A REVIEW OF THE INCORPORAION AND MOBILIZATION OF ARSENIC IN HYDROTHERMALLY ALTERED ROCKS EXCAVATED DURING TUNNEL CONSTRUCTION

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Abstract

In 2002, a new environmental regulation in Japan addressed the potentially hazardous nature of hydrothermally altered rocks excavated from tunnel projects. Prior to the formulation of this new regulation, excavated rocks from tunnel projects have been widely considered non-hazardous and used as embankment material for the construction of roads. Tunnels for roads and railways will continue to be constructed in the foreseeable future because of the continued economic prosperity in most of South East Asia, which will produce large volumes of excavated rocks including considerable amounts of those that were hydrothermally altered because of the many active volcanoes and faults located in the region. These altered rocks generally have high amounts of environmentally-regulated hazardous elements like arsenic (As). However, not much has been reported regarding the distribution and mobilization of As in tunnel excavated rocks because of the relatively recent nature of the problem. This paper presents a review of the current knowledge pertaining to the incorporation of As into altered rocks as well as the mobilization of this element in altered rock-water systems. Moreover, this paper compares the leaching behavior of As from altered rocks to other solid-liquid systems that have been extensively studied in the past like mine wastes/tailings, contaminated soils/sediments and aquifers.

Keywords: Arsenic, Hydrothermally altered rocks, Incorporation, Mobilization

Introduction

Arsenic (As), which is the 33rd element in the periodic table, is a silver-grey brittle solid with atomic weight of 74.9 g/mol. Although very toxic, As is widely utilized in the manufacture of ceramics and semiconductors because of its metallic and non-metallic properties. Arsenic poisoning in humans is categorized into either acute or chronic. Acute poisoning pertains to the intake of As in large doses through food, water or air that is fatal if left untreated. In contrast, chronic As poisoning is associated with the minute intake of As for an extended period of time usually from contaminated drinking water. Chronic As poisoning has been implicated in a number of serious health problems that include arsenicosis, keratosis and certain types of cancers (*e.g.*, skin, lungs, liver, bladder and kidneys) [1,2,3,4,5,6,7,8,9].

The sources of As contamination can be grouped into either natural or anthropogenic (man-made). Local geologic settings and anomalies are responsible for the former while human activities such as mining, agriculture, manufacturing and sewage account for the latter. One famous example of As contamination due to natural causes is the high-As groundwater in

Bangladesh and West Bengal, India used for drinking and cooking that has been affecting more than 70 million people [10,11,12,13,14]. Other cases of As contamination, which are due to either natural or anthropogenic causes, have also been reported in many countries around the world including Taiwan, China, Vietnam, Cambodia, Hungary, Romania, United States, Mexico, Chile, Argentina, Thailand, Ghana, Greece, SW England, South Africa and Zimbabwe [8,9,15,16,17,18,19,20,21,22].

Until recently, excavated rocks especially from tunnel projects are not considered hazardous wastes because they generally contain low concentrations of environmentally-regulated elements like As, boron (B), selenium (Se) and heavy metals. In Japan, these tunnel excavated rocks are usually reused as embankment material during road construction. However, a new and stricter construction waste disposal regulation was enacted in 2002, which showed the potential hazard associated with excavated rocks especially those that have been hydrothermally altered or of marine origin. Among the environmentally-regulated hazardous elements enumerated above, As is the most commonly encountered toxic element in excavated altered rocks. However, altered rocks that contain, in addition to As, other hazardous elements like Se and B as well as heavy metals like lead (Pb), copper (Cu) and zinc (Zn) are excavated from time to time. Therefore, contamination of the environment by these hazardous elements present in this new source is a serious problem and must be addressed accordingly.

Extensive reviews about As are found in the literature that helped in explaining the sources, distribution, mobilization, speciation and geochemistry of this element in the natural environment [23,24,25,26]. However, these reviews did not include excavated rocks from tunnel construction because most of them were published before environmental concerns related to these rocks became significant. Therefore, this paper aims to present a summary of the current knowledge regarding the distribution and mobilization of as in hydrothermally altered rocks excavated during tunnel constructions. Moreover, this paper would provide a comparison of the mobilization of as in these altered rocks-water systems with those that have been more extensively studied like contaminated soils and sediments, mine wastes/tailings and aquifers. This review would provide engineers and scientists with knowledge for the proper management of these hazardous excavated rocks to avoid future environmental problems related to as leaching and contamination.

