

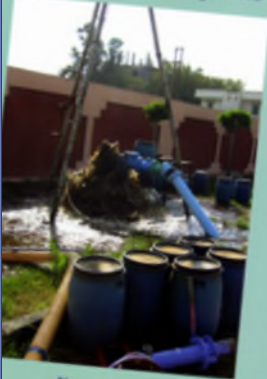


KWR 2021.034 | Mei 2021

Inzicht in ijzerchemie helpt ons chemische putverstopping en ontijzering te doorgronden

Resultaten uit het 'post-pensionering'-onderzoek van Kees van Beek

Cause and prevention of clogging of wells abstracting groundwater from unconsolidated aquifers



Kees van Beek



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en ontijzering te doorgronden**
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KWR 2021.034 | Mei 2021

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Summary

In this series of papers, experiences and field observations on chemical well clogging by accumulation of Hydrous Ferric Oxide (HFO) precipitates, and on iron(II) removal by aeration and filtration in drinking water preparation from groundwater, including Subsoil Iron Removal (SIR), have been compared with the chemistry of iron(II) as presented in handbooks and papers.

Iron(II) may be precipitated as HFO by oxygen by homogeneous, heterogeneous and biological oxidation. The homogeneous iron(II) oxidation rate is proportional to $(H^+)^{-2}$: the higher the pH, the faster the homogeneous iron(II) oxidation rate. The heterogeneous iron(II) oxidation rate is proportional to $(H^+)^{-1}$ and to FeAC, the iron(II) adsorption capacity: the higher the pH and the greater the FeAC, the faster the heterogeneous iron(II) oxidation rate.. Consequently, the transition pH between predominant occurrence of homogeneous and of heterogeneous iron(II) oxidation is governed by the FeAC: low FeAC values resulting in lower values for this transition pH, and higher FeAC values in higher pH values. Biological iron(II) oxidation by *Gallionella* spp will occur everywhere where conditions for homogeneous and/or heterogeneous iron(II) oxidation are less favorable: at lower pH and at lower FeAC values. Biological iron(II) oxidation is also relevant, because heterogeneous iron(II) oxidation is initiated by biological HFO precipitates.

Applying these “rules” to chemical well clogging by accumulation of HFO precipitates learns: At “high” pH there will be continuous precipitation of HFO’s by homogeneous oxidation of iron(II), resulting in clogging of field-lines (conveying the abstracted groundwater from the well field to the treatment plant), but hardly in clogging of the well screen. As at “high” pH iron(II) concentrations are low, this is a rather slow process (depending on residence times in these field-lines).

At “neutral” pH chemical well clogging is caused by accumulation of *Gallionella* spp biomass and of HFO precipitates. *Gallionella* spp possess excellent adhering skills, and are able to accumulate in or along the slots of the well screen where oxygen containing groundwater enters the well. As from greater depth iron(II) containing groundwater is flowing upwards, this is an excellent environment for *Gallionella* spp: from the one side oxygen containing water and from the other side iron(II) containing water, and *Gallionella* spp in between. Depending on conditions the clogging rate may be variable. After complete mixing of both water types, after the pump, HFO precipitation will be minimal, as biological oxidation will be (nearly) absent, and pH is too low for relevant homogeneous oxidation.

Contrary to chemical well clogging, in drinking water treatment by aeration and filtration conditions may be optimized to either homogeneous or to heterogeneous/biological iron(II) oxida-

tion. Optimal conditions for homogeneous oxidation are a “high” pH and sufficient residence time in the supernatant water on the sand-filter. Under non-optimal conditions minuscule HFO flocs may pass the sand-filter and enter the drinking water distribution system. Optimal conditions for heterogeneous/biological oxidation are a “neutral” pH and a thin layer of supernatant water in order to arrive at an equal load over the sand-filter.

In Sub-soil Iron Removal (SIR) aerated water is infiltrated into an aquifer, after which a greater volume of iron-free water may be abstracted. This phenomenon may be explained by heterogeneous iron(II) oxidation, where adsorption and oxidation are separated in time. The role of biological oxidation needs further research.

After evaluation of many groundwater chemistry data, it appeared that the concentration of iron(II) in groundwater is governed by continuous reduction of HFO's from the one side and precipitation of Siderite (FeCO_3) at the other side, and in this way also of the concentrations of As, Co, Ni and Zn.

Eventual subjects of further research may be:

1. Properties of HFO precipitates, as function of method of drinking water preparation, as raw material for further use.
2. Application of SIR above ground in large upward flow vessels, comparable to water softening, with continuous or intermittent oxygen supply, etc.

Inhoud

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Inzicht in ijzerchemie helpt ons chemische putverstopping en ontijzering te doorgronden

Resultaten uit het 'post-pensionering'-onderzoek van Kees van Beek, zoals beschreven op de KWR-website

KWR-onderzoeker Kees van Beek heeft zich na zijn pensionering gebogen over de theorie van de ijzerchemie, omdat de ijzerchemie niet alleen relevant is voor het optreden van chemische putverstopping, maar ook voor de ontijzering in de drinkwaterbereiding. Bij de ontijzering zijn drie processen te onderscheiden: homogene, heterogene en biologische ijzeroxidatie. Bij een hogere pH van het grondwater, zoals bij duinwaterbedrijven, domineert homogene oxidatie. Homogene oxidatie verloopt traag en leidt daarom vooral in terreinleidingen tot verstopping. Bij lagere pH, zoals in de meeste andere grondwaterwinningen, spelen heterogene oxidatie en biologische oxidatie de grootste rol, met als resultaat ernstige chemische en biologische verstopping van het putfilter. Van Beek's onderzoek leverde niet alleen een verklaring op voor de waargenomen putverstoppingen onder verschillende omstandigheden, maar is ook van toepassing op een belangrijk proces bij de drinkwaterbereiding, de ontijzering van grondwater - ook een ijzeroxidatieproces. Waar bij putverstopping de omstandigheden vastliggen, zijn bij ontijzering tijdens de drinkwaterzuivering de condities wél te optimaliseren. Van Beek: "Ik heb veel hulp gehad van technologen uit de drinkwatersector en KWR. Door hun ervaringen met ontijzering in de zuivering te vergelijken met optreden van chemische putverstopping en af te zetten tegen de theorie van de oxidatie van ijzer door zuurstof, was het mogelijk een grotere vinger achter de ontijzering te krijgen." Dat leidde bijvoorbeeld tot de suggestie om het ontijzeringproces anders in te richten, zodat de kwaliteit van het verwijderde ijzerslib meer te sturen is naar de behoefte voor hergebruik.



Kennis over putverstopping kan bijdragen aan het optimaliseren van ijzerverwijdering in de drinkwaterbereiding

In 2006 ging Kees van Beek officieel met pensioen, na 33 jaar toegepast onderzoek bij KWR. Hij was specialist in putverstopping en hij heeft onder meer een grote bijdrage geleverd aan een methode om mechanische putverstopping te voorkomen, namelijk door putten volgens een plan afwisselend aan en uit te schakelen. Dit kwam onder meer aan de orde op het symposium Putmanagement in 2017. Putschakeling kan voorkomen dat kleine deeltjes zich ophopen op de boorgatwand. Graag wilde hij ook zijn vingers krijgen achter de oorzaken van chemische putverstopping, een ander fenomeen dat bij veel puttenvelden voor problemen zorgt. Daarom heeft hij zich na zijn promotie in 2010 gebogen over de theorie van de ijzerchemie die ten grondslag ligt aan chemische verstopping en aan ontijzering. Voor dit werk kon hij zijn werkplek bij KWR behouden en gebruik blijven maken van de KWR-faciliteiten, tot wederzijds genoegen. Maar nu vindt Van Beek het genoeg: het wordt tijd om écht met pensioen te gaan. Graag wil hij zijn bevindingen uit deze laatste periode delen met de drinkwatersector. De zes artikelen waarin hij de afgelopen jaren zijn bevindingen heeft vastgelegd zijn daarom gebundeld en gecombineerd met deze toelichting op de KWR-website, die een samenvatting geeft van de belangrijkste resultaten. Van Beek's gespit in de theorie van de ijzerchemie heeft sterk bijgedragen aan de verklaring van de waarnemingen van diverse collega's bij KWR en waterbedrijven.



“De processen die bij putverstopping en ontijzering een rol spelen, zijn in essentie gelijk,” zegt Van Beek. “Vergelijking van kennis en ervaringen met ontijzering en met chemische putverstopping levert daardoor meer zinvolle kennis voor beide toepassingen.”

3 SOORTEN IJZEROXIDATIE

Kees van Beek: “Bij de oxidatie van ijzer(II) door zuurstof zijn drie processen te onderscheiden. In de eerste plaats de homogene oxidatie: die treedt op bij beluchting van ijzerhoudend water of bij menging van ijzer(II)-houdend water en van zuurstofrijk water. Hierover is vrij veel bekend. Bij homogene oxidatie ontstaan vlokken ijzer(III)hydroxide. Daarnaast heb je heterogene oxidatie: oxidatie van ijzer(II) nadat het is geadsorbeerd aan het oppervlak van eerder gevormd ijzer(III)hydroxide. Over dit proces is minder bekend. Daarnaast is er nog biologische oxidatie, en daarover weten we het minst. De ijzeroxiderende *Gallionella*-bacteriën gedijen onder omstandigheden waar ijzer(II) bevattend water en zuurstof bevattend water met elkaar mengen, daaraan ontleen zij hun energie. Om de vrijkomende energie tot hun voordeel te kunnen gebruiken, beschikken *Gallionella*-bacteriën over uitstekende hechtende eigenschappen: zij “overleven” stroming in putfilters en terugspoelen van ontijzerings-filters. Zodra beide waterstromen of -typen zijn gemengd, vervalt het bestaansrecht van *Gallionella*-bacteriën en zal alleen nog homogene oxidatie optreden.”

VERKLARING VOOR GRONDWATERWATERONTIJZERING EN PUTVERSTOPPING

Oxidatie van ijzer(II) naar ijzer(III) speelt op meerdere plaatsen in de drinkwatervoorziening een rol. Zoals gezegd ontstaat chemische putverstopping door oxidatie van ijzer. Begrip van de ijzerchemie helpt om te verklaren onder welke condities en op welke plekken er wel of juist geen putverstopping optreedt. Tegelijkertijd geeft de ijzerchemie meer inzicht in de ontijzering van eenmaal opgepompt water, en mogelijk zicht op meer optimale methoden om dat water te ontijzeren. “De processen die bij putverstopping en bij ontijzering een rol spelen, zijn in essentie gelijk,” zegt Van Beek.



Grondwaterputten raken regelmatig verstopt door accumulatie van neerslagen, gevormd door oxidatie van ijzer uit het grondwater.

PUTVERSTOPPING PH-AFHANKELIJK

Chemische putverstopping is een hinderlijk fenomeen en er zijn nauwelijks mogelijkheden om de condities onder de grond aan te passen. Begrijpen hoe de verstopping ontstaat, is al een stap vooruit. Van Beek: “Bij het oppompen van water met een hoge pH – zeg maar boven 7,5 – domineert na menging met zuurstof de homogene oxidatie. Dit is bijvoorbeeld het geval bij duinwaterbedrijven. De ijzerconcentraties in het water zijn laag en de homogene oxidatiereactie verloopt relatief traag. Er is dan dus nauwelijks verstopping van de filterspleten, waarschijnlijk mede doordat de ijzer(II)-concentraties laag zijn, zodat *Gallionella*-bacteriën onvoldoende energie kunnen verkrijgen. In deze winningen zie je juist dat ijzerhydroxidevlokken ontstaan wanneer het water al een poosje onderweg is, door homogene oxidatie in de terreinleidingen. Voortdurende vorming van ijzer(III)hydroxideneerslagen en -vlokken, ondanks de lage concentratie van ijzer(II), kan daar leiden tot ernstige verstopping.”

Anders is het bij lagere pH. “Bij een pH onder 7,5, zoals bij de meeste andere grondwaterwinningen, spelen heterogene oxidatie en biologische oxidatie de grootste rol. In putten die (gescheiden) waterstromen onttrekken van zuurstof-bevattend en van ijzer-bevattend water zijn de omstandigheden ideaal voor *Gallionella*-bacteriën. Om de maximale energie uit deze menging te halen, zullen zij zich “stroomopwaarts” bewegen naar de spleten van het putfilter. Dankzij hun uitstekende hechtende eigenschappen kunnen zij zich daar handhaven, wat resulteert in ernstige chemische en biologische verstopping van het putfilter. Zodra beide waterstromen volledig zijn gemengd - na de onderwaterpomp - is de rol van *Gallionella*-bacteriën uitgespeeld. In de terreinleidingen vind je daarom maar verwaarloosbaar verstopping door

heterogene oxidatie, want ook al zijn er hogere concentraties ijzer(II), er is geen biologische of andere hechting.”

ONTIJZEREN: STUREN VIA DE CONDITIES

Dezelfde processen als bij putverstopping zijn actief bij de bovengrondse verwijdering van ijzer(II) uit grondwater door beluchting en filtratie, zoals bij de bereiding tot drinkwater. De beste resultaten worden behaald door de procescondities zo in te richten dat de omstandigheden voor één van de oxidatie-reacties optimaal zijn, dus homogene oxidatie “alleen in het bovenwater” of heterogene oxidatie “alleen in het (zand)filter”. De rol van biologische oxidatie van ijzer(II) in deze “klassieke” zuiveringsmethode is slecht bekend.

Een al bekende methode die momenteel weer in de belangstelling staat is de verwijdering van ijzer(II) uit grondwater door middel van ondergrondse ontijzering. Van Beek: “Hierbij wordt zuurstofrijk water in het watervoerend pakket geïnfiltreerd, waarna, discontinu, een groter volume ijzerloos grondwater kan worden onttrokken. Het onderliggende proces bij deze methode is heterogene oxidatie, waarbij vooral de adsorptie van ijzer aan het oppervlak van de bodemdeeltjes bepalend is voor het rendement van ondergrondse ontijzering.”

IS DE KWALITEIT VAN IJZERSLIB TE STUREN?

Bij de verschillende soorten oxidatie ontstaan ook verschillende soorten slib, met van elkaar verschillende fysieke eigenschappen. Deze eigenschappen kunnen bepalend zijn voor de verdere gebruiksmogelijkheden, wat maakt dat de keuze voor de soort oxidatie veel effect kan hebben op verder nuttig gebruik van het slib. “Hier liggen mogelijk nog kansen,” vermoedt Van Beek. “De resultaten van onderzoek naar ondergrondse ontijzering zijn potentieel ook relevant voor toepassing in de ‘klassieke’ ontijzering. In het optimale toepassingsgebied van heterogene oxidatie, waarbij je dus bovenwater vermijdt, moet het mogelijk zijn ontijzering in een fluïde bed toe te passen, analoog aan ontharding in korrelreactoren. Ontijzering in korrelreactoren heeft veel voordelen: geen terugspoelen, geen doorslag van ijzervlokjes tijdens opstarten na terugspoelen, hoge hydraulische belasting, reststof met een hoog droge stof gehalte en mogelijk een hogere marktwaarde, etc. Door de bedrijfsvoering te variëren, bijvoorbeeld tussen continue of juist discontinu toevoer van zuurstof, is het wellicht ook mogelijk de kwaliteit van de ijzerkorrels te variëren tussen volledig anorganisch gevormde korrels en anorganisch/organisch gevormde korrels en daarmee af te stemmen op een gevraagde kwaliteit ijzerkorrels.”

SIDERIET BEPAALT CONCENTRATIE VAN IJZER(II) IN GRONDWATER

Een leuke “bijvangst” van het onderzoek van Van Beek was de constatering dat de concentratie van ijzer(II) in het Nederlandse grondwater wordt bepaald door het mineraal sideriet (FeCO_3). Dit mineraal wordt in de ondergrond gevormd zodra ijzer(II)-houdend grondwater oververzadigd raakt ten opzichte van sideriet. Ijzer(II) komt vrij onder invloed van verschillende bodemchemische processen, onder andere door het oplossen van ijzerhydroxiden (ijzerhuidjes op zand). De omzetting van deze ijzerhuidjes in sideriet-neerslagen is ook bepalend voor de concentratie van sporenelementen in grondwater, zoals arseen, kobalt, nikkel en zink. ■

Understanding iron chemistry helps us understand chemical well clogging and iron removal in drinking water preparation

[Results from Kees van Beek's 'post-retirement' research \(article on the KWR website\)](#)

KWR researcher Kees van Beek studied iron chemistry after he retired because iron chemistry is not only relevant for the occurrence of chemical well clogging but also for the removal of iron in the preparation of drinking water. Three processes are distinguished in iron removal: homogeneous, heterogeneous and biological iron oxidation. When groundwater has a higher pH, as at the dune waterworks, homogenous oxidation predominates. Homogenous oxidation is a slow process and therefore leads to blockage, particularly in field lines, conveying the abstracted groundwater from the well to the treatment plant. At lower pH levels, as in most other groundwater abstractions, heterogeneous oxidation and biological oxidation are relevant, resulting in serious chemical and biological well clogging. Van Beek's research not only provided an explanation for the observed well clogging under various conditions but also applies to a vital process in the preparation of drinking water, removal of iron from groundwater – also an iron oxidation process. Whereas in well clogging conditions are fixed, in iron removal during drinking water treatment, conditions may be optimised. Van Beek: "I got a lot of help from technologists from the drinking water sector and from KWR. By comparing their experiences with iron removal during drinking water preparation with the occurrence of chemical well clogging and comparing these experiences with the chemistry of the oxidation of iron by oxygen, it was possible to get a better understanding of the iron removal process. This resulted, for example, in the suggestion to remove iron in such a way that the quality of the produced iron sludge better suits further use as raw material.

Kees van Beek officially retired in 2006, after 33 years of applied research at KWR. He was a specialist in well clogging and, among other things, made a significant contribution to the prevention of mechanical well-clogging by switching wells on and off regularly. This was, amongst others, discussed at the 2017 Well Management symposium. Switching wells regularly on and off prevents accumulation of small particles on the borehole wall. He also wanted to get a better understanding of the causes of chemical well-clogging, another phenomenon that causes problems in many



Kees van Beek: "Chemical well clogging and iron removal in drinking water preparation are identical processes."

well fields. That is why, after his PhD thesis in 2010, he studied the chemistry of iron underlying chemical well clogging and iron removal. For this research, he could retain his position at KWR and take advantage of the KWR facilities, much to our mutual delight. But now it has been enough: it is time for Van Beek to retire for real. He would like to share his findings from this last period with the drinking water sector. The six papers in which he summarised his findings over the last few years have been put together and combined with this summarising article on the KWR website. Van Beek's "digging" into the iron chemistry has contributed significantly to the explanation of experiences and observations of various colleagues at KWR and at drinking water utilities.



Van Beek: "Comparing experiences and observations with chemical well clogging and with iron removal by aeration and precipitation provides useful information for both applications."

3 TYPES OF IRON OXIDATION

Kees van Beek: "Three processes may be distinguished in the oxidation of iron(II) by oxygen. Firstly, homogenous oxidation occurs when ferrous water is aerated or when ferrous water is mixed with oxygenated water. A great deal is known about this. Homogenous oxidation produces flocs of ferric hydroxide. Then there is heterogenous oxidation: oxidation of iron(II) after adsorption on the surface of previously precipitated iron(III) hydroxides. Less is known about this process. Then there is biological oxidation, about which we know the least. The iron-oxidising *Gallionella* bacteria thrive under conditions where iron(II)-containing water and oxygen-containing water are mixing, deriving their energy from this mixing process. In order to use the released energy to their advantage, *Gallionella* bacteria possess excellent adhesive properties: they "survive" flow in well screens and backwashing of sand filters. As soon as both water flows or types are mixed, growth conditions for *Gallionella* bacteria are over, and only homogeneous oxidation will occur."

EXPLAINING REMOVAL OF IRON FROM GROUNDWATER AND CHEMICAL WELL CLOGGING

Oxidation of iron(II) to iron(III) plays a role in several parts/steps in the public drinking water supply. As mentioned above, chemical well clogging is caused by iron oxidation. Understanding iron chemistry helps to explain under which conditions and at which locations well clogging will or will not occur. At the same time, iron chemistry provides a better understanding of the removal of dissolved iron in the abstracted groundwater and eventually into more optimal methods for iron removal. "The processes relevant in well clogging and in iron removal are essentially the same," says Van Beek.



Groundwater wells regularly become clogged by the accumulation of deposits precipitated by the oxidation of iron from the groundwater.

PH-DEPENDENT WELL CLOGGING

Chemical well clogging is a nuisance phenomenon, and there are hardly any possibilities for adjusting underground conditions. Understanding the conditions resulting in clogging is already a step forward. Van Beek: "In groundwater containing iron as well as oxygen, with a high pH - say, above 7.5 - homogeneous oxidation dominates. This high pH is prevalent at water utilities abstracting dune water and some outside well fields. Because the iron concentrations in the abstracted groundwater are low, and the homogenous oxidation reaction is relatively slow, there is hardly any clogging of the screen slots. Moreover, because the iron (II) concentrations are low, *Gallionella* bacteria probably cannot obtain enough energy for abundant growth. Observations on these well fields show that iron hydroxide flocs develop after the water has been underway for some time in the field lines. This continuous precipitation of iron(III) hydroxides may result, despite the low concentration of iron(II), in severe clogging of these field lines."

Conditions are different at lower pH. "At a pH below 7.5, as in most well fields, heterogeneous oxidation and biological oxidation are dominant. In wells that abstract (separate) flows of oxygen-rich and of iron-rich water, conditions are ideal for *Gallionella* bacteria. To get the maximum energy from this mixing, they will move "upstream" to the slots of the well screen. Thanks to their excellent adhesive properties, they are able to maintain themselves there, resulting in severe chemical and biological clogging of the well screen. As soon as both water flows are completely mixed - after the (submersible) pump - the role of *Gallionella* bacteria is over. In the field lines, clogging will be negligible because, despite higher iron(II) concentrations, heterogeneous and biological oxidation will be (almost) absent."

IRON REMOVAL: CONTROLLING THROUGH CONDITIONS

The same processes as in well clogging are active in the above-ground removal of iron(II) from groundwater by aeration and filtration, as in the preparation of drinking water. The best results are achieved by designing the process conditions in such a way that these conditions are optimal to one of the oxidation reactions, i.e. homogenous oxidation “only in the supernatant water” or heterogeneous oxidation “only in the (sand) filter”. The role of biological oxidation of iron(II) in this “classic” treatment is poorly known.

An already well-known method that is currently attracting renewed attention is removing iron(II) from groundwater through underground iron removal. Van Beek: “This involves infiltrating oxygen-rich water into the aquifer, after which a larger volume of iron-free groundwater can be abstracted discontinuously. The underlying process in this method is heterogeneous oxidation, in which the adsorption of iron on the surface of the soil particles determines the efficiency of this method.”

CAN THE QUALITY OF IRON SLUDGE BE CONTROLLED?

Different types of oxidation also result in different kinds of sludge with different physical properties. These properties may determine further possibilities for use as raw material, which means that the selection of the oxidation process may significantly influence further meaningful use of the sludge. “There may still be opportunities here,” Van Beek supposes. “The results of research into underground iron removal are potentially also relevant for application in ‘classic’ iron removal. In the optimal application range of heterogeneous oxidation, it should be possible to remove iron in a fluidised bed, analogous to softening in pellet reactors. Iron removal in pellet reactors has many advantages: no backwashing, no iron flocs passing the filter during start-up after backwashing, high hydraulic load, residue with a high dry matter content and possibly a higher market value, et cetera. By varying operation, for example, between the continuous or discontinuous supply of oxygen, it may also be possible to vary the quality of the iron pellets between completely inorganic and inorganic/organic pellets and thus to produce a requested quality of iron pellets.”

SIDERITE DETERMINES CONCENTRATION OF IRON(II) IN GROUNDWATER

An interesting “by-catch” of Van Beek’s research was the observation that the concentration of iron(II) in Dutch groundwater is determined by the mineral siderite (FeCO_3). This mineral is formed in the subsurface as soon as groundwater containing iron(II) becomes supersaturated with respect to siderite. Iron(II) is released by various soil chemical processes, among others, by the reduction of iron hydroxides (iron skins on sand). The conversion of these iron skins into siderite precipitates also determines the concentration of trace elements in groundwater, such as arsenic, cobalt, nickel and zinc. ■

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ORIGINAL ARTICLE



Concentration of Iron(II) in Fresh Groundwater Controlled by Siderite, Field Evidence

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Abstract

Iron(II) concentrations in fresh groundwater in Dutch aquifers range from absent up to 50 mg/l. Evaluation of extensive chemical data sets learned that the maximum logarithmic concentration of iron(II) in aquifers, between $\pm 6.5 < \text{pH} < \pm 8$, is a linear function of pH, governed by Siderite. It is a broad relation due to oversaturation with respect to Siderite and to variation in alkalinity. Iron(II) is continuously supplied to groundwater by reduction of hydrous ferric oxides (HFO), until becoming saturated with respect to Siderite, and from then on, HFO reduction and Siderite precipitation occur simultaneously. In Dutch aquifers, the electron supply rate (equivalent to the organic matter oxidation rate) apparently exceeds the HFO electron uptake rate (equivalent to the HFO reduction rate) and the excess supply is taken up by sulfate (equivalent to the sulfate reduction rate): HFO reduction, sulfate reduction and FeS precipitation occurring simultaneously, where the presence of Siderite prevents a dip in the iron(II) concentration. After sulfate becomes exhausted, the excess electron supply is transferred to methane production: HFO reduction and methane production occurring simultaneously. This evaluation also demonstrated that the organic matter oxidation rate and the HFO reduction rate decrease over time. The results of this study are also relevant for the behavior of As and of Co, Ni and Zn in groundwater, as HFO, Pyrite and Siderite may contain variable contents of these elements.

Keywords Iron(II) concentration in fresh groundwater · Redox zoning · Hydrous ferric oxides · Siderite

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1 Introduction

Iron plays an important role in the (redox)chemistry of groundwater. Understanding the concentration of iron(II) in aquifers requires information about production of dissolved iron(II) by reduction of hydrous ferric oxides (HFO) on the one hand and precipitation of dissolved iron(II) by solid iron phases like iron sulfides (FeS , FeS_2) or iron carbonate (Siderite, FeCO_3) on the other hand. Because these solid phases may contain all kinds of admixtures, information about the chemistry of iron is also relevant for the chemistry of arsenic (Postma et al. 2007), cobalt, nickel and zinc (van Beek and van der Jagt 1996), phosphate (Geelhoed et al. 1997), etc.

Research on the chemistry of iron(II) in fresh groundwater was initiated by Hem (1967) and by Langmuir (1997) and later on extensively summarized in handbooks by Stumm and Morgan (1996) and by Appelo and Postma (2007). However, extensive field data corroborating the presented information remain scarce. Water utilities, distributing drinking water prepared from groundwater, intensively monitor the quality of groundwater flowing toward their well fields. As a result, these water utilities have acquired large databases, comprising concentrations of many parameters over many years, also of iron(II). Figure 1 shows the concentration of iron(II) as function of pH, subdivided in several sulfate concentration classes. This figure shows several interesting phenomena:

- (1) At $\text{pH} > \text{ca. } 6.5$, the maximum log concentration of iron(II) is a linear function of pH,
- (2) This relationship is independent of the sulfate concentration, i.e., independent of the occurrence of sulfate reduction, and

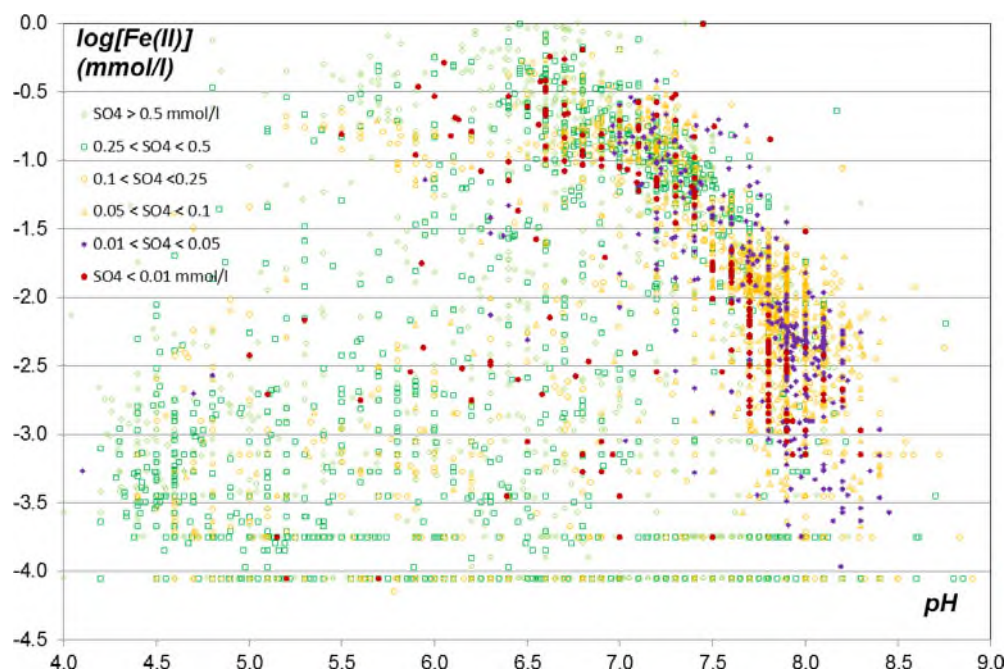


Fig. 1 Concentration of iron(II) (=total concentration of all Fe^{2+} -species) as function of pH in fresh groundwater in aquifers, subdivided into sulfate concentration classes

- (3) This relationship is independent of aquifer type and aquifer material, as the well fields involved are abstracting groundwater from phreatic and (semi-)confined aquifers, consisting of fluvial, marine, aeolian and ice-pushed sediments.

