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Application of Chemical Oxidation Followed by Anaerobic Degradation Remedial Technologies for Trichloroethene in a Multi-System Aquifer

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ABSTRACT: Remedial enhancements to an existing pump-and-treat (P&T) system were selected for a pilot study to address trichloroethene (TCE)-impacted groundwater within a fractured bedrock system extending into a residential neighborhood. The focus for implementing the remedial enhancements was the farthest downgradient area of the dissolved plume not fully responding to P&T system operations due to pumping well distance as predicted by groundwater modeling. This area is hydrogeologically complex due to an upward vertical gradient where TCE impacted bedrock groundwater moves into overlying unconsolidated sediment. To enhance treatment of this area, an aggressive in situ treatment train was implemented to quickly reduce groundwater impact using RegenOx™ and then establish a long-term remedy using NewmanZone® to stimulate microbial growth as part of an anaerobic reductive dechlorination (ARD) bioremediation process. Application of RegenOx™ and NewmanZone® was accomplished via permanent injection points into the bedrock and unconsolidated sediments (alternating points screened within glacial till and fluvial deposits/fill).

INTRODUCTION

An area located approximately 1,250 feet north from a Facility with an operating pump-and-treat (P&T) remedial system addressing volatile organic compounds (VOCs), specifically trichloroethene (TCE) in bedrock groundwater, was selected for a pilot study to evaluate remedial enhancements. The pilot study area was selected based on groundwater data indicating the existing P&T system would not effectively treat groundwater within a reasonable time frame (as predicted by groundwater modeling). This area is located at the northern end of a residential neighborhood and was the most downgradient edge of TCE concentrations in the bedrock aquifer that was being addressed under a Consent Order.

Based on the Remedial Investigation/Feasibility Study (RI/FS) work, project characterization data, and a review of the most applicable remedial technologies the following remedial technologies were selected for combined application to evaluate remediation of TCE in groundwater with continued Pump and Treat remediation system operation.

- In situ chemical oxidation (ISCO) technologies (specifically using RegenOx™) and
- In situ anaerobic bioremediation via anaerobic reductive dechlorination (ARD) process technologies (specifically using Newman Zone®).

The use of the above technologies was envisioned to be applied as a treatment train with initial passive injection of RegenOx™ for ISCO to peak-shave TCE concentrations followed by active injection/recirculation of Newman Zone® for ARD to continue TCE reductions. Ultimately, the use of these remedial technologies was projected to address residual TCE concentrations at the northern portion of the residential neighborhood (pilot study area) while enhancing the long term effectiveness of the existing P&T system to address current (pre-pilot study) TCE concentrations ranging from non-detect to 9,100 µg/L.

The RegenOx™ chemical oxidant formulation consists of sodium percarbonate and sodium carbonate monohydrate activated by ferrous sulfate (comparable with Fenton's Reagent chemistry, but is not as strongly reactive and is less exothermic). RegenOx™ reacts with chlorinated solvents such as TCE as well as other carbon based (organic) materials and breaks these constituents down into harmless byproducts (CO_2 and H_2O). RegenOx™ has been shown to react with VOCs over a relatively short time frame (up to 30 days). The oxidizing conditions initialized by the RegenOx™ formulation have been shown to subside with groundwater conditions returning to pre-injection conditions over time. This characteristic allows for use of this product as an initial treatment to quickly reduce VOC concentrations and subsequent application of in situ bioremediation treatment for long-term VOC reductions (Regenesis: http://www.regenesis.com/products/chemOx/regenOx/).

NewmanZone® is an electron donor formulation consisting of sodium lactate, soybean oil, food-grade additives, and proprietary surfactants and stabilizing agents that stimulates the ARD process. ARD is an electron donor/carbon source (substrate) rate driven, microbial mediated, oxidation-reduction reaction capable of degrading chlorinated solvents (i.e. TCE) to the final end products, chloride, ethene and ethane. The use of NewmanZone® for ARD process stimulation was selected based on the formulations ability to be long lasting and readily distributable in a groundwater system (Remediation & Natural Attenuation Services, Inc.: http://www.rnasinc.com/newman-zone/).

