TechData Sheet

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In-situ Chemical Oxidation of Organic Contaminants in Soil and Groundwater Using Fenton's Reagent

Introduction

Remediation of soil and groundwater contaminated with organic contaminants is accomplished by injecting a strong chemical oxidizer, like a mixture of hydrogen peroxide, together with a catalyst, ferrous sulfate and an optimum pH (3-5) adjuster, using sulfuric acid. This particular reagent mixture is called Fenton's Reagent (FR), which was discovered by H. J. H. Fenton in 1894; hereafter named as Fenton's Reagent Oxidation Process (FROP). The principal active component of the FROP is the hydroxyl free radical, which is produced by catalytical chemical reaction between hydrogen peroxide and ferrous iron. The free radical thus produced cleaves and oxidizes organic compounds non-selectively that successively form smaller chained hydrocarbon compounds. The intermediate compounds formed are generally mono- and di-carboxylic acids which are non-hazardous, naturally occurring substances that are easily oxidized to carbon dioxide and water (mineralized) during subsequent sequential reactions. The cleaving of the organic substrate does not and will not produce volatile organic compounds that can be released into the atmosphere.

The FROP is effective in treating contaminants such as VOCs, SVOCs, LNAPL, DNAPL, TPH, PCBs and/or total chlorinated hydrocarbons (TCHs) etc. in saturated soils, sediment, and groundwater. This FROP chemical reactions are simplified and expressed as:

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + OH^- + OH^\bullet \quad (1)$$

$$H_2O_2 + Fe^{3+} \longrightarrow Fe^{2+} + H^+ + HO_2^\bullet \quad (2)$$

$$RH\ X\ Fe^{2+} + H_2O_2 \longrightarrow H_2O + CO_2 + H^+ + X^- \quad (3)$$

Equation (3) represents a simplified overall reaction for oxidizing an halogenated (X) hydrocarbon molecule (RH) in the presence of ferrous catalyst into the final products consisting of water, carbon dioxide, and the halogen salt.

In an in-situ application, the FR is injected into the subsurface environment using a specially designed injector well assembly. The total quantity of hydrogen peroxide to be injected in the FROP treatment is calculated based on contaminant quantity existing in the in-situ environment. Pressure and temperature in the well during the FR injection are monitored in order to use the data for control of the FR injection rates.

Advantages and Limitations of FROP

The following are the benefits that are found in addition to using conventional remediation techniques:

- Fast, in-situ destruction of a wide range of volatile and semi-volatile organics to very low residual levels.
- Inexpensive application and short-term duration treatment method.

- Lower, long-term liability exposure by completely destroying contaminants on site.

- Contaminant concentration and the variety of organic contaminants are not limited.

The following are the limitations of the FROP:

- Groundwater must have moderate (< 400 ppm) calcium carbonate, hardness, and naturally occuring organic matter content.

- Saturated soils need adequate hydraulic conductivity, 10^{-5} cm/sec or greater.

- Soils require low clay content to allow FR penetration.

- Groundwater pH needs to be adjusted to the optimum range of 3-5.

NAS Pensacola Demonstration

Field demonstration of the FROP was conducted at a Wastewater Treatment Plant Sludge Drying Bed site at NAS Pensacola, Florida. As shown in Figure 1, the FROP system is simple in operation. The process control panel, which resides in the van, serves as pump-and-rate regulation center. Hydrogen peroxide solution is pumped through the milky-colored line, catalyst through the blue line, and compressed air through red line to the injection well via the injector head assembly.

The demonstration was conducted in two phases, each lasted for about a week. Phases 1 and 2 were carried out during 8-12 December 1998 and 11-17 May 1999, respectively.

The main remedial objective was to substantially reduce contaminant concentrations of chlorinated hydrocarbons at the source area, which would ensure on-going in-situ natural attenuation in the groundwater to continue to remediate the VOC contaminants in the downgradient groundwater. Initial concentration of TCE had historically exceeded 3,000 µg/L in the source area. Also an estimated 5,000 pounds of TCH existed in the source area, which covered a surface area of about 50 by 50 feet.

