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Model based verification and prognosis of acidification and sulphate releasing processes downstream of a former sewage field in Berlin (Germany)

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ABSTRACT

An ammonium contamination plume originating from sewage field management practices over several decades is affecting the water quality at the well fields of the Friedrichshagen waterworks in Berlin, Germany. Because hydraulic measures were unsuccessful due to the fixation of ammonium on the aquifer matrix by cation exchange, an in situ nitrification measure by injection of oxygen gas was chosen to protect the extraction wells. In order to assess the hydro chemical processes accompanying this in situ measure, reactive transport modelling was performed. The relevant processes are the dissolution of oxygen gas and the nitrification of ammonium which initiate secondary geochemical processes like sulphate release, acidification and hardening. The reactive transport modelling began with the deduction of a reaction network, followed by the mathematical formulation and incorporation of reactive terms into a reactive transport solver. Two model versions were set up: (1) a simplified large scale model to evaluate the long-term reaction zoning to be expected due to permanent oxygen gas injection, and (2) a verification of the monitored hydrochemistry during a first field test performed near the contamination source. The results of reactive transport modelling demonstrate that in situ injection of oxygen gas will be effective in reducing the ammonium load from the well fields, and that acidification processes near the production wells can be minimized. Finally, a line of gas injection wells extending over the whole width of the ammonium contamination plume will be constructed to protect the well fields from further ammonium load.

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1. Introduction

A subject of the work presented here is the reactive modelling of a remediation measure of an ammonium contamination by oxygen gas sparging, which in Europe and at least in Germany is unique and is still undergoing evaluation by pilot tests.

At a distance of about 3 km from the northern well field A of the Friedrichshagen waterworks (one of the largest water works in Berlin) industrial and municipal waste water were infiltrated at a sewage field between 1900 and 1976.

* Corresponding author. *E-mail address:* horner@igb-berlin.de (C. Horner). Increasing wastewater input, especially since the 1950s resulted in an overload of the sewage field capacity. Since 1955, the wastewater input exceeded the maximum infiltration capacity of the sewage field. During the following years, the excess of waste water input in relation to the available sewage field capacity has continuously worsened. For example, in 1973 the wastewater input increased to 48000 m³/d in relation to a sewage field infiltration capacity of 13000 m³ d⁻¹ (UWG, 1992). The highest ammonium concentrations especially came from gas work effluents. The wastewater effluent affected the receiving water near the sewage field and infiltrated the capture zone of well field A and the aquifer upstream of the well fields A and B of the Friedrichshagen waterworks as well (Fig. 1). Since the 1970s, the Berlin Water Company has been assessing the ammonium

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Fig. 1. Site map of the ammonium contamination.

contamination by an extensive monitoring network of multilevel observation wells. After 1992 the monitoring network was extended. The extent of the ammonium contamination plume shown in Fig. 1 was derived from monitoring measurements in 1995.

In 1978, a wastewater treatment plant was built, but its sludge drainage capacity was limited so that about 2.8 million m³ of sludge had to be deposited in unsealed sludge reservoirs and in case of emergency also on the sewage field. By the wastewater plant management, only the load of organic substances could be eliminated, while a total removal of the ammonium load has failed. In this way, there was further ammonium input into the local receiving water course and as well into the aquifer. In total, 30000–35000 tons of ammonium nitrogen were infiltrated into the receiving water course and on the sewage field.

The first clean-up activities were initiated in 1994 (UWG, 1992). Due to the migration properties of ammonium within the aquifer involving fixation on the aquifer matrix by ion exchange, a pure hydraulic pump and treat remediation strategy was rejected. As promising alternatives, two clean-up technologies were chosen to be tested during pilot tests at this site: The infiltration of highly oxygenated water and the in situ oxygen/air gas sparging to provide the clean-up also at the neighboring downstream area, supporting pumping was applied. As a unique approach for ammonium at this time in Germany and in whole Europe, these field tests were funded by the Ministry of Technology and Research of the Federal Republic of Germany (BMFT).

As shown by Fig. 1, the ammonium contamination plume still has reached the wells of well field A, but also by now affects the production wells in the western part of the well

field B. The northern well fields of the Friedrichshagen waterworks are generally screened at a depth of more than 20 m within an unconfined aquifer. At about 40 m average depth, the Holstein interglacial deposit composed mainly by silt and peat clay acts as the aquifer system aquiclude (UWG, 1992). The aquifer itself is composed by coarse to medium grained sands with only minor intermediate silt and till layers. The sewage field is situated within the transition zone between the glacifluvial outwash sands ("Warsaw Berlin glacial valley") and the glacial drift tableland in the North of the Friedrichshagen waterworks capture zone. From the drilling campaign at the test site Machnow (BIOXWAND project), a similar geological situation but with more intermediate fine sand and silt layers was demonstrated. Below the glacial drift table land, the main aquifer continues but changes to confined flow conditions. Due to the sandy composition of the local aquifer, the hydrodynamic contaminant input and transport was additionally facilitated due to the upconing of groundwater level at the sewage field as long as the sewage field was operated. Due to a preliminary cleanup at the top of the sewage field, the contaminant input has recently stopped, but due to sorption on the aquifer matrix a great stock of contaminant is still available. It was demonstrated by elution experiments on drilling cores sampled from the local aguifer that about 80% of the abundant ammonium is fixed by ion exchange on the aquifer matrix. The regional groundwater flow is directed South from the contamination source to the well fields A and B. The mean groundwater flow velocity is 0.3 m d^{-1} .

During the last decades, reactive transport modelling has become an important tool to assess the effect of clean-up measures on contaminated sites. Reactive transport models for assessing hydro geochemical conditions have been developing continuously since the 1970s, starting with batch reactive simulation software such as EQ3/6 (Wolery, 1979), MINEQL (Westall et al., 1976), and PHREEQE (Parkhurst et al., 1980), and leading to reactive transport codes that link these modules with hydrodynamic transport codes. The basic principles of reactive transport models are available from Rubin (1983). Based on this fundamental work, a great number of reactive codes were established, including those developed by Šimůnek and Suarez (1994), Engesgaard and Kipp, (1992), Parkhurst and Appelo (1999), Prommer et al. (1999), and Prommer (2002).

Among remediation measure approaches, focus is increasingly set on natural attenuation measures which aim to stimulate the activities of in situ available bacteria populations to eliminate biodegradable aquifer contaminations by supplying of terminal electron acceptors like oxygen or nitrate nitrogen species. In particular, oxygen gas sparging has become a more significant method of remediation not only at organic hydrocarbon contamination sites (e. g. Lahvis and Baehr, 1996; Johnson, 1998), but also at sites with other oxidable contaminants like ammonium.

