

## *Effect of Arsenic Speciation on Remediation of Arsenic-Contaminated Soils and Waters*

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### **Abstract**

There are many Technologies for removing arsenic from drinking water and soils. Before selecting a treatment technology, it is necessary to know forms of As present in water or soil. Arsenic mobility and toxicity is greatly affected by its speciation. In groundwater, inorganic As commonly exists as As(V) (arsenate) and As(III) (arsenite), the latter being considered to be more mobile and toxic for living organisms, While Organic arsenic species are very much less harmful to health, and are readily eliminated by the body. Additionally, As(III) is more mobile in soils than As(V) and organic As is less mobile compared to inorganic forms of As. There for Conversion of As(III) to As(V) is a critical element of any arsenic treatment process. In this article, arsenic species in different environmental conditions (i.e. Eh and pH) was compared and efficiency of different remediation technologies for these conditions was discussed.

**Keywords:** Arsenic, Environment, Toxicity, Remediation

### **Introduction**

Arsenic is a metalloid with the atomic number 33, atomic weight 74.9216, symbol As and placed in the group VA of the periodic table of elements together with nitrogen, phosphorus, antimony and bismuth. Its electron configuration is  $[Ar]18 4s^2 3d^{10} 4p^3$ ; elemental As has therefore 5 valence electrons (Petrusevski et al., 2007).

Arsenic is 20th in abundance in the Earth's crust (2-3 mg As/kg). Major As-containing primary minerals are arsenopyrite ( $FeAsS$ ), realgar ( $As_4S_4$ ), and orpiment ( $As_2S_3$ ). Realgar ( $As_4S_4$ ) and orpiment ( $As_2S_3$ ) are the two common reduced forms of As. Arsenic occurs in oxidized form in the mineral arsenolite ( $As_2O_3$ ) (Bhattacharya et al., 2007).

Arsenic is released into the environment from two principal pathways: natural processes and industrial activities. Arsenic released in the environment through natural processes such as weathering of rocks and sediments, hydrothermal ore deposits, volcanic eruptions, geothermal activities, forest fire, wind-blown dust, and seasalt. Arsenic is also released in the soil environment due to Mining, smelting, ore processing, pesticides, fertilizers, and chemical industries (Bhattacharya et al., 2007; Henke and Hutchison, 2009).

The typical concentration of As in fresh water is 0.1-80  $\mu g/L$  (Naidu et al., 2006). In general, As(III) is more mobile in

soils than As(V). The mobility and bioavailability of As are reported to be greater in sandy soils compared to clayey soils and only a limited amount (20%) of the total As in soils is easily mobile and the greater fraction (80%) is not available for plants due to strong binding of As with Fe and Al mineral phases (Bhattacharya et al., 2007).

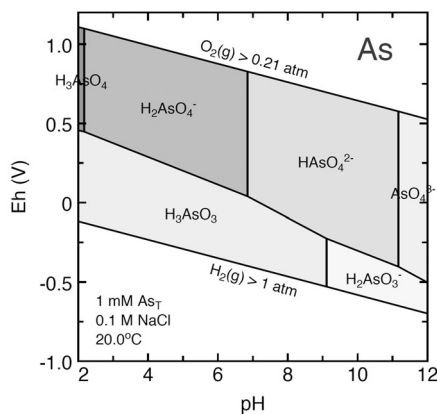
The most important As species in the aquatic and terrestrial environments are the oxyacids, arsenite ( $H_3AsO_3$ ;  $pK_1=9.2$ ; undissociated at neutral pH) and arsenate ( $H_3AsO_4$ ;  $pK_1=2.2$ ; anionic at neutral pH). Dissolved organic compounds may also influence As mobility by several mechanisms. Stable complexes of fulvic or humic acids may block arsenic absorption by Fe oxides, alumina, and quartz. In this environment, microbes play an important role by causing a reductive dissolution of metal oxides and release of As bound in the oxides and organic phases. The presence of dissolved organic carbon (DOC) in reducing aquifers is associated with increased As mobilization (Bhattacharya et al., 2007).

Total arsenic is the sum of both particulate arsenic, which can be removed by a 0.45- micron filter, and soluble arsenic. Soluble arsenic occurs in two primary forms: inorganic and organic. Organic arsenic species are abundant in seafood, and include such forms as monomethyl arsenic acid (MMAA), dimethyl arsenic acid (DMAA), and

arseno-sugars. They are very much less harmful to health, and are readily eliminated by the body (Petrusevski et al., 2007).

As(V) exists in four forms in aqueous solution based on pH:  $H_3AsO_4$ ,  $H_2AsO_4^-$ ,  $HAsO_4^{2-}$ , and  $AsO_4^{3-}$ . Similarly, As(III) exists in five forms;  $H_4AsO_3^+$ ,  $H_3AsO_3$ ,  $H_2AsO_3^-$ ,  $HAsO_3^{2-}$ , and  $AsO_3^{3-}$ . The ionic forms of As(V) dominate at pH > 3, and As(III) is neutral at pH < 9 and ionic at pH > 9 (Petrusevski et al., 2007).

Since the net charge of As(III) is neutral at natural pH levels (6-9), this form is not easily removed. Figure 1 shows the Eh-pH diagram of arsenic species (Petrusevski et al., 2007).



**Figure 1.** Eh-pH diagram of arsenic species (Petrusevski et al., 2007)

The redox stability of As(III) and As(V) is dependent on the pH and Eh in solution. At low pH, As(III) is prevalent between 0 and 500 mV and As(V) is stable above 500 mV. As the pH increases, As(III) is stable only if the Eh continuously decreases. The stability of As(V) increases beyond 0 mV as the pH increases. (Naidu et al, 2006; Ravenscroft et al, 2009; Nordstrom and Archer, 2003; Nriagu et al., 2007).

Iron and its eventual oxidation are important controls on arsenic speciation in water. If a water contains little iron, as could be the case in many groundwaters and high pH mine drainages, an appreciable amount of arsenate may be found at pH > 4 (Bednar et al., 2005).

This article is a review of arsenic removal technologies with emphasize on their ability to remove different arsenic species.

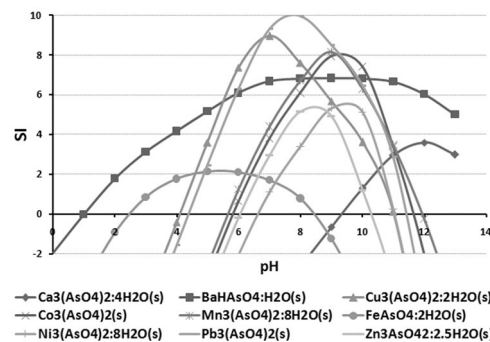
**Precipitation processes**

Both As(V) and As(III) behave as chelates and precipitates with many metallic cations.  $Ca_3(AsO_4)_2$  is the most stable

As(V) species in well-oxidized alkaline environments. Under reducing conditions and high concentrations of Mn in the soils the solubility of As is controlled by  $Mn_3(AsO_4)_2$ . (Naidu et al., 2006). Saturation index is a appropriate criterion for comparing tendency of different metals to precipitate with arsenic, and is defined as bellow:

$$SI = \log [IAP / K_s] \quad (1)$$

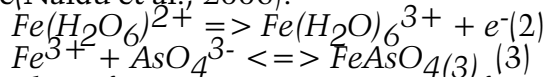
Where IAP and  $K_s$  are ion activity and solubility constant, respectively. Positive SI values suggests that precipitation occurs. Fig. 2. shows SI for different metal-arsenic compounds in different pH values of solution (this figure was drawn using Visual MINTEQ software).



**Figure 2.** Saturation index for arsenic precipitates with different metals, As(III)=As(V)=10 mM, metal con.=100 ppm, I=0.1, Eh=0.2, T=25 °C.

It can be seen from fig. 2 that arsenic (As(V)) forms solid species with many metallic cations, especially in pH range 4 to 12.

Sims et al. (1986) described a fixation process in which As(V) contaminated solids are treated by the 1:1 addition of ferrous sulfate ( $FeSO_4 \cdot 4H_2O$ ) solution to produce ferric arsenate. It is apparent that  $O_2$  availability is one of the key factors controlling the process.  $FeAsO_4$  is an insoluble phase(Naidu et al., 2006).



