Chemistry of arsenic

removal during coagulation and Fe–Mn oxidation

Recent studies have indicated that arsenic in drinking water is as hazardous as radon in homes and secondhand tobacco smoke.

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lthough arsenic has long served as a choice poison and is of legendary toxicity, the presence of trace (parts per billion or micrograms per litre) arsenic levels in public drinking water supplies has not previously caused alarm. However, recent studies have indicated that arsenic in drinking water is more dangerous than previously suspected, with risks comparable to that of radon in homes and secondhand tobacco smoke.[1] The US Environmental Protection Agency (USEPA) is currently considering more stringent arsenic regulations to minimize these risks.[2]

The newfound concern is based on evidence collected from epidemiological studies in Taiwan for long-term human

Arsenic removal during coagulation or Fe–Mn oxidation is examined to aid utilities that desire to improve arsenic removal. Fundamental mechanisms of arsenic removal are discussed, optimization strategies are forwarded, and some new insights are provided to guide future research. Specifically, As(III) removals by coagulation are primarily controlled by coagulant dose and relatively unaffected by solution pH, whereas the converse is true for As(V). When compared on the basis of moles iron or aluminum hydroxide solid formed during coagulation, iron and aluminum coagulants are of demonstrably equal effectiveness in removing As(V) at pH <7.5. However, iron-based coagulants are advantageous if soluble metal residuals are problematic, if pH is >7.5, or if the raw water contains As(III). Arsenic removal during Fe–Mn oxidation is controlled by the quantity of iron removed [$Fe(OH)_3$ formed] and is relatively independent of the quantity of manganese removed (MnOOH formed).

exposures, that arsenic can cause liver, lung, kidney, and bladder cancers in addition to the previously acknowledged risk of skin cancer.[1,3,4] Earlier studies with laboratory animals probably confounded timely identification of the high arsenic risk, because it is an essential trace nutrient and does not cause cancer in laboratory rodents.[2,5] For humans, consideration of the new risks at the current maximum contaminant level (MCL) of 50 μg/L arsenic suggests a lifetime risk of dying from arsenic-induced cancers as high as 13/1,000 people at 1 L/d.[1] Although arsenic toxicity clearly depends on its chemical form, with arsenite [As(III)] much more toxic than the oxidized arsenate [As(V)] species, the proposed regulations will probably target only total arsenic.[2,6,7]

With respect to the proposed regulation, much is uncertain at this time. Given that arsenic has been categorized as a class A carcinogen by USEPA, the MCL goal (MCLG) will likely be set at 0 μg/L, although analytical and cost considerations will probably result in a final MCL between 0.5 and 10 μg/L.[2] The USEPA deadline for input into the rule-making process is currently scheduled for June 1995. The final regulation (promulgation) was recently delayed to November 1997.[7,8]

The water industry has responded aggressively to fill obvious gaps in the knowledge and address technical challenges posed by the anticipated regulation. Consequently, current understanding is likely to dramatically improve pending results of new research projects in areas of arsenic analytical techniques, national arsenic occurrence surveys, examinations of arsenic removal in conventional water

Removal of arsenic during physiochemical treatment processes will be an important line of defense in meeting the proposed arsenic regulation.

oluble arsenic occurs in natural waters only in the arsenate and arsenite oxidation states.

treatment processes, compliance cost estimates, and new treatment options. Nevertheless, this article provides a review of arsenic geochemistry, occurrence, and treatment options for researchers and utility personnel.

Geochemisty of arsenic

Soluble arsenic occurs in natural waters only in the As(V) and As (III) oxidation states. Although both organic and inorganic forms of arsenic have been detected, organic species (methylated arsenic) are rarely present at concentrations >1 μg/L and are generally considered of little significance compared with inorganic arsenic species in drinking water treatment.[9] Thus, this discussion focuses exclusively on the geochemistry and behavior of inorganic arsenic.

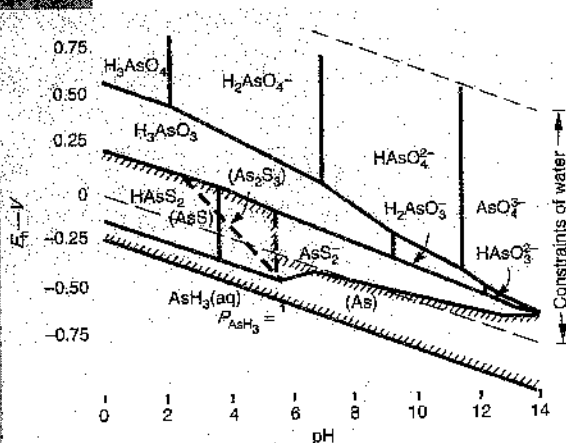Thermodynamic predictions provide useful insight into the equilibrium chemistry of inorganic arsenic species (Figure 1). In oxygenated waters, As(V) is dominant, existing in anionic forms of either $H_2AsO_4^-$, $HAsO_4^{2-}$, or AsO_4^{3-} over the pH range typically encountered in water treatment (pH 5–12). Under anoxic conditions, As(III) is stable, with nonionic (H_3AsO_3) and anionic ($H_2AsO_3^-$) species dominant below and above pH 9.22, respectively. In the presence of sulfides, precipitation of AsS (realgar) or As_2S_3 (orpiment) may remove soluble As(III) and exert considerable control over trace arsenic concentrations.[10] For example, from pH 5 to 9 and in the presence of only 0.2 mg/L H_2S, <0.075 μg/L (1 × 10⁻⁹ M) total As(III) is soluble, based on orpiment equilibrium.[11]

Although thermodynamics can provide an accurate prediction of possible changes in a given nonequilibrium condition, they give no insight to the rate at which those changes will occur. In general As(III) and As(V) acid–base reactions can be assumed to occur instantaneously, whereas changes between oxidation states require indeterminate time

Arsenate [As(V)] is anionic above about pH 2 and is thermodynamically favored in oxygenated waters. Arsenite [As(III)] is nonionic at pH values less than about 9.6, is anionic at higher pH, and is thermodynamically favored in anoxic waters. Stability diagram at $25^\circ C$, 1 atm with 10^{-5} M total arsenic, and 10^{-3} M total sulfur. Solid species enclosed in hatched area, indicating $< 10^{-5.3}$ M solubility. Reprinted from Water Research, volume 6, J.F. Ferguson & J. Garvis. A Review of the Arsenic Cycle in Natural Waters. Page 1259 (1972), with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.

periods in natural waters. For instance, the conversion of As(III) to As(V) in oxygenated water is thermodynamically favored, yet the rate of the transformation may take days, weeks, or months, depending on the specific conditions. Strongly acidic or alkaline solutions, the presence of copper salts, carbon, unknown catalysts, and higher temperatures can increase the oxidation rate,[10,12,13] and manganese oxide, chlorine, permanganate and other oxidants can directly transform As(III) to As(V) in the absence of oxygen.[14–17] Unexpectedly, As(III) oxidation has been observed to be independent of oxygen concentration in seawater.[13] Likewise, the reduction of As(V) to As(III) in the absence of oxygen is also chemically slow and may require bacterial mediation.[18] As a result of these kinetic limitations on arsenic redox equilibria, correlations between redox conditions and arsenic speciation are quite poor.[19–21]

Iron (Fe) and manganese (Mn) exert a strong influence on arsenic concentrations in the environment. Though scorodite ($FeAsO_4 \cdot 2H_2O$) is not observed to form at levels of arsenic typically found in natural systems,[22,23] other solids such as $Ca_3(AsO_4)$, $Ba_3(AsO_4)_2$, and especially arsenopyrite (FeAsS) and $Mn_3(AsO_4)$ are believed to exert some control over arsenic solubility.[21,24–27] Perhaps more important at

lower arsenic concentrations, however, is the coprecipitation–adsorption of arsenic with iron and manganese oxide solids.[10,21,26–29] Arsenic can be immobilized through adsorption–coprecipitation with iron and manganese hydroxides, mobilized when such solids are dissolved under reducing conditions, or released from the oxide surfaces in the event of competition (for sorptive surface sites) in the presence of orthophosphate and natural organic matter (NOM).[30–32] The latter factors can explain why arsenic may be correlated to high Mn(II) (dissolved and reduced manganese oxide), Fe(II) [dissolved and reduced $Fe(OH)_3$], and orthophosphate (competition with arsenic for adsorption sites) in certain waters.[10,21,26,27,29,31–34]

