Review

Geochemical processes controlling fate and transport of arsenic in acid mine drainage (AMD) and natural systems

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ABSTRACT

Acid mine drainage (AMD) is often accompanied with elevated concentrations of arsenic, in the forms of arsenite, As(III), and/or arsenate, As(V), due to the high affinity of arsenic for sulfide mineral ores. This review summarizes the major geochemical processes controlling the release, speciation, fate, and distribution of inorganic arsenic in mine drainage and natural systems. Arsenic speciation depends highly on redox potential and pH of the solution, and arsenite can be oxidized to the less toxic arsenate form. Homogeneous oxidation of arsenite occurs rather slowly while its heterogeneous oxidation on mineral surfaces can greatly enhance the reaction rates. Little evidence suggests that precipitation reaction limits the concentrations of arsenic in natural water, while co-precipitation may lead to rapid arsenic removal when large amount of iron hydroxides precipitate out of the aqueous phase upon neutralization of the mine drainage. Both arsenate and arsenite adsorb on common metal oxides and clay minerals through formation of inner-sphere and/or outer-sphere complexes, controlling arsenic concentration in natural water bodies. Arsenite adsorbs less strongly than arsenate in the typical pH range of natural water and is more mobile. Part of the adsorbed arsenic species can be exchanged by common anions (e.g., PO_4^{3-} and SO_4^{2-}), especially phosphate, which leads to their re-mobilization. Understanding the geochemistry of arsenic is helpful for predicting its mobility and fate in AMD and natural systems, and for designing of cost-effective remediation/treatment strategies to reduce the occurrence and risk of arsenic contamination.

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Contents

1. Introduction

Arsenic ranks 20th among the most abundant elements in the earth's crust, and it is associated with igneous and sedimentary rocks, particularly with sulfidic ores [1]. Chemically, arsenic is very similar to its predecessor, phosphorus, and it can partially substitute for phosphorus in biochemical reactions. Arsenic is toxic to plants and soil biota [2]; in humans, chronic exposure to inorganic arsenic can cause skin, lung, liver, bladder, and kidney cancers [3–5]. Arsenite, As(III), is generally considered to be more acutely toxic than arsenate, As(V) [6], and is also more potent than arsenate in chronic toxicity [7–9]. Arsenite is more difficult to be removed
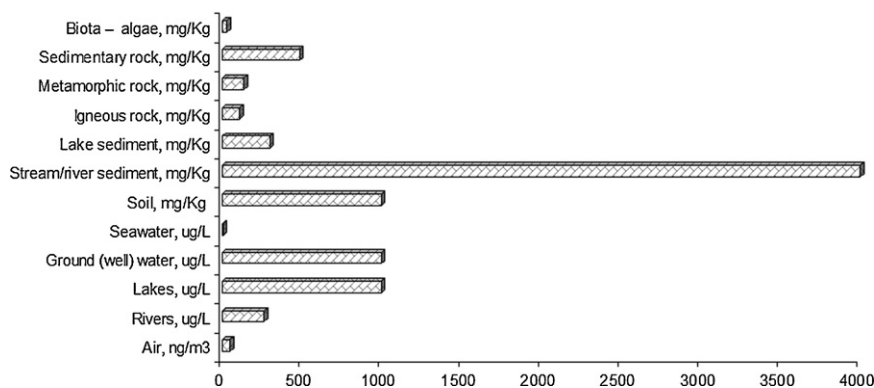
Fig. 1. Arsenic concentrations in environmental media (data from [164]).

from drinking water supplies than arsenate as it is present in neutral form in the pH range of drinking water. The current drinking water standard (10 ppb) of arsenic set by the Environmental Protection Agency (EPA) [10] and the limit (10 ppb) recommended by the World Health Organization (WHO) [11] make no differentiation between arsenite and arsenate. Concentrations of arsenic detected in environment are generally reported as total arsenic (i.e., without regard to speciation) [12–14], although analytical methods are available to distinguish between the organic and inorganic forms and between the two valence states of arsenic (e.g., [15–21]). It is believed that arsenate is the major water-soluble species in groundwater, but there is increasing evidence that arsenite may be more prevalent than anticipated. Improved methods of sampling, sample preservation, and analysis have contributed to this conclusion [22]. This is not surprising given the fact that there are multiple natural processes that effectively scavenge arsenate from water, while they are much less efficient for arsenite removal.

Arsenic is found in soils, air, and water as a metalloid and as chemical compounds of both inorganic and organic forms. The concentration ranges of arsenic found in environmental media are shown in Fig. 1. Arsenic can enter terrestrial and aquatic environments through both natural geologic processes (geogenic) and human (anthropogenic) activities [23]. Anthropogenic sources of arsenic include mineral processing, glass manufacturing, wood preserving, pesticide production and application, landfill/waste pile leaching, and coal/oil production and processing [24]. Anthropogenic sources of arsenic is mainly released into the atmosphere through emissions (total input 2.5×10^4 ton/year, mostly due to copper smelting and coal combustion) and into the pedosphere and lithosphere through wastes of all sorts ($2.8–9.4 \times 10^4$ ton/year) [23]. While anthropogenic sources may be important in some settings, the majority of the arsenic problems are caused by naturally occurring inorganic arsenic [25–28]. There are no less than 245 arsenic-bearing minerals in nature, which release arsenic when subjected to weathering [29]. In addition, many sulfide minerals, especially pyrite, contain appreciable amount of arsenic (up to 0.5%) in solid solution [29].

Acid mine drainage (AMD) is polluted water that normally contains high levels of iron, aluminum, and sulfuric acid. The contaminated water often has an orange or yellowish-orange color, indicating high levels of iron, and may also have the smell of rotten egg (hydrogen sulfide). Arsenic is one of the priority pollutants commonly associated with AMD, especially that from gold mining operations [30,31]. Under the extremely acidic conditions of some AMD, high concentrations of a wide range of solutes are often found, including iron and arsenic. Plumlee et al. [32] reported arsenic concentrations ranging from detection limits (<1 μg/L or more) to 340,000 μg/L based on the results from 180 samples of

mine drainage from the U.S. The highest reported arsenic concentration in AMD is 850,000 μg/L which was found in an acid seep at Iron Mountain, California [33]. In comparison, the concentrations of arsenic found in natural water bodies range from <0.5 μg/L to greater than 5000 μg/L, with typical concentrations in freshwater being less than 10 μg/L and frequently less than 1 μg/L [34].

Being a metalloid, arsenic forms no single cations but reacts readily to form oxyanions and the corresponding salts. Occurrence and removal of arsenic in natural water bodies are related to the pH and the redox conditions of the solution, its oxidation state, and sorption or exchange reactions [35]. A thorough understanding of the geochemical interactions of arsenic with its surrounding environment is required in order to prevent arsenic pollution and to predict the risk of arsenic in AMD and natural water bodies. Knowledge on the sources of arsenic, the mechanisms controlling its release and mobility, and its natural attenuation processes is crucial to minimize the occurrence of arsenic in aquatic system, to assess the risk of arsenic contamination, and to design and implement remediation and treatment plans.

The fate and mobility of arsenic are mainly controlled by five categories of processes in surface water and groundwater: (1) redox reactions; (2) adsorption and desorption; (3) competitive adsorption (ion exchange); (4) solid phase precipitation and dissolution; and (5) biological activity. These processes interact with each other and the mobility of arsenic may be controlled by multiple processes under a given set of conditions. Many factors, such as redox potential (Eh), pH or acidity, chemical composition of the system (e.g., redox pairs, competing anions, aquifer minerals, etc.), and reaction kinetics also play a role in these processes [28,36]. Consequently, the occurrence, distribution, and mobility of arsenic are dependent on the interplay of these geochemical factors. Arsenic occurrence in groundwater world-wide shows significant spatial and temporal (to a less extent) variations [34,37], owing to the interplay among changes in the chemical composition and redox state of groundwater, microbiological activity, and adsorption and precipitation processes in the subsurface that establish and evolve within the overall hydrologic framework [36]. This work is mainly concerned with inorganic arsenic species in AMD and groundwater and only the first four mechanisms are considered in the following discussion. Cullen and Reimer [1] and Sadiq [2] have excellent reviews on organoarsenicals and microbiological arsenic transformations in natural environment.

