

Arsenic. An environmental problem limited by solubility*

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Abstract: Arsenic is a toxic element for animals and the majority of plants, in spite of evidence that it is also an essential element. The long-term intake of small doses of arsenic has a carcinogenic effect. There are well-identified regions where arsenic ground water concentrations can reach values higher than 2 mg/L. Water purification and waste treatment techniques based on (1) precipitation of calcium, magnesium, and iron(III) arsenates, and/or (2) adsorption or coprecipitation of arsenic oxyanions are unlikely to produce aqueous solutions with arsenic concentrations below the guideline values proposed for arsenic dissolved in potable water and treated sewage effluents. As(III) species are more toxic than As(V) species. Arsenate species are predominant at moderate and high redox potentials, while arsenite species occur under more reducing conditions. Metal arsenites are much more soluble than the corresponding metal arsenates, and arsenites are adsorbed less by solid phases.

Remediation techniques must consider the available information on solubility and adsorptive properties of As(III) and As(V). The less-soluble lead and barium arsenates are not suitable for arsenic decontamination. New remediation methods must consider solubility data for arsenic-containing materials and minerals.

INTRODUCTION

Arsenic is a minor terrestrial element that occurs primarily in association with sulfur-containing minerals such as realgar (AsS), orpiment (As₂S₃), or arsenopyrite (FeAsS). The mean values of arsenic content in soils, the earth's crust, and sediments are quoted by Sparks [1] as 6, 1.5, and 7.7 mg kg⁻¹, respectively. The natural oxidation of air-exposed sulfide minerals is one of the origins of crustal chemical elements mobilization associated with the generation of acid mine drainage. Mobilization of arsenic in the environment arises also from anthropogenic activities related to mining and ore processing, metallurgy, agriculture, wood preservation, and industry.

The major environmental concern about arsenic is not related to its presence in soils and sediments in anomalous amounts, but to its anomalous concentration in surface waters and its availability to living beings. Natural waters, in general, contain low levels of total arsenic as As(V) and/or As(III)—1 to 10 µg/L in normal waters [2].

Arsenic is a toxic element for animals and the majority of plants in spite of there being some evidence that it is also an essential element. High arsenic concentrations can inhibit nitrification, and there are data that indicate growth inhibition of microorganisms in arsenate-rich soils. It is known that arsenic is responsible for the development of liver, bladder, skin, and kidney cancer, and long-term intake of small doses of inorganic arsenic compounds is a factor in many other diseases [3]. The World Health Organization (WHO), the European Union, the United States, and many other countries' governments

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have established 0.050 mg/L arsenic as the maximum contaminant level for total arsenic in potable water. However, there is evidence of adverse health effects at lower exposure levels, and WHO promoted 0.010 mg/L arsenic as the new guideline value for arsenic in potable water [2]. Water is essential for living beings and is the dominant arsenic exposure pathway. Humans are the main concern of the arsenic environmental problem. Arsenic-contaminated waters are used by populations of some parts of the world, with large-scale disasters occurring in particular regions of Asia, Africa, and Central and South America [2–5] involving some millions of inhabitants. In some Bengal districts of India, arsenic ground water concentrations range between 0.05 and 1.25 mg/L, reaching 3.7 mg/L in some places [3]. In this context, the control of arsenic concentrations in surface waters [pore water, ground water, and other animal feeding water supplies (lakes, rivers, and oceans)] are of main relevance as well as the knowledge of its bioavailability from agriculture soils. Another important aspect consists of finding powerful methods of water decontamination.

Immobilization of arsenic in the environment occurs through precipitation of low-solubility salts and adsorption on soils and sediments. Remediation processes will follow the same principles, and the most common techniques are based on precipitation and adsorption phenomena. The objective of this work is to show that the water purification and waste treatment techniques based on (1) precipitation of calcium, magnesium, and iron(III) arsenates, and/or (2) adsorption or coprecipitation of arsenic oxyanions are unlikely to produce aqueous solutions with arsenic concentrations below the guideline values proposed for arsenic dissolved in potable water and treated sewage effluents. Lead arsenates are presented as an example of less-soluble metal arsenates that control lead and arsenate concentrations in natural aquatic systems and can be used for remediation techniques under certain conditions.

PRECIPITATION

Calcium, magnesium, and iron have been used to immobilize arsenates in remediation techniques, as they are easily available, environmentally friendly, some of their compounds are inexpensive, and their solubility is generally considered to be extremely low. Robins [6] was one of the first to doubt the effectiveness of the arsenic remediation techniques based on the precipitation of these metal arsenates.

