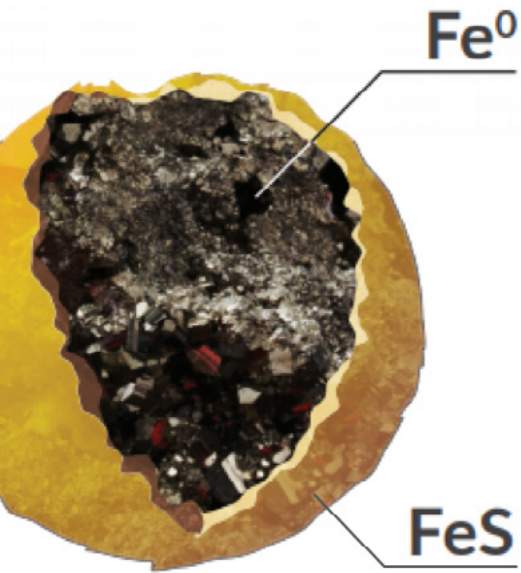


ZVI FAQ

Commonly Asked Questions About Zero Valent Iron



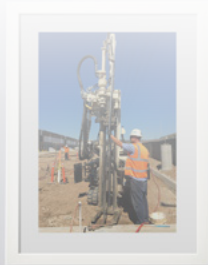


Overview

Frequently Asked Questions About Zero Valent Iron (ZVI)

The following frequently asked questions about zero valent iron are taken from the questions and answers portion of a webinar given by John Freim PhD, ZVI Product Manager and Director of Materials Science at REGENESIS.

A recording of the webinar, "Optimization of ZVI Technology for the *In Situ* Remediation of Chlorinated Contaminants" is available online and can be accessed in full at www.regenesis.com/en/webinars



Overview

John Freim, ZVI Product Manager and Director of Materials Science



With a career that includes research grants from the Environmental Protection Agency (EPA) Department of Energy (DOE), Missile Defense Agency (MDA), along with grants from the National Institutes of Health (NIH) and U.S. Air Force (USAF), and successful entrepreneurial environmental remediation experience, Dr. John Freim brings a distinguished track record to his role as Director of Materials Science at REGENESIS®. With over 30 years of expertise in materials processing, and 15 years in the environmental remediation industry, Dr. Freim would seem to be the ideal choice to join REGENESIS and lead the effort to establish the company's first state-of-the-art colloidal product manufacturing facility. Before joining REGENESIS, Freim had been serving as President of OnMaterials, which he founded to use his expertise in the synthesis and processing of nanopowders and other engineered materials. His research grants from the EPA, NIH, and USAF enabled Freim to develop procedures to affordably manufacture and apply ZVI remediation amendments to contaminated soil and groundwater. Subsequently, in 2003, OnMaterials began selling ZVI products and services to environmental contractors that resulted in several hundred product applications.



How do you calculate the dose of S-MicroZVI and how long does it last?

When modeling a site, we take into consideration the concentration of electron acceptors in the water. These include not only the contaminants such as Trichloroethylene (TCE) but also some other species such as dissolved oxygen and nitrate. Using porosity and groundwater flow, our modeling software calculates the electron acceptor flux in a time period such as a year, and what we'll do is dose the site with the knowledge that the iron is consumed as the electron acceptors pass through the treatment zone. A typical site is dosed for a longevity of about five years and we employ a safety factor of two to five on top of that.

Does S-MicroZVI promote biogeochemical reductive processes?