These reactions are generalized to a groundwater and surface water source in Figure 2. For each water source, three distinct zones are demarcated, including aerobic, anoxic without sulfide, and anoxic with sulfides. These zones might correspond to the epilimnion, hypoliminion, and sediments within a stratified lake or, analogously, to increasing depth within a groundwater aquifer. Within oxygenated zones, As(V) is stable and may remain soluble or sorb–coprecipitate with iron and manganese oxides if present. High concentrations of orthophosphate may compete with As(V) for adsorption sites in this zone, increasing soluble arsenic concentrations and mobility. In anoxic regimes without sulfides, As(III) is stable, and dissolved forms of iron and manganese are favored. Arsenic mobility (or solubility) is highest in this zone because (1) As(III) is believed to sorb less strongly onto oxides than As(V) and (2) coprecipitated–sorbed arsenic is released upon dissolution of

> **oagulation and Fe–Mn removal processes can convert soluble arsenic into insoluble reaction products, facilitating their subsequent removal from the water by filtration or sedimentation.**

arsenic-containing iron and manganese oxides. In anoxic zones with sulfides, As(III) becomes immobilized because of the formation of orpiment, realgar, or arsenopyrite, or is coprecipitated with iron pyrite.

In this treatment, the formation of $Mn_3(AsO_4)$ and $Ca_3(AsO_4)_2$ are not illustrated because they require anomalously high ambient As(V) or manganese concentrations, whereas barium arsenate $[Ba_3(AsO_4)_2]$ is not illustrated because of the relative rarity of barium occurrence. Nevertheless, under

certain circumstances such solids might be important in controlling arsenic speciation and concentrations in natural systems. For example, even trace barium (0.1 mg/L Ba^{2+}) can maintain As(V) concentrations at <0.075 µg/L because of $Ba_3(AsO_4)_2$ precipitation over the range pH 6–10. In contrast, even in the presence of 5 mg/L Mn(II) and at pH 8.0, as much as 2.5×10^{-6} (190 µg/L) As(V) is predicted to be present from dissolution of $Mn_3(AsO_4)_{11}$

Occurrence of arsenic

At this time the magnitude of the arsenic problem is unclear and remains a topic of considerable discussion. Although data on low-level occurrence are rare, this author's synthesis (Table 1) and other surveys indicate that roughly 30 percent of medium to large utilities may have >2 µg/L As in the raw water,[21,34–38] with a much higher frequency of problems expected in the western United States and in smaller systems that rely to a greater extent on groundwater sources.[21,39] With respect to treated water, a recent nationwide survey of large utilities conducted by the Metropolitan Water District of Southern California suggests that about 15 percent of large utilities exceed a 2-µg/L As level, with groundwater plants about twice as likely to exceed this level as surface water plants. More specifically, 21 and 10 percent of groundwater and surface water treatment plants, respectively, had effluent concentrations >2 µg/L.[38]

Technologies for arsenic removal

The current advanced treatment options include activated alumina, iron-oxide-coated sand, green sand, reverse osmosis, ion exchange, and electrodialysis.[6,40–42] The term "advanced" is used in the context that the technologies are not yet proven at full-scale treatment plants (at least for low-level arsenic removal), and

Key arsenic reactions in aquatic regimes

Groundwater	Key Reactions	Surface Water
Aerobic	Oxidation of As(III) to As(V). Sorption–coprecipitation of As to oxides. Exchange of phosphate for sorbed As(V). $Mn^{2+} \rightarrow Mn^{4+} \rightarrow MnO_2 \cdot H_2AsO_4$. $Fe^{2+} \rightarrow Fe^{3+} \rightarrow Fe(OH)_3 \cdot H_2AsO_4$. $HAsO_2 \rightarrow HAsO_4^{2-}$. HPO_4^{2-} $HAsO_4^{2-}$	Epilimnion
Anaerobic No H_2S	$HAsO_4^{2-} \rightarrow HAsO_2$. $Fe(OH)_3 \cdot H_2AsO_4 \rightarrow Fe^{2+} + HAsO_2$. $MnO_2 \cdot H_2AsO_4 \rightarrow Mn^{2+} + HAsO_2$. Reduction of As(V) to As(III). Reduction of Fe/Mn oxides. Release of soluble As	Thermocline / Hypolimnion
Anaerobic H_2S	$HAsO_2 + HS^- \rightarrow As_2S_3$ or AsS. $Fe^{2+} \rightarrow FeS \cdot HAsO_2$. Precipitation of soluble As(III) as realgar or oripment, or coprecipitation with FeS	Sediments

TABLE 1   Summary of low-level arsenic occurrence data—November 1993*

Location or Agency Conducting Survey	Number of Samples	Average As Concentration µg/L	Percent >2 µg/L As	Reference
Wisconsin water utilities†	181	NA‡	16	35
California Central Basin Water District	227	3.8	69	36
West Basin Water District	35	0.8	6	
Southern California Water Co.§	200	0.2–3.4	25	
Maine†	460	0.5	NA	34
North central New Hampshire†	43	0.3	NA	
Wells in S.E. New Hampshire**	35	NA	66	
Random US survey of raw water conducted by the University of Colorado, Boulder††	44	4	27	37
Treated water samples††	140	1.6	15	38

*Raw water sources unless otherwise stated
†Wisconsin, north central New Hampshire, and Maine are not noted for As problems.
‡NA—not applicable; indicates that the relevant average or percent >2 µg/L could not be calculated from the cited reference
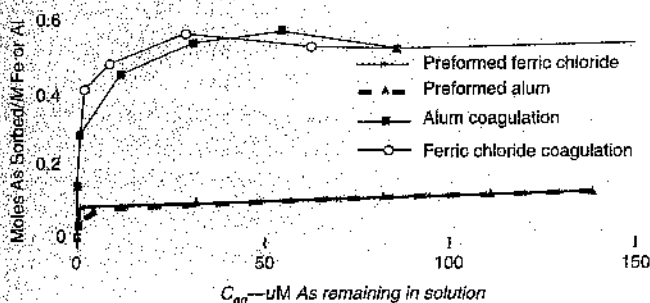§16 divisions sampled
**Area noted for As problems in New Hampshire
††Utilities same as randomly selected for AWWARF-sponsored bromide survey
‡‡Metropolitan Water District: US survey of large utilities (serving 83 million people)

their use generally requires an entirely new treatment step. However, existing processes such as coagulation with metal salts, softening, and Fe–Mn treatment are capable of removing significant concentrations of arsenic. Because a large majority of water treatment plants currently use at least one of these processes (Table 2) and thereby obtain some incidental arsenic removal, it is possible that these existing techniques could serve as a first line of defense in meeting the new standard.[43,44] Unfortunately, current understanding is not adequate to exploit the intrinsic arsenic removals possible by these existing processes, much less to formulate strategies that can substantially

A comparison of arsenic removal by alum and ferric chloride and of preformed solids and solids formed in situ (coagulation)

Legend:
- Preformed ferric chloride
- Preformed alum
- Alum coagulation
- Ferric chloride coagulation

