

Arsenic removal by ferric chloride

Source water composition affects removal efficiency.

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Recent epidemiological studies on the carcinogenicity of arsenic have triggered increased concern about the concentrations of arsenic in drinking water and have prompted reevaluation of arsenic's current maximum contaminant level (MCL) of 50 $\mu\text{g/L}$. The range for the arsenic MCL proposed by the US Environmental Protection Agency (USEPA) is between 2 and 20 $\mu\text{g/L}$; final determination of the

MCL will be based on risk assessment, the practical quantitation limit, and estimates of treatment costs, which are likely to be significant.^{1,2}

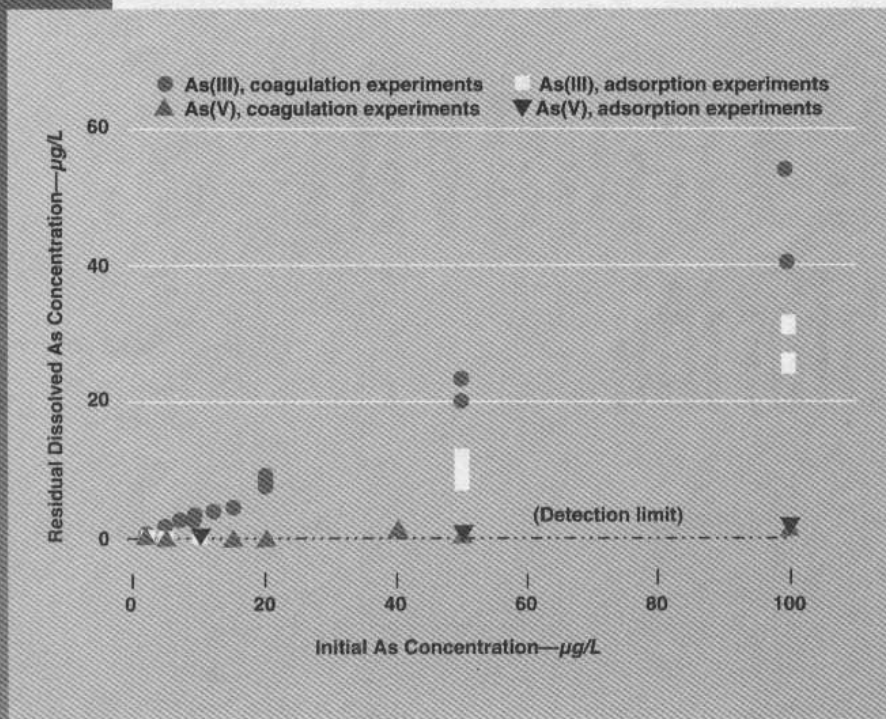
US drinking water supplies typically contain less than 5 $\mu\text{g/L}$ arsenic. However, accurate determinations of low-level arsenic occurrence are only now becoming available through intensive efforts by USEPA and water utilities. These findings indicate that arsenic occurrence is highest for groundwater systems in the southwestern United States.³

Water treatment with coagulants, specifically

Bench-scale studies were conducted in model freshwater systems to investigate how various parameters affected arsenic removal during coagulation with ferric chloride and arsenic adsorption onto preformed hydrous ferric oxide. Parameters included arsenic oxidation state and initial concentration, coagulant dosage or adsorbent concentration, pH, and the presence of co-occurring inorganic solutes. Comparison of coagulation and adsorption experiments and of experimental results with predictions based on surface complexation modeling demonstrated that adsorption is an important (though not the sole) mechanism governing arsenic removal during coagulation. Under comparable conditions, better removal was observed with arsenic(V) [As(V)] than with arsenic(III) [As(III)] in both coagulation and adsorption experiments. Below neutral pH values, As(III) removal-adsorption was significantly decreased in the presence of sulfate, whereas only a slight decrease in As(V) removal-adsorption was observed. At high pH, removal-adsorption of As(V) was increased in the presence of calcium. Removal of As(V) during coagulation with ferric chloride is both more efficient and less sensitive than that of As(III) to variations in source water composition.

FIGURE 1

Residual dissolved arsenic concentrations achieved during coagulation with 4.9 mg/L FeCl₃ (30 μM total iron) and adsorption with 50 μM total iron at pH 7 as a function of initial As concentration



hydrolyzing metal salts such as alum and ferric chloride, has long been recognized as an effective method for removing arsenic from source waters. In the late 1960s, coagulation with ferric chloride was used in Taiwan to treat deep-well water with naturally elevated arsenic concentrations; residual arsenic concentrations in treated water met the current MCL of 50 μg/L.⁴ More recently, coagulation treatment has been assessed in bench-, pilot-, and full-scale studies in order to meet the more stringent standards under consideration by the USEPA.⁵⁻⁹

With regard to the potential applicability of coagulation treatment for arsenic removal, a critical question is the extent to which removal efficiencies may be affected by source water composition. In this article, laboratory studies of arsenic removal during coagulation with ferric chloride and of arsenic adsorption onto preformed hydrous ferric oxide are compared to elucidate the mechanisms of arsenic removal and the effects of source water composition on arsenic removal efficiency. The authors also examine the extent to which arsenic removal during coagulation can be attributed to adsorption of arsenic onto freshly precipitated amorphous iron(III) [Fe(III)] hydroxide and the application of an adsorption model

(i.e., the surface complexation model) for predicting effects of source water composition on arsenic removal.

Background and theory

Occurrence of arsenic in source waters. Naturally elevated arsenic concentrations are common in groundwaters of the western United States, particularly in geothermal waters and groundwaters in mining areas.¹⁰ Although the concentrations of arsenic in rivers and lakes are usually low (<1-40 μg/L),¹¹⁻¹³ higher concentrations (up to several hundred micrograms per litre) occur in surface waters influenced by hydrothermal inputs, such as the tributaries to Lake Crowley in Mono County, Calif.¹⁴ Extremely elevated concentrations have been reported in alkaline lakes (e.g., up to 17 mg/L in Mono Lake).¹⁵

Recent estimates by the USEPA and water agencies

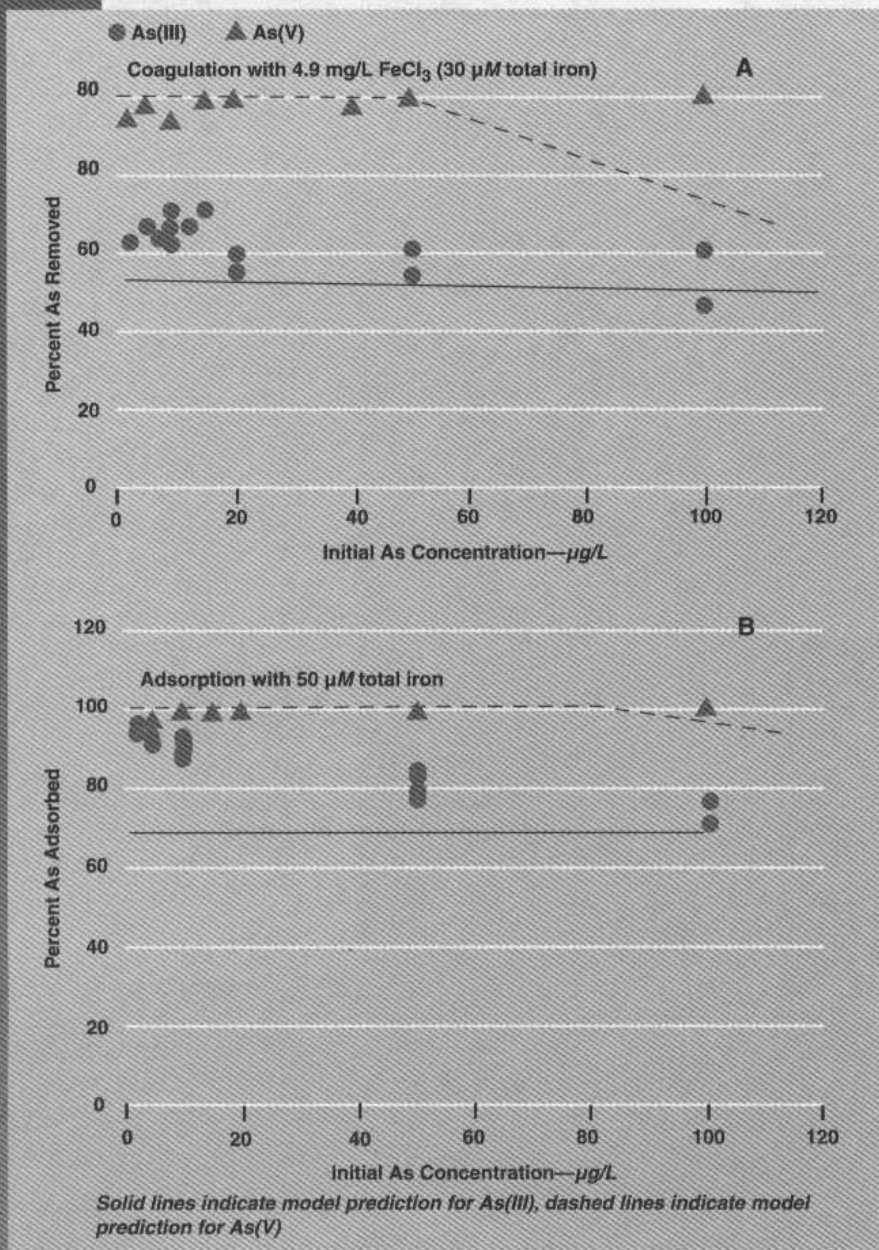
indicate that relatively few water utilities use source waters with arsenic concentrations at or near the current MCL of 50 μg/L.^{2,3} However, a significant number of utilities (approximately 18,000 by USEPA estimates) rely on source waters with arsenic concentrations in the 2- to 5-μg/L range.^{2,16} Given these figures, revision of the arsenic rule is likely to have a considerable impact on the water industry.