Incorporation and Distribution of Arsenic in Hydrothermally Altered Rocks Excavated from Tunnel Construction

Hydrothermally altered rocks are enriched with metals like Pb, chromium (Cr), Cu, gold (Au) and silver (Ag) or with metalloids like as due to the interactions of the host rock (i.e., unaltered rock) with hydrothermal solutions/fluids. When hydrothermal solutions/fluids containing solutes derived from magmatic water or from the wall rock migrate upward, changes in equilibrium with space and time allow the deposition of the dissolved solutes onto the host rock [27]. In certain exceptional cases where the hydrothermal solution/fluid is highly mineralized, ore deposits are formed during alteration through the concentration of valuable metallic elements (e.g., Au, Ag and Cu) in sulfide minerals. In most cases, however, the hydrothermal solution/fluids interacting with the host rock are less mineralized, which causes substantial chemical and mineralogical changes to the host rock but with little enrichment of economically-valuable metallic minerals. The extent of alteration of the host rock depends on the inherent physical (e.g., temperature) and chemical properties (i.e., degree of mineralization) of the solution/fluid interacting with the rock as well as its distance from the "core" of the alteration area. Because of this, rocks excavated in tunnels constructed through altered rock beds have very complex chemical and mineralogical compositions. In addition, variability of the chemical and mineralogical properties of the excavated rock is compounded by the mixing of altered and unaltered rocks, which are both excavated during construction. Take for example the tunnel project in the Nakakoshi area of Kamikawa province in Hokkaido, Japan, which was built as part of the national highway connecting the cities of Asahikawa and Monbetsu. Hydrothermally altered rock extended from the mouth to more than 175 m into this tunnel, and a mineralized zone accompanied the hydrothermal alteration with a maximum width of 2.5 m, composed of quartz-pyrite vein and veinlets [28]. In addition, a strongly-altered andesitic dike with a width of 4 m was observed near the center of alteration. The hydrothermal alteration of slate in this area is characterized by silicification, pyritization and argillic alteration of kaolinite resulting in a high As abundance of the rock (up to 513 mg/kg). A summary of the mineral composition of rock samples collected from different parts of this tunnel (e.g., around the quartz-pyrite vein, andesitic dike and unaltered rock) clearly shows large variations in mineral composition depending on the extent of alteration (Table 1). Rocks situated in the "core" of alteration (i.e., around the veins and veinlets) have more complex compositions and contain minerals ranging from sulfides (e.g., pyrite, marcasite and arsenopyrite) and clays (e.g., kaolinite and illite) to carbonates (e.g., calcite, siderite). In contrast, the unaltered host rock (slate) is only composed of quartz and trace amounts of chlorite. From Table 1, occurrences of primary As minerals (e.g., arsenopyrite) in these altered excavated rocks are limited to the "core" of alteration, and their relative abundance was too low to be of importance especially after the mixing of the altered and unaltered rocks during excavation.

Table 1. Mineralogical Composition of the Altered, Unaltered and Bulk Excavated Rock from the Nakakoshi Tunnel [28]

Sample Description		Qz	Pl	Ab	Ill	Chl	Kao	Cal	Sid	Ank	Py	Apy	Pyh	Mar
Altered rock	Altered slate	++++	+++		-	+		++			-			
	Strongly altered slate	++++		+	-	+	+	+++	-		-			
	Strongly altered slate near vein	++++	+		+	+	++				-			
	White clay vein	+					++++		+	+				
	Silicic rock	++++		-	-	-					-			
	Quartz vein with pyrite	++++		+	-						++			++
	Andesite	+++	+	+	+	+	-							
Altered mineral	White vein	++					++++		+					
	White vein							++++						
	Vein	+					+++		+++					
	Non magnetized bulk pyrite	+	+					+			++++			
	Non magnetized flaked pyrite	+++					-					+		
	Magnetized pyrite	++				-		+					+++	
Unaltered rock	Slate	++++				-								
Bulk rock	Mixed altered and unaltered	++++	+++			+	+	+			-			

++++: Very high; +++: high; ++: medium; +: minor; - : trace

Even pyrite, which is relatively abundant in the altered rocks, was “diluted” in the bulk excavated rock as a result of this mixing (Table 1).

Although hydrothermal alteration causes large spatial variations in the chemical and mineralogical properties of the host rock, Tabelin et al. [29] found a distinct pattern regarding the enrichment of the rock with toxic elements especially As. They analyzed the As contents of pyrite crystals found in two different tunnels: one rock underwent phyllic-type alteration while the other experienced sericitic-type alteration. They found that As enrichment primarily occurred in precipitated pyrite grains and not the silicate-aluminate matrix of the host rock regardless of the type of alteration [29]. In addition, as was only incorporated into pyrite formed during hydrothermal alteration and not in those formed during the diagenesis of the sedimentary rock, which highlighted the importance of an as-rich fluid in the formation of “arsenian” pyrite. This important condition for the formation of as-rich pyrite has also been observed in sedimentary and other hydrothermal systems by other researchers [5,30,31,32,33]. Incorporation of As into pyrite could occur probably as non-stoichiometric substitution or as a metastable $Fe(As,S)_2$ solid solution [34,35]. Thus, pyrite (FeS_2) should be considered as the most common toxic element-bearing mineral precipitated during hydrothermal alteration and one of the primary sources of as in excavated hydrothermally altered rocks.

