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REVIEW

Arsenic Geochemistry of Acid Mine Drainage

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Abstract Due to geochemical similarity between arsenic and sulphur, polymetallic sulphide deposits and pyrite/arsenopyrite-bearing coal beds often contain exceptionally high concentrations of arsenic. Arsenic release from mine waste occurs after oxidative dissolution of sulphide minerals. Both arsenite and arsenate forms coexist in many mine drainage localities, with the latter oxidation state more common. The rate of arsenite oxidation to arsenate in such environments is mostly controlled by the availability of oxygen and arsenic-oxidizing microbes. Most released arsenic gets naturally attenuated within few meters downstream by adsorption and co-precipitation; amorphous precipitates such as schwertmannite or hydrous ferric oxides are better sinks than crystalline counterparts, such as goethite and jarosite. Because arsenate has a stronger affinity than arsenite for sorbents at acidic pH, arsenate-dominated mine water often contains lower levels of arsenic than arsenite-dominated mine water. Secondary mineral precipitation is largely controlled by distribution of acid-neutralizing minerals, such as carbonates and aluminosilicates. In addition to natural attenuation, active and passive treatment of mine water can lower arsenic levels to meet legal limits.

Keywords Active versus passive treatment · Adsorption versus co-precipitation · Microbial attenuation · Mine tailings · Secondary precipitates

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Introduction

Arsenic (As) is a carcinogen and has been linked to skin, nerve, and digestive disorders (Mandal and Suzuki 2002). Inorganic As, in particular As^{3+}, has been shown to be the most carcinogenic (Smedley and Kinniburgh 2002). The oxidative dissolution of As-containing minerals, such as arsenical pyrite (FeS_2-As), arsenopyrite (FeAsS), realgar (As_2S_2), orpiment (As_2S_3), and cobaltite (CoAsS), and their presence as accessory phases in polymetallic deposits and in coal seams are the prime source of As in mine drainage. These minerals are normally stable under reducing conditions but can release As during chemical dissolution. Arsenic is a contaminant of concern in many mining districts and can cause problems downstream (Cheng et al. 2009; Williams 2001; Younger et al. 2005). Leaching of As is accelerated by microbial activities, e.g. by *Acidithiobacillus ferrooxidans* sp. (Baker and Banfield 2003). Romero et al. (2010) and Asta et al. (2010) reported more than 3,500 and 39,900 mg/kg As in mine wastes in Cuba and Spain, respectively. Up to 850 mg/L of As was reported in mine water from Iron Mountain, California (Druschel et al. 2004; Nordstrom and Alpers 1999a). Table 1 provides As concentrations at selected mine drainage localities.

Acid mine drainage (AMD) arises due to oxidative leaching of mine dumps or waste rocks. Centuries of historic mining activities have produced vast quantities of solid wastes, which were mostly abandoned untreated. Mine drainage discharges are serious environmental threats globally (Gemici 2008; Ravengai et al. 2005). For example, the Carnoulès mine, in France, generated about 1.5 Mt of solid waste rich in As and other contaminants that released >350 mg/L As, mainly as As^{3+}, and up to 7,500 mg/L of SO_4^{2-} (Elbaz-Poulichet et al. 2006). In severe AMD, Fe and SO_4^{2-} concentrations can reach up to 10,000 and 20,000 mg/L,

Table 1 Arsenic concentration variation in different acid mine drainage environments and associated stream or reservoir waters

AMD locality	pH	Source of As	As species in the aqueous media	As content (mg/L)	Nature of aqueous media	Sources
Mount Bischoff, Tasmania, Australia	~2.5	Arsenical pyrite/arsenopyrite	As^{5+}	2.5	Mine water	Gault et al. (2005)
Iberian pyritic belt, SW Spain	2.62–3.42	Arsenical pyrite/arsenopyrite	As^{3+} and As^{5+} ($As^{5+} > As^{3+}$)	2.2	Stream water	Asta et al. (2010)
Carnoulès mine, France	2.73–3.37	Arsenical pyrite/arsenopyrite	As^{3+} and As^{5+} ($As^{3+} > As5 +$)	350	Acid spring	Casiot et al. (2003b)
Gubong mine, Korea	6.5	Arsenopyrite	–	0.17	Flood plain GW	Woo and Choi (2001)
Enguialès mine, France	2.7	Arsenical pyrite, arsenopyrite	–	0.20	Stream water	Courtin-Nomade et al. (2005)
Pezinok mine, Slovakia	6.1–8.3	Arsenical pyrite/arsenopyrite	–	80.9	Mine tailing impoundment	Majzlan et al. (2007)
Mátra mountain mine, Hungary	~6.0	Arsenical pyrite	–	0.24	Mine water	Ódor et al. (1998)
Beatrice gold mine, Zimbabwe	~7.0	Arsenopyrite/arsenical pyrite	–	0.18	Dump tributaries	Ravengai et al. (2005)
Santa Lucia mine, Cuba	~2.5	Arsenical pyrite	–	0.30	Stream water	Romero et al. (2010)
						Marszatek and Wąsik(2000)
Zloty Stok mine, Poland	7.13–7.35	Lőllingite/arsenopyrite/pyrite/pyrrhotite	–	26.2	Mine adit	
Western Hunan mine, China	~7.0	Arsenical pyrites	–	16.5	River water	Lu and Zhang (2005)
Alaşehir Hg mine, Turkey	2.6–2.7	Arsenical pyrite	$As^{3+} \gg As^{5+}$	3.2	Mine water	Gemici (2008)
Sherridon tailing, Canada	~2.5	Arsenical pyrite, arsenopyrite	$As^{3+} \gg As^{5+}$	36	Mine tailing water	Moncur et al. (2009)
Carnoulès mine, France	3.4	Arsenical pyrite/arsenopyrite	$As^{3+} \gg As^{5+}$	205	Mine 1adit discharge	Egal et al. (2009)
Blackwater mine, New Zealand	~3.0	Arsenical pyrite/arsenopyrite	–	59	Wetland water near to mine adit	Haffert and Craw (2008)
Richmond mine, USA	0.83	Arsenical pyrite/arsenopyrite	–	187	Mine water	Druschel et al. (2004)
Carnoulès mine, France	1.2	Arsenical pyrite/arsenopyrite	$As^{3+} \gg As^{5+}$	12,137	Mine water	Casiot et al. (2003a)

Possible As-rich source contributing As into the aqueous media is mentioned. The concentration values show only the highest As content in the aqueous phase to get an overview of the As enrichment in the corresponding mine drainage affected localities. For detailed concentration ranges cited references can be referred

'–' represents data not avail; *GW* groundwater respectively (Kuyucak 2002). Although precise assessment of mine drainage pollution is impossible, Johnson and Hallberg (2005) estimated, based on 1989 available data, that 19,300 km of rivers and 72,000 ha of lakes and reservoirs are adversely affected by mine water effluents, worldwide.

Mine tailings containing hazardous elements are often isolated by dykes or retention dams. The breaching of such isolators can cause severe ecological disasters, such as in England, where breakdown of the Wheel Jane tin mine in 1992 contaminated the Carnon River and the Fal estuary (Younger et al. 2005), and in Spain, where the Aznallcollar mine tailings dam gave way (Achterberg et al. 1999).

The U.S. Environmental Protection Agency (USEPA) has assessed the use of monitored natural attenuation (MNA) techniques as a remediation strategy to control many inorganic contaminants, including As (Reisinger et al. 2005).

Understanding arsenic biogeochemistry is crucial in order to formulate treatment guidelines or elucidate its environmental hazards. Insights on As biogeochemistry around AMD-affected localities becomes extremely important because of its close association with sulphur, redox dynamics, and sensitivity to biogeochemical changes. The main objective of this review is to provide an overview of our current level of knowledge on arsenic biogeochemistry in AMD environments, its release mechanisms, redox thermodynamics, role of microorganisms, its interaction with secondary precipitates, mechanisms of attenuation, and treatment options.

