

Performance and Persistence Differences Between Abiotically- and Biotically-Generated Mackinawite-Structured Iron Sulfides

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1. INTRODUCTION

The introduction of reactive iron species for treatment of inorganic contaminants is well known, yet the efficiencies of these various irons – zero valent iron (ZVI), ferrous or ferric sulfate, and iron sulfides, differ greatly in reactivity, efficiency, and cost. One group of reactive iron species are “reactive iron sulfides” which have been successfully used for the reduction and precipitation of inorganic contaminants such as chromium, arsenic, and mercury.

This memorandum focuses on the use of a particular subset of reactive iron sulfides - mackinawite structured iron sulfide and sulfonated iron-aluminum layered double hydroxide (LDH), collectively referred in this paper as “FeS”.

Another standalone reductant the environmental remediation industry has long studied and recognized for its usefulness is ZVI. However, ZVI may have its own set of constraints, limitations, and variabilities in successfully meeting remediation goals when deployed at a particular site. In addition, compared with these forms of FeS, ZVI is less chemically efficient (due to passivation) and persistent in the environment than other FeS.

These constraints, limitations, and variability in success when using ZVI are related to many factors, including but not limited to:

- The iron source used to manufacture the ZVI itself
- Particle sizing of the ZVI
- Low reactivity due to its intrinsic passive layer
- Narrow working pH
- Reactivity loss with time due to the precipitation of metal hydroxides and metal carbonates
- Low selectivity for target contaminants (especially under oxic conditions)
- Limited efficacy for treatment of some refractory contaminants
- Passivity of ZVI arising from certain contaminants
- Geochemical variability between sites and even within sites location (Guan, 2015).

To counteract some of these challenges, during the past decade, ZVI reagent providers have begun to sulfidate (sulfonate) their ZVI, chiefly with the intent is to increase the ZVI's reactivity, selectivity, and longevity for various reductive processes. Although these sulfidated or sulfonated ZVIs (S-ZVI) have become a more commonly used product for both inorganic and organic contaminant reduction applications, consistently meeting a site's long-term remediation goals has remained elusive.

2. FERROUS SULFIDE CREATION

Multiple university and industry research papers have proven that FeS can be generated abiotically (chemically) or biotically (biogeochemically) (Wang et al., 2024, Mangayayam et al., 2019). While the formation of a stable, highly reactive FeS is possible in both abiotic and biotic scenarios, there are significant performance differences between chemically synthesized FeS (abiotic FeS) and biogeochemical generated FeS (biotic FeS)

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Biogeochemically generating ferrous sulfides in-situ for site remediation has become a more prevalent practice in the past decade and a half, primarily based upon the research and evaluation of sulfate-rich aquifers with sulfate-reducing microbes that produced free sulfide (Rickard 2012 and Picard et al., 2018). The introduction of an iron component for oxidation and reaction with this free sulfide produced in these environments completed the FeS formation process. It is interesting to note that this concept traces its roots back to paleo-geochemical environments where biotic FeS was generated in low-temperature, anoxic surface water and groundwater settings by sulfate reducing microorganisms (SRM) (Wacey et al., 2015). In both settings, sulfate is utilized as an electron acceptor by indigenous or imported facultative microbes that produce (hydrogen) sulfide. This reductive metabolic process is known as biosulfidogenesis (Jameson et al., 2010).

This concept of biologically produced sulfide combined with an iron source has evolved over the years into the practice of mixing S-ZVI with microbes to jumpstart this process or provide the necessary components to facilitate the reaction and precipitation of iron sulfides, most notably for reductive dechlorination applications.

More recently, it has become common for environmental practitioners to optimize this biotic formation of FeS by adding additional nutrients and kinetic additives to condition the aquifer and promote more optimal geochemical conditions that improve the speed, efficiency, and quantity of FeS produced biogeochemically. This combined injectate has been referred to as S-ZVI and enhanced reductive dechlorination (ERD), (SZVI+ERD), S-ZVI and enhanced in situ bioremediation (EISB) (S-ZVI+EISB), or S-ZVI and anaerobic bioremediation (AB), (S-ZVI+AB).