PILOT STUDY AREA SETTING

The pilot study area is situated within the north end of a small residential community which is bordered to the south by the Facility. The geology and hydrogeology of the area consists of unconsolidated sediments that are underlain by bedrock with an interconnected aquifer system. The unconsolidated glacial till sediments (clay and silt with unsorted variable grained sand, coarse gravel and boulders) has a thickness of 15 to 20 feet and has been reworked by surface water leaving alluvial deposits. Portions are underlain by fill material observed within ten feet of grade. The above material is underlain by compacted glacial till (lodgment till) 10 to 15 feet thick. The lodgment till is underlain by fractured sedimentary bedrock consisting of shale inter-bedded with sandstone and siltstone and/or mudstone with high clay content at about 30 to 37 feet below grade (bg).

Groundwater flow direction in the unconsolidated sediments (overburden) is northward, and in bedrock is southward in the pilot study area. A vertical groundwater flow component for the groundwater system was observed to upward at wells MW-12A and MW-12B at the north end of the pilot study area, which becomes downward at cluster well MW-24 (S,I,D) on the southern end of the area.

Bedrock groundwater quality in the pilot study area for TCE historically ranged from non-detect to 8,400 µg/L. Overburden groundwater quality in the pilot study area for TCE historically ranged from 16 µg/L (estimated) to 19,000 µg/L. The presence of TCE degradation product cis-1,2-dichloroethene (cis-1,2-DCE) has been typically observed at one to two orders of magnitude below TCE concentration with an occasional exception. The presence of vinyl chloride (VC) was typically not observed in the pilot study area with exceptions of wells MW-12A, MW-12B, MW-19A, and MW-20A.

PILOT STUDY OVERVIEW

The pilot study activities were conducted in two phases to accommodate the batch injection of RegenOx™ followed by the active injection of NewmanZone®. The pilot study work included the following activities.

- Installation of twenty overburden (OIW-1 through OIW-20) injection wells in two off-set parallel rows of ten with alternating well depths to top of lodgment till and top of bedrock.
- Installation of three bedrock (IW-1 through IW-3) injection wells; IW-2 and IW-3 to 80 feet and IW-1 to 100 feet.
- Conduct baseline monitoring for RegenOx™ injection.
- Initiate batch injections of RegenOx™ solution into the twenty three injection wells and monitoring pilot study area.
- Construction of active recirculation/injection system to use groundwater pumped from former potable well 41 that was treated via activated carbon, amended with Newman Zone®, and injected into the injection wells via subsurface plumbing.
- Following stabilization and return of groundwater conditions to pre-injection levels, conduct baseline monitoring event for NewmanZone® injection.
- Initiate active injection of NewmanZone® via recirculation system start-up with operation & maintenance (O&M) and monitoring pilot study area.

RegenOx™ Pilot Study. Baseline monitoring of groundwater geochemical parameters (via field analysis) and groundwater quality (via laboratory analysis) was conducted at select monitoring wells to evaluate pre NewmanZone® injection groundwater. Field geochemical parameters collected were pH, temperature, conductivity, Oxidation-Reduction Potential (ORP), and Dissolved Oxygen (DO). Groundwater was also field screened via colorimetric test strip for peroxide (indicates presence of RegenOx™). Groundwater samples were laboratory analyzed for VOCs (EPA 8260). Additionally, groundwater samples from MW-21AS and MW-22AI were laboratory analyzed for dissolved gases—methane, ethane, ethane (EPA 5021A), anions - chloride, sulfate, nitrate, formate, acetate, lactate/propionate, and butyrate (EPA 6500), ammonia (Hach 8155), phosphate (Hach 8048), and pH.

RegenOx™ batch injection activities were conducted over a four week period with a one week break (third week) in conducting injections to allow relaxation of subsurface back-pressures encountered during the second week of injections. The injection process consisted of mixing and injecting the Part B activator complex (5% solution), flushing with 1.5-3 well volumes of clean water, mixing and injecting the Part A oxidant complex (5% solution), and flushing with 1.5-3 well volumes clean water. A total of 8,561 gallons of RegenOx™ was injected to the pilot study area with 3,535 gallons injected to the overburden and 4,981 gallons injected to the bedrock.

Monitoring during and after RegenOx™ injection activities were implemented. An overall increase in groundwater geochemical parameters from baseline data and detection of peroxide was expected to show RegenOx™ was reacting with carbon sources (i.e. VOCs) in the pilot study treatment zone. The following field geochemical and peroxide data was observed (see Figure 1 for well locations).