Arsenic Release Mechanisms

Arsenic has a crustal abundance of 3 mg/kg (Smedley and Kinniburgh 2002). There are numerous As-bearing sulphide minerals; the ‘mindat’ online database lists more than 156 such minerals. The most important of these minerals at mine sites include arsenical pyrite (FeS_2-As), arsenopyrite (FeAsS), realgar (As_2S_2), orpiment (As_2S_3), cobaltite (CoAsS), engartite (Cu_3AsS_4), and tennantite [$(Cu,Ag;Zn,Fe)_{12}(As,Sb)_4S_{13}$]. Most of these minerals occur as hydrothermal vein or volcanic sublimates and are commonly associated with Cu–Zn-Fe–Pb-Ag-Au polymetallic deposits, while amorphous arsenic minerals precipitate near hot springs or along active hydrothermal systems (Lengke et al. 2009). Researchers have extensively reviewed the geochemistry of such mineral phases, including the amorphous As minerals, such as As_2S_3 and AsS (e.g. Drahota and Filippi 2009; Lattanzi et al. 2008; Lengke et al. 2009; Lowson 1982; Nordstrom 1982; Williamson and Rimstidt 1994). Therefore, the nature of individual minerals is not detailed in this article; instead, the broad geochemical processes that control As leaching in the AMD environment are summarised.

Abiotic Release Mechanisms

The oxidation reaction of arsenopyrite (FeAsS), which generates acidity and As in AMD, is shown in Eq. 1 (Dold 2005; Woo and Choi 2001). The generated Fe^{2+} quickly oxidizes to Fe^{3+} (Eq. 2) and the produced Fe^{3+} further acts as an oxidant, accelerating As release. At low pH (<3.5), As release is enhanced by both dissolved O_2 and Fe^{3+}, while at pH >3.5, Fe^{3+} is precipitated as insoluble $Fe(OH)_3$ (Eq. 3), minimizing its role in FeAsS oxidation (Walker et al. 2006; Yu et al. 2004, 2007). Excess protons may be generated during As^{3+} oxidation to As^{5+} by dissolved O_2 (Eqs. 4 and 5), but the reaction kinetics are extremely slow in normal environmental settings and generation of acidity is insignificant. Yu et al. (2007) demonstrated that the As release rate from FeAsS is directly influenced by increasing pH and temperature when dissolved O_2 is the sole oxidant. Arsenopyrite dissolution also follows an incongruent pattern where the secondary precipitates are crystalline ferric arsenates, such as scorodite ($FeAsO_4 \cdot 2H_2O$), amorphous ferric arsenates, ferric oxyhydroxides such as goethite, and hydrous ferric oxides with high As (Murciego et al. 2010). This process also introduces significant amount of As into the mine water. Oxidative dissolution of metal sulphides are generally exothermic reactions and can raise the interior temperature of mine waste pile up to 80 °C (Kuyucak 2002), which further increases reaction rates (Baker and Banfield 2003; Kuyucak 2002).

$$FeAsS + 3.25O_2 + 1.5H_2O \rightarrow Fe^{2+} + SO_4^{2-} + H_2AsO_4^- + H^+ \tag{1}$$

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \tag{2}$$

$$Fe^{3+} + 3H_2O \rightarrow FeOH_3 + 3H^+ \tag{3}$$

$$0.5As_2S_3 + 3.5O_2 + 3H_2O \rightarrow H_2AsO_4^- + 1.5SO_4^{2-} + 4H^+ \tag{4}$$

$$0.5As_2S_3 + 3.5O_2 + 3H_2O \rightarrow HAsO_4^{2-} + 1.5SO_4^{2-} + 5H^+ \tag{5}$$

Oxidative dissolution of arsenical pyrites follows a similar pathway as FeAsS, generating acidity, ferrous iron, ferrous iron oxidation, and final precipitation of ferric hydroxide phases. The structurally bound As or substituted fraction for S (and sometimes, possibly iron) in FeS_2 is released into the mine drainage (Eq. 6). Pyrite is the most abundant metal sulphide in earth’s crust (Moncur et al. 2009; Rimstidt and Vaughan 2003) but, based on the weatherability trend proposed by Moncur et al. (2009), arsenopyrite is more prone to dissolution than pyrite.

$$FeS_2 - As + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ + As^{3+}/As^{5+} \quad (6)$$

In contrast, because of the absence of Fe in orpiment (As_2S_3), its dissolution is controlled by dissolved O_2 (Eqs. 7 and 8). Its arsenic release rate with respect to pH and temperature is identical to arsenopyrite, and is normally triggered in carbonate-bearing horizons (pH >8) (Lengke and Tempel 2002). Besides the effects of pH and dissolved O_2 on As release (Al-Abed et al. 2007; Beauchemin and John Kwong 2007; Langmuir 1997; Štrbac et al. 2009), degrees of As redox changes have also been reported. For example, based on realgar and amorphous AsS oxidation reactions, Lengke and Tempel (2003) have proposed partial oxidation of As^{3+} to As^{5+} due to electron transfer (Eqs. 7–9) where intermediate sulphur species such as thiosulfate ($S_2O_3{}^{2-}$) and sulphite ($SO_3{}^{2-}$) can be generated. In a similar study, Lengke and Tempel (2001) showed that polythionates ($S_nO_6{}^{2-}$, n = 3, 4, 5, 6) are major intermediate sulphur species and up to 50 % of As^{3+} can be oxidized to As^{5+} during oxidation of amorphous As_2S_3 (Eqs. 10 and 11).

$$0.5As_2S_2 + 7H_2O \rightarrow H_3AsO_3 + HSO_4^- + 10H^+ + 9e^- \quad (7)$$

$$H_3AsO_3 + H_2O \rightarrow H_3AsO_4 + 2H^+ + 2e^- \quad (8)$$

$$AsS + 2.25O_2 + 2.5H_2O \rightarrow H_3AsO_3 + SO_4^{2-} + 2H^+ \quad (9)$$

$$As_2S_{3(s)} + \frac{(3n+15)}{2n}O_{2(aq)} + \frac{(3n+3)}{n}H_2O_{(aq)} \rightarrow 2H_3AsO_3^0 + \frac{3}{n}S_nO_6^{2-} + \frac{6}{n}H^+ \quad (10)$$

$$As_2S_{3(s)} + \frac{(5n+15)}{2n}O_2 + \frac{(3n+3)}{n}H_2O_{(aq)} \rightarrow 2HAsO_4^{2-} + \frac{3}{n}S_nO_6^{2-} + \frac{(4n+6)}{n}H^+ \quad (11)$$

where n is the number of sulphur ions.

The rate of oxidation is variable for different minerals and depends completely on the availability of oxidants such as dissolved O_2 and/or Fe^{3+} and aqueous pH. For example, the rate of As_2S_3 dissolution at highly alkaline pH (pH >13.5) is 6 to 8 orders magnitude higher in anoxic conditions than in the pH range 2.3–8.2 in oxic conditions, resulting in variable proportions of As^{3+}, As^{5+}, and thioarsenic compounds (Lengke et al. 2009). In a similar manner, biological dissolution is several orders faster than abiotic oxidation reactions. *A. ferrooxidans* can increase As-sulphide dissolution 2–6 times under similar conditions in their absence by acting directly as an oxidant and by oxidizing Fe^{2+} to Fe^{3+}, and thus further accelerating the dissolution process.

