S-MicroZVI:
Frequently Asked Questions

S-MicroZVI®
Sulfidated Zero-Valent Iron

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Contents

Introduction

S-MicroZVI® is an *In Situ* Chemical Reduction (ISCR) reagent that promotes the destruction of many organic pollutants and is most commonly used with chlorinated hydrocarbons. It is engineered to provide an optimal source of micro-scale zero valent iron (ZVI) that is both easy to use and delivers enhanced reactivity with the target contaminants via multiple pathways. S-MicroZVI can destroy many chlorinated contaminants through a direct chemical reaction. S-MicroZVI will also stimulate anaerobic biological degradation by rapidly creating a reducing environment that is favorable for reductive dechlorination.

The following resource provides answers to frequently asked questions regarding the science, technology and application of REGENESIS' S-MicroZVI reagent.

S-MicroZVI Properties

What is S-MicroZVI and how does it differ from other sulfur-containing iron products?

S-MicroZVI® contains sulfidated iron particles suspended in a glycerol-based liquid carrier. Sulfidated iron consists of zero-valent iron particles with a thin surface layer of reduced iron sulfide. This unique configuration provides exceptional reactivity with many common groundwater contaminants. Sulfidation also inhibits reactions between iron and water that are unproductive, prolonging S-MicroZVI's reactive lifetime.

Not all sulfur-containing iron products provide the core-shell microstructure provided by S-MicroZVI. Products that do not provide the benefits of core-shell configuration include:

- Iron with sulfur impurities
- *In situ* precipitated biogeochemical-produced minerals
- Chemically synthesized mackinawite
- Mixtures of ordinary ZVI and mackinawite powders

Contaminants Treated

Can S-MicroZVI be used where there are few to no parent products in a plume (e.g., plume contains mostly cis-DCE and/or VC)?	S-MicroZVI can be a viable remediation approach to treat plumes containing mostly daughter products (like cis-DCE or VC) in environments with slow-moving or stagnant groundwater. When addressing faster-moving groundwater containing daughter products, combining S-MicroZVI with a fermentable organic donor or colloidal activated carbon may be beneficial. Abiotic degradation rates for daughter products like cis-DCE are slower than parent compounds like TCE. Therefore, combining S-MicroZVI with an electron donor will usually result in a more effective treatment of daughter-product-dominant groundwater plumes.
What is S-MicroZVI's efficiency with chloromethanes and chloroethanes?	S-MicroZVI exhibits rapid reactivity with compounds containing higher chlorine contents. Carbon tetrachloride, a perchlorinated compound, has a half-life of less than one day at typical dosing. Chloroform is degraded more slowly, and dichloromethane is recalcitrant. Similarly, S-MicroZVI degrades 1,1,1-trichloroethane rapidly while 1,2-dichloroethane is recalcitrant. Similar to treating chlorinated ethenes, combining S-MicroZVI with enhanced biological processes is often better suited for addressing daughter products since it can address the full spectrum of chlorinated methanes and ethanes.
Does S-MicroZVI treat PFAS?	S-MicroZVI does not actively degrade PFAS. Information to effectively treat PFAS can be found on the REGENESIS website at https://www.REGENESIS.com/en/pfas-treatment-solutions/
Does S-MicroZVI treat 1,4-Dioxane?	There is no evidence for the reactivity of 1,4-dioxane with S-MicroZVI or any other type of iron and it is not believed to be an effective solution for that contaminant.
Can S-MicroZVI treat DNAPL?	S-MicroZVI does not directly react with free-phase DNAPL because abiotic reduction occurs in the aqueous phase. However, when co-applied with organic emulsions such as 3-D Microemulsion® (3DME), S-MicroZVI is very effective at addressing DNAPL in source zones. This product combination solubilizes the DNAPL within the emulsion droplets that are subsequently biodegraded. This releases the contaminants into the aqueous phase where they are rapidly degraded by both abiotic and biological processes.

Will S-MicroZVI treat hexavalent chromium and arsenic?

