

CHAPTER 7

CHEMICAL FORMS OF ARSENIC IN WATER SUPPLIES AND THEIR REMOVAL

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INTRODUCTION

Concern about toxic elements in water supplies and receiving waters seems to have abated slightly from the virtual hysteria that was recently focused on mercury and cadmium, two elements which exert toxic effects on man through the aquatic food chain rather than through his drinking water. Though arsenic is accumulated by plants and aquatic organisms, it is not known to have caused toxic effects on man as a result of consumption of foods that have high concentrations accumulated from polluted waters. Rather, acute and chronic arsenic poisoning is due to ingestion of polluted drinking water. The potential problems of arsenic toxicity are water to man interactions with organisms altering the chemical state of arsenic but not accumulating toxic quantities through a food chain.

Arsenic in water supply systems is not a current problem in the United States. McCabe *et al.*¹ found arsenic exceeding the U.S.P.H.S. recommended limiting concentration (0.01 mg/l) in 0.5 per cent of the treated water samples, and exceeding the maximum permissible limit (0.05 mg/l) in 0.2 per cent of the samples. The U.S.P.H.S. standards are stringent, and water purveyors are doing an excellent job of providing water free of this and other toxic elements. However, arsenic is found in fresh surface waters of the

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U. S. frequently enough to merit interest in arsenic removal in natural systems and in water treatment processes. In analyses of fresh surface waters in the U. S., arsenic was found in about 7 per cent of the 1500 samples from 150 rivers,² and in 21 per cent of 727 samples from rivers and lakes.³ In almost every case in which arsenic was detected, the concentration exceeded the recommended limiting concentration of 0.01 mg/l. In the first survey, the mean of arsenic values in violation of the U.S.P.H.S. permissible limit was 0.1 mg/l, a factor of 10 above the permissible limit and 2 above the maximum limit. Arsenic concentrations exceeded the U.S.P.H.S. standards far more frequently than any other element potentially hazardous to human health. It is not known whether arsenic is effectively removed by any water treatment system in the U. S. Conventional wisdom has conservatively assumed ineffective removal of toxic elements, including arsenic,⁴ although studies have appeared from time to time demonstrating rather high removal of arsenic to residual levels within the U.S.P.H.S. standards. The U.S.P.H.S. standards are customarily applied to the raw water source with no assumed removal of the element in the water treatment process. It is very likely that water supply systems have used alternative sources when high levels of arsenic have been encountered, rather than relying upon removal in processing. In future decades, as demand for water continues to increase, it is highly likely that some localities will prefer to process water to remove arsenic in order to meet standards for drinking water rather than find an alternative source.

Treatment technology for removing arsenic from water supplies has been reviewed recently by Patterson and Minear.⁵ A bewildering variety of chemical processes have been successfully used, as summarized in Table 7.I. Either arsenic can be readily removed by almost any process, or arsenic removal processing is subject to few generalizations. Review of the studies cited in Table 7.I discounts the former possibility. Processes that were effective in some instances were often used unsuccessfully in others.

The purpose of this paper is to review the chemical speciations of arsenic in natural waters, the possible conversions between species, and the significance of this speciation for removal technology. Included are a discussion of the removal of different forms of arsenic and a description of the results of experimental work on adsorption of arsenic.

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Table 7.I

Arsenic Treatment Methods and Removals Achieved.
Adapted from Patterson and Minear.⁵

<i>Treatment</i>	<i>Initial Arsenic mg/l</i>	<i>Final Arsenic mg/l</i>	<i>Per Cent Removal</i>	<i>Reference</i>
Lime Softening	0.2	0.03	85	5
Precipitation with Lime (plus iron)	---	0.05 or less	--	5
Charcoal Packed Bed	0.2	0.06	70	5
Ferrous Sulfide Filter Bed	0.8	0.05	94	7
Coagulation with Ferric Sulfate	25.0	5 or less	80 or more	26
Coagulation with Ferric Chloride	3.0	0.05	98	27
Precipitation with Ferric Hydroxide	---	0.6	--	5
Precipitation with Ferric Hydroxide	272.0	11-15	94-96	5
Precipitation with Sulfide Salt	---	0.05	--	5
Alumina Packed Bed	0.06	0.006	90	21

SPECIATION AND MECHANISMS OF CONVERSION

The equilibrium relations among arsenic species can be computed using thermodynamic data. An Eh-pH diagram for the arsenic system (10^{-5} M arsenic), including 10^{-3} M sulfur summarizes information on predominant soluble species and solids.⁶