Figure 1 raises several questions:

- (1) Which equilibrium is (equilibria are) determining this relationship?
- (2) Which (geochemical) process is (processes are) governing this relation?
- (3) What is causing the rather wide spread in concentration of iron(II) as function of pH (1.5 log-unit)?

In order to answer these questions, some well fields have been rather arbitrarily selected for detailed research. Before starting this evaluation, some information about these well fields will be presented.

2 Materials and Methods

2.1 Location and Description of the Field Sites

In this study, the chemical data obtained from monitor wells around the well fields Beerschoten, Culemborg, Edese Bos, Havelterberg, Holten and Klooster have been evaluated; for location of these well fields, see Fig. 2. These monitor wells are equipped with screens with a length of 1 or 2 m, with up to circa 5 screens in one well. Around well field Klooster, besides monitor wells also mini-screen wells have been installed with the explicit purpose of groundwater chemistry studies. These mini-screen wells are equipped with up to 40 mini-screens in one well, consisting of 25-mm-diameter 6-cm-long gravel-coated screens.

In this study, the data of Beerschoten (characterized by a rather sharp $\text{NO}_3/\text{Fe}(\text{II})$ redox boundary) and Klooster (equipped with mini-screen-wells) will be discussed in detail. Information about the remaining well fields is presented as Supplemental Information.

Figure 3 presents the location of the groundwater quality monitor wells around the well fields Beerschoten and Klooster. The figure of Klooster also presents the location of the miniscreen-wells. The location of the monitor wells around the other well fields is presented as Supplemental Information.

Tables 1 and 2 summarize some information about the well fields involved. Four of the six well fields, i.e., Beerschoten, Edese Bos, Havelterberg and Holten, are located on ice-pushed ridges, consisting of old Pleistocene (Weichselian Ice Age) lime-less sediments with low contents of (less reactive) organic material. Water utilities prefer these ice-pushed ridges: excellent water quality and aquifer conditions and hardly interaction with human activities like groundwater abstraction or groundwater pollution. The well fields Culemborg and Klooster are located in young (Holocene) deposits, containing high contents of lime and (reactive) organic material.

As a result, groundwater at the well fields Culemborg and Klooster is already anoxic at shallow depth; the other well fields become gradually more anoxic with increasing depth.

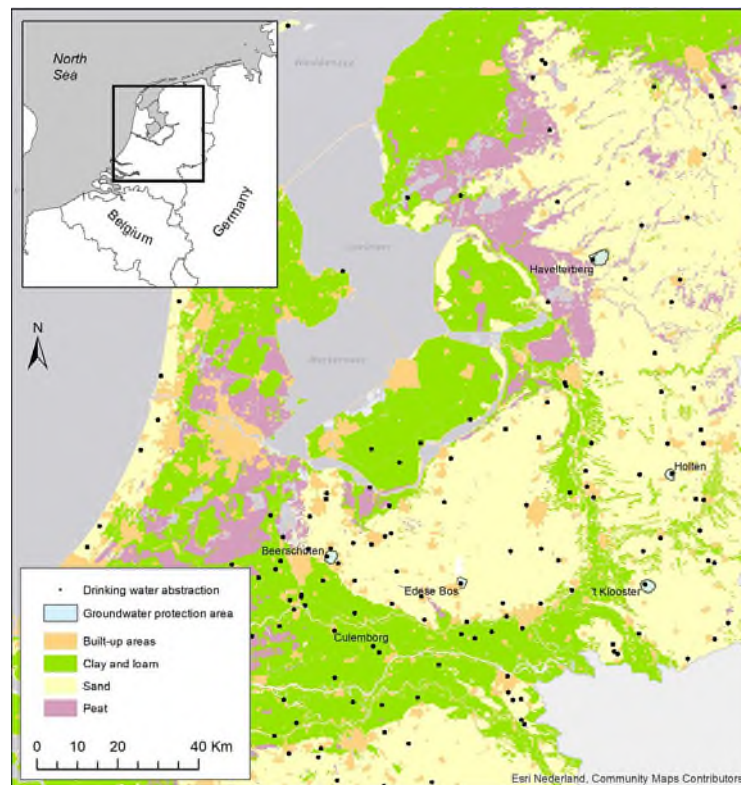


Fig. 2 Location of all well fields exploited by the waterworks in the Netherlands, and location of the well fields involved in this study, with corresponding groundwater protection area (Culemborg has no protection area)

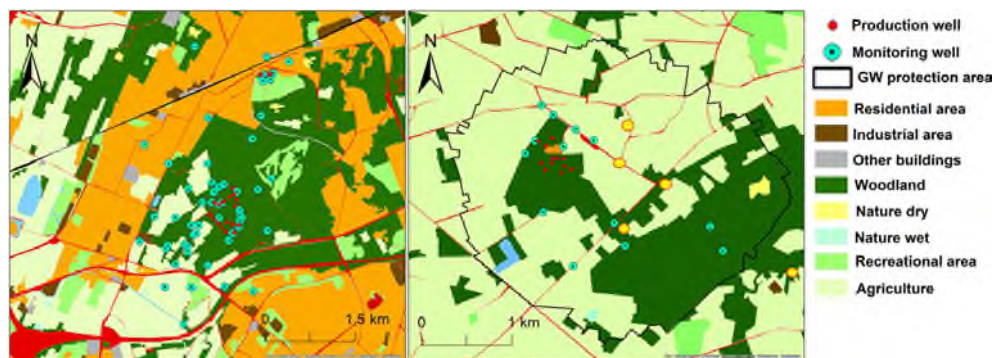


Fig. 3 Location of the groundwater monitor-wells around well fields Beerschooten (left) and Klooster (right). Mini-screen wells at Klooster marked by yellow circles

2.2 Chemical Data Set

The results of all the groundwater chemical analyses of the monitor-wells, going back to 1985 and earlier, have been compiled by Water Utility Vitens in (identical) chemical databases, one for each well field. The quality of the chemical analyses may be variable:

Table 1 Summary of some site characteristics of the well fields involved

Well field	Production 10 ⁶ m ³ /year	Aquifer	Depth well screen m below surface	Physiography
Beerschoten	8	Phreatic	60–100, 160–180	On the lower slope of an ice-pushed ridge
Culemborg	2	Confined	100–150	Fluvial river Rhine deposits
Edese Bos	3.5	Phreatic	35–75	On top of an ice-pushed ridge
Havelterberg	6.3	Phreatic	20–80	On top of an (overridden) ice-pushed ridge
Holten	2.5	Phreatic	15–75	On the lower slope of an ice-pushed ridge
Klooster	5	Phreatic	15–35	Sand filled glacial valley

Table 2 Summary of some groundwater characteristics of the well fields involved

Well field	Organic matter	Lime	Groundwater depth	Land use/vegetation
Beerschoten	Low	Absent	Deep uphill, moderate downhill	Natural reserve with wood
Culemborg	Moderate	Moderate	Shallow (ca 1 m below surface)	Dairy farms
Edese Bos	Low	Absent	Deep	Natural reserve with wood
Havelterberg	Low	Absent	Deep	Wood and agriculture
Holten	Low	Absent	Deep uphill, moderate downhill	Wood and agriculture
Klooster	High	Rich	shallow (ca 1 m below surface)	Agriculture

chemical analyses have been executed by different laboratories applying different analytical chemical methods, over time analytical-chemical methods have been modified, lower chemical analytical boundaries have become lower, sampling methods have been standardized, etc. In order not to lose information with respect to lower concentrations, analytical results “less than” have been modified into half this value: $A < x \text{ mg/l} \rightarrow A = 0.5 x \text{ mg/l}$. No attempts have been made to remove divergent results, possibly originating from polluted sites, apparent errors, etc. The number of parameters analyzed per sample may vary considerably: from a few to all macro parameters, together with none to many inorganic and/or organic micro parameters.

With respect to the concentration of iron(II), there is one more complication: the rather wide spread in the results of the chemical iron(II) analyses in Fig. 1 may (partly) be attributed to the complicated sampling procedure: refreshing the volume of the monitor well, sampling by suction, and filtration over a 0.45- μm membrane, all without entry of oxygen, and acidification of the sample for storage and transport. Moreover, there is no convenient way to check the quality of the results obtained, as is possible to some extent for macro parameters.

2.3 Groundwater Flow Toward Wells

In flat to gently sloping areas, regional groundwater flow in (semi-)phreatic aquifers is characterized by an almost horizontal laminar flow more or less parallel to the surface. Variations in the vertical chemical profile are caused by variations in surface conditions until far upstream. Well(-field)s in (semi-)phreatic aquifers develop their own corresponding recharge area, characterized by a much more vertical flow (Todd and Mays 2005). This

more vertical flow makes well fields more appropriate for groundwater chemistry research: variations in chemical groundwater profiles may be explained by variations in surface conditions over a much shorter distance.

Departing from a groundwater recharge of 300 mm/year, the recharge area of well field Beerschoten (drinking water production: $8 \cdot 10^6$ m³/year) amounts to 2400 ha, corresponding with a radius of 2764 m, and of well field Klooster ($5 \cdot 10^6$ m³/year) to 1500 ha, and to a corresponding radius of 2185 m. However, in the presence of a regional groundwater flow, the recharge area is egg shaped: the upward “radius” being much longer than the downward “radius”.

3 Relevant Chemical Equilibria

Solid phases relevant for the chemistry of iron(II) in fresh groundwater are:

- (1) Hydrous ferric oxides (HFO). As Dutch aquifers for the greater part consist of sand (=HFO coated quartz grains) (Breeuwsma 1990), they contain an immense reservoir of HFO. The older the HFO precipitate, the more the recalcitrant, and the slower the dissolution/reduction process (Postma et al. 2016). The contribution to the concentration of iron(II) by weathering of primary minerals is negligible.
- (2) Ferrous iron sulfides (FeS) like amorphous sulfides, Mackinawite, etc. These are the initial iron(II) sulfide precipitates, slowly converting into the final stable phase Pyrite (FeS₂).
- (3) Ferrous iron carbonate (FeCO₃) like Siderite.
- (4) Ferrous iron hydroxide (Fe(OH)₂).

The redox-reactions involved under (1) and (2) are usually initiated by the oxidation of organic material, present in groundwater recharge, or as solid dispersed in the aquifer matrix or in intercalated peat/clay layers. The electron supply rate depends on the stability of the organic material involved: the older the organic material the more recalcitrant, and the slower this oxidation process (Postma et al. 2016; Appelo and Postma 2007, p. 443). Table 3 presents a summary of the chemical (half) reactions involved.

As several redox reactions may occur simultaneously, electron exchange is here described as an electron supply rate equal to an electron uptake rate.

4 Results and Discussion

4.1 Concentration of Iron(II) as Function of pH

Elaboration of the (redox-)system summarized in Table 3 (Appelo and Postma 2007; Stumm and Morgan 1996; Drever 1988; Hem 1967) yields Fig. 4, representing a pH-pe diagram for iron(II). This diagram shows the solubility of iron(II) for two concentrations: 1 mmol/l as about the maximum concentration in Dutch fresh groundwaters and 1 μmol/l as about the lowest relevant concentration.

Figure 4 demonstrates that with decreasing redox potential the concentration of iron(II) increases, until between $\pm 6 < \text{pH} < \pm 9$ and $(\text{HCO}_3^-) = 1$ mmol/l, groundwater becomes saturated with respect to Siderite, and Siderite starts to precipitate [at higher

Table 3 Summary of chemical (half-) reactions relevant for the behavior of iron(II) in fresh groundwater (where “e” represents an electron)

1	Oxidation of organic material, represented as CH_2O : $\text{CH}_2\text{O} + 2\text{H}_2\text{O} \rightarrow \text{HCO}_3^- + 5\text{H}^+ + 4e$	(1)
2	Denitrification: $\text{NO}_3^- + 6\text{H}^+ + 5e \rightarrow \frac{1}{2}\text{N}_2 \uparrow + 3\text{H}_2\text{O}$	(2)
3	Reduction of HFO: $\text{FeOOH}(\text{s}) + 3\text{H}^+ + e \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O}$	(3)
4	Reduction of sulfate, together with precipitation as $\text{FeS}(\text{s})$: $\text{SO}_4^{2-} + \text{Fe}^{2+} + 8e + 8\text{H}^+ \rightarrow \text{FeS}(\text{s}) + 4\text{H}_2\text{O}$	(4)
5	Reduction of organic material (methanogenesis): $\text{CH}_2\text{O} + 4\text{H}^+ + 4e \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	(5)
6	Solubility of Siderite (no distinction has been made between the mineral Siderite and the chemical precipitate FeCO_3): $\text{FeCO}_3(\text{s}) + \text{H}^+ = \text{Fe}^{2+} + \text{HCO}_3^-$	(6)
7	Next to Siderite, at high pH and low alkalinity $\text{Fe}(\text{OH})_2(\text{s})$ may become relevant: $\text{FeCO}_3(\text{s}) + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2(\text{s}) + \text{H}^+ + \text{HCO}_3^-$	(7)

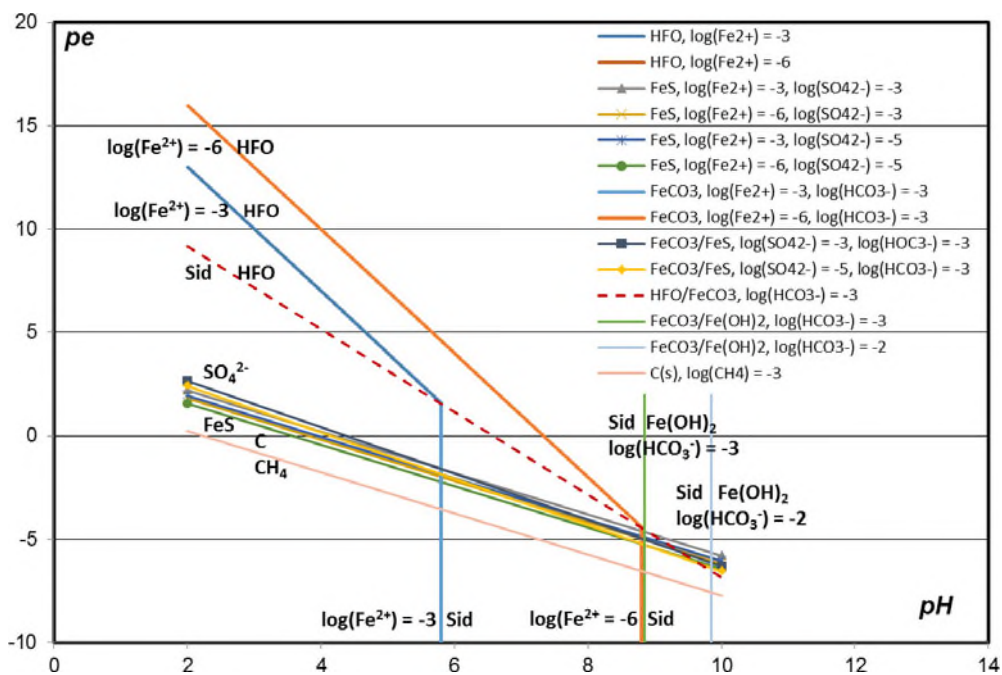


Fig. 4 pH-pe diagram for Fe^{2+} in equilibrium with the solid phases HFO, Siderite (FeCO_3) and Mackinawite (FeS) for representative Dutch fresh groundwater conditions: Fe^{2+} : 1 $\mu\text{mol/l}$ and 1 mmol/l , alkalinity: 1 meq/l , and SO_4^{2-} : 1 and 0.01 mmol/l . (other redox reactions like NO_3^-/N_2 and $\text{MnO}_2/\text{Mn}^{2+}$ neglected). This diagram was constructed with the help of standard (Gibbs) free energy of formation data as provided by Stumm and Morgan (1996) and for Mackinawite by Rickard and Luther (2007)

pH $\text{Fe}(\text{OH})_2$]. Conditions becoming more reducing, HFO reduction and Siderite precipitation continue, until sulfate reduction starts, and FeS as well as Siderite will precipitate. During further reduction, both reduction processes will continue, until all sulfate

has been reduced. Then, methanogenesis, producing methane, will start together with HFO reduction and Siderite precipitation.

Consequently, under Dutch aquifer conditions, at $\pm 6 < \text{pH} < \pm 8.5$, the maximum concentration of iron(II) in fresh groundwater is a function of pH, governed by the solubility of Siderite, and at $\text{pH} > \pm 8.5$ by $\text{Fe}(\text{OH})_2(\text{s})$, independent of redox conditions. Important conclusions from Fig. 4 are: sulfate reduction occurs only under Siderite saturated conditions (provided sufficient HFO supply), and sulfate reduction is not accompanied by a dip in the concentration of iron(II).

4.2 Geochemical Processes Producing Iron(II)

Figure 5 presents the chemical groundwater profiles, consisting of the concentrations of iron(II), nitrate and sulfate, alkalinity and pH against depth, for the well fields Beerschoten and Klooster, where Beerschoten, like Edese Bos, Havelterberg and Holten, is representative for a geological old, leached, site, poor in reactive soil components, and Klooster, like Culemborg, is representative for a geological young site, from the surface down rich in reactive soil components, like calcite and organic matter, see also Table 2. The chemical profiles of the second sites are presented as Supplemental Information.

The chemical profiles in Fig. 5 show several (chemical) interruptions, for instance, at Beerschoten at 70 and 90 mbs (meters below surface) and at Klooster at 80 mbs, caused by the presence of clay layers.

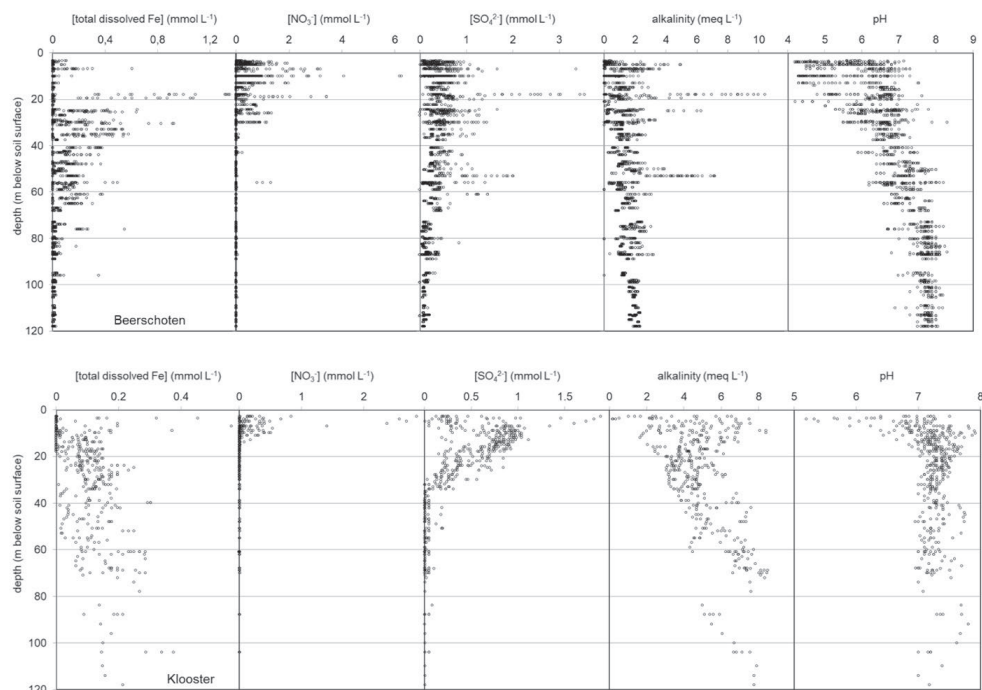


Fig. 5 Concentrations of iron(II), nitrate and sulfate, alkalinity and pH against depth for well fields Beerschoten (upper) and Klooster (lower). Many of the low iron(II), nitrate and sulfate concentrations are actually “ $\frac{1}{2}$ ” values. Beerschoten: the exceptional high concentrations of sulfate and alkalinity are probably caused by polluted sites. Klooster: only data from the mini-screen wells are presented. See Supplemental Information for all other sites

Due to their large difference in stability as function of redox potential, nitrate and iron(II) cannot occur together (Appelo and Postma, 2007). As a result of this mutual exclusion, the infiltration of nitrate containing water into a pyrite containing soil results in a sharp nitrate/iron(II) front. This redox front has been extensively described by a.o. Jessen et al. (2016), Postma et al. (1991), van Beek et al. (1989) and Strebel et al. (1985), but is still matter of debate (Zhang 2012).

As a result of differences in groundwater level and in reactivity of the soil column, the depth of the “nitrate front” varies at Beerschoten from surface to ca. 30 mbs and at Klooster from surface to ca. 10 mbs, while sulfate reaches a depth of at least 70 mbs at Beerschoten and of ca. 30 mbs at Klooster, confirming that at Klooster the aquifer is much more reactive than at Beerschoten.

Beerschoten is representative for old, leached sediments, containing traces (less reactive) organic material and no lime (see Table 2). Between 30 and 70 mbs, there is a minimal decrease in concentration of sulfate, together with a gradual increase in alkalinity over depth. At the same depth (30 mbs) the concentration of iron(II) is maximal, decreasing downwards as the produced iron(II) is precipitated as Siderite by an excess alkalinity increasing with depth. Moreover, produced iron(II) is also precipitated as FeS(s). Apparently, the electron supply rate by oxidation of organic material exceeds the electron uptake rate by reduction of HFO into iron(II), and because sulfate is the next redox species and is readily available, the surplus supply is used by sulfate reduction. According to Fig. 5, the produced alkalinity, iron(II) and sulfide result in the simultaneous precipitation of FeS and of Siderite.

Klooster is a former seepage area, where close to the surface sulfides have been accumulated. As a result of lowering the groundwater level, these sulfides are oxidized into sulfate. Beyond 10 mbs, there is a minimal gradual increase over depth of the concentration of iron(II) and a sharp decrease in the concentration of sulfate. Apparently, here too reduction of HFO and of sulfate occur together, where the produced alkalinity is buffered by Calcite and by Siderite, and the produced dissolved iron(II) is precipitated as Siderite and as FeS(s). During further reduction, the redox potential decreases continuously as well as the sulfate concentration, until all sulfate has been reduced and the redox potential corresponding with methane production is reached. Then, HFO reduction and methane production occur simultaneously. The production of methane is confirmed by its presence in the abstracted groundwater: at Culemborg 6 mg/l and at Klooster 0.6 mg/l.

The simultaneous reduction of HFO and sulfate, and of HFO reduction and methane production, has been described before by Jakobsen and Postma (1999).

4.3 Variation in Iron(II) Concentration

As a result of the continuous reduction of HFO, an increase in concentration of iron(II) with depth would be expected, but at Beerschoten the concentration of iron(II) decreases with depth, and at Klooster increases only very slightly, see Fig. 5. Apparently the concentration of iron(II) is bound to a maximum: the solubility of Siderite, see Fig. 4. Because chemical analyses are not complete, activities cannot be estimated, and the solubility product of Siderite has been approximated by the concentration product, see Table 3:

$$pK_{\text{Siderite}} = -\log K_{\text{Siderite}} \approx -\log [\text{Fe(II)}] - \log [\text{HCO}_3^-] - \text{pH} - \log K_2 \quad (8)$$

where [X] represents the total concentration of X, and K_2 the second dissociation constant of carbonic acid.

Figure 6 shows the value of pK_{Siderite} , estimated according to Eq. (8), as function of depth for the sites Beerschoten and Klooster.

Figure 6 shows that the values estimated for pK_{Siderite} vary near the surface, becoming more and more constant with increasing depth: deeper than 5 à 10 mbs at Klooster, and deeper than 25 à 30 mbs at Beerschoten. These values agree reasonably well with the values of the preceding paragraph. For the relation between pK_{Siderite} and depth for the other well fields, refer to the Supplemental Information.

As the solubility product of Siderite equals $pK_{\text{Siderite}} \approx 10.7$ (Stumm and Morgan 1996), groundwater, at both sites, is apparently super-saturated with respect to Siderite; where super-saturation at the geological “younger” site Klooster is greater than at the geological “older” site Beerschoten. Postma et al. (2007) ascribe the super-saturation with respect to Siderite to the sluggishness of precipitation. Of “our” sites, the presence of Siderite has been experimentally confirmed around well field Klooster (Hartog et al. 2005) and has been reported at other sites in the Netherlands by Huisman (1998), Cirkel et al. (2014), etc.

Reworking of Eq. (8) yields:

$$\log [\text{Fe(II)}] \approx \log \frac{K_{\text{Siderite}}}{[\text{HCO}_3^-]} - \text{pH} - \log K_2 \quad (9)$$

Accordingly, the concentration of iron(II) is a function of pH and the variation in this relationship is caused by the ratio between solubility product of Siderite and concentration of HCO_3^- : by equal relative changes of K_{Siderite} and of $[\text{HCO}_3^-]$, the concentration of iron(II) remains the same.

At $\text{pH} > \pm 8$, the concentration of iron(II) is governed by the solubility of $\text{Fe(OH)}_2(\text{s})$ (Stumm and Morgan 1996), see Table 3:

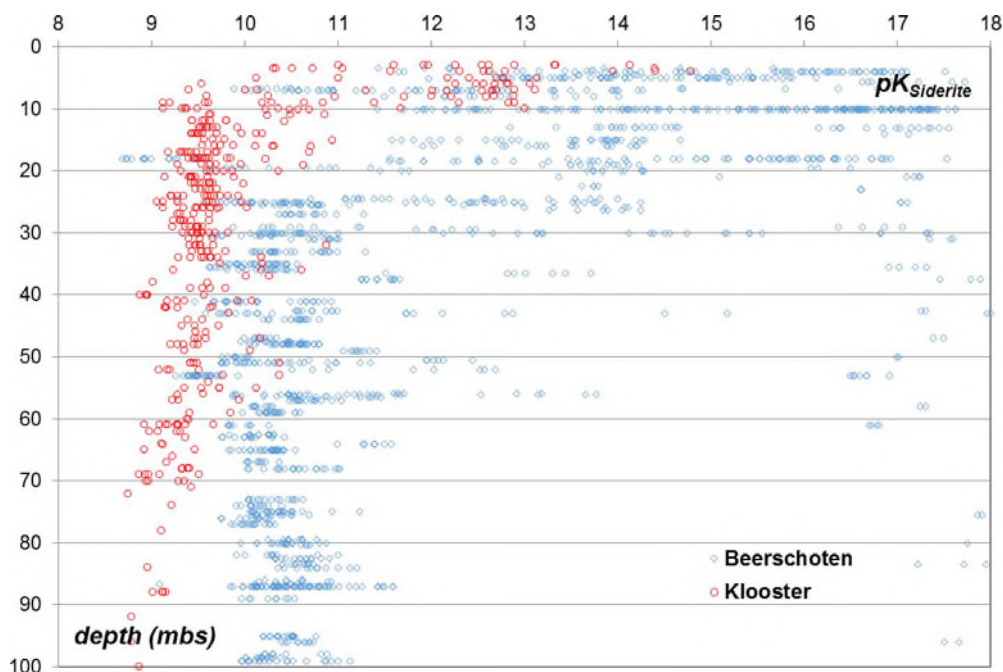


Fig. 6 pK_{Siderite} , approximated by the concentration product, as function of depth for well fields Beerschoten and Klooster

$$\log [\text{Fe(II)}] \approx \log K_{\text{Fe(OH)}_2(\text{s})} K_w^2 - 2\text{pH} \quad (10)$$

with $K_w = (\text{H}^+)(\text{OH}^-)$. Figure 7 shows the concentration of iron(II) as function of pH for all six well fields. From this figure, it appears that observations from a single site, for instance Klooster, do not show the iron(II) concentration–pH relation, but the observations of all sites together do. Many observations of Beerschoten, Culemborg, Holten and Klooster fit within the range of ratios between solubility product of Siderite and alkalinity. The observations of Havelterberg are all undersaturated with respect to Siderite, while the data of Edese Bos seem to fit better the $\text{Fe(OH)}_2(\text{s})$ solubility product.