2. Release of arsenic in mineral weathering

Composition of AMD from a mining area is controlled collectively by local hydrology, geology, and geochemistry. AMDs are discharged from millions of abandoned mine drainage tunnels and

tailings piles all over the world. The acidic water poses a threat not only to the aquatic life in mountain streams and rivers, but can also contaminate groundwater and downstream water bodies. Most organisms have a well defined range of pH tolerance, and the acidity of water alone has long been recognized to have direct toxic effects on aquatic life as well as indirect effects on their food sources [38–41]. Mine drainage is often discolored due to the presence of Fe^{2+} and Fe^{3+}, and the pH of AMD can be as low as −4 [42]. AMD is mainly caused by the physical and chemical weathering (with an important microbiological component) of one ubiquitous mineral in the Earth's crust – pyrite (FeS_2), and it often also contains high concentrations of toxic metals such as lead, arsenic, copper, and zinc. The level of acidity and the concentration of heavy metals in AMD are directly related to the amount of pyrite undergoing weathering in the drainage basin. Mining activities inadvertently accelerated physical weathering of pyrite by grinding up the ore and placing the waste residues in tailings impoundments. The initiating reaction in the geochemical processes of forming AMD is oxidation of pyrite:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \tag{1}$$
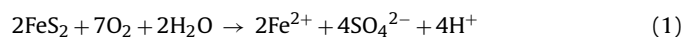
Fe^{2+} and H^+ are released into the water that flows from the mine drainage tunnels or tailings piles to surface water or groundwater. Fe^{2+} is oxidized to Fe^{3+} in the presence of dissolved oxygen in water:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \tag{2}$$
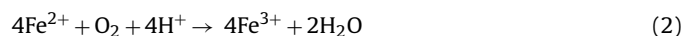
The conversion of ferrous to ferric iron is the rate-limiting step in the overall pyrite reaction sequence [43], and it has long been known that *Acidithiobacillus ferrooxidans* and several other bacteria species can greatly accelerate this conversion [43,44]. Fe^{3+} can further hydrolyze in water and precipitate as $Fe(OH)_3$, which releases more H^+ into the stream:

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

The ferric iron hydroxide formed is a yellowish-orange precipitate that turns the acidic runoff in the streams to an orange or red color and covers the stream bed with a slimy coating. In addition, iron-(oxy)hydroxysulphates often precipitate in iron-rich, acid-sulfate waters, with jarosite present under the most severe (pH < 3) AMD conditions and schwertmannite present under the most moderate (pH 3–5) AMD conditions [45,46]. Under acidic conditions, the soluble Fe^{3+} reacts spontaneously with more pyrite and leads to more pyrite oxidation (an autocatalytic process):

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{4}$$
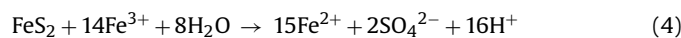
Although the reactions causing oxidation of pyrite and formation of AMD occur in an abiotic environment, lithotrophic microbial consortia greatly accelerate this process. The oxidation of pyrite to Fe^{2+} and SO_4^{2-}, which occurs slowly at neutral pH, becomes much faster at pH values below 4 due to the action of acidophilic chemolithotroph bacteria [47]. In particular, *A. ferrooxidans* is known as a key contributor to pyrite oxidation [48]. Besides pyrite, sulfides of copper, zinc, cadmium, lead, and arsenic in the drainage tunnels and tailings piles also undergo similar geochemical reactions, releasing toxic metals and more H^+ into the mine drainage. More details on the geochemistry of AMD can be found in a recent review by Blowes et al. [49].

Depending on the scale of the mines, the tailings impoundments can vary from less than 10 ha to several square kilometers in surface area and from a few meters to more than 50 m in thickness [49]. Because of the relatively low groundwater velocities, a series of acid-neutralization reactions occur when AMD contacts carbonate-, hydroxide, and other base-containing solids. The pH-buffering reactions result in the development
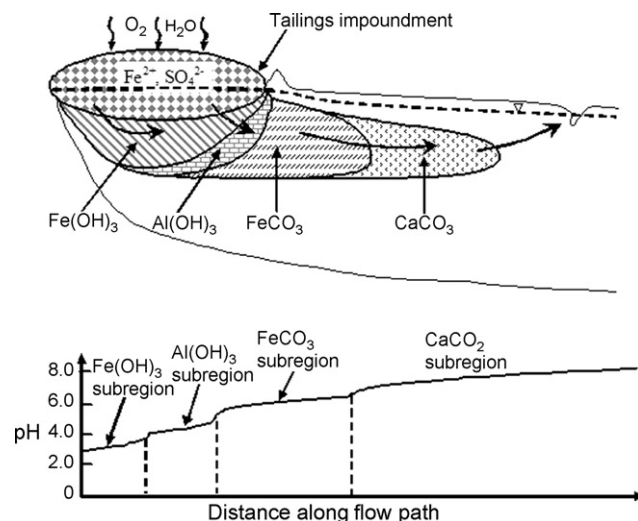

Fig. 2. Schematic diagram of mine tailings impoundment and underlying aquifer, and the associated geochemical pH-buffering regions (after [49,50]).

of a series of pH regions, as illustrated in Fig. 2. Precipitation of metal-bearing hydroxide and hydroxysulfate minerals occurs with increases in the pH of the water, and dissolved metals are removed in this process [50]. For example, dissolved arsenic in AMD is known to be rapidly scavenged through co-precipitation and adsorption as the pH increases and as iron is oxidized and precipitated [34,51].

Arsenic is commonly concentrated in sulfide-bearing mineral deposits, especially those associated with gold mineralization, and it has a strong affinity for pyrite [26]. Arsenic can exist in sulfide minerals either as a dominant mineral-forming element or as an impurity. Arsenic is also concentrated in hydrous iron oxides and is known to adsorb to clay minerals and associate with organic carbon [28]. Arsenic is released slowly as these minerals weather or are subjected to significant changes in physical/chemical conditions under normal circumstances, but grinding, crushing and pulverizing from mining activities greatly increase its releasing rate, besides the exposure of large quantities of arsenic-bearing minerals to weathering. AMD frequently contains arsenic in the form of arsenite, As(III), and/or arsenate, As(V), along with much higher concentrations of dissolved iron. The geochemistry of arsenic is very complex and arsenic release and mobilization can occur under a wide variety of conditions, which make it difficult to predict and control arsenic occurrence in mine drainage.

3. Redox reactions of arsenic and pH effects

Arsenic is a redox-sensitive element, and its main oxidation states are −3, 0, +3, and +5. Arsine (AsH_3) is a highly poisonous and flammable gas and rarely occurs in nature, while arsenate and arsenite are the most commonly found arsenic species in AMD and groundwater. Fig. 3 shows the Eh–pH diagram for arsenic species. Arsenate generally predominates under oxidizing conditions, while arsenite predominates when conditions become sufficiently reducing. Thermodynamic calculations [2] and experimental results [52,53] indicate that at high redox levels (pe + pH > 10), arsenate is the predominant arsenic species while under moderately reduced and reduced conditions (pe + pH < 8), arsenite is the most abundant form of arsenic. Redox reactions can control aqueous arsenic concentrations by their effects on arsenic speciation, and hence, arsenic adsorption and desorption. Through the inter-conversion between
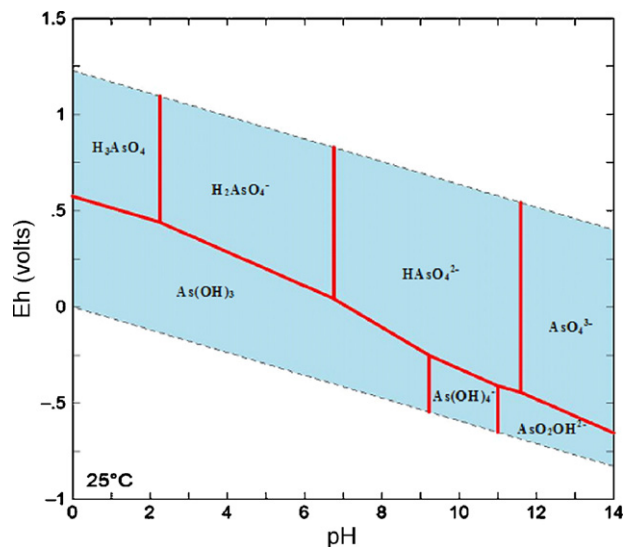
Fig. 3. Eh–pH diagram for arsenic species.

arsenate and arsenite, redox reactions involving either aqueous or adsorbed arsenic can affect arsenic mobility [54].

Arsenite oxidation by oxygen is very slow in homogeneous solutions. No oxidation of arsenite in distilled and demineralized water was observed after 37 days [55], and a half-life of 1 year has been reported for arsenite oxidation by oxygen [56]. Heterogeneous oxidation of arsenite on naturally occurring mineral surfaces is a key process for its rapid oxidation and this reaction significantly influences the environmental fate of arsenite. Manganese oxides are highly redox-sensitive compounds and they play a distinctive role in the surface soil or near surface environments due to their narrow Eh–pH stability field. Reduced species arsenite can be readily oxidized by manganese oxides in lake water [57], sediments [58,59], and aquifer materials [60], and by biogenic manganese oxide as well [61]. Oxidation of arsenite by birnessite (δ-MnO$_2$), a representative of many naturally occurring manganese oxides, has been extensively studied [62–67]. The net reaction of arsenite oxidation by manganese oxides is:

$$MnO_2 + H_3AsO_3 + 2H^+ \rightarrow Mn^{2+} + H_3AsO_4 + H_2O \qquad (5)$$
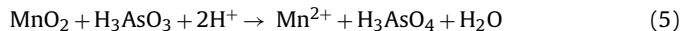
This reaction not only converts the more toxic arsenite species to less toxic arsenate, but may also result in precipitation of manganese arsenate compounds and reduce the total concentration of arsenic species in solution [67]. Scott and Morgan [66] found that oxidation of arsenite in solution could be completed within 10 min at pH 4 by synthetic birnessite particles. They concluded that birnessite directly oxidizes arsenite through a surface mechanism and that adsorption of arsenite is the slowest step in the production of arsenate. For well-crystallized hexagonal birnessite, Tournassat et al. [67] concluded that the surface reaction sites are likely located on the edges of birnessite layers rather than on the basal planes. Su and Puls [68] reported complete oxidation of arsenite occurred in a synthetic birnessite suspension at pH 2.5–11.5 after 24 h of reaction. Sun and Doner [69] also reported that birnessite was an active oxidant of arsenite both in solution and on the goethite surface and hypothesized that the adsorption–oxidation system composed of goethite and birnessite may be significant in decreasing arsenic toxicity in terrestrial environments. Manning et al. [70] reported that zero valent iron corrosion reaction could slowly oxidize arsenite to arsenate under aerobic conditions, and they also observed that maghemite and hematite minerals caused arsenite oxidation while goethite and lepidocrocite did not. Chiu and Hering [71] reported

that the oxidation of arsenite by manganite occurred on the time scale of hours at near-neutral pH. Johnston and Singer [72] found that Fe(II) could reduce arsenate in the presence of goethite, but not in homogeneous solution at near-neutral pH under anoxic conditions, while the oxidation of arsenite and Fe(II) depended heavily on pH buffer type and concentration under aerobic conditions. It has been commonly observed that oxidation of Fe(II) by dissolved oxygen causes partial oxidation of arsenite [70,72,73]. It was proposed that a radical species, Fe(IV), produced during the oxidation of divalent iron, Fe(II), facilitates the oxidation of arsenite in this process [74,75]. Manning and Goldberg [54] found that oxidation of arsenite to arsenate could be enhanced by heterogeneous oxidation on kaolinite and illite surfaces as well. Light-induced arsenite oxidation in the presence of dissolved iron has also been reported [76,77].

The oxidation of arsenite by (hydr)oxide minerals observed in different studies may not agree well with each other because of the specific experimental conditions and materials used, which makes it difficult to interpret the important oxidants under natural conditions. On the other hand, arsenic redox reactions can be predicted from thermodynamic properties of the redox couples. Fig. 4 shows pe–pH diagrams for some common redox couples (they may not always exist for a given system) that may be important for arsenate/arsenite redox reaction in groundwater and soils at free metal ion concentrations of 10^{-6} mol/L. Theoretically, the oxidized species of couples having positive Eh can oxidize the reduced species of couples having negative Eh at a given pH. Redox couples Co^{3+}/Co^{2+}, Mn^{3+}/Mn^{2+} have high oxidizing potential and are not stable in aqueous solution, while Fe^{3+}/Fe^{2+} cannot be stable in alkaline solution, either. Among the minerals, Fe(III) (hydr)oxide minerals can generally oxidize arsenite at pH below 4–5, but they are no longer capable of oxidizing arsenite at pH above 8. Mn(IV) (hydr)oxide minerals are not stable at pH below 4 to near 6, but they can serve as the general oxidants for arsenite oxidation at pH above 6. In addition, cobalt spinel can cause arsenite oxidation at solution pH higher than around 8. Together, these results suggest that manganese (hydr)oxides are responsible for arsenite oxidation under near-neutral to alkaline conditions, while iron (hydr)oxides are important oxidants under acidic conditions in general.

Besides directly affecting the speciation of arsenic, redox reactions also control the stability of most sulfide and (hydr)oxide minerals, which are sources and sinks of arsenic species. Eh–pH diagrams of sulfide minerals (not shown) indicate that they are generally stable under reducing conditions, but they will be oxidized under oxidizing conditions, which will release the arsenic contained in them into the environment. Eh and pH play a key role in controlling stabilities of (hydr)oxide minerals (e.g., iron, manganese and aluminum oxides or hydroxides), which not only affect the stability of arsenate and arsenite through redox reactions, but can also adsorb dissolved arsenate (and some arsenite) effectively. The Eh–pH diagrams of these minerals (not shown) suggest that they are generally stable at neutral to high pH range, but are dissolved in acidic or highly alkaline solutions as they are amphoteric. For example, although Fe(III) (hydr)oxide minerals can oxidize arsenite at pH below about 4–5, they are no longer stable at pH below 2. At low pH range, Fe(III) and Mn(IV) (hydr)oxides are only stable at highly oxidizing conditions, and they will undergo reductive dissolution when Eh is low enough. The stabilities of these metal (hydr)oxides control the redox speciation and distribution of arsenic species between solid phase and aqueous phase. Dissolution of these arsenic "sinks" may change the oxidation rate of arsenite and trigger release of the immobilized arsenic. Burton et al. [78] reported that the process of Fe(III)-reduction released high concentrations of Fe(II) and was associated with significant mobilization of arsenic during re-flooding of iron- and organic-
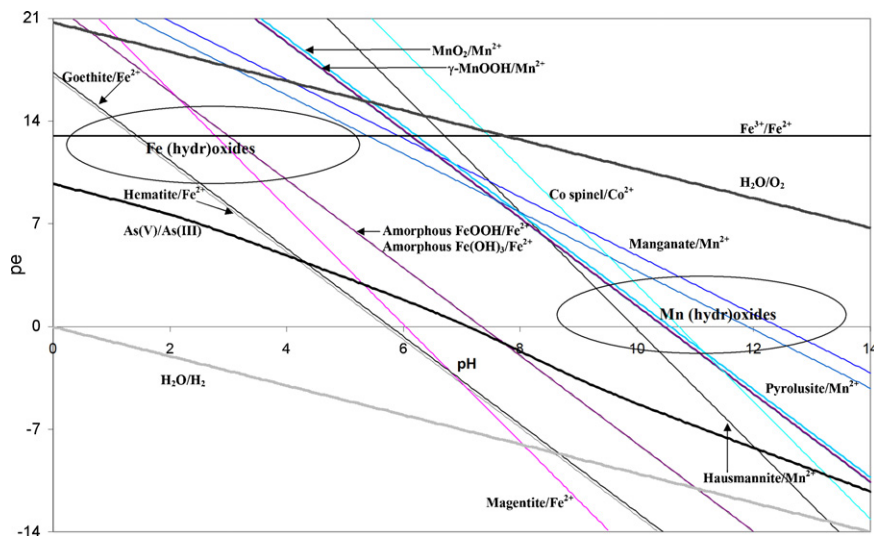
Fig. 4. pe–pH diagrams for different redox couples that may be important for arsenate/arsenite redox reaction in nature environment.
Notes:
- Fe^{2+}, Mn^{2+}, Co^{2+}, Fe^{3+}, Co^{3+}, Mn^{3+} concentrations are assumed to be constant at 10^{-6} mol/L at the entire pH range without any speciation;
- Redox couples Mn^{3+}/Mn^{2+} and Co^{3+}/Co^{2+} are not shown because they are outside of the stability field of water in the entire pH range of interest;
- Thermodynamic data for species are from Stumm and Morgan [167];
- For accurate description of the pe of As(V)/As(III) redox couple with respect to pH change, speciation of both As(V) and As(III) with solution pH are considered in pe calculation (based on total As concentration of 10^{-6} mol/L).
- The upper and lower boundaries for water stability are based on the partial pressures of O_2 and H_2 at 1 atm.

rich acid-sulfate soils. Joensson and Sherman [79] showed that dissimilatory reduction of iron oxides, followed by precipitation of fougerite, magnetite or siderite released dissolved arsenate at pH > 8; however, sorption of arsenic was enhanced when arsenate was also reduced to arsenite in this process. Tufano and Fendorf [80] revealed that with the initial phase of Fe reduction, ferrihydrite undergoes transformation to secondary phases and increases arsenite retention, but with increased reaction time, cessation of the phase transitions and ensuing reductive dissolution result in prolonged release of arsenite to the aqueous phase. Results of this study suggest that arsenite retention during Fe reduction is temporally dependent on secondary precipitation of Fe phases. Under very reduced conditions, arsenic has been observed to accumulate at redox boundaries in sediments and associate with sulfide [30,81–83]. Spectroscopic evidence and geochemical modeling by O'Day et al. [36] show that maximum dissolved arsenic concentrations occur in the redox transition between conditions where arsenate sorbed on Fe(III) oxyhydroxide is stable and the stability region where sufficient reduction of arsenate and sulfate leads to the formation of realgar or other arsenic sulfide phases.

Overall, redox conditions can determine the speciation of dissolved arsenic in the aqueous phase. Arsenate will be the predominant species under well oxygenated conditions. Arsenite heterogeneous oxidation on surfaces of oxidative minerals plays key roles in arsenic transformations. On the other hand, if the solution is rich in reduced species (e.g., S^{2-}), arsenic will mainly exist in form of arsenite species, although arsenic sulfide phases may form if the environment in highly reducing.