During the Phase 1 pilot test, 14 FR injection wells, ranging from 10 to 40 feet, were installed in the plume/source area as shown in Figure 2. A total of 8,000 gallons of FR solution, which consisted of about 4,000 gallons of hydrogen peroxide solution (a 50% solution) and about

Figure 1. FROP operation at NAS Pensacola.

equal amount, or 4,000 gallons of ferrous sulfate in 100 ppm concentration solution was injected into the 14 wells during the pilot test period. As stated previously, the FR was injected into the subsurface media (soil and groundwater) through the pre-installed injection wells and injector head assembly. FR injection rate was controlled at the control panel based on the measured pressure and temperature data. After the Phase 1 pilot test, it was determined that it was necessary to have an additional FR injection primarily due to results of subsequent samples taken and the chemical analysis. The Phase 2 injection tests began in early May 1999. An additional 6,000 gallons of hydrogen peroxide solution (that made a total of 10,000 gallons) was pumped into the injection wells, which were all 35 to 40 feet deep, since the highest concentrations of chlorinated hydrocarbons were detected after Phase I injection at those depths. Concentrated pumping of FR into this area was done in order to oxidize/destroy those contaminants to the maximum extent possible.

Test Results and Discussion

The performance of the FROP treatment test is depicted in the Figure 3. The test result as shown in this figure is very promising. During the Phase 1 test, the FROP application was able to reduce TCH, represented by TCE concentrations, from 3,000 and 1,700 ppb, respectively

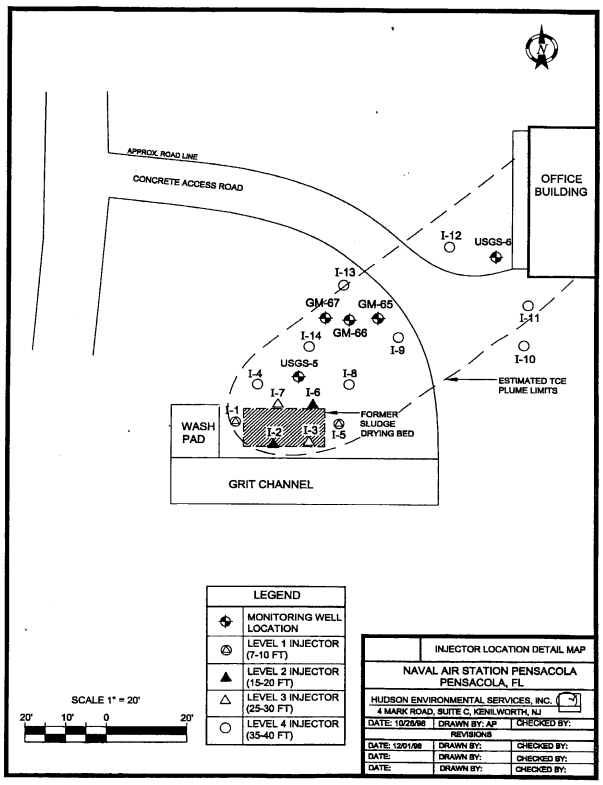

Figure 2. Injection and monitoring wells locations.

in IMW-66 and USGS-5 wells' water sample down to 130 ppb and below detection limit (of <1 ppb). USGS, as part of their natural attenuation investigation program for the Navy at the site, had also sampled groundwater from these wells a month after the Phase 1 FROP test (post-treatment sampling). Results of these samples showed a higher TCE values (see December 1998 and January 1999 data point in Figure 3), which are generally called "rebound" phenomena. The data review concluded that a second round of FR injection was necessary to eliminate/mitigate such an unwanted condition. A second FR injection was then planned and executed. The Phase 2 injection did bring down the TCE value to about 100 ppb and less which has ensured the natural attenuation can easily simulate the residual contaminant and guard safely for the environmental encroachment problem.

Cost Analysis

Model Site (the plume/source area)

- ❑ Soil and groundwater volume: 50'x50'x40' = 100,000 ft^3 or 3,700 yd^3
- ❑ TCE contamination: 250 ppm in soil = 2,800 lb
  10 ppm in GW = 40 lb
  2,160 lb free product
  Total: 5,000 lb
- ❑ Plume remediation cost:
  - H_2O_2: \$0.50 x 10 lb/gal x 5,000 gal x 2 = \$50,000
  - Injection wells installation: \$1,500 each x 20 = \$30,000
  - Injection equipment and transportation to site: \$20,000
  - Labor: \$1,000 x 3 people x 14 days (for two injections) = \$42,000
  - \$200 x 3 people x 14 days (per diem) = \$8,400
  - \$1,000 x 30 (others) = \$30,000
  - Misc. at 10% of all costs = \$18,040
    Subtotal \$198,440
    Sampling and Analysis: ..... \$ 21,560
    Total: \$220,000
- ❑ Unit Cost: \$220,000/3,700 yd^3 = \$60/yd^3 or \$45/ton (1 yd^3 soil weighs 1.33 tons)
- ❑ Cost savings realized: (\$2M* - \$220K)/\$2M = 89%

*Life cycle cost of pump-and-treat for an estimated 20 years of on-site treatment.

Lessons Learned

The in-situ chemical oxidation using Fenton's Reagent method was very successful at the NAS Pensacola site.

