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The influence of speciation in the removal of arsenic from mine waters

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Abstract

Arsenic is a common constituent that requires removal prior to the discharge of water from metal and from some coal mines. The release of the element in high concentration can lead to toxic and carcinogenic risks. Current worldwide standards require a concentration of less than 50 μg/L, except in Australia and the USA where the standard has been tightened to 10 μg/L.

A fundamental control on arsenic release, migration and toxicity is redox chemistry. Arsenic occurs naturally in two inorganic states, As(III) and As(V). The former is more toxic but is dominant only in anoxic systems, whilst the latter is the more common in oxic systems.

To assess the level of influence that speciation has on treatment and to devise alternative approaches, solutions of both As (III) and As(V), as well as natural mine waters, were treated in the laboratory with different reagents and methods.

Arsenic (III) solutions and mine waters with a high As(III)/As(V) ratio required a more aggressive oxidant and higher Fe:As ratio than As(V) dominated solutions and mine waters. The principal method of removal was through adsorption on to Fe oxyhydroxides and synthetic resins. In the case of As(V), reaction kinetics are such that in conventional plants co-precipitation also occurs with Fe, Ca, Mg, and, if present, Cu and Zn to form more stable insoluble arsenate salts.

Speciation of arsenic, and thus attenuation, is also strongly influenced by pH for both species, with the optimum treatment pH being in the range 3–5 for both species. This is related to the Fe-chemistry of the solution. For many natural mine waters and, more importantly, tailings and spent heap leach process solution, this requires pH control through the addition of ferric sulphate and CO_2-sparging.

Combined oxidation–precipitation processes provide the most cost effective and efficient approach to arsenic removal to comply with the increasingly stringent environmental legislation. In this paper, a focus is made on low-cost methods or those that could be applied within the framework of neutralisation and sludge precipitation treatment plants or passive treatment cells that are the most common applications for mine water treatment in Europe.

Key words: arsenic, mine water, oxidation, speciation

INTRODUCTION

Arsenic is a common constituent of many metal ores and a trace element in sulphides associated with coal deposits (Thornton and Farago 1997; Bowell and Parshley 2001; Nordstrom 2001). Both natural and accelerated weathering of these arsenic-bearing materials result in the release of arsenic into the environment. Due to its potential toxicity, the United States Environmental Protection Agency (US EPA) has reduced the maximum contaminant level for arsenic in drinking or receiving water to 10 μg/L, which for mine waters will be the active standard as of 2006. As many mining dis-

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charges emit water above this concentration, it is necessary to manage such drainage.

The common practice is to remove and fix arsenic through its co-precipitation with ferric species. Arsenic removal by this method is more effective if arsenic is present in the pentavalent state (Tozawa *et al.* 1977; Robbins 2001). Also, the sludge produced from arsenic (V) with iron (III) has a significantly lower solubility than the corresponding iron (III)- arsenic (III) precipitate (Krause and Ettel 1989). Therefore, as arsenic (V) is desired for successful treatment it is essential to fully characterise the form of arsenic prior to implementing treatment.

ARSENIC GEOCHEMISTRY

Over 200 As-containing minerals have been identified in nature. Of these 60% are arsenates, 20% sulphides and sulphosalts, 10% are oxides and the remainder arsenides, native elements and metal alloys. Arsenic naturally occurs in chalcophile hydrothermal mineral deposits and more rarely associated with volcanic or magmatic rocks. Rare arsenic phases are also known to occur in fumaroles and geothermal systems (Benson and Spencer 1983). Occasionally arsenic can also occur associated with sedimentary pyrite in sedimentary rocks, and in this environment it has been considered to be the source for anomalous concentrations of arsenic in drinking water in Wisconsin, Maine and Bangladesh (Welch *et al.* 2000; Nordstrom 2000). The most common arsenic mineral, globally, is arsenic-bearing pyrite. Arsenic has long been used as an excellent ‘pathfinder element’ because of its low abundance in most rock types and concentration in hydrothermal deposits, as well as its generally low mobility. This, coupled with sensitive analytical protocols by conventional methods, makes the element extremely useful in mineral exploration (Boyle and Jonasson 1973).

