Modeling In Situ Iron Removal from Ground Water

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Abstract

In situ iron removal is conducted routinely in a number of European countries. A volume of oxygenated water is injected, and subsequently a larger volume of ground water can be pumped with a lower iron concentration than is found in native ground water. The underlying reaction mechanism has not been well described so far, and the process has not been modeled quantitatively. The essential problem is how the electron transfer takes place between the dissolved oxygen in injection water and the dissolved iron in ground water. An intermediate reaction step, involving cation exchange of ferrous iron and subsequent oxidation by oxygen of injection water, explains the efficiency increase during the initial cycles and the absence of clogging by precipitated iron-oxyhydroxide. A hydrogeochemical transport model has been used to model column experiments with good results. The quantification of the reaction mechanism allows the assessment of operational conditions. For example, it can be shown that increasing the oxidant concentration in the injected water has an insignificant effect when exchangeable ferrous iron is low.

Introduction

In situ iron removal has proven to be a viable technique for diminishing the iron concentration in ground water. The technique involves a cyclic injection of oxygenated water into the aquifer, and withdrawal of injected water and ground water in which iron (and manganese) concentrations are lower than in the native ground water. It is applied in a number of European countries (Hallberg and Martinell 1976; Rott et al. 1978; Booch and Barovich 1981; Van Beek, 1980, 1983; Rott and Lamberth 1993; Meyerhoff 1996). The lower iron concentrations are beneficial since further water treatment can be abated or sometimes even omitted.

The gross chemical mechanism of in situ oxidation appears to be simple, in that a given amount of oxidant is injected, and is consumed by reduced substances in the aquifer. The redox balance must apply to amounts of oxidants and reductants. The problem is how the dissolved oxidant (such as 0,) in injected water reaches the dissolved reductant (Fe^{2+}) in ground water, while the latter is being displaced during injection. The essence of in situ treatment is, in fact, that iron removal continues even after the complete withdrawal of the injected water. Several reactions have been proposed to explain the extended reaction, but the chemical consequences and relationships have not been calculated or fully explored.

The mechanisms and their implications are presented here. The most probable reaction has been incorporated in the hydrogeochemical transport model PHREEQC (modified from Parkhurst [1995]), and the model is used to simulate the column experiments of Olthoff (1986, 1988). The mechanism, based on the oxidation of exchangeable Fe^{2+}, explains the initial increase of efficiency during successive cycles and the absence of clogging during operation. The model is also able to indicate how operational conditions can be improved, for example, where it might be profitable to increase the oxidant concentration in injected water.

Reaction Stoichiometry and Process Efficiency

The oxidation of dissolved ferrous iron with oxygen follows the reactions:

$$Fe^{2+} \rightarrow Fe^{3+} + e- \qquad (1)$$

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O \qquad (2)$$

The resulting ferric iron is highly insoluble and precipitates readily as an oxyhydroxide such as goethite or lepidocrocite:

$$Fe^{3+} + 2\,H_2O \rightarrow FeOOH + 3\,H+ \qquad (3)$$

The precipitate can adsorb additional Fe^{2+}:

$$x\,Fe^{2+} + FeOOH \rightarrow FeOOH_{1-y}Fe_x^{(2x-y)+} + y\,H+ \qquad (4)$$

where x and y are the stoichiometric coefficients for Fe^{2+} sorption and H+ release (the value of x is discussed later).

The solubility of 0, at 0.2 atm in water at 10°C is 11 mg/L or 0.35 mmol/L (mM). It follows from Reactions 1 to 4 that 1 L with 0.35 mM 0, can remove iron from 4(1 + x) L ground water with 0.35 mM Fe^{2+} (19.5 mg Fe^{2+}/L). The redox balance for in situ iron removal consists similarly of the amount of oxidant that is injected and the amount of oxidation that has taken place.

The amount of injected oxidant is

$$Ox_{in} = \int_0^{V_{inj}} \nu_i \; \mathrm{Ci} \; dV \qquad (5)$$

where ν_i gives the electron-equivalents per mole reduction of i (ν_{O_2} = 4 according to Reaction 2),c_i is the concentration of i (mM), and V_{inj} is the injected volume (m^3). Part of the injected oxidizer is with-

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drawn again when the operation switches to pumping. The consumed oxidant equals

$$Ox_{react} = Ox_{in} - \int_0^{V_{gw}} \nu_i \, C_i \, dV \qquad (6)$$

where V_{gw} is the extracted volume of ground water (m^3).
It is balanced by the decrease of reductants:

$$Red_{react} = \sum_j \int_{V_{inj}}^{V_{gw}} \nu_j \, (C_{j,0} - C_j) \, dV + \sum_k \nu_k (q_{k,0} - q_k) V_{ox} \qquad (7)$$

where c_j is the concentration of reductant j in pumped ground water (mM), c_{j0} is the concentration in pristine ground water, V_{ox} is the oxidized 'pore volume of the aquifer (m^3) in which $q_{k,0}$ is the averaged initial concentration of solid reductant k (mmol/L pore water), and q_k is the averaged final concentration. The reaction of the solid reducers k may be deduced from changes in water composition. For example, the oxidation of pyrite can be manifest in an increase of the sulfate concentration. Otherwise, if sulfate is sorbed, the reaction of the components k must be a lumped parameter deduced from electron balance, $Ox_{react} = Red_{react}$. The occurrence of sorption of Fe^{2+} on newly created sites (Equation 4) also complicates the construction of the redox balance.