Sophisticated approaches to model gas transport coupled to hydrodynamic flow and transport are available from Šimůnek and Suarez (1994), Donaldson et al. (1997), Fry et al. (1997), Geistlinger and Synakh (2000), Lazik et al. (2002), Holocher et al. (2003), and Geistlinger et al. (2005). All these approaches result in multi-phase flow and transport models which link gaseous concentrations to concentrations of dissolved gas via the Henry distribution coefficients and kinetic mass transfer rates derived from gas bubble specific parameters. But most of these codes set the focus on liquidgas transport without addressing hydro-chemical calculations, and an extensive set of input parameters is required owing to the highly stochastic character of gas transport within the aquifer.

Other programs, such as MODFLOW and MT3DMS which comprise the flow and transport modules of the PMWIN suite (Chiang and Kinzelbach, 2001), are designed to model only water saturated hydrodynamic transport, but not gas transport. Thus, the oxygen gas phase cannot be treated properly for applications to gas sparging. One simplifying option is to treat the oxygen gas phase analogously to a stationary non aqueous liquid phase allowing oxygen dissolution from the gas phase to provide aqueous-phase electron acceptor for subsequent oxidation reactions.

In this study, the reactive transport model software PHT3D (Prommer, 2002) was selected because it can be handled using the PROCESSING MODFLOW (PMWIN) suite (Chiang and Kinzelbach, 2001). PHT3D itself links PHREEQC-2 (Par-khurst and Appelo, 1999) as the reactive subset software to MT3MS as the multi species transport program (Zheng and Wang, 1998). The groundwater flow field necessary to perform hydro dynamical transport simulations is calculated using the MODFLOW software (McDonald and Harbaugh, 1988).

Examples for modelling ammonium contamination using PHT3D, but without oxygen gas sparging remediation measure, are given by Haerens (2002) and Serapliglia (2002).

In comparison, the paper presented here focuses mainly on the hydro-geochemical changes caused by the entrapment of oxygen gas in the aquifer. The basis of the reactive transport model is a reaction network (conceptual model) including the key processes (dissolution of oxygen gas and nitrification) and secondary processes initiated by those, such as the autotrophic and heterotrophic denitrification reaction involving organic carbon and pyrite (FeS₂), ion exchange reactions and dissolution of calcite. Due to these secondary reactions, hardness increase and some acidification of the groundwater takes place. The monitoring results at the test site suggested that the acidification is limited by pH buffering caused by calcite dissolution (NIDESI, 2000; BIOXWAND, 2004).

In order to assess these hydro-geochemical changes, reactive transport modelling was performed in two steps:

- A simplified regional model was developed to simulate all chemical processes discussed above in order to estimate the extent of chemical changes due to a long-term oxygen bubble wall management, as a prognostic tool to decide if oxygen gas sparging is an appropriate remediation method. A further issue was to decide if this method is adequate to reduce/eliminate the ammonium contamination load from the well field as long as the remediation is operated. This model is referred to as the "simplified large scale model".
- A detailed 3D model, incorporating the geological setting and pumping well configuration on the BIOXWAND pilot test site was developed to simulate selected phases of the field test campaign conducted in 2002/2003. This model is referred to as the "oxygen bubble wall test site model".

2. Simplified large scale model

2.1. Model set up

Before modelling reactive transport, a reaction network comprising all relevant hydro-geochemical reactions was formulated. The reaction network describing the hydrogeochemical changes caused by the oxygen gas sparging of the aquifer was derived from former investigations on the test site (NIDESI, 2000; BIOXWAND, 2000) and is given by the chemical reactions outlined in Table 1. The principal process, the nitrification is provided by the dissolution of oxygen from

Table 1Reaction network.

Process	Reaction equation
Nitrification	$NH_4^+ + 2O_2 \Rightarrow NO_3^- + 2H^+ + H_2O$
Oxygen dissolution from the	$O_{2, gas} \Leftrightarrow O_{2, dissolved}$
Heterotrophic denitrification	$5CH_2O + 4NO_3^- \Rightarrow 5HCO_3^- + 2N_2 + H^+ + 2H_2O_3^-$
Autotrophic denitrification	$5FeS_2 + 15NO_3^- + 10H_2O \Rightarrow 5Fe(OH)_3 + 7\frac{1}{2}N_2 + 10SO_4^2 - + 5H^+$
Aerobic respiration	$CH_2O + O_2 \Rightarrow HCO_3^- + H^+$
Oxygen consumption by pyrite	$FeS_2 + \frac{15}{4}O_2 + \frac{7}{2}H_2O \Rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$
Supply of organic carbon Dissolution of calcite	$CH_2O_{\text{particular}} \Leftrightarrow CH_2O_{\text{dissolved}}$ $CaCO_2 + H^+ \Leftrightarrow Ca^{2+} + HCO_2^-$
lon exchange reactions	$Ca^{2+} + 2NaX \Leftrightarrow CaX_2 + 2Na^+$
	$Mg^{2+} + 2NaX \Leftrightarrow MgX_2 + 2Na^+$ K ⁺ + NaX \Leftrightarrow KX + Na ⁺
Fixation of Ammonium by	$NH_4^+ + NaX \Leftrightarrow NH_4X + Na^+$
ion exchange	$Fe^{2+} + 2NaX \Leftrightarrow FeX_2 + 2Na^+$

Table 2			
Mathematical	formulation	of reaction	kinetics.

Process	Rate formulation	Reference
Nitrification	$r_{\rm Amm} = -\frac{\partial C_{\rm Amm}}{\partial t} = f_{\rm lag} \cdot k_{\rm Nitr} \frac{C_{\rm O_2}}{C_{\rm O_2} + k_{\rm m,O_2}} \cdot \frac{C_{\rm Amm}}{C_{\rm Amm} + k_{\rm m,Amm}}$	1
	$f_{\text{lag}} = 0$ if $(t \le t_{\text{lag}}), f_{\text{lag}} = 1 (t > t_{\text{lag}})$	
DOC degradation	$r_{\text{DOC}} = -\frac{\partial C_{\text{DOC}}}{\partial r_{\text{OC}}} = \left(k_0 \cdot \frac{c_{0_2}}{r_{0_2}} + k_{NO^-} \cdot \frac{c_{NO_3^-}}{r_{0_3}} + \frac{l_{0_2}}{r_{0_2}}\right) \cdot C_{\text{DOC}}$	2
Pyrite degradation	$\frac{\partial c}{\partial t} = \begin{pmatrix} -c_0 & c_{0,2} & k_{m,0_2} & k_{m,0_3} & k_{m,0_$	3,4,5
	$r_{Pyrite} = -\frac{c_{Pyrite}}{\partial t} = \left(C_{0_2}^{0.5} + f_2 \cdot C_{NO_3^{-}}^{0.5}\right) \cdot C_{H^{+}}^{-0.11} \cdot \left(10^{-10.15} \cdot \left(\frac{r_{Pyrite}}{V}\right)\right) \cdot \left(\frac{c_{Pyrite}}{C_{0_{Pyrite}}}\right)$	
DOC supply from matrix	$r_{\text{POC}} = -\frac{\partial C_{\text{POC}}}{\partial t} = k_{\text{sol}} \cdot C_{\text{POC}} \cdot (C_{\text{sat,DOC}} - C_{\text{DOC}})$	2
O ₂ gas phase dissolution	$r_{0_{2,n}} = \frac{\partial C_{0_{2,n}}}{\partial t} = k_{\text{sol},0_{2}} \cdot C_{0_{2,n}} \cdot (C_{\text{sat},0_{2}} - C_{0_{2,n}}) - \sum r_{0,\text{consumption}}$	2
O ₂ gas phase input	$r_{O_{2,gas}} = \frac{\partial C_{O_{2,gas}}}{\partial t} = k_{input,O_2} - k_{sol,O_2} \cdot C_{O_{2,gas}} \cdot \left(C_{sat,O_2} - C_{O_{2,aq}}\right)$	3

