



***In Situ* Remediation of Chlorinated Solvents via Admixing Reactive Media and Stabilizing Agents (ZVI-Clay)**

Tom Sale and Mitchell Olson

Department of Civil and Environmental Engineering • Colorado State University

OVERVIEW

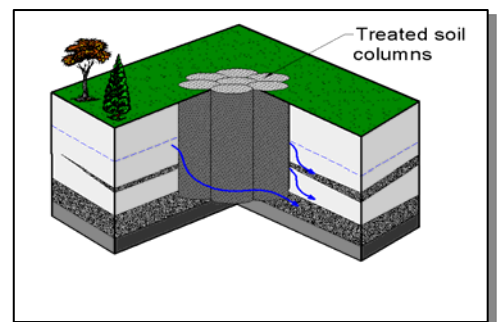
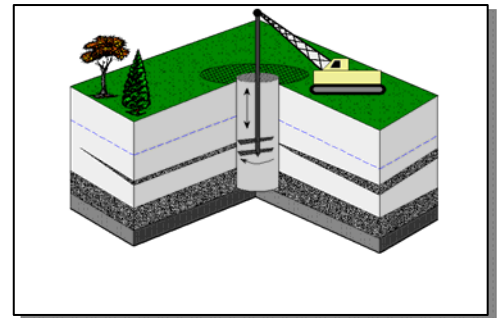
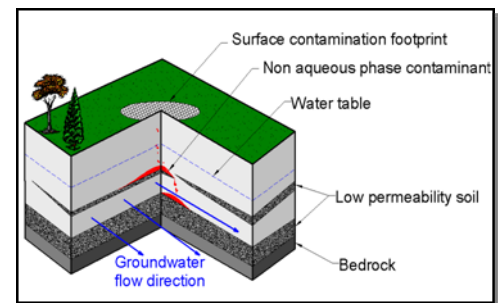
ZVI-Clay is an *in situ* remediation technology that involves admixing reactive media (zero valent iron), stabilizing agents (clay), and soils containing chlorinated organic compounds using conventional soil mixing equipment. Through this process, chlorinated compounds in source zones are depleted and hydraulic conductivity of the targeted zone is decreased. The net benefit is a reduction in future releases of contaminants from the treated intervals. This technology offers the potential of faster, less costly, and more effective treatment than competing technologies for a significant set of sites.

DuPont and the University of Waterloo pioneered ZVI-Clay in the 1990s and early 2000s. In 2003, DuPont donated patents for the technology (Batchelor et al. 1998 and 2002) to Colorado State University (CSU). CSU is currently advancing the technology through research and commercialization initiatives. CSU's partners in advancing ZVI-Clay include DuPont, CH2M HILL, TetraTech-NUS, Arcadis, Geo-Solutions Inc., and Chevron.

To date seven full-scale field projects have been completed involving treatment of 25,000 cubic yards of impacted media. Observed treatment of PCE, TCE, and CT in soils and groundwater (in the treated body) fall in the range of 99 to 99.99%. Contractor costs for mobilization, mixing, materials, and demobilization have ranged from \$71/cubic yard (7,000 cubic yards site) to \$175/cubic yard (1,100 cubic yard site).

PROCESS DESCRIPTION

ZVI-Clay uses conventional construction equipment to admix reactive media and stabilizing agents with contaminated soil. Through soil mixing, 1) heterogeneous source zones are turned into



uniform bodies, 2) contaminants are intimately commingled with reactive media, and 3) hydraulic conductivity is reduced. Soil mixing greatly reduces the need to rigorously delineate contaminant distribution within source zones and overcomes the challenge of delivering reactive media through complex geologic media. In addition, treatment is completed in one pass. This can provide significant scheduling and cost benefits. Conditions through the process of soil mixing are illustrated below.