The efficiency of the process is defined to be the volume of ground water recovered until c_j reaches a maximum concentration divided by the volume of injected water:

$$E = V_{gw} / V_{inj} \qquad (8)$$

The efficiency can be related to the reaction stoichiometry. For oxygen and iron (reactions 1 to 4), it becomes specifically

$$E = \frac{4 \, C_{O_2} (1 - Ox_{out} - R_k)(1 + x)}{C_{Fe^{2+},0} - C_{Fe^{2+}}} \qquad (9)$$

where Ox_{out} is the fraction of oxygen which is pumped out again and R_k is the fraction of oxygen used for oxidation of nonferrous chemicals. In the aquifer the fronts spread out due to dispersion and the combined effects of transport and reaction. The concentration of iron will therefore increase gradually in the well on pumping, and the efficiency depends on the limiting concentration of Fe^{2+} where a new run is started with the injection of oxygenated water. Figure 1 shows the increase of Fe^{2+} concentrations for a case in The Netherlands (modified from Van Beek [19801). With each cycle 1000 m^3 of oxygenated water are injected and about 7000 m^3 are pumped. The ensuing runs show a delayed rise of the iron concentration in the pumped ground water. In other words, the process efficiency increases with the number of runs. The increasing efficiency in successive runs is a common feature of in situ iron removal.

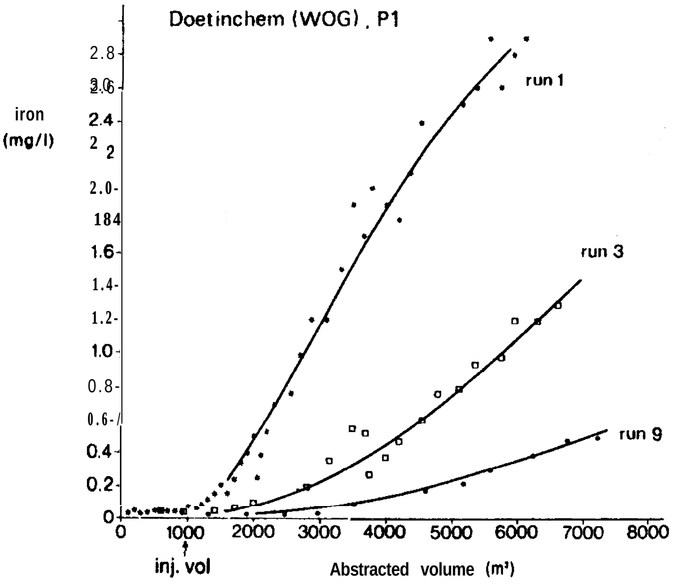

Figure 1. Iron concentration in ground water as function of pumped volume and number of injections of oxygenated water (modified from Van Beek [1980]).

Contact of Fe^{2+} and Oxidant

Several theories have been advanced on in situ iron removal, and specifically, how the electron acceptor in injection water contacts dissolved Fe^{2+} in ground water. Boochs and Barovich (198 1) considered the effects of mixing at the injection front due to physical dispersion. Their theory implies that the efficiency is equal to the mixing ratio of ground water and injection volume. It requires an unreasonably large dispersivity since observed efficiencies of five and higher must be explained by a mixing ratio of five and higher. For example, if the injected volume travels 10 m from the well, it must mix with water up to 50 m (in the case of linear flow). This implies that the dispersivity should be about 50 / 3 ≈ 17 m, which is high. This theory cannot explain why efficiency increases during successive runs.

Hallberg and Martinell(1976) and Rott and Lamberth (1993) suggested that bacteria play a decisive role in the process. The repeated injection of oxygenated water and withdrawal of reduced ground water supplies nutrients and creates favorable growth conditions for microorganisms. Increase of efficiency with successive runs was related to growth of the bacterial community. This theory implies that the microorganisms are able to take away and store the oxidant, and to use it again when flow is inverted and the iron-containing ground water flows by. It requires changes in the oxidation state of organic matter, and organic matter reactions must be invoked to capture a considerable part of the oxidant. A large proportion of oxidant is indeed consumed by organic matter when nitrate is the oxidizer (Vanek 1990). However, the reaction of organic matter is less conspicuous when oxygen is used (Van Beek 1983). Furthermore, it can be expected that the growth of the bacterial population delays the onset of iron removal, whereas the process is observed to start immediately during the first run (Van Beek 1983). Olthoff (1986) has performed a series of column experiments (discussed later), and observed only a small effect on the efficiency of in situ iron removal when hypochlorite was injected to sterilize the column.