pH and Eh as Master Variables of Arsenic Mobilization

Arsenic in rocks, sediments and soils predominantly occur together with minerals like Fe-oxyhydroxides/oxides and sulfides as explained in the reviews of Drahota and Filippi [24] and Smedley and Kinniburgh [26]. Thus, stability of these minerals in solid-liquid systems has a direct influence on as mobilization. Based on thermodynamic considerations, stability of minerals in an aqueous solution at a given temperature is largely a function of the pH and redox potential (Eh). Figure 1 illustrates the pH and Eh dependence of pyrite and hematite dissolution at 25°C. Under acidic conditions, dissolution of metallic oxides like hematite is thermodynamically favorable, which releases dissolved Fe^{2+} into solution. In addition, strongly acidic solutions tend to support higher concentrations of dissolved metallic species of Fe like Fe^{2+} and Fe^{3+}. Under acidic conditions, the dissolution of metallic hydroxides, oxyhydroxides and oxides starts with the attachment of protons (i.e., H^+ ions) onto the oxide surfaces that weakens critical bonds and ends with the detachment of the metal species into solution [36]. Proton-promoted dissolution of these minerals is a surface-controlled process where the rate-limiting step is the detachment of Fe units from the crystalline framework of the minerals [37,38,39,40,41,42,43,44,45,46]. Under circumneutral and alkaline conditions, dissolved metallic species begin to precipitate forming metallic hydroxides, oxyhydroxides and oxides thereby limiting their mobilities in solution.

On the other hand, pyrite is stable throughout the entire pH range provided that the Eh is moderately oxidizing (Eh ≈ 0.25 V) to strongly reducing (Eh ≈ -0.75 V) (Figure 1). Under strongly oxidizing conditions generally found in surface waters in equilibrium with the atmosphere, pyrite dissociates releasing Fe, SO_4^{2-}, H^+ and it’s associated as load as explained by the following equations:

$$FeS_{2(s)} + 3.5\ O_{2(aq)} + H_2O \longrightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-} \qquad \text{Equation 1}$$

$$FeS_{2(s)} + 14\ Fe^{3+} + 8\ H_2O \longrightarrow 15\ Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad \text{Equation 2}$$

$$Fe^{2+} + 0.25\ O_{2(aq)} + H^{+} \longrightarrow Fe^{3+} + 0.25\ H_2O \qquad \text{Equation 3}$$

Oxidation of pyrite with pH is a very complicated process because of the combined effects of different oxidants like O_2 and Fe^{3+} as well as the mediation of microorganisms. Ferric ion (Fe^{3+}) and O_2 are two of the most important oxidants of pyrite [42,48,49,50,51]. Under abiotic conditions, dissolved oxygen (DO) is important both as direct oxidant of pyrite and indirectly as an oxidant of Fe^{2+} (Equations 1 and 3). However, Fe^{3+} is more powerful than O_2 as an oxidant when these two are both present in a system [50]. Thus, in the acidic region where the solubility of Fe^{3+} is high, it becomes the most important oxidant of pyrite. As the pH increases towards the alkaline region, the rate of Equation 3 increases dramatically, but under these conditions Fe^{3+} is also easily precipitated [52]. Regardless of these very low concentrations of Fe^{3+} in the alkaline region, it is still an important oxidant of pyrite as reported by Moses et al. [50]. According to these authors, O_2 becomes more important to replenish the diminishing Fe^{3+} through Fe^{3+}/Fe^{2+} recycling under alkaline conditions because of the very low concentrations of Fe^{3+} [50]. In the presence of microorganisms like *Thiobacillus ferroxidans*, which oxidizes Fe^{2+} to Fe^{3+}, equation 3 is catalyzed increasing the rate of pyrite oxidation by several-fold [53].

