EXPEDITING CLEANUP OF A PUMP AND TREAT SITE BY USE OF CHEMICAL OXIDATION TECHNOLOGY

Gary Cronk, P.E. (JAG Consulting Group)
Lanita Stevens (U.S. Gypsum Company)

ABSTRACT: Pump and treat systems have been commonly implemented for the past 20 years to cleanup groundwater contaminant plumes. While pump and treat systems are often effective in controlling the migration and reducing the size of the plume, they have one common drawback in that contaminant levels usually reach a low asymptotic level after several years of pumping. This situation is magnified in large groundwater plumes (over 100 feet in length).

At the U.S. Gypsum Company site in La Mirada, CA, a pump and treat system has operated for over ten years (1996 to 2006). The pump and treat system was successful in reducing the size of two co-mingled contaminant plumes; one with benzene and one with TCE. During this time period, groundwater was pumped from nine recovery wells, resulting in the treatment of over 45 million gallons of groundwater and the removal of over 408 pounds of VOCs. After 10 years of operation, asymptotic levels of benzene (3,000 µg/l range) and TCE (500 µg/l range) were still present at two locations at the site.

As a means of expediting groundwater cleanup, two in-situ chemical oxidation (ISCO) technologies were implemented. For the TCE plume, a pilot test using potassium permanganate was performed to demonstrate its effectiveness on TCE, its persistence in the environment, and its large radius of treatment. Reductions of TCE from 100% to 85% were achieved in 120 days. Based on this successful pilot test, a full scale permanganate treatment consisting of nine injection wells is planned in March 2008 to treat the remaining TCE plume.

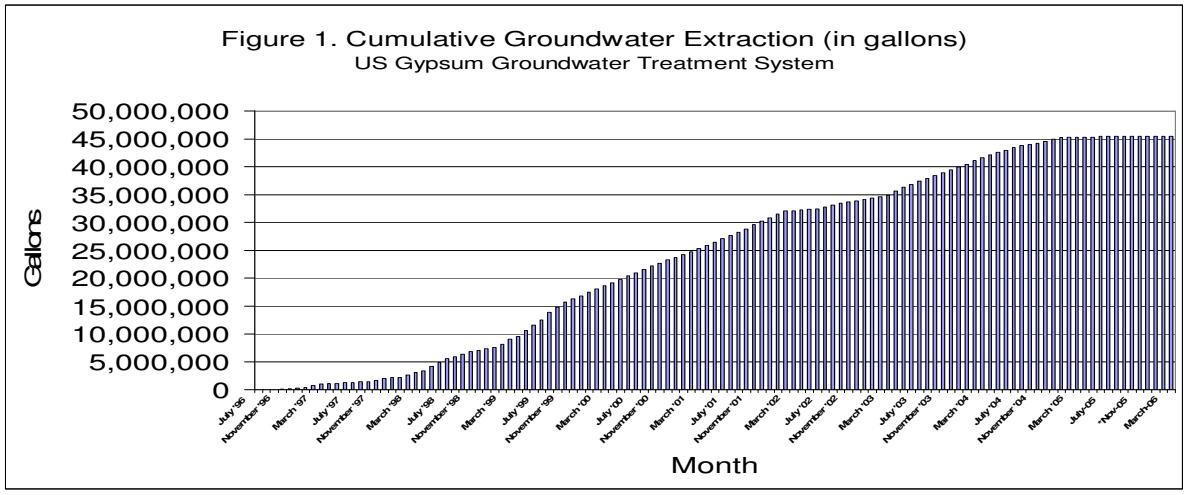
For treatment of the benzene plume, catalyzed hydrogen peroxide and activated sodium persulfate were injected. These oxidants were selected because they are highly effective on benzene. Benzene concentrations have been reduced from a pre-ISCO maximum of 5,500 µg/l to 98 µg/l (98% reduction). Other wells have shown benzene reductions from 99.9% to 96%. Based on these highly successful ISCO results, closure of both groundwater plumes is expected from the Los Angeles RWQCB by the end of 2008.