C_{aq}—uM As remaining in solution

Arsenic removal density as a function of arsenic equilibrium concentration (C_{eq}) during coagulation with (A) ferric chloride or (B) alum
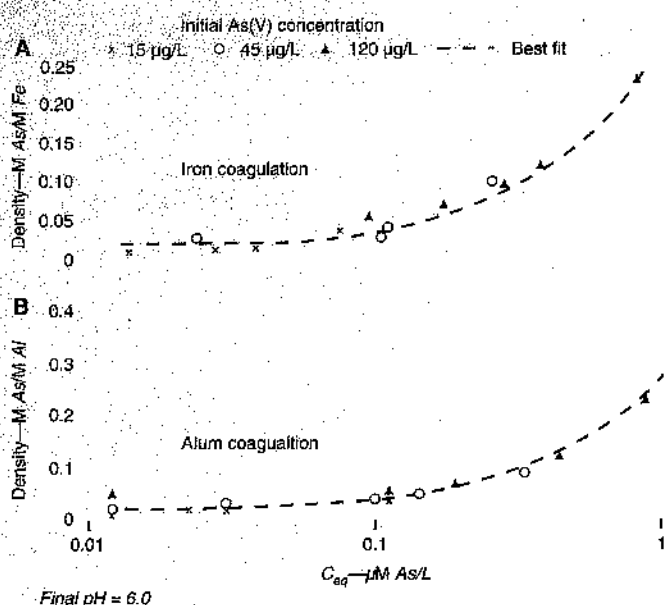
Initial As(V) concentration
- 15 µg/L
- 45 µg/L
- 120 µg/L
- Best fit

A — Density—M As/M Fe
Iron coagulation

B — Density—M As/M Al
Alum coagualtion

C_{eq}—µM As/L

Final pH = 6.0

TABLE 2 — **Percentage of groundwater or surface water treatment plants using softening, coagulation, or Fe–Mn removal processes[43] and percentage of surveyed utilities obtaining ≥80 percent arsenic removal from raw waters[38]**

Treatment Step	Plants—percent	
	Groundwater	Surface Water
Softening	16	20
Coagulation	0	89
Fe–Mn removal	23	Not available
Utilities attaining ≥80 percent As removal from raw water*	11	39

*Excludes plants with nondetectable arsenic

enhance removals. The current work attempts to address these deficiencies for arsenic removal via coagulation and Fe–Mn removal processes.

Materials and methods
Batch coagulation experiments.

Batch experiments were conducted to test key hypotheses and optimization strategies related to arsenic removal during coagulation. The general experimental procedure involved adding ferric or alum coagulant to arsenic-containing solutions, pH adjustment, equilibration, and then centrifugation. The experiments differed in the initial concentrations of arsenic, arsenic oxidation state, coagulant dosage, the form of the coagulant when added (preformed versus conventional), and the final solution pH.

Stock alum and ferric chloride solutions were prepared with equimolar concentrations of trivalent ion by diluting 25 g $Al_2(SO_4)_3 \cdot 18H_2O$ or 20.28 g $FeCl_3 \cdot 6H_2O$ in a 1-L volumetric flask [0.075 M as Al(III) or 0.075 M as Fe(III)]. The coagulant was then dosed directly to 0.1-L beakers at concentrations of $9 \times 10^{-5} M$ Al(III) or Fe(III) (i.e., 30 mg/L as alum or 14.6 mg/L as $FeCl_3$ or as noted in specific experiments), and the pH was adjusted to a predetermined endpoint. In experiments with preformed solids, arsenic was added subsequent to the formation of the corresponding metal hydroxide solid in situ, preventing removal of arsenic via coprecipitation or precipitation reactions. In all other experiments, however, the arsenic was present prior to coagulant addition.

After a 1-h equilibration period on a test-tube shaker, the solutions were centrifuged for 10 min (at 1,000 rpm) and filtered through a 0.45-µm-pore-size membrane filter. All experiments were performed with a constant background ionic strength of 0.001 M sodium nitrate ($NaNO_3$) with pH adjustments via dropwise addition of 0.1 M sodium hydroxide (NaOH). Blank samples (without the coagulant addition) confirmed that no arsenic was lost through adsorption onto the glassware. The final pH was carefully measured and recorded before analysis.

All samples were analyzed for arsenic using the method of Johnson et al.[45] To each 45 mL of sample, 4.5 mL of colorimetric reagent was added. The As(V) reacts with the molybdate in the reagent to form a blue complex that can be quantified in a spectrophotometer.* The method does not detect As(III) unless it is converted to As(V) by addition of 1 mL of

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*UV-160, Shimadzu, Tokyo, Japan

1 N hydrochloric acid (HCl) and a drop of potassium iodate solution. After a reaction time of 4 h to allow development of color, absorbance is measured at 865 nm using a 10.0-cm cell. The minimum detection limit is 1.5 µg/L as As.

Arsenic adsorption modeling. Adsorption of arsenic to iron hydroxide solids was modeled using a chemical equilibrium program developed at the University of Colorado. The program is based on the Minteqa2 (USEPA software) database and computer program, but it has been fitted with a user-friendly interface and sophisticated graphical output. Minteqa2 uses a diffuse-layer model and an attached database to predict As(V) and As(III) adsorption onto freshly formed iron hydroxide solids.[46] Data output from this program was analyzed to produce the contour plots presented in this article.

Results and discussion

Considerable evidence exists that significant arsenic may be removed during conventional treatment processes. Coagulation and Fe–Mn removal processes can convert soluble arsenic into insoluble reaction products, facilitating their subsequent removal from the water by filtration or sedimentation.

Isopleths (contours) of constant percentage arsenate removal as a function of pH and coagulant dosage for a system with an initial arsenic concentration of (A) 5 µg/L As and (B) 50 µg/L As
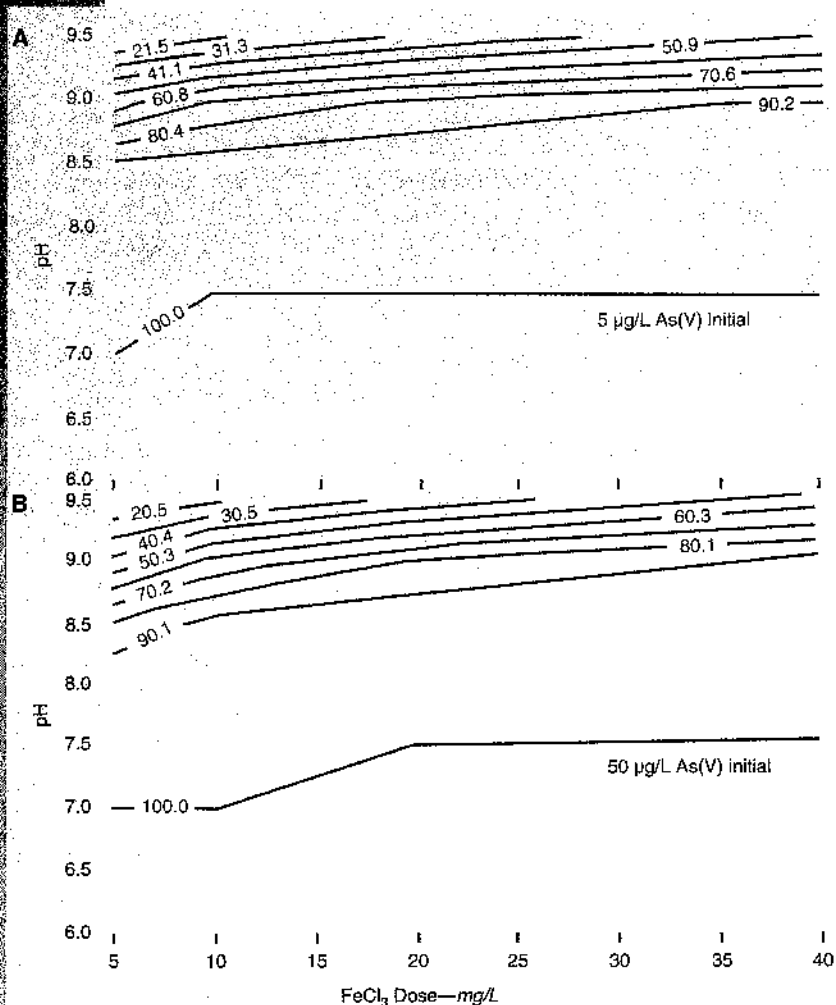
Arsenate removal is primarily dependent on pH and is independent of initial concentration and coagulant dosage. Predictions are derived from the Dzomback diffuse-layer adsorption model.

Thus, arsenic removal efficiency depends on the removal of soluble arsenic and of the resulting particulates, and problems with either process can limit arsenic removal.

