Recent Advances to Reductive Liquid Reagents: Benefits of Using Ultra Fine Zero Valent Iron

Soil & Groundwater Remediation Webinar | October 30, 2025





Presentation Outline

EHC® Reagent - Early Reagent for combined microscale ZVI + Organic Carbon ISCR

Continued ISCR Reagent Development

ELS® + Microscale ZVI

EHC® Liquid

Physical limitations for reagent distribution

Particle settling

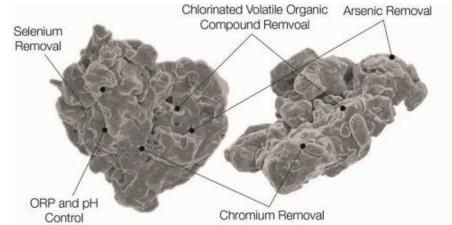
Flow velocity required to maintain suspension

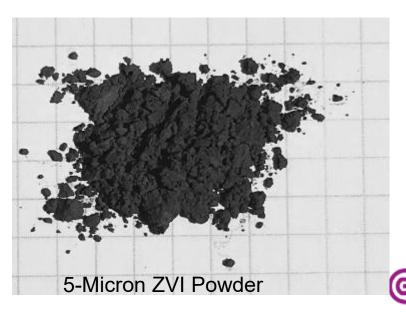
ELS® + Evonik 5 Micron ZVI Improved Liquid ISCR Reagent

Evonik 5-Micron ZVI with GeoForm® Soluble

Conclusions

Questions???





EHC® Reagent Over 25 years of combined biological & chemical (ISCR) treatment of chlorinated organics

EHC® in situ chemical reduction (ISCR) reagent is the original patented combination of controlled-release solid organic carbon and microscale zero valent iron (ZVI) used for the treatment of groundwater and saturated soil impacted by persistent halogenated compounds, including chlorinated solvents, pesticides and organic explosives. The EHC® formula is the culmination of years of research and successful field use. EHC® is comprised of a synergistic mixture of micro-scale ZVI and a solid organic carbon source, stimulating both abiotic

EHC® Reagent is delivered as a dry powder and includes the following:

Micro-scale zero valent iron (standard ~30 to 40%)

Controlled-release, <u>food grade, complex carbon (plant fibers</u>)
 (standard ~60% to 70%)

• Major, minor, and micronutrients

and biotic dechlorination mechanisms

- Food grade organic binding agent
- Sustainable solution
 - recycled metal
 - food production by-products

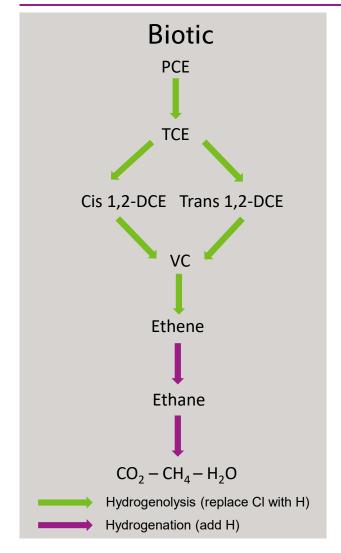


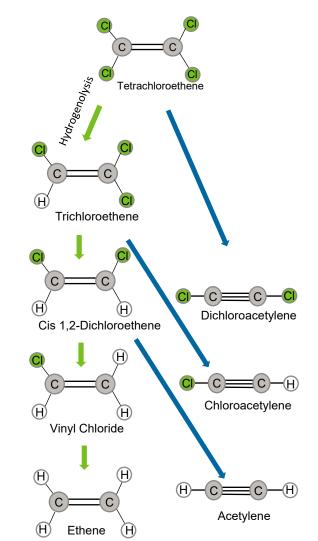
EHC

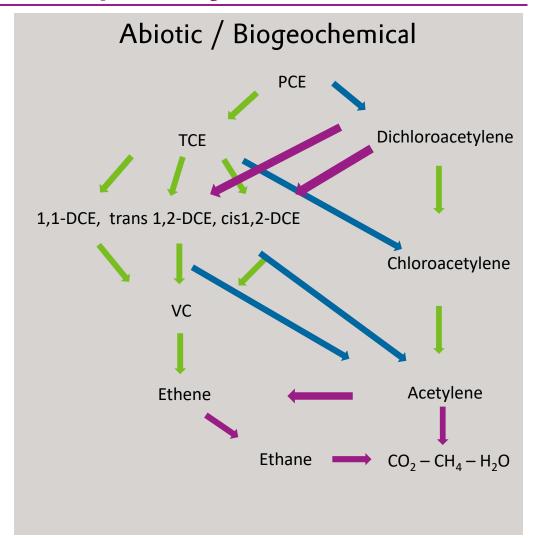




Combined organic carbon and zero valent iron enhance both biotic and abiotic chlorinated ethene degradation pathways



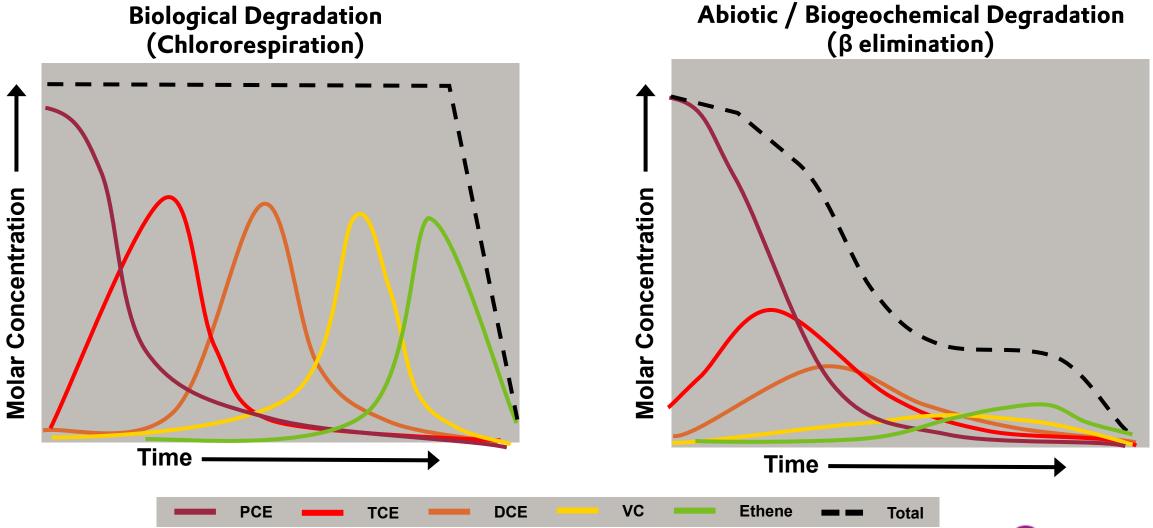








Anticipated Change in Chlorinated Ethene Molar Concentration



Emulsified Lecithin Substrate (ELS) - Biological Reduction Microscale ZVI

ELS® Concentrate creates a microemulsion of <u>food-grade carbon</u> that supports the treatment of a wide range of groundwater contaminants. ELS creates reducing conditions and promotes biologically enhanced reductive dechlorination reactions. ELS is specially designed for easy on-site handling, emulsification and addition to the subsurface via typically constructed wells, hydraulic injection networks, or direct push technology.



Composition

- > Food-grade lecithin, including:
 - Polysaccharides & sugars to support rapid creation of reducing conditions
 - ✓ Phospholipids for long-term release of organic carbon
 - ✓ Slow-release nitrogen & phosphorus

Availability

Provided as 100% concentrate (no added water)

Packaging:

> 55-gal. drum.



Adding Microscale ZVI to ELS = ISCR

ZVI added to:

- Maintain pH in range favorable for biological degradation
- Bypass generation of toxic daughter products
- Reduction of daughter products more rapidly achieves goals
- Provide long term process for continued dechlorination.





Design Optimization Test: Evaluate ELS® (liquid organic reagent)with Microscale ZVI

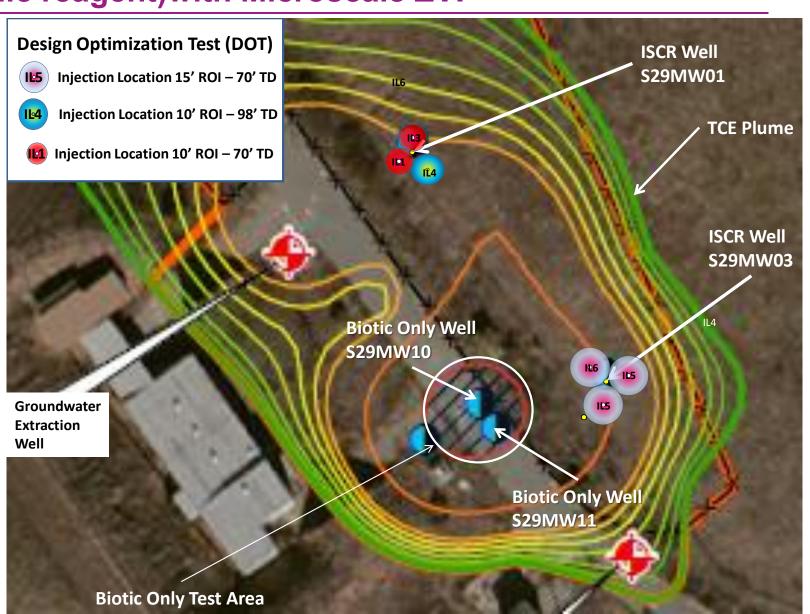
TCE in groundwater > 1,000 μg/L

Aerobic aquifer (~7 mg/L)

Applied organic substrate (buffered EVO) in Biotic Only Area

Applied organic substrate (ELS) + Microscale ZVI in ISCR Area

High Pressure direct push technology

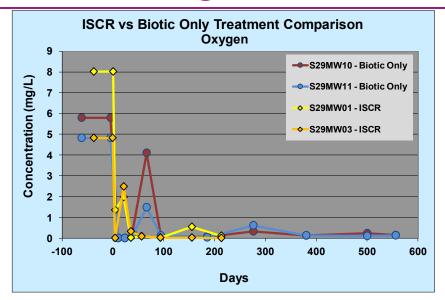


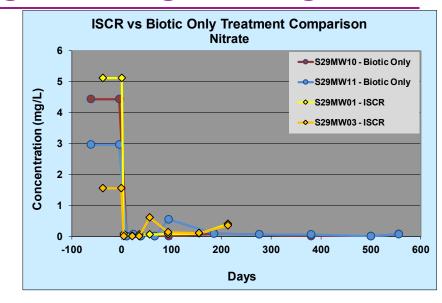
ELS + Microscale ZVI: Evaluating benefits of adding ZVI to organic reagents

Analytical Results

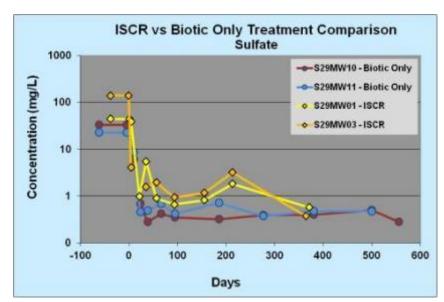
ISCR _____

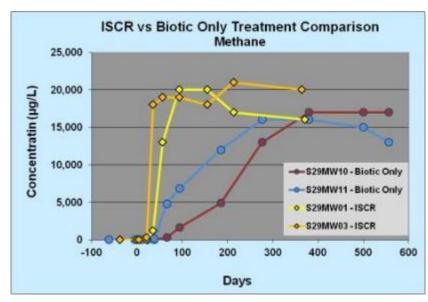
Bio Only





Electron acceptors rapidly reduced



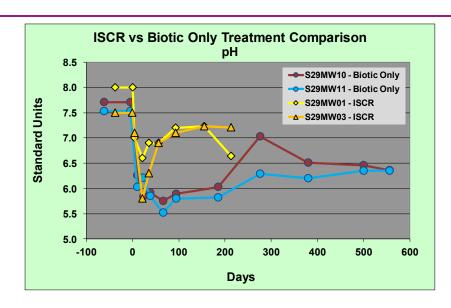


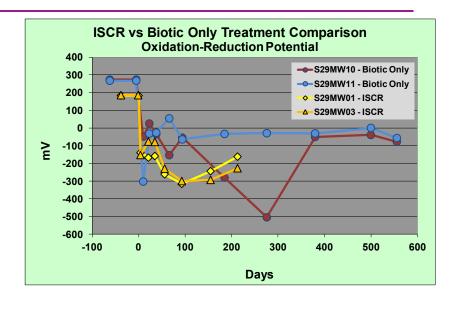
Analytical Results ELS + Microscale ZVI

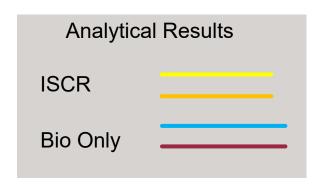
pH and ORP in optimal range

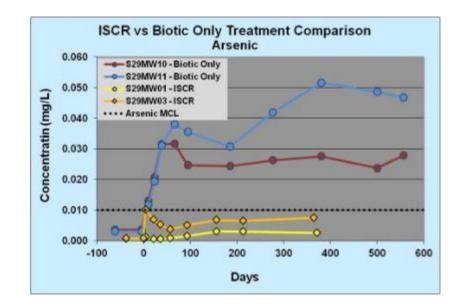
Iron prevented arsenic in solution > MCL

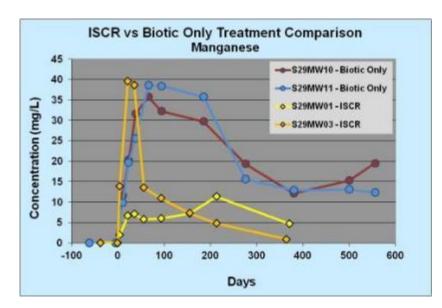
Quickly reduced mobilized manganese





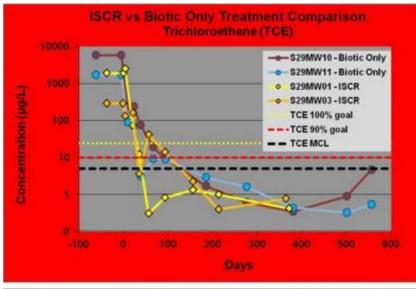


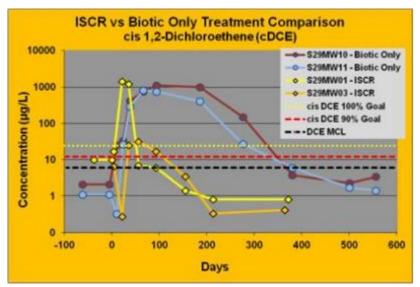


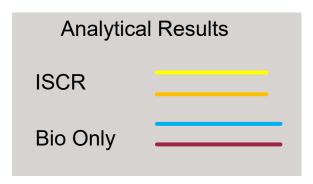


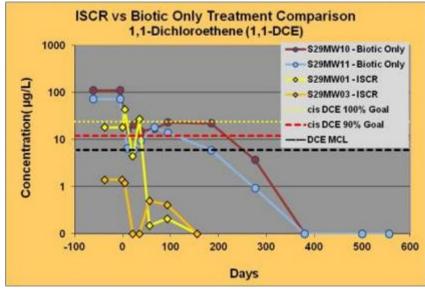
Analytical Results ELS + Microscale ZVI

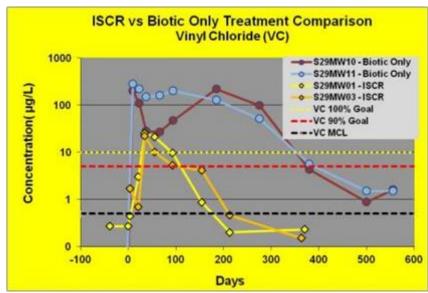
Minimal generation of chlorinated ethene daughter products substantially reduced cleanup time.











ELS + Microscale ZVI Field Test Results and Conclusions

- Inclusion of ZVI substantially increased the degradation rates of the chlorinated ethenes
- Increased degradation rates partially due to the β elimination degradation pathway (limited daughter product generation)
- Addition of ZVI limited the mobilization of toxic metals (i.e., arsenic)
- Organic substrate was mobile however ZVI is immobile
- Limitation of application is that the ZVI slurry must be injected by highpressure injection
- Due to contaminant depth (>100 feet) and large plume size and very permeable aquifer, distribution through wells may be a more preferable application method.

Solution:

Evaluate ways to inject iron and ELS through well screens





Limitations and Benefits: Injection by Direct Push Technology and Injection Wells

High Pressure Direct-Push Injection

- Depth: Typically, less than 100 feet BGS
- Limited radius of distribution ~ 20 ft
- One application
- Can inject thick slurries
- Can inject reagents in low K aquifers

Well Application

- Unlimited Depth
- Larger radius of distribution >100 feet
- Multiple applications
- Dependent on well slot size
- Flow rate limited by aquifer hydraulic conductivity (K)

Application method selection is site-specific and both well injection and direct push technologies are well understood.



Continued Development of Liquid Reagents: Soluble Ferrous-Iron Enhanced Biological Reduction

EHC® Liquid Reagent is an *in situ* chemical reduction (ISCR) product for the treatment of impacted groundwater. It is a cold-water soluble formulation that is specially <u>designed for injection via existing wells or hydraulic injection networks</u> for the treatment of a wide range of groundwater contaminants. EHC Liquid creates strong reducing conditions and promotes both biotic and abiotic dechlorination reactions.

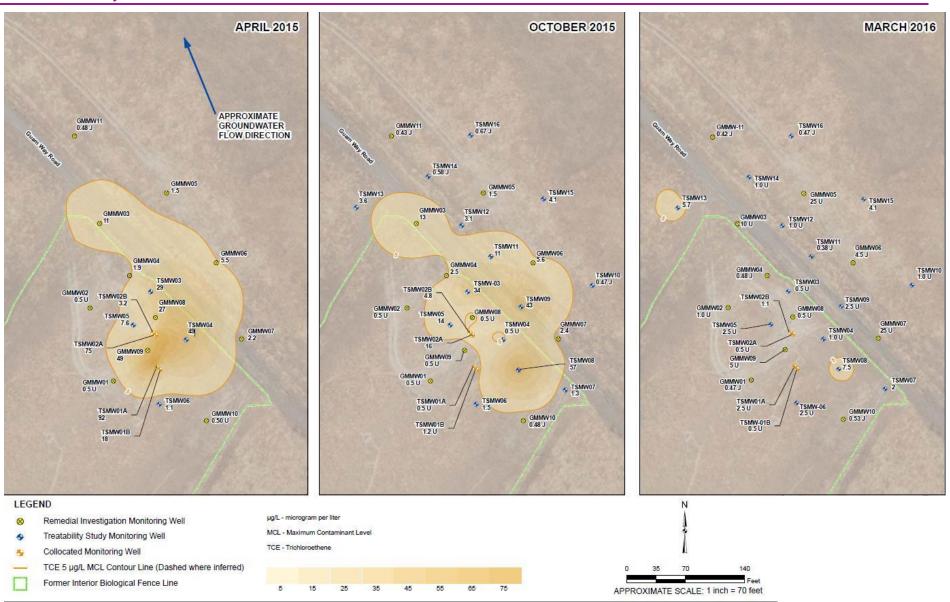
- Cold-water soluble ISCR product injection via existing wells or hydraulic injection networks
- Composition controlled-release <u>organic carbon</u> with a <u>soluble ferrous</u> <u>iron</u> compound - all food grade
- Delivered in two parts:
 - (i) liquid organic carbon (ELS Concentrate)
 - (ii) soluble ferrous iron powder.
 - > pH buffer, if needed, delivered as powder
- Water content will vary with desired injection volume and physical conditions





EHC® Liquid Treatment of TCE Plume, Concord NWS

EHC® Liquid applied to treat TCE in aerobic aquifer



Comparison of EHC® Reagent and EHC® Liquid: Chemical and Biogeochemical Treatment of PCE in High-Sulfate Aquifer

Sediment and groundwater samples collected from source area wells

Some sediment in each of the microcosms

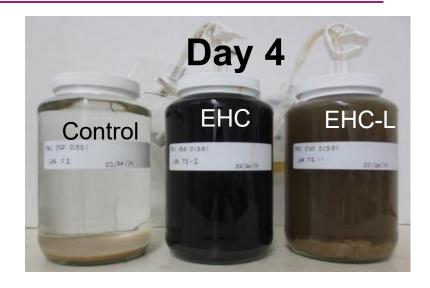
PCE – 170 μ g/L - Spiked to 1,800 μ g/L

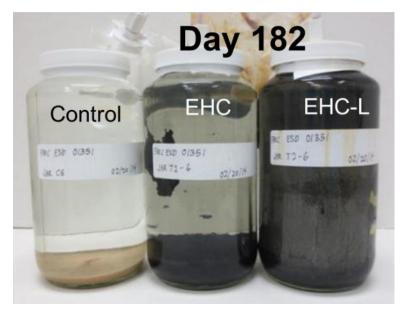
Sulfate – 1,800 mg/L - Spiked to ~2,300 mg/L

SDC-9TM Dhc ~ 1X10⁸ cells/L

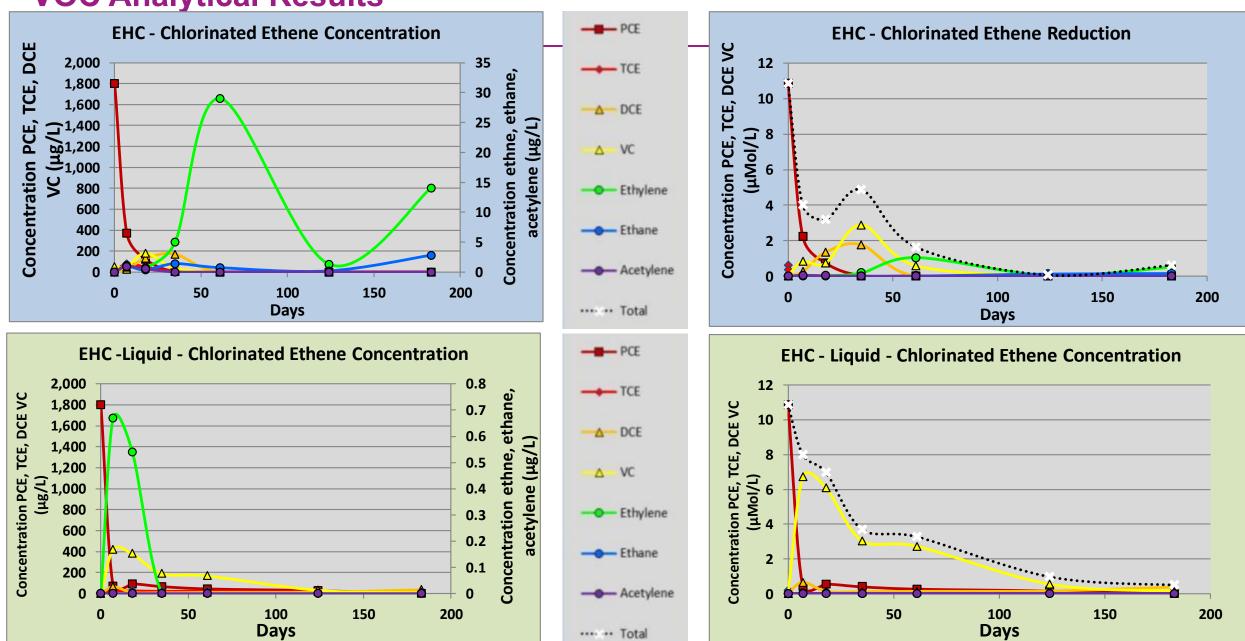
EHC® Liquid 10 g/L + additional 14 g/L soluble iron

EHC® Reagent - 10 g/L





VOC Analytical Results



How big of a particle can move through wells and unconsolidated sediments?

How big of a particle can move through a well screen?

Typical monitoring well screen = 0.01 inches (0.254 mm = 254 μ M to 0.02 inches = 0.508 mm = 508 μ M

Typical size range in microscale ZVI

Approximately 0.040mm to 1.000 mm

So, technically some microscale ZVI will fit through an 0.01 and 0.02 slot well screen

However,

Multiple particles suspended in water can clog the well screen

But some may get through the screen

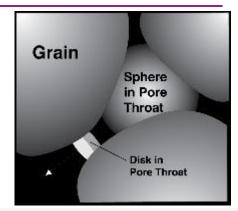


Microscale ZVI on magnet collected from inside monitor well after injection



Next Step: Getting through the aquifer: limitation of pore throat size

The pore size of sand varies significantly based on its particle size and packing, but it generally ranges from approximately 0.01 mm to 1 mm (10 to 1000 micrometers). Coarse sand has larger pores, while fine sand has smaller pores. For example, studies on specific types of sand show pore sizes can be distributed from 1 to 300 μ m

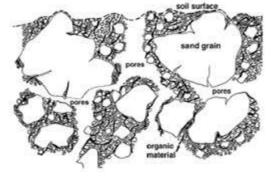


Pore throat size is related to sand grain size.

- smaller sand grains lead to smaller pore throats,
- larger grains can lead to larger pores and throats,
- the relationship is complex
 - depends on factors like grain shape and sorting
- A general guide is that for a random close packing of spheres, the largest throat is about \(1/4.5\) to \(1/6.6\) of the grain size.

Estimated Pore Throat of Spherical Particles							
	μМ	Pore Throat Size					
		4.5 6.6					
	2000	444.4444 303.0303					
Coarse Sand	1000	222.2222 151.5152					
medium Sand	500	111.1111 75.75758					
	250	55.55556 37.87879					
Fine Sand	125	27.77778 18.93939					
Silt	62.5	13.88889 9.469697					
clav	3.9	0.866667 0.590909					

Sediments are not perfect spheres





Settling Velocity: ZVI has a high settling velocity

Larger particles settle faster: A larger particle experiences a greater gravitational force and less relative drag, allowing it to achieve a higher settling velocity. The settling velocity is roughly proportional to the particle's diameter squared, so a doubling of the diameter quadruples the settling velocity.

Smaller particles settle slower: A smaller particle has a higher surface area to mass ratio, leading to more frictional drag from the fluid. This significant drag force slows its descent, keeping it suspended in the fluid for a longer period.

For very fine iron particles (e.g., below (2.0) µm), the settling velocity can be so low it is negligible compared to fluid flow.

Other factors: While size is a primary factor, settling velocity is also influenced by the particle's density, shape, and the fluid's viscosity and density. For iron, its high density is a key reason for its relatively high settling velocity compared to less dense materials like some plastics.

Because Microscale particles are so large they tend to settle out of water quickly, thereby limiting distribution Guar often used to suspend microscale ZVI to reduce the settling velocity by increasing the water viscosity.



Bench Test: Evaluate settling velocity of Evonik Ultra Fine 5 micron ZVI in water



Settling Velocity ~ 0.3 cm / Sec

So what flow rate is required to keep ZVI in suspension in 2" and 4" diameter wells?								
		_	_					
Diameter	Radius	Area	Area	Volume	Volume			
Inches	Inches	<u>In2</u>	cm2	cm3/min	gpm			
	0.5	3.141593	6.4516	31.8	0.000264			
2	1	3.141593	20.2683	644.5319	0.170267			
4	2	12.56637	81.0732	2578.128	0.681069			
6	3	28.27433	182.4147	5800.787	1.532406			

So, relatively low flow rate should maintain 5-micron ZVI in suspension

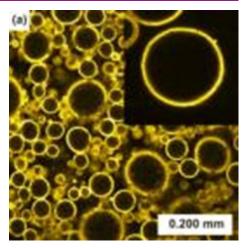


Evonik Ultra Fine ZVI Mixed with ELS® and/or EHC® Liquid

ELS with soluble ferrous iron (EHC® Liquid Mix) easy to mix in field and inject through wells.

Enhances both biological and biogeochemical degradation (in high sulfate aquifers)

Recently, ultra fine (5 micron) zero valent iron is now available in the United States for environmental remediation



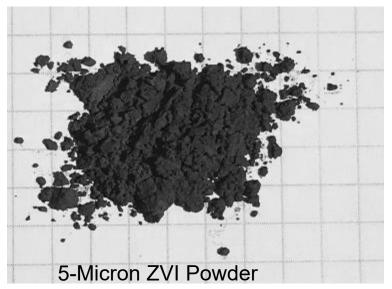
Benefit of Zero Valent Iron vs soluble ferrous iron:

5 Micron ZVI buffers ELS® so no needed buffer to keep pH in range appropriate for biologically mediated reductive treatment results in significant savings.

5 Micron ZVI added at higher concentration than soluble iron powder

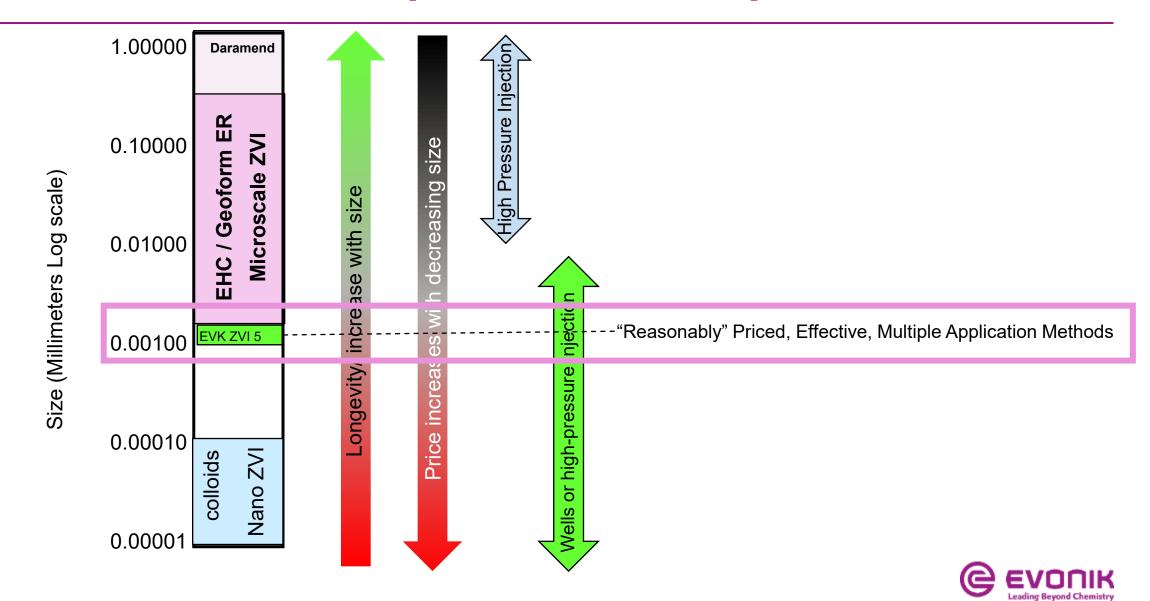
ZVI donates 3 electrons versus 1 electron from ferrous iron

Evonik 5 micron ZVI generates ~ 20X the reducing capacity of organo iron





Iron size selected depends on multiple factors?



Evonik Ultra Fine Zero Valent Iron

Evonik's Ultra Fine ZVI was developed to provide a source of ZVI for application with ELS through typically constructed injection wells

Uniform 5-micron diameter ZVI in organic suspension

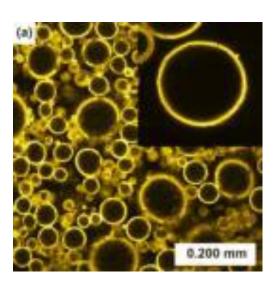
Liquid suspension reduces the potential for combustion of ZVI powder

Provided in 55-gallon drum containing 500 lbs of 40% 5-micron iron in organic liquid suspension.

ELS concentrate is easily emulsified in the field.

Iron is mixed with ELS emulsion and applied directly through wells or by direct high-pressure injection.









ELS® and Evonik Ultra Fine ZVI Batch Test setup, ORP and pH results

Bench test conducted to evaluate pH and ORP changes with reductive dechlorination processes.

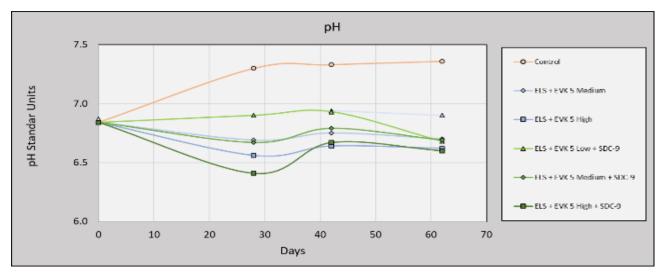
Tested 3 iron and ELS® doses (Low, Medium, High)

ORP remained in range optimal for biological reductive dechlorination.

pH remained in range optimal for biological reductive dechlorination without added buffer.

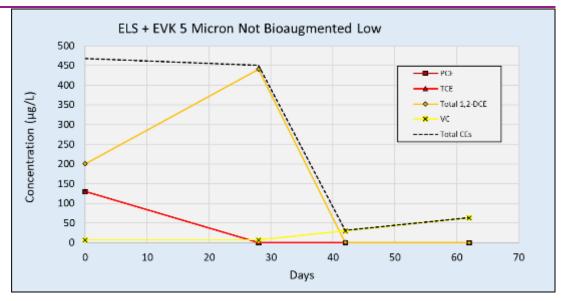
Condition	Treatment	ELS (mg/L)	EVK ZVI (mg/L)	Culture (µL)	Sampling (Days)
0	Control				21, 42, 62
1	EHC-L Low	1000	250		21, 42, 62
2	EHC-L Med	2000	500		21, 42, 62
3	EHC-L High	3000	750		21, 42, 62
4	EHC-L Low + Bio	1000	250	yes	21, 42, 62
5	EHC-L Med + Bio	2000	500	yes	21, 42, 62
6	EHC-L High + Bio	3000	750	yes	21, 42, 62

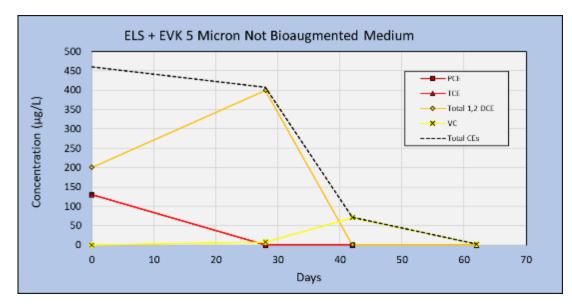
DRP (mV)										
Condition	Test	Treatment	Water	Day 0	Day 1	Day 5	Day 8	Day 14	Day 28	Day 60
1		Control		339	261	-302	-236	-266	-158	
2	EHC-Liquid	ZVI Low	Well	336	85		-69	-239	-164	
3	Eno-Liquiu	ZVI Medium	VVEII	334	106		-144	-204	-216	
4	ZVI	ZVI High		319	127	-447	-147	-189	-229	

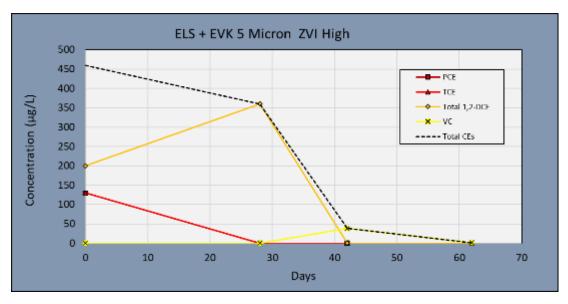


Bench Test ELS® + Evonik Ultra Fine ZVI: Enhances Both Biological and Chemical Reduction









Cost Benefit of Evonik Ultra Fine ZVI Relative to EHC® Liquid Mix

EHC® Liquid Mix - organo iron added approximately 27 to 83 mg/L of ferrous iron (Fe^{II} to the aquifer)

Current blend of ELS® and Evonik Ultra Fine (5 Micron) ZVI range dosing ~100 mg/L to 300 mg/L Fe⁰

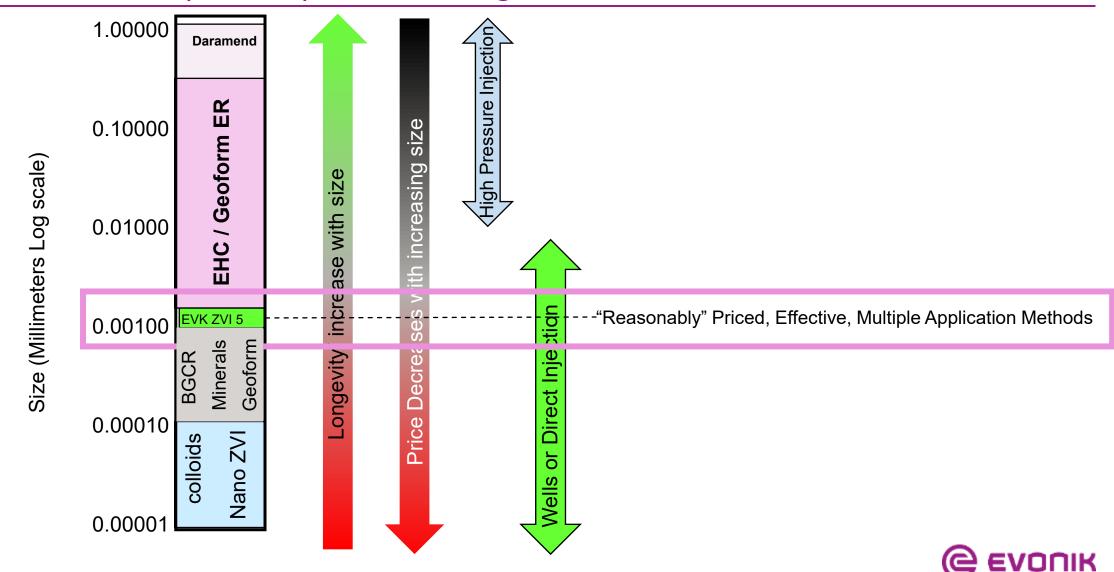
New blend provides approximately ~20 X the reducing power of soluble ferrous iron blend.

Because ZVI raises pH during corrosion, additional buffer is not required for most circum neutral pH aquifers

Because of the added electrons and mass of iron, Evonik Ultra Fine 5-micron ZVI is moderately less expensive than soluble organo-iron application while providing more aggressive treatment.



Evonik Ultra Fine ZVI (5 micron) Enhances Biogeochemical Treatment Processes



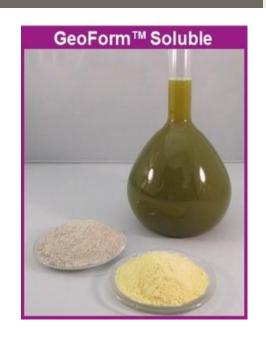
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GeoForm® Formulations

GeoForm® Soluble

GeoForm® Extended Release

- Injects as a solution forming long lasting solids.
- Proprietary blend of Soluble Organic Carbon, Sulfate, Ferrous Iron, pH buffer and nutrients.
- Delivered in 2 parts allowing for custom designs
- Longevity of 2-3 years or more



- Provides a longer lasting source of electron donors for continued rejuvenation of reactive minerals.
- Extended Release Organic Carbon, Micro-Scale ZVI, Sulfate, Ferrous Iron, pH buffers and nutrients
- Longevity of 5-10 years



	Treatment Mechanisms					
GeoForm® Formulation	Biotic Reduction	Abiotic Reduction				
		Reductive Minerals	ZVI			
GeoForm® Soluble	$\sqrt{}$	$\sqrt{}$	\checkmark			
GeoForm® Extended Release	$\sqrt{}$	$\sqrt{}$	$\sqrt{}$			



Sulfidation Increases ZVI reactivity and Longevity

"Sulfidation" ... can refer to any modification or transformation of a metal-based material by exposure to sulfur compounds of various oxidation states..."

GeoForm™ Soluble In Situ Sulfidation Process:

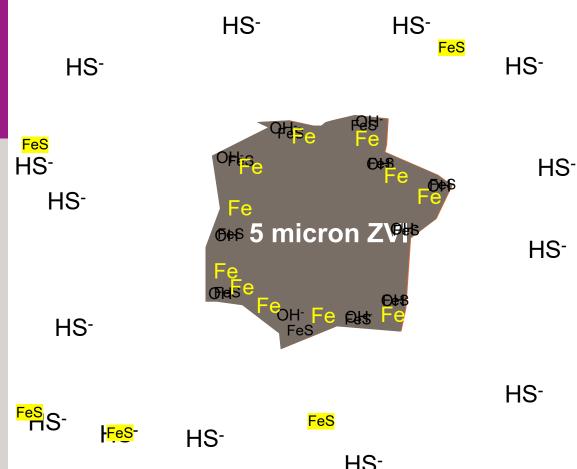
ZVI, sulfate (SO_4^{2-}), ferrous iron (**Fe**), and organic carbon (**OC**) are distributed in aquifer

ZVI reacts with water to generate ferrous iron and OHon surface

Sulfate is biologically reduced to sulfide (HS-)

Sulfide replaces OH- on ZVI

Fe²⁺ (ambient, supplied or from ZVI oxidation,) combines with HS⁻ to form FeS coating on ZVI and precipitate on aquifer matrix

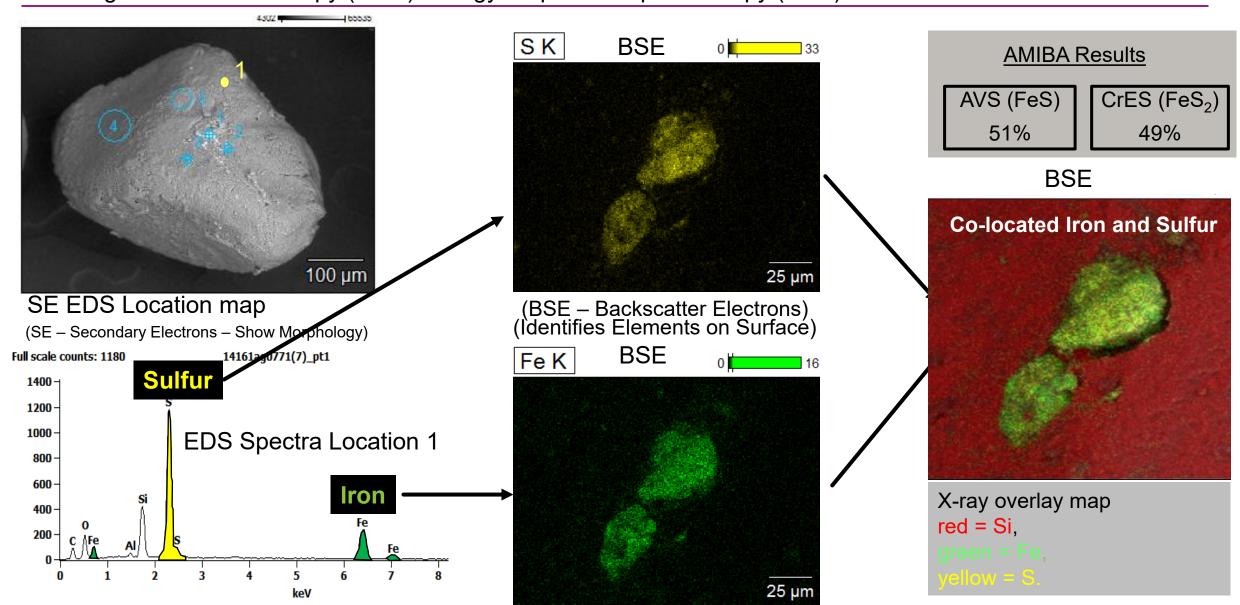


Sulfidation of Iron-Based Materials: A Review of Processes and Implications for Water Treatment and Remediation

Dimin Fan, Ying Lan, Paul G.Tratnyek, Richard L. Johnson, Jan Filip, Denis M. O'Carroll, Ariel Nunez Garcia, and Abinash Agrawal. Environmental Science & Technology

SEM-EDS Results Following GeoForm® Extended Release Application

Scanning Electron Microscopy (SEM)-Energy Dispersive Spectroscopy (EDS)



Evonik Ultra Fine ZVI with GeoForm® Soluble applies all major contaminant destruction pathways

GeoForm® Soluble mix adds source of soluble ferrous iron and sulfur.

Biological reduction of sulfate generates reactive iron-sulfide minerals (pyrite, mackinawite).

Sulfide in GeoForm® Soluble mix sulfidizes the ZVI

Both ZVI and iron-sulfide mineral create an abiotic degradation pathway (β Elimination).

Result: Sulfidation extends ZVI longevity and increases reactivity to chlorinated organics.

Combination of ZVI, ELS and GeoForm[®] Soluble reagents provide all major reductive CVOC degradation processes: Biological reduction, electron shuttle enhancement, chemical reduction, biogeochemical reduction, sulfidation.



When to use GeoForm® Soluble vs EHC® Liquid and Evonik Ultra Fine ZVI

GeoForm® Soluble is custom designed to achieve ~500 to 3,000 mg/L sulfate (You decide).

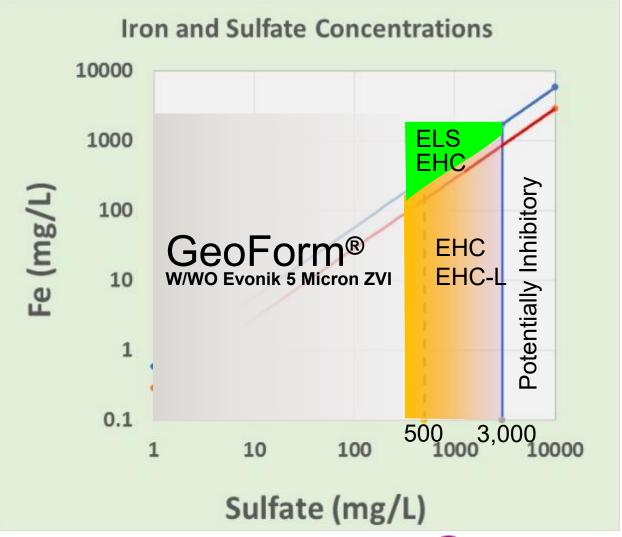


ELS (organic component) exceeds demand from sulfate, contaminants and other acceptors

In high sulfate – low iron aquifers consider adding iron in form of EHC, or EHC-L

In high sulfate – high iron aquifers consider ELS or EHC.

Sulfate in excess of 3,000 mg/L may be inhibitory (may try more iron)





Conclusions

Evonik 5-Micron ZVI:

- Applied with ELS enhances both biological and abiotic degradation of chlorinated ethenes
- Can be applied with ELS through typically screen wells (i.e., 0.01" & 0.02" factory screens)
- Small particle size
 - Allows wider distribution through very fine-grained sediments and pore throats
 - Allows for suspension and transport at substantially lower flow rates than micro-scale ZVI
- Applied with ELS provides substantially more iron and reducing electrons than reagents using organo-irons.
- Cost-effective substitute for soluble organo irons in many aquifers.
- Applied with GeoForm[®] Soluble provides all the major chlorinated organic destruction mechanisms including:
 - Biological reduction (ELS + Dhc),
 - Chemical reduction (ZVI),
 - Biogeochemical reduction (FeS minerals),
 - Sulfidation of ZVI