BACKGROUND

A pump and treat system has operated for over ten years (1996 to 2006) at the U.S. Gypsum Company site in La Mirada, CA. The pump and treat system consists of nine groundwater recovery wells (RW-1 through RW-7, BH-21, and MW-3) as well as seven air sparging wells (EW-25 through EW-31). The primary groundwater zone beneath the site is referred to as the "upper aquifer" and extends from approximately 77 to 120 feet below ground surface (bgs).

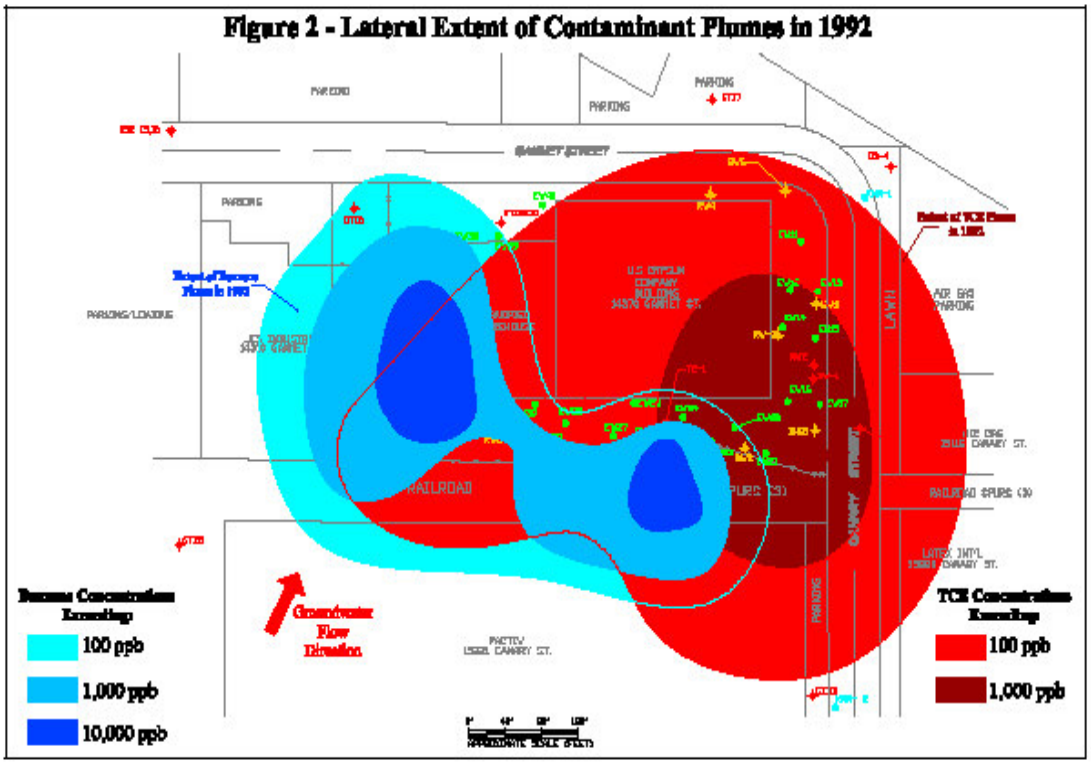
The pump and treat system began operation in July 1996 and operated on a nearly continuous basis until March 2006 (10 years). As of March 30, 2006, when the system was turned off, the system had pumped and treated a cumulative total of 45.4 million gallons of groundwater. Over the 10 years of operation, the pump and treat system

maintained an average flow rate of approximately 9 gallons per minute (gpm) and a daily flow rate of 13,000 gallons per day (gpd). Figure 1 summarizes the monthly and cumulative volume of groundwater treated over the period of 1996 to 2006.



The pump and treat system has been used for treatment of two co-mingled contaminant plumes at the U.S. Gypsum site. A highly concentrated benzene plume exists along the southern boundary of the site. The original benzene plume in 1992 measured over 600 feet in length and 240 feet wide and had benzene concentrations over 90,000 micrograms per liter (µg/l). The original benzene plume extended off-site to the south and west of the U.S. Gypsum site.

