

CASE STUDY COMPARISON OF MULTIPLE ACTIVATION METHODS FOR SODIUM PERSULFATE ISCO TREATMENT

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ABSTRACT: Several methods are available for activating sodium persulfate, including hydrogen peroxide, ferrous iron or chelated iron, alkaline conditions (high pH), and heat. This paper discusses in-situ chemical oxidation (ISCO) case studies (both full scale and pilot studies) which were designed and implemented using varying methods for activating persulfate. A total of six case studies are discussed with regards to selection of activator, reduction in contaminant levels, and site conditions affecting the ISCO treatments.

To obtain optimal contaminant destruction and efficiency, the proper activation method for persulfate must be selected. Selection of the activation method is dependent upon both the contaminant(s) of concern and the site conditions. As a general rule of thumb, FMC Corporation has stated the most aggressive means of persulfate activation is by use of high pH and/or hydrogen peroxide. However, there are certain site conditions where these activators might not be the best choice. For shallow groundwater UST sites, the high pH or peroxide might cause corrosion or damage to utilities and metal objects that may come into contact with the activator or the persulfate. In addition, hydrogen peroxide often reacts very aggressively in the subsurface and care must be taken to adequately vent off-gas production and control the reaction so that peroxide does not come to the surface. FMC does not recommend iron activation for destruction of gasoline range and diesel range organics, although it is effective on MTBE, TBA, BTEX, and other hydrocarbons. In addition, iron activation is not recommended for treatment of vinyl chloride, methylene chloride, carbon tetrachloride, TCA or DCA.

The six ISCO case studies were all sites located in California. The following is a breakdown of the activators used on the sites:

- Hydrogen peroxide activation – 2 sites
- High pH activation – 2 sites
- Iron activation - 2 sites

Good to excellent contaminant reductions (generally exceeding 85% reduction) were achieved in all these case studies, due in large part to the matching of site conditions to the best activation method.

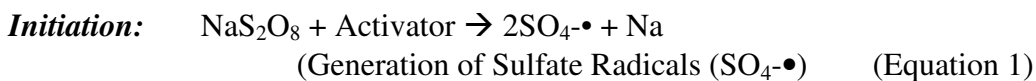
INTRODUCTION

In recent years, sodium persulfate has become a commonly used oxidant for many contaminated groundwater sites. Persulfate is a strong and versatile oxidant capable of treating a wide spectrum of organic contaminants. The activation of sodium persulfate can be achieved by any of the following methods:

- Hydrogen Peroxide
- Ferrous Iron or Chelated Iron
- High pH
- Heat

Once the persulfate is activated by one of the above methods, it results in the formation of sulfate free radicals ($\text{SO}_4\text{-}\bullet$) as represented in Equations 1 through 4 below. The sulfate radicals can also produce hydroxyl radicals (see Equation 2). Free radicals are molecular fragments that have an unpaired electron causing them to be strong oxidizing agents and are known to rapidly oxidize many VOCs. In addition to its oxidizing strength, persulfate and sulfate radical oxidation has several advantages over other oxidants. First, it is kinetically fast. Second, the sulfate radical is more stable than the hydroxyl radical and thus able to transport (diffuse) greater distances and create a larger radius of treatment.

Sulfate Radical Generation and Reactions:



Where: RH represents an organic compound;

R• represents oxidized organic compound

Soil oxidant demand and metals also contribute to oxidant consumption.

Note: Free radical chemistry is not necessarily stoichiometric or straightforward.

SELECTION OF THE RIGHT ACTIVATOR

To obtain optimal contaminant destruction and efficiency, the right activation method must be selected. Selection of the activation method is dependent upon both the contaminant of concern(s) and the site conditions. For example, for cleanup of gasoline or diesel contaminated UST sites, the best activator would be high pH or hydrogen peroxide. Heat could also be used, but generating or obtaining a source of heat is often costly (unless the site is already producing steam or another source of heat). FMC Corporation does not recommend iron activation for destruction of gasoline range and diesel range organics, although it is effective on MTBE, TBA, BTEX, and other hydrocarbons.

