

Removal of Arsenic (V) From Water by Adsorption on Aluminum and Ferric Hydroxides

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The removal of arsenic from drinking water at water-treatment plants is shown here to be affected by pH and doses of suitable coagulants.

A study of the removal of arsenic (V) from water by adsorption on aluminum and ferric hydroxides was undertaken to simulate the removal of arsenic (V) by conventional water-treatment processes. To follow this removal, a radioactive isotope, As^{75} , added in the form of sodium arsenate, Na_2HAsO_4 , was used as a tracer. A carrier solution of sodium arsenate was added to bring the arsenic concentration in the test solutions to the USEPA limit of 0.05

mg/l. The conventional water-treatment practices simulated in the study included coagulation with aluminum or ferric sulfate, rapid mix, slow mix, sedimentation, and filtration.

Source of Arsenic in the Environment

There is no one distinct source of arsenic in the environment. Arsenic is naturally distributed throughout the earth's biosphere and can be found just about anywhere. In the

ocean the arsenic concentration is approximately 14 tons/cu mi³ in many areas. On land, arsenic makes up approximately 0.00005 per cent² of the earth's crust. The concentrations of arsenic shown in Table I represent typical values in some soils and rocks.

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Arsenic is found in many soils and deep-sea sediments. Common mineral forms of arsenic compounds are arsenopyrite ($FeS_2 \cdot FeAs_2$), realgar (As_2S_3), and orpiment (As_2S_3).² Arsenic forms permanent compounds in virgin soils at a concentration varying between 1.3 and 2.3 ppm.⁴ Deep-sea sediments have been found to have an arsenic concentration ranging from a few parts per million to as much as 435 ppm on a carbonate-free basis in unconsolidated, noncontaminated sediments.⁵

The highest concentrations of arsenic in the deep-sea sediments are found in areas where active oceanic ridges are present. Several theories have been developed as to why the high concentrations of arsenic have been found on these active ridges. One of these theories is that the arsenic is adsorbed from the sea water on a colloidal ferromanganese precipitate that is quite characteristic of many of the active ridges.

From the use of geochemical balance calculations it has been determined that these high arsenic concentrations have not developed through the normal methods of weathering of continental rocks containing arsenic. It is possible that these high concentrations arise from the leaching and depletion of arsenic in rocks or buried sediment. However, the leaching of pelagic sediments containing 40 ppm arsenic in the ocean could not account for the high concentrations of arsenic on active ridges. Another possibility that has been suggested is that as these active oceanic ridges bring forth gas and other materials from the earth's interior, a high concentration of arsenic is also brought forth and deposited on the ridges.⁶ This latter theory would be consistent with the fact that many soils surrounding volcanoes contain high concentrations of arsenic (20 ppm).⁴

Arsenic is very widely used in industry. Arsenicals have been used as part of agriculture for many years as insecticides, herbicides, and algaecides (see Table 2).

In recent years, with the development of organic arsenicals such as DEMSA, $[(CH_3)_2AsO(CH_3)]$, and cacodylic acid, $[(CH_3)_2AsO(CH_2)]$, many of the inorganic forms have dropped out of use.⁷

Arsenic trioxide has been used for sheep-dip and to preserve hides and

skins of animals. Also referred to as "white arsenic," it is the basic source for manufacture of other arsenic compounds. Arsenic trioxide is a fine white powder. Odorous and tasteless, it makes an excellent poison.⁸

Lead arsenate and calcium arsenate are used as insecticides and are highly toxic. Paris green is also used as an insecticide.

Other industrial applications of arsenic compounds include utilization as wood killers, rusticides, wood preservatives, decolorizers in glass manufacturing, formulation of pigments, and manufacture of lead shot.⁹ Arsenic is also used indirectly in industry through the burning of coal containing pyrite. According to a study published by Dunn in 1933, English industrial cities were found to have arsenic concentrations varying between 50 and 400 ppm in their atmospheres.¹⁰

Arsenic is also added to the environment when fertilizers are applied to croplands. Many fertilizers are made using calcium phosphate, which may contain over 20 ppm of arsenic.⁷

The application of 25×10^6 pounds of arsenic compounds to the environment annually for weed control has increased the arsenic concentrations in the environment.⁷ Similarly, the use of phosphate detergents has resulted in additional release of arsenic to the environment. Arsenic is found in detergents as a constituent of phosphate builders at concentrations of 70-80 ppm.¹¹ As a result, laundry waters have been found to contain from 5 to 100 ppb of arsenic. The concentration of arsenic in the Kansas River has been found to be in the range of 2 to 8 ppm.¹²

It can be seen that through man's actions in industrial, agricultural, and domestic endeavors the arsenic concentration in the environment has increased. There increases need careful scrutiny to determine the effect of arsenic on public water supplies.

