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INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT

In Situ Injection Strategies

Eric J. Holcomb
Governor

Bruno L. Pigott
Commissioner

(317) 232-8603 • (800) 451-6027 www.idem.IN.gov 100 N. Senate Ave., Indianapolis, IN 46204

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Notice

IDEM Technology Evaluation Group (TEG) completed this evaluation of in-situ injection strategies based on review of items listed in the "References" section of this document. IDEM OLQ technical memorandum *Submittal Guidance for Evaluation of Remediation Technologies* describes criteria for performing these evaluations.

This evaluation explains the technology but does not verify its effectiveness in conditions not identified here. Mention of trade names or commercial products does not constitute endorsement or recommendation by IDEM for use.

Background

Development of a successful injection strategy begins with a refined conceptual site model (CSM) that conveys a detailed understanding of site conditions and physical limitations necessary to design and implement an injection remedy. Once the geology, hydrology, aqueous geochemistry, groundwater biogeochemistry, and spatial distribution of contaminant mass are understood, amendment screening and selection, dosing, delivery technologies, and performance metrics can be developed.

Before a treatment plan using in-situ injection methods can be evaluated, remedial design characterization (ITRC 2020) should be completed containing:

- The extent and amount of contamination (especially free product), the location of utility lines, piping, possible migration pathways, all subsurface heterogeneities, groundwater depth/elevation, and direction/gradient of groundwater flow. It needs to cover site topography, aquifer geochemistry (reduced mineral content, organic content, mineral demand for ferrous iron, sulfite, nitrite, dissolved oxygen, etc.), potential receptors, detailed lithology, hydraulic parameters (conductivity, transmissivity, storativity, effective porosity, etc.), particle size distribution, and soil porosity.
- Laboratory results showing the natural oxygen demand (NOD) of the site soils.
- Results of an on-site pilot study, which establishes the amendment concentrations, injection rates and volumes, temperature, pressures, time of injection, and radius of influence.
- If in-situ bioremediation is used a microcosm study is needed.
- Plans for an SVE system for the hydrogen peroxide application, if needed to handle significant quantity of explosive off-gassing (USEPA 2004).
- Plans for methane monitoring system for certain biological applications and SVE system if needed because excessive methane is generated.
- A detailed contingency plan which incorporates the information above.

- A site safety plan, which covers the special problems presented by handling and use of amendments,
- Plans for site monitoring, with quarterly sampling in the injection area and immediate surroundings, typically for a **minimum** of one year. If plume behavior is being used to close the site at least an additional 4 to 10 quarters (or more) of monitoring data may be needed to evaluate long-term trends.

Types of In-Situ Amendments

In-situ injections delivers materials to the subsurface to degrade or transform COCs. In-situ injection can be used for treating the vadose and saturated zones. In-situ injection is effective in treating a wide variety of contaminants at both the source area and within the aqueous plume, and some forms of in-situ injection often produce decreased groundwater COC concentration results within weeks to months after the application.

- **Oxidizing agents (In situ Chemical Oxidation (ISCO)):** Common oxidizing agents include catalyzed hydrogen peroxide (CHP, sometimes called modified Fenton's reagent), ozone, peroxone (the combination of ozone and hydrogen peroxide), activated and catalyzed persulfate, sodium percarbonate, and sodium or potassium permanganate. These oxidants are supplied in various forms. ISCO is amenable to treat groups of organic compounds (for example, BTEX, MTBE, cVOCs, SVOCs, carbon tetrachloride, select pesticides (for example, DDT, chlordane, lindane, etc.)), and some energetics (for example, dinitrotoluene or DNT, trinitrotoluene or TNT, and hexahydro-1,3,5-trinitro-1,3,5-triazine or RDX). ISCO is less effective on PAHs, PCBs, DCA, pesticides, chloroform, and metals that require reducing reactions and radicals. Some oxidants have narrow ranges of target compounds; for example, permanganate can attack only double bonds in compounds like PCE or TCE. Permanganate injection also calls for the manganese concentration in groundwater to be determined. Persulfate injection also needs sulfate levels and the baseline iron content. Peroxide injection calls for the baseline iron content, and alkalinity. Ozone injection in the vadose zone adds moisture content to the large list above.
- **Zero Valent Iron (ZVI):** Although this is sometimes listed as an ISCO method, ZVI removes contaminants via reduction rather than oxidation. This is a completely different set of reactions and geochemistry.
- **Oxygen releasing compounds (ORCs):** ORCs are chemicals that when hydrated release oxygen. There are several different types of ORCs available. ORC is an amendment used when aerobic bioremediation is the remedial method selected. Additional details can be found in Bioremediation Guidance Document updated 2017 (See Reference Section).
- **Hydrogen releasing compounds (HRC):** HRCs are chemicals that when hydrated release hydrogen. There are several different types of HRCs available. HRC is an amendment used when anaerobic bioremediation is the remedial method selected. Additional details can be found in Bioremediation Guidance Document updated 2017 (See Reference Section).
- **Active bacteria:** Active bacteria injection is a method where live bacteria cultures are injected into the subsurface to supplement either aerobic or anaerobic bioremediation. When using live cultures, a microcosm study is conducted prior to injection. Most studies like this find that there is a lack of nutrients and not a lack of bacteria. Additional details can be found in Bioremediation Guidance Document updated 2017 (See Reference Section).
- **Trap and Treat Materials:** Trap and treat is a method that uses porous activated carbon saturated with materials that will reduce concentrations of the target COCs. As the contaminants enter the porous carbon, they encounter the injection materials thus reducing the contaminant. The constant change in equilibrium between the aquifer and the carbon allows additional contaminants to enter the carbon and are treated. Additional information can be found in USEPA 2018.

