



## Project Summary

# Arsenic (III) Oxidation and Removal from Drinking Water

Phyllis Frank and Dennis Clifford

The oxidative pretreatment of As(III) using chlorine and oxygen was studied following quantification of As(III) and As(V) removals by activated alumina columns.

Activated alumina removed 100  $\mu\text{g/L}$  As(V) from a typical groundwater at pH 6.0 much more effectively than it did As(III). Approximately 23,500 bed volumes of water could be treated by activated alumina columns before As(V) reached the 0.05-mg/L maximum contaminant level (MCL), whereas only 300 bed volumes could be treated before As(III) reached that level.

Variables affecting the oxidation of As(III) by chlorine include the pH, chloride concentration, other ions, chloramine formation, and total organic carbon (TOC). In artificial groundwater containing no ammonia or TOC with 100  $\mu\text{g/L}$  As(III) present initially and 1.0 mg/L chlorine dosage, the reaction reached 95 percent completion in less than our shortest possible observation time of 5 sec. Thus, with 1.0 mg/L chlorine dosage, the As(III) oxidation rate was greater than 20  $\mu\text{g/L}$  per sec. The extent of oxidation at 30 sec was insensitive to pH in the range of 6.5 to 9.5, with decreasing reaction outside this range. Increasing chloride concentration slowed the reaction slightly, but not significantly for water treatment. The counterion (sodium or calcium) did not appear to affect the extent of reaction in the artificial groundwater or in chloride solutions up to 0.010 M. Monochloramine is capable of oxidizing 40 percent of the initial 100  $\mu\text{g/L}$  As(III) in the pH range of 6.5 to 10.5. The presence of 5 mg/L TOC substantially slowed the oxidation kinetics of 100  $\mu\text{g/L}$  As(III) by 1.0 mg/L chlorine dosage. Although the reaction reached 50 percent completion in less than 30 sec, it

did not reach 80 percent completion until approximately 30 min.

In artificial groundwater, sparging 1 hr with oxygen did not oxidize 100  $\mu\text{g/L}$  As(III); in deionized water, however, 14 percent was oxidized. However, capped samples of As(III) in deionized water and artificial groundwater were completely oxidized after 61 days on the shelf with air in the headspace.

*This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Arsenic is a well-known toxic element and not an uncommon contaminant of groundwaters used for potable water supply. Worldwide, the concentration of arsenic in contaminated groundwaters ranges from a few  $\mu\text{g/L}$  to 8 mg/L. Contaminated wells included in a 1982 American Water Works Association survey of inorganic contaminants in the United States had a modal total arsenic concentration within the 0.075- to 0.100-mg/L concentration range. Data on the speciation of arsenic-bearing groundwaters is relatively scarce; however, it is known that the valence state of arsenic in groundwater varies with location. Inorganic arsenic may occur totally as As(III), as As(V), or any mixture of these two valence states. Water drawn from an infiltration gallery 4 m (13 ft) deep in San Ysidro, New Mexico, had a total arsenic concentration of 80  $\mu\text{g/L}$  with 40 percent of the total occurring as As(III). Nineteen wells sampled in Hanford, California, had total

arsenic concentrations ranging from 30 to 90  $\mu\text{g/L}$ , all of which was trivalent arsenic.

The speciation of arsenic is important because trivalent arsenic is considered to be 3 to 20 times as toxic as pentavalent arsenic. The exact role of arsenic in human metabolism remains obscure with some researchers claiming that it is carcinogenic and others believing that it may be an essential trace element. Despite the lack of knowledge about the consequences of ingesting very small amounts of arsenic, the ultimate toxicity of this element is well recognized. The National Interim Primary Drinking Water Regulations set a maximum contaminant limit (MCL) for arsenic at 0.05 mg/L.

A survey of the literature and our own experimental studies have shown that arsenic may be removed by iron or alum coagulation, filtration, reverse osmosis, ion-exchange, electrodialysis, and adsorption onto activated alumina. With all of these processes, however, it was found that As(V) (arsenate) is much more effectively removed than is As(III) (arsenite) because the former exists in natural water as a monovalent or divalent anion of arsenic acid ( $\text{H}_3\text{AsO}_4$ ,  $\text{p}K_2 = 7.0$ ). Arsenite, on the other hand, exists predominantly as a neutral species—arsenious acid ( $\text{H}_3\text{AsO}_3$ ,  $\text{p}K_1 = 9.2$ ). And it is well known that coprecipitation, sorption, ion exchange, electrodialysis membrane transport, and reverse osmosis membrane rejection are much more effective with ions like the arsenates than with neutral species like arsenious acid. However, the removal of As(III), particularly by activated alumina columns, has not been quantified.

One purpose of this study was, therefore, to quantify and compare the columnar removal of both As(III) and As(V) at the known optimum pH of 6.0. This study was performed in a typical high-sulfate, high total-dissolved-solids water containing 3.0 mg/L fluoride.

Following this short alumina adsorption study, a more comprehensive study was performed on the oxidation of As(III) to As(V). The kinetics of oxidation by chlorine were studied as a function of pH and ionic composition. The oxidation of As(III) by oxygen was studied because of its potential low cost and because the oxidation of As(III) in stored water samples was inadvertently observed.

This study was undertaken at the University of Houston as part of a comprehensive research effort on arsenic removal from drinking water. Related field studies using the University of Houston/U.S. Environmental Protection Agency (EPA) Mobile Drinking Water Treatment

Research Facility have been performed in San Ysidro, New Mexico, and are continuing in Hanford, California. Related laboratory studies have been done on establishing the As(V) capacity of activated alumina, regenerating arsenic-spent alumina, establishing the fundamentals of As(V) uptake by ion-exchange resins, and developing an analytical method for the separation and determination of As(III) and As(V).