1) Serapiglia (2002), 2) Prommer (2002), 3) Williamson and Rimstidt (1994), 4) Eckert and Appelo (2002), 5) Prommer and Stuyfzand (2004), 3) This work.

the oxygen/air gas phase. As secondary processes initiated by the dissolution of oxygen, the aerobic respiration and, in the case of presence of pyrite, the oxidation of pyrite are important. Farther from the oxygen/air bubble wall, the nitrate formed by nitrification reaction is removed by the denitrification processes, such as autotrophic and heterotrophic denitrification. Due to a lacking database, other possibly important nitrogen species like intermediate N₂O were not considered. Secondary processes are acidification in the aquifer (especially the reactions in which pyrite is involved) and a hardening of the groundwater due to calcite dissolution. The consumption of pyrite during oxidation and autotrophic denitrification is reflected by an increase of the sulphate concentration. As evident at the test site, pH buffering caused by the dissolution of calcite limits the acidification. Further, ion exchange processes are considered which limit the mobility of NH⁺₄. Ion exchange is regarded as the one reaction involving NH₄⁺ under pristine conditions as typical for the upstream region of the oxygen bubble wall Supply of dissolved organic carbon (DOC) by dissolution of matrix bound organic carbon is a further important reaction to assess by reactive transport modelling.

After establishing the reaction network, mathematical formulations for the chemical reaction kinetics, such as nitrification, oxygen gas dissolution, pyrite oxidation, mobilization and degradation of organic carbon, were implemented as available from the literature, and are given by Table 2. Other reactions, such as precipitation/dissolution reactions of minerals, like calcite and iron hydroxides, were formulated as chemical equilibrium.

As mentioned above, PHT3D is conceptualized only for hydrodynamic, but not for gas phase flow and transport. The oxygen/air gas phase input and dissolution process are formulated analogously to the dissolution of a stationary NAPL/DNAPL phase using a saturation concentration of oxygen and a kinetic mass transfer coefficient (Prommer, 2002). Of course, this is a very raw simplification. The O₂ gas input during a gas sparging period is estimated using the ideal gas law based on the field experience of O₂ gas sparging which resulted in operating pressures ranging from 0.8 to 1.1 bars and a mean groundwater temperature of 10 °C (BIOXWAND, 2004). Among oxygen saturation, the oxygen gas solubility was related to the temperature dependent Henry constant of oxygen as given by the PHREEQC database (Parkhurst and Appelo, 1999). The kinetic mass transfer coefficient of oxygen was estimated from laboratory experiments performed with adjacent soil material (BIOXWAND, 2004).

The model domain of the simplified large scale model was formulated with a longitudinal extension of 3 km (approximately the extent of the ammonium contamination plume, see Fig. 1). The inflow boundary represents the contamination source near the sewage field, whereas the outflow boundary is related to the well fields A and B of the Friedrichshagen waterworks, which already show elevated ammonium concentrations. For simplicity, the well field was formulated as a constant head boundary condition rather than to specify a row of pumping wells. Both inlet and outlet boundary conditions were termed time constant. The model design is shown by Fig. 2, and its spatial discretization and flow parameters are given by Table 3. The applied hydraulic gradient and the aquifer hydraulic conductivity represent a typical average for the capture zone of the Friedrichshagen waterworks (UWG, 2002) and were specified to such an extent that the observed average pore velocity of 0.3 m/d resulted after flow simulation under stationary conditions.



Fig. 2. Model design of the simplified large scale model.

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Table 3

Simplified large scale model: discretization parameters, flow and hydrodynamic parameters.

Parameter	Unit	Value
Number of rows	-	60
Number of columns	-	3
Length of model	m	3000
Discretization rows	m	50
Discretization columns	m	50
Top level of model	m above sea level	39.0
Bottom level of model	m above sea level	-2.0
Piezometer head (inflow)	m above sea level	35.0
Piezometer head (outflow)	m above sea level	30.0
k _f value	$m s^{-1}$	5×10^{-4}
Porosity	-	0.25
Flow velocity	$m s^{-1}$	0.3
Longitudinal dispersivity	m	10.0
Ratio longitudinal to transversal dispersivity	-	10

From the applied flow boundary conditions, a parallel flow field results after the flow simulation. Therefore the simplified large scale model is in fact a 1D model.

The hydro-geochemical reaction network derived for both reactive transport models is summarized by Table 4. It consists of 31 components related to kinetics and/or partial chemical equilibrium. The relevant solid components and minerals were selected and specified according to the recorded aquifer matrix composition. The initial groundwater concentrations (Table 5) were based on a representative sample for the contaminated groundwater available from the monitoring database, and assigned homogeneously for the whole model domain. The solid matrix concentrations (Table 6) were derived from solid matrix analyses performed at the start of the field remediation experiments (NIDESI, 2000). Before running the reactive transport model, both groundwater analysis and solid matrix analysis were processed using PHREEQC-2 (Parkhurst and Appelo, 1999). Normally, the calculated pH value results from electroneutrality, but chemical analyses to be processed normally have an analytical ion balance error. In order to achieve electroneutrality as requested for reactive transport simulation (Prommer, 2002) and to preserve the assigned pH value of the initial water composition, electroneutrality was provided by varying slightly the chloride concentration.

Table 4

Summary of hydrogeochemical components.