Benefits of Arsenic

Arsenic can be used by man to provide tremendous benefits. For instance, DEMSA and cacodylic acid are well-known organic herbicides used for control of weeds. DEMSA is used to kill the perennial weeds and Johnson grass. It has proven to be an extremely economical herbicide, es-

TABLE 1
Arsenic in Soils and Rocks

Material	Arsenic Concentration—ppm
Impure realgar	1-9
Soils (USA)	1.3
Phosphate rocks	20.0
Coal (Illinois, W.V.)	0.5
Pyrite (USA)	1,000
Sphalerite (Germany)	1,000

TABLE 2
Inorganic Arsenic Compounds Used for Pest and Weed Control

Arsenic Compound	Chemical Formula
Lead arsenate	$Pb_3(PO_4)_2 \cdot 3As_2O_3$
Lead arsenite	$Pb_3(PO_3)_2 \cdot 3As_2O_3$
Lead hypophosphite	$Pb_3H_2P_2O_7$
Arsenic trioxide	As_2O_3
Arsenic pentoxide	As_2O_5
Calcium arsenate	$Ca_3(AsO_4)_2$
Barium arsenate	$Ba_3(AsO_4)_2$
Lead arsenite	$Pb_3(AsO_3)_2$
Lead arsenate	$Pb_3(AsO_4)_2$
Calcium arsenite	$Ca_3(AsO_3)_2$
Paris green	$Cu_3(AsO_4)_2 \cdot 4CuSO_4 \cdot 5H_2O$

TABLE 3
Effect of Arsenic in the Ration Diet for Baby Pigs

Addition of 0.1% 4-Hydroxyphenyl arsinic acid to ration— ppm	Improvement—ppm	
	Weight Gain Growth Rate	Feed Conversion Efficiency
0	100	100
1.1	27.4	26.4

pecially for use in areas where weed growth is heavy. Cacodylic acid is also effective against weeds and functions as a contact herbicide to defoliate and desiccate a large variety of plants.⁷ These organic arsenicals have greatly increased in popularity and have replaced many of the inorganic arsenicals.

Arsenic also seems to be of nutritional value in the diet of pigs. In a study to determine the effects of growth rate and feed-conversion efficiency, 3-dimethyl-4-hydroxyphenyl-arsinic acid supplemented the diet of 60 pigs. The results are presented in Table 3.¹³

The results of the experiment make it apparent that the arsenic improved both the growth rate and the feed-conversion efficiency. On the basis of these data alone, it appears that arsenic compounds may have a place in the raising of livestock in the future.

In the present light of environmental concerns, the beneficial effects of arsenicals are being relegated to a position of little importance. The major emphasis in studies concerning arsenic is on the deleterious effects of arsenic on the environment.

Many arsenic compounds are known for their toxicity to man as both poisons and carcinogenic

agents. The carcinogenic effect of arsenic is a fairly recent discovery, and little is known of its exact mechanism.¹⁰ The molecular biology of arsenic carcinogenesis involves the human epidermal cells. Inorganic-bound arsenite inhibits replication of DNA and interrupts the repair mechanisms.¹¹ A possible cause is the blockage of DNA polymerase by the linkage of arsenate to guanine groups.

Lead arsenate and sodium arsenite are both toxic compounds of arsenic. The poisoning is caused by the absorption of the compound through the skin or by inhalation or ingestion of the compounds.