Van Beek and Vaessen (1979) were the first to propose that Fe^{2+}, sorbed on iron-oxyhydroxide in the aquifer, may become oxidized by the injected oxidant. The resulting Fe^{3+} precipitates and forms a new layer on the existing iron-oxyhydroxide, which is able to sorb Fe^{2+} from ground water when flow is reversed. The positions of the concentration fronts according to this theory are illus-

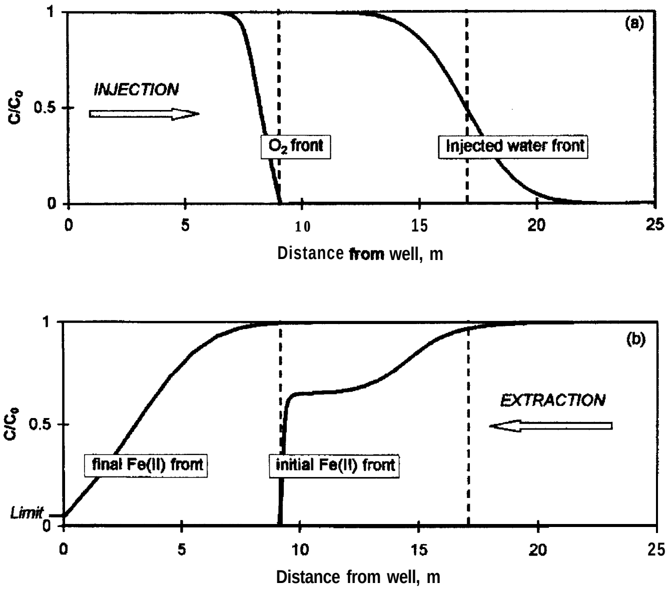

Figure 2. Concentration fronts of oxygen and iron during in situ iron removal with oxidation of exchangeable Fe^{2+}. (a) O$_2$ front and extent of injected water at the end of injection. (b) Solute Fe^{2+} fronts at the beginning and end of extraction.

trated in Figure 2. The reactions and the front positions can best be understood going upstream from the injection water front.

First, cations from the injection water exchange with Fe^{2+} from the exchange sites. In solution Fe^{2+} reacts with oxygen, oxidizes to Fe^{3+} and precipitates as iron-oxyhydroxide. Oxygen is retarded since it is consumed by the reaction. The oxygen front therefore lags behind the injection water front (Figure 2a), and Fe^{2+} remains in solution between the oxygen- and the injection water fronts (Figure 2b).

The exchanger is devoid of Fe^{2+} where the ground water contains oxygen. During pumping, ground water with Fe^{2+} passes the depleted exchanger and iron is sorbing again. Thus, the iron front lags behind the ground water front, and ground water without iron can be pumped until the Fe^{2+} front arrives at the well (Figure 2b).

This theory demands that the ratio of sorbed and solute iron is at least equal to the efficiency. Van Beek and Vaessen (1979) did not perform the calculations to assure that this can be the case and assumed that only iron-oxyhydroxide would be active as sorber for Fe^{2+}. Eichhom (1985) (cited by Meyerhoff [19961) suggested that the cation exchange capacity of the sediment (which includes clay minerals and other exchangers besides iron-oxyhydroxide) is also available for exchange of Fe^{2+}. He did not calculate how much exchangeable Fe^{2+} is available.

The increase in efficiency was related by Van Beek and Vaessen to the initial consumption of oxidant by other reductants than Fe^{2+}, and to the increase of iron-oxyhydroxide during successive cycles. However, the oxidation reaction of sorbed and exchangeable Fe^{2+} during in situ iron removal can explain, by itself, the observed efficiency increase that is shown in Figure 1. When the injection of oxygenated water is resumed before the iron concentration in ground water in the well reaches the level of the foregoing run, the exchanger is not refilled with Fe^{2+} to the previous level. The smaller amount of exchangeable Fe^{2+} allows the oxygen to penetrate further into the aquifer, and to create a larger oxidized zone, which in turn can sorb Fe^{2+} from a larger volume of ground water.