4. Adsorption and desorption of arsenic species

Adsorption reactions between arsenic and mineral surfaces are generally considered the most important control on the concentration of dissolved arsenic in groundwater environments [37]. Adsorption of arsenic is a complex function of the interrelationship between the properties of the solid surface, pH, the concentration of arsenic and competing ions, and arsenic speciation [37]. There are

two general mechanisms for adsorption of arsenate and arsenite on a mineral surface: non-specific adsorption and specific adsorption. Non-specific adsorption, also known as outer-sphere surface complexation, involves the electrostatic attraction between a charged surface and an oppositely charged ion in solution (Fig. 5a). The adsorbed ion resides at a certain distance from the mineral surface. Specific adsorption, or inner-sphere complexation, involves the formation of a coordinative complex with the mineral surface (Fig. 5b–d). Inner-sphere complex bonds are more difficult to break than outer-sphere complex bonds and result in stronger adsorption of ions. Changes in ionic strength affect the electrostatic forces near the mineral surface [84]. Anions that form inner-sphere com-
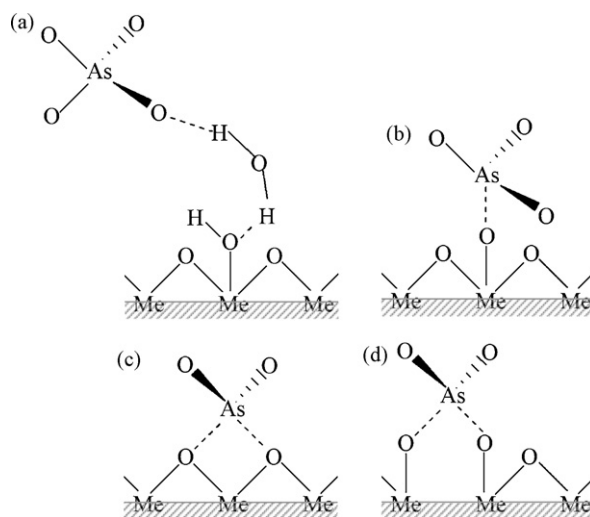

Fig. 5. Schematic representation of configurations of arsenate molecules adsorbed on metal (hydr)oxide surfaces: (a) outer-sphere surface complexation; (b) mononuclear monodentate inner-sphere complexation; (c) mononuclear bidentate inner-sphere complexation; and (d) binuclear bidentate inner-sphere complexation. Arsenite binds on metal oxide surfaces in a similar way (after [170]).

Table 1
The point of zero charge, pH_{PZC}, of clays and common soil oxides and hydroxides.

Mineral	pH_{PZC}[*]
Birnessite (δ-MnO_2)	2.2
Montmorillonite	<2.5
Quartz (SiO_2)	2.9
Kaolinite	4.6
α-$Al(OH)_3$	5.0
α-MnO_2	5.1
Rutile (TiO_2)	5.8
Hydroxyapatite ($Ca_5OH(PO_4)_3$)	7.6
Hematite (α-Fe_2O_3)	8.5
γ-Al_2O_3	8.5
$Fe(OH)_3$	8.5
Corundum (α-Al_2O_3)	9.1
Goethite (α-$FeOOH$)	9.3
Calcite ($CaCO_3$)	9.5
δ-Al_2O_3	9.5
MgO	12.3

Note: [*] values reported in [167,168].

Fig. 6. Arsenate and arsenite speciation as a function of solution pH (pK_a values of H_3ASO_4 and H_3AsO_3 are from [138]).

plexes coordinate directly with the oxide surface in a manner that is relatively independent of ionic strength, while the formation of outer-sphere complexes by weakly adsorbed anions is sensitive to ionic strength [37]. This section focuses on the adsorption of arsenate and arsenite on metal (hydr)oxides and other minerals alone, while their adsorption in the presence of competing ions is covered in the next section.

Arsenic species can adsorb on many soil colloids, including (hydr)oxides of iron, aluminum, and manganese, clay, calcium carbonate and organic matters. The adsorption capacity and behavior of these colloids are dependent on ever-changing factors, such as hydration, soil pH, specific adsorption, changes in cation coordination, isomorphous substitution, and crystallinity [2]. As a result of the altering tendencies of soil colloids properties, arsenic adsorption is complex, empirical, ambiguous, and often a self-contradicting process in soils [2]. In general, iron (hydr)oxides are the most commonly involved natural minerals in the adsorption of arsenic in both acidic and alkaline soils, while aluminum (hydr)oxides, clay, manganese oxides, and organic matters may play some roles only in acidic soils [2,28,85–89]. The non-specific adsorption of inorganic arsenic species on mineral surfaces depends on the charges of both the solid surfaces and the arsenic species, both of which are pH dependent. Mineral surface appears to be positively charged when solution pH is below its point of zero charge (pH_{PZC}, pH at which the net surface charge is equal to zero), and *vice versa*. The pH_{PZC} values of some common soil minerals are summarized in Table 1. In the near-neutral pH range, iron and aluminum (hydr)oxides, and calcite are positively charged while the clay minerals are negatively charged, which suggests that the former ones are important sorption "sinks" for negatively charged species under such conditions. Charges of dissolved arsenic species originate from the association and dissociation of H^+ as a function of solution pH. Fig. 6 shows the distribution of different arsenate and arsenite species as function of solution pH. At the low pH range of AMD, H_3AsO_4 and $H_2AsO_4^-$ are the major species for arsenate, while arsenite primarily exists in the form of H_3AsO_3 in AMD. Under the typical pH conditions (4–9) of most surface water and groundwater, arsenate is present as the negatively charged oxyanions $H_2AsO_4^-$ or $HAsO_4^{2-}$, whereas arsenite is present as a neutral species H_3AsO_3. Based on the speciation behaviors of arsenate and arsenite and the pH dependence of mineral surfaces, electrostatic attraction can cause arsenate to be sorbed by iron, manganese, and aluminum (hydr)oxides, and even clay minerals, but little adsorption of arsenite under typical soil and groundwater aquifer conditions. The simultaneous pH dependence of both mineral surface charge and arsenic species charge may
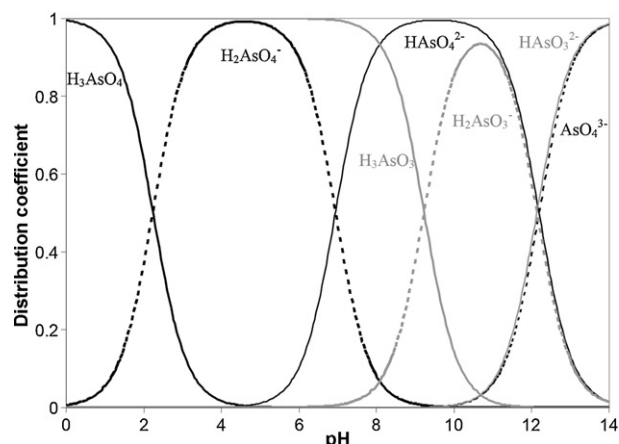
result in complex arsenic sorption patterns. For example, Gulens et al. [85] observed that arsenate is more mobile than arsenite at a pH of 5.8 on a sandy loam, which is probably due to the fact that the surfaces of both clay and sand (the major components of this soil) were negatively charged at this pH, which repel the negatively charged $H_2AsO_4^-$. Increasing pH reduces the surface charge of minerals, while more arsenate and arsenite species become negatively charged. Consequently, increased mobility is expected for both arsenite and arsenate at higher pH.

The stronger adsorption of arsenate by iron and aluminum (hydr)oxides and clay minerals than arsenite at acidic and neutral pH ranges has been observed in many experimental studies (e.g., [89–91]). Smith et al. [91] observed that sorption of arsenate decreased with increasing pH due to two interacting factors, the increasing negative surface potential on the plane of sorption and the increasing amount of negatively charged arsenate species present in soil solution, while sorption of arsenite increased with increasing pH. They also observed that there was a pH (approximately 3) below which arsenate sorption decreased with increasing ionic strength and above which the reverse occurred, while increasing ionic strength had little effect on the amount of arsenite sorbed. Smith et al. [27] observed that Ca^{2+} increased arsenate sorption through changes in the surface charge characteristics of the soils, but the presence of Ca^{2+} had little effect on the amount of arsenite sorbed. These results suggest that arsenate adsorbs mainly through non-specific sorption (electrostatic attraction) while specific sorption (inner-sphere complexation) probably plays a major role for the sorption of arsenite.

Dixit and Hering [89] found that sorption of arsenate onto amorphous iron oxide and goethite is more favorable than that of arsenite below pH 5–6, whereas, above pH 7–8, arsenite has a higher affinity for the solids. Raven et al. [92] reported that arsenite adsorbed faster than arsenate on ferrihydrite at relatively high arsenic concentrations, but arsenate adsorption was faster at low arsenic concentrations and high pH. Jain et al. [93] also observed that arsenite sorbed at a higher rate than arsenate on ferrihydrite at solution pH above 8. Robertson [35] found that arsenic concentration does not correlate with dissolved Fe but may be partially controlled by Fe in the solid phase, and that arsenic in groundwater is controlled in part by sorption or desorption of $HAsO_4^{2-}$ on active $FeO(OH)$ surfaces under oxidizing conditions. Aluminum oxides and clay minerals also adsorb arsenate and arsenite, but to a much weaker extent compared with iron oxides in normal groundwater pH range [54]. It has also been observed that arsenite adsorbs less strongly to most aluminum oxide and aluminosilicate soil min-

erals than arsenate [54,94]. Bostick et al. [95] observed that surface sulfhydryl groups on galena (PbS) and sphalerite (ZnS) reacted with arsenite to form sulfide complexes similar to $As_3S_3(SH)_3$ clusters observed in solution, which can be oxidized by residual oxidants on the PbS surface but form stable inner-sphere complexes on ZnS surface. Wolthers et al. [96] found that both arsenate and arsenite sorb on disordered mackinawite (FeS) at fast rates and form dominantly outer-sphere complexes at the surface. Soil organic matters such as humic acids are also capable of sorbing arsenate and arsenite [97].

