A review of acidity generation and consumption in acidic coal mine lakes and their watersheds

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Abstract

Lakes developing in former coal mine pits are often characterized by high concentrations of sulfate and iron and low pH. The review focuses on the causes for and fate of acidity in these lakes and their watersheds. Acidification is primarily caused by the generation of ferrous iron bearing and mineralized groundwater, transport through the groundwater–surface water interface, and subsequent iron oxidation and precipitation. Rates of acidity generation in mine tailings and dumps, and surface water are often similar (1 to >10 mol m^{-2} yr^{-1}). Weathering processes, however, often suffice to buffer groundwaters to only moderately acidic or neutral pH, depending on the suite of minerals present. In mine lakes, the acidity balance is further influenced by proton release from transformation of metastable iron hydroxysulfate minerals to goethite, and proton and ferrous iron sequestration by burial of iron sulfides and carbonates in sediments. These processes mostly cannot compensate acidity loading from the watershed, though. A master variable for almost all processes is the pH: rates of pyrite oxidation, ferrous iron oxidation, mineral dissolution, iron precipitation, iron hydroxide transformation, and iron and sulfate reduction are strongly pH dependent. While the principle mechanism of acidity generation and consumption and several controls are mostly understood, this cannot be said about the fate of acidity on larger spatial and temporal scales. Little is also known about critical loads and the internal regulation of biogeochemical iron, sulfur, and carbon cycling in acidic mine lakes.
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1. Introduction

Many acidified lakes have formed in ore mine pits and strip mines in North America and Central Europe since the 1990s, owing to the economic end of mining or the exploitation of existing resources (Eary, 1999; Geller et al., 1998; Miller et al., 1996). In addition, many natural lakes have been reported to be polluted by acid mine drainage (AMD) (e.g. Herlihy and Mills, 1985; Kaufmann et al., 1992). Consequently, several overview papers called for an investigation of the geochemistry and biogeochemistry of these environments as a prerequisite for effective management and remediation strategies (Klapper and Schultze, 1995; Miller et al., 1996). The ensuing studies now allow for a more accurate analysis of the mechanisms of acidification and neutralization than possible only a few years ago.

Acidification of lakes can be induced by a variety of processes in their watersheds, for instance the release of organic acids from incomplete mineralization, organic matter accumulation, natural mineral weathering in weakly buffered catchments, and acidic atmospheric deposition (Schnoor and Stumm, 1985). In post-mining

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landscapes, acidification of lakes is primarily caused by AMD after oxidative weathering of metal sulfides (Bonnissel-Gissinger et al., 1998; Nordstrom, 2000; Singer and Stumm, 1970). The pollution of surface waters by AMD is a world wide problem (Young, 1992; Younger, 1992), and basically occurs anywhere where coal or sulfidic ores are mined. Occasionally, this process is also observed in natural environments (Schwertmann et al., 1995).

Several reviews and books have been written about AMD related issues. To mention are the books edited by Alpers and Blowes (1994), Jambor and Blowes (1994), and Plumlee and Logsdon (1999), which cover basic principles, mineralogy, hydrogeology, analytical and remediation techniques, as well as case studies on the environmental geochemistry of mineral deposits. A survey of mine water related environmental issues in European countries has been collated in a series of special issues edited by Wolkersdorfer and Bowell (2003), and information about many case studies and several more technically oriented reviews are provided in the book edited by Younger and Robins (2002a,b). The review by Evangelou and Zhang (1995) is primarily concerned with the mechanisms of pyrite oxidation and oxidation prevention. Nordstrom (2000) reported recent advances in the hydrogeochemistry and microbiology of acid mine waters. Plant life in extremely acidic waters have recently been reviewed by Nixdorf et al. (2001), and geochemical and equilibrium trends in mine pit lakes by Eary (1999), Shevenell et al. (1999) and Bowell (2002). Microbial processes in the sediments have been focussed on by Küsel (2003).

The objective of this review is to collate and synthesize recent scientific progress regarding acidity generation and consumption in watersheds and lakes polluted by AMD, primarily from coal mining. To these ends, acidity is defined, and rates and mechanisms of acidity generation and consumption in tailings, dumps, aquifers, surface waters, and sediments are discussed. Some emphasis is placed on case studies from coal mining regions in Eastern Germany; however, the author believes that much of the information provided will also be useful regarding other types of mining and other regions.

2. Acidity and alkalinity in AMD polluted waters

Acidity and alkalinity, i.e. acid and base neutralizing capacity, can be defined in a variety of ways that depend on the chemical composition of a water and the intentions of the investigator (Stumm and Morgan,

1996; Morel and Hering, 1993). In general terms, the concept aims at quantifying proton deficiency and excess in a water sample relative to a chosen reference state. Of particular importance for quantification of acidity and alkalinity is thus the – operationally defined – reference pH, which stipulates the reference state for the acid–base species that may be considered. For carbonate dominated systems, the well known definitions of CO_2- alkalinity and CO_2- and H-acidity can be derived:

$$Alk_{(CO_2)} = 2[CO_3^{2-}] + [HCO_3^-] - [OH^-] + [H^+];$$

$$Ac_{(HCO_3^-)} = [H_2CO_3] + [H^+] - [OH^-]$$

and

$$Ac_{(H^+)} = -Alk_{(CO_2)}.$$

These definitions are not adequate to describe proton deficiency and excess in acidic and metal-rich waters. In case studies on acidity generation and consumption, however, the definition of acidity and alkalinity used is not always stated, potentially causing confusion about the meaning of 'acidity' generation and consumption. A clear definition of the concept is thus necessary, stipulating a reference pH and appropriate reference states. As reference pH, the equivalence point of HCO_3^-, i.e. the pH of a $NaHCO_3$ solution (pH 8.3; $C_{tot} = 10^{-4}$ mol L^{-1}) may be kept because it lies in a range typical for many hardwater lakes. Given the composition of AMD polluted waters, the relevant iron, sulfur, aluminium, and other metal species need to be included in the definition. Furthermore, precipitation of hydroxides should be included because iron and aluminium are often in thermodynamic equilibrium with solid phases in these waters, as will be discussed below. Therefore, the hydroxides constitute the reference states for iron and aluminium at the reference pH. As this review focuses on lake water as a receptor for acidity, it is further useful to define the oxic lake water as a reference space. This is important because reduced, more soluble species that enter a lake from an adjacent, more reduced compartment will be oxidized and precipitate as hydroxide. These considerations are in agreement with the following definition:

$$\begin{aligned} Ac_{(HCO_3^-)} = {} & 2[Fe^{2+}] + 3[Fe^{3+}] + 2[Fe(OH)^{2+}] \\ & + [Fe(OH)_2^+] + 3[Al^{3+}] + 2[Al(OH)^{2+}] \\ & + [Al(OH)_2^+] + [H_2S] + [H^+] + [HSO_4^-] \\ & + [H_2CO_3] - [S^{2-}] - [NH_3] - [OH^-] \\ & - [Fe(OH)_4^-] - [Al(OH)_4^-]. \end{aligned}$$

Acidity in this context subsumes both homogenous and heterogeneous reactions, assuming FeOOH, Al(OH)$_3$, HCO$_3^-$, H$_2$O, NH$_4^+$, HS$^-$, and SO$_4^{2-}$ and H$_2$O as reference states, and the oxic lake water as reference space. Other relevant elements may be included in the same manner. It is important to note that the nature of the precipitates has to be considered for each system, as the stoichiometric coefficients of the metal species may change and thus alter the acidity definition.

3. Acidity generation and consumption in the watershed

3.1. Primary geochemical and biogeochemical processes

3.1.1. Pyrite occurrence and oxidation

Iron sulfides are commonly associated with metal ores and coal, predominantly in form of pyrite (FeS$_2$), or the less abundant and stable marcasite, which may form at lower pH and possibly lower sulfur concentration (Ward, 2002). In ores, often also pyrrhotite (Fe$_{1-x}$S) and other metal sulfides, such as sphalerite (ZnS), galena (PbS), chalcopyrite (CuFeS$_2$), and arsenopyrite (FeAsS) occur in appreciable quantities (Ljungberg and Öhlander, 2001; Plumlee et al., 1999). Pyrite contents in the overburden and mine wastes associated with lignite mining ranged from 0.1% and 5% (weight) in various pyrite oxidation and AMD case studies (Knöller et al., 2004; Ludwig and Balkenhol, 2001; Ludwig et al., 1999; Rolland et al., 2001; Seoane and Leiros, 1997; Wisotzky and Obermann, 1995). Contents are often substantially higher in ore mining areas (e.g. Strömberg and Banwart, 1994; Yanful et al., 1999) and may reach 85% (weight) in mine tailings at some sites (Blowes et al., 1991). For lignite, a global average sulfur content of 2.1±4.99% (s.d.) weight was determined, and sulfur contents of 0.5% to 3% are most common in major coal fields (Bouska and Pesec, 1999; Greb et al., 2002; Dai et al., 2002).

The variation in sulfur content has been linked to the depositional and diagenetic conditions during peat and coal formation. Sulfur content tends to increase with marine influence during peat formation and to decrease with ombrothrophy, i.e. restriction to atmospheric sulfur input (Greb et al., 2002; Dai et al., 2002 and references therein). As a result, sulfur contents vary among stratigraphic units and spatially within and between coal fields (Bouska and Pesec, 1999; Greb et al., 2002; Dai et al., 2002). On a smaller scale, pyrite primarily occurs above and below coal seams and it is often, but not always, concentrated in clusters and scattered

pockets (Evangelou and Zhang, 1995). The spatial distribution is influenced by the mechanism of pyrite formation, which can be syngenetic or epigenetic, i.e. precede or follow the diagenesis of coal seams. Epigenetic pyrite formation, which may be caused by hydrothermal activity, results in a more discontinuous distribution of pyrite, for example in veins (Ward, 2002). At individual sites, contents may further decrease with increasing average grain size of coal bearing strata (Rolland et al., 2001).

Pyrite oxidation takes place when the mineral is exposed to water and air. To a certain extent, oxidation is thus inevitable following the relocation of pyrite bearing materials to mine dumps or tailings, or the dewatering of aquifers during mining operations (Fig. 1). The process of pyrite oxidation is complex and involves both chemical and biological mechanisms, as well as a number of controls. It has, however, been conceptualized by three basic processes (Table 1, Eqs. (1)–(3)). As a first step, pyrite is oxidized by oxygen, either chemically or by microbial mediation. The chemical oxidation is fairly slow, which has been attributed to the low affinity of molecular oxygen to the pyrite surface (Luther, 1987). The microbially mediated process may begin with the dissolution of pyrite by attached *Thiobacilli ferrooxidans.* Subsequently, dissolved sulfide is enzymatically oxidized (Konishi, 1990). The process is further accelerated by the formation of elemental sulfur on pyrite surfaces (Mustin et al., 1993). Kinetically faster compared to oxidation of pyrite by oxygen is the oxidation by dissolved ferric iron (Luther, 1987; Table 1, Eq. (2)), which predominates probably even at circumneutral pH (Moses and Herman, 1991; Moses et al., 1987). Critical for the rate of pyrite oxidation is thus the supply of ferric iron from ferrous iron oxidation by oxygen (Table 1, Eq. (3)). At high pH values, ferrous iron is chemically rapidly oxidized and pyrite oxidation may be maintained without biological mediation (Singer and Stumm, 1970). At low pH values, microbially mediated oxidation of ferrous iron by acidophilic lithoautotrophic bacteria, such as *Acidithiobacillus ferrooxidans* (Pronk and Johnson, 1992), *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* (Johnson, 1993) predominates. Microbial mediation can decrease the half-life of ferric iron from about 1000 days to 20–1000 min, hence increase the reaction rate by a factor 10^6 at pH 3 (Singer and Stumm, 1970).

Chemical and microbial pyrite oxidation are directly controlled by the mineral and crystal type (Malmström et al., 2000) and by particle size, i.e. mass normalized surface area (Strömberg and Banwart, 1999). Among a variety of morphologies, such as framboids, octahedral
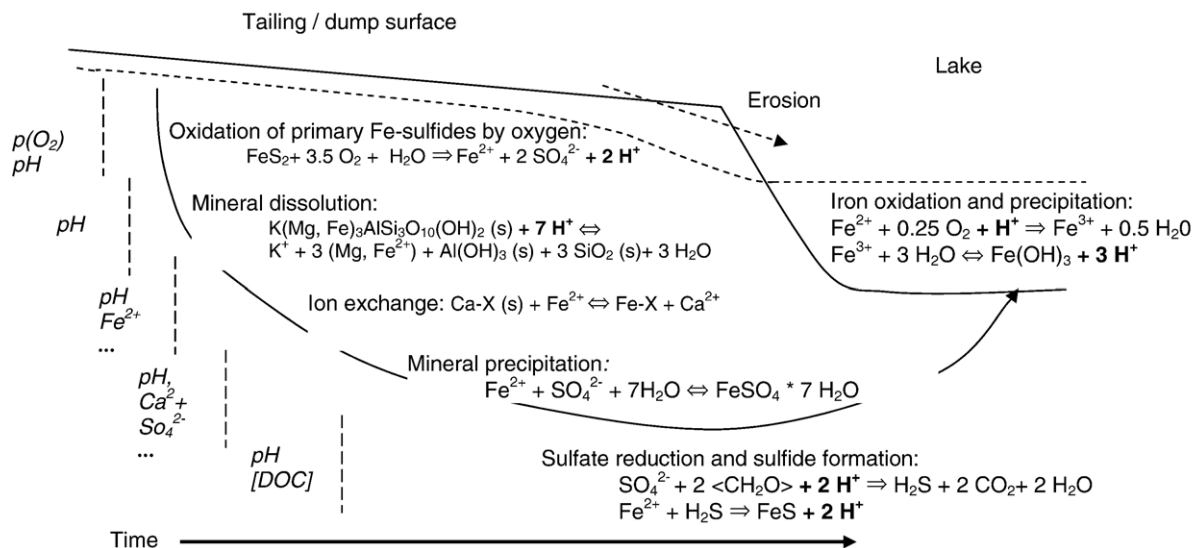
Fig. 1. Schematic of processes and controls involved in acidity generation and consumption in mine dumps and lakes. Controls (italics) are enumerated for the processes on the left hand side. For further description see text.

and cubic crystals, and conglomerates with irregular surfaces, the small, polycrystalline framboids are particularly susceptible to oxidation owing to their porosity and large surface area (Evangelou and Zhang, 1995). Oxidation rates increase with partial pressure of oxygen (Williamson and Rimstidt, 1994) and temperature (Jaynes et al., 1984), and are furthermore controlled by the pH (Bonnissel-Gissinger et al., 1998; Williamson and Rimstidt, 1994), and concentrations of ferric iron and ferrous iron (Williamson and Rimstidt, 1994). Siderophores may facilitate pyrite oxidation by transfer of electrons from dissolved ferric iron to pyrite surfaces (Peiffer and Stubert, 1999). Accelerated pyrite oxidation also ensues from presence of CO_2 or HCO_3^-, which form ferrous bicarbonate complexes on pyrite surfaces and facilitate the abiotic oxidation of ferrous iron to ferric iron (Evangelou et al., 1998). This effect may, for example, occur as a consequence of AMD neutralization by carbonate addition to AMD generating materials. Surface coatings with ferric oxyhydroxides can, in contrast, reduce the rate due to physical protection and immobilization of Fe^{3+} (Evangelou and Zhang, 1995; Nicholson et al., 1988, 1990).

Oxidant fluxes often constrain pyrite oxidation in mine tailings and overburden dumps. Oxygen is included during tipping of dumps (Rolland et al., 2001), but otherwise it has to be transported to the reaction front, which advances from the exposed tailing or dump surface downwards (Blowes and Jambor, 1990; Blowes et al., 1991; Ljungberg and Öhlander, 2001). A limitation of pyrite oxidation by supply of oxidants may

then occur around individual pyrite grains (Davis and Ritchie, 1986; Elberling et al., 1994; Wunderly et al., 1996), and in entire strata owing to water saturation (Elberling and Damgaard, 2001) and development of cemented layers (Blowes et al., 1991; Gilbert et al., 2003). Application of soil or clay covers and capillary barriers have a similar effect (Carlsson et al., 2003; Yanful et al., 1999; Bussiere et al., 2004). Pyrite oxidation rates were reduced by up to 99.8% in predictions for a 100 year period using reactive transport modeling and assuming coverage by water and fine-grained, low-sulfur waste materials (Romano et al., 2003). Decreases in moisture content can potentially slow down iron sulfide oxidation as well (Wunderly et al., 1996).

The spatial distribution of pyrite in geologic materials may also play a role for pyrite oxidation rates. Gerke et al. (2001) suggested that a heterogeneous distribution of sulfides slows the oxidation, based on results from 2D reactive transport modeling of a mine dump. Rolland et al. (2001) estimated in a case study that over the operation of a coal strip mine the majority of pyrite was oxidized on dump surfaces. The oxidation process is hence strongly influenced by the mining technology used (Rolland et al., 2001; Wisotzky and Obermann, 2001).