Figure 1 shows some observations with a low sulfate concentration, not corresponding to saturation with respect to Siderite: apparently the HFO reduction rate here is so slow with respect to the electron supply rate that sulfate reduction already occurs before ground-water is saturated with respect to Siderite.

4.4 Consequences for As and Trace Element Chemistry

The solid phases HFO and iron sulfides are known to contain great amounts of As and trace metals like Co, Ni and Zn (Appelo and Postma 2007), higher than in Siderite en Calcite. Consequently, trace element concentrations in ground water are governed by the same processes governing the concentration of iron(II): supply by oxidation of Pyrite and by reduction of HFO from the one side, and removal by slow (co)precipitation with FeS and with Siderite (and Calcite) from the other side. As organic matter and HFO become more recalcitrant over time, the corresponding oxidation and reduction rates will decrease over time, resulting in an overtime decreasing concentration of As and trace metals.

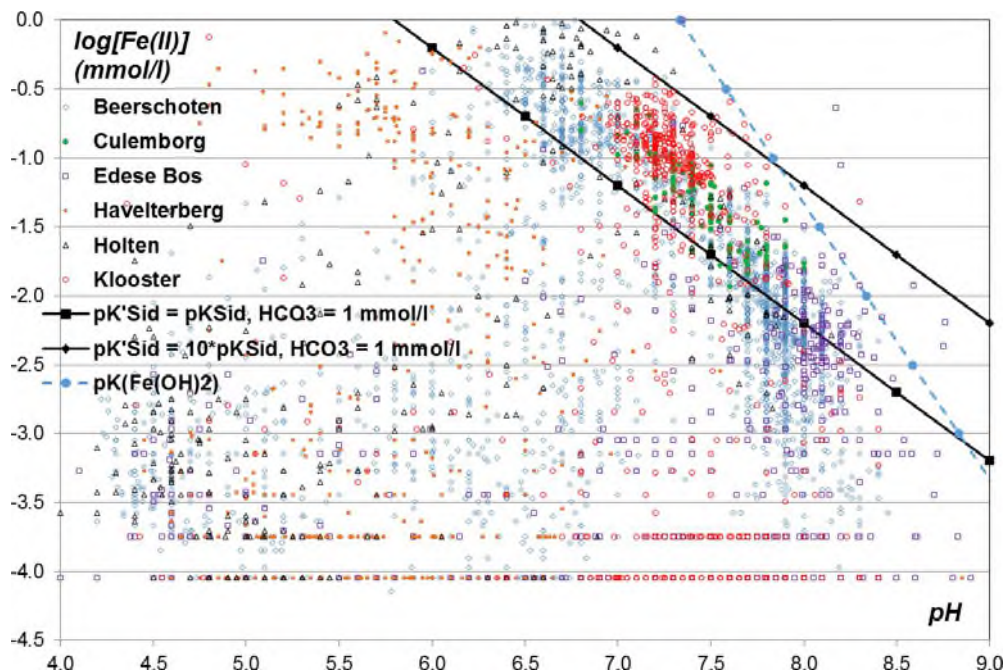


Fig. 7 Concentration of iron(II) as function of pH for all well fields involved

This reasoning was confirmed experimentally by Postma et al. (2016) with regard to the behavior of As: over time a decreasing reduction capacity, resulting in a decreasing HFO reduction rate, together with a slow Siderite precipitation rate, resulting in an overtime decreasing concentration of As in groundwater, in their case intensified by a low concentration of sulfate, resulting in a low co-precipitation of As by iron sulfides.

5 Conclusions

- (1) Under neutral to mildly alkaline conditions ($\pm 6.5 < \text{pH} \pm 8$), the maximum concentration of iron(II) in groundwater is governed by (over)saturation with respect to Siderite [and at high pH ($\text{pH} > \pm 8$) with respect to $\text{Fe}(\text{OH})_2(\text{s})$]. Iron(II) concentrations show some variation due to supersaturation with respect to Siderite, resulting from sluggish precipitation, and due to variation in alkalinity.
- (2) Usually redox processes are presented as a sequence, but HFO reduction and sulfate reduction occur simultaneously, as well as HFO reduction and methane production. Apparently, the electron supply rate by oxidation of organic matter exceeds the electron uptake rate by reduction of HFO, and the excess supply is transferred to reduction of sulfate. After all sulfate has been reduced, HFO reduction and methanogenesis will occur simultaneously.
- (3) As a result of continuous oxidation of organic matter, alkalinity increases with depth. Despite continuous supply of iron(II) as a result of HFO reduction, the concentration of iron(II) decreases (or remains constant) over depth due to precipitation as Siderite.
- (4) Over time, organic matter and HFO are becoming more recalcitrant, resulting in decreasing organic matter oxidation and HFO reduction rates. Because the reduction rate of sulfate is governed by the difference between these both rates, the sulfate reduction rate is decreasing over time too.
- (5) HFO and iron sulfides may contain high contents of As and of trace metals like Co, Ni and Zn, and Siderite lower contents. This makes the behavior of these precipitates relevant for the actual concentration of these trace elements in groundwater.

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Concentration of iron(II)

1 CONCENTRATION OF IRON(II) IN FRESH GROUNDWATER

2 CONTROLLED BY SIDERITE, FIELD EVIDENCE.

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6

7 SUPPLEMENTAL INFORMATION

8 1. LOCATION MONITORING WELLS

9 The location of the monitoring wells around the well fields Culemborg (upper left), Edese

10 Bos (upper right, Havelterberg (lower left), and Holten (lower right) is shown below.

11



12

Iron(II) in Dutch fresh groundwaters

1

2020 November

Concentration of iron(II)

13 *Figure S1: Location of the groundwater monitor-wells around well fields Culemborg, Edese Bos,*
 14 *Havelterberg and Holten.*

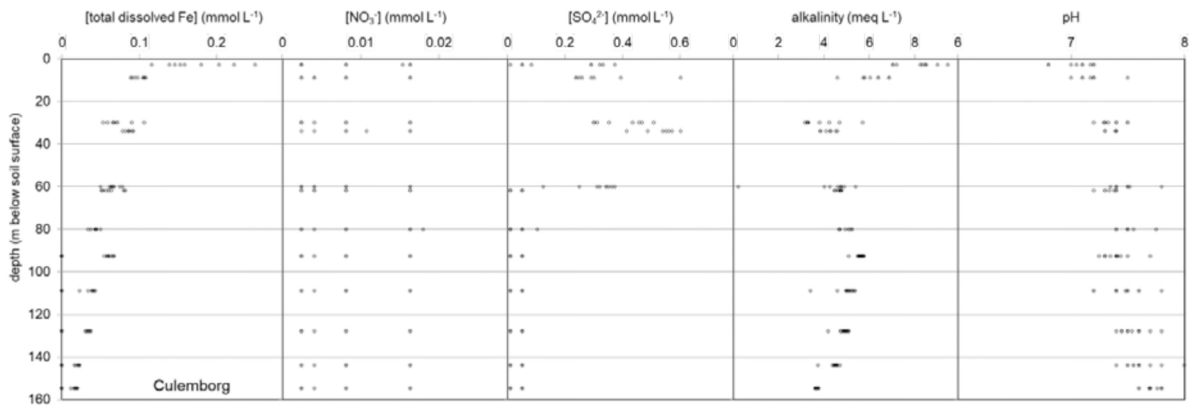
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16 **2. DEPTH PROFILES CHEMICAL COMPOSITION**

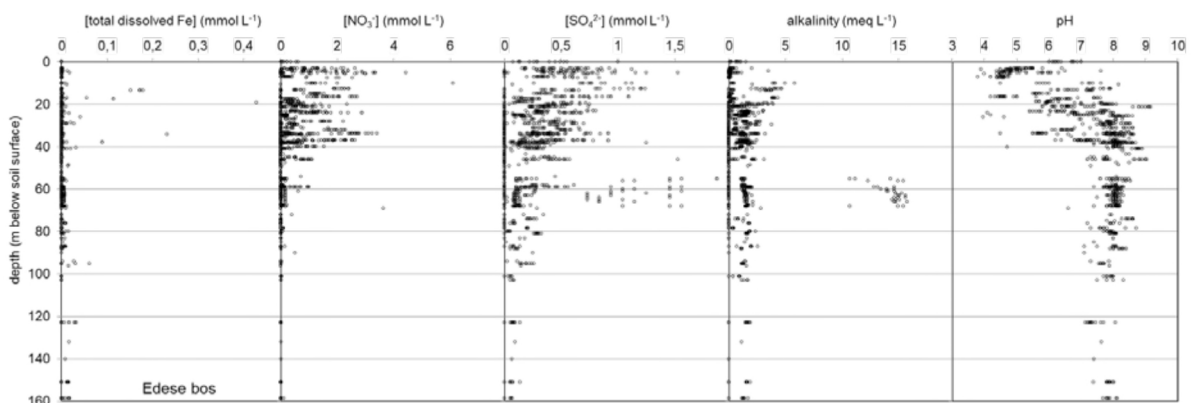
17 Concentrations of iron(II), nitrate and sulfate, alkalinity and pH as function of depth in the
 18 monitoring wells around the well fields Culemborg, Edese Bos, Havelterberg and Holten
 19 respectively is shown below.

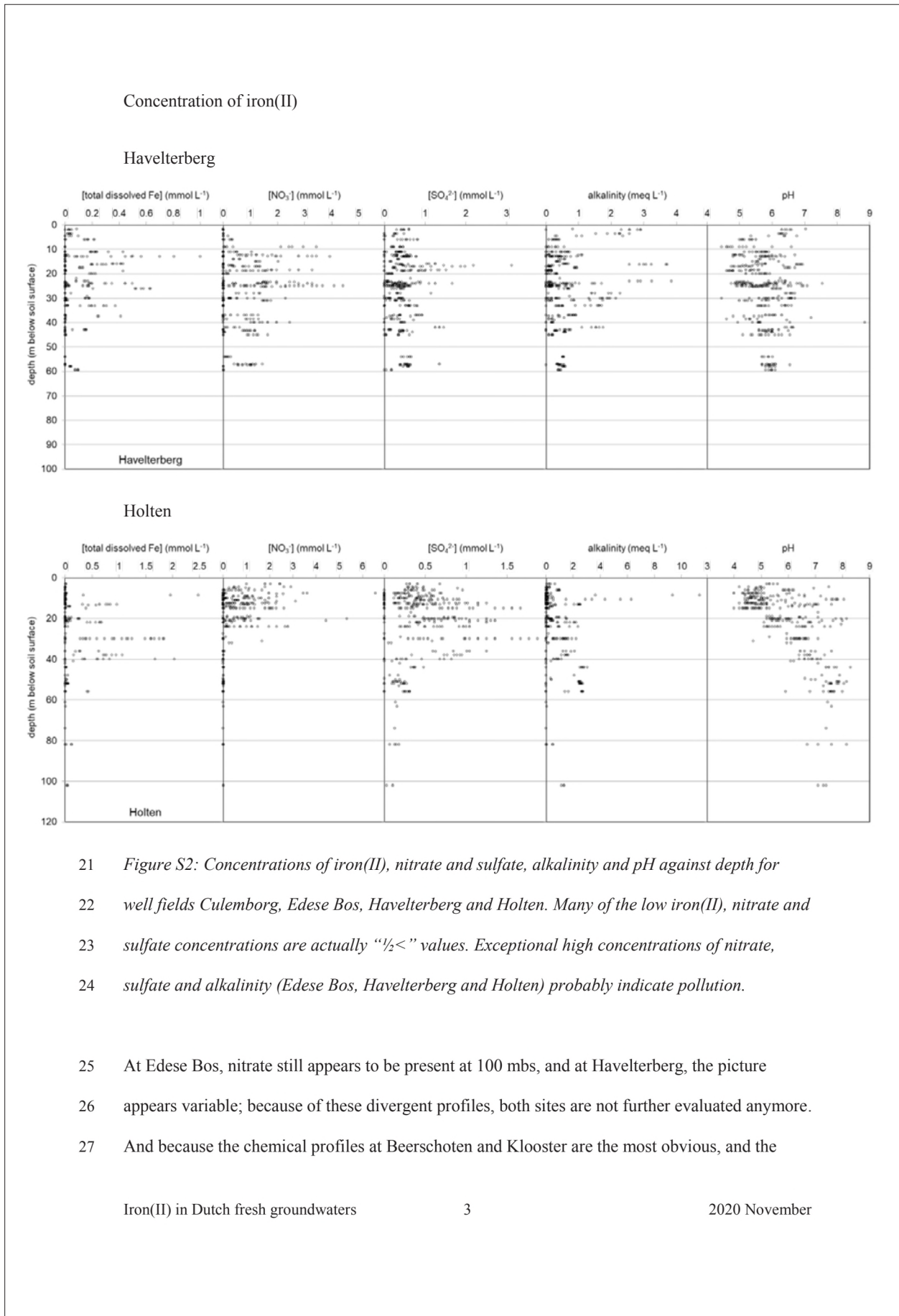
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Culemborg



Edese Bos





Concentration of iron(II)

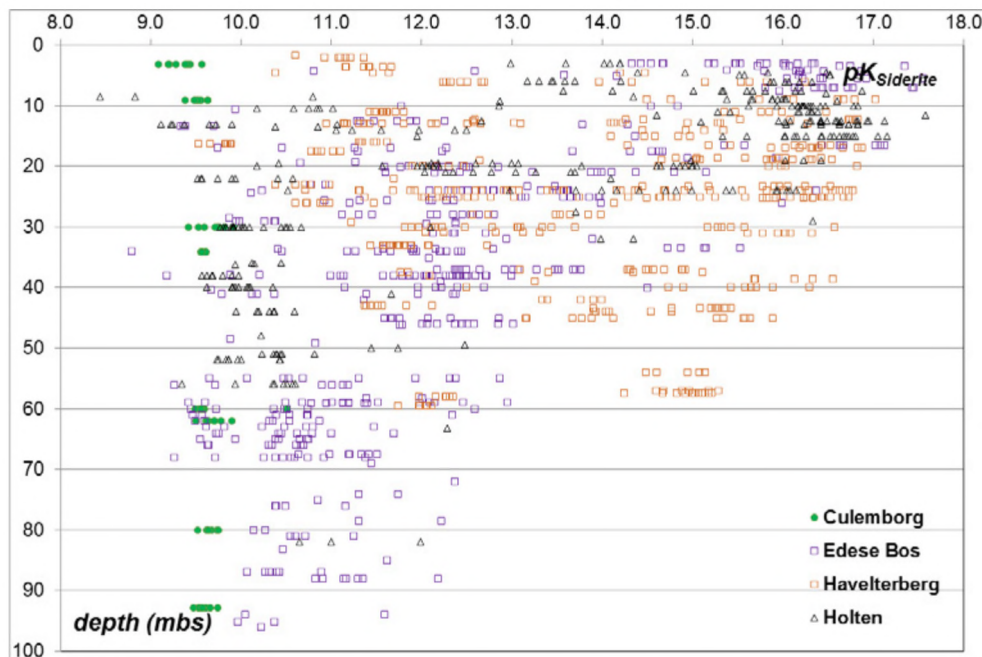
28 profile of Culemborg is comparable with Klooster, and the profile of Holten with Beerschoten,
29 only the sites Beerschoten and Klooster are discussed in detail.

30

31 **3. SOLUBILITY-PRODUCT OF SIDERITE AS FUNCTION OF DEPTH**

32 The Figure below shows the solubility product of Siderite as function of depth for the remaining
33 sites. From this Figure it may be derived that Culemborg over its whole depth is saturated with
34 respect to Siderite, Edese Bos only at greater depth, Havelterberg not, while Holten shows a wide
35 range: some sites saturated, and many shallow sites very unsaturated.

36



37

38 *Figure S3: $pK_{Siderite}$ approximated as the concentration product, as function of depth for well*
39 *fields Culemborg, Edese Bos, Havelterberg and Holten.*

Drinking water treatment and chemical well clogging by iron(II) oxidation and hydrous ferric oxide (HFO) precipitation

C. G. E. M. van Beek, C. H. M. Hofman-Caris and G. J. Zweere

ABSTRACT

Removal of iron(II) from groundwater by aeration and rapid sand filtration (RSF) with the accompanying production of drinking water sludge in the preparation of drinking water from groundwater, and chemical well clogging by accumulation of hydrous ferric oxide (HFO) precipitates and biomass after mixing of oxygen containing and of iron(II) containing groundwater, are identical processes. Iron(II) may precipitate from (ground)water by homogeneous, heterogeneous and/or biological oxidation, where the contribution of these processes, and thus the characteristics of the corresponding HFO precipitates, is a function of pH and process-conditions. Under current conditions in drinking water treatment, homogeneous oxidation dominates above $\text{pH} \approx 7.75$, and heterogeneous and biological oxidation below this value. In chemical well clogging, this transition occurs at $\text{pH} \approx 7.0$. This information is relevant for the optimization of removal of iron(II) from groundwater by aeration and RSF and the corresponding quality of the produced drinking water sludge, and for the operation of wells clogging by accumulation of HFO precipitates and biomass.

Key words | aeration, chemical well clogging by accumulation of hydrous ferric oxide (HFO), drinking water production from groundwater, homogeneous, heterogeneous and biological oxidation of iron(II), rapid sand filtration (RSF)

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HIGHLIGHTS

- Removal of iron(II) by aeration and rapid sand filtration (RSF) in drinking water treatment and accumulation of hydrous ferric oxides (HFOs) and biomass in chemical well clogging are identical processes.
- Consequently, information and experiences gained in the one field may be compared and applied in the other field and vice versa.
- This information is helpful in optimization of the drinking water treatment process and of the quality of the produced HFO-sludge.

ABBREVIATIONS

AMD	Acid mine drainage	FeOB	Iron(II) oxidizing bacteria
Fet	Total (divalent and trivalent) (dissolved and solid) iron concentration	HFO	Hydrous ferric oxide
Fe(II)	Total divalent iron concentration	RSF	Rapid sand filtration
FeAC	Iron(II) adsorption capacity	SIR	Subsoil iron removal

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INTRODUCTION

In the Netherlands (Western Europe) drinking water distributed by water utilities may contain not more than 0.2 mg/l total iron. This standard has been decreased by the water utilities to 0.05 mg/l, and even 0.02 mg/l. About two-thirds of the drinking water in the Netherlands is prepared from groundwater, abstracted at somewhat more than 200 well-fields from alluvial sediments at depths between 25 to 150 m. As the abstracted groundwater may contain up to circa 25 mg/l iron(II), removal of iron(II) is a relevant item. Usually, iron(II) is removed by aeration, producing hydrous ferric oxide (HFO) precipitates, which are removed by rapid sand filtration (RSF). The same applies to manganese(II). After removal of iron and manganese, this water is distributed as drinking water. About 10% of the plants need additional treatment for removal of DOC/color, and many more for pH/hardness correction. For extensive information see Gimbel *et al.* (2004) and Sommerfeld (1999).

In the Netherlands, about a third of the number of well fields, abstracted groundwater consists of a mixture of iron(II) as well as oxygen containing water (Supplementary material, Figure A1). In such waters HFOs will precipitate, resulting in clogging of these wells and raw water lines. For extensive information see Houben & Treskatis (2012), Smith & Comeskey (2010) and Tyrrel & Howsam (1994).

Removal of iron(II) by aeration and RSF, and chemical clogging of wells by accumulation of HFOs and biomass are identical chemical/biological processes occurring under very different conditions. Here both processes will be compared mutually and with physical-chemical and microbiological information. The purpose of this review is to arrive at a clear understanding of the relevant processes, elucidate, and if possible remedy eventual problems, and apply experiences from the preparation of drinking water on the occurrence of chemical well clogging and vice versa.

OXIDATION OF IRON(II) BY OXYGEN

Dissolved iron(II) may be oxidized by oxygen by three processes, i.e. homogeneous, heterogeneous and biological

oxidation (Supplementary material, section C), producing HFO precipitates:

$$\frac{d}{dt}[\text{Fe(II)}] = \frac{d}{dt}[\text{Fe(II)}]_{\text{homo}} + \frac{d}{dt}[\text{Fe(II)}]_{\text{hetero}} + \frac{d}{dt}[\text{Fe(II)}]_{\text{biol}} \quad (1)$$

This combination of processes occurs everywhere where dissolved iron(II) and oxygen mix: in nature (groundwater-seeps), in preparation of drinking water from groundwater by aeration and RSF, in wells clogging by abstraction of a mixture of oxygen containing and of iron(II)-containing water, etc. The contributions of the various iron(II) oxidizing processes in Equation (1) depends on the circumstances.

In homogeneous oxidation, iron(II) as well as oxygen are present in solution, producing HFO-flocs. The accompanying rate-equation reads (Stumm & Morgan 1996):

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

with k_{homo} rate-constant, [Fe(II)] and [O₂] concentrations of iron(II) and oxygen, and t time. Assuming constant concentration of oxygen and constant pH, Equation (3) is obtained:

$$[\text{Fe(II)}] = [\text{Fe(II)}]_0 \exp\left(-k_{\text{homo}} \frac{[\text{O}_2]}{(\text{H}^+)^2} t\right) \quad (3)$$

with [Fe(II)]₀ and [Fe(II)] as initial and actual concentration of iron(II). Under favorable conditions (high pH, oxygen saturation) this is a fast process (Supplementary material, section C) producing large HFO flocs; under unfavorable conditions small flocs, which may pass the sand-filter and enter the drinking-water distribution-system, and after back washing hardly will settle down in the sludge basin.

Heterogeneous oxidation of iron(II) by oxygen is a two stage process: first adsorption of iron(II) by HFO surfaces, and subsequently oxidation of adsorbed iron(II) by oxygen. The accompanying rate-equation, somewhat modified after Tamura *et al.* (1976), may be represented as:

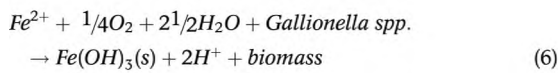
$$\frac{d}{dt}[\text{Fe(II)}] = -k_{\text{hetero}} \frac{[\text{Fe(II)}][\text{O}_2]}{(\text{H}^+)} \text{FeAC} \quad (4)$$

with FeAC as the iron(II) adsorption capacity of HFO, which is a function of pH and HFO mineralogy (Schwertmann & Fechter 1982). Solution of (4) at constant oxygen concentration, pH and adsorption-capacity yields:

$$[Fe(II)] = [Fe(II)]_0 \exp\left(-k_{hetero} \frac{[O_2]FeAC}{(H^+)} t\right) \quad (5)$$

This relation has been experimentally confirmed by, among others Demir & Tufekci (2002), Tufekci *et al.* (2000) and Dietz & Dempsey (2017): the higher the pH and the more HFO-sludge present (the greater the surface area), the faster the oxidation. Subsoil iron removal (SIR) is based on this process (van Beek 1985).

In the oxidation of iron(II), (a small amount of) energy is produced, which may be used by neutrophilic iron(II) oxidizing bacteria (FeOB):



Gallionella spp. completely depend on this process for their energy supply, while others, like *Leptothrix* spp., in the (near) absence of iron(II) or oxygen may switch to another chemical process/energy source (Kappler *et al.* 2015). Until recently, it was assumed that *Gallionella* spp. especially occur in acidic micro-aerophilic environments, but recently it has been demonstrated that they play an important role in the removal of iron(II) under neutral oxygen-rich conditions (Hanert 2006; de Vet *et al.* 2011; Eggerichs *et al.* 2014; Wullings 2016).

Gallionella spp. excrete the produced HFOs, covered by 'extracellular polymeric substances' (EPS), in twisted stalks (spirals), characteristic for *Gallionella*, as amorphous HFO, Ferrihydrite, Lepidocrocite or Akaganeite (Chan *et al.* 2011). These biologically produced HFO precipitates serve as a substrate for further heterogeneous oxidation of iron(II) (Chan *et al.* 2011; Melton *et al.* 2014; Wang *et al.* 2014), in some way preventing encapsulation of FeOB by these precipitates. Bruins (2016) demonstrated the same phenomenon for manganese removal by oxidation and RSF: initially biological oxidation, after some time followed by heterogeneous oxidation.

DISTRIBUTION OF IRON(II) OXIDATION PROCESSES AS FUNCTION OF PH

A rough distribution of the various iron(II) oxidizing processes as a function of pH may be obtained in water treatment, as processes here are designed for ease of study. The contribution of homogeneous oxidation may be estimated by calculation (van Beek *et al.* 2016), of heterogeneous oxidation from bed-height growth, and of homogeneous and heterogeneous oxidation from back-washing. The complement is ascribed to biological oxidation. However, de Vet *et al.* (2011) was able to arrive at correct global estimates between two consecutive back-washings (van Beek *et al.* 2016).

Bed-height growth

As a result of heterogeneous oxidation of iron(II), the grains of the sand filter will grow, increasing the height of the filter bed (van Beek *et al.* 2016). As homogeneous and biological oxidation will not or negligibly contribute to bed-height-growth, the contribution of heterogeneous iron(II) oxidation may be estimated from this increase as the product of bed-height-growth, and density and iron content of this iron-precipitate. Due to mutual friction of the grains during back-washing, a part of the HFO precipitates will be removed. Comparison of this calculated value with the iron load of the sand-filter, yields a (relative) minimum contribution of heterogeneous oxidation. Disturbance of the bed-height-growth rate by leaching of filter sand during back washing, or supply of sand by sand-delivering wells is not considered here.

Figure 1 shows the calculated bed-height-growth-rate as a function of bed load for various relative contributions of heterogeneous iron(II) oxidation (van Beek *et al.* 2016). The observed values for the bed-height-growth-rate will be lower than the maximum calculated values: next to heterogeneous oxidation also homogeneous and biological oxidation of iron(II) may occur, and during back washing abrasion of the 'coated' grains results in the release of iron-sludge, which will be carried off.

Figure 1 shows high relative contributions of heterogeneous oxidation (25 to 90%) at high loads, and low

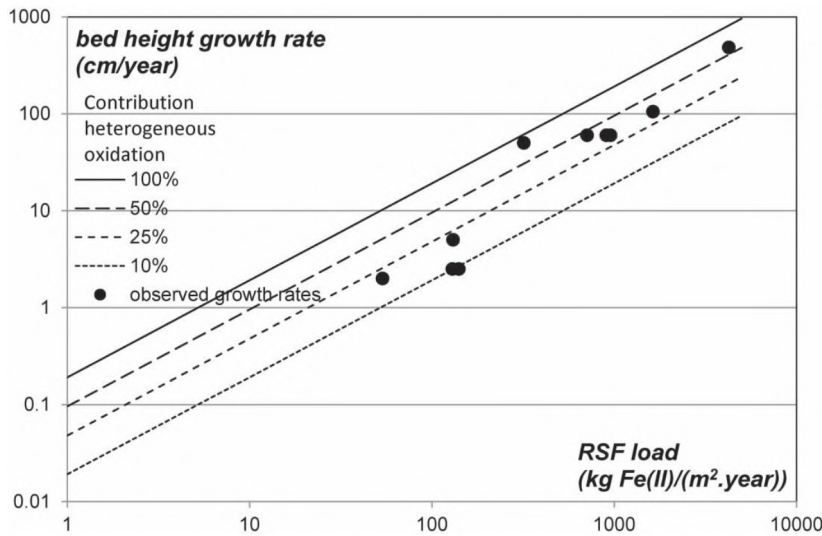


Figure 1 | Calculated bed-height-growth-rate, in cm/year, as function of bed load, in kg Fe(II)/(m²·year), for various relative contributions by heterogeneous oxidation. A bed-height-growth-rate of 10 cm/year and a bed-load of 100 kg Fe(II)/(m²·year) compare with a contribution by heterogeneous oxidation of (minimal) 50%. Applied values: volume density of the accretion: 1.22 kg dry matter/l, and iron content of the accretion: 0.428 kg Fe/kg dry matter. Data provided by several drinking water utilities.

relative contributions (10 to 25%) at low loads: high loads are treated in open basins, which are easy to clean, and low loads in closed vessels, which are hard to clean.