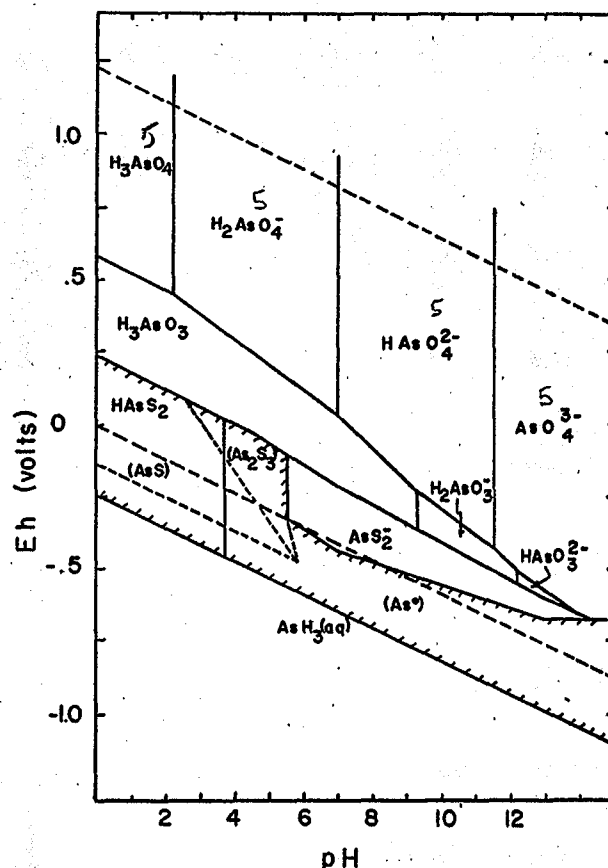


Figure 7.1. The Eh-pH diagram for As at 25°C and one atmosphere with total arsenic 10^{-5} M and total sulfur 10^{-3} M. Solid species are enclosed in parentheses with dashed boundary line. Cross-hatched area indicates solubility less than $10^{-5.3}$ M. Stability of water is indicated by dashed lines. Adapted from Ferguson and Gavis.⁶

In oxygenated waters, arsenic acid species (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-}) are stable. Under mildly reducing conditions, arsenious acid species (H_3AsO_3 , H_2AsO_3^- and HASO_3^{2-}) become stable. The arsenic oxides, As_2O_5 and As_2O_3 , are too soluble to appear in the diagram. Under conditions where sulfide is stable, realgar (AsS) and orpiment (As_2S_3) occur as stable solids at pH values below approximately 5.5 and Eh values of approximately 0 volts. The predominant species at low pH in the presence of sulfide is $\text{HASs}_2(\text{aq})$. It has maximum solubility of $10^{-6.5} \text{ M}$ (0.025 mg/l As). AsS_2^- predominates at pH greater than 3.7; above pH 5.5 its concentration is 10^{-5} M . At still lower Eh values elemental arsenic is thermodynamically stable. Although As^0 solubility in water has not been reported, it is undoubtedly low. At very low Eh values, arsine (AsH_3) may be formed. Arsine is only slightly soluble; the calculated line for a concentration of $10^{-5.3} \text{ M}$ in solution corresponds to a partial pressure of about 1 atm. If iron were included, ferric arsenate ($\text{pK}_{\text{sp}} 20.24$) would have a small region of stability at pH below 2.3 and Eh above +0.74 V. There are no other arsenic-containing solids with measured solubilities low enough to result in arsenic concentrations less than 0.05 mg/l ($10^{-6.2} \text{ M}$).

The available thermodynamic data indicate that low Eh conditions in the presence of sulfide should result in effective removal of As(III). Packed beds of ferrous sulfide and the addition of hydrogen sulfide have been used in removal processes.⁷ Precipitation of ferrous sulfide in a solution originally containing arsenate adsorbed on ferric hydroxide did not cause removal of arsenic, probably because the arsenate was not reduced to arsenic(III).⁸ Thermodynamic data provide few other clues about possible removal processes. There are several stable, soluble arsenic species, but few sufficiently insoluble arsenic solids. The data, of course, provide no information about rates of any of the possible reactions.

It is necessary to look elsewhere in order to understand arsenic concentrations in nature and the removal of these concentrations in water treatment processing. In Figure 7.2, a schematic cycle of reactions is shown for arsenic in a stratified lake.⁶ The diagram indicates that arsenic may be oxidized from 0 to (III) to (V), that ligand exchange reactions with OH^- , H_2O , and S^{2-} may occur, and that removal to sediments may occur through precipitation as well as sorption and biological uptake. The cycle is hypothetical

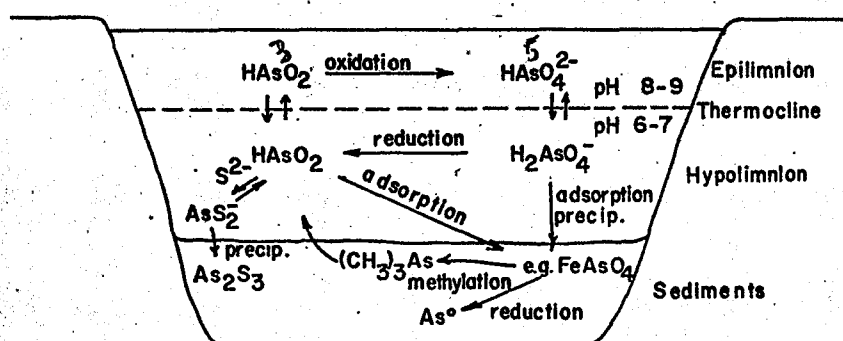


Figure 7.2. Cycle proposed for arsenic in a stratified lake. Adapted from Ferguson and Gavis.⁶

since some of the reactions shown have not been studied in an aquatic environment; however, all the reactions are consistent with experimental observations.