Yes, it does. Biogeochemical reductive dechlorination is often described using the acronym BiRD. BiRD occurs when ferrous iron combines with other groundwater species *in situ* to produce reductive minerals. These reactive minerals include iron sulfides and hydroxides that serve as abiotic reductants for the elimination of toxic compounds. For example, a common reaction would be to have the ferrous iron that is produced by the oxidation of the ZVI react with native sulfate in groundwater to form reduced iron sulfide. These minerals can also react with and eliminate TCE and other contaminants. I will caution that if you look at the chemistry behind this reaction, reducing sulfate to sulfide is an eight electron reaction so this will consume a lot of reductant. To best accomplish this, it's a good idea to co-apply the ZVI with an organic electron donor such as 3-D Microemulsion (3DME)® to supply the electrons for the formation of the biogeochemical reductants. Because the reactants are all water soluble, they can migrate further than solid materials and this advantage can extend the zone of influence for the injection.

Being that the surface given by iron sulfide is hydrophobic, can it attract also other hydrophobic compounds such as, for example, TPH in the case of a commingled plume?

We've done a lot of injections with other materials that you would think might adsorb to S-MicroZVI such as the organic droplets that are present in 3DME or emulsified vegetable oil (EVO). The presence of these species does not appear to interfere with the activity of the ZVI. And given how much attraction these would have for a hydrophobic surface, I think it's unlikely that total petroleum hydrocarbon (TPH) compounds at typical concentrations in groundwater would interfere with the iron. I will caution that if you have NAPL or free-phase hydrocarbons in the groundwater this could possibly be a problem. But for dissolved species it's unlikely that it will have any negative effect.

What are the chemical reactions involved in the treatment of chromium and arsenic?

I'll premise this answer with my opinion that metals immobilization is not very well understood. My understanding is that the iron is used to promote the reduction of hex chrome to trivalent chromium hydroxide. This first involves reducing the hex chrome to tri chrome followed by a reaction with water to produce insoluble chromium hydroxide, chromium oxyhydroxide, and possibly other insoluble minerals.

I speculate that the same mechanism could apply for arsenic where the arsenic is reduced and then precipitated as insoluble minerals. One such reaction is when the arsenic atoms substitute for iron within an iron sulfide lattice. So, you might have, say 1% or so arsenic precipitating into the biogeochemically produced iron sulfide minerals.

When more than one product is applied, what order are the amendments applied?

When S-MicroZVI is co-applied with other remediation amendments they are usually applied together by adding each product into a mixing tank and co-injecting a colloidal suspension. Because the product characteristics such as particle size and mobility are similar, the amendments will go to the same place in the ground and react together. This applies to both PlumeStop and 3DME co-injections. There might be a few instances where you would do separate injections. Sometimes anaerobic microbes are added separately at the end of the project. If Hydrogen Release Compound (HRC)®, which is another organic donor is used it must be applied separately from the S-MicroZVI for health and safety reasons.

What sort of pH adjustments and buffers are you typically applying with ZVI injections? What are you looking for in pH trends immediately after injections versus long term?

Our experience suggests that reductive dechlorination processes operate effectively at a pH from slightly below pH 6 to slightly above pH 8. Most sites have groundwater within this pH range. If the pH is on the low side, a soluble pH modifier such as sodium bicarbonate can be used although the effects are often temporary. A stronger base such as colloidal calcium carbonate can also be used, but with the caveat that carbonate can react with and passivate iron if present in high concentrations. We generally avoid using stronger bases such as magnesium hydroxide because they are subject to overshoot and it is difficult to control pH. Groundwater pH will usually trend slightly basic when ZVI alone is applied. When fermentable bioremediation amendments are applied, groundwater pH will generally trend acidic. These pH excursions are usually minor and acceptable provided the pH doesn't move outside the previously mentioned ranges.

Are there any safety protocols with the ZVI injections?

We use the same protocols that are used for injecting any amendments. You're going to need eye protection, wear gloves and use common sense. There are pressurized injection lines, so use normal safety protocols. After completing applications for the day you want to make sure that you leave all valves open to atmospheric pressure to avoid gas buildup in hoses. Beyond that, 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. Instead you'd want to rinse them with clean water. If the ground is a particularly acidic environment, it would be a good idea to talk to us before you inject the sulfidated iron to make sure that you're not going to produce hydrogen sulfide *in situ*. In addition to that, all our field personnel use hydrogen sulfide sensors in the trailers, so we've been trained on this. We've only seen this issue once in an injection well at only 2 ppm which is under the OSH PEL for hydrogen sulfide.