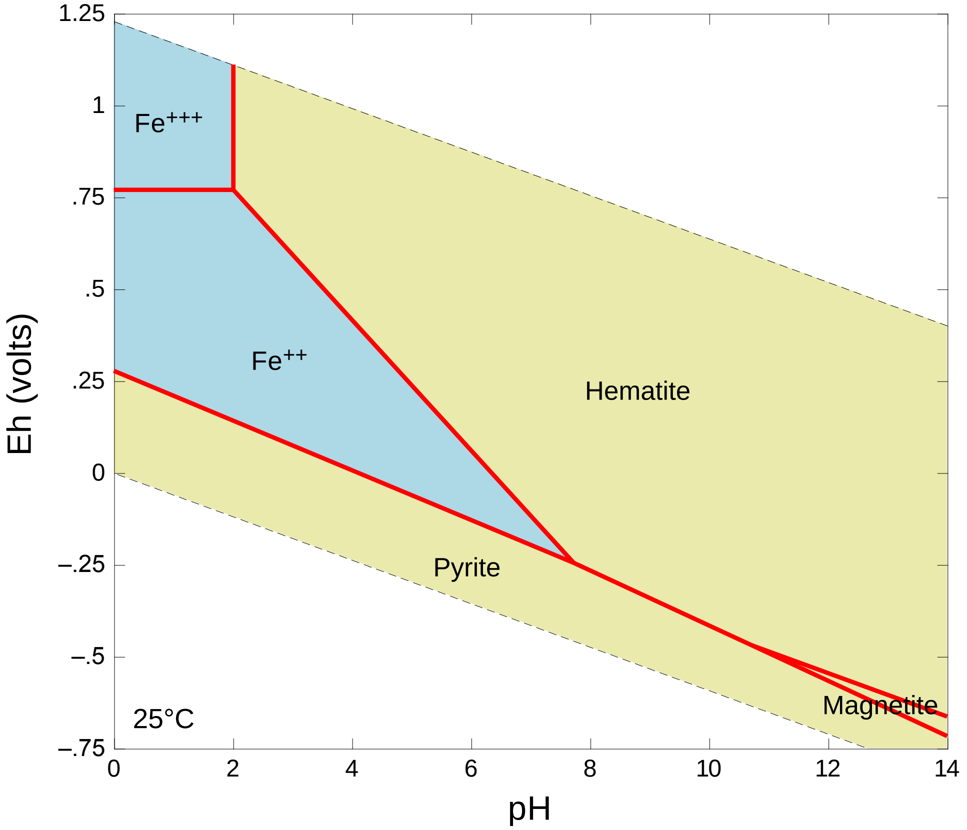

Figure 1. Eh-pH predominance diagram of Fe at 25°C, 1.013 bars, activity of Fe and SO_4^{2-} = 10^{-3}. Yellow and blue regions in the diagram represent solid and liquid phases, respectively

Figure 2 illustrates the strong pH dependence of both As mobilization and dissolution of Fe-bearing minerals in altered rock-water systems. The leaching of As in altered rocks is enhanced at acidic and alkaline pH while a minimum is observed in the circumneutral pH that is identical to the leaching behavior of Fe. According to the previously published works of the authors, the processes controlling the release of As from altered rocks include dissolution, desorption/adsorption and pyrite oxidation [28,29,54,55,56,57]. In the acidic region, dissolution of soluble phases and Fe-bearing minerals that contain As predominates whilst pyrite oxidation and desorption of adsorbed As are the main release mechanisms in the alkaline region [55]. Desorption/adsorption of As, which is generally present in solution as a negatively charge anion, is strongly pH dependent because of the variable surface charges found in natural adsorbents like Al- and Fe-oxyhydroxides/oxides. These minerals possess a variable-charged surface as a result of chemically-bound water to metal atoms at the interface between the mineral phase and aqueous solution [53]. The surfaces of these minerals become protonated when the solution contains high concentration of H^+ (acidic conditions) that results in a strong positively-charged surface.

