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Diffusive/Dispersive and Reactive Fronts in Porous Media: Fe(II)-Oxidation at the Unsaturated/Saturated Interface

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Impact Statement

Using a combined experimental and modeling approach we investigate the coupling between diffusive/dispersive processes and kinetic iron(II) oxidation in batch, 1-D column, and 2-D flow-through systems.

1   **Abstract**

2   Diffusive/dispersive mass transfer is important for many groundwater quality problems as it drives the

3   interaction between different reactants, thus influencing a wide variety of biogeochemical processes. In

4   this study we performed laboratory experiments to quantify oxygen transport in porous media, across the

5   unsaturated/saturated interface, under both conservative and reactive transport conditions. As reactive

6   system we considered the abiotic oxidation of ferrous iron in the presence of oxygen. We studied the

7   reaction kinetics in batch experiments and its coupling with diffusive and dispersive transport processes

8   by means of 1-D columns and 2-D flow-through experiments, respectively. A non-invasive optode

9   technique was used to track oxygen transport into the initially anoxic porous media at highly resolved

10   spatial and temporal scales. The results show significant differences in the propagation of the conservative

11   and reactive oxygen fronts. Under reactive conditions oxygen, continuously provided from the

12   atmosphere, was considerably retarded due to the interaction with dissolved iron(II), initially present in

13   the anoxic groundwater. The reaction between dissolved oxygen and ferrous iron led to the formation of

14   an iron(III) precipitation zone in the experiments. Reactive transport modeling based on a kinetic

15   PHREEQC module tested in controlled batch experiments allowed a quantitative interpretation of the

16   experimental results in both 1-D and 2-D setups.

17   *Keywords: diffusion; transverse dispersion; unsaturated/saturated interface; iron(II) oxidation; porous media.*

18

19   In natural systems, the geochemical and biological activity at the interface between different

20   compartments, such as the unsaturated and the saturated zone in the subsurface, is determined by the

21   fluxes and exchange rates across the interface. Interface regions are highly active in terms of

22   physicochemical and microbiological processes (e.g., Sobolev and Roden, 2001; Bauer et al., 2009; Jost et

23   al., 2014). A number of experimental and modeling studies have identified diffusive and dispersive

24   processes as key mechanisms for mass transfer of volatile compounds to or from groundwater systems

25   (e.g., Barber and Davis, 1987; Barber et al., 1990; McCarthy and Johnson, 1993; Klenk and Grathwohl,

26   2002; Werner and Höhener, 2002; Prommer et al., 2009; Haberer et al., 2011, 2012; Freitas et al., 2011).

27   Of particular importance is the mass transfer of oxygen to anoxic groundwater since dissolved oxygen

28   plays a key role for many biogeochemical processes. The supply of oxygen influences the subsurface

29   redox conditions and the rates of many biological and geochemical reactions (e.g., Stumm and Morgan,

30   1996; Chapelle, 2001; Mächler et al., 2013; Rezanezhad et al., 2014). The importance of oxygen transport

31   across the capillary fringe has been shown in detailed experimental and modeling studies focusing on

32   conservative transport (e.g., Williams and Oostrom, 2000; Haberer et al., 2011, 2014a, 2014b),

33   microbially-mediated reactions (e.g., Sobolev and Roden, 2001; Maier et al., 2007; Dobson et al., 2007;

34   Jost et al., 2014), and abiotic reactions (Farnsworth et al., 2012). The objective of this work is the

35   simultaneous investigation of diffusive/dispersive oxygen transport under conservative and reactive

36   conditions. As a reactive system we selected the abiotic oxidation of ferrous iron that is a process of great

37   environmental relevance in shallow groundwater systems (e.g., Sung and Morgan, 1980; Appelo et al.,

38   1999; Appelo and Postma, 2005; Martin, 2005; Vencelides et al., 2007). In fact, iron(II) oxidation affects

39   the mobility and fate of many organic and inorganic contaminants. One notable example is the coupling of

40   iron cycling with arsenic release and transport (e.g., Smedley and Kinniburgh, 2002; Stollenwerk, 2003;

41   Wallis et al., 2011; Sharma et al., 2011; Voegelin et al., 2014). Dissolved ferrous iron is a common

42   constituent of anoxic groundwater and, when it comes into contact with dissolved oxygen, it is oxidized to

43   ferric iron. Once ferric iron is formed it readily undergoes hydrolysis and precipitates as solid ferric

44   hydroxides ($Fe(OH)_3$). With time, ferric hydroxides are transformed into progressively more stable and

45   crystalline minerals such as maghemite, lepidocrocite, hematite, and goethite (e.g., Sung and Morgan,

46   1980; Cornell and Schwertmann, 2003; Martin, 2005; Voegelin et al., 2010), which are the principal forms

47   of mineralized ferric iron found in soils and aquifer sediments. Changes in redox and pH conditions

48   influence iron speciation as well as the kinetics of iron(II) oxidation (Stumm and Morgan, 1996; Frini and

49   Maaoui, 1997).

50   In this study, we experimentally investigate the coupling of abiotic iron(II) oxidation and transport

51   processes in porous media. We focus on the interface between the unsaturated and the saturated zone and

52   we perform (*i*) reactive batch experiments to characterize the kinetics of iron(II) oxidation under different

53 pH conditions and in the presence and absence of a catalyzer; (ii) 1-D conservative and reactive column

54 experiments to investigate the propagation of oxygen fronts under diffusive conditions; and (iii) 2-D flow-

55 through experiments to quantify oxygen transfer across the capillary fringe and the propagation of

56 conservative and reactive fronts under advection-dominated flow-through conditions. Numerical transport

57 simulations have been carried out to interpret the experimental results and to assess the implications of the

58 experimental findings at larger temporal and spatial scales.

59

60 # THEORETICAL BACKGROUND

61 ## Diffusive/Dispersive Transport in Porous Media

62 A correct description of diffusive/dispersive processes in porous media is of primary importance since

63 these physical processes determine the transport and distribution of chemical species in the subsurface.

64 Such processes are typically coupled and often limit the overall rate of biogeochemical reactions. In the

65 absence of advective movement of groundwater, diffusion is the main process governing solute transport.

66 In porous media, diffusion of a dissolved species is hindered by the reduced cross-sectional area available

67 for the movement of solute molecules as well as by the size and the tortuous nature of the pores (e.g.,

68 Shackelford, 1991; Grathwohl, 1998; Appelo and Postma, 2005). In a 1-D porous medium diffusive

69 transport of a conservative solute is described as:

70
$$\varepsilon \frac{\partial C(z,t)}{\partial t} = D_p \varepsilon \frac{\partial^2 C(z,t)}{\partial z^2} \qquad (1)$$

71 where C [M L^{-3}] is the concentration of the diffusing compound depending on distance, z [L], and time, t

72 [T], ε [-] represents the porosity, and D_p [L T^{-2}] is the pore diffusion coefficient. The latter is related to the

73 aqueous diffusivity of the dissolved species as well as to the properties of the porous medium by (e.g.,

74 Boudreau, 1996; Sabatini, 2000; Boving and Grathwohl, 2001; Delgado, 2006):

75
$$D_p = \frac{D_{aq}}{\tau} \approx D_{aq} \varepsilon^{m-1} \qquad (2)$$

76   where τ [-] is the tortuosity, a coefficient encompassing the effects of all geometrical and chemical

77   interactions on the apparent diffusional constant in the porous medium (D_p) compared to that found in free

78   aqueous solution, D_{aq} [$L^2 T^{-1}$] (Clennel, 1997). The right hand side of Eqn. 2 is a common empirical model

79   relating the pore diffusion coefficient to the porosity of the packed bed (e.g., Epstein 1989; Boudreau,

80   1996; Grathwohl 1998; Boving and Grathwohl, 2001; Hu and Wang, 2003). m [-] is an empirical exponent

81   for which different values have been reported in the literature. For instance, Peng et al. (2012) reported a

82   value of 1.33 for soils, a range from 1.92-2.93 for limestone and sandstone, and a range from 2.5-5.4 for

83   clays.