Arsenic removal via coagulation. Although the potential to obtain high-efficiency arsenic removal by coagulation is unquestioned, an understanding of removal mechanisms and optimization strategies is currently lacking.
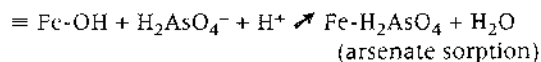
Addition of iron or aluminum coagulants to water can facilitate the conversion of soluble As(V) and As(III) species into insoluble reaction products.[16,44,47-53] These products might form through precipitation, coprecipitation, or adsorption mechanisms. Precipitation refers to the insolubilization of contaminants by exceeding a solubility product, in this case that of either $Fe(AsO_4)$ or $Al(AsO_4)$ solids.[22]

Coprecipitation is defined as an incorporation of soluble arsenic species into a growing hydroxide phase via inclusion, occlusion, or adsorption. Finally, adsorption refers to formation of surface complexes between soluble arsenic and the solid oxyhydroxide surface site as indicated in the following example reactions:

$$\equiv Fe\text{-}OH + H_2AsO_4^- + H^+ \rightleftharpoons Fe\text{-}H_2AsO_4 + H_2O$$
(arsenate sorption)

$$\equiv Fe\text{-}OH + H_3AsO_3 \rightleftharpoons \equiv Fe\text{-}H_2AsO_3 + H_2O$$
(arsenite sorption)

in which $\equiv Fe\text{-}OH$ is an hydroxide surface site.

The batch experiments described in this article were designed to shed light on operative As(V) removal mechanisms during coagulation. For these

Isopleths (contours) of constant percentage arsenic removal by adsorption for a system with an initial arsenic concentration of (A) 5 μg/L As(III) and (B) 50 μg/L As(III)
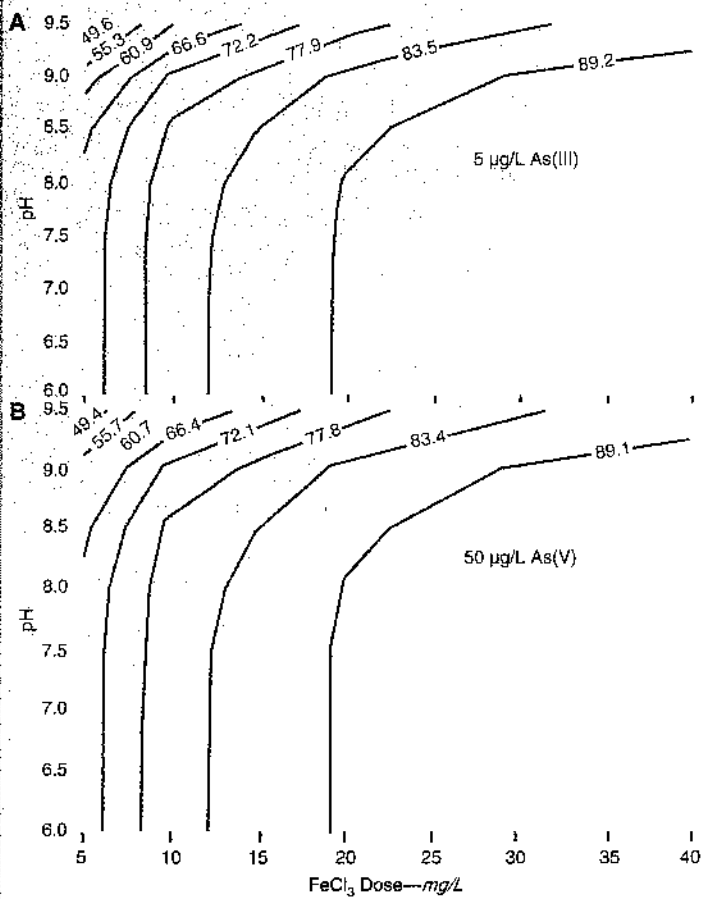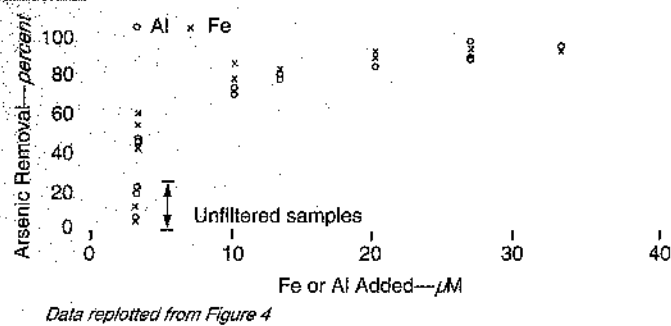
A 9.5 — 49.6, 55.3, 60.9, 66.6, 72.2, 77.9, 83.5, 89.2

5 μg/L As(III)

pH: 9.5, 9.0, 8.5, 8.0, 7.5, 7.0, 6.5, 6.0

B 9.5 — 49.4, 55.7, 60.7, 66.4, 72.1, 77.8, 83.4, 89.1

50 μg/L As(V)

pH: 9.5, 9.0, 8.5, 8.0, 7.5, 7.0, 6.5, 6.0

$FeCl_3$ Dose—mg/L : 5, 10, 15, 20, 25, 30, 35, 40

FIGURE 7 Percentage arsenate removals are independent of initial arsenate concentration for all aluminum dosages and when iron dosages are >10 μM

o Al x Fe

Arsenic Removal—percent: 100, 80, 60, 40, 20, 0

Unfiltered samples

Fe or Al Added—μM: 0, 10, 20, 30, 40

Data replotted from Figure 4

experiments, increasing concentrations of As(V) solution (0.03 to 30 mg/L) were coagulated with a fixed 90 μM dose of Fe(III) as $FeCl_3$ or Al(III) as alum. This corresponds to coagulant doses of 27 mg/L as alum or 14 mg/L as $FeCl_3$. The initial solution pH of 6.0 was decreased to about pH 5.0 after coagulant

addition and was subsequently raised to and maintained at 6.0 ± 0.1 with NaOH addition. For comparison, the experiment was repeated by forming an identical concentration of $Fe(OH)_3$ or $Al(OH)_3$ in the absence of the As(V), after which the solids were added directly to the As(V)-containing solutions at pH 6.0. The two variations of this experiment are identified here as in situ formation or preformed hydroxide solids formation.

When preformed hydroxides were added to the As(V)-containing solution, the density of sorbed As(V) increased as a function of soluble As(V) remaining in solution (Figure 3). As the sorbed As(V) concentration approached about 0.1 M As/M hydroxide solid, the surface became saturated, and only incremental increases in adsorption density occurred at higher arsenic concentrations [even at As(V) concentrations >25 mg/L or >330 μM]. Similar tendencies were observed in the data for hydroxide solids formed in situ; however, in this case surface saturation (or maximum adsorption density) occurred at about 0.5–0.6 M As removed/M hydroxide solid. In the experiments with preformed oxides only surface adsorption occurs, whereas in the experiments with coagulation coprecipitation is also operative.

Another experiment examined the effects of coagulant dosage and As(V) concentration on in situ arsenic removals (Figure 4). Coagulant doses as high as 33 μM Al(III) or Fe(III) were examined, corresponding to alum or ferric chloride doses as high as 11.6 or 5.8 mg/L, respectively. Each coagulant was dosed to solutions containing either 15, 45, or 120 μg/L As(V) at pH 6.0, after which the solution was centrifuged and filtered through a 0.1-μm-pore-size filter. When plotted in terms of normalized arsenic removal density versus arsenic remaining in solution, all of the experimental results may be approximated by a single curve for the range of initial As(V) concentrations and coagulant dosages tested. It is hypothesized that the scatter in the data is due to unintended variations in the rate of base addition, because the scatter was also present in replicate samples for a given coagulant dosage and initial As(V) concentration.