The technology was demonstrated to be a simple, safe, fast, and cost-effective in-situ treatment method for chlorinated hydrocarbons like TCE at the test site. The discrete, limited size of the source area and fairly homogeneous sandy soils were important charateristics contributing to the cost effectivenss of using this FROP technology at the site.

For the small, discrete source area at NAS Pensacola, the technology was cost-effective. For larger treatment applications (such as large source area and low concentrations of TCH), the cost-effectiveness may be diminished and should be compared with other technologies. The site at NAS Pensacola had nearly ideal conditions for the demonstration, which included sandy silt soils with relatively high hydraulic conductivity, low carbonate/bicarbonate content, and low pH.

Application of the technology at other sites should be examined on a site-specific basis. The general effectiveness and cost efficiency of the technology depends on the volume to treat and other site specific conditions, as do other technologies. For example, the buffering capacity of carbonate aquifers would prevent pH adjustment that is required to facilitate the FR reaction. Likewise, the cost-effectiveness of remediating low permeability zones (like clayey tight soils) will be lowered by the reduced ability to distribute/disperse the chemicals. Nevertheless, the in-situ FROP carries a short-term duration treatment cost advantage over any other alternative technologies.

Points of Contacts

For more information on FROP, contact:

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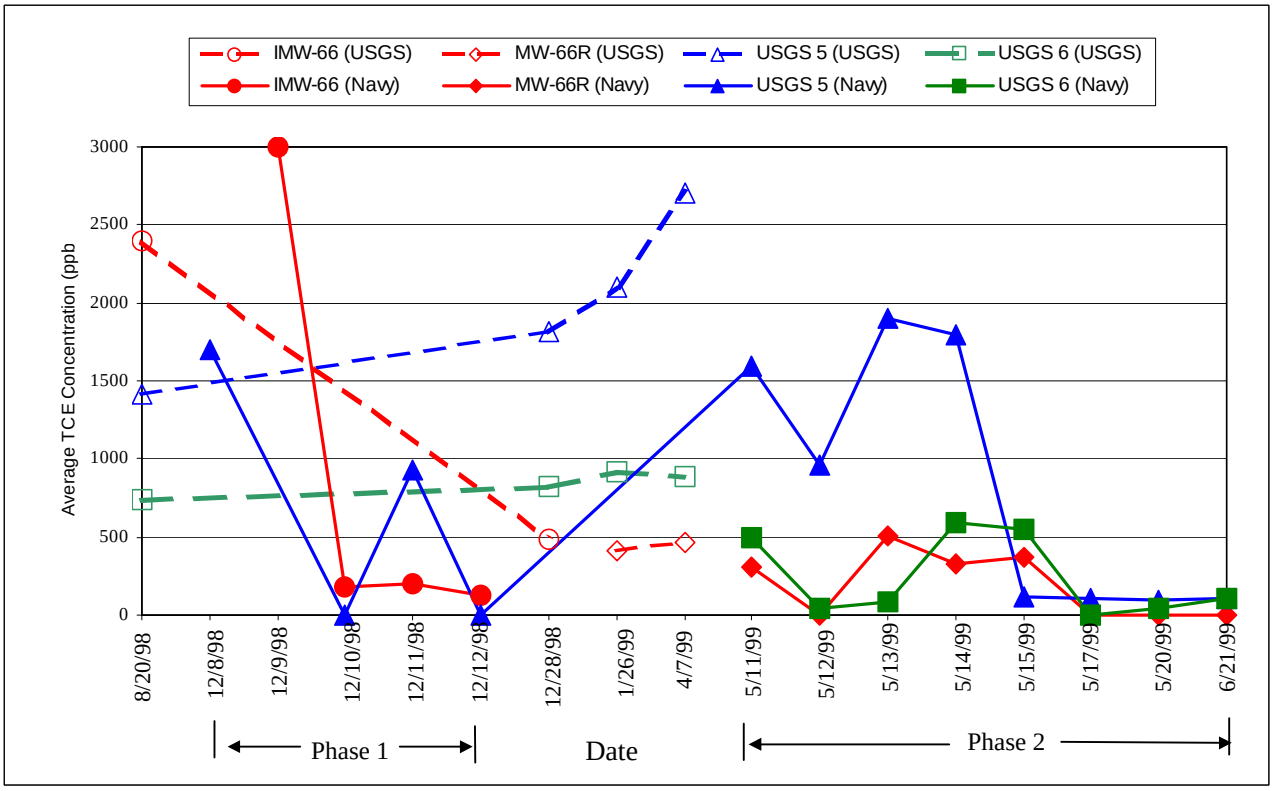

Figure 3. FROP performance.