Physical state	Chemical state	Components
Hydrodynamically transported	Chemical equilibrium	NO ₃ -N, N ₂ -N, NO ₂ -N, O ₂ , H ₂ , HCO ₃ , CH ₄ , Fe(2), Fe(3),SO ₄ , Cl, HS ⁻ , Ca, Mg, Na, K
Hydrodynamically transported	Kinetics	NH ₄ –N, DOC
Milieu parameters	Chemical equilibrium	pH, Pe
Immobile	Kinetics	O ₂ gas phase
Solids	Precipitation/ Dissolution chemical Equilibrium	Calcite, Ferrihydrite(Fe OH) ₃ ,am)
Solids	Ion Exchange equilibrium	NH ₄ X, NaX, CaX ₂ , MgX ₂ , KX, FeX ₂
Solids	Kinetics	Pyrite, particulate OC

Table 5

Representative hydrogeochemical initial conditions of dissolved components for
the simplified large scale model (pH and Pe dimensionless, otherwise mol l^{-1}
and mg l^{-1}).

Component	mol l ⁻¹	mg l ⁻¹	Representative values within the ammonium contamination (Database Berliner Wasserbetriebe), mg l ⁻¹
pН	7.06		7.10
Pe	12.81		-
NH4-N	1.662×10^{-3}	23.28	23.3
NO ₃ –N	1.71×10^{-7}	0.0024	-
NO ₂ –N	5.9×10^{-17}	0.00	-
N ₂ –N	1.15×10^{-7}	0.0016	-
02	1.42×10^{-12}	0.00	-
HCO ₃	7.175×10^{-3}	437.75	440.0
CH ₄	0	0	-
Ca	3.964×10^{-3}	158.9	160,0
Mg	6.131×10^{-4}	14.91	15.0
Na	2.608×10^{-3}	59.96	60.0
K	5.104×10^{-4}	19.96	20.0
SO_{4}^{2-}	2.501×10^{-3}	240.25	240.0
HS ⁻	0	0	-
Cl ⁻	3.028×10^{-3}	107.35	80.0
DOC	5.0×10^{-4}	6.0	6.0
Fe(2)	4.89×10^{-16}	0	1.0
Fe(3)	5.94×10^{-9}	0.0003	-

The domain of the oxygen bubble wall was assigned to the nodes situated at a distance of 500 m from the outflow model boundary (see Fig. 2) as designed by the Berlin Water Company for the final remediation. As a realistic guess derived from the BIOXWAND field test campaign (BIOXWAND, 2004), an input of 156 kg $O_2 d^{-1}$ along the oxygen bubble wall lateral extension (150 m) was assumed. The reach assigned to the oxygen bubble wall towards the groundwater flow direction was 50 m.

The reactive kinetic parameters (see Table 2 and Appendix A for symbols) specified for the conceptual model are listed in Table 7. Most of these parameters were assigned as a first guess based on literature references. Because of the magnitude of the simulated time span (50 years), the lag time

Table 6

Hydrochemical initial conditions of solid components for the large scale model.

Component	Measured variation, (NIDESI, 2000)	Unit	Specified value	mol dm ⁻³
Cation exchange capacity	$1.3 \times 10^{-4} - 1.67 \times 10^{-1}$	³ mol (eq)/ 100 g	1.67×10 ⁻¹	³ 0.03674
ТОС	100-300	mg C/kg dry soil	200	0.0367
Calcite	2.0-6.0 ¹⁾	weight % dry soil	2.0	0.39
Pyrite	0-187 ²⁾	mg/kg dry soil	187	3.43×10^{-3}
Ferrihydrite	-	-	0	0
NH ₄ X	-			1.69×10^{-3}
CaX ₂	-			1.5365×10^{-2}
MgX_2	-			1.499×10^{-3}
NaX	-			$6,382 \times 10^{-4}$
KX	-			6.875×10^{-4}
FeX ₂	-			5.4×10^{-15}

¹⁾ NIDESI (2000), ²⁾ calculated from 100 mg Sulphur/kg dry soil by assuming 0.25 for porosity and 2.2 kg dm⁻³ for bulk density.

Table 7
Reactive kinetic parameters applied to the simplified large scale model

Process	Kinetic parameter	Notation	Value	Unit	Reference
Nitrification	Rate constant Monod	k _{Nitr} k _{m,O2}	1×10^{-10} 1×10^{-6}	mol $l^{-1} s^{-1}$	1 1
	Monod	km _{Amm}	1×10^{-6}		1
	Lag time	t _{lag}	0	d	3
Degradation	Rate	k _{O2}	0.0001	$mol l^{-1} d^{-1}$	4
Doc	Rate	k _{NO3}	0.0001	$mol l^{-1} d^{-1}$	4
	Monod	km _{O2}	1×10^{-6}	mol l^{-1}	4
	Monod	km _{NO3}	1×10^{-6}	mol l^{-1}	4
	Inhibitor constant O ₂	I ₀₂	1×10^{-6}	mol l ⁻¹	4
Kinetics pyrite	Reactive surface parameter	A _{Pyrite} /V	10 ¹⁾	dm ⁻¹ mol ⁻¹ l	2.3
Sorption/	Solubility	C _{sat,DOC}	0.0005	mol l^{-1}	6
DOC	Solution	$k_{\rm sol,DOC}$	1×10^{-5}	d ⁻¹	6
O ₂ gas phase input at bubble wall	Input rate O ₂	k _{Input,O2}	3.255× 10 ^{−5}	$mol d^{-1} dm^{-3}$	5
Kinetics solution O ₂	Saturation concentration	C _{sat,O2}	0.00125	mol l ⁻¹	5
gas pilase	Solution rate constant O ₂	k _{sol,O2}	2.0	d^{-1}	4

1) Serapiglia (2002), 2) Williamson and Rimstidt (1994), 3) Prommer and Stuyfzand (2004), 4) NIDESI (2000), 5) BIOXWAND (2004), 6) Horner (2005a).

needed by the microbial nitrifier population for adaptation to perform the nitrification was neglected.

2.2. Results

The results of the simplified large model over a 50 year time period are shown as breakthrough curves in Figs. 3 and 4. Due to the 1D model character, equal component concentrations result for the three columns stacked next to one another.

The simulated breakthrough curves for dissolved oxygen and the nitrogen species ammonium, nitrate, and dissolved nitrogen at four different sample points (bubble wall, 100 m, 250 m from the bubble wall, and at the outlet) are shown in Fig. 3. At the oxygen bubble wall, the build up of an aerobic domain starts by performing the nitrification reaction and competing reactions such as pyrite oxidation reaction which at first provide a deficit in oxygen. After degrading the local pyrite stock, an excess of oxygen results from permanent oxygen gas input, and the oxygen bubble wall can develop. At 100 m downstream from the bubble wall, the nitrate load leaving the oxygen bubble wall is denitrified by pyrite as indicated by the nitrogen breakthrough curve. After consumption of pyrite, the breakthrough of both oxygen and nitrate can be expected also downstream to the oxygen bubble wall. The elimination of ammonium due to nitrification was demonstrated to be restricted to the oxygen bubble wall. At farther distances (250 and 500 m from the oxygen bubble wall), only hydrodynamic transport can be expected for the depleted ammonium load and for the dissolved nitrogen generated by denitrification. After an operation time span of 50 years, the pyrite reaction front was simulated to proceed at about 250 m from the oxygen bubble wall, as indicated by the start of the nitrate breakthrough. Upstream to the oxygen bubble wall, the initial anaerobic conditions will be stable. Here, ammonium will only be subjected to ion exchange equilibrium. Further reactions to address here are the Ferrihydrite /Fe⁺² redox pair and the calcite precipitation/ dissolution equilibrium.