Additional amendments (to inhibit migration or deal with potential safety issues) including:

- **Activated Carbon**: Additional information can be found in USEPA 2018.

- **Surfactants:** Surfactants can also be used to remove sludge, silty fines, and organic/mineral matter during monitoring well redevelopment with the intent to re-establish contact between the well screen and formation water. Such surfactants are non-toxic/food grade and are particularly useful in hydrocarbon mass mobilization within fine sands and sandy silts (ITRC 2003).
  The inherent agitation of surfactant well redevelopment can result in biased or even useless analytical data. Monitoring wells need to be given enough time to equilibrate before analytical results can be considered useable. IDEM OLQ recommends 1 month of post-redevelopment to reach equilibrium conditions.
- **pH Buffers:** pH is influenced by a complex relationship between organisms, contaminant chemistry, and physical and chemical properties of the local subsurface environment. For example, in low-alkalinity systems, fermentation of complex substrates generates acids, and hydrochloric acid (HCl) is formed during anaerobic dechlorination. These processes may significantly decrease groundwater pH. Reducing groundwater pH to below 5 will likely inhibit microbial growth. Adding pH buffers can mitigate this potential problem. Additional information can be found in ITRC 2020.
- **Methane inhibitors:** Methane concentrations may increase due to the proliferation of methane-producing bacteria, which occurs when high levels of carbon substrate such as emulsified vegetable oil are introduced into the subsurface. Methane can be metabolized by many microbes to carbon dioxide under aerobic conditions in the vadose zone. To ensure the complete mitigation of any potential methane issue, injection of small amounts of commercially available methane inhibitors is recommended to retard the proliferation of methanogens. Additional information can be found in ITRC 2020 and IDEM 2017.

INJECTION AND THE USE OF PNEUMATIC FRACTURING

There are two generally used methods to deliver the in-situ amendments:

- Direct injection into a borehole, and
- Using an injection well (both horizontal and vertical). (USEPA 2004)

The common method for delivering amendments is using a direct push device. This device can be used for most of the unconsolidated materials encountered in Indiana. To implement an effective injection program a complete CSM is needed. Injection can also use wells; however, if a monitoring well is used to inject materials, the well can no longer serve as a monitoring well to evaluate long-term post-treatment plume trends. If a compliance monitoring well is within the effective radius of influence of an injection and the well shows direct evidence of the injected materials, data from these wells would be considered questionable and replacement monitoring wells may need to be installed. These wells can still be used for evaluating the effectiveness of the injection during the treatment period. Instead of using monitoring wells, dedicated injection wells may be needed if multiple injections are anticipated or planned.

However, when fine grained materials are encountered there can be an extra step introduced to the injection process. Pneumatic fracturing can be used in fine-grained materials to introduce beneficial substrates (ISCO, ORC, bioremediation, etc.) into the formation. For pneumatic fracturing to be successful a complete CSM is needed. Pneumatic fracturing, by itself, is not a treatment technique but is used with injection methods creating a network of artificial fractures in a geologic formation. Pneumatic fracturing serves two principal functions for enhancing injection methods. First, the fractures can facilitate removal of contaminants out of the geologic formation. Second, the fractures may be used to introduce beneficial substrates into the formation. The overall objective of fracturing is to overcome the transport limitations that are inherent at many remediation sites. Even with all the necessary information, pneumatic fracturing may not be effective.

