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TECHNICAL ARTICLE

Effect of Temperature on Arsenic Treatment and Mobility in Mine Influenced Water

Drummond Earley III[1]

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Abstract

Natural and artificial sorption of arsenic on iron hydroxides is one of the most important reactions controlling arsenic mobility in mine water and other water resource systems. Thermodynamic equilibrium modeling can be used to design and optimize water treatment systems as arsenic sorption is a function of speciation, dose, pH, Eh, and water composition. However, the effects of temperature on arsenic treatment systems have not been extensively considered in mine water quality investigations and treatment designs. Laboratory and field studies have shown that adsorption of arsenic oxyanions onto iron hydroxide particles is endothermic and the equilibrium concentration of arsenic in water is lower at higher temperatures and higher at lower temperatures. Data from two field sites are presented to investigate the effect temperature has on arsenic treatment. At a site in Canada, ferric sulfate coagulation is used to treat arsenic in tailings contact water when not frozen. The dosage of ferric sulfate is held constant but is much less efficient during spring thaw than in the summer. Thermodynamic modeling shows that the dosage must be increased in the spring to meet discharge water quality standards because the sorption equilibrium constant is temperature dependent. At another site in the Rocky Mountains of the USA, the USGS studied and modeled passive treatment of arsenic and other contaminants in AMD-affected stream flows without including temperature dependent sorption. Thermodynamic modeling was used to reexamine the effect of temperature on arsenic sorption onto iron hydroxide precipitates.

Keywords Sorption · Thermodynamic · Modeling · Geochemistry · Tailings · AMD

Introduction

Environmental Regulation of Arsenic in Water

Arsenic in surface and groundwater resources is highly regulated because elevated levels of arsenic pose a risk to human health and the environment (Smith and Huyck 1999). Arsenic in drinking water has been regulated in the U.S. since 1942 and the current standard in drinking water and groundwater aquifers is 10 µg/L (Southwest Hydrology 2002a). Similar water quality standards are enforced around the globe and arsenic is the second most common contaminant of concern at Superfund sites in the U.S. (EPA 2002). Because of this focus on human health and the environment, arsenic geochemistry has been extensively studied (Bowell et al. 2014; Campbell and Nordstrom 2014).

Mine Sources of Arsenic in Water

Many metal ore deposits are associated with relatively high concentrations of arsenic, as compared to average crustal abundance, which is used as a geochemical tracer of mineralization for gold, silver, and other metals (Boyle and Jonasson 1973). The most common mineral sources of arsenic include arsenopyrite, arsenic-bearing pyrite, and other arsenic sulfide minerals in ore deposits that end up in mill tailings and other mining wastes. However, mined arsenopyrite or arsenic-bearing pyrite oxidizes in the tailings as oxygenated water infiltrates into the pile and dissolves, releasing iron and arsenic in the mining-influenced water (MIW) at rates faster than natural weathering rates.

✉ Drummond Earley III
dearley@d3geochem.com

[1] D3 Geochemistry LLC, 5055 Burch Creek Drive, South Ogden, UT, USA

Arsenic Speciation and Mobility in Aqueous Solutions

Arsenic is usually present in water as arsenate (As[V]) oxyanions (e.g. $HAsO_4^-$) under oxidizing and neutral to slightly alkaline pH, which is the predominant condition of surface water discharges and groundwater at mine sites (Campbell and Nordstrom 2014). Arsenic is most mobile in neutral to alkaline pH ranges and intermediate redox conditions conducive to sulfide oxidation but not oxidizing enough to form iron hydroxides that sorb arsenic (Smith and Huyck 1999). Arsenic is particularly mobile in variably saturated sediments or tailings where water levels rise and fall. In such environments, arsenic is released from sulfide minerals when water levels fall, creating oxidizing conditions, and can also be immobilized by iron hydroxides under these conditions. Conversely, it can also be desorbed and remobilized from iron hydroxides when pH changes (Feng et al. 2012, 2013). Arsenic can also be mobilized under reducing conditions by re-saturation of sediment and tailings and surface-bound arsenic is released as the iron hydroxides dissolve (Bowell et al. 2014). Eh conditions need to be oxidizing (0 V or above) at circumneutral pH to ensure that arsenic is bound to iron hydroxides such as ferrihydrite ($Fe(OH)_3$). Arsenic may also be precipitated as sulfides at low Eh via sulfate reduction reactions, but this reaction is usually much slower than sorption onto iron hydroxides. Therefore, elevated arsenic concentrations may persist in reduced groundwater or anaerobic wetlands (Bowell et al. 2014).