Acute poisoning involves four major areas. The first area is the digestive system. Symptoms include vomiting of blood-stained or bile-stained mucus and constipation, accompanied by increased temperature and pulse. The second area of disturbance is the skin, which suffers eruptions characterized by redness and swelling of the eyelids and nostrils, erythema over the entire body, and loss of nails and hair. The third dis-

turbance is a sensitivity that is accompanied by such symptoms as headache, numbness, stiffness, crawling and pecking sensations in the toes, feet, and legs; and the partial cramping of muscles. The final disturbance is motor paralysis, which causes death upon paralysis of the heart.¹²

In the past there have been several instances of toxicity effects being directly related to arsenical poisoning. The miners of the Schneeberger schistite arsenide mines in Saxony, Switzerland, had a high percentage of malignant tumors of the lungs from breathing coal dust. Chénobryevsky's cancer and leukemias among the miners have been attributed to the high percentage of arsenic in the coal that was burned. In Haffner in 1902, an epidemic of arsenical poisoning was caused by drying beer malt in air heated by burning coal that contained arsenic.¹³

Additional problems with arsenic in the environment arise because of its phytoxic effects on certain plants. The phytoxic effect of certain arsenic compounds is related to its structural analogy to other compounds. Arsenic is capable of replacing phosphorus in the plant cell, but it is unable to perform the biological functions of phosphorus.¹⁴

Obviously, arsenic can have beneficial effects on the environment when used under controlled conditions. However, when looking at the entire spectrum of arsenic in the environment, it becomes apparent that arsenic has the potential to be extremely hazardous to both plants and animals.

Aqueous Chemistry of Inorganic Arsenic

Sodium arsenite, NaAsO_2 , is the form of arsenic that is most frequently used as a weed killer. When sodium arsenite is added to water with a pH less than 9.3, the predominant aqueous form is HAsO_2 . If the solution pH is greater than 9.5, then AsO_2^- is the predominant aqueous species. Arsenite, As (III), is oxidized to arsenate, As (V), in the presence of oxygen, chlorine, or potassium permanganate.

The other species of arsenic that is commonly found in water is the arsenate ion, AsO_4^{3-} . Although the arsenate ion is toxic, it is not so toxic as arsenite. The chemistry of arsenate is very similar to that of phosphate, PO_4^{3-} . Arsenic (V) exists in four forms in aqueous solution: H_2AsO_4^- , HAsO_4^{2-} , HAsO_3^- , and AsO_4^{3-} . The predominant form is dependent upon the pH of the water. A representation of the predominant ionic form of arsenic (V) for a given pH is given in Fig. 1. The equilibrium expressions used by constructing Fig. 1 are given in Table 4.

Experimental Procedure

Batch studies of the removal of arsenate by coagulation, sedimentation, and filtration utilized radioactive tracer, As^{75} , carried in the form of sodium arsenate. A dilution of the tracer was made so that the test water would exhibit a count rate of 10,000 to 20,000 cpm, using a 10-ml sample in a well-type NaI crystal scintillation counter. This would permit the observation of a two order of magnitude reduction in arsenic concentration with great accuracy.

The USEPA recommended limit for arsenic concentration in drinking water is 0.01 mg/l and the required limit is 0.05 mg/l. Since the half-life of arsenic constituted only 0.00041 $\mu\text{g/l}$, it was necessary to augment the jar-test solutions with a carrier solution of nonradioactive sodium arsenate to bring the initial arsenic concentration to 0.05 mg/l.

In performing each jar test the following procedure was followed: One liter of Champagne-Urbain tap water was added to a test beaker, followed by 0.1 ml of the radioactive-tracer solution and the sodium arsenate carrier solution to bring the arsenic concentration to 0.05 mg/l. This solution was then divided into

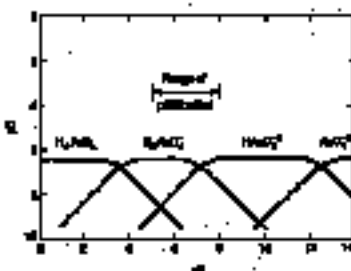


Fig. 1. Distribution of Arsenic (V) Species in 6.7×10^{-3} M Solution (pH 6.7) of Arsenic Acid

