

## Mechanisms of Arsenic Immobilization by MetaFix<sup>®</sup> Reagent

### Formation of Mixed Iron-Arsenic Mineral Precipitates

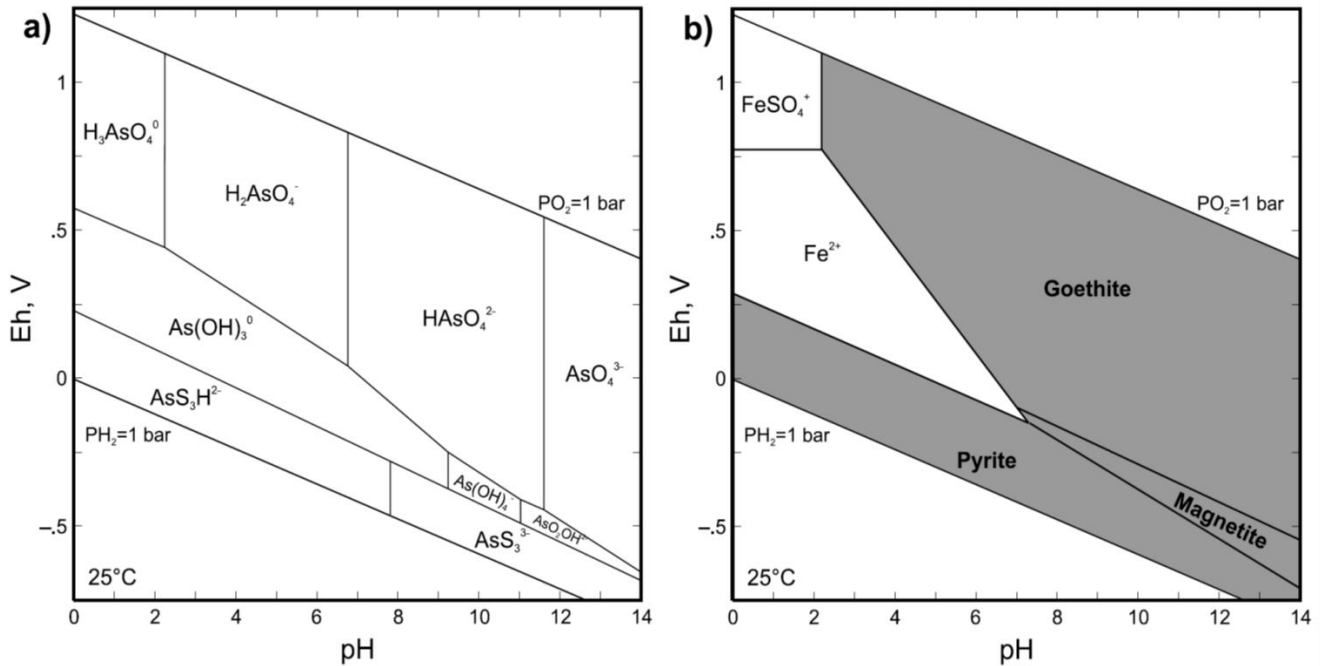
MetaFix reagents treat dissolved metals such as arsenic via long-term sequestration as solid arsenic species by means of reductive precipitation and adsorption onto the surfaces of iron oxides, iron oxyhydroxides, and other iron corrosion products.

A primary mechanism of arsenic immobilization in soil or groundwater treated with MetaFix is the reduction of arsenate [As(V)] anions to arsenite [As(III)]. This reduction step is facilitated by two components of MetaFix: zero valent iron (ZVI) and iron sulfides, both of which are powerful reductants (electron donors), as indicated in the following redox half-reactions:



These reactions generate free ferrous iron and electrons, which subsequently produce stable As-Fe sulfide phases. Corrosion (oxidation) of solid ZVI particles produces dissolved iron that subsequently forms secondary iron minerals, including iron oxides [e.g.; magnetite, Fe<sub>3</sub>O<sub>4</sub>] and iron oxy-hydroxides (goethite, FeOOH). These mineral phases provide reactive surface areas where arsenic oxyanions [As(V) and As(III)] can be bound or co-precipitated (Manning *et al.*, 2002; Kober *et al.*, 2005). Similarly, oxidation of solid FeS provides free iron (Fe<sup>2+</sup>) and sulfide to react with As(III) resulting in precipitation of insoluble iron-As-S phases including arsenopyrite.

MetaFix reagents are designed to have near neutral pH and do not affect the native soil or groundwater pH. MetaFix creates geochemical conditions (i.e., low Eh and neutral pH) that are conducive to the creation of secondary iron minerals, such as goethite and magnetite, and As-S species (Figure 1).

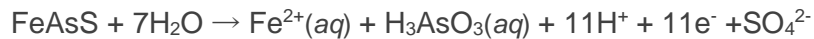


**Figure 1.** Eh-pH diagrams for arsenic and iron at 25°C for coupled iron- and sulfate-reducing systems. These paired diagrams show the relative distribution of potentially adsorbing arsenic species (left) relative to representative types of Fe-bearing sorbents (right) that are predicted to occur as a function of Eh and pH. (a) System As-S-H<sub>2</sub>O, with ΣAs=10<sup>-5</sup> and ΣS=10<sup>-3</sup>; all solids suppressed to show stability fields for the aqueous species. (b) System Fe-C-S-H<sub>2</sub>O with ΣFe=10<sup>-4</sup>, ΣC=10<sup>-3</sup>, and ΣS=10<sup>-3</sup>; Hematite is suppressed. (From EPA/600/R-07/140)

### Long Term Stability of Iron-Arsenic-Sulfide Solid Phases

The creation of Fe-As-S phases was demonstrated experimentally with the use of iron + sulfide treated soil columns (Przepiora *et al.*, 2008). These results showed that a significant part of the arsenic mass immobilized in the soil was associated with secondary iron oxides and oxyhydroxides, which is in agreement with previous published results in iron rich systems (Manning *et al.*, 2003; Koeber *et al.*, 2005).