84   For the 1-D diffusion experiments at the unsaturated/saturated interface performed in this study, the

85   following boundary conditions apply:

86
$$C = C_{bg} \text{ at } t = 0 \text{ for } 0 < z \leq \infty$$
$$C = C_0 \text{ at } z = 0 \text{ for } t \geq 0$$
$$C = C_{bg} \text{ at } z \to \infty \text{ for } t \geq 0$$
(3)

87   Under these conditions, the analytical solution of the 1-D diffusion equation (Eqn. 1) is:

88
$$C_{norm} = \frac{C - C_{bg}}{C_0 - C_{bg}} = erfc\left(\frac{z}{2\sqrt{D_p t}}\right)$$
(4)

89   where the concentration of the diffusing compound is normalized by the background concentration

90   prevailing in the porous medium, C_{bg} [$M L^{-3}$], and the concentration at the unsaturated/saturated interface,

91   C_0 [$M L^{-3}$]. This analytical solution is used to analyze the results of the conservative transport experiments

92   in the 1-D setup and to estimate the value of the pore diffusion coefficient.

93   Under flow-through conditions solute transport of a conservative species is determined by advective and

94   dispersive processes. Considering a 2-D domain, the governing transport equation reads as:

95
$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} + D_T \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial x}$$
(5)

96   where v [$L T^{-1}$] is the seepage velocity, and D_L [$L^2 T^{-1}$] and D_T [$L^2 T^{-1}$] are the longitudinal and transverse

97   components of the hydrodynamic dispersion tensor, respectively.

98   Mass transfer and mixing in the transverse direction are typically more important in subsurface transport

99   problems (e.g., Kitanidis, 1994); particularly for a continuous release of dissolved species, as in the flow-

100   through experiments performed in this study, for which the concentration gradients in the longitudinal

101   direction become negligible compared to the ones in the transverse direction (e.g., Chiogna et al., 2011

102   and 2012). Thus, an accurate description of the transverse hydrodynamic dispersion coefficient is

103   fundamental to properly describe dilution and reactive mixing processes. Recent pore-scale and laboratory

104   studies have shown the important interplay between the fundamental physical processes of advection and

105   diffusion not only at slow but also at high seepage velocities, resulting in compound-specific incomplete

106   dilution in the pore channels (Rolle et al., 2012; Rolle and Kitanidis, 2014) and influencing the transport

107   of uncharged polyatomic species as well as charged ions in porous media (Rolle et al., 2013a,

108   Muniruzzaman et al., 2014). Such effects at the subcontinuum scale propagate and are relevant also at

109   larger macroscopic scales (Rolle et al., 2013b). Hence, such effects need to be captured in dispersion

110   parameterizations at the continuum scale. An example is the compound-specific model for transverse

111   dispersion proposed by Chiogna et al. (2010). This parameterization of D_T, inspired by an earlier statistical

112   model of Bear and Bachmat (1967), takes into account the influence of aqueous diffusion not only on the

113   pore diffusion but also on the mechanical dispersion term:

114   $$D_T = D_p + D_{aq} \left(\frac{Pe^2}{Pe + 2 + 4\delta^2} \right)^\beta \tag{6}$$

115   where $Pe = vd/D_{aq}$ is the dimensionless grain Péclet number with d [L] representing the grain diameter, δ

116   [-] is the ratio between the length of a pore channel and its hydraulic radius, and β [-] is an exponent

117   accounting for incomplete dilution of the solute in the pore channels. Average values of $\delta = 6.2$ and $\beta =$

118   0.5 were determined experimentally considering a wide range of flow-through conditions in different

119   porous media and were found in good agreement with the outcomes of pore-scale simulations (Rolle et al.,

120   2012, Hochstetler et al., 2013).

121   In reactive systems coupled transport and biogeochemical transformation occurs. In the description of

122   such systems, the reactive terms are included in the governing diffusion and advection-dispersion

123 equations (Eqs. 1 and 5). In this study we consider the abiotic oxidation of ferrous iron by dissolved

124 oxygen, for which the reactive term is described in the following section.

125

126   **Abiotic Iron(II) Oxidation**

127 The abiotic oxidation of ferrous iron in the presence of oxygen is described by the following chemical

128 reaction:

129 $$Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3(s) + 2H^+ \tag{7}$$
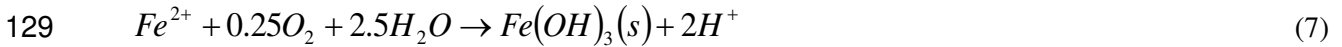
130 An intermediate step in this overall chemical reaction is the formation of ferric iron, which readily

131 undergoes hydrolysis and precipitates as solid ferric hydroxide (Cornell and Schwertmann, 2003).

132 Depending on the solution's pH and temperature, as well as on the ions participating in the reaction, the

133 presence of organic constituents and oxidizing agents, various oxidation products are formed in different

134 ratios (e.g., Stumm and Morgan, 1996; Voegelin et al., 2010). As an example, the slow oxidation of

135 ferrous iron due to aeration can result in the formation of magnetite, lepidocrocite, hematite, and goethite

136 (e.g., Frini and Maaoui, 1997). The oxidation of iron(II) (Eqn. 7) also results in the formation of H^+-ions

137 and thus, depending on the buffering capability of the system, in a possible decrease of pH.

138 Due to the importance of iron(II) oxidation in many aquatic systems, the kinetics of this reactive process

139 has been extensively studied. In aqueous solutions at pH $\geq$ 5 the oxygenation kinetics of ferrous iron

140 follows the general rate law (e.g., Stumm and Lee, 1961; Sung and Morgan, 1980; Davison and Seed,

141 1983; Millero et al.1987; Stumm and Morgan, 1996):

142 $$-\frac{d[Fe^{2+}]}{dt} = k^*[Fe^{2+}][OH^-]^2 p_{O_2} \tag{8}$$

143 where k^* is the reaction rate constant for which Stumm and Morgan (1996) report a value of $8(\pm2.5)\times10^{13}$

144 mol^{-2} L^2 atm^{-1} min^{-1} at 20 °C. Expressing the dependence on oxygen as function of the dissolved aqueous

145 concentration, the rate law reads as:

146 $$-\frac{d[Fe^{2+}]}{dt} = k[Fe^{2+}][OH^-]^2[O_2(aq)] \tag{9}$$

147   in which the reaction rate constant, k, now has units of $mol^{-3} L^3 min^{-1}$.

148   According to Eqs. 8 and 9, the oxidation rate of ferrous iron is of first-order with respect to the

149   concentration of both ferrous iron and oxygen, whereas it is of second-order with respect to pH. Therefore,

150   the reaction rate is strongly pH-dependent, and below pH 6 the oxidation of ferrous iron is very slow (e.g.,

151   Martin, 2005; Morgan and Lahav, 2007). To increase the reaction rate catalysts, such as Cu^{2+} and Co^{2+},

152   may be added in trace quantities (Stumm and Lee, 1961; Stumm and Morgan, 1996).