There seems to be a well-developed biogeochemical cycle for arsenic. Microorganisms enter the cycle by mediating reactions that are kinetically slow or in some cases thermodynamically unfavored. In any particular water, arsenic may be present in various chemical forms that will react differently in water treatment processes, as well as pose different hazards to consumers of the water.

The two parts of this cycle that will be discussed in some detail are the balance between arsenite and arsenate in aerobic waters and the possible methylation of arsenic.

Recent measurements by Johnson and Pilson⁹ of arsenic (III) and (V) in the Sargasso Sea can be interpreted with care for implications for concentrations in freshwaters. These measurements confirmed earlier ones by Sugawara and Kanamori¹⁰ that arsenic in seawater is present in significant amounts in the (III) oxidation state, as well as the stable (V) state. The persistence of 20 to 75% of the total arsenic as arsenite can be explained by postulating addition of mostly As(III) and a negligible rate of oxidation, or a steady state between the rate of oxidation of As(III) and the reduction of As(V) . Johnson and Pilson¹¹ explored these possibilities for seawater and found the rate of arsenite oxidation to be very slow, but still much higher than needed to oxidize arsenite completely in the oceans, where the residence time for arsenic is estimated at 60,000 years. They also demonstrated that arsenate in non-sterile seawater enriched with glucose can be reduced to arsenite, and postulated that in the sea

a steady state exists between the chemical oxidation and the bacterial reduction. The authors have not found measurable chemical oxidation of arsenite in fresh water systems over a four month period and believe chemical oxidation to be unimportant in freshwaters. Others have found rapid oxidation of arsenite solutions to be catalyzed by bacteria.^{12,13}

Reduction of arsenic species to either dimethyl or trimethyl arsine has been identified in several systems but not yet in water.¹⁴⁻¹⁷ The authors are not aware of any study of the rate of oxidation of methylarsines in water. It is possible that the reduction observed by Johnson and Pilson was to a methylarsine, which was subsequently oxidized to arsenite during their experiment or to arsenate during chemical analysis. There is no doubt that methylarsines occur in nature. The possible production of another methylated species in water, its importance in aquatic cycling of arsenic, its stability, accumulation, toxicity, and removal in processing all merit study, even though there is no reason to suspect toxic effects like those found for mercury.

In lakes or other fresh surface waters there is likely to be a partitioning of arsenic between the oxidation states. Depending on the arsenic sources, the relative rates of chemical and bacterial oxidation of As(III), the rate of bacterial reduction of As(V) and the presence or absence of an anaerobic hypolimnion, the As(III) content could be large or small. Though the concentrations of the species are important, little more can be reported at present. No measurements in freshwaters are reported, and information about the rates of the reactions is insufficient to make predictions.

In addition to the single sweep polarographic technique described by Whitnack and Brophy,¹⁸ with modifications given in this paper, there are now colorimetric techniques for separately measuring arsenic(III) and (V) at environmental levels.^{19,10} The measurement of the forms of arsenic should become routine in any case where levels approach the drinking water standard. Toxicity is associated primarily with As(III), and removability is affected by the chemical state. Future drinking water standards might well be set for both arsenic(III) and total arsenic, as is done for hexavalent and total chromium.

The oxidation state of arsenic is equally important in ground waters. It seems likely that the soluble species would be near equilibrium with their environment.

ARSENIC REMOVAL

In the face of uncertainty about species, the task of removing arsenic has been approached by trial and error. Plausible, though not necessarily accurate, explanations can be contrived for chemical conditions leading to success or failure of the processes listed in Table 7.I.

Removal in water treatment by precipitation processes with calcium, iron or aluminum salts may be accomplished by precipitation of an insoluble solid, for which thermodynamic information is not available, by occlusion in the precipitated solids, or by adsorption on their surfaces. The terms precipitation, occlusion and adsorption are used to distinguish loosely between the following:

1. Formation of a stoichiometric phase, which may be undetectable by conventional chemical or X-ray analysis and constitutes only a minor fraction of the precipitate;
2. Incorporation into the interior of a solid either in lattice sites or in interstices; or,
3. Association with the surface of the precipitate without specifying the kind of bonds causing the association.²⁰

There are no data to indicate that any solids formed with arsenic or arsenious acid species are insoluble enough to cause removal to low levels in water treatment. However, there are no thermodynamic solubilities reported for arsenite solids and only a few reported arsenate solubilities. For arsenate, which is very similar to phosphate, it seems probable that the variety and complexity of the possible precipitated solids have not been appreciated. There may be highly insoluble solids that can be precipitated from solution.

The experimental studies described later in this paper are intended to determine the importance of adsorption of arsenite and arsenate onto amorphous ferric and aluminum hydroxides. The findings cast doubt on the importance of adsorption as a removal mechanism in water treatment precipitation processes. The remaining phenomenon, occlusion, seems the most likely mode of arsenic removal. Occlusion has been restricted to include only phenomena such as ion entrapment, lattice substitution and solid solution formation. Even so, occlusion is vague, hard to measure, and difficult to distinguish from adsorption in rapid precipitations.