For example, the average concentration of As in hydrothermal ore deposits ranges up to 500 ppm up to 10 wt% of an ore or altered host rock. In unmineralised rocks the average concentration is less than 10 ppm but can be up to 20 ppm in argillaceous sediments (White *et al.* 1963; Smedley and Kinneburgh 2002). Mining does not produce arsenic, although it can be liberated when exposed to conditions in which the primary host mineral is unstable and thus oxidises or weathers, for example, placement on a heap or waste rock dump. Alternatively where an As-hosting ore is chemically treated prior to liberation of the ore element, such as smelting, the arsenic mineral may also be liberated from the matrix and in this form becomes mobile.

The concentration of arsenic liberated from such reactions is dependent on several factors:

- total concentration available, this in turn is related to the geology of the original hydrothermal deposit;
- the Eh–pH regime of the environment in which the arsenic is liberated;
- the chemistry of natural waters in promoting release or attenuation of arsenic.

The total amount of arsenic available is entirely dependent on the proportion of arsenic minerals available in the deposit. So for example, for a volcanogenic massive sulphide or high sulphide-gold deposit or for a Carlin deposit, high concentrations of arsenic would be anticipated.

Control on the release of this arsenic is then dependent on environmental conditions. Typically in very acidic environments, for example those of Iron Mountain in California, arsenic mobility would be high (Nordstrom and Alpers 1999). Equally, in high-pH environments high arsenic mobility would also be anticipated, as the major control would be adsorption on to mineral phases and this would be predicted to be low at higher pH for arsenic oxyanions (Bowell 1994; Bowell and Parshley 2001). Within ambient systems arsenic can occur as arsenate ($H_nAsO_4^{3-n}$) or arsenite ($H_nAsO_3^{3-n}$) complexes or in the presence of methylat-

Table 1. Arsenic geochemistry in water draining some European mines

Mining district	As concentration, μg/L	Reference
Cornwall, Sn–Cu mines	<0.1–95 600	Haswell *et al.* 1985; Thornton and Farago 1997
Tamar Estuary, Devon	2–9	Smedley and Kinniburgh 2002
Parys Mountain, Wales	<0.1–770	Fuge *et al.* 1994; Bowell *et al.* 1996; unpublished data
South Wales coalfield	<10–240	Bowell *et al.* 1996
Avoca, Ireland	<5–1160	Bowell 2002; unpublished data
Carnoules, France	Up to 189 000	LeBlanc *et al.* 2002
Rio Tinto, Spain	Up to 22 000	Bowell 2002; unpublished data
Ural Mountains	Up to 400 000	Smedley and Kinniburgh 2002

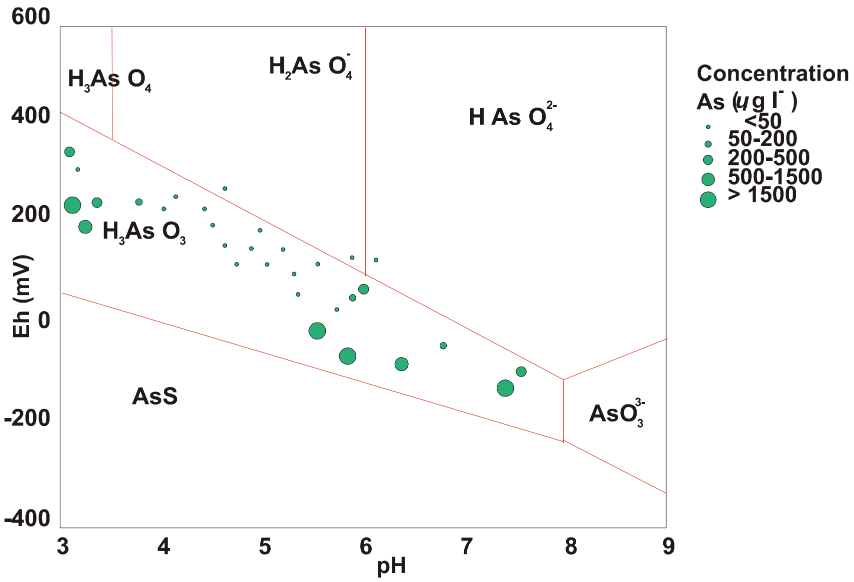

Figure 1. Arsenic speciation in Cornish mine waters

ing agents such as monomethylarsonic acid (MMAA) or dimethylarsinic acid (DMAA).