Back-washing

Information about the contributions of the various oxidation processes may also be obtained from back-washing of sand-filters. Figure 2 shows the results of such experiments of well-field ‘Holten’ (pH after filtration ca. 6.3), and of well-field ‘Manderveen’ (pH after filtration ca. 8).

By back washing, all HFOs, precipitated during the preceding filtration period by homogeneous oxidation (in the supernatant water and accumulated upon the top of the sand filter), will be removed with minimal effort, see well-field Manderveen. At well-field Holten, with heterogeneous and biological oxidation, not all HFOs, accumulated during the preceding filtration period, could be removed, even not with more extensive backwashing procedures (involving higher flow rates, longer back washing times or a combination of water and air). The remaining part is considered the minimum contribution by heterogeneous oxidation.

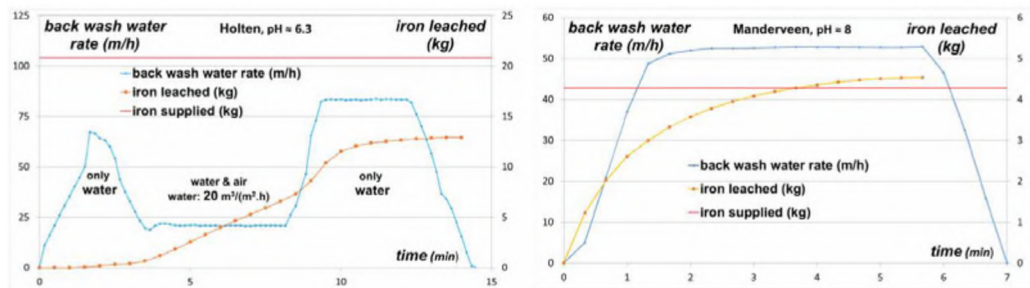


Figure 2 | Amount of iron (kg) removed by back-washing, compared with the amount accumulated during the preceding filtration period. Left: well-field Holten (iron concentration in abstracted groundwater: 3–8 mg/l, pH effluent 6.2–6.3). Right: well-field Manderveen (iron: 0.7–0.9 mg/l, pH effluent 7.9–8.0), both operated by water utility Vitens.

Figure 3 shows the contribution of the oxidation processes distinguished in the removal of iron(II) by aeration and RSF (augmented after van Beek *et al.* 2016) as a function of pH. In Figure 3, the contribution by homogeneous oxidation has been calculated from the residence time in the supernatant water, or estimated from back-wash experiments (Manderveen). At none of the well fields a complete removal was estimated, which may be explained by a too low value of the reaction-constant, or the removal of the last traces of iron(II) in the top of the sand-filter. Due to the small surface area (the sides and the bottom of the water-volume on top of the sand-filter, versus the grains of the sand-filter) resulting in a few attachment possibilities, and the low concentration of iron(II), the contribution of biological oxidation is considered negligible.

The contribution of heterogeneous oxidation of iron(II) has been estimated from the bed-height-growth and from back-wash experiments. Both ways of estimation are by definition too low, as back-washing will remove an unknown part of the HFO precipitates. The remaining part of

iron(II) has been removed by biological oxidation. Apparently, *Gallionella* spp. is able to survive backwashing (in the sand-filter, in the air-sprayers?).

Notice in Figure 3 the distinction between homogeneous oxidation of iron(II) by oxygen at $\text{pH} > \text{ca. } 7.75$ and heterogeneous and biological oxidation at $\text{pH} < \text{ca. } 7.75$.

The presence of water on top of the sand-filter serves two different goals: a thick layer of water at 'high' pH serving as a reaction volume for homogeneous oxidation, and a thin layer at 'low' pH facilitating a uniform distribution of water over the filter-surface.

The contributions of heterogeneous and of biological oxidation may be manipulated: the lower the filter velocity, the greater the contribution of biological oxidation (van Beek *et al.* 2016); the lower the pH, the lower the adsorption capacity of HFOs for iron(II) and the lower the contribution of heterogeneous oxidation; the less frequent and the less rough back washing, the less the loss of FeOB and the greater the contribution of biological oxidation, etc. In

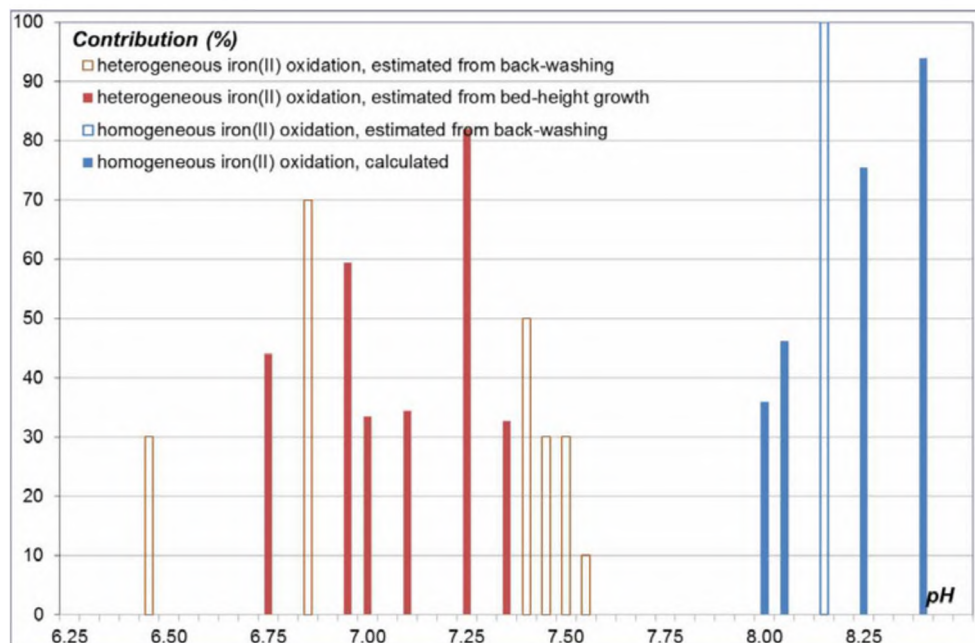


Figure 3 | Distribution of iron(II) oxidation processes in the removal of iron(II) by aeration and RSF as function of pH (extended after van Beek *et al.* 2016). The values for heterogeneous oxidation are by definition too low; the phenomenon 'bed height growth' is relevant.

order to prevent agglomeration of filter-sand, (and to prevent the filter bed exceeding the sand-vessel,) regular back washing is necessary. In order to avoid competition with heterogeneous oxidation of iron(II) as much as possible, biological oxidation of iron(II) will predominantly occur on and just below the top of the sand-filter, as there competition with heterogeneous oxidation will be minimal.

Well clogging by accumulation of HFO precipitates and biomass

Wells, abstracting a mixture of iron(II)- and of oxygen containing groundwater (Supplementary material, sections A and B), will clog by accumulation of HFO precipitates, whether or not together with accumulation of biomass consisting of *Gallionella* spp. Figure 4(a) shows schematically a sand-filter. Due to the unfavorable conditions for biological and heterogeneous oxidation, in the supernatant water almost only homogeneous oxidation of iron(II) will occur.

Figure 4(b) schematically shows the occurrence of chemical well clogging by accumulation of HFO precipitates and biomass. Comparison of Figure 4(a) and 4(b) demonstrates

that conditions in a clogging well are far more comparable with those in the supernatant water of the sand-filter than those in the sand filter itself (small versus large surface area for precipitation of HFOs and for attachment of *Gallionella* spp.). Consequently, in chemical well clogging conditions are much more favorable for homogeneous oxidation than for heterogeneous and biological oxidation (however not optimal, because in chemical well clogging the abstracted groundwater cannot be saturated with respect to oxygen). The HFO flocs, precipitated as a result of homogeneous oxidation, which cannot or hardly attach on surfaces, will accumulate in the (long) raw-water lines, over time resulting in ever smaller effective diameters of these lines, and consequently ever smaller yields, see Figure 5 (van Beek 2018). Burté *et al.* (2019) present a fine example of a heat extraction system: no clogging of the abstraction well, but accumulation of HFO deposits in the waterlines and clogging of the infiltration well. During periods of rest, homogeneous oxidation of iron(II) will continue: small HFO flocs precipitated during these periods may accumulate inside the well, and may, in the presence of a (small) hydraulic gradient over the height of the well-screen, leave the well and accumulate in the

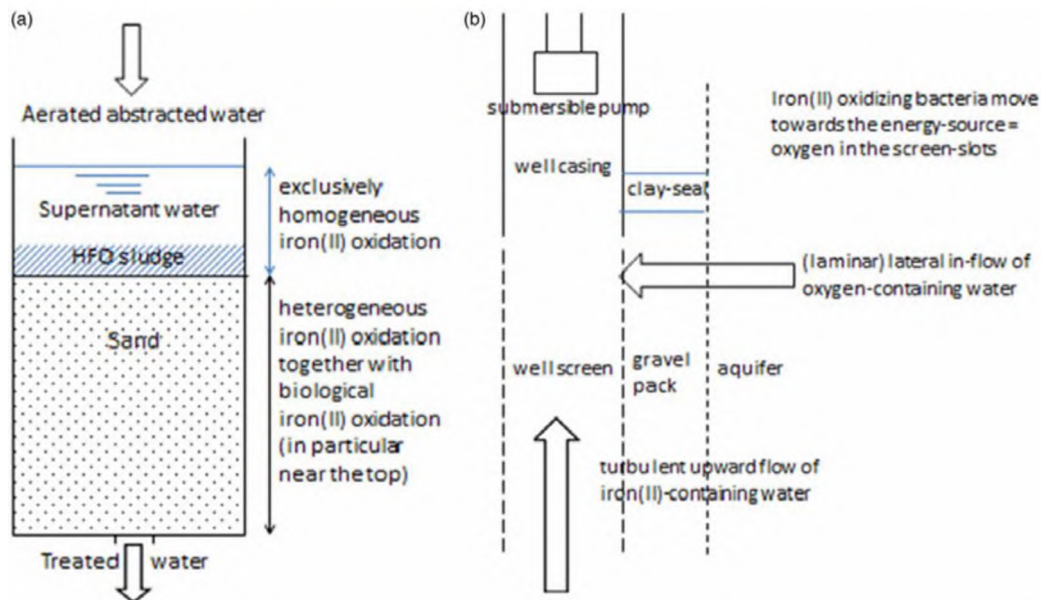


Figure 4 | (a) (left): Longitudinal section through a sand-filter and (b) (right): longitudinal section through a well suffering chemical well clogging resulting from abstracting a mixture of (deep) iron(II) containing and (shallow) oxygen containing water (not to scale).

screen slots, gravel pack, well bore and further away in the aquifer (Houben & Weihe 2010; van Beek 2018).

With decreasing pH, conditions for homogeneous oxidation become less favorable, whereas both heterogeneous and biological oxidation are favored. *Gallionella* spp. will look for the most favorable conditions (energy source): the slots of the well-screen, along which oxygen-containing groundwater enters the well (similar to the accumulation of chemical precipitates and biomass around ‘deep sea vents’). The accumulation of biomass and HFO precipitates, and thus clogging of (the slots of) the well-screen will start where oxygen containing water enters the well (boundary layer oxygen-containing and iron(II)-containing water), and subsequently extend in the downstream as well as slowly in the upstream direction, causing well-screen and well-head clogging, see Figure 5. Over time, the well-screen will become clogged more and more, obstructing the inflow more and more, resulting in an increasingly

deeper water level inside the well, in the end ceasing production, if not rehabilitated in time.

DISCUSSION

Substitution of Equations (2) and (4) into (1) yields:

$$\begin{aligned} \frac{d}{dt}[Fe(II)] = & -k_{homo} \frac{[Fe(II)][O_2]}{(H^+)^2} \\ & - k_{hetero} \frac{[Fe(II)][O_2]}{(H^+)} FeAC(pH) \\ & + \frac{d}{dt}[Fe(II)]_{biol} \end{aligned} \quad (7)$$

Figure 6 shows the homogeneous oxidation rate of iron(II) by oxygen as a function of pH for three concentrations of iron(II) together with the heterogeneous oxidation rate for various values of the iron(II) adsorption

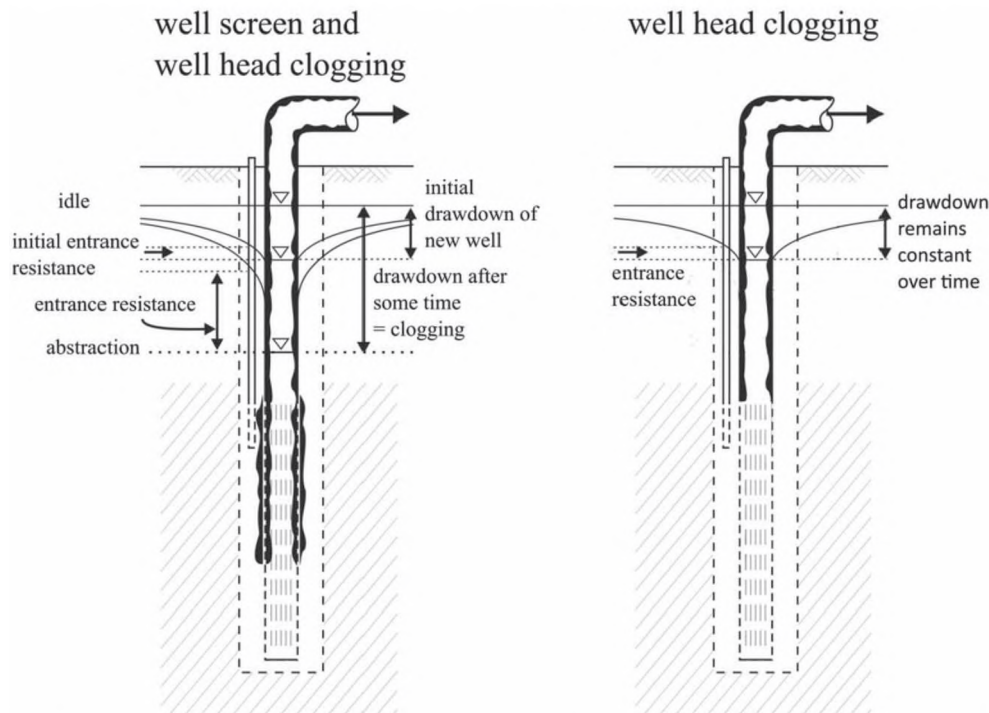


Figure 5 | Difference between well-head and well screen clogging (left) and only well-head clogging (right). In well-head clogging the well casing, the submersible pump (not represented here), but in particular the raw-water lines are covered/clogged by HFO precipitates, resulting in an ever decreasing yield; in well-screen clogging the clogging of the screen becomes ever more serious, until the well ceases to deliver water.

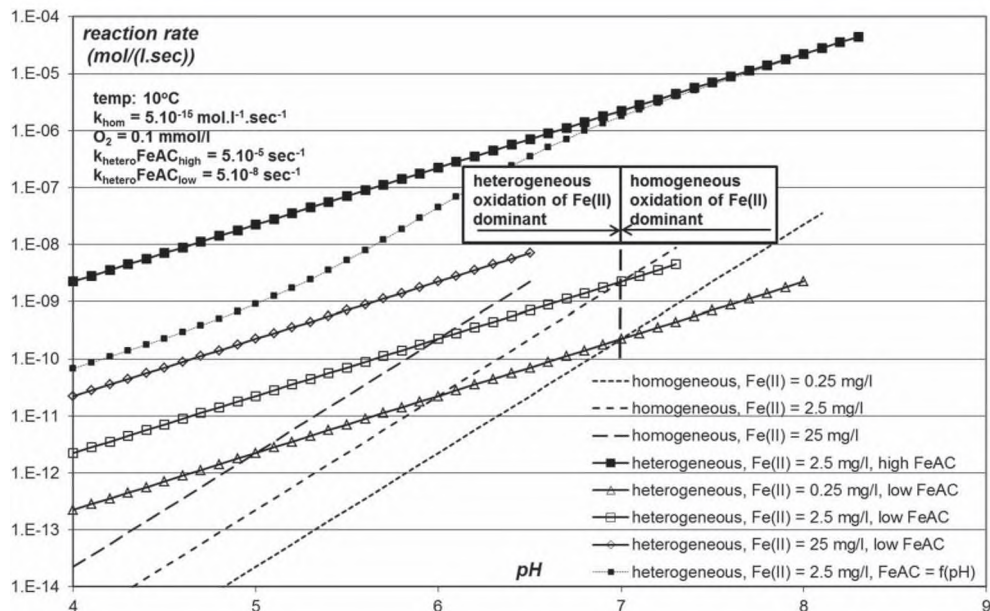


Figure 6 | Reaction rate as a function of pH for homogeneous and for heterogeneous oxidation of iron(II) by oxygen for various concentrations of iron(II) and for various iron(II) adsorption capacities. Values applied: $k_{\text{homo}} = 5.10^{-15} \text{ mol.l}^{-1}.\text{sec}^{-1}$, and $k_{\text{hetero-FeAC}}$: respectively 5.10^{-8} (chemical well clogging) and $5.10^{-6} \text{ sec}^{-1}$ (RSF), in such a way that heterogeneous and homogeneous oxidation occur next to each other as function of pH.

capacity (FeAC). Figure 6 demonstrates that for low values of FeAC, as in chemical well clogging, homogeneous and heterogeneous oxidation of iron(II) occur next to each other as function of pH: homogeneous oxidation at 'high' pH (in Figure 6: $\text{pH} > 7$), and heterogeneous oxidation at 'low' pH (in Figure 6: $\text{pH} < 7$). This distribution provides an elegant explanation for the occurrence of both clogging phenomena: well-head clogging by homogeneous oxidation if $\text{pH} > 7$, and well-screen (and also, to a lesser extent, well-head) clogging by heterogeneous and biological oxidation if $\text{pH} < 7$ (van Beek 2018).

Figure 6 also shows the heterogeneous iron(II) oxidation rate for a high value of the FeAC, representative for RSF, and, as the negative charge of HFO's increases with increasing pH, also for a pH-dependent value of the FeAC (Dempsey *et al.* 2012). Under these conditions, over the whole pH-range, heterogeneous oxidation of iron(II) is dominant over homogeneous oxidation.

Because the reaction rates of homogeneous and of heterogeneous oxidation increase with increasing pH,

conditions for *Gallionella* spp. are most favorable at low pH, see Figure 6.

Conditions for biological oxidation are even becoming more unfavorable with increasing pH due to a concomitant decreasing concentration of iron(II) (Supplementary material, section A).

Figure 6 also shows that for lower FeAC values, the dominant iron(II) oxidation process in particular is a function of pH, and to a lesser extent of the concentrations of iron(II) and of oxygen: at high pH the occurrence of homogeneous oxidation of iron(II) is dominant, at neutral pH of heterogeneous oxidation and at low pH of biological oxidation by *Gallionella* spp., moreover favored by a high iron(II) concentration. This distribution is in line with the distribution demonstrated by Dempsey *et al.* (2012) and by Kirby & Kostak (2002): at low pH HFO's still have some negative charge and some heterogeneous oxidation will occur, advantageously utilized in the treatment of acid mine drainage (AMD). Minimum pH values with respect to the removal of iron(II) in the treatment of drinking

water by aeration and RSF are presented by Czekalla (1997): pH = 6.0, and later a value of pH = 5.5 (Czekalla 2008).

This distribution of iron(II) oxidation processes as a function of pH is in line with the experimentally observed distribution in the removal of iron(II) from groundwater by aeration and RSF, see Figure 3: homogeneous oxidation of iron(II) if pH >7.75, and heterogeneous and biological oxidation of iron(II) if pH <7.75. The same distribution appears present in the occurrence of chemical well clogging, see Figure 7: if pH >7: homogeneous oxidation of iron(II) resulting mainly in well-head clogging (van Beek 2018), and if pH <7: heterogeneous and biological oxidation, resulting mainly in well-screen clogging, where the contributions of heterogeneous and of biological oxidation will cross each other as function of pH. Besides pH and concentrations of oxygen and of iron(II) also other parameters are relevant with respect to this distribution: growth conditions for *Gallionella* spp. (adequate supply of nutrients), well operation (pump capacity,

operation hours/year), well maintenance (well rehabilitation: method and frequency), etc.

If the abstracted groundwater besides iron(II) contains no oxygen, chemical well clogging will not occur; and if the abstracted groundwater contains oxygen but the concentration of iron(II) is below ca. 0.02 mg/l, there will be some, but hardly relevant well clogging.

CONCLUSIONS

In the removal of iron(II) in the production of drinking water from groundwater by aeration and RSF and in the occurrence of chemical well clogging by accumulation of HFOs and biomass, identical iron(II) oxidation processes are active: homogeneous, heterogeneous and biological oxidation, but under very different conditions. Which oxidation process dominates is determined by chemical (pH, O₂ concentration), physical (specific surface area) and operational

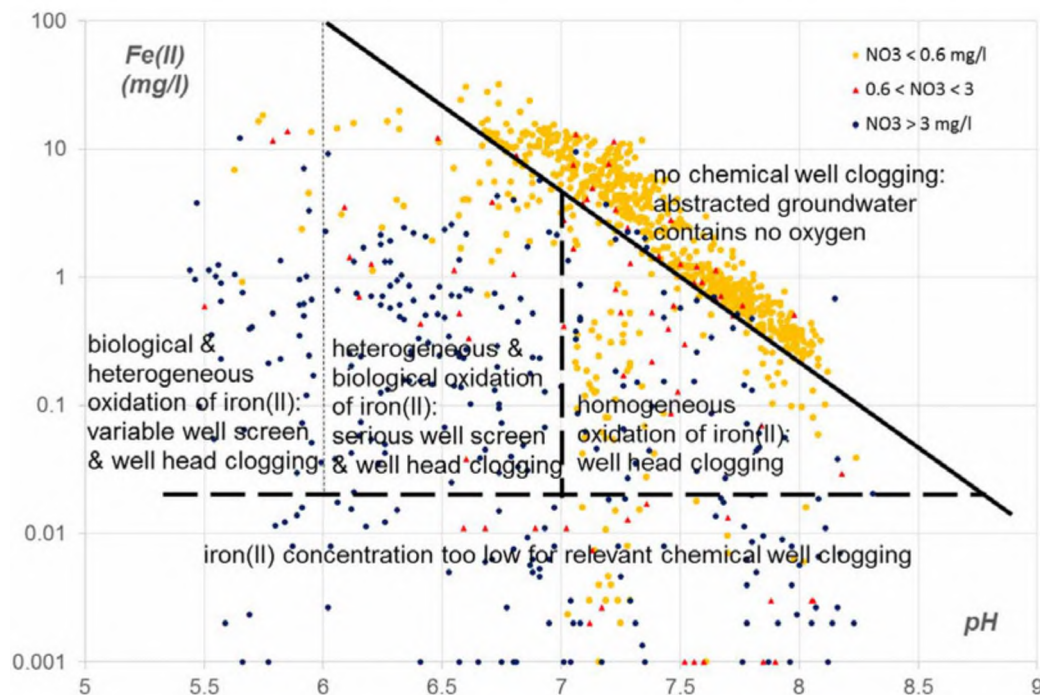


Figure 7 | Preliminary classification for the occurrence of chemical well clogging by accumulation of HFO precipitates and biomass as function of pH, iron(II) concentration, and presence of nitrate (oxygen, Supplementary material, section A) in groundwater abstracted by 1186 wells operated by water utility Vitens.

(flow velocity, continuous vs. intermittent operation) conditions, and may be, within limits, manipulated. Obviously, there are more options for process-optimization in drinking water treatment than in well clogging: flow direction, method of back-washing, volume of 'supernatant water', etc. Under current conditions the boundary pH between on the one hand homogeneous oxidation, and on the other hand heterogeneous and biological oxidation of iron(II) equals for drinking water treatment $\text{pH} \approx 7.75$ and for chemical well clogging $\text{pH} \approx 7$. The oxidation/precipitation process also governs the characteristics and properties of the HFO precipitates and the contribution of biomass, and consequently of the drinking water sludge and of the clogging material (HFO particle size, HFO floc size, ratio inorganic/organic material).

Many of the phenomena described, as bed-height-growth, differences in back washing of sand-filters, passage of HFO particles, presence of *Gallionella* spp. in sand-filters and in clogging wells, etc., are well known. Making these phenomena quantitative, as a function of pH and also of concentration of oxygen, will result in a better understanding and thus in a more efficient operation.

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Dirk Vries (KWR Water Research) and Koen Huysman (PIDPA) are acknowledged for commenting on an earlier draft of this paper. Two anonymous reviewers suggested considerable improvements.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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Well-screen and well-head clogging by hydrous ferric oxides

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Abstract

In the production of drinking water from groundwater by aeration and rapid sand filtration (RSF), iron(II) may be removed in two ways: at $\text{pH} > \sim 8$ by homogeneous oxidation and precipitation, and at $\sim 6.0 < \text{pH} < \sim 7.5$ by combined heterogeneous and biological iron(II) oxidation and precipitation. In line with this distinction, wells may become clogged by the accumulation of hydrous ferric oxide (HFO) precipitates in two ways: at “high” pH ($\text{pH} > \sim 7$) by development of HFO flakes resulting in minimal clogging of the screen slots, and at “low” pH ($\text{pH} < \sim 7$) by massive HFO precipitates and biomass resulting in extensive clogging of the screen slots. As HFO precipitation continues, both processes result in extensive well-head clogging, i.e. fouling of submersible pumps, collector lines, etc. While well-screen clogging may be monitored conveniently, no general method is available for monitoring well-head clogging. Recognition of both chemical clogging types is important for effective well construction, operation and maintenance. During rest, HFO precipitation processes continue, further blocking pumps and water lines. If a vertical hydraulic gradient is present over the height of the well screen, HFO precipitates may accumulate on the well screen and enter the aquifer. Consequently, the behavior of the well is important not only during operation, but also during rest. These findings are illustrated by numerous observations on well fields exploited by the drinking water utilities in the Netherlands.

Keywords Homogeneous, heterogeneous and biological iron(II) oxidation · Well clogging · Well enhancement · The Netherlands

Introduction

Figure 1 shows a series of submersible pumps, hoisted from groundwater abstraction wells, displayed as a function of pH: from $\text{pH} \sim 5.6$ (Fig. 1a) to $\text{pH} \sim 7.3$ (Fig. 1e). All these pumps are covered by hydrous ferric oxide (HFO) precipitates, ranging from massive deposits consisting of HFOs and organic matter covering the whole pump at low pH, to a mixture of slimy flakes of organic matter and HFOs covering only the inlet of the pump at high pH. These differences in HFO deposits cannot be ascribed to differences in chemical composition of the abstracted groundwater, as all these wells abstract fresh groundwater serving the public drinking water supply. The volumes of groundwater abstracted and the number of operation hours since the last installation of the submersible pump may vary between the wells, but these variations will result in differences in the amount of precipitation, and not in its appearance or pattern.

All these wells abstract groundwater consisting of a mixture of oxygen-containing and iron-containing water. As soon as these waters mix, HFOs will start to precipitate, regardless of whether favored by the presence of iron(II)-oxidizing bacteria (FeOB), and may clog the well screen (Howsam et al. 1995; McLaughlan 2002; Houben and Treskatis 2007; Smith and Comeskey 2010). Further downstream, the HFO precipitation process will go on, causing submersible pumps (see Fig. 1) and the insides of water lines to be covered by HFO precipitates. The HFO precipitates may contain all kinds of admixtures, such as aluminum, manganese, phosphates and silicates, present in the abstracted groundwater (Houben 2003), resulting in differences in appearance, such as a change in color (Fig. 1). If the abstracted water also contains methane, clogging will be more serious by the production of biomass.