Accompanying secondary processes such as acidification by release of sulphate due to pyrite oxidation reactions and the release of HCO₃⁻ from calcite dissolution are illustrated together with the oxygen breakthrough by Fig. 4. The shape of the sulphate breakthrough showing increasing concentrations towards downstream can be explained by the progression of the pyrite reaction front due to oxidation and denitrification reactions. The maximal concentration level of sulphate released by pyrite degradation can be stated significantly above the limit value of the German and EU drinking water limit (250 mg SO₄ l^{-1}). Fig. 4 demonstrates also that after complete consumption of the pyrite stock, the upstream sulphate concentration will propagate towards downstream. The sulphate release causes a moderate drop in the groundwater pH at about 0.3 pH units (from pH 7 to pH 6.7, here not shown). pH buffering by calcite dissolution is demonstrated by the HCO_3^- breakthrough nearly simultaneous to the sulphate breakthrough.

The oscillations of the breakthrough curves shown in Figs. 3 and 4 are only partially caused by the coarse model discretization. It is clear that an element wise step by step consumption of pyrite will generate a pulsing sulphate signal which is propagated in a damped manner towards the model outlet. The overshot in the ammonium breakthrough (Fig. 3) is not numerical but due to the release from the ion exchanger.

In summary, the reach of reaction zones caused by a permanent gas sparging within the oxygen bubble wall over 50 years is shown in Fig. 5. Due to the quasi 1D character of the simplified large scale model, the component concentration at any longitudinal position is the same in each of the three transverse gridblocks. From the model results it can be concluded that neither the aerobic zone nor the anaerobic nitrate zone will extend to the model outflow (here symbolizing the well field A of the Berlin Friedrichshagen water works). Within a time span of 50 years operation, nitrate concentrations exceeding the limit value of the German drinking water limit (40 mg $NO_3^- l^{-1}$) within the production wells are avoidable. If the contamination source is not eliminated as modelled by the simplified large scale model, at a very long extent the secondary nitrate can be expected to break through at the

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Fig. 3. Simulation results of the simplified large scale model: Breakthrough of oxygen and nitrogen species.

well field. But the monitoring results (personal communication Berlin Water Company) demonstrate a continuous leaching of the contamination source during the last 20 years.

3. Oxygen bubble wall test site model

3.1. Description of the oxygen bubble wall test site and of the field test campaign

The oxygen bubble wall test site Machnow (BIOXWAND project) is situated immediately South to the sewage field (see Fig. 1). A detail map of this test site is available from Fig. 6. Here, the monitoring well and pumping well configuration, the extent of the oxygen bubble wall after 160 day operation, and estimated groundwater flow paths with time markers are shown. The test site has a surface of 30×50 m². An important remediation element is the pumping well situated at about 30 m south of the bubble wall to capture the remediate groundwater. The oxygen bubble wall was found to be placed in 15–25 m depth with a maximal lateral extension in 20 m depth as shown by Fig. 6.

The local geology is characterized by alternating layers of fine and middle grained sand. The shallow part of the local aquifer until a depth of 15 m below surface is made up by middle and coarse grained sand. Finer sands prevail within the shallower part from 15 m up to 20 m depth, and a gradual change to middle sand was found at the deeper level down to 40 m below surface. This geological stratification determines the shape and distribution of the oxygen bubble wall. The local groundwater level depth was met at 4–5 m below surface with a groundwater gradient towards south. Around the pumping well which is operated using a pumping rate of $25 \text{ m}^3 \text{ d}^{-1}$ the regional groundwater flow field is superposed by a local depression cone indicated by flow paths shown in Fig. 6.

At the test site, two pilot clean-up tests were conducted. The first clean-up campaign was performed in 1998/1999 (NIDESI, 2000) by an infiltration of oxygenated water via a recharge well to initiate the in situ nitrification of the ammonium contamination. Based on the evaluation which showed only a limited success for this clean-up method, a second clean-up experiment providing in situ oxygen gas and air into the contaminated aquifer was performed in 2002 and 2003 over a total time interval of 336 days.

The oxygen gas sparging field experiment itself was made up by 8 intervals. The oxygen/air gas infiltration schedule is given by Table 8. During intervals 1 to 4, a coherent oxygen gas domain was built up as shown by Fig. 6, and the latter intervals of the experiment were used to maintain a stable gas domain within the aquifer. Intervals 3 and 4 during which the oxygen bubble wall was built up were chosen for the reactive transport simulation, as indicated by the shaded stable elements in Table 8.

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Fig. 4. Simulation results of the simplified large scale model: Breakthrough of oxygen, sulphate and hydrogen carbonate.

3.2. Model setup

In order to verify the hydro-chemical changes observed during the selected field experiment phases, a 3D flow and reactive transport model was set up ("oxygen bubble wall field test site model"). The 3D model was derived from the simplified large scale model by refining the horizontal model grid until grid element sizes of $5 \times 10 \text{ m}^2$ in the close-up range of the oxygen bubble wall and the aerobic zone at the test site. The position of the condensed domain figuring the oxygen bubble wall test site is indicated in Fig. 7. A detailed view of the model domain showing the extent of the oxygen bubble wall, and the pumping and monitoring wells is also available from Fig. 7.

In order to incorporate adequately the observed hydrogeological profile and the lateral and vertical extension of the oxygen bubble wall into the reactive transport model, the 40 m thick aquifer modelled by the simplified large scale model was vertically sub-divided into 8 model layers. The pumping well was assigned to the model layers 3 to 7 according to its screen position at a depth of 10 to 30 m below surface (NIDESI, 2000; BIOXWAND, 2004). The observed hydraulic conductivities were found to vary vertically from 2×10^{-4} to 8×10^{-4} m s⁻¹. Higher hydraulic conductivity was found typical for the shallow parts down to a depth of 15 m below surface (BIOXWAND, 2004; Horner, 2005b). The longitudinal dispersivity was termed at 2 m d⁻¹, and the transversal as well as the



Fig. 5. Simplified large scale model: Simulated reaction zoning after 50 years.



Fig. 6. Site map of the oxygen bubble wall test site with oxygen gas sparging wells, selected monitoring wells, pumping well, and estimated groundwater streamlines, modified after BIOXWAND (2004).

vertical dispersivities were set at 10% of the longitudinal dispersivity.

