More Lessons Learned from Common Mistakes Applying In-Situ Remediation Technologies in the Field

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ISCO IN AN ELONGATED TCE PLUME

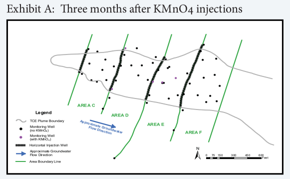
In-situ chemical oxidation (ISCO) bench test results for Areas C-F of an elongated trichloroethylene (TCE) plume indicated that 3.8 to 9 grams per kilogram (g/Kg) of potassium permanganate ($KMnO_4$) were needed to treat the TCE dissolved in groundwater in these areas. The bench test results were ignored because the previous pilot study in Area J used 0.03 g/Kg $KMnO_4$.

For full-scale treatment in Areas C-F and J, modeling was used instead of bench test results. Approximately 13,000 to 27,500 gallons of 3% $KMnO_4$ was injected into horizontal wells during July and August 2011.

In October 2011, three months after $KMnO_4$ injections, sampling results showed:

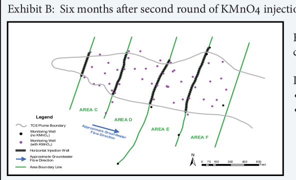
- No $KMnO_4$ was detected in Areas C and F
- $KMnO_4$ was detected in only two wells in Area D and only three wells in Area E

Exhibit A: Three months after $KMnO_4$ injections



In June-July 2013, an additional 13,000 to 27,500 gallons of 3% $KMnO_4$ was injected into the horizontal wells. This achieved a much better short-term distribution of $KMnO_4$, reaching all but four wells within six months.

Exhibit B: Six months after second round of $KMnO_4$ injections

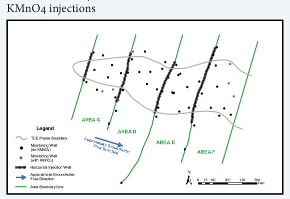


However, after 20 to 21 months, very few wells had measurable concentrations of permanganate.

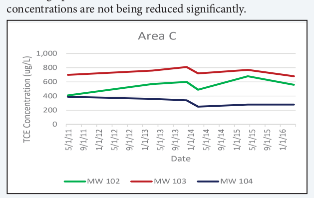
In March 2014, sampling results showed:

- No $KMnO_4$ was detected in Area E
- $KMnO_4$ was detected in two wells south of the TCE plume in Area C; one well north of the plume and one well south of the plume in Area D; and, in three wells in Area F

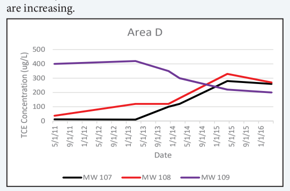
Exhibit C: Twenty-one months after second round of $KMnO_4$ injections



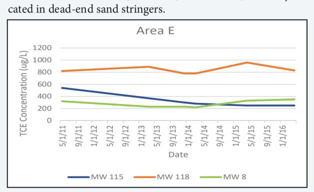
A trend graph for selected wells in Area C indicates that TCE concentrations are not being reduced significantly.



Area D, a trend graph for selected wells indicates that TCE may have desorbed and/or have been displaced into the vicinity of some wells where concentrations are increasing.



In Area E, the trend graph shows mixed results; concentrations are decreasing in some wells, but are virtually unchanged in others. Wells where $KMnO_4$ remains (see Exhibit C) are likely located in dead-end sand stringers.



Observations and Mistakes:

- Little progress remediating the plume has been made except at the edges where concentrations were lower.
- $KMnO_4$ concentrations were not maintained at levels sufficient to treat TCE continuously. ISCO is a Contact Sport!
- Injections were too infrequent.
- $KMnO_4$ likely follows preferential pathways and displaced TCE in some areas.
- Horizontal wells may not be the best way to deliver $KMnO_4$ to large areas with heterogeneous geology.

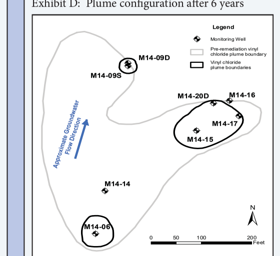
Lessons Learned:

- $KMnO_4$ injections should be frequent. If there is no $KMnO_4$, no treatment is occurring.
- Understand the geology – heterogeneous geology results in preferential pathways.
- More injection wells are needed in high concentration areas of the plume.