The outlined controls are partly reflected in published rates of *in situ* pyrite oxidation. At an ore mining site in Baffin Island, Canada, pyrite oxidation rates decreased by a factor of 3 in a chronosequence of mine tailings covering a period of 7 years and decreased by two orders

Table 1
Selected processes causing changes in acidity of mine waters

Processes involved in acidity generation

I Redox reactions	Stoichiometry	
(1) Pyrite oxidation	$FeS_2 + 3.5O_2 + 3H_2O \Rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$	
(2) Pyrite oxidation	$FeS_2 + 14Fe^{3+} + 8H_2O \Rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$	
(3) Ferrous iron oxidation	$Fe^{2+} + 0.25O_2 + H^+ \Rightarrow Fe^{3+} + 0.5H_2O$	
(4) Pyrrhotite oxidation	$FeS + 2O_2 \Rightarrow Fe^{2+} + SO_4^{2-}$	
(5) Sulfur oxidation	$S(0) + 1.5O_2 + H_2O \Rightarrow 2H^+ + SO_4^{2-}$	
(6) Chalcopyrite oxidation	$CuFeS_2 + 4O_2 \Rightarrow Cu^{2+} + Fe^{2+} + 2SO_4^{2-}$	
(7) Sphalerite oxidation	$ZnS + 2O_2 \Rightarrow Zn^{2+} SO_4^{2-}$	

II Heterogeneous reactions — precipitation (secondary)		
(8) Ferrihydrite	$Fe(OH)_3 + 3H^+ \Leftrightarrow Fe^{3+} + 3H_2O$	$pK_s = -4.81^2$
(9) Jurbanite	$Al^{3+} + SO_4^{2-} + H_2O \Leftrightarrow AlOHSO_4 + H^+$	$pK_s = 3.8$
(10) Alunite	$K^+ + 3Al^{3+} + 2SO_4^{2-} + 6H_2O \Leftrightarrow KAl_3(SO_4)_2(OH)_6 + 6H^+$	$pK_s = 1.4^2$
(11) K-Jarosite	$K^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \Leftrightarrow KFe_3(SO_4)_2(OH)_6 + 6H^+$	$pK_s = 9.21^2$
(12) H-Jarosite	$3Fe^{3+} + 2SO_4^{2-} + 6H_2O \Leftrightarrow HFe_3(SO_4)_2(OH)_6 + 5H^+$	$pK_s = 5.39^4$
(13) Schwertmannite	$Fe_8O_8(OH)_x(SO_4)_y + (24-2y)H^+ \Leftrightarrow 8Fe^{3+} + ySO_4^{2-} + (24-2y+x)/H_2O$	$pK_s = -18$ $\pm 2.5^1$; 10.5 $\pm 2.5^3$
(14) Goethite	$FeOOH + 3H^+ \Leftrightarrow Fe^{3+} + 2H_2O$	$pK_s = -1.4^1$
(15) Melanterite	$Fe^{2+} + SO_4^{2-} + 7H_2O \Leftrightarrow FeSO_4 * 7H_2O$	$pK_s = 2.46^6$
(16) Gibbsite	$Al^{3+} + 3H_2O \Leftrightarrow Al(OH)_3(s) + 3H^+$	$pK_s = -8.04$
(17) Siderite	$Fe^{2+} + CO_2(g) + H_2O \Leftrightarrow FeCO_3 + 2H^+$	$pK_s = -10.45$
(18) Rhodotrosite	$Mn^{2+} + CO_2(g) + H_2O \Leftrightarrow MnCO_3 + 2H^+$	
(19) Gypsum	$Ca^{2+} + SO_4^{2-} + 2H_2O \Leftrightarrow CaSO_4 * 2H_2O$	$pK_s = 4.58^2$

III Mineral transformation		
(20) Schwertmannite[8]–goethite	$Fe_8O_8(OH)_{5.5}(SO_4)_{1.25}(s) + 2.5H_2O \Leftrightarrow 8FeOOH(s) + 2.5H^+ + 1.25SO_4^{2-}$	

Processes involved in consumption of acidity

I Heterogeneous reactions — dissolution	
(21) Calcite	$6.4 < pH < 10.4 : CaCO_3 + H^+ \Leftrightarrow Ca^{2+} + HCO_3^-$
(22) Calcite	$pH < 6.4 : CaCO_3 + 2H^+ \Leftrightarrow Ca^{2+} + CO_2(g)$
(23) Dolomite	$6.4 < pH < 10.4 : MgCa(CO_3)_2 + 2H^+ \Leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$
(24) Dolomite	$6.4 < pH < 6.4 : MgCa(CO_3)_2 + 4H^+ \Leftrightarrow Ca^{2+} + Mg^{2+} + 2CO_2(g) + 2H_2O$
(25) Biotite	$K(Mg, Fe(II))_3 AlSi_3O_{10}(OH)_2(s) + 7H^+ \Leftrightarrow K^+ + 3(Mg^{2+}, Fe^{2+}) + Al(OH)_3(s) + 3SiO_2(s) + 3H_2O$
(26) Plagioclase	$Na_{0.7}Ca_{0.3}Al_{1.3}Si_{2.7}O_8(s) + 1.3H^+ + 1.3H_2O \Leftrightarrow 0.3Ca^{2+} + 0.7Na^+ + 1.3Al(OH)_3(s) + 2.7SiO_2(s) + 3H_2O$
(27) Orthoclase	$K(Fe(II)_{1.5}Mg_{1.5})AlSi_3O_{10}OH_2(s) + 7H^+ + 3.75H_2O + 0.375O_2(aq) \Leftrightarrow K^+ + 1.5Mg^{2+} + Al^{3+} + 3H_4SiO_4 + 1.5Fe(OH)_3(s)$

II Cation exchange	
(28) Iron	$Ca–X(s) + Fe^{2+} \Leftrightarrow Fe–X + Ca^{2+}$
(29) Protons	$Ca–X(s) + H^+ \Leftrightarrow H–X + Ca^{2+}$

Table 1 (*continued*)

Processes involved in acidity generation

III Redox/precipitation reactions

(30) Pyrrhotite formation　　$2.25 < CH_2O > +FeOOH + SO_4^{2-} + 2H^+ \Rightarrow FeS + 2.25CO_2 + 3.75H_2O$

(31) Sulfur formation　　$1.5 < CH_2O > +SO_4^{2-} + 2H^+ \Rightarrow S\!\!/\!\!\int + 1.5CO_2 + 2.5H_2O$

(32) Pyrite formation　　$3.75 < CH_2O > +FeOOH + 2SO_4^{2-} + 4H^+ \Rightarrow FeS_2 + 3.75CO_2 + 6.25H_2O$

(33) Sulfate reduction　　$SO_4^{2-} + 2 < CH_2O > +2H^+ \Rightarrow H_2S + 2CO_2 + 2H_2O$

(34) Iron reduction　　$Fe(OH)_3 + 1/4 < CH_2O > +2H^+ \Rightarrow Fe^{2+} + 1/4CO_2 + 11/4H_2O$

Source: [1]Bigham et al. (1996b); [2]Parkhurst (1995); [3]Yu et al. (1999); [4]Ball and Nordstrom (1991); [5]Nordstrom (1982); [6]Lindsay (1979); [8]example composition.

of magnitude along a transect from unsaturated to submersed tailings (Elberling et al., 2003). Seasonal differences in acid mine drainage fluxes related to changes in water contents of the unsaturated zone of lignite mine dumps have also been reported (Knappe et al., 2004). Collated results suggest that in mine tailings and dumps containing <5% pyrite, initially ≥10 mol S m^{-2} yr^{-1} are released and that rates decrease to 1– 10 mol S m^{-2} yr^{-1} after several decades (Table 2). In unsaturated and pyrite rich tailing deposits, rates may, in contrast, reach hundreds of moles of S per m^{-2} yr^{-1} (Table 2).

3.2. Secondary geochemical and biogeochemical processes

The chemical composition of groundwater polluted by AMD is further affected by "secondary" processes along the flow path (Fig. 1). These processes encompass homogenous chemical reactions close to thermodynamic equilibrium (complexation), heterogeneous chemical reactions being often in disequilibrium (mineral precipitation and dissolution), and microbially mediated redox processes (Alpers and Nordstrom, 1999).

3.2.1. Complexation

The role of homogeneous complexation reactions in acid mine drainage is tractable to chemical equilibrium modeling (reviewed in Nordstrom, 2000; Nordstrom and Alpers, 1999). The reactions are kinetically fast, and speciation adjusts rapidly to changes in geochemical forcing. Complexation of metal cations changes both transport characteristics and precipitation behaviour of metals and ligands, and potentially also alters pH, because many complexes possess acid–base properties. In AMD polluted groundwater, concentrations of ferrous iron and sulfate are often in the range of tens of millimoles in dumps of coal deposits, and even higher in tailings associated with ore deposits. As a consequence, a substantial part of the dissolved iron and aluminum is present as sulfate complexes, particularly when the pH is acidic (Alpers and Nordstrom, 1999).

Complexation of ions at reactive surfaces also occurs in dump and tailing materials and provides a mechanism

Table 2

Examples of iron sulfide oxidation rates in mine tailings and dumps

Rate (mol S m^{-2} yr^{-1})	Deposit	Saturation	FeS/FeS$_2$ content (%)	Age	Source
1040	Ore tailing	No	40–85	'Fresh'	(1)
440	Ore tailing	No	40–85	'Old'	(1)
250–350	Ore tailing	No	26	–	(2)
43	Coal dump	No	<1%	–	(3)
25	Coal dump	No	<1%	6	(4)
12.8–14.6	Ore tailing	Yes	40–85	'Fresh'–'old'	(1)
10	Coal dump	No	<1%	19	(4)
1.9–4.9	Coal dump	No	<1%	43 (av.)	(5)
2	Coal dump	No	<1%	50	(4)
1	Coal dump	No	<1%	27	(4)
0.43	Ore tailing	No	<5%	50	(6)

(1) Elberling and Damgaard (2001); (2) Yanful et al. (1999); (3) Wilden et al. (2001); (4) Schaaf (2001); (5) Rolland et al., 2001; (6) recalculated after Ljungberg and Öhlander, 2001.

for the retention of acidity (Balkenhol et al., 2001; Hoth et al., 2001; Ludwig et al., 2001; Strömberg and Banwart, 1999). Instructive in this respect is, for instance, the column experiment by Ludwig et al. (2001) using weakly pyritic (0.5% weight), kaolinite-(45% weight) and illite-(43% weight) rich dump materials. Over a 2-year period, natural precipitation rates were applied to the columns. A total of 94 mmol H^+ kg^{-1} were released. Surface complexation and ion exchange buffered 20 mmol H^+ kg^{-1}, whereas only 3.6 mmol H^+ kg^{-1} were buffered by Al release due to silicate weathering.

3.2.2. Weathering

The dissolution of carbonates and silicates changes the chemical composition of groundwater by consuming protons and releasing metal cations, in particular Ca^{2+}, Mg^{2+}, K^+, and Al^{3+}. A number of carbonate minerals might contribute to the neutralization of acidity. Calcite, dolomite, and magnesite ($MgCO_3$) have the highest neutralization potential, followed by carbonates that contain various amounts of oxidizable cations, such as ankerite (e.g. $Ca_{0.5}Fe(x...y)Mg(y...x)CO_3$), and magnesian siderite ($Fe(x...y)Mg(y...x)CO_3$; Paktunc, 1999). Dissolution of iron carbonates is acidity neutral in terms of the given definition because protons are exchanged for ferrous iron. The neutralization potential of silicates varies according to their stoichiometric composition and the products of silicate dissolution, because secondary clay minerals, such as montmorillonite and kaolinite, may form (Sherlock et al., 1995). Most protons per formula unit of the mineral can be buffered in case of congruent, i.e. complete, dissolution. Carbonate and silicate weathering further differ with respect to characteristic pH values that develop in the buffered waters. Values of pH attained by silicate weathering are generally lower because the process releases dissolved Fe^{3+}, Mn^{2+}, and Al^{3+}. The dissolved metals contribute to acidity and proton load by re-precipitation as hydroxides (Hammarstrom et al., 2005; Totsche et al., 2004) and by deprotonation of aquocomplexes in the pH range of 2–5 (e.g. Stumm and Morgan, 1996, p. 273).

Weathering rates are controlled by a number of factors. Surface-normalized dissolution rates of carbonates are directly controlled by pH (Lund et al., 1973; Plummer and Busenberg, 1982), which is reflected in first-order kinetic laws of carbonate dissolution that have been established (Eq. (35), Appendix). A raise in pH from 0 to 5 decreased the dissolution rate by about 4 orders of magnitude (Gautelier et al., 1999). Temperature changes had smaller and concentrations of Ca^{2+} and Mg^{2+} little to no effect on the dissolution rate. A strong

pH dependency of silicate dissolution was also demonstrated (White and Brantley, 1995, and references therein). Particle size, i.e. mineral surface area, further controls metal sulfide, carbonate, and silicate dissolution rates (Strömberg and Banwart, 1999). In the authors' study more than 80% of the sulfide and silicate dissolution was contributed by particles with diameters <0.25 mm.

Dissolution rates of pyrite, carbonate minerals, and silicates further differ under standardized conditions, when normalized to mineral surface area. At pH 5 and 25 °C, pyrite oxidation rates were determined as about 10^{-9} mol m^{-2} s^{-1} (Williamson and Rimstidt, 1994, and references therein), whereas calcite and dolomite dissolution rates were found to be about three order of magnitude faster (10^{-5}–10^{-6} mol m^{-2} s^{-1}; Chou et al., 1989; Gautelier et al., 1999). Dissolution rates of various silicates were 2–3 orders of magnitude slower than pyrite oxidation rates (10^{-12}–10^{-13} mol m^{-2} s^{-1}; Sverdrup, 1990; White and Brantley, 1995, and references therein). Similar differences between pyrite and silicate weathering rates were also found using tailing materials in batch, column, and field investigations (Malmström et al., 2000).

If similar surface areas of these minerals are present, water discharging from a pyrite oxidation front may thus attain a near-neutral pH in the presence of carbonates, and otherwise acidify. Differently stated, much longer residence times and flow distances are required for effective buffering of protons in carbonate-free aquifer materials. This simple concept is adequate for a qualitative prediction of groundwater pH in many cases. Circumneutral pH values have been reported from carbonate rich dumps, tailings, and aquifers in ore and coal mining areas (e.g. Elberling and Damgaard, 2001; Hoth et al., 2001; Mayo et al., 1992, 2000; Rolland et al., 2001; Wirries and McDonnell, 1983). In the absence of carbonates, pH values in dump and tailings were lower and more variable. Values of pH typically ranged from 3.5 to 5.5 in the water saturated dumps of lignite mines devoid of carbonates (Bozau and Strauch, 2002; Werner et al., 2001) and values of 0.8 and 2.4 were determined in incubation and column studies (Balkenhol et al., 2001; Ludwig et al., 2001; Seoane and Leiros, 1997). If carbonate contents are low, such predictions are likely unsuccessful, though. A wide span of pH values (3.8–7.4) was, for instance, determined in water saturated coal mining dumps that were characterized by low carbonate (0.01 wt.%) and variable pyrite contents (Wisotzky and Obermann, 2001).

While laboratory studies have been useful to interpret geochemical patterns in field investigations, the

appropriate application and extrapolation of laboratory derived knowledge remains a somewhat open question. In laboratory based batch or column studies weathering rates were much larger than *in situ* (Malmström et al., 2000; Salmon and Malmström, 2004). The extrapolation of laboratory studies is, therefore, very likely inaccurate. In some cases, a correction of rates can be accomplished using scaling factors that account for factors such as temperature, pH, mineral content, hydrological flow paths, and particle size distribution (Malmström et al., 2000). Eq. (36) (Appendix), provides an example how batch-scale chemical reaction rates can be extrapolated to column- or field-scale conditions. However, such an approach is limited by the spatial and mineralogical heterogeneity of acidity sources and sinks in the field. The modeling study by Salmon and Malmström (2004) showed that scaling approaches may not be successful. Rates in the field were still systematically and consistently overestimated by extrapolation of batch-scale experiments, even if corrected by Eq. (36), (Appendix).

3.2.3. Precipitation

The precipitation and mineralogy of secondary minerals has been reviewed in great detail (e.g. Alpers and Nordstrom, 1999; Cornell and Schwertmann, 1996; Hammarstrom et al., 2005) and is only briefly summarized. With respect to the acidity balance of mine lakes, the formation of secondary minerals in groundwater is important since these processes sequester metals and sulfate. They also change the ratio of protons to metals in the acidity that is discharged (Hammarstrom et al., 2005; Table 1), and potentially reduce the trace metal load by co-precipitation with ferric iron hydroxides (e.g. Davis, 2003). In comparison to the dissolution of minerals, precipitation is on average kinetically faster and often attains a thermodynamic equilibrium with respect to particular phases (Nordstrom and Alpers, 1999).