After mixing, contaminants are degraded *in situ* by the reactive media. In the case of iron and chlorinated solvents, corrosion of the iron drives dechlorination via reductive pathways (Gillham and O'Hannesin 1994). Reaction rates generally follow pseudo first-order kinetics. In soils treated by ZVI-Clay, observed half lives for most chlorinated solvent fall in the ranges of 1 to 30 days (Olson 2005). With these conditions, remaining contaminant mass is reduced by 90 percent every few days to few months. Where media is well-mixed, this process has been shown to achieve total

depletions of 99 to 99.99% in soil and groundwater. Degradation rates are dependent on the specific contaminants, the type of iron used, the amount of iron used, and the mineralogy of the soils. Granular ZVI



Stabilizing agents (typically clay) provide multiple benefits. Foremost, admixing clay and soil results in large reduction in hydraulic conductivity. This limits discharge of contaminants during and after mixing from the treated body. Furthermore, stabilizing agents also 1) facilitates drilling, 2) provides a high viscosity delivery fluid for suspension and deliver of granular iron, 3) improves subsurface mixing, 4) reduces inflow of competing electron acceptors, 5) increases residence time for the reaction to proceed, 6) enhances capillary rise precluding air entry into treated material above the water table, and 7) constrains adverse migration of dense non-aqueous phase liquids.

LABORATORY RESEARCH

Over the last four years, in excess of \$500,000 has been invested in laboratory research conducted at Colorado State University. Key focus areas include:

- Resolving governing reaction processes and developing models for prediction of performance.
- Site specific treatability studies focusing design optimization and resolving effectiveness.
- Analysis of the post treatment geotechnical properties of soils and development of post treatment design options.

Key results from laboratory efforts include are noted below.

ZVI Size and Amount – Reaction rates increase with greater amount of iron and with smaller iron particle sizes. Results from field sites indicate that fine-grained granular iron (i.e., -50 +100 mesh) has a favorable cost, can remain reactive in the subsurface for at least two years, and is typically sufficient, at ~2% by weight, to address high concentrations of chlorinated solvents.



DNAPL Emulsification – Clay particles bridge the DNAPL/water interface, promoting the formation of Pickering emulsions. Furthermore, the viscosity imposed by the clay inhibits coalescing of DNAPL droplets. Benefits of emulsification include higher rates of DNAPL dissolution and limiting adverse DNAPL migration during treatment.

Post Treatment Compressive Strength – During delivery of ZVI and clay, water is added to the targeted media. This decreases the compressive strength of the soil. Promising options for restoring the compressive strength of the treated media include addition of cement to the top of the targeted interval, placing a surcharge on the treated media to enhance drainage (see images on the left) and/or use of wick drains to enhance drainage. To date, cement stabilization has been employed post treatment at two sites. Initial addition of cement has been avoided since high pH conditions (associated with many cements)



can inhibit the desired depletion of chlorinated solvents.



Laboratory Treatability Studies – To date, nine laboratory treatability studies have been completed. Through these efforts, methods for conducting laboratory studies have been refined. The current approach involves use of an automated mixing system (right) that allows repeatable mixing of multiple columns. Reactor vessels are constructed of transparent PVC (left) with multiple sampling ports. Performance is evaluated via soil samples, which are collected through the ports over time. Comparisons between lab and field results are favorable.



Up to four nines of removal in a year –

Results from laboratory studies conducted to date indicate half-lives of common chlorinated solvent on the order of 1 to 30 days. In general, PCE is the slowest and carbon tetrachloride is the fastest. Given even the slowest rates up to four nines of removal appear to be obtainable within one year. A number of optimization studies are currently ongoing. Key focus areas are improving reaction rates and limiting formation of reaction byproducts such as methylene chloride.

Site Location	Contaminant	Iron Source	Iron Amount (%)	Soil Treatment	Half-Life (h)
Camp Lejeune, North Carolina (DoD) (2005)	PCE	Peerless	1	UnS, B	1,033
		GMA	1	UnS, B	484
		Peerless	3	UnS, B	465
		Peerless	5	UnS, B	539
		Peerless	7	UnS, B	517
	PCE	Peerless	1	S, B	664
		GMA	1	S, B	621
		Peerless	3	S, B	787
		Peerless	5	S, B	699
Florence, South Carolina (Industrial)	CT	Peerless	1	S, K	140
		Peerless	2	S, K	120
		GMA	2	S, K	230
		Connelly	2	S, K	62
		Peerless	5	S, K	87
	CF	Peerless	1	S, K	350
		Peerless	2	S, K	140
		GMA	2	S, K	35
		Connelly	2	S, K	51
		Peerless	5	S, K	69
	1,1,2,2-TCA	Peerless	1	S, K	170
		Peerless	2	S, K	46
		GMA	2	S, K	9
		Connelly	2	S, K	40
		Peerless	5	S, K	46
Yellowstone County, Montana	Toxaphene	Peerless	2	UnS, K	72
		GMA	2	UnS, K	55
		Connelly	2	UnS, K	46
		Peerless	5	UnS, K	33
		GMA	5	UnS, K	55
		Connelly	5	UnS, K	33