153   Abiotic iron(II) oxidation may not only occur by direct oxidation of ferrous iron in the solution

154   (homogeneous reaction), but also by specific adsorption of ferrous iron to hydrous oxide surfaces (e.g.,

155   Stumm and Morgan, 1996; Park and Dempsey, 2005; Schmidt et al., 2009). Iron (hydr)oxides, formed as

156   reaction products in the homogeneous oxidation of iron(II), may further accelerate the reaction rate by

157   providing a surface for the autocatalytic oxidation. The autocatalytic oxidation process depends on the

158   amount of ferric iron (Wolthoorn et al., 2004) and is noticeable only for pH-values greater than about pH

159   7 (Sung and Morgan, 1980). At pH-values greater than 7 the oxidation of ferrous iron is a mixture of both

160   the homogeneous and the autocatalytic process with the former representing the dominating mechanism at

161   circumneutral pH (Wolthoorn et al., 2004). Hence, only the homogeneous reaction rate is considered in

162   this study to describe the abiotic oxidation of ferrous iron.

163

164   **MATERIAL AND METHODS**

165   **Experimental Setups**

166   In the following, we present the different experimental setups used to investigate diffusive/dispersive and

167   reactive transport of oxygen at the interface between the unsaturated and the saturated zone. A schematic

168   overview is given in Fig. 1. We performed batch experiments, 1-D diffusion experiments, and 2-D flow-

169   through experiments in a thermostatic room at 22 °C.

170

171   < Figure 1 >

172

173   *Batch experiments*

174   Batch experiments were performed to characterize the abiotic iron(II)-oxidation reaction (Eqn. 7) and to

175   determine the reaction rate constant needed for simulating reactive transport in the 1-D and 2-D

176   experiments (k in Eqn. 9). In particular, we investigated the impact of pH and a catalyzer (Cu^{2+}) on the

177   observed reaction rate. Table 1 summarizes the different conditions tested.

178

179   < Table 1 >

180

181   Before starting the experiments, four 250 mL-Schott bottles were equipped with an oxygen-sensitive

182   sensor spot (SP-PSt3-NAU from PreSens GmbH, Regensburg, Germany). The sensor spot was attached to

183   the inner wall of each Schott bottle to facilitate oxygen measurement during the experiment by applying a

184   non-invasive optode technique (Fibox3 from PreSens GmbH, Regensburg, Germany; e.g., Haberer et al.,

185   2011). Subsequently, the Schott bottles were filled with 250 mL air-equilibrated MilliQ water. To keep pH

186   stable and to avoid mineral precipitation, an organic pH buffer (here: PIPES, CAS: 5625-37-6, with pK_a =

187   6.80 at 20 °C; Good et al., 1966) was added in experiments B, C, and D with a concentration of c(PIPES)

188   = 1×10^{-3} mol L^{-1}. Complete dissolution of the pH buffer was achieved by heating up the solutions and

189   allowing them to cool down to room temperature. To investigate the effect of a catalyzer we also added

190    $CuSO_4$ to one of the Schott bottles (Batch D; $c(Cu^{2+})$ = 3×10^{-7} mol L^{-1} according to Stumm and Lee,

191   1961). If needed pH was adjusted to the desired initial pH-value with 1 mol L^{-1} NaOH. All Schott bottles

192   were stirred continuously to achieve uniform distribution of the reactants and to enhance oxygen resupply

193   from the atmosphere. After addition of Fe^{2+} as $FeCl_2 \cdot 4H_2O$ (CAS: 13478-10-9, final concentration: $c(Fe^{2+})$

194   = 1.79×10^{-4} mol L^{-1}), we followed $c(O_2)$, pH, $c(Fe^{2+})$, and $c(Fe_{tot})$ over time. During the experiment, the

195   oxygen concentration was detected with an optical fiber from the outside, pH was measured with a pH-

196   electrode (pH 540 GLP, WTW Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany),

197   and water samples were taken to determine the concentrations of Fe^{2+} and Fe_{tot} by performing a ferrozine

198   assay (Stookey, 1970; Viollier et al., 2000). To prevent oxidation of ferrous iron before the analysis, we

199 diluted the samples with 1 mol L^{-1} HCl in a 1:1 ratio. An additional dilution step, using multiwell plates,

200 was necessary to measure $c(Fe^{2+})$ and $c(Fe_{tot})$. That is, 20 µL of the diluted sample were again mixed with

201 either 80 µL HCl $(c(HCl) = 1$ mol L$^{-1})$ to measure ferrous iron, or 80 µL hydroxylamine hydrochloride

202 solution (i.e., 10 % (m/v) hydroxylamine hydrochloride in 1 mol L^{-1} HCl) to measure total iron. 100 µL

203 ferrozine solution (50 % (m/v) ammonium acetate with 0.1 % (m/v) ferrozine in MilliQ water) were added

204 to each sample to measure the concentration of ferrous iron at a wavelength of 562 nm using a microplate

205 reader (FLASHScan® 550 from Analytik Jena AG, Jena, Germany).

206

207 *1-D diffusion experiments*

208 Glass columns (length: 11.6 cm, inner diameter: 1.75 cm), filled with a fully water-saturated porous

209 medium, were used to study diffusive conservative and reactive mass transfer of oxygen from the

210 atmosphere to anoxic water (Fig. 1). In particular, we characterized pore diffusion in different porous

211 media (i.e., in glass beads and in River Rhine sand with grain diameters of 0.4-0.6 mm) under

212 conservative conditions and we investigated the impact of abiotic iron(II) oxidation on oxygen transport in

213 1-D reactive transport experiments, using the same conditions and reaction kinetics investigated in the

214 batch systems (experiment B). In the conservative setup an initial solution identical to the one prepared for

215 batch system B (Table 1), but without addition of ferrous iron, was used as pore water solution; in the

216 reactive case we additionally added ferrous iron with a concentration of 1.79×10^{-4} mol L^{-1}. Such solutions

217 were flushed with nitrogen and stored in Tedlar® gas sampling bags.

218 Before starting the experiment, we glued an oxygen-sensitive sensor strip (SP-PSt3-NAU from PreSens

219 GmbH, Regensburg, Germany) with dimensions of 4.7 cm × 0.5 cm onto the inner wall of the glass

220 column (Fig. 1) to obtain temporal and spatial profiles of oxygen concentration in one experimental run.

221 The glass column was placed into a polystyrene box (Fig. 2) to minimize temperature effects and to keep

222 humidity high, thus resulting in minimal evaporation rates and, hence, in the approximately constant

223 location of the unsaturated/saturated interface. During the experiment temperature was recorded and used

224 for temperature compensation of the measured oxygen concentrations. Moreover, the evaporation rate was

225 determined with a separate column (with same dimensions as the measurement column and filled with the

226 same fully water-saturated porous medium) based on weight measurements at the beginning and at the end

227 of the experiment.

228

229 < Figure 2 >

230

231 To prepare the setup the glass columns were closed on one end using screw caps with silicon/PTFE septa.

232 Before filling the measurement vial, we pierced hollow needles through the septum of the bottom screw

233 cap. The needles were connected to pump tubing, through which we injected the prepared anoxic solutions

234 into the column using a peristaltic pump (IPC 12, IDEX Health and Science GmbH, Wertheim, Germany).

235 Subsequently, the porous medium was filled into the column, always keeping the water table above the

236 upper limit of the porous medium packing. When the column was packed completely, a second cap was

237 screwed onto the measurement vial and a hollow needle was punched through the septum to facilitate

238 upward flow (Fig. 2). The anoxic solution was flushed through the system until a constant low background

239 concentration of oxygen was measured.

240 We started the experiment (time = 0) by switching off the inlet pump (no-flow condition), unscrewing the

241 upper cap, and removing the supernatant liquid in the measurement vial, such that the water meniscus,

242 representing the unsaturated/saturated interface, was at the upper limit of the porous medium packing.

243 Oxygen immediately started to diffuse into the anoxic porous medium (Fig. 2) and we measured the

244 breakthrough of oxygen concentrations at a specific point (13 mm) below the porous medium/atmosphere

245 interface as a function of time (10 s intervals). Additionally, every three to six hours the oxygen

246 distribution in the column was determined by measuring spatial profiles of oxygen concentration at high

247 resolution (2.5 mm) along the oxygen-sensitive sensor strip.