Applications of coagulation in water treatment. Potable water treatment with coagulants has

Water treatment with coagulants, specifically hydrolyzing metal salts such as alum and ferric chloride, has long been recognized as an effective method for removing arsenic from source waters.

traditionally been used to reduce turbidity by removing nonsettling and slowly settling solids from source waters. At low dosages of the coagulants ferric chloride and alum, charge neutralization by hydrolyzed metal coagulant species results in the formation of flocs through aggregation of destabilized colloidal particles. At high dosages of these coagulants, the constituent metal of the coagulant precipitates as an

FIGURE 2 Efficiency of arsenic removal and adsorption at pH 7 as a function of initial arsenic concentration



amorphous metal hydroxide floc in which the colloidal particles become entrapped.¹⁷

Treatment with coagulants, particularly at high dosages, can also achieve significant reductions in color and trihalomethane formation potential through the removal of dissolved or colloidal organic carbon.^{17,18} Under the Disinfectants/Disinfection By-Products Rule, enhanced coagulation will be included as a best available technology for meeting the total trihalomethane standard.¹⁹

Dissolved inorganic contaminants, such as arsenic, can also be removed during coagulation treatment with alum or ferric chloride through adsorption (association of the dissolved contaminant with the surface of the precipitate), occlusion (entrapment of

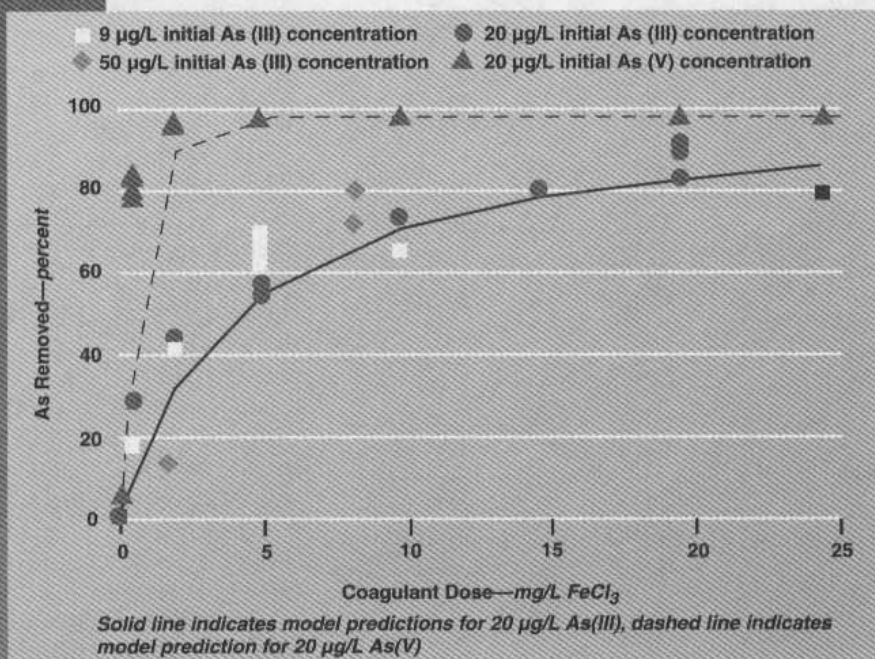
adsorbed contaminants in the interior of the growing particle), and solid-solution formation (incorporation of the contaminant into the bulk phase, rather than only onto the surface of the precipitate).²⁰ At high coagulant dosages, adsorption of inorganic contaminants to precipitated metal hydroxide solids is likely to be the predominant mechanism for contaminant removal. Precipitation of solid phases with the contaminant as a constituent ion of the solid (such as ferric arsenate or solid solutions of ferric arsenate with ferric hydroxide) can occur only if the solubility product of the solid is exceeded, which is unlikely at low contaminant concentrations.

Previous studies of arsenic removal during coagulation. The efficacy of coagulation treatment for arsenic removal has been demonstrated in bench-, pilot-, and full-scale studies. Many of these studies have been directed toward achieving residual arsenic concentrations meeting the current MCL of 50 µg/L, although more recent studies⁵⁻⁹ have examined the possibility of meeting more stringent standards. Most work has focused on removal of As(V), the thermodynamically stable form of inorganic arsenic in oxic waters. As(III) removal during coagulation with alum, ferric chloride, and ferric sulfate has been shown to be less efficient than As(V) removal under comparable conditions.^{4,21-23}

For As(V), better removal is achieved during coagulation with Fe(III) than with aluminum salts on a weight basis (i.e., mg/L as ferric chloride or alum);^{4,6,21,22} removal efficiencies are similar, however, on a molar basis (i.e., mole Fe(III) or Al(III) per litre).⁹ In the circumneutral pH range, As(III) removal is unaffected by pH,^{22,23} whereas removal efficiencies for As(V) decrease above pH 8 with ferric chloride and above pH 7 with alum.^{9,22,23} In general, higher removal efficiencies can be achieved with increased coagulant dosages.^{6,9,21}

These observations of how pH, arsenic oxidation state, and coagulant dose affect removal of arsenic

FIGURE 3 Efficiency of arsenic removal in coagulation experiments at pH 7 and adsorption experiments at pH 6 [with 50 µg/L As(III)] as a function of coagulant dose (or equivalent adsorbent concentration)



upon addition of coagulants are consistent with trends observed in studies of arsenic adsorption onto hydrous metal oxides; a brief review of arsenic adsorption studies is provided by Wilkie and Hering.²⁴ Some comparative studies of As(V) adsorption and coprecipitation have shown that higher adsorption densities can be achieved by coprecipitation than by adsorption.^{9,25} However, these effects were most pronounced at high sorbate-sorbent ratios and were also observed to be slowly reversible, i.e., the excess As(V) associated with the solid formed in the coprecipitation experiments was gradually released back into solution and the ultimate adsorption density converged (on a time scale of approximately 20 days) with that observed in adsorption experiments.²⁵

The consistent behavior of arsenic in adsorption and coagulation studies indicates that adsorption is a dominant mechanism for arsenic removal by coagulants and suggests that physicochemical models for adsorption, such as the surface complexation model, may be useful in predicting the effects of source water composition on arsenic removal during coagulation treatment.