## Experimental Procedures

### Column Studies

The objective of the column studies was to verify the reportedly efficient removal of pentavalent arsenic and the nonremoval of trivalent arsenic on activated alumina. Since some groundwaters in the United States contain both excess arsenic and fluoride, and since activated alumina is known as a successful adsorbent for fluoride, these column studies were conducted on water that contained typical concentrations of both fluoride and arsenic.

Two column runs were conducted simultaneously. Each column was constructed from 1/4-in-ID Plexiglas\* tubing with stainless steel Swagelock fittings at each end and was loaded with 5 mL of conditioned Alcoa F-1 activated alumina (U.S. standard mesh size 24 X 48). Milton Roy metering pumps were used to control the flowrate at 1.7 mL/min for an empty bed contact time (EBCT) of 2.9 min. These pumps provided a steady flow rate over the entire length of the longest column run (58 days).

The column feedwater was prepared to resemble groundwater that had been acidified to pH 6.0 with sulfuric acid. This pretreatment creates a sulfate-enriched, bicarbonate-free water. An arsenic concentration of 0.100 mg/L was chosen because it is twice the MCL and not uncommon in arsenic-contaminated groundwaters (e.g., Hanford, California, and San Ysidro, New Mexico). The same line of reasoning was used in choosing 3 mg/L as the fluoride concentration. The composition of the pH 6.0 column feedwater was 100  $\mu\text{g/L}$  arsenic, 3.0 mg/L fluoride, 71 mg/L chloride, 384 mg/L sulfate, 210 mg/L sodium, and 20 mg/L calcium. The influent to each column differed only in the valence state of the arsenic; one column received 100  $\mu\text{g/L}$  As(V), and the other received 100  $\mu\text{g/L}$  As(III), which was prepared fresh daily to avoid oxidation.

\*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

A fraction collector was used to collect 25.5-mL samples every 15 min. Selected samples were analyzed for total arsenic content with a Perkin-Elmer Model 5000 atomic absorption spectrophotometer with a graphite furnace (GFAAS), Zeeman background correction, and an HGA-400 furnace temperature programmer. An electrodeless discharge arsenic lamp was used as the source lamp, and nickel nitrate was used as a matrix modifier. Fluoride analyses were conducted using a fluoride-ion-selective electrode and a digital pH/ion analyzer.

### Oxidation Studies

#### Objectives

The oxidation studies were undertaken to establish the kinetics of As(III) oxidation by chlorine and monochloramine as influenced by pH, anions, cations, and TOC. The oxidation of As(III) by pure oxygen and by air was also studied in the hope that the use of chlorine could be avoided.

#### Procedure Development for Chlorine Oxidation

No method was available for instantaneous arsenic speciation and quantification. The methods available for analytical As(III) separation from As(V) include ion exchange, pH-controlled arsine generation, and selective extraction. Each of these methods requires subsequent analysis for total arsenic in various fractions. An ion-exchange method previously developed at the University of Houston was chosen for arsenic speciation. Five milliliters of chloride-form IRA-458 anion-exchange resin contained in a mini-column was exposed to a sample at a flow rate of 10 mL/min and was used to separate As(III) from As(V) in a 100-mL sample. Under these conditions, the fastest possible separation time was about 10 min.

An oxidation quenching agent was found to be necessary because the reaction time of the As(III) oxidation was discovered in screening tests to be much faster than the minimum separation time of 10 min. Several criteria are required of such a quenching agent: (1) the quenching agent must react with chlorine instantaneously in a manner to prevent further oxidation of As(III), (2) it cannot oxidize As(III) or reduce As(V), (3) it must not deleteriously affect the separation procedure, and (4) it should not substantially interfere with arsenic analysis by GFAAS.

Several quenching agents were tried. Ammonia, which had been used previously in Se(IV) oxidation studies, appeared to

be a good candidate. However, ammonia could not be used as a quenching agent because the resulting monochloramine was found to oxidize As(III).

Thiosulfate, a common dechlorinating agent, was also considered but was abandoned without testing because it is known to react with chlorine in a somewhat slow, stepwise manner. Sodium sulfite, another common dechlorinating agent, is reported to react instantaneously with chlorine. However, experiments indicated that As(V) was reduced to As(III) when a threefold excess of sodium sulfite was used to quench the 1.0 mg/L Cl<sub>2</sub> dosage.

N,N-diethyl-p-phenylene diamine oxalate (DPD), which is used in the colorimetric test for chlorine, is reported to react instantaneously with free chlorine under the proper conditions. This reaction is one-to-one, follows Beer's Law, and results in the destruction of free chlorine. A 4.3-fold excess of DPD added during turbulent mixing proved to be an excellent quenching agent. It immediately consumed the free chlorine without oxidizing As(III) or reducing As(V). The pH was adjusted into the 6.2 to 6.5 range by adding a predetermined amount of HCl or NaOH followed by one-tenth the usual amount of phosphate buffer. The amount of phosphate buffer had to be reduced because phosphate interferes with the GFAAS determination of total arsenic.

### Chlorine Oxidant Experiments

The composition of the background water used for the As(III) oxidation tests, unless otherwise indicated, was 10 milliequivalents (meq)/L comprising 96 mg/L sulfate, 71 mg/L chloride, 366 mg/L bicarbonate, and 230 mg/L sodium. The pH was adjusted, if needed, by dropwise addition of either 0.1 N HCl or 1.0 N NaOH solution. An initial As(III) concentration of 0.100 mg/L was chosen because it is twice the MCL and is not an uncommon concentration in arsenic contaminated groundwaters. A chlorine dosage of 1.0 mg/L was considered to be sufficient for the batch tests because, with the exception of As(III), there was no chlorine demand in the artificial groundwater. The batch chlorine oxidation tests were conducted in 2-L polyethylene beakers containing 1-L samples. A plastic-coated propeller mixer provided rapid mixing for the addition of stock chlorine solution and quenching agent. All time increments were measured with a laboratory timer. A 100-mL pipette was used to collect the sample, which was immediately separated. An initial sample and the As(III) fraction were stored in a 60-mL or 125-mL polyethylene bottle for

subsequent GFAAS analysis. An occasional As(V) fraction was eluted and collected as a spot check of separation recovery; otherwise, As(V) was determined by difference.