ISCO AT A FIRE TRAINING AREA

A Former Fire Training Area had vinyl chloride with minor amounts of tetrachloroethylene (PCE), TCE, and cis-1,2-dichloroethene (cis-1,2-DCE) contamination at 5-15 feet (ft) below ground surface (bgs). Site investigations indicated that there were interbedded fine grained units present. Bench tests and a pilot study using permanganate in the north and persulfate in the south were conducted. Full-scale implementation involved 17 recirculation modules with 22 extraction wells and seven injection wells in each cell. Iron-activated sodium persulfate was injected for full-scale treatment. The first round of injections targeted three high-concentration areas over four days. The second round of injections treated the whole plume over four days. The third round (six months later) treated four higher concentration areas. The monitoring wells were sampled after six weeks, then three quarterly sampling events were conducted. The injection and extraction wells were abandoned because the contract said the wells had to be abandoned. The site was transitioned to monitored natural attenuation (MNA) even though there were high concentrations of vinyl chloride remaining and the concentration criterion for transition to MNA had not been met. When asked why the wells were abandoned, the consultant said "it never works to inject ISCO more than twice." MNA was projected to achieve project goals in 5 years. However, this did not occur.

Exhibit D: Plume configuration after 6 years



Monitoring has been conducted for nine years, but some hot spots are persistent. It also appears that there are seasonal effects, likely due to matrix back diffusion of contamination followed by dilution during the rainy season as shown on the following graph:

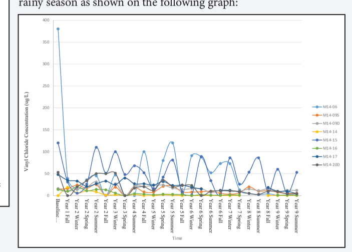
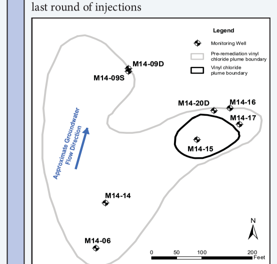


Exhibit E: Plume configuration 9 years after last round of injections



At least one hot spot remains above cleanup criteria and it is unclear how long it will take to achieve remedial goals (RG). However, dilution due to infiltration of unusually high rainfall during the 2016-2017 rainy season may be masking the extent of contamination. Matrix back-diffusion may result in rebound in other hot spots in the future. The site remains in long-term monitoring.

The original RG for vinyl chloride of 15 micrograms per liter (ug/L) is no longer protective. In addition, per- and polyfluoroalkyl substances (PFAS) sampling of soil and groundwater has revealed high concentrations of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) in soil and groundwater.

Observations and Mistakes:

- Conditions for transition to MNA were not achieved, but the transition was made because of the mistaken idea that ISCO injections could only be done twice.
- MNA was predicted to achieve cleanup within five years, which did not occur because of rebound; back diffusion was not considered at any time during this project.
- Natural attenuation had previously stalled at vinyl chloride, based on several years of data collected during the remedial investigation phase. It is unclear why it was assumed that MNA would be effective after ISCO.
- Although testing was not conducted, it is likely that the native microbial population was repressed or killed by persulfate, inhibiting MNA.
- The original cleanup goal for vinyl chloride is no longer considered protective for vapor intrusion. This issue will be addressed in an upcoming Five-Year Review Report.

Lessons Learned:

- The active treatment phase should continue until the rebound evaluation is complete, so that additional injections can be conducted if necessary. Transition to MNA should not occur before this determination is made.
- Remediation systems should not be abandoned until it is certain that remedial objectives have been achieved
- There are misconceptions about the effectiveness of ISCO and why rebound occurs.
- Contracts should not be written so tightly that necessary remediation is precluded. The consultant should have freedom to modify the design so that RGs can be achieved.
- If contaminant concentrations were not decreasing by natural attenuation prior to ISCO, MNA is not likely to be effective within a reasonable timeframe if there are high target compound concentrations after ISCO injections are terminated.

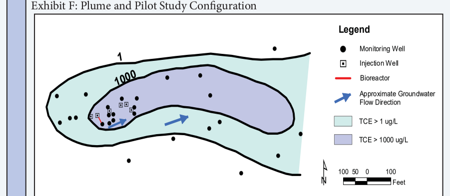
ISB IMPLEMENTATION PROBLEMS

In 2010, a contractor injected emulsified vegetable oil (EVO) into an 18-foot deep bioreactor trench at a concentration of 2-3% oil at a site with 5 to 30 ft of interbedded sands and clays over weathered bedrock to conduct an in-situ bioremediation (ISB) pilot study for treatment of TCE. Groundwater was extracted from another trench and recirculated through the bioreactor.