Application of the surface complexation model to arsenic removal during coagulation. In the surface complexation model, adsorption of protons or hydroxide ions to oxide surfaces is interpreted in terms of acid-base reactions of the sur-

face hydroxyl groups of the oxide and the adsorption of other cations or anions in terms of the corresponding complexation reactions.^{26,27} Formation of surface complexes at the oxide surface are modeled by using mass balance and equilibrium expressions in which the apparent equilibrium constant for formation of the surface complex contains a coulombic term because of the electrostatic effects of surface charge. Surface charge is developed by reactions yielding charged surface species (such as protonated or deprotonated surface hydroxyl groups).

The surface complexation model has three central features. The extent of adsorption is limited by the number of exchangeable surface hydroxyl groups, which is a function of surface area. All adsorbing species (including

protons) compete for available surface sites; the effect of pH on adsorption thus derives from the acid-base reactions both of the oxide surface and of the adsorbing species. Apparent equilibrium constants for adsorption vary with the extent of adsorption of all species that form charged surface species (such as protons) because of long-range electrostatic interactions on the surface.

Several computer programs are available that include surface complexation modeling of ion adsorption at the oxide-water interface; one such program

Naturally elevated arsenic concentrations are common in groundwaters of the western United States, particularly in geothermal water and groundwater in mining areas.

is MINEQL+, v. 3.0.²⁸ The application of such computer models requires (1) characterization of the solid suspension (i.e., surface area and total concentration of surface sites for adsorption); (2) equilibrium constants for complexation reactions (including protonation reactions) in solution and at the oxide surface; (3) an expression for long-range electrostatic effects at the oxide surface; and (4) composition of the source water.

TABLE 1

Equilibrium constants used in adsorption modeling^{26,28}

Solution Reactions	Log K
$\text{AsO}_4^{3-} + \text{H}^+ = \text{HAsO}_4^{2-}$	11.60
$\text{AsO}_4^{3-} + 2\text{H}^+ = \text{H}_2\text{AsO}_4^-$	18.35
$\text{AsO}_4^{3-} + 3\text{H}^+ = \text{H}_3\text{AsO}_4$	20.60
$\text{AsO}_3^{3-} + \text{H}^+ = \text{HAsO}_3^{2-}$	13.41
$\text{AsO}_3^{3-} + 2\text{H}^+ = \text{H}_2\text{AsO}_3^-$	25.52
$\text{AsO}_3^{3-} + 3\text{H}^+ = \text{H}_3\text{AsO}_3$	34.74
Surface Reactions	Log K ^{int}
$\equiv\text{Fe}^{\text{w},\text{s}}\text{OH} + \text{H}^+ = \equiv\text{Fe}^{\text{w},\text{s}}\text{OH}_2^+$	7.29
$\equiv\text{Fe}^{\text{w},\text{s}}\text{OH} = \equiv\text{Fe}^{\text{w},\text{s}}\text{O}^- + \text{H}^+$	-8.93
$\equiv\text{Fe}^{\text{w},\text{s}}\text{OH} + \text{Ca}^{2+} = \equiv\text{Fe}^{\text{w},\text{s}}\text{OCa}^+ + \text{H}^+$	-5.85
$\equiv\text{Fe}^{\text{w},\text{s}}\text{OH} + \text{Ca}^{2+} = \equiv\text{Fe}^{\text{w},\text{s}}\text{OHCa}^{2+}$	4.97
$\equiv\text{Fe}^{\text{w},\text{s}}\text{OH} + \text{SO}_4^{2-} + \text{H}^+ = \equiv\text{Fe}^{\text{w},\text{s}}\text{SO}_4^- + \text{H}_2\text{O}$	7.78
$\equiv\text{Fe}^{\text{w},\text{s}}\text{OH} + \text{SO}_4^{2-} = \equiv\text{Fe}^{\text{w},\text{s}}\text{OHSO}_4^{2-}$	0.79
$\equiv\text{Fe}^{\text{w},\text{s}}\text{OH} + \text{PO}_4^{3-} + 3\text{H}^+ = \equiv\text{Fe}^{\text{w},\text{s}}\text{H}_2\text{PO}_4 + \text{H}_2\text{O}$	31.29
$\equiv\text{Fe}^{\text{w},\text{s}}\text{OH} + \text{PO}_4^{3-} + 2\text{H}^+ = \equiv\text{Fe}^{\text{w},\text{s}}\text{HPO}_4^- + \text{H}_2\text{O}$	25.39
$\equiv\text{Fe}^{\text{w},\text{s}}\text{OH} + \text{PO}_4^{3-} + \text{H}^+ = \equiv\text{Fe}^{\text{w},\text{s}}\text{PO}_4^{2-} + \text{H}_2\text{O}$	17.72
$\equiv\text{Fe}^{\text{w},\text{s}}\text{OH} + \text{AsO}_4^{3-} + 3\text{H}^+ = \equiv\text{Fe}^{\text{w},\text{s}}\text{H}_2\text{AsO}_4 + \text{H}_2\text{O}$	29.31
$\equiv\text{Fe}^{\text{w},\text{s}}\text{OH} + \text{AsO}_4^{3-} + 2\text{H}^+ = \equiv\text{Fe}^{\text{w},\text{s}}\text{HAsO}_4^- + \text{H}_2\text{O}$	23.51
$\equiv\text{Fe}^{\text{w},\text{s}}\text{OH} + \text{AsO}_4^{3-} = \equiv\text{Fe}^{\text{w},\text{s}}\text{OHAAsO}_4^{3-}$	10.58
$\equiv\text{Fe}^{\text{w},\text{s}}\text{OH} + \text{AsO}_3^{3-} + 3\text{H}^+ = \equiv\text{Fe}^{\text{w},\text{s}}\text{H}_2\text{AsO}_3 + \text{H}_2\text{O}$	40.20

$K^{\text{app}} = K^{\text{int}} (\Delta Z F / RT)$, in which ΔZ = change in charge of surface species, F = Faraday constant, Ψ = surface potential, R = gas constant, T = absolute temperature

At coagulant dosages high enough to allow precipitation of the corresponding amorphous metal hydroxide, the surface complexation model can be applied to model the removal of dissolved constituents during coagulation by assuming (1) that the added coagulant is stoichiometrically converted to the hydroxide solid, (2) that removal of the dissolved constituents can be attributed to adsorption, (which occurs to the same extent as would adsorption on an equivalent concentration of preformed sorbent), and (3) that the adsorbed contaminant is entirely removed by settling and filtration such that the concentration of the contaminant in the product water corresponds to its calculated dissolved concentration. For ferric chloride, stoichiometric conversion to the hydroxide solid (hydrated ferric oxide or HFO) yields 0.55 mg/L HFO per mg/L FeCl_3 added. The properties of HFO (including surface complexation constants) have been compiled by Dzombak and Morel.²⁶

The laboratory studies described in this article compare adsorption and coagulation experiments and evaluate the applicability of surface complexation modeling for predicting the effects of source water composition on arsenic removal.