Even with these advancements mentioned, one of the greatest challenges to overcome in these types of biogeochemical systems is the amount of time (and timing) required to create the desired environment for successful remediation.

Many chemical and biological processes must occur concurrently and sequentially over a period of months to generate the quantity and type of FeS required. Some of these processes include the *transformation and maintenance* of the aquifer into a sulfate-reducing environment depleted of dissolved oxygen to promote biosulfidogenesis. This biosulfidogenesis must be coupled with oxidation of the iron source (e.g., ZVI) to produce several iron oxide species plus ferrous iron, and all these processes must be present and maintained for direct microbial interaction and formation of FeS. Additionally, the availability of sulfate (total or mass flux) also has a direct bearing on the formative size, iron morphology, and mineralogy of the iron sulfide; again, influencing the reactivity and mass of FeS generated.

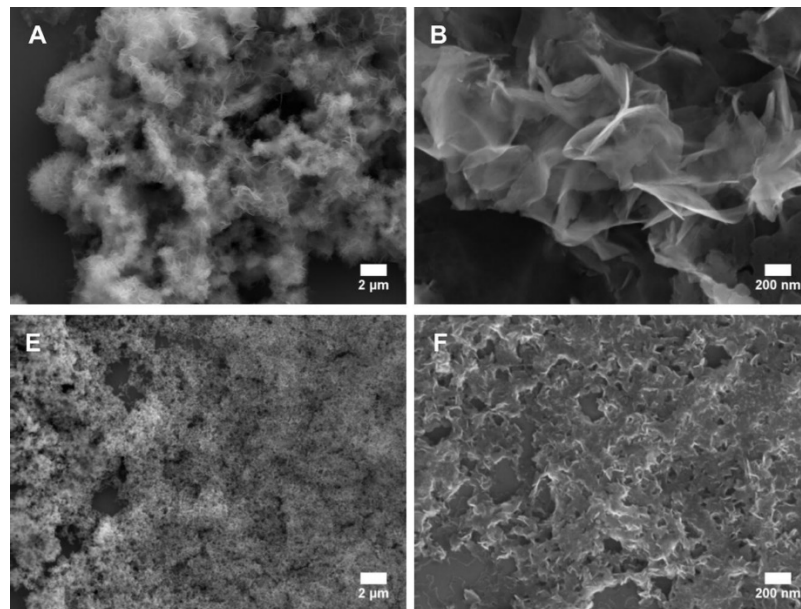
While earlier laboratory studies (Rickard, 1969) inferred that biotic FeS did not physically differ from abiotic FeS, more recent research suggests that this is not necessarily the case. Over the past five decades, more sophisticated laboratory experiments confirmed the issues with verifying the viability of usable biotic FeS and have found that non-reactive species of FeS may be generated (e.g., pyrite, greigite) and not the quantities of the reactive FeS desired.

Using modern laboratory technologies, the physical and chemical characteristics (i.e. crystal size, morphology, texture, solubility) of the minerals formed in the presence of sulfate-reducing microorganisms (SRM) “have not been thoroughly investigated” and were “likely limited by the technology available at time” (Picard et al., 2018). Further, several factors influencing the ability of SRM to biotically form reactive FeS were highly affected by the geochemical setting- mainly influenced by the geological environment and anoxic conditions. Thus, the generation (derivation) and reactivity/utilization (consequence) of these biotic compounds can be more readily predicted

in modern experiments where instrumentation is more appropriate for in-depth analysis, but also the equipment can control environmentally germane factors that play a role(s) in biotic FeS formation.

3. STRUCTURAL DIFFERENCES

Iron sulfide mineralization experiments examining the influences of several biogenic parameters on the formation of biotic FeS after one week of incubation and then monthly for one year revealed significant structural differences. These biotically formed FeS particles were compared to abiotically prepared FeS at the same Fe:S ratios (Picard et al., 2016).