S-MicroZVI is effective for removing hexavalent chromium from groundwater. This involves reducing the hexavalent chrome to trivalent chromium followed by a reaction with water to produce insoluble chromium hydroxide, chromium oxyhydroxide, and other insoluble minerals. These are thermodynamically stable and will not revert to hexavalent chromium compounds.

Arsenic immobilization involves the biogeochemical reductive dechlorination (BiRD) process and other coprecipitation reactions to produce iron sulfide compounds *in situ*. Arsenic is incorporated within and immobilized within iron sulfide (arsenopyrite) particles.

Design and Application

How is the S-MicroZVI dose calculated and how long will it last?

When modeling a site, the concentration of electron acceptors in the water is considered. These include not only the contaminants (e.g., TCE) but also other species such as dissolved oxygen and nitrate. REGENESIS' modeling software calculates the S-MicroZVI dose required to meet the electron acceptor flux demand, with an engineering safety factor applied. A typical S-MicroZVI application is designed assuming a longevity of about five years.

Can S-MicroZVI be mixed with and co-applied with other amendments?

Yes, S-MicroZVI is co-applied with other advanced remediation amendments like colloidal activated carbon (PlumeStop®), fermentable organic emulsions (3DME), or colloidal solid donors (AquiFix®).

Can S-MicroZVI be used in permeable reactive barriers?	Yes. Permeable reactive barriers intercept groundwater plumes where contaminants moving through the barrier are eliminated. Due to the finite residence time within the barrier, rapid reaction kinetics are beneficial in preventing contaminant breakthroughs. S-MicroZVI's rapid kinetics provide distinct advantages over ordinary iron products. However, it is usually beneficial to co-apply S-MicroZVI with PlumeStop within a PRB. PlumeStop increases contaminant retention time within the barrier by orders of magnitude. The increased residence time is particularly beneficial when addressing cis-1,2-DCE and other slower-degrading daughter products.
Can S-MicroZVI be applied alone or is it only made for co-application with PlumeStop and organic electron donors?	S-MicroZVI can be applied alone to treat dilute plumes where the contaminant flux is low or moderate, and residence time in the treatment area is sufficient to facilitate complete reduction before leaving the treatment area. In very high contaminant mass flux barrier applications where the residence time is too short for S-MicroZVI to be effective as a standalone technology, it is best to pair S-MicroZVI with PlumeStop to increase the contaminant retention time. This allows for the complete elimination of daughter compounds. Additionally, S-MicroZVI is not recommended as a standalone treatment technology in source zones where residual DNAPL is likely. It should be co-applied with an organic electron donor emulsion product like 3DME.
Can S-MicroZVI be applied in low permeability geologic materials like silt and clay?	Experience suggests that few if any, injectable remediation amendments can be uniformly emplaced into clay. Where injecting into clay is required, it often involves using tight injection point spacings with top-down direct push technology (DPT) injections and higher injection pressures. If the soil contains permeable sand lenses within clays, colloidal products like S-MicroZVI can usually be preferentially emplaced into these permeable zones. Back diffusion from the clays can bring the contaminants in contact with the amendments placed into these zones.
Can it reduce the permeability of the site?	S-MicroZVI, when properly diluted and injected, will not result in a significant reduction of the permeability at a site.