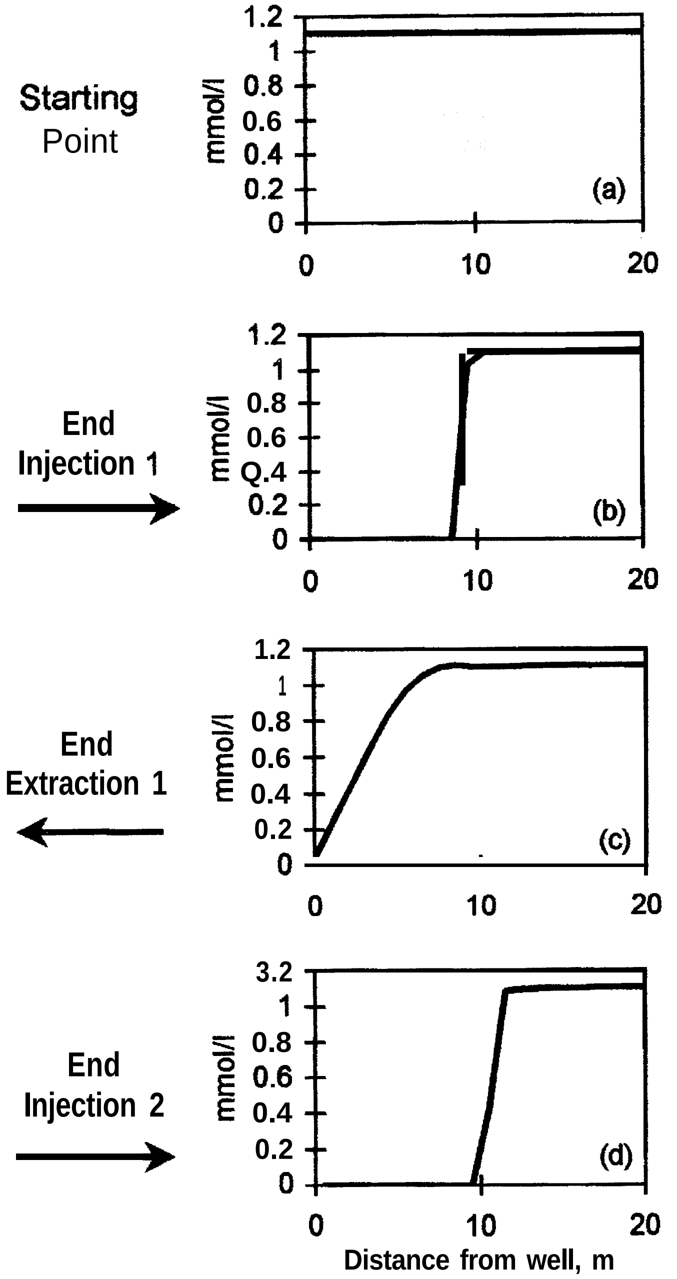

Figure 3. Profiles of total exchangeable and sorbed Fe^{2+} during the first two cycles of in situ iron removal. (a) Concentration of sorbed Fe^{2+} in the pristine aquifer. (b) Concentration profile after the first injection of oxygenated water. (c) The exchange complex is not completely refilled with Fe^{2+} at the end of the first extraction. (d) Less sorbed Fe^{2+} near the well permits the oxygen to enter the aquifer further with the second injection.

The process is illustrated in Figure 3, where the sorbed Fe^{2+} concentration is shown as function of distance to the well during the first two cycles. Initially, the aquifer exchanger contains uniformly 1.05 mmol Fe^{2+}/L pore water in this example (Figure 3a). At the end of the first injection the sorbed Fe^{2+} concentration is zero in an oxidized zone near the well (Figure 3b). Subsequently, ground water is extracted until the iron concentration reaches a limiting value in the well and the first cycle ends. The sorbed iron profile is given in Figure 3c, and it will be noted that it is different from the initial, uniform profile in that less iron is sorbed near the well. During the second injection, oxygen can enter a few meters further into the aquifer and create a larger oxidized zone (Figure 3d). The larger oxidized aquifer volume permits more sorption of iron and consequently longer extraction is possible before the iron concentration in the well reaches the limit. The efficiency increase is therefore connected to the transient character of the operation in the initial stages.

It may be noted that the profile shapes of solute and sorbed Fe^{2+} at the end of the injection stage are not identical in Figures 2b and 3b. Between the injected water front and the oxygen front, the solute Fe^{2+} concentration is lower than in the pristine ground water (Figure 2b). However, in that part, the exchangeable concentration remains about equal to the original concentration in the aquifer (Figure 3b). The reason is that the Ca^{2+} concentration has decreased markedly in the oxygenated zone where it has exchanged with Fe^{2+}. Thus, Ca^{2+} offers less competition for the exchange sites and the concentration of FeX_2 does even increase after the oxygen front despite the lower Fe^{2+} concentration in solution.

Rott et al. (1978) hypothesized that sorption of oxygen on aquifer sediment occurred and enabled contact with dissolved iron. The oxygen would be released when iron-containing ground water passed the sorption sites when flow is reversed. The theory may produce results that are indiscernible from oxidation of sorbed Fe^{2+} (Aleksejew and Kommunar 1983). However, sorption of oxygen on aquifer sediment is not well documented, and this theory has not been considered here.