Over the natural pH range of most mine waters the principal species of As (V) is $H_2AsO_4^{2-}$ and of As (III) is H_3AsO_3, of which the reduced form is the more mobile. For example, the speciation of arsenic in filtered mine waters from several Cornish mines (Figure 1). The concentration of arsenic observed in European mine waters is shown in Table 1.

As can be observed in Table 1, a wide range of is shown for many deposits depending on the leached source as well the physicochemical nature of the leaching fluid. However, in all cases the concentration does show levels above those acceptable for discharge to the environment (typically <50 µg/L). The principal reactions of arsenic attenuation from acidic mine waters are: adsorption by ferric oxyhydroxide, and to a lesser extent Al–Mn oxides, clays and organic matter; and scorodite precipitation. Another important mechanism in acid mine waters observed at the Carnoules mine in France, is the removal of arsenic by bacteria forming an Fe–As rich precipitate (LeBlanc *et al*. 2002). In circum-neutral to alkaline solutions, co-precipitation of As in the form of arsenate and arsenite salts becomes a more important attenuation mechanism. However, the rate of change in the oxidation state of arsenic is not rapid, so the predicted proportions of arsenic species based on thermodynamic calculations does not always correspond to actual analytical results.

TREATMENT THROUGH OXIDATION

In this study the preliminary results of bench scale testing are reported for pure arsenic solutions and mine waters. Reactions took place in a glass reactor with automated stirring. Electrodes for oxidation–reduction potential (ORP) and pH were used to monitor the testwork and all experiments were conducted in a water bath to control temperature.

Arsenic oxidation was achieved by bubbling oxygen into the container. The arsenic (III) concentration was determined by chromatography-hydride generation AAS. Filtrates were analysed by ICP using EPA method 200.8 and by hydride generation AAS using method 200.2. All reagents used in the testwork were of reagent grade.

Arsenic removal through Fe (III) oxidation

Arsenic removal by iron (III) has been studied by several authors and has been found to be more effective for arsenic (V) than arsenic (III) (e.g. Tozawa *et al*. 1977; Robbins *et al*. 1988; Wang 1997; Robbins 2001).

In this study both arsenic (V) and arsenic (III) solutions were utilised as pure solutions and as a mixed solution at variable total arsenic concentration, at 25°C and at varying Fe(III)/As molar ratios to assess the effects of arsenic speciation on arsenic removal.

As observed in Figure 2, the two arsenic species show different optimum ranges for co-precipitation with iron (III) and in this study as with previous workers, arsenic (V) is more readily removed to lower concentration over a wider pH range than arsenic (III). Initial As concentration = 78 mg/L; temperature = 298 K; reaction time = 30 minutes

In order to meet water quality standards of 50 µg/L or lower it can be observed that it would be necessary to