Fig. 8 refers to the representation of the immobile oxygen gas phase domain in the model. The simulated steady-state groundwater flow field is demonstrated using flow lines generated by running PMPATH (Chiang and Kinzelbach, 1994) in the right side plot of Fig. 8 and demonstrates the local convergent flow field due to running the pumping well situated downstream. Arrows along the streamlines indicate time markers depicting 10 days time intervals of progression.

Table 8

Schedule	of	the	"BIOXWAND"	field	experiment	campaign	on	the	test	site
Machnow	Ι.									

Interval no.	O_2/air gassing rate (Nm ³ $O_2 h^{-1}$)	O ₂ amount sparged (kg)	Space of time	Duration of phases (d)
1	0.5, intermittently	860	07-01-02 until	25
	gassing		08-03-02	(effective)
2	0	0	08-03-02 until	18
			08-21-02	
3	0.5, permanently	1090	08-21-02 until	63
	gassing		10-23-02	
4	1.0, permanently	2050	10-23-02 until	61
	gassing		12-23-02	
5	0	0	12-23-02 until	15
			01-07-03	
6a	1.0, permanently	518	01-07-03 until	15
	gassing		01-22-03	
6b	1.0, permanently	968	01-22-03 until	28
	gassing		02-19-03	
7	0	0	02-19-03 until	48
			04-08-03	
8	0.75–1 Nm ³	740	04-08-03 until	63
	Air/h+0-0.25		06-10-03	
	$Nm^3 O_2/h$,			
	permanently gassing			

After about one month, groundwater referred to the oxygen bubble wall can be expected to be captured by the pumping well. Reliable pristine chemical initial conditions were not available at the monitoring wells because the local groundwater composition was demonstrated to be just affected by earlier remediation campaigns such as the NIDESI campaign (NIDESI, 2000) during which oxygenated drinking water was applied to the test site. Therefore the chemical initial state addressed to the simplified large scale model was assigned using an adaptation of the ammonium concentration to the analytic value monitored at well P2/M before start of the simulated oxygen gas sparging cycle. This modified dissolved initial chemical state is available from Table 9. The solid concentration initial state was resumed from the simplified large scale model (see Table 6) and equilibrated using PHREEQC-2 (Parkhurst and Appelo, 1999) with the modified initial groundwater composition.

The monitoring well groups P2O/M/U, P3O/M/U and P4/ O/M/U shown by Fig. 11 were selected for modelling, because monitored chemical analyses were extensively available on these monitoring wells. Monitoring demonstrated that after 160 days duration the whole capture zone of the pumping well downstream to the oxygen bubble wall had changed from pristine anaerobic to aerobic conditions (BIOXWAND, 2004).

3.3. Sensitivity analysis

Simulation runs of the oxygen bubble wall test field model demonstrated that the monitoring measurements (BIOX-WAND, 2004) could not be verified by using simply the reactive parameters as assigned to the simplified large scale model (Table 7). Therefore, at first a sensitivity analysis based on spatially uniform reactive parameters was performed. Possible sensitive parameters affecting the simulation results



Fig. 7. Design of the oxygen bubble wall test site verification model within the refined model portion with oxygen bubble wall, aerobic zone and selected monitoring wells.

are especially the nitrification rate constant, the reactive surface of pyrite, and the cation exchange capacity. The variation of the reactive parameter values is available from Table 10.

The nitrification lag time as an indicator of microbial adaptation to redox conditions changing from anoxic to oxic is not included in Table 10, because it was recognized as essential parameter after subsequent simulation runs.

From the program limitations of the software package PHT3D (Prommer, 2002) which addresses only flow and transport under water saturated conditions, it is clear that the oxygen breakthrough only can be verified sufficiently as long as an immobile oxygen gas phase is available within a model element. This is demonstrated for sample point P2/M by Fig. 11. At the monitoring wells P3/M and P4/m situated outside of the oxygen gas domain, the discrepancy of the simulated to the monitored oxygen breakthrough was found to increase in relation to the distance from oxygen gas phase domain shown by Fig. 8.

As mentioned above, aerobic conditions prevail at the simulated test site depicting the nitrification and the pyrite oxidation as main reactions to model. Due to the aerobic redox milieu that persists from former gas injection periods, denitrification reactions are not active at the oxygen gas bubble test site although they are present in the reaction network. Of course, both nitrification and pyrite oxidation reactions are linked to the oxygen release and transport demonstrated as insufficiently modelled by the PHT3D software. Despite this fact only a limited impact of these program limitations on the simulation of both reactions was found.

Extensive simulation runs demonstrated that a spatially uniform assignment of the reactive parameters (such as the nitrification rate constant and the reactive surface of pyrite) meets the measured breakthrough of NH₄–N and NO₃–N either within the oxygen gas phase domain (monitoring well P2/M), or at the monitoring wells situated outside (Horner, 2005b). Therefore spatially non-uniform parameter values were assigned to theses reactive parameters at the oxygen gas phase domain and the downstream domain which reflect different aggregation states of the matrix bound pyrite, and different microbial activity. To the nitrification lag time parameter, which is additionally decisive for microbial activity, a different value at the oxygen gas phase domain can refer to a preconditioning of the microbial population due to former gas sparging periods.

Among the reactive parameters included, the lag time was found to be the most sensitive parameter in relation to the other reactive parameters. Therefore, the main focus in presenting simulation results is put on NH₄–N and NO₃–N simulation results which are available from Figs. 9 and 10. Starting from neglecting the lag time over whole the model (variant 4, see Table 11, and Figs. 9 and 10), the lag



Fig. 8. Oxygen bubble wall test site model: O₂ gas phase domain and simulated streamlines with time markers figuring 10 day time intervals.

Table 9

Hydrogeochemical initial conditions of dissolved components for the test site (pH and pe dimensionless, otherwise mol l^{-1} and mg l^{-1}), after BIOXWAND (2004).