Arsenic Attenuation and Mobility in Water

Oxidation of pyrite at the surface of the Earth releases ferrous iron ions. Minor amounts of arsenic occur within pyrite and may also be released by this mechanism. However, as the ferrous iron oxidizes it precipitates owing to the low solubility of iron hydroxides. Hence mobilized arsenic may reprecipitate by sorption onto the newly formed iron oxide solid. This reaction may be indicated by a correlated decrease in concentrations of dissolved iron and arsenic in open water bodies that receive MIW. The sorption and coprecipitation effect is so effective that iron precipitation and coagulation is commonly used to remove arsenic from drinking water in remote villages, small municipal water treatment systems, and large industrial wastewater treatment facilities around the globe (Nicomel et al. 2015; Southwest Hydrology 2002b). However, the sorption reaction is reversible, and even in oxidizing conditions, arsenic can re-dissolve into surface and groundwater if the pH increases significantly. This is because arsenic is an oxyanion, and the surface charge of precipitated iron hydroxide particles becomes more negative as pH rises according to the generalized two-layer theory of sorption (Dzombak and Morel 1990). Hence proper disposal of the treatment sludge is required to prevent release of arsenic back into the environment.

This paper describes two cases where geochemical modeling was used to assess water treatment efficiency by iron coagulation and flocculation of arsenic. The generalized two-layer model of Dzombak and Morel (1990) was used in the modeling, and the comprehensive thermodynamic parameter database MINTEQ (Allison et al. 1991) is available for arsenic sorption and potentially competing ions for specific iron hydroxide surface sites. Briefly, the double electric layer theory of Gouy-Chapman is based on a conceptual model of interactions at solid surfaces in contact with aqueous solutions that results when one layer of surface charges attached to the solid countered by opposite charges in a diffuse layer in the solution. The net charge balance within the double layer is maintained by proton exchange, cation binding, and anion binding via ligand exchange. The surface charge at the solids is usually created by hydroxyls as the predominant earth minerals are oxides. Common hydroxides of iron, aluminum, silicon, and manganese are the predominant sorbents in nature as they form high surface area coatings on the matrix minerals in soils and in groundwater systems. They also form mobile colloids, which can form naturally or artificially by precipitation of saturated solutions. These colloids can then be removed by flocculation. A more detailed explanation of adsorption phenomena and the double layer model of sorption is provided in Dzombak and Morel (1990) and Stumm (1992).

Modeling Arsenic Fate, Transport, and Water Treatment

Modeling of arsenic sorption–desorption by iron hydroxides has been applied to mine influence waters such as acid mine drainage (Runkel et al. 2011), pit lakes (Tempel et al. 2000), and heap leach solutions (Decker et al. 2006). These studies used laboratory isotherms for experiments conducted at or close to standard state conditions (25 °C, 1 bar pressure), and a few studies at higher and lower temperatures are available to provide thermodynamic data for modeling (Smith 1999). Some theoretical considerations of sorption behavior at variable temperature suggest that specific sorption of anions trends inversely and that of cations trends positively with increasing temperature (Machesky 1990; Smith 1999; Stumm 1992). Hence, oxyanions of arsenic should sorb more strongly at lower temperatures according to these theories and experimental data for a limited number of other anion species. However, a laboratory study by Banerjee et al. (2008) showed that adsorption of arsenic onto synthetic iron hydroxide particles is endothermic and that the equilibrium concentration of arsenic in water is lower at higher temperatures and higher at lower temperatures. In addition, arsenic sorption onto naturally formed soils and laterite iron concretions was also observed to be endothermic (Feng et al. 2013; Partey et al. 2008). A field study conducted in the Altiplano region of Bolivia showed that arsenic concentrations are lower in water from high temperature geothermal springs than in lower temperature shallow aquifer samples (Munoz et al. 2015). While arsenic is commonly associated with hot springs, arsenic concentration data compiled by Boyle and Jonasson (1973) indicate that high arsenic concentrations are also associated with cold springs. Machesky (1990) estimated that adsorption enthalpies are often ± 20 kJ/mole or greater, which implies that 20° temperature gradients could double or halve the concentration of a sorbate, which is enough to significantly affect water quality with respect to applicable standards. A water treatment plant in Billings, Montana has difficulty treating arsenic in the Yellowstone River source with ferric coagulation in the winter (EPA 2015).

