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Innovative Injection Technique to Treat DNAPL in Granular and Fine-Grained Matrices

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ABSTRACT: High-energy, low-volume pulses of a water-based suspension of a unique treatment material (BOS 100®) consisting of granular activated carbon that has been impregnated with metallic iron were employed to remediate DNAPL at a large urban industrial facility. Initially, injections were completed using conventional hydraulic fracturing and large portions of the dissolved phase plume responded to this technique. However, selected areas of the plume were resistant to this approach, and it became apparent that an unknown source or sources were present. High-resolution sampling demonstrated that localized thin seams of DNAPL impacted soils were present at several locations in the vicinity of the former TCE UST. Successful remediation of these impacts required surgical placement of treatment at fairly high loading. Deep soil mixing was evaluated however the estimated cost for this approach was prohibitive given the relatively small area of interest. A modified "jetting" approach was developed that allowed extremely accurate placement and mixing of injectate with impacted soil over a relatively thick zone. This effect was realized using a high-flow, high-energy pulse of a water-based suspension of BOS 100®.

INTRODUCTION

The site is a large, urban industrial facility where trichloroethylene (TCE) had been used extensively as a cleaning solvent. Conventional "nature and extent" site characterization suggested that historical releases of TCE had resulted in a dissolved-phase plume of roughly 6,600 m^2 and a source area located nearby the former UST where groundwater TCE concentration was 54 mg/l. The UST used for bulk storage of TCE had been removed and soils over-excavated. Based on post-removal site investigation results, DNAPL was not suspected to be present.

Site Description. The site is underlain by river deposits and sedimentary bedrock. Alluvial sediments within the impacted zone primarily consisted of well-graded, fine- to coarse-grained sand approximately 50 feet thick. However, over much of the southern portion of the site an aquitard is present at a depth of roughly 15 meters consisting of interbedded sand, silt, and clayey silt deposits. The thickness of this formation varies from 1 to 2 meters and underlies the former TCE storage UST and residual source area.

Regional groundwater seep is generally to the north-northeast however the gradient is very flat and historical changes in the piezometric surface coupled with localized variation in hydraulic conductivity as a function of site stratigraphy resulted in unpredictable flow directions and distribution of TCE.

Remedial Technology. The selected remedy for this site was an immiscible, activated carbon injectate (BOS 100® manufactured by Remediation Products Inc.) designed for rapid degradation of chlorinated solvents. The product consists of activated carbon that has been impregnated with metallic iron. The manufacturing process results in an extremely large (metallic iron) surface area that is highly active. The product is mixed with water and the resulting slurry is then injected using high pressure pumps. Hydraulic fracturing is employed to enhance its distribution and place the material throughout the impacted formation. First, contaminants are “trapped” by the activated carbon and then degraded by reaction with the metallic iron residing within the inner pore structure. Reaction byproducts include low levels of dissolved iron, chloride, and a series of non-toxic and unregulated hydrocarbon gases such as ethylene, and methane. No significant amounts of daughter products are generated.

INJECTION APPROACH AND METHODS

For much of the plume, conventional hydraulic fracturing techniques were adequate and had achieved the desired results. However, certain regions of the plume were resistant to this treatment approach and it became increasingly apparent that something was being overlooked. As a result, a high resolution sampling strategy was implemented to evaluate poor performance in selected areas of the plume. The sampling strategy enabled detection and definition of numerous disjointed and highly localized pockets of DNAPL distributed over an area of approximately 230 square meters. Percent level TCE impacts as high as 5.4% (wt) were observed within extremely narrow zones ranging from a fraction of a centimeter to several centimeters in thickness.

High Resolution Sampling. This sampling strategy involved use of groundwater data to guide subsequent soil sampling in an effort to locate small source areas. A more detailed description of this methodology is available in another conference paper by Mr. Thomas A. Harp. By way of example, representative data showing the highly localized distribution of TCE in sub-surface soils is shown in the following table.