Role of Microorganisms on Arsenic Leaching

The most common bacterial species in acidic environments involved in oxidation of sulphide to sulphur belong principally to the genus *Thiobacillus, Leptospirillum, Sulfolobus, sulfobacillus*, *metallogenium*, and the colourless sulphur oxidizing bacteria, with *Thiobacillus* sp. being the dominant species (Baker and Banfield 2003; Harrison 1984; Kuyucak 2002; Wichlacz and Unz 1981). The prime role of this bacterial community, especially *A. ferrooxidans*, is to catalyze the oxidation of Fe^{2+} to Fe^{3+} (Eq. 2) and sulphide to sulphur (Eq. 12) and sulphate (Eq 14) that eventually generates acidity in form of protons (H^+) and sulphuric acid (H_2SO_4), respectively. Depending on the pH, the *Thiobacillus* sp. may differ in their genus distribution (Table 2), while *A. ferrooxidans* plays the most important role in iron and sulphur geochemistry in acidic mine waters (Baker and Banfield 2003; Harrson 1984). Other bacteria also contribute significantly to sulphide dissolution. For example, *L. ferrooxidans* sp. oxidizes Fe^{2+} to Fe^{3+} at temperatures > 20 °C, even though it is incapable of S oxidation (Kuyucak 2002). *Sulfolobus* sp. and *Sulfobacillus* sp. are thermophilic acidophiles and capable of oxidizing both Fe and S at pH 1–3 at temperatures between 50 and 90 °C (Kuyucak 2002).

$$CO_2 + 2H_2S \rightarrow 2CH_2O + 2S + H_2O \quad (12)$$

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \quad (13)$$

$$2CO_2 + H_2S + 2H_2O \rightarrow 2CH_2O + H_2SO_4 \quad (14)$$

Microbial activities act as strong catalysts for accelerating the leaching of As. Sulphide dissolution is intensified so that acid dissolution can increase more than 1,000 times (Williamson and Rimstidt 1994). Bacteria such as *A. ferrooxidans* or *L. ferrooxidans* facilitate mobilization due to direct physical contact with the As-bearing phases (e.g. FeAsS) in the direct mechanism (Eq. 1), while indirectly, they catalyse Fe^{2+} oxidation to Fe^{3+} (Eq. 2) and the latter acts as an oxidant for As release (Eq. 15) (Zhu 2010). Nordstrom and Alpers (1999b) showed that the microbially mediated rate of pyrite oxidation by ferric iron (Fe^{3+}) is two to three times faster than abiotic oxidation by O_2 at pH 2. Oxidation of Fe^{2+} serves as the rate-limiting step in

Table 2 Distribution of *Thiobacillus sp.* at different pH conditions

Thiobacillus sp.	pH
T. intermedius	1.9–7.0
T. thiooxidans	2.0–3.5
T. ferrooxidans (now *A. ferrooxidans*)	2.5–4.0
T. thioparus	7.0–8.5
T. denitrificans	7.0–8.5

biologically-mediated acid production as bioavailable organic carbon is almost negligible in acid drainage, and iron oxidizers compete with other bacterial species for O_2 and nutrients. This was shown by Zhu (2010) with arsenical pyrites of the Newark basin, in New Jersey, USA, where As release was seven times greater in bacterially-controlled reactors than abiotic release. The mobilization continued for ≈4 weeks, while As release stopped after only 2 days in abiotic sulphide exchange conditions (Zhu et al. 2008). Active bacterial leaching of As by *T. ferrooxidans* (which was subsequently renamed *A. ferrooxidans*) from sulfidic gold mine material was reported by Luong et al. (1985) in Alaska, USA, and Yukon, Canada.

$$FeS_2 - As + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ + As^{3+}/As^{5+} \quad (15)$$

Arsenic may be mobilized from arsenopyrite by reaction with hydrogen sulphide (HS^-) in the presence of dissolved oxygen (DO). This release process is thermodynamically more favourable ($\Delta G^0_{298} = -510$ kJ/mol) than release in the absence of dissolved sulphide ($\Delta G^0_{298} = -271$ kJ/mol) (Eqs. 16 and 17). Arsenic mobilization from FeAsS is also triggered by exchange with aqueous sulphide (Zhu et al. 2008). This sulphide-arsenide exchange reaction results in greater As release than normal O_2 oxidation reactions. Sulphate-reducing bacterial activity in the mine water further enhances these processes because of continuous production of sulphides (HS^-).

$$FeAsS + HS^- + H^+ + 1.25O_2 + 0.5H_2O \leftrightarrow FeS_2 + As(OH)_{3(aq)}, \Delta G^0_{298} = -510\text{kJ/mol} \quad (16)$$

$$FeAsS + 0.75O_2 + 1.5H_2O \leftrightarrow FeS + As(OH)_{3(aq)}, \Delta G^0_{298} = -271\text{kJ/mol} \quad (17)$$

Mine Tailings

Processing of sulphide-rich ores produces large quantities of pyritic wastes (Langmuir 1997; Marszatek and Wąsik 2000). Because of finer grain size (0.2 mm, Kuyucak 2002) and large surface area, a large portion of these tailings are exposed to the atmosphere. As-bearing minerals associated either with mine dumps or products from metallurgical sludge are the primary source of As in mine water. Physical weathering processes mainly drive the As-bearing mineral phases directly to the depositional site or the soil profile through mechanical transport, while chemical erosion leads to oxidative dissolution of the As-incorporated mineral phases, which subsequently move down-gradient as dissolved ionic As. Although physical weathering partly contributes to the overall As leaching processes, chemical leaching plays a crucial role through dissolution reactions (Ganne et al. 2006). Two chemical processes dominantly govern As mobilization: first, oxidation of As-bearing sulphide minerals such as $Fe(As, S)_2$ or FeAsS by oxidising agents such as atmospheric O_2 (Lengke et al. 2009) and second, dissolution/desorption of sorbed As from Fe-(oxyhydr)oxides due to changes in Eh and pH or the presence of $PO_4{}^{3-}$, $HCO_3{}^-$, and $HSiO_4{}^{3-}$ as competitive ions.

Mine tailings are characterized by three broad zones based on the degree of chemical weathering (Fig. 1). The top few centimetres (≈50 cm) are extremely active for weathering, for most biogeochemical processes are greatest at the water–sediment-air interface. This horizon is followed by an underlying intermediate zone of chemical leaching where the tailings are not directly exposed to the atmosphere but receive some oxygen from percolating surface water or the fluctuating water table. The bottom-most horizon remains water saturated much of the year, maintaining a relative uniformity in physico-chemical

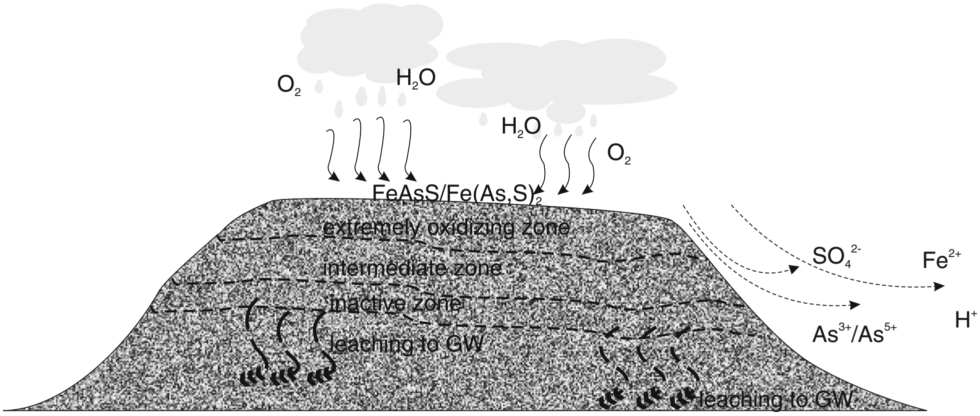

Fig. 1 A schematic diagram demonstrating the overview of geochemical processes takes place in mine tailing impoundments that eventually cause high concentrations of arsenic and acidity in mine drainage and surrounding aqueous media including stream waters. Soils and secondary precipitates also are rich in arsenic because of adsorption and/or co-precipitation

conditions (Lin 1997). The role of DO on As release has been observed in the Carnoulès mine, Gard, France (Casiot et al. 2003a) and is also related to seasonal variations. Between April and November, low DO availability causes relative low As in groundwater around impoundments compared to between January and March in the same borehole samples. The authors report 162 mM of As in January, but only 1.7 mM in October. Higher O_2 availability enhances the degree of FeS_2 weathering and hence, the release of As and acidity.