A trichloroethylene (TCE) plume exists along the eastern boundary of the U.S. Gypsum site. The original TCE plume (1992) extended off-site to the east and north across Canary Street and Gannet Street. The TCE plume originally measured over 680 feet long and 560 feet wide with maximum TCE levels over 2,600 µg/l. The lateral extent of the co-mingled benzene and TCE plumes are shown in Figure 2.



Over the 10 years of operation, a total estimated dissolved mass of 408 pounds of VOCs has been removed by the pump and treat system. While the pump and treat system was successful in controlling the off-site migration of the groundwater plume and reducing the elevated levels of VOCs, after approximately eight years of operation the system

reached low asymptotic levels of VOCs. Little or no substantial reduction in VOC levels was attained in the last two years of operation. Figure 3 and 4 illustrates the low asymptotic levels of TCE and benzene (respectively) that have been attained over ten years of operation. After ten years of operation, the levels of TCE (500 µg/l range) and benzene (3,000 µg/l range) remaining in the groundwater still require further remedial action to meet cleanup requirements of the Los Angeles Regional water Quality Control Board (RWQCB).

Figure 3. Reductions in TCE Levels Using Pump and Treat, 1995-2006

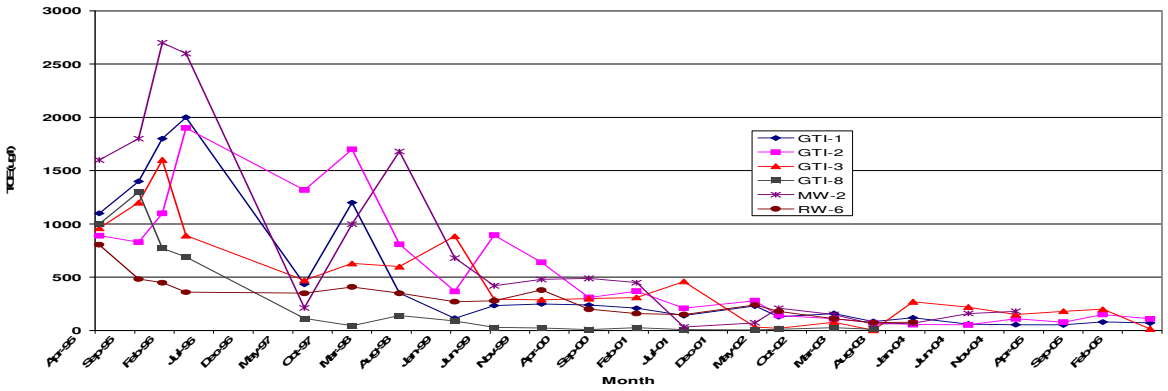
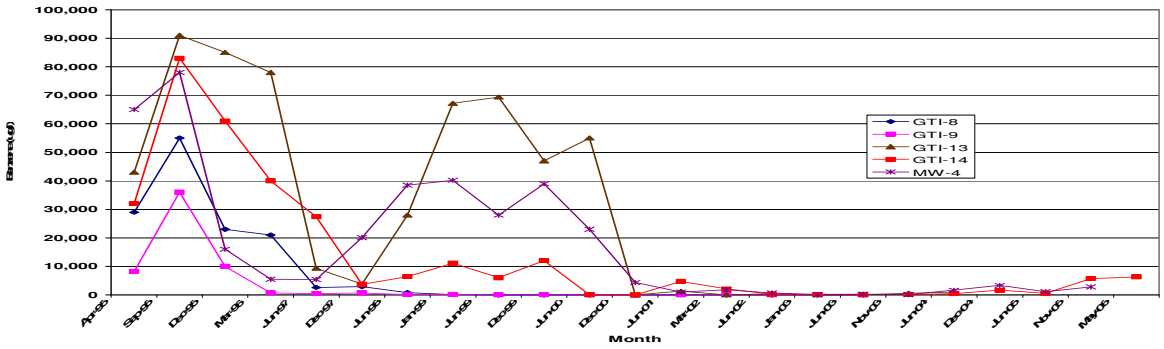


Figure 4. Reductions in Benzene Levels Using Pump and Treat, 1995-2006



A more rapid and economical method of treating the remaining groundwater contamination was sought. Based on recent advances using in-situ chemical oxidation treatment, this technology was proposed for use at U.S. Gypsum because it could achieve the rapid reduction in contaminant levels and be cost-effective as well.