Exchange and Sorption of Fe^{2+}

The remarkable operational success of in situ iron removal can probably be explained by the oxidation of exchangeable and sorbed Fe^{2+}. However, this process has not been quantified yet. Exchange of Fe^{2+} can be calculated with equations given by Appelo and Postma (1993). The relative importance of iron-oxyhydroxide as a sorbing agent for Fe^{2+} can be estimated using data on hydrous ferric oxide (HFO, or goethite) (Dzombak and Morel 1990). Assume a sandy sediment with bulk density $\rho_b = 1.8$ g/cm^3, porosity $\varepsilon_w = 0.3$, cation exchange capacity (CEC) of 1 meq/100g, and 100 mg Fe per kg sediment in the form of goethite. Laboratory goethite has 0.2 mol weak sorption sites per mol HFO, which translate to $\rho_b/\varepsilon_w \times 0.2 \times 100/55.85 = 2.14$ mmol weak sites/l pore water. There are also 0.005 mol strong sites per mol HFO, or 0.05 mmol/l pore water. A proportion of the HFO sites and of the exchange complex will be occupied by Fe^{2+}, depending on the other ions in solution and on the sorption/exchange constants.

Exchange constants can be obtained from Appelo and Postma (1993, Table 5.5). Binding constants for Fe^{2+} sorption on HFO have not been determined, as far as we know. However, the constants can be estimated with a linear free energy relation. According to guidelines provided by Dzombak and Morel (1990, Table 10.5) log K's for the reaction

$$\equiv SOH + Fe^{2+} \leftrightarrow \equiv SOFe^{+} + H+ \qquad (10)$$

are expected to be 0.7 and -2.5 for strong and weak sites, respectively.

The hydrogeochemical computer model PHREEQC (Parkhurst 1995) was used to calculate for a 3 mM $Ca(HCO_3)_2$ solution with 0.1 mM Fe^{2+} at pH = 7.0 and 25°C, that exchangeable FeX_2 is 0.31 mM, and that 5% of the weak sites and 100% of the strong sites on HFO are occupied by Fe^{2+} (0.14 and 0.05 mM respectively). The input file for PHREEQC is given in the Appendix.

The calculated concentrations of exchangeable and sorbed Fe^{2+} will change in proportion with CEC and HFO. Sorption on HFO accounts initially for 38% of total exchangeable Fe^{2+} in the previous example. With each cycle a maximum of 0.5 mM HFO precipitates, which adds additional sorption sites and allows for an increase of efficiency. It will also be clear that solution parameters influence exchangeable and sorbed Fe^{2+}. Halving of the $Ca(HCO_3)_2$ concentration will more than double the concentration of exchangeable FeX_2 (more than double, because a lower alkalinity gives less Fe^{2+} complex in solution). An increase of pH will greatly favor sorption of Fe^{2+} on HFO. For example, a pH increase from 7 to 8 will increase the percentage of weak sites occupied by Fe^{2+} from 5% to 30%. This increase is related to the decreasing positive charge on HFO when the point of zero charge (PZC = 8.3) is approached from lower pH. Thus, the value of x in Equation 4 is variable and depends on solution composition.

Front Retardation and Efficiency

It has been often proposed to use pure oxygen to obtain higher concentrations of oxidant in the injection fluid and to attain a higher efficiency, as is suggested by Equation 9 (Meyerhoff 1996). However, the oxidation of exchangeable Fe^{2+} as an intermediate in the reaction leads to front retardation and imposes a limit on the maximal attainable efficiency. This interesting consequence has gone unnoticed so far.

Suppose that in the previous example with 0.5 mM exchangeable and sorbed Fe^{2+}, water is injected with an oxygen concentration of 0.5 mM electron equivalents. The oxygen front will then show a retardation of $R = 1 + \Delta q/\Delta c = 1 + 0.5/0.5 = 2$. Half of the injected oxygen is not used to oxidize Fe^{2+}, but will be pumped out again. The amount of oxidized exchangeable Fe^{2+}, divided by the iron concentration in ground water, yields an efficiency of 2.5. The retardation of the oxygen front becomes R = 1.5 when the oxygen concentration is doubled. The efficiency now increases to $1/1.5 \times 5 = 3.3$, or only 4/3 higher than beforehand, whereas Equation 9 suggests that the efficiency would increase by a factor of 2. The reason is that (in Equation 9) an increase of c_{O_2} is accompanied by an increase of Ox_{out}. The efficiency can probably better be improved in this case by optimizing the well arrangement, for example, by installing separate injection and pumping wells to prevent the last part of the oxygenated water being withdrawn without reaction.