Owing to the high degree of complexity of arsenic chemistry and sorption processes as a function of pH, redox potential, ionic strength competing ionic species, and temperature (Campbell and Nordstrom 2014), computer modeling is necessary to accurately predict treatment efficiency and arsenic concentrations in mine influenced water and the fate and transport of arsenic in other field settings (Earley et al. 2019; Wallis et al. 2015). In this study, geochemical reaction path modeling was used to simulate active treatment at a mine site in Canada and acid rock drainage discharge in the Rocky Mountains of Colorado, USA at temperatures below standard laboratory testing conditions. This paper does not attempt to derive internally consistent thermodynamic parameters for more accurate sorption prediction but uses modeling to assess the relative effects of temperature on arsenic sorption by iron hydroxides, which has not been routinely considered.

Methods

A thermodynamic model of arsenic sorption onto iron hydroxides based on the hydrogeochemical model described by Earley et al. (2019) was used to simulate active and passive treatment systems at two different mining sites in North America. This study also provided data and modelling results that suggest that arsenic sorption is temperature dependent in natural geothermal waters. Data from the Canadian site was provided by the mine operator and data from the Rocky Mountain site was obtained from published literature sources (Runkel et al. 2009, 2011). The author was not involved with the sampling and analysis during monitoring at these sites, but these sources provided available field datasets for testing the hypothesis that arsenic sorption is endothermic below standard state temperatures of 25 °C. The model was created using the geochemical reaction path code React, which is part of the Geochemist's Workbench® software (Bethke et al. 2021). In addition to simulating dilution, aqueous speciation, and equilibrium precipitation/dissolution, the model also simulates arsenic and other ion sorption reactions. The generalized two-layer model of Dzombak and Morel (1990) is implemented in the geochemical model because it calculates pH-dependent arsenic sorption for specific iron hydroxide surface sites.

When added to water during arsenic treatment, ferric sulphate dissociates and forms iron hydroxide particulates and sulfuric acid:

$$Fe_2(SO_4)_3 + 6\,H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4 \qquad (1)$$

Arsenic adsorbs onto the iron hydroxide ($Fe(OH)_3$) that precipitates due to its low solubility. The iron hydroxide particulates coagulate with arsenic and then flocculate, which separates the arsenic from the water column. At high concentrations and over time, sorbing cations or anions may form a surface precipitate, which has been described as an ideal solid solution of the surface phase, and the sorbate may eventually be incorporated into the bulk solid during recrystallization of the amorphous phase (Campbell and Nordstrom 2014).

Because the coprecipitation occurs via a surface sorption mechanism, the dosage stoichiometry depends on the mass and surface area of the iron hydroxide particulates. The primary arsenic species in oxygenated water is arsenate (As^{+5}), which adsorbs onto the surface of precipitated ferric hydroxide (Dzombak and Morrel 1990), according to surface reactions such as the following for arsenate:

$$\equiv FeOH^o + AsO_4^{3-} + 3H^+ \rightarrow \equiv FeH_2AsO_4^o + H_2O \qquad (2)$$

Under reducing conditions arsenite is the predominant species:

$$\equiv FeOH^o + H_3AsO_3^o \rightarrow \equiv FeH_2AsO_3^o + H_2O \qquad (3)$$

The $\equiv FeOH^o$ term in these equations represents the precipitated iron hydroxide surface. Similar weaker iron hydroxide surface sorption reactions are also responsible for arsenate sorption. The sorption reaction is reversible under changing pH and other chemical and physical conditions. The sorption model is based on the thermodynamic data compiled by Dzombak and Morel (1990).

The MINTEQ thermodynamic database (Allison et al. 1991), and sorption database supplied with the Geochemist's Workbench software was modified slightly to account for the endothermic sorption of arsenic onto precipitated iron hydroxide by inclusion of the heat of sorption determined by calibration. The heat of sorption (enthalpy) extracted from a linear fit of log K_d with 1/T using the Van 't Hoff equation is endothermic at approximately 204 kJ/mol (used for both As[III] and As[V] as As III levels were relatively low). This sorption enthalpy is approximately five times higher than the reported enthalpies of sorption calculated by laboratory sorption test data (Banerjee et al. 2008). However, the laboratory studies were conducted at temperatures between 25 and 60 °C on synthetic iron hydroxide media and it is possible that the enthalpy of sorption is temperature dependent and becomes more endothermic as the freezing point of water is approached in natural systems. The sorption enthalpy measured in experiments conducted by Partey et al. (2008) and Feng et al. (2013) on natural soil materials at 25 to 60 °C is on the same order of magnitude as the synthetic iron hydroxide media.