Oxidation of iron(II) in groundwater by mixing with oxygen-containing water

In the oxidation of iron(II) in (ground)water by oxygen, three processes may be distinguished (van Beek et al. 2016): homogeneous, biological and heterogeneous iron(II) oxidation. In homogeneous oxidation, iron(II) is

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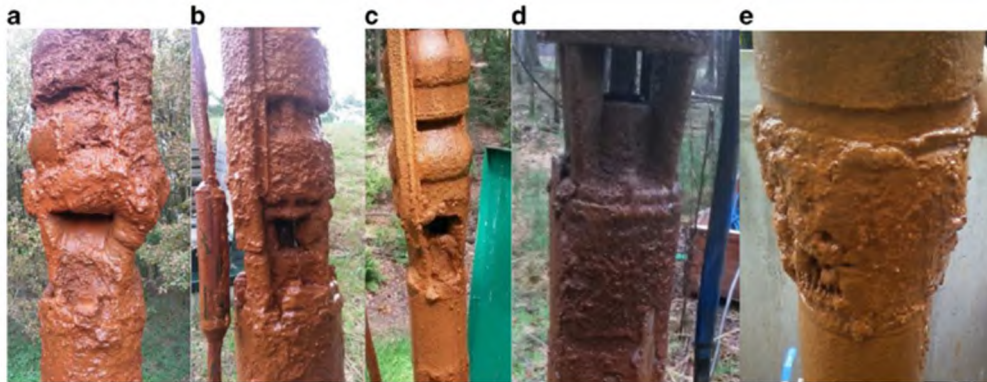
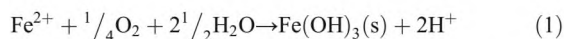


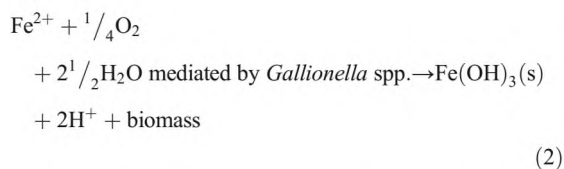
Fig. 1 Submersible pumps, hoisted from wells abstracting fresh groundwater in the Netherlands, covered by HFO precipitates, arranged as a function of pH (from left to right): **a** well-field Manderveen (water utility Vitens) pH ~5.6, **b** Holten (Vitens) pH ~6.0, **c** Havelterberg

(Vitens) pH ~6.1, **d** Heumensoord (Vitens) pH ~6.6, and **e** Heel (WML) pH ~7.3. For reference, the diameter of the pumps varies from 15 to 20 cm

oxidized in solution, resulting in the production of HFO flakes, and may be represented as (*s* = solid):



In biological oxidation, oxidation of iron(II) is mediated by FeOB, in particular *Gallionella* spp., which have excellent adhesive properties. This process results in the production of biological HFO precipitates, consisting of a mixture of HFO precipitates and biomass, and may be represented as:



In heterogeneous oxidation, iron(II) is adsorbed by HFO surfaces and subsequently oxidized, resulting in growth of HFO precipitates. This composite process may be represented in a simplified way as:

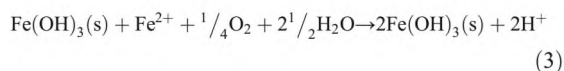


Figure 2 shows the distribution of the various iron(II) oxidation processes as a function of pH in the production of drinking water from groundwater by aeration and rapid sand filtration (RSF) (van Beek et al. 2016). In this figure, the contribution of homogeneous iron(II) oxidation has been calculated based on the residence time in the supernatant water on top of the RSF. The eventual remaining dissolved iron(II) is removed in the very top of the sand filter. The contribution of

heterogeneous iron(II) oxidation has been calculated by measuring the increase in the RSF bed height over time. Due to material loss by backwashing, the estimated contributions are probably (highly) underestimated, the magnitude depending on the vigor of backwashing. The remainder is oxidized by biological iron(II) oxidation. Nowadays, the contribution of biological iron(II) oxidation may also be measured experimentally (de Vet et al. 2011).

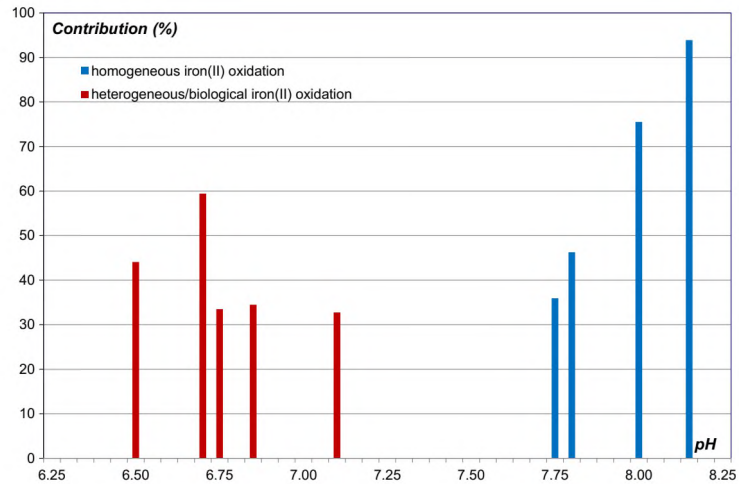
Figure 2 demonstrates that there is, in drinking water treatment, a clear difference in iron(II) removal by aeration and RSF depending on pH. At high pH, removal is by homogeneous oxidation in the supernatant water. At low pH, removal is by heterogeneous and biological oxidation in the sand filter. Supernatant water is here only necessary to arrive at a homogeneous distribution of the water to be treated over the sand filter.

Comparison of precipitation of HFOs in aeration and RSF and in chemical well clogging

In a drinking water treatment plant, the distribution of the various iron(II) oxidation processes by oxygen depends on the construction and the operation of the plant. Figure 3a shows schematically the construction of a RSF setup consisting of aeration and filtration. In the supernatant water, conditions are favorable for homogeneous iron(II) oxidation, as there are hardly any surfaces for chemical or biological attachment. These conditions are comparable to those in abstraction wells: hardly any surfaces are available for attachment, see Fig. 3b. Only the insides of the pipes and the submersible pump, in particular the inlet, provide some surface area (see also Fig. 1).

The experimental conditions between iron(II) precipitation in drinking water treatment and in chemical well clogging are quite different, see Fig. 3. However, the similarity in the

Fig. 2 Contribution of the various iron(II) oxidation processes as a function of pH in the removal of iron(II) by aeration and RSF (modified after van Beek et al. 2016)



sequence of iron(II) precipitation processes in chemical well clogging, on the one side (Fig. 1), and in drinking water treatment on the other side (Fig. 2) is remarkable.

The objective of this study is to compare the removal of iron(II) in drinking water treatment by aeration and RSF with chemical well clogging by accumulation of HFO precipitates as a function of pH: at high pH ($pH > \sim 7$) chemical well clogging by accumulation of HFO flakes by homogeneous oxidation of iron(II), and at low pH ($pH < \sim 7$) chemical well clogging by accumulation of massive HFO precipitates and biomass by heterogeneous and biological oxidation of iron(II). If such a difference is present, this will have consequences for well construction, well operation and well maintenance.

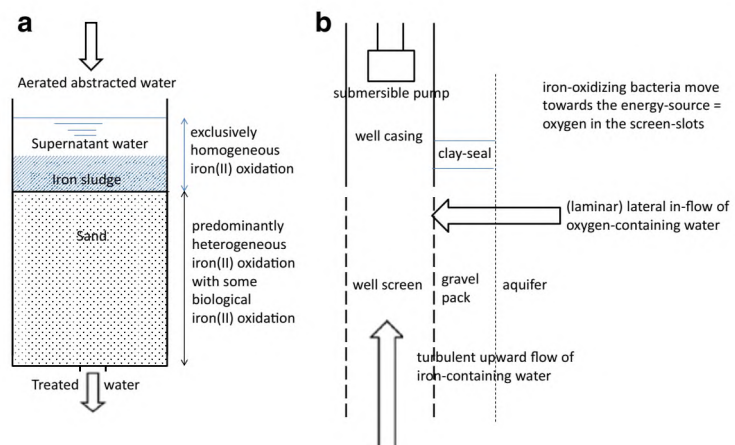
As conditions in wells are much more similar to oxidation of iron(II) in the supernatant water than in the sand filter (limited vs. abundant surface area), the value of the transition pH will be somewhat lower than in Fig. 2 ($pH \approx 7$ vs. $pH \approx 7.5$). The value of this transition pH value is provisional and may

depend on the chemical composition of the abstracted groundwater (concentration of iron(II) and oxygen after mixing, presence of silicate, phosphate, hardness, etc.), the operation of the well(-field), and other factors.

Chemical well clogging in the Netherlands

In the Netherlands, the occurrence of chemical well clogging by accumulation of HFO precipitates is limited to phreatic aquifers: oxygen being present in the shallow part of these aquifers, and iron(II) in the deeper part. Figure 4 shows the concentration of iron(II) in groundwater abstracted by the drinking water utilities from all phreatic well fields in the Netherlands (ca. 100), as a function of pH, subdivided into several classes as a function of the nitrate concentration. As there are only a few reliable results for oxygen concentration measurements available, the presence of nitrate has been used as a surrogate parameter for the presence

Fig. 3 **a** Schematic of a rapid sand filtration (RSF) unit consisting of aeration and filtration, and **b** conditions in a well suffering chemical well clogging by abstracting a mixture of (deep) iron(II)-containing and (shallow) oxygen-containing water (not to scale)



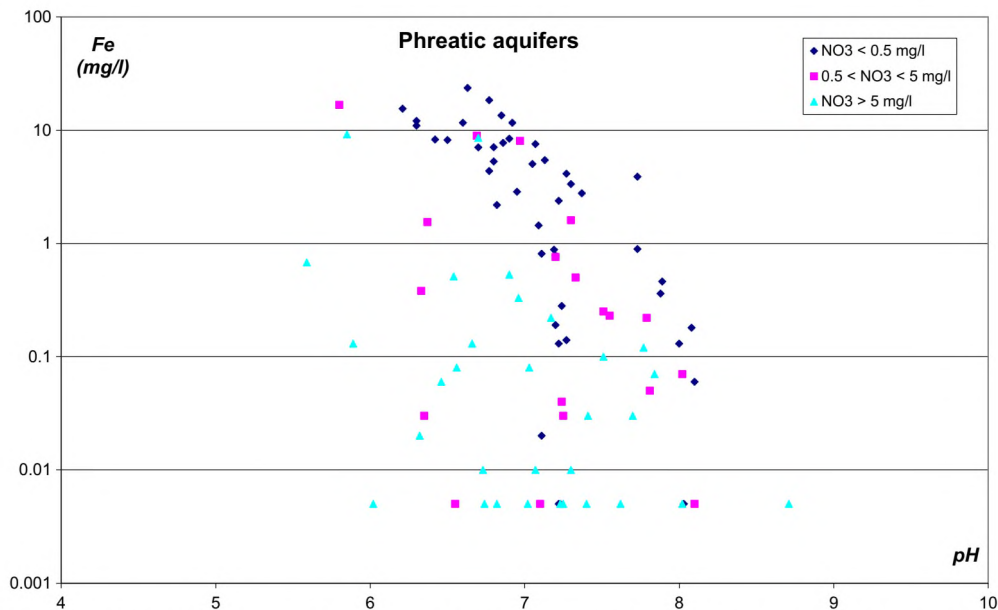


Fig. 4 Concentration of iron(II), in mg/l, in groundwater abstracted by the Dutch water utilities from phreatic aquifers as a function of pH, subdivided into several nitrate concentration classes. Data from Mendizabal (2011)

of oxygen. Chemical well clogging occurs at all well fields abstracting a mixture of iron(II)-containing and nitrate-containing groundwater and in about half the phreatic well fields abstracting groundwater with no discernable nitrate.

In the Netherlands, the water utilities abstract ca. $250 \times 10^6 \text{ m}^3$ (MCM)/year from ca. 100 phreatic well fields, i.e. on average 2.5 MCM/year/well field, each well field comprising on average 10 to 15 wells. As the recharge rate amounts to ca. 250 mm/year, the corresponding recharge area of an average phreatic well field covers ca. 1000 ha.

The chemical composition of the abstracted groundwater is governed by the chemical composition of the recharge water and its interaction with vegetation and the soil and/or aquifer matrix. Land uses in the recharge area include agriculture (arable land, dairy farming, pig farming), nature (heather, stunted trees,

Douglas firs), habitation (extensive urbanized areas, summer resorts) and surface water. Table 1 presents a summary of the characteristics of the well fields represented in Fig. 1.

Table 2 presents the chemical composition of the abstracted groundwater of the well fields involved. If the land use within the recharge area of a well field is very heterogeneous, the chemical composition of the abstracted groundwater of the individual wells will reflect the associated variations. This is particularly relevant in sloping areas (deep and shallow groundwater depth), in ice-pushed areas with sloping clay layers, and in recharge areas with heterogeneous land use. For example at well-field Holten the average pH of the abstracted groundwater of all wells equals 6.82, while the pH of the abstracted groundwater of the well with the hoisted pump equals 6.0.

Table 1 Some characteristics of the well fields in the Netherlands involved in this study

Well field	Number of wells	Surface level (m + MSL) ^a	Well screen depth (mbs) ^b	Geology	Land-use recharge area (%)		
					Agriculture	Nature	Urbanized
Havelterberg	14	12.5	30–79	East German river deposits	40	50	10
Heel ^c	29	26	40–85	River Meuse deposits	60	30	10
Heumensoord	35	20	30–50	Ice-pushed river Rhine deposits	10	70	20
Holten	19	19	11.5–72.5	Ice-pushed river Rhine deposits	55	35	10
Manderveen	8	25	25–55	East German river deposits	65	30	5

^a MSL = mean sea level, ^b mbs: meters below surface

^c Heel: artificial basin fed by exfiltrating groundwater and surface water (see also: van Beek et al. 2017)

Table 2 Chemical composition of the abstracted groundwater of each well field (not the individual well) involved in this study (Mendizabal 2011). Temperature of groundwater in phreatic aquifers in the Netherlands equals 10 °C

Well field	EC mS/m (20 °C)	pH	mmol/l										Sum cations mmol _e /l	Sum anions			
			Cl	HCO ₃	NO ₃	SO ₄	Ca	Mg	Na	K	Fe μmol/l	Mn			NH ₄	PO ₄	SiO ₂ mmol/l
Havelterberg	15.5	6.37	0.45	0.69	0.08	0.12	0.51	0.11	0.49	0.03	27.50	1.65	2.06	3.81	0.33	1.74	1.45
Heel	42.4	7.30	1.13	2.03	0.02	0.64	1.50	0.27	1.19	0.08	28.57	3.44	6.44	2.97	0.09	4.81	4.46
Heumensoord	31.9	6.95	0.76	1.23	0.20	0.39	0.96	0.28	0.86	0.07	5.89	1.65	0.17	1.03	0.23	3.42	2.98
Holten	31.0	6.82	0.54	1.48	0.14	0.59	1.14	0.25	0.60	0.09	0.09	6.55	4.72	0.64	0.23	3.46	3.33
Manderveen	28.2	5.59	0.68	0.20	0.46	0.60	0.72	0.28	0.70	0.09	12.14	1.53	1.33	2.33	0.29	2.79	2.54

Figure 5 shows the locations of the studied well fields in the Netherlands.

Monitoring chemical well clogging

Characteristics of well clogging

The oxidation of iron(II) by oxygen and precipitation of HFOs does not end in the well screen, but goes on during flow towards the point of destination (drinking water treatment plant, etc.), resulting in well-head clogging by narrowing of the diameter of the pipes and increasing the flow resistance and the energy needed for transport, or decreasing the yield. Consequently, well clogging may be defined as a decrease in production (volume of abstracted groundwater) per unit energy over time, other conditions remaining constant. Table 3 and Fig. 6 present an overview of definitions in well clogging as used here.

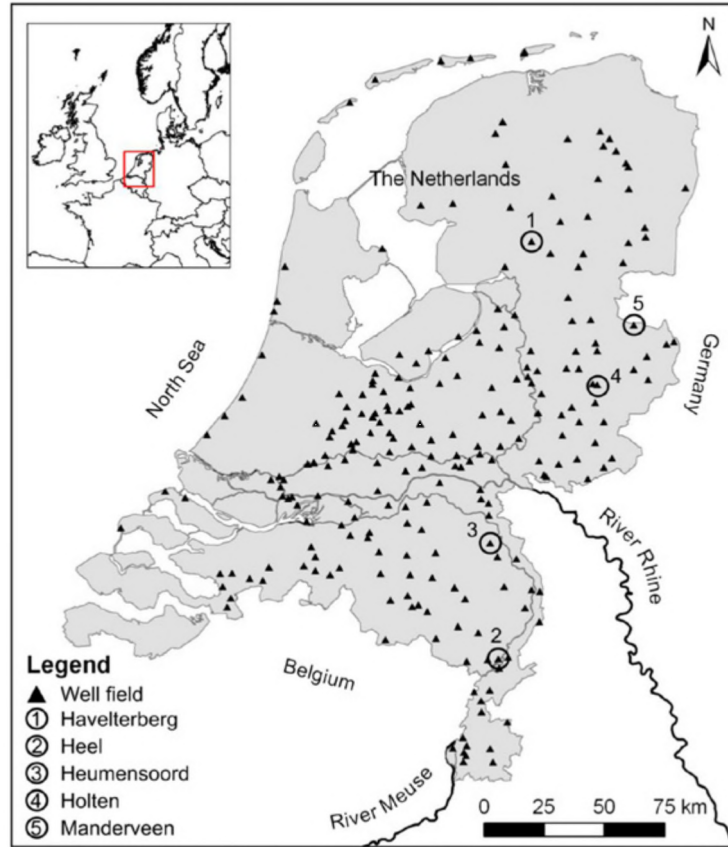
The consequences of well clogging with regard to production very much depend on the method of abstraction. In the case of abstraction by a submersible pump [in its correct discharge (Q) to height (h) range], the production remains about constant (as long as the pump does not start sucking air), but the energy used increases. In the case of vacuum abstraction, the energy applied remains constant, but the production decreases (until zero).

Typically, well clogging is defined as hydraulic well clogging (van Beek 1984), characterized by a decrease in specific volume flow (volume flow per unit drawdown) over time. This decrease may be caused by an accumulation of particles on the well bore (van Beek et al. 2009) or by an accumulation of chemical precipitates in the screen slots (see Fig. 6a and b).

If a well abstracts a mixture of oxygen and of iron(II) containing water, this iron(II)-containing water is usually delivered through the lower part of the well screen. In the upper part of the well screen, iron(II)-containing water from below mixes with sideward inflowing oxygen-containing water, and HFOs will start to precipitate, continuing downstream, see also Fig. 3b.

At “high” pH, HFO flakes will develop, accumulating downstream, giving rise to “well-head” clogging, see Fig. 6c. The well screen may contain some HFO precipitates developed during rest, etc. At “low” pH, HFO precipitates and biomass will accumulate in the screen slots and further downstream, giving rise to “well-screen” and “well-head” clogging, see Fig. 6b. Well-screen clogging is characterized by a decrease in the specific volume flow over time, where the specific volume flow is defined as the volume flow per unit drawdown (drawdown: water level in the well during abstraction minus water level during rest, see also Fig. 6) and by an increase in entrance resistance (over the screen slots) over time. Chemical well-head clogging is characterized by an increase in resistance through the pump and pipes over time.

Fig. 5 Location of all well fields operated by the Dutch water utilities, and of the well fields involved in this study



Hydraulic head monitoring

Well-screen (and well-bore) clogging may be monitored by measuring the specific volume flow over time. The specific volume flow of a well may be calculated as:

$$Q_{spec,t} = \frac{Q_t}{\Delta s_t} \tag{4}$$

with:

- $Q_{spec,t}$ specific volume flow at time t [$m^3 \cdot h^{-1} \cdot m^{-1}$]
- Q_t volume flow at time t [$m^3 \cdot h^{-1}$]
- Δs_t drawdown at time t [m]

And the hydraulic condition of the well may be evaluated by comparing the actual value of the specific volume flow with the original value:

$$f_t = \frac{Q_{spec,t}}{Q_{spec,0}} \tag{5}$$

with:

- f_t hydraulic condition of the well at time t [-]
- $Q_{spec,0}$ specific volume flow on commissioning [$m^3 \cdot h^{-1} \cdot m^{-1}$]

Nowadays, many wells have been equipped with devices that continuously measure the hydraulic and barometric pressure, which may be conveniently converted into hydraulic head. If the well has been equipped with a submersible pump, working in its correct Q - h range (where $Q_t = Q_0$), with the help of the results of these measurements, the hydraulic condition of the well may be continuously accurately monitored as:

$$f_t = \frac{Q_{spec,t}}{Q_{spec,0}} = \frac{Q_t \Delta s_0}{\Delta s_t Q_0} \approx \frac{\Delta s_0}{\Delta s_t} \tag{6}$$

with:

- Q_0 volume flow on commissioning [$m^3 \cdot h^{-1}$]
- Δs_0 drawdown on commissioning [m]

As long as there is no clogging (and the volume flow of the pump is not changed), drawdown remains constant ($\Delta s_t = \Delta s_0$), and as soon as there is clogging, drawdown increases ($\Delta s_t > \Delta s_0$). The advantage of these continuous

Table 3 Nomenclature and characteristics of the various types of well clogging, defined as the decrease in production per unit energy over time due to functioning of the well (not due to lowering of the water table, pump-wear, etc)

Hydraulic well clogging		Non-hydraulic well clogging
Mechanical well clogging (or well-bore clogging)	Chemical well clogging (or well-screen clogging)	Well-head (incl. pump and water lines) clogging
Cause of clogging		
Accumulation of particles on the well bore	Accumulation of chemical and/or biological precipitates in the slots (in the upper part) of the well screen	Accumulation of chemical and/or biological precipitates
Field characteristics		
1. Decrease in specific volume flow over time 2. No entrance resistance 3. Well, well head and water lines spotlessly clean	1. Decrease in specific volume flow over time 2. Entrance resistance 3. (Upper part of) well screen, (submersible) pump, well head and water lines clogged by massive HFO precipitates and biomass	1. No or negligible decrease in specific volume flow over time 2. No or negligible entrance resistance 3. (Submersible) pump, well head and water lines clogged by HFO flakes

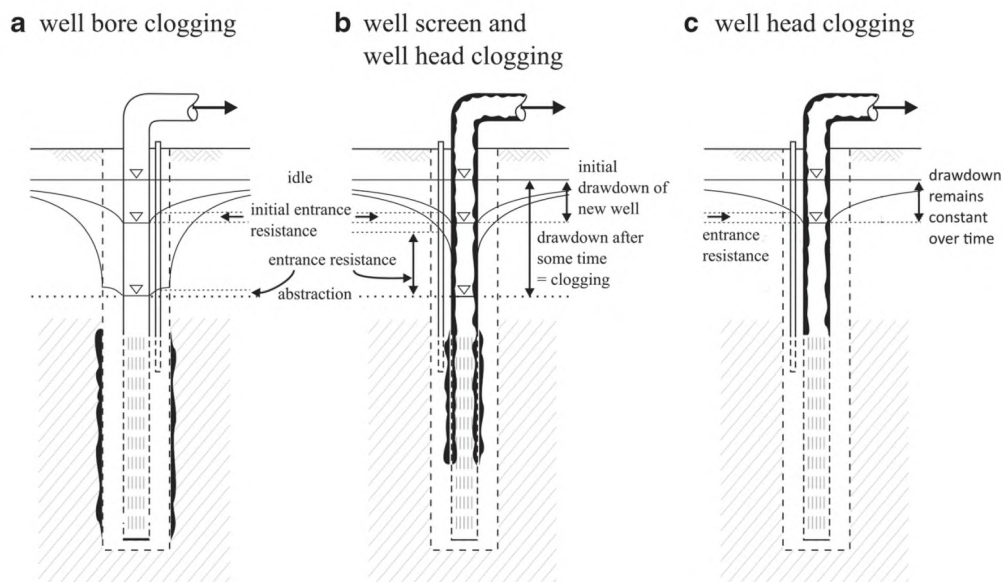
measurements is that their results are highly representative of field/operational conditions, and they produce an immediate warning in case of increasing drawdown.

Most wells of the Dutch drinking water utilities are equipped with a monitoring well in the gravel pack at the top of the well screen (see Fig. 6), enabling measurement of the entrance resistance. In the absence of well-screen clogging, the entrance resistance is negligible (< 1 to 2 cm). If a well is clogging, the presence of this observation well makes it possible to distinguish between well-screen and well-bore clogging (without opening the well).

In past days, the hydraulic condition of the wells was monitored by measuring the water level in all wells of a well field,

then switching all wells on or off, and measuring the water level again. Subtracting the values produced the drawdown. By repeating these measurements over time under comparable conditions, a fair impression of the hydraulic condition of the wells was obtained. The value for the specific volume flow may also be obtained with the help of (short) pumping tests, where the well has been disconnected from the system, by measuring drawdown Δs after a standardized period of abstraction with volume flow Q .

These field measurements show an advantage over continuous measurements by also providing information about the location of the clogging: if an entrance resistance is present, the screen slots are clogging; if there is no entrance resistance,

**Fig. 6** a Schematic representation of (mechanical) well-bore clogging, b combined (chemical) well-screen and well-head clogging, and c (chemical) well-head clogging

clogging is located somewhere else, most probably on the well bore. However, after some time the well operator will know which kind of well clogging is active.

A disadvantage of these field measurements is the variability in results, due to the variability in physical conditions (variations in groundwater level over the seasons and over the years), operational conditions (neighboring wells turning on and off, etc.) and individual variations (variable pumping times).

Monitoring pump/well-head clogging

There are no general ways for monitoring well-head (incl. pump) clogging. Increasing power consumption or decreasing water production may be indicators. An experienced well operator will pick up signals such as non-return valves not working properly, relatively short life span of submersible pumps, etc., and will know how to maintain the wells/well field in good condition.

Results

Chemical well clogging at “low” pH

Figure 7 shows the results of hydraulic head measurements in the well and in the monitor well at the top of the well screen in the gravel pack of well 72-23 of well-field Holten (water utility Vitens) over a period of about 10 years (van Beek 1984). This figure shows a year-after-year increase in drawdown of about 2 m, indicating serious well clogging. Moreover, during the same period, drawdown in the (upper) monitor well decreases by about 0.5 m. Consequently, the entrance resistance (the difference in hydraulic head between the monitoring well

in the gravel pack and the abstraction well) increases in one year from negligibly to about 2.5 m, indicating considerable clogging of the screen slots. The presence of HFO precipitates, clogging the screen slots, has been confirmed by the results of numerous video-camera recordings and the execution of many well rehabilitations. Figure 7 also shows that these wells are conveniently simple to rehabilitate (e.g. by brushing or jetting and concomitant abstraction), and that the clogging process recommences immediately after the well has been rehabilitated.

Actually, this is the classical picture: fast clogging of the well-screen slots by accumulation of HFO precipitates and slimes, for which the wells are easy to rehabilitate again and again, provided the situation is managed in good time.

Well-screen clogging is not an exceptional phenomenon. Figure 8 shows, as an example, well 19 of well-field Vierakker (Vitens), albeit much less severe. Notice the gradual increase in the entrance resistance.

Chemical well clogging at “high” pH

Figure 9 shows the results of continuous hydraulic head measurements of wells 14 and 21 of well-field Heel (van Beek et al. 2017; Bustos Medina et al. 2013), where the top of the band of observations represents the hydraulic head in the well during rest and the bottom of the band during abstraction. This figure shows that drawdown varies a few decimeters over time, indicating that in well 21 there is minor transitory clogging (compare with Fig. 7, several meters in well 72-23 of well-field Holten). However, drawdown in well 14 remains largely constant during nearly continuous abstraction from October 2010 to October 2012, but drawdown decreases after well (and pump) cleaning around January 2014 and January 2015.