Kinetics of the Oxidation Reactions

The kinetics of oxidation of solute Fe^{2+} by oxygen increase with the square of the OH- concentration with pH > 5 (Singer and Stumm 1970). The oxidation is essentially complete within an hour at pH = 7, and 91% complete within 24 hours at pH = 6. The reaction produces protons according to Reactions 1 through 3, which slow down the rate when the solution is unbuffered. The other common reductants in aquifers are pyrite and organic matter for which rate equations are also known (Williamson and Rimstidt 1994; Appelo and Parkhurst 1998). The rates for pyrite and organic matter are much slower, and oxygen injected in an aquifer will preferentially consume Fe^{2+}. The fast rate of the exchange reaction, and of Fe^{2+} oxidation with oxygen when pH is above 6.5, permit use of the local equilibrium assumption when the flow velocity is less than about 300 m/year.

Model Calculations of Olthoff's (1986) Experiment

Olthoff (1986) performed column experiments to assess the relationship between efficiency and the limiting iron concentration for which the cycle of injection and pumping is completed. Twelve columns, each with a length of 2.4 m and a diameter of 18 cm, were filled with sand and coupled in series. One cycle involved the injection of 150 L of water at 25 L/hour, a rest period of 16 to 20 hours, and the withdrawal of water at 12.5 L/hr until the iron concentration reached a threshold level of 1 mg/L. Dissolved iron was analyzed in the column during recovery in the 24th cycle. The material properties of the sand are given in Table 1. Note that the iron content of the sediment is quite high, and that it will be an important sorber compared to the relatively low CEC of 0.8 meq/100g. The water composition is shown in Table 2. The injection water has the same composition, but it contains 10.5 mg oxygen/L and no iron.

The experiment has been modeled with the hydrogeochemical transport model PHREEQC, version 2 (Parkhurst and Appelo 1997, 1999). The model includes dispersion (dispersivity was 10 cm according to Olthoff (19861). The pore water flow velocity during injection was 20 km/yr, which is too high for local equilibrium for exchange and redox reactions. Olthoff (1986) noted that the efficiency increased in his experiments when the flow velocity was decreased, which also points to nonequilibrium conditions. However, it was assumed that the rest period of 20 hours would be sufficient to reach at least near-equilibrium, and only equilibrium calculations were done. The amount of sorption sites on iron-oxyhydroxide in the sediment is not known; it is probably not identical for the amorphous and the crystalline oxides. The total number of sites was therefore used as a fit parameter. The number of weak sites and strong sites was 0.066 and 0.00165 per mol total iron, respectively.

The model results are compared with Olthoff's data in Figure 4. The C/C, = 0.5 front for dissolved iron has penetrated 5.1 m in the column after the injection of oxygenated water. The corresponding profile is labeled with "3 L" in Figure 4, indicating that 3 L were pumped out before the first sampling was performed. The iron front returned to 1 m when 607 L of water were recovered, and the concentration profile is labeled as "607 L". A volume of 607 L is identical to a travel distance of 50 m for a conservative tracer. Thus, the iron front shows a retardation of R = 50 / (5.1- 1) = 12.2.

Table 1
Properties of Sand Used by Olthoff (1986)

	Column 1-2	**Column 3-12**
Grain size (mm)	0.44	0.47
Porosity (-)	0.42	0.42
$CaCO_3$ (g/kg)	10	19
TOC (g/kg)	0.8	1.8
CEC (meq/ 100g)	0.82	0.77
Fe total (g/kg)	2.3	2.23
Am. Fe-ox. (mg Fe/kg)	84	129

Note that Fe total includes crystalline and amorphous iron oxides.

Table 2
Water Composition in Olthoff's (1986) Experiment

pH	**Na**	**K**	**Mg**	**Ca**	**Fe**	**Cl**	**HCO,**	**SO_4^{2-}**
6.83	**16.8**	**2.4**	**8.3**	**61.7**	**9.8**	**36**	**124**	101

Concentrations in mg/L or pH units.

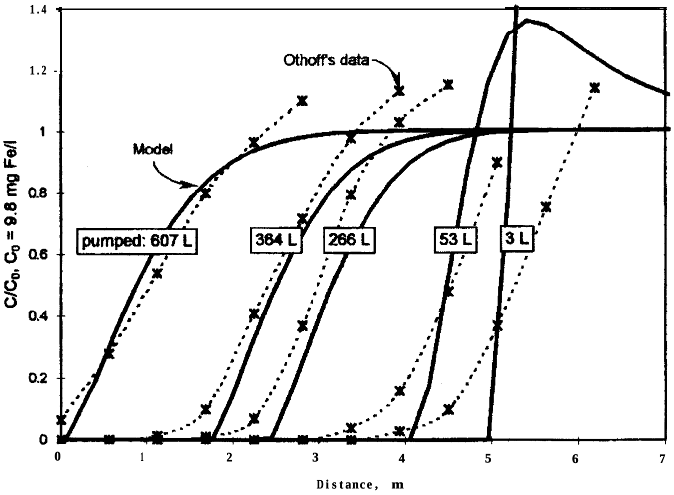

Figure 4. Dissolved iron as a function of distance and recovered volume in Olthoff's (1986) column experiment on in situ iron removal. Dotted lines indicate experimental results from Olthoff; thick lines are model simulations. The labels with the profiles indicate the liters pumped from the column after 150 L oxygenated water had been injected.