While the kinetics of sorption and flocculation are somewhat slower at lower temperatures, there is enough residence time in the field systems modeled to reach sorption equilibrium, given that the rate of sorption is on the order of minutes to a few hours under laboratory conditions (Banerjee et al. 2008; Feng et al. 2012; Razzouki et al. 2015).

Site Descriptions

Two sites, one in central Canada and one in the Rocky Mountain region of Colorado, USA with different mine water arsenic impacts and treatment pathways were simulated using the Geochemists Workbench® React Software and the modified MINTEQ thermodynamic database described above.

Central Canada

Active ferric sulfate coagulation treatment at a tailings storage facility located in central Canada required greater dosages than vendor recommendations in order to meet discharge requirements during spring runoff, but lower dosages during the late spring through fall seasons. Arsenic is elevated in the tailings pond water before entering the polishing pond and a chemical compound, ferric sulfate, is used as a coagulant to lower arsenic concentrations at the decant between the ponds (Fig. 1). The tailings pond water flows into a polishing pond, whichis discharged in the spring and fall to manage run-off. The reagent solution is 50 to 60% polyferric sulphate, $Fe_2(SO_4)_3$, which usually contains $\approx$ 12% of the active component ferric iron (Fe^{+3}). Sulfuric acid is also added to the solution during manufacturing to keep the ferric sulphate dissolved. The amount of sulfuric acid added is not known but the pH of the polishing pond water is monitored and remains weakly alkaline during the ferric sulfate treatment. The ferric sulphate solution is dosed into water pumped from the tailings pond to the polishing pond. At the average dosage rate of ferric sulfate, the tailings pond decant iron concentration is $\approx$ 20 mg/L. Iron particles are formed when the ferric sulphate reacts with pond water and the particles flocculate and are deposited with arsenic in the polishing pond with the other suspended solids (Fig. 1).

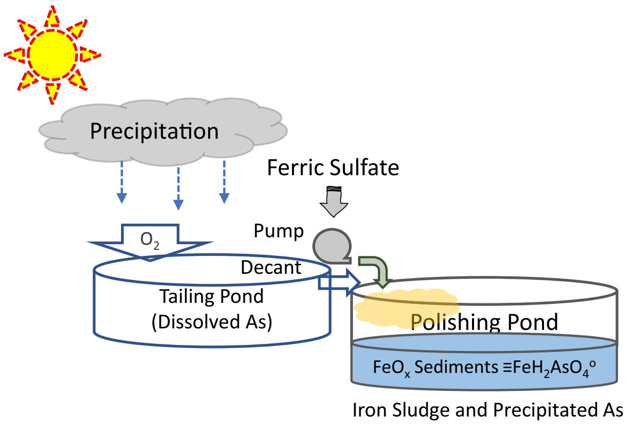

Fig. 1 Schematic tailings pond treatment system using ferric sulfate addition and ferric hydroxide (FeO_x) coagulation

While the basic principle of water treatment by coagulation is relatively simple, as illustrated in Fig. 1, the operation of real water treatment systems can be complex because of the variability in flows and treatment efficiency in large-scale MIW systems, which is affected by:

- Precipitation and flow
- Water chemistry including:
    - Influent arsenic concentration
    - Dominant arsenic species
    - pH and ORP
    - Total dissolved solids and competing species
- Temperature
- Flocculant density and surface area
- Reagent form and composition
- Mixing efficiency
- Residence time

During the ice-free season, the operator doses about 1 L of ferric sulfate per 40,000 L of effluent using a dosing pump discharging to a 1.27 cm (½ inch) hose that drips into the decant culvert transferring water from the tailings pond to the polishing pond (Fig. 1). The treatment system consumes a barrel of ferric sulfate about every six days. Typically, the total arsenic concentrations peak in the water entering the polishing pond under the springtime ice and drops by a factor of six during open water at a constant dose. Ferric sulphate addition is adjusted to meet the discharge limit for total arsenic. Samples of treated water from the polishing pond are collected monthly during the ice-free season and submitted to an analytical laboratory for analysis of dissolved arsenic, pH, and other constituents of concern. The quality control and quality assurance measures are consistent with Provincial regulations, which are consistent with Canada's national standards.