Calcium arsenates and magnesium arsenates

Acid mine drainage and industrial waste waters are commonly treated with calcium oxide and calcium hydroxide to increase final pH and reduce the amount of dissolved matter discarded into aquatic systems. Some dissolved arsenic can be precipitated as a rich calcium arsenate solid whose composition will be related to the composition of the aqueous solutions [7]. As can be seen from data in Table 1, these solids are moderately soluble to be effective in the reduction of arsenic mobility in the environment. Table 1 only reports the solubility of well-defined solid phases. Other values exist in the literature, but the solid phases are not well defined. The lowest value for arsenic concentration in equilibrium with solid calcium arsenates, 0.01 mg/L arsenic, was found by Bothe and Brown [9] at pH 12.6 in closed systems. The introduction of air that contains carbon dioxide in the Ca–As–H₂O system causes significant instability of calcium arsenates for pH > 8.3 [7], and calcium carbonate will be the stable solid phase above this pH value. The change of calcium arsenate to calcium carbonate will release arsenic in the environment. For pH ranging from 4.5 and 8.5, the total arsenate concentrations in aqueous solutions in equilibrium with calcium arsenates are around 200 times higher than the maximum contaminant level for total arsenic in potable water and treated sewage effluents and wastes.

The presence of the rare calcium arsenate minerals weilite (CaHAsO₄), pharmacolite (CaHAsO₄·2H₂O), haidingerite (CaHAsO₄·H₂O), and phaunouxite [Ca₃(AsO₄)₂·11H₂O] must indicate high concentrations of total dissolved arsenate, taking into account that calcium concentrations in the environment are usually controlled by equilibria with other less-soluble, calcium-containing solid phases.

Table 1 Total concentration of arsenate in aqueous solutions in equilibrium with calcium arsenates, magnesium arsenate, and iron(III) arsenates.

Solid phase	T/K	pH ^a	Arsenate _{total} /(mol/L) ^a	References
CaHAsO ₄ ·H ₂ O	308	acid	0.12–1.2	[8]
Ca ₃ (AsO ₄) ₂	293	6.90–8.35	1.5 × 10 ⁻² –3.5 × 10 ⁻³	[11]
Ca ₃ (AsO ₄) ₂ ·4.25 H ₂ O	296	7.32–7.55	1.1 × 10 ⁻² –6.5 × 10 ⁻³	[9]
Ca ₁₀ (AsO ₄) ₆ (OH) ₂	310	5.56–7.16	7.5 × 10 ⁻³ –4.4 × 10 ⁻⁴	[12]
Ca ₁₀ (AsO ₄) ₆ Cl ₂	310	4.67–7.42	1.9 × 10 ⁻³ –3.7 × 10 ⁻⁵	[12]
Mg ₃ (AsO ₄) ₂	293	6.50–7.40	1.5 × 10 ⁻² –4.6 × 10 ⁻³	[11]
FeAsO ₄	293	1.90–2.95	3.7 × 10 ⁻³ –8.5 × 10 ⁻⁵	[14]
FeAsO ₄ ·2 H ₂ O	298	5.53–6.36	1.4 × 10 ⁻⁴ –2.5 × 10 ⁻⁵	[13]

^apH and total arsenate values are the highest and lowest numbers presented in the references, but a direct relation does not exist between the values of the two columns.

Magnesium salts are used to a much lesser extent to promote arsenic fixation in soils, sediments, and wastes. In spite of magnesium arsenates being considered extremely insoluble solids, their solubility is similar to the calcium arsenates, as can be seen from the data in Table 1. Hoernesite [Mg₃(AsO₄)₂·8H₂O] was found in arsenic-contaminated soils and in toxic waste sites [10]. The solubility of this mineral is poorly known, but it must be not much different from the value determined by Chukhlantsev [11], and its crystallization must occur in arsenic- and magnesium-rich environments. In fact, Voigt et al. [10] assume that hoernesite was formed in arsenic-contaminated soils because of the high magnesium content of the ground water.