Removal in water treatment by packed bed processes is evidently accomplished by adsorption in the case of charcoal beds and alumina beds. Epitaxial precipitation may be important in the case of ferrous sulfide beds, as arsenic readily forms strong, predominantly covalent bonds with both iron and sulfur. The tendency to bond with these elements causes arsenic to change its coordinative partners readily, especially if it is in the (III) oxidation state. In the presence of sulfide, arsenic(V) should be reduced; however, it is doubtful whether this reaction occurs rapidly.⁸ In Taiwan,⁷ removal of arsenic from ground water onto ferrous sulfide beds is consistent with the presence of As(III). The chronic arsenicism found in the area also implies that As(III) was present. In Fallon, Nevada, the removal onto both alumina columns and charcoal beds provides no clues to the oxidation state.² Arsenate species have a high affinity for aluminum, though perhaps no greater affinity than arsenite has.

The need to know the chemical state of arsenic in order to understand its removal is repeatedly apparent. This knowledge is certainly not vital as there is no immediate need to remove arsenic. Trial and error has served well when removal methods have been needed. However, arsenic, as a constituent of surface waters, is important enough to merit serious study of the removal of its various chemical forms. The tools are at hand to acquire a detailed understanding of arsenic removal. The experimental work described in the remainder of this paper is an attempt to begin this task.

Procedure

All glassware used in the experiments was soaked in 0.25 *N* HCL for 24 hours or more, washed, and then rinsed three times with distilled deionized water, which was also used in all sample and reagent preparations. Polarography cells were treated in similar fashion, but were rinsed five times.

Standard arsenate solutions were prepared by weighing Fisher reagent grade sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7 \text{H}_2\text{O}$) and diluting it to a working stock of $2.67 \times 10^{-2} \text{ M As(V)}$. Standard arsenite solutions were prepared with Baker "Dilut It" (NaAsO_2) vials and kept under nitrogen to prevent oxidation. A working stock solution was $2.51 \times 10^{-2} \text{ M As(III)}$. Arsenate must be reduced to arsenite to facilitate

polarographic analysis of samples. The reducing agent used by Johnson and Pilson¹⁹ was used in this instance. Fresh reagent was prepared daily and kept stoppered during use.

In order to obtain solids with reproducible characteristics, it was necessary to prepare aluminum and ferric hydroxide precipitates using the procedures which follow:

To prepare aluminum hydroxide, 33.32 g of Fisher reagent grade $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ was weighed out and dissolved in 950 ml water. This was stirred for 1 hour and then titrated with 30 ml of 10 *N* NaOH at a dropping rate of 1 ml/30 sec. At the end of the titration, the pH, which was above 8.0, was adjusted to pH 7.0 by adding 0.1 *N* HCL. After aging the precipitate for another hour, the suspension was washed with 950 ml water over Whatman 42 filter paper. The aluminum hydroxide precipitate was then resuspended in another 950 ml water. The washed, resuspended precipitate was aged once more for 12 to 20 hours before use. The pH in each batch was monitored and was stable at the end of the aging. In various batches the final pH ranged from 6.2 to 6.9.

To prepare iron hydroxide, 48.20 g of reagent grade $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 950 ml water. The solution was then treated using a similar procedure as was used for aluminum hydroxide. However, it should be noted that the final pH, after adding 30 ml of 10 *N* NaOH, was very close to 7.0; therefore, no attempt was made to adjust it further.

Measures of the characteristics of an amorphous precipitate that affect its adsorptive behavior might include surface charge and isoelectric point, the amount of hydrolysis, the surface area, and any structural features the solid may have. The pH change was used as a surrogate for a direct measure of the precipitate characteristics. The solids were aged until pH changes were negligibly slow as compared to the reaction times in the experiments. From X-ray analyses of the precipitates with time, the suspensions used at the time of the experiments were amorphous $\text{Al}(\text{OH})_3(\text{s})$ and $\text{FeOOH}(\text{s})$. Only after one and one-half months did $\text{FeOOH}(\text{s})$ show some poorly characterized ordering peaks of goethite. The $\text{Al}(\text{OH})_3(\text{s})$ showed no signs of ordering even after one and one-half months.

Surface areas were not measured in the experiments but can be expected to be of the order of $100 \text{ m}^2/\text{g}$ for these precipitates. Isoelectric points from 6.6 to 7.3 for amorphous $\text{Al}(\text{OH})_3(\text{s})$ and from 6 to 8.6 for amorphous

FeOOH(s) have been reported.²² The precipitates used in these experiments were prepared in a manner similar to procedures used by Mattson,²³ who found isoelectric points of 7.1 for FeOOH(s) and 7.5 for Al(OH)₃(s). Because the isoelectric point of metal hydroxide precipitates is variable as a function of sample history, it is quite possible that in these tests the isoelectric point was as much as a pH unit away from reported values.