Where has sulfidated ZVI been applied?

Since 2017 sulfidated ZVI has been applied at over 100 project sites in the United States, in Canada and Europe. To my knowledge there hasn't been any material applied in Asia, Africa, Australia or South America.

How well will the ZVI go into soils heavily consisting of clay? As compared to water or PlumeStop?

Our experience suggests that few if any injectable remediation amendments can be uniformly emplaced into clay. The best application method in clay will often involve using tight spacings with top down direct push technology (DPT) injections and high injection pressures – basically a brute force method. If the soil has more permeable sandy lenses within clays, the colloidal products can usually be emplaced in these areas and back diffusion from the clays can bring the contaminants in contact with the amendments. Using membrane interface probe (MIP) or other investigative techniques to determine the location of the permeable layers is especially important in these circumstances.

How much does it cost?

Project cost is variable and depends on design factors including contaminant concentration, groundwater flux, soil porosity etc. A good rule of thumb for S-MicroZVI, is \$30 per cubic yard. This does not include the cost of other amendments, drilling, injection services etc.

What are the most important site characterization parameters to collect to assess the feasibility of ZVI?

We recommend sampling groundwater for the typical geochemical parameters (pH, ORP, dissolved iron) along with concentrations of both the contaminants of concern (TCE) and other electron acceptors notably dissolved oxygen (DO), nitrate and sulfate. It is also beneficial to quantify groundwater flux. The best way is to use MIP or similar methods to determine the more permeable zones with preferential groundwater flow. Passive flux meters are often effective for measuring flux through these zones.

How is S-MicroZVI made, and have you ever observed S-MicroZVI being formed *in situ*?

The manufacturing process for S-MicroZVI is proprietary and results in a 40% by weight suspension of colloidal particles that have a ZVI core and an iron sulfide shell, as depicted on page 2 of this FAQ. Although the thermodynamics of the reaction of ZVI with sulfate are favorable, we have observed that the kinetics are very slow. Bacteria can reduce native sulfate to sulfide which can then combine with ferrous iron to produce mackinawite and other reduced iron sulfides. Some ferrous iron is produced by S-MicroZVI degradation and when combined electrons supplied by an organic electron donor and native sulfate this will result in the *in situ* formation of reactive iron sulfides in groundwater.

Does S-MicroZVI work effectively against polyfluoroalkyl substances, or PFAS, aka, PFOA (perfluorooctanoic acid) and PFOS (perfluorooctane sulfonate)?

ZVI does not actively degrade PFAS. However, PlumeStop activated carbon does adsorb most PFAS compounds. There is information on our website on this technology.

Learn more at <http://pfastreatment.org>

You discussed bench and lab comparison of sulfidated ZVI with some other conventional ZVI. Any field results showing comparison?

We have recently published a case study about a sulfidated ZVI project that was performed in Southern California. Several years ago, another product was applied at this site without success using pneumatic fracturing. This prior work resulted in daylighting and an uneven distribution of product.

[Click Here to Read the Case Study](#)

Has there been any evidence of 1,4-dioxane degradation with this technology?

No, I haven't seen any evidence for reactivity of 1,4-dioxane with S-MicroZVI or any other type of iron. Oxidation or *ex situ* fluidized bed reactors are the only technologies that I am aware of.

How does the ZVI technology overcome a naturally aerobic environment?

Dissolved oxygen (DO) is relatively easy to electrochemically reduce with favorable kinetics and thermodynamics. DO does consume ZVI however and there are situations with a high groundwater flow and high DO where the dosing requirements can be quite large. In these instances, this can be overcome by co-applying an organic donor to help sustain a reducing environment.