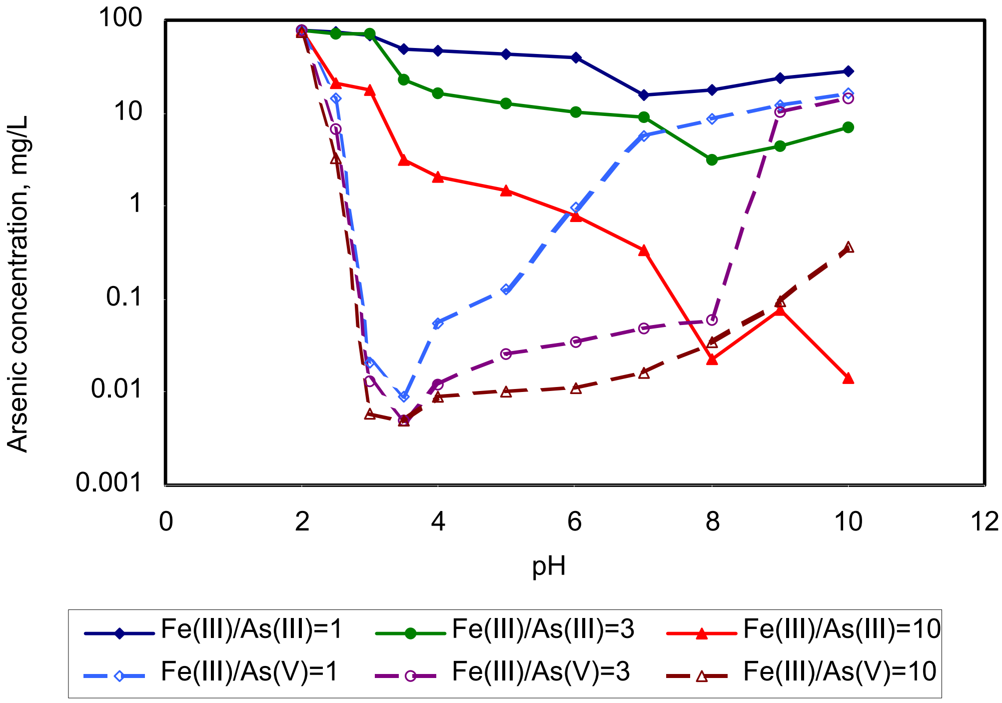

Figure 2. Arsenic removal from solution as a function of Fe(III)/As ratio

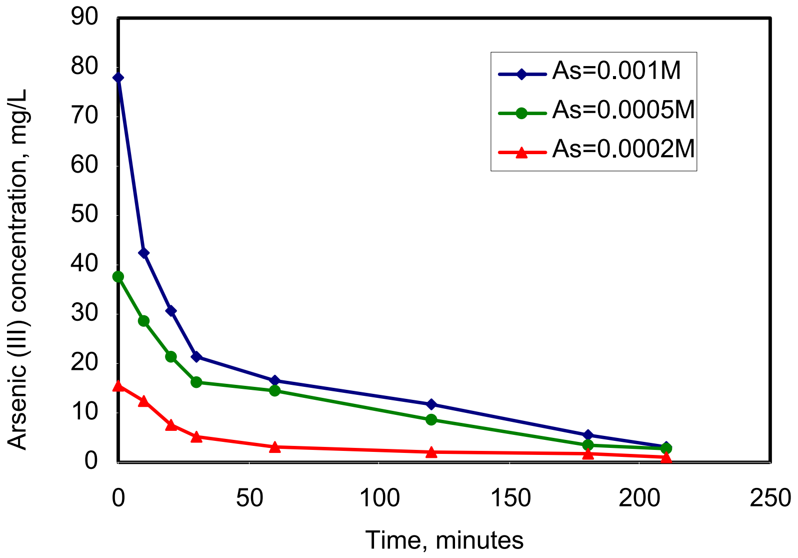

Figure 3. Arsenic (III) removal through oxidation (analysis for As III) by hydrogen peroxide over time

convert almost all arsenic (III) to arsenic (V) over the natural pH range for water.

Arsenic removal through addition of oxidising reagents

The oxidation of arsenic (III) can be commercially achieved using a wide range of oxidising agents such as hydrogen peroxide, ozone, and potassium permanganate. The emphasis in this study was the assessment of these agents in oxidising low concentrations of arsenic (III). The benefit of using oxidising agents was tested on iron (II)-arsenic (III) and iron (III)-arsenic (III) solutions so as to consider arsenic oxidation and attenuation. Hydrogen peroxide oxidation without pH control has been reported in early studies on arsenic chemistry (Tozawa and Nishimura 1976). They observed rapid oxidation in alkaline solutions but much slower with pH <6. More recently the system $FeSO_4$–AsO_3–H_2O_2–H_2O has been studied to evaluate the effectiveness of arsenic (III) removal by hydrogen peroxide (Wang 1997).