Furthermore, the remedial design characterization needs to thoroughly evaluate the geotechnical characteristics of the formation during the design phase of a fracturing project. Exploratory borings in the proposed injection zone with continuous sampling or coring are recommended. The borings are normally supplemented with geotechnical tests performed on collected samples of the geologic material to be fractured. The TEG finds that pilot testing is useful to screen a site for full-scale remediation incorporating fracturing.

Additional information and techniques used to optimize injection-based remedies can be found in the ITRC Guidance Document titled "Optimizing Injection Strategies and In Situ Treatment Performance," (ITRC 2020).

ADVANTAGES

- Chemical oxidation is usually much faster (weeks or months) than most other injection methods.
- Addition of key nutrients can accelerate biodegradation that was already ongoing,
- Except for off gassing from hydrogen peroxide and ozone use, ISCO does not leave wastes to treat or transport.
- Oxidization destroys the contaminant molecules. This reduces, or eliminates the potential for more toxic breakdown products, as may be the case in bioremediation.
- Oxidation enhances the mass transfer (desorption) of contaminants into vapor and dissolved phases, where they can be more easily captured or treated in-situ.
- Some in situ applications are less invasive and cause less site disruption than other treatment methods.
- Some oxidants produce oxygen, which will help aerobic microbial decomposition of some hydrocarbons.
- Chemical oxidation can also be applied to plumes of mixed contaminants (such as petroleum mixed with solvents) that are not easily remediated in-situ with other technologies.
- Adding Surfactants can:
  - Reduces volatility,
  - Increases solubility,
  - Improves bioavailability and accelerates biodegradation,
  - Most surfactants are non-flammable, non-hazardous, water-based formulations,
  - Versatility – Can be blended as foaming agents, emulsifiers, and dispersants which suspend gases, immiscible liquids, or solids in water or other liquid, and
  - Any surfactants remaining in the subsurface are easily biodegradable.

LIMITATIONS

There are numerous limitations to in-situ injections. Some are inherent to the chemistry, others to site conditions, or both. The limitations include:

- Because of the necessary monitoring and safety precautions, chemical oxidation may have potentially higher initial and overall costs relative to other source area solutions (USEPA 2004).
- There are notable health and safety issues involved with the handling and application of strong oxidizers. Permanganates are hazardous to handle ex-situ, and hydrogen peroxide has a violently exothermic reaction to free product.
- Even if the oxidants are effective on the contaminants, the contaminants may be mobilized. There may be an increase in vapors, or redistribution of contamination from the sorbed phase into groundwater. Chemical oxidation enhances mass transfer (desorption) of contaminants into vapor and dissolved phases. This may allow contaminant mobilization outside the monitoring area. Some injected materials can generate methane and at high enough concentrations can be an explosion hazard.
- Groundwater contaminant levels often rebound, and multiple injection events are necessary.
- It is difficult to deliver amendment into areas having heterogeneous geology. It is nearly impossible to deliver amendment into low permeability units (USEPA 2004).
- Typical radius of influence (ROI) for injections range from 2.5 feet for tight clays to 25 feet in permeable saturated soils (ITRC 2005).

- Some amendments tend to react quickly, which greatly limits their radius of influence beyond the injection point. Closely spaced, low volume injection points are usually best.
- The high natural oxidant demand in many Indiana soils means that there are many non-target compounds competing for the oxidant. Larger volumes of oxidant may be needed to achieve meaningful results. Peat layers generally prohibit use of oxidants. Inorganic oxidant demands come from nitrification and the oxidation of sulfide, iron, iron sulfide, chromium, selenium, manganese, etc.
- In situ remedies rarely remediate the entire contaminant mass; residual contaminants typically need additional injections, monitoring and/or risk assessment.
- The manganese from permanganates and the iron catalysts used for Fenton's Reaction and persulfate precipitate out in the formation and cause notable reductions in permeability.
- Metals can be mobilized by changes in their oxidation state. It is important to know what metals are present in the soil and groundwater because this treatment technology can oxidize some metals, including iron, chromium, and selenium, to a more soluble form, thereby increasing their migration potential (ITRC 2005).
- Inadequate evaluation of existing microcosms can lead to not reaching remedial goals when using in-situ bioremediation.
- A major consideration in all liquid in situ applications is the amount of fluid introduced during emplacement, particularly in the source area. The same volume of fluid will be displaced as is introduced. This can spread contamination further. Also, it can cause a misleading impression that the oxidant is reducing contamination, when only dilution or dispersion is taking place.
- Adding Surfactants can:
  - Surfactants remedial effects on petroleum contamination are limited to the well bore and immediate formation outside the well bore, especially if short-term vacuum recovery is applied,
  - Monitoring well surfactant application and the agitation of vacuum recovery will severely bias analytical results,
  - Monitoring wells need sufficient time to reach steady-state or equilibrium conditions before returning to a regular network monitoring program, Phosphorous-containing surfactants can increase biofouling and decrease well productivity, and
  - Most surfactants are toxic to aquatic organisms due to their surface activity which will react with the biological membranes of organisms (ETSA, 2010).