Iron(III) arsenates

Iron(III) arsenate with the chemical composition and crystal structure of scorodite (FeAsO₄·2H₂O) is widespread in arsenic-bearing ore deposits [13]. The persistence of this mineral in these special environments with low pH and high total concentrations of iron and arsenic suggested that its solubility could control the concentration of arsenates in natural waters. Dove and Rimstidt [13] found that scorodite was stable under oxidized conditions, for pH < 3, iron total activity around 10⁻³, and arsenate activity greater than 10^{-1.29}. Iron(III) oxides and oxyhydroxides are the stable solid phases for pH > 3. The incongruent dissolution of scorodite with its transformation into iron(III) hydroxides was observed by Dove and Rimstidt [13] in 16 of 20 experimental runs for times up to 8 weeks. Langmuir et al. [15] showed that arsenic concentrations of tailings solutions may increase with time from the breakdown of the arsenate solid phases (mainly scorodite). This phase change reaction was very rapid at first and approaches zero after 72 h at 298 K [15]. Data in Table 1 show that total arsenate concentration in aqueous solutions in equilibrium with iron(III) arsenates is around 200 times higher than the maximum contaminant level for total arsenic in potable water. Iron(III) arsenates are not only too soluble, to provide an adequate decrease of arsenic in natural waters from precipitation processes, but their formation is very pH- and pE-dependent. Figure 1 shows the pH and pE dependence of the reduced and oxidized iron species and its relation with dissolved As(III) and As(V) species. The region between MnO₂(s)/Mn²⁺(aq) and Fe₂O₃(s)/Fe(s) equilibria is described by Stumm and Morgan [16] as the zone of representative redox potentials for many ground and soil waters where oxygen is consumed by degradation of organic matter, but reduction of sulfates does not occur. The interconversion between iron(II) and iron(III) oxidation states is very dependent on the redox potential of the media, which for soils is also related to the organic matter content. Iron(III) arsenates are more soluble than calcium arsenates when redox potentials are lower than 0 V [17,18] as a result of iron and arsenic reduction.

Lead arsenates

Lead arsenates were employed for decades as pesticides in agriculture, and residues of these compounds remain in soils. Murphy and Aucott [19] estimate that 22 × 10⁶ kg of lead arsenate had been used in

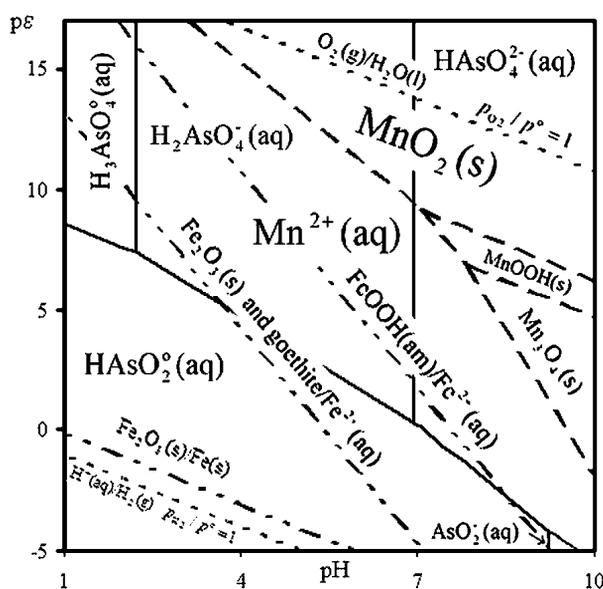
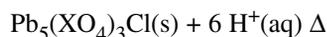


Fig. 1 Relevant arsenic (—), iron (---), and manganese (----) redox equilibria in environmental arsenic-related processes, at 298.15 K. Mn_T and $Fe_T = 10^{-5}$ mol/L.

New Jersey, USA, during the period 1900 to 1980. Concentrations of dissolved lead in aqueous suspensions of soils contaminated with lead arsenates as high as 35 mg/L were found, but more often very low levels were observed [20]. The ability of lead to form less-soluble crystals than arsenic with the widespread ions present in soils and sediments contributes to its lower environmental mobility.

Lead is also a toxic element, and methods to minimize its bioavailability and mobility in the environment, based on the solubility of lead phosphates, have been studied [21]. The precipitation of lead as $PbHPO_4$ and as $Pb_5(PO_4)_3Cl$, with the crystal structure of pyromorphite, was proposed by Nriagu [22] in the early 1970s as a method to immobilize lead in contaminated soils and wastes due to low solubility of lead phosphates. The total concentration of phosphates in the environment is controlled in the long term by the solubility of calcium phosphate minerals. This fact was used by Ma et al. [21] to study the viability of using apatite and other calcium phosphates for lead immobilization. They concluded that the immobilization process was near completion within 30 min with a final lead concentration in the aqueous solutions lower than 0.015 mg/L after 1 h, which is below the maximum contaminant level for total lead in potable water allowed in many countries.