For mixed solvent plumes containing chlorinated ethenes, such as TCE, PCE, DCE, and vinyl chloride, any of the four activation methods would work well. However, if the site contains high levels of vinyl chloride, methylene chloride, carbon tetrachloride, TCA or DCA, activation by iron activation is not recommended. In this situation, high pH or

hydrogen peroxide would be the activator of choice. 1,4-dioxane can be treated by activation by iron, high pH, or peroxide.

As a general rule of thumb, FMC has stated the most aggressive means of persulfate activation is by use of hydrogen peroxide and/or high pH. However, there are certain site conditions where these activators might not be the best choice. For shallow groundwater UST sites, the high pH or peroxide might cause accelerated corrosion of utilities and metal objects that it comes into contact with. In addition, hydrogen peroxide often reacts aggressively in the subsurface and care must be taken to adequately vent off-gas production and to minimize peroxide coming to the surface. Sensitive sites where the surfacing of hydrogen peroxide could cause issues for the owner's business operations would not be good candidates for peroxide.

Site 1. Hydrogen Peroxide Activation

Site 1 is an industrial site located in Ranch Dominguez, CA (Los Angeles County). Hydrogen peroxide activation was selected for treatment of this methylene chloride DNAPL site. This activation technique, which incorporates combined oxidizing power of peroxide and persulfate along with heat given off by the Fenton's reaction, was selected because of the recalcitrant nature of methylene chloride and the difficult site conditions. This project was extremely difficult because most of the contaminant plume was under an active industrial building and the contaminants were isolated within a clayey formation at a depth of 40 to 50 feet. A total of 16 of the 23 injection wells were located inside the building with several slant wells installed in sensitive areas where the owner's equipment could not be re-located.

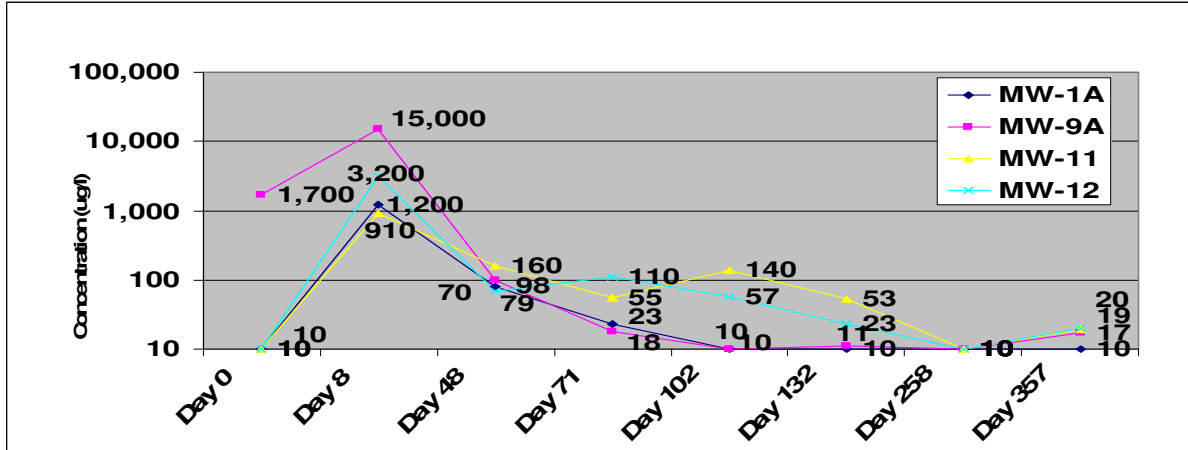
FIGURE 1. Tank used for mixing sodium persulfate



Results – Site 1.

Pre-treatment methylene chloride levels over 15,000 µg/l were reduced to levels less than 50 µg/l within 258 days. “Surfacing” of hydrogen peroxide occurred at this site and off-gas venting issues caused some minor damage to the asphalt pavement. Closure of this site has recently been granted by the Los Angeles Regional Water Quality Control Board.

FIGURE 2. Reductions in methylene chloride following persulfate treatment



Site 2. Hydrogen Peroxide Activation

Site 2 is an industrial site located in Huntington Beach, CA (Orange County). Hydrogen peroxide activation was selected for the 8 well pilot scale treatment of 1,4-dioxane and chlorinated solvents, due to the extremely elevated levels of these recalcitrant contaminants. Depth to groundwater was approximately 12 feet.