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Chemistry and Reactivity

Does the sulfidation layer made of iron sulfide react over time? Would a reaction of iron sulfide increase sulfur concentrations?	Because the amount of iron sulfide is small (< 5 wt%) significant changes in the sulfur chemistry in the treated environment from the iron sulfide are not expected.
Will nitrate in groundwater consume or passivate S-MicroZVI?	Nitrate directly reacts with and consumes S-MicroZVI and is accounted for in remediation designs. Nitrate does not alter the sulfidation layer or passivate S-MicroZVI.
Does S-MicroZVI promote biogeochemical reductive processes?	Yes. Biogeochemical reductive dechlorination is often described using the acronym BiRD. BiRD occurs when ferrous iron combines with other groundwater species *in situ* to produce reduced minerals. These reactive minerals include iron sulfides and hydroxides that serve as abiotic reductants for eliminating chlorinated and other high oxidation-state contaminants. For example, a common reaction involves ferrous iron produced by the oxidation of the S-MicroZVI reacting with native sulfate in groundwater to form reduced iron sulfide. These minerals can also react with and eliminate TCE and other contaminants. Note that reducing sulfate to sulfide is an eight-electron reaction that will consume a lot of reductants. BiRD treatment efficiency is maximized when co-applying the S-MicroZVI with an organic electron donor such as 3DME or AquiFix. These electron donors will supply the electrons to form the biogeochemical reductants. Because the degradation products such as ferrous iron and acetate are all water soluble, they can migrate further than solid materials and this advantage can extend the zone of influence for the injection.
What impact does aerobic groundwater have on S-MicroZVI?	Dissolved oxygen (DO) is relatively easy to electrochemically reduce with favorable kinetics and thermodynamics. Along with nitrate, DO does consume ZVI, and in high groundwater flow environments with elevated DO the dosing requirements may be large. In these environments, the DO demand can be overcome by co-applying an organic donor to help establish and sustain a reducing environment.
Will the hydrophobic iron sulfide surface also attract other hydrophobic compounds such as TPH?	Hydrophobic compounds such as TPH do not appear to interfere with the activity of the S-MicroZVI. An exception may be where there is NAPL or free-phase hydrocarbons in the groundwater. However, dissolved hydrocarbons are not likely to have a negative effect.
Does pH Affect S-MicroZVI performance?	Reductive dechlorination processes operate most effectively at a pH range from 6 to 8. Most sites have groundwater within this pH range. If the pH is below 6, a soluble pH modifier such as sodium bicarbonate may be used but the effects are often temporary. A solid-phase base such as colloidal calcium carbonate may also be used for longer results.

Safety

What safety considerations are there for injecting S-MicroZVI?

The same protocols that are used for injecting other remediation amendments are recommended. These include eye protection, gloves, and applying common sense when working with pressurized systems. After completing applications for the day, all valves should be left open to atmospheric pressure to avoid gas buildup in hoses. Regularly flush the lines with water and employ good housekeeping practices.

One thing to consider is that sulfidated iron reacts with strong acids such as hydrochloric acid which produce hydrogen sulfide and a rotten egg odor. Because this is toxic at relatively low concentrations, you don't want to clean or rinse the mix tanks with HCl or other acids. Instead, you'd want to rinse them with clean water. If the subsurface is acidic, contact us before injecting the S-MicroZVI to ensure that no hydrogen sulfide is produced *in situ*.

REGENESIS Remediation Services (RRS) employs hydrogen sulfide sensors in the trailers as a standard practice.

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Price and Performance

Is sulfidated ZVI more cost-effective than using commodity iron?

S-MicroZVI is engineered to meet the unique requirements of the environmental remediation industry. Because of the colloidal particle size and sulfidation layer, unit costs are greater than commodity iron. Although the unit product price may be more expensive, reactivity and distribution advantages mean that a project typically needs only 10% to 20% of the iron by mass compared to commodity products. Injecting less volume results in lower product application costs, so from a total project cost basis, the economics are much closer than many initially realize.

How long does sulfidation last?

A column study demonstrated that reactivity was maintained for 4 years with complete and rapid conversation of TCE to ethene and ethane. For comparison, other colloidal ZVI products, such as nanocrystalline zero-valent iron (NZVI), have a reactive lifetime of a few months at best (Rajajayavel et al). No other ZVI product provides this unique combination of reactivity and longevity. This combination results in superior long-term treatment of contaminants introduced into flux zones by back-diffusion from clays and low permeability zones, increasing the probability of achieving closure goals with a single application. Learn more

How does sulfidated ZVI compare to Enhanced Reductive Dechlorination in price and performance?