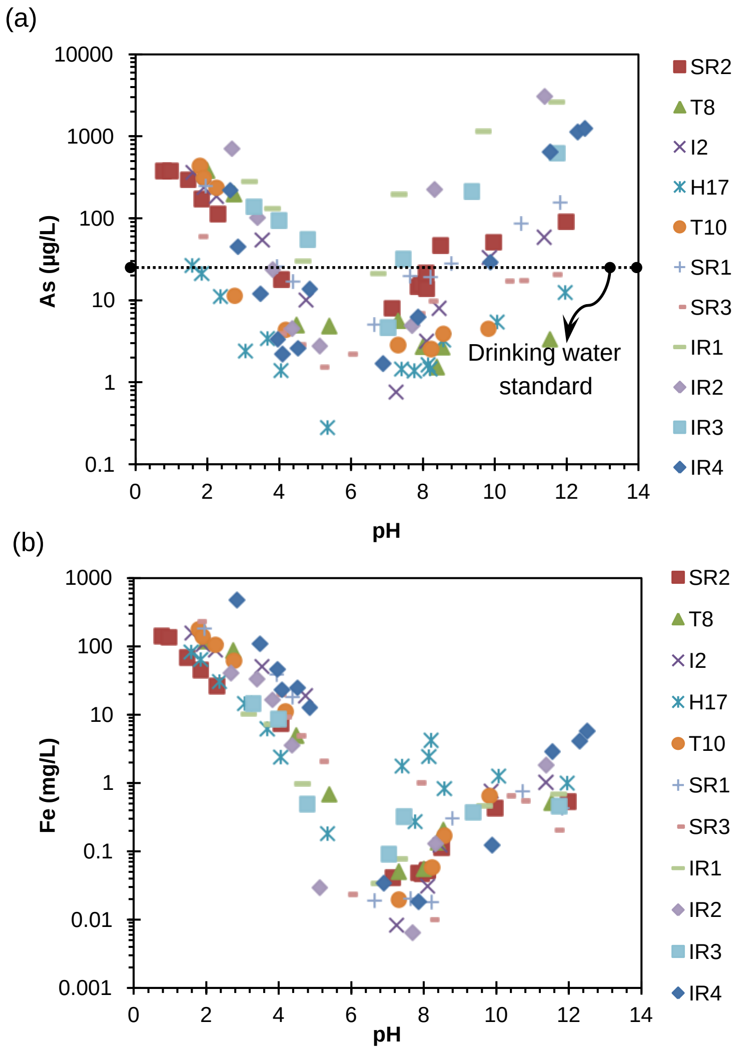

Figure 2. Leaching behavior of as and Fe in the entire pH from several altered rock samples: (a) as concentration as a function of pH, (b) Fe concentration as a function of pH

Because of these positively charged surfaces, adsorption of As onto Al and Fe-oxyhydroxides is favorable especially around slightly acidic to circumnetral pH (pH 4 – 8) where the dissolution of these minerals is still negligible. As the pH increases, the positively charged surfaces of these minerals slowly diminish and changes to negative under alkaline conditions (e.g., goethite: pH > 8.1; δ-Al_2O_3: pH > 10) [53,58]. On the other hand, pyrite oxidation increases under abiotic-alkaline conditions because of the availability of surface OH^- species that are involved in more rapid electron transfer at the pyrite surface [52]. The low mobility of As in the circumneutral pH is attributed to the strong adsorption of As onto Fe- and/or Al-oxyhydroxides/oxides found or precipitated in the rock, which are stable at this pH range [58,59,60,61].

The importance of pH on the mobility of As is well documented in mine waste rocks/tailings, industrial processing wastes like fly ash, and contaminated soils or sediments. According to Ritcey [62], as together with cyanide are the main toxic substances of concern in tailings of most gold plants. Dissolved as in these tailings are precipitated as ferric arsenate ($FeAsO_4$), with Ca and Mg arsenates or adsorbed onto Fe-oxyhydroxides at higher pH through the addition of lime [62]. However, as immobilized or adsorbed could be solubilised from these precipitates during years of weathering due to the acidic pH generated by sulfide weathering [62]. The same observation of enhanced as leaching at acidic pH was reported by Doyle et al. [63] who evaluated the stability of treated copper smelter flue dusts. These authors identified scorodite ($FeAsO_4 \cdot 2H_2O$) as the principal As-bearing phase in this treated flue dust and attributed the higher leaching of As in the continuous reactor test (1,000 – 1,400 µg/L) compared with the batch reactor test (100 – 300 µg/L) to more acidic pH. Acidic pH also enhanced the mobility of as in iron-rich mineral processing wastes [64].

The importance of pH in the mobilization of As in aquifer systems have also been reported by many researchers. Peters and Burkert [65], who investigated the groundwater in the Mesozoic sedimentary strata composed of sandstone and red mudstone with interbedded gray shale, and gray to black siltstones and shale, found that the concentration of As strongly correlated with variations in the pH, with highest concentrations observed at pH values greater than 6.4. Smedley et al. [66] also reported positive correlations of As concentration and pH from the Quarternary loess aquifer in La Pampa, Argentina. The pH of the groundwater in this loess aquifer ranges from 7 to 8.7, which is attributed to carbonate and silicate interactions under arid conditions. In both of these aquifer systems, the authors attributed the high As concentrations at higher pH values to the increased desorption of As [65,66].

Under anoxic and reducing conditions, the release mechanisms of As from altered rocks did not dramatically change. The depleted supply of DO under anoxic conditions resulted in lower leaching of As, but only in the alkaline region, which was attributed to the reduced extent of pyrite oxidation [29]. DO become more important in pyrite oxidation under alkaline pH because of its role both as direct oxidant of pyrite and in the recycling of Fe^{3+}/Fe^{2+} [49,50]. In the acidic and circumneutral region, the effect of depleted DO was not apparent because of the availability of Fe^{3+}, which is a stronger oxidant of pyrite than DO [50]. Under reducing conditions, leaching of As from altered rocks was more pronounced because of the reductive dissolution of Fe-oxyhydroxides/oxides, which released both adsorbed (labile) and irreversibly-bound (non-labile) As [55]. Oxides of redox-sensitive metals like Fe undergo reductive dissolution via the direct reduction of the oxide surface by reducing organic ligand or reducing metal complexes that weaken the bonds between reduced Fe and O^{2-} in the crystal lattice (i.e., reduction of the Madelung energy) [67,68,69]. Some of the dissolved As under reducing conditions could be removed via co-precipitation with pyrite or its direct precipitation as amorphous orpiment (As_2S_3) [70,71,72]. However, the extent of As removal by these processes under reducing conditions were less effective than the scavenging capability of Fe-oxyhydroxides/oxides under oxic conditions, which was apparent in the higher As concentrations throughout the entire pH range under reducing conditions [55].