Materials and methods

Standards and reagents. All chemicals were reagent-grade and were used without purification. All solutions were prepared with deionized (DI) water purified by reverse osmosis and deionized using a commercial system.* All glassware was acid-washed. Arsenite standards were prepared from the solid ACS primary standard arsenic trioxide, As_2O_3 ,† dissolved in 0.18 M (1.5 percent v/v) trace metal-grade HCl.‡ The arsenate standard was prepared from sodium salt heptahydrate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$,§ dissolved in DI

water. Secondary arsenic stock solutions (1 mg/L As for analytics, 100 mg/L As for coagulation, and 10 mg/L for adsorption experiments) were always freshly prepared from the arsenic stock solution (1 g/L As) by dilution with DI water. Hydride generation was accomplished using analytical grade 4 percent w/v sodium borohydride (NaBH_4) pellets** dissolved in 1 percent w/v sodium hydroxide.‡ Ultrapure 0.14 M potassium iodide** was used as a prereductant for analysis of As(V). Acetylene†† was used as the atomic absorption spectrophotometry (AAS) flame fuel, and 99.999 percent nitrogen‡‡ was used as the purge gas for the hydride generator. For coagulation experiments, a primary ferric chloride stock

solution (2.5 M FeCl_3 or 405.5 g/L FeCl_3) was prepared from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ‡ and stored in a dark polyethylene bottle. Secondary stock solutions (0.3 M FeCl_3 or 48.7 g/L FeCl_3) were prepared immediately before use.²⁹

Background electrolyte solutions were prepared from the reagent-grade salts NaNO_3 and NaHCO_3 ‡ Calcium, sulfate, and phosphate stock solutions used to amend the background electrolyte solutions were prepared from the salts $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$.‡ Kaolin stock solutions (500 mg/L) were prepared from US pharmaceutical-grade kaolin‡ without further purification. Stock solutions were sonicated for 30 min in a sonicating bath§§ prior to each experiment.

Arsenic analysis. Arsenic concentrations were determined by hydride generation-flame atomic absorption spectrometry^{30,31} using an atomic absorption spectrometer*** equipped with an electrodeless discharge lamp and coupled to a hydride generation system.††† Basic sodium borohydride solution was delivered to the generation system's reaction flask at a rate of 22–25 mL/min until the maximum absorbance (193.7 nm) was obtained (i.e., for approximately 6–8 s). The reaction vessel and quartz cell were continuously purged with nitrogen gas.

This analytical procedure was followed for As(III) calibration standards and for samples from adsorp-

*Barnstead, Dubuque, Iowa

†Aldrich, Milwaukee, Wis.

‡Fisher, Pittsburgh, Pa.

§Sigma, St. Louis, Mo.

**Alfa Products, Ward Hill, Mass.

††Liquid Air, Walnut Creek, Calif.

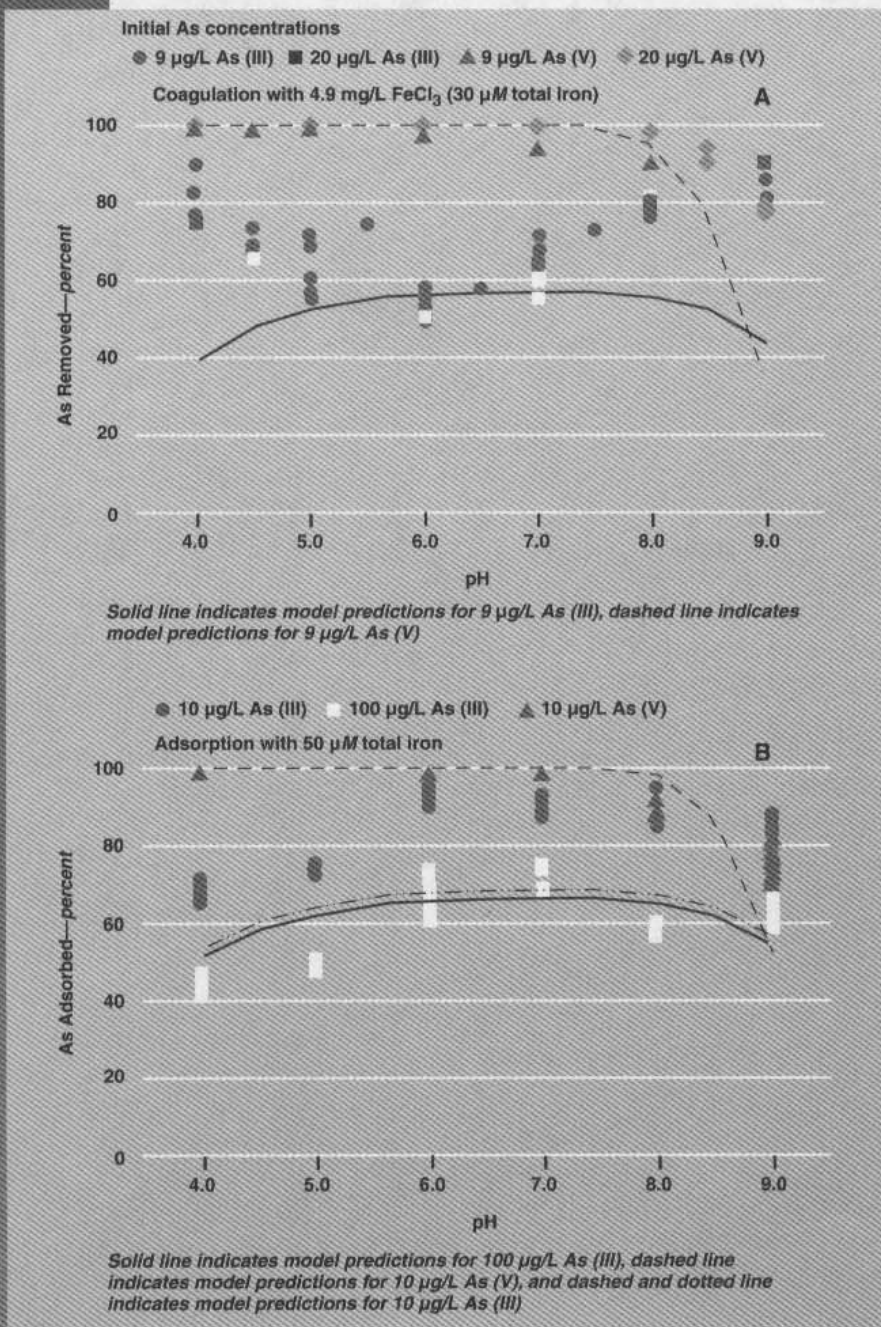
‡‡Liquid Carbonic, Oak Bridge, Ill.

§§Branson B-220, Branson Ultrasonics, Danbury, Conn.

***Model 3300, Perkin-Elmer, Norwalk, Conn.

†††MHS-10, Perkin-Elmer, Norwalk, Conn.

FIGURE 4 Efficiency of arsenic removal during coagulation and adsorption as a function of pH



tion experiments conducted with As(III) and analyzed on the same day as the adsorption experiment. Samples and calibration standards containing As(V) and all stored samples were analyzed for total inorganic arsenic by including a prereduction step with potassium iodide.

For analysis of total arsenic in samples containing As(V), 2 mL of 0.14 M KI (10 percent w/v),* and 5 mL of concentrated, trace metal-grade HCl† were added to 20 mL of sample, and at least 1 h was allowed for complete prereduction. Hydride generation was performed as described earlier. When samples con-

taining As(V) were analyzed, calibration standards were also prepared with As(V). This procedure was adopted for all stored samples from adsorption experiments (i.e., samples not analyzed the same day as the experiment) and for all samples from adsorption and coagulation experiments performed with As(V).

Analyses of calibration standards and samples were performed under the same conditions (i.e., total acid concentration, sample volume, and KI prereduction). Stored samples from coagulation experiments with As(III) were analyzed with KI prereduction but with only 0.18 M HCl. This is insufficiently acidic to guarantee complete reduction of As(V) to As(III) and is not recommended. However, because storage experiments indicated negligible oxidation of As(III) to As(V) over a period of one week, it is unlikely that the analytical procedure used would have introduced any significant artifacts.

Samples not analyzed on the same day adsorption or coagulation experiments were performed were acidified to about pH 1 with concentrated HCl and stored in acid-washed high-density polyethylene (HDPE) containers. All samples were analyzed within seven days of collection.

