

Pollution Engineering

Solutions for Air, Water, Waste and Remediation

Oxidants & Reductants Work Together





While oxidants and reductants do not mix, they can be used together to accomplish specific tasks.

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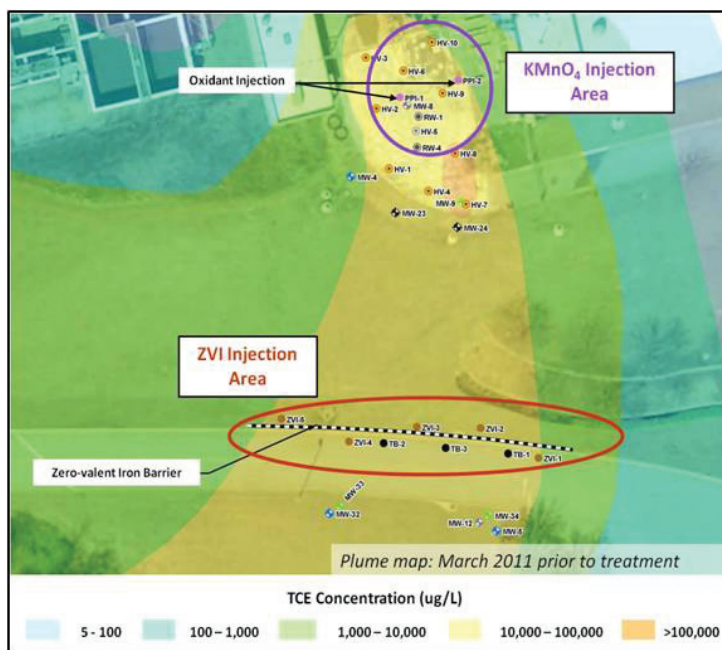
Chlorinated solvent DNAPL site remediation remains a daunting challenge that often requires the integration of multiple technologies to achieve cleanup objectives. Technologies must be adapted to variable site conditions and flexible to the evolving nature of the source and plume as the remediation progresses.

Geo-Cleanse International, Inc. was contracted to design and implement a pilot test for a particularly challenging site characterized by relatively high source area trichloroethene (TCE) concentrations, low permeability saprolite geology overlying highly transmissive bedrock, low natural attenuation, and a large plume area with limited accessibility. The proposed remedial plan was an integrated in-situ chemical oxidation using potassium permanganate in the source area, with in-situ chemical reduction using zero-valent iron (ZVI) barriers in the downgradient plume area. Reagents were injected as high-solid slurries to effectively distribute large reagent volumes within specific and focused target zones in the low-permeability saprolite and a fractured zone in bedrock. Modeling and monitoring were conducted as part of the design and implementation, respectively, as a basis for reagent requirements, injection point horizontal and vertical spacing, scale-up for future expansion of the treatment, and to ensure that the antagonistic reagents do not interact and consume each other.

The site

The site is a former manufacturing facility in Greenville County, S.C. The site geology consists of fill material (mostly silty sands) underlain by saprolite and bedrock. The saprolite consists of thinly laminated, variably micaceous silty sand weathered from the underlying schist and gneiss bedrock. The saprolite ranges in depth from approximately 2.5 to 26 feet below ground surface (ft bgs) and partially weathered rock ranges from approximately 10 to 35 ft bgs. Groundwater moves in a southwestern direction, and ranges from approximately 50 to 65 ft bgs. The depth to water-bearing units varies across the site, depending upon the fractured zones within the saprolite. However, groundwater throughout the majority of the site is located in the saprolite. The groundwater seepage velocity is approximately 60 feet per year.

Figure 1. KMnO_4 and ZVI Treatment Areas



A TCE handling unit located near the southwest corner of the facility, which was in operation for about 10 years, was determined to be the primary source, with an estimated discharge of approximately 1,365 gallons of solvent. Site investigations revealed a groundwater plume of TCE and breakdown products (cis-1,2-dichloroethene and vinyl chloride) migrating offsite. The plume covers approximately 16 acres with concentrations historically greater than 250 mg/L in the source area and up to 96 mg/L in the mid-plume area near the on-site access road. Site access is limited in much of the plume, with a steep slope onsite near the source area and a forested area offsite.