Reductive dechlorination of TCE to cis-1,2-DCE was observed in nearby wells; concentrations of TCE dropped by approximately 50% after 17 months of operation. However, little vinyl chloride was detected and concentrations did not change in wells located 35 to 70 ft from the bioreactor. No reductive dechlorination was observed in downgradient wells screened in the clayey weathered igneous bedrock, which ranges in thickness from 10 to 60 ft at the site.

In 2016, a second pilot study involving injection of an approximate 10% Wesblend® mixture into three injection wells with 5-ft screens in the lower weathered bedrock zone and three monitoring wells with 10-foot well screens was attempted. About 4,600 gallons of Wesblend® mixture consisting of molasses, hydrolyzed vegetable oil, whey and nutrients was delivered to an open-top 6,000 gallon tank. Four days later, 50 gallons of Wesblend® mixture was mixed with 550 gallons of water by pumping the mixture back and forth between two 650 gallon tanks. The contractor had difficulty mixing the solution due to the density of the Wesblend® mixture (10.84 pounds per gallon). After a day of mixing, injections began at 5 pm and continued over the next two days. In addition, about 500 gallons of a 30% Wesblend® mixture was injected into the bioreactor trench until the pump failed. On the fifth day, the Wesblend® mixture fermented, overtopped the tank and had to be disposed off-site.

Exhibit F: Plume and Pilot Study Configuration



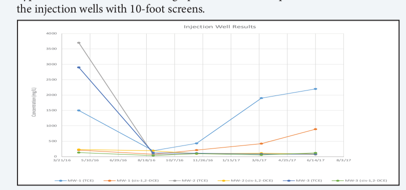
Injection Well	Planned Injection Volume (10% Wesblend®)	Actual Volume Injected (10% Wesblend®)	Estimated ROI
MW-1	8,044 gallons	4 gallons	0.24 ft
MW-2	8,044 gallons	7.8 gallons	0.33 ft
MW-3	8,044 gallons	3 gallons	0.21 ft
IW-1	8,044 gallons	12 gallons	0.58 ft
IW-2	8,044 gallons	3 gallons	0.29 ft
IW-3	8,044 gallons	3.5 gallons	0.32 ft

Observations and Mistakes:

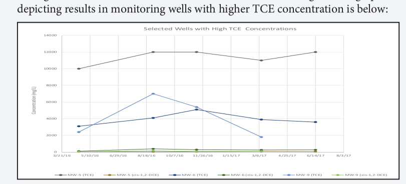
- The injection well heads were pushed off the wells by the injection pressure, starting when injections began.
- The planned injection volume was more than 8,000 gallons per well, but the actual amount injected varied from 3 to 12 gallons per well. This was attributed to low permeability, but it is likely that the diluted mixture was too thick for effective injection and distribution.
- The radius of influence (ROI) was calculated to range from about 0.2 to 0.6 ft from the injection wells.
- On the fifth day after delivery, the Wesblend® mixture became biologically active, expanded and overflowed the open-top tank, and had to be disposed off-site.
- Pre-injection testing of a groundwater sample found only 14.6 cells of dehalococcoides per milliliter and 9.67×10^3 cells of dehalobacter per milliliter. There was insufficient dehalococcoides for reductive dechlorination. Testing for the vinyl chloride reductase gene was not conducted.
- Characterization work performed during and after the second pilot test indicated that the injection wells were installed in a line that was sub-parallel, rather than perpendicular to the groundwater flow direction. Ideally, wells would have been installed in a line that was perpendicular to the groundwater flow direction.

Results:

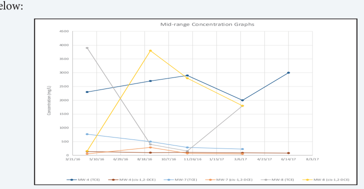
- TCE concentrations decreased, but cis-1,2-DCE was produced in only 2 of 6 injection wells. Small amounts of vinyl chloride were produced in 5 of 6 injection wells with concentrations ranging from non-detect to 12 ug/L in the wells with 5-foot screens and from 0.57 ug/L to 22 ug/L in the wells with 10-foot screens. In some wells, vinyl chloride was only detected during the final sampling event. Typical results are shown on the graph below, which depicts concentrations in the injection wells with 10-foot screens.