TABLE 1. Partial boring log for soil boring 108

Moisture Content	PID (ppm)	TCE Result (µg/kg)	Sample Interval (m)	Depth (m)	Recovery (m)	Soil/Rock Type
WET	1		10.89 - 10.95		1.5	CL
	ND	97		11.08		ML
	1		11.2 - 11.26			
	333	428		11.4		
	9	53,760	11.54 - 11.6			CL
	9,999+	25,477,000	11.66 - 11.72	11.7		ML
MOIST	390	915,300	11.78 - 11.85			CL
	124			12		
	4	193	12.12 - 12.19			
	9			12.3		ML

A 1.5 meter section of the soil core is displayed showing the inter-bedding of sandy silt and sandy clay lenses. Field PID readings are shown along with associated laboratory results for TCE at specific sample intervals denoted in meters. Massive changes in concentration occur over very narrow zones. For example, a change of nearly 3-orders of magnitude was noted in less than 0.1 meters of depth as TCE increased from roughly 54 ppm to over 25,000 ppm. Such highly localized seams of percent level TCE required a far more surgical injection technique than that which had been previously utilized at the site.

Sub-Surface Injection Dynamics. Conventional hydraulic fracturing techniques applied to fine grained soils do not allow for control of the path taken by injectate. Rather, injected fluid tends to take the path of least resistance. Although conventional wisdom may suggest that contaminants and groundwater also follow these same groundwater pathways, this is typically only achieved with low-flow, low pressure injection techniques and this technique will fail when suspended slurries are to be injected (In Situ Remediation Reagents Injection Working Group, August 2009). When high pressure pumps are used to inject fluids into the formation, as pressure builds, soil structure fails and the fluid causes soil to separate or “fracture”. As the injection progresses, this separation propagates through the formation in very unpredictable directions. Now, the “path of least resistance” means the path traveled by the lowest pressure required to separate the soil structure. This may coincide with bedding planes, cracks, and other discontinuities in the soil structure. The point is that such random pathways are not conducive to targeting highly localized seams of DNAPL.

Another issue associated with DNAPL in general and highly a localized seam in particular is the amount of material required to treat the mass on any volume basis. Depending on the technology or chemical chosen, it is not possible or realistic to place enough material within the DNAPL impacted zone to address the resident mass. As a result, it would be advantageous to dilute or smear the mass over a larger thickness so that treatment became more practical. One way of doing this is through deep soil mixing techniques that use large diameter augers to churn soil and mix amendments into specific depth horizons. In the process, impacted soils are well mixed and tend to become smeared over a somewhat thicker zone. Cost is the principal impediment to use of this technique in that mobilization of the equipment alone will generally exceed $100,000. Deep soil mixing was considered to address DNAPL at the subject site however the extent of impacts were too small to support the expense.

An alternative to deep soil mixing is use of a modified “jetting” technique to mix injectate and impacted soil. Jetting uses high velocity streams (jets) of fluid to cut swathes in and displace soil. It is often used to construct slurry walls or to stabilize contaminants with clay or pozzolan-cements. The objective would be to modify the technique so that radial mixing of soil with injectate occurs to the extent that soils become “fluidized” and this fluidized zone is propagated out from the point of injection. A technique was developed that created high energy low volume pulses of slurry. A customized injection tool was fabricated that was able to create narrow zones of injectate well mixed with impacted soils. As a result, high densities of injectate could be installed with virtually surgical precision.

Tip Design. Industry-standard direct-push injection equipment often relies on pumping equipment capable of no more than 6.9 x 10E6 pascals at 120 lpm. Using commercially available injection tips the injectate would exit the tip at a velocity of approximately15 m/sec. This exit velocity lacked sufficient energy to ensure penetration of the formation at the depths of interest.

Extensive field testing of over 30 different rod and hole configurations led to the development of an injection tip that consisted of a standard, five-foot long, 5.72 cm O.D., Geoprobe rod sealed with a standard drive-point on the end. Six 3.97 mm holes were drilled over a 7.6 cm section of the rod approximately one foot down from the upper end. The geometric placement of the holes, allowed the injectate to exit the rod into the formation every 60 degrees when looking down on the rod. Table 2 provides injection tip details including the size and number of holes drilled through the rod. The tip was tested over a wide range of flow rates from approximately 200 lpm (50 gpm) to nearly 950 lpm (250 gpm).