Farquhar et al. [98] studied the mechanisms of arsenic interaction with the surface of goethite, lepidocrocite, mackinawite, and pyrite with X-ray absorption spectroscopy, and they found that arsenate and arsenite formed inner-sphere complexes involving bidentate on the oxyhydroxide substrate while the complexes formed with sulfide minerals are outer-sphere. Previous studies have shown that arsenate specifically sorbed onto iron oxides such as goethite through an inner-sphere complex via a ligand exchange mechanism [99–102]. Extended X-ray absorption fine structure (EXAFS) studies [99,102,103] indicate that bidentate binuclear complexation was the major binding mechanism for arsenate adsorption on goethite. Fendorf et al. [99] and Grossl et al. [100] further demonstrated that three types of surface complexes can form during arsenate adsorption on goethite surface: monodentate surface complexes at low surface coverage; bidentate mononuclear complexes at high surface coverage; and bidentate binuclear complexes at surface coverage near monolayer capacity. O'Reilly et al. [104] observed bidentate binuclear bond formation between arsenate and goethite surface and they reported that the bond remained unchanged over 1 month. EXAFS studies by Manning et al. [62] indicated that arsenate forms an inner-sphere bidentate binuclear complex on both arsenite-altered and unaltered MnO_2 surfaces and they hypothesized that arsenite also forms an inner-sphere complex on MnO_2 before being oxidized. *In situ* EXAFS investigations conducted by Foster et al. [105] show that arsenate adsorbs primarily to Mn(IV) sites on hydrous manganese oxides and forms a bidentate, bridging sorption complex analogous to that formed on ferric hydroxides. Manning and Goldberg [54] found that ionic strength only had a minor effect on arsenite adsorption on kaolinite, illite, monmorillonite, and amorphous aluminum hydroxide, which is indicative of inner-sphere complexation. Based on EXAFS and X-ray absorption near edge structure (XANES) analyses, Manning et al. [106] concluded that arsenite formed an inner-sphere, bidentate binuclear bridging complex on the surface of α-FeOOH, which was only influenced slightly by pH and arsenite surface coverage, and that the arsenite-α-FeOOH surface complex is stable toward heterogeneous oxidation to arsenate. Randall et al. [107] showed that arsenate adsorbed on green rust by forming two different inner-sphere surface complexes: edge-sharing between AsO_4 and FeO_6 polyhedra and double-corner sharing between AsO_4 tetrahedra and adjacent FeO_6 polyhedra, while sorption onto lepidocrocite occurs via an inner-sphere complex resulting from bidentate corner sharing between AsO_4 tetrahedrons and adjacent FeO_6 octahedrons. EXAFS results by Morin et al. [108] indicate that both arsenate and arsenite form inner-sphere complexes on the surface of maghemite under high surface coverage conditions (0.6–1.0 monolayer), with the predominance of single binuclear bidentate double-corner complexes for arsenate, a dominant contribution from bidentate binuclear double-corner complexes with additional contributions from bidentate mononuclear edge-sharing complexes and monodentate mononuclear corner-sharing complexes for arsenite. Based on spectroscopic, sorption, and electrophoretic mobility measurements, Goldberg and Johnston [109] concluded that arsenate forms inner-sphere surface complexes on both amorphous aluminum and iron oxides while arsenite forms both inner- and outer-sphere surface complexes on amorphous iron oxide and

outer-sphere surface complexes on amorphous aluminum oxide. EXAFS and XANES analyses by Arai et al. [110] indicate that both arsenite and arsenate form inner-sphere complexes with bidentate binuclear complexes on aluminum oxide surface, and that in addition to inner-sphere complexes, outer-sphere complexes also form increasingly with pH increases (5.5–8) for arsenite adsorption. Based on the results of batch sorption experiments and EXAFS spectroscopy, Joensson and Sherman [79] concluded that arsenate sorbs to secondary Fe(II) and mixed Fe(II)/Fe(III) minerals, fougerite, magnetite and siderite, by forming inner-sphere surface complexes resulting from corner sharing between AsO_4 groups and FeO_6 octahedra, while arsenite also forms inner-sphere surface complexes on magnetite and fougerite but only a (presumably) weak outer-sphere complex on siderite. Recently, Wang et al. [111] reported that during magnetite precipitation at near-neutral pH arsenite forms predominantly tridentate hexanuclear As(III)O_3 complexes, which is the first time such a tridentate surface complex has been observed for arsenic. Because of the different experimental conditions, techniques, and uncertainties associated with the analyses, results from investigations on arsenate and arsenite adsorption on soil minerals do not necessarily agree with each other well. Nonetheless, these studies provide molecular level insights into the possible mechanisms responsible for arsenate and arsenite sorption.

Sorption and desorption of arsenic species on minerals are primarily affected by pH and control the transport of arsenic. Decreasing pH generally leads to increased arsenic retention because of the shift in mineral surface charges from negative to more positive, and consequently, the arsenic species become less mobile. At very low pH range (less than 1) when nearly all arsenic species exist in neutral form, arsenic is no longer sorbed and becomes mobile again. Also, oxide minerals may dissolve when pH is low enough, and all the arsenic retained on their surfaces will be released into the aqueous phase. Such events may bring exceedingly high arsenic input to downstream water bodies. The pH of AMD is very low in the source zone (drainage tunnels and tailings piles). As the drainage travels along the streambed, pH rises from very low values to near or above neutral (Fig. 2). Precipitation of Fe^{3+} as iron (hydr)oxides effectively scavenges most arsenate from water through sorption and other mechanisms. Arsenite is sorbed less by iron hydroxides, and some of the arsenite may continue to travel downstream, causing contamination of downstream water bodies. The arsenic-rich iron (hydr)oxides may re-dissolve when the surrounding water becomes acidic enough and the arsenic will be released again. Alternatively, if the pH of the surrounding becomes more basic (>9.5), arsenate may be partially released due to the change in surface charge (less positive) of iron (hydr)oxides. Nonetheless, the fraction of arsenic that adsorbed through inner-sphere complexation will not be released unless the iron hydroxides minerals are dissolved. As AMD is often in contact with many different minerals, it is expected that the predominant sink for the negatively charged arsenic species may shift as the pH of the mine drainage changes. It is also expected that the arsenic released from the dissolution of a particular mineral might be captured by another mineral that remains stable under the conditions [49–51]. Therefore, the interactions of arsenate and arsenite with multiple minerals can be beneficial in retarding arsenic migration.

5. Competitive adsorption (ion exchange) of arsenate and arsenite

As electrostatic attraction with positively charged mineral surfaces is a major force responsible for arsenate sorption, other anions (e.g., PO_4^{3-} and SO_4^{2-}) with similar or higher charge densities may compete for the same sorption sites on mineral surfaces

and cause reduced arsenate adsorption and even desorption. The reported anion exchange selectivity sequence on activated alumina surfaces in the pH range of 5.5–8.5 is: $OH^- > H_2AsO_4^-$, $Si(OH)_3 O^- > F^- > HSeO_3^- > SO_4^{2-} > CrO_4^{2-} \gg HCO_3^- > Cl^- > NO_3^- > Br^- > I^-$ [112,113]. This suggests that aqueous silicate, selenate, fluoride, and sulfate ions, which occur frequently in natural water bodies, may compete with arsenates for adsorption sites.

