

# **In Situ Application of Potassium Permanganate Solution for VOCs-Impacted Groundwater Cleanup – The Regulatory Perspective**

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**Abstract:** In-situ chemical oxidation has been an attractive option as an expedited restoration of aquifers impacted by chlorinated volatile organic compounds (VOCs). Both pilot tests and full-scale application of potassium permanganate (KMnO<sub>4</sub>) solution have been demonstrated in the field. Compared to typical pump-and-treat technologies, use of chemical oxidation can be significantly faster and more cost-effective to reach cleanup goal. In this paper, the pros and cons of using KMnO<sub>4</sub> solution in in-situ restoration of VOCs-impacted aquifer are discussed from a regulatory perspective.

## **Introduction**

Traditionally, pump-and-treat technology has been used to restore groundwater aquifers impacted by chlorinated volatile organic compounds (VOCs). However, pump-and-treat approaches to aquifer restoration have demonstrated a distinct lack of success (National Research Council, 1994). In recent years, a number of innovative remedial technologies have been investigated. One example of these innovative remedial technologies for groundwater contamination is in situ chemical oxidation using potassium permanganate (KMnO<sub>4</sub>).

## **Technology Description**

Remediation of groundwater contamination using potassium permanganate (KMnO<sub>4</sub>) involves injecting KMnO<sub>4</sub> solution (2%~4%) directly into the source zone and down-gradient plume.

Permanganate is an oxidizing agent with a unique affinity for oxidizing organic compounds containing carbon-carbon double bonds, aldehyde groups or hydroxyl groups. Therefore, the technology is suitable for the cleanup of groundwater impacted by tetrachloroethene (PCE) and trichloroethene (TCE). Under normal subsurface pH and temperature conditions, the carbon-carbon double bond of alkenes is broken spontaneously and the unstable intermediates are converted to carbon dioxide through either hydrolysis or further oxidation by the permanganate ion. Permanganate can also be used to treat organic compounds that contain hydroxy functional groups such as primary and secondary alcohols, as well as some organic acids such as phenol.

The effectiveness of in situ chemical oxidation in the subsurface relies on the adequate and uniform distribution of the oxidant to the source zone. Due to the complex nature of groundwater aquifers, the dynamic in situ oxidation process in subsurface environment is less predictable than most other cleanup alternatives.

## **Pros & Cons**

In situ application of potassium permanganate solution offers several advantages over conventional treatment technologies such as pump and treat. For example, the technology does not generate large volumes of contaminated groundwater that must be treated and disposed of. The life cycle of this innovative technology is also much shorter. These advantages will, therefore, result in savings on material, monitoring and maintenance. However, successful application of the technology relies on the effective delivery of the  $\text{KMnO}_4$  solution to the source zone. The chemical oxidation process may also cause temporal changes in geochemistry and aquifer permeability in localized spots. Although potassium permanganate is a relatively safe chemical with respect to toxicity, the typical dangers associated with the handling of this oxidizing chemical are present.

## **Requirements**

Because in situ chemical oxidation is an emerging technology, there are regulatory issues to be addressed before they are implemented. Three consistently mentioned concerns are as follows (EPA, March 2000):

- Permitting processes for innovative treatment technologies are inconsistent, involve numerous levels and are time- and resource-intensive.
- Permitting and manifesting requirements under the Resource Conservation and Recovery Act (RCRA) often inhibit the development of innovative treatment technologies.
- Users (contractors) of environmental technologies are concerned about liabilities they might incur through the use of innovative treatment technologies.

California has not developed a statewide policy regarding the use of this technology at groundwater cleanup sites. In the State of California, groundwater cleanup oversight is delegated to two CalEPA agencies. The State Water Resources Control Board (State Water Board) regulates groundwater cleanup through its 9 Regional Water Quality Control Boards (Regional Water Board). The California Department of Toxic Substances Control (DTSC) regulates groundwater cleanup through its four Regions. Each agency has jurisdiction over separate groundwater programs but shares responsibilities in some areas. Typically, a lead agency is appointed to avoid duplication.