Other analytical methods. In all experiments, pH was measured with a pH meter‡ with the pH electrode calibrated with three buffers (pH 4.0, 7.0, and 10.0). Total iron analysis was performed by

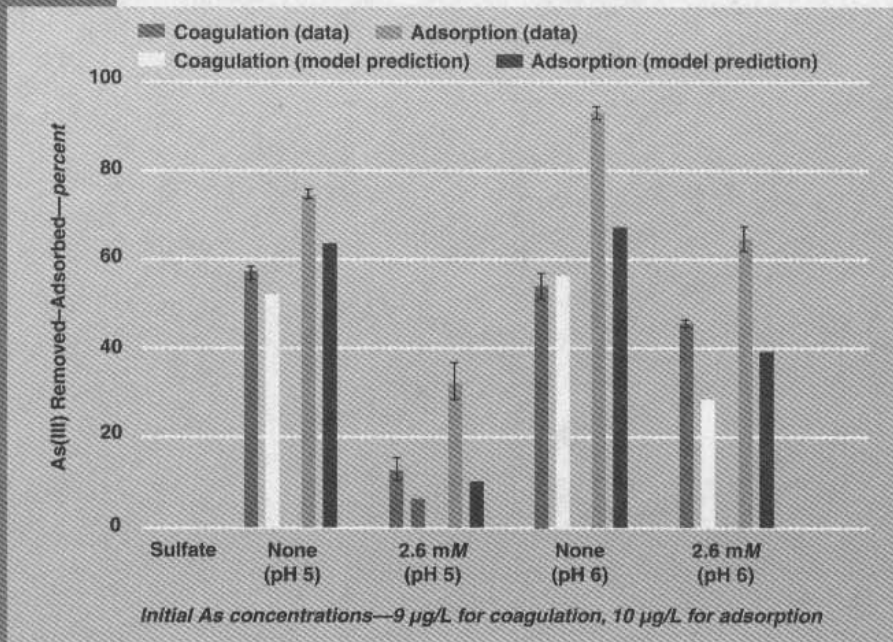
flame atomic absorbance spectrometry following standard procedures.³¹ Samples were analyzed by direct aspiration into an air-acetylene flame; absorbance was measured at 248.3 nm. Samples containing iron oxide suspensions were acidified with concentrated HNO₃ to dissolve the solid before AAS analysis. Calibration standards were prepared in the same acid matrix (final concentration 0.08 M HNO₃) as the sample.

*Alfa, Ward Hill, Mass.

†Fisher, Pittsburgh, Pa.

‡Model 15, Fisher, Pittsburgh, Pa.

FIGURE 5 Effect of sulfate on the efficiency of As(III) removal during coagulation with 4.9 mg/L FeCl₃ (30 μM total iron) and adsorption with 50 μM total iron



Conditions and apparatus for adsorption experiments. HFO was freshly prepared for each adsorption experiment by adding 45 mL of 0.5 M NaOH dropwise with stirring to 150 mL of 0.05 M Fe(NO₃)₃ at 25°C to reach a final pH of about 8. The final pH was stable approximately 5 to 10 min after base addition was complete. After precipitation of the solid, the HFO stock suspension was centrifuged and the supernatant solution was discarded. The solid was washed four times with DI water and then resuspended in aging medium. The composition (pH and major ion composition) of the aging medium was preadjusted to the values appropriate for the subsequent adsorption experiment.

All adsorption experiments were conducted using 50 mLs of background electrolyte (0.01 M NaNO₃) in 85-mL polycarbonate centrifuge tubes. Blank losses (e.g., to centrifuge tubes and filters) were evaluated in triplicate for As(III) and As(V) at initial concentrations of 2.5, 10, and 100 μg As/L and pH values of 4, 6, and 8, respectively. After 2 h on a wrist-action shaker, half of the solution from each reaction vessel was filtered through a 0.1-μm cellulose nitrate membrane filter.* Filtered and unfiltered samples were analyzed for arsenic. Blank losses for both As(III) and As(V) were low (≤ 5 percent), and negligible filter losses were observed.

Adsorption experiments were run in triplicate with both As(III) and As(V) at varying initial concentrations. The reaction vessels were filled with electrolyte solution amended as appropriate with other major ion salts and adjusted to the desired pH. For experiments conducted at pH 8 and 9, the background electrolyte was also amended with 0.001 M NaHCO₃.

Solutions were spiked with the secondary arsenic stock solution and then with the HFO stock suspension (about 2.67 g/L) to obtain the desired concentrations. Nominal HFO concentrations were verified by total iron analysis. The pH values of the arsenic stock solution and of the HFO stock suspension were adjusted to the pH of the adsorption experiment prior to their addition to the background electrolyte.

The suspensions were continuously mixed on a wrist-action shaker for 2 h. At the end of the reaction period, the final pH was measured, and the suspensions were filtered through a 0.1-μm membrane filter. Filtered solutions were either analyzed immediately or acidified and stored for arsenic analysis. Dilution attributable to

acid additions to stored samples was accounted for in calculations of arsenic adsorption.

Conditions and apparatus for coagulation experiments. Experiments were conducted with background electrolyte 0.01 M NaNO₃ and 0.001 M NaHCO₃; pH before adjustment was 8.3 ± 0.1. Test solutions were contained in 1-L cylindrical heat-resistant glass beakers and mixed using a variable-speed, six-paddle stirrer.† The pH values of the background electrolyte solutions were preadjusted to the target value (± 0.1 pH unit) by addition of HCl or NaOH solutions. Solutions of pH-adjusted background electrolyte were amended with stock solutions of inorganic salts [Ca(NO₃)₂, Na₂SO₄, or NaH₂PO₄] as appropriate before spiking with As(III) or (V) to the desired concentration. To maintain the target pH, predetermined amounts of NaOH solutions were added simultaneously with the ferric chloride coagulant under rapid-mix conditions. The mixing conditions were: 1-min rapid mix at 100 rpm ($G = 160 \text{ s}^{-1}$), 30-min slow mix at 45 rpm ($G = 48 \text{ s}^{-1}$), and 15 min quiescent settling. After the settling period, a 20-mL disposable syringe was used to collect approximately 100 mL of solution from 2 cm below the liquid surface; the solution was then filtered through a 0.1-μm membrane filter using a vacuum filter flask assembly. In some experiments, disposable syringe filter assemblies‡ were employed.

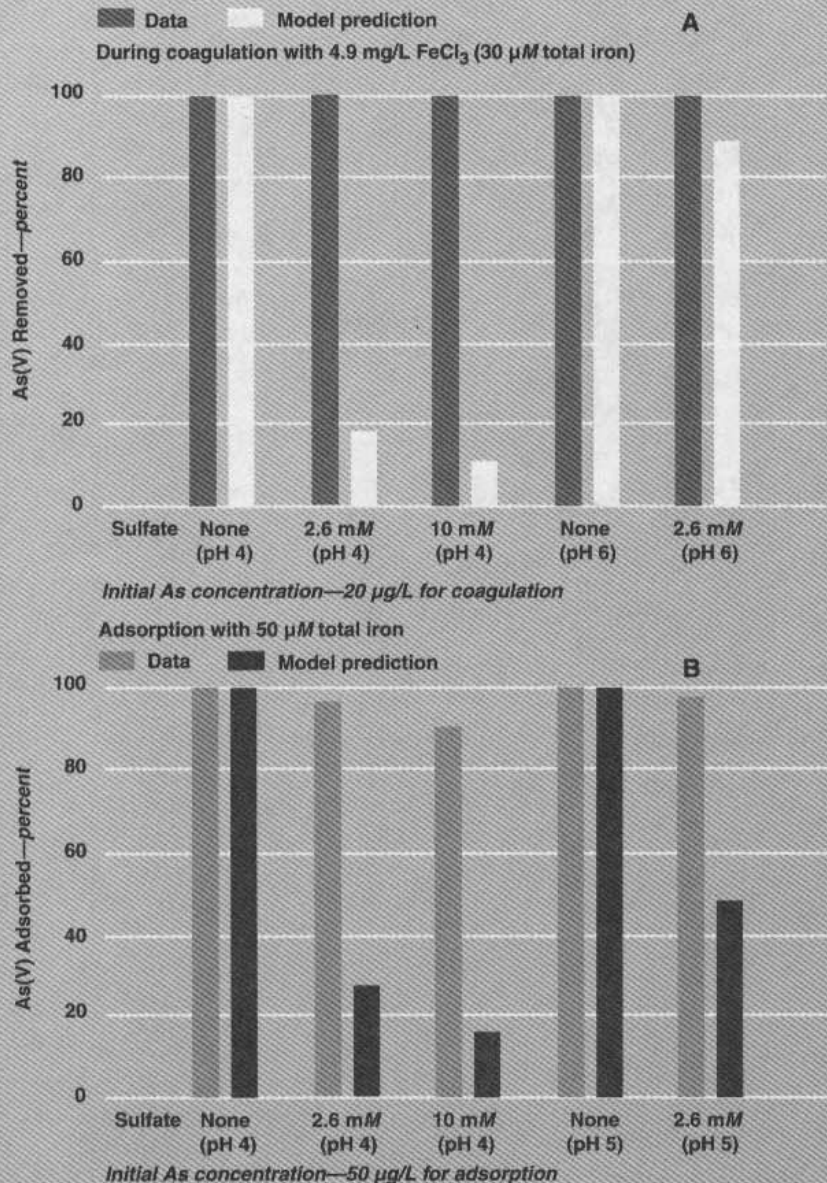
The pH was measured after the settling period. Filtrate from coagulation experiments was transferred to 60-mL, acid-washed HDPE bottles and acidified

*Sartorius, Englewood, N.Y.