The pH of the tailings pond effluent is circumneutral to slightly alkaline (pH ranges between 7 and 9) and so an average pH of 8 was used in the model simulations for this site. The predominant form of arsenic is arsenate as the pond is open to the atmosphere and is relatively large. However, in the winter, the tailings pond becomes reduced when covered with ice. This condition is indicated by a relatively low oxidation reduction potential (ORP) reading of ≈ − 250 mV in the tailings and polishing ponds during the spring thaws in April. However, arsenic speciation testing determined that the predominant form of dissolved arsenic in the influent water is still arsenate, despite the relatively anoxic conditions.

Rocky Mountains, Colorado, USA

Iron hydroxide precipitates naturally from mine water containing ferrous iron during oxidation at the surface to ferric iron. The precipitates sorb arsenic and other metals. For the purposes of this paper, this process is referred to as passive treatment although it may be called natural attenuation depending on the degree of water management used to promote this process. Passive treatment occurs in Mineral Creek in San Juan County, Colorado, which is influenced by acid rock drainage from historic underground mining operations (Runkel et al. 2011). The USGS performed a synoptic field sampling study along the creek to analyze downstream concentrations of metals and other constituents downstream of the mine sources. The USGS also conducted geochemical transport modeling using this dataset and included simulations of iron hydroxide sorption of arsenic and many other metals in the system using the code OTEQ. The USGS water quality dataset is published, and open source (Runkel et al. 2009), and was used to test the temperature-dependent sorption model for arsenic in a passive treatment setting. The USGS model was based on the two-layer pH-dependent sorption model and MINTEQ thermodynamic dataset (Allison et al. 1991) but did not have a temperature-dependent sorption isotherm. Instead, the USGS empirically calibrated the model to fit the data by adjusting the sorption equilibrium constant in the database.

Figure 2 is a temperature and total arsenic vs. distance profile for MIW drainage flows and Mineral Creek at selected sampling stations near tributary confluences before treatment (Runkel et al. 2009). The temperature ranged from about 15 to 11 °C before MIW discharges from the northeast to the main branch of Mineral Creek. Mineral Creek is the main drainage and flows southeast to the confluence of the mine drainage, as shown in the Fig. 3. Mixing at the confluence lowers the temperature to 7 °C and total arsenic concentrations also diminish from 3.5 mg/L to the detection limit of 0.001 mg/l. Mineral Creek continues to flow south, and downstream temperatures fall to as low as 5.5 °C where cold meltwater fed alpine stream tributaries discharge

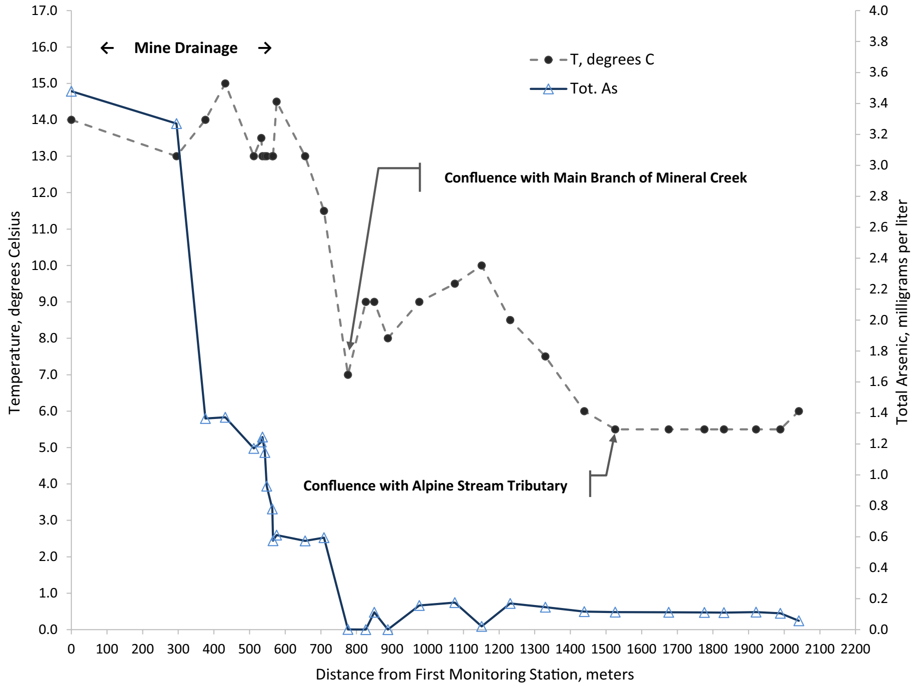

Fig. 2 Temperature and total arsenic versus distance along mine drainage and Mineral Creek