Biological approaches (ERD) are more cost-effective on some projects, for instance, where iron alone is known to be less effective (i.e., DCE and VC-only plume). However, S-MicroZVI is synergistic with ERD, overcoming the shortfalls of ERD-only approaches. For example:

- S-MicroZVI quickly lowers redox potential into productive biological dechlorination ranges, accelerating the onset of biological degradation.
- Abiotic degradation converts about 90% of PCE and TCE into ethene and ethane, bypassing the accumulation of daughter products. This improves the efficiency of combined ERD/S-MicroZVI remedies because less DCE and VC are produced. The small amount of daughter products that are produced are degraded more rapidly.
- Co-applying S-MicroZVI with oil-in-water emulsions results in DNAPL partitioning into hydrophobic oil droplets. When the hydrophobic oils biodegrade, the contaminants are introduced into the aqueous phase where ISCR-enhanced bioremediation occurs.

How does sulfidated ZVI compare to mackinawite and larger micron-scale amendments?

S-MicroZVI is a technically superior and more cost-effective solution. It has a much higher reactivity–approximately 30x higher–than bare iron and provides longer effective treatments that average approximately 4 years.

S-MicroZVI® Sulfidated Zero-Valent Iron

Summary of S-MicroZVI Performance Benefits

Zero valent iron (ZVI) is a powerful reductant that can react with and eliminate many groundwater contaminants. However, not all ZVI products are alike. Most are manufactured for other applications. S-MicroZVI is engineered specifically for the environmental remediation industry and outperforms commodity iron in 3 important areas:

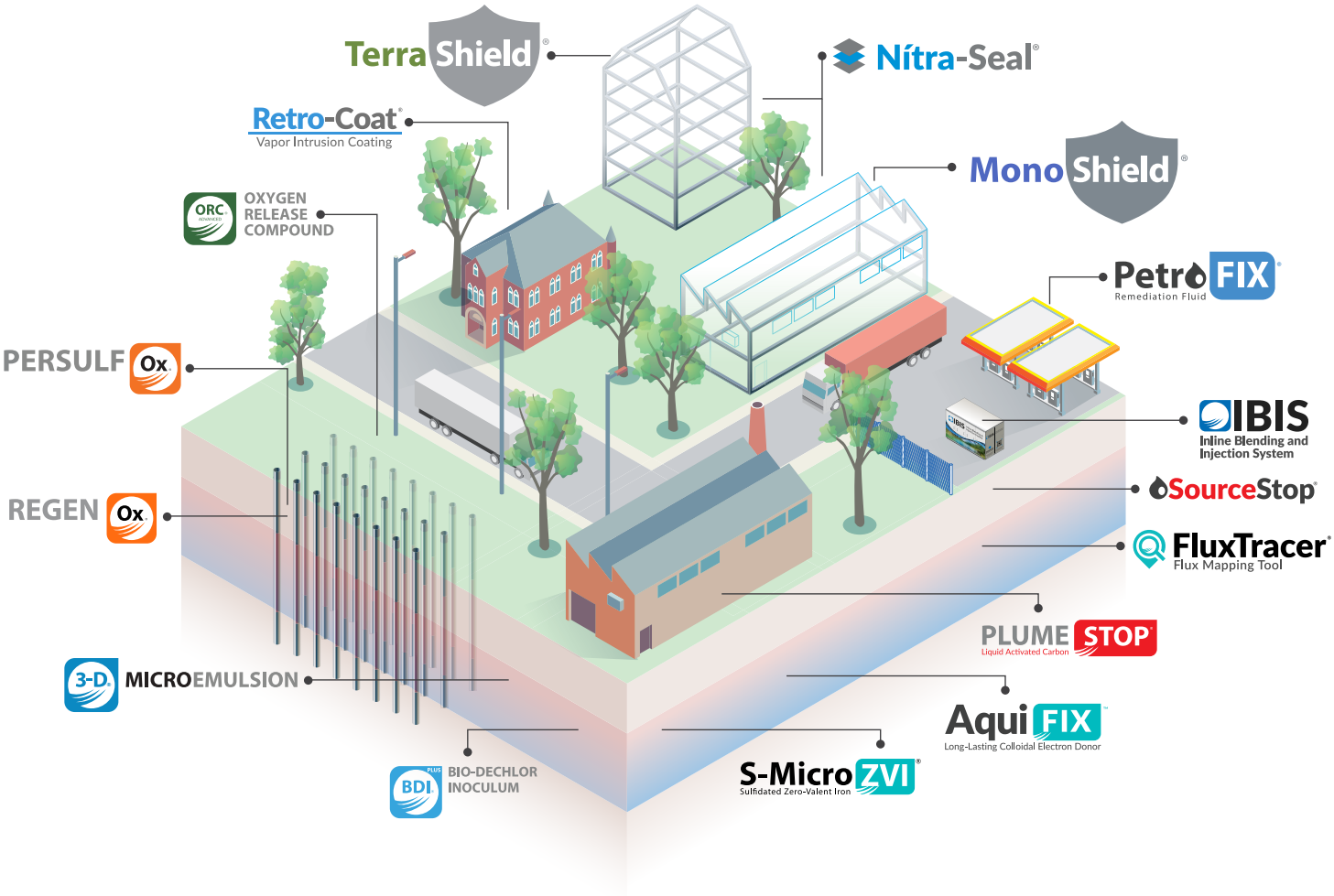
1. S-MicroZVI particles contain a thin surface layer of iron sulfide (< ~ 5 wt. %). Sulfidated iron provides reaction kinetics with TCE that are 30x faster than bare iron (reference?). Sulfidation also inhibits hydrolysis, with laboratory studies showing that reactivity is maintained for over 4 years. This is unmatched in the industry, and the speed and longevity result in significant performance gains.
2. Small particle-size iron particles distribute more uniformly within the aquifer flux zones providing superior contact and destruction potential.
3. S-MicroZVI is provided as a liquid suspension and is unmatched in handling by any ZVI product. Unlike commodity products, S-MicroZVI doesn't produce dangerous iron dust, requires no powder feeders, and requires no thickening with guar. It can be applied at low injection pressures without using pneumatic or hydraulic fracturing. These features are superior from a health and safety standpoint.

