

Effects of Iron on Arsenic Speciation and Redox Chemistry in Acid Mine Water

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Abstract

Concern about arsenic is increasing throughout the world, including areas of the United States. Elevated levels of arsenic above current drinking-water regulations in ground and surface water can be the result of purely natural phenomena, but often are due to anthropogenic activities, such as mining and agriculture. The current study correlates arsenic speciation in acid mine drainage and mining influenced water with the important water-chemistry properties Eh, pH, and iron(III) concentration. The results show that arsenic speciation is generally in equilibrium with iron chemistry in low pH AMD, which is often not the case in other natural-water matrices. High pH mine waters and groundwater do not always hold to the redox predictions as well as low pH AMD samples. The oxidation and precipitation of oxyhydroxides depletes iron from some systems, and this also affects arsenite and arsenate concentrations differently through sorption processes.

Keywords: Arsenic, Speciation, Iron, Acid Mine Drainage, Remediation

1. Introduction

Because of a rich history of mining, acid mine drainage (AMD) is a common problem in areas of the Western United States. Oxidation of pyritic ores is a major cause of acidic drainage (Wildeman et al., 1974; Black and Craw, 2001; Gault et al., 2001). The production of iron(III) and hydrogen ions can catalytically dissolve secondary minerals, thereby increasing the metal load to the drainage (Wildeman et al., 1974; Plumlee et al., 1993). In addition to the generally

low pH (~1!4) of AMD systems, toxic metal concentrations often can be well above maximum contaminant levels (MCL's) for drinking water (U.S. Environmental Protection Agency, 1996; Welch et al., 2000). Arsenic is one element in particular that can be associated with metal sulfide deposits that are responsible for AMD and arsenic is common in many mineralized regions (Gault et al., 2001; Williams, 2001). Certain areas of Colorado and Nevada have such mineralization, producing acidic drainages that contain arsenic. On the other hand, circumneutral drainages and mining influenced waters from different mineralogies in Colorado, Utah, and Idaho can also contain arsenic but only minor concentrations of iron.

The present study originated from a need to remediate arsenic-containing AMD. Much work has been done recently on removal of arsenic from contaminated systems, usually focused on sorption or co-precipitation mechanisms (Joshi and Chaudhuri, 1996; Hering et al., 1997; Thirunavukkarasu et al., 2001). Redox speciation of arsenic in such systems is important in these remediation techniques because the sorptive properties of inorganic As(III) [arsenite] and As(V) [arsenate] vary with pH (Bowell, 1994; McGeehan, 1996; Goldberg, 2000). Furthermore, the effect of pH on arsenic sorption differs between arsenite and arsenate. Many publications describe specific mining sites that have arsenic-containing AMD (Mok and Wai, 1990; Elbaz-Poulichet et al., 2000; La Force et al., 2000; Black and Craw, 2001). However, there are few studies that attempt to compare different sites in depth or propose mechanisms that explain the distribution of arsenic species (Plumlee et al., 1993; Roussel et al., 2000; Williams, 2001), despite the importance of this information.

The work presented in this paper show trends in AMD matrices where thermodynamic predictions based on field measured Eh values are correlated to arsenic speciation (Daus et al.,

2002). It is suggested that the presence of the dominant iron redox couple will yield a poised system that will control the speciation of arsenic, particularly in lower pH AMDs. In addition to the redox control on arsenic speciation, a secondary effect can be deduced based on the control of iron solubility by pH, thus causing oxyhydroxides to precipitate at higher pH, thereby preferentially removing arsenate through sorption. The results reported here suggest a trend in arsenic speciation that is controlled by pH, redox potential (Eh), and indirectly, by iron.

2. Field Site Descriptions

Samples were collected from 10 AMD effluents throughout Colorado, 1 AMD from Nevada, and 1 tailings leachate from Idaho. A groundwater extraction treatment well and mine process water from a Utah copper mine were also collected. All of the samples studied have arsenic concentrations substantially greater than the current (2004) drinking-water maximum contaminant level (MCL) of 10 :g/L. Other samples were collected from these sites with total arsenic concentrations near the 10 µg/L MCL and showed similar trends to those reported. All samples were analyzed for chemical properties (Eh, pH, conductivity), chemical composition, and arsenic species distribution. The mines investigated for this study vary in metals composition and pH, which provides for a diverse group of samples for comparison.