Ten-ml aliquots of stirred suspended precipitates were taken and filtered on pre-weighed Whatman 42 filter paper. These were dried for 4 hours at 104° C and weighed to establish the weight concentration of the suspension. Experimental samples were prepared in volumetric flasks by adding, in order, a small portion of water, arsenic stock, and an aliquot of suspension, and then filling the flask to mark. "Zero time" was considered to be after the prepared solution was shaken 20 times, at which time the samples were transferred to stoppered Erlenmeyer flasks. Kinetic experiments were run in a 25 ± 0.5° C temperature bath. Samples were stirred with a magnetic stirring bar. After drawing an aliquot from the flask for analysis, the flask was flushed with N₂ and resealed to prevent oxidation. The pH and adsorption isotherm samples were placed in a shaker in a thermostatically controlled room at 25 ± 0.5° C.

The duration of equilibrium adsorption experiments was between 20 to 24 hours after which aliquots were drawn for analysis. Arsenic(III) analysis was performed immediately. Ten-ml aliquots of samples to be assayed for As(V) were placed in 25-ml Erlenmeyer flasks, to which 0.4 ml of reducing agent was added. These samples were stoppered and analyzed the following day.

Arsenic analysis was done on a Model 1660 Davis Differential Cathode Ray Polarotrace. Traces were reproduced on a Honeywell strip chart recorder with a chart speed of 1 in./sec. Mercury dropping rate was set at 0.037 g/min. Bath temperature was 26.4° C. One ml of Hg was used in each polarography cell. Arsenic(III) was polarographed with a start potential of 0.8 volts; the sweep takes the applied potential through 1.3 volts. RC derivative proved useful to lessen slope complications. Three drops of concentrated H₂SO₄ were used as a carrier electrolyte in 3 ml of sample. Degassing with N₂ was done for two minutes without skirt and for one minute with skirt in place. A standard curve plotting log units for peak height against log concentration proved to be linear at concentrations from 1 × 10⁻³ to 5 × 10⁻⁵ molar As(III).

Arsenic(V) will not produce a polarotrace and must be reduced to arsenic(III). Prior to running the arsenic(V) samples, the Erlenmeyer flasks were unstoppered and aerated for 30 minutes to relieve the systems of dissolved SO_2 . It was found that 0.4 ml would reduce up to $5.0 \times 10^{-3} M$ As(V); however, at lower concentrations between $1 \times 10^{-5} M$, 0.2 ml would be more satisfactory. A concentration of 0.4 ml can be used for all samples, but lower ranges require greater amplification. The unused portion of the reducing agent causes a reduction wave which tends to reduce the size of the peaks. The scanning potential was the same as for As(III). Sample size was 4 ml, and no supporting electrolyte was needed as it was already present in the reducing agent itself. Degassing with N_2 was done for two minutes without skirt and for two minutes with skirt in place. Standard curves were prepared for As(III), as previously mentioned.

EXPERIMENTAL RESULTS

Adsorption Kinetics

In all cases adsorption was initially rapid with 50 to 95 per cent of the total removal taking place before the first sample was taken as shown in Figure 7.3. Removal continued

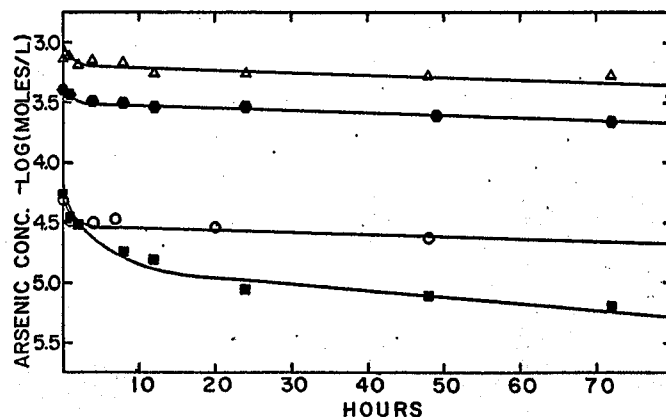


Figure 7.3. Arsenic adsorption as a function of time (initial As Conc. $1 \times 10^{-3} M$) ● As(V) on FeOOH (.766 g/l), ○ As(V) on $\text{Al}(\text{OH})_3$ (1.29 g/l), ■ As(III) on FeOOH (.685 g/l), △ As(III) on $\text{Al}(\text{OH})_3$ (1.04 g/l).

slowly over the 72 hour length of the experiments. The extent of the reaction varied significantly with about 99.5% removal of As(III) on FeOOH(s), 97% removal of As(V) on Al(OH)₃(s), 86% of As(V) of FeOOH(s), and 50% of As(III) on Al(OH)₃(s). Adsorption varied from 0.435 mmol/g for As(III) on Al(OH)₃(s) to 1.45 mmol/g for As(III) on FeOOH(s). These values are large and indicate that specific adsorption of the molecules was involved.