Approximately 140 tons of impacted soil was excavated from the source area during the removal of the TCE storage tank and associated sumps and piping. Several remedial technologies were applied to address the remaining impacted groundwater and soils within the source area, including soil vapor extraction, in-situ thermal desorption, and groundwater extraction. Elevated concentrations still remained in the saprolite and bedrock zones after these efforts, thus the responsible party sought remedial options to obtain maximum contaminant levels for the chemicals of concern within a reasonable period of time.



The KMnO_4 solids are delivered to the fractured well cavity via a steel drum.

Thus, Geo-Cleanse proposed pilot-scale tests that integrated in-situ chemical oxidation using potassium permanganate (KMnO_4) in the source area, with in-situ chemical reduction using a ZVI permeable reactive barriers where access was available in the downgradient plume. Hydraulic slurry emplacement was selected to apply the reagents to the subsurface due to the low permeability of the saprolite.

The process

Permanganate is a chemical oxidant that is capable of destroying a variety of contaminants, particularly unsaturated chlorinated solvents such as TCE. The active oxidant is the permanganate anion (MnO_4^-), which is a strong and persistent oxidant. Permanganate is a soluble salt, supplied either as potassium (solid form) or sodium (liquid form). KMnO_4 has a modest solubility (approximately 2 percent under practical environmental conditions, with an equilibrium solubility of approximately 6 percent). Permanganate oxidation of TCE does not generate hazardous intermediates or breakdown products. Furthermore, permanganate can chemically diffuse into fine-grained soil and bedrock, thus it can inhibit back-diffusion of VOCs from low-permeability matrices. Based upon these factors, hydraulic slurry emplacement of solid KMnO_4 was selected to provide an aggressive remedy for the source area.

This injection method provides the ability to deliver large oxidant volumes in a time-efficient manner in a

relatively low permeability formation. The emplaced slurry then provides a high-permeability zone within a low-permeability formation, which preferentially draws groundwater into the permanganate-filled structure. As groundwater moves through the permanganate-filled zone, the oxidant will slowly dissolve over periods of months to more than a year and destroy the TCE and breakdown products in the groundwater. In addition, permanganate will diffuse and advect with groundwater. This allows vertical and horizontal migration of permanganate away from the slurry emplacements and through the aquifer.

The use of ZVI for groundwater remediation is well established, with applications at over 150 sites around the world since the early 1990s. The ZVI (a strong reductant) reacts with TCE and its breakdown products through electron transfer. Dechlorination is relatively rapid and complete, producing ethane and ethene as the final carbon-containing compounds. Ethene/ethane mass balance of 80 percent and higher have been reported from closed-system tests with chlorinated ethenes and ethanes.

Like KMnO_4 , ZVI is also a granular solid that can be injected with hydraulic slurry emplacement, providing high-permeability zones within the low-permeability matrix to draw groundwater into the treatment zone, and can provide treatment for many years with a single application. ZVI will not diffuse from the emplaced zone and thus cannot migrate outside the immediate treatment area; this is advantageous because groundwater discharges to a stream at the downgradient edge of the plume.

One of the primary concerns with coupling these seemingly antagonistic technologies was the possibility the permanganate migrating downgradient from the source area and reaching the ZVI, resulting in nonproductive degradation of both reagents and shortening the ZVI lifetime. However, there was very little potential for the permanganate treatment in the upgradient source area to impact the ZVI barrier in the plume due to the distance between the areas, groundwater velocity, and soil oxidant demand for the permanganate.

Groundwater that has been treated by permanganate has an elevated oxidation-reduction potential (ORP), which will persist after the permanganate has degraded below detectable levels. The ORP is a very general measure of the overall electron activity in the groundwater and reflects a wide range of chemical species and reactions. Similar to attenuation of permanganate, the elevated ORP will also attenuate due to the reaction with aquifer solids, but is more complicated to model because the reaction kinetics are affected by the wide range of chemical species involved. Given the anticipated permanganate attenuation rate, the ORP of