The strong influence of Eh (redox potential) on the mobility of As is more pronounced in aquifer systems because of their nearly constant pH values. Arsenic in most aquifer systems is concentrated in Fe-oxyhydroxides/oxides [11,14,73,74] and/or sulfide minerals like arsenian pyrite, marcasite and realgar-like As-sulfide [5,32,65,73]. Because all of these above mentioned mineral phases are redox sensitive, the release of their associated As loads is also highly dependent on the Eh of the system. Thus, pyrite and Fe-oxyhydroxides/oxides could act either as sources or sinks of As depending on the prevailing redox conditions. In Wisconsin, USA, Schreiber et al. [73] reported that the high As concentration in the groundwater was the result of the oxidation of sulfide minerals like pyrite and marcasite. Oxidation of these sulfide minerals appear to have been promoted by groundwater abstraction that has led to the lowering of the piezometric surface of the aquifer since the 1950s [73]. In contrast, Lowers et al. [32] reported that As is being partitioned into pyrite in the reducing groundwater of the Bengal basin when adequate sulfate is available, which results in the low concentration of dissolved As in the deeper parts of the aquifer. In addition, O'Day et al. [5] identified the formation of a realgar-like arsenic sulfide that could act as a sink of As if the groundwater As concentrations are sufficiently high (i.e., μM) under sulfate-reducing conditions. However, reductive dissolution of Fe-oxyhydroxides poses a bigger problem in aquifers than the oxidation of sulfide minerals. In the Bengal basin, high As concentrations in the groundwater has been attributed to the reductive dissolution of ferric oxyhydroxides mediated by bacteria, which are present in the sediment as grain coatings [11,14]. Reductive dissolution of Fe-oxyhydroxides was also pointed by other authors as the primary mechanism of As release into groundwater in reducing aquifers found in Taiwan, Japan, China, USA, Vietnam, Hungary and Romania [15,74,75,76,77,78,79]. Aside from aquifers, reducing conditions induced by anthropogenic sources such as landfills could also mobilize naturally occurring As in sediments. According to Keimowitz et al. [80], dissolved As in groundwater plumes reached concentrations of ca. 300 μg/L because of the strongly reducing conditions induced by leachates from landfills onto the subsurface sediments. These As did not appear to originate from within the landfill but was leached out from the subsurface natural glacial aquifer solids found beneath the landfill that contained an average of 5 mg/kg of As [80].

Effects of Coexisting Ions on the Leaching of Arsenic from Altered Rocks

Coexisting ions are important in the mobilization of As because of their positive or negative effect on As adsorption onto mineral phases especially those of Al and Fe. Dissolved As is generally found in solution as either a negatively (e.g., $HAsO_4^{2-}$ and $H_4AsO_4^{-}$) or uncharged oxyanion (e.g., H_3AsO_4 and H_3AsO_3). Based on electrostatic effects, adsorption of As could be enhanced by cations through the formation of more positively-charged surfaces on oxide minerals. According to Ghosh and Teoh [81], the adsorption of arsenate (As(V)) onto Al oxides was enhanced at pH above 8 in the presence of Ca^{2+}. This positive effect of Ca^{2+} on the adsorption of As(V) was also observed by Wilkie and Hering [82] in their experiments using ferrihydrite as adsorbent at pH 9. Meng et al. [83] reported that addition of Ca^{2+} and Mg^{2+}

enhanced As(V) co-precipitation and adsorption onto ferric hydroxide by negating the competitive effects of silicate. Similarly, Stachowicz et al. [84] found that Ca^{2+} and Mg^{2+} promoted the adsorption of As(V) onto goethite in the pH range of 5 – 9. In addition, these authors showed that Ca^{2+} has a minor effect on the adsorption of arsenite (As(III)) only at very high pH values, but not in the pH range (6 – 9) relevant for natural groundwater while Mg^{2+} ions had no significant effect on As(III) oxyanion binding over a very large pH range [84]. The reaction of Mg^{2+} and Ca^{2+} with goethite surfaces is governed by the formation of bidentate and monodentate inner sphere complexes, respectively, which are hydrolyzed in water [84,85].