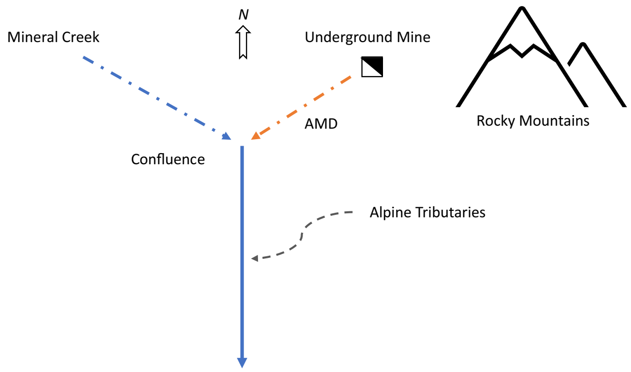

Fig. 3 Schematic of Rocky Mountain watershed study area and mine drainage source

Table 1 Selected USGS water quality sample results for dissolved metals and sulfate plus pH and temperature (Runkel et al. 2009) used in Rocky Mountain AMD site model simulations

Analyte	0 m	512 m	656 m	888 m	2041 m
pH	2.96	3.10	3.11	4.18	4.75
Temperature (C)	14.0	13.0	14.5	9.0	6.0
Al (mg/L)	39.75	19.63	14.49	1.924	0.949
As (mg/L)	3.195	1.025	0.464	0.018	0.009
Ca (mg/L)	217.6	118.7	96.57	24.63	19.24
Cl (mg/L)	0.660	6.372	7.067	2.344	1.318
Cu (mg/L)	13.86	6.824	4.402	0.749	0.412
Fe (mg/L)	224.8	89.01	53.53	3.126	1.572
K (mg/L)	1.710	1.044	0.991	0.358	0.328
Mg (mg/L)	39.23	19.74	17.84	2.976	1.986
Mn (mg/L)	31.97	16.32	11.47	1.621	0.825
Na (mg/L)	24.42	16.03	13.10	2.559	1.777
SO_4 (mg/L)	1681	809.3	610.6	105.7	71.89
Zn (mg/L)	88.15	43.82	29.51	4.653	2.788

into Mineral Creek. However, total arsenic increases to about 0.1 mg/L and remains relatively constant at 0.10 to 0.18 mg/L to the end of the monitoring segment of the creek. The MIW flow temperatures are higher as a result of discharges of mine adit and groundwater seeps that enter the mine workings at depth below the surface.

These variations were significant enough to test the temperature- and pH-dependent sorption model in a setting where natural attenuation of arsenic is occurring. Selected samples collected along the USGS stream surveys (Runkel et al. 2009) were used to simulate temperature-dependent sorption effects. The temperature, pH, and water chemistry of these samples (Table 1) was used as input to the arsenic sorption model. Dissolved arsenic was analyzed along with total arsenic and the dissolved measurements were used in the model. Dissolved arsenic was only ≈ 10% less than total arsenic in the modeled data set except at the last station where dissolved arsenic was about 17% of the total arsenic in the stream. The model calculates the concentration of arsenic sorbed from the aqueous dissolved arsenic concentration (Dzombak and Morel 1990). The temperature-corrected simulation results were compared to results from simulations at a constant temperature of 25 °C using the standard MINTEQ thermodynamic database. Sorption parameters (i.e. surface area, sorbent molecular weight, low affinity site density) were set using the default database values.

For simplicity, the modeling was conducted in selected stream segments where pH and temperature differences were significant enough to test the model's ability to predict the expected arsenic concentration given the mass of iron precipitated as iron hydroxide. The mass of iron hydroxide was taken as the dilution-corrected drop in ferrous iron concentration from one station to the next downstream station resulting from oxidation (Table 1). The predicted arsenic concentration was used as input for the next segment simulation in temperature-compensated and uncompensated comparative model scenarios. As conceptualized in the USGS model (Runkel et al. 2011), arsenic sorption equilibrium is reversible and arsenic concentrations are in equilibrium with the iron precipitate in the bed load. For example, in Table 1, the ferrous iron concentration falls from 224.8 to 89.01 mg/L in the 0 to 512 m reach of stream below the AMD source (Fig. 2), and the amount of ferrihydrite precipitated is ≈ 100 mg/L of water. The sorption model calculates the expected amount of arsenic depleted from the water column and the output concentration is provided with other concentration results. The first temperature simulation occurs between 656 and 888 m and the second between 888 and 2041 m with corresponding dilution factors from sulfate mass balance. The pH was adjusted in the Geochemist's Workbench React code (Bethke et al. 2021) to simulate the effects of pH changes downstream.