On the basis of these simple experiments, several points are noteworthy. First, the presence of a clear maximum in the ratio of As removed to solid formed (Figure 3) suggests that $Al(AsO_4)$ or $Fe(AsO_4)$ solids

apparently did not form in these systems despite the presence of high As(V) concentrations (>20 mg/L). If such solids had formed, the adsorption density would have increased rapidly after an appropriate solubility product had been exceeded. Second, the performance of aluminum and iron were nearly identical when compared on a molar basis (at pH 6.0) in both the in situ and preformed systems (Figure 3). Last, As(V) removal for the in situ system was about five times higher than was observed for the preformed solids. This strongly suggests that a solid with a higher surface area forms in situ or that coprecipitation is an operative removal mechanism, which is consistent with the results of previous research.[54] Differentiation between As(V) removal via coprecipitation and sorptive removal mechanisms would require a more detailed analysis.
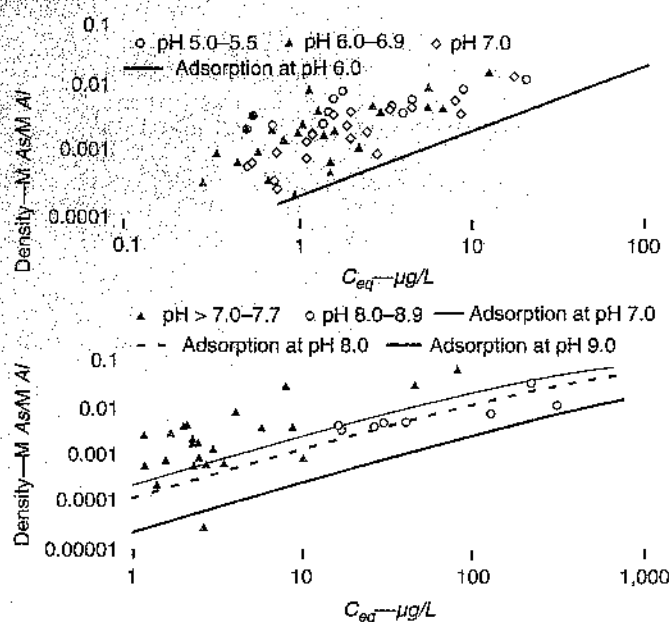
Although many authors have determined that arsenic adsorption onto iron and aluminum hydroxides may be described with adsorption isotherms, this treatment of the data need not apply for arsenic removal by hydroxides formed in situ (analogous to coagulation). Nevertheless, Figure 4 illustrates that in situ hydroxide formation does reduce final arsenic concentrations to levels dependent on adsorption density [expressed as M As removed/M Fe(OH)$_3$ or Al(OH)$_3$ formed]. In other words, arsenic removal during coagulation might still be described by appropriate isotherm models.
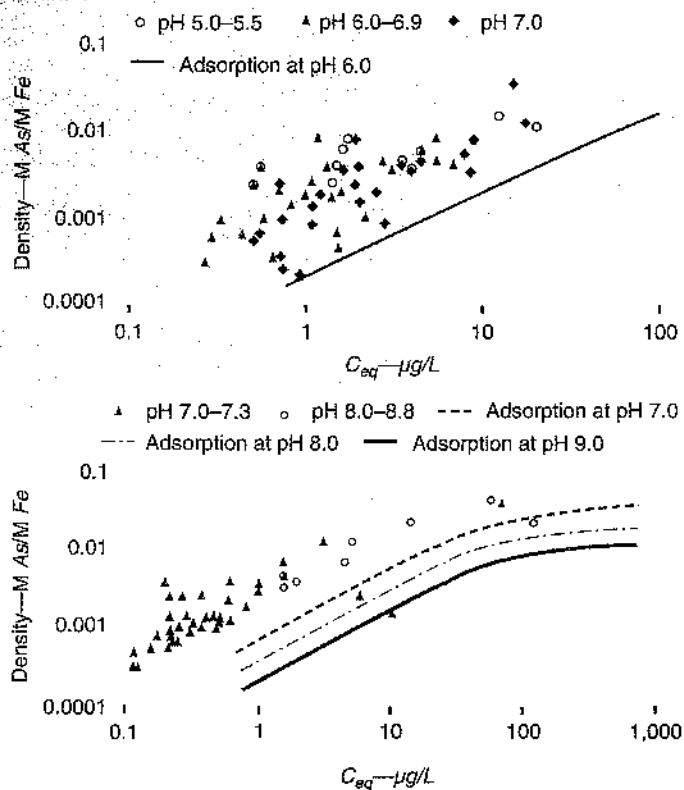

Isotherm predictions (lines) for arsenate removal by aluminum oxides at various pH values (points from database on final arsenic concentrations after coagulation removal are sorted according to pH ranges and are plotted for comparison)

reliminary survey data indicate that many water treatment plants would exceed an arsenic standard of 2 μg/L.

Prediction of arsenic removal via adsorption reactions. Assuming that As(V) and As(III) removals are controlled by adsorption reactions, it is instructive to examine predictions based on previously collected adsorption data for arsenic in systems containing preformed iron and aluminum hydroxides. Although Figure 3 clearly illustrates that predictions of arsenic removal based solely on adsorption will underpredict removals obtained in practice (i.e., preformed versus in situ), the analysis of sorptive removals provides a foundation for examining previously collected data and formulating optimization strategies.

Two types of approaches might be used. The first is to use available Langmuir parameters applicable at a given pH, whereas the alternative is to use a dif-

fuse-layer model valid for any pH and coagulant dosage.[46] For the work described here, the latter approach was deemed more desirable, and contour plots predicting sorptive removal of As(III) or As(V) as a function of pH and coagulant dosage are shown in Figures 5 and 6.[46] Two levels of initial arsenic concentrations were modeled, i.e., 5 and 50 μg/L, for adsorption onto iron hydroxide [plotted as a function of coagulant dosage, assuming that 1 M FeCl$_3$ produces 1 mol Fe(OH)$_3$ solid].

As expected, pH, coagulant dosage, and initial arsenic concentration all affect As(V) and As(III) removal, although the relative sensitivity to each parameter depends on the specific conditions. From pH 5.0 to 8.0 and coagulant doses >5 mg/L as FeCl$_3$, coagulant dosage is of secondary importance to pH in determining the extent of As(V) removal (Figure 5). For example, a system using a coagulant dose of 5 mg/L as FeCl$_3$ at pH 8.3 would increase As(V) adsorption by about 10 percent by lowering the pH to 7.0 (system with 50 μg/L As), whereas quadrupling the coagulant dosage would yield only about a 2 percent increase in arsenic removal. In contrast, predicted sorptive removals of nonionic As(III) are not dependent on pH but are more strongly controlled by the initial As(III) concentration and coagulant dosage (Figure 6). To illustrate, for a system at pH 8.0 and a coagulant dose of

Isotherm predictions (lines) for arsenate removal by iron oxides at various pH values; data points on final arsenic concentrations after coagulation are sorted according to pH ranges and are plotted for comparison

The necessity to obtain efficient particulate removal subsequent to coagulation is also illustrated in Figure 7. A sample subjected to centrifugation only (no membrane filtration) achieved overall As(V) removals 20–50 percent lower than for a similar sample with both centrifugation and membrane filtration (indicated on the graph for lowest Al or Fe dose). Low coagulant dosages are likely to form stabilized colloids in natural waters as well, and obtaining high-efficiency solid–liquid separation (removal of the floc with sorbed arsenic) is obviously essential for effective arsenic control in such systems.

To summarize these observations, at coagulant doses >5 mg/L as $FeCl_3$, sorptive removal of As(V) is a relatively strong function of pH and a lesser function of coagulant dosage or initial As(V) concentration. It was confirmed that percentage As(V) removals were consistent at As(V) concentrations <120 µg/L. For As(III), removal is expected to be insensitive to pH and dominated by coagulant dosage and initial As(III) concentration. Of course, predictions based on sorptive models need not apply to real systems, because formation of coagulant in situ would tend to enhance arsenic removal whereas competition from other anions would tend to hinder arsenic removal (the water used in these experiments contained no background calcium, magnesium, sulfate, chloride, or bicarbonate). Nevertheless, these general observations provide a foundation for analyzing previous research results.

Previous research results. To test the previous predictions for consistency and to formulate tentative optimization strategies, an arsenic removal database was compiled containing all previous published work on arsenic coagulation in water treatment.[44,47,53,55] The database includes a diverse collection of water qualities and initial arsenic concentrations ranging from 3 to 1,200 µg/L (data >1.2 mg/L arsenic were not considered), providing a particularly rigorous test of the predictions in the earlier section.