Component	mol l ⁻¹	mg l ⁻¹
pH	6.983	
ре	12.898	
NH ₄ –N	1.297×10^{-3}	18.16 ¹⁾
NO ₃ –N	1.71×10^{-6}	$0.024^{1})$
NO ₂ -N	5.9×10^{-17}	0.001)
N ₂ -N	1.15×10^{-6}	0.016 ¹⁾
02	3.19×10^{-12}	0.00
HCO ₃	7.747×10^{-3}	472
CH ₄	0	0
Ca	4.473×10^{-3}	179
Mg	6.498×10^{-4}	15.79
Na	2.624×10^{-3}	60.32
K	5.211×10^{-4}	20.38
SO_{4}^{2-}	2.084×10 ⁻³	200.20
HS ⁻	0	0
Cl	4.347×10^{-3}	154.11 ²⁾
DOC	5.0×10^{-4}	6.0
Fe(2)	6.68×10^{-16}	0 ¹⁾
Fe(3)	6.52×10^{-9}	0.000371)

After equilibration using PHREEQC-2 (Parkhurst and Appelo, 1999),
 chloride used for charge balancing.

time parameter was varied at the oxygen gas phase domain whereas the lag time outside the oxygen gas phase domain was fixed at 50 days after first arrival of dissolved oxygen. This value was set up close to the upper limit termed by the laboratory experiments of the BIOXWAND campaign (BIOXWAND, 2004). For NH₄-N, the characteristic shape of the measured breakthrough showing a concentration maximum prior to the start of the nitrification is confirmed by the simulation (Fig. 9). This phenomenon can be explained by flushing out the NH₄⁺ exchange complex from the ion exchanger and its substitution mainly by the Ca²⁺ exchanger complex. The variation of the lag time is demonstrated by a shift on the simulated NH₄-N breakthrough. By including the lag time, for NO₃–N simulation results closer to the measured NO₃–N breakthrough are obtained rather than by neglecting the lag time. Without considering the lag time as simulation parameter, in general a too rapid NO3-N breakthrough is simulated as shown by Fig. 10.

For the secondary processes such as sulphate release and groundwater acidification, simulation results are presented by Fig. 11. As mentioned above, an autotrophic denitrification reaction releasing additional sulphate from pyrite decomposition can be excluded for the oxygen bubble wall test site because of an aerobic redox environment not only generated by the modelled gas sparging cycle but also by former gas sparging. Due to the lack of reliable initial sulphate concentrations in the database, a calibration of the monitored sulphate values seemed less promising rather than confirming the observed trend of concentration change. At the sample points P2/M and P3/M, the observed sulphate breakthrough is confirmed by the simulation as shown by Fig. 11. At monitoring well P4/M, the measured sulphate concentrations in general exceed the simulated sulphate concentrations based on the initial chemical concentration conditions given by Table 9. Here an additional influence due to the convergent flow field can be suggested which activates a more concentrated sulphate load from an upstream aquifer domain outside of the oxygen bubble wall. The pH variation observed during the modelled gas sparging cycle was simulated sufficiently well. These results confirm the conception that buffering by calcite dissolution as discussed by NIDESI (2000) and BIOXWAND (2004) delimits the acidification (Table 12).

4. Summary and conclusions

In order to prevent a continuous impairment of the northern well fields of the Berlin Friedrichshagen waterworks by an ammonium contamination resulting from sewage field management a reactive transport model was developed. Due to the migration properties of ammonium which is retarded by cation exchange processes, a pure hydraulic clean-up measure was estimated to be less successful than an in situ attenuation measure using oxygenating groundwater or oxygen gas/air to eliminate/reduce the ammonium load from the production wells. Preliminary pilot tests performed near the contamination source (NIDESI, 2000; BIOXWAND, 2004) have demonstrated that a clean-up by applying oxygen gas is a more promising clean-up method than the infiltration of oxygenated groundwater. Oxygen/air gas sparging initiates in situ nitrification of dissolved and matrix bound (exchangeable) ammonium. The efficiency of this process is related to the availability of dissolved oxygen and competes with secondary chemical reactions such as oxidation of pyrite, oxidation of dissolved iron and aerobic respiration. Evidence of the occurrence of both pyrite and reactive organic carbon in the local aquifer was demonstrated by extensive soil matrix investigations (NIDESI, 2000; BIOXWAND, 2004). A mathematical formulation of the reaction network was performed using PHREEQC-2 (Parkhurst and Appelo, 1999) which is linked to the reactive transport code PHT3D (Prommer, 2002) applied for reactive transport modelling.

First, a long-term prognosis of the impact of oxygen gas sparging within an oxygen bubble wall over 50 years was established to extrapolate the reach of the different reaction zones induced by oxygen gas sparging towards the well fields. For this purpose, a simplified large scale quasi 1D model was established which covers the local capture zone between well field A and the sewage plant as contamination source. Based on mean flow velocities observed, the prognosis calculations showed that the elimination of ammonium finally will

 Table 10

 Oxygen bubble wall test site model: range of selected reactive parameters.

Reactive parameters				
Nitrification rate constant $k_{\text{Nitr}} \pmod{1^{-1} \text{s}^{-1}}$ $2 \times 10^{-10} - 6 \times 10^{-10}$	Surface parameter of pyrite $A_{Pyrit}/V (dm^{-1} mol^{-1})$ 2–10	Dissolution rate constant of $O_2 k_{sol,O2} (d^{-1})$ 20	Saturation concentration of $O_2 C_{sat,O2}$ (mg l^{-1}) 60	Ion exchange capacity (meq/100 g) 0.835

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Fig. 9. Simulated and measured breakthrough of NH₄-N (oxygen bubble wall test site model).

eventually reach the well fields. A smaller reach can be predicted for the nitrification and denitrification reaction zones so that the well field itself probably will not be impacted by elevated nitrate concentration after 50 years. Secondary reactions affecting the groundwater quality are the acidification due to sulphate release from pyrite consumption,



Fig. 10. Simulated and measured breakthrough of NO₃-N (oxygen bubble test site model).

5

5

Oxygen bu	ibble wall test site model: Inv	vestigation of paramete	er sensitivity for spatially differ	ing kinetic parameters.	
Model	Reactive parameters				
version	Nitrification rate constant $k_{\text{Nitr}} \pmod{l^{-1} \text{s}^{-1}}$	Surface parameter of <i>P</i> yrite $A_{Pyrit}/V(dm^{-1}mol^{-1})$		Nitrification lag time	
	Oxygen bubble wall	Downstream	Oxygen bubble wall	Downstream	Oxygen bubble wall
1	4×10^{-10}	2×10^{-10}	10	5	20
2	4×10^{-10}	2×10^{-10}	10	5	10

10

10

 $2\!\times\!10^{-10}$

 2×10^{-10}

and the hardening of the groundwater due to pH buffering by calcite dissolution. Depending on the progress of pyrite reaction, an elevated sulphate load is generated and transported. After complete pyrite consumption by oxidation and denitrification reactions, a successive dilution to pristine sulphate concentrations was demonstrated by reactive transport modelling. This prognosis is confirmed by the long-term monitoring performed by the Berlin Water Company. Theoretically, if the contamination source is permanently active (as modelled), also nitrate can reach the well field, In practice, during the last 20 years, due to the elimination of additional ammonium input, a leaching of the contamination plume is observed (BIOXWAND, 2004) so that a dilution of the contaminated load can be foreseen.