248

249

250   At the end of the experiment, we determined gravimetrically the porosity of the porous medium packing in

251   the column:

$$\varepsilon = \frac{V_w}{V_{tot}} = \frac{\dfrac{m_w}{\rho_w}}{\dfrac{m_w}{\rho_w} + \dfrac{m_s}{\rho_s}} \tag{10}$$

253   where V_w [L^3] and V_{tot} [L^3] are the volumes of the water and the porous medium packing, m_w [M] and m_s

254   [M] are the masses of the water and the solid phase, and ρ_w [M L^{-3}] and ρ_s [M L^{-3}] are the density of the

255   water and the solid phase, respectively.

256

257   *2-D flow-through experiments*

258   Flow-through experiments were performed to investigate the propagation of dispersive oxygen fronts in a

259   quasi 2-D setup. The flow-through chamber was constructed with two 5-mm thick glass panes, separated

260   by a Viton® septum, and had inner dimensions of 16.2 cm (length, *L*) × 12.7 cm (height, *H*) × 0.5 cm

261   (width, *W*). An oxygen-sensitive sensor strip was glued onto the inner wall of the chamber (at $x = 13$ cm

262   from the inlet, see Fig. 1) to detect oxygen concentrations at high spatial resolution (2.5 mm spacing). We

263   filled the flow-through chamber with glass beads with grain diameters of $d = 0.4$-0.6 mm. At the inlet and

264   at the outlet of the chamber, hollow needles, connected to pump tubing (Fluran-HCA, ID 0.64 mm from

265   IDEX Health & Science GmbH), were pierced through the Viton® septum separating the two glass panes.

266   These needles were equally spaced by 0.75 cm, and served as inlet (12 ports) and outlet ports (13 ports) to

267   induce a horizontal flow-field in the chamber during the experiment by means of two high-precision

268   peristaltic pumps (IPC-N 24, IDEX Health & Science GmbH). An overview of the porous medium

269   properties and of the flow and transport parameters in the 2-D setup is given in Table 2.

270

271   < Table 2 >

272

273 The conservative and reactive transport experiments were performed under the same conditions as the 1-D

274 column systems, i.e., using anoxic buffered solutions without and with addition of ferrous iron,

275 respectively (the latter solution corresponding to Batch B, Table 1). To minimize the contamination of the

276 prepared anoxic solutions by atmospheric oxygen, after flushing the solutions with nitrogen, we added a

277 small amount of ascorbic acid (CAS: 50-81-7) resulting in a concentration of 6.25×10^{-5} mol L^{-1}.

278 Subsequently, the pH of the solutions was adjusted to the desired value of 7. Similarly, to minimize

279 oxygen contamination on the long term of the flow-through experiments (days to weeks) we placed an

280 AnaeroGen sachet (Fisher Scientific, Schwerte, Germany) in the gas phase of the glass bottles that were

281 used to store the inlet solutions. The ascorbic acid in the sachet absorbed oxygen, which reduced the

282 oxygen content in the gaseous phase to below 1 %. To extract water from the glass bottles and pump it in

283 the flow-through setup, a thoroughly nitrogen-flushed Tedlar® gas sampling bag, serving as gas reservoir,

284 was connected to the reservoir of the inlet anoxic solution (Fig. 1).

285 After flushing the system with at least two pore volumes, high-resolution vertical oxygen profiles were

286 measured along the oxygen-sensitive sensor strip located close to the outlet of the flow-through chamber.

287

288 **Modeling Approach**

289 Numerical modeling was performed to quantitatively evaluate the experimental results in the batch, 1-D

290 and 2-D systems. A reactive module for kinetic oxidation of ferrous iron was developed using the

291 geochemical code PHREEQC-3 (Parkhurst and Appelo, 2013). The module was first developed for batch

292 conditions and validated with the experimental dataset B (Table 1). The stoichiometry of ferrous iron

293 oxidation was described as in the balanced redox reaction (Eqn. 7); the kinetics of iron(II) oxidation was

294 implemented according to Eqn. 9. To simulate the reaction kinetics we decoupled the valence states of

295 ferrous and ferric iron, following an approach similar to the one described in example 9 of Parkhurst and

296 Appelo (2013), and we allowed the precipitation of ferrihydrite. Mimicking the experimental conditions,

297 we used the same initial concentration of the major reactants (ferrous iron and dissolved oxygen) and a pH

298 buffer with identical concentration and pKa of PIPES (Table 1). The only parameter that was adjusted was

299   the specific rate constant of iron(II) oxidation (k in Eqn. 9). To this end, we took advantage of the new

300   capabilities of the recently released IPHREEQC, and specifically of IPHREEQC-COM which allows

301   performing all geochemical PHREEQC calculations directly from MATLAB as well as from any other

302   software that can interface with a COM (component object model) server (Charlton and Parkhurst, 2011;

303   Wissmeier and Barry, 2011). Thus, an automatic fitting routine based on the trust-region-reflective

304   algorithm implemented in the MATLAB function lsqnonlin was used to determine the value of the

305   reaction rate constant through the minimization of the non-linear least squares problem between the

306   computed and measured concentrations.

307   The PHREEQC module for kinetic iron(II) oxidation was directly applied in the 1-D and 2-D systems.

308   The simulation of the diffusive/reactive transport in the 1-D column setup was performed in PHREEQC,

309   where the 10 cm saturated porous medium domain was discretized into 100 cells ($\Delta z = 1$ mm). The

310   simulations were performed for simulation times corresponding to the experimental duration and the

311   spatial and temporal profiles obtained from the model runs were compared to the experimental

312   measurements.

313   Flow and transport simulations were performed for the 2-D flow-through system. Since this and previous

314   experimental studies conducted using similar porous media (e.g., Haberer et al., 2011) have shown that a

315   sharp interface between the unsaturated and the underlying fully water-saturated zone can be identified,

316   and that steep oxygen gradients form only in the saturated zone, the system can be accurately described by

317   exclusively focusing on the fully water-saturated medium. Thus, we solved the flow problem using the

318   code MODFLOW (Harbaugh, 2005) and the transport problem with PHT3D (Prommer et al., 2003),

319   which couples the solute transport code MT3DMS (Zheng and Wang, 1999) with PHREEQC. The

320   geometry and the boundary conditions in the 2-D model closely represent the experimental setup and a

321   fine discretization (grid cells with Δx and Δz up to 0.5 and 0.25 mm, respectively) was used to allow

322   capturing the steep concentration gradients observed in the experimental setup.

323

324

RESULTS AND DISCUSSION

Batch Experiments

Batch experiments were performed to study the kinetics of iron(II) oxidation under different conditions. Figure 3 shows the time-dependent reduction in ferrous iron concentration for the batch experiments summarized in Table 1. In Batch A, no buffer was added to the solution and we measured a rapid decrease in pH from 7 to 5.5. This caused a significant decrease in the reaction rate, which strongly depends on pH (Eqs. 8 and 9), and thus only a slight decrease of the ferrous iron concentration was observed. In Batch B the pH was buffered and the results show a fast oxidation of iron(II) in the solution. Increasing the initial pH (Batch C) and adding $CuSO_4$ as catalyzer (Batch D) caused a further increase in the reaction rate and in the oxidation of dissolved ferrous iron.