†Phipps and Bird, Richmond, Va.

‡Anotop, Maidstone, England

FIGURE 6 Effect of sulfate on the efficiency of As(V) removal and adsorption



by addition of 1.0 mL concentrated HCl. Although dilution effects were neglected in calculating residual arsenic concentrations, sample dilution was less than two percent. Samples were not stored more than seven days before analysis.

Evaluations of blank losses of arsenic (by adsorption to apparatus) were performed as described except that coagulant was not added. Mixing and filtration conditions were identical to those in the coagulation experiments. Blank losses averaged approximately 5 percent for As(III) and As(V) over a range of pH values.

Use of computer programs for surface complexation modeling. Calculations were performed using a computer program* that calculates equilibrium chemical speciation and includes surface com-

plexation modeling of ion adsorption.²⁸ Characteristics of HFO recommended by Dzombak and Morel²⁶ [including stoichiometry ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, 89 g HFO/mol Fe), specific surface area (600 m^2/g), surface site concentrations, and adsorption constants] were applied for calculations of the extent of adsorption during coagulation experiments based on the total concentration of Fe(III) added. Intrinsic adsorption constants are listed in Table 1 for weak ($\text{Fe}^{\text{w}}\text{OH}$) and strong ($\text{Fe}^{\text{s}}\text{OH}$) sites with concentrations of 0.2 mol weak sites/mol Fe and 0.005 mol strong sites/mol Fe. For proton and anion binding, identical constants are used for strong and weak adsorption sites. No attempt was made to optimize surface complexation parameters in modeling coagulation or adsorption experiments.

Results and discussion

The laboratory studies examined the effects of various parameters (including arsenic oxidation state and initial concentration, coagulant dosage or adsorbent concentration, pH, and concentrations of co-occurring inorganic solutes) on arsenic removal during coagulation with ferric chloride and arsenic adsorption onto preformed HFO. Experiments were conducted with a background electrolyte solution of 0.01 M NaNO_3 , 0.001 M NaHCO_3 for all coagulation and for adsorption experiments at pH 8 and 9 and 0.01 M NaNO_3 for other adsorption experiments. Addition of carbonate was observed to have negligible effects on adsorption results at pH 6 and to increase adsorption of As(III) slightly at pH 9. Observed results are compared with predictions of computer calculations.

Arsenic removal from simple pH-adjusted background electrolyte was studied for both As(V) and As(III) over the range of conditions, with initial As concentrations from 2 to 100 $\mu\text{g}/\text{L}$, pH from 4 to 9, and coagulant dose (or equivalent total iron concentration in adsorption experiments) from 0.49 to 24.3

*MINEQL+, v. 3.0, Environmental Research Software, Hallowell, Maine

TABLE 2 Effects of filter size on arsenic removal in coagulation experiments*

As Oxidation State	pH ± 0.1	Percent Removal 0.1 μm	Percent Removal 0.5 μm	Percent Removal 1.0 μm	Percent Removal Without Filtration
V	4.0	≥ 99.5	99	96	†
	4.5†	≥ 99.5	†	≥ 99.5	30
	5.0	≥ 99.5	96	97	†
	5.0†	≥ 99.5	†	≥ 99.5	28
	6.0	≥ 99.5	≥ 99.5	≥ 99.5	†
	6.0†	99	†	≥ 99.5	73
III	4.0	76	73	72	54
	4.5	66	65	68	54
	6.0	51	51	54	51

*Initial As concentration—20 $\mu\text{g/L}$, coagulant dose—4.9 mg FeCl_3/L
 †Amended with 3 mM calcium, 2.6 mM sulfate, and 0.8 μM phosphate
 ‡Not determined

mg FeCl_3/L . The effects of these parameters on arsenic removal are discussed in detail later. In general, however, it was observed that for the range of conditions tested, residual As(V) concentrations $< 2 \mu\text{g/L}$ could be achieved under all but the least favorable conditions (e.g., elevated pH or low coagulant-to-arsenic ratios) and even lower residual As(V) concentrations ($< 0.5 \mu\text{g/L}$) were attained in many cases. In contrast, residual As(III) concentrations $< 2 \mu\text{g/L}$ could be achieved only under the most favorable conditions (e.g., very high coagulant-to-arsenic ratios).

Although As(V) is the thermodynamically stable form of inorganic arsenic in oxic waters, oxidation of As(III) to As(V) by oxygen is sufficiently slow that As(III) may occur as a metastable species in oxygenated waters.^{11,12,32} Conventional oxidants used in water treatment (e.g., chlorine, ozone, and permanganate) are capable of rapidly oxidizing As(III) to As(V).³³ In some cases, however, treatment of raw source waters with oxidants may result in unacceptable levels of disinfection by-products. Thus, studies of removal efficiencies for As(III) may have some consequences for water treatment as well as provide insight into the general mechanisms for removal of trace inorganic contaminants by coagulants.

Effect of initial arsenic concentration. Very low residual arsenic concentrations could be achieved at pH 7.0 with a coagulant dose of 4.9 mg/L FeCl_3 over a wide range in initial arsenic concentrations for As(V) but only at lower initial arsenic concentrations for As(III). Similar results were obtained in adsorption studies at pH 7.0 with a total Fe concentration of 50 μM , which corresponds to a coagulant dose of 8.1 mg/L FeCl_3 (Figure 1). The residual concentrations obtained in coagulation experiments correspond to a constant percent removal of arsenic independent of initial concentration (Figure 2, part A). This behavior is generally consistent with model predictions (shown by the lines in Figure 2). In adsorption studies, increased percent adsorption was observed with As(III) at low initial As(III) concentrations (Figure 2, part B). This effect may be attributable to oxidation of As(III) at the HFO surface³⁴ or to preferential adsorption of

As(III) to strong binding sites on the HFO surface. The observed effect is consistent with the extent of heterogeneity of the HFO surface previously invoked to describe adsorption of transition metals.^{24,26}