Commonly occurring solutes, including phosphate (PO_4^{3-}), silica (SiO_2), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-), adsorb onto hydrous ferric oxide, and the competition from them has been observed to reduce arsenic removal by hydrous ferric oxide [114]. In particular, phosphate, which has similar chemical properties and behaviors as arsenate, strongly competes with arsenate for sorption sites on metal oxide surfaces. Significant reductions in arsenate adsorption by phosphate on amorphous iron oxide [115,116], goethite [117], gibbsite [117], kaolinite [115,118], montmorillonite [118], illite [118], aluminum oxide [115], and quartz [115] have been reported, while sulfate was also observed to have a minor competitive effect on arsenate adsorption [115,116,119]. Smith et al. [27] observed that the presence of PO_4^{3-} in solution decreased the amount of arsenate and arsenite sorbed on selected soils, but PO_4^{3-} was not able to completely desorb all the arsenate. Similar observations have been made by Darland and Inskeep [120] on arsenate transport in sand columns containing free iron oxides, and Smith et al. [27] suggested that some oxide surfaces contain preferential sorption sites for arsenate and PO_4^{3-} and others that are common to both. EXAFS studies by O'Reilly et al. [104] also indicate that significant amounts of arsenate could not be replaced by PO_4^{3-} even at a concentration three times higher than the initial arsenate sorptive solution, and that PO_4^{3-} was more effective to promote arsenate desorption from goethite than SO_4^{2-}. Arsenite adsorption on amorphous iron oxide is also reduced by competing phosphate and sulfate [116,119]. Acharyya et al. [25] suggested that one of the mechanisms causing arsenic pollution of groundwater in Bengal Basin, Bangladesh is that arsenic anions sorbed on aquifer minerals were displaced into groundwater by competitive exchange of phosphate anions sourced from over-application of fertilizer to surface soils, although some researchers disagree with this [121]. Like arsenate, PO_4^{3-} is adsorbed on goethite surface sites as an inner-sphere complex via a ligand exchange mechanism [122–124]. Infrared spectroscopic studies by Lumsdon et al. [101] show that arsenate is adsorbed on the surface of synthetic goethite as the acidic $HAsO_4^{2-}$ ion, replacing singly coordinated surface –OH groups, and that the larger size of arsenate allows it to interact more strongly with some of the –OH groups that remain on the surface than phosphate. Sulfate can be adsorbed as either an outer- or inner-sphere complex. He et al. [122] found that sulfate adsorption on γ-Al_2O_3 and kaolinite was better modeled by assuming outer-sphere complex formation, while X-ray photoelectron spectroscopy (XPS) studies of sulfate adsorption on goethite suggest inner-sphere complexation [125]. In situ attenuated total reflection (ATR)-Fourier transform infrared spectroscopy (FTIR) studies of sulfate sorption on hematite indicate formation of monodentate bisulfate or bidentate sulfate on dry hematite [77]. Peak et al. [126] found that sulfate formed both outer-sphere and inner-sphere surface complexes on goethite at pH less than 6 but only an outer-sphere complex at pH values greater than 6 through ATR-FTIR studies.

Dissolved silicate also has a significant effect on the adsorption of arsenate and arsenite on ferrihydrite and other iron and aluminum oxides [127,128], which is caused by the adsorption and polymerization of silicic acid (H_4SiO_4) on ferrihydrite surface. The competitive effect of molybdate on arsenate adsorption on goethite [117], gibbsite [117], kaolinite [118], montmorillonite [118], illite [118], and Cecil clay [129] at pH below 5 has been reported, but the effect is weaker than phosphate [117,129]. Robertson [35] observed

that the occurrence of arsenic in groundwater in southwest U.S. is correlated with dissolved Mo, Se, V, and F^- and with pH, and that leachable arsenic in the basin-fill sediments is about 10 times more abundant than that of the crust, suggesting competitive sorption among negatively charged ions. Compared to the sorption suppression brought by specifically sorbed ligand ions such as phosphate, monovalent anions such as chloride and nitrate seem to have an insignificant effect on arsenate sorption [130]. Besides the competition from inorganic anions, organic species may also interfere with arsenic sorption. Yean et al. [88] observed substantial decrease of arsenic sorption to magnetite nanoparticles in the presence of natural organic matter. Mobilization of arsenic from synthetic iron oxides, soils, aquifer and lake sediments by dissolved organic matter was attributed to the competition between arsenic and organic anions for sorption sites with redox reactions probably of minor importance [131]. Bowell [132] found that organic acids competed for surface binding sites on iron mineral surfaces and reduced sorption of arsenic species. The presence of fulvic acid was also observed to reduce arsenate adsorption on aluminum and iron oxides, kaolin, and quartz [115]. Redman et al. [133] reported that natural organic matter dramatically delayed achievement of sorption equilibria and diminished the extent of sorption of both arsenate and arsenite on hematite, and greatly affected arsenic redox and complexation speciation in freshwater environments. Competition effects for arsenate and arsenite sorption on soil organic matters from anions including $H_2PO_4^-$, CO_3^{2-}, and SO_4^{2-} have also been reported [97].

As shown above, the competing anions can play an important role in arsenic fate and transport. In groundwaters, SO_4^{2-} concentrations are low (typically 1 mg/L or less), while large concentration of phosphate, bicarbonate, silicate and possibly organic matter can enhance the desorption of arsenic through competition for adsorption sites [34]. Sudden rise in concentration of a strongly adsorbing anion (e.g., PO_4^{3-}) can also re-mobilize the arsenic sequestered on iron, aluminum, and manganese (hydr)oxides and clay minerals through competitive adsorption. In AMD, the concentration of SO_4^{2-} can be several orders of magnitude higher than that of arsenate, and can significantly reduce arsenate sorption on iron and aluminum (hydr)oxides, despite its relatively weak affinity. The co-occurring anions in AMD and groundwater systems must be taken into consideration when designing an arsenic removal treatment via sorption.

6. Precipitation and co-precipitation of arsenate and arsenite

Formation of earth alkaline or transition metal–arsenate complexes as limiting mineral phases, which readily precipitate when supersaturated, may potentially control concentrations of dissolved arsenic in water and alter its distribution between solution and solid phases. However, of the more than 320 minerals identified that contain arsenic, only few are present in most geochemical environment [28]. Table 2 lists the solubility product constants (K_{sp}) of some arsenic-containing inorganic salts and the corresponding free arsenate concentrations at metal concentration of 10^{-6} mol/L. Arsenate may react with Fe^{3+}, which exists in very high concentrations in AMD to yield insoluble ferric arsenate, but ferric arsenate is not thermodynamically stable in neutral to high pH region [1]. Other metal arsenates, such as those of Zn(II), Cu(II) and Pb(II) are less soluble and more stable in the neutral pH region. Although lime softening is one of the methods commonly used in water treatment for arsenic removal [134], K_{sp} value of $Ca_3(AsO_4)_2$ suggests that arsenic cannot be removed to very low concentrations by calcium arsenate precipitation alone unless lime is added at very high doses. In the experimental studies of Bothe and Brown [135], $Ca_3(AsO_4)_2$ was not observed in

Table 2
Dissolved arsenate concentration controlled by solubility of different arsenate salts.

Compound	Solubility product constant (K_{sp})[a] at 25 °C	AsO_4^{3-} concentration (mol/L)[b]
$AlAsO_4$	1.6×10^{-16}	1.60×10^{-10}
$Ba_3(AsO_4)_2$	8.0×10^{-51}[c]	8.94×10^{-17}
$BiAsO_4$	4.4×10^{-10}	4.40×10^{-05}
$Ca_3(AsO_4)_2$	6.8×10^{-19}	8.25×10^{-01}
$Cd_3(AsO_4)_2$	2.2×10^{-33}	4.69×10^{-08}
$CrAsO_4$	7.7×10^{-21}	7.70×10^{-15}
$Co_3(AsO_4)_2$	7.6×10^{-29}	8.72×10^{-06}
$Cu_3(AsO_4)_2$	7.6×10^{-36}	2.76×10^{-09}
$FeAsO_4$	5.7×10^{-21}	5.70×10^{-15}
$Pb_3(AsO_4)_2$	4.6×10^{-36}	2.14×10^{-09}
$Mg_3(AsO_4)_2$	2.1×10^{-20}	1.45×10^{-01}
$Mn_3(AsO_4)_2$	1.9×10^{-29}	4.36×10^{-06}
$Ni_3(AsO_4)_2$	3.1×10^{-26}	1.76×10^{-04}
Ag_3AsO_4	1.0×10^{-22}	1.00×10^{-04}
$Sr_3(AsO_4)_2$	8.1×10^{-19}	9.00×10^{-01}
$Zn_3(AsO_4)_2$	1.3×10^{-28}	1.14×10^{-05}
As_2S_3	2.1×10^{-22}	1.45×10^{-02}[d]

[a] Values reported in [169].

[b] AsO_4^{3-} concentration when the corresponding cation concentration is 10^{-6} mol/L.

[c] Value of the solubility product constant of $Ba_3(AsO_4)_2$ is believed to be incorrect [1,28].

[d] Reported as concentration of $HAsO_2$ instead of AsO_4^{3-}. As_2S_3 solubility is based on reaction: $As_2S_3 + 4H_2O = 2HAsO_2 + 3H_2S$, where $H_2S_{(aq)}$ concentration is assumed to be 10^{-6} mol/L.

the precipitates, rather $Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O$, $Ca_5(AsO_4)_3OH$, and $Ca_3(AsO_4)_2 \cdot 3\frac{2}{3}H_2O$ formed. They also observed that the equilibrium concentrations of arsenate were the lowest at high pH (>12) and that the minimum arsenate concentrations in equilibrium with $Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O$ and $Ca_5(AsO_4)_3OH$ were 0.01 and 0.5 mg/L, respectively. Lime precipitation, which was widely used in the past by the metallurgical industry is being abandoned as a result of strong evidence showing that calcium arsenate compounds decompose slowly in contact with atmospheric CO_2 to form calcium carbonate and soluble arsenic acid [136].