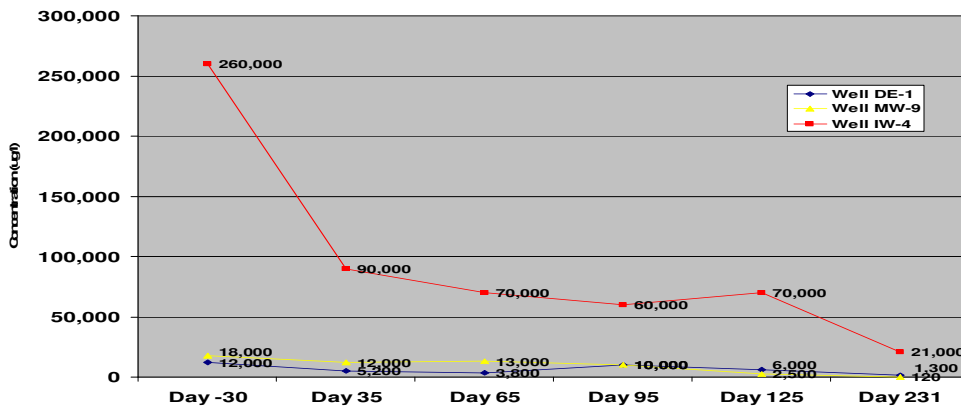
FIGURE 3. Hydrogen peroxide tanks used for activation of persulfate.



Results – Site 2.

After 231 days, the 1,4-dioxane levels were reduced substantially, with levels as high as 260,000 µg/l being reduced to 21,000 µg/l (92% reduction). “Surfacing” of peroxide did occur at this site. As a result of the highly successful pilot test, further ISCO treatment of the site is being planned.

FIGURE 4. Reductions in 1,4-dioxane following persulfate treatment



Site 3. High pH Activation

Site 3 is an industrial site located in Santa Ana, CA. Alkaline activation of sodium persulfate using 25% sodium hydroxide was used for the pilot scale treatment of a mixed chlorinated solvent plume. Two injection wells were utilized. Depth to groundwater was approximately 25 feet.

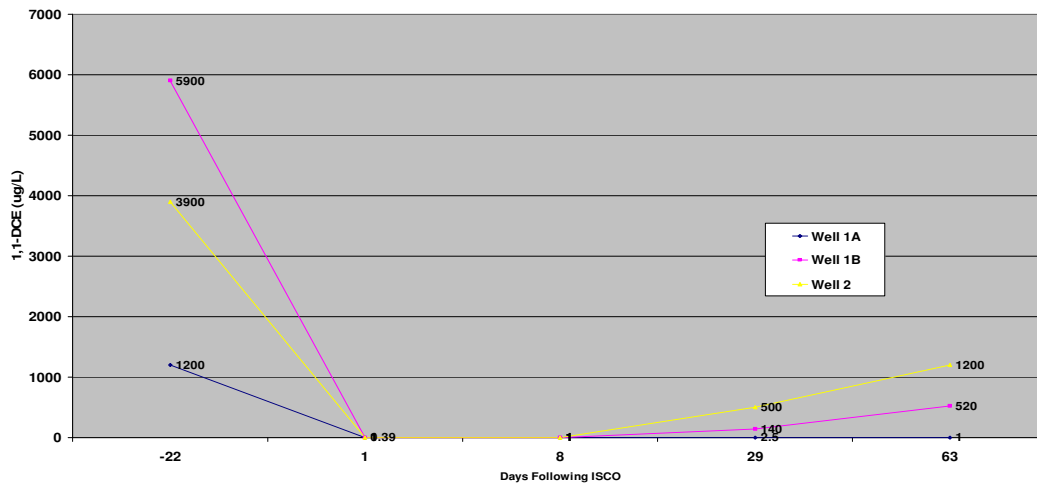
FIGURE 5. Injection of sodium hydroxide solution.



Results – Site 3.