Application of the surface complexation model to coagulation implies that the concentration of surface binding sites available to remove contaminants is proportional to the coagulant dosage and that the surface binding sites can become saturated at high contaminant concentrations. However, at

initial arsenic concentrations that are small compared with the concentrations of surface binding sites of the preformed HFO or the comparable solid formed in coagulation experiments, no surface saturation effects are expected. Thus, the percent of arsenic removal is expected to be independent of initial arsenic concentration over a limited range. This expected behavior can be explained by applying, for a given pH and major ion composition, a simplified (Langmuir) expression for adsorption that relates the adsorbed As concentration, $[\text{As}]_{\text{ads}}$, to the dissolved concentration, $[\text{As}]_{\text{diss}}$:

$$[\text{As}]_{\text{ads}} = \frac{[\text{As}]_{\text{diss}} K_{\text{ads}} [\equiv\text{FeOH}]_{\text{T}}}{1 + [\text{As}]_{\text{diss}} K_{\text{ads}}} \quad (1)$$

in which K_{ads} = an apparent adsorption constant and $[\equiv\text{FeOH}]_{\text{T}}$ = the total concentration of surface binding sites that is proportional to the coagulant dosage (with all concentrations in mol/L). At low concentrations of $[\text{As}]_{\text{diss}}$, this expression simplifies to

$$[\text{As}]_{\text{ads}} = [\text{As}]_{\text{diss}} K_{\text{ads}} [\equiv\text{FeOH}]_{\text{T}} \quad (2)$$

that may be combined with a mass balance for arsenic

$$[\text{As}]_{\text{total}} = [\text{As}]_{\text{ads}} + [\text{As}]_{\text{diss}} \quad (3)$$

to obtain the expression for percent As adsorbed-removed

$$\text{Percent As adsorbed} = \frac{K_{\text{ads}} [\equiv\text{FeOH}]_{\text{T}}}{1 + K_{\text{ads}} [\equiv\text{FeOH}]_{\text{T}}} \times 100 \quad (4)$$

This expression indicates that as long as the surface sites are not saturated by adsorbed As, the percent of As removal for a given coagulant dosage should be independent of the dissolved (or initial) As concentration. This result has been confirmed by similar observations in jar tests of As(V) removal from natural waters spiked with As(V)⁶ and is supported by

TABLE 3

Effects of kaolin on As(III) removal in coagulation experiments*

pH ± 0.1	Percent Removal Without Kaolin	Percent Removal Preconditioned Media†	Percent Removal With 5-mg/L Kaolin
4.0	81 \pm 7	56 \pm 1	52 \pm 6
5.0	64 \pm 7	63 \pm 3	62 \pm 3
7.0	67 \pm 3	58	59

*Initial As concentration—9 μ g/L, coagulant dose—4.9 mg/L FeCl₃
 †Solutions of pH-adjusted background electrolyte were preconditioned with 5 mg/L kaolin for 45 min with slow mixing at 45 rpm and filtered before use in coagulation experiments.

excellent removal observed in full-scale treatment with low influent concentrations of As(V).⁸ The predicted decrease in percent of As(V) removal above an initial concentration of 50 μ g/L As(V) is not a result of saturation of surface sites but rather of the indirect effect of As(V) adsorption on surface charge (which is discussed later in more detail).

Effect of coagulant dosage. Eq 4 is also consistent with the observed dependence of percent of arsenic adsorbed-removed on adsorbent concentration or coagulant dosage. A pronounced effect of coagulant dosage on As removal from background electrolyte pH-adjusted to 7.0 \pm 0.1 was observed for both As(III) and As(V) with initial arsenic concentrations of 9 and 20 μ g/L as shown in Figure 3. Under comparable conditions, As(V) was more efficiently removed than As(III). Complete removal of As(V) was observed for coagulant doses above 5 mg/L FeCl₃. Complete removal of As(III) was not observed under the range of conditions examined. Although adsorption experiments were performed for only a limited range of total iron concentrations, observations from these experiments [for 50 μ g/L As(III)] were consistent with those from coagulation experiments (Figure 3).

Effect of pH. The results of adsorption and coagulation experiments performed over the pH range 4 to 9 for similar (though not identical) conditions of total iron and arsenic concentrations are shown together with model predictions in Figure 4. Total iron and initial arsenic concentrations were 30 μ M Fe (4.9 mg/L FeCl₃) and 9 and 20 μ g/L As for coagulation and 50 μ M Fe (equivalent to 8.1 mg FeCl₃/L) and 10 and 100 μ g/L As for adsorption. The results of model calculations for the appropriate total iron and arsenic concentrations are shown with each data set. As Figure 4 shows, the observed pH effects are distinctly different for the coagulation and adsorption experiments with As(III), particularly at the extreme pH values. Comparison

of the results of the adsorption experiments and the model (Figure 4, part B) indicate that the observed pH dependence is slightly stronger than predicted, though unlike the coagulation experiments, the observed and predicted trends are generally consistent. Figure 4, part B, also shows a much better (absolute) agreement between observed and predicted As(III) adsorption at higher (100 μ g/L) than at lower (10 μ g/L) initial As(III) concentrations.

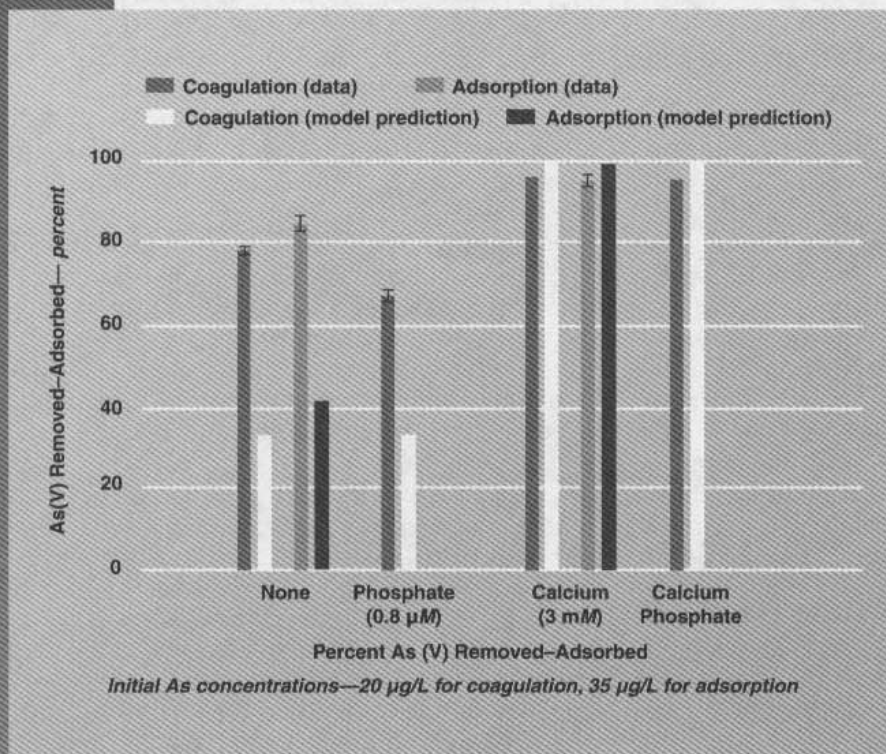
The different pH trends observed in the coagulation and adsorption experiments and the inconsistency between observed and predicted trends in coagulation experiments suggest that arsenic removal during coagulation is influenced by factors that do not significantly affect adsorption onto preformed HFO. One possibility is that the characteristics of the amorphous Fe(III) hydroxide precipitated in the coagulation experiments differ from those of the preformed HFO. The size of the Fe(III) hydroxide precipitated upon addition of coagulants clearly varies with pH, as demonstrated by the absence of visible flocs at the extreme pH values. However, the absence of detectable iron passing through the 0.1- μ m filters and the complete removal of As(V) indicate that the added Fe(III) is effectively precipitated even at pH 4. The observed effects in the coagulation experiments with As(III) are consistent with the formation of smaller Fe(III) hydroxide precipitates at the extreme pH values because smaller precipitates would provide a higher effective surface area for arsenic adsorption. In addition, even the short 2-h aging period in the HFO preparation may result in some evolution of the properties of the HFO surface.²⁶ A short aging period was chosen as the most appropriate surrogate for the in situ precipitation (and 45-min equilibration during slow mixing and settling) in the coagulation experiments. Nonetheless, some differences between the results of coag-

In general, consistent trends were observed in adsorption and coagulation experiments, and observed trends were in agreement with model predictions.

ulation and adsorption experiments may have been because of aging effects.