Mimetite [$Pb_5(AsO_4)_3Cl$] is isostructural with pyromorphite, and it can be considered that all members of the pyromorphite-mimetite solid solution have the same value for the solubility constant, at 298.15 K, within experimental error [23]. For the reaction



with $X = P$ and/or As , the value of the solubility constant K_{H^+} extrapolated to zero ionic strength, was found to be $\log K_{H^+} = -27.9(4)$ [23]. The composition of the solid solutions is congruent with the composition of the aqueous solution in relation to the relative total amounts of dissolved phosphates and arsenates. Mimetite is the most stable lead arsenate phase in the pH range of natural waters. Aqueous systems with $pH > 7$ must have lead and arsenate total concentrations lower than 10^{-7} mol/L. In very acidic solutions, $pH < 2.5$ and chloride concentrations lower than 10^{-3} mol/L, lead and arsenate concentrations can be controlled by the equilibrium of aqueous solutions with schultenite ($PbHAsO_4$). An

aqueous solution in equilibrium with schultenite at pH = 3.2 contains around 5×10^{-5} mol/L of total arsenate [24].

The use of phosphates as fertilizers or in soil amendments induces the arsenate release and increases its mobility. It is observed that the arsenate released to aqueous solutions by phosphate amendment reverts to sparingly soluble solid phases [25]. Arsenic precipitates during drying processes and arsenate–phosphate coprecipitation is usually observed. The crystallization of aluminum arsenophosphates solid solutions is also quoted by Peryea [25] but, in this case, the composition of the solid solutions is not congruent with the composition of the aqueous solutions—the phosphate/arsenate ratio is four to eight times higher in the solid phases than in the aqueous solutions.

The crystallization of mimetite is a method already used to remove dissolved arsenic from aqueous solutions, and the final arsenic concentration can be lower than 0.2 $\mu\text{g/L}$ [9].

Soils and sediments containing lead arsenates will pose low environmental problems of lead and arsenate bioavailability if they are not in contact with phosphate-containing solutions. The very low solubility of lead arsenates will assure trace concentrations of these two elements in the aquatic systems under oxidizing conditions.

These considerations show the importance of solubility in the design of programs for environmental remediation related to lead and arsenate.

Arsenites and arsenic sulfides

Arsenate species are predominant at moderate and high redox potentials, while arsenite species occur under more reducing conditions as shown in Fig. 1. Metal arsenites are much more soluble than the corresponding metal arsenates, and the concentrations of arsenic in waters increase with the reduction of As(V) as a consequence of more-soluble arsenite solid phases and lower extent of adsorption [17,26]. However, the changes between As(III) and As(V) are kinetically controlled [18]. Mine drainage waters can contain more than 30 % of their total arsenic as arsenite in moderate oxidation conditions with arsenic enrichment in waters with low redox potential and pH > 6 [2]. Arsenic can be either oxidized or reduced by bacterial activity in mine waters, aquatic sediments, raw and activated sewages, and soils [26]. Manganese oxides are very effective in the oxidation of As(III) to As(V) [27,28] and play an important role controlling arsenic toxicity in the environment as arsenite is around 60 times more toxic for humans than arsenate [3]. As can be seen from Fig. 1, As(V) is the most stable species under normal atmospheric conditions, but the oxidation of As(III) by atmospheric oxygen is slow [28].

Arsenic sulfides are the less-soluble, arsenic-containing solid phases, but they become very soluble due to the oxidation of sulfide that occurs at very low redox potentials and the consequent generation of acid drainage.

Adsorption

Arsenic concentrations in soil pore waters are generally very low even in contaminated soils [29] as a result of the combination of the multiple processes occurring in soils: chelation, cation exchange, adsorption, and mineralization. Arsenic contamination is generally localized in spite of arsenic being relatively more mobile than other contaminants [29]. Adsorption can occur mainly in phyllosilicates (e.g., micas and clays), hydrous metal oxides (aluminum, manganese, and iron), carbonates, and organic matter. These secondary minerals are important in soil chemical processes owing to their reactivity and high specific surface areas, both internal and external.