### Oxygen Oxidant Tests

Oxygen oxidation was tried using two methods—stagnant and bubbling. The bubbling oxygen oxidation tests were conducted using different background waters containing 100 µg/L As(III). For all these experiments, a 500-mL sample in a Pyrex gas washing bottle was bubbled with O<sub>2</sub> at a flow rate of 300 to 400 mL/min for 60 min. A control sample to serve as a blank was bubbled with nitrogen under these same conditions.

In the stagnant oxygen tests, As(III) samples were allowed to sit in 125-mL polyethylene bottles with air in the headspace for 61 days. Samples were 200 µg/L As(III) in deionized water at pH 6.0, 7.0, and 8.0; 50 µg/L As(V) and 50 µg/L As(III) in deionized water at pH 6.0, 7.0, and 8.0; and 50 µg/L As(III) and 50 µg/L As(V) in artificial groundwater described

previously except with 1 meq Ca<sup>2+</sup> at pH 7.3 and 8.3.

### Reagents

All stock As(V) solutions were prepared according to *Standard Methods* using reagent grade KH<sub>2</sub>AsO<sub>4</sub>. All stock As(III) solutions were prepared immediately preceding their use according to *Standard Methods* using reagent grade As<sub>2</sub>O<sub>3</sub>. All other solutions, with the exception of chlorine oxidant, were prepared using the appropriate reagent-grade chemicals. Stock chlorine oxidant was prepared from a commercial bleach (Clorox) containing sodium hypochlorite. The titer of this solution was checked immediately preceding use. GFAAS analysis showed no arsenic to be present in the bleach.

### Results

#### Column Studies

The breakthrough curves for arsenic and fluoride from the As(III) and As(V) columns are shown in Figures 1 and 2. As(III) reached the MCL almost immediately

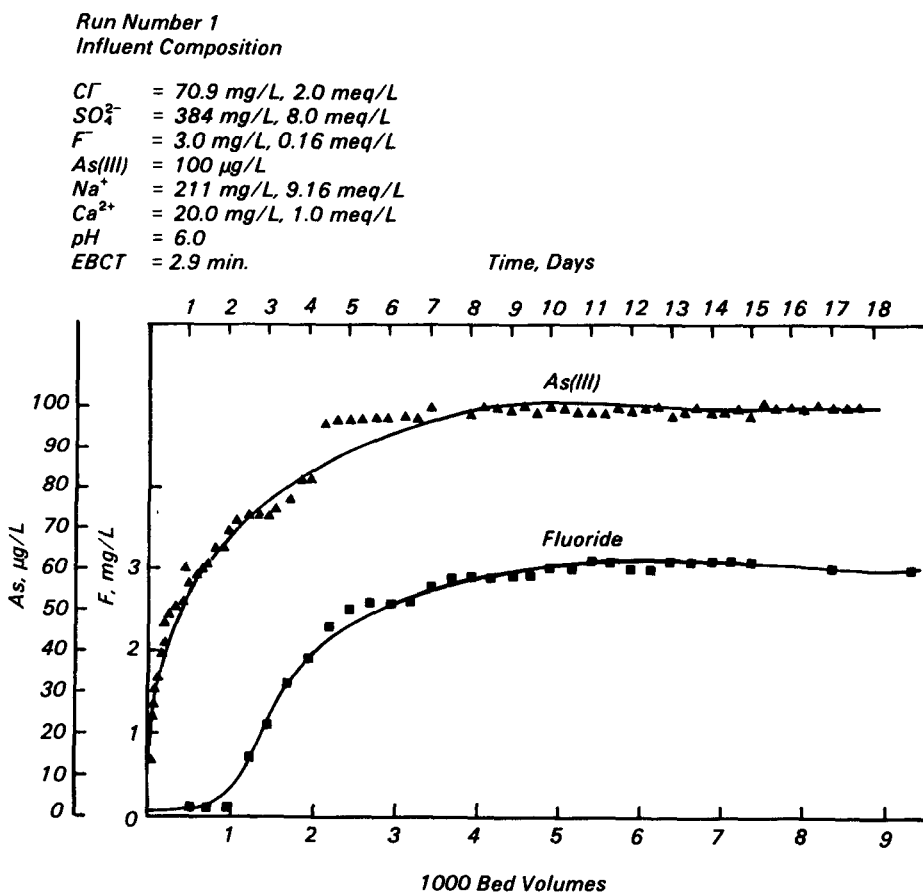


Figure 1. As(III) (arsenite), and fluoride breakthrough curves from a minicolumn containing 28 X 48 mesh, F-1 activated alumina.

(Figure 1) at 300 bed volumes (0.6 days), whereas As(V) did not reach the MCL until 23,400 bed volumes (48 days) (Figure 2). Thus the presence of pentavalent arsenic results in column runs nearly 80 times longer than trivalent arsenic (Figure 3). Therefore, preoxidation of As(III)-containing waters is essential for efficient treatment using activated alumina.

Even though trivalent arsenic appeared in the effluent very quickly, some As(III) was removed. In fact, when the effluent As(III) concentration reached 90 percent of the influent value, a mass balance showed that 0.344 mg As(III) had been removed, yielding an average mass loading of 0.078 mg As(III)/g alumina. Speciation of both the influent and the effluent showed the arsenic to be totally As(III). Thus it appears that it is the trivalent species that is actually absorbed onto the alumina, since no oxidation of As(III) occurred.

Fluoride adsorption was little affected by the difference in adsorption of As(III) and As(V). The effluent concentration of fluoride reached the MCL at 1600 bed volumes for the column with As(III) and at 1500 bed volumes for the column with As(V). Although As(V) is more preferred than fluoride and As(III) is less preferred, the difference in arsenic adsorption is unlikely to affect fluoride adsorption because the molar ratio of F<sup>-</sup> to arsenic is 117.