Alum and iron precipitations are also common methods used in water treatment for arsenic removal [134,137]. The solubility product constants of the corresponding arsenate salts suggest that they can limit aqueous arsenate concentration to very low levels, but metal arsenate precipitation is not generally believed to be the major arsenate removal mechanism in these processes. The poorly crystalline ferric arsenate precipitate produced during arsenic removal is similar to "arsenical ferrihydrite", which is ferrihydrite containing strongly adsorbed arsenate anions, and it appears to be stable for many years under slightly acidic pH and oxidizing conditions [136]. Sadiq et al. [138] observed that the solubility of arsenic in Kelly Lake, Ontario is controlled by the equilibrium of $Fe_3(AsO_4)_2 \cdot 8H_2O(c)/Fe_4Fe_2(OH)_{12} \cdot SO_4(c)$. Scorodite ($FeAsO_4 \cdot 2H_2O$) is widespread in arsenic-bearing ore deposits and its solubility has been suggested to limit the concentration of arsenate in natural waters with low pH and high total concentrations of iron and arsenic [137]. Based on the K_{sp} value, barium arsenate is extremely insoluble and may severely limit dissolved arsenic concentration. If this is true, $Ba_3(AsO_4)_2$ would be supersaturated over a wide range of Eh, pH, and dissolved solid concentrations, but there is no evidence for the geological occurrence of this material [2,28] and dissolved barium is still detected in waters with low arsenic concentrations (e.g., [139,140]). It is believed that there is a major error in the thermodynamic data associated with $Ba_3(AsO_4)_2$ [1,28].

As shown earlier, arsenate species are predominant at moderate to high redox potentials, while arsenite species occur under reducing conditions. As(III) does not appear to directly precipitate
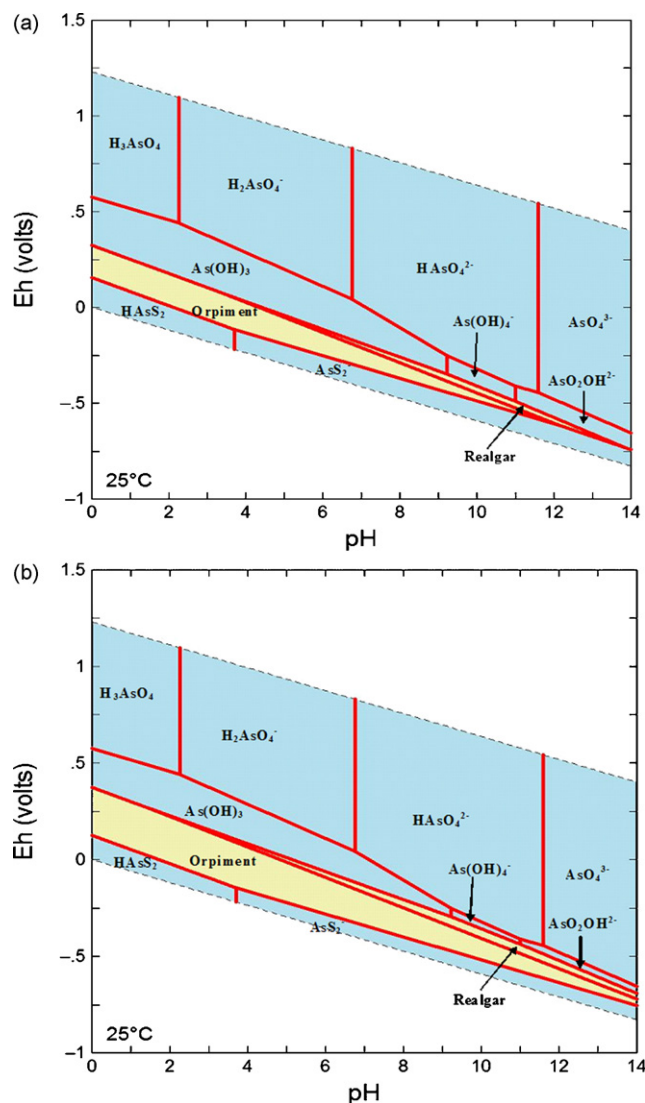

Fig. 7. Eh–pH diagram of arsenic in the presence of sulfur species: (a) at the total concentration of 10^{-6} mol/L for both arsenic and sulfur; and (b) at the total concentration of 10^{-2} mol/L for both arsenic and sulfur.

in salt form with metal ions, but it precipitates in form of orpiment (As_2S_3) under reducing and sulfide rich environment. Precipitation of arsenic sulfide may be an important natural attenuation process for inorganic arsenic and provide a solubility control on dissolved arsenic concentration at low pH [1]. Fig. 7a and b shows the Eh–pH diagram of arsenic species in the presence of sulfur at 10^{-6} and 10^{-2} mol/L (for both arsenic and sulfur), which may represent the conditions in groundwater and AMD, respectively. In both cases, As_2S_3 is supersaturated in the presence of sulfide at low Eh and low pH, with slightly greater solubility (due to formation of $HAsS_2$ and AsS_2^-) at Eh close to the boundary of H^+ reduction. However, arsenic sulfide may not reach saturation to limit dissolved arsenic concentration even under reducing environment because sulfide activity in water bodies is frequently limited by other elements (e.g., iron). Furthermore, orpiment is only stable within a relatively narrow range of redox potentials and its oxidation results in arsenic release.

Fig. 8a and b shows the Eh–pH diagram of arsenic in the presence of iron, aluminum, manganese, magnesium, calcium, and sulfur at 10^{-6} and 10^{-2} mol/L (for all species), which may represent the conditions in groundwater and AMD, respectively. In groundwater
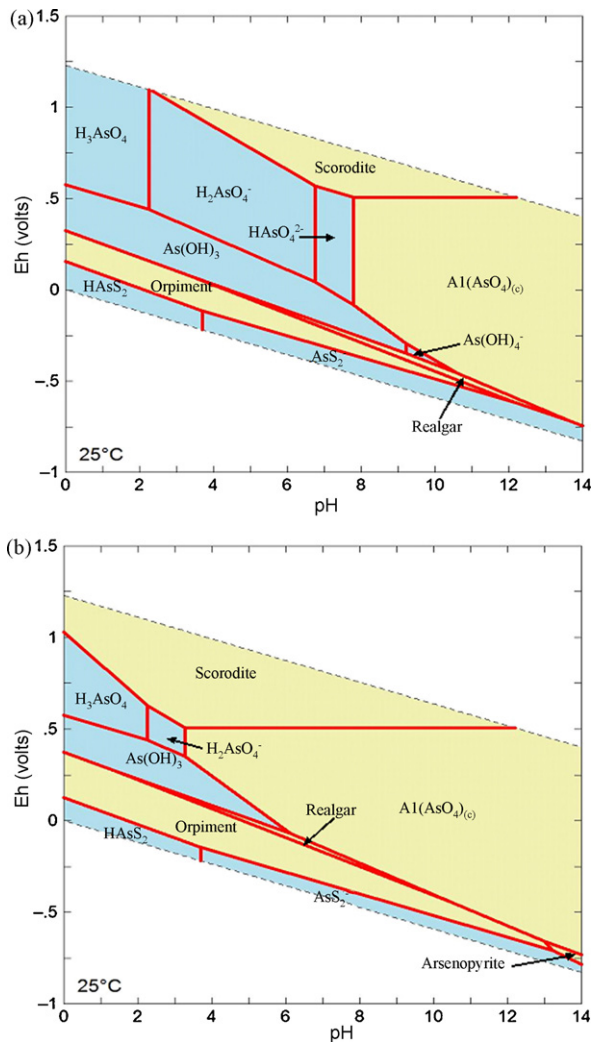
Fig. 8. Eh–pH diagrams for arsenic in the presence of iron, manganese, magnesium, aluminum, calcium, and sulfur: at the total concentration of 10^{-6} mol/L for all species; and (b) at the total concentration of 10^{-2} mol/L for all species. The partial pressure of CO_2 is at $10^{-3.5}$ atm.

environment, $AlAsO_4$ controls the dissolved arsenic concentration at high pH, while scorodite and orpiment control arsenic solubility in narrow ranges of high and low Eh, respectively. For neutral and acidic pH ranges with slightly reducing to highly oxidizing conditions, dissolved arsenic concentration is not limited by precipitation of aluminum or other minerals. In contrast, the stability fields of $AlAsO_4$, scorodite, and orpiment greatly expand when high levels of metals are present in the solution, as in the case of AMD. Arsenic is mobile (as dissolved H_3AsO_4 and $H_2AsO_4^-$) only at pH < 3.5 in a narrow range of Eh. These results agree with the observed occurrence of dissolved arsenic in AMD and other types of natural water [2,34,36,49,51]. Overall, field observations suggest that direct precipitation of discrete arsenic solid phase may not occur except in contaminated soils [2]. The concentrations of dissolved arsenic observed in groundwater environments are often orders of magnitude less than the solubilities of most arsenic-bearing minerals [37]. Thermodynamic predictions show that some arsenic minerals could potentially control arsenic concentrations in groundwater under common geochemical conditions, but these minerals are rarely if ever documented outside of mineralized area [141]. The limited thermodynamic data available does not allow full assessment of solubility controls on dissolved arsenic con-

centrations, and the lack of precipitation and dissolution kinetic information further constrains the applicability of solubility control by mineral precipitation. It appears that direct precipitation or dissolution of arsenic minerals is not limiting inorganic arsenic solubility in natural waters. Arsenic concentrations observed in aquatic environment probably reflect availability from geological materials and direct input, versus removal via adsorption processes [1].