The retardation can be used to estimate the total amount of exchangeable and sorbed iron with the formula R = 1 + $\Delta q/\Delta c$, where Ac is the change in solute iron (9.8 mg/L) and Aq is the change in exchangeable and sorbed iron. After subtraction of exchangeable iron (calculated in equilibrium with the ground water composition of Table 2), the number of sorption sites on goethite (in equilibrium with ground water) could thus be estimated from Aq. The obtained value led to the model results in Figure 4 and shows an excellent agreement of the average front locations in experiment and model.

Compared to the model simulation, the experimental data show more disperse fronts, especially during the initial stages of recovery (Figure 4). This is likely the result of nonequilibrium of the redox and exchange reactions related to the high flow velocity in the experiment. It appears that the kinetics become less important during recovery when the front has traveled a longer distance, and when only exchange and sorption reactions take place, although smearing of the low concentrations is still evident in Figure 4. Another conspicuous feature in Figure 4 is that the dissolved iron concentrations can become higher than in native ground water during the process. The model indicates that the decrease of pH, due to oxidation and precipitation of Fe^{2+}, is the major factor for the concentration increase of Fe^{2+}.The lower pH increases the solubility of iron hydroxide, and leads to iron concentrations almost twice than those found in native ground water. The concentration increase extends over a greater distance in the experiment compared to model simulations. However, the overall concentration profiles of Fe^{2+} are well matched, which indicates that the dominant reaction terms have been correctly identified by the model.

On Clogging During In Situ Iron Removal

Iron precipitates can be quite massive and often cause serious clogging of drinking water wells. However, clogging has not been reported for in situ iron removal, even though systems have been operating for more than 20 years (Meyerhoff 1996). The lack of clogging suggests that precipitation of iron takes place at some distance away from the well, and possibly at varying locations in time. The model presented in this paper shows that the exchangeable iron concentration near the well is limited by the maximum solute iron concentration where the cycle ends. Thus, the iron precipitate builds up slowly near the well when the maximum concentration of Fe^{2+} in the pumped ground water is kept low (which is the essence of in situ iron removal). The precipitation of iron mainly takes place at some distance away from the well, where the ground water iron concentration is not diminished by exchange and sorption.

It is not unlikely that the point where the iron precipitation becomes maximal moves away from the well in time. The iron-hydroxide may precipitate on the exchange sites and form a coating which renders the sites less easily accessible. The exchange rate for Fe^{2+} would thus be limited, permitting oxygen to pass the point where Fe^{2+} is exchangeable and to penetrate further in the aquifer. Thus, the oxidized zone becomes more extended, and oxidation of Fe^{2+} and precipitation occurs further away from the well. A similar extension of the oxidized zone takes place in the initial transient stage, as was shown in Figure 3.

The important, overall effect of the intermediate reaction with exchangeable Fe^{2+} is that it reduces the possibility that iron hydroxide builds up in a limited space and near the well. This appears to be the major reason why clogging is insignificant during in situ iron removal.

Operational Flaws

It is known that ground water pH should be above 6 for in situ iron removal. This may well be related to the rapid decrease of the oxidation rate of Fe^{2+} when pH is below 6. The aquifer must not contain sulfides (pyrite) as the oxidation acidifies the system. The sections of the aquifer should be selected to be as homogeneous as possible, and without extremely coarse layers to prevent preferential flow of injected water through the most permeable parts, which generally have a relatively low exchange capacity.

Conclusions

The injection of oxygenated water for in situ ground water removal of iron is a viable treatment option. The reaction involves the displacement of ferrous iron from exchange and sorption sites and subsequent oxidation by oxygen. The exchange sites sorb Fe^{2+} again when Fe^{2+}-containing ground water flows by. The efficiency increases in successive runs because the operation is initially transient. Clogging has not been observed with in situ iron removal and appears to be unimportant by virtue of the self regulating nature of the Fe^{2+} exchange and sorption mechanism. The model can explain the results from column studies by Olthoff (1986) well.

The quantitative approach followed in this paper allows appraisal of operational conditions. For example, increasing the oxidant concentration in injected water is useless when the efficiency is limited by the amount of exchangeable Fe^{2+}, capable of consuming the oxidant during the injection stage.