These laboratory results were in general agreement with studies on arsenic and fluoride removal conducted in San Ysidro, New Mexico, in 1984 using the University of Houston/EPA Mobile Drinking Water Treatment Research Facility. The San Ysidro water contained 48 µg/L As(V) and 32 µg/L As(III), and based on the laboratory results just presented, it performed generally as expected with regard to the bed volumes required to reach the arsenic MCL. A comparison of results from the field and laboratory data for arsenic and fluoride removal are presented in Table 1. Although more bed volumes were required to exceed the fluoride MCL in the San Ysidro water, which contained only 2.0 mg/L fluoride, the capacity to the fluoride MCL was almost exactly the same as that obtained in laboratory tests. The shape of the arsenic breakthrough curve in the field study was surprisingly sharp; a much earlier breakthrough of trivalent arsenic was expected. The explanation may be that some oxidation of As(III) to As(V) occurred in the field column; also, the trivalent arsenic concentration of the influent in the field study was only 0.032

**Run Number 2  
Influent Composition**

Cl <sup>-</sup>	= 70.9 mg/L, 2.0 meq/L
SO <sub>4</sub> <sup>2-</sup>	= 384 mg/L, 8.0 meq/L
F <sup>-</sup>	= 3.0 mg/L, 0.16 meq/L
As(V)	= 100 µg/L
Na <sup>+</sup>	= 211 mg/L, 9.16 meq/L
Ca <sup>2+</sup>	= 20.0 mg/L, 1.0 meq/L
pH	= 6.0
EBCT	= 2.9 min.

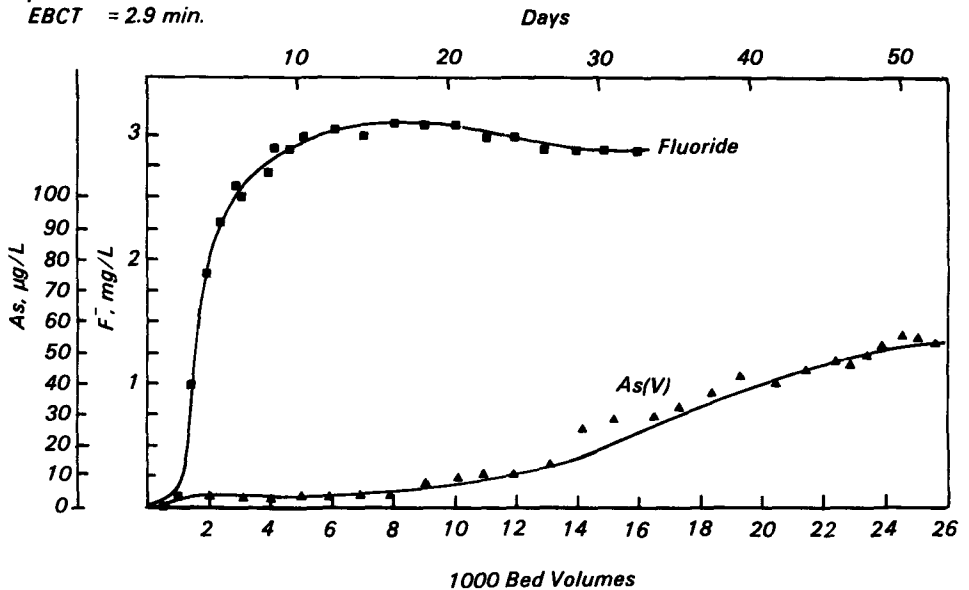


Figure 2. As (V) (arsenate), and fluoride breakthrough curves from a minicolumn containing 28 X 48 mesh, F-1 activated alumina.

mg/L — one-third the concentration in the laboratory study. Furthermore, the pentavalent arsenic breakthrough curve indicated early breakthrough of As(V). This effect was presumably because of the shorter EBCT of the lab column, its shallow bed depth, and the fact that the adsorption zone was a large fraction of the bed depth.

**Chlorine Oxidant Studies**

The data in Figure 4 indicate the results of the kinetic experiments on the oxidation of arsenic(III) by chlorine in artificial groundwater with sodium as the cation. This figure indicates that the reaction reached a stable 95 percent completion within the fastest possible measuring time—5 sec. This result is not in agreement with equilibrium calculations, which predict essentially 100 percent completion. The residual As(III) concentration (Figure 4) may, however, be attributable to leakage of As(V) during the speciation procedure. In any event, the apparent 95 percent complete reaction is surely sufficient for water treatment practice.

The experimentally observed effect of pH on the oxidation of As(III) by chlorine

is shown in Figure 5. In the neutral pH range of 6.5 to 9.5, the pH does not significantly affect the extent of reaction. Not until pH values are greater than 10.5 is the oxidation reaction affected adversely. The relative insensitivity of the oxidation reaction of As(III) to As(V) by chlorine in the neutral pH range may be attributed to the fact that As(III) exists predominantly as arsenious acid in this pH range and that the changes in pH do not significantly affect the activation of the species. The slight decrease in reaction extent at pH 5.5 may be explained by the fact that the reaction produces acid, H<sup>+</sup>, in the 2.2 to 7.0 pH range. As the pH decreases, the H<sup>+</sup> concentration increases, representing an accumulation of products. Another contributing factor may be the increase in Cl<sup>-</sup> as a result of acidification from pH 8.3 with HCl.

