

## **Reactive Contact System for Arsenic Removal Using Iron and Sulfur-Based Environment**

\*Bahngmi Jung<sup>1)</sup>, Dong Suk Han<sup>1)</sup>, Ahmed Khodary<sup>1)</sup>, and Ahmed Abdel-Wahab<sup>2)</sup>

Chemical Engineering Program, Texas A&M University at Qatar, PO Box 23874, Doha, Qatar

\*[bahngmi.jung@qatar.tamu.edu](mailto:bahngmi.jung@qatar.tamu.edu)

### **ABSTRACT**

Arsenic contamination has seriously threatened public health and the environment in many countries because of its carcinogenicity. Recent research has demonstrated that particulate iron sulfides can remove arsenic from solution and bind it in a stable solid phase. In this study, an attempt to remove arsenic by reductive precipitation with mixtures of iron and sulfur were investigated. Experimental results showed the formation of strong bonds between arsenic and iron sulfide mixtures. However, the stability of final residuals was dependent on pH, and ratios of Fe, S, and As concentrations. Consequently, the interaction of arsenic with particulate iron sulfides or aqueous-phase mixtures of Fe and S may regulate arsenic solution concentration in reducing environment and could be considered to be reactive contact system, resulting in less release back to environment.

### **1. INTRODUCTION**

The maximum contaminant level (MCL) of arsenic has been lowered recently from 50 µg/L to 10 µg/L. This will require installation of many new treatment facilities that will produce large amounts of residuals contaminated with arsenic. Concerns have been raised as to the technical feasibility of existing technologies and regulatory implication of the new standard on the disposal of these residuals. The toxicity characteristic leaching procedure (TCLP) limit for arsenic is anticipated to be lowered to 1000 µg/L from the current level of 5000 µg/L, causing a larger number of residuals to be classified as hazardous wastes and thereby come under additional regulatory control. Landfilling is the best method for disposal of arsenic bearing residuals, but high concentrations of dissolved organic carbon in landfills allow microorganisms to produce moderately reducing conditions. Such conditions result in reduction of As(V) to As(III) and release of this more soluble and more toxic form of arsenic to the surrounding

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<sup>1)</sup> Research Associate

<sup>2)</sup> Associate Professor

environment. Furthermore, iron (oxy)hydroxides that may stabilize arsenic can suffer reductive dissolution and release more arsenic. Stabilization processes should be designed so that arsenic is strongly immobilized under conditions in the disposal zone. Reductive stabilization processes do this by forming low-solubility solids that are stable under reducing conditions. Such solids would contain arsenic, sulfide and sometimes ferrous iron. Sulfide and ferrous iron are obvious reductants to apply in order to achieve formation of these solid phases. Although existing knowledge demonstrates the potential for sulfide-based stabilization methods to effectively immobilize arsenic, it is not sufficient to indicate how such technologies can be made to perform optimally. Therefore, the goal of this study is to understand reductive stabilization processes for arsenic by evaluating reactions of arsenic with sulfur and ferrous iron.

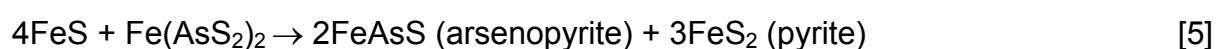
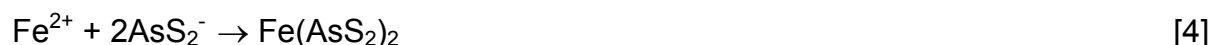
## 2. CHEMISTRY OF ARSENIC AND ARSENIC CONTAINING SOLIDS

Arsenic is a metalloid that occurs in a variety of forms, oxidation states, and valences. Arsenic is perhaps unique among the heavy metalloids and oxyanion-forming elements in its sensitivity to mobilization at pH values typically found in groundwaters (pH 6.5 – 8.50) and under both oxidizing and moderately reducing conditions. The two primary oxidation states of importance in natural waters are the +5 oxidation state (arsenate or arsenic acid) and the +3 oxidation state (arsenite or arsenious acid) (Ferguson and Gavis 1972; O'Neil 1995). However, arsenic can also exist in oxidation states such as As(II) in realgar (As<sub>2</sub>S<sub>2</sub>) and As(-I) in arsenopyrite (FeAsS). Arsenic acid has pK<sub>a</sub> values at 2.20, 6.97 and 11.53 while arsenous acid has pK<sub>a</sub> values of 9.22, 12.13, and 13.40. Therefore, the pK<sub>a</sub> values indicate that in the pH range of most natural waters, arsenate is present as a mono- or divalent anion while arsenite is neutrally charged (O'Neil 1995). The difference in the charge of the two oxidation states in natural waters plays an important role in the respective environmental chemistry because arsenite is more mobile and adsorbs less strongly than arsenate. Under oxidizing conditions, arsenate is the thermodynamically stable form. In reducing conditions, arsenite becomes the thermodynamically stable form. In anoxic water systems, bacterial actions will result in reducing conditions, as indicated by the reduction of SO<sub>4</sub><sup>2-</sup> to S<sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> to CH<sub>4</sub>. Under the influence of these reducing conditions As(III) will become more thermodynamically important. When sulfide is present in such reducing environment, arsenic sulfide solid phases such as realgar (As<sub>2</sub>S<sub>2</sub>) and orpiment (As<sub>2</sub>S<sub>3</sub>) can form. These solids occur as stable solids over a range of pH values at Eh values of about or below 0 Voltage (Cullen and Reimer 1989; Vink 1996). The primary forms of naturally occurring arsenic minerals are sulfides and iron sulfides, such as arsenopyrite (Smedley and Kinniburgh 2002). Moore et al. (1988) stated that sulfide can reduce As(V) to As(III) prior to formation of arsenic sulfide solid phases. These reactions can be described as (Moore et al. 1988; Rochette et al. 2000).





Rochette et al. (2000) indicated that under moderately reducing conditions dissolved arsenic-sulfur complexes may account for sizable levels of As, provided the solution is undersaturated with respect to solid arsenic-sulfides such as orpiment ( $\text{As}_2\text{S}_3$ ). Results of these studies proposed the formation of  $\text{H}_x\text{As}_3\text{S}_6^{x-3}$  species (Rochette et al. 2000). At highly reducing conditions and excess of sulfide, these species react with  $\text{H}^+$  and/or  $\text{S}^{2-}$  in order to form orpiment. Under acidic conditions, the reaction of sulfide and thioarsenite with ferrous iron can result in the formation of sulfoslats, of which reaction was proposed as follows: (Kim et al. 2000):



Arsenic-containing minerals such as arsenopyrite, orpiment and realgar are generally believed to form at high temperature and pressure (Smedley and Kinniburgh 2002). However, orpiment can be easily formed in the laboratory and arsenopyrite has been reported to be formed by microbial action in the lab (Rittle and Drever 1995). Even if formation of arsenopyrite is difficult, it may be possible to form arsenian pyrite ( $\text{Fe}(\text{S,As})_2$ ) (Smedley and Kinniburgh 2002), which may approach the low solubility of arsenopyrite.

### 3. MATERIALS AND METHODS

All reagent solutions were prepared using reagent grade chemicals and deoxygenated deionized water. Deoxygenated deionized water (18.2 M $\Omega$ ) was acquired by a Barnstead Nanopure filter system and purged with  $\text{N}_2$  gas (purity > 99.99 %) for at least 2 hours, then the purged water was stored in an anaerobic chamber.  $\text{NaAsO}_2$  (Sigma-Aldrich) and  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (Sigma-Aldrich) were used for As(III) and As(V), respectively. All batch reactors were prepared in anaerobic chamber to characterize the removal of arsenic in solution containing iron and sulfide. Arsenic-sulfide solutions were created using stock solutions of arsenic (III) and sulfide, made with  $\text{NaAsO}_2$  and  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (Sigma-Aldrich). The pH of solution was controlled using 1 N HCl or 1 N NaOH.

Analytical procedures were developed for arsenic (As(III) and As(V)). The technique for arsenic analysis was based on the continuous hydride generation/atomic absorption spectrometer (model AA240 FS fast sequential AAS) with a hydride generator manufactured by Varian (model VGA 77AA) using Standard Method 3114C (Masscheleyn et al. 1991). At low pH, both As(III) and As(V) will be reduced by sodium borohydride (1.5 %  $\text{NaBH}_4$  in 0.5% NaOH) in strong acid (6N HCl) to arsine gas ( $\text{AsH}_3$ ). The arsine gas was removed from the solution by purging with a flow of argon and it is transferred to the flame AA where its concentration is determined by comparison with standard responses. The detection limit for total arsenic was found to be 0.59 ppb.

## 4. RESULTS AND DISCUSSION

Figure 1 shows total arsenic concentration, final solution pH, and oxidation-reduction potential with reaction time. Total arsenic concentration was rapidly decreased by 82% ~ 92% in 1 hour in sulfidic solution. Here, the loss of arsenic may be caused by sulfide converting arsenite to arsenic-sulfur complexes which was not measured by the current hydride-generation AA technique. No solid phase was formed when the concentrations of As, S, and Fe are 1 mg/L (~13.3  $\mu\text{M}$ ), 5 mM, and 5 mM, respectively. The absence of Fe(II) may increase the formation of arsenic-sulfur complexes showing more arsenic removal (Fig. 1a). Many studies have demonstrated that the formation of arsenic-sulfur complexes (thioarsenates) plays a key role for the mobility and toxicity of arsenic in sulfidic conditions (Bostick et al. 2005; Stauder et al. 2005) and they were identified using ion chromatography with inductively coupled plasma mass spectrometry (IC-ICP-MS). Stauder et al. (2005) have found that thioarsenates are formed in sulfidic groundwater and artificial arsenite hydrogen sulfide solutions. The dominant thioarsenate-anions were  $\text{HAsO}_3^{2-}$ ,  $\text{HAsO}_2\text{S}_2^{2-}$ ,  $\text{AsOS}_3^{3-}$ , and  $\text{AsS}_4^{3-}$ . In this study, the As-S-Fe solution showed a high pH of 11.5 under no additional pH adjustment and reducing condition showing ORP reaching to - 270 mV (Fig. 1b).