Figure 2. Cross Section

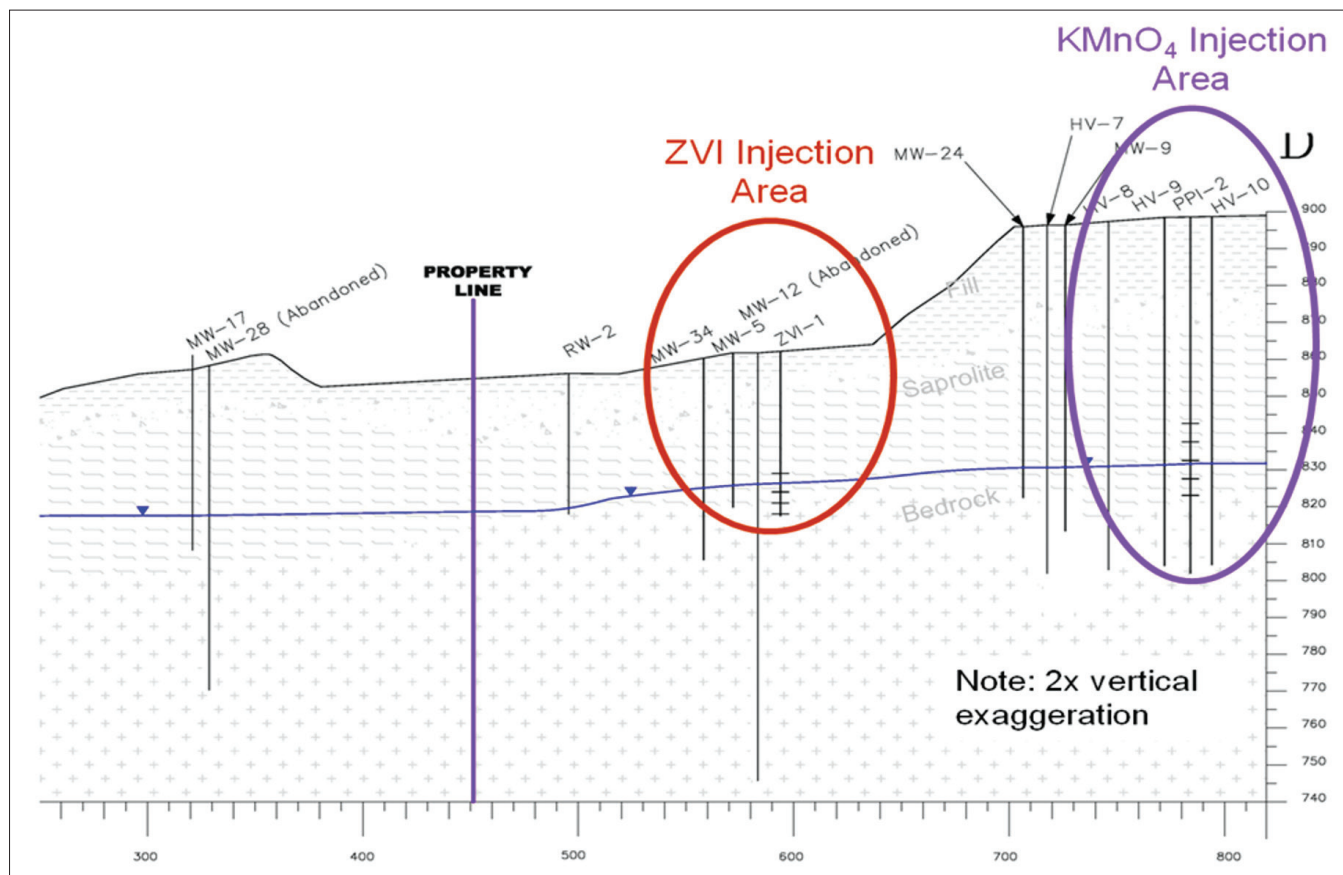