The USGS also modeled stream chemistry after the trial addition of lime to neutralize the low pH in Mineral Creek (Runkel et al. 2011). The comparative temperature simulations are not discussed in this paper as the much higher pH conditions in the creek resulted in faster oxidation and precipitation of iron (Stumm and Morgan 1981) and low downstream arsenic concentrations. Hence, the arsenic concentrations were less affected by temperature, which results in greater uncertainties in model inputs and simulation results and loss of resolution. It is also uncertain whether the stream reached a new steady state condition after treatment, which would be necessary to fulfil the model assumptions.

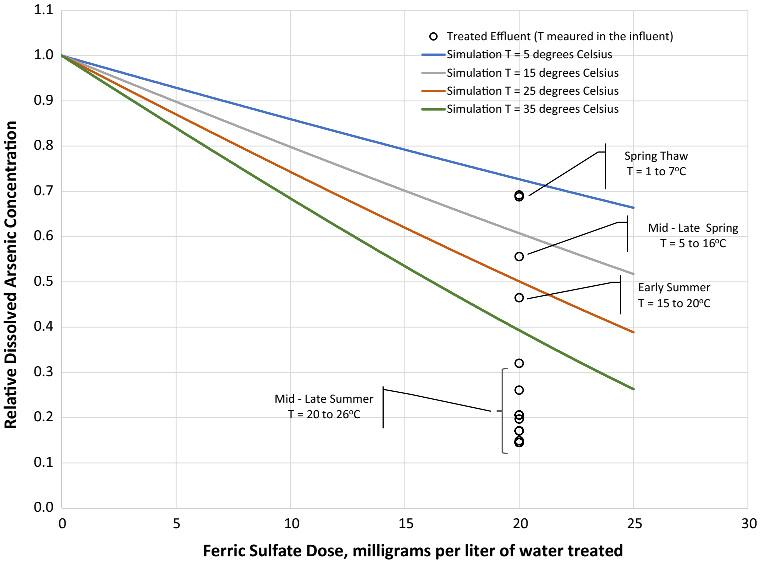

Fig. 4 Model simulation results for Canadian tailings pond water treatment simulations at pH = 8

Results and Discussion

Central Canada Tailings Pond Treatment System

Figure 4 shows sorption model results and seasonal variations in relative arsenic concentration observed at the Canadian tailings pond discharge site. The relative % change in dissolved arsenic concentrations in the treated water over a season, from highest concentrations in spring to lowest concentrations in early summer, was ≈ 120%. However, the influent arsenic concentrations to the treatment system only varies by 22%, with the spring concentrations being lower and the summer concentrations higher. The inflow pH ranges from 7 to 9, but a constant pH of 8 was used in the simulations. Sensitivity runs based on the relative arsenic concentrations indicate that the temperature effect on sorption efficiency decreases at higher pH because arsenic sorption decreases with pH (Dzombak and Morel 1990). At the Canadian site, the pH increases from about 7.8 in the spring to about 9 during the summer. Because arsenic sorption decreases in this pH range, the observed relative change in ferric coagulation efficiency from spring to summer would be even greater if the pH remained constant. This may be due to ferric hydroxide having less sorption capacity at higher pH values.

The highest dissolved arsenic concentrations in treated water sample analyses shown in Fig. 4 were observed during the spring thaw and the lowest in mid-summer. Measured water temperatures in the tailings pond decant ranged from close to freezing to about 25 °C in the influent, but there may be greater temperature variations in the polishing pond where the iron sludge precipitates. The predicted range of seasonal mine tailings pond discharge treatment modeling is in good agreement with the observed variations. The highest simulated arsenic levels at 5 °C were close to the measured spring thaw concentrations and the lowest simulated concentrations were measured in the early summer. Some effluent samples collected later in the summer had lower concentrations of arsenic than in early summer and were lower than the simulated arsenic concentrations at 35 °C. The lower arsenic concentrations observed at the Canadian site may be due to biological activity in the pond and sorption of arsenic onto organic matter (Boyle and Jonasson 1973) in addition to the ferric precipitate. Another reason for the low late-summer arsenic could be the ferric precipitate from the early season treatment, which can sorb additional arsenic as temperatures warm. Hence the effective treatment dose from previous ferric sulfate addition may be higher than the active dose in late summer.