On the other hand, several anions inhibit the adsorption of As primarily due tocompetition with adsorption sites. Phosphate (PO43-) has been shown to strongly suppress the adsorption of both As(V) and As(III) onto Al and Fe oxyhydroxides/oxides, natural iron-ores and polymetallic sea nodules [84,86,87,88,89,90]. Other anions documented in the literature that have slight to moderate negative effects on As adsorption include dissolved Si (H4SiO4), bicarbonate (HCO32-) and sulfate (SO42-) [83,86,89,90,91,92]. According to Meng et al. [83], adsorption of H4SiO4 onto ferric hydroxide inhibited As adsorption because of the increased electrostatic repulsion for As anions and reduced concentration of available surface sites. In addition, H4SiO4 could hinder the precipitation of ferric hydroxide at pH greater than 8.6 and H4SiO4 concentration of ca. 5 mg/L, which could further decrease As adsorption. On a ferrihydrite surface, the adverse effect of H4SiO4 to As adsorption is further compounded by polymerization [92]. Polymerization of H4SiO4 inhibits the adsorption of As by making the ferrihydrite surface more negatively charged due to the increased acidity of remaining silanol groups when the number of siloxane linkages increased [92,93]. Bicarbonate also has a moderate negative effect on the adsorption of As(III) onto ferric hydroxides [89]. However, the effect of HCO3- on As adsorption is negligible in a multi-ionic system containing PO43-[84]. The differences in the inhibitory effects of these anions could be related to their relative binding affinity onto the iron hydroxides surface. Meng et al. [89] evaluated the binding affinities of these anions together with those of As(III) and As(V) and found that the affinity of the adsorption sites decreased in the following order As(V) > PO43- > As(III) > H4SiO4 > HCO32-. For SO42-, its negative effects on the adsorption of As is more pronounced at high concentrations (> 250 mg/L) and onto Al2O3 or adsorbents with heterogeneous surfaces [86,94,95]. Other common anions found in groundwater like Cl- and NO3- did not have detectable effects on As adsorption onto Fe2O3 and Al2O3, which could be attributed to the weaker complexes of Cl- and NO3- compared to those of As(V) and As(III) [86,96].

A piper diagram is illustrated in Figure 3 showing the major ions in the pore water and effluent/drainage of in situ impoundment experiments using excavated altered rocks. The altered rock in site H was taken from the same bulk excavated rock used by Tabelin et al. [28,56], which were excavated in the Nakakoshi area that was described previously. On the other hand, the sample used in site T was taken from the Teine mine area, which is consists of Late Miocene andesite tuff breccia and mudstone extruded by altered andesite (propylite) [97]. The pore water and effluent/drainage from site H are characterized as sodium-sulfate type indicating that the major cation and anion are Na+ and SO42-, respectively. In contrast, the major cation and anion in the pore water and effluent/drainage from site T are Ca2+ and SO42-, respectively, and these waters are classified as calcium-sulfate type. These results show that Ca2+, Na+ and SO42- are the major coexisting ions in altered rock-water systems.

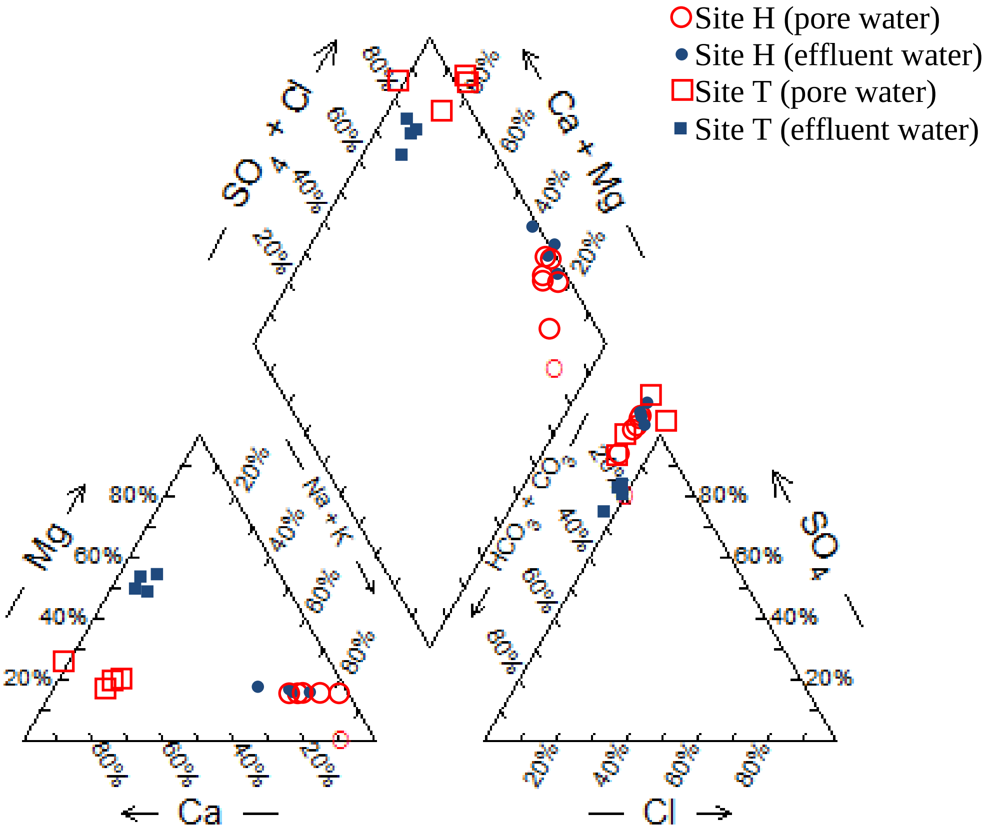

Figure 3. Piper diagram showing the major ions and classification of pore water and effluent/drainage samples collected from in situ impoundment-type experiments using altered rocks from two tunnel projects. Site H utilized altered sedimentary rock from the Nakakoshi area while site T used altered volcanic rock from Teine mine area