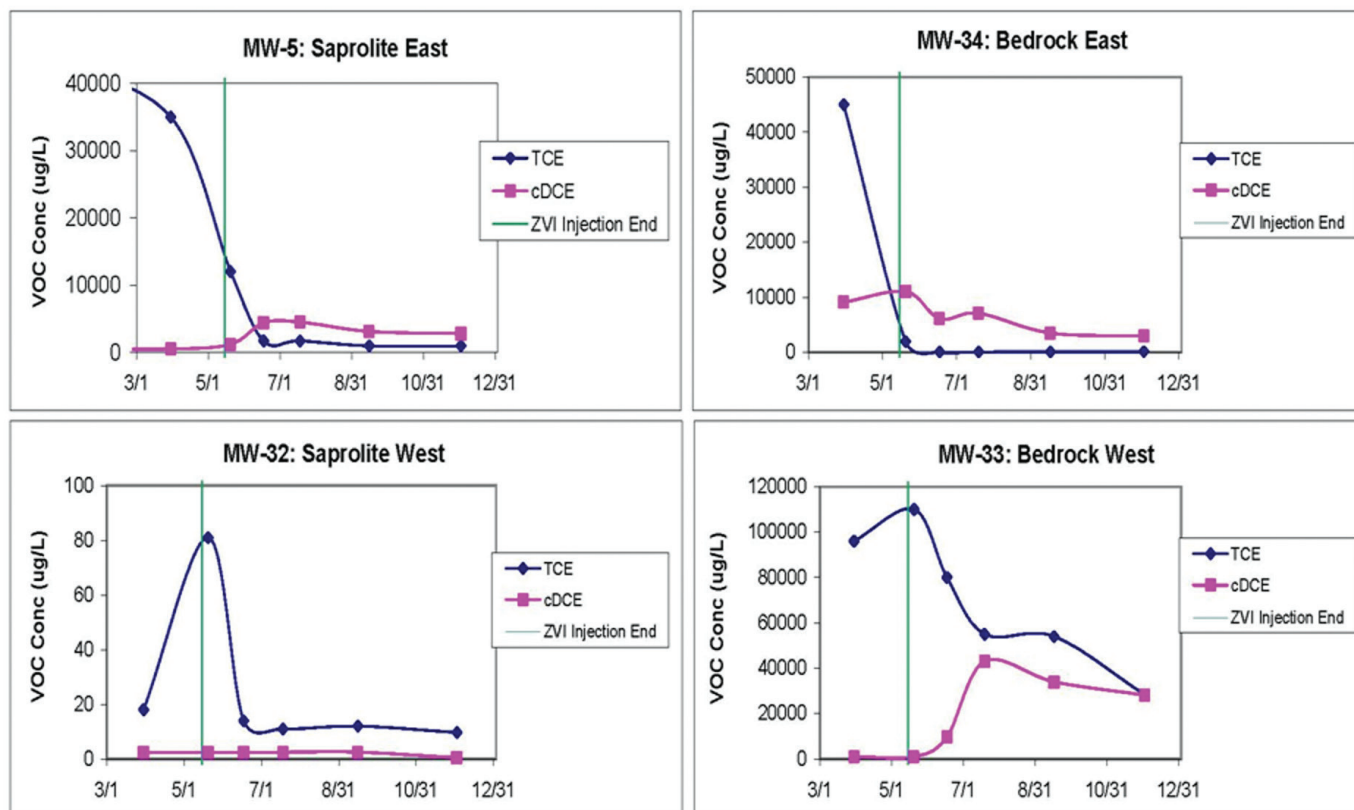