ISCO TREATMENT OF TCE USING POTASSIUM PERMANGANATE

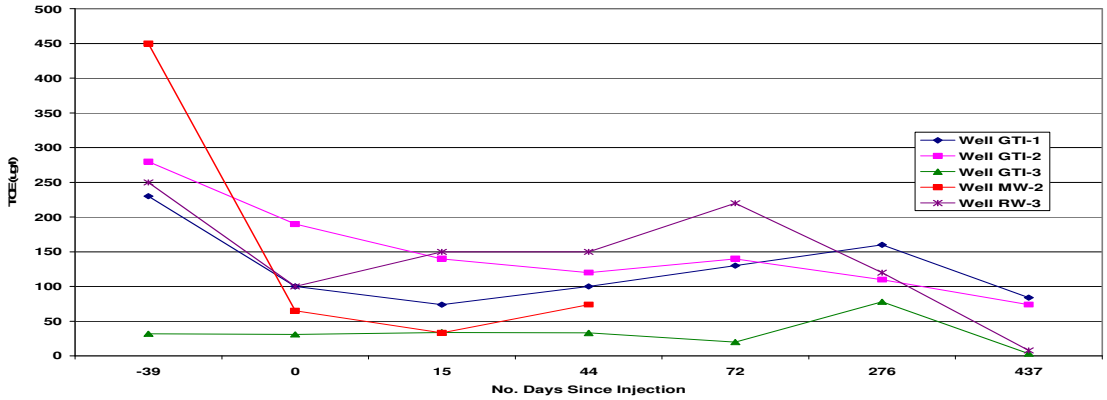
A pilot test was initially performed in April 2002 to demonstrate that the TCE and 1,1-DCE levels in the groundwater along the east side of the US Gypsum property could be effectively treated using potassium permanganate. The following major activities were completed during the pilot test:

- A new injection well (RW-7) was installed for the permanganate injection
- A bench scale treatability test was completed to assist in the design of the field pilot test,

- Six injections of 1,500 gallons each of permanganate solution (up to 4% by weight) was performed into injection well RW-7 over a 46 day period (starting on March 29, 2002)
- Pumping from downgradient well RW-2 (located 60 feet from the injection well) was performed to extend the radius of treatment of the permanganate,
- Groundwater field measurements and laboratory samples were collected and analyzed per the requirements of the Los Angeles RWQCB Waste Discharge Requirements permit.