FIELD APPLICATIONS

To date, ZVI-Clay has been used in seven full-scale site remediation efforts. Key attributes of the projects are summarized in the Table below. In addition, three sites are currently in varied phases of evaluating use of ZVI-Clay in 2007.



- Complete
- Pending

ZVI-Clay Field Applications Through 2007

Site	Date	Primary Contaminant	Volume of Treated Soil (cubic yards)	Facility	Soil Mixing Technique	Contractors Costs (\$ per cubic yard)	Performance in the Treated Body (Soils or <u>Water</u>)
Kinston, VA	1999	TCE	~ 600	Manufacturing Facility	Jet Grouting	NA	90% after 1 year – Performance limited by incomplete mixing
Martinsville, VA	2002	CT 20 tons	4,000	Nylon Plant	Crane – Soil Mix Sys.	\$120	CT 99.99%, total CVOCs 99% removal (2 years)
Camp Lejeune, NC	2005	PCE 13 tons	7,000	Dry Cleaner	Crane – Soil Mix Sys.	\$71	Removal after two years – Soils, PCE >99.95% & TCE >96% removal over most of site – <u>Water</u> >99% PCE, >99% TCE
Arnold AFB, TN	2005	TCE	4,000	Disposal Area	Surface Rotary Sys.	NA	NA
Vint Hill Farm, VA	2006	Mixture of chlorinated solvents	1,100	NA	Crane – Soil Mix Sys.	\$175	Removal at 11 months – Soils BDL <u>Water – Total VOCs – 98.6%, DCE – 99.4%, PCE>98.9%, TCE>98.9%, DCE-99.3%, CT>80 (BDL), MC-92%, 1,1,2-TCA 91%, 1,2-DCA 77%</u>
DOD Site, MO	2007	TCE in Cutting Oil	~7,000	Munitions Manufacturing	Crane – Soil Mix Sys.	NA	NA
Florence, SC	2007	Mixture of chlorinated solvents	800	Manufacturing Facility	Surface Rotary Sys.	NA	NA

Approaches employed to date to resolve field-scale performance, and associated results, are noted below:

- Soils Concentrations – Soils have been collected before and after soil mixing at four sites. With the exception of a few local hot spots, all sites have shown 99 to 99.99% removal of chlorinated solvents in soils.
- Groundwater concentrations
 - In the treated body - At two of the sites wells in the treated bodies have been used to evaluate performance. Observed depletion of PCE, TCE and CT and related byproducts is on the order of 99%. Also, degradation of more recalcitrant compounds (MC, 1,1,2-TCA, and 1,2-DCA) is being observed
 - Downgradient of the treated body – At two of the sites downgradient water quality has been monitored during and after mixing. No adverse downgradient impacts have been observed during mixing. Post mixing, downgradient concentrations of targeted chlorinated solvents in groundwater have improved by one to two orders of magnitude
 - Hydraulic conductivity – Pre and post treatment hydraulic conductivity has been measured at two sites. Results indicate reductions in hydraulic conductivity by factors of 300 and 1000.
- Subsequent land use – At three of the sites (images below) post treatment capping has led to subsequent use of the land for parking vehicle. At the remaining sites the land is in an undeveloped state.



SUMMARY

ZVI-Clay is an innovative *in situ* remediation technology targeting chlorinated solvent source zones. Conventional soil mixing equipment is used to deliver granular iron and clay into target media. Zero Valent Iron (ZVI) drives degradation and clay reduces the hydraulic conductivity of the treated body. The combination provides synergistic benefits of contaminant depletion and stabilization.

ACKNOWLEDGMENT

We greatly appreciate, TetraTech-NUS, Arcadis, Geo-Solutions Inc. and numerous students at Colorado State University. Support for this work provided by DuPont, faculty at the University of Waterloo, EnviroMetals Technologies Inc., CH2M HILL .