Oxidation tests performed using 1.0 mg/L chlorine at pH 6.0 in 0.00 to 0.002 M chloride solutions (0 to 710 mg/L chloride) made from sodium chloride or calcium chloride indicates that the extent of As(III) oxidation was slightly diminished with increasing chloride concentration. The reaction was essentially 100 percent

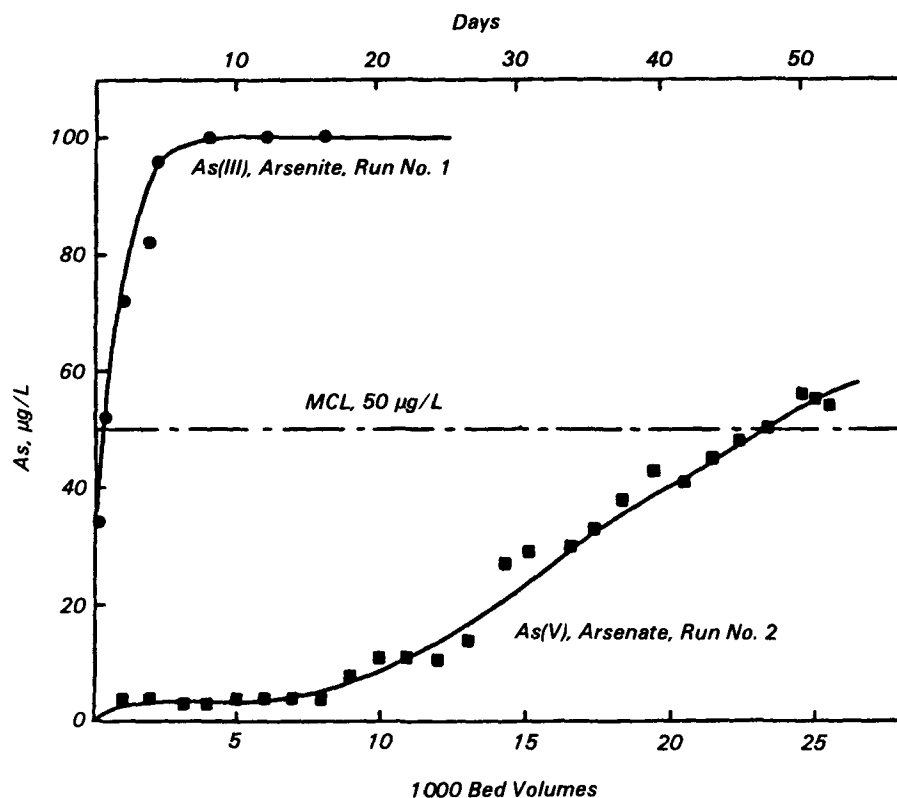


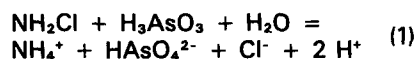
Figure 3. Comparison of As(III) and As(V) breakthrough curves from minicolumns of activated alumina.  $C_T = 100 \mu\text{g/L}$ , EBCT = 2.9 min, and pH = 6.0.

complete in deionized water, but only 90 to 95 percent complete with 350 mg/L chloride present. This trend may be expected from the oxidation reaction in which chloride is a product. Regarding the effect of calcium as compared with sodium as the chloride counterion, calcium seemed to have a slightly greater effect on diminishing the extent of reaction. These data indicate, however, that neither chloride nor the presence of sodium as opposed to calcium should be considered important during As(III) oxidation by chlorine in water treatment practice.

### Effect of Chloramines

Figure 6 shows the kinetics of oxidation of  $100 \mu\text{g/L}$  As(III) in artificial groundwater containing a dosage of 1.0 mg/L chlorine with a 10-fold stoichiometric excess of ammonium chloride at pH 8.3. As expected, analysis of the chloramine species showed only the presence of monochloramine— $\text{NH}_2\text{Cl}$ . Figure 6 has two salient points. First, the reaction appears to reach completion at an As(V)/As(III) ratio of approximately two-thirds. And, secondly, the reaction appears to have slower kinetics than the oxidation of As(III)

by free chlorine. The following reaction can be written:



This reaction has a standard free energy of  $-82.4 \text{ kcal/mol}$  and an equilibrium constant of  $2.57 \times 10^{60}$ . Under the experimental conditions, thermodynamic calculations predict an As(V)/As(III) ratio of  $5.66 \times 10^{78}$  at equilibrium. The observed data do not match the predicted value. Although the thermodynamic data available may be somewhat in error, these errors cannot account for the total difference between observed and predicted values.

One possible explanation for the incomplete oxidation is that although the

above reaction is feasible, it does not actually occur because the energy barrier of activation is too high. In this case, oxidation may be accomplished by analytically undetectable amounts (less than  $0.1 \text{ mg/L}$ ) of free chlorine remaining in solution in equilibrium with monochloramine. The sequence of reactions, beginning with the known-to-be-slow hydrolysis of monochloramine followed by the observed fast oxidation of As(III), for pH 6.0, makes the overall reaction appear as if monochloramine were the oxidant, as shown in Equation 1. However, HOCl may be the true oxidant. Note, however, that the experimentally observed 40 percent oxidation of As(III) does not quantitatively agree with the expected oxidation based upon the most recent studies of monochloramine hydrolysis. Significantly less As(III) oxidation is predicted based on the amount of free chlorine computed from the published equilibrium constant and the slow rate of reaction. More work is required to elucidate the monochloramine oxidation mechanism.

As Figure 7 shows, the solution pH does not appear to substantially affect the extent of reaction in the pH range of 6.5 to 10.5. This pH sensitivity of the chloramine reaction is very similar to that obtained for oxidation of As(III) by free chlorine where a somewhat decreased rate is observed at pH 5.5. Although pH-dependent, the reaction of monochloramine to dichloramine is not considered here because the reaction occurs slowly and only at a pH of less than 6.0. Calculations from kinetic data show that after 1 hr, only 7 percent of the monochloramine should be converted, and at the 1 min quenching time used in this experiment, less than 0.1 percent of the monochloramine should be converted to dichloramine at the lowest pH examined.