Arsenate. Owing to higher removal efficiency during coagulation and ease in oxidative transformation [i.e., converting As(III) to As(V)],[16] most work examining arsenic removal to date has focused on As(V). As mentioned earlier, within certain arsenic concentration–coagulant dosage regimes As(V) removal is predicted to depend primarily on pH and secondarily on coagulant dosage. Moreover, initial examinations suggested that alum and ferric salts are nearly equally efficient when compared on an equivalent molar basis. To examine the validity of these hypotheses, data were first sorted into pH categories. Thereafter, moles arsenate removed per mole

6 mg/L as $FeCl_3$, decreasing pH to 7 tends to decrease predicted As(III) removal by only 1 percent, whereas tripling the coagulant dosage yields a predicted 12 percent increase in As(III) removal efficiency.

The prediction that percentage As(V) removals are relatively independent of initial As(V) concentration was examined by replotting the data from the earlier batch experiments (i.e., Figures 4 and 7). The analysis confirms that percentage removals were constant regardless of initial As(V) concentration for all aluminum dosages tested and when removals using ferric chloride were above about 60 percent (Figure 7). However, when percentage arsenic removal decreased to about 50 percent at the lowest ferric chloride dosage, removals obtained at 15 µg/L initial As(V) were 12 percent higher compared with the system with 120 µg/L initial As(V). A sensitivity analysis using Langmuir isotherm predictions indicates that if initial arsenic concentrations are <100 µg/L, percentage arsenic removals are predicted to be constant (±5 percent) at all typical alum dosages (and hydroxide surface concentrations). Percentage removals are also predicted to be relatively constant if arsenic removals are >50 percent in systems using ferric coagulants. This is consistent with observations in the batch experiments.

trivalent ion added was calculated and plotted as a function of final soluble As(V) concentrations. Predictions of removal based on adsorption data were plotted for comparison.[48,56]

As might be expected on the basis of Figure 3, As(V) removals by alum, ferric chloride, and ferric sulfate at a given pH were nearly always greater than predictions based on isotherm data (Figures 8 and 9). Indeed, for the diverse range of data represented, predictions based on isotherms might be considered to represent a lower bound to the observed removals; that is, observed removals at a given pH are usually greater than predicted by sorptive mechanisms and are only rarely lower than those predicted. The degree to which predicted removals underestimated actual removals (in terms of M As removed/M coagulant applied at a given soluble As concentration) was typically about a factor of 5 in terms of adsorption (or removal) density. This corresponds roughly to a fivefold increase in adsorption density when preformed and in situ removals are compared. It is noteworthy, however, that adsorption densities varied by about an order of magnitude for a given As(V) equilibrium concentration, probably due to the presence of competing ions

Results for adsorption of arsenate and arsenite onto iron and aluminum hydroxides*

Sorbent	Type	Sorbate	Time h	Highest Density M As/M Oxide	Reference
Al(OH)$_3$	Preformed	As(V)	48	0.12 at pH 6.0	56
Al(OH)$_3$	Preformed	As(V)	24	0.11 at 6.6	57
Al(OH)$_3$	Preformed	As(III)	24	0.04 at 6.2	57
Fe(OH)$_3$	Preformed	As(V)	24	0.25 at pH 8.0	54
Fe(OH)$_3$	In situ	As(V)	24	>0.70 at pH 8.0	54
Fe(OH)$_3$	Preformed	As(V)	24	0.09 at pH 6.0	48
Fe(OH)$_3$	Preformed	As(V)	24	0.09 at pH 7.2	57
Fe(OH)$_3$	Preformed	As(V)	72	0.05 at pH 7.7	14
Fe(OH)$_3$	Preformed	As(III)	24	0.053 at pH 6.1	48
Fe(OH)$_3$	Preformed	As(III)	24	>0.4 at pH 6.7	57
Fe(OH)$_3$	Preformed	As(III)	72	0.10 at pH 6.9	14

*Highest density refers to highest density reported in this article and may or may not correspond to the actual maximum possible removal density.

Adsorption densities are generally higher at lower pH for each coagulant tested, despite obvious scatter in the data within various pH regions.

and other effects. These effects must be considered in the development of any universally applicable model that can predict As(V) removal by coagulation.

Absolute differences between predictions and the data notwithstanding, some qualitative agreements in general tendencies exist. For instance, it appears that the best-fit of the real data collected at various pH ranges follows the trends predicted by adsorption. In addition, it is also clear that adsorption densities are generally higher at lower pH for each coagulant tested, despite obvious scatter in the data within various pH regions. This is particularly true for alum coagulants at pH >8.0.

It is also illustrative to discuss the coagulant dosages required to obtain a given effluent arsenic concentration. For a potential regulation of 10 µg/L arsenic, removal densities greater than 3.0×10^{-3} M

As/M coagulant (as trivalent ion) were obtained in more than 90 percent of the samples in the database. This approximation is valid for iron < pH 8.5 and alum < pH 7.9. Consequently, for an initial As(V) concentration of 20 µg/L, a coagulant dose of 7 mg/L as FeCl$_3$ (14 mg/L as alum) would meet a 10-µg/L standard for most samples. For a system exhibiting an average removal density, the required coagulant doses would be about two to three times lower (2–4 mg/L as FeCl$_3$ or 4–7 mg/L as alum).

Although the systems within the database do not meet previously described constraints for predicted constant percentage arsenate removals, this treatment of the data is presented in Figure 10. At all dosages $>1.2 \times 10^{-4}$ M Al(III) or Fe(III) (i.e., 20 mg/L as ferric chloride or 40 mg/L as alum) and pH <8.0, >90 percent removal of As(V) was always achieved. At lower coagulant dosages there is considerable scatter to the data, probably reflecting combined effects of poor particle removal (i.e., as per Figure 7), the previously mentioned effects of higher surface loading and high initial As(V) concentrations, and possible interferences from other anions in the different waters tested.

Comparing the relative performance of alum and ferric-based coagulants is also of interest. At pH ≤7.0, alum and ferric salts are nearly equally effective, with average removals only 5 percent higher in systems using ferric at a dose of 0.06 and 0.12 mM (10 and 20 mg/L ferric chloride or 20 and 40 mg/L alum). This is consistent with the data presented in Figure 7. However, the advantages of ferric over alum become significant at higher pH values. At pH 7.0–7.5, average removals at a coagulant dose of 0.06 mM were 87 percent in the system with ferric versus 67 percent for alum. The very large differences in performance observed above pH 8.0 (Figure 10) are somewhat deceptive because of the much higher solubility of

Reported percentage arsenate removals for alum or ferric coagulants in various pH ranges