The results of titrating hydrogen peroxide at a pH = 2.0 ± 0.5 with arsenic (III) solutions are shown in Figure 3.

The rate of arsenic removal is initially rapid, but decreases over time, with a more rapid decrease in the rate observed with higher concentration (Figure 3). This indicates that the process is limited in application to low-level arsenic solutions for rapid arsenic (III) oxidation. Even with higher pH, complete oxidation of arsenic (III) is limited in low-concentration solutions. The method of arsenic removal was through oxidation to arsenic (V) by a reaction such as:

$$H_2O_2 + H_3AsO_3 = H_3AsO_4 + H_2O \qquad (1)$$

Another influence on arsenic (III) oxidation by oxidants appears to be the presence of competing species. In the presence of iron (II), arsenic (III) oxidation is rapid with more than half of the initial solution removed in the first five minutes of reaction (Robbins 2001). The decrease in the rate of arsenic removal suggests that the oxidation of both iron and arsenic proceeded quickly due to rapid co-precipitation, with almost complete removal within an hour. By comparison the oxidation of arsenic (III) by hydrogen peroxide in the presence of iron (III) occurs much more slowly, probably as a consequence of arsenic removal by adsorption rather than co-precipitation. The removal was much more effective at low to neutral pH (pH range 4–7) than at higher pH (>9) due to the increased solubility of arsenic at higher pH. In natural mine waters this removal would occur through a stepwise process of formation of arsenic (V), and removal either through co-precipitation (such as with Fe to form scorodite) or through surface adsorption of arsenic (V) on to mineral surfaces.

The oxidation of arsenic (III) by ozone shows zero order kinetics and almost complete removal occurs in the presence of both iron (II) and iron (III) (Wang 1997). Similarly, potassium permanganate also produces almost complete arsenic removal in the presence of excess permanganate solution (Figure 4). The oxidation of manganese (II) results on the competitive formation of $MnAsO_4.2H_2O$ as well as MnO_2 proceeds according to the reactions:

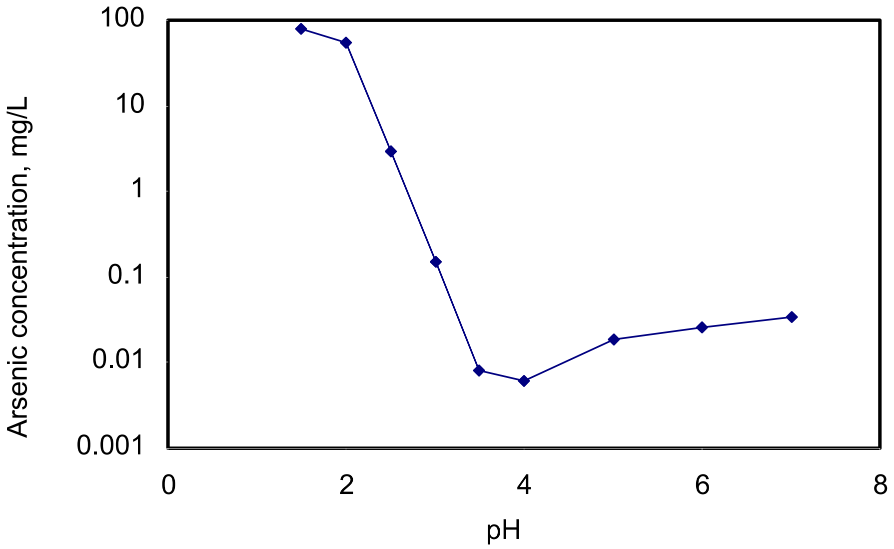

Figure 4. Arsenic (III) removal by oxidation in the presence of Iron (II) by addition of KMnO4 at variable pH
Initial As = 78 mg/L; Initial Fe = 168 mg/L; $KMnO_4$ solution strength of 0.001 M; Temperature = 298 K; Reaction time = 60 minutes