< Figure 3 >

The conditions of Batch B were selected to investigate the impact of kinetic effects on reactive transport in the 1-D and 2-D experiments. Under these conditions, we measured the temporal evolution of dissolved ferrous iron concentration, oxygen, and pH over a time period of 80 min. The reactive PHREEQC module for kinetic iron(II) oxidation described above was used to simulate the experimental results and to directly obtain a best-fit value for the reaction rate constant (k). As shown in Fig. 4 a reasonably good agreement was found between the experimental data and the results of the simulations for the different parameters measured in the batch experiment. Furthermore, the automated fitting procedure implemented using the capability of IPHREEQC-COM yielded a value of the reaction rate constant of $k = 9.84(\pm0.23)\times10^{15}$ L^3 mol^{-3} s^{-1} (at 22 °C). This value is comparable with previously reported values of reaction rate constants for abiotic ferrous iron oxidation (e.g., Stumm and Lee, 1961; Davison and Seed, 1983; Stumm and Morgan, 1996).

< Figure 4 >

1-D Oxygen Diffusive Fronts under Conservative and Reactive Conditions

351

352 Oxygen diffusive fronts were tracked in the 1-D column setup, and conservative transport experiments

353 were performed in different porous media (i.e., in glass beads and River Rhine sand packings). Figure 5

354 shows the oxygen concentrations for a conservative diffusion experiment conducted in the 1-D column

355 setup using glass beads with grain diameters d = 0.4-0.6 mm as porous medium. The symbols represent

356 the measurements, whereas the continuous lines are the modeling results obtained by fitting the analytical

357 solution of the conservative 1-D transport problem (Eqn. 4) to the experimental data. The spatial profiles

358 measured at different time intervals along the oxygen-sensitive sensor strip show a progressive penetration

359 of the oxygen front into the anoxic porous medium (Fig. 5a). The breakthrough of oxygen at the

360 measurement location, 13 mm below the unsaturated/saturated interface, is shown in Fig. 5b.

361

362 < Figure 5 >

363

364 The simultaneous fitting of the analytical solution to the spatial and temporal profiles allowed us to

365 determine the value of the pore diffusion coefficient of oxygen in the packed column. We obtained a value

366 of D_p = 1.18×10^{-9} m^2 s^{-1}. Knowing the free aqueous diffusion coefficient for dissolved oxygen (Table 2)

367 the tortuosity of the porous medium can be estimated using Eqn. 2. We obtained a value of tortuosity of

368 1.67 for the column packed with glass beads and 1.73 for the one packed with river Rhine sand (Table 3).

369 These values compare well with previously reported results and also with estimates using an empirical

370 correlation with the packed bed porosity (Eqn. 2, right hand side), with an empirical exponent of m = 1.5

371 (e.g., Bruggeman 1935; Boudreau, 1996; Sabatini, 2000; Boving and Grathwohl, 2001; Delgado, 2006;

372 Coutelieris and Delgado, 2012).

373

374 < Table 3 >

375

376   We also performed a reactive experiment in the porous medium packed with glass beads with the aim of

377   investigating the coupling of diffusive oxygen transport with the kinetic oxidation of ferrous iron. The

378   oxygen concentration profiles measured along the oxygen-sensitive sensor strip at specific time intervals

379   are presented in Fig. 6b. Reactive transport simulations were performed with a 1-D PHREEQC model

380   including the pore diffusion coefficient determined in the conservative experiment ($D_p = 1.18 \times 10^{-9}$ m^2 s^{-1})

381   and the reaction rate constant obtained from the best fit analysis of the abiotic iron(II) oxidation in the

382   batch system ($k = 9.84 \times 10^{15}$ mol^{-3} L^3 s^{-1}, Batch B). As can be observed in Fig. 6b, the pure forward

383   modeling simulations of the reactive system using the experimentally determined transport and reaction

384   parameters are in excellent agreement with the experimental data. In Fig. 6 we also included the spatial

385   profiles of the conservative experiments in the same porous medium as well as the simulation outcomes of

386   a hypothetical case of instantaneous reaction (Liu et al., 2010; Haberer et al., 2011), shown in Fig. 6a and

387   Fig. 6c, respectively.

388

389   < Figure 6 >

390

391   The comparison between the spatial profiles for the three different cases presented in Fig. 6 is illustrative

392   of the propagation of the oxygen fronts in the anoxic porous medium. The location of the oxygen fronts 18

393   hours after the start of the respective experiment is depicted for the three distinct cases. Due to the absence

394   of a chemical reaction, the penetration depth of oxygen is largest for the conservative case and can be

395   described by:

396    $$z_{cons} = 2 erfc^{-1}(C_{norm})\sqrt{D_p t} \qquad (11)$$

397   where erfc^{-1} is the inverse complementary error function. For $C_{norm} = 0.05$, $D_p = 1.18 \times 10^{-9}$ m^2 s^{-1}, and $t =$

398   18 h, the penetration depth was $z_{cons} = 25$ mm (Fig. 6a). Tracking the same normalized concentration,

399   significantly smaller penetration depths were obtained in the reactive cases. The smallest penetration

400   depth was found in the case of instantaneous reaction: $z_{reac,ins} = 17$ mm. For the reactive transport

17

401   experiments with kinetic iron(II) oxidation, the oxygen profile reached a penetration depth of $z_{reac,kin} = 18$

402   mm that is in-between the conservative and the instantaneous reaction cases, but closer to the latter.

403   The oxygen penetration depth at different times (also for $C_{norm} = 0.05$), corresponding to the measurement

404   of the spatial profiles in the conservative and reactive experiments, as well as the simulation results for the

405   three scenarios discussed above are reported in Fig. 7a. Considering the ratio of the penetration depth

406   increments over time we estimated the velocities of propagation of the oxygen fronts which appear to

407   follow a $1/\sqrt{t}$ -trend. The speed of propagation of the diffusive fronts is larger in the conservative case,

408   whereas for reactive transport the interaction with the dissolved ferrous iron results in the retardation of

409   the oxygen fronts.

410

411   < Figure 7 >

412

413   Figure 8 shows the temporal oxygen concentration profiles determined at 13 mm depth below the

414   unsaturated/saturated interface. The fastest propagation of the oxygen front in the conservative case is

415   reflected also by its earlier breakthrough compared to the observations in the reactive experiments. The

416   breakthrough curves in Fig. 8 also illustrate that the effect of the iron(II)-oxidation kinetics is significant at

417   early times when the experimental and simulated results are clearly distinct from the conservative and

418   instantaneous cases. However, as time progresses the oxygen breakthrough for the kinetic iron(II)

419   oxidation tends to approach the behavior of an instantaneous reaction.

420

421   < Figure 8 >

422

423   Numerical simulations were also performed to further investigate the propagation of conservative and

424   reactive oxygen fronts at spatial and temporal scales beyond the ones considered in the experiments. In

425   these scenarios, besides the three cases illustrated above, we also considered the kinetic oxidation of

426   ferrous iron in an unbuffered system (corresponding to Batch A in Table 1). The results are reported as

427   spatial profiles in Fig. 9. Over a time period of 0.5 days, comparable with the temporal scale of the 1-D

428   diffusion experiments, the conservative, reactive instantaneous, and buffered reactive kinetic profiles are

429   distinct, whereas the unbuffered reactive kinetic profile overlaps with the conservative case. As time

430   increases (5, 50, and 500 days) the differences in the velocity of propagation of the oxygen fronts lead to

431   increasingly different penetration depths. Moreover, the profiles for the buffered kinetic system tend to

432   merge with the ones of the instantaneous reactive scenario since under these conditions the relatively fast

433   reaction kinetics is limited by the diffusive transport. Conversely, kinetic effects start to be remarkable for

434   the unbuffered kinetic reaction system at later time as shown by the spatial profiles in Fig. 9b (especially

435   for $t = 500$ days). In fact, at later times the slow reaction kinetics, determined by the absence of pH

436   buffering capacity, starts to have a noticeable effect and results in a slower propagation of the oxygen

437   front compared to the conservative case.