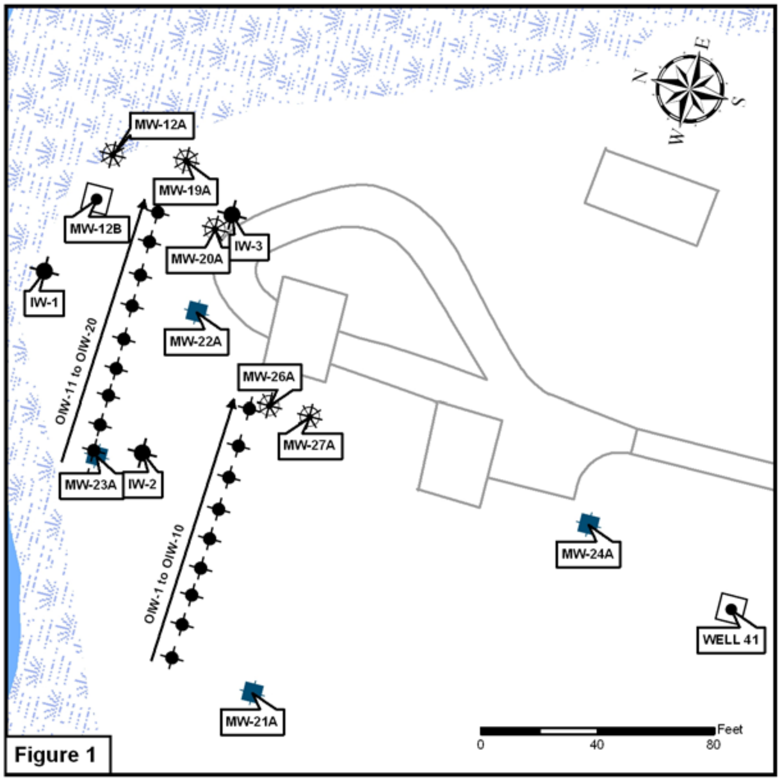

FIGURE 1, Well location map.

- DO values fluctuated from event to event with only MW-19A, MW-20A, and MW-22AI showing increased values.
- ORP values increased at MW-20A, MW-23AS, and MW-23AI.
- Conductivity values increased at MW-12B, MW-19A, MW-20A, MW-23AS, MW-23AI, MW-23AD, MW-26A, and MW-27A.
- The pH values increased at MW-12A, MW-12B, MW-21AS, MW-22AI, MW-23AI, and MW-23AD.
- Temperature values increased at MW-12B and MW-19A.
- Peroxide monitoring showed the presence of peroxide at MW-12B and MW-23AD.

Based on increases of three or more field geochemical parameters and detection of peroxide over 12 weeks of monitoring at wells MW-12B, MW-19A, MW-20A, MW-23AI, and MW-23AD, the occurrence of an oxidation reaction/presence of RegenOx™ is apparent in the pilot study treatment zone.

VOC analysis for TCE from baseline to post injection sampling for wells in the pilot study treatment zone showed seven wells to decrease, three wells to increase and two wells to continue showing non-detectable concentrations (see Table 1). For the most part, the presence of cis-1,2-DCE concentrations, followed TCE concentrations with cis-1,2-

DCE concentrations an order of magnitude lower than TCE concentrations which is similar to pre-injection conditions.

TABLE. RegenOx™ pilot study TCE concentrations.

Wells	Baseline RegenOx™ TCE Data*	Post-RegenOx™ TCE Data* (Eight Weeks)	TCE Percent Change
MW-12A	9,100	4,700	-48%
MW-12B	5,500	3,900	-29%
MW-19A	2,800	3,700	+32%
MW-20A	180	150	-17%
MW-21AS	94	44	-53%
MW-21AI	660	750	+14%
MW-22AI	1,500	5,100	+240%
MW-23AS	2,600	190	-93%
MW-23AI	6,100	5,100	-16%
MW-23AD	4,800	3,500	-27%

* - Concentrations in µg/L

The RegenOx™ monitoring data shows the distribution of RegenOx™ in the groundwater system to be limited to the pilot study treatment area. The oxidation reaction induced by RegenOx™ was successful in the reduction of VOCs (specifically TCE) in the areas where RegenOx™ was believed to be more thoroughly distributed within the groundwater system via batch injections. Considering the monitoring data and the identified heterogeneous nature of the subsurface lithology that hinders complete contact of the RegenOx™ with VOCs in groundwater the effectiveness of RegenOx™ to remediate VOCs at the Facility is highly dependent upon distribution through the subsurface environment. Typically, multiple RegenOx™ injection events are suggested by the manufacturer to address the distribution issue as well as potential rebound of VOC concentrations associated with the de-adsorption from the material matrix.