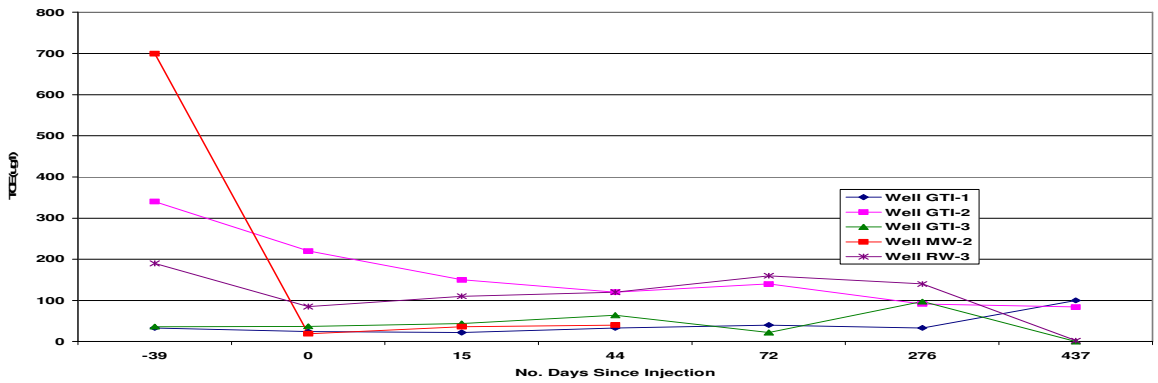
Substantial reductions in TCE and 1,1-DCE concentrations were detected immediately following the permanganate injections. Within 30 to 60 days of the injections, the TCE concentrations in the closest wells to the injection well (within 50 feet) all showed significant reductions, including RW-3 (250 µg/l to 100 µg/l), well MW-2 (450 µg/l to 65 µg/l), EW-12 (220 µg/l to 30 µg/l), and EW-15 (280 µg/l to ND). Three additional wells located 90 feet or more away from the injection well also influenced by the pilot test, with significant TCE reductions in GTI-1 (230 µg/l to 74 µg/l), GTI-2 (280 µg/l to 140 µg/L), and GTI-3 (32 µg/l to 20 µg/l). A graph illustrating the TCE reductions achieved by the potassium permanganate pilot test (over 15 months) is provided in Figure 5.

Figure 5. Reductions in TCE Levels During and Following Permanganate Pilot Test



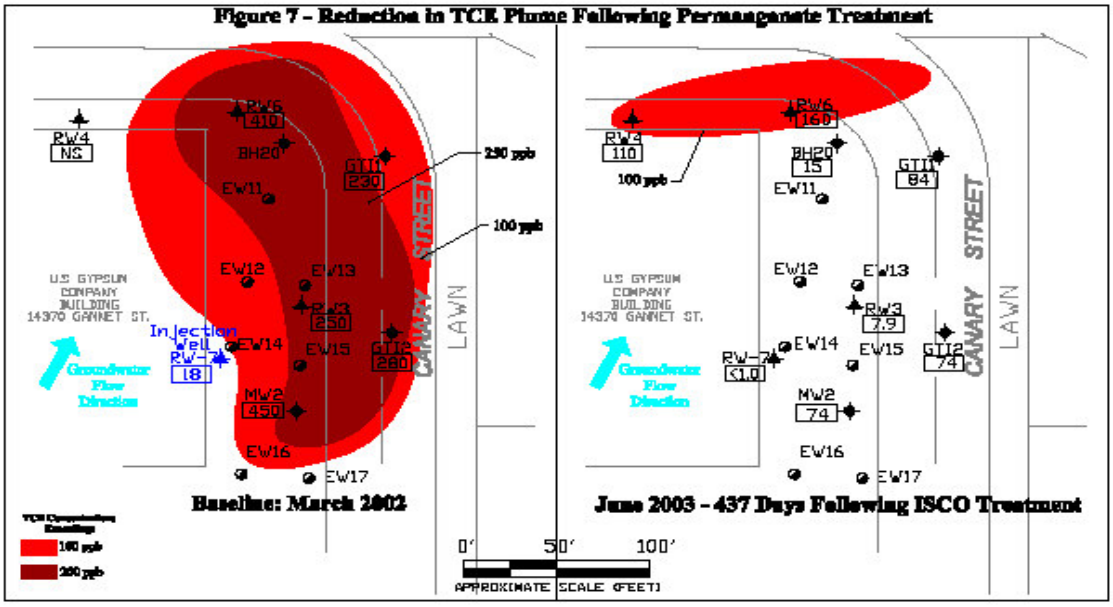
Significant reductions in 1,1-DCE concentrations were observed in wells RW-3 (190 µg/L to 110 µg/l), EW-12 (180 µg/l to 6.2 µg/L), EW-15 (270 µg/L to ND), MW-2 (700 µg/l to 19 µg/L), and GTI-2 (340 µg/l to 130 µg/L). A graph illustrating the 1,1-DCE reductions achieved by the potassium permanganate pilot test (over 15 months) is provided in Figure 6.