Benefits of Sulfidation Reference

> These unique properties increase the certainty of achieving remedial goals with a single application. For example, S-MicroZVI was used at a site in California where a prior fracture injection of ZVI was unsuccessful, leading the regulators to seek a more predictable delivery approach. Learn more

References

Rajajayavel, S. R. C., & Ghoshal, S. (2015). Enhanced reductive dechlorination of trichloroethylene by sulfidated nanoscale zerovalent iron. Water Research, 78, 144-153. doi:10.1016/j.watres.2015.04.009



About REGENESIS

At REGENESIS we value innovation, technology, expertise and people which together form the unique framework we operate in as an organization. We see innovation and technology as inseparably linked with one being born out of the other.

Inherently, innovation imparts new and better ways of thinking and doing. For us, this means delivering expert environmental solutions in the form of the most advanced and effective technologies and services available today.

We value expertise, both our customers' and our own. We find that when our experienced staff collaborates directly with customers on complex problems, there is a high potential for success including savings in time, resources and cost.

At REGENESIS we are driven by a strong sense of responsibility to the people charged with managing the complex environmental problems we encounter and to the people involved in developing and implementing our technology-based solutions. We are committed to investing in lasting relationships by taking time to understand the people we work with and their circumstances. We believe this is a key factor in achieving successful project outcomes.

We believe that by acting under this set of values, we can work with our customers to achieve a cleaner, healthier, and more prosperous world.