In terms of acidity balances, a number of different cases have to be distinguished. Precipitation of ferrous iron or aluminum with the anion of a strong acid, such as H_2SO_4, for example as the mineral melanterite ($FeSO_4 \cdot 7H_2O$) or halotrichite ($Fe(Al_2(SO_4)_4 \cdot 22H_2O)$), decreases the acidity load in the pH range of 2.5 to 3.5 (Table 1, Eq. (15)). Since these precipitates are quite soluble, they are likely to precipitate only in heavily AMD polluted aquifers (Blowes et al., 1991), and otherwise occur as a product of evaporation of acid mine solutions (Nordstrom and Alpers, 1999). Precipitation of ferrous iron or aluminum with anions of weak acids is acidity-neutral under acidic conditions because the

anion is present in its protonated form. If carbonates precipitate for instance, >90% of the carbonate is present as carbonic acid and dissolved CO_2 at pH values below 5.4. Ferrous iron is thus almost quantitatively exchanged for two protons. Precipitation of oxidized metal species as hydroxides or hydroxysulfates, e.g. as ferrihydrite or schwertmannite, does not change the acidity concentration according to the definition presented, but also results in a proton gain of the discharging water (Table 1, Eqs. (8), (13)). Noteworthy is also the precipitation of gypsum ($CaSO_4 \cdot 2H_2O$, Table 1, Eq. (19). Gypsum frequently precipitates in coal mine dumps and dump materials (Ludwig et al., 2001; Wisotzky and Obermann, 2001), in ore tailings (Blowes and Jambor, 1990), and also in discharging surface waters of ore deposits (Hammarstrom et al., 2005). Although less important in terms of the acidity balance of mine lakes – the balance is only altered if pH values are very low and close to the acidity constant of HSO_4^- ($pK_s = 1.9$) – gypsum precipitation is important for limiting the mineralization of mine waters and the sulfate export, which may entail significant environmental problems downstream.

3.2.4. Reductive processes

Mine tailing and dump aquifers may contain organic electron donors stemming from soil percolates, soil organic matter, coal, and bituminous materials associated with the geologic parent material. With the exception of oxic respiration, the utilization of these electron donors consumes protons (e.g. Table 1, Eqs. (33), (34)). Iron reduction further releases ferrous iron, which entails geochemical consequences downstream. Sulfate reduction reverses pyrite oxidation if iron sulfides are formed, and diagenetically transformed to pyrite. The speciation of precipitating sulfide and the redox state of the endproduct further influence the net effect on acidity and proton balances and need to be considered (see definition, and Eqs. (30)–(32)).

Iron reducing bacteria (IRB) seem comparatively insensitive to pH (Johnson, 1995; Küsel, 2003), but sulfate reducing bacteria (SRB) may be limited by low pH and low availability of electron donors in AMD polluted aquifers. Investigations documented low most probable number concentrations (<102 MPN g^{-1}) of SRB and low sulfate reducing activity in the acidic zones of tailing and dump aquifers (Benner et al., 2000; Fortin et al., 1996; Knöller et al., 2004). In reactive barriers, in which electron donors are abundant and pH values are elevated, high MPN numbers of up to 10^8 MPN g^{-1} were determined (Benner et al., 2000). MPN counts of SRB and carbon contents of the tailing

materials were also positively correlated (Benner et al., 2000). Amending coal dump and ore mine tailing materials with organic substrates furthermore increased sulfate reduction rates in batch experiments (Wisotzky, 1998; Karnachuk et al., 2005).

Despite such constraints on sulfate reduction, a number of studies suggested that this process may effectively remove acidity from AMD polluted aquifers by natural attenuation, when the limitation by pH is eased. Knöller et al. (2004) combined concentration measurements and ^{34}S and ^{18}O isotope analyses along the flow path of highly mineralized, but only moderately acidic (pH 5.2), dump waters into an aquifer. Within a flow distance of a few hundred meters, sulfate concentrations in the aquifer decreased from 860 to 40 mg L^{-1}, δ^{34}S values of sulfate in the pore water increased from −11‰ to 23‰, and δ^{18}O values increased from about 0‰ to 12‰. The isotopic shifts indicated that sulfate reduction was at least partly responsible for the sulfate removal from the groundwater. Sulfate reducing activity was also reported from other near-neutral and water saturated lignite dumps using this approach and corroborated by enumeration of sulfate reducing bacteria (Hoth et al., 2005). Increase in groundwater pH>4 coincided with increases in SRB counts to $5 \cdot 10^4$–10^6 MPN g^{-1}. Similar results were reported from shallow layers (0–50 cm depth) of Cu–Zn ore mine tailings in Canada. Fortin and Beveridge (1997) and Fortin et al. (2002) documented substantial quantities of SRB ($<10^3$–10^6 MPN g^{-1}) reaching a maximum in reduced, pH-neutral layers. The presence of SRB was further related to the occurrence of iron sulfides and sulfate consumption. Recently, in such tailing materials very high rates of sulfate reduction (100–1000 nmol cm^{-3} d^{-1}) were determined using ^{35}S radiotracer techniques (Praharaj and Fortin, 2004).

The nature and origin of the electron donor sources supporting this activity is of considerable interest but has hardly been investigated. Fortin et al. (2002) suggested that bacterial biomass fixed by lithotrophic iron and sulfur oxidizing activity at the oxidation front was recycled in the reduced zone below. Utilization of geogenic organic matter may further provide a carbon and energy source, particularly when weakly coalified lignite is present. Lignite mostly consists of hydrophobic bitumen, insoluble humins, and humic and fulvic acids (Fakoussa and Hofrichter, 1999). The latter chemical moieties are accessible to unspecific exoenzymatic attack by lignin peroxidases, manganese peroxidases, laccases, and hydrolases, which produce more accessible and reactive monomers, and which are partly fairly stable against degradation (Hofrichter and

Fritsche, 1997; Fakoussa and Hofrichter, 1999). The enzymes are commonly produced by lignin degrading fungi and partly also by higher plants (Fakoussa and Hofrichter, 1999).

In agreement with the possibility of *in situ* lignite degradation, Hoth et al. (2005) reported mineralization of tertiary geogenic carbon in lignite mine dumps based on ^{14}C dating of CO_2 produced *in situ*. Several investigations further suggested a mineralization of geogenic carbon in the unsaturated zone of other coal mine dumps in the coal fields of Eastern Germany, where geogenic carbon contents of 0.5–5% commonly occur (Waschkies and Hüttl, 1999). Carbon mineralization rates typically ranged from 20 to 400 μg CO_2–C g^{-1} d^{-1} at 20 °C to 25 °C in incubation experiments (Waschkies and Hüttl, 1999; Rumpel and Kögel-Knabner, 2002), translating into volume based rates of about 50 to 1000 nmol cm^{-3} d^{-1} (assuming a carbon content of 3% (weight) and a bulk density of 1 g cm^{-3}). It can be speculated that geogenic organic matter also supports iron and sulfate reduction in the saturated zone of mine dumps and aquifers. The low efficiency of anaerobic carbon mineralization has to be considered, though, and transport of exoenzymes with seepage water into the saturated zone may be required.

In conclusion, little is yet known about the spatial distribution of reductive processes within mining landscapes and with regard to the electron donor sources supporting anaerobic activity in the subsurface. To understand natural attenuation of acidity by reductive processes, studies are needed that quantify iron and sulfate reduction rates and their environmental, geochemical and biochemical controls within the subsurface of polluted watersheds.

3.3. Hydrologic processes

Water and gas fluxes locally sustain the chemical disequilibrium that drives geochemical and biogeochemical processes in the subsurface of mine lake watersheds. On the watershed scale, water flow further constrains the acidity loading to surface waters and plays a most crucial role in the acidification process. To mention are groundwater–surface interactions, the heterogeneity of fluxes in space and time, surface runoff and erosion, and evaporation from surface waters.

Groundwater–surface water interactions, mostly seepage of groundwater into surface waters, generally occurs along lakeshores situated in unconsolidated deposits (Sebestyen and Schneider, 2004, and references therein). Rates of inflow ranged from −14.6 to 14.7 L m^{-2} d^{-1} in these studies. This is a similar range as

reported from a variety of coal mine lakes after rebound of the local groundwater surface had occurred (Knoll et al., 1999; Werner et al., 2001; Bozau and Strauch, 2002). Apart from direct acidity loading, inflow rates of this magnitude may substantially alter sediment pore water chemistry, lead to the mobilization of iron and sulphur from sediments, and reinforce acidification (Blodau, 2004, 2005; Knorr and Blodau, 2006). Any generalization regarding groundwater–surface water interactions is, however, difficult owing to the uncertainty about the hydrogeologic properties of aquifers in mining areas (Younger and Robins, 2002a,b).

Relevant with respect to acidity loading is the spatial differentiation of groundwater inflow. Lake 77, a small shallow lake located in the Plessa watershed in Lusatia, Germany (Fig. 2), for example, received an estimated <2 L m^{-2} d^{-1} in the lake center, whereas close to mine dumps inflow rates were estimated at >10 L m^{-2} d^{-1} (Weber, 2000). High inflow rates and ferrous iron concentrations lead to an estimated acidity loading on the order of 20–30 mol m^{-2} yr^{-1} in the affected lake area (Blodau, 2005). Similar patterns, flow rates, and spatial variability have been found in other coal mine lakes, including seepage from lakes into aquifers (Bozau
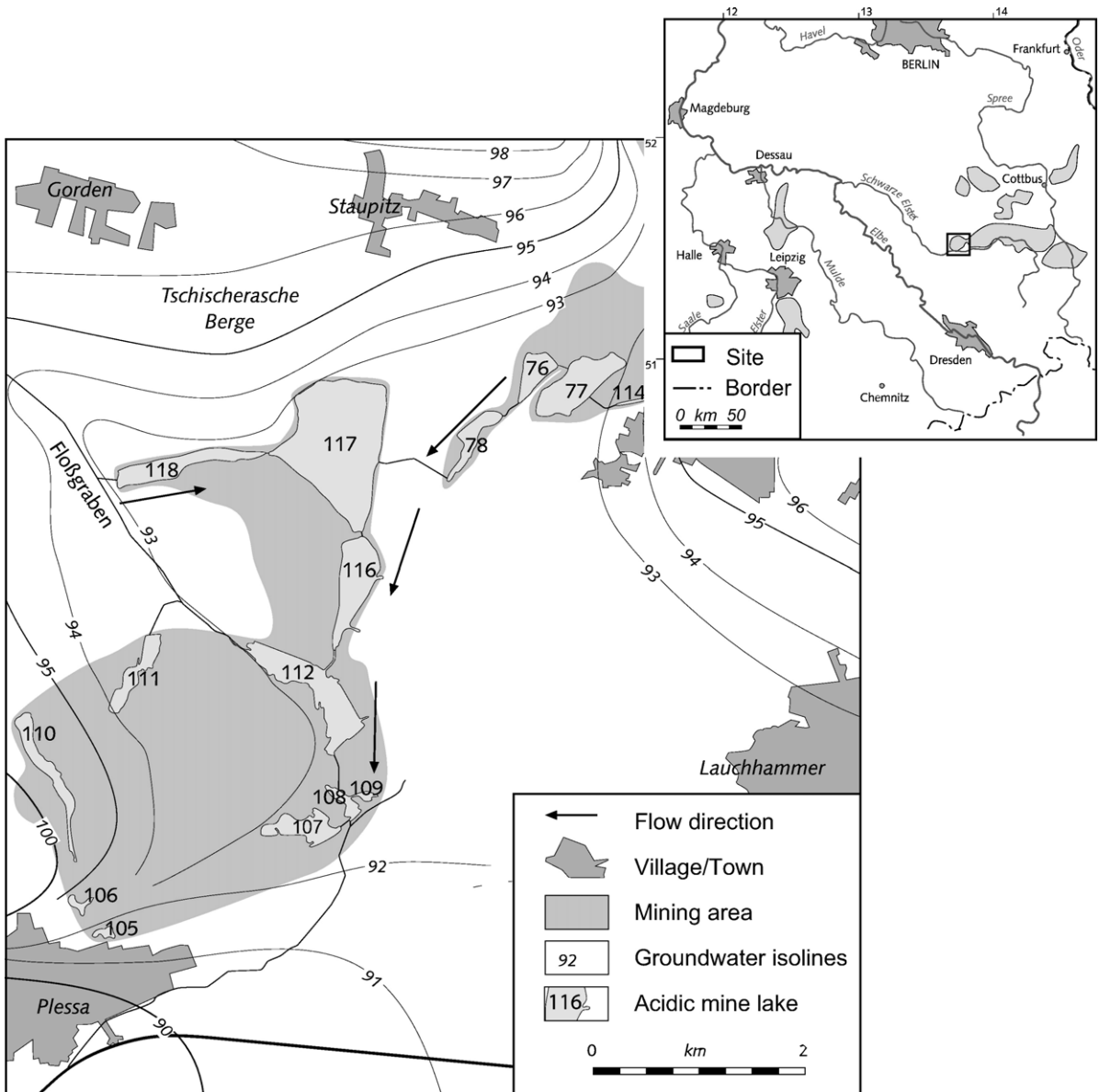

Fig. 2. Map of the Plessa watershed in Lusatia, Germany. (after Peine, 1998; modified).

and Strauch, 2002; Werner et al., 2001). Also in streams polluted by AMD, subsurface inflow was found to be an important local source of the overall metal load (e.g. Kimball et al., 2002). To be considered is also the temporal variation of groundwater inflow that occurs in lakes among seasons and years (Kenoyer and Anderson, 1989; Sebestyen and Schneider, 2004). Such temporal variation is exacerbated in mining landscapes, where groundwater flow reversal may occur with changes in mining operations and groundwater management, as has been pointed out by Werner et al. (2001).

The Plessa watershed illustrates some hydrologic characteristics that affect acidity flow on the watershed scale (Bozau and Strauch, 2002; Heidenreich et al., 1999; Knoll et al., 1999; Knöller and Strauch, 2002; Rolland et al., 2001). As a result of strip mining, lakes were arranged as chains within the watershed (Fig. 2). The water and acidity balances of these lakes varies considerably and systematically along the flow path (Bozau and Strauch, 2002; Knoll et al., 1999; Knöller et al., 2004; Weber, 2000). Headwater lakes located downgradient of mine dumps, such as Lakes 77 and 111, are heavily polluted by AMD and receive most of their water (>50%) from dump aquifers. Within a few kilometres distance downstream, the groundwater contribution to the lakes diminishes and water residence time decreases. In Lake 116, for instance, which is located 4 lakes downstream from Lake 77 (Fig. 2), only an estimated 2.5% of the total water input was contributed by surrounding dump aquifers and <1% from the remaining aquifer (Weber, 2000).

The headwater lakes thus receive acidity with a high iron to proton ratio and larger iron deposits developed on the lake ground, as a comparison between Lakes 77 and 116 illustrates (Table 3). A similar situation was found between upstream Ausee and downstream Murnersee along the Rauberweiher lake chain in northern Bavaria (Table 3, Peine and Peiffer, 1996, 1998). Downstream, the proton load increased relative to the iron load, as the lakes were dominated by the input of surface waters poor in iron. Such differences in the composition of the supplied acidity will likely have consequences for in-lake acidity sinks and sources but systematic investigations of this issue are lacking to date.

In semi-arid or arid regions, such as the southwestern part of the U.S.A., evapoconcentration has been identified as a process leading to continued salinization and acidification (Shevenell et al., 1999). Surface runoff from mine dumps and tailings and wave action can lead to acidity loading as well (Abel et al., 2000; Werner et al., 2001). At a mine lake located in central Germany, Lake Cospuden, Abel et al. (2000) estimated erosion of up to 90 kg yr^{-1} m^{-2}, causing a total acidity load of 500 keq yr^{-1} to the lake. Surface erosion is facilitated by the frequent hydrophobicity and lack of vegetation on mine dump and tailing surfaces, which promotes surface runoff and gully erosion (Biemelt et al., 2005).

3.4. Occurrence and longevity of acidity generation and acid mine drainage

The occurrence and longevity of AMD in watersheds has been analyzed based on chemistry of discharging water over time in sites, areas, and regions (Koryak et al., 2004; Younger, 1992, 1997), based on geochemical data obtained during the operation of mines (Morin, 2001), and based on the mineral life-time concept (Banwart and Malmström, 2001). AMD dynamics within tailings and aquifers has also been analyzed

Table 3
Iron fluxes, TRIS formation rates and pore water pH in acidic mine lake sediments

Site	pH	Iron (III) sedimentation/long-term deposition	Iron (III) transformation reactive-crystalline	Fe^{2+} fluxes	Fe (III) reduction	TRIS formation
77 (S)[1]	3–3.5	5.5/7.7	5.6	0.97	2.4	0.0047
77 (N)[1]	5–6.5	5.9/5.3	0.27	17.4	1.5	0.035
77 centre[3]	3–6.5	10.3/3.5	1.9	0.7–3.0	2.5	0.011
116[2,5]	>6 4.9	3.9	0.55	1.8	1.8	0.38
76[2,6]	4–7	1.6	0.54	0.61		0.050
Ausee[5,7]	3–3.5	2.0	1.4	0.14		0.0019
Murnersee	>6	0.67[8]	0.48[8]	0.95[6]		0.047[7]

All fluxes are given in mol m^{-2} yr^{-1}. For the iron (III) transformation fluxes it has been assumed that reactive iron was initially deposited. This has only been verified for Lake 77 and Ausee. Schwertmannite is generally assumed to be contained in the reactive iron fraction (24 h extraction with 1 M HCl), goethite in the crystalline fraction (Peine et al., 2000).
[1]This study, [2]Blodau and Peiffer (2003) [3]Peine et al. (2000); [4]Blodau et al. (2000); [5]Blodau et al. (1998); [6]Blodau, unpublished; [7]Peine and Peiffer (1996); [8]Röckman, unpublished.

using reactive transport modelling (Bain et al., 2000; Gerke et al., 1998; Hoth et al., 2001).