Figure 3. VOC Concentrations – ZVI Area



*Note: All samples reported < RDL are plotted at a value of half of the RDL.

groundwater entering the ZVI treatment area was not anticipated to be elevated due to the permanganate. Other permanganate reaction byproducts (such as chloride and potassium) do not significantly react with ZVI.

The permanganate component of the pilot test targeted a portion of the source area and the ZVI portion targeted a mid-plume location located near the property boundary (**Figure 1**). The treatments each targeted the vertical interval from the water table in the saprolite to approximately 10 feet into bedrock, covering the zones in which impacted groundwater is found (**Figure 2**). The primary objectives of the pilot study were to evaluate the potential overall effectiveness of each technology, and to assess engineering assumptions relevant for full-scale project design and implementation.

The boring locations were oriented in a line perpendicular to the direction of groundwater flow (**Figure 1**). The boring locations were installed with a horizontal spacing of approximately 30 feet to provide horizontal



Visual indication of KMnO_4

aqueous matrix, which thickens the slurry to suspend it in the fluid. An enzyme is included in the slurry, which slowly breaks down the guar gum over a period of hours following injection in order to expose the ZVI to react with the groundwater. Approximately 73 tons of ZVI were emplaced into the five boring locations forming a 150-ft barrier line.

Two locations were utilized for the KMnO_4 slurry emplacement application. Based upon the results of the ZVI injections, it was determined that constructing the borehole with the PVC casing was the optimal design. Therefore, the two locations were constructed with 4-inch diameter, schedule 40 PVC casing that was grouted into place. The locations were approximately 25 feet apart, which was considered a conservative spacing. The KMnO_4 product that was emplaced was RemOx-S, manufactured by Carus Corporation. Sand was blended into the permanganate in order to reduce “crusting” of the KMnO_4 due to MnO_2 precipitation.

The permanganate slurry was prepared using bentonite to suspend the solid permanganate in the slurry, rather than guar gum as used with the ZVI, because permanganate reacts with the guar gum. Tests and calculations demonstrated that the very small amount of bentonite utilized was insufficient to measurably reduce the permeability of the emplaced slurry. The amount of KMnO_4 required for the pilot test was based upon residual contaminant mass estimates and permanganate oxidant demand bench tests. The amount of permanganate utilized reflected the combined total of the soil oxidant demand plus the VOC oxidant demand, which was 28,225 pounds of KMnO_4 and sand blend. Permanganate was emplaced at five vertical intervals in each boring location.

The results

The monitoring program included groundwater sampling events prior to, during and after the emplacement



overlap, which was primarily selected based upon the empirical experience of the hydraulic emplacement subcontractor. The ZVI was injected into four to six discrete depth intervals within each boring, ranging in depth from the static water table to approximately 10 feet into bedrock. The vertical spacing was selected based upon hydrologic modeling of groundwater capture into the permeable slurry emplacements.

The granular form of ZVI was utilized rather than microscale or nanoscale form. The amount of ZVI required was based upon three main factors: initial VOC concentrations entering and exiting the barrier; the VOC travel velocity; and the length and vertical thickness of the treatment zone. The ZVI slurry was prepared by blending the iron with guar gum in an

of each reagent. Tiltmeter monitoring was conducted during the injections and post-injection soil borings adjacent to the injection locations were collected to determine reagent distribution. The monitoring program in the permanganate and ZVI areas were slightly different, reflecting the different influence of each reagent on groundwater chemistry.

The groundwater analytes in the permanganate pilot test area consisted of VOCs, color, ORP, specific conductivity and pH. Permanganate imparts a distinctive light pink to purple color to groundwater, which provides direct evidence of reagent distribution and is easily observed in the field. The groundwater analytes in the ZVI pilot test area consisted of VOCs, ferrous iron, ORP, specific conductivity and pH. The ZVI does not impart a characteristic color to the groundwater, so reagent distribution was evaluated by monitoring water levels during the injection and by advancing soil borings after the injection was conducted.

Three soil borings were advanced and soil cores were analyzed with a magnetic susceptibility meter to quantify the presence of ZVI, visually examined for the presence of ZVI particles, and a magnet was used on core sections and in the borings to collect ZVI particles to evaluate the physical distribution. The particles collected from the borings were analyzed by X-ray diffraction to confirm their identification. Tiltmeters were used to measure surface deformation during the pilot test. The tiltmeters data were analyzed to calculate vectors whose orientation and length represent the direction and magnitude of the tilt, respectively for each tiltmeter.

The source area pilot test proved to be very effective at reducing VOCs. Permanganate was physically observed (based upon the distinctive pink to purple color of the reagent in groundwater) at 11 of the 15 well locations in the pilot test area, at distances of up to approximately 40 feet from the emplacement boring locations. After 18 months, permanganate was still observed in the source area. The overall TCE concentrations were reduced by 84 to 100 percent relative to the baseline concentrations. Concentrations were reduced by two to five orders of magnitude, in one case from 82,000 µg/L to non-detectable. Permanganate was not observed in any of the wells located outside the pilot test area; therefore the permanganate did not come into contact with the ZVI, which was a primary concern.