Besides direct precipitation as pure minerals, arsenic may also co-precipitate with hydrous oxides and hydroxides of iron, aluminum, and manganese. Co-precipitation is the simultaneous precipitation of a normally soluble component with a macro-component from the same solution by the formation of mixed crystals, by adsorption, occlusion or mechanical entrapment [142]. Arsenic may be sequestered from solution during the precipitation of soluble iron resulting in the formation of a poorly crystalline hydrous ferric oxide containing co-precipitated arsenic [102,143–146]. Adsorption and co-precipitation of arsenate with iron and aluminum flocs are believed to be the primary arsenic removal mechanisms in water treatment plants [147,148]. At high Fe/As weight ratio (>5:1) and elevated pH, surface complexation and electrostatic attraction lead to co-precipitation of arsenate [149]. Mamtaz and Bache [144] found that Fe(III) was more efficient than Fe(II) at removing arsenite from groundwater through co-precipitation, possibly due to the low oxidation rate of Fe(II) (i.e., oxidation of Fe(II) to Fe(III) limited the formation of ferric hydroxide, which is a more effective arsenic scavenger than ferrous hydroxide). They also suggested that adsorption may be the primary mechanism controlling arsenite removal when the Fe/As weight ratio is greater than 10. Meng et al. [150] found that Fe/As weight ratios of greater than 40 were required to reduce arsenic concentration to less than 50 μg/L in Bangladesh well water due to the presence of elevated phosphate and silicate concentrations. Bowell [132] observed that the proportion of arsenic associated with amorphous iron oxyhydroxides was much greater than that associated with crystalline iron oxyhydroxide and oxide minerals. Ford [151] reported that arsenate co-precipitated with hydrous ferric oxide was stabilized against dissolution during transformation of hydrous ferric oxide to the more crystalline hematite and goethite.

Waychunas et al. [102] compared both the As and Fe EXAFS spectra of ferrihydrite with adsorbed and co-precipitated arsenate. Inner-sphere bidentate (bridging) arsenate complexes on the ferrihydrite surface and on the surfaces of the crystalline FeOOH polymorphs were observed, while monodentate arsenate linkages also occurred on the ferrihydrite surface, but were not generally observed on the crystalline FeOOH polymorphs. They also observed that the Fe–Fe correlations in the ferrihydrite were progressively disrupted in the co-precipitated samples as the Fe/As ratio was decreased, and no Fe oxyhydroxyl octahedra corner-sharing linkages (as would be present in FeOOH polymorphs) at the lowest Fe/As ratios. It was suggested that the strong arsenate bidentate adsorption prevented further Fe–O–Fe polymerization at high As/Fe ratios, and resulted in an enlarged surface area and a larger proportion of sites for bidentate arsenate bonding in co-precipitated samples as compared to the adsorbed samples. Kinetic studies of arsenate adsorption and co-precipitation by Fuller et al. [143] showed that the initial arsenate uptake by co-precipitation was significantly greater than by adsorption, and that the uptake rate was not diffusion limited because arsenate was coordinated by surface sites before crystallite growth and coagulation processes could proceed. They also observed that arsenate was slowly released from the precipitates for at least 1 month after the initial adsorption caused by crystallite growth, and that the adsorption densities by co-precipitation (0.7 mole arsenate per mole of Fe) may be near

three times higher than those by adsorption (0.25 mole arsenate per mole of Fe).

Precipitation and dissolution of minerals that do not contain arsenic also influence dissolved arsenic concentration through arsenic sorption and co-precipitation. Iron and aluminum (hydr)oxides are of particular importance because of their wide occurrence and high arsenic sequestering capacity. Fe and Al are dissolved in solution at low pH, but precipitate out in form of (hydr)oxides in near-neutral to alkaline solutions (iron hydroxide may re-dissolve under highly reducing conditions while aluminum hydroxide re-dissolves at pH above 8). As these minerals are important sinks of arsenic species, changes in their stabilities can bring about transfers of large amounts of arsenic between the solid phase and aqueous solution. The pH of AMD is usually very low, which does not allow metal arsenate salts or metal (hydr)oxides to precipitate unless the acidity is neutralized. When pH of AMD rises back to near-neutral, dissolved arsenate concentrations begin to drop rapidly with the precipitation of iron (hydr)oxides through precipitation, co-precipitation, and sorption. Arsenite species are also removed in this process, but to a less extent. This naturally occurring attenuation mechanism significantly reduces the concentrations of arsenic transported downstream after iron (hydr)oxide precipitation.

7. Remediation of arsenic contamination

Soil contaminated with arsenic has traditionally been addressed with conventional cleanup technologies such as soil removal, soil washing, and physical stabilization (capping), which are expensive and disruptive to the environment [152]. *In situ* remediation of arsenic-contaminated soil and groundwater can provide a relatively inexpensive alternative to above ground treatment. Geochemical fixation and phytoremediation have been developed for cost-effective treatments of arsenic contamination. Proper modification of the chemistry of soil, groundwater or aquifer materials to create conditions that favor arsenic sorption on the solid phases is the principal mechanism immobilizing arsenic in soils and removing it from groundwater. Hydroxides of iron, aluminum and manganese, clay and sulfide minerals, and natural organic matter are commonly associated with soils and aquifer sediments, and have been shown to be significant arsenic sorbents [153–160]. As discussed in previous sections, the extent of sorption is influenced by arsenic speciation and the site geochemical conditions such as pH, redox potential, and the co-occurring ions [78,131,157,161]. In addition, microbial activity can catalyze the transformation of arsenic species, or mediate redox reactions thus influencing arsenic mobility, while plants capable of hyperaccumulating arsenic may translocate it from contaminated soils and groundwater to their tissues, providing the basis for phytoremediation [152,154,162–164].

Various options are available for remediating AMD, which can be divided into those that use either chemical or biological mechanisms to neutralize AMD and remove metals (iron, aluminum and manganese, and possibly other heavy metals) and metalloids (of which arsenic is generally of greatest concern) from solution [165]. In both abiotic and biotic processes, arsenic species are removed through a combination of precipitation, co-precipitation, sorption, and ion-exchange processes with the neutralization of AMD's acidity and precipitation of iron/aluminum/manganese species [165,166].

8. Conclusion

Accelerated weathering of sulfide minerals, which are rich in arsenic, results in AMD containing arsenic at elevated concentrations. Speciation with respect to Eh and pH determines how arsenic species interact with the environment and is the primary reason for the different behaviors of arsenate and arsenite. Arsenate species are more abundant under oxidizing conditions while arsenite species are predominant in reducing environment. Heterogeneous oxidation on manganese (hydr)oxide mineral surfaces at high pH and on iron (hydr)oxide mineral surfaces at low pH probably plays a key role in arsenite oxidation because of the slow homogeneous oxidation kinetics. H_3AsO_4 and $H_2AsO_4^-$ are predominant arsenate species in AMD and natural water, while the total aqueous arsenate concentration is not controlled by solubilities of arsenate minerals. Arsenite mainly exists in the form of H_3AsO_3 in AMD and natural water, and is very mobile because of its neutral nature. Arsenate and arsenite adsorb on many metal (hydr)oxides and clay minerals through formation of inner-sphere and/or outer-sphere surface complexes, and solution pH and competing anions can have major effect on their sorption. Arsenate is sorbed more strongly by (hydr)oxides and clay minerals, and is less toxic than the more mobile arsenite in the typical pH range of natural water. Many anions (especially phosphate and sulfate) in AMD and groundwater can compete for the sorption sites on mineral surfaces and reduce arsenic adsorption, and sudden input of such anions may lead to arsenic desorption. Compared to groundwater and other natural water bodies, the pH of AMD vary significantly. A series of acid-neutralization reactions occur as the acidic water travel downstream/downgradient, and the pH can increase from very acidic to slightly above neutral. Such change in solution pH controls arsenic fate and transport in AMD system through its effects on arsenate and arsenite speciation, redox reactions of arsenic species and other redox pairs, precipitation and dissolution of minerals and metal (hydr)oxides, and the surface charges of solid phases, as discussed in the previous sections. When acidity of AMD is neutralized, arsenate is effectively scavenged through a suite of precipitation, co-precipitation, and adsorption reactions, while a portion of arsenite may remain in the aqueous stream. The arsenic sequestered in solid precipitates can be re-mobilized due to change in surface charge, structural re-organization of the precipitated minerals, or their re-dissolution at low pH.

Thermodynamic principles can be used to determine the predominant arsenic species under given conditions, although this is limited by the availability and quality of the thermodynamic data. The kinetics of many chemical reactions may be slow and equilibrium states may not be reached for reactions involving arsenic species in natural systems because of the ever-changing conditions. The kinetic limitation of chemical reactions further complicates the fate and transport of arsenic in AMD and natural systems. Nonetheless, thermodynamics is a powerful tool in studying arsenic geochemistry. With appropriate caution it can help to interpret the observed arsenic occurrence and speciation, to predict its mobility, and to design remediation and treatment strategies minimizing arsenic contamination in AMD and natural systems.

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