The moderate positive effect of Ca^{2+} on the adsorption of As was observed by Tabelin et al. [28] in column experiments under oxidizing and slightly alkaline pH. However, they noted that this positive effect was only temporary, and as the concentration of Ca^{2+} decreased below ca. 50 mg/L, As desorption increased drastically. In addition, their results also illustrate that if both Ca^{2+} and SO_4^{2-} are present, the positive effect of Ca^{2+} far outweighed the negative effects of SO_4^{2-} on the adsorption of As [28]. Another important coexisting ion that should be considered in altered rock-water systems is H_4SiO_4, but this oxyanionic species is not shown in the piper diagram. The H_4SiO_4 concentrations of the pore waters in site H and T were in the ranged of 4 – 9 and 8 – 10 mg/l as Si, respectively. On the other hand, the concentration of H_4SiO_4 in the effluent/drainage ranged from 0.9 to 6 mg/l as Si in site H and 2 to 11 mg/l as Si in site T. These values of H_4SiO_4 are similar to those found in natural waters (0.45 – 14 mg/l as Si) [98]. Small amounts of H_4SiO_4 (0 – 1 mg/l as Si) had negligible negative effects on As adsorption onto Fe-hydroxides [83]. Although 10 mg/l of H_4SiO_4 decreased the amount of As adsorbed onto Fe-hydroxide by ca. 50% [83], this was not observed in altered rock-water systems [28,55,97]. The observation of this effect was difficult because of the nearly constant concentrations of H_4SiO_4 in the effluents/drainage and pore waters from altered rocks [28,55]. In general, effects of coexisting ions on the adsorption of As in altered rock-water systems may not be as significant as those reported by other authors in pure mineral-water systems, which could be attributed to the absence or very low concentration of powerful competing ions like PO_4^{3-}.

Conclusions

In recent years, growing evidence of As toxicity, widespread natural/anthropogenic As contaminations especially of aquifers and reductions in regulatory environmental limits for As brought renewed interests in the distribution and mobilization of As. This review has attempted to summarize the growing knowledge of As incorporation and geochemistry in hydrothermally altered rocks excavated during tunnel construction. Arsenic in hydrothermally altered rocks is incorporated mostly in pyrite grains regardless of the type of alteration. However, the degree of As enrichment is dependent on the inherent chemical and physical properties of the hydrothermal fluid/solution that caused the alteration, that is, As content of the rock increases as the hydrothermal fluid becomes more mineralized. The release of As from altered rocks is strongly dependent on the pH and Eh, which could be considered as the two master variables controlling its mobilization. Acidic and alkaline pHs generally favor the mobilization of As from altered rocks. In contrast, the effects of Eh on As mobility is dependent on the predominant source of As in the rock. If the main source of As is sulfide minerals like pyrite, oxidizing conditions would enhance the leaching of As especially in the presence of microorganisms that catalyze pyrite oxidation through the oxidation Fe^{2+} to Fe^{3+}. However, a portion of the released As could be immobilized through co-precipitation/adsorption with/onto Fe-oxyhydroxides/oxides, which are precipitated as a consequence of pyrite oxidation. In cases where As is predominantly associated with Fe-oxyhydroxides/oxides, reducing conditions would enhance the leaching of As because of the reductive dissolution of these oxyhydroxides/oxides. Under reducing conditions, As could also be immobilized through co-precipitation with pyrite and other sulfide minerals, but the As scavenging effect of this process is less effective as compared to Fe-oxyhydroxides/oxides. Among the coexisting ions that could affect As adsorption, only Ca^{2+}, H_4SiO_4, and SO_4^{2-} are found in the altered rock-water system in substantial amounts. High Ca^{2+} concentrations enhanced the adsorption of As in altered rock-water systems at slightly alkaline pH, but this effect was only temporary. On the other hand, the effects of H_4SiO_4 and SO_4^{2-} on the leaching of As from altered rocks was not apparent. In hydrothermally altered rocks, the distribution of As as well as the factors important to its mobility were similar to those reported in mine tailings and waste rocks, contaminated soils and sediments, and aquifer systems. Because of these similarities, As mitigation techniques that have been applied to these more extensively studied systems (i.e., mining wastes, contaminated soils and aquifer systems) could be utilized in the disposal of altered rocks excavated from tunnel construction.

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