There for arsenic can precipitate from solution either by metallic cations directly or by co-precipitation with metallic hydroxides. Conventional coagulation involves the formation of large, non-dispersed particles from a colloid, such as hydrated  $Fe_2(SO_4)_3$ , and a solute, such as  $H_2AsVO_4^-$ (Naidu et al., 2006).

**Ion exchange**

Small-scale systems and point-of-entry (POE) systems (treating water as it enters the

home or building) often use ion exchange (IX) for arsenic removal because of ease of handling and sludge-free operation. However, treatment costs are higher than for conventional treatment in large-scale systems. The predominant species of As(V),  $H_2AsO_4$  and  $HAsO_4$ , are negatively charged, and thus are removable by IX. Ion exchange does not remove As(III) because As(III) occurs predominantly as an uncharged ion ( $H_3AsO_3$ ) in water with a pH value of less than 9. If As(III) is present, it is necessary to oxidise As(III) to As(V) before removal by IX (Petrusevski et al., 2007). The IX process has been cited as best available technology for the removal of As from water with low sulfate (<50mg/l) and low nitrate (<5mg/l). Total dissolved solids should be less than 500mg/l (Bhattacharya et al., 2007). Sulfate and nitrate ions are negative and so can compete with negative arsenic species for ion exchange process. Higher pH values may be preferred because arsenic species become not only more ionic but also more negative.

#### Membrane filtration

Membrane processes can remove arsenic through filtration, electric repulsion, and adsorption of arsenic-bearing compounds. The viability for arsenic removal is highly dependent on the size distribution of arsenic bearing particles in the source water. Membrane filtration is effective in removing both As(III) and As(V) species. However, efficiency in removing As(V) is higher than for As(III) (Petrusevski et al., 2007).

#### Adsorption processes

Adsorption involves the use of granular adsorptive media for the selective removal of arsenic from water with or without pH adjustment and with or without spent media regeneration. Several granular adsorptive filter media have shown high effectiveness in arsenic removal from water. These include activated alumina, activated carbon, iron oxide coated or based filter media including some commercial media like Aqua-Bind MP, ArsenX, Bayoxide E33 ferric oxide, Granular Ferrichydroxide (GFH), MEDIA G2, manganese greensand etc (Petrusevski et al., 2007).

Above pH 2.20, the charge on the As(V) oxo-acid is negative. In soils and sediments, the surfaces of quartz grains and secondary clay minerals are coated with pH-dependent metal oxides whose charge is positive until approximately pH 8, where the

point of zero charge for most aluminum (Al) and iron (Fe(III)) oxides occurs. Arsenate is therefore electrostatically attracted to surfaces of ferrihydrite, goethite, hematite or  $\gamma$ - $Al_2O_3$ . Arsenate is hence less mobile than the non-ionic As(III) in the environment. Arsenate adsorption increases with decreasing pH, while As(III) adsorption maximum generally occurs near its first dissociation constant (9.22). Interestingly, methylated As species also sorb onto Fe-oxides with an affinity in the order from As(V) > DMAA > As(III) > MMAA (Naidu et al., 2006).

Knowledge of the composition of the soil solution and its relative concentration is critical, because potential competitors for surface sorption sites can be assessed (e.g.  $PO_4$ ,  $MoO_4$ ,  $SeO_4$ ,  $SO_4$ ) and will help to determine if As forms ion complexes in solution, which would affect its sorption characteristics. Phosphate and molybdate in suspensions of metal oxides and clays decrease the adsorption of As(V) on these sorbents (Naidu et al., 2006).