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Appendix

PHREEQC (Parkhurst 1995) is a computer model for performing hydrogeochemical calculations such as exchange and surface complexation equilibrations, mineral reactions and equilibrations, and mixing of water. PHREEQC operates with input files in which the calculation instructions are arranged according to keywords. These keywords are largely self-instructive, as is illustrated by the example input file below where the keywords have been capitalized. Several databases are available with constants for the various reactions. The database has been extended with surface complexation reactions for Fe^{2+}. The input file illustrates how exchangeable and surface complexed Fe^{2+} can be calculated. Exchangeable FeX$_2$ is calculated with constants from Appelo and Postma (1993).

```
                                        Comment

SURFACE-SPECIES
 Hfo_sOH + Fe+2 = Hfo_sOFe+
    + H+ log_k 0.7
 Hfo_wOH + Fe+2 = Hfo_wOFe+
    + H+ log_k -2.5
SOLUTION 1
 -units mmol/kgw                        the standard input units
 -temp 25                               deg. C
 pH     7.0
 Pe     0.0 Goethite 3.0                pe in equilibrium with Goethite, SI = 3
 Ca     3
 C(4) 6 charge                          Total C is adapted for charge balance
 Fe     0.1
EXCHANGE 1
 X     0.06                             60 meq X-/l
 -equil 1                               exchange composition is defined
                                        to be in equilibrium with solution 1
SURFACE l-50
 Hfo_w 2.le-3 600 0.6                   weak sites, moles, m2/g, g
 Hfo_s  5.4e-5                          strong sites, moles
 -equil 1                               surface composition is defined
                                        to be in equilibrium with solution 1
END
```

PHREEQC has been enhanced with several new features to increase applicability, such as one-dimensional transport with dispersion and diffusive exchange with stagnant zones, exchangers and surfaces that can be coupled to varying amounts of minerals or reactants, and generalized kinetics (Parkhurst and Appelo 1997; Appelo and Parkhurst 1998; Parkhurst and Appelo 1999). This version has been used to calculate the profiles shown in Figures 2 through 4 of the paper.

The input file for calculating the data in Figure 2 is presented next. Figure 2 illustrated the effects of injection of oxygenated water in a sediment column of 50 m, and of subsequent pumping. The sediment is reduced, and contains Fe^{2+} in solution and exchangeable. The first part (until the first END) defines the chemical characteristics of the aquifer and the ground water. The aquifer is split up in 50 cells, and exchangers and sorbing surfaces are defined to be in equilibrium with the given solution. Subsequently a block of keywords defines the injection. SOLUTION 0 is the water injected in cell 1. The TRANSPORT parameters identify 50 cells, the length, boundary conditions at column ends, etc. The PRINT statement is used to limit lengthy output, which may otherwise overflow the hard disk, and printing of which also slows down program performance. A spreadsheet type file is defined with the keywords SELECTED_OUTPUT and USER_PUNCH. After the END, the extraction is defined.

```
                                        Comment
SOLUTION_SPECIES
 H20 + 0.01e- = H2O-0.01                For program convergence
 log_k -9.0
EQUILIBRIUM-PHASES l-50                 Define sediment
 Goethite 3.0 10.7e-3                   Goethite equilibrium, SI, moles
EXCHANGE l-50
 x 0.15
 -equil 1
SURFACE l-50
 Hfo_w Goethite 0.2 5.3e4               Coupled to Goethite, proportion, m2/mol
 Hfo_s Goethite 5e-3                    Coupled to Goethite, proportion
 -equil 1
SOLUTION l-50                           Define groundwater, 50 cells
 -temp 10
 pH     7.0
 Pe     0.0 Goethite 3.0
 Ca     3
 C(4) 6 charge
 Fe     0.1
END

SOLUTION 0                              Inject oxygenated water
 -temp 10
 pH 7.0
 pe 14.0 02(g) -0.68
 Ca 3
 C(4) 6 charge
 Cl le-3
TRANSPORT
 -cells 50
 -length 1                              Flowtube 50 X lm = 50 m.
 dispersivity 0.1                       Dispersivity, m
 -diffusion_coefficient 0.0             Diffusion coefficient, m2/s
 -bcon flux flux                        Boundary conditions at column ends
                                        Inject 1 m3...
 -shifts 17                             No of cell transfers
 -flow_direction forward
 -time 2.16e4                           1 shift = 6 hours residence time
                                        v = 4.63e-5 m/s
 -punch-frequency 17                    output at 17th shift only
PRINT
 -reset false
SELECTED-OUTPUT
 -file gw.prn                           For convenient output format..
 -reset false
USER-PUNCH
 -heading _Dist_ f___inj_w_ _O2/O2in__ __Fe/Feaq_
 -start
 10 punch Dist
 20 punch tot("Cl")/le-6
 30 punch mo1("02")/2.286e-04
 40 punch tot( "Fe( 2)")/ 1 e-4
 -end
END
                                        Pump 4.52 m3
TRANSPORT
 -shifts 77                             No of shifts
 -flow_direction backward
 -punch-frequency 77
END
```

Transport in the example is calculated for a column, but radial flow in well injections can be modeled by adapting the lengths of the cells in agreement with the radial extension of the injection front (Appelo and Postma 1993, Chapter 10). PHREEQC is available on the Web: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html.