### Effect of TOC

The data in Figure 8 show the kinetics of As(III) oxidation in aged Houston, Texas, tap water with 1.0 mg/L chlorine dosage. Although the oxidation reaction was appreciably slowed in this water, it reached the same 95 percent completion as did the oxidation of  $100 \mu\text{g/L}$  As(III) in artificial groundwater. Presumably, the chlorine de-

Table 1. Comparison of Laboratory and Field Data for Fluoride and Arsenic Removal

Item	UH Laboratory Test		San Ysidro
	As(III)	As(V)	40% As(III)
Bed volumes to As MCL	300	23400	8760
Arsenic capacity, $\text{g/m}^3$	18	1610	575
Bed volumes to $\text{F}^-$ MCL	1600	1550	2520
Fluoride capacity, $\text{g/m}^3$	4190	4280	4160

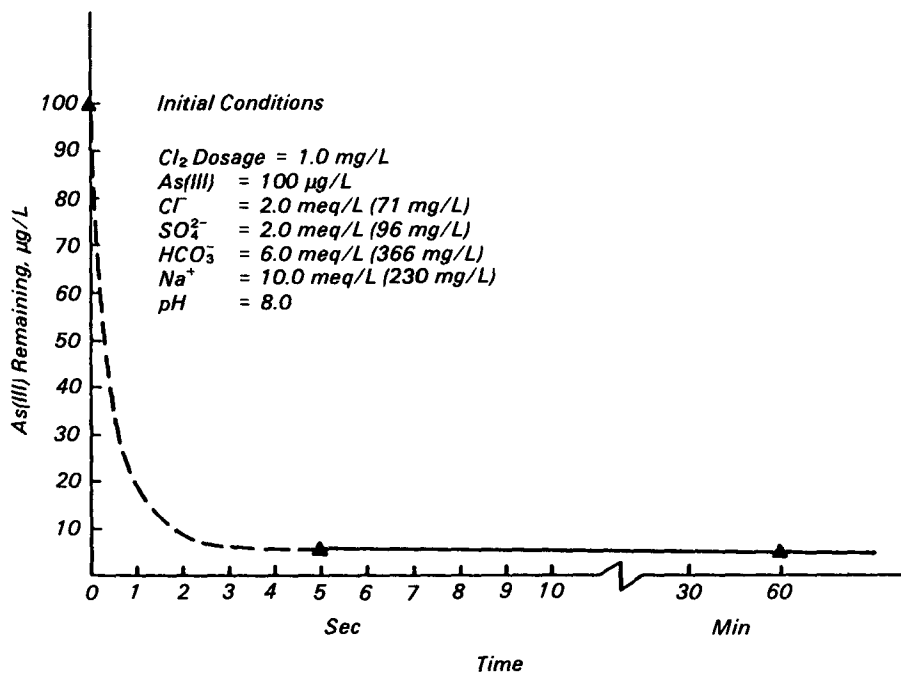


Figure 4. The oxidation kinetics of 100 µg/L As(III) using 1.0 mg/L chlorine with DPD quenching.

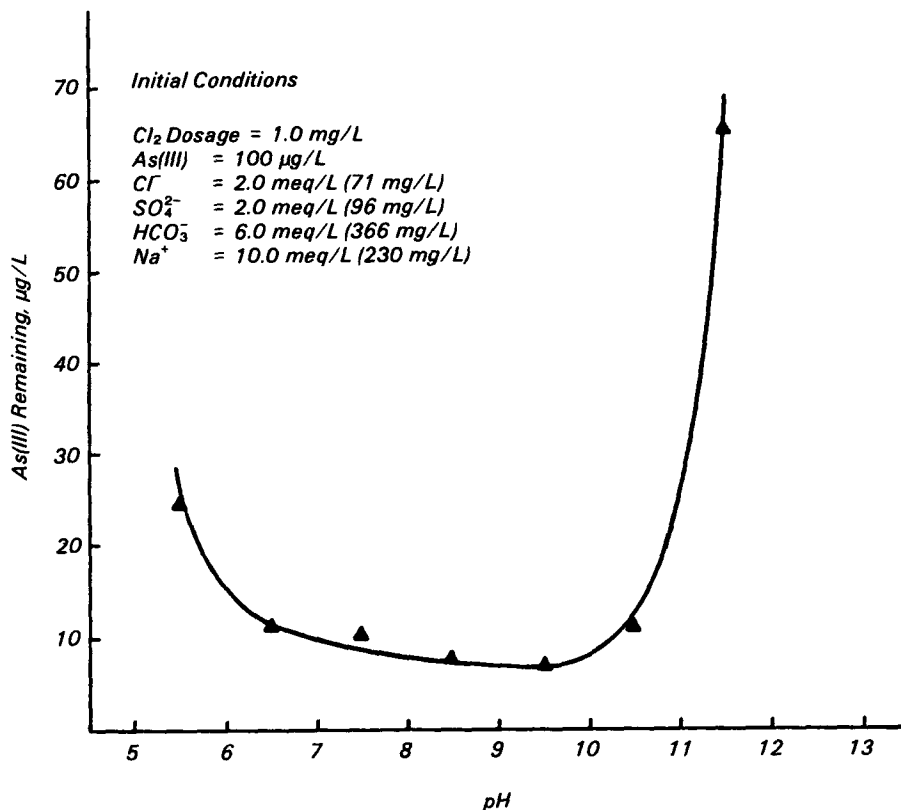


Figure 5. The effect of pH on As(III) oxidation of chlorine with DPD quenching after 30 sec.

mand exerted by the 5 mg/L TOC in the aged tap water was responsible for slowing the reaction, which took 720 times longer in the presence of TOC. Note, however, that even in the TOC-contaminated tap water, the original 100 µg/L As(III) was reduced to less than 50 µg/L As(III) in less than 30 sec. Hypochlorous acid may undergo many reactions with organic constituents in water. In general, at least part of the chlorine demand of a water is exerted immediately, with other slower reactions occurring at longer chlorine contact times. In fact, the overall oxidation may comprise parallel reactions, with oxidation by free chlorine occurring immediately and oxidation by combined chlorine, either chloramines or organic chloramines, occurring at a slower rate for the second stage.