Release of As is greater under more acidic pH conditions. Lee et al. (2005) showed up to 4.2 % release at pH 1, but only 0.1 % at pH 5 from the same tailing samples (45 wt% As).

In many cases, mine tailings are covered with impermeable layers (discussed later) to reduce oxidation. However, failures of such barriers can shift the oxidation-dissolution reactions to the discharges of such piles, producing more than 12 g/L of As during wet seasons (e.g. Carnoulès, France, Elbaz-Poulichet et al. 2006).

The released fraction of As is usually quickly adsorbed by or co-precipitated with secondary precipitates, as previously discussed, but may still flow downstream as colloidal nanoparticles (<20–200 nm) of As-rich co-precipitates or As-sorbed precipitates (Majzlan et al. 2007; Slowey et al. 2007). Hence, relatively low As content in mine water (Table 1) in many scenarios is not surprising; it is completely dependent on the extent of secondary precipitates in the environment. On the other hand, in a few scenarios, even if the mine water pH is neutral (e.g. Pezinok, Slovakia), elevated As concentrations (up to 101 mg/L) have being reported (Majzlan et al. 2007). The As release might have occurred in acidic conditions after sulphide (FeS_2, FeAsS present in tailings) oxidation, while the neutral pH might have resulted from neutralization by carbonate minerals, as was observed at these tailing impoundments.

$H_n(AsO_3)^{n-3}$-$H_n(AsO_4)^{n-3}$ Redox Dynamics

Both organic and inorganic arsenic species are present in nature. Considering their lower toxicity and relative abundance, organic species such as monomethyl (MMA) or dimethyl (DMA) forms are of less concern than inorganic forms. Arsenite (As^{3+}) and arsenate (As^{5+}) are the most abundant and environmentally significant species of the four inorganic forms, i.e. +3, +5, 0, and −3. Both species undergo redox conversions when Eh–pH conditions change, or in the presence of microbial activity and mineral surfaces. Arsenic bound to AMD precipitates, mainly Fe-oxyhydroxides, exists either in reduced (i.e. As^{3+}) or oxidized (i.e. As^{5+}) form, depending on the geochemical conditions and activity of arsenic-oxidizing bacteria. Nevertheless, most research shows that the oxidized form, i.e. As^{5+}, is the most commonly observed state (Table 3). Gault et al. (2005) reports As^{5+} associated with hydrous ferric oxides (HFO) and jarosite 40 m downstream of a mine adit. Pentavalent As (As^{5+}) has a stronger affinity for Fe^{3+} minerals than trivalent As (As^{3+}) in acidic pH (Casiot et al. 2003a). Hence, in AMD environments, the oxidation state of As partly regulates the dissolved As fraction in mine water and the removal efficiency on precipitates, especially ferric (oxy) hydroxides/hydroxysulfates. In general, greater As concentrations occur in AMD environments when As^{3+} species is predominant (Table 1), possibly because of this As entrapment based on species distribution. Although As^{3+} oxidation kinetics to As^{5+} in abiotic condition is relatively slow, certain bacteria, such as *Thiomonas ynys1*, trigger As^{5+} formation and enhance its natural attenuation onto Fe^{3+} precipitates (Casiot et al. 2003b). Casiot et al. (2003b) reports such a scenario in the As^{3+} dominated Carnoulès mine, France, where As removal was minimal. After bacterially catalyzed oxidation of As^{3+} to As^{5+}, almost 75 % of the As was removed in the acidic pH conditions (pH 2.73–3.37, Table 1).

Fe-rich rims around sulphide minerals like FeS_2, FeAsS, or $FeSb_4S_6$ contain high amounts of As^{5+}. The As is bonded in both a bidentate binuclear and monodentate complex manner, with bond distances comparable to other Fe precipitates (Table 4). The nature of the precipitate is HFO type, with substantial amounts of Ca^{2+}.

The redox chemistry of As can also be influenced by climate. Morin et al. (2003) demonstrated that in the Carnoulès mine, As^{3+} is dominant during wet seasons, while As^{5+} is dominant in the dry season. The authors have proposed that Fe-oxidizing bacteria such as *A. ferrooxidans*, which can oxidize Fe^{2+} but not As^{3+}, dominate during the wet season, while the *Thiomonas* community actively oxidizes As^{3+} along with Fe^{2+} during the dry season, leading to incorporation of relevant As species onto ferric oxyhydroxide precipitates.

Role of atmospheric O_2 as an As^{3+} oxidant has been observed in numerous laboratory studies, with a general agreement of slow reaction kinetics when atmospheric O_2 is the only oxidant (Eary and Schramke 1990; Tallman and Shaikh 1980), though this gets accelerated by reactive mineral surfaces in heterogeneous media (Cheng et al. 2009). This has been observed in the Carnoulès mine tailings, where Casiot et al. (2003a) reported dominance of As^{3+} species (≥90 %) during summer, when availability of DO was relatively poor (<63 μM) compared to winter, with DO was considerably higher (>218 μM). This can also cause seasonal variations in As species distribution in mine water being controlled by O_2 levels in the As-containing aqueous media.

Table 3 Summary of arsenic species, As-O and As-Fe bonding distances and nature of bonding in the Fe^{3+} (oxy)hydroxide/hydroxysulfate precipitates around acid mine drainage affected environment

AMD locality	pH	Nature of precipitates	As species on the precipitates	Bonding distances (Å)		Nature of bonding	Sources
				As-O	As-Fe		
Mount Bischoff, Tasmania, Australia	~2.5	Jarosite and HFO	As^{5+}	1.69	3.28–3.30	Inner sphere bidentate complexes with HFO or FOH and substitution for SO_4^{2-} in jarosite	Gault et al. (2005)
Iberian pyritic belt, SW Spain	2.93–3.42	Schwertmannite, HFO, jarosite, goethite	As^{5+}	1.68	3.30–3.32	Substitution for SO_4^{2-} in jarosite and schwertmannite and inner sphere bidentate complexation with FOH	Asta et al. (2010)
Pezinok Sb mine, Slovakia	~7.0	HFO	As^{5+}	1.70	3.32	Bidentate binuclear and monodentate complexes	Majzlan et al. (2007)
Carnoulès mine, France	3.4	Schwertmannite, tooeleite, jarosite	As^{3+}	–	–	–	Egal et al. (2009)
Carnoulès mine, France	3.4	Schwertmannite	As^{5+}	–	–	–	Egal et al. (2009)
Sulphur bank mine, USA	~3.0	Alunite, jarosite	As^{5+}	–	–	–	Slowey et al. (2005)

GW groundwater, *HFO* hydrous ferric oxides, *FOH* ferric oxyhydroxides

'–' represents data not available

Table 4 Brief overview of arsenic concentrations in solid precipitates around selected acid mine drainage affected localities in different countries, pH of the aqueous media from which precipitates appear, and mineralogical character of the precipitates