SAFETY

Most of the safety precautions and monitoring that the USEPA states are needed, and the ITRC advises, have not been included on Indiana sites. For public safety, they need to be considered.

- Both liquid and solid peroxides have the same limitations, in that they cannot be safely applied to free product, or around piping, tanks, or utility lines. The heat produced by even dilute hydrogen peroxide can also produce significant hydrocarbon vapors in the subsurface, with attendant dangers to nearby structures or utility corridors. To prevent problems with off-gassing, the USEPA requires special precautions when implementation of remedial action involving Fenton's Reagent/hydrogen peroxide (USEPA 2004). Some states currently require an SVE system with peroxide injections.
- Sodium permanganate often comes in a liquid solution, at 40% strength. This poses an explosion risk (USEPA 2004).
- Without a detailed knowledge of the subsurface (i.e. complete CSM), use pneumatic fracturing could create preferential pathways that allow both injected materials and contamination to migrate unintended directions.
- Methane generation can be an issue with certain materials injected to enhance bioremediation. Vapor sampling and groundwater sampling will need to include collection of methane samples. Additional information about methane can be found in Technical Evaluation Guidance:

  - Bioremediation (IDEM 2017)
  - Methane Monitoring Monitoring (IDEM 2019)

Optimization and Verification

- Oxidant injection is not an easy to assess, one-time application strategy. Both USEPA 2004 and ITRC 2005 call for monitoring of oxidant treatment sites for a minimum of one year after injection, to guard against rebound. According to Regenesis 2007, 88% of sites using chemical oxidation had contaminant rebound in at least one well.
- There is also additional monitoring needed during the treatment process, as mentioned above. Huling and Pivetz 2006, recommends process monitoring of all ISCO applications for:
  - Oxidants,
  - Metals,
  - Iron, phosphates, and chelators,
  - pH,
  - Alkalinity/Buffer Capacity,
  - Eh (electrode potential), and
  - Groundwater level.

  Additionally, peroxide use calls for continuous temperature measurements, and both peroxide and ozone injection call for continuous measurements of oxygen gas, carbon dioxide, and the Lower Explosive Limit (LEL). Transducers are the best way to monitor water levels over time.
- Most injection methods will not completely eliminate contamination. Usually injection treatments are conducted in series with plume behavior evaluations. Once the injection monitoring is complete and the injection zone has equilibrated (usually between 6- and 12-months following injection), four to eight additional sampling events are needed to evaluate the residual contamination that remains.

RECOMMENDATIONS

The presence of free product, underground utility lines, or low permeable soils limits the in-situ injection treatments at a site (USEPA 2004). The information reviewed for this guidance document supports using amendments for in-situ applications in low permeable soil, provided suitable pathways for the amendments can be created through available fracturing techniques. Because of the safety issues, IDEM OLQ recommends disapproval of any corrective action plan using liquid hydrogen peroxides in-situ without an aggressive vapor and groundwater capture system.

None of the chemical oxidants can economically remediate free product, and the peroxides can be extremely dangerous if they contact it. Underground utilities can be adversely affected by the heat, VOC vapors, elevated oxygen levels, and potential corrosion that can occur with chemical oxidation injections. The problems of low permeable soils may be helped by soil fracturing, using the less reactive oxidants, or repeated injections. However, none of these are guaranteed to work, and all this adds to the expense and time needed.

FURTHER INFORMATION

If you have any additional information regarding In-Situ Injection Strategies or any questions about the evaluation, please contact the Office of Land Quality, Science Services Branch at (317) 232-3215. IDEM TEG will update this technical guidance document periodically or on receipt of new information.

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