### Oxygen Oxidant Studies

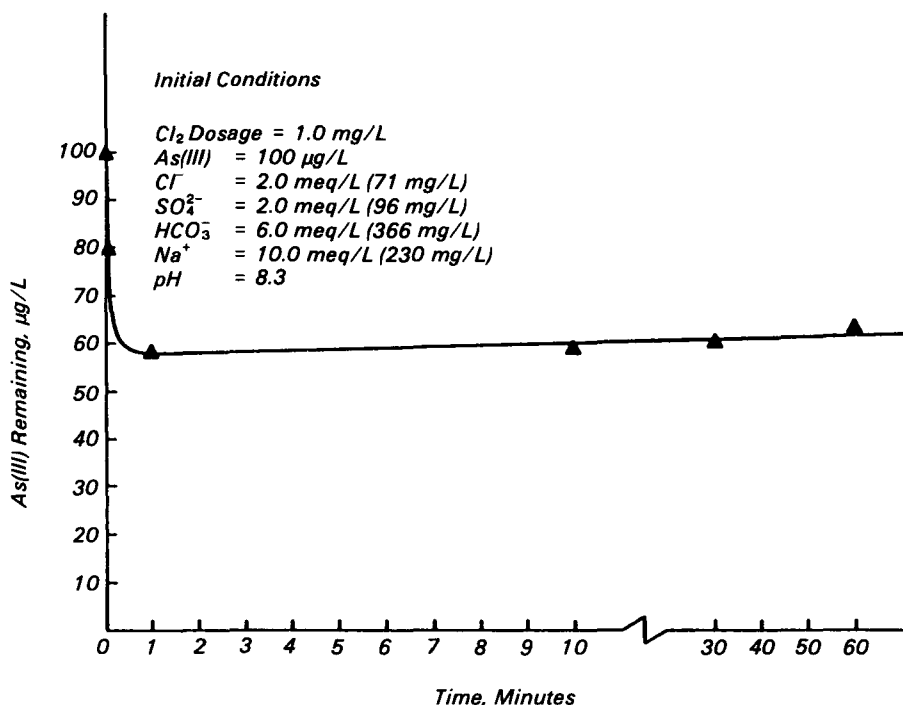
#### Sparging Tests

The results of the oxygen sparging tests are presented in Table 2. Even though glass surfaces reportedly adsorb arsenic, 97 percent of the As(III) was recovered after the nitrogen-sparged control test. In the oxidation tests in artificial groundwater, very little if any oxidation occurred; but in the deionized water, somewhat greater oxidation occurred. Because chloride ion slightly inhibits As(III) oxidation by chlorine, it may also stabilize As(III) with respect to oxygen oxidation. However, the effects of the other ions in solution cannot be ignored. The presence of 1.0 mg/L Fe(III) appeared to enhance the oxidation reaction by oxygen slightly. Despite highly favorable thermodynamic conditions, the oxidation of As(III) appears to occur only very slowly. Possibly that the actual oxidizing species is not O<sub>2</sub>, but H<sub>2</sub>O<sub>2</sub>, a compound postulated to account for the slow oxidation reactions of many species.

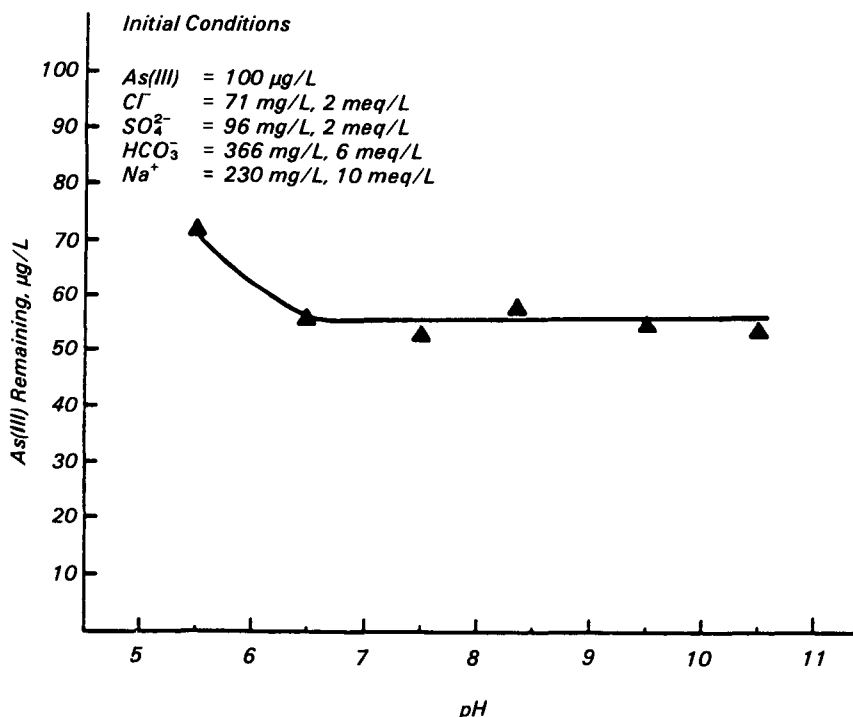
#### As(III) Shelf-Life Experiments

Various standard arsenic solutions were stored in polyethylene bottles and left on a shelf at room temperature away from direct sunlight. After 61 days, the percent As(III) remaining was determined. In all the bottles, As(III) was completely oxidized to As(V) by the end of 2 months. The observed complete oxidation of As(III) was not affected by the following factors:

1. pH in the range of 6.0 to 8.3,
2. concentration of As(III) in the range of 50 to 100 µg/L,
3. the initial presence or absence of As(V), and



**Figure 6.** The oxidation kinetics of 100  $\mu$ g/L As(III) using 1.0 mg/L monochloramine in the presence of excess ammonia.



**Figure 7.** The effect of pH on the oxidation of 100  $\mu$ g/L As(III) using 1.0 mg/L monochloramine and excess ammonia.