As the needs for the application of in situ chemical oxidation increases, California Regional Water Boards have been evaluating and developing policies for the innovative technologies. The North Coast Regional Water Quality Control Board has recently adopted a General Permit for addition of oxygen releasing compounds to groundwater. The Los Angeles Regional Water Quality Control Board is currently drafting a General Waste Discharge Requirements (WDR) for using in situ chemical oxidation for contaminated aquifer restoration. Before the general WDR is adopted, a site specific WDR is required for using in situ chemical oxidation in the Los Angeles Region.

According to the provisions in Section 13260 of the California Water Code, any injection of potassium permanganate into the groundwater is a discharge of waste. However, the discharge of potassium permanganate is intended to provide more efficient remediation of contaminated groundwater and is consistent with the antidegradation provisions of State Water Resources Control Board Resolution No. 68-16 (Anti-degradation Policy). Therefore, such a discharge may be permitted after the discharger meets the relevant regulations such as the California Environmental Quality Act and prescribes Waste Discharge Requirements for their discharge.

Under the California Environmental Quality Act, an Initial Study (in the format of an expanded Environmental Checklist) should be conducted in accordance with Title 14, California Code of Regulations, Section 15063, entitled Guidelines for Implementation of the California Environmental Quality Act. Based on the Initial Study, a Mitigated Negative Declaration will be prepared when it is found that the project will not have a significant adverse effect on the environment.

The WDR is intended to provide monitoring and discharge guidelines and requirements to provide full and complete containment of any by-products of the chemical oxidation process; to prevent any discharge of potassium permanganate or any by-products into any surface, surface water drainage course, or surface waters; and to minimize any adverse impacts caused by the injection of potassium permanganate solution.

### **Field Demonstration Data**

The use of  $\text{KMnO}_4$  injection for the cleanup of TCE/PCE-impacted groundwater can be very effective based on the published data from sites overseen by California Regional Water Quality Control Boards and DTSC. In summary, field data collected from these field demonstrations indicate the following:

1. The technology is most suitable for the cleanup of groundwater impacted by tetrachloroethene (PCE) and trichloroethene (TCE). For example, TCE removal of up to 99% over a period of 22 weeks was observed in monitoring wells at a site in Ripon, California. However, the technology is less effective for vinyl chloride and dense nonaqueous-phase liquid (DNAPL) such as in the case of Santa Clara and Menlo Park, respectively.
2. Based on pre-injection and post-injection data, no impact to aquifer permeability has been observed.
3. Chloride and manganese concentrations, two of the major by-products after injection, were within the range of background levels in the testing area thus did not appear to be impacted by the oxidation process.
4. Data collected from the sites where chromium changes in the aquifer were evaluated suggest that some trivalent chromium (insoluble at neutral pH) will temporarily convert to hexavalent chromium (soluble). However, the hexavalent chromium was attenuated by the natural processes with an average half-life of two weeks at Santa Clara. Another site at Pinole overseen by the Department of Toxic Substance Control (DTSC) reported that hexavalent chromium was attenuated from 0.050 part per

million (ppm) to below detection limit (0.01 ppm) in two weeks. All these published field data indicate that hexavalent chromium converted from trivalent chromium caused by the injection of  $\text{KMnO}_4$  solution is a transitional state. Once the oxidizing conditions disappear (reaction between  $\text{KMnO}_4$  and VOCs is complete), the hexavalent chromium will convert back to trivalent state shortly (within days to weeks).

5. It is very effective when the  $\text{KMnO}_4$  solution can be adequately delivered to the impacted saturated soil matrix. However, the success is limited for clayey formation where both the delivery of oxidant and inter-phase mass transfer rate are limited.

### **Disclaimer**

The opinions in this paper are solely of the authors and are not necessarily endorsed by the State of California regulatory agencies.

### **References**

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