The approximate locations of the sampling sites are listed in table 1, and extend across mineralized regions of Colorado, Nevada, Utah, and Idaho, yet generally are located in small clusters. The Summitville EPA Superfund site and the Platoro mining district to the south of Summitville are within the Platoro caldera in south-central Colorado. Samples from the Koehler Tunnel and adjacent Koehler Breakdown were taken from near the summit of Red Mountain Pass, southeast of Ouray, Colo. The third grouping of Colorado sites, which includes the Argo

Tunnel, Quartz Hill Tunnel, and Virginia Canyon Mine, are in the Central City mining district near Idaho Springs, Colo., about 50 km west of Denver. All the Colorado drainage samples were collected from inactive mine sites, whereas the Nevada, Utah, and Idaho sites are from active operations. The Nevada sample was collected northwest of Elko, Nev.; the Utah samples were collected in the copper mining district west of Salt Lake City, Utah. Samples from Idaho were in the phosphate-mining district north of Soda Springs, Idaho.

Current remediation efforts for AMD at these mines vary greatly. Sites such as Summitville, the Argo Tunnel, Platoro, Nevada, and Utah sites have active pH-induced precipitation facilities installed to treat the mine effluents and affected waters. Both Koehler sites, the Virginia Canyon Mine, and Quartz Hill Tunnel all flow unremediated into local creeks, where the effects of iron precipitation are clearly visible. No iron precipitation is noted at the Idaho site, as the drainage enters a wetland area shortly after emerging from the tailings pile. Most of the sites investigated were effluents draining directly out of mine adits or tailings piles except for the Platoro Wetland Seep and Pumphouse Sump, which represent secondary surfacing groundwater within a wetland area actively receiving mine drainage, and the Utah samples which are a mine process water and an AMD impacted groundwater being treated for arsenic.

3. Experimental

All chemicals used for preservation or speciation of samples were reagent grade or higher purity and used without further purification; the deionized water used had a resistivity of 18.3 M Ω cm. Samples collected for total elemental analysis were filtered to 0.45 μ m, acidified with nitric acid (pH<2), and stored in high-density polyethylene plastic bottles. Total elemental concentrations were determined by ICP-AES (Inductively Coupled Plasma-Atomic Emission

Spectroscopy, Perkin Elmer Optima 3000) using scandium as an internal standard [EPA Method 200.7] (U.S. Environmental Protection Agency, 1991); total arsenic was determined by ICP-AES and ICP-MS (Inductively Coupled Plasma-Mass Spectrometry, Perkin Elmer Elan 6100), the latter using germanium as an internal standard [EPA Method 200.8] (U.S. Environmental Protection Agency, 1991).

Accurate measurement of the arsenic species distribution in AMD is required to establish the proper remediation procedures and to correlate the species distribution with the water-chemistry properties. Development of improved speciation methods as well as preservation techniques was required for the current work and has been described in detail elsewhere (Bednar et al., 2001a; Bednar et al., 2002a; Garbarino et al., 2002; Bednar et al., 2004). Photooxidation has been shown to efficiently convert arsenite to arsenate, particularly in matrices that contain dissolved iron (Khoe et al., 2000; Emmett and Khoe, 2001; Hug et al., 2001); therefore, excluding light from the samples after collection is critical. Opaque bottles were used for 0.45- μ m filtered samples collected for laboratory speciation and preserved in 12.5 mM EDTA (ethylenediaminetetraacetic acid). It is hypothesized that the binding of iron by EDTA reduces its capability to participate in redox reactions (photo-induced or otherwise) with arsenic species. Addition of nitric or hydrochloric acids has been used for arsenic species preservation and total elemental analysis (Hall et al., 1999; Williams, 2001; Bednar et al., 2002a), yet these practices can increase arsenite oxidation, particularly in iron-containing matrices (Khoe et al., 2000; Bednar 2001b; Emmett and Khoe 2001).