AMD locality	As content in solid phase (mg/kg)	pH	Nature of solid phase	Source
Kumho mine, Korea	67,336	~7.0	Quartz, kaolinite, jarosite, ferric hydroxide, pyrite	Lim et al. (2009)
Western Hunan mine, China	4.7–17.2	~ 7.0	Clayey shales/slates, carbonaceous rock	Lu and Zhang (2005)
Western Hunan mine, China	64.2–496.2	~ 7.0	Paddy carbonaceous soil	Lu and Zhang (2005)
Alaşehir Hg mine, Turkey	1,164	~2.6	Mine waste piles	Gemici (2008)
Alaşehir Hg mine, Turkey	999	~2.6	Stream sediment	Gemici (2008)
Erzgebirge mountains, Czech Republic	650,000	~1.0	Mine mill dumps	Filippi (2004)
Erzgebirge mountains, Czech Republic	13,622	~1.0	Fine sandy soil with clays and humus material	Filippi (2004)
Angleur mine, Belgium	903	~8	Arsenopyrite, smythite (Zn milling slag dump)	Ganne et al. (2006)
Seobo W mine, Korea	360,000	3.2–1.4	Fe^{3+}-oxyhydroxide rims around FeS_2	Lee et al. (2005)
Seobo W mine, Korea	310,000	3.2–1.4	Fe-As amorphous rims around FeAsS	Lee et al. (2005)
Seobo W mine, Korea	14,400	6.0	Contaminated soil	Lee et al. (2005)
Sherridon tailings, Canada	53,000	~2.7	Fe^{3+}-rich rims around FeS_2	Moncur et al. (2009)
Sherridon tailings, Canada	71,000	~2.7	Fe^{3+}-rich rims around FeAsS	Moncur et al. (2009)
Pezinok mine, Slovakia	294,200	6.1–8.3	Fe^{3+}-rich rims around $FeAsS/FeS^2$	Majzlan et al. (2007)
Enguialès mine, France	2,268	2.7	Ochreous precipitates (schwertmannite, goethite, HFO)	Courtin-Nomade et al. (2005)
Nevada Cu mine waste, USA	471	3.1	Silicates, hematite, organic matter	Al-Abed et al. (2007)
Mount Bischoff, Tasmania, Australia	12,700	~2.5	HFO, jarosite	Gault et al. (2005)
Iberian pyritic belt, SW Spain	39,900	2.62–3.42	Jarosite, goethite, schwertmannite	Asta et al. (2010)
Blackwater mine, New Zealand	400,000	~3.0	Pyrite, arsenopyrite, clays (mine tailings)	Haffert and Craw (2,008)
Sulfurbank mine, USA	74.3	~3.0	Pyrite, alunite, jarosite	Slowey et al. (2007)

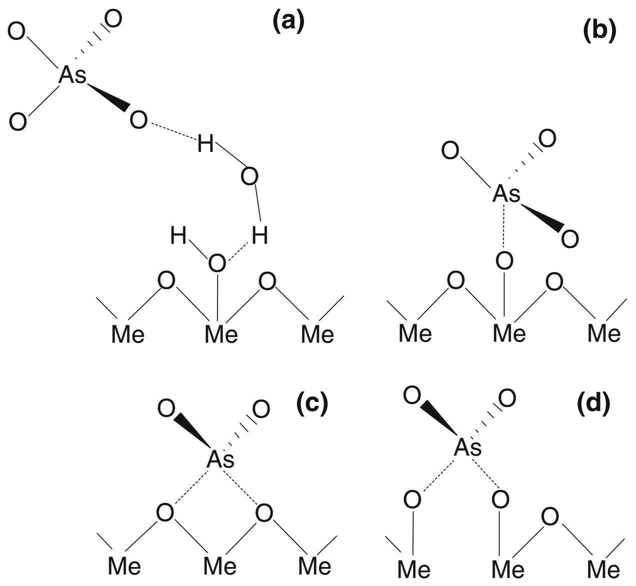

Fig. 2 A schematic diagram shows nature of bonding of arsenic in metal (dominantly Fe^{3+} in AMD) oxyhydroxide/hydroxysulfate precipitates. **a** outer sphere complexes, **b** monodentate mononuclear inner sphere complexes, **c** bidentate mononuclear inner sphere complexes, **d** bidentate binuclear inner sphere complexes. Me represents 'metal' (after Cheng et al. 2009)

Extended X-ray absorption fine structure (EXAFS) studies show the binding nature of As^{3+}/As^{5+} with Fe^{3+} and O in the ferric hydroxide precipitates. The As-O and Fe-As bond distances vary slightly, presenting an almost identical bonding nature (Table 3). The As^{3+}/As^{5+} bond as inner sphere bidentate complexes or substitute for SO_4^{2-} in jarosite and schwertmannite (Gault et al. 2005). Similar findings were also reported from the Iberian pyritic belt, in Spain, with a predominant pentavalent state of As on Fe precipitates, while both As^{5+} and As^{3+} states are present in the mine water (Asta et al. 2010). The dominance of As^{5+} in the solid phase can be explained by both oxidation of As^{3+} to As^{5+} and subsequent adsorption of As^{5+} and/or adsorption of As^{3+} followed by oxidation in the solid phase. However, insufficient oxidation of As^{3+} has been seen in mine precipitates (e.g. Carnoulès mine, France, Egal et al. 2009) in As^{3+} dominated (91 %) mine water. Majzlan et al. (2007) report that As^{5+} can coexist with As^{3+} in the same mineral phase (i.e. HFO). As^{3+} oxidation on the solid phase or leaching of As^{3+} into mine water and subsequent oxidation to As^{5+} and co-precipitation with Fe^{3+} might explain this coexistence. A clear distinction between these processes is not possible.

Courtin-Nomade et al. (2005) report that the fraction of dissolved As decreased from ≈195 to ≈7 μg/L immediately downstream of the mine water adit, which is in accordance with the greater association of As with amorphous phases such as schwertmannite than the more crystalline ferric oxides, such as goethite and jarosite, which schwertmannite transforms into with time.

Natural Attenuation Processes

Arsenic leached due to oxidation processes can reach concentrations up to several hundred milligrams per litre of both As^{3+} and As^{5+}, depending on As enrichment in waste piles, hydrogeochemical conditions, or microbial activities. For example, Bruneel et al. (2006a) reported >430 mg/L As in Carnoulès AMD, France, while Woo and Choi (2001) reported only 0.17 mg/L As in the Gubong mine drainage, Korea. However, in most cases, the leached fractions decrease below permissible limits by natural processes due to interaction with the precipitated minerals during the course of down-gradient migration; of particular importance is the precipitation of Fe^{3+} minerals. Secondary Fe^{3+}-oxyhydroxides commonly precipitate immediately after dissolution of sulfide minerals. Before leaching into the aqueous media, most of the released As is trapped by these secondary products within the mine tailings, occupying the micro-fractures of tailings and/or form as outer rims around primary sulfidic minerals, such as FeS_2 or FeAsS (Lee et al. 2005; Majzlan et al. 2007). Although aluminosilicates and clay minerals constitute the major mineralogy along the flow path, their relative low affinity towards potentially toxic elements (PTE) compared to secondary Fe^{3+}-minerals, make them less significant in attenuation. Principally, four natural attenuation processes generally act together to govern mine water As fate and mobility: (1) sorption onto solid media, e.g. onto iron (hydr)oxides (Asta et al. 2010; Carlson et al. 2002; Choi et al. 2009; Fukushi et al. 2003); (2) complexation or co-precipitation with secondary precipitates, e.g., precipitation of scorodite ($FeAsO_4 \cdot 2H_2O$), toeilleite ($Fe_6(AsO_3)_4$-$SO_4(OH)_4 \cdot H_2O$), or pitticite ($FeSO_4As_2O_5 \cdot H_2O$) (Haffert and Craw 2008a, 2008b; Morin et al. 2003); (3) microbially induced removal, e.g., activity of *A. ferrooxidans* (Bruneel et al. 2006b; Cassiot et al. 2003a, 2003b), and; (4) dilution by drainage water intermixing, e.g., tributary water mixing with the Reefton gold mine water discharge, New Zealand (Haffert and Craw 2008a, , b).