The endothermic sorption model results indicate that doubling the dose is required to lower arsenic concentrations in the cold weather months, accounting for the lower coagulation efficiencies. The equilibrium model accurately predicts ferric sulfate dose requirements but there may be some additive kinetic effects (Banerjee et al. 2008; Campbell and Nordstrom 2014; Razzouki et al. 2015). At the alkaline pH of the tailings and polishing pond, ferric dosage rates do not significantly affect the treatment efficiency of arsenite vs. arsenate species. The model results were used to refine ferric sulfate dosage in the treatment system over the course of the year to meet discharge water quality requirements while minimizing reagent consumption.

Mineral Creek Colorado

Figure 5 compares the Mineral Creek modeling results with the observed dissolved arsenic concentrations without lime treatment. The temperature-dependent sorption model

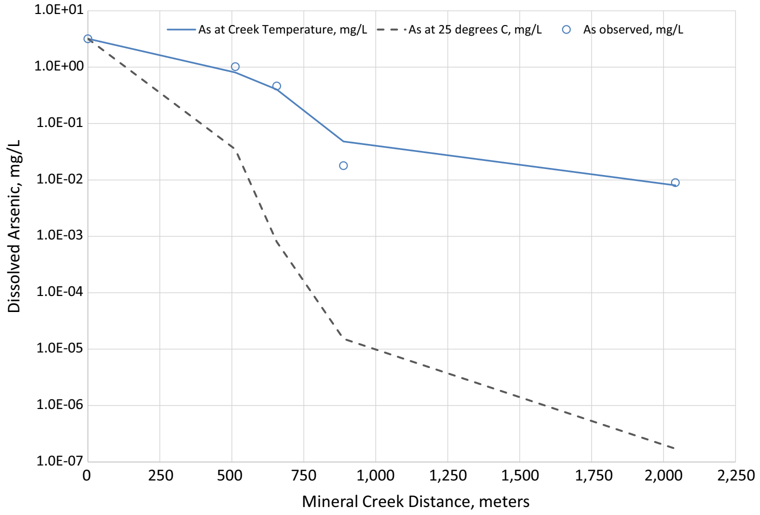

Fig. 5 Model simulation results for Rocky Mountain site at stream temperatures and 25 °C

generates a better fit to the measured concentrations than an isothermal model using only the 25 °C sorption equilibrium constant. The sorption model without temperature compensation results in higher attenuation of arsenic with iron precipitation downstream. The USGS calibrated the model empirically to achieve this fit for arsenic (Runkel et al. 2011), but several other constituents were also modeled Fig. 5. A comprehensive analysis of model fit to other contaminants was not attempted in this modeling study but major and trace ions were included in the model to simulate the effects of sorption site competition and ionic strength. Most of the commonly used thermodynamic sorption equilibrium constants in standard thermodynamic databases are for 25 °C, which is the commonly applied laboratory temperature for isotherm experiments (Smith 1999).

Conclusions

Aqueous arsenic chemistry, speciation, and surface complexation is highly complex and sensitive to pH, redox, competing aqueous species, and temperature. This study shows that geochemical computer modeling can be used to better understand arsenic treatment systems for MIW and predict arsenic mobility.

Numerical simulation of active treatment of arsenic at a tailings pond in Canada using ferric sulfate coagulation accurately predicts that treatment efficiency is adversely affected by cold temperatures. Thermodynamic data and geochemical modeling show that arsenic sorption onto iron hydroxide precipitates is endothermic and equilibrium arsenic concentrations are higher during the winter than in the summer, so that higher doses of iron sulfate are needed in the spring to attain the same level of arsenic reduction. In another example, natural attenuation of arsenic in AMD is negatively affected by cold temperatures in a high elevation mountain stream in the Rocky Mountains of the USA.

These findings suggest that temperature effects on arsenic sorption can be significant over the range of surface and groundwater temperatures commonly encountered in near-surface water resources. This may necessitate additional consideration of temperature variations for water treatment design and monitoring systems where natural attenuation is relied on to reduce the risk of arsenic contamination.

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