For As(V), the model prediction of a sharp decrease in removal at higher pH values (above pH 8.5) was not consistent with observations in coagulation experiments. The sharpness of the predicted pH edge is largely attributable to the inclusion in the model of a highly charged As(V) surface species (\equiv FeOHAsO₄³⁻); the apparent adsorption constant for this surface species is strongly affected by surface charge and consequently by both pH and the extent

FIGURE 7 Effects of phosphate and calcium on the efficiency of As(V) removal during coagulation with 4.9 mg/L FeCl₃ (30 μM total iron) and of calcium on As(V) adsorption with 50 μM total iron at pH 9



of As(V) adsorption. Formation of the negatively charged surface species becomes increasingly unfavorable at pH values above the zero point of charge of the oxide and with increasing coverage of the oxide surface by As(V). As also indicated by the deviations between model predictions and observations shown in Figure 2, some optimization of the adsorption constants in the model may be necessary.

Effect of arsenic oxidation state. In examining the effects of various parameters on arsenic removal-adsorption, it is clear that, consistent with previous observations,^{4,21-24} arsenic removal from background electrolyte during coagulation with ferric chloride and by adsorption onto preformed HFO is significantly more efficient for As(V) than for As(III) under comparable conditions. As discussed in the following section, removal-adsorption is also more strongly affected by the presence of co-occurring inorganic solutes for As(III) than for As(V).

Effect of co-occurring inorganic solutes. The major ion composition of source waters can influence the extent of arsenic adsorption onto oxide surfaces and thus its removal during coagulation. Co-occurring inorganic solutes, such as calcium, sulfate, and phosphate, may directly compete for surface binding sites and may also influence the surface charge of the oxide (Table 1), thus indirectly affecting the adsorption of trace contaminants, such as arsenic.

Effects of sulfate on arsenic removal-adsorption were examined for both As(III) and (V) in coagulation and adsorption experiments. For As(III), these ex-

periments were conducted at pH 5 and 6; the observed results and model predictions are shown in Figure 5. For both types of experiments, the addition of sulfate decreased the observed efficiency of As(III) removal-adsorption but not to the extent predicted by the model. That is, the model overpredicts the competitive effect of sulfate on As(III) removal-adsorption.

For As(V), adsorption experiments with sulfate were conducted at pH 4 and 5 and coagulation experiments at pH 4 and 6. As shown in Figure 6, neither As(V) removal during coagulation nor As(V) adsorption onto preformed HFO was observed to be significantly decreased in the presence of sulfate even at concentrations up to 10 mM (960 mg/L SO₄). It is clear from Figure 6 that the competitive effect of sulfate is drastically overemphasized by the model.

In comparing the observed and predicted effects of sulfate on adsorption of As(III) and As(V), it appears that the discrepancies between observations and predictions are greater for As(V) than for As(III). For both As(III) and As(V), the predicted effect of sulfate on adsorption is partly attributable to direct competitive binding of the anions. For As(V), an indirect effect of sulfate on As(V) adsorption is predicted. Because both sulfate and As(V) form negatively charged surface species (Table 1), the effect of sulfate adsorption on surface charge is predicted to make As(V) adsorption less favorable. Further work is required to reconcile the model predictions with the observed results.

The presence of co-occurring inorganic solutes can, under certain conditions, increase rather than decrease the adsorption-removal of trace contaminants. At pH 9.0, the removal of As(V) (at an initial concentration of 20 μg/L) during coagulation with 4.9 mg/L FeCl₃ (30 μM total iron) was increased in the presence of 3.0 mM calcium; the presence of calcium also counteracted the slight competitive effect of phosphate (Figure 7). Similar effects were observed for the adsorption of As(V) (at an initial concentration of 35 μg/L) onto preformed HFO (with 50 μM total iron). Comparison with model predictions is difficult because of the poor agreement between predicted and observed As(V) removal and adsorption at pH 9 in the absence of calcium. However, the model predictions are consistent with the observed trend of increased As(V) removal and adsorption in the pres-

ence of calcium. The predicted effect of calcium derives from the increase in surface charge that accompanies adsorption of calcium; the resulting positive surface charge (even at pH 9) favors As(V) adsorption.²⁴

Effects of filter size and background particulates. Obviously bench-scale tests provide only an approximation of processes at pilot- or full-scale levels. Differences in arsenic removal in bench-, pilot-, and full-scale tests have been observed previously.^{6,8} Two significant differences between the bench-scale tests described here and larger-scale operations are the type of filtration and the lack of background particulates (turbidity) in the bench-scale tests. Both of these differences may affect the concentration of arsenic in the product water if the arsenic is associated with fine colloidal particles.

The effect of variable removal of fine particulate material was examined by comparing arsenic removal efficiencies with different sizes of membrane filters (0.1, 0.5, and 1.0 μm) and without filtration. Arsenic removal from pH-adjusted background electrolyte during coagulation with 4.9 mg/L FeCl_3 was determined with an initial As concentration of 20 $\mu\text{g/L}$. Some samples were amended with calcium, sulfate, and phosphate. As shown in Table 2, variations in filter size (from 0.1 to 1.0 μm) had only minor effects on As(V) and As(III) removal. Marked decreases in As removal efficiencies were observed with unfiltered samples, as also reported by Edwards.⁹ These decreases were particularly notable at low pH, again indicating the formation of smaller, nonsettleable Fe(III) hydroxide particulates under these conditions.

Although the presence of background particulates is known to improve the efficiency of coagulation processes,¹⁷ the addition of kaolin particles had no consistent effect on arsenic removal. The observed decrease in As(III) removal in the presence of 5 mg kaolin/L (with a corresponding turbidity of 8 ntu) was also observed when the background electrolyte was exposed to the kaolin particulates and the kaolin was removed before the coagulation experiment (pre-conditioned media) as shown in Table 3. Thus the effect of kaolin appears to be associated with changes in solution composition rather than with the presence of the particles per se.

Conclusions

Experiments were conducted in model freshwater systems to examine the effects of various parameters (such as arsenic oxidation state and initial concentration, adsorbent concentration or coagulant dosage, pH, and the presence of co-occurring inorganic solutes) on the removal of arsenic by adsorption onto preformed HFO and during coagulation with FeCl_3 .

In general, consistent trends were observed in adsorption and coagulation experiments, and observed trends were in agreement with model predictions. Under comparable conditions, better removal was observed for As(V) than for As(III) in both coagulation and adsorption experiments. For both As(V)

and As(III), removal was dependent on coagulant dosage or adsorbent concentration. In coagulation experiments, arsenic removal was independent of initial concentration. Increased adsorption of As(III) was observed at low initial concentrations. Below neutral pH values, As(III) removal-adsorption was significantly decreased in the presence of sulfate. However, only a slight decrease in As(V) removal-adsorption was observed. At high pH, adsorption-removal of arsenic(V) was increased in the presence of calcium.

Under the experimental conditions studied, effects of pH on As(V) removal-adsorption could not be easily discerned; slight decreases were observed at high pH. For As(III), a weak pH dependence was observed in adsorption experiments. In contrast, an unexpectedly strong pH dependence was observed in coagulation experiments with a minimum in removal efficiency at pH 6.

In conclusion, these studies demonstrate the significance of adsorption processes in governing arsenic removal during coagulation but also suggest that other processes, such as the nucleation and growth of amorphous Fe(III) hydroxide precipitates upon coagulant addition and the oxidation of As(III) to As(V), may influence the efficiency of arsenic removal. Surface complexation modeling is useful in evaluating observed experimental trends, but its application to natural waters is limited by the discrepancies between observed results and model prediction (particularly for As(V) in the presence of sulfate), by the difficulty in modeling the interactions of natural organic matter with oxide surfaces, and by the implicit assumptions of chemical equilibrium and complete separation of dissolved and adsorbed arsenic in the model. In practice, the effectiveness of arsenic removal will depend on the efficiency of the solid-liquid separation process. Efficient filter performance is necessary to prevent increased arsenic concentrations in product water caused by breakthrough of colloidal particles, with which arsenic may be associated.

Acknowledgment

This work was supported in part by the AWWA Research Foundation and by the Metropolitan Water District of Southern California. Instrumentation used in this project was purchased with partial funding from the National Science Foundation. This work benefited from the comments of Marc Edwards at the University of Colorado in Boulder, Ruth Hund of AWWARE, as well as the reviewers.

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