Among these approaches, the mineral-life time concept is least demanding regarding data input. The current rates of pyrite, carbonate, and silicate weathering in a deposit can be estimated from the chemical composition of discharging water according to Eqs. (37)–(39), (Appendix), as Banwart and Malmström (2001) pointed out. The flow of a solute is assigned to a particular process with a known stoichiometry and used as tracer for this process. For meaningful application, the water residence time must be short in comparison to the time scale of processes and solutes must not accumulate within the deposit. The life time of a particular mineral can then be estimated based on the current flow rate of the tracer ((38), Appendix) and the available reservoir ((39), Appendix). As the time dependence of rates is not accounted for, more accurate estimates require the consideration of a rate limiting step, such as inner-particle oxygen transfer, or surface reaction limitations, and its implementation in reactive transport models (Bain et al., 2000; Wunderly et al., 1996). For a detailed review of geochemical and reactive transport modeling the reader may consult Alpers and Nordstrom (1999).

Based on the application of the outlined approaches, pyrite reservoirs may persist from decades to many centuries in surface deposits (Banwart and Malmström, 2001; Blowes and Jambor, 1990; Rolland et al., 2001). Similar life times were obtained for underground coal mines (Younger, 1997). In these mines, a pulse of ferrous iron and sulfate was typically released within the first 10 to 40 years after closure and flooding. Subsequently, "juvenile" acidity may be generated over centuries until sulfide stocks are depleted.

4. Acidity generation and consumption in acidic mine lakes

The change of water chemistry along a generalized flow path within watersheds impacted by mining is illustrated by a collation of studies covering the chemical composition of dump aquifers, AMD point sources, and affected creeks and lakes (Fig. 4). The chemical composition strongly varies between individual waters, but geochemical trends are visible. Iron concentrations decreased from an average of 7.5 mmol L^{-1} in AMD polluted aquifers to <2 mmol L^{-1} in point sources and creeks, and to <1 mmol L^{-1} in lakes. The pH decreased by about 2 units comparing dump aquifers and surface waters. In Fig. 4, sulfate concentrations may be taken as a proxy for mineralization by pyrite

oxidation, using the rough approximation that sulfate behaves mostly conservative (Bencala et al., 1987). This is, of course, not a strictly valid assumption in view of secondary sulphate mineral precipitation, sulfate reduction, and sulphate adsorption.

Much of this change in water chemistry can be attributed to dilution by unpolluted waters and precipitation of iron hydroxides in the oxic surface waters. Once ferrous iron has entered oxygen rich surface waters, it is oxidized chemically (Singer and Stumm, 1970), or microbially (Noike et al., 1983), and mostly precipitates in its ferric form (Table 1, Eqs. (8), (11)–(14); Peine et al., 2000; Regenspurg et al., 2004). The chemical composition of mine lakes is furthermore influenced by a combination of redox-, precipitation and transformation processes of iron and sulfur in the sediments (Fig. 3), which are also reviewed.

4.1. Processes in surface waters

4.1.1. Ferrous iron oxidation

In running waters, ferrous iron oxidation is often only completed over some distance downstream from point sources, allowing for estimates of *in situ* oxidation rates (Fillipek et al., 1987; Herlihy et al., 1990; Hudson-Edwards et al., 1997). Related studies documented iron oxidation rates ranging from 0.03 mol L^{-1} yr^{-1} to 350 mol L^{-1} yr^{-1}, with initial ferrous iron concentrations being 3.9 to 10 mmol L^{-1} (Foos, 1997; Kirby and Elder Brady, 1998; Noike et al., 1983). Downstream of point sources, iron is thus typically oxidized at similar or higher rates than in mine tailings and dumps (Table 2).

Much lower iron oxidation rates (0.003 mol L^{-1} yr^{-1}, recalculated after Peine, 1998) were estimated in acidic mine lakes (Peine et al., 2000; Regenspurg et al., 2004). Across a total of 18 lakes, ferrous iron concentrations were further, with one exception, <0.1 mmol L^{-1} in epilimnic waters (Herzsprung et al., 1998; Regenspurg et al., 2004). Concentrations were thus at least 1–2 orders of magnitude lower than in the inflowing ferrous iron rich groundwater (Fig. 4). Iron oxidation in larger water bodies may thus be limited by the supply of ferrous iron from the watershed. An exception might be periods of mixing during autumn and spring, when ferrous iron and oxygen rich waters mix (Herzsprung et al., 1998).

The factors influencing ferrous iron oxidation rates have been addressed in laboratory (e.g. Pesic et al., 1989; Singer and Stumm, 1970; Sung and Morgan, 1980; Theis and Singer, 1974) and field studies (Barry et al., 1994; Davison and Seed, 1983; Kirby and Elder
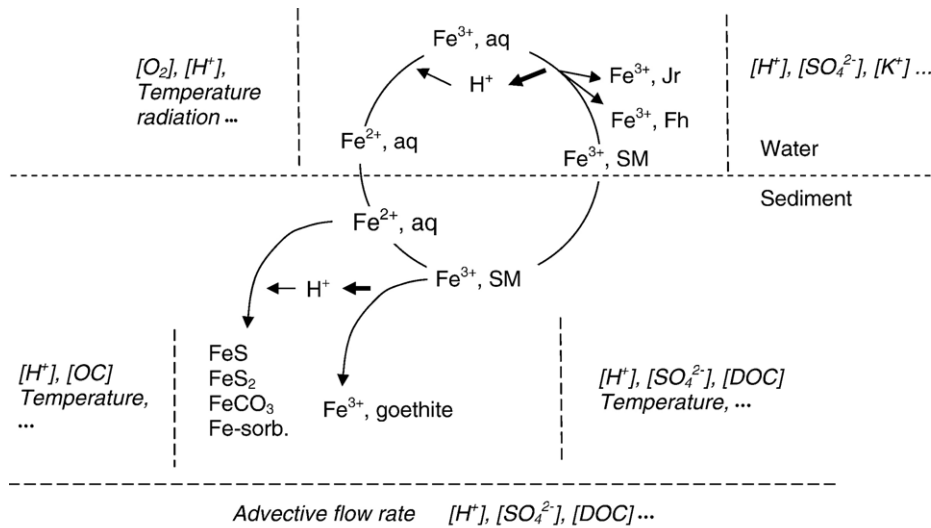
Fig. 3. Schematic of iron cycling at the sediment–water boundary of acidic mine lakes. Controls on iron cycling and proton production and consumption are shown in italics. For further description see text.

Brady, 1998; Noike et al., 1983). According to these studies, chemical and microbially mediated oxidation rates are a function of pH, partial pressure of oxygen, and ferrous iron concentrations. A combined rate law (Eq. (40), Appendix) adequately described the oxidation process across a variety of shallow ponds used as acid mine drainage treatment sites (Kirby et al., 1999).
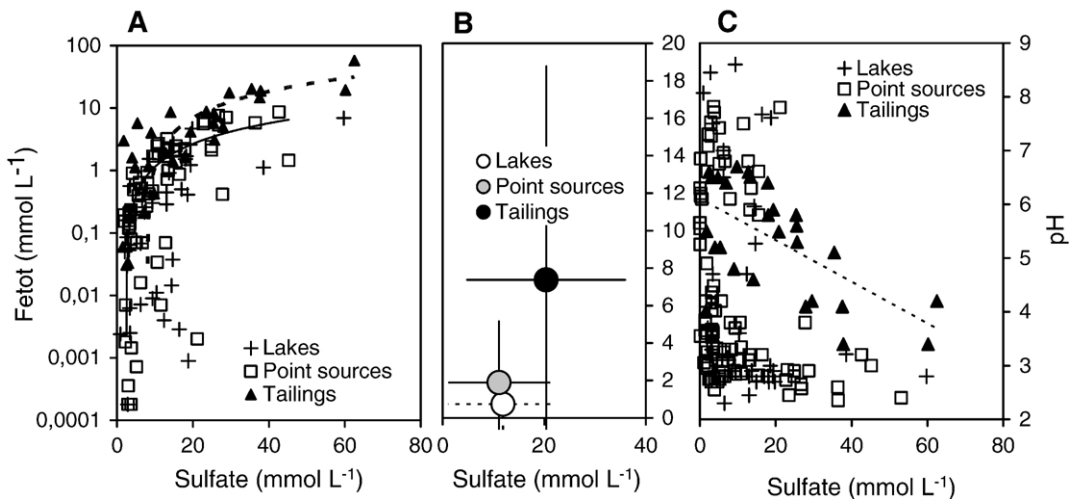

Fig. 4. Total dissolved iron (A, B) and pH (C) vs. sulfate concentrations in mining lakes, point sources, and tailings, dumps, and aquifers (labelled 'tailings') of mining environments. Panel B shows median and standard deviations for the data presented in panel A. Iron and sulfate concentrations are related by

Groundwater: $[Fe] = 0.57 \times [SO_4^{2-}] - 4.6$ R^2: 0.62
Point sources: $[Fe] = 0.15 \times [SO_4^{2-}] - 0.4$ R^2: 0.56
Lakes: $[Fe] = 0.09 \times [SO_4^{2-}] - 0.4$ R^2: 0.57
The figure thus illustrates the elimination of iron along a "generalized" flow path in watersheds. In panel C, the regression line between groundwater and sulfate concentrations shows the decrease in pH with sulfate concentrations, i.e. stronger pollution by pyrite oxidation. Data were taken from Bigham et al. (1996b), Blodau (2004), Bozau and Strauch (2002), Cairney and Frost (1975), Hoth et al. (2001), Miller et al. (1996), Nixdorf and Kapfer (1998), Nixdorf et al. (1998), Regenspurg et al. (2004), Rolland et al. (2001), Werner et al. (2001), Wisotzky (1998), Yu et al. (1999).

As can also be seen from Eq. (40), Appendix), the two oxidation mechanisms differ with respect to their dependency on proton concentrations. Chemical oxidation rates decrease, as the pH is lowered from 7 to 4.5, and remain constant below pH 4.5. In contrast, microbial oxidation rates linearly increased with proton concentrations at pH values of 2.2 to 3 (Pesic et al., 1989). The rate was independent of H^+ concentrations only below a pH of 2.2. This difference in pH dependency has two consequences. First, microbially mediated oxidation may be orders of magnitude faster than chemical oxidation at pH of 2–4, whereas above pH 5 the chemical oxidation mechanism should prevail (Kirby et al., 1999). Second, overall oxidation rates should be at a minimum at intermediate pH values of about 4.5 to 5.5. Kirby and Elder Brady (1998) found this prediction in rough agreement with a collation of field data.

The importance of microbial mediation for iron oxidation in surface waters has been confirmed by several studies. The half-live of ferrous iron in streams may be as short as 160 min at pH 3.8 (McKnight et al., 1988), although chemical iron oxidation is slow at pH < 5 with a half life of about 200 days (Davison, 1993; Singer and Stumm, 1970). Below pH 3, rates were 3 and 5 orders of magnitude faster than chemical oxidation rates ($\sim 1.6 \cdot 10^{-3}$ mol L^{-1} yr^{-1} with $[Fe^{2+}]=1$ mmol L^{-1}, p(O_2)=0.2 atm, rate law from Stumm and Morgan (1996)). In the study by McKnight et al. (1988), a difference of six orders of magnitude was found. Rates were still elevated also at higher pH (5.4) (Sulzberger et al., 1990). In agreement with these observations, a decrease in iron oxidation rates was found when mixtures of surface water and sediment samples from a slightly acidic (pH 5.2) alpine lake were sterilized by gamma irradiation (Barry et al., 1994).

It should be mentioned that ferric iron is also photochemically reduced in AMD polluted lakes. Photoreduction of either solid phase or unspecified ferric iron was for instance observed in radiation batch experiments with samples from an acid mine impacted creek, and with surface water samples from acidic mine Lake 111 in Lusatia (Friese et al., 2002; Herzsprung et al., 1998; Hrncir and McKnight, 1998). The presence of simple organic ligands accelerated photoreduction rates (Hrncir and McKnight, 1998).

4.1.2. Precipitation of iron

Following oxidation of ferrous iron, a variety of precipitates may form depending on the geochemical conditions in the lake water, in particular goethite, jarosite, ferrihydrite, and schwertmannite (Bigham et al.,

1990, 1996a,b; Peine et al., 2000; Regenspurg et al., 2004; Table 1). The predominant iron precipitate in acidic mine lakes is probably the poorly crystalline oxohydroxysulfate mineral schwertmannite (Fe_8O_8 $(OH)_xSO_y$, $8-x=2y$, $1.0 < y < 1.75$), first described by Bigham et al. (1990). Its formation was found to be directly linked to the bacterially mediated oxidation of Fe^{2+} (Kawano and Tomita, 2001). The thermodynamic stability constants of the mineral are still debated (Majzlan et al., 2004). Estimates range from $\log K_{sp}=7.09\pm0.09$ to $\log K_{sp}=18.0\pm2.5$ (Bigham et al., 1996b; Yu et al., 1999; Kawano and Tomita, 2001).

Schwertmannite is characterized by a tunnel structure akin to that of akaganéite (β-FeOOH). Instead of chloride stabilizing the tunnel structure, sulfate shares its oxygen with iron atoms at the tunnel wall (Bigham et al., 1990). Optimum conditions for schwertmannite formation were found to be between pH 2.8 and 3.2 (Bigham et al., 1996b). Jarosite forms at pH < 2.5 and in the presence of K^+ (Cravotta et al., 1999; Göttlicher and Gasharova, 2000; Regenspurg et al., 2004). Ferrihydrite precipitates at pH > 4.5 and lower sulfate concentrations (Lee et al., 2002; Yu et al., 1999). Mixtures of these minerals may precipitate in-between stability fields (Karathanasis and Thompson, 1995; Yu et al., 1999). Goethite, although the thermodynamically stable phase at a pH > 2 (Bigham et al., 1996b) only occurred in minor quantities within precipitates (Bigham et al., 1996a, 1996b; Yu, 1996).

The precipitation of schwertmannite has consequences for the acidity and proton balance of acidic mine lakes because about 2.6 H^+ are released per ferric iron, depending on the exact stoichiometric composition of the mineral (Table 1, Eq. (13)). The resulting iron sedimentation rates in acidic mine lakes ranged from 2 to >10 mol m^{-2} yr^{-1} (Table 3; Blodau, 2004, 2005; Langner, 2004; Peine et al., 2000). Iron sedimentation rates are thus comparable to pyrite oxidation rates in dumps of lignite mines (see Section 3.1).

Schwertmannite precipitation rates can be estimated from ferrous iron loading. Dissolved ferric iron activities in surface waters were found to be controlled by solubility equilibrium with schwertmannite (Bigham et al., 1996b; Regenspurg et al., 2004; Yu et al., 1999). The crystal growth of schwertmannite should hence be faster than the supply of ferrous iron and its oxidation. Not considering seasonal anoxia in the water body (Bachmann et al., 2001; Herzsprung et al., 1998), sedimentation and export with discharge are stipulated by discharge, ferrous iron input, and the iron concentration in equilibrium with the mineral. The partitioning should hence be a function of the water balance, K_{sp} and

pH, with lower pH increasing the export of ferric iron with discharge.

4.2. Processes in sediments

4.2.1. Acidity generation from iron transformations

Total iron contents of AMD polluted lake and pond sediments typically range from 5% to 60% of dry weight (Bachmann et al., 2001; Blodau et al., 2000; Lessmann et al., 1999; Meier et al., 2004; Peine and Peiffer, 1996; Holmström and Öhlander, 2001) and are thus much higher than in marine and freshwater lake sediments (typically 1% to 7%, e.g. Canfield et al., 1993; Cook et al., 1986; Gagnon et al., 1995; Haese et al., 1997). As outlined above, schwertmannite initially often predominates in these iron deposits. The mineral transforms with burial via re-dissolution into goethite (Bigham et al., 1996a; Regenspurg et al., 2004; Schwertmann and Carlson, 2005) and its relative content decreases with burial (Blodau, 2004; Peine et al., 2000).