1) What other chlorinated contaminants can benefit from your S-MicroZVI?

1). Chlorinated ethenes are the most commonly treated contaminant, but S-MicroZVI can also be used to treat some chlorinated methanes (carbon tetrachloride and chloroform) and ethanes (1,1,1- trichloroethane). A rule of thumb is that more chlorinated compounds will be eliminated more effectively (PCE is better than DCE). We've also had some success with some chlorinated pesticides/herbicides. **2.)** Injection is accomplished using either direct push points or screened wells typically using 5 foot vertical intervals.

2) Where and how should it be injected?

How well does ZVI respond to significantly high cVOC concentrations in groundwater, such as PCE at 30-60 mg/L? Is ZVI a good technology to treat NAPL?

ZVI reactions occur in the aqueous phase so, sorbed or free phase contaminant needs to be solubilized into water for degradation to occur. At locations where we believe that non-aqueous phase contaminant is present, we recommend using a mixture of S-MicroZVI, 3DME, and our BDI Plus® dechlorinating microbe culture (*Dehalococcoides sp*). PCE and TCE are non-polar compounds and thus, will partition into the similarly non-polar droplets in 3DME. As the organic droplets biodegrade the contaminant is then released back into the aqueous phase where the reactions occur. We have some literature describing the ZVI enhanced ERD process; please see the link below. Specifically, adding S-MicroZVI to the traditional bioremediation amendments accelerates degradation and minimizes daughter product formation.

[Click Here to Read the Tech Bulletin](#)

Have you measured any pH effects as a result of the FeS shell?

In microcosm experiments at a typical S-MicroZVI dose we see a small increase in pH. Since sulfidated iron inhibits reactivity with water I would anticipate that this would result in a lesser pH increase compared to bare ZVI because hydroxide is a reaction product of hydrolysis.

In the presentation, you mentioned TCE breaking down via a different pathway, but still showed results for cDCE and vinyl chloride. Could you elaborate on this?

Beta-elimination of chlorinated ethenes is a two-electron reaction that involves removing one chlorine from each side of the carbon-carbon bond that changes from a double bond to a triple bond. So PCE is first converted to dichloroacetylene, TCE is first converted to chloroacetylene, and cDCE is converted to acetylene. Vinyl chloride (VC) doesn't have a chlorine on each side of the carbon-carbon bond so it doesn't degrade by beta-elimination. Also, each of these compounds can also degrade via hydrogenolysis, a two-electron reaction where a chlorine atom is replaced by hydrogen. These two process operate simultaneously with beta-elimination generally having faster kinetics.

Have you used this in fractured rock, specifically dolostone, and if so, have you seen passivation of the iron (e.g., from calcium and iron carbonates)?

Yes, this product has been applied into fractured rock. It's generally not as easy as injecting into sand, and packers or similar devices are often used to control vertical distribution within the boreholes. Regarding carbonate based minerals I don't know the specific geology of the fractured rock sites but it possible that these could passivate ZVI. However, I've used small amounts of insoluble pH buffers (calcium carbonate) in the past and haven't noticed any appreciable lessening of performance.