Fig. 7 Results of hand measurements of the hydraulic head in the well and in the monitor well in the gravel pack at the top of the well screen of well 72-23 of well-field Holten (Vitens) (van Beek 1984)

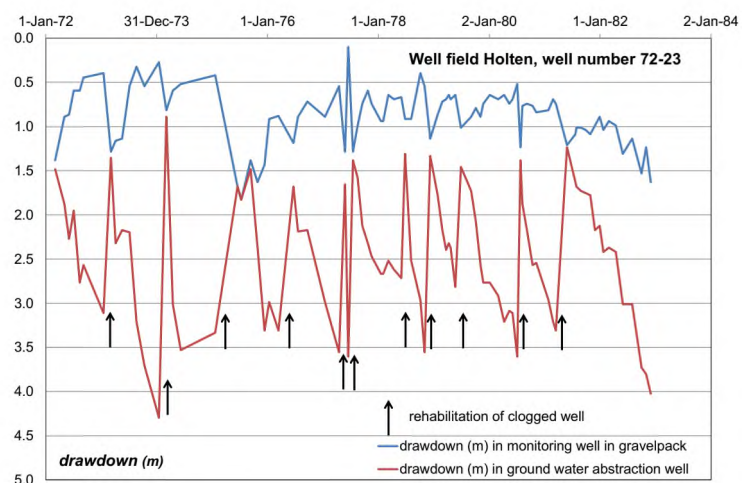
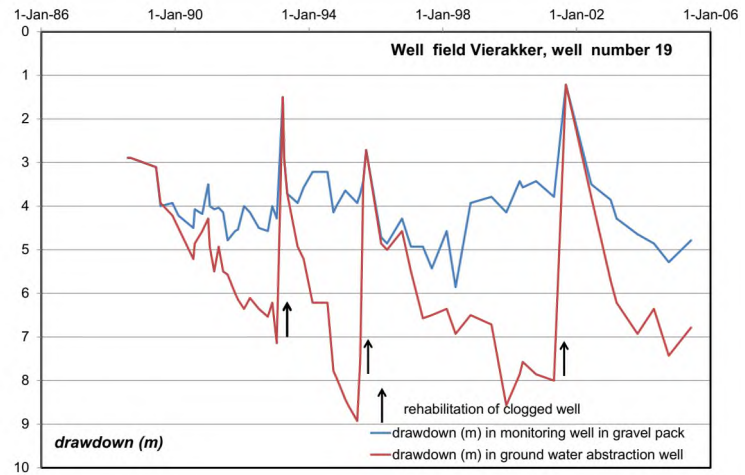


Fig. 8 Results of hand measurements of the hydraulic head in the well and in the monitor well in the gravel pack at the top of the well screen of well 19 of well-field Vierakker (Vitens) (van Beek 2010)



The well screens of wells 14 and 21 showed the presence of some HFO precipitation; however, conditions were complicated by the presence of a vertical hydraulic gradient over the well screen, resulting in short-circuit flow during rest, continuously producing some HFO precipitates.

Figure 10a shows the results of the continuous hydraulic head measurements of well 48 of well-field Heel. Remarkable is the decrease in drawdown between February 2010 and May 2011. Drawdown may only decrease if the abstraction rate decreases. Figure 10b shows a picture of the corresponding submersible pump, which is completely choked with HFO precipitates, and it is immediately quite understandable why drawdown decreased over time. Here, eventual well-screen clogging is completely masked by well-head clogging, but as wells 14 and 21 do not show well-screen clogging, it may be assumed that in well 48 well-screen clogging is absent too. Fig. 10a shows that well-head clogging started by frequent intermittent operation, and progressed much more slowly during almost continuous operation. Perhaps, also, the location of the well, near the end of the collector line, might be relevant.

The observations at well-field Heel, abstraction of groundwater containing iron(II) and (traces of) oxygen at pH ~7.3, causing minimal well-screen clogging but extensive well-

head fouling, are wholly comparable to the observations concerning the abstraction of artificially infiltrated water in the dune area along the coast of the Netherlands (Lafort, water utility Evides, and Dammers, water utility Dunea, personal communication, 2017) and with those of riverbank recharge in Berlin, Germany (Menz 2016).

Discussion

In drinking water treatment, iron(II) removal by aeration and RSF is either optimized to homogeneous iron(II) oxidation by increasing pH to ~8 and oxygen concentration to about saturation in the supernatant water, or to heterogeneous/biological iron(II) oxidation by optimizing pH and oxygen concentration in an environment with a large surface area (sand), facilitating attachment (adhesion), in the near absence of supernatant water (Fig. 2). Consequently, in drinking water treatment, two different physical environments are present.

In chemical well clogging, physical conditions are identical over the whole pH range. Because, compared with a sand filter the surface area of the submersible pump and the insides of the well and all pipes is negligible, actually the occurrence of

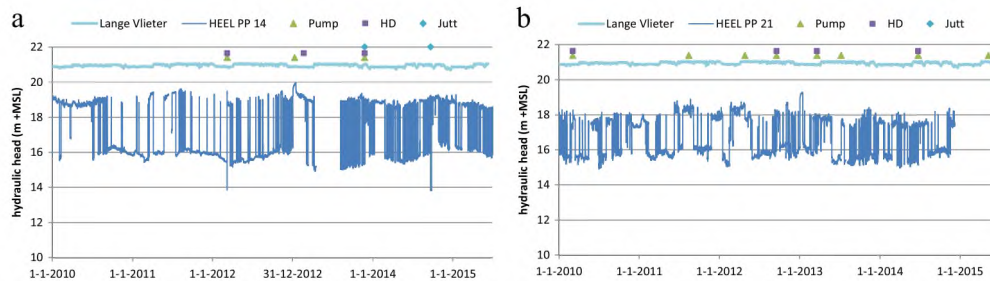


Fig. 9 Results of continuous measurements of hydraulic head in **a** well 14 and **b** well 21 of well-field Heel between 2010 and 2015 (van Beek et al. 2017). Upper light-blue line: water level in the basin; symbols refer to well maintenance

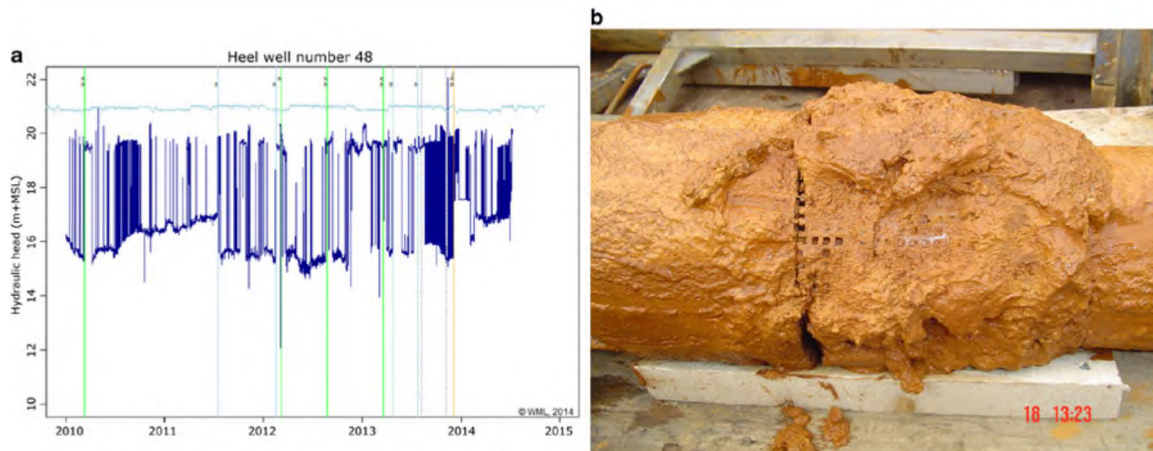


Fig. 10 **a** Results of continuous measurements of hydraulic head in well 48 of well-field Heel between 2010 and 2015. *Upper light-blue line*: water level in the basin; *symbols*: well maintenance. **b** Photograph of the hoisted submersible pump (courtesy Water Supply Utility WML)

homogeneous iron(II) oxidation is favored. HFO flakes produced in this process possess negligible adhesive properties, and will start to accumulate in quiet areas, after (sharp) bends, constrictions, valves etc., slowly expanding to less quiet areas. As soon as the reaction rate of homogeneous iron(II) oxidation becomes too slow, heterogeneous and biological iron(II) oxidation will take over, producing massive HFO and biological deposits. This reasoning is confirmed by the results of monitoring: “well-head” clogging at “high” pH, and “well-screen” and “well-head” clogging at “low” pH.

Chemical well clogging at “high” pH

An obvious conclusion of Fig. 1 might be that the higher the pH, the less HFO precipitation develops (and the less serious the chemical well clogging). This is contrary to what one might expect from Eqs. (1), (2) and (3): the higher the pH, the more favorable the conditions for iron(II) oxidation and HFO precipitation (and the more serious the chemical well clogging).

This would be correct if the concentration of iron(II) were independent of pH. Figure 4 shows the concentration of iron(II) in groundwater abstracted by the drinking water utilities in phreatic aquifers in the Netherlands, as a function of pH. This figure shows that oxygen (nitrate)-containing groundwater is present over the whole pH range. Figure 4 also shows that the maximum concentration of iron(II) in the abstracted groundwater varies by a factor of 100 over the pH range of interest: from about 0.25 mg/l at pH \approx 8 to about 25 mg/l at pH \approx 6.5. However, the concentration of iron(II) in nitrate (oxygen)-containing groundwater is usually lower.

The rate equation generally applied for homogeneous oxidation of iron(II) by oxygen reads (Stumm and Morgan 1996):

$$\frac{d}{dt} [\text{Fe}^{2+}] = -k_1 \frac{[\text{Fe}^{2+}][\text{O}_2]}{[\text{H}^+]^2} \quad (7)$$

where k_1 represents the rate constant for homogeneous oxidation. After integrating Eq. (7) at constant oxygen concentration and constant pH, and after inserting the appropriate initial condition, the concentration of iron(II) after time t may be calculated as:

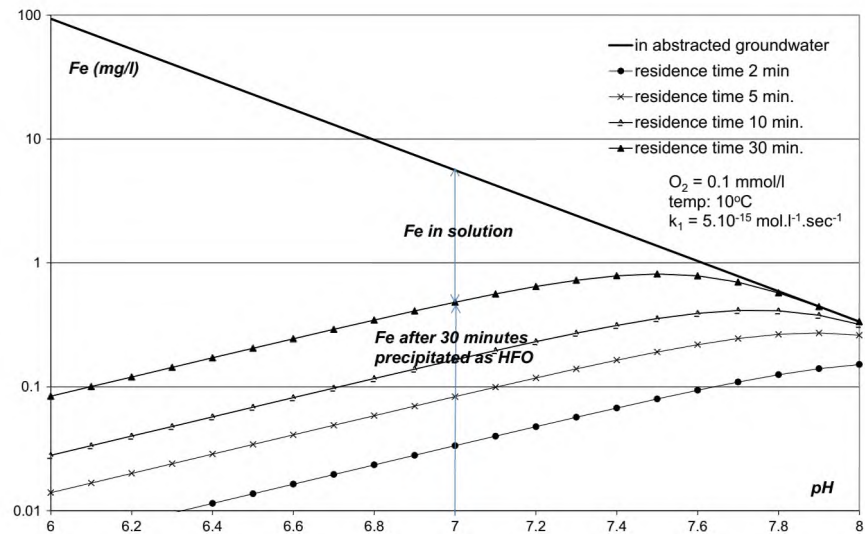
$$[\text{Fe}^{2+}]_t = [\text{Fe}^{2+}]_0 \exp\left(-k_1 \frac{[\text{O}_2]}{[\text{H}^+]^2} t\right) \quad (8)$$

where $[\text{Fe}^{2+}]_0$ represents the concentration of iron(II) at $t=0$, and $[\text{Fe}^{2+}]_t$ the concentration at time t . The “concentration” of iron(II) precipitated after time t , $[\text{Fe}^{2+}]_{\text{prec},t}$, may be calculated as the difference between the initial and the actual concentrations:

$$[\text{Fe}^{2+}]_{\text{prec},t} = [\text{Fe}^{2+}]_0 - [\text{Fe}^{2+}]_t = [\text{Fe}^{2+}]_0 \left(1 - \exp\left(-k_1 \frac{[\text{O}_2]}{[\text{H}^+]^2} t\right)\right) \quad (9)$$

Figure 11 shows the concentration of iron(II) in abstracted groundwater as a function of pH, as derived from Fig. 4. This figure also shows the “concentration” of iron(II) precipitated by homogeneous iron(II) oxidation after various residence times, which appears highly dependent on pH. Because the residence time in the mixing zone of the well screen (where oxygen-containing water enters the well and mixes with the upward-flowing iron(II)-containing water; see Fig. 3b) is short, only minute amounts of HFO will precipitate in the upward-flowing water and not necessarily in the screen slots, causing well-screen clogging. This behavior explains the absence of well-screen clogging by homogeneous iron(II)

Fig. 11 Concentration of iron(II) in abstracted groundwater and “concentration” of iron(II) precipitated by homogeneous oxidation after several residence times, as a function of pH. [At pH = 7.5, the maximum concentration of iron(II) equals 1.37 mg/l; after 5 min, 0.19 mg/l iron(II) has been precipitated (leaving 1.18 mg/l in solution); at pH = 7, the maximum concentration of iron(II) equals 5.60 mg/l; after 5 min, 0.08 mg/l iron(II) has been precipitated (leaving 5.52 mg/l in solution)]



oxidation at high pH. However, as the precipitation process continues, HFO precipitates will accumulate in and on the pump, in the collector lines, and so on. This HFO precipitation process will also continue during rest, which explains the problems caused by frequent switching of the submersible pump on and off, i.e. continuously refreshing the water column, including the oxygen and iron(II) supply. Problems may arise during rest if non-return valves do not work properly, or if there is a vertical hydraulic head over the well screen.

In this contribution, chemical well clogging was limited to clogging by precipitation of HFO, and not by aluminum hydroxides, manganese oxides, etc. (Houben 2003). Because in these chemical precipitation processes no biology is involved, their behavior will be comparable to “well-head” clogging.

This reasoning does not explain the absence of biological and heterogeneous iron(II) oxidation in well-screen clogging at high pH. This is surprising, as in the production of drinking water from groundwater by aeration and RSF, heterogeneous iron(II) oxidation is active to at least pH > 7, see Fig. 2.

As *Gallionella* spp. depend solely on the oxidation of iron(II) by oxygen for their energy, and little energy is produced by this reaction (Stumm and Morgan 1996; Emerson and de Vet 2015; de Vet 2011), in order to maintain a reasonable colony of *Gallionella* spp., a considerable amount of iron(II) must be oxidized. Figure 4 shows that the (maximum) concentration of iron(II) decreases with increasing pH. It is hypothesized that with increasing pH, the concentration of iron(II) becomes too low, and the competition with homogeneous (and heterogeneous) iron(II) oxidation too fierce, to sustain a viable colony of *Gallionella* spp., which may initiate biological iron(II) oxidation and chemical well clogging.

Chemical well clogging at “low” pH

In the preceding section it was demonstrated that at low pH, the development of HFO precipitates by homogeneous iron(II) precipitation is negligible. Consequently, flakes precipitated by homogeneous iron(II) precipitation cannot serve as a nucleus for adsorption of iron(II). At low pH, chemical well clogging must be initiated by heterogeneous and/or biological iron(II) precipitation.

It has been demonstrated that on the outside of HFO-containing fibrils of *Gallionella* spp., HFO (Neubauer et al. 2002) and even lepidocrocite (Chan et al. 2011) may start to precipitate. As *Gallionella* spp. show excellent adhesive properties, it is postulated that chemical well clogging is initiated by these microorganisms. Posth et al. (2014) elaborate extensively on the intertwining between chemical and biological oxidation of iron(II). In order to obtain a maximum amount of energy in this upward flowing iron(II)-containing water, *Gallionella* spp. will encroach as close as possible the supply of oxygen, i.e. the screen slots, and in order to obtain maximum concentrations of oxygen, possibly even enter these slots, thus in this way causing maximum (chemical) well-screen clogging. This is in line with the findings of Eggerichs et al. (2014) who determined the optimal conditions for *Gallionella* spp. as pH between 6 and 7, and oxygen concentration between 0.4 and 4 mg/l. The encroaching of screen slots by *Gallionella* spp. and HFO precipitates may be compared with the encroaching of deep sea vents by biomass and chemical precipitates (Jannasch and Mottl 1985). Fragments of this clogging material, consisting of *Gallionella* and HFO precipitates, may tear off and adhere downwards in the groundwater abstraction system, like the submersible pump and the waterlines, and start growing there.

Wang et al. (2014) found no relation between the encrustation level of wells dewatering open-cast lignite mines and iron concentration (varying from 25 to 425 mg/l), pH (varying from 4.5 to 7.3) or oxygen concentration (varying from 1.8 to 5.8 mg/l). This is contrary to the findings of this study, where the kind of clogging showed at least a relation with pH. It is possible that the heterogeneity of the chemistry of their abstracted waters overshadowed any relationship.

Recommendations for well operation

Based on the foregoing, a number of recommendations for well operation under iron(II) precipitating conditions may be presented.

Rehabilitation Wells (screens and heads) clogged by accumulations of only HFO, at “high” pH, are convenient to clean mechanically by brushing and jetting under simultaneous abstraction.

Wells clogged by accumulations of biomass and HFO, at “low” pH, may be approached in two ways: extensive cleaning by brushing and jetting or intensive cleaning by brushing and jetting, if necessary together with some hydrochloric acid aiming for complete removal of HFO deposits and biomass, whether or not followed by disinfection of *Gallionella* spp. Whether the costs of intensive rehabilitation, inclusive of disposal of spent chemicals, outweigh the costs of extensive rehabilitation, will depend on the extension of the rehabilitation interval.

There are experiences that it sometimes took a long time before a newly drilled well started clogging, but once clogging started, there was no difference anymore with the wells on the same well field.

Continuous abstraction At “high” pH, HFO flakes may develop, which settle down and stick together during rest. In order to prevent this accumulation, continuous abstraction is recommended. By frequent intermittent abstraction the water column in the well is continuously refreshed, inclusive the oxygen and iron(II) supply.

In previous research (van Beek et al. 2017; Bustos Medina et al. 2013), it was demonstrated that due to the presence of a downward vertical hydraulic gradient over the well screen during rest, HFO flakes may enter the aquifer. This downward hydraulic gradient may also develop due to neighboring running wells. Also, Houben and Weihe (2010) found recent HFO precipitates at some distance from the well. Apparently, HFO flakes invading the aquifer is a rather common phenomenon. In order to prevent accumulation of HFO flakes in the gravel pack and in the aquifer, continuous abstraction is recommended.

Short residence times However, *Gallionella* spp. have excellent adhesive properties. In drinking water treatment systems

their contribution decreases with increasing flow velocity (van Beek et al. 2016). If this also holds for groundwater abstraction, this would ask for high abstraction volume flows, short well screens, etc. Short well screens also present more flexibility in positioning the screen over the height of the oxic/anoxic aquifer (positioning the screen as much as possible in the oxic or anoxic part of the aquifer), and decrease the magnitude of an eventual vertical hydraulic gradient over the well screen.

Complete removal of dissolved iron(II) during transport from the well to the drinking water treatment plant will not occur due to presence of a limited surface area compared to complete removal in a RSF with a much greater surface area.

Installation of easy-to-clean equipment As long as it is not possible to prevent chemical well clogging, it is best to cope with it conveniently. Figure 12 shows the well head of a small vacuum well abstracting groundwater with a high pH: after opening the well head, the well screen is easy to clean; after opening the cleaning pipe, the connection line is easy to clean (brush); cleaning the collector line may pose no problem at all.

This construction resembles that mentioned by van Beek (2010), but no special abstraction pipe is necessary, because there is no danger of well-screen clogging.

Installation of equipment less sensitive to chemical clogging

In the dune area in the Netherlands, artificially recharged groundwater, containing iron(II) and oxygen at a high pH, is continuously abstracted with the help of drain pipes laid under a small slope. These long straight drain pipes do not become clogged, and need minimal maintenance (Appeldoorn et al. 2000). This demands the simplest well-head construction: minimal bends, variations in diameter (constrictions), installation of valves, etc.

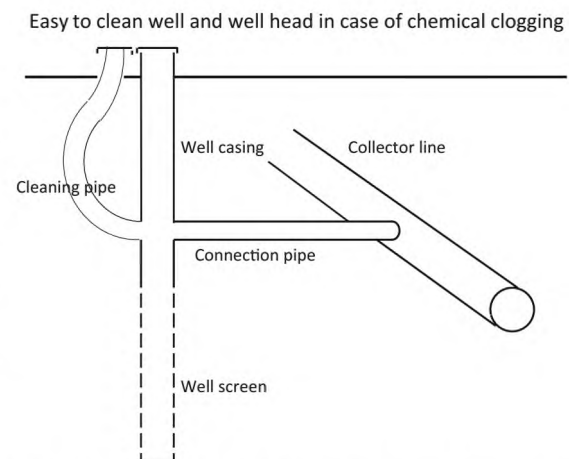


Fig. 12 Well-head construction facilitating easy access for cleaning the well head in case of well-head clogging (by HFOs at high pH)

Regular disinfection By regular disinfection of the well by chlorine, the development of *Gallionella* spp. may be prevented. This will only be helpful at low pH. Such experiments have been executed in Germany: Krems (1979) reported positive, and Moser (1979) negative results, but they did not mention the pH of the abstracted water. However, as the introduction of chemicals into drinking water is rejected, application of non-adhesive materials would be a better option.

Recommendations for research

The results of the research described here are based on observations under more or less average conditions. Additional observations encompassing a wide range of pH and of iron and oxygen concentrations would allow firmer conclusions. Moreover, a number of questions may have already been formulated, such as:

Sequence in chemical well clogging Here, well clogging at “high” and at “low” pH has been discussed, resulting in predominantly chemical well-head and chemical well-screen clogging, respectively. But what happens at intermediate pH? Is there a sharp or gradual transition between the two occurrences? Or is there a dip between processes? Is this transition influenced by the chemical composition of the abstracted water, as this chemical composition determines the chemical composition of the HFO precipitates? Kobus and Vlasblom (1975) inserted strings of Perspex plates into wells abstracting dune infiltration water in order to determine the depth of the oxygen entrance front. By inserting these strings over a wide variety of abstracted water chemistries, much information about the occurrence of homogeneous, biological and heterogeneous HFO precipitation, as well as the properties of these HFO precipitates in chemical well clogging, may be obtained. This information might also be obtained by comparing the pH of the abstracted groundwater and the presence/absence of an entrance resistance.

Optimal conditions for *Gallionella* spp. In order to obtain oxygen as well as iron(II), *Gallionella* spp. need adhesive surfaces. In a well, oxygen-containing water will enter the well at the top of the well screen and mix with upward-flowing iron(II)-containing water, and due to the turbulent flow, the boundary layer will disappear over a short distance: both water types will be completely mixed. Information regarding the distribution of *Gallionella* spp. over the height of the well screen and the well casing may be obtained by inserting strings with plates at regular distances. By inserting strings with all kinds of plates (smooth, rough, treated with anti-fouling paint, consisting of anti-fouling material, etc.), much information about adhesion of *Gallionella* spp. and HFO precipitates may be obtained.

Presence of short-circuit flows during rest The presence of these flows has been demonstrated for some wells, but information about the frequency of this phenomenon is lacking. Such information might be obtained by inserting long lines with Perspex plates to the bottom of the well: if all plates are covered by HFO deposits, short-circuit flow is present; if only the top plates are covered, short-circuit flow is absent. This information may also be obtained with the help of very accurate flow measurements during rest.

Development of monitoring procedures for well-head clogging Well-bore and well-screen clogging can be conveniently monitored. The results of this monitoring should be combined with readily available information, for instance water production and/or power consumption, to arrive at efficient operation and maintenance procedures for well-head clogging.

Conclusions

In the precipitation of HFOs, three processes may be distinguished: homogeneous, biological and heterogeneous iron(II) oxidation. As in iron(II) removal in drinking water treatment by aeration and RSF, these three precipitation processes result in two chemical well-clogging processes by accumulation of HFO precipitates. Chemical well clogging by homogeneous iron(II) oxidation, producing HFO flakes, occurs at high pH ($\text{pH} > \sim 7$); these flakes may accumulate in the well head and further downward, all along the collector line, resulting into well-head clogging and much less in well-screen clogging. At $\text{pH} < \sim 7$, conditions are favorable for heterogeneous and biological iron(II) oxidation, resulting in well-screen clogging and well-head clogging. It is postulated that this precipitation process is initiated by biological iron(II) oxidation, and is thereafter taken over by heterogeneous iron(II) oxidation. Recognition of these HFO precipitation processes is important for the operation of the well fields concerned, prevention of well clogging and rehabilitation of clogged wells.

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Chemical and mechanical clogging of groundwater abstraction wells at well field Heel, the Netherlands

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Abstract Well field Heel, in the south east of the Netherlands, consists of a row of wells drilled in an anoxic pyrite-containing aquifer alongside a former gravel pit, which now serves as a recharge basin, where water is actively aerated. All wells are seriously affected by chemical (screen slot) and/or mechanical (well bore) clogging. The objective of this study is to explain this combined occurrence. A combination of chemical, hydraulic and well-maintenance data indicate three groundwater quality types: (1) oxic basin water, (2) anoxic iron-containing basin water after oxidation of the traversed aquifer, and (3) deeply anoxic native groundwater. Wells abstracting a mixture of oxic basin water and anoxic basin water and/or native groundwater experience chemical well clogging, whereas wells abstracting (only or partly) native groundwater are vulnerable to mechanical well clogging. In the end, after oxic basin water has completely oxidized the traversed the aquifer, only two groundwater quality types will be present. Wells abstracting only oxic basin water will show no clogging, and wells abstracting a mixture of native groundwater and oxic basin water will experience chemical and possibly also mechanical well clogging. In this reasoning, the sequence in abstracted groundwater quality types coincides with a sequence in well clogging: from mechanical to chemical to no clogging. As well field Heel is situated in sloping terrain, the interplay between regional hydraulic gradient and different water qualities results in one-sided chemical

clogging in the upper part of the well screen during abstraction, and in the lower part during the resting phase.

Keywords Artificial recharge · Hydrochemistry · Sedimentary rocks · Well clogging · The Netherlands

Introduction

Well clogging is a disturbing problem in groundwater abstraction, showing up unexpectedly during periods of greatest demand (when water levels are lowest) and in this way interrupting smooth operation. Moreover, the occurrence of well clogging causes higher expenditures for extra wells, energy, monitoring and rehabilitation and, if rehabilitation is not successful, for the replacement of the clogged wells.

Well clogging is characterized by an increase in drawdown over time, where drawdown is defined as the difference in water level in the well during abstraction and during the preceding rest period. Wells abstracting groundwater may become clogged in two ways: (1) chemically by precipitation of hydrous ferric oxides (HFO) in the screen slots, whether or not accompanied by other precipitates and/or biomass (Howsam 1995; McLaughlan 2002; Houben and Treskatis 2007; Smith and Comeskey 2010) or (2) mechanically at the interface between aquifer and gravel pack by accumulation of soil particles (or colloids; van Beek et al. 2009a). Both types can be distinguished with the help of a monitoring well in the gravel pack at the top of the well screen: screen-slot clogging is characterized by the presence of an entrance resistance (over the screen slots), and well-bore clogging by the absence of this resistance (cf. Fig. 1). This diagnosis may be confirmed by visual inspection: in screen-slot clogging, reddish-brown precipitates and slimy biomass are present on the well screen, on the submersible pump and in the raw water transport pipes,

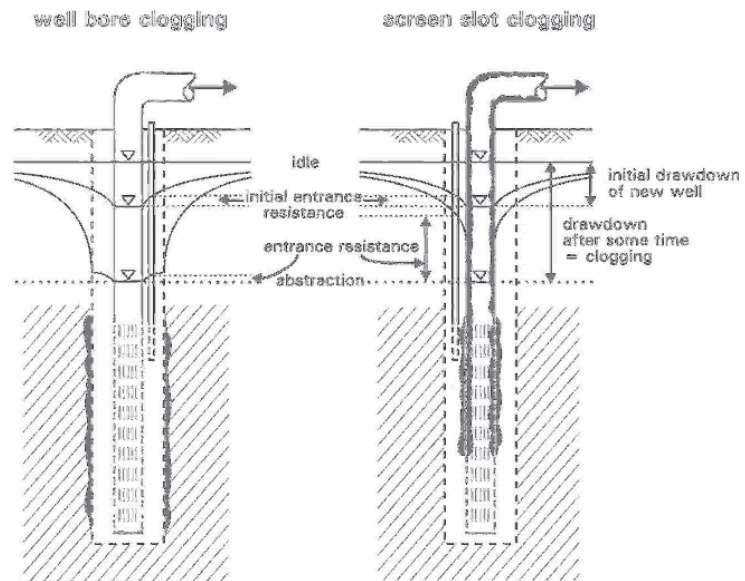
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Fig. 1 Schematic representation of wells clogged by accumulation of particles on the well bore characterized by the absence of an entrance resistance, and of wells clogged by an accumulation of HFO precipitates and biomass in the screen slots, characterized by the presence of an entrance resistance. The concept of entrance resistance is here restricted to the resistance over the screen slots. In the Netherlands, abstraction wells exploited by the water works are equipped with a monitor well in the gravel pack at the upper side of the well screen. The wells at Heel also contain a monitor well in the gravel pack at the bottom of the well screen. Modified after van Beek (1982)



whereas in well-bore clogging, the well screen, pump and transport pipes are clean.