Acidity generation from schwertmannite transformation has been estimated using mineral inventories and dating, and ranged from 2.4 mol m^{-2} yr^{-1} to 3.5 mol m^{-2} yr^{-1} in the case study of Lake 77 (Blodau et al., 1998, 2000; Peine et al., 2000; Blodau, 2005). Acidity generation rates of this magnitude are probably common in other acidic mine lakes (Table 3) and AMD treatment ponds as well. From sediments in AMD treatment ponds, Gagliano et al. (2004) reported transformation rates of 30 μmol cm^{-3} yr^{-1}. Given the reported bulk density of 0.4 g cm^{-3}, and a sediment thickness of 33 cm, rates amounted to 4.0 mol m^{-2} yr^{-1}. A number of experimental studies documented that pH controls schwertmannite transformation rates (Bigham et al., 1996b; Knorr and Blodau, submitted for publication; Regenspurg et al., 2004; Schwertmann and Carlson, 2005). Raising pH from 3 to 5 increased transformation rates by a factor of 5.8 (±2.1) (Knorr and Blodau, submitted for publication). Schwertmann and Carlson (2005) reported a doubling of the transformation rate, when the pH was increased from 4.0 to 7.2.

Transformation rates are further controlled by temperature, sulfate, and DOC concentrations in the pore water. An increase in temperature from 10 to 20 °C increased transformation by a factor of 3.8 (±1.6) (Knorr and Blodau, submitted for publication). A similar effect was reported by Jonsson et al. (2005). The inhibiting effect of sulfate on transformation rates was already mentioned by Bigham et al. (1996b). In the study by Knorr and Blodau (submitted for publication),

sulfate (20 mmol L^{-1}) and DOC (20 mg L^{-1}) concentrations lowered transformation rates by a factor of 2.5 and 2.4, respectively, compared to an unamended control. A combination of low pH, high sulfate and DOC concentrations, and low temperatures thus effectively impedes schwertmannite transformation. Such results have not been validated by field investigations yet.

4.2.2. Acidity consumption by reductive processes

Sediment organic matter is utilized by oxic respiration and a number of suboxic processes, including iron and sulfate reduction. Langner (2004) and Holmström and Öhlander (1999) documented oxygen penetration depths of about 1 cm in mining lakes and ponds. Koschorreck and Tittel (2002) further showed that benthic photosynthesis is an effective source of oxygen at the trophogenic sediment–water interface. A substantial fraction of organic matter recently deposited or fixed *in situ* should thus be utilized by oxic respiration, in analogy to conditions in soft water lakes (Furrer and Wehrli, 1996; Müller et al., 2003). Sulfate and iron reduction have been documented to occur at substantial rates, whereas methanogenesis is probably of little importance (Küsel, personal communication, Blodau, unpublished data). Studies on denitrification and manganese reduction in acidic mine lakes do not seem to have been published yet.

Sulfate reduction rates were determined with the ^{35}S radiotracer technique (Fossing and Jørgensen, 1989), and ranged from 0.15 mol m^{-2} yr^{-1} to 1.9 mol m^{-2} yr^{-1} (Blodau et al., 1998; Blodau and Peiffer, 2003; Gyure et al., 1990; Meier et al., 2004). In Lake 116 in Lusatia, higher rates were determined in littoral than in pelagial sediments (Blodau et al., 1998). Rates were similar as in freshwater lakes, such as Little Rock and Wintergreen Lake in the north-central U.S. (Smith and Klug, 1981; Urban et al., 1994), in which sulfate reduction is limited by sulfate availability. Iron reduction rates ranged from 0.14 to 2.5 mol m^{-2} yr^{-1} (Table 3) and were determined in incubation experiments or derived from pore water profiles. Proton consumption by iron and sulfate reduction, therefore, has the potential to balance proton release from schwertmannite transformation in highly acidic systems.

Sulfate reduction rates can be considerably higher in moderately acidic lakes (pH $\sim$4), such as the reservoir Lake Anna in Virginia, USA (Herlihy and Mills, 1985). Sulfate reduction rates reached 82 mol m^{-2} yr^{-1} and only 4.9 mol m^{-2} yr^{-1} at an unpolluted control site. These rates by far exceed a maximum of 6.6 mol m^{-2} yr^{-1} determined in several marine

sediments (Canfield et al., 1993; Chanton et al., 1987; Jørgensen, 1997) and document the potential for sulfate reduction in sediments of AMD polluted lakes. As a result, reduction removed 50% of the sulfate in the inflow (490–750 μmol L^{-1}) within a 2 km distance along the lake and raised the pH in the surface water from 3.9–4.3 to 6.1–6.3 (Herlihy et al., 1987).

Such differences in sulfate reduction activity may reflect three possible scenarios. In unpolluted lakes, sulfate reduction is generally limited by sulfate availability (Ingvorsen et al., 1981; Urban et al., 1994). In highly acidic mine lakes, sulfate reduction is carbon limited due to the low productivity of these waters (see below). In moderately polluted lakes, both limitations are eased and higher rates are possible. Results from soft water lake acidification experiments support this view. There, increases in sulfate concentrations also raised sulfate reduction rates (Schindler et al., 1986) and sulfur burial in sediments (Urban and Monte, 2001).

The most important constraint on sulfate reduction, therefore, seems to be electron donor availability, despite carbon contents reaching 5% to 30% of dry weight (Blodau et al., 2000). Electron donor addition to sediment batch and microcosm assays generally enhanced reduction rates (Fauville et al., 2004; Frömmichen et al., 2003, 2004; Küsel, 2003; Küsel and Dorsch, 2000). This pattern can be most likely attributed to the relative recalcitrance of coal derived organic matter and the small pool of labile, plankton derived material (Blodau et al., 2000; Laskov et al., 2002; Chabbi et al., 2006).

Sulfate and iron reduction are further controlled by temperature and pH. Iron and sulfate reduction rates accelerated by a factor of 2.0 and 2.6, respectively, in iron rich and acidic sediments with a 10 °C temperature increase (Blodau et al., 1998; Meier et al., in press). The response of both processes to changes in pH strongly differed, though. Sulphate reduction required pH values of 4.5–5 and higher to proceed (Peine et al., 2000; Koschorreck et al., 2002; Blodau and Knorr, in press), whereas iron reducers isolated and cultivated from sediments were acidophilic and had a pH optimum of 3.2 (Küsel et al., 1999). Iron reduction rates also decreased in incubation experiments when pH was raised from 3 to 6 (Blodau and Gatzek, submitted for publication). This effect can likely be attributed to precipitation of dissolved ferric iron at higher pH, which is preferentially reduced over ferric iron hydroxides (Straub et al., 2001).

The low availability of electron donors in mining lakes can be attributed to a lack of carbon fixation and to

slowed decomposition in AMD polluted waters. Terrestrial litter, which stems for example from acidity tolerant *Phragmites*, *Typha* and *Juncus* species (Fyson, 2000), decomposes slowly in the sediments, owing to absence of shredders, and the formation of iron coatings (Chabbi and Rumpel, 2004; Nyogi et al., 2002; Siefert and Mutz, 2001). Primary production and deposition of organic matter are limited by phosphate coprecipitation with ferric iron and by degassing of dissolved inorganic carbon (DIC) at low pH (Beulker et al., 2003; Lessmann et al., 2003; Nixdorf and Kapfer, 1998; Duffek and Langner, 2002; Kleeberg and Schubert, 2000; Nixdorf et al., 2001). Primary production is thus spatially restricted to the benthos, the metalimnion, and the littoral, where DIC and phosphorus become available (Koschorreck and Tittel, 2002; Nixdorf et al., 2001; Nixdorf and Kapfer, 1998). The resulting primary production rates ranged from 0 and 12.5 mg C m^{-3} h^{-1} in three mining lakes and were far lower than in natural lakes of the same region (27–230 mg C m^{-3} h^{-1}; Beulker et al., 2003; Nixdorf et al., 2003). Similar rates were determined by Gyure et al. (1987) in coal strip mining lakes at pH 2.8–3.1. In the sediments, the organic matter may further be stabilized against microbial attack by an intense association of organic matter with iron hydroxides (Laskov et al., 2002). In marine sediments, this association reduces microbial availability (Hedges and Keil, 1995; Hedges and Oades, 1997).

Acidic mine lakes are not unproductive waters under all circumstances, though. As food webs in acidic mine lakes are poorly stabilized, mass developments of phytoplankton can occur when the nutrient constraints are eased (Woelfl et al., 2002). The concentrations of grazing zooplankton are low (Deneke, 2000) and the structure of the food chain is simple (Wollmann et al., 2000), often consisting only of a few species, in particular *Ochromonas* sp. and *Chlamydomonas* sp. (Nixdorf et al., 2001; Deneke, 2000; Nixdorf and Deneke, 2004). Owing to these characteristics and uncertainty about phosphorus dynamics (Kleeberg and Grüneberg, 2005), primary production and organic matter sedimentation may be highly volatile and difficult to predict for different geochemical conditions in the lake water.

4.2.3. Iron sulfide formation and acidity sequestration

Acidity is only sequestered by iron and sulfate reducing activity in sediments if reduced species are buried. This is often not the case, as the collation of iron reduction rates, iron fluxes, and total reduced inorganic sulfur (TRIS) formation rates in Table 3 shows. In most cases, TRIS formation and acidity sequestration rates

were one to two orders smaller than rates of iron and sulfate reduction (Blodau, 2005; Peine et al., 2000). One reason for the inefficient sequestration is a common predominance of iron reduction close to the sediment water interface, where electron donors are rapidly consumed (Blodau and Peiffer, 2003; Blodau et al., 2000). From there, ferrous iron mostly re-enters the surface waters, as shown in Fig. 3, and is partly oxidized at the sediment–water interface (Meier et al., 2004). The retention of ferrous iron by carbonate formation (at pH $>\sim 5$), or unspecific adsorption, avoids proton generation in the lake water and may be quantitatively more important (Blodau, 2004). However, burial still remained far smaller than proton generation in the investigated case studies.

A more effective sequestration of acidity can be expected under certain conditions. First, iron and sulfate must be reduced concurrently or in close vicinity. Second, the precipitation of iron sulfides must be fast compared to the oxidation of hydrogen sulfide with iron oxides (Peiffer, 1994; Peiffer et al., 1992), as the later process "competes" for the produced hydrogensulfide.

Conducive for the development of an iron sulfide forming regime is the formation of sediments dominated by goethite and a near-neutral pH (Peine et al., 2000; Blodau, 2004; Meier et al., 2004). This observation can be interpreted within a thermodynamic framework. Under such conditions, iron reduction loses in thermodynamic competitiveness relative to sulfate reduction, and the available energy for sulfide oxidation to sulfate with ferric iron as electron acceptor decreases. These factors potentially strengthen sulfate reducers and facilitate precipitation (Blodau and Peiffer, 2003). A pore water pH value of about 4.5 to 5 seems to be a critical threshold for iron sulfide accumulation to occur. Several published studies are in agreement with this simple concept (Blodau and Knorr, in press; Küsel et al., 2001; Koschorreck et al., 2002; Peine et al., 2000; Wendt-Potthoff et al., 2002), and iron sulfide accumulation in pH-circumneutral sediments of Lake 116 in Lusatia provides a good example (Table 3). High rates of sulfate reduction and iron sulfide formation have also been reported from the pH-circumneutral, AMD-polluted sediments of Lake Anna, Virginia (Herlihy et al., 1988).

The effect of pH and other potential controls on the oxidation rate of sulfides with ferric iron hydroxides has experimentally not been firmly established in sediments of AMD polluted lakes yet. Currently, only incidental observations from batch and lake enclosure experiments suggest that high pH values discourage sulfide oxidation with ferric iron hydroxides (Küsel et

al., 2001; Wendt-Potthoff et al., 2002). It should also be noted that iron sulfide formation may only be controlled by pH and thermodynamic factors in iron rich and carbon limited sediments. In other environments, sulfate reduction can be a viable process at pH 3 (Christensen et al., 1996; Elliot et al., 1998; Koschorreck et al., 2003). Surface area, surface properties, and passivation of ferric iron hydroxides may also be more important controls on reduction rates than thermodynamic constraints (e.g. Roden, 2003; Roden and Urrutia, 2002).

A further complication arises from a possible lack of competition between iron and sulfate reducing bacteria due to different electron donor requirements (Küsel, 2003). Iron reducers were capable of utilizing more complex organic molecules than fermentation products, such as short chain fatty acids and alcohols, and did not utilize acetic acid under acidic conditions (Küsel, 2003; Küsel and Dorsch, 2000). Inhibition of fermenting activity by low pH, or a successful competition of iron reducers with fermenters for more complex molecules, such as sugars, may thus contribute to the absence of sulfate reduction, and the lack of iron sulfide formation at low pH.

The time scale necessary to establish iron sulfide forming conditions are apparently on the order of a few weeks to months and mainly depend on the provision of electron donors to the sediments (Frömmichen et al., 2004; Fyson et al., 1998; Herzsprung et al., 2002; Koschorreck et al., 2002; Wendt-Potthoff et al., 2002). A depletion of electron donors resulted in a re-establishment of pH 3 and iron reducing conditions within similar time periods (Wendt-Potthoff et al., 2002). The microbial communities involved are, therefore, able to adapt to changing geochemical conditions in the sediments fairly rapidly. This is no surprise, as generally genera are present that are capable of various terminal electron accepting processes (Küsel, 2003). Sulfide accumulating conditions can rapidly establish also in newly deposited, acidic, iron rich sediments (pH 3.4) on the time scale of weeks (Bell et al., 1990). After a classical redox sequence had been completed, a sulfate reducing, pH 5 circumneutral regime was attained in this field study.

4.2.4. Potential system dynamics of acidity generation and consumption

The constraints on the internal iron and sulfur cycle have implications for the long-term development of acidic mine lakes, and for the success of remediation measures, e.g. by increases in carbon deposition to the sediments (Koschorreck et al., 2002; Wendt-Potthoff et

al., 2002). Enhanced carbon deposition would increase sequestration of acidity if iron reduction became iron limited and, consequently, sulfate reduction proceeded even at low pH (Koschorreck et al., 2003). A similar effect would ensue if proton consumption by iron reduction exceeded proton release from schwertmannite transformation, and sulfate reduction was initiated with increasing pH (Blodau and Knorr, in press). However, negative feedbacks on acidity consumption are likely because the transformation of metastable iron (hydr)oxysulfates to goethite accelerates with rising pH in the sediments, and because increasing export of ferrous iron from the sediments implies increased sedimentation of the metastable precipitates. An "internal acidity loading" phenomenon, well known from phosphorus and the eutrophication debate, would be the result.

Previous enclosure experiments support this view. A short term pulse of 11.8 kg m^{-2} organic/inorganic carbon ("Carbokalk") initiated sulfate reduction in sediments of highly acidic Lake 111, Lusatia, but most of the carbon was used in iron reduction (Wendt-Potthoff et al., 2002). Most of the ferrous iron entered the water column and was oxidized to ferric iron and precipitated. Furthermore, carbon additions also led to disintegration of jarosite

(Göttlicher and Gasharova, 2000) and reprecipitation of goethite (Herzsprung et al., 2002). Owing to this process pattern, in-lake neutralization proved difficult to stimulate.

Two feedback loops may diminish in-lake acidification and enhance neutralization, though (Fig. 5). If iron input into a lake decreased and less schwertmannite was deposited, less would also be transformed. With rising sediment pH, more iron sulfides would be formed. The related sequestration of acidity could further raise the pH in the surface waters, and may at some point suffice to impede schwertmannite deposition when the pH reaches values >4.5. This change would encourage sulfate reduction in the sediments, as the schwertmannite reservoir was subsequently depleted. The development of a sulfidic sediment, such as in Lake Anna, Virginia (Herlihy et al., 1987, 1988) seems possible. If this development was initiated and pH in the lake water increased, primary production and sedimentation of organic matter might also increase, as less of the limiting nutrient, phosphate, was co-precipitated (Fig. 5). Increasing organic matter sedimentation would enhance proton consumption in the sediments, resulting in a further pH increase in the surface waters. While these positive feedback loops on in-lake neutralization represent an intriguing concept,
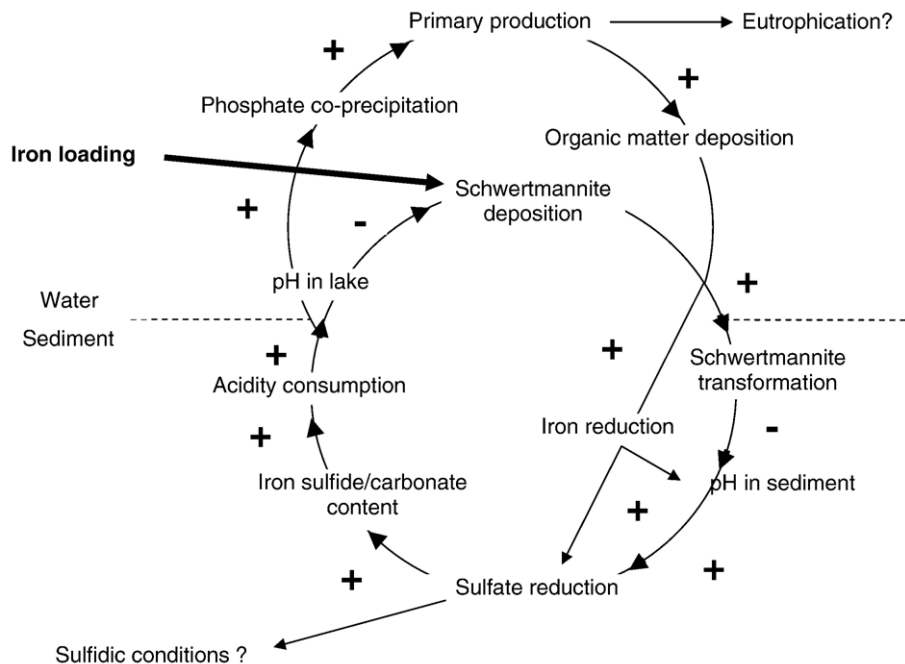

Fig. 5. Schematic of potentially important feedback loops in the biogeochemical system "mine lake". (+) signs indicate positive, (−) signs negative correlation. For further description see text.

the critical iron loads that would allow for such a dynamics are unknown.