The Eh and pH were measured in the field because of the instability of these properties during sample storage and transport to the laboratory. The pH meter was calibrated with two

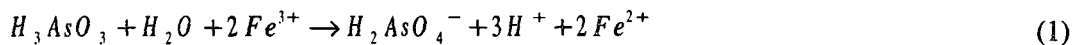
buffers (pH = 4 and 7) and recalibrated periodically in the field to reduce instrumental drift. The Eh measurements were made with a platinum electrode using a silver:silver chloride reference. Accuracy of the Eh meter was checked periodically in the field using Light's Solution, which should yield a value of 475 mV at 25 °C (Light, 1972); readings obtained for this reference solution were considered acceptable if they were 475 ± 10 mV (Light, 1972).

4. Results and Discussion

Fourteen mine effluents or mine-impacted waters were investigated for this study, with total arsenic concentrations ranging from 0.1 to 14 mg/L. The samples have a wide range of iron and sulfate concentrations, pH, and Eh values as listed in table 2. There is no direct correlation between total arsenic and iron concentration. However, as the sample pH increases, higher As(III):(V) ratios are observed (table 2). The Eh values show an inverse relation to pH as might be theoretically expected. Manganese most likely will show similar effects to iron because oxidized manganese tends to precipitate as pH increases (Clayton et al., 1998). At higher pH, soluble iron and manganese are in their reduced state, thereby supporting a lower Eh and a more stable environment for arsenite (McGeehan and Naylor, 1994).

The results listed in table 2 indicate a relation among arsenic speciation and the water chemical properties Eh, pH, and iron(III) concentration. It is postulated that arsenic speciation is controlled by the pH-effected speciation and solubility of iron (Roussel et al., 2000; Daus et al., 2002). In AMD with a pH greater than ~4, the Eh-pH relation shows that iron(II) is strongly susceptible to oxidation to iron(III), which then precipitates as an oxyhydroxide or oxyhydroxysulfate. Sorption of arsenic to these oxyhydroxides will affect the arsenic speciation in mine drainages at pH greater than ~3.5 where iron(III) solubility is negligible. The higher

degree of sorption of arsenate over arsenite to oxyhydroxides results in arsenite being the dominant form of arsenic in the higher pH drainages. At less than pH~3.5, where substantial amounts of dissolved iron(III) exist, arsenite is expected to be oxidized to arsenate according to Eq. (1):



Available Eh-pH diagrams and a favorable E_{cell} of ~0.4 V calculated for the oxidation of arsenite by iron(III) [Eq. (1)] in a typical AMD matrix support this explanation. Figure 1 is a simplified Eh-pH diagram taken from the literature (Vink, 1996), and represents an AMD-type system. Using the data from table 2, the water samples fall in the bold outlined areas. A bimodal distribution is noted, with the samples grouped into high Eh–low pH and low Eh–high pH clusters with particularly small variations in Eh and pH within the low pH cluster. The intermediate pH samples (pH~3–4) are grouped with the lower pH cluster, and all are within the Fe_2O_3 - $H_2AsO_4^-$ stability field. The higher pH group (figure 1) appears to be transitional between the arsenite and arsenate fields.

The field-measured Eh and pH values listed in table 2 are plotted in figure 2. Also in figure 2 is the calculated Eh based on the arsenic species ratios measured (table 2) and typical iron ratios that might be expected at the pH measured and assuming iron (III) concentrations are controlled by ferrihydrite solubility (Wildeman et al., 1997). It is clear that the arsenic- and iron-calculated Eh values agree with the field measurements at lower pH. The arsenic-calculated Eh values differ slightly from the field measurements at low pH but agree well at high pH. Additionally, the iron-calculated Eh values (figure 2) are from expected iron(II):(III) ratios that might exist in AMD's with the pH conditions measured.