Arsenopyrite (FeAsS), the major solid arsenic phase created during MetaFix treatment, is extremely insoluble under reducing conditions (Eh < 0 mV), but it is highly soluble in oxic conditions (Craw *et al.*, 2003):



Ferrous iron in MetaFix prevents arsenic remobilization under oxic conditions by:

- Creating protective coatings on the precipitated reduced arsenic mineral phases; and,
- Facilitating precipitation and/or adsorption of any arsenic that is potentially mobilized under extreme changes in geochemical conditions.

This has been validated in laboratory testing demonstrating the long-term stability of arsenic in iron + sulfide treated soil under geochemical conditions that could, in theory, reverse the arsenic immobilization processes (Przepiora *et al.*, 2008). Such conditions include extremes of pH and ORP. The observed persistence of As-Fe reduced mineral phases in the iron + sulfide treated column under highly oxic conditions and extreme pH could be attributed to development of protective submicron iron oxide and oxyhydroxide coatings on As-bearing soil surfaces. A similar phenomenon has been observed in natural geologic systems where a primary or authigenic arsenopyrite is present on earth’s surface (Craw *et al.*, 2003). Based on this research, the As-Fe-S phases will be stable in water-saturated and moderately reducing systems, such as those created with MetaFix.

Table 1 provides a summary of the potential arsenic mobilization processes in natural environments and the corresponding anticipated MetaFix treatment mechanisms that prevent arsenic remobilization.

**Table 1.** Potential As Mobilization Processes and MetaFix treatment Mechanisms

Attenuation Processes*	Mobilization Processes*	MetaFix Treatment Mechanisms
Precipitation of metal arsenates or arsenites or precipitation of arsenic sulfides	Dissolution of metal arsenates/ arsenites due to change in pH; dissolution of arsenic sulfides due to increase in pH or shift changes in ORP conditions.	MetaFix is a pH neutral reagent , therefore pH is maintained at levels below zero point charge (ZPC) of iron oxides and oxyhydroxides (< pH 8). MetaFix treatment provides a long term source of free iron from oxidation of ZVI and FeS. This enables continuous formation of secondary iron precipitates, including iron oxides and iron sulfides that function as a sink for arsenic, if any is remobilized.
Co-precipitation of arsenic as a trace component in oxyhydroxides or sulfides of iron or manganese	Dissolution of host oxyhydroxide due to decrease in pH or shift from oxidizing to reducing conditions; dissolution of host sulfide due to shift from reducing to oxidizing conditions.	
Adsorption to iron oxyhydroxides, iron sulfides, or other mineral surfaces	Desorption at high pH for oxyhydroxides and sulfides; complexation/stabilization in the presence of DOC. Reductive dissolution of iron hydroxides or oxidative dissolution of iron sulfides.	

\* EPA/600/R-07/140

## REFERENCES

Craw D., Falconer D., and Youngson J.H., 2003. Environmental arsenopyrite stability and dissolution: theory, experiment, and field observations. *Chemical Geology*, Vol. 199, pp. 71-78.

Dolfing J, van Eekert M, Seech A, Vogan J, Mueller J. 2008. *In situ* chemical reduction (ISCR) technologies: Significance of low Eh reactions. *Soil Sed. Contam.* 17(1): 63-74.

Drever, J.I., 1997. *The Geochemistry of Natural Waters. Surface and Groundwater Environments.* 3rd Ed., Prentice Hall, NJ, pp. 436.

EPA, 2007. *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water. Volume 2, Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium.* EPA/600/R-07/140.

Islam, F. S., A. G. Gault, C. Boothman, D. A. Polya, J. M. Charnock, D. Chatterjee, J. R. Lloyd. 2004. Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. *Nature.* 430: 68-71.

Islam, F. S., R. L. Pederick, A. G. Gault, L. K. Adams, D. A. Polya, J. M. Charnock, J. R. Lloyd. 2005. Interactions between the Fe(III)-reducing bacterium *Geobacter sulfurreducens* and arsenate, and capture of the metalloid by biogenic Fe(II). *Appl. Environ. Microbiol.* 71: 8642-8648

Kober, R , E . Welter, E., Ebert, M, And Dahmke, A., 2005. Removal of Arsenic from Groundwater by Zerovalent Iron and the Role of Sulfide. *Environ. Sci. Technol.*, Vol. 39, pp. 8038-8044.

Manning, B.A., Hunt, M.L., Amrhein, C. and Yarmoff, J.A., 2002. Arsenic(III) and arsenic(V) reactions with zerovalent iron corrosion products. *Environ. Sci. Technol.*, Vol. 36, pp. 5455-5465.

Przepiora, A., Hill, D., and Seech, A. 2008. *In situ* Reductive Immobilization of Dissolved Metals Using Iron and Organic Carbon Substrate. *Proceedings of the Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds.* Monterey, CA, May 19-22, 2008. Paper A-026.

Seech, A.G., J.E. Cairns and I.J. Marvan. 2000. *Composition and Method for Dehalogenation and Degradation of Halogenated Organic Contaminants.* US Patent 6, 083,394.

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