5. Summary and outlook

We have made considerable progress regarding rates and mechanisms of acidity generation and consumption in acidic mine lakes and their watersheds. In most general terms, the review suggests that several of the involved processes, such as pyrite oxidation and carbonate weathering in the watershed, and ferrous iron oxidation and iron(hydro)xide precipitation in lakes, may occur at similar rates. A mineralization of the affected waters seems inevitable; but a strong acidification primarily occurs where imbalances between proton production and consumption develop. This is often the case in silicate dominated aquifers and in lakes heavily loaded with ferrous iron. There, neutralization often cannot compensate proton release. Acidity dynamics is thus controlled externally by the fluxes of oxidants and reductants into individual compartments and internally by the kinetics of processing oxidants and reductants. The pH is arguably the most effective 'internal' mastervariable on kinetics and causes characteristic biogeochemical process patterns within these compartments. In contrast to the outlined progress on mechanisms, rates, and controls, we still know little about spatial distribution patterns of acidity sources and sinks on the watershed scale, and about the temporal dynamics of acidity generation and consumption. Without further progress on these issues, it will remain difficult to predict the future of acidic mine lakes.

To make this progress, we will likely have to reframe scientific strategy, which has focussed on disciplinary research, individual compartments, and on a reductionistic approach. To enter a new phase of research on AMD related acidification of lakes, we need to focus more strongly on material flow within larger watersheds, and on natural attenuation by reductive processes within the landscape. The review revealed, for example, that little is known about the consumption of acidity by iron sulfide formation in aquifers and riparian zones. If material flow of the decisive elements, iron, sulfur, and carbon, within and between landscape units was quantitatively better understood, we would gain a more thorough understanding where organic matter availability leads to effective acidity sequestration. If effective acidity sinks along hydrologic flow paths were identified more precisely, the scientific basis for efficient remediation could further be improved.

Such a strategy needs to be complemented by a focus on the biogeochemical system dynamics within lakes. Currently we know little about the chemical controls on some critical processes, such as primary production, organic matter sedimentation and phosphate co-precipitation. The controls on the kinetics of proton release from accumulated 'proton reservoirs', for example in form of schwertmannite, are also insufficiently understood. The response of these processes to changes in iron, proton, and sulfur loading will to a large degree determine whether- and on what time scale-attenuation of acidity will eventually proceed. More research on these issues is thus needed. Equally important will be a strategy focussing on the interaction of the various processes involved in acidity generation and consumption over time. To these ends, dynamic mathematical models have to be developed that ease the assumption of thermodynamic equilibrium where appropriate, and that are capable of capturing the critical biogeochemical structures, processes, and mass balances without being burdened by excessive detail. To calibrate and validate such models, observation of lake ecosystems in transition between acidic and neutral states is required. Ecosystem experiments, using either enclosures or whole lakes, will further be instrumental for identifying the dynamic regulation of acidity generation and consumption.

Acknowledgement

Appendix A

$$r = k \circ a(\text{H}^+, \text{ surface}]^n \qquad (35)$$

and n being a temperature dependent factor and H^+ hydrogen ion activity adjacent to the mineral surface. (Gautelier et al., 1999).

$$\frac{R_a}{\gamma_m^a \circ a_s} = \alpha \circ 10^{-\frac{E_a}{R}\left(\frac{1}{T^a} - \frac{1}{T^b}\right)} \circ 10^{n(\text{pH}^a - \text{pH}^b)} \circ \sum_i^a \frac{x_{a,i} k_{a,i}}{k_b} \circ k_b$$

$$(36)$$

with α: mobile fraction of pore water; R^a: weathering rate in column or field; γ_m^a: mineral content; a_s: total specific surface area; E_a: activation energy; R: gas constant; T: absolute temperature; n: reaction order with respect to protons; $x_{a,i}$: particle size fraction associated with reaction,

$k_{a,i}$: rate coefficient of particle size class i at column or field scale (a); k_b: rate coefficient at batch sale (b).

$$F_c = \sum_i F_{w,i} C_{c,i} - \sum_i F_{w,j} C_{c,j} \qquad (37)$$

with F_c: flow of the contaminant, F_w: flow of water; C_c: contaminant concentration; i and j denote flows from and to the deposit.

$$R_{w,M} = \frac{F_{t,M}}{\eta_{t,M}} \qquad (38)$$

with $R_{w,M}$: weathering rate of mineral (M); $F_{t,M}$: flow of tracer (t) specific to mineral (M); $\varsigma_{t,m}$: stoichiometric coefficient for tracer (t).

$$N_M = \frac{A \circ H \circ \gamma_M \circ \delta}{M_{w,M}} = \frac{A \circ H \circ \delta \circ x_i}{n_{t,M} \circ M_{w,t}} \qquad (39)$$

with N_M: mineral content in deposit; A: areal extent of the deposit; H: height of the deposit; γ_M: volume fraction of mineral (M); δ: density of the rock, sediment, or ore; $M_{w,m}$: molecular weight of mineral (M); $M_{w,t}$: molecular weight of tracer (t), x_t: mass fraction of tracer (t); $n_{t,M}$: stoichiometric coefficient of tracer (t) in mineral (M).

$$\frac{d[Fe^{2+}]}{dt} = -\frac{k_{abiotic} \circ [Fe^{2+}][O_2]}{[H^+]^2} - k_{bio} \circ c_{bact} \circ [Fe^{2+}][O_2][H^+] \qquad (40)$$

with: $k_{abiotic}$: rate constant of abiotic ferrous iron oxidation, k_{biotic}: biotic rate constant associated with *Thiobacillus ferrooxidans*; c_{bact}: concentration of *Thiobacillus ferrooxidans*.

References

Abel A, Michael A, Zartl A, Werner F. Impact of erosion-transported overburden dump materials on water quality in Lake Cospuden evolved from a former open cast lignite mine south of Leipzig, Germany. Environ Geol 2000;39(6):683–8.

Alpers CN, Blowes DW. Environmental geochemistry of sulfide oxidation. Am. Chem. Soc. Symp. Series 550. Am Chem Soc 1994 681 pp.

Alpers N, Nordstrom DK. Geochemical modeling of water–rock-interactions in mining environments. In: Plumlee GS, Logsdon MJ, editors. The environmental geochemistry of mineral deposits, vol. 6. Rev. Econ. Geol.; 1999. p. 289–323.

Bachmann TM, Friese K, Zachmann DW. Redox and pH conditions in the water column and in the sediments of an acidic mining lake. J Geochem Explor 2001;73(2):75–86.

Bain JG, Blowes D, Robertson WD, Frind EO. Modelling of sulfide oxidation with reactive transport at a mine drainage site. J Contam Hydrol 2000;41:23–47.

Balkenhol R, Ludwig B, Ufer K, Jochum J, Friedrich G. Pyrite oxidation in sediment samples from the German open-cut brown coal mine Zwenkau: mineral formation and dissolution of silicates. J Plant Nutr Soil Sci 2001;164:283–8.

Ball JW, Nordstrom DK. User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters, U.S. Geol. survey; 1991.

Banwart SA, Malmström ME. Hydrochemical modelling for preliminary assessment of minewater pollution. J Geochem Explor 2001;74:73–97.

Barry RC, Schnoor JJ, Sulzberger B, Sigg L, Stumm W. Iron oxidation kinetics in an acidic alpine lake. Water Res 1994;28(2):323–33.

Bell PE, Herlihy AT, Mills AL. Establishment of anaerobic, reducing conditions in a lake sediment after deposition of acidic, aerobic sediment by a major storm. Biogeochemistry 1990;9:99–116.

Bencala KE, McKnight DM, Zellweger GW. Evaluation of natural tracers in an acidic and metal-rich stream. Water Resour Res 1987;23(5):827–36.

Benner SG, Gould WD, Blowes DW. Microbial populations associated with the generation and treatment of acid mine drainage. Chem Geol 2000;169:435–48.

Beulker C, Lessmann D, Nixdorf B. Aspects of phytoplankton succession and spatial distribution in an acidic mining lake (Plessa 117 Germany). Acta Oecol 2003;24:S25–31.

Biemelt D, Schapp A, Kleeberg A, Grünewald U. Overland flow, erosion, and related phosphorus and iron fluxes at plot scale: a case study from a non-vegetated lignite mining dump in Lusatia. Geoderma 2005;129:4–14.

Bigham JM, Schwertmann U, Carlson L, Murad E. A poorly crystallized oxohydroxysulfate of iron formed by bacterial oxidation of Fe(II) in acidic mine waters. Geochim Cosmochim Acta 1990;54(10):2743–58.

Bigham JM, Schwertmann U, Pfab G. Influence of pH on mineral speciation in a bioreactor simulating acid mine drainage. Appl Geochem 1996a;11(6):845–9.

Bigham JM, Schwertmann U, Traina SJ, Winland RL, Wolf M. Schwertmannite and the chemical modeling of iron in acid sulfate waters. Geochim Cosmochim Acta 1996b;60(12): 2111–21.

Blodau C. Evidence for a hydrologically controlled iron cycle in acidic and iron rich sediments. Aquat Sci 2004;66(1):47–59.

Blodau C. Groundwater inflow controls acidity fluxes in an iron rich and acidic lake. Acta Hydrochim Hydrobiol 2005;33(2):104–17.

Blodau C, Gatzek C., submitted for publication. Chemical controls on iron reduction rates in schwertmannite-rich sediments. Chem Geol.

Blodau, C., Knorr, K.H., in press. Experimental inflow of groundwater induces a biogeochemical regime shift in acidic and iron rich sediments. J. Geophys. Res. B.

Blodau C, Peiffer S. Thermodynamics and organic matter: constraints on neutralization processes in sediments of highly acidic waters. Appl Geochem 2003;18(1):25–36.

Blodau C, Hoffmann S, Peine A, Peiffer S. Iron and sulfate reduction in the sediments of acidic mine lake 116 (Brandenburg, Germany): rates and geochemical evaluation. Water Air Soil Pollut 1998;108 (3–4):249–70.

Blodau C, Peine A, Hoffmann S, Peiffer S. Organic matter diagenesis in acidic mine lakes. Acta Hydrochim Hydrobiol 2000;28:123–35.

Blowes DW, Jambor JL. The pore-water geochemistry and the mineralogy of the vadose zone of sulfide tailings. Waite Amulet, Quebec, Canada. Appl Geochem 1990;5(3):327–46.

Blowes DW, Reardon EJ, Jambor JL, Cherry JA. The formation and potential importance of cemented layers in inactive sulfide mine tailings. Geochim Cosmochim Acta 1991;55(4):965–78.

Bonnissel-Gissinger P, Alnot M, Ehrhardt JJ, Behra P. Surface oxidation of pyrite as a function of pH. Environ Sci Technol 1998;32(19):2839–45.

Bouska V, Pesec J. Quality parameters of lignite of the North Bohemian basin in the Czech Republic in comparison with the world average lignite. Int J Coal Geol 1999;40:211–35.

Bowell RJ. The hydrogeochemical dynamics of mine pit lakes. In: Younger PL, Robins NS, editors. Mine water hydrogeology and geochemistry, vol. 198. Geological Society of London, Geol. Soc. Spec. Publ. 2002. 396 pp.

Bozau E, Strauch G. Hydrogeological basis for biotechnological remediation of the acidic mining lake 'RL 111', Lusatia (Germany). Water Air Soil Pollut Focus 2002;2(3):15–25.

Bussiere B, Benzaazoua M, Aubertin M, Mbonimpa M. A laboratory study of covers made of low-sulphide tailings to prevent acid mine drainage. Environ Geol 2004;45:609–22.

Cairney T, Frost RC. A case study of mine water quality deterioration, Mainsworth Colliery, County Durham. J Hydrol 1975;25:275–93.

Canfield DE, Thamdrup B, Hansen JW. The anaerobic degradation of organic matter in Danish coastal marine sediments: iron reduction, manganese reduction, and sulfate reduction. Geochim Cosmochim Acta 1993;57(16):3867–84.

Carlsson E, Öhlander B, Holmström H. Geochemistry of the infiltrating water in the vadose zone of a remediated tailings impoundment, Kristineberg mine, northern Sweden. Appl Geochem 2003;18:659–74.

Chabbi A, Rumpel C. Decomposition of plant tissue submerged in an extremely acidic mining lake sediment: phenolic CuO-oxidation products and solid state (13)C NMR spectroscopy. Soil Biol Biochem 2004;36(7):1161–9.

Chabbi A, Rumpel C, Grootes PM, Mariotti A, Hüttl RF. Isotopic tracers for the analysis of vegetation-derived organic matter in lignite-containing soils and sediments along a transect ranging from a forest soil to submerged lake sediment. Org Geochem 2006;37(6):740–53.

Chanton JP, Martens CS, Goldhaber MB. Biogeochemical cycling in an organic-rich coastal marine basin. 7. Sulfur mass balance, oxygen-uptake and sulfide retention. Geochim Cosmochim Acta 1987;51(5):1187–99.

Chou L, Garrels RM, Wollast R. Comparative study of the kinetics and mechanisms of dissolution of carbonate minerals. Chem Geol 1989;78:269–82.

Christensen B, Laake M, Lien T. Treatment of acid mine drainage by sulfate-reducing bacteria; results from a batch scale experiment. Water Res 1996;30(7):1617–24.

Cook RB, Kelly CA, Schindler DW, Turner AA. Mechanisms of hydrogen ion neutralization in an experimentally acidified lake. Limnol Oceanogr 1986;31(1):134–48.

Cornell RM, Schwertmann U. The iron oxides. VCH; 1996.

Cravotta CA, Brady KBC, Rose AW, Douds JB. Frequency distribution of the pH of coal-mine drainage in Pennsylvania. In: Morganwalp DWH, editor. U.S. Geological Survey Toxic Substances Hydrology Program—Proc. Technical Meeting, vol. 99-4018A. US Geol. Surv. Water-Res. Invest. Rep.1999. p. 313–24.

Dai S, Ren D, Tang Y, Shao L, Li S. Distribution, isotopic variation and origin of sulfur in coals in the Wuda coal field, Inner Mongolia, China. Int J Coal Geol 2002;51:237–50.

Davis A. A screening-level laboratory method to estimate pit lake chemistry. Mine Water Environ 2003;22:194–205.

Davis GB, Ritchie AIM. A model of oxidation in pyritic mine wastes: Part 1. Equations and approximate solution. Appl Math Model 1986;10(5):314–22.

Davison W. Iron and manganese in lakes. Earth-Sci Rev 1993;34 (2):119–63.

Davison W, Seed G. The kinetics of the oxidation of ferrous iron in synthetic and natural waters. Geochim Cosmochim Acta 1983;47 (1):67–79.

Deneke R. Review on rotifers and crustaceans in highly acidic environments of pH <=3. Hydrobiologia 2000;433:167–72.

Duffek A, Langner C. P retention in an acidic mine lake under the influence of flooding with river water. Verh. - Int. Ver. Limnol. 2002;28:1717–20.

Eary LE. Geochemical and equilibrium trends in mine pit lakes. Appl Geochem 1999;14(8):963–87.

Elberling B, Damgaard LR. Microscale measurements of oxygen diffusion and consumption in subaqeous sulfide tailings. Geochim Cosmochim Acta 2001;65(12):1897–905.

Elberling B, Nicholson RV, Scharer JM. A combined kinetic and diffusion-model for pyrite oxidation in tailings — a change in controls with time. J Hydrol 1994;157(1–4):47–60.

Elberling B, Balic-Zunic T, Edsberg A. Spatial variation and controls of acid mine drainage variation. Environ Geol 2003;48:806–13.

Elliot P, Ragusa S, Catcheside D. Growth of sulfate-reducing bacteria under acidic conditions in an upflow anaerobic bioreactor as a treatment system for acid mine drainage. Water Res 1998;32 (12):3724–30.

Evangelou VP, Zhang YL. A review: pyrite oxidation mechanisms and acid mine drainage prevention. Crit Rev Environ Sci Technol 1995;25(2):141–99.

Evangelou VP, Seta AK, Holt A. Potential role of bicarbonate during pyrite oxidation. Environ Sci Technol 1998;32:2084–91.

Fakoussa R, Hofrichter M. Biotechnology and microbiology of coal degradation. Appl Microbiol Biotechnol 1999;52:25–40.