Figure 6. Reductions in 1,1-DCE Levels During and Following Permanganate Pilot Test



Nearby monitoring wells all showed significant changes in field water quality parameters within days of the injections, notably in permanganate ion, oxidation-reduction potential, turbidity, and conductivity. These field measurements were very useful for tracking the movement and dispersion of permanganate in groundwater. Based on field water quality measurements, the observed radius of treatment was between 35 and 45 feet.

The overall size of the TCE plume was reduced substantially following the permanganate treatment. The 250 ppb (µg/l) contour line present during the baseline sampling event was eliminated entirely following ISCO treatment and the 100 ppb contour line was significantly reduced in size. Figure 7 shows the reduction in TCE plume size from March 2002 to June 2003.



Overall, the permanganate pilot test was deemed highly successful. TCE and 1,1-DCE concentrations were reduced significantly within a radius of 40 feet following the injections. By use of groundwater pumping, the radius of influence was extended to up to 90 feet.

ISCO TREATMENT OF BENZENE USING SODIUM PERSULFATE

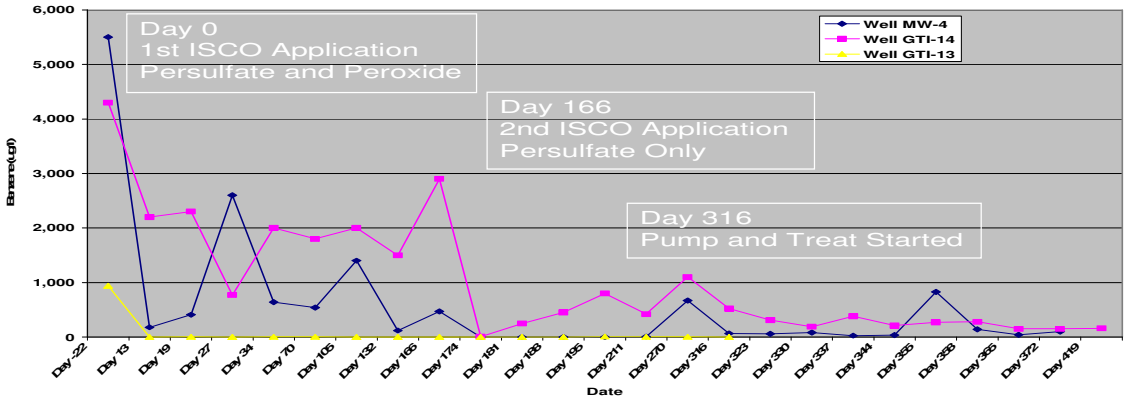
Two sodium persulfate injection events were performed at the US Gypsum site. The first ISCO injection occurred in October 2006 and consisted of the application of 14,190 pounds of sodium persulfate that was activated by injection of 7,218 gallons of 17.5% hydrogen peroxide and 600 pounds of ferrous sulfate. The second injection occurred in March 2007 and consisted of application of 7,000 pounds of sodium persulfate and

activation by injection of 600 pounds of ferrous sulfate. The oxidants were injected using six dedicated injections wells that were installed to cover the approximate 3,500 square foot plume area.

The two sodium persulfate applications at the US Gypsum site have proved to be highly successful during the 419 monitoring days following the initial injection. The overall benzene concentrations have been reduced significantly in well MW-4 from a pre-ISCO level of 5,500 µg/l to 98 µg/l after the injection (98% reduction), in well GTI-13 from 940 µg/l to 1.3 µg/l (99.9% reduction), and in well GTI-14 from 4,300 µg/l to 160 µg/l (96% reduction).