Significant reductions were observed within 30 days for TCE (95%), 1,1-DCE (99%), and other contaminants, but a moderate rebound effect was observed after 45 days of the injection. The rebound effect was believed to be due to release of adsorbed contaminants from the soil. In addition, continued migration of contaminants from the source area likely masked the results in the treatment area, which was located downgradient of the source area.

FIGURE 6. Reductions in 1,1-DCE Following Persulfate Treatment.



Site 4. High pH Activation

Site 4 is an active gas station site located in Huntington Harbor, CA. High pH activation of persulfate using 25% sodium hydroxide was selected for this site because of its treatment effectiveness on gasoline range hydrocarbons. Depth to groundwater was at 30 feet bgs, so no interference with shallow utilities was anticipated. Three existing

monitoring wells surrounding the UST source area were used as injections wells for this treatment project.

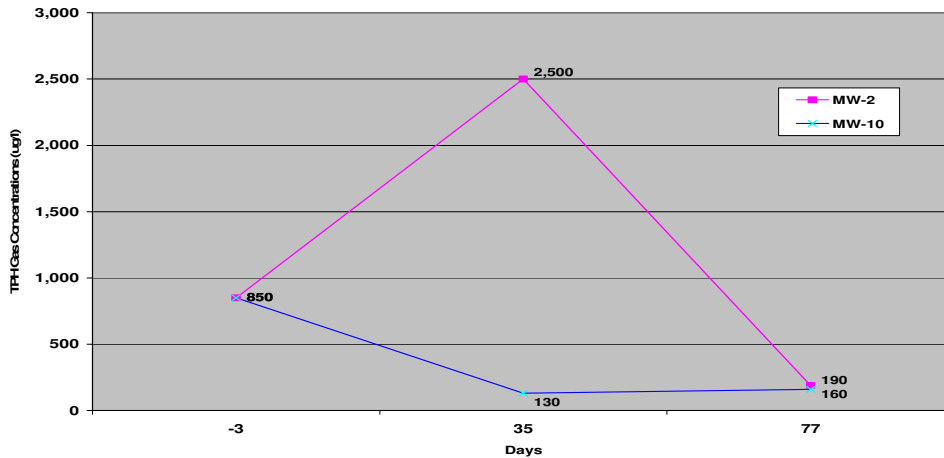
FIGURE 7. Mixing of persulfate solution.



Results – Site 4.

After 77 days, the TPH gas levels were reduced substantially, with levels as high as 860 $\mu\text{g/l}$ reduced to 160 $\mu\text{g/l}$ and BTEX levels reduced by 82% to 100%. This site is early in the monitoring phase and additional results over the next several months will likely continue to show reductions in contaminant levels.

FIGURE 8. Reductions in TPH as gas following persulfate treatment.



SITE 5. Ferrous Sulfate Activation

Site 5 is an industrial site located in La Mirada, CA (Los Angeles County). Ferrous iron was selected to activate sodium persulfate for treatment of a small but highly concentrated benzene plume. Three injection wells were utilized. Depth to groundwater was approximately 80 feet.

FIGURE 9. Mixing of ferrous sulfate into solution.



Results – Site 5.

Reduction of benzene levels from 2,900 µg/l to 160 µg/l was achieved after 253 days of the persulfate injection. A mild rebound effect occurred at this site after 30-60 days, due primarily to a rising water table and cross contamination from the deep vadose zone. Following removal of the deep vadose zone contamination using soil vapor extraction, the benzene levels did not rebound again and have remained below 160 µg/l. Closure of the benzene plume at this site is currently being pursued with the Los Angeles RWQCB.

FIGURE 10. Benzene reductions following persulfate treatment (iron activation)



Site 6. Chelated Iron Activation

Site 6 is an industrial site located in La Mirada, CA (same site as Case Study 5). Chelated iron (EDTA) was selected to activate sodium persulfate for treatment of a TCE and 1,4-Dioxane plume. A three well injection was recently performed using existing monitoring wells. Depth to groundwater is approximately 80 feet.

Figure 11. Well head injection apparatus.



Results – Site 6

Analytical results from this site are pending at the time this paper was written.

REFERENCES

FMC Corporation, 2008. “Activation Know How”, located on the FMC website.

FMC Corporation, 2008. Table of Klozur Activation Chemistries, located on the FMC Website.