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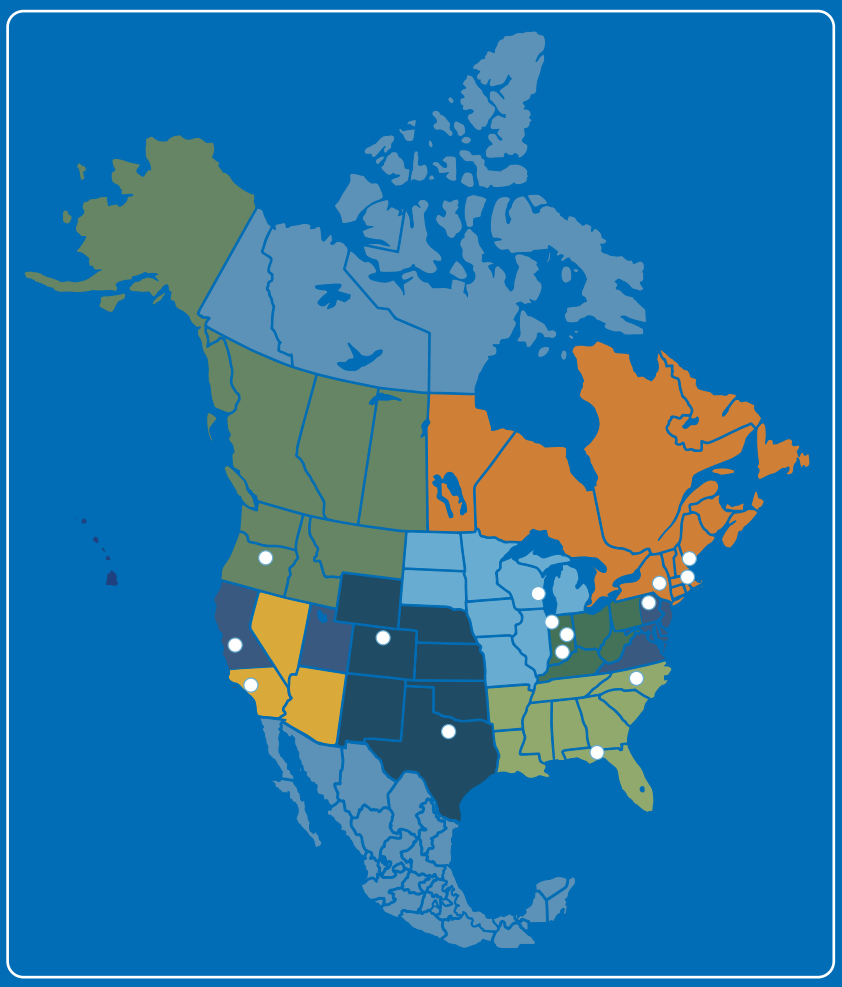
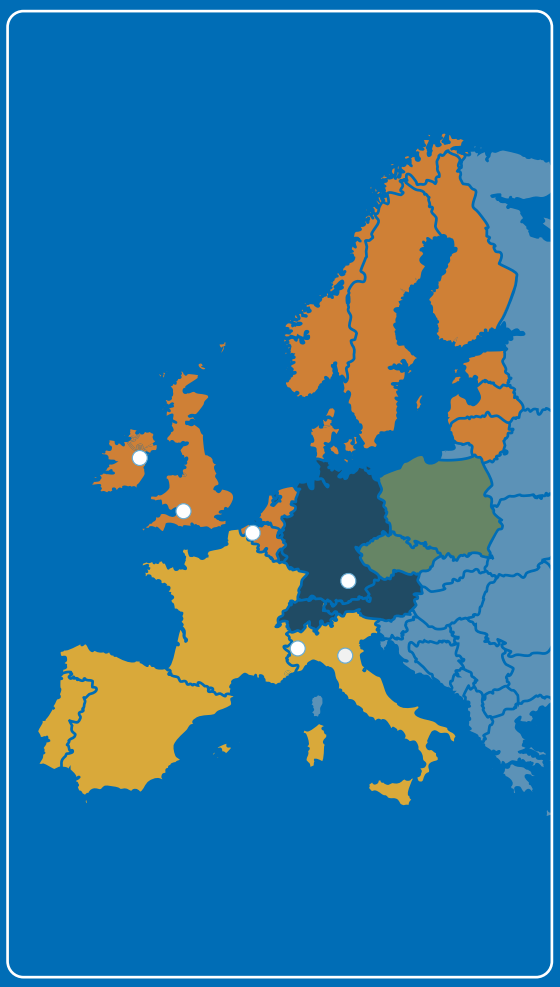
We're Ready to Help You Find the Right Solution for Your Site





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