Scanning Electron Microscope (SEM) images of biotic (upper row) and abiotic (lower row) iron sulfide precipitates, washed and air-dried in an anaerobic chamber, after one week of incubation. (from Picard et al., 2018)

The Picard, et al., 2018 team concluded the following:

1. Despite having similar Fe:S ratios and formed at similar pH, the mineral precipitates formed under biotic and abiotic experiments had visually distinct bulk morphologies.
2. Biotic precipitates appeared less opaque (i.e. absorbed less light) than abiotic precipitates.
3. After the minerals settled back to the bottom of the vials, the precipitates formed in biotic Fe experiments formed a sticky aggregate, while abiotic precipitates appeared finer and more homogeneously distributed.
4. Precipitates in the biotic treatments aggregated more than the abiotic precipitates and thus formed larger particles. Aggregates of biotic particles in solution were much larger (1354 ± 120 nm) than abiotic aggregates (428 ± 148 nm).
5. The massive aggregation of biogenic iron sulfide minerals is consistent with observations of 'sticky' mineral precipitates in the serum vials.
6. The binding of Fe^{2+} to microbial compounds before the precipitation of FeS seems to play an important role in determining the final properties and morphology of iron sulfide minerals.
7. Different mineral morphologies are observed when minerals precipitate in the presence of dead SRM.

Overall, the application and applicability of these “controlled” laboratory experiments to actual remediation applications assumes the ability to efficiently create biotic FeS in an “uncontrolled” environment. This means that:

- Since the increased surface area (smaller sized particles) and uniformity within the structure has a direct impact on reactivity in-situ, and
- The distribution and reactivity of the biotically formed FeS in-situ is hampered by agglomeration and massing, abiotically formed FeS would be favored.

4. IMMEDIATE REMEDIATION

Deploying an abiotically, manufactured (chemically synthesized) FeS presents several advantages and resolutions to the limitations of the biogeochemically generated version. An FeS synthesized with an excess of sulfide (S-FeS) exhibits a larger interlayer spacing and unit cell volume that contains an interlayer of polysulfides which is structured as a wave pattern that has a greater surface area for contaminant reduction, degradation, and/or removal (Wang, et al., 2024).

- Abiotically produced FeS (e.g., S-FeS) is not dependent on biogeochemical processes.
- Pyrite and greigite are not formed or introduced to the system, a conversion process which depletes the reductive setting.
- Phosphate in the geochemical setting does not retard or inhibit the formation of these types of abiotically produced FeS (or S-FeS) – the phosphate mineral complex (vivianite) is not a chemically available form of FeS.
- Extracellular materials, byproducts of microbial respiration, do not aggregate and produce irregular or outsized FeS particles.
- Agglomerated FeS particles are not present, which may reduce aquifer porosity.
- Multi-metal contaminants, or commingled inorganic and organic contaminants, settings do not shift the production or reactivity of the abiotically produced FeS which may occur during biotic FeS formation.

5. CONCLUSIONS

Biogeochemically generated FeS has gained acceptance in the environmental remediation industry for groundwater remediation of inorganic and organic contaminants. The introduction of bioremediation components with S-ZVI to generate FeS in situ is a demonstrated technology. A chemically manufactured version (S-FeS) has also been utilized with prevalence in recent years in similar deployments. It has proven to be effective immediately and demonstrate subsurface persistence.

The differences in these two FeS materials, outside of performance and timeframe, are also realized in project cost and timeline. The intent of proponents of biotic FeS is to reduce the cost of the injectate on a per pound basis. Yet, because of many in situ factors, it is difficult to estimate the total mass of FeS that will be generated, even if conditions remain constant and optimal, which is difficult to control longer than weeks or months in most cases. The agglomerate structure is also not conducive to high-capacity reduction or degradation. With S-FeS, the weight of available irons and sulfides is straightforward to calculate and evaluate on a stoichiometric and cost basis.

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Conflict of Interest Statement

Derek Pizarro declares no conflicts of interest. Thomas McCullough and Gary Meyer are the owners of Redox Solutions, LLC, which owns the intellectual property and manufacturing facility for a commercialized mackinawite structured iron product (FerroBlack®).