The pH values of the unbuffered suspensions were monitored throughout the test, and the values, shown in Figure 7.4,

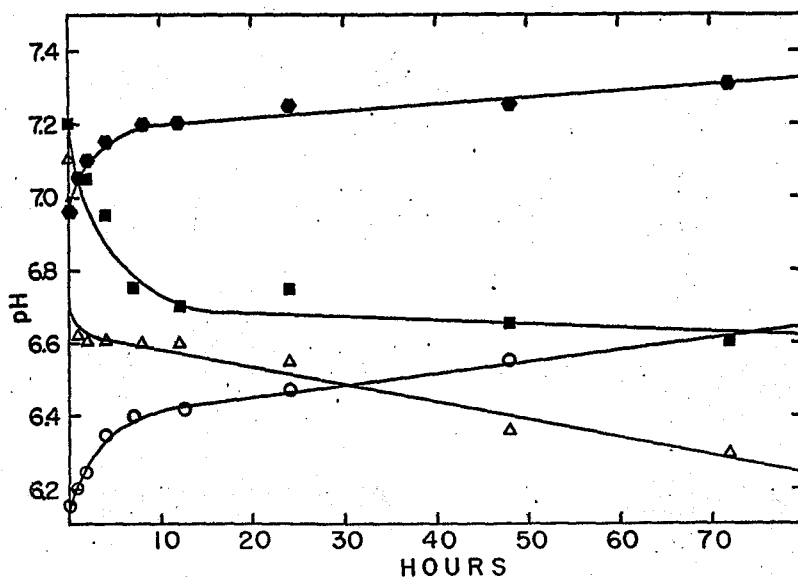
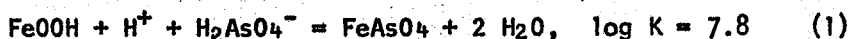


Figure 7.4. Arsenic adsorption pH changes as a function of time (initial arsenic Conc. 1×10^{-3} M)
 ● As(V) on FeOOH (.766 g/l), ○ As(V) on Al(OH)₃ (1.29 g/l) ■ As(III) on FeOOH (.685 g/l), △ As(III) on Al(OH)₃ (1.04 g/l).

drifted slowly upward for As(V) adsorption and slowly downward for As(III) adsorption. Initially, the pH values changed more slowly than the As concentrations. The precipitates showed no pH drift in the absence of arsenic.

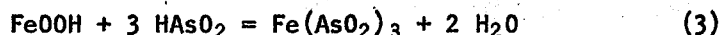
Using solubility data for ferric and aluminum arsenate and amorphous hydroxides, it was calculated that the initial arsenate solutions were undersaturated ($K/Q \approx 10^{-1}$) with respect to conversion of the hydroxide to the arsenate (Equations 1 and 2).



At the end of the experiment, undersaturation was increased ($K/Q \approx 10^{-3.1}$).

Arsenate was taken up only slightly by ferric hydroxide and much more extensively by aluminum hydroxide. Precipitation is evidently not involved, and adsorption does not follow the relative solubilities of the arsenates. Aluminum, which demonstrates more extensive removal, has a solubility product for arsenate more than four orders of magnitude greater than ferric iron.

The removal of arsenite might be accomplished by precipitation of aluminum or ferric arsenite (Equations 3 and 4).



Ferric orthoarsenite is reported to be slightly soluble; however, no solubility products have been located for either solid.

For "equilibrium" adsorption studies, a time period of 20 to 24 hours was selected and then used in all subsequent experiments.

Effect of pH.

Experiments were conducted in which the initial pH was varied by addition of acid or base so that the final pH would range between 6 and 8. The final pH values for arsenite adsorption were 0.3 to 0.5 units lower than the initial values, while the pH for arsenate adsorption drifted upward 0.2 to 0.3 pH units. The results of these experiments are shown in Figure 5. As(V) adsorption is at maximum or saturation values, but, as described in the following section, no saturation adsorption was found for As(III). There was considerable "scatter" in the data but little variation in removal with pH over the range tested.

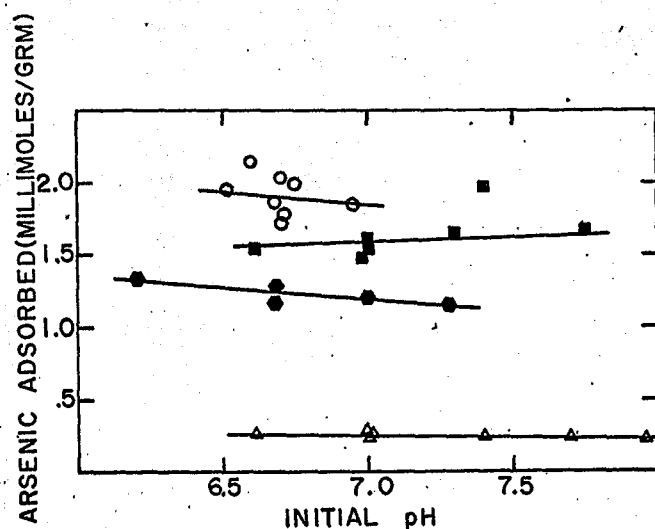


Figure 7.5. pH effects on adsorption (initial As conc. 1×10^{-3} M) ● As(V) on FeOOH, ○ As(V) on Al(OH)₃, ■ As(III) on FeOOH, △ As(III) on Al(OH)₃.