S-MicroZVI™

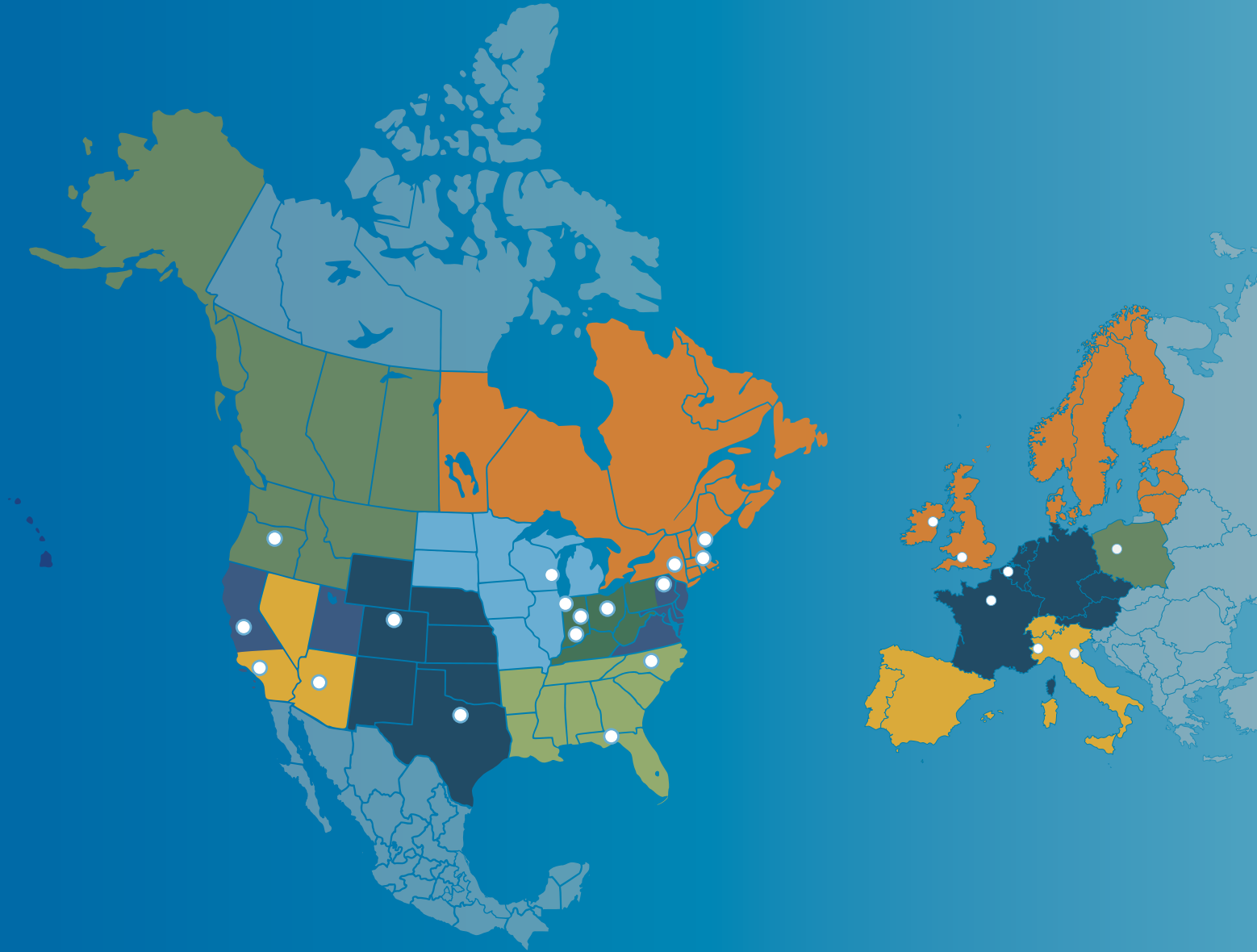
Sulfidated Zero-Valent Iron

REGENESIS offers S-MicroZVI®, an advanced zero-valent iron (ZVI) product proven to accomplish *In Situ* Chemical Reduction (ISCR) of contaminants within the subsurface environment. S-MicroZVI is delivered as a colloidal suspension 40% ZVI by weight in glycerol with a particle size of less than 5 microns. S-MicroZVI is manufactured using a state-of-the-art sulfidation process resulting in a particle coating which increases activation toward specific contaminants and extends performance longevity. S-MicroZVI destroys contaminants abiotically and applied to stimulate ISCR-enhanced bioremediation.

- Easy to Apply
- Disperses Widely in the subsurface aquifers
- Excellent reactivity
- Extended longevity



WE'RE READY TO HELP YOU FIND THE RIGHT SOLUTION FOR YOUR SITE



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