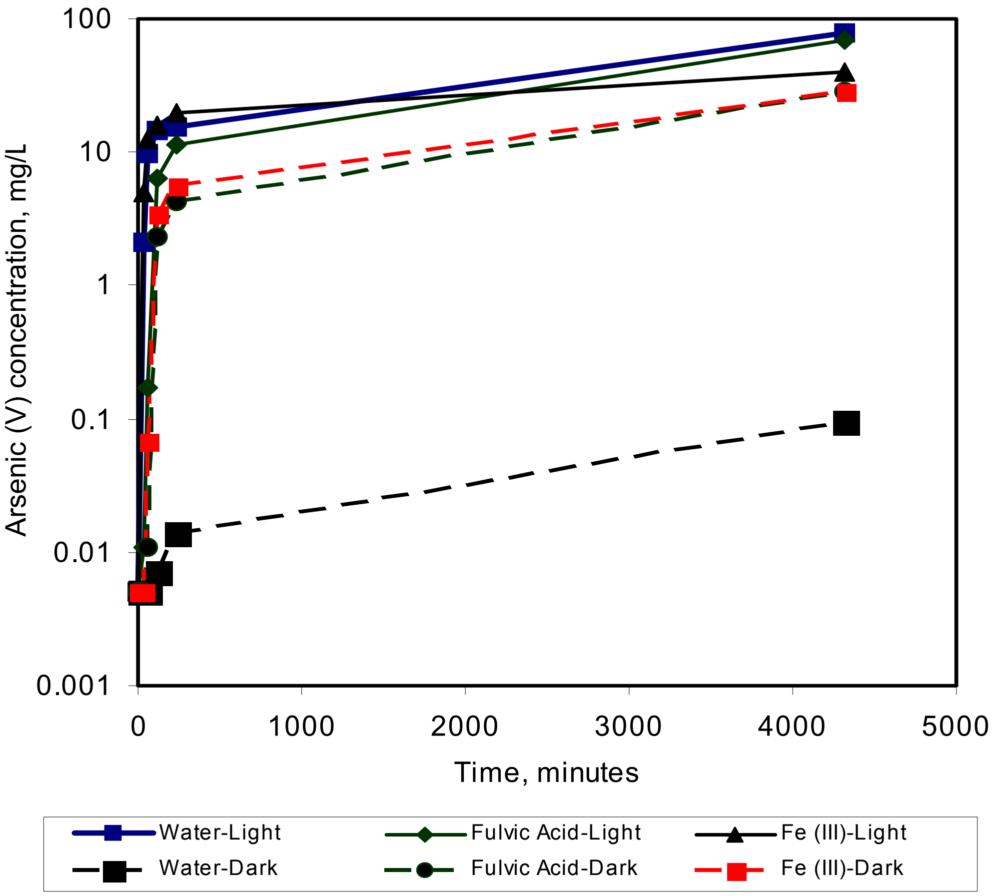

Figure 5. Arsenic oxidation over time in the presence of fulvic acid and iron (III) when exposed to, and in the absence of, sunlight

$$5H_3AsO_3 + 2MnO_4^- + 6H^+ = 5H_3AsO_4 + 2Mn^{2+} + 3H_2O \quad (2)$$

$$4Mn^{2+} + 5H_3AsO_4 + MnO_4^- + 6H_2O = 5MnAsO_4.2H_2O + 7H^+ \quad (3)$$

Additionally, the formation of MnO_2 through the reaction of Mn^{2+} and MnO_4^- will result in further adsorption of arsenic (V) oxyanions contributing to the lower final arsenic concentration. This occurs through a reaction such as:

$$3Mn^{2+} + 2MnO_4^- + 2H_2O = 5MnO_2 + 4H^+ \quad (4)$$

Treatment through UV exposure

The oxidation of arsenic (III) to arsenic (V) can be catalysed by UV light and has been shown in several studies to result in the removal of arsenic (Brockbank *et al.* 1988; Wensheng *et al.* 2000). This opens up the possibility of passive treatment cells being effective primary treatment methods for arsenic (III) removal. Under this method, arsenic (III) would oxidise to arsenic (V) on exposure to light and this would compete with or be contemporaneous to iron (II) to iron (III) oxidation. Assuming that the water chemistry promotes adsorption, and/co- precipitation, then this would be effective in removing arsenic from a mine water. Such a mechanism is likely to be the most obvious one in the removal of arsenic (III) at Carnoules mine in France (Le Blanc *et al.* 2002). In the presence of another oxidising agent, arsenic (III) oxidation occurs at a greater rate, for example, in the presence of fulvic acid and/or iron (III) (Figure 5). In the absence of daylight the oxidation rate slows considerably (Figure 5).