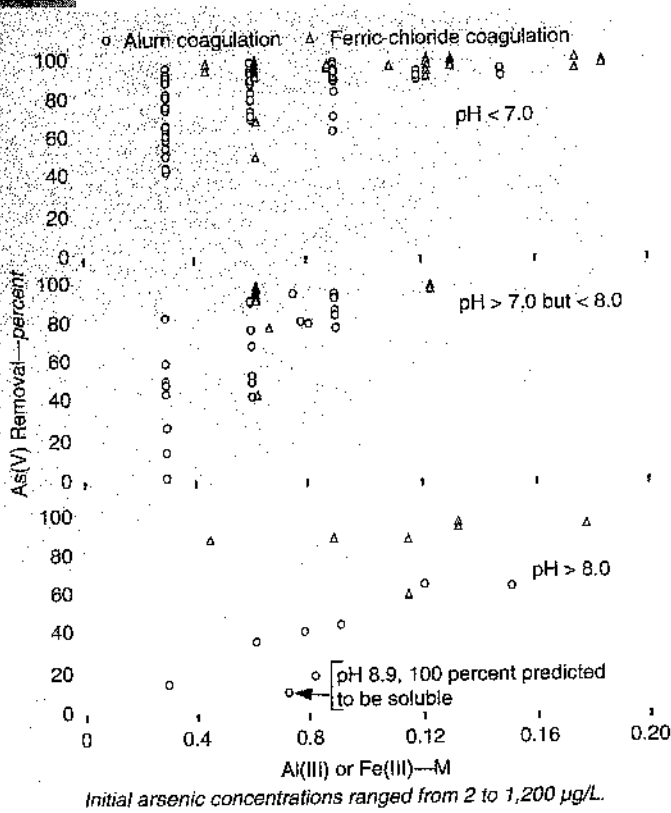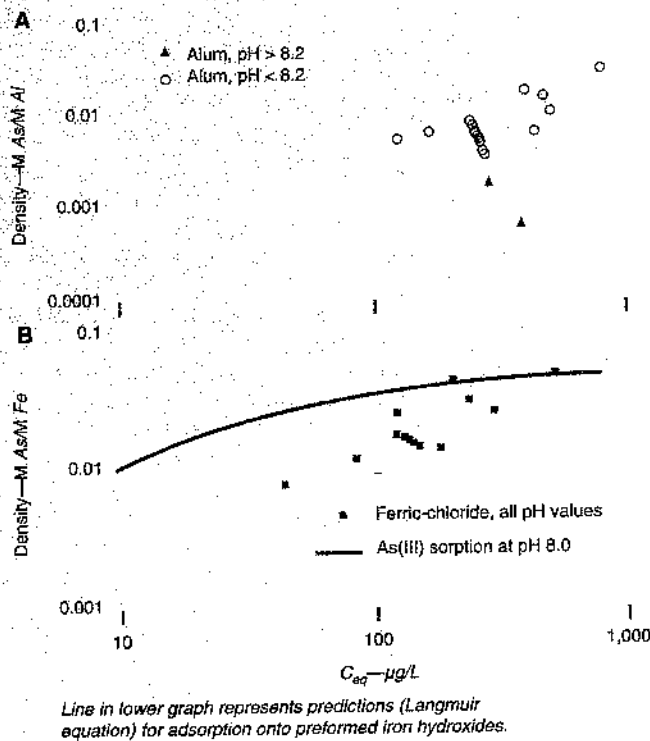Initial arsenic concentrations ranged from 2 to 1,200 µg/L.

FIGURE 11 Removal of arsenite by (A) alum coagulation and (B) ferric coagulation

Line in lower graph represents predictions (Langmuir equation) for adsorption onto preformed iron hydroxides.

$Al(OH)_3$ than $Fe(OH)_3$. For example, solubility calculations for one point (indicated by the arrow in Figure 10) in which As(V) removals were particularly low suggest that no $Al(OH)_3$ would have precipitated. This observation does not change the fact that ferric outperforms alum at the higher pH values, but rather, it substantially alters the possible rationale for these differences. It is noteworthy that these observations are completely consistent with the earlier comments.

Arsenite. Only limited information has been collected to date regarding As(III) removal by iron and aluminum hydroxides. Nevertheless, one factor influencing sorptive As(III) removals is the maximum number of sites available on the hydroxide surface. On fresh preformed hydroxide surfaces, the maximum number of sites is generally considered to be as high as about 0.25 M sites/M hydroxide, with lower site densities possible depending on the specific sorbing species and solution pH.[46,54] Maximum adsorption densities for As(V) and As(III) adsorption onto various hydroxides are presented in Table 3. An examination of the As(V) data reaffirms previous observations; that is, maximal As(V) adsorption densities are as high as 0.25 M As/M Fe or 0.12 M As/M Al for preformed hydroxides. Of course, densities may increase to as high as 0.7 M As/M Fe when the hydroxide solid is formed in situ (Figure 3).

In contrast, something novel is obviously occurring in As(III) adsorption onto iron and aluminum hydroxides. First, maximum surface densities for As(III) adsorption onto preformed aluminum hydroxides are about 0.04 M As/M Al, roughly three times lower than observed for As(V). This is consistent with the notion that As(III) sorbs less strongly to oxide surfaces than does As(V). However, the maximum adsorption densities onto iron are not only higher than those observed for aluminum, but they are so high as to be completely inconsistent with an adsorption-based removal mechanism. Two researchers (Table 3) reported maximum adsorption densities for As(III) onto preformed $Fe(OH)_3$ that were >0.4 M As/M Fe, a value beyond the maximum number of sites for preformed $Fe(OH)_3$ and nearly as high as removal densities for in situ As(V) removal.[48,57] Indeed, one of the researchers even reported removal densities as high as 5 M As/M.[48]

Although the higher of these two reported densities is difficult to justify, particularly because formation of a $Fe(AsO_4)$ precipitate can remove only a maximum of 1 M As/M Fe, it would seem presumptuous to attribute two consistent results from different researchers to experimental error. A few phenomena that might explain the results include

- Arsenite reduction of ferric solids:

$$As(III) + 2Fe(III) \rightarrow 2Fe(II) + As(V)$$
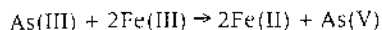
with subsequent oxidation of ferrous iron back to ferric iron (by oxygen) could cause coprecipitation of As(V), explaining removal densities up to about 0.5 M As/M Fe as observed during iron coagulation of arsenate. Despite the thermodynamic favorability of this reaction at pH values less than about 7.0, no one has ever observed the oxidation of As(III) by iron solids.[14,48]

- Formation of some as yet unknown ferric arsenite solids. This is a possibility but seems somewhat unlikely.

- Formation of arsenic polymers at the surface analogous to polyphosphates, allowing a single arsenic species on the chain to sorb to the surface while removing several arsenic atoms. Although this sounds attractive and arsenic polymers are known to exist as solids, they have never been observed in solution.[58]

- Formation of ferric arsenite or ferric arsenate complexes that could subsequently resorb to the oxide surface. Others have demonstrated that this phenomenon can lead to high adsorption densities for polyphosphates onto iron oxide,[59] but an analogous

Percentage arsenite removal as a function of pH for alum and ferric coagulants

Coagulants were formed in situ, coagulant dose was 90 µM, and the initial arsenic concentration was 300 µg/L.

nly limited information has been collected to date regarding As(III) removal by iron and aluminum hydroxides.

reaction sequence or even the existence of ferric arsenite complexes have not yet been discovered.

In any case, this analysis and speculation might serve as a basis for some productive future research.

Moreover, Table 3 also refutes the conventional wisdom that As(III) adsorption to oxides is less effective than As(V) adsorption. Although this is quite true for adsorption onto aluminum hydroxides [i.e., sites for As(III) are about 5 percent of the total As(V) sites for activated alumina and bauxite in water], it is clearly not the case for As(III) adsorption onto iron. In fact, two researchers have reported higher adsorption densities for As(III) adsorption onto iron oxides than for As(V) under similar circumstances.[14,57] Thus,
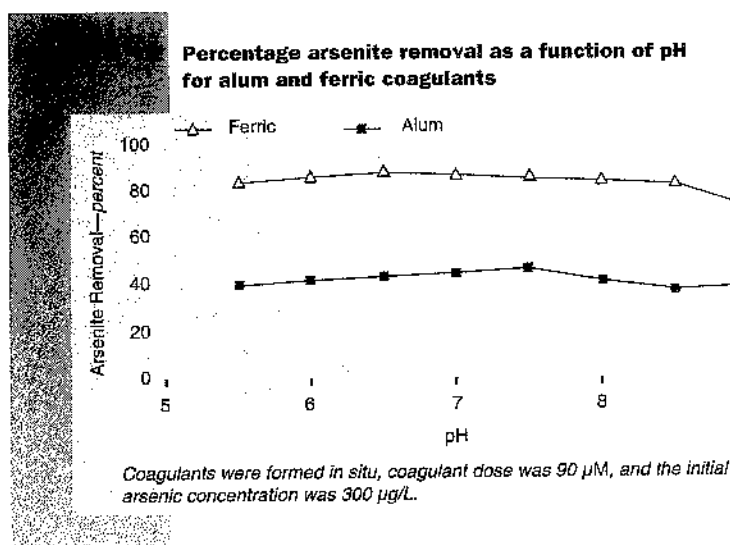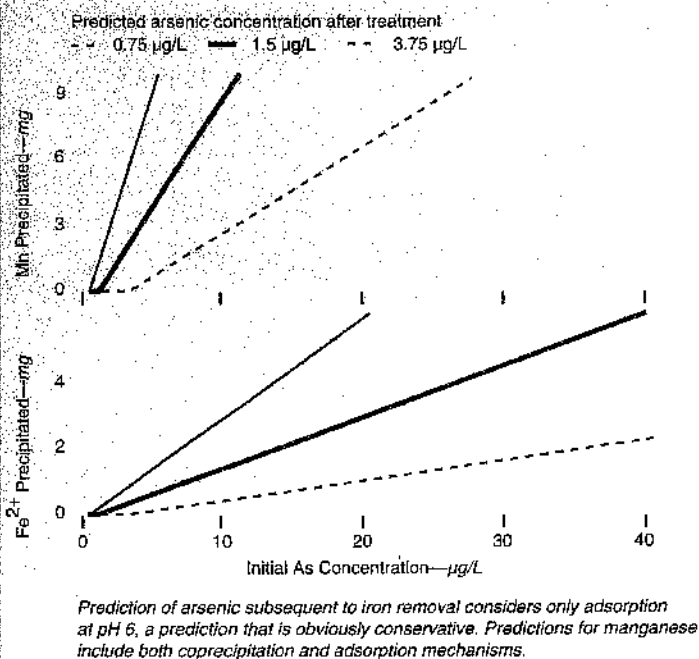
something interesting is occurring during arsenite removal by iron hydroxides.