Chemical well clogging

Aquifers, in particular phreatic aquifers, may show a vertical chemical stratification: shallow groundwater containing oxygen (and no iron) and deeper groundwater containing iron (and no oxygen). Appelo and Postma (2005) present several examples of this sequence. In a well, drilled in such an aquifer, mixing of both water quality types will occur, resulting in the precipitation of HFO inside the well and further downstream. These HFO precipitates will clog the upper part of the well screen from the lower boundary of the oxygen-containing groundwater upwards and cover the well casing, the submersible pump and the raw water pipes. These precipitates may also hinder proper functionality of the foot valve of the submersible pump and clog the inlet-screen. Malfunction of the foot valve may result in back-flow of water during periods of pump shutdown, and clogging of the inlet screen of the pump in a decrease of the abstraction rate.

In well clogging, not only the abstraction period is important, but also the rest period. During rest, water present in the well consists of a mixture of oxygen-containing and of iron-containing water. Now there is ample time for the development of HFO precipitates; moreover, HFO flocs may dwindle down from the submersible pump. If there is a hydraulic potential gradient over the height of the well, there may be an outward bound flow, resulting in the development of HFO precipitates clogging the screen slots and the gravel pack. This flow may be temporarily upward induced by filling up

the cone of depression around the well along the gravel pack (in particular if there is no clay seal above the well screen; van Beek et al. 2009b). If there is a downward hydraulic potential gradient during rest, this flow will be continuously downward: the well acts as a short-circuit with water entering the upper part of the well and leaving the lower part (Bustos Medina et al. 2013). The presence of HFO precipitates outside the well was also described by Houben and Treskatis (2007), who showed gravel packs completely cemented by HFO precipitates and by Houben and Weihe (2010), who demonstrated the presence of recent HFO deposits in the gravel pack and further downstream in the aquifer.

Mechanical well clogging

Groundwater contains particles (or colloids), especially in deeply anoxic (sulfate-reducing) aquifers (McDowell-Boyer et al. 1986; McCarthy and Degueldre 1993; Kretzschmar et al. 1999; van Beek et al. 2010) and in groundwater not in equilibrium with the aquifer matrix (Vaidya and Fogler 1990). The latter is often the case in artificial recharge, where water is directly infiltrated into an aquifer. These particles consist of organic material and of mineral particles, more or less representative for the aquifer matrix, like quartz, feldspars, clay minerals and, if present, calcite, but also of in situ chemical precipitates like FeS and phosphates (Chanudet and Filella 2006; van Beek 2010).

As it is hard to develop a well completely, during abstraction these organic and mineral particles may accumulate on the well bore, actually increasing the “skin”. Obviously, the number of particles accumulated on the well bore is directly

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proportional to the “concentration” of particles in groundwater and to the length of each individual abstraction period (van Beek et al. 2009b). Because the well bore becomes clogged, the entrance resistance remains negligible.

What happens during rest is not completely clear, but one may hypothesize that these particle accumulations will disintegrate, as there is no force of flowing water on the accumulated particles anymore. Starting the (submersible) pump produces a shock around the well rinsing the accumulated particles out. As long as by each start of the pump all particles accumulated on the well bore during the preceding abstraction period are removed, no clogging will occur. If not, the well will clog (van Beek et al. 2009a). Table 1 presents a summary of well clogging characteristics under conditions in the Netherlands.

Well field heel

As chemical clogging of the screen slots by an accumulation of HFO precipitates occurs under slightly anoxic conditions (the abstracted groundwater should contain oxygen and iron(II)) and mechanical clogging of the well bore by accumulation of particles under deeply anoxic (sulfate reducing) conditions (these waters contain the highest concentrations of particles), these types of clogging do not occur together (cf. Table 1). In the Netherlands, chemical clogging occurs only in wells abstracting water from phreatic aquifers and mechanical clogging occurs in wells abstracting water from (semi-) confined aquifers. However, at well field Heel both clogging phenomena have been found occurring together, which has never been reported before. Apparently, conditions at well field Heel are quite different from the norm. The objective of this study is to understand the processes resulting in the concurrent occurrence of chemical and mechanical well

clogging. This will be done by evaluating chemical, hydraulic and well-maintenance data. Based on this understanding, a picture of future developments will also be presented.

Field site

Site description

Well field Heel is located in the south east of the Netherlands close to the River Meuse (Fig. 2). The wells are located in a single row along the eastern and southern shore of the manmade basin “Lange Vlieter” (Fig. 2). This basin is the result of gravel exploitation for the cement industry, which started in 1983 and finished in 1996. In the exploitation process, the useless topsoil was removed and set aside along the southern shore (at sub fields Langven and De Reut, see the next section).

Drinking water production started in 2001 and increased to 16×10^6 m³/year by the end of 2007, after which it remained constant. However, the design capacity of the well field amounts to 20×10^6 m³/year.

The volume of the Lange Vlieter basin equals 25×10^6 m³, and is fed by surface water pumped up from the Lateral Canal (Fig. 2). The water level below the lock in this channel is kept at 14.4 m + MSL (mean sea level), and in the basin at 21.0 m + MSL in summer and at 20.85 m + MSL in winter. The hydraulic gradient between Lange Vlieter and Lateral Canal therefore corresponds to circa 0.5 %.

The basin is located on a terrace in the valley of the River Meuse. Consequently, there has always been a considerable hydraulic gradient towards this river, and at present to the Lateral Canal. Currently, the basin acts as a flow-through basin: exfiltration of groundwater on the

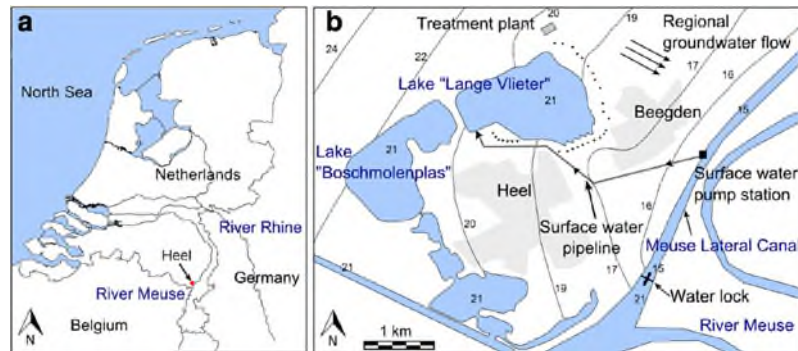
Table 1 Summary of criteria and supporting evidence with respect to well clogging in the Netherlands (van Beek and Breedveld 2007)

Criteria	Chemical (or screen slot) well clogging	Mechanical (or well bore) well clogging
Characteristic	Presence of entrance resistance ^a	Absence of entrance resistance ^a
Cause	Accumulation of chemical precipitates (and biomass) in screen slots	Accumulation of particles on well bore
Characteristic phenomenon	Inside well, pump and raw water pipes completely covered by precipitates	Inside well, pump and raw water pipes spotless clean
Groundwater quality characteristic	Abstracted groundwater contains iron and oxygen (nitrate)	Abstracted groundwater shows signs of sulfate reduction (?)
Aquifer characteristic ^b	Phreatic aquifer	(Semi-)confined aquifer
Geological profile ^b	Abstraction from brown and gray colored unconsolidated sediments	Abstraction from gray colored unconsolidated sediments
Rehabilitation	Easily rehabilitated, as long as the precipitates are fresh	Difficult to rehabilitate, as the accumulation is present at some distance from the well

^a Entrance resistance refers only to the head loss over the screen slots

^b Conditions in the Netherlands

Fig. 2 a–b Location of well field Heel. The wells (black dots) are located along the southern and eastern shore of the basin *Lange Vlieter* (modified after Bustos Medina et al. 2013)



upstream (W and NW) side, and infiltration of basin water at the downstream (SE) side. Also some overflow of the neighboring gravel-pit Lake Boschmolenplas may contribute to the Lange Vlieter. The yearly contribution of the sum of precipitation and evaporation is negligible. By supplying the basin with surface water, the water level in the basin has been raised, resulting in a decrease of exfiltration of native groundwater at the upstream side, and in an increase of infiltration of basin water at the downstream side. According to the legal permission for exploitation of the Lange Vlieter for drinking water production, the infiltrated water should be abstracted as much as possible and the water level in the basin should be at prescribed level.

Description of the well field

Well field Heel consists of 29 wells, subdivided into three sub-fields, Galgenberg: 12 wells, Langven: 10 wells, and De Reut: 7 wells (see also Table 2). Figure 3 shows schematic cross-sections of the eastern (Galgenberg) and southern (Langven and De Reut) shores of the basin. Note the presence of the back-fill material on the southern side up to a depth of ~ 0 m + MSL, impeding (shallow) flow of basin water towards the wells.

The hydraulic conductivity of the aquifer, as determined with the help of pumping tests by the water utility, is higher on the eastern side of the basin ($K_h = 80$ m/day) than on the southern side ($K_h = 50$ m/day). This difference is caused by the presence of two different geological units.

All wells have been drilled with the help of air lift/rotary with a borehole diameter of 600–750 mm. In these boreholes, wells completely constructed of PVC have been placed with well screens with a diameter of 300 mm, resulting in a thickness of the gravel-pack of 15–22.5 cm. Table 2 presents a summary of the dimensions of the wells of the various well clusters. At some distance (~ 2 m) above the top of the well screen, the gravel pack is sealed by bentonite mud. After construction, all wells were developed with high capacity and sectional pumping, until no relevant improvement of the specific volume flow (abstraction volume flow over drawdown) occurred anymore.

Basin hydrology

For the purpose of this study, the flow and origin of water to each well under continuous abstraction was calculated with the help of backward particle tracking with a stationary finite element groundwater model (see Fig. 4). In a similar way, the

Table 2 Summary of well dimensions (for location of the wells see Figure 4)

Subfield	Well cluster	Number of wells	Pump capacity ($\text{m}^3 \text{h}^{-1}$)	Surface (m MSL)	Screen (m MSL)		Blind (m MSL)		Gravel diameter (mm)
					Top	Bottom	Top	Bottom	
Galgenberg	N	4	150–175	25.7	8.7	−8.8	–	–	1.7–2.5
Galgenberg	NE	4	100(−175)	29	10.8	−8.1	3.5	0.5	1.7–2.5
Galgenberg	E	4	100–150	30.7	8.1	−9.7	0.3	−2.2	1.7–2.5
Langven	SE	5	100	22.9	1.8	−18.2	−7.6	−12.6	1.4–2.0
Langven	S	5	100	22.8	−1.1	−20.0	−6.3	−10.3	1.4–2.0
De Reut	SW-1	4	(85–)100	24.4	−0.6	−15.0	–	–	1.0–1.6
De Reut	SW-2	3	100	23.3	−2.5	−20.5	–	–	1.0–1.6
Total	–	29	–	–	–	–	–	–	–

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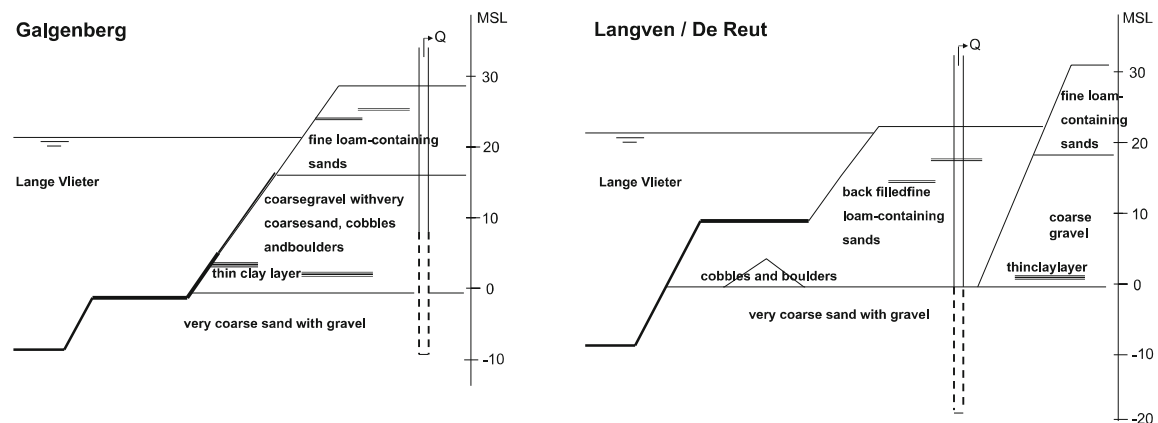


Fig. 3 Schematic cross-section of the eastern (*Galgenberg*) and southern (*Langven* and *De Reut*) bank of the basin, with average position of the well screens. Back-fill material is *gray-colored*

fate of the basin water was calculated, showing that besides the $16 \times 10^6 \text{ m}^3/\text{year}$ abstracted by the wells, circa $2 \times 10^6 \text{ m}^3/\text{year}$ escapes from abstraction along the SE corner to the Lateral Canal.

Figure 4 shows that under conditions of continuous abstraction, the wells of well clusters NE and E abstract only basin water, and the wells of the other well clusters (N, SE, S and SW) abstract a mixture of basin water and more or less native groundwater. If a well in one of these clusters is not abstracting, at that site there will be infiltration of basin water, either to neighboring wells or to the Lateral Canal. After this well starts abstracting again, it will take some time before equilibrium conditions are again attained.

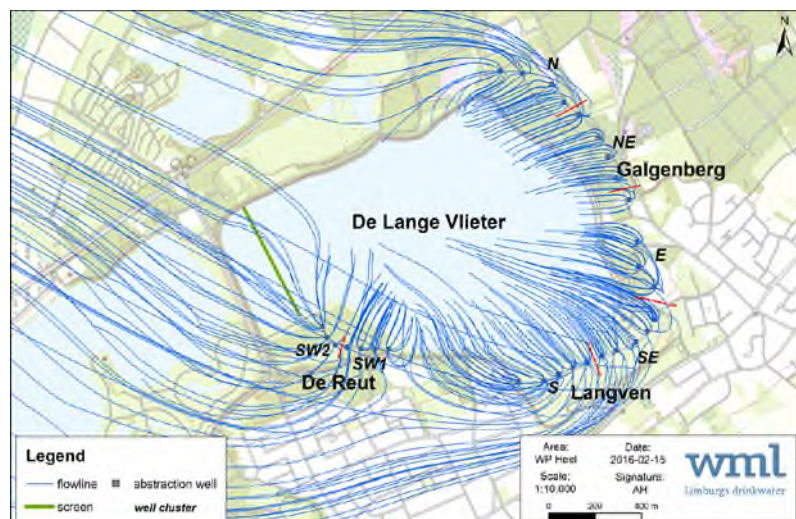
Consequently, Fig. 4 is not representative for current conditions: due to the discontinuous operation, the contribution of native groundwater to abstracted groundwater, in particular in

the subfields S and SE (*Langven*), will be less than indicated. This is confirmed by Bustos Medina et al. (2013) who found nearly identical chemical compositions over the height of the aquifer 2 m from well 21 (well cluster S) at the basin side as well as on the inland side. Consequently, only wells belonging to the well clusters N and SW will abstract relevant, but variable, contributions of native groundwater. Thus, native groundwater contributes in two ways to the drinking-water production: an indirect contribution via the basin, and a direct contribution via some wells belonging to well cluster N, and all wells belonging to well clusters SW, S and SE.

Basin and groundwater chemistry

(Wet) gravel mining started in the Meuse River just south of Heel (bottom part of Fig. 2), moved forward in NW direction

Fig. 4 Groundwater flow to each individual well at Heel under average conditions (year 2010: drinking water production $16 \times 10^6 \text{ m}^3/\text{year}$, continuous production distributed evenly over all wells). The flow lines crossing both basins are present in the aquifer underneath the basin. The locations of the subfields (*Galgenberg*, *Langven* and *De Reut*) and of the well clusters (SW2 to N) are indicated



and thereafter in NE direction around the village of Heel. As a result, during excavation, there was infiltration of surface water consisting of a mixture of Meuse River water and exfiltrated groundwater. After shutting down the gravel mine, the (surface water) connection to the Meuse River was closed, and the water in the basin Lange Vlieter was gradually replaced by exfiltrating anoxic native groundwater. After commissioning of the basin as a reservoir for public drinking-water supply, the basin was recharged with oxidic surface water and aerated through compressed air diffusers. The concentration of nitrate reached equilibrium around 2009 (Fig. 5), and the chemical composition of the basin water has since then remained more or less constant.

Figure 5 shows that the concentration of nitrate in the basin water increased and attained a nearly constant concentration of ~ 7 mg/l NO_3^- . Infiltration of this oxidic (nitrate containing) basin water replaces the native anoxic groundwater, thereby over time oxidizing the originally anoxic aquifer. With some delay, this oxidic basin water entered some wells (over the most coarse, and least reducing, part of the aquifer), reaching at present a concentration of > 4 mg/l in water abstracted in wells 2, 3 (well cluster NE), 13 and 14 (cluster E). Water abstracted in wells 4, 5 (cluster NE), 15 (cluster E), 21, 23 (cluster SE), 41 and 48 (cluster SW1) contains 1–3 mg/l NO_3^- and water abstracted in the other wells contains no or temporary low concentrations of nitrate.

In the end, the area between the basin and wells will become completely oxidized, characterized by the presence of oxygen and nitrate in the abstracted water in concentrations comparable to that in the basin water, and by

the disappearance of reduced species like iron and manganese. Apparently, up till now, there is nowhere that the aquifer between the basin and the wells has been oxidized over its complete height.

Well monitoring and well clogging

There are many ways to monitor the operational condition of a well. Here the wells were monitored by continuous drawdown monitoring with the help of water level loggers, regular video inspections, and regular specific volume flow (specific capacity) or pumping tests. In the next sections, the results of these measurements are presented.

Continuous drawdown monitoring

All wells have been equipped with water level loggers enabling continuous measurement of the water level every 3 h. Figure 6 shows the results of such measurements. The upper level represents the water level during rest, the lower level the water level during abstraction. The difference between these levels equals drawdown. As long as drawdown remains constant over time, at constant abstraction rate, there is no clogging. As soon as drawdown increases, the well clogs, whereas in the case that the drawdown decreases, the well is improving. In Fig. 6 well maintenance has also been indicated.

Figure 6 also provides information about well operation: a high frequency of vertical lines represents frequent switching on and off (high frequency, intermittent abstraction).

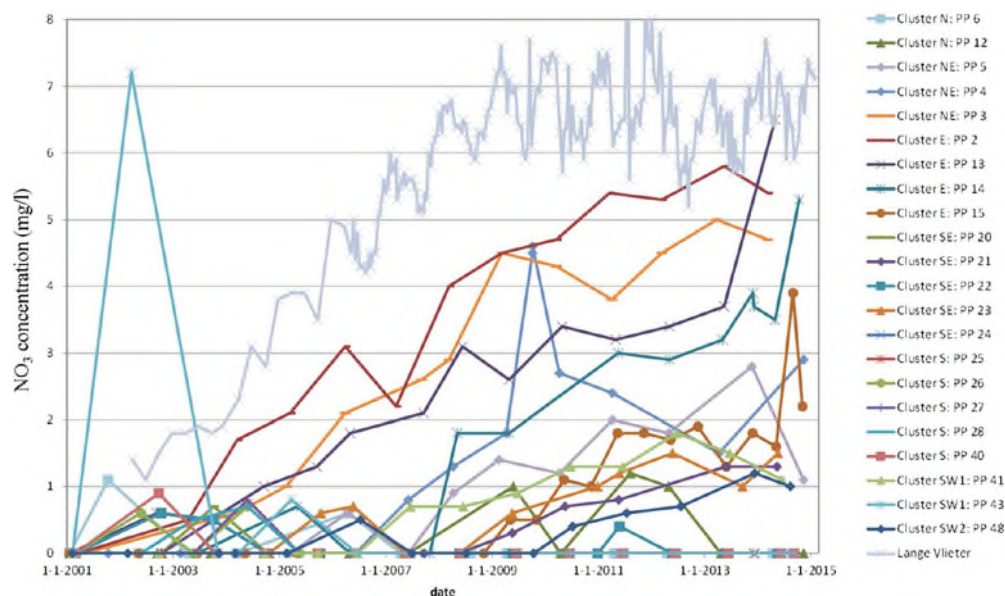


Fig. 5 Concentration of nitrate in the basin and in the abstracted water. Only wells that (temporarily) contain nitrate are represented

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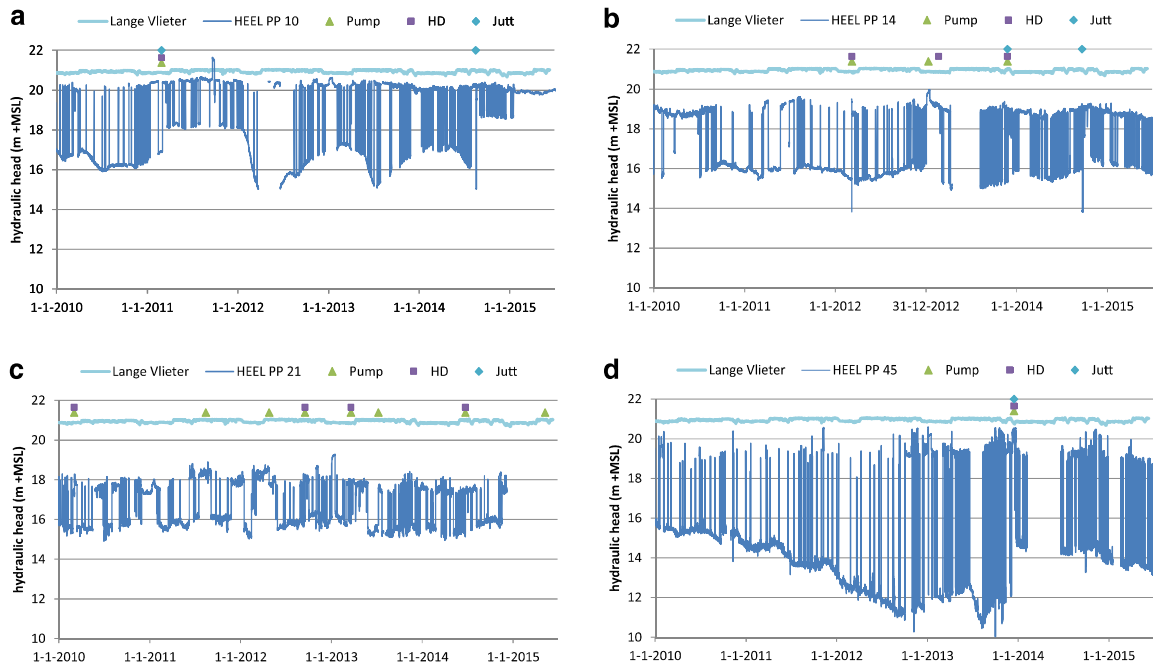


Fig. 6 Results of continuous drawdown measurements of well **a** 10, **b** 14, **c** 21 and **d** 45, and water level in basin Lange Vlieter (nearly horizontal line at 21 m +MSL). Maintenance is also indicated: pump pump cleaning, HD high pressure jetting of the well screen, and

Jutt (juttering) refers to repeatedly pressing the water level in the well down, with the help of compressed air, and suddenly releasing this pressure

Continuous lower lines represent periods of prolonged continuous abstraction, such as well 14 from September 2010 to March 2012 and well 21 from January to March 2012. Continuous upper lines represent periods of prolonged rest, such as well 21 from December 2010 to February 2011 and from December 2011 to January 2012. Small variations at the upper and lower level represent interference by neighboring wells. Sudden changes in drawdown represent interventions by the well operator, for instance rehabilitation of a clogged well (February 2011 in well 10, and January 2014 in well 45).

The slowly fluctuating upper level of drawdown indicates that conditions at rest slowly change over time, due to different water levels in the basin in summer and winter, and due to a greater abstracted volume in summer than in winter. Moreover, the basin sides are clogging by accumulation of suspended material present in the basin, increasing the potential difference between basin and well during abstraction.

Noteworthy is the difference in behavior of the wells over the period considered: drawdown in wells 14 and 21 remaining constant, and in wells 10 and 45 varying over time, representing clogging and improvement. The variation in drawdown over time as function of well operation is characteristic for well bore (or mechanical) clogging: clogging during nearly continuous abstraction and improvement during high frequency intermittent abstraction (van Beek et al.

2009a). Apparently, well 14 and 21 are not sensitive to well clogging.

From Fig. 6 the current condition of the well may be calculated as the current specific volume flow as a fraction of its value on commissioning. The specific volume flow is defined as the volume flow per meter drawdown, where drawdown equals the difference in water level in the well during rest and during operation (the vertical lines in Fig. 6):

$$f_t = \frac{Q_{spec,t}}{Q_{spec,0}} = \frac{Q_t}{Q_0} \frac{\Delta s_0}{\Delta s_t} \approx \frac{\Delta s_0}{\Delta s_t} \quad (1)$$

With:

- f_t Current hydraulic condition of a well, at time t [-]
- $Q_{spec,t}$ Current specific volume flow [$m^3/h/m$]
- $Q_{spec,0}$ Specific volume flow on commissioning [$m^3/h/m$]
- Q_t Current volume flow [m^3/h]
- Q_0 Volume flow on commissioning [m^3/h]
- Δs_t Current drawdown [m]
- Δs_0 Drawdown on commissioning [m]

As long as the volume flow remains fairly constant ($Q_t \approx Q_0$), Eq. (1) shows that the ratio of $\Delta s_0/\Delta s_t$ presents a reasonable indication of the hydraulic condition of the well. Depending on the pump characteristic, the volume flow may

decrease with increasing drawdown. If so, Eq. (1) presents a number that is proportionally too optimistic.

Video inspection

Video inspections were applied to examine the well for structural defects, damage, signs of screen slot clogging, results of well rehabilitation, etc. Figure 7 shows the result of two such inspections of well 21 and 23. Both wells show the presence of HFO precipitates. Noteworthy is the uneven distribution of these precipitates, both vertically and horizontally. Both wells show HFO precipitates starting at one side at the upper part of the well screen. Through the slots of, in particular, well 21, it may be observed that the gravel pack is reddish brown colored, indicating the presence of HFO precipitates behind the well screen in the gravel pack. Both wells also show HFO precipitates in the lower part of the well screen, inside and outside the screen. In well 23, the presence of these HFO precipitates is one sided. The HFO precipitates at the upper and the lower part of the well screen are separated by a clean part in between.