- TCE concentrations increased in three monitoring wells, decreased in two monitoring wells and increased, then decreased on one monitoring well. A graph depicting results in monitoring wells with higher TCE concentration is below:



- Cis-1,2-DCE concentrations decreased in two monitoring wells, had no trend in one monitoring well, and increased slightly in two monitoring wells. Significant concentrations of cis-1,2-DCE were produced in only one monitoring well, as shown in the graph below:



- Vinyl chloride was only detected in one monitoring well during two quarters (2.3 ug/L and 1.5 ug/L)
- Dissolved oxygen (DO) only decreased below 0.5 milligrams per liter (mg/L) in 1 of 12 injection and monitoring wells
- Oxidation reductive potential (ORP) < -150 millivolts (mV) developed in only two monitoring wells. ORP ranged as high as 296 mV.
- Nitrate concentrations were low, mostly below 1 mg/L.
- Sulfate ranged from 52 to 160 mg/L in all but 1 monitoring and up to 360 mg/L in the three injection wells monitored for sulfate.
- Ethene was observed in one injection well (3.5 ug/L); ethane was observed in three injection wells (3.9 to 9.1 ug/L); and, three injection wells were not monitored for ethene/ethane.
- Methane was observed in all three injection wells and seven monitoring wells (concentrations ranging from non-detect to 16,000 ug/L), but it took as much as 10 months to detect methane in some monitoring wells.
- It does not appear that reductive dechlorination occurred in most wells, given the minimal production of cis-1,2-DCE, vinyl chloride, ethene, and ethane, the high DO and ORP, and the high sulfate concentrations.

Lessons Learned:

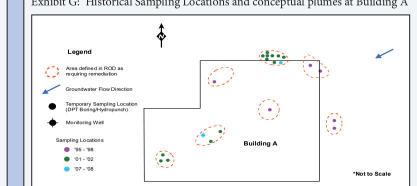
- A fluid acceptance test using water should be conducted to refine injection volumes before any amendment is ordered.
- The project team should practice mixing a small amount of amendment with water in a laboratory setting before attempting to mix amendment and water in the field to test whether the proposed mixing technique works.
- Fermented and biologically active amendment should not be injected.
- Additional delineation should be done before installing pilot test wells; if necessary the injection well configuration should be modified so the line of injection wells is perpendicular to the groundwater flow direction.
- Sugar or molasses-based amendments should be delivered in small quantities (i.e., only enough for one or two days) or in sterile sealed drums.
- 14.6 cells of dehalococcoides per milliliter is insufficient for reductive dechlorination. It is unclear if the vinyl chloride reductase gene was present; testing for this gene should have been conducted.

OLD DATA USED FOR ISCO REMEDIAL DESIGN

Building A, an industrial building erected in the 1940s, was historically used for cleaning, reworking, and manufacturing of metal parts; plating, painting, and tool maintenance operations; and specialty operations. The building contained a main paint shop that consisted of two paint bays and several smaller paint spray booths. In addition, the building houses a plating shop with operations involving degreasing; caustic and acid etching; metal stripping and cleaning; and chrome, nickel, silver, cadmium, and copper plating.

The investigation at Building A included 20 grab groundwater samples from direct push technology (DPT) soil borings and one groundwater sample from a monitoring well. Sampling was conducted in 1995, 1997, 1998, 2001, 2002, 2007, and 2008. The investigation identified seven areas where concentrations were above the RGs. Of the seven areas, two areas were only defined by a single grab groundwater sampling location (See Exhibit G) and no additional sampling was proposed or conducted to define the lateral or vertical extent of contamination. This conceptual site model (CSM) was carried forward to the Feasibility Study (FS) and Record of Decision (ROD) and did not account for treatment under Building A using electrical resistance heating (ERH) that occurred after 2008.

Exhibit G: Historical Sampling Locations and conceptual plumes at Building A



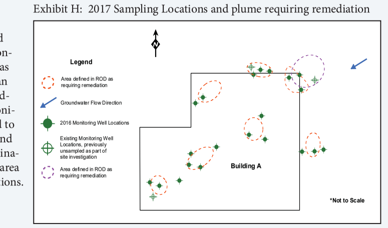
The ROD was submitted in 2014, 6-21 years after sampling was conducted, and proposed ISCO injections within each plume area to treat a few volatile organic compounds (VOCs) based on the CSM.

Other VOCs were not considered including:

- 1,1,1-trichloroethane (1,1,1-TCA) was present at concentrations up to 100 mg/L
- 1,1-dichloroethane (1,1-DCA) was present at concentration up to 110 mg/L
- Other VOCs were detected at concentrations up to 37 mg/L

Due to concerns with the dated sampling data and the lack of lateral and vertical delineation, additional sampling was conducted in October/December 2017 to update the CSM (See Exhibit H). The additional sampling included the installation of 21 groundwater monitoring wells and the use of three existing site monitoring wells that had not been sampled recently. As a result of the additional sampling, only one of the seven areas identified for treatment in the ROD was determined to have VOC concentrations above RGs. This is likely a result of the previous treatment conducted under Building A using ERH, which was not accounted for in the CSM.