TABLE 4
Equilibrium Expressions for the Products of Arsenic Acid

$\text{H}_2\text{AsO}_4^- = \text{H}^+ + \text{HAsO}_4^{2-}$	$K_1 = 2.4 \times 10^{-2} = \frac{[\text{H}^+][\text{HAsO}_4^{2-}]}{[\text{H}_2\text{AsO}_4^-]}$
$\text{HAsO}_4^{2-} = \text{H}^+ + \text{AsO}_4^{3-}$	$K_2 = 1.1 \times 10^{-7}$, where $[\text{H}^+][\text{AsO}_4^{3-}] = [\text{HAsO}_4^{2-}]$
$\text{H}_2\text{AsO}_3 = \text{H}^+ + \text{HAsO}_3^-$	$K_3 = 6.6 \times 10^{-2} = \frac{[\text{H}^+][\text{HAsO}_3^-]}{[\text{H}_2\text{AsO}_3]}$
$\text{HAsO}_3^- = \text{H}^+ + \text{AsO}_3^{2-}$	$K_4 = 2.1 \times 10^{-7}$, where $[\text{H}^+][\text{AsO}_3^{2-}] = [\text{HAsO}_3^-]$
$\text{HAsO}_3^- = \text{H}^+ + \text{AsO}_2^-$	$K_5 = 2 \times 10^{-11} = \frac{[\text{H}^+][\text{AsO}_2^-]}{[\text{HAsO}_3^-]}$
$\text{AsO}_2^- = \text{H}^+ + \text{AsO}_3^{2-}$	$K_6 = 2.1 \times 10^{-11}$, where $[\text{H}^+][\text{AsO}_3^{2-}] = [\text{AsO}_2^-]$
Arsenic (V) concentration = 0.05 mg/l = $[\text{H}_2\text{AsO}_4^-] + [\text{HAsO}_4^{2-}] + [\text{HAsO}_3^-] + [\text{AsO}_4^{3-}]$	
$\frac{0.05 \text{ mg/l}}{75 \text{ g/mol}} = 6.67 \times 10^{-4} = 6.7 \times 10^{-4} \text{ M/l}$	
$\frac{0.05 \text{ mg/l}}{75 \text{ g/mol}} (6.7 \times 10^{-4}) = 6.7$	

two 300-ml aliquots. One aliquot served as a control and the other was used for testing purposes. Finally, the pH was adjusted in both the control and the test solution. The original count rate was then determined on 10-ml aliquots of both solutions.

The stock solution of alum, $(Al_2(SO_4)_3 \cdot 18H_2O)$, was made by adding 1 g of alum to 1 l of deionized water, giving a concentration of alum equaling 1 mg/ml. The stock solution of ferric sulfate, $(Fe_2(SO_4)_3 \cdot 9H_2O)$, was made by adding 1 g of hydrated ferric sulfate to 1 l of deionized water, giving a concentration of hydrated ferric sulfate equal to 1 mg/ml.

Once the control and test solutions had been made, the initial flocculation steps were taken. The coagulant was added to the test solution along with any coagulant aids. No coagulant was added to the control solution, because it was used to determine how much of the As^{5+} was adsorbed on the glassware, mixing paddles, and filter medium.

In performing the rapid mix and slow mix flocculation, a mechanical stirring device with a variable-speed motor was used. A 1-min period of rapid mixing was followed by 30 min of slow mixing and 20 min of sedimentation in the beakers. At the end of this time, 10-ml samples from both the control and test solutions were taken and rotated to determine the percentage removal of the As^{5+} .

The final step in the simulated water-treatment process was the filtration of 10-ml samples of both the control and test solutions through 0.45- μ m cellulose acetate-membrane filters.

Experimental Results

Arsenic removal was observed as a function of pH and coagulant dose. The results are given in tables 3 and 6.

The experimental results, expressed as the percentage removal of arsenic (V), show that arsenic adsorption on ferric hydroxide exceeds the adsorption on aluminum hydroxide. In both cases, increased coagulant dosage results in increased arsenic removal. The results also indicate that arsenic removal is somewhat pH dependent. This is shown in Fig. 2, 3. Although there is little difference in arsenic removal at the

lower pH reactions, a noticeable decrease in removal is seen at pH 3.0. These decreases are observed for both

ferric and aluminum coagulants. The decrease in the adsorption of arsenic at pH 3.0 on both aluminum

hydroxide and ferric hydroxide may be the result of the change in the ionic form of the arsenic (V) from $H_2AsO_4^-$ to $HAsO_4^{2-}$ (Fig 1). Alternatively, at the higher pH, the hydroxyl ion may begin to compete for the exchange sites on the ferric and aluminum hydroxide precipitates.

Summary

The use of conventional water-treatment practices as simulated in jar-test studies shows a substantial removal of the arsenic (V). The removal of the arsenic (V) was accomplished by the adsorption of the arsenic (V) on aluminum and ferric hydroxide.

The main variables affecting the adsorption process as determined in this experiment were the pH and coagulant dosage. With increasing coagulant dosage there was a consistent increase in the removal of arsenic (V) at all pH levels. It appears that the pH became important because of the change in the ionic form of the arsenic (V).

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