#### 4. the type of background water.

Adsorption of arsenic onto the polyethylene bottle surfaces was not observed during this experiment, as determined by before-and-after total arsenic analyses.

### Conclusions

Preoxidation of As(III) to As(V) is essential to achieve efficient arsenic removal using activated alumina.

1.0 mg/L free chlorine dosage readily oxidizes As(III) to As(V) in the pH range of 6 to 10, although the reaction is slowed when TOC is present.

1.0 mg/L combined chlorine (monochloramine) oxidizes about 45 percent of the As(III) to As(V) in the pH range of 6 to 10.

Fresh As(III) solutions should be prepared as needed because during storage dilute As(III) solutions may be completely oxidized to As(V).

### Recommendations

#### Laboratory Studies

Further studies of the chloramine oxidation of As(III) should prove useful in elucidating both the mechanism of As(III) oxidation and the means by which monochloramine acts as an oxidant in general. The extent of As(III) oxidation by monochloramine may vary with the monochloramine concentration and the amount of excess ammonia present. Experiments under the conditions used in this work with different monochloramine dosages (i.e., 0.5, 2.0, 5.0, and 10.0 mg/L) and different amounts of excess ammonia should help determine whether free chlorine or combined chlorine is the actual oxidant. Also, further study of longer reaction times may indicate which is the true oxidant.

#### Pilot Studies

Pilot studies of As(III) oxidation by chlorination of actual arsenic-contaminated waters will be beneficial. The presence of reduced species such as sulfides, Fe(II), and Mn(II) may adversely affect the ease of As(III) oxidation. Furthermore, species such as copper are known to catalyze the destruction of HOCl, which may adversely affect the extent of reaction at a given chlorine dosage.

The full report was submitted in fulfillment of Cooperative Agreement No. CR 807939 by the University of Houston under the sponsorship of the U.S. Environmental Protection Agency.

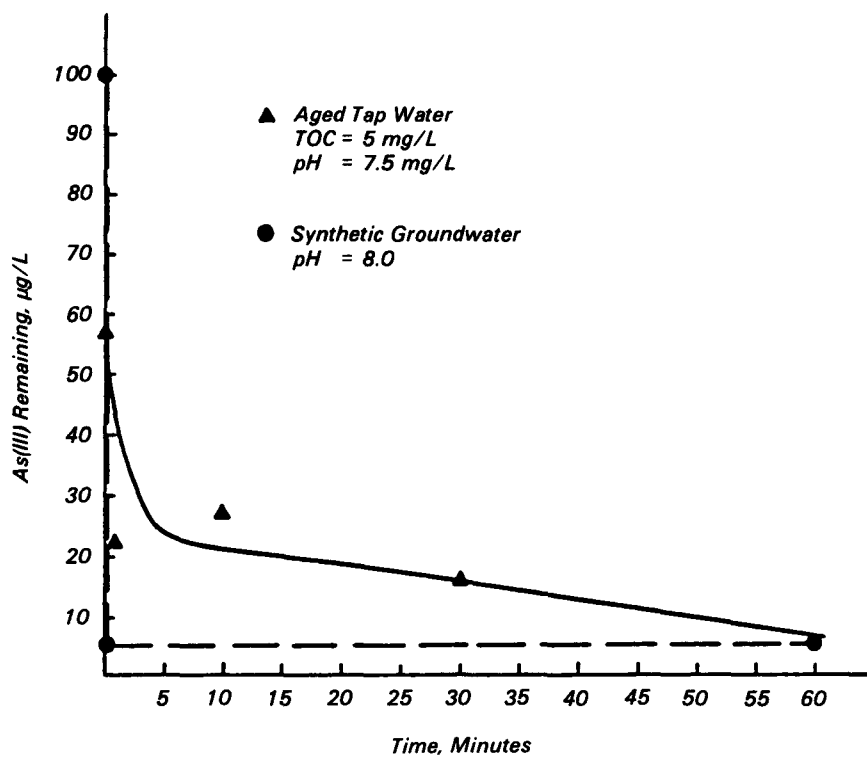


Figure 8. Comparison of the kinetics of oxidation of 100 µg/L As(III) by 1.0 mg/L chlorine dosage in aged tap water and artificial groundwater.

Table 2. The Results of O<sub>2</sub> Oxidation Batch Tests\*

Conditions	Arsenic (III) Oxidized in:	
	Synthetic Groundwater <sup>+</sup>	Deionized Water
pH 6.0	3%	14%
pH 7.5	5%	
pH 8.3	5%	
1.0 mg/L Fe(II)		16%
1.0 mg/L Fe(III)	8% (pH 7.3)	28% (pH 6)

\*All tests were of 60 min duration with 100 µg/L As(III) initially.

+ Composition: 2 meq/L Cl<sup>-</sup>, 6 meq/L HCO<sub>3</sub><sup>-</sup>, 2 meq/L SO<sub>4</sub><sup>2-</sup>,  
1 meq/L Ca<sup>2+</sup>, 9 meq/L Na<sup>+</sup>



---

*Phyllis Frank and Dennis Clifford are with the University of Houston, Houston, TX 77004.*

*Thomas J. Sorg is the EPA Project Officer (see below).*

*The complete report, entitled "Arsenic(III) Oxidation and Removal from Drinking Water," (Order No. PB 86-158 607/AS; Cost: \$11.95, subject to change) will be available only from:*

*National Technical Information Service*

*5285 Port Royal Road*

*Springfield, VA 22161*

*Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:*

*Water Engineering Research Laboratory*

*U.S. Environmental Protection Agency*

*Cincinnati, OH 45268*



Environmental Protection Information Cincinnati OH 45268

Business  
Private Use, \$300  
S2-86/021



U.S. OFFICIAL MAIL  
PENALTY FOR PRIVATE USE \$300  
U.S. POSTAGE  
0.49

0000329 PS  
U S ENVIR PROTECTION AGENCY  
REGION 5 LIBRARY  
230 S DEARBORN STREET  
CHICAGO IL 60604

ID