The small apparent deviation of arsenic speciation from thermodynamic equilibrium at low pH is likely a function of the extremely low concentration of arsenite in these samples [reflected in the low As(III):(V) ratios in table 2]. This is analogous to the low concentration of iron (III) in waters with $\text{pH} > 4$ resulting in more (analytical) error being associated with the species ratio calculations than with the field Eh measurements. The samples with circumneutral pH show a deviation from theoretical predictions of the iron redox couple, likely suggesting that another redox couple dominates in these systems. For example, the Platoro Wetland Seep sample had an odor of hydrogen sulfide, indicating that sulfide may be controlling redox reactions in that system. Samples, such as the Arsenic Extraction Well, Mining Process Water, and South Maybe Canyon Tailings Leach, had little dissolved iron, further supporting the idea that precipitation of oxyhydroxides had removed enough iron from the system to allow another redox couple to dominate.

The agreement between theoretical predictions of arsenic speciation from the published Eh/pH diagram and the observed Eh of natural AMD samples actually is not normally the situation and probably occurs because the dominant iron redox couple in most AMD effluents gives a meaningful field Eh measurement. In other natural samples investigated, primarily domestic and agricultural irrigation wells containing arsenic in the 10- to 1,000- $\mu\text{g/L}$ range and iron in the 1- to 5- mg/L range, a similar agreement is not observed (Bednar et al., 2002c). Often, redox disequilibrium is found with iron (III) and arsenite coexisting as well as arsenate being found in wells containing dissolved iron (II) and traces of hydrogen sulfide (Bednar et al., 2002b). These apparent speciation anomalies in non-AMD samples are not uncommon and have been reported by others (Yan et al., 2000; Daus et al., 2002).

6. Summary and Conclusions

The thermodynamic explanations of arsenic speciation are derived directly from comparison of various mine drainages with a range of pH and Eh conditions. Although the correlations between speciation and water chemistry are not perfect, particularly in the higher pH range, the low pH extreme does show a good arsenic speciation agreement with predicted values. The lowest pH/highest Eh sites investigated (Gold Mine Waste Rock, Koehler Breakdown, and Virginia Canyon Mine) have total arsenic concentrations of 65, 7, and 3.6 mg/L, respectively, present almost entirely as arsenate. One of the highest pH/lowest Eh sites (Parole Shaft), however, has a total arsenic concentration of 14 mg/L, which is composed of ~90% arsenite.

The intermediate region (pH~3–4), where a nearly 50:50 arsenic speciation ratio might be expected (as in the case of the Koehler Tunnel), could be explained by kinetics. Water samples were collected as near to the actual adit as possible. If a precipitation/sorption reaction is taking place, then a sampling location farther downstream might show a higher As(III):(V) ratio, thus making a better agreement with the expected result. Photooxidation also could be important in AMD systems where the oxidation of arsenite would increase with distance from the “dark” underground source.

The high pH sites (>6) show arsenic speciation ratios of near 1, although not as high as the Parole Shaft. Treatment processes favoring arsenate for remediation purposes likely influence the Arsenic Extraction Well arsenic speciation ratio. The chemical reactions occurring in the Mining Process Water are not entirely known, yet it still shows a high pH and As(III):(V) as theoretically expected. The South Maybe Canyon sample shows a reasonably high As(III):(V), in agreement with what would be predicted.

Use of the type of field investigations described here as preliminary data for implementing a passive-treatment system for arsenic-containing AMD is possible (Wildeman and Updegraff, 1997). Photooxidation, for example, would be advantageous for high pH systems because the oxidation of iron by atmospheric oxygen or microbial populations would create a photolysis counterpart and a sorption substrate for the oxidation and removal of arsenite. Further work is needed before a passive treatment system could be implemented, and in-depth investigations on a prospective site would be required. However, the findings presented here can be used to predict the speciation of arsenic for remediation options in such systems owing to the speciation of arsenic being in near thermodynamic equilibrium with iron.