438

439   < Figure 9 >

440

441   **Oxygen Dispersive Fronts under Flow-Through Conditions**

442   The impact of the kinetic iron(II)-oxidation reaction on oxygen transfer across the unsaturated/saturated

443   interface was also investigated in a quasi 2-D flow-through system. In such setup we performed

444   sequentially conservative and reactive experiments. First, the flow-through chamber, filled with glass

445   beads with grain diameters in the range of $d = 0.4$-0.6 mm, was flushed with an anoxic solution,

446   containing the pH-buffer but no ferrous iron, at an average flow velocity of 1.9 m d^{-1}. Due to the oxygen

447   gradient between the atmosphere and the anoxic water phase, oxygen was transferred across the

448   unsaturated/saturated interface into the anoxic water. After reaching steady state, we measured the vertical

449   oxygen concentration profile for this conservative experiment at the oxygen-sensitive polymer strip

450   located at $x = 13$ cm from the inlet. Successively, we performed the reactive experiment by injecting at the

451   inlet an anoxic solution containing ferrous iron and the pH buffer. As can be observed in the photograph

452   of Fig. 10a, the contact between dissolved oxygen and ferrous iron caused the precipitation of iron

453 hydroxides close to the unsaturated/saturated interface. The shape of the iron precipitation zone is also

454 significantly influenced by the flow field in the flow-through system, as substantiated by the flow model

455 and by the computed flow lines (Fig. 10b). Reactive transport was simulated by incorporating the kinetic

456 geochemical PHREEQC module, previously applied in the batch and 1-D system, into the

457 multidimensional transport simulator PHT3D (Prommer et al., 2003). The comparison of the experimental

458 data and the outcome of forward simulations with the same reaction kinetics described above and with the

459 key transport parameter, the local transverse hydrodynamic dispersion coefficient calculated according to

460 Eqn. 6, is shown in Fig. 10c. Despite the limited spatial scale of the setup, a significant difference can

461 already be appreciated between the spatial oxygen profiles in the conservative and reactive experiments.

462 Similarly to the observations in the 1-D diffusion system, also in the flow-through setup the dispersive

463 oxygen front penetrates further in the anoxic porous medium in the case of conservative transport.

464

465   < Figure 10 >

466

467 Figure 11 shows the penetration depth and the velocity of propagation of the dispersive oxygen fronts for

468 two distinct seepage velocities: v = 1.9 m d^{-1} (as in the flow-through experiments) and for a scenario at

469 lower flow velocity, v = 0.19 m d^{-1}. The symbols refer to the conservative and kinetic reactive cases and

470 are plotted in the region of the flow-through domain where the flow is approximately horizontal. The

471 penetration depths are larger and more distinct between the conservative and reactive cases for the low

472 flow velocity scenario, due to the tenfold higher residence time of oxygen in the flow-through system.

473 However, as can be observed in Fig. 11b, the velocity of propagation of the dispersive oxygen fronts is

474 considerably larger for the case with higher seepage velocity.

475

476   < Figure 11 >

477

478

CONCLUSIONS

The quantitative understanding of mixing processes in porous media is of critical importance for many environmental applications. A challenging task is to address the coupling between transport and biogeochemical reactions in subsurface environments. This is particularly true for mixing-induced mineral precipitation, which typically occurs along multi-component chemical gradients in narrow mixing zones and at the interface between different compartments. An increasing number of recent studies have addressed the complexity of these reactive systems in porous media (e.g., Tartakovsky et al., 2008; Zhang et al., 2010; Yoon et al. 2012; Molins et al., 2012; Gebrehiwet et al., 2014; Redden et al., 2014). In this work we investigated the abiotic oxidation of ferrous iron resulting in the precipitation of ferric hydroxides at the interface between the unsaturated and the saturated zones. In particular, we focused on the effects of abiotic iron(II) oxidation on the propagation of oxygen fronts in diffusive transport regimes as well as under flow-through conditions. Through the direct comparison of conservative and reactive transport in the same setups, our experiments allow quantifying the significant influence of ferrous iron oxidation on the penetration depth and on the speed of propagation of oxygen fronts in anoxic, water-saturated porous media. We also show that the chemistry of the anoxic solution, and in particular its pH buffering capability, plays a significant role in the propagation of oxygen fronts and on the importance of the kinetics of abiotic iron(II) oxidation for reactive transport. In pH-buffered systems we found that the kinetics of iron(II) oxidation becomes less important with increasing time and that at larger time scales the reaction can be described as an instantaneous process. Conversely, the iron(II)-oxidation kinetics can be important also at large time scales in unbuffered systems, where the decrease in pH strongly affects the reaction rates. Thus, under these conditions the slow reaction rate may become the controlling factor in the coupling with typically slow, and thus rate-limiting, diffusive and dispersive processes. Although our study was performed under simplifying conditions compared to physical and chemical heterogeneous groundwater systems, the results on the coupling between transport processes and abiotic ferrous iron oxidation have important implications for relevant subsurface environmental processes such as transport of inorganic contaminants and their interaction with iron minerals (e.g., Smedley and Kinniburgh, 2002),

505 acidification of groundwater (e.g., Kjøller et al., 2004; Franken et al., 2009), pyrite oxidation (e.g.,

506 Prommer and Stuyfzand, 2005), formation of gley soils and oxidized iron mineral inclusions in open

507 framework gravel lenses in braided river sediments (e.g., Cornell and Schwertmann, 2003).

508 Finally, our experiments and their model-based interpretation also show that the accurate and independent

509 determination of key transport parameters (i.e., pore diffusion coefficient in the 1-D setups and the

510 transverse dispersion coefficient in the 2-D flow-through system) as well as the detailed study and

511 description of reaction kinetics allows the predictive use of numerical simulations for reactive systems

512 where transport and reactive processes are coupled.

513

522

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FIGURE CAPTIONS, TABLES, AND FIGURES

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723   experiments.

724

725   Fig. 2: Photograph of the experimental setup used to perform the 1-D diffusion experiments (right panel) and

726   schematics of system operation in different experimental phases, i.e., flow-through mode before starting the

727   experiment (to achieve constant background concentrations) vs. no-flow conditions during the experiment (oxygen is

728   allowed to diffuse into the system).

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731   buffered), Batch B: pH 7 (buffered), Batch C: pH 8 (buffered), Batch D: pH 7 (buffered) and with catalyzer.

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736   medium: (a) Spatial profiles measured at increasing times (i.e., in 3 to 6 hour-time intervals) along the oxygen-

737   sensitive sensor strip. The depth = 0 mm indicates the location of the unsaturated/saturated interface. (b) Oxygen

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739   medium (symbols indicate the experimental data and are shown at lower temporal resolution than the actual

740   measurements, performed every 10 s).

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743   case with kinetic iron(II) oxidation, and (c) instantaneous reaction. The depth of 0 mm indicates the location of the

744   unsaturated/saturated interface.

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747    $C_{norm} = 0.05$ and (b) velocity of the propagating oxygen fronts.

748

749   Fig. 8: Temporal oxygen concentration profiles in the 1-D diffusion experiments (detected at 13 mm depth below the

750   interface between the atmosphere and the saturated porous medium) for the conservative, reactive kinetic, and

751   reactive instantaneous cases.

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753   Fig. 9: Long-term propagation of oxygen concentration fronts in 1-D diffusive systems. Spatial profiles at (a) 0.5

754   days and 5.0 days, and at (b) 50 days and 500 days.

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756   Fig. 10: 2-D flow-through experiment: (a) Photograph of the experimental setup during the reactive phase of the

757   experiment (with kinetic iron(II) oxidation and buffered pH), (b) simulated flow lines using MODPATH (Pollock,

758   1994) and color map showing the simulated precipitation of ferrihydrite (with maximum concentration close to the

759   inlet: 2.97×10^{-4} mol L^{-1} of bulk volume at 0.2 days). The vertical orange line shows the location of the vertical

760   oxygen-sensitive polymer strip ($x = 13$ cm). (c) Concentration profiles for the conservative and reactive experiments

761   (the y-axis represents the distance from the upper boundary of the flow-through setup).

762

763   Fig. 11: Penetration depth (a) and velocity of propagation of the dispersive oxygen fronts (b) in the quasi 2-D flow-

764   through setup as function of the longitudinal distance from the inlet of the flow-through chamber for two seepage

765   velocities ($v = 1.9$ and 0.19 m d^{-1}, respectively).

766   Table 1. Overview of the batch experiments.

Batch	Ferrous Iron, $c(Fe^{2+})$	Initial pH [-]	pH-buffer, $c(PIPES)$	Catalyzer, $c(Cu^{2+})$
A	1.79×10^{-4} mol L^{-1}	7	-	-
B	1.79×10^{-4} mol L^{-1}	7	1×10^{-3} mol L^{-1}	-
C	1.79×10^{-4} mol L^{-1}	8	1×10^{-3} mol L^{-1}	-
D	1.79×10^{-4} mol L^{-1}	7	1×10^{-3} mol L^{-1}	3×10^{-7} mol L^{-1}

767

768   Table 2. Summary of porous medium properties and flow and transport parameters in the 2-D setup.

Parameter	Value
Inner dimensions of the flow-through chamber, $L \times H \times W$ [cm]	$16.2 \times 12.7 \times 0.5$
Average grain diameter [mm]	0.50
Porosity of the porous medium [%]	39.7
Flow rate, Q [m^3 s^{-1}]	5.63×10^{-9}
Cross-sectional flow-through area [m^2]	5.93×10^{-4}
Hydraulic conductivity, K [m s^{-1}]	2.5×10^{-3}
Aqueous diffusion coefficient for oxygen, D_{aq} [m^2 s^{-1}] (at 22 °C)	1.97×10^{-9}

769

770   Table 3. Summary of parameters and results for the conservative experiments in the 1-D setup.

Porous medium	Glass beads	River Rhine sand
D_p [m^2 s^{-1}]	1.18×10^{-9}	1.14×10^{-9}
τ (diffusion) [-]	1.67	1.73
τ (ε, $m = 1.5$) [-]	1.57	1.52
ε (porosity) [%]	40.6	43.5

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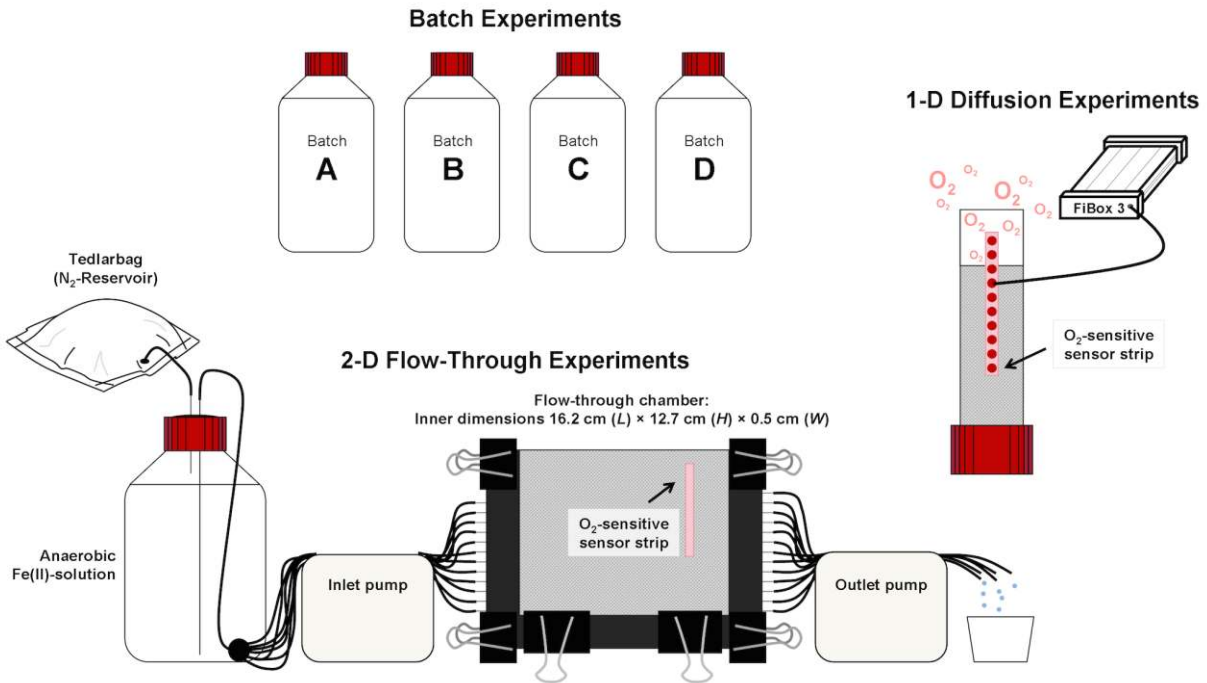
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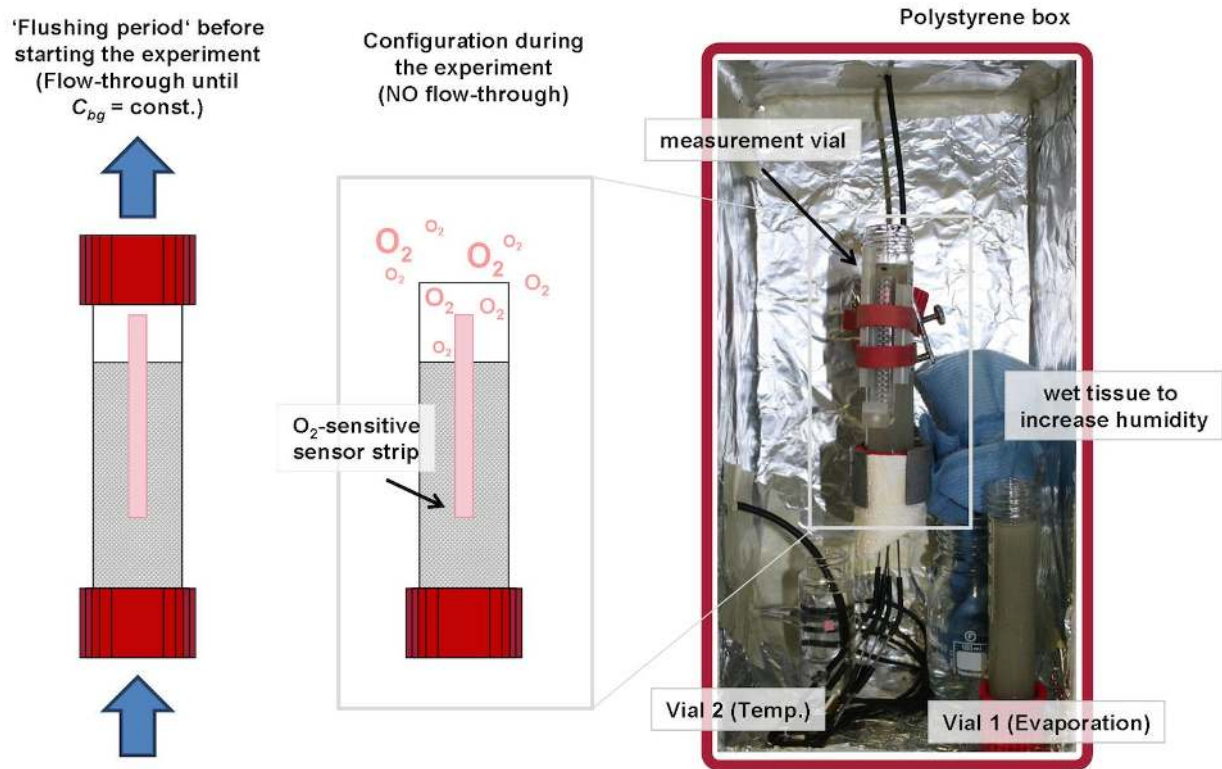
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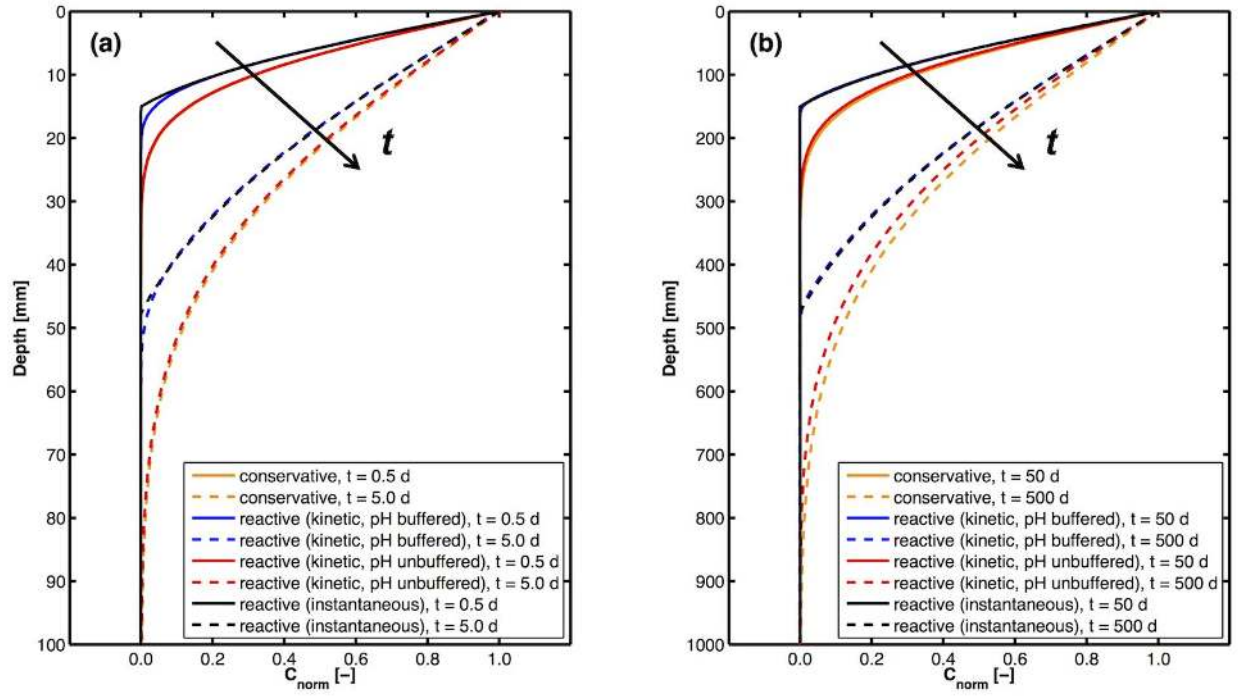
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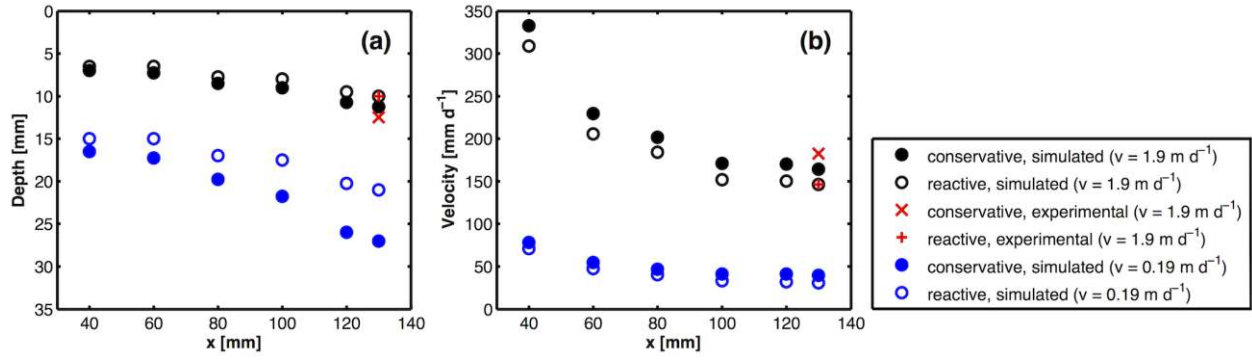
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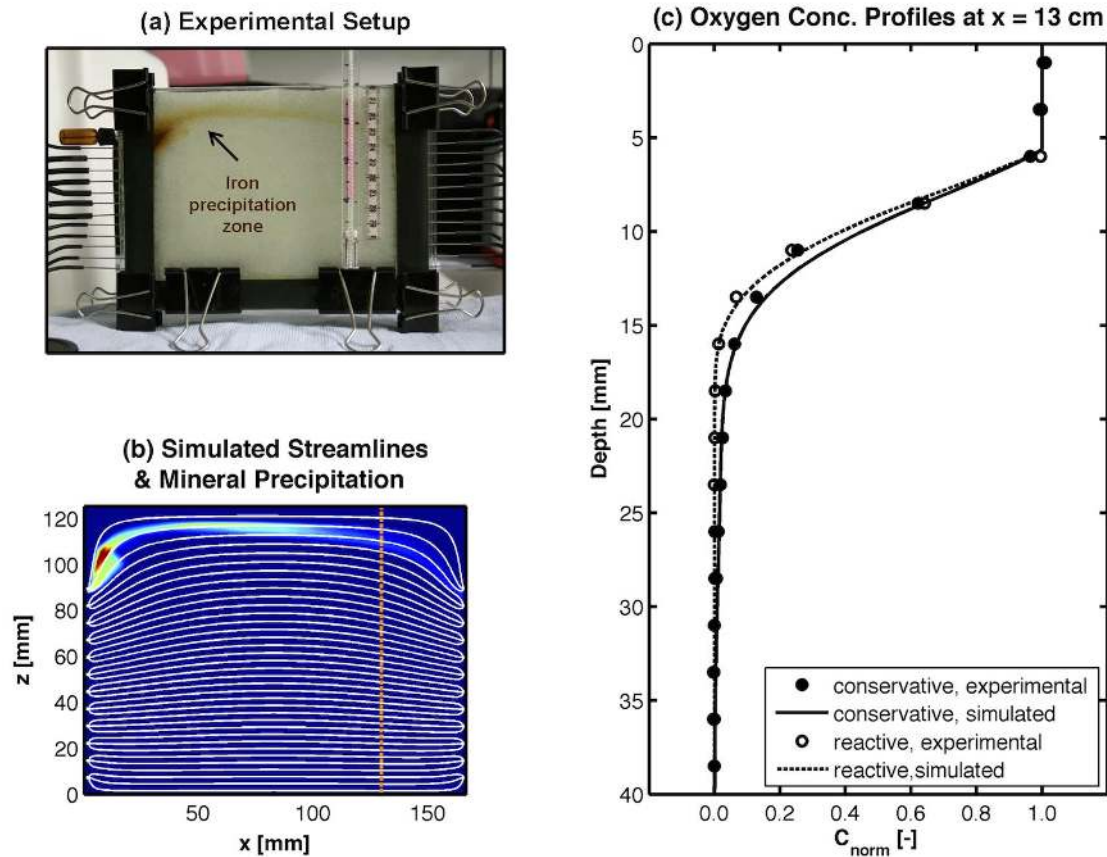
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