Analyzing previously collected research data for As(III) removal by iron and aluminum coagulation is also instructive. First, no isotherm data for As(III) adsorption onto aluminum hydroxides are yet available, but the data that have been collected suggest that As(III) removal decreases markedly above pH 8.0 (Figure 11). This might be due to the high solubility of the aluminum hydroxide at this pH range or to other factors.[60] For adsorption of As(III) onto iron hydroxides, it is clear that isotherm predictions consistently overestimate the amount of As(III) that is sorbed, in contrast to isotherm results for As(V) that consistently underestimated overall removals (Figure 11). This overestimation might be due to competitive anion effects (i.e., sulfate competition for sites in natural waters), kinetic limitations to adsorption during short-term conventional water treatment steps, or some other and as yet unknown factor or factors as described previously.

Removal densities are much higher for As(III) removal during iron coagulation when compared with those for alum. Although there is significant scatter to the data, the lowest removal densities onto iron are about 0.01 M As/M Fe, whereas this molar ratio is clearly the upper range for aluminum-based coagulants (Figure 11). Thus, iron coagulants are much more effective in removing As(III) than are aluminum-based coagulants. This was also confirmed in bench-scale work at the University of Colorado at Boulder (Figure 12).[61]

In sum, this analysis clearly points to the fact that much productive research remains to be completed before As(III) removal onto iron hydroxides can be fully explained. In particular, understanding the causes for occasionally high As(III) removal densities seems particularly important, given that the key phenom-

Predictions of final soluble arsenate resulting from (A) manganese removal and (B) iron removal

Predicted arsenic concentration after treatment
- - 0.75 µg/L ⎯⎯ 1.5 µg/L - - 3.75 µg/L

(Y-axis top: Mn Precipitated—mg, values 9, 6, 3, 0)
(Y-axis bottom: Fe²⁺ Precipitated—mg, values 4, 2, 0)
(X-axis: Initial As Concentration—µg/L, values 0, 10, 20, 30, 40)

Prediction of arsenic subsequent to iron removal considers only adsorption at pH 6, a prediction that is obviously conservative. Predictions for manganese include both coprecipitation and adsorption mechanisms.

ena might be harnessed to significantly enhance As(III) removal during water treatment.

Arsenic removal via Fe–Mn oxidation. Because arsenic geochemistry reveals that high arsenic concentrations are often correlated with high Fe(II)–Mn(II), understanding arsenic behavior during Fe(II)–Mn(II) removal is of particular interest. Though scant information is currently available, basic removal mechanisms may be expected to be those operative during coagulation; i.e., oxidation to remove Fe(II) and Mn(II) leads to formation of hydroxides that remove soluble arsenic by coprecipitation or adsorption reactions. The production of oxidized Fe–Mn species and subsequent precipitation of hydroxides are analogous to an in situ coagulant addition, with the quantity of Fe or Mn removed translating into a "coagulant dose." No arsenic is expected to be removed by soluble Mn(II) or Fe(II).

Even when based on conservative estimates of adsorption alone, arsenic removal during Fe(II) precipitation is expected to be fairly efficient (Figure 13). For example, removal of 2 mg/L as Fe(II) is predicted to achieve a 0.75-µg/L soluble effluent concentration from a 10-µg/L As(V) initial concentration via adsorption alone. Even removal of 1 mg/L as Fe(II) is capable of sorbing 83 percent of a 22-µg/L As(V) influent concentration, producing soluble arsenic concentrations of about 3.5 µg/L. The accuracy of these predictions is supported by the results of Clifford and Lin,[62] who reported that 60 percent of a 188-µg/L As(V) influent was removed by oxidation pre-

cipitation of 2 mg/L Fe(II). The observed removal compares favorably with the adsorption-only prediction of 58 percent (as per the prediction shown in Figure 12).

Even when removal by both adsorption and coprecipitation are considered, removal of arsenic during manganese precipitation is relatively ineffective when compared with iron. For instance, precipitation of 1 mg/L Mn(II) is predicted to remove only 25 percent of a 5-mg/L influent concentration. When much higher concentrations of Mn(II) are precipitated, however, removal can become more significant; precipitation of 3 mg/L Mn(II) is predicted to produce a 3.75-µg/L As soluble effluent concentration with a 12-µg/L influent. Although Mn(II) concentrations >3 mg/L are rare, they can occur in some instances when arsenic is troublesome.

Given the relative importance of iron oxides and manganese oxides in mediating arsenic removal, if roughly equal concentrations of iron and manganese were removed, it might be expected that the effects of manganese could be ignored. Magyar[63] demonstrated that 89 percent of a 52-µg/L As(V) influent could be removed during greensand filtration. During the process, 2.9 mg/L Fe(II) and 0.47 mg/L Mn(II) were also removed by addition of KMnO₄. If only sorptive removal by precipitated iron oxides is considered, total arsenic removal is predicted to be 92 percent, a number in excellent agreement with the observed value.

As discussed earlier, pH is predicted to play an important role in arsenic removal via adsorption to iron hydroxides. In addition, given the low concentrations of iron hydroxides formed during iron removal, the coagulant dosage (or ferrous iron removed) is more important than indicated in the earlier discussion. Interestingly, the limited data collected for manganese suggest that pH is not significant in arsenic removal during manganese precipitation.[17] These points must be refined and investigated during future research, and the reality will undoubtedly be much more complex than is the framework proposed here.

Conclusions
- Arsenic geochemistry is dominated by redox processes, sulfide precipitation, and adsorption–coprecipitation to iron and manganese hydroxides. Formation of manganese, calcium, and barium arsenate solids may be important under some circumstances, and competition from high levels of orthophosphate and NOM could increase arsenic mobility.
- Initial survey data indicate that many water treatment plants would exceed an arsenic standard of 2 µg/L. Plants with groundwater supplies appear more

likely to exceed a given effluent standard than plants treating surface water supplies.

• Coagulation is an effective treatment technique for arsenic removal, with alum and ferric coagulants about equally effective (on a molar basis) in removal of As(V) < pH 7.5. However, iron is more effective than alum in removing As(III), in removing As(V) > pH 7.5, and in preventing formation of soluble coagulant metal residuals above about pH 8.0. Obtaining effective removal of sorbed–coprecipitated arsenic-containing flocs may be a limiting factor in overall arsenic removals at lower coagulant dosages. Percentage As(V) removals are expected to be independent of initial As(V) concentration over a limited coagulant dosage–initial arsenic concentration regime.

• Soluble As(V) removals during oxidation of ferrous iron are expected to be very significant, whereas soluble removals during Mn(II) oxidation is likely to be of lesser importance in achieving low arsenic residuals (< 5 µg/L).

Acknowledgment

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