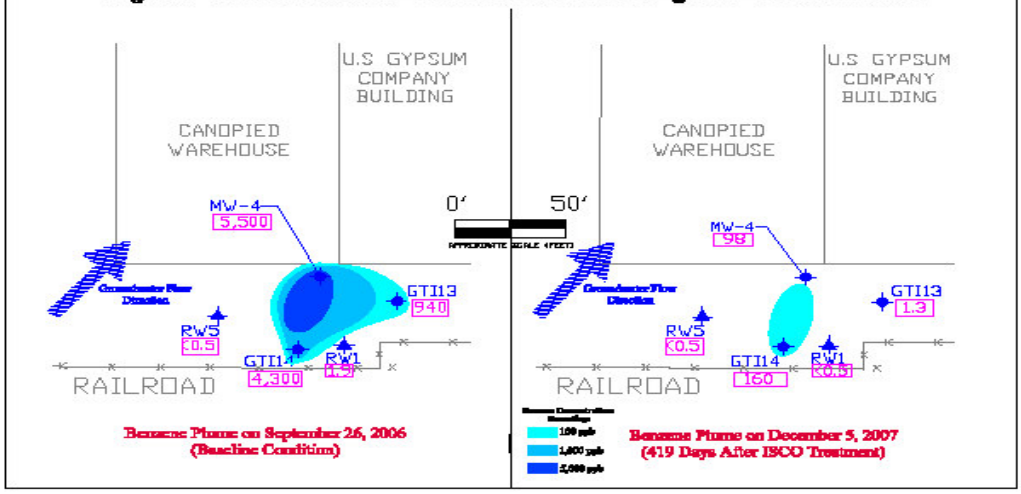
Due to a benzene rebound after about 8 months, the groundwater pump and treat system was re-started for a short period on August 24, 2007, with submersible pumps being placed directly into the two monitoring wells, GTI-14 and MW-4. In the 70 days of operation (through November 2, 2007), the groundwater treatment system has helped to reduce the benzene level in GTI-14 from 1,100 µg/l (before start-up) to 160 µg/l. In well MW-4, the benzene level was reduced from 670 µg/l before start-up to 98 µg/l. The cause of this rebound is believed to be due to a rising water table and continued leaching from the deep vadose zone (60 to 80 feet bgs). The soil vapor extraction system was also re-started in August 2007 to remove benzene contamination from the deep vadose zone in the vicinity of the groundwater problem. In five months of operation (through February 15, 2008), the SVE system has removed an additional 700 pounds of VOCs from the vadose zone. No rebound of dissolved benzene levels has occurred since the SVE system has been re-started.

Figure 8. Dissolved Benzene Reductions Following ISCO Treatment



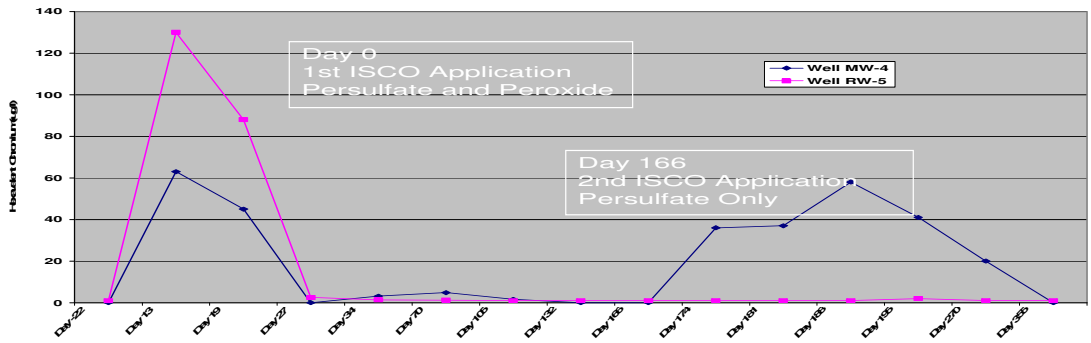
The size and shape of the benzene plume has been reduced substantially in the 419 days following ISCO treatment. During the baseline event (September 2006), a large 5,000 ppb contour line was present, encompassing MW-4 and stretching south towards GTI-14. By December 5, 2007, 419 days after the initial ISCO treatment, the 5,000 ppb and the 1,000 ppb contour lines are completely eliminated and the 100 ppb contour line is much reduced in size. A side by side comparison of the lateral extent of the benzene plume before and after persulfate ISCO treatment is shown in Figure 9.

Figure