Fauville A, Mayer B, Frömmichen R, Friese K, Veizer J. Chemical and isotopic evidence for accelerated bacterial sulfate reduction in acid mining lakes after the addition of organic carbon: laboratory batch experiments. Chem Geol 2004;204:325–44.

Fillipek LH, Nordstrom DK, Ficklin WH. Interaction of acid mine drainage with waters and sediments of West Squaw Creek in the West Shasta mining district, California. Environ Sci Technol 1987;21:388–96.

Foos A. Geochemical modeling of coal mine drainage, Summit County, Ohio. Environ Geol 1997;31(3/4):205–10.

Fortin D, Beveridge TJ. Microbial sulfate reduction within sulfidic mine tailings: formation of diagenetic Fe sulfides. Geomicrobiol J 1997;14:1–21.

Fortin D, Davis B, Beveridge TJ. Role of *Thiobacillus* and sulfate-reducing bacteria in iron biocycling in oxic and acidic mine tailings. FEMS Microbiol Ecol 1996;21:11–24.

Fortin D, Rioux JP, Roy M. Geochemistry of iron and sulfur in the zone of microbial sulfate reduction in mine tailings. Water Air Soil Pollut Focus 2002;2:37–56.

Fossing H, Jørgensen BB. Measurement of bacterial sulfate reduction in sediments — evaluation of a single-step chromium reduction method. Biogeochemistry 1989;8(3):205–22.

Friese K, Herzsprung P, Witter B. Photochemical degradation of organic carbon in acidic mine lakes. Acta Hydrochim Hydrobiol 2002;30(2–3):141–8.

Frömmichen R, Kellner S, Friese K. Sediment conditioning with organic and/or inorganic carbon sources as a first step in alkalinity generation of acid mine pit lake water (pH 2–3). Environ Sci Technol 2003;37(7):1414–21.

Frömmichen R, Wendt-Potthoff K, Friese K, Fischer R. Microcosm studies for neutralization of hypolimnic acid mine Pit Lake Water (pH 2.6). Environ Sci Technol 2004;38(6):1877–87.

Furrer G, Wehrli B. Microbial reactions, chemical speciation, and multicomponent diffusion in porewaters of a eutrophic lake. Geochim Cosmochim Acta 1996;60(13):2333–46.

Fyson A. Angiosperms in acidic waters at pH 3 and below. Hydrobiologia 2000;433:129–35.

Fyson A, Nixdorf B, Kalin M, Steinberg C. Mesocosm studies to assess acidity removal from acidic mine lakes through controlled eutrophication. Ecol Eng 1998;10:229–45.

Gagliano WB, Brill MR, Bigham JM, Jones FS, Traina SJ. Chemistry and mineralogy of ochreous sediments in a constructed mine drainage wetland. Geochim Cosmochim Acta 2004;68:2119–28.

Gagnon C, Mucci A, Pelletier E. Anomalous accumulation of acid-volatile sulfides in a coastal marine sediment, Saguenay Fjord, Canada. Geochim Cosmochim Acta 1995;59(13): 2663–2676.

Gautelier M, Oelkers EH, Schott J. An experimental study of dolomite dissolution rates as a function of pH from −0.5 to 5 and temperature from 25 to 80° C. Chem Geol 1999;157:13–26.

Geller W, Klapper H, Schultze M. Natural and anthropogenic sulfuric acidification of lakes. In: Geller W, Klapper H, Salomons W, editors. Springer: Acidic Mining Lakes; 1998. p. 3–14.

Gerke HH, Molson JW, Frind EO. Modelling the effect of chemical heterogeneity on acidification and solute leaching in overburden mine spoils. J Hydrol 1998;209:166–85.

Gerke H, Molson JW, Frind EO. Modelling the impact of physical and chemical heterogeneity on solute leaching in pyritic overburden mine spoils. Ecol Eng 2001;17:91–101.

Gilbert SE, Cooke DR, Hollings P. The effects of hardpan layers on the water chemistry from the leaching of pyrrhotite-rich tailings material. Environ Geol 2003;44:687–97.

Göttlicher J, Gasharova B. Interactions of iron and sulfur bearing solid phases with water in surface coal mining pits and acidic mining lakes. In: Rammlmair D, Mederer J, Oberthür TH, Heimann RB, Pentinghaus H, editors. Applied Mineralogy in Research, Economy, Technology, Ecology and Culture, vol. 2. Rotterdam: Balkema; 2000. p. 557–60.

Greb SF, Eble CF, Chesnut DR. Comparison of the Eastern and Western Kentucky coal fields (Pennsylvanian, USA) — why are coal distribution patterns and sulfur contents so different in these coal fields? Int J Coal Geol 2005;50:89–118.

Gyure RA, Konopka A, Brooks A, Doemel W. Algal and bacterial activities in acidic (pH 3) strip mine lakes. Appl Environ Microbiol 1987;53(9):2069–76.

Gyure RA, Konopka A, Brooks A, Doemel W. Microbial sulfate reduction in acidic (pH 3) strip mining lakes. FEMS Microbiol Ecol 1990;49:179–86.

Haese R, Wallmann K, Dahmke A, Kretzmann U, Müller PJ, Schulz HD. Iron species determination to investigate early diagenetic reactivity in marine sediments. Geochim Cosmochim Acta 1997;61(1):63–72.

Hammarstrom JM, Seal RR, Meier AL, Kornfeld JM. Secondary sulfate minerals associated with acid drainage in the eastern US: recycling of metals and acidity in surficial environments. Chem Geol 2005;215(1–4):407–31.

Hedges JI, Keil RG. Sedimentary organic matter preservation: an assessment and speculative synthesis. Mar Chem 1995;49(2–3): 81–115.

Hedges JI, Oades JM. Comparative organic geochemistries of soils and marine sediments. Org Geochem 1997;27(7–8):319–61.

Heidenreich H, Boehrer B, Kater R, Hennig G. Gekoppelte Modellierung geohydraulischer und limnologischer Vorgänge in Tagebaurestseen und ihrer Umgebung. Grundwasser 1999; 2:49–54.

Herlihy AT, Mills AL. Sulfate reduction in freshwater sediments receiving acid mine drainage. Appl Environ Microbiol 1985;49 (1):179–86.

Herlihy AT, Mills AL, Hornberger GM, Bruckner AE. The importance of sediment sulfate reduction to the sulfate budget of an impoundment receiving acid mine drainage. Water Resour Res 1987;23:287–92.

Herlihy AT, Mills AL, Herman JS. Distribution of reduced inorganic sulfur compounds in lake sediments receiving acid mine drainage. Appl Geochem 1988;3:333–44.

Herlihy AT, Kaufmann PR, Mitch ME. Regional estimates of acid mine drainage impact on streams in the mid-Atlantic and southeastern United States. Water Air Soil Pollut 1990;50: 91–107.

Herzsprung P, Friese K, Packroff G, Schimmele M, Wendt-Potthoff K, Winkler M. Vertical and annual distribution of ferric and ferrous iron in acidic mining lakes. Acta Hydrochim Hydrobiol 1998;26 (5):253–62.

Herzsprung P, Friese K, Packroff G, Schimmele M, Wendt-Potthoff K, Winkler M. Chemical changes in sediment pore-waters of an acidic mining lake after addition of organic substrate and lime for stimulating lake remediation. Water Air Soil Pollut Focus 2002;2 (3):123–40.

Hofrichter M, Fritsche W. Depolymerization of low-rank coal by extracellular fungal enzyme systems: III. In vitro depolymerization of coal humic acids by a crude preparation of manganese peroxidase from the white-rot fungus *Nematoloma frowardii* b19. Appl Microbiol Biotechnol 1997;47:566–71.

Holmström H, Öhlander B. Oxygen penetration and subsequent reactions in flooded sulphic mine tailings: a study at Stekenjokk, northern Sweden. Appl Geochem 1999;14:747–59.

Holmström H, Öhlander B. Layers rich in Fe- and Mn-oxyhydroxides formed at the tailings–pond interface, a possible trap for trace metals in flooded mine tailings. J Geochem Explor 2001; 74:189–203.

Hoth N, Wagner S, Häffner F. Predictive modelling of dump water impact on the surroundings of the lignite dump site Jänschwalde (Eastern Germany). J Geochem Explor 2001;73:113–21.

Hoth N, Feldmann H, Rinker A, Glombitza F, Häffner F. Reductive processes within lignite dumps — chance of a long-term natural attenuation process. Geoderma 2005;129:19–31.

Hrncir DC, McKnight D. Variation in photoreactivity of iron hydroxides taken from an acidic mountain stream. Environ Sci Technol 1998;32(14):2137–41.

Hudson-Edwards K, Macklin M, Taylor M. Historic metal mining inputs to Tees river sediment. Sci Total Environ 1997;194–195:437–45.

Ingvorsen K, Zeikus JG, Brock TD. Dynamics of bacterial sulfate reduction in a eutrophic lake. Appl Environ Microbiol 1981;42 (6):1029–36.

Jambor JL, Blowes D. Environmental geochemistry of sulfidic mine wastes. Nepean, Ontario: Mineral Association of Canada; 1994. 438 pp.

Jaynes DB, Rogowski AS, Pionke HB. Acid mine drainage from reclaimed coal strip mines. I. Model description. Water Resour Res 1984;20:233.

Johnson DB. Biogeochemical cycling of iron and sulfur in leaching environments. FEMS Microbiol Rev 1993;11:63–70.

Johnson DB. Acidophilic microbial communities: candidates for bioremediation of acidic mine effluents. Int Biodeterior Biodegrad 1995;35(1–3):41–58.

Jonsson J, Persson P, Sjoberg S, Lovgren L. Schwertmannite precipitated from acid mine drainage: phase transformation, sulfate release and surface properties. Appl Geochem 2005;20 (1):179–91.

Jørgensen BB. Bacterial sulfate reduction within reduced microniches of oxidized marine sediments. Mar Biol 1997;41:7–17.

Karathanasis AD, Thompson YL. Mineralogy of iron precipitates in a constructed acid mine drainage wetland. Soil Sci Soc Am J 1995;59:1773–81.

Karnachuk OV, Pimenov NV, Yusupov SK, Frank YA, Kaksonen AH, Puhakka JA, et al. Sulfate reduction potential in sediments in the Norilsk mining area, northern Siberia. Geomicrobiol J 2005;22:11–25.

Kaufmann PR, Herlihy AT, Baker LA. Sources of acidity in lakes and streams of the United States. Environ Pollut 1992;77(2–3):115–22.

Kawano M, Tomita K. Geochemical modeling of bacterially induced mineralization of schwertmannite and jarosite in sulfuric acid spring water. Am Mineral 2001;86(10):1156–65.

Kenoyer GJ, Anderson MP. Groundwaters dynamic role in regulating acidity and chemistry in a precipitation-dominated lake. J Hydrol 1989;109(3–4):287–306.

Kimball BA, Runkel RL, Walton-Day K, Bencala KE. Assessment of metal loads in watersheds affected by acid mine drainage by using tracer injection and synoptic sampling: Cement Creek, Colorado, USA. Appl Geochem 2002;17:1183–207.

Kirby CS, ElderBrady JA. Field determination of Fe^{2+} oxidation rates in acid mine drainage using a continuously-stirred tank reactor. Appl Geochem 1998;13(4):509–20.

Kirby CS, Thomas HM, Southam G, Donald R. Relative contributions of abiotic and biological factors in (FeII) oxidation in mine drainage. Appl Geochem 1999;14:511–30.

Klapper H, Schultze M. Geogenically acidified mining lakes — living conditions and possibilities of restoration. Int Rev Hydrobiol 1995;80(4):639–53.

Kleeberg A, Grüneberg B. Phosphorus mobility in sediments of acid mine lakes, Lusatia, Germany. Ecol Eng 2005;24:89–100.

Kleeberg A, Schubert H. Vertical gradients in particle distribution and its elemental composition under oxic and anoxic conditions in a eutrophic lake, Scharmutzelsee, NE Germany. Arch Hydrobiol 2000;148(2):187–207.

Knappe S, Haferkorn U, Mattusch J, Meissner R, Rupp H, Wennrich R. Water and solute balances in recultivated lignite mining dump soils—field data and lysimeter experiments. Water Air Soil Pollut 2004;157:85–104.

Knoll D, Weber L, Schafer W. Groundwater influx to old residual lakes in the brown coal open-pit mining area of Niederlausitz, Germany. Grundwasser 1999;4(2):55–61.

Knöller K, Strauch G. The application of stable isotopes for assessing the hydrological, sulfur, and iron balances of acidic mine lake ML 111 (Lusatia, Germany) as a basis for biotechnological remediation. Water Air Soil Pollut Focus 2002;2: 3–14.

Knöller K, Fauville A, Mayer B, Strauch G, Friese K, Veizer J. Sulfur cycling in an acidic mining lake and its vicinity in Lusatia, Germany. Chem Geol 2004;204:303–23.

Knorr KH, Blodau C. submitted for publication. Controls on schwertmannite transformation rates and products. Environ Sci Technol.

Knorr KH, Blodau C. Altered groundwater inflow remobilizes acidity from sediments of an iron rich and acidic lake. Environ Sci Technol 2006;40:2944–50.

Konishi Y. Bacteria dissolution of pyrite by Thiobacillus ferrooxidans. Bioprocess Eng 1990;5:231.

Koryak M, Stafford LJ, Reilly RJ. Declining intensity of acid mine drainage in the northern Appalachian bituminous coal fields: major Allegehny river tributaries. J Am Water Resour Assoc 2004;40 (3):677–89.

Koschorreck M, Tittel J. Benthic photosynthesis in an acidic mining lake (pH 2.6). Limnol Oceanogr 2002;47(4):1197–201.

Koschorreck M, Frömmichen R, Herzsprung P, Tittel J, Wendt-Potthoff K. Functions of straw for in situ remediation of acidic mining lakes. Water Air Soil Pollut Focus 2002;2 (3):97–109.

Koschorreck M, Wendt-Potthoff K, Geller W. Microbial sulfate reduction at low pH in the sediment of an acidic lake in Argentina. Environ Sci Technol 2003;37(6):1159–62.

Küsel K. Microbial cycling of iron and sulfur in acidic coal mining lake sediments. Water Air Soil Pollut Focus 2003;3(1):67–90.

Küsel K, Dorsch T. Effect of supplemental electron donors on the microbial reduction of Fe(III), sulfate, and CO_2 in coal mining-impacted freshwater lake sediments. Microb Ecol 2000;40 (3):238–49.

Küsel K, Dorsch T, Acker G, Stackebrandt E. Microbial reduction of Fe(III) in acidic sediments: Isolation of Acidiphilium cryptum JF-5 capable of coupling the reduction of Fe(III) to the oxidation of glucose. Appl Environ Microbiol 1999;65:3633–40.

Küsel K, Roth U, Trinkwalter T, Peiffer S. Effect of pH on the anaerobic microbial cycling of sulfur in mining-impacted freshwater lake sediments. Environ Exp Bot 2001;46:213–23.

Langner C. Frühdiagenetische Prozesse in jungen Sedimenten von entstehenden Seen des Braunkohletagebaus. Ph.D. thesis, UFZ Halle-Leipzig GmbH, Magdeburg, 2004.

Laskov C, Amelung W, Peiffer S. Organic matter preservation in the sediment of an acidic mining lake. Environ Sci Technol 2002;36 (20):4218–23.

Lee G, Bigham JM, Faure G. Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown mining district, Tennessee. Appl Geochem 2002;17:569–81.

Lessmann D, Deneke R, Ender R, Hemm M, Kapfer M, Hartwig K, et al. Lake Plessa 107 (Lusatia, Germany) — an extremely acidic shallow mining lake. Hydrobiologia 1999;408/409:293–9.

Lessmann D, Fyson A, Nixdorf B. Experimental eutrophication of a shallow acidic mining lake and effects on the phytoplankton. Hydrobiologia 2003;506(1–3):753–8.

Lindsay WL. Chemical equilibrium in soils. John Wiley and Sons; 1979. 449 pp.

Ljungberg J, Öhlander B. The geochemical dynamics of oxidising mine tailings at Laver, northern Sweden. J Geochem Explor 2001;74(1–3):57–72.

Ludwig B, Balkenhol R. Quantification of the acidification potential of pyrite containing sediment. Acta Hydrochim Hydrobiol 2001;29 (2–3):118–28.

Ludwig B, Khanna P, Balkenhol R, Friedrich G, Dohrmann R. Pyrite oxidation in a sediment sample of an open-cut brown coal mine: mineral formation, buffering of acidity and modeling of cations and sulfate. J Plant Nutr Soil Sci 1999;162:499–509.

Ludwig B, Prenzel J, Obermann P. Modelling ion composition in seepage water from a column experiment with an open cut coal mine sediment. J Geochem Explor 2001;73:87–95.

Lund LJ, Fogler HS, McCune CC. Acidization-I. The dissolution of dolomite in hydrochloric acid. Chem Eng Sci 1973;28:691–700.

Luther GW. Pyrite oxidation and reduction: molecular orbital theory considerations. Geochim Cosmochim Acta 1987;51:3193–9.