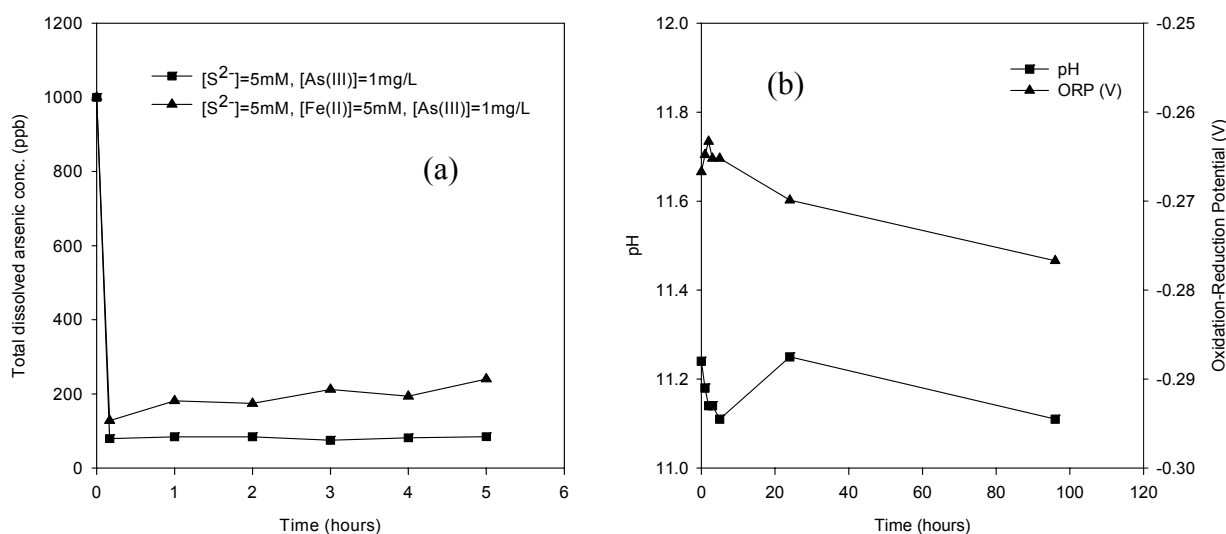


Fig. 1. Measured total arsenic concentration (a), pH and oxidation-reduction potential (b) in As-S-Fe solution. The initial concentrations of initial As(III),  $\text{S}^{2-}$ , and Fe(II) in Fig. 1b were 1 mg/L, 5mM, and 5 mM, respectively.

At the same molar ratio of sulfide and iron as shown in Fig.1, the effect of pH was investigated for arsenic removal in As-S-Fe solution. The initial arsenic concentration was 100 mg/L. The results showed that total arsenic was removed by 89.6%, 67.9 %, and 16.9 % at pH 4, 6, and 8, respectively in 1 day. After filtering using 0.45 $\mu\text{m}$  filter, the color of the remnant solid was different (Fig. 2a and 2b). At pH 8, no solid was formed on the filter. Another experiment was conducted at pH 4 and at different molar ratio of sulfide. In this case, a yellowish solid was observed on the filter as shown in Fig.

2c. This result demonstrates that different reactions will occur at different pH conditions. Stauder et al. have suggested that the acidification of samples to pH 4-6 resulted in a transformation of thioarsenates. This is supported by the solid identification with another analytical method, attenuated total reflection using infrared Fourier transform (ATR-FTIR) in a further study.

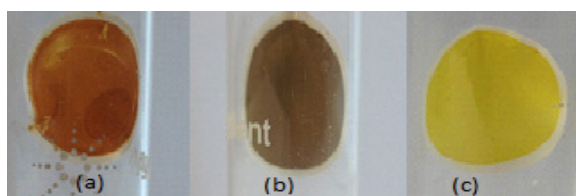


Fig. 2. The remnant solids after filtering. The pH in (a) ~ (c) was 4, 6, and 4. The initial arsenic concentration was 100 mg/L. Sulfide and Fe(II) concentrations were 5 mM and 5 mM in both (a) and (b), whereas 0.05 mM and 0.5 mM in (c).

## CONCLUSION

In this study, it was found that arsenic-sulfur complexes are formed in sulfidic environments. The identification of arsenic speciation in sulfidic waters by means of hydride generation atomic absorption spectrometry (AAHG) was not appropriate. However, a rapid loss of total soluble arsenic concentration and lack of solid formation supports the formation of arsenic-sulfur complexes (thioarsenates). In addition, it can be concluded from laboratory tests that insoluble arsenic precipitates or thioarsenates are sensitive to changes in pH in As-S-Fe solution.

Therefore, the optimal experimental conditions for minimizing the occurrence of arsenic-sulfur complexes and maximizing formation of As precipitates should be investigated for the effective reductive stabilization of arsenic residuals.

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