Table 11

3

4

 $4\!\times\!10^{-\,10}$

 4×10^{-10}

On the basis of the long-term prognosis available from the simplified large scale model simulation, a 3D model was set up for the oxygen bubble wall test site to simulate selected intervals of the test campaign. As a result of extensive simulation runs, magnitude order of ranges were estimated for the relevant reactive parameters, such as the denitrification rate constant, the reactive surface parameter of pyrite, and the dissolution rate constant for oxygen. By setting spatial non uniform reaction parameter values for two reaction zones-the oxygen bubble wall environment and the downstream area which changed during the field test to aerobic conditions-the simulation results were only slightly improved. By introducing additionally the lag time parameter for the nitrification reaction, the simulation results were substantially improved. The lag time parameter refers to a time span which the nitrifier bacteria need to adapt to a redox environment changing from anaerobic to aerobic conditions. Within the oxygen gas phase domain, more appropriate conditions can be expected for the nitrifier bacteria population also from earlier gas sparging cycles than under initially pristine anoxic redox conditions as prevailing outside of the oxygen gas domain. Owing to fact that the reactive transport code PHT3D (Prommer, 2002) is only designed for saturated flow conditions, but not for simultaneous water/gas transport, the greatest discrepancies between monitoring values and simulated values resulted for dissolved oxygen. Reliable simulation results were obtained for dissolved oxygen only at the oxygen gas phase domain. Here an (of course strongly simplified) approach analogous to an exchange between stationary NAPL or DNAPL phase and water was shown

0

0



Fig. 11. Simulated and measured breakthrough of SO₄, pH, and O₂ (oxygen bubble wall test site model).

Downstream

50

50

50

0

(d)

Table 12

Range of reactive parameters based on the Oxygen bubble wall test site model simulations.

Parameter	Unit	Range		Referenced
		Oxygen bubble wall	Downstream	values
Nitrification rate constant k _{Nitr}	$mol l^{-1} s^{-1}$	$2 \times 10^{-10} - 4 \times 10^{-10}$	1×10^{-10} - 2×10^{-10}	$\begin{array}{c} 1 \times 10^{-10} \text{-} \\ 2 \times 10^{-10} \text{1,2)} \end{array}$
Reactive surface parameter of pyrite <i>A</i> _{Pvrit} / <i>V</i>	$\mathrm{dm}^{-1}\mathrm{mol}^{-1}$	5-10	1–5	10 ³⁾
Cation exchange capacity	meq/100 g dry soil	0.167–1.67	0.167–1.67	0.13–1.67 ⁴⁾
O ₂ dissolution rate constant	d^{-1}	2–20	-	2.0 ⁴⁾
O ₂ saturation constant	mg l^{-1}	60	-	60 ⁶⁾
Nitrification lag time	d	0–20	10–50	10-50 ⁵⁾

¹⁾ Serapiglia (2002), ²⁾ Haerens (2002), ³⁾ Prommer and Stuyfzand (2004), ⁴⁾ NIDESI (2000), ⁵⁾ BIOXWAND (2004), ⁶⁾ Horner (2005a,b).

efficient. Despite of the limitations of the PHT3D code to adequately simulate the breakthrough of dissolved oxygen outside of the oxygen gas phase domain, the resulting error was demonstrated to have only a minor impact on the simulation results achieved for the nitrification kinetics, and the secondary processes such as sulphate release and acidification due to pyrite decomposition, and buffering by calcite dissolution.

Based on the long-term prognosis for the clean-up using oxygen gas sparging provided by the simplified large scale model and on the first field test site monitoring results approached by the reactive transport modelling, the Berlin Water Company has decided to continue the oxygen/air gas sparging field experiments at a new location within 500 m from the well field A of the Berlin Friedrichshagen water works. In 2006, the field test devices and a detailed framework of monitoring wells were installed, and simultaneously a regional 3D reactive transport model based on a regional flow model established by (UWG, 2002) and on monitored hydrochemistry was set up (Horner, 2006). From this regional model, the area of interest (the surrounding of the new test site) will be depicted by telescoping to simulate the new field test experiment as a steering tool to assess all field test experiment intervals planned for a time interval of two years (2008/2009).

As a final remediation measure, a line of oxygen gas injection wells extending laterally over about 1 km across the ammonium contamination plume is planned to clean-up the well fields recently affected by elevated ammonium concentrations. A design of this measure and a preliminary prognosis of remediation impact after a management duration of 5 years are given by Fig. 12. This preliminary prognosis (UWG, 2002), based on kinetics not coupled to hydrochemistry simulation gives a first plausible guess about the reach of ammonium elimination caused by a permanent oxygen gas infiltration along the projected line.

After eliminating the contamination source at the sewage field, the contamination plume itself is expected to be flushed out without any attenuation remediation measure after about 80 years (BIOXWAND, 2004). Therefore, the oxygen bubble has to be managed at least over this time span to provide security for the production wells. Further experiments and reactive modelling have to be carried out in order to provide appropriate gas injection rates, so that a steady oxygen bubble wall can be kept viable.



Fig. 12. Preliminary prognosis of operating a long-term projected oxygen bubble wall after 5 years (modified from BIOXWAND, 2004).

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Appendix A. Notation of symbols

Symbol	Explanation
$A_{\rm Pyrite}/V$	Surface parameter of pyrite [dm ⁻¹]
C _{Amm}	Ammonium concentration [mol l ⁻¹]
C _{DOC}	DOC concentration [mol l^{-1}]
$C_{\rm H+}$	H^+ concentration [mol l^{-1}]
C _{NO3}	Nitrate concentration [mol l^{-1}]
C ₀₂	Dissolved oxygen concentration [mol l ⁻¹]
C _{POC}	Particulate organic carbon concentration [mol dm ⁻³]
$C_{\rm sat,DOC}$	Solubility of DOC [mol l^{-1}]
C _{sat,O2}	Solubility of oxygen gas phase [mol l^{-1}]
$C_{O2,gasphase}$	Oxygen gas phase concentration [mol dm ^{-3}]
C _{pyrite}	Concentration of pyrite [mol dm ⁻³]
$C_{0,pyrite}$	Initial concentration of pyrite [mol dm ⁻³]
f_2	Factor in pyrite kinetics equation, set as 1 [–]
I ₀₂	Inhibition factor for oxygen [mol l^{-1}]
k _{input,O2}	Input rate of oxygen gas phase $[d^{-1}]$
k _{m,Amm}	Monod factor for ammonium [mol l^{-1}]
k _{m,NO3}	Monod factor for nitrate [mol l^{-1}]
k _{m,O2}	Monod factor for oxygen [mol l^{-1}]
k _{Nitr}	Nitrification rate constant [mol $l^{-1} s^{-1}$]
k ₀₂	Rate constant for DOC degradation with O_2 [mol $l^{-1} d^{-1}$]
k _{NO3}	Rate constant for DOC degradation with NO ₃ [mol $l^{-1} d^{-1}$]
t _{lag}	lag time interval for nitrifier microbes to start nitrification
f_{lag}	Toggle factor to switch on nitrification
k _{sol,DOC}	Solution rate of DOC from particulate organic carbon [d ⁻¹]

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