Majzlan J, Navrotsky A, Schwertmann U. Thermodynamics of iron oxides: Part III. Enthalpies of formation and stability of ferrihydrite $(Fe(OH)_3)$, schwertmannite $(FeO(OH)_{3/4}(SO4)_{1/8}$, and ϵ-Fe_2O_3. Geochim Cosmochim Acta 2004;68(5):1049–59.

Malmström ME, Destouni G, Banwart SA, Strömberg BHE. Resolving the scale-dependence of mineral weathering rates. Environ Sci Technol 2000;34(7):1375–8.

Mayo AL, Nielsen PJ, Loucks M, Brimhall WH. The use of solute and isotopic chemistry to identify flow patterns and factors which limit acid mine drainage in the Wasatch Range, Utah. Groundwater 1992;30(2):243–9.

Mayo AL, Petersen JN, Kravits C. Chemical evolution of coal mine drainage in a non acid producing environment, Wasatch Plateau, Utah, USA. J Hydrol 2000;236:1–16.

McKnight DM, Kimball BA, Bencala KE. Iron photoreduction and oxidation in an acidic mountain stream. Science 1988;240:637–40.

Meier J, Babenzien HD, Wendt-Potthoff K. Microbial cycling of iron and sulfur in sediments of acidic and pH-neutral mining lakes in Lusatia (Brandenburg Germany). Biogeochemistry 2004;67(2):135–56.

Meier, J., Costa, R., Smalla, K., Boehrer, B., Wendt-Potthoff, K., in press. Temperature dependence of Fe(III) and sulfate reduction rates and their effect on growth and composition of bacterial enrichments from an acidic pit lake neutralization experiment. Geobiology.

Miller GC, Lyons WB, Davis A. Understanding the water quality of pit lakes. Environ Sci Technol 1996;30(3):118A–23A.

Morel FMM, Hering JG. Principles and applications of aquatic chemistry. New York: Wiley-Interscience; 1993.

Morin KA. Prediction of minesite-drainage chemistry through closure using operational monitoring data. J Geochem Explor 2001;73:123–30.

Moses CO, Herman JS. Pyrite oxidation at circumneutral pH. Geochim Cosmochim Acta 1991;55:471–82.

Moses CO, Nordstrom K, Herman JS, Mills AL. Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. Geochim Cosmochim Acta 1987;51(6):1561–71.

Müller B, Wang Y, Dittrich M, Wehrli B. Influence of organic matter decomposition on calcite dissolution in surficial sediments of a freshwater lake. Water Res 2003;37:4524–32.

Mustin C, de Donato P, Berthelin J, Marion P. Surface sulfur as promoting agent of pyrite leaching by *Thiobacillus ferrooxidans*. FEMS Microbiol Rev 1993;11:71–8.

Nicholson RV, Gillham RW, Reardon EJ. Pyrite oxidation in carbonate-buffered solution. 1. Experimental kinetics. Geochim Cosmochim Acta 1988;2(5):1077–85.

Nicholson RV, Gillham RW, Reardon EJ. Pyrite oxidation in carbonate-buffered solution. Geochim Cosmochim Acta 1990;54:395–402.

Nixdorf B, Deneke R, editors. Grundlagen und Maβnahmen zur biogenen Alkalinisierung von sauren Tagebauseen. Berlin: Weiβensee Verlag; 2004.

Nixdorf B, Kapfer M. Stimulation of phototrophic pelagic and benthic metabolism close to sediments in acidic mining lakes. Water Air Soil Pollut 1998;108:317–30.

Nixdorf B, Mischke U, Leβmann D. Chrysophytes and chlamydomonads: pioneer cplonists in extremely acidic mining lakes (pH<3) in Lusatia (Germany). Hydrobiologia 1998;369/370:315–27.

Nixdorf B, Fyson A, Krumbeck H. Review: plant life in extremely acidic waters. Environ Exp Bot 2001;46(3):203–11.

Nixdorf B, Krumbeck H, Jander G, Beulker C. Comparison of bacterial and phytoplankton productivity in extremely acidic mining lakes and eutrophic hard water lakes. Acta Oecol 2003;24:281–8.

Noike T, Nakamura K, Matsumoto J. Oxidation of ferrous iron by acidophilic iron-oxidizing bacteria from a stream receiving acid mine drainage. Water Res 1983;17:21–7.

Nordstrom DK. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. Acid sulfate weathering. Soil Sci Soc Am Spec Publ 1982:37–46.

Nordstrom DK. Advances in the hydrogeochemistry and microbiology of acid mine waters. Int Geol Rev 2000;42:499–515.

Nordstrom DK, Alpers CN. Geochemistry of acid mine waters. In: Plumlee GS, Logsdon MJ, editors. The environmental geochemistry of mineral deposits, vol. 6. . Rev. Econ. Geol.; 1999. p. 133–60.

Nyogi DK, McKnight D, Lewis JR. Effects of mine drainage on breakdown of aspen litter in mountain streams. Water Air Soil Pollut Focus 2002;2:329–41.

Paktunc AD. Mineralogical constraints on the determination of neutralization potential and prediction of acid mine drainage. Environ Geol 1999;39(2):103–12.

Parkhurst DL. User's guide to PHREEQC — a computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. US Geol Surv Water-Resour Invest Rep 1995;95:4227–370.

Peiffer S. Reaction of H_2S with ferric oxides. Environ Chem Lakes Reservoirs 1994;11:371–90.

Peiffer S, Stubert I. The oxidation of pyrite in the presence of reducing and non-reducing Fe(III)-chelators. Geochim Cosmochim Acta 1999;63(19/20):3171–82.

Peiffer S, dos Santos Afonso M, Wehrli B, Gächter R. Kinetics and mechanism of the reaction of H_2S with lepidocrocite. Environ Sci Technol 1992;26(12):2408–13.

Peine A. Saure Restseen des Braunkohletagebaus — Charakterisierung und Quantifizierung biogeochemischer Prozesse und Abschätzung ihrer Bedeutung für die seeinterne Neuralisierung. Ph.D. thesis. Universität Bayreuth, Bayreuth, 1998. 165 pp.

Peine A, Peiffer S. Neutralisation processes in acid mine lake sediments. Arch Hydrobiol Spec Issue Adv Limnol 1998;48:261–7.

Peine A, Peiffer S. In-lake neutralization of acid mine lakes. In: Geller W, Klapper H, Salomons W, editors. Acidic mining lakes. Berlin: Springer; 1998.

Peine A, Tritschler A, Küsel K, Peiffer S. Electron flow in an iron-rich acidic sediment—evidence for an acidity-driven iron cycle. Limnol Oceanogr 2000;45(5):1077–87.

Pesic B, Oliver DL, Wichlacz P. An electrochemical method of measuring the oxidation rate of ferrous to ferric iron with oxygen in the presence of *Thiobacillus ferrooxidans*. Biotechnol. Bioeng. 1989;33:428–39.

Plummer LN, Busenberg E. The solubilities of calcite, aragonite and vaterite in CO_2–H_2O solutions between 0 and 90 °C, and an evaluation of the aqueous model for the system $CaCO_3$–CO_2–H_2O. Geochim Cosmochim Acta 1982;46:1011–40.

Plumlee GS, Logsdon MJ, editors. The environmental geochemistry of mineral deposits, 6. Rev Econ Geol 1999.

Plumlee GS, Smith KS, Montour MR, Ficklin WH, Mosier EL. Geologic controls on the composition of natural waters and mine waters draining diverse mineral-deposit types. In: Plumlee GS, Logsdon MJ, editors. The environmental geochemistry of mineral deposits, 6. Rev Econ Geol 1999. p. 373–407.

Praharaj T, Fortin D. Indicators of microbial sulfate reduction in acidic sulfide-rich mine tailings. Geomicrobiol J 2004;21 (7):457–67.

Pronk J, Johnson DB. Oxidation and reduction of iron by acidophilic bacteria. Geomicrobiol J 1992;10:153–71.

Regenspurg S, Brand A, Peiffer S. Formation and stability of schwertmannite in acidic mining lakes. Geochim Cosmochim Acta 2004;68(6):1185–97.

Roden EE. Fe(III) oxide reactivity toward biological versus chemical reduction. Environ Sci Technol 2003;37:1319–24.

Roden EE, Urrutia MM. Influence of biogenic Fe(II) on bacterial crystalline Fe(III)oxide reduction. Geomicrobiol J 2002;19: 209–51.

Rolland W, Wagner H, Chmielewski R, Grunewald U. Evaluation of the long term groundwater pollution by the open cast lignite mine Jänschwalde (Germany). J Geochem Explor 2001;73 (2):97–111.

Romano CG, Mayer KU, Jones DR, Ellerbroek DA, Blowes DW. Effectiveness of various cover scenarios on the rate of sulfide oxidation of mine tailings. J Hydrol 2003;271:171–87.

Rumpel C, Kögel-Knabner I. The role of lignite in the carbon cycle of lignite containing mine soils: evidence from carbon mineralisation and humic acid extraction. Org Geochem 2002;33:393–9.

Salmon SU, Malmström ME. Geochemical processes in mill tailings deposits: modelling of groundwater composition. Appl Geochem 2004;19:1–17.

Schaaf W. What can element budgets of false-time series tell us about ecosystem development on post-lignite mining sites? Ecol Eng 2001;17:241–52.

Schindler DW, Turner MA, Stainton MP, Linsey GA. Natural sources of acid neutralizing capacity in low alkalinity lakes of the precambrian shield. Science 1986;232(4752):844–7.

Schnoor JL, Stumm W. Acidification of aquatic and terrestrial systems. Chemical processes in lakes. John Wiley; 1985. p. 311–38.

Schwertmann U, Carlson L. The pH-dependent transformation of schwertmannite to goethite at 25 degrees C. Clay Miner 2005;40 (1):63–6.

Schwertmann U, Bigham JM, Murad E. The first occurrence of schwertmannite in a natural stream environment. Eur J Mineral 1995;7:547–52.

Sebestyen SD, Schneider RL. Seepage patterns, pore water, and aquatic plants: hydrological and biogeochemical relationship in lakes. Biogeochemistry 2004;68:383–409.

Seoane S, Leiros MC. Weathering processes under various moisture conditions in a lignite mine spoil from As Pontes (N. W. Spain). Water Air Soil Pollut 1997;96:347–66.

Sherlock EJ, Lawrence RW, Poulin R. On the neutralization of scid rock drainage by carbonate and silicate minerals. Environ Geol 1995;25:43–54.

Shevenell L, Connors KA, Henry CD. Controls on pit lake water quality at sixteen open-pit mines in Nevada. Appl Geochem 1999;14:669–87.

Siefert J, Mutz M. Processing of leaf litter in acid waters of the post-mining landscape in Lusatia, Germany. Ecol Eng 2001;17: 297–306.

Singer PC, Stumm W. Acidic mine drainage: the rate-determining step. Science 1970;167:1121–3.

Smith RL, Klug MJ. Reduction of sulfur compounds in the sediments of an eutrophic lake basin. Appl Environ Microbiol 1981;41: 1230–7.

Straub KL, Benz B, Schink B. Iron metabolism in anoxic sediments at near neutral pH. FEMS Microbiol Ecol 2001;34:181–6.

Strömberg BHE, Banwart SA. Kinetic modelling of geochemical processes at the Aitik mining waste rock site in northern Sweden. Appl Geochem 1994;9:583–95.

Strömberg BHE, Banwart SA. Experimental study of acidity consuming processes in mining waste rock: some influences of mineralogy and particle size. Appl Geochem 1999;14: 1–16.

Stumm W, Morgan JJ. Aquatic chemistry — chemical equilibria and rates in natural waters. New York: Wiley-Interscience; 1996.

Sulzberger B, Schnoor JL, Giovanoli R, Hering JG, Zobrist J. Biogeochemistry of iron in an acidic lake. Aquat Sci 1990;52(1): 56–74.

Sung W, Morgan JJ. Kinetics and product of ferrous iron oxygenation in aqueous systems. Environ Sci Technol 1980;14 (5):561–8.

Sverdrup HU. The kinetics of base cation release due to chemical weathering. Lund: Lund University Press; 1990.

Theis TL, Singer PC. Complexation of iron(II) by organic matter and its effect on iron(II) oxygenation. Environ Sci Technol 1974;8 (6):569–73.

Totsche O, Pöthig R, Uhlmann W, Büttcher H, Steinberg CEW. Buffering mechanisms in acidic mining lakes — a model based analysis. Aquat Geochem 2004;9:343–59.

Urban NR, Monte AE. Sulfur burial in and loss from the sediments of Little Rock Lake, Wisconsin. Can J Fish Aquat Sci 2001;58 (7):1347–55.

Urban NR, Brezonik PL, Baker LA, Sherman LA. Sulfate reduction and diffusion in sediments of little rock lake, Wisconsin. Limnol Oceanogr 1994;39(4):797–815.

Ward CR. Analysis and significance of mineral matter in coal seams. Int J Coal Geol 2002;50:135–68.

Waschkies C, Hüttl RF. Microbial degradation of geogenic organic C and N in mine spoils. Plant Soil 1999;213:221–30.

Weber L. Modellierung von Porenwasserprofilen in sauren Bergbaur-estseen unter Berücksichtigung der advektiven Strömung im Sediment. Ph.D. thesis. Universität Heidelberg, Heidelberg; 2000.

Wendt-Potthoff K, Frömmichen R, Herzsprung P, Koschorreck M. Microbial Fe(III) reduction in acidic mining lake sediments after addition of an organic substrate and lime. Water Air Soil Pollut Focus 2002;2(3):81–96.

Werner F, Bilek F, Luckner L. Impact of regional groundwater flow on the water quality of an old post mining lake. Ecol Eng 2001; 17:133–42.

White AF, Brantley SL. Chemical weathering rates of silicate minerals. Rev Miner 1995;31:1–22.

Wilden R, Schaaf W, Hüttl RF. Element budgets of two afforested mine sites after application of fertilizer and organic residues. Ecol Eng 2001;17:253–73.

Williamson MA, Rimstidt JD. The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. Geochim Cosmo-chim Acta 1994;58(24):5443–53.

Wirries DL, McDonnell AL. Drainage quality at deep coal mine sites. Water Res Bull 1983;19(2):235–40.

Wisotzky F. Assessment of the extent of sulfate reduction in lignite mining dumps using thermodynamic equilibrium models. Water Air Soil Pollut 1998;108(3–4):285–96.

Wisotzky F, Obermann P. Hydrogeochemie der Pyritoxidation am Beispiel des Rheinischen Braunkohlereviers, Tagungsband. Grundwassergüteentwicklung in den Braunkohlegebieten der neuen Länder; 1995. p. 167–83.

Wisotzky F, Obermann P. Acid mine groundwater in lignite overburden dumps and its prevention — the Rineland lignite mining area (Germany). Ecol Eng 2001;17:115–23.

Woelfl S, Tittel J, Zippel B, Kringel R. Occurrence of an algal mass development in an acidic (pH 2.5), iron and aluminum-rich coal mining pond. Acta Hydrochim Hydrobiol 2002;28:305–9.

Wolkersdorfer C, Bowell R, editors. Contemporary reviews of mine water studies in Europe, Part 1, vol. 23. Mine Water Environ 2004. p. 162–82.

Wollmann K, Deneke R, Nixdorf B, Packroff G. Dynamics of planktonic food webs in three mining lakes across a pH gradient (pH 2–4). Hydrobiologia 2000;433:3–14.

Wunderly MD, Blowes DW, Frind EO, Ptacek CJ. Sulfide mineral oxidation and subsequent reactive transport of oxidation products in mine tailings impoundments: a numerical model. Water Resour Res 1996;32(10):3173–87.

Yanful EK, Simms PH, Payant SC. Soil covers for controlling acid generation in mine tailings: a laboratory evaluation of the physics and geochemistry. Water Air Soil Pollut 1999;114(3–4):347–75.

Young JE. Mining the earth. Worldwatch Paper, vol. 109. Worldwatch Institute; 1992. 53 pp.

Younger PL. Minewater pollution: the revenge of old king coal. Geoscientist 1992;4(5):6–8.

Younger PL. The longevity of mine water pollution: a basis for decision making. Sci Total Environ 1997;194:457–66.

Younger PL, Robins NS, editors. Mine water hydrogeology and geochemistry, vol. 198. Geological Society of London, Geol. Soc. Spec. Publ.; 2002a. 396 pp.

Younger PL, Robins NS. Challenges in the characterization and prediction of the hydrogeology and geochemistry of mined ground. In: Younger PL, Robins NS, editors. Mine water hydrogeology and geochemistry, vol. 198. . Geological Society of London, Geol. Soc. Spec. Publ.; 2002b. 396 pp.

Yu JY. Precipitation of Fe and Al compounds from the acid mine waters in the Dogyae area, Korea: a qualitative measure of equilibrium modeling applicability and neutralization capacity? Aquat Geochem 1996;1:81–105.

Yu JY, Heo B, Choi I, Cho J, Chang H. Apparent solubilities of schwertmannite and ferrihydrite in natural stream waters polluted by mine drainage. Geochim Cosmochim Acta 1999;63(19/20):3407–16.