Iron in AMD and its eventual oxidation are important controls on arsenic speciation in mine water (Daus et al., 2002). If a water contains little iron, as could be the case in many groundwaters and high pH mine drainages, an appreciable amount of arsenate may be found at $\text{pH} > 4$ (Robertson, 1989). For example, some groundwater samples from Fallon, NV and Golden, CO contain iron at 1 to 5 mg/L with a circumneutral pH, yet have As(III):As(V) near 1 (Garbarino et al., 2002). AMD is rather unique among natural systems because a dominant redox couple [iron (II):(III)] exists, whereas in many groundwater, surface water, and soil systems this might not be the case. Therefore, the relations found in the present study for AMD are not always applicable to other natural systems.

Acknowledgments

The authors wish to thank Jim Herron of the Colorado Division of Minerals and Geology for providing helpful information on possible sample sites for the study. We also thank Dick Laird of Umicore USA for allowing us to sample in Platoro, Colo., and Mary Scott of the

Colorado Department of Public Health and Environment for allowing us to sample the Summitville site. We thank Jeffrey Jones of the U.S. Forest Service and Scott Sprague for assistance in sampling in Idaho, Charles Bucknam for allowing us to sample in Nevada, and Jennifer Saran for allowing us to sample in Utah. This research was funded by the U.S. Geological Survey and by a Sigma Xi Grant-in-Aid of Research from the National Academy of Sciences. Kenneth Stollenwerk and David Rutherford of the U.S. Geological Survey provided internal review of the subject manuscript. The use of trade, product, or firm names in this paper is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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Table 1: Mine drainage sites investigated and approximate locations.

Table 2: Field and laboratory measured properties and chemical analysis results of the 11 mine drainages investigated. All elemental concentrations are given in milligrams per liter and were determined by ICP-AES. Arsenic concentrations were determined by ICP-AES and ICP-MS. Redox potential (Eh, in volts) values were adjusted by adding 200 mV to the silver:silver chloride referenced reading to normalize the value to the standard hydrogen electrode. BDL represents below detection limit, for copper and phosphate by ICP-AES, 2 and 100 :g/L, respectively. Sulfate and phosphate concentrations were determined by ICP-AES elemental analysis of sulfur and phosphorous.

Figure 1: Eh-pH diagram for an acid mine drainage-type system with sampling sites plotted (bold outlined areas) over the calculated stability fields. Figure adapted from Vink (1996).

Figure 2: Field-measured Eh and calculated Eh from measured arsenic species ratios and expected iron species ratios.

Table 1:

Site	Approximate Location
Argo Tunnel	Idaho Springs, Colo.
Quartz Hill Tunnel	10 km north of Idaho Springs, Colo., 1 km west of Central City, Colo.
Virginia Canyon Mine	1 km north of Idaho Springs, Colo.
Koehler Tunnel	Red Mountain Pass, 15 km south of Ouray, Colo.
Koehler Breakdown	Red Mountain Pass, 15 km south of Ouray, Colo.
Summitville Pump Vault	Summitville EPA Superfund Site, 30 km southwest of Del Norte, Colo.
Parole Shaft	Platoro, 15 km south of Summitville, Colo.
Wetland Seep	Platoro, 15 km south of Summitville, Colo.
Pumphouse Sump	Platoro, 15 km south of Summitville, Colo.
Mammoth Shaft	Platoro, 15 km south of Summitville, Colo.
Arsenic Extraction Well	West of Salt Lake City, Utah
Mining Process Water	West of Salt Lake City, Utah
South Maybe Canyon Tailings	North of Soda Springs, Idaho
Gold Mine Waste Rock	West of Elko, Nevada

Table 2:

Site	[As]	[Fe]	[Mn]	[SO ₄ ²⁻]	[Cu]	[PO ₄ ³⁻]	pH	Eh	As(III):(V)
Argo Tunnel	0.091	128	74	2690	4	0.386	2.9	652	0.047
Quartz Hill Tunnel	0.170	639	66	4720	38	BDL	2.8	648	0.082
Virginia Canyon Mine	3.610	381	36	2940	18	12.3	2.7	678	0.008
Koehler Tunnel	0.900	105	3	560	4	BDL	3.5	626	0.805
Koehler Breakdown	7.030	493	16	2230	50	BDL	2.8	713	0.013
Summitville Pump Vault	0.204	210	16	1290	66	BDL	3.6	620	0.058
Parole Shaft	13.970	99	11	870	BDL	BDL	5.8	162	8.924
Wetland Seep	0.415	213	23	900	BDL	BDL	6.3	100	5.554
Pumphouse Sump	1.400	346	28	1500	0.2	BDL	3.1	566	0.968
Mammoth Shaft	0.740	601	38	2520	BDL	BDL	4.3	80	1.230
Arsenic Extraction Well	5.870	0.04	0.14	338	BDL	BDL	6.7	360	<0.001
Mining Process Water	0.200	BDL	3	2760	0.1	BDL	7.5	422	1.391
South Maybe Canyon Tailings	0.125	BDL	BDL	632	BDL	0.324	7.2	300	0.526
Gold Mine Waste Rock	64.651	3300	117	32900	55	1030	2.2	760	<0.001

Figure 1:

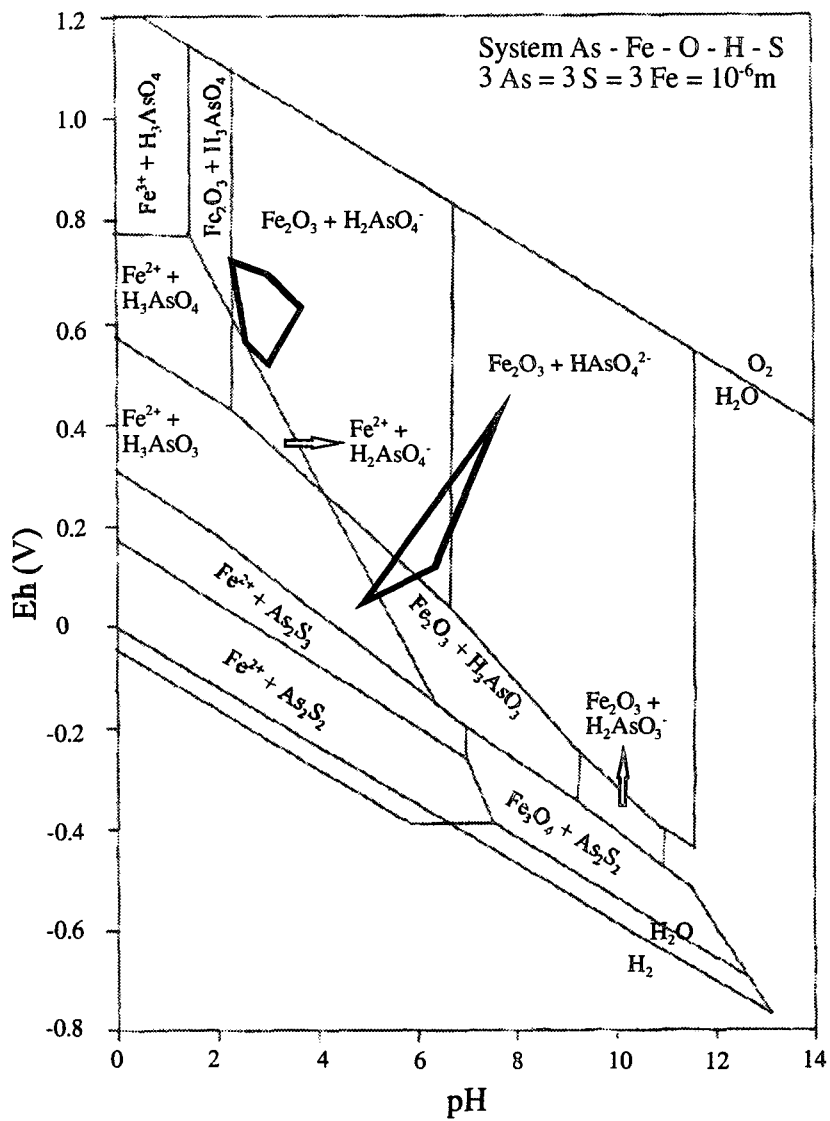


Figure 2:

