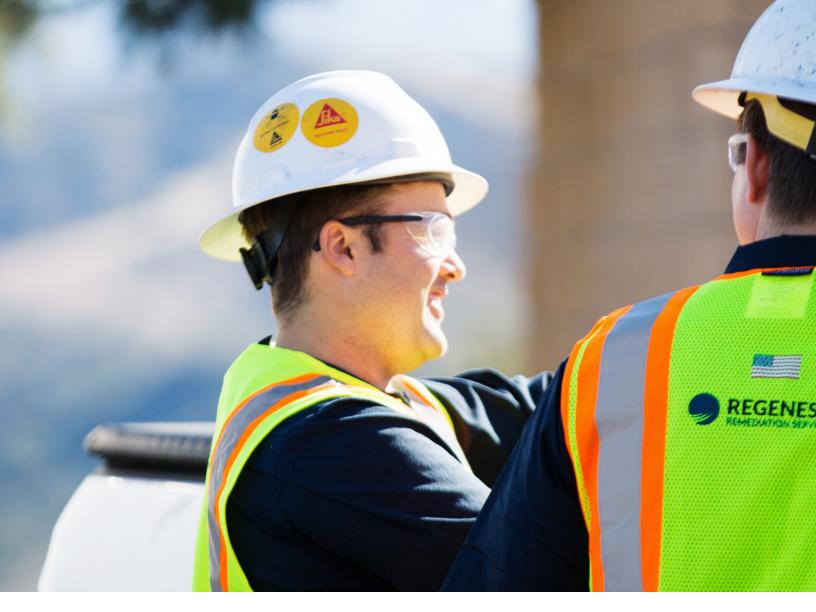
TO CONSIDER IN SITU CHEMICAL REDUCTION TO TREAT YOUR SITE

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Introduction

Many potential remediation strategies are available for the cleanup of an environmentally impacted property, and these strategies possess unique advantages and disadvantages. The key to a successful strategy is the selection of a technology or combination of technologies that is suitable for the target contaminants, site-specific conditions, and budget/time frame for completion.

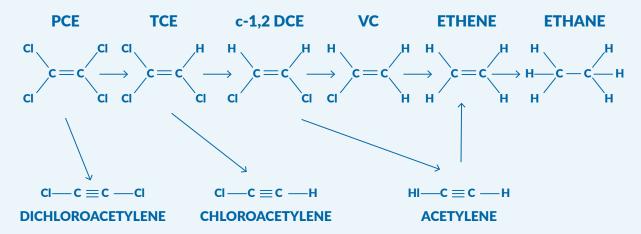
Though *in situ* chemical reduction (ISCR) has been in use for some time, recent technological advances have improved it as a remedial approach. Chemical reduction involves the transfer of electrons from a reductant such as zero-valent iron (ZVI) to a molecule such as a perchloroethylene (PCE), during which the molecule is converted to harmless compounds. In essence, chemical reduction is the mirror process of *in situ* chemical oxidation (ISCO), a technique commonly used to treat environmental contaminants in soil and groundwater. ISCR can be an effective approach that should be considered whenever designing a remedial strategy.

A proliferation of remedial technologies based on chemical reductants such as ZVI, which is highly effective against chlorinated solvents, some metals, and other contaminants, has been recently developed. REGENESIS has recently developed S-MicroZVI^M, a sulfidated, colloidal suspension of ZVI micro-scale particles less than 5 μ m in size that can easily be injected and is chemically reactive in the subsurface. While no single technology is optimal for all situations, under the right circumstances, ISCR can be an effective approach that should be considered whenever designing a remedial strategy.



The Chemical Reduction Pathway Can Bypass Toxic Daughter Products

This diagram shows the chemical formulations of PCE and its reduced daughter products all the way down to ethane. The compounds on the top of the diagram represent the sequential process that is typical of bioremediation. In this process, PCE is reduced to trichloroethylene (TCE) and then subsequently to dichloroethylene (DCE), vinyl chloride, and finally benign ethane. This transformation occurs through the sequential removal of one chlorine atom from the molecule coupled with its replacement with a hydrogen molecule. Like the bioremediation process, the reduction of PCE by the colloidal ZVI technologies from REGENESIS is a two-electron process; however, instead of TCE, DCE, and vinyl chloride, the latter process reduces PCE to dichloroacetylene and then to chloracetylene and acetylene. These acetylene derivatives are short-lived intermediate compounds, and the parent compounds which are typically PCE and TCE, are directly reduced to ethene or ethane, as denoted at the bottom of the diagram.



Importantly, the process can bypass the formation of vinyl chloride which is more toxic than PCE and TCE and often has a lower MCL than the parent compounds. This avoidance of vinyl chloride formation is a benefit that remediation professionals can leverage when developing solutions to reach site closure quickly and with minimal harm to sensitive receptors.

An ISCR Approach Offers Flexibility

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A Versatile Remediation Approach

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An ISCR approach can treat a wide variety of contaminants, including chlorinated solvents such as percloroethylene (PCE), tetrachloroethylene (TCE), dichloroethylene (DCE), and vinyl chloride (VC), pesticides (i.e., toxaphene, pentachlorophenol), energetics (i.e., Trinitroluene (TNT), cyclotrimethylenetrinitramine (RDX)), and heavy metals (chromium). In cases where a property is impacted by mixed plumes of these contaminants, an ISCR approach can often be used to treat all of the contaminants simultaneously, eliminating the need to utilize multiple technologies and/or perform the cleanup process in stages. With a long list of treatable contaminants and the ability to treat a wide range of concentrations, ISCR is a versatile tool applicable to many different situations.

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Additionally, ISCR solutions can be effective at a wide range of concentrations. At high concentrations, some technologies, such as adsorptive amendments, can be overwhelmed, while at low concentrations, biological processes may be ineffective because of insufficient food sources required to fuel their metabolism. ISCR, however can be effective in both types of environments. With a long list of treatable contaminants and the ability to treat a wide range of concentrations, ISCR is a versatile tool applicable to many different situations.

The shorter the project life cycle, the more money that can be saved on overhead costs and administrative expenses.

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Shorter Project Life Cycles Lead to Cost Savings Overall

The reaction kinetics exhibited by ISCR are rapid relative to those of other processes. For many contaminants, reduction occurs almost immediately upon contact with the reductant. Therefore, a well-designed project based on ISCR can be completed on the timescale of weeks to months, whereas alternative approaches (such as bioremediation or monitored natural attenuation) can take months to years.

For example, at the Hunter's Point Naval Shipyard in California, microscale ZVI injected as a permeable reactive barrier (PRB) showed significant (>99%), rapid (<12 weeks), and sustained (multiple years) reduction of chloroform concentrations within a dilute chlorinated plume.

A rapid time to site closure is particularly important for properties with a pending sale or a short timetable for development. Additionally, the shorter the project life cycle is, the more money that can be saved on overhead costs (operation and maintenance, ongoing monitoring, etc.) and administrative expenses.

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The need to return to the site every 3-5 years to install a new permeable reactive barrier PRB versus once every 15-30 years would obviously have a significant impact on the bottom line.

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Longevity Offered with ISCR Extends Contact with Reactive Zone

In addition to the fast reduction kinetics of ISCR, the reductant itself can remain active for a long period. For example, coarse-grained ZVI applied as a semipermeable reactive barrier via trenching can last in the subsurface for decades, whereas a similar permeable reactive barrier (PRB) made of a slow-release electron donor that promotes biological degradation may last only five years or less. The need to return to the site every 3-5 years to install a new PRB versus once every 15-30 years would obviously have a significant impact on the bottom line. With its lengthy lifespan, ISCR can provide a viable long-term solution for plume control to prevent offsite migration and treat large plumes, as the extended time frame allows the contaminant to more effectively come into contact with the reactive zone via advection or diffusion.

In cases where ISCR is applied for long-term plume control, the longevity of the strategy means that a single application could be sufficient for the life of the project. The longevity of ISCR can help clients save on the cost of contractors, product, and maintenance.

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Proven Cost-Effective Compared to Other Remedial Technologies

In addition, ISCR can help cut costs and the technology can be more cost-effective than alternative remedial options. For example, installing a ZVI barrier can be an economical alternative to a pump and treat system.

In the case of a US Department of Defense (DOD) site near Grand Island, Nebraska, that was impacted by explosives in the groundwater, the initial capital cost of a ZVI barrier was higher than that of a proposed pump and treat system. However, once applied, ISCR worked passively, obviating the requirement for the continued operation and maintenance (O&M) that is associated with mechanical systems. Due to the accumulated cost of O&M, the pump and treat option was 42% more expensive than the ZVI approach over an estimated project life cycle of 30 years. This figure includes the assumption that the ZVI barrier would require replacement after 15 years.

In some cases, ISCR has been applied to replace existing pump and treat systems, thereby theoretically eliminating maintenance costs over multiple years and leading to an overall cost savings.

ISCR can also be less expensive than excavation, particularly in cases where the nearest landfill is a substantial distance from the site, causing transportation costs to be prohibitive.