Reported zero point of charge (ZPC) values for amorphous Al(OH)₃(s) and amorphous FeOOH(s) are slightly basic. Negatively charged or uncharged molecules were removed onto an initially neutral or slightly positively charged surface. It was expected that if electrostatic interactions were important, adsorption of As(V) would decrease as the pH increased towards pH_{ZPC}. Alternatively, based on studies of anion adsorption onto goethite,²⁴ decreasing adsorption of arsenate and arsenite species with increasing pH might be expected, with inflections in the adsorption pH curve at pK values. No significant effects were observed.

For arsenate, the pH drifted upwards indicating an exchange, qualitatively similar to Equations 1 and 2, where an initially uncharged or positively charged surface hydroxyl group reacts with H₂AsO₄⁻ and takes up protons during the process. The stoichiometry of the proton exchange has not been determined; however, it is believed that the adsorption process results in a net uptake of anions and, hence, a reduction of the surface charge (Stern Layer) of the particles and in a reduction in

pH_{ZPC}.²⁵ Further experiments are planned to determine the reaction stoichiometry and the effect on electrophoretic mobility.

For arsenite, H_3AsO_3 is adsorbed with the release of protons. The experimental pH range is far from the pK_1 of 9.2. Since the adsorption reaction is probably between an uncharged surface hydroxyl group and an uncharged molecule, the observed lack of an effect of initial pH on adsorption is not surprising. Additionally, electrostatic interactions should have little influence.

Adsorption Isotherms

A series of experiments was conducted to measure the adsorbent/adsorbate concentration relations for the two solutes onto the two solids. Conditions for the experiments are shown in Table 7.II. The results are given in Figure 7.6 and Figure 7.7, which show, respectively, the entire concentration range and an expanded diagram of the low concentration range. Adsorption of As(V) shows saturation at high concentrations. The lines are Langmuir isotherms fitted to the data. The data in a linearized form are shown in Figure 7.8, together with the selected isotherms. As(III) adsorption showed no saturation up to surface excesses of several mmol/g of adsorbate, which are extremely large values even for a high surface area material.

If the isotherms are extrapolated to the low concentrations of interest in water treatment, it can be calculated that for a dose of 100 mg/l of alum or 50 mg/l of ferric chloride, removal of an initial arsenic concentration of 0.1 mg/l would be 34% for As(V) on $Al(OH)_3(s)$, 3.8% for As(III) onto $Al(OH)_3(s)$, and 11% for As(III) or (V) onto $FeOOH(s)$. These calculations are made assuming the same surface area to weight ratios as for the precipitates. Such an extrapolation to the origin is legitimate only to make the observation that adsorption on hydroxides does not appear promising for purposes of removal to meet drinking water standards. The literature provides examples of iron and alum precipitation that uphold these results,²⁶ as well as ones that do not.²⁷ It is believed that another mechanism, precipitation or occlusion, must be operating in the cases where high removals to low residuals have been observed.

Table 7.II

Adsorption Isotherm Experimental Conditions

Adsorption	Precipitate Concentration g/l	pH Range		Final Concentration Range (mol/l)	
		Initial	Final	Initial	Final
As(V) on Al(OH) ₃	0.29 - 1.40	6.9 - 8.0	7.2 - 8.3	5×10^{-6} - 5×10^{-3}	
As(V) on FeOOH	0.29 - 2.90	5.4 - 6.4	5.6 - 6.6	5×10^{-6} - 5×10^{-3}	
As(III) on Al(OH) ₃	0.20 - 1.30	6.8 - 7.8	6.3 - 7.3	2×10^{-4} - 6×10^{-4}	
As(III) on FeOOH	0.12 - 0.78	7.0 - 8.0	6.5 - 7.5	1×10^{-4} - 6×10^{-4}	

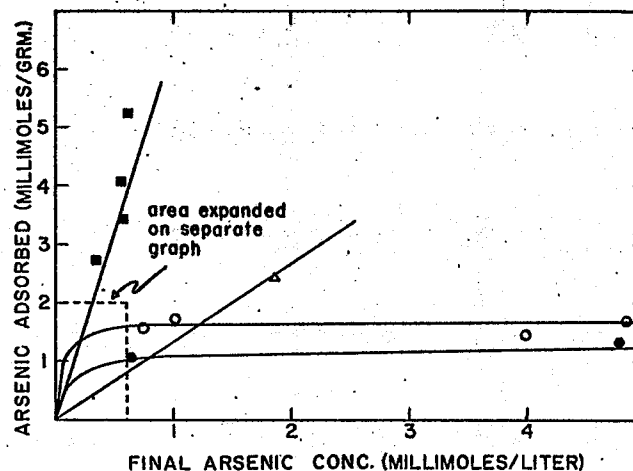


Figure 7.6. Arsenic adsorption isotherms (not showing data points in dashed area) ● As(V) on FeOOH, ○ As(V) on Al(OH)₃, ■ As(III) on FeOOH, △ As(III) on Al(OH)₃.