Binding of As onto these mineral surfaces take place through both inner sphere and outer sphere pathways, which affects the strength of the bond between the As and mineral sites (Fig. 2). Breaking of inner sphere bonding is commonly more difficult and limits mobilization, even when geochemical conditions change.

A(d/b)sorption Processes

Adsorption and/or absorption processes, which occur together in AMD environments, are the primary mechanisms by which As is naturally eliminated from mine discharges. Secondary minerals such as Fe-oxides, hydroxides, or oxyhydroxysulfates, which are primarily produced through dissolution-precipitation processes, have a strong retention affinity for arsenic because of their relatively high surface area and surface reactivity. Other potential natural sorbents include zeolite (Payne and Abdel-Fattah 2005), alumina (Lin and Wu 2001), and natural organic matter (Paikaray et al. 2005). Vermiculite, smectite, and/or illite-type clay minerals have been reported to form during weathering of aluminosilicates (Lin 1997). Although other clay minerals are common around mining districts and carry highly charged surface sites for metal complexation, As retention by these minerals is less significant than the Fe-minerals.

Schwertmannite is the most common and abundant Fe-mineral precipitated in acidic mine water (pH 3.0–4.5, Bigham et al. 1990) in the presence of high dissolved sulphate (≈3,000 mg/L) through bacterial oxidation (e.g. *A. ferrooxidans*) of leached Fe^{2+} from waste dumps to Fe^{3+}. Schwertmannite precipitation removes major fractions of leached As from the aqueous phase by ionic exchange with solid phase SO_4^{2-} (Carlson et al. 2002; Roman-Ross et al. 2010), which as a consequence, increases the SO_4^{2-} loading in stream flows (Paikaray and Peiffer 2010). High surface area (>200 m^2/g, Bigham et al. 1990; Childs et al. 1998) and highly amorphous nature facilitate considerable trapping of As. Fukushi et al. (2003) demonstrated that schwertmannite and goethite are the prime scavengers of As, removing up to 255 µg/L within 200 m downstream of mine tailings, enriching As^{5+} in these precipitates by up to 61 mg/g. Other potential As scavengers in mine drainage areas include ferrihydrite ($Fe(OH)_3$), which is often present as an intermediate product of schwertmannite transformation to goethite (Peretyazhko et al. 2009), and has been demonstrated to have a higher As retention affinity due to its higher surface area (Carlson et al. 2002). Romero et al. (2010) found that presence of hematite (Fe_2O_3), goethite (FeOOH), or magnetite (Fe_3O_4) in mine water can substantially reduce As content in schwertmannite-absent localities. Goethite and/or jarosite formed during mineralogical transformation of schwertmannite are dominant secondary phases downstream of mine discharges and also can act as potential scavengers of mine water As (Asta et al. 2010). Approximately 40 g/kg of As (Table 4) was associated with schwertmannite, goethite, and jarosite, with the highest fraction often sorbed to schwertmannite, relative to jarosite and goethite.

In many mine tailings, the low pH pore waters in the extreme oxidized horizon (i.e., the top few centimetres, Fig. 1) mobilizes metals, especially Fe^{2+} and Al^{3+}, along with more toxic elements such as As. Presence of carbonated aquifers in such acidic environments raises the pore water pH to near neutral, which, as a consequence, can cause precipitation of Fe-oxyhydroxides a few centimetres below the ground. During $Fe(OH)_3$ precipitation, As get trapped and confined in such a horizon (Haffert and Craw 2008a, 2008b; Woo and Choi 2001). As the pH starts increasing, secondary minerals precipitate, further buffering the pH, in addition to acting as sinks for As. A schematic plot shows the commonly observed pH buffering AMD precipitates (Fig. 3). The Fe-precipitates form an impermeable hardpan layer, restricting not only O_2 diffusion, but further migration of As downwards, hence playing a major role in natural attenuation processes within the tailings pile (Lin 1997; Ódor et al. 1998). Moncur et al. (2009) demarcated such hardpans into two distinct

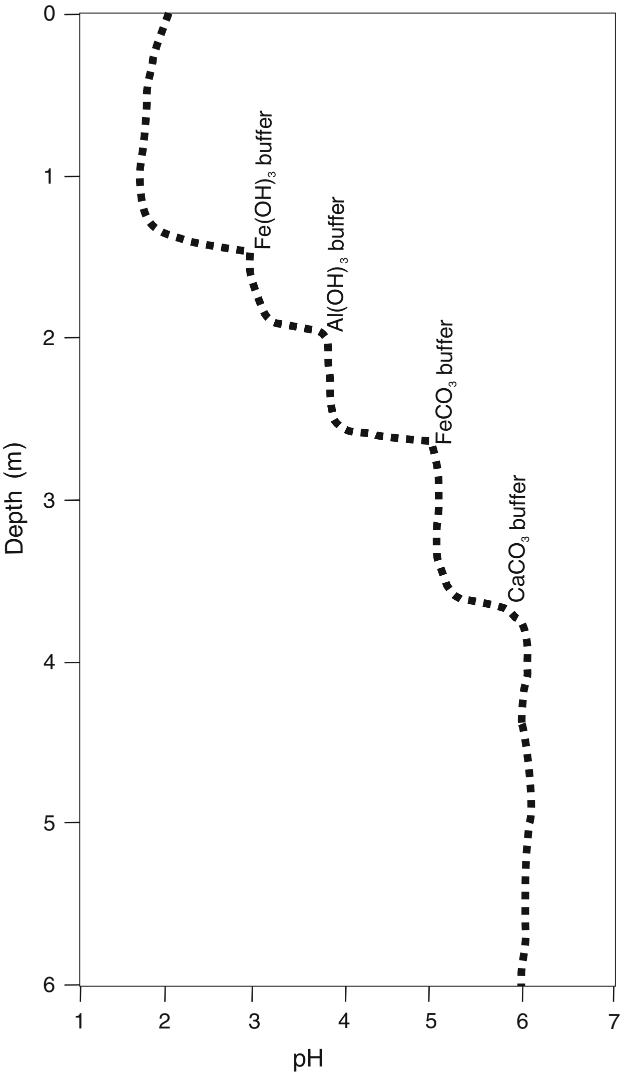

Fig. 3 A schematic representation of development of pH buffering zones in tailing impoundments with respect to depth of respective pile after oxidative dissolution of sulfide minerals and subsequent precipitation of secondary products

horizons; the top few centimetres (<10 cm), where active oxidation results in precipitation of Fe^{3+} minerals, is distinctly different than the underlying massive (>1 m thick) compact horizon, which is dominantly Fe^{2+} minerals, such as rozenite ($FeSO_4 \cdot 4H_2O$), melanterite ($FeSO_4 \cdot 7H_2O$), and gypsum ($CaSO_4 \cdot 2H_2O$). Arsenic concentrations below this hard pan are almost negligible. Moncur et al. (2009) reports such a scenario from the Sherridon tailings, Canada where As concentrations are almost zero below the hardpan, while above it, As concentrations were ≈40 mg/L.