CHLORINATED SOLVENT CONTAMINATION: REMEDIAL OPTIONS



DIRECT PUSH INJECTION





Most of the compounds encountered in the remediation of chlorinated contaminants are fairly recalcitrant, and natural attenuation is generally slow. As a result, bringing a site to closure often requires a remedial option. These options can be classified into three general categories.

One category is direct push injection, in which temporary injection points are used to inject the remediation amendments into the subsurface. Remediation practitioners can also use permanent wells, which are similar to monitoring wells and have a screened section within the contaminated aquifer. Finally, mechanical options are available and can vary from something as simple as excavation to more complex approaches such as soil mixing, in which the remediation amendments are brought into contact with the contaminants through physical mixing. In many circumstances, only *in situ* remediation is both efficient and cost-effective. By using the ISCR technologies from REGENESIS, environmental consultants are able to shut down permanent, engineered systems and reach remediation targets at a much lower cost to closure than that achieved with pump and treat systems.



An ISCR Solution Can Make Other Approaches Better

ISCR approaches can not only be compatible with other technologies but can also work together synergistically as a more effective combination. For example, combining an electron donor such as HRC® or 3D-Mircoemulsion® (3DME) with a chemical reductant can create parallel degradation pathways, which can extend the longevity of the iron and, depending on the application method, improve the coverage of the impacted areas, as a slow-release electron donor can move through the aquifer and fill gaps that less-mobile chemical reductants such as ZVI may not reach. ISCRenhanced bioremediation can be particularly effective because it stimulates anaerobic biological degradation by rapidly creating a reducing environment favorable for reductive dechlorination.

ISCR-enhanced bioremediation can be used to treat contaminants such as chlorinated solvents, haloalkanes, and chlorinated pesticides. Contaminants resistant to abiotic degradation like 1,2-dichloroethane or dichloromethane and compounds that typically inhibit bioremediation (e.g., 1,1,1-trichloroethane or chloroform) can also be effectively treated by ISCRenhanced bioremediation. ISCR-enhanced bioremediation can be used for source zones, plumes, and barrier applications. Such a system can also be co-applied with specialized microbes, such as Bio-Dechlor Inoculum Plus® (BDI+), which can further enhance its effectiveness.

Adding an iron-based amendment such as Chemical Reducing Solution (CRS[®]) to an electron donor such as 3DME can enhance chlorinated contaminant reduction by precipitating reduced iron sulfides, oxides, and hydroxides, as these compounds facilitate various chemical reduction pathways. This combination of biological and chemical processes is referred to as biogeochemical contaminant reduction and can have very rapid results. At a former dry cleaning site in western New York, CRS, 3DME, and BDI+ were applied, and the combination achieved 97% reduction in contaminant concentrations within two months. ISCR can also be combined with adsorptive carbon technologies such as PlumeStop®. Adding ZVI can expand the range of sites that can be treated with PlumeStop by reducing the overall contaminant load, which would otherwise make such an approach infeasible. Combining ISCR with complementary technologies can enhance the performance of each technology, leading to more effective remediation and better results.



ZVI and Colloidal Activated Carbon



- Sorption sites become available for additional contaminants
- Contaminant sorbs to AC or ZVI particle
- Microbes and ZVI degrade contaminants

How the Process Works

The combination of colloidal ZVI and colloidal activated carbon (PlumeStop) makes for a powerful, long-lasting *in situ* groundwater remediation strategy. PlumeStop sorbs contaminants quickly and prevents them from migrating offsite. Once sorbed, two mechanisms of contaminant degradation promoted by S-MicroZVI are possible: microbial processes and direct reaction with the contaminants.

As the contaminants are degraded, the sorption sites on the activated carbon become available to bind additional contaminants.

As a result, the combination of the ISCR technology with colloidal activated carbon allows for long-term, sustained treatment.

Colloidal ZVI can also be mixed and co-applied with other engineered remediation products, such as 3DME, PlumeStop, and BDI+

PLUME STOP

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ZVI Is Easy To Apply

The most common ISCR amendment, ZVI, comes in a variety of forms. One important specification for ZVI is its particle size, which can range from the macroscale (> 1,000 μ m) to the nanoscale (<40 nm). The particle size can impact the effectiveness of the process by causing variations in the available surface area, radius of influence, cost, and method by which ZVI is applied.

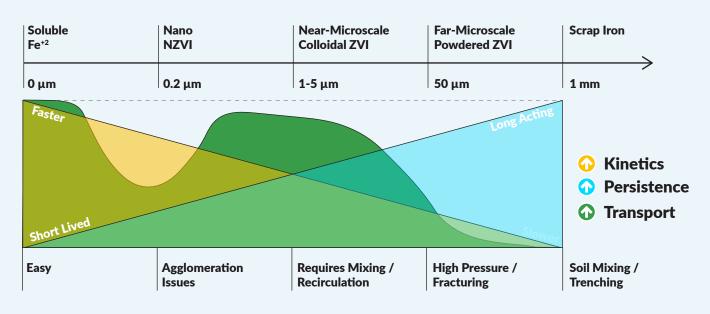
ZVI can be applied in a variety of ways, i.e., via trench back filling, soil mixing, or injection, where the size of the particles typically determines the practicality of each method. While coarse-grained ZVI has a longer subsurface longevity than fine-grained ZVI, the latter has gained popularity because its installation via injection is more practical, more cost-efficient, and less invasive. Whereas the application of larger-particle ZVI can require high-pressure injection and even hydraulic or pneumatic fracking, innovative formulations of microscale ZVI such as S-MicroZVI can be injected under low pressure into either temporary push points, or permanent injection wells through a process that is both easier and safer.

These highly injectable ZVI products can be installed into areas (i.e., underneath existing buildings) that would be more difficult, and in some cases impossible, to reach with a material of larger particle size. Additionally, the combination of the improved injectability with the relatively higher mobility of these smaller-particle ZVI products allows reactive zones to be created at depths greater than previously possible.

In terms of on-site health and safety, ZVI is non-toxic and relatively safe to handle, requiring only standard PPE (safety glasses and gloves) and no special equipment. S-MicroZVI is shipped as a liquid suspension and does not require powder feeders or thickening with guar prior to application.

The ease of use can facilitate smoother and more efficient injection work, potentially lowering the overall cost.

The ZVI Particle Size Impacts the Ease of Injection



Small (0.2 micron) particles of nano ZVI (nZVI) have a large surface area and strong inner particle forces, so instead of discrete nanoparticles that are 0.2 microns in diameter, which theoretically should be easy to inject, the particles exist as clumps, and the remediation practitioner must inject large aggregates of iron. A fitting analogy is that instead of injecting a single grape into the ground, a bunch of grapes must be injected. Because of this complication, remediation professionals have struggled to achieve effective reagent distribution with nZVI.

At the larger particle sizes found in powdered ZVI (30 microns and up), gravity starts to create a major challenge, and the particles are also larger than the pore spaces within the ground particles into which the reagent is being applied. As a result, the ZVI must be applied via high-pressure techniques or soil mixing. In the middle of the particle size scale is the REGENESIS technology S-MicroZVI which is $1-5 \ \mu m$ in size. The particles are large enough to avoid agglomeration issues, and as a result, their injection into the subsurface is much more manageable. Remediation field scientists can apply dispersants to keep these materials from agglomerating, resulting in much better distribution and a material that is easy to inject. A slight amount of mixing is required for recirculation, but the material is easy to inject under low pressure.

As this graph demonstrates, these technologies also provide the optimal amount of reactivity and longevity.

Because ISCR works in the subsurface, once installed, humans aboveground will not be exposed to either the chemicals or contaminants.

Reduces Risk To Human Health

When handled properly, ISCR amendments are not harmful to the environment or people. Because ISCR works in the subsurface, once applied, humans above ground will not be exposed to either the amendments or the contaminants. Of course, ISCR produces a benefit to human health by destroying contaminants such as chlorinated compounds. However, unlike biological processes that remove chlorine atoms sequentially and produce intermediates that can be more toxic than the parent compound, abiotic chemical reduction produces fewer daughter products. This fact is particularly important in cases where chlorinated compounds are being treated below buildings. Daughter products such as vinyl chloride are far more volatile and carcinogenic than their parent compounds and can enter occupied spaces through vapor intrusion, thereby posing a risk to human health. By using ISCR and circumventing the generation of harmful daughter products, clients can reduce risk, avoid exposure, and eliminate the cost associated with an expensive vapor intrusion mitigation system.

Conclusion

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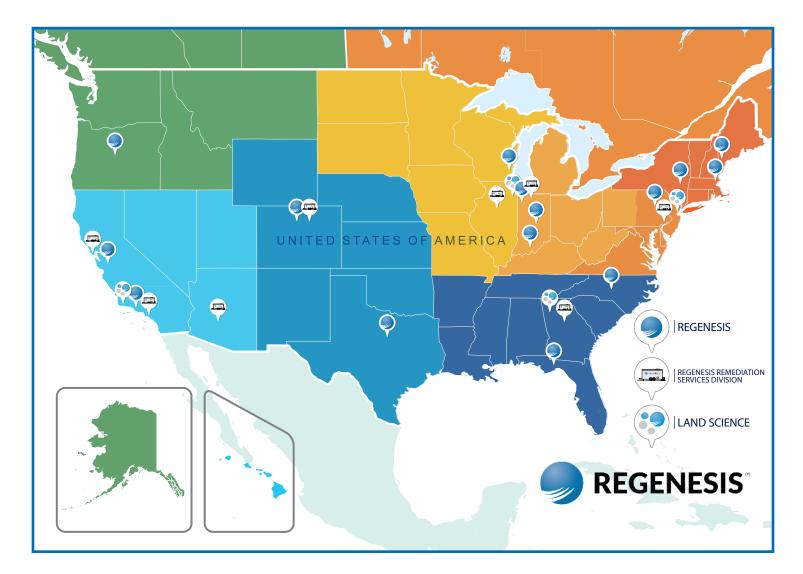
Gaining in popularity, ISCR technology gives environmental professionals promising options for site cleanup. With the advancements to the state of the technology made by highly injectable products like S-MicroZVI, ISCR is a valuable tool that should be a part of any remedial strategy discussion.

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Proven Technologies for Remediation Success

S-Micro	S-MicroZVI [™] is an <i>In Situ</i> 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.
	S-MicroZVI is composed of colloidal, sulfidated zero-valent iron particles suspended in glycerol using proprietary environmentally acceptable dispersants. The passivation technique of sulfidation, completed using proprietary processing methods, provides unparalleled reactivity with chlorinated hydrocarbons like PCE and TCE and increases its stability and longevity by minimizing undesirable side reactions.
	In addition to superior reactivity, S-MicroZVI is designed for easy handling that is unmatched by any ZVI product on the market. Shipped as a liquid suspension, S-MicroZVI requires no powder feeders, no thickening with guar, and pneumatic or hydraulic fracturing is not mandatory. When diluted with water prior to application, the resulting suspension is easy to inject using either direct push or permanent injection wells.
PLUME STOP Liquid Activated Carbon	PlumeStop Liquid® Activated Carbon™ is a fast-acting groundwater remediation reagent which captures and biodegrades a range of contaminants, thus accelerating the successful treatment of impacted sites and leading to their permanent closure. As a science-based, <i>in situ</i> treatment technology, REGENESIS' PlumeStop rapidly removes contaminants from groundwater and stimulates their permanent degradation.
CHEMICAL REDUCING SOLUTION	CRS® (Chemical Reducing Solution) is an iron-based amendment for <i>in situ</i> chemical reduction (ISCR) of halogenated hydrocarbon contaminants such as chlorinated ethenes and ethanes. It is a pH neutral, liquid iron solution that provides a soluble, food-grade source of ferrous iron (Fe ²⁺), designed to precipitate reduced iron sulfides, oxides, and/or hydroxides. These Fe ²⁺ minerals are capable of destroying chlorinated solvents via chemical reduction pathways, thus improving the efficiency of the overall reductive dechlorination process by providing multiple pathways for contaminant degradation in groundwater.
	3-D Microemulsion® is an injectable liquid material specifically designed for <i>in situ</i> remediation projects where the anaerobic biodegradation of chlorinated compounds through the enhanced reductive dechlorination (ERD) process is possible. ERD is the primary anaerobic biological process by which problematic chlorinated solvents such as tetrachloroethylene (PCE) and trichloroethene (TCE), dichloroethene (DCE) and vinyl chloride (VC) in groundwater are biologically transformed into less harmful end products such as ethene.
BIO-DECHLOR INOCULUM	Bio-Dechlor INOCULUM Plus (BDI Plus) is designed for use at sites where chlorinated contaminants are present and unable to be completely biodegraded via the existing microbial communities. BDI Plus is an enriched, natural microbial consortium containing species of Dehalococcoides sp. (DHC) which are capable of completely dechlorinating contaminants during <i>in situ</i> anaerobic bioremediation processes. BDI Plus has been shown to stimulate the rapid dechlorination of chlorinated compounds such as tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), and vinyl chloride (VC). It also contains microbes capable of dehalogenating halomethanes (e.g. carbon tetrachloride and chloroform) and haloethanes (e.g. 1,1,1 TCA and 1,1, DCA) as well as mixtures of these halogenated contaminants.

REGENESIS Is Ready To Assist You In Determining The Right Solution For Your Site



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