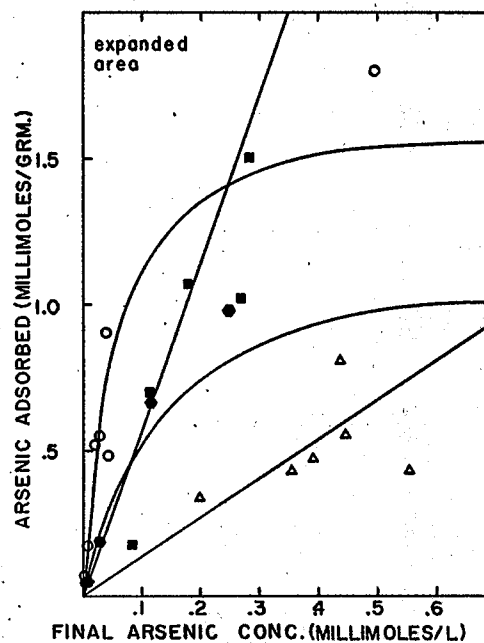


Figure 7.7. Adsorption isotherms (low concentration range) ● As(V) on FeOOH, ○ As(V) on Al(OH)₃, ■ As(III) on FeOOH, △ As(III) on Al(OH)₃.

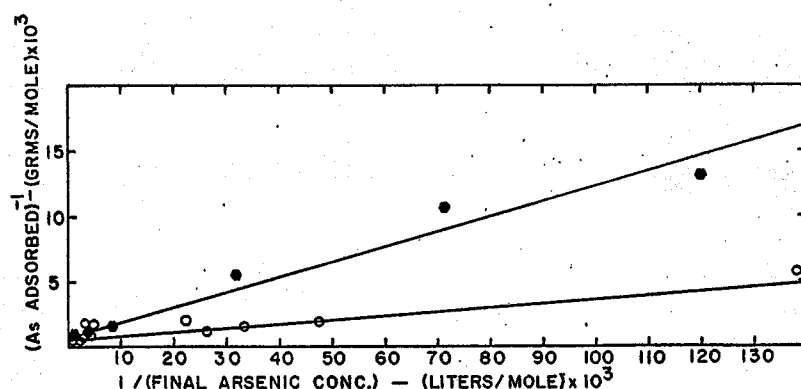


Figure 7.8. Linearized adsorption isotherms using Langmuir equation $\left(\frac{1}{\Gamma} = \frac{1}{\Gamma_o K_L S} + \frac{1}{\Gamma_o}\right)$

● As(V) on FeOOH ($\Gamma_o = 1.25 \text{ m M/g}$, $K_L = 7.30 \times 10^3 \text{ l/mol}$),

○ As(V) on Al(OH)₃ ($\Gamma_o = 1.70 \text{ m M/g}$, $K_L = 19.7 \times 10^3 \text{ l/mol}$).

SUMMARY AND CONCLUSIONS

It was found that arsenic species may be adsorbed in large quantities onto the surfaces of amorphous ferric and aluminum hydroxides. The adsorption varies greatly with the oxidation state of the arsenic, but not with the pH within the range of 5.5 to 7.5. This adsorption evidently does not account for the high removals that are sometimes found in arsenic removal studies. The adsorption of arsenic species has posed many interesting questions. These relate first to understanding interactions between anions or neutral molecules and hydroxide surfaces. It is not clear, for instance, whether arsenate adsorption can be explained solely in terms of the molecule-surface interaction or whether the charge, concentration and identity of the cation must also be considered. Also, the question remains as to why the same initial removal of both As(III) and (V) is found on FeOOH(s), and why saturation is not observed with As(III). At the highest surface excesses, on the order of mmol/g, the cation to arsenic ratio is between 10 and 2.

At these values can there be a useful conceptual distinction between adsorption, occlusion and precipitation for removal onto an amorphous solid?

A second set of questions concerning the mechanism of arsenic removal in water treatment arises. Does the surface area or the nature of the surface change enough during precipitation so that adsorption, or occlusion, may be the removal mechanism in contradiction to the present results with aged precipitates? What is the role of precipitation of arsenic solids in removal? To what extent can removal be maximized by controlling mixing and flocculation in a precipitation process?

A final set of issues is related to the speciation of arsenic in water sources. The concentrations of arsenite and arsenate can now be measured at environmental levels, and information about the cycling of arsenic species is rapidly accumulating. These advances can be utilized in routine measurement of arsenic species and the establishment of separate standards for arsenic(III) and (V). Relaxation of standards for arsenic(V) may allow use, without removal processing, of many of the surface waters that now equal or exceed the recommended limiting concentration of the U.S.P.H.S. Drinking Water Standards. In other cases, water sources that present a true hazard can be identified with certainty.

The relative abundance in the past of uncontaminated water sources near metropolitan areas no longer exists. Present understanding of arsenic removal mechanisms is still not advanced; however, studies to date indicate that removal processing seems to be approaching technological feasibility. Perhaps it is now reasonable to rely on processing to remove arsenic. In any case, the high levels of arsenic in surface waters and the demand for increased quantities of water for municipal supply indicate that careful consideration of standards and policies with respect to treatment is in order.

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