Exhibit H: 2017 Sampling Locations and plume requiring remediation



Further, the extent of the contamination associated with the one area with concentrations above RGs was significantly different than previously presented. Additional groundwater monitoring wells are proposed to better define the lateral and vertical extent of contamination associated with this area and to target ISCO injections.

Observations and Mistakes:

- The conceptual designs presented in the FS and ROD were based on dated/obsolete data that did not sufficiently delineate the lateral or vertical extent of contamination.
- The result of other removal actions conducted at the site were not considered during the development of the conceptual designs presented in the FS and ROD. The conceptual design associated with the selected remedy in the ROD was then used as the basis for the remedial design.
- Non-target compounds were not considered.

Lessons Learned:

- Conceptual designs are just that, conceptual.
- Sufficient recent data should be obtained during the development of a remedial design to target injections to areas that require treatment.
- Site history and removal actions need to be accounted for when developing a remedial design.
- Both target and non-target compounds need to be considered when developing a remedial design.
- Flexibility is needed. Contracts should not be written to implement a conceptual design that is based on obsolete data. Collection of recent data should be required before finalizing a remedial design.
- When only old data is available, expect surprises when new data is obtained.

INSUFFICIENT DATA PROVIDED FOR A ISB REMEDIAL DESIGN

In the later 1980's, VOCs and radionuclides were detected in private wells north of the site. Site investigations discovered considerable contaminant loading from TCE source areas associated with an industrial building historically used for cleaning machinery parts, decontaminating the interiors of used radioactive materials cylinders, disassembling and testing cascade components, laundering clothes, and various other processes and activities.

An interim remedial action was initiated to retard the migration of the highest TCE concentration area within the groundwater plume. By 1997, two extraction wells and a treatment facility were installed to initiate hydraulic control of the high TCE concentration plume (i.e., concentrations greater than 1,000 ug/L) and reduce TCE migration offsite.

In 2015, agreement was reached to optimize the interim remedial action to increase TCE mass removal and to enhance control of the TCE concentration plume migration at the northern edge of the site. The optimization consisted of two new extraction wells (EWs), and the installation of 11 monitoring wells to evaluate performance and effectiveness (See Exhibit I).

To increase TCE mass removal, ISB was proposed in 2017 using six injection wells along and east-west transect (See Exhibit J).

Exhibit I: Optimized Interim Remedial Action

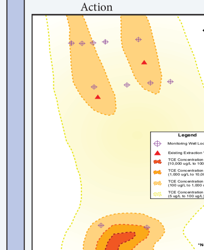
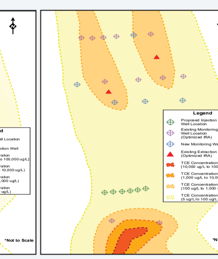


Exhibit J: Proposed ISB Remedial Design



Insufficient design details were provided in the remedial design and numerous data gaps were identified, including:

- No information was provided to support the locations proposed for ISB injection wells
- No baseline TCE concentration or groundwater quality parameter data was provided for the area of the proposed ISB injection wells
- The impacts of the EWs on contaminant migration were unknown
- No hydraulic characteristics of the subsurface were provided
- No pilot study was conducted to assess ROI or injection rates and pressures
- No microbial studies were conducted to assess microbial populations before ISB injection
- No bench scale testing was conducted using site soil and groundwater for ISB amendment dosages

Observations and Mistakes:

- The ability to conduct required injections is unclear because there is insufficient information.
- The CSM is undefined.
- The effectiveness of ISB is uncertain because it is not known if required microbial populations are present.
- Justification for application parameters was not provided.
- Target depths for the injections are unsupported due to the unknown vertical and horizontal extent of contamination. The potential exists that zones that do not need treatment will be treated and/or that zones that require treatment will be missed.
- The potential for failure is high.

Lessons Learned:

- Sufficient pre-design information from pilot studies, microbial studies, and bench scale testing is necessary to ensure an effective remedial design can be implemented.
- Adequate time and budget need to be allocated to remedial design projects to ensure critical data for implementation are obtained and assessed.
- Having a clearly defined CSM based on sufficient data is critical for successful implementation of a remedial design. Know what needs to be treated!