The application of this remedial technology (more than the one injection event conducted for this pilot study) appears to be appropriate to address small to moderate impacted areas in the lithology of the Facility based on the pilot study. However, due to the heterogeneous nature of overburden and bedrock in the Facility area, the application of RegenOx™ would likely yield variable results dependent upon the lithology and structure of one area versus another. The limited reaction life expected of RegenOx™ in conjunction with monitoring data showing positive results (groundwater geochemical affect) for the treatment area, indicated this phase of the pilot study was complete eight weeks after injection completion, which permitted the ARD phase of the pilot study to be initiated four weeks later.

ARD/NewmanZone® Pilot Study. Baseline monitoring (post RegenOx™ portion of pilot study) of groundwater geochemical parameters (via field analysis) and groundwater quality (via laboratory analysis) was conducted at wells in the pilot study area. The field geochemical parameters collected were pH, temperature, conductivity, ORP, and DO. Baseline monitoring for Newman Zone also consisted of lowering a bailer into a well to visually inspect pre-injection conditions with post-injection effects as the presence of a milky white appearance would indicate the presence of NewmanZone® substrate. Groundwater samples were laboratory analyzed for VOCs (EPA 8260). Additional groundwater samples were laboratory analyzed for dissolved gases - methane, ethane, ethane (EPA 5021A), anions - chloride, sulfate, nitrate, nitrite, formate, acetate, lactate/propionate, and butyrate (EPA 6500), total organic carbon (SW 5310C) ammonia (Hach 8155), phosphate (Hach 8048), and pH to evaluate NewmanZone® pre-injection activities.

Active injection of NewmanZone® was immediately initiated upon baseline monitoring completion. The injection process involved pumping groundwater from Well #41 at approximately 2 gallons per minute (gpm), clearing groundwater of sediment via bag filter, treating groundwater through two activated carbon units (in series), amending treated groundwater with a 10 percent solution of NewmanZone® to water at a rate of 0.25 gpm, and injecting the treated/amended groundwater via a manifold system to the three bedrock injection wells and to the two parallel overburden injection well lines (north and south) consisting of ten wells each. Due to the observed amended solution in the nearby surface water, flow to the 23 injection locations was adjusted to stop the flow to surface water, with continued injections in the treatment area (predominately to bedrock groundwater). Approximately five weeks after active injection initiation, the system was shut down to allow the NewmanZone® to spread through the treatment area with natural groundwater flow. A total of 2,825 gallons of NewmanZone® amended groundwater was injected to the pilot study area with approximately 587 gallons injected to the overburden and approximately 2,238 gallons injected to the bedrock.

ARD monitoring after initiation of the active injection of NewmanZone® continued at wells initially monitored as part of the baseline monitoring with wells. The following field geochemical data was observed (see Figure 1 for well locations).

- DO values decreased (below 1 mg/L) at MW-12B, MW-22AS, and MW-22AI with wells MW-20A, MW-21AS, MW-23AD, MW-23AI, and MW-26A decreased DO levels fluctuating above and below 1 mg/L. The decreased DO suggest possible initiation of an anaerobic environment.
- ORP values decreased at MW-20A, MW-22AS, MW-22AI, and MW-26A. The decreased ORP suggest possible initiation of an anaerobic environment.
- Conductivity values increased at MW-12A, MW-12B, MW-20A, MW-21AS, MW-21AI, MW-23AI, MW-23AD, and MW-27A. Increased conductivity values correlate with observed NewmanZone® presence.
- The pH values increased at MW-12A, MW-20A, MW-21AS, MW-21AI, and MW-22AI and decreased at MW-12B, MW-23AI, MW-23AD, and MW-27A. Decreased pH levels correlates with observed NewmanZone® presence.
- Temperature values showed variable trends from event to event that do not correlate.
- NewmanZone® presence was observed at MW-12B, MW-23AI, MW-23AD, MW-26A, and MW-27A.