Co-precipitation

Co-precipitation normally occurs together with sorption and it can be difficult to differentiate between these two processes in natural settings. Sorption reactions predominate at low aqueous As concentrations whereas surface precipitation is facilitated at higher aqueous concentrations. Although sorption reactions is responsible for most arsenic retention from mine drainage (e.g. Fukushi et al. 2003), arsenic incorporation is partly controlled by formation of Fe-OH-As or Fe–S-OH-As surface precipitates (Carlson et al. 2002; Paikaray et al. 2011; Sarmiento et al. 2009). The formation of such additional poor crystalline phases are normally favoured at higher As/(As + S) molar ratios. Arsenic can also incorporate within Fe–O–H structures, forming a stable insoluble product along with other toxic elements, e.g., Pb and As precipitation in Santa Lucia mine, Cuba (Romero et al. 2010) producing an insoluble precipitate in acidic mine waters. The binding of As during co-precipitation of such compounds resist susbsequent As mobilization. The higher As leached in many AMD discharges are trapped by precipitation of scorodite. Precipitation of such minerals is reported in several AMD areas (e.g. Flemming et al. 2005; Haffert and Craw 2008a, b; Slowey et al. 2007). Iron is released in a reduced oxidation state (Fe^{2+}) during sulphide oxidation (Eqs. 1 and 6), is rapidly oxidized to Fe^{3+} within a few meters downstream, and is eventually removed by Fe^{3+}-mineral precipitation. The dissolved As (either As^{3+} or As^{5+}) form strong complexes or nano-crystaline precipitates during Fe^{3+} precipitation. High As^{3+}-rich mine waters such as Carnoulès, France (Egal et al. 2009; Morin et al. 2003) or Sherridon, Manitoba (Moncur et al. 2009) produce nano-cyrystaline As^{3+}-$SO_4{}^{2-}$-Fe^{3+} mineral precipitates, e.g. tooeleite (Egal et al. 2009; Morin et al. 2003). Because of weaker partitioning of As^{3+} than As^{5+} on Fe-precipitates, As^{3+} content on these solid phase is relatively low compared to As^{5+} (Morin et al. 2003). Morin et al. (2003) reported about >350 mg/L As^{3+} being removed by tooeleite precipitation within 30 m downstream and that this processes is catalysed by bacterial activity. Arsenate-dominated mine waters also form such amorphous precipitates of ferric arsenate type or Fe^{3+}-As-OH (Carlson et al. 2002; Egal et al. 2009; Morin et al. 2003). The nature of As bonding with As^{5+} differs, with inner-sphere bidentate complexes forming during As^{5+} co-precipitation with schwertmannite and inner-sphere monodentate complexes responsible for As^{5+} adsorption onto previously precipitated schwertmannite (Fernández-Martinez et al. 2010; Roman-Ross et al. 2010).

In addition to co-precipitation of As on Fe^{3+} precipitates from the mine water, Majzlan et al. (2007) reports Fe-rich weathering rims around the original mineral, e.g. pyrite, arsenopyrite, and berthierite ($FeSb_2S_4$). These rims also act as sinks for As released by sulphide oxidative dissolution, even if As is not present in the original mineral, e.g. $FeSb_2S_4$. Because of Fe-enrichment in these rims, As from mine water can co-precipitate with Fe^{3+} by virtue of its strong affinity, leading to solid phase enrichment up to 30 wt% (Majzlan et al. 2007). Lee et al. (2005) reports up to 36 wt% As in amorphous Fe^{3+} precipitates formed around FeS_2 with only 0.7–0.8 wt% As. The total As in the secondary phases is likely contributed from As-rich primary minerals such as FeAsS (45 wt% As) occurring in the same tailings. This is consistent with studies by Moncur et al. (2009) who report 5.3 and 5.6–7.1 wt% As_2O_5 on the rims around FeS_2 and FeAsS, respectively, in tailings in Manitoba, Canada.

Other co-precipitated secondary minerals include jarosite ($KFe_3(SO_4,AsO_4)(OH)_6$) (Savage et al. 2005), alunite ($KAl_3(SO_4,AsO_4)_2(OH)_6$) (Slowey et al. 2007), pharmaco siderite ($K_2Fe_4(AsO_4)_3(OH)_5 \cdot 6H_2O$) (Morin et al. 2002), and arseniosiderite ($Ca_2Fe_3(AsO_4)_3 \cdot 3H_2O$). Precipitation of these secondary products is strongly controlled by hydrogeochemical conditions and As:cation ratios in the drainage water (Slowey et al. 2007).

Microbial Removal

Microbial removal of As proceeds in two ways (Bruneel et al. 2006b) in AMD environments: (1) microbial oxidation of As^{3+} to As^{5+}, and 2) oxidation of Fe^{2+} to Fe^{3+}. In the first scenario, As^{5+} is less toxic than As^{3+} (Smedley and Kinniburgh 2002) and has a better sorbing potential to Fe-oxyhydroxides than As^{3+} in acidic conditions (Sadiq 1997). In the second scenario, because of elevated Fe concentrations, iron-oxidizing bacteria such as *A. ferrooxidans* and *Leptospirillum ferrooxidans* grow in AMD environments (Baker and Banfield 2003), which catalyse Fe^{2+} oxidation and facilitates ferric hydroxide precipitation. These precipitates act as major sinks for As (Casiot et al. 2003b; Morin et al. 2003). Both processes occur together in AMD environments, as reported from Carnoulès mine, France (Bruneel et al. 2006a, 2006b; Casiot et al. 2003a) where Fe^{3+}-As^{3+} oxyhydroxide (tooeleite)

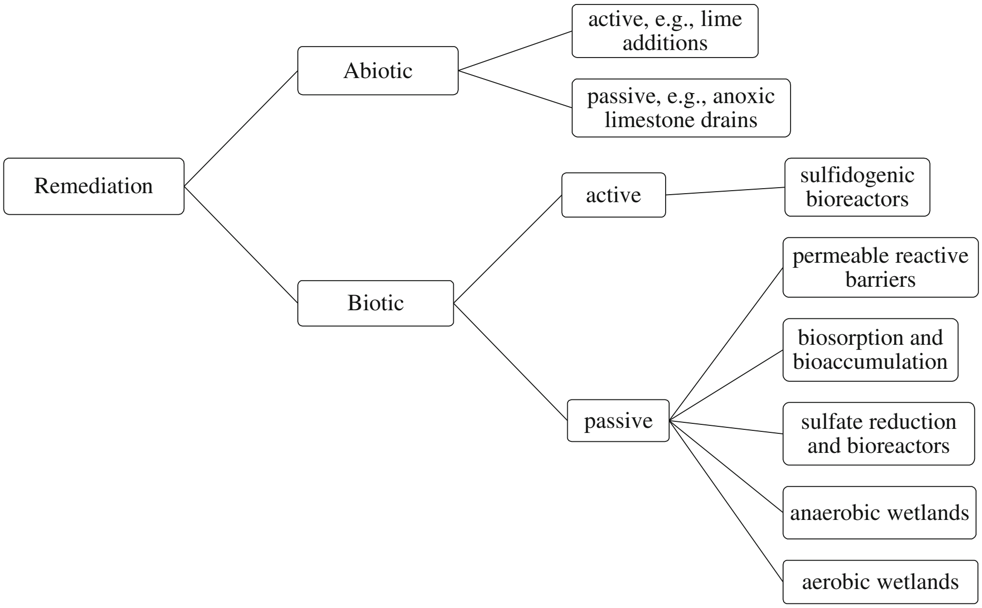

Fig. 4 Commonly adopted treatment techniques for remediation of acid mine hazards including arsenic contamination (modified after Johnson and Hallberg 2005)

precipitation is favoured in winter, while Fe^{3+}–As^{5+} is favoured in summer (Bruneel et al. 2006a), due to the activity of both *A. Ferrooxidans* and *Gallionella ferruginea*. *T. ynysl* also grow there, catalyzing As oxidation and As retention by the Fe minerals (Casiot et al. 2003b).

Bacterially-catalysed Fe^{2+} oxidation can be a major factor controlling precipitation of Fe^{3+} precipitates. For example, Egal et al. (2009) showed that slow oxidation of Fe^{2+} favoured formation of tooeleite, while relatively rapid oxidation favoured schwertmannite formation. In both cases, significant amounts of As, mainly As^{3+}, was co-precipitated from the mine water, resulting in almost negligible As about 150 m downstream of the adit.