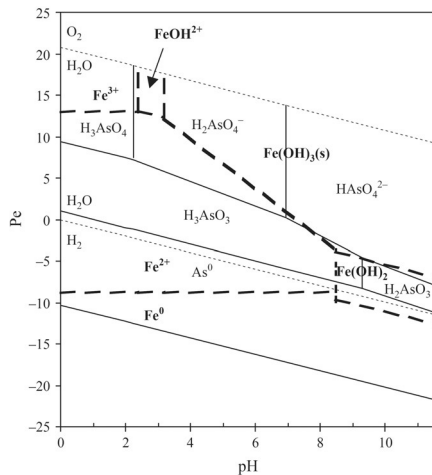
In a short column study it was observed that pyritic and oxidic materials sorbed between 2500 and 5000 mg/kg of As(V), respectively. As(III) was removed far more successfully than As(V) over a wide pH range between 2 and 10 in goethite concentrations of 0.5 and 1 g/L in solution (Naidu et al., 2006).

#### Arsenic removal by zero-valent iron

Bang et al. (2005) studied removal of arsenic with zero valent iron filings in water. Batch experimental results showed that As(III) removal rate was faster than As(V) removal rate at pH 4 and 7 under anoxic conditions. XPS spectra showed that As(III) was reduced to As(0) by Fe(0) under anoxic conditions within 5 days. The reductions from As(V) to As(III) occurred slowly in As(V)-Fe(0) system. As(III) inhibited the anoxic corrosion of iron more dramatically than did As(V). Under oxic conditions, As(III) removal was slower than As(V) removal at pH 7. The removal of arsenic under oxic conditions was attributed to the adsorption on ferric hydroxides formed rapidly through oxidation of Fe(0). Fig. 3 shows the pe-pH diagram for the As-Fe- $H_2O$  system at 25 °C. Fe(0) can reduce highly soluble As(V) and As(III) to sparsely soluble As(0). On the other hand, iron hydroxides possess a high adsorption capacity for As(V) and As(III) (Bang et al., 2005).

It can be seen from Fig. 3 that ferric

hydroxide ( $\text{Fe}(\text{OH})_3$ ) precipitates from solution in a wide area with high pe and pH. In these conditions arsenic species such as  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  can be adsorbed on ferric hydroxide surface and easily removed from aqueous solution. While in more reducing areas reduction of As(III) to As(0) by oxidation of iron is dominated, resulting in removal of neutral As(III) species.



**Figure 3.** Pe-pH diagram for the As-Fe- $\text{H}_2\text{O}$  system at 25 °C. Total As = 4  $\mu\text{M}$ ; total Fe =  $10^{-4}$  M (Bang et al. (2005)).

### Electroremediation of As-contaminated soils

The electroremediation process involves the application of a direct voltage between electrodes placed in the soil. The concept is based on the electrophoretic mobility of contaminant ions in the direction of charged electrodes. The process also involves the movement of pore-water dragged along by ions, usually cations, to the cathode. The latter process, described as the electrokinetic phenomenon or electroosmosis, enables the removal of both ionic and non-ionic forms of contaminants (Naidu et al., 2006).

### Bioremediation of As-contaminated soil

Bioremediation is based on the remediation of contaminated sites using either microorganisms or plants to detoxify the site, largely by transforming or degrading the pollutants. Bioremediation of As-contaminated soils is based on the ability of the microbes or mold and fungi to transform As either into a less toxic form (particularly through bio-oxidation) or into a form that allows the concentration to be reduced by volatilization or leaching (particularly through biomethylation) (Naidu et al., 2006).

They are also beneficial because of their role in facilitation of oxidation of ferrous ions

to ferric that lead to the precipitation of iron compounds like ferric hydroxide or jarosite. Precipitation of these compounds cause further arsenic removal by co-precipitation or adsorption processes.

Microorganisms or plants which are used to detoxify the arsenic contaminated sites should be able to grow and live in presence of high concentrations of heavy metals that is common in contaminated soils and waters. For example, bacteria, called as *Bacillus arsenoxydans*, could grow in culture media containing up to 1%  $\text{As}_2\text{O}_3$  as arsenite and brought about its oxidation to arsenate (Naidu et al., 2006).

### Conclusion

As discussed above, arsenic removal from water and soil is greatly dependent on its oxidation form. While As(V) can be removed easily by different remediation methods, As(III) species are more mobile since their neutral charge in a wide pH values. As(III) hardly forms ionic species even in presence of strong complexing agents and there for its oxidation to As(V) is essential for its removal from contaminated soils or waters.

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