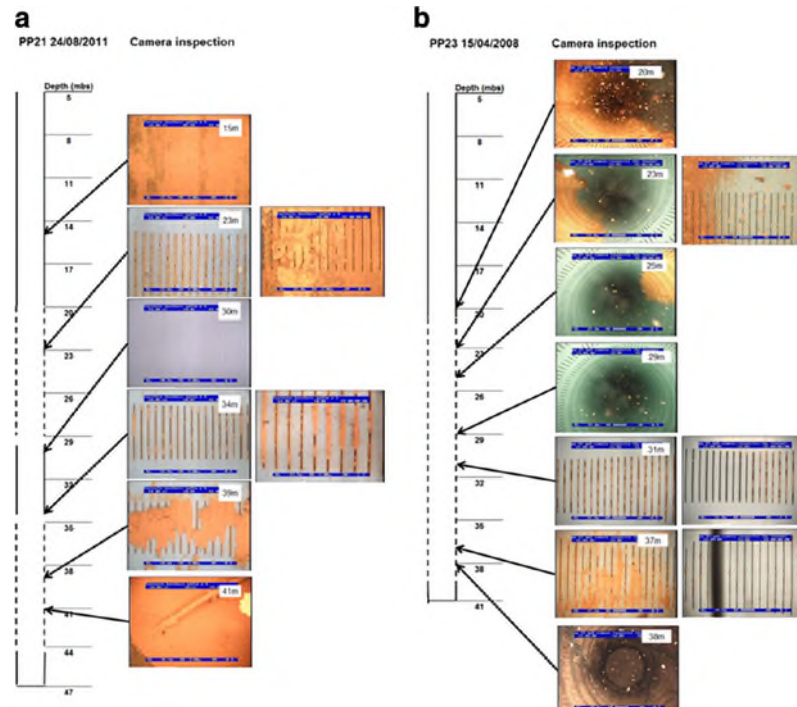
As already mentioned, phreatic aquifers may become with increasing depth increasingly reduced, groundwater containing in the upper part of the aquifer oxygen and in the lower part iron(II). This was for well field Heel confirmed by Bustos Medina et al. (2013) for well 21. During well operation

iron(II)-containing water and oxygen-containing water will mix above the boundary depth between both layers due to upward flow towards the pump. Here HFO precipitation will lead to chemical well clogging in the upper part of the well screen (Fig. 1). By consequence, the observed distribution of HFO precipitates in Fig. 7 over the well screen and outside the screen is remarkable.

The one-sided presence of HFO precipitates inside the well in the upper part of the well screen may be explained by the one-sided entrance of oxygen-containing (basin) water during abstraction. Oxygen and dissolved iron(II) will become well mixed by the turbulent upward flow in the well, and HFOs will immediately start to precipitate resulting in a one-sided coating and further downstream in a complete coating of the well screen, well casing, intake of the submersible pump, etc. This one-sided HFO clogging has been described in greater detail for well 21 by Bustos Medina et al. (2013) but is not unique for Heel and has been reported from other sites too (Krems 1972; Houben and Treskatis 2007).

The presence of HFO precipitates outside the well in the gravel pack, and in the lower part of the well screen cannot be explained in this way. The basin at Heel is located in a recharge area, characterized by a downward hydraulic gradient. As a result, during rest, the well may act as a short circuit flow: water entering the well in the upper part of the well screen and leaving the well at greater depth (Bustos Medina et al. 2013).

Fig. 7 Horizontal and vertical video inspections of **a** well 21 (date of inspection: August 24, 2011, last cleaning before inspection: March 4, 2010) and **b** well 23 (date of inspection April 15, 2008, last cleaning before inspection October 16, 2007). The screen of well 21 extends from 20.4 to 43.6 m below surface (mbs), with a blind part between 30 and 34 mbs, and of well 23 from 20.5 to 39.5 mbs. In five places there are two pictures at one depth



If this entering water contains only oxygen, the alternating flow of oxygen-containing water during rest and of iron-containing water during abstraction will result in heterogeneous iron(II) oxidation as in subsoil iron removal (SIR; van Beek 1980, 1985), as shown by the iron deposits present in the gravel pack. Houben and Weihe (2010) demonstrated the presence of HFO precipitates in the gravel pack and adjacent aquifer. At their well field, the surface showed an (estimated) slope of ~0.3 %, even smaller than the hydraulic gradient of ~0.5 % here. If the water inside the well consists of a mixture of oxygen- and of iron(II)-containing water, HFO precipitates may develop in the well screen, gravel pack and further downstream.

The same reasoning applies to the presence of HFO precipitates outside the well in the upper part of the gravel pack. Their presence may be explained by the occurrence of short outward-bound hydraulic gradients, for instance for filling in the cone of depression after switching off the pump (van Beek et al. 2009b).

Pumping tests

The hydraulic condition of a well may be expressed as the value of the current specific volume flow compared to the value on commissioning. The current value may be obtained with the help of a short pumping test. The results of these tests are summarized in Table 3. The results of these tests must be in line with the results of the continuous drawdown monitoring.

During the pumping test, the entrance resistance is estimated by comparing the water level inside the well and the level in a monitoring well in the gravel pack. If a well is clogged, the type of clogging may be determined by the presence or absence of an entrance resistance (cf. Table 1). The results of these measurements are also summarized in Table 3.

If necessary, after the pumping test, the well and pump were cleaned. The kind and intensity of these well maintenance activities may also provide information about the type of well clogging. Notice in Fig. 6 the difference in frequency of well maintenance in wells 14 and 21 on the one hand, and wells 10 and 45 on the other hand. These frequencies are summarized in Table 3.

The type of well clogging must be confirmed by the chemical composition of the abstracted groundwater (cf. Table 1): abstracted groundwater in chemical well clogging characterized by the presence of oxygen and iron. Information about the chemical composition of the abstracted groundwater is summarized in Table 3.

Discussion

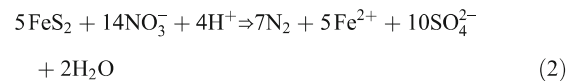
Table 3 presents a summary of all data with respect to well clogging and behavior. This table shows that on

commissioning the specific volume flows of the wells belonging to well clusters N, NE and E are, on average, twice as high than in clusters SE, S and SW. This difference is due to the difference in transmissivity of the aquifers between the eastern and the southern side of the basin, and due to the presence of backfill material at the southern side.

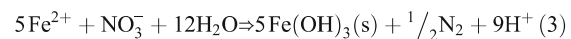
Table 3 also shows that well clogging is a serious problem. In 2014 only 4 of the 29 wells (well numbers 21, 24, 41 and 48) were not clogged; all other wells showed little to serious clogging. All clogged wells have been rehabilitated, but it was not possible to rehabilitate most of these clogged wells to their original capacity. The capacity of the wells of the clusters N, NE and E now varies between ~25–75 % of the original capacity, and of the wells of the clusters SE, S and SW between ~50–100 %.

Table 3 also displays the concentration of some chemical parameters in the basin and in the water abstracted by each well, averaged over the second half of 2014 (cf. Fig. 4 for nitrate). The chemical compositions of the basin water and of the waters abstracted by the wells are not directly comparable, as these last compositions are averaged values weighted by residence time. And even the residence time distribution of the water abstracted by each well may not be constant (depending on the season and on the operation of neighboring wells); however, as information over the chemical composition over the last 15 years is available, some cautious conclusions may be derived. From the chloride and sulfate concentrations it may be derived that (under current operational conditions) the wells of well clusters NE (except well 5), E, SE and S abstract nearly pure basin water. Apparently, in all these wells the “basin water front” has reached all these wells. This is confirmed by Bustos Medina et al. (2013) who found nearly constant chloride and sulfate concentrations over depth in the exploited aquifer at well 21.

The somewhat higher concentration of sulfate in the abstracted water compared to the basin water may be explained by the oxidation of traces of sulfides (pyrite) present in the aquifer (Loma et al. 2012). The presence of iron(II) in the water abstracted by well clusters NE, E, SE and S is caused by incomplete oxidation of pyrite:



followed by:



where the second reaction (Eq. 3) is usually not complete. The incomplete oxidation of iron(II) may be caused by the steep decrease of the redox potential at the pyrite oxidation front and

governed by the rates of the two reaction steps. In the literature, many vertical nitrate/iron(II) profiles with a sharp transition between nitrate and iron(II) are presented (Kölle et al. 1990; Postma et al. 1991; van Beek 2000; Appelo and Postma 2005). As there are no wells abstracting ironless water, the “nitrate front” or “oxic basin water front” has not yet reached any of the wells over their complete screen length.

However the increase in concentration of sulfate is too small to explain the encountered concentrations of iron(II). Possible additional sources may be cation exchange, desorption of adsorbed iron(II) and reduction of HFO precipitates. Also Bustos Medina et al. (2013) report increasing concentrations of iron(II) with depth together with decreasing pH-values, without concurrent changes in other parameters.

As results of oxygen concentrations are not available, nitrate has been used as a surrogate-parameter for oxygen. As soon as nitrate is present in fair concentrations ($>1\text{--}2\text{ mg/l NO}_3^-$), oxygen is usually also present. Water abstracted by the well clusters NE and E contains nitrate, as do some wells located close to the basin (well 21, 23 (cluster SE), 41 and 48 (cluster SW); Table 3). The presence of nitrate is accompanied by lower concentrations of iron(II).

All other wells (well clusters N and SW and well 5) abstract either only native groundwater or a mixture of native groundwater and anoxic basin water. Over the years, depending on well operation, this distribution may vary somewhat, as illustrated in Fig. 5 by the variable presence of nitrate over time.

During the yearly pumping test, besides the specific volume flow of the well, the entrance resistance was also measured between the abstraction well and both the upper and lower monitoring well in the gravel pack. As the results of these measurements are not completely reliable (not double-checked), an entrance resistance was considered present if the difference between the monitoring well and the production well was $>10\text{ cm}$ (at a drawdown in the abstraction well $>100\text{ cm}$) during at least two yearly inspections.

If necessary, after the yearly pumping test, maintenance activities were executed, like removal of HFO precipitates from the submersible pump and cleaning or rehabilitation of wells by high pressure jetting or by jutting (repeatedly pressing the water table down with the help of compressed air, and suddenly removing this pressure), not farther than at least 2 m above the top of the well screen. Table 3 summarizes which wells, during the years 2010–2014, showed the characteristics of well bore clogging: increase of drawdown during continuous or low frequency intermittent abstraction, and decrease of drawdown or constant drawdown during frequent intermittent abstraction (well 10 and well 45 in Fig. 6). Table 3, moreover shows the frequency of these well maintenance activities.

Table 3 shows several interesting features: wells that abstract nitrate- and iron(II)-containing water experience chemical well clogging, necessitating intensive well maintenance. Most of these wells show an entrance resistance, at the top and

at the bottom of the well screen. However, this entrance resistance is so small that it does not show as an increase in drawdown (well 14 and well 21 in Fig. 6). This need for intensive maintenance is caused by the rather high pH (~ 7.5) of the abstracted water, resulting in a fast precipitation of HFO. Probably due to this intensive maintenance, HFO accumulations are removed before they could result in a measurable increase in drawdown.

As demonstrated by the temporary presence of nitrate in the water abstracted by some wells (cf. Fig. 5), the distribution between native groundwater and basin water abstracted by one well may vary over time, and also the sensitivity to well clogging. As the occurrence of well bore clogging is confined to wells abstracting deeply anoxic water, the sensitivity for well bore clogging may vary under comparable well operation conditions. This is demonstrated by well 10 in Fig. 6: under comparable frequencies of intermittent abstraction, the well is sometimes sensitive to well bore clogging (see January 2012 and April 2013) and sometimes not (see 2010). It is, however, unknown, whether or not during this period (2010) particles accumulated on the well bore segment where deeply anoxic groundwater entered the well, but did not result in an increase in drawdown.

Conclusions and outlook

At well field Heel, three groundwater quality types may be distinguished, i.e. native groundwater, infiltrated anoxic basin water, and infiltrated oxic basin water. The wells located around the basin may abstract one of these or mixtures of these groundwater types, with corresponding consequences with regard to the occurrence of well clogging. Table 3 presents a summary of the current and final mixtures of abstracted water quality types, the wells concerned, and the consequences with regard to well clogging. These results are presented in the same sequence as the wells are present in the field, in this way also providing a spatial view from N to SW.

At the moment the wells in the central part (well clusters NE, E and SE minus wells 16, 20, 22 and 24) abstract a mixture of anoxic and oxic basin water (cf. Fig. 4), resulting in chemical (or screen slot) well clogging. The wells at both ends (well clusters N and SW minus wells 41 and 48) abstract native groundwater with a variable admixture of anoxic basin water, under incorrect (van Beek et al. 2009a) well operation resulting in mechanical (or well bore) well clogging.

In between these groups there is a transition group (well cluster S and wells 5, 24, 41 and 48) abstracting anoxic and oxic basin water and a variable admixture of native groundwater. The contribution of native groundwater will be small and variable, depending on the operation of the well field, clogging of the banks of the basin, etc. If these wells are not correctly operated, particles may accumulate over that

(vertical) segment of the well bore where native groundwater is entering the well. Whether this particle accumulation will manifest itself as an increase in drawdown (well clogging) is unknown, depending on the size of that segment, the amount of particles accumulated, etc. The well field conditions in 2010–2014 compare rather well with the occurrence of well clogging in 2014 (Table 3). Differences may be due to variations in well field operation (not all wells are operated continuously as represented in Fig. 4) and to variations in geology such as hydraulic conductivity, reduction capacity of the aquifer, etc.

Over time the aquifer will become more and more oxidized, until the traversed aquifer will be oxidized completely. Then the wells in the central part of the well field (Table 3) will abstract only oxidic basin water, and chemical well clogging will not occur anymore. At both ends of the well field, the wells will abstract a mixture of oxidic basin water and native groundwater, resulting in chemical well clogging and possibly also mechanical well clogging.

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

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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 $\text{pH} \approx 7.5$ 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)

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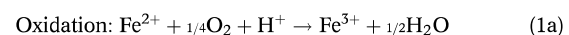
INTRODUCTION

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, [Tekerekopoulou et al. \(2013\)](#) reviewed this process.

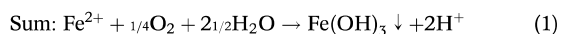
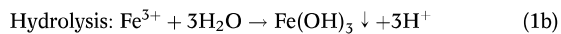
In the oxidation of iron(II) to HFO, three processes may be distinguished ([Böhler 1999](#); [van Beek et al. 2012](#)):

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:

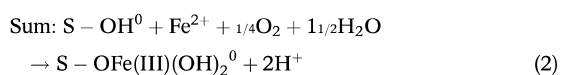
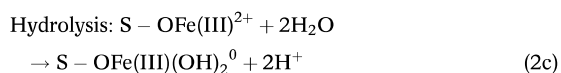
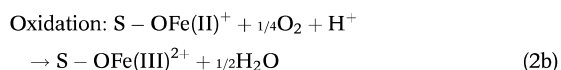
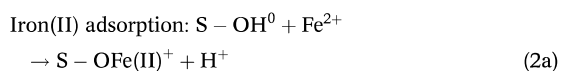


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From Equation (1) it is clear that homogeneous oxidation is favored by a high oxygen concentration and a high pH. These conditions are achieved by very intensive aeration, as in aeration-degassing-towers. In this process HFO flocs will develop and 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:

$$\frac{[\text{Fe}^{2+}]_0 - [\text{Fe}^{2+}]}{[\text{Fe}^{2+}]_0} = 1 - \exp\left(-k_1 \frac{[\text{O}_2]}{[\text{H}^+]^2} \tau\right) \quad (5)$$

where $[\text{Fe}^{2+}]_0$ represents the concentration of iron in the abstracted groundwater (mol/l), $[\text{Fe}^{2+}]$ 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.

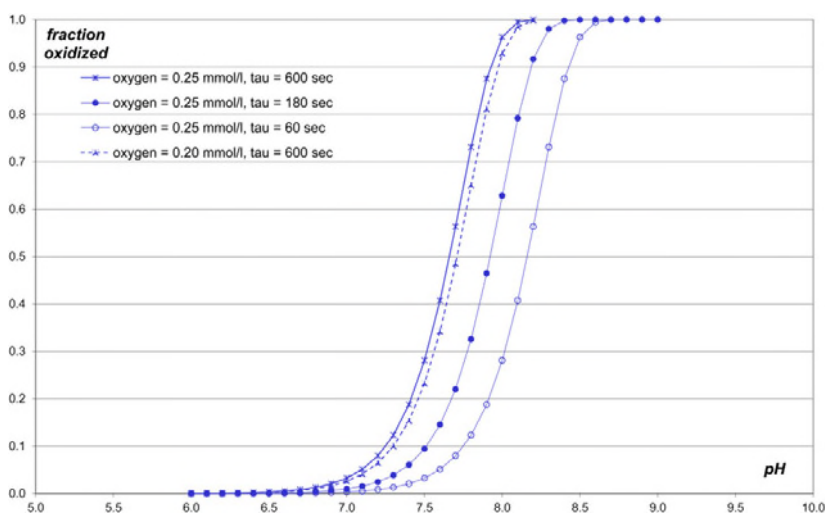


Figure 1 | Fraction of iron(II) oxidized by homogeneous oxidation as function of pH for three values of residence time and two values of oxygen concentration ($k_1 = 2.2 \cdot 10^{-15} \text{ mol.l}^{-1}.\text{s}^{-1}$).

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 ($l \cdot mol^{-1} \cdot sec^{-1}$), 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 ($kg \ Fe \cdot m^{-2} \cdot day^{-1}$), 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 ($m^3 \cdot m^{-2} \cdot h^{-1}$) 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 Grobendonk 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: Reststoffenu-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 'Reststoffenuic', 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 or 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 ($k_1 = 2.2 \cdot 10^{-15} \text{ mol} \cdot \text{L}^{-1} \cdot \text{sec}^{-1}$, $k_{\text{dissolving}} = 1.22 \text{ kg/L}$, and $F_{\text{Fe}} = 0.428 \text{ kg/kg}$)

Water treatment plant	Balen		Bunnik		Dalen		Grobbe-donk		Haaren		Groene-kan		Harder-broek		Heren-tals		Loos-drecht		Macharen		Veghel		Vliertden		
	Pidpa	Vitens	Vitens	VMD	Pidpa	Brabant	Water	Vitens	Vitens	Vitens	Vitens	Vitens	Vitens	Vitens	Pidpa	Vitens	Brabant	Water	Water	Water	Water	Water	Water	Water	
Chemical composition abstracted groundwater																									
pH	6.60	7.59	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	44.0	44.7	47.3	45.9	39.9	16.7	34.4	26.6	59.5	65.6	45.9													
Alkalinity (mmol _e /l)	2.92	4.43	1.07	3.94	2.57	1.72	4.00	1.90	4.16	5.80	5.20														
Iron concentration (mg/l)	27	3.25	12	34.7	0.46	1.41	19.7	5.34	12	2.5	4.3														
Aeration and RSF class	III	I	III	III	I	II	I	I	III	II	III	I	I	I	III	II	III	I	III	I	I	I	I	I	
Calculation contribution iron(II) removal by homogeneous oxidation (%)																									
Oxygen concentration after aeration (mg O ₂ /l)	5	9	2	5.5	9	6.5	8.5	3	6.5	6	9	9	9												
pH after aeration	6.7	7.8	6.5	6.7	7.95	7.75	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	8	9	8.1	8	14	8.8	7													
Residence time in aeration tower (min)	0	0	0	0	3	0	0	0	0	0	3	3													
Residence time in supernatant water (min) ¹	0.8	1.8	0.0	2.7	3.4	2.3	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	3.0	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	5.3 ^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	36	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	0.386 ^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	2.5 [#]	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	0.036	0.029	0.858	0.072	0.858	negl	negl													
Calculated contribution heterogeneous oxidation (%)	59	10 [#]	44	33	negl	9 [#]	19 [#]	34	20 [#]	33	negl	negl													

(continued)

Table 2 | continued

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

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.

²Initial filter bed height 2 m, in WTPs Balen and Herentals 1.8 m, in WTP Dalen 2.5 m.

³Full length of filter bed available, ⁴upper half of filter bed 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 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 ($\varnothing = 1 \text{ m}^2$) 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) ($k_1 = 2.2 \times 10^{-15} \text{ mol.l}^{-1}.\text{sec}^{-1}$, $d_{\text{coating}}^{\text{bulk}} = 1.22 \text{ kg/l}$, and $f_{\text{Fe}} = 0.428 \text{ kg/kg}$)

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 (%)	45	48	59
Calculation contribution iron(II) removal by biological oxidation (%)			
Sum homogeneous and heterogeneous oxidation (%)	45	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.

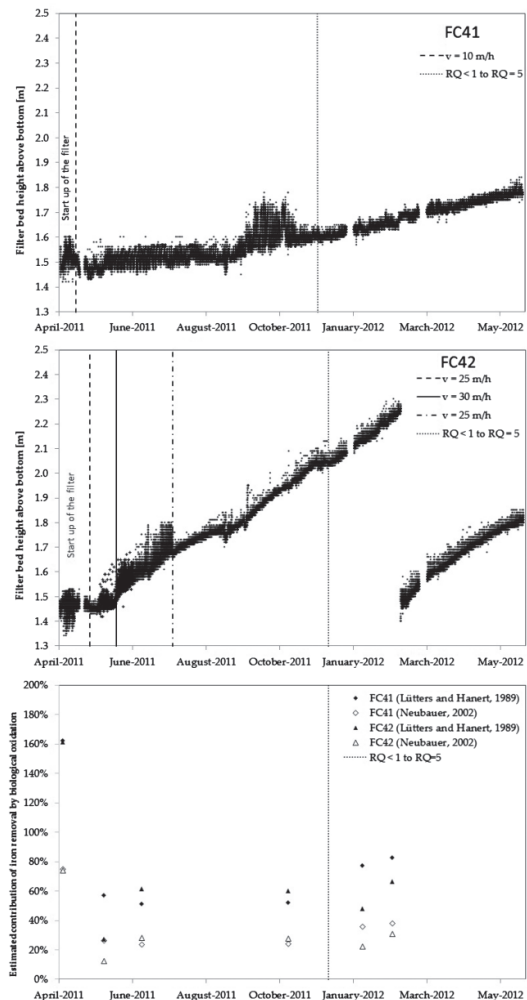


Figure 2 | Results of the continuous bed height measurements of the pilot plant trickling filters FC41 (filter flux 10 m/h) and FC42 (filter flux 25 m/h) and of the contribution of biological iron(II) oxidation to total iron(II) removal at WTP Lekkerkerk (Oasen). At the start of the experiments the filter 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) ($K_1 = 2.2 \times 10^{-15}$ mol/L¹·sec⁻¹, $d_{\text{coating}}^{\text{bulk}} = 1.22$ kg/L, and $f_{Fe} = 0.428$ kg/kg)

Water treatment plant (Oasen)	Lekkerkerk				De Hooze Boom		
	FC41		FC42		FF11	FF12	
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

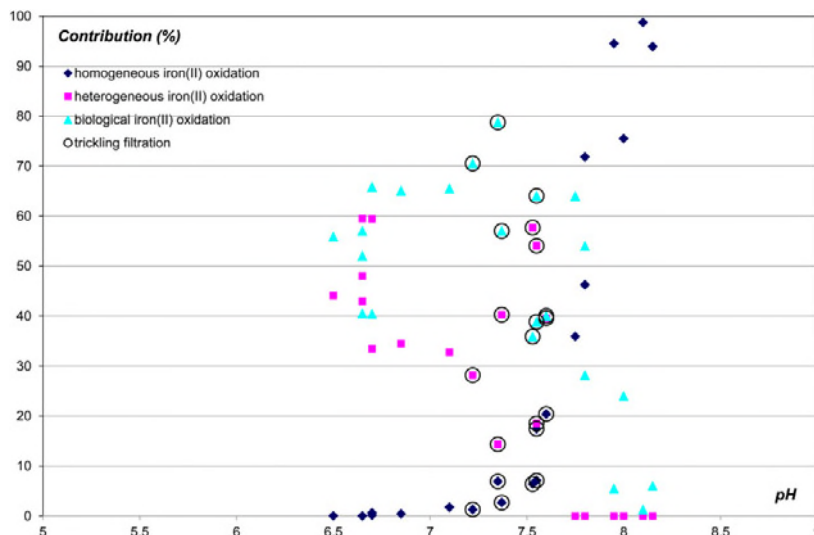


Figure 3 | Contribution of the various iron(II) oxidation processes as a function of pH (in aerated water) in iron(II) removal by aeration and RSF. The results from trickling (or dry) filtration have been indicated separately.

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. Sogaard *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.

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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 & Czekalla 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).

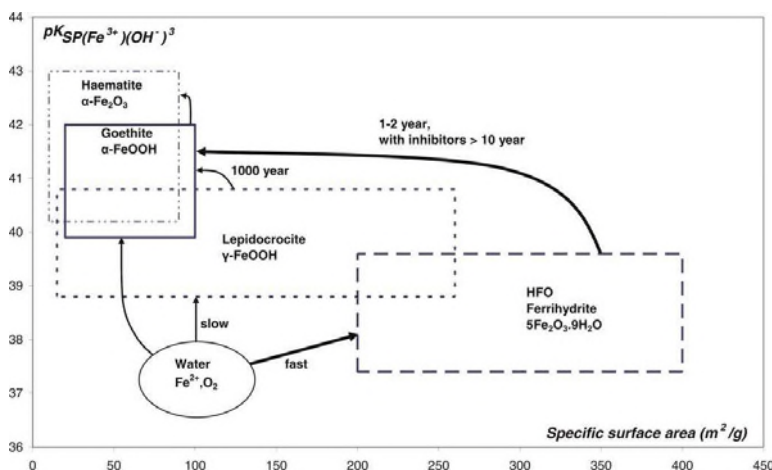


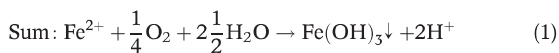
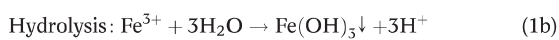
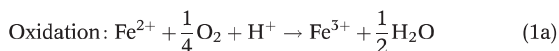
Figure 1 | Relations between various iron(III) hydroxides (modified after Stuyfzand (2007), based on data from Houben & Treskatis (2007) and Appelo & Postma (2006). Arrows without numbers denote unknown rates.

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):

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

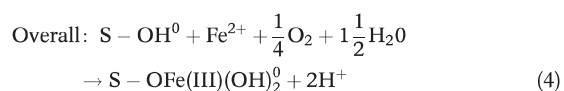
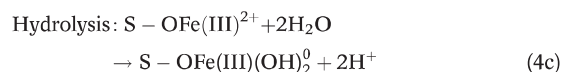
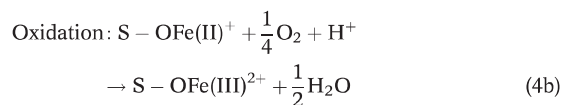
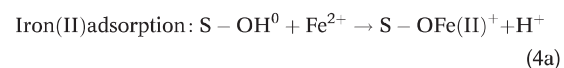
The value for the rate constant k_1 at 25 °C equals $1.08 \times 10^{-13} \text{ mol L}^{-1} \text{ s}^{-1}$ (Stumm & Morgan 1996). This value is very much dependent on the temperature. At 10 °C, which is the average temperature of groundwater in

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

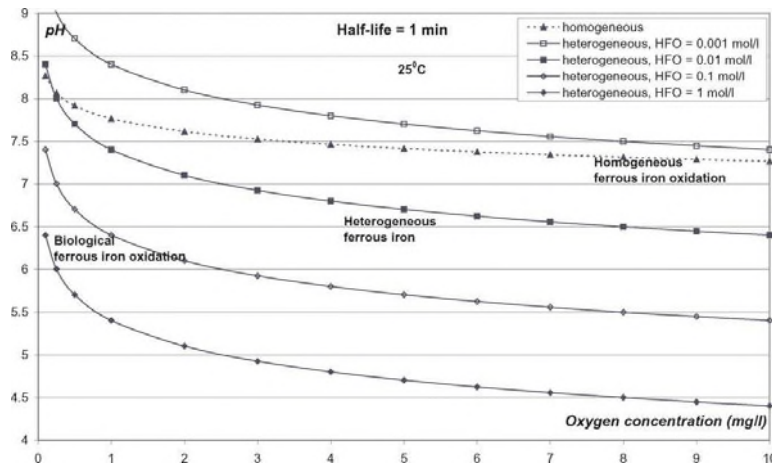


Figure 2 | Half-life of 1 minute for homogeneous oxidation of iron(II) as a function of oxygen concentration and pH at 25 °C (dotted line), and for heterogeneous oxidation for four concentrations of HFO (solid lines). The lines were calculated using the rate constants for systems with only iron(II). 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 $>$ goethite $>$ 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:

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

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

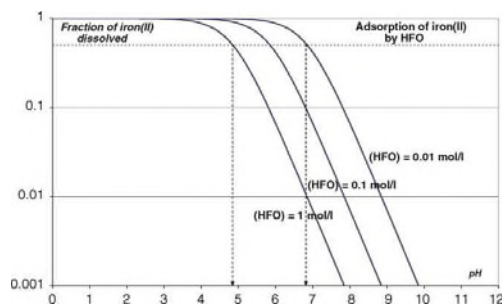


Figure 3 | Fraction of iron(II) dissolved as function of pH for several HFO concentrations. The horizontal dotted line represents the 50% adsorption/solution.

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 2001; 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, [Sogaard *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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