DISCUSSION

The treatment of mine waters to remove arsenic has been shown to be highly dependent on speciation. For the most common and cost effective methods of arsenic removal it is essential to have knowledge of the major species of both arsenic and iron in a system. On the basis of this, treatment methods can be modified so as to promote the oxidation of arsenic (III) and iron (II), in order that efficient removal can occur.

Bench scale testwork has shown that for low-level arsenic (III) concentration, removal in acidic solutions is slow and inefficient, but in the presence of iron can be significantly catalysed. In iron (III)–arsenic (III) solutions the catalytic effect of iron was strongly pH dependent. In highly acidic solutions the extent of iron hydrolysis is slow and consequently more iron is available to catalyse arsenic (III) oxidation and, as such, both oxidation and removal of arsenic becomes more efficient. If pH > 4 then the benefit of iron (III) catalysis is largely lost, due to iron hydrolysis. However, in the case of iron (II)–arsenic (III) the reactions between iron (II), water and an oxidizing agent such as hydrogen peroxide involve the formation of intermediate radicals such as OH (Deng and Stumm 1990). These radicals assist in rapid oxidation of arsenic (III) and so oxidation was more effective and less pH dependent.

Ozone oxidation is highly effective at arsenic oxidation and thus removal; however, it has considerable cost disadvantages. Likewise, potassium permanganate is also useful in promoting arsenic oxidation in the presence of either iron (II) or iron (III). However, problems with this method include not only the high reagent costs but also potential for the release of high-Mn concentrations in any discharge.

In applying these results to mine water treatment, all show the same essential components that lead to the removal of arsenic:

- oxidation of arsenic (III) to arsenic (V);
- presence of chelating ions or preferential adsorption surface;
- physicochemical environment promotes either arsenic precipitation or adsorption of arsenate.

Within the context of UK and European mine water treatment, the majority are based on aerobic passive treatment cells in which the priority is the removal of iron through iron (II) oxidation and hydrolysis to form iron (III) oxyhydroxides and oxyhydroxy-sulphate precipitates. Addition of additional oxidising agents would help to promote arsenic (III) to arsenic (V) oxidation. In the majority of mine waters the Eh–pH conditions are such that arsenate adsorption is the most likely mechanism for arsenic removal associated with the iron (III) precipitates.

In some environments sufficient solar UV light my occur, such that this is adequate to promote significant arsenic (III) oxidation, but in more temperate environments additional oxidising agents may need to be included.

CONCLUSIONS

This paper provides an overview of potential treatment options for arsenic removal within the context of passive and ‘semi-passive’ treatment plants of the type that are currently being applied to mine water treatment in the UK and Europe.

In applying any of these methods, arsenic speciation and good water geochemical characterisation are essential. All of the reagents discussed appear to be effective in arsenic removal with ozone and potassium permanganate, demonstrating efficient and complete oxidation of arsenic (III) and consequent removal as a co-precipitate or adsorbed on to mineral particles. The application of other methods is dependent on arsenic speciation, pH and chemistry of the mine water.

For acidic solutions of low-arsenic (III) concentration, oxidation will be slow and difficult in the absence of iron or where pH >4. In highly acidic solutions (pH <4), iron is typically present and catalyses arsenic (III) oxidation and removal through co-precipitation.

In the treatment of higher pH solutions, the simultaneous oxidation of iron (II) with arsenic (III) or the oxidation of arsenic (III) followed by attenuation on iron (III) oxyhydroxides are more efficient methods in treating mine waters.

This approach to improving mine water quality with respect to trace elements, within a passive treatment cell, may also be applicable to other elements such as chromium, antimony and selenium.

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