TABLE 2. Injection rod orifice geometry and flow dynamics.

Injection Rate (lpm)	Size of Orifice (cm)	Area of Single Orifice (sq cm)	Number of Holes	Total Area of Holes (sq cm)	Exit Velocity (m/sec)
202	0.3969	0.1226	6	0.735	44.6
310					68.7
419					92.7
442					97.9
508					112.5
597					132.2
698					154.5
775					171.7
856					189.7
942					208.6

The visual effect at these higher flow rates is quite dramatic as shown in Figure 1. During one such test, it was noticed that a hole had been created in the soil by the downward facing jet. Insertion of a tape measure showed that the hole was nearly 5-feet (1.5 meters) deep. This is just another indication of the effects of the high energies involved.

FIGURE 1.

Pump Specification. The effectiveness of this injection tip was made possible by the injection equipment that was used. The BOS 100® slurry was blended on a custom designed mixing trailer. The slurry was then transferred to the injection rig equipped with a 165 hp, triplex, positive displacement oilfield service pump. The inlet side of the pump had a special design to maintain the BOS 100® in suspension while the valves and seats within the pump were engineered to tolerate the abrasive nature of the material. Valving on the outlet side of the pump permitted the slurry to be circulated within the injection rig until it was time to direct the slurry to the injection rod.

This author is not aware of any other pump system similar to that used anywhere in the USA. Figure 2 shows Summit who weighs 31 kg and the pump, which weighs 2300 kg. The equipment and all modifications to perform this work were provided by Well Improvement Company of Fort Collins, CO.

FIGURE 2.

The injection pump is powered by the truck engine and is coupled to its transmission. Depending on the transmission gear selected and the speed of the engine, injection rates between 31 and 1160 lpm were possible. At each flow rate, the system is able to deliver a pressure up to 17.2 x 10E6 pascals. The best results in targeting the sandy silt lenses were achieved with injection rates between 580 and 970 lpm. At these flow rates the slurry exit velocities were approximately132 and 215 m/sec respectively. Due to safety considerations, high flow injections are not instantaneously initiated. The flow is gradually increased to the set-point and then disengaged when the targeted volume was installed. Typically, 50 gal (194 L) volumes were installed at an injection rate of 850 lpm (exit velocity of 190 m/sec).

Typical Installation Design. Typically the pulse volume was 30 to 50 gallons injected at a rates ranging from 150 to 250 gpm. Exit velocity of injectate ranged from 12,000 to over 20,000 ft/min. Injections were completed in 10 to 15 seconds. Sentinel wells surrounding the injected area were used to monitor for any movement of contamination.

RESULTS

Much has been written about the difficulties associated with return of sites to pre-contamination conditions when DNAPL is present. DNAPL represents a long term source of groundwater contamination and one of the most difficult problems is that DNAPL is very often nearly impossible to locate (Bedient et al., 1999). US EPA conducted a detailed technical evaluation at 24 ground water pump-and-treat sites and concluded that the key factor responsible for poor performance was the presence of DNAPL in the water bearing units (US EPA, 1989). Further, in May of 1992, US EPA issued a directive that recognized full remediation of ground water at sites impacted by DNAPL may be technically impractical (US EPA, 1992). Given the well known difficulty associated with clean-up of DNAPL, expectations were not high.

Injection Distribution. Testing of various tip designs was a challenge. An injection would be completed and then soil sampling was performed to elucidate the extent of radial mixing, effective radius of influence, and the overall distribution. It was determined that much better distributions were obtained when holes were drilled within a narrow length of rod rather than spread out over a 30 to 60 cm section. Figure 3 shows a distribution obtained during testing of the chosen injection tip. A very homogeneous mixture of soil and BOS 100® roughly 5 inches (12.7 cm) thick is shown. Recalling data from Table 1, DNAPL impacted soil at that location resides within a 6 cm seam. Based on the test, estimated product loading in the soil should be adequate to address known seams of DNAPL impacts.