Stream Water Dilution

Dilution of acid mine effluents mainly occurs by three physical processes: (1) dilution by natural drainage such as rainfall or glacial melting, (2) dilution by tributaries (Yu and Heo 2001), and (3) groundwater base flow (Fillpek et al. 1987). Lowering of As concentrations by the first process is insignificant in most cases, while tributaries carrying almost As-free water can dilute As levels dramatically. Haffert and Craw (2008a, b), reported such As dilution at the Reefton gold mine in New Zealand. In well-saturated areas, the water table is likely to be very close to the surface, hence causing base flow or discharges into the flowing stream. Fillpek et al. (1987) reported that base flow and an undetected seep dramatically lowered dissolved metal concentrations where no visibly remarkable Fe-precipitate was present.

Another major pathway of natural attenuation takes place at the surface- and groundwater intermixing zones (called hyporheic zones). Contamination attenuation dynamics in this zone was excellently reviewed by Gandy et al. (2007). Understanding the complex biogeochemistry in this zone merits attention because of its contribution to contaminant elimination by sorption, precipitation, biodegradation, and dilution, during groundwater recharge-discharge processes. Frequent switching of redox zonation caused by dry and wet seasons result in precipitation and dissolution of environmental minerals or growth of specific microorganisms that eventually govern overall metal remediation.

Treatment Techniques

One or all of the above discussed natural attenuation processes act together in most AMD environments, efficiently reducing dissolved As levels below regulatory standards. However, the degree and extent of such processes solely depend on the abundance of sorbing media and geochemical conditions. Therefore, numerous treatment methods have been adopted to decrease dissolved As levels to below threshold values. Akcil and Koldas (2006), Costello (2003), Johnson and Hallberg (2005) and Kuyucak (2002) have summarized such processes; the salient techniques are discussed below and listed in Fig. 4.

Abiotic Techniques

Johnson and Hallberg (2005) discussed several preventive AMD generation procedures: (1) flooding or sealing of underground mines; (2) underwater storage of mine tailings; (3) land based storage in sealed heaps; (4) blending of mineral waste; (5) total solidification of tailings; (6) application of anionic surfactants; and (7) microencapsulation. None of these techniques are typically 100 % effective. For example, underwater submergence, although considered a cost effective technique to reduce acid generation, can cause the release of metals like Pb and Zn if organic material is also present (Kuyucak 2002). Clay capping, which is widely used in several countries, can be affected adversely by cracking during wet and dry periods. Such a scenario has been reported by Filippi (2004) from the Erzgebirge mountains, Czech Republic where destruction of concrete bunker enclosing ≈65 wt% As rich mine mill caused soil As enrichment as high as 13,622 mg/kg within 1.5 m downstream. Numerous attempts have been made to stop AMD production by applying chemicals such as phosphates (e.g., apatite) to precipitate ferric phosphate, hence, reducing Fe^{3+} efficiency as an oxidant (Evangelou 1998) or injection of anionic surfactants such as Na-dodecyl sulphate to reduce the activity of iron-oxidizing species such as *A. ferrooxidans* that catalyze sulphide oxidation. The latter approach has been cost-effective at some sites, most notably in treating coal preparation (washing) reject material (Kleinmann and Erickson 1983; Kuyucak 2002; Loos et al. 1989; USEPA 1995).

However, since none of these techniques are typically 100 % effective, some water treatment is usually necessary. The most commonly used treatment techniques are broadly categorised as active and passive. Active techniques require continuous monitoring of treatment processes. Lime, Ca- or Na-carbonate, or Na- or Mg-hydroxides are normally used to raise the mine water pH (Johnson and Hallberg 2005). The ferric oxyhydroxide precipitates formed at such pH conditions act as potential scavengers for As. However, such treatment techniques have high chemical and maintenance costs. In contrast, passive methods, which use natural and constructed wetlands as remediation tools and have relatively low maintenance costs (Johnson and Hallberg 2005), but usually require a great deal of land area and are not usually applicable to extremely acidic water or high acid loads. Limestone dissolution is usually used to raise the pH, with various approaches used to keep the limestone from getting armoured (Kleinmann et al. 1998; Watzlaf et al. 2004).

Biotic Techniques

Microorganisms play an important role in As removal processes, by raising the net alkalinity through sulphate reduction, denitrification, and methanogenesis. Microbial reduction of Fe- and $SO_4{}^{2-}$ produces net alkalinity and precipitation of metal sulfides has special significance in AMD neutralization processes. Photosynthetic microorganisms use weak bases (e.g., $HCO_3{}^{-}$) and produces strong bases (OH^{-}), neutralizing acidity (Eqs. 18–20).

Acidophilic heterotrophic bacteria such as *Acidiphilium* sp. play a passive role by metabolising organic matter those are toxic to iron oxidizing bacteria and inhibiting biologically mediated iron oxidation (Johnson 1995; Kuyucak 2002). Metabolism of certain heterotropic bacteria such as *Pseudomonas*, *Clostridium*, and *Desulfovibrio* can reduce manganese and iron (e.g., Eq. 21) by using them as electron acceptors under anaerobic conditions (Kuyucak 2002). Once Fe^{3+} is converted to Fe^{2+}, its removal is facilitated by interaction with sulphides produced by sulphate reduction and generating additional alkalinity. Sulphate reduction adds alkalinity to AMD once H_2S gas released from mine waste environment.

Microbial Reduction

$$SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2H_2CO_3 \tag{18}$$

$$Me + H_2S \rightarrow MeS + 2H^+ \tag{19}$$

$$6HCO_3^- + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 + 6OH^- \tag{20}$$

$$Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O \tag{21}$$

Such bioremediation processes are relatively inexpensive but can be less predictable than more conventional chemical techniques. Microbial oxidation of Fe^{2+} to Fe^{3+} is widely known, removing As on Fe precipitates (Kuyucak 2002). The sludge produced during treatment steps are followed by addition of adequate flocculant to promote aggregation of precipitates that are subsequently removed in settling ponds. Other major biological treatment processes include compost bioreactors, permeable reactive barriers, and composite aerobic and anaerobic reactors (Costello 2003).

Conclusions

Arsenic pollution in AMD localities draws special attention worldwide, due to its chronic toxicity and very low tolerance limits (10 µg/L). Because of its close geochemical resemblance to sulphur, almost all metal sulphide mines and coal deposits are enriched with variable amounts of As, either via S replacement or solid solution. Oxidative dissolution of these As-rich sulphides can generate environmentally toxic levels of As in mine water. The degree of dissolution and hence, arsenic generation is governed by many factors, including DO, aqueous pH, and the activity of iron-oxidizing bacteria. In oxygen-deficient environments, dissolved Fe^{3+} generated by both abiotic and biotic processes control the rate of arsenic release; acidity generation by Fe^{3+} is commonly several orders greater than that by only oxygen. Certain microbes, e.g. *A. ferrooxidans* sp., accelerates sulphide dissolution and hence, arsenic release.

Both arsenite and arsenate species are found in AMD localities. Their distribution is controlled by hydrogeochemical conditions and the availability of arsenic-oxidizing bacteria. However, prolonged exposure to atmospheric oxygen and ferric iron mineral surfaces often leads to the predominance of arsenate species in most mine drainage. Arsenic-oxidizing bacteria, such as *T. ynysl*, trigger arsenate formation in aqueous media and ultimately on secondary precipitates. Sometimes, because of inefficient oxidizing potential of microbes, arsenite-rich ferric precipitates occur, e.g. Carnoulès mine, France.

Adsorption of released arsenic on secondary precipitates and co-precipitation are the prime processes controlling natural arsenic attenuation. Availability of acid-neutralizing minerals around mine tailings impoundments facilitates pH buffering and precipitation of secondary products from mine drainage. Active and passive mine water treatment techniques are used at severely contaminated sites where natural attenuation processes cannot sufficiently lower arsenic levels to threshold limits.

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