Each ZVI slurry emplacement boring achieved a radius of influence of at least 15 feet based upon sampling data from the three soil borings (visual evidence, magnetic susceptibility and X-ray diffraction analysis of ZVI particles in soil) advanced after the emplacement, and indirectly based upon tiltmeter data reflecting surface deflections. The inorganic geochemistry results from groundwater downgradient of the treatment bar-

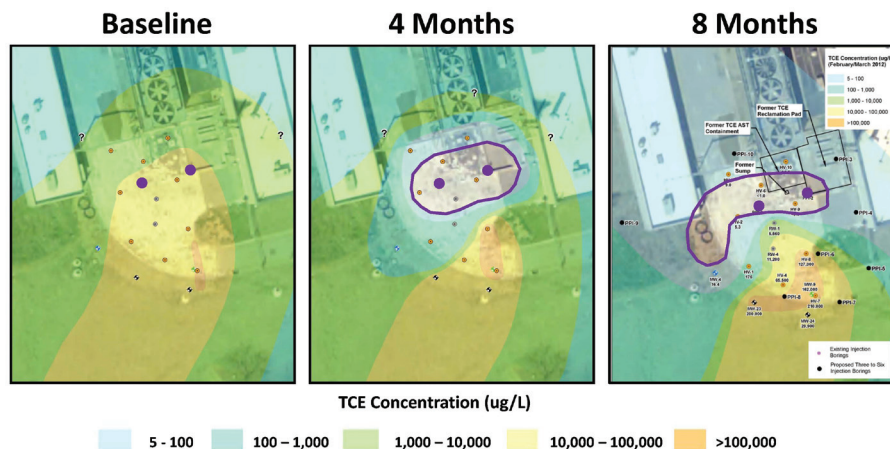


Figure 3: VOC concentrations - KMnO₄ Area

rier also reflected the influence of ZVI. Groundwater ORP is particularly sensitive to the ZVI and decreases were observed in all four monitoring wells (two in the saprolite and two in the bedrock) located approximately 30 to 40 feet downgradient from the barrier location. The groundwater pH and specific conductivity also reflected transient shifts associated with ZVI applications, which can also be influenced by the soil buffering capacity and other factors in addition to the ZVI.

The VOC concentrations in the groundwater downgradient from the barrier also exhibited significant reductions. The TCE concentrations were reduced by 46 to 100 percent relative to the baseline concentrations in the four downgradient monitoring wells (Figure 3). The TCE concentrations were reduced from approximately 35,000 µg/L to 950 µg/L and from 18 µg/L to 9.7 µg/L in the two saprolite monitoring wells. The TCE concentrations in the two bedrock wells were reduced from approximately 96,000 µg/L to 28,300 µg/L, and from 45,000 µg/L to non-detect. Cis-1,2-dichloroethene, formed from ZVI degradation of TCE, initially increased following the injection, however additional post-injection sampling has shown a subsequent decrease as a function of time. ☞

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Company Profiles



Geo-Cleanse
INTERNATIONAL, INC.

Since 1995, Geo-Cleanse International, Inc. (Geo-Cleanse) has been dedicated exclusively to the design and implementation of in-situ chemical remediation technologies within the U.S., Canada, and Europe. We have experience remediating a wide range of contaminants under various site conditions. All of our in-situ remediation program designs are site-specific and range from in-situ catalyzed hydrogen peroxide injections to slurry emplacements of zero valent iron. A critical step in ensuring the success of our remedial programs is selection of the appropriate chemical reagent and the application design, which is based on our extensive field and laboratory experience. Geo-Cleanse evaluates each of the reagent's strengths and weaknesses as they apply to the site and its' relevant conditions, and then recommends the most effective remedial approach.

To date, Geo-Cleanse has field experience on hundreds of contaminated sites, including complex multi-acre plumes consisting of non-aqueous phase liquids (e.g., LNAPL and DNAPL), bedrock contamination, and comingled plumes. As the chemical remediation field continues to evolve, we have consistently provided innovative remedial solutions to our diverse clientele network, as well as developed our own proprietary in-situ technologies. Our extensive experience, together with independently published results of our work, and our knowledgeable staff of professionals, ensures that Geo-Cleanse continues to be one of the world's top environmental remediation firms.

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