

# Evaluation of Iron and Sulfur Supplements to Promote Reactive Mineral Formation in In Situ Reactive Zones

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**Background/Objectives.** It is well established that abiotic treatment mechanisms contribute to the overall treatment capacity in organic carbon-based anaerobic biological in situ reactive zones (IRZs). In addition to the targeted biological treatment mechanisms, reduced iron minerals (such as troilite, mackinawite, pyrite, green rusts, and magnetite) provide an abiotic component that contributes to overall contaminant destruction that is not frequently documented during remedial performance assessment. While reagents containing supplemental iron and sulfur claim to promote abiotic treatment in IRZs, questions remain regarding their contribution to reactive mineral formation, abiotic mass destruction, and treatment efficacy in comparison to reagents without supplements. For many aquifer systems, the native mineralogy contains sufficient sources of geogenic iron and significant reduced iron minerals can be generated. As a result, remedial costs associated with additional iron reagents to enhance abiotic treatment may not be necessary. Although less common than natural sources of iron, natural sources of sulfur can also contribute to iron sulfide mineral formation. Though iron and sulfur supplements to carbon-based biological programs in theory enhance the synergy between biotic and abiotic transformation processes, side-by-side testing is valuable for the development of cost-effective full-scale remedial programs.

**Approach/Activities.** Field performance results from side-by-side testing of carbon-only and carbon with iron and/or sulfur supplements are presented to evaluate the efficacy of added supplements. Case Study A is an 18-month, side-by-side field-scale evaluation of emulsified vegetable oil (EVO) and an iron-infused emulsified lecithin in a cold weather application in the northeastern U.S. A review of ex situ material handling and in situ treatment performance observations is presented. Case Study B is a side-by-side field-scale evaluation of soluble carbon substrate with and without sulfur supplements in the southeastern U.S. Advanced analytical tools including scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy were used to characterize mineral precipitates formed during the pilot test.

**Results/Lessons Learned.** For Case Study A, field-scale implementation of the iron-infused organic substrate resulted in significant ex situ solids precipitation induced by cold weather during the injection event, significantly reducing the delivery of carbon and iron to the aquifer. Similar levels of dissolved iron and other geochemical indicators were observed for both the carbon-only and carbon with iron supplement, suggesting that supplemental iron addition is not necessary. For Case Study B, the precipitation of iron sulfide minerals was observed, and SEM was used to better understand the composition and size of the minerals formed. The SEM results demonstrate that these biologically-generated precipitates form in the presence of significant microbial growth, and the expected reactivity and treatment contribution of these precipitates is discussed in the context of available literature.