The above indicate a positive step towards distribution of the NewmanZone® through the treatment area and establishment of an anaerobic environment in the pilot study treatment zone.

The best indicator for the evaluation on the effectiveness of the ARD pilot study is the reduction of VOCs, specifically the reduction of TCE to its degradation products by naturally occurring microorganisms (microbes) in the subsurface environment. The geochemical analytical data provides a basis to evaluate whether the environmental conditions in groundwater is being effectively changed to support those anaerobic microbes that can reduce TCE to associated degradation daughter products. Based on the monitoring data collected over an approximate six week period for the pilot study, the laboratory geochemical data showed indications of a reducing (anaerobic) environment. Minor reductions in nitrate and sulfate were observed MW-12B, MW-22AI, and MW-23AD suggesting the potential presence of microbes that use these chemicals as an energy source and may potentially degrade TCE once these chemicals are depleted. The presence/ increase presence of TOC observed in the treatment zone indicates improved groundwater conditions for the proliferation of microbes. An increased presence of methane, ethane, and ethane as well as acetate observed at several well locations indicate the presence of an improving anaerobic environment that could ultimately lead to the reduction of TCE and daughter products to base breakdown products.

The VOC analytical data over the six week period of the ARD portion of the pilot study indicated significant reductions (over an order of magnitude) of TCE at MW-12B, MW-21AI, MW-22AI, MW-23AI, and MW-23AD. Notable reductions of TCE from 6,500 µg/l to non-detectable concentrations were observed at MW-12B and MW-23AI. The reduction of TCE to cis-1,2-DCE was observed at MW-12B, MW-23AI, and MW-23AD. Cis-1,2-DCE was also shown to decrease at MW-21AI and MW-22AI, which is a positive indication of daughter product elimination from the ARD process being induced with the injection of substrate. The presence of VC (daughter product of cis-1,2-DCE) was observed at MW-12A (concentrations below 6 µg/L) and MW-20A (concentrations below 18 µg/L). The remaining wells in the pilot study treatment zone did not show the presence of VC above the analytical detection limits.

A summary of TCE data and percent change for the ARD pilot study treatment area wells is provided in Table 2, which indicate that after one month of ARD pilot study application, significant reductions greater than an order of magnitude was demonstrated at five of the nine wells in the treatment area. The four wells not showing a significant reduction in TCE concentration may be indicative of potential fluctuations in concentrations associated with the natural condition affects on groundwater and/or ineffective distribution patterns for substrate injections. In addition, long-term monitoring of the pilot study will assist in determining the potential effects of the substrate in adsorbing TCE concentrations, which may lead to short-term false positive effects. Previous experience on similar sites indicates this short-term effect would be offset by the continued development of the ARD conditions.

TABLE 2. ARD pilot study TCE concentrations.

Well	Baseline ARD TCE Data*	ARD Injection (Six Weeks) TCE Data*	TCE Percent Change
MW-12A	1,900	4,600	+142%
MW-12B	6,500	<6.8	- >99%
MW-19A^	3,700	2,300	-38%
MW-20A	320	290	-9%
MW-21A-S	450	620	+38%
MW-21A-I	3,200	820	-74%
MW-22A-I	5,200	300	-94%
MW-23A-I	5,200	<6.8	->99%
MW-23A-D	5,900	220	->99%

* - Concentrations in µg/L

^ - MW-19A TCE data from April 2008 (post RegenOx event)

Wells MW-26A and MW-27A showed non-detectable VOCs

Overall, the observed distribution of substrate in the pilot study area in conjunction with the field/analytical geochemical data can provide insight to the areas where TCE concentration reductions occurred. The area where TCE reductions and appearance of degradation products occur correlates well with the groundwater ARD parameter monitoring data. Considering the monitoring results for the ARD pilot study, the use of this remedial technology may be beneficial to expedite the further remediation of groundwater impacts and the cost beneficial analysis would be highly driven by the associated cost of application infrastructure while balancing against the significant yearly operation and maintenance cost of the current pump-and-treat technology.