Adsorption of As(III) and As(V) on clays [30], activated alumina grains [31] and hydrated manganese, aluminum, and iron(III) oxides [28,32–38] has been studied, and the influence of pH [30–35,38], size, and structure of the sorptive particles [38], and the competition of other ions and dissolved organic matter [35,36] on the extent of adsorption, have been investigated. The mechanism of adsorption has also been studied, and the most amorphous hydrated oxides seem to be the most effective in arsenate adsorption processes [32,37]. As(V) adsorption capacity of different iron(III) hydrox-

ides, aluminum hydroxides, and clays follow the order: amorphous aluminum hydroxide > synthetic iron(III) oxyhydroxide > goethite > clays [38]. The adsorption extent depends also on the initial concentration, pH, and competing ions present in solution. Pierce and Moore [32] found a maximum of 92 % of arsenate removed by amorphous iron(III) hydroxides at pH 4 and an arsenate concentration of 1.33 $\mu\text{mol/L}$. The percentage of removal decreased with increasing concentration of total arsenate but could be enhanced by increasing the amount of the adsorber [32].

Desorption of arsenate from goethite was studied by O'Reilly et al. [39] over a period of 12 months, in order to get information on the mobility, persistence, and fate of arsenic in the environment. Phosphates are also competitor ions for the same specific adsorption sites on solid particles as arsenate [25,36,39], increasing the extension of its desorption. Arsenate desorption in the presence of phosphate was rapid, with about 45 % arsenic desorbed within the first 24 h [39]. Sulfate ions had much less effect on arsenate desorption.

Remediation techniques based on adsorption phenomena can be an efficient arsenic removal process depending on the initial total arsenate concentrations in the waters. Adsorption and desorption are relatively rapid processes, making it difficult to monitor the arsenic concentrations in the final waters if a continuous flow process is used. Desorption processes must be considered on the global processes of arsenic water purification. The environment is the ultimate destination of human activities, and the disposal of the arsenic-contaminated sortive materials has to be done in a way that does not lead to its remobilization.

CONCLUSIONS

The market demands for arsenic-containing compounds and materials is decreasing as a consequence of materials technological advances and the focuses on the manufacture and use of less hazardous compounds to humans and the environment. New solutions have to be found to prevent environmental accumulation of arsenical residues or their mobilization into water supplies.

The environment is an open dynamic system characterized by a succession of transitory states translating the complex interactions between living organisms and local physical and chemical parameters. The study of paragenetic mineral sequences in supergene-enriched zones can give some insights into the relation of percolating waters composition and the crystallized solid phases. Nevertheless, it is important not to forget that environmental changes occur over a wide time scale and the actual conditions of the presence of given solid phases. The occurrence of certain metal arsenates is only possible under fixed conditions of temperature, pressure, and chemical composition of the precursor solutions. Robins [6] mentioned that stabilization of arsenic as calcium, magnesium, or iron(III) arsenate solids arose from the idea that metal arsenates (under specific pH values) were extremely insoluble and will not allow substantial leaching into ground waters. This opinion emerged from the extrapolation to high pH values of the linear relationship between log solubility of metal arsenate and pH calculated to low pH values, without considering the conditions of maximum stability of each solid phase [6]. The idea that calcium, magnesium, manganese(II), and iron(III) salts form extremely insoluble solid arsenates and can be used for arsenic immobilization and water purification is unfounded. The aqueous solutions in equilibrium with these metal arsenates have extremely high arsenic concentrations [6,17,28]. These, in general, can be 200 times the maximum contaminant level for total arsenic in potable water and often exceed the maximum contaminant level for total arsenic content in treated sewage effluents and wastes. Unfortunately, attempts to remove arsenic from mining, metallurgy, and industry sewage effluents and wastes by addition of lime and/or iron(III) salts still persist.

Hydrated amorphous aluminum hydroxides, iron(III), and manganese oxyhydroxides are more efficient at adsorbing arsenates than more crystalline materials, but the optimal adsorption conditions occur at low pH values. Adsorption techniques also require pH control and consideration of the final destination of the arsenic-contaminated residues.

To be economically viable, remediation techniques have to produce solutions with arsenic concentrations lower than the maximum contaminant level, use relatively fast processes, and produce environmentally safe arsenic-concentrated residues. Adsorption is, in general, a faster phenomenon than solid crystallization [1] and can be used for rapid reduction of large amounts of arsenic in solutions. Crystallization processes are kinetically controlled by the high activation energies of formation of solid phases, but this energetic barrier can be overcome by the presence of other solid phases. There is no simple solution, and present remediation techniques must combine adsorption, crystallization, and oxidation processes. New solutions have to be found, and research on solubility of new arsenic-containing materials and minerals has to be conducted.

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