FIGURE 3.

Groundwater Results. One way to think of the installation is to envision a bed of activated carbon installed within the impacted soil and groundwater. Adsorption of organic contaminants by activated carbon is a very fast process. As a result, if the BOS 100® product is properly placed in contact with contamination, concentrations of contaminants will rapidly fall.

Within regions of DNAPL, groundwater TCE concentrations up to 1,280 mg/l were observed. As expected, measured concentrations of TCE in groundwater were not a good indicator of progress until DNAPL was reduced. In most cases, the total amount of BOS 100® required was installed in divided doses over a few injection events. Once the prescribed amount of BOS 100® had been installed, TCE concentrations in groundwater began to decline. Table 3 summarizes ground water data from key wells within DNAPL impacted areas. The first area where a DNAPL impact was delineated and treated is the PZ-055 area. As a consequence, treatment has been in place for roughly one year longer than at other locations on the site.

TABLE 3. TCE concentrations in groundwater.

Well ID	Historical Maximum TCE Result (µg/L)	Most Recent TCE Result (µg/L)	Percent Reduction
PZ-052	106,250	630	99.41
PZ-055	1,280,000	2.4	100.00
PZ-127	149,260	790	99.47
PZ-138R	140,825	980	99.30
PZ-154	589,870	240	99.96
PZ-156R	594,125	694	99.88
PZ-157R2	210,000	512	99.76
PZ-184	256,000	410	99.84

As part of the closure plan, a pair of monitor wells was installed within the PZ-055 area. One well was screened across the upper portion of the water table and the second well targeted the zone right at the bedrock. After treatment was completed, TCE concentration fell to less than 5 µg/l in both monitor wells and has remained below the standard for over a year. The dissolved phase plume was also mitigated and site-closure monitoring began in 2011.

LESSONS LEARNED

There are a multitude of opinions about injection of water based solutions and slurries and how best to install them. Guidance documents have been written. However, the key feature when targeting highly localized impacts will be control over where injectate goes and the ability to install high densities of treatment material. Conventional hydraulic fracturing or low-flow/low-pressure injections will not accomplish this goal.

Extensive evaluation of numerous injection tips showed that the distribution resulting from injection is a strong function of both the exit stream energy and geometry of hole layout. The premise that drilling holes over a wider length of the injection tip will enable a more uniform distribution of injectate proved to be inaccurate. Instead, it was found that fewer small diameter holes drilled within a short section spanning a few centimeters produced much better results.

It is possible to remediate DNAPL using in situ technologies however the keys to success will turn on the adequacy of data and specialized injection techniques. Given the recognized difficulty associated with detecting and delineating DNAPL, it is clear that conventional “nature and extent” investigations are inadequate to the task. Only specialized sampling techniques can produce data of sufficient resolution to define source impacts like those existing at this site.

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REFERENCES

Bedient, P.A., H.S. Rifai, and C.J. Newell. 1999. *GROUNDWATER CONTAMINATION Transport and Remediation.* 2^{nd} Edition, Prentis Hall.

Harp, T.A. 2012. *Obtaining High Resolution Data to Characterize and Design Treatment for DNAPL and Associated Plume in Granular and Fine-Grained Matrices*. Battelle, Proceedings of the Eighth International Conference (May 21-24, 2012).

In Situ Remediation Reagents Injection Working Group. 2009. Subsurface Injection of In Situ Reagents (ISRRs) within the Los Angeles Regional Water Quality Control Board Jurisdiction. A technical report compliments of REGENESIS.

U.S. Environmental Protection Agency. 1989. *Evaluation of Ground-Water Extraction Remedies*, Volume 1 Summary Report, EPA/540/2-89/054.

U.S. Environmental Protection Agency, 1992. *Estimating Potential for Occurrence of DNAPL at Superfund Sites*, R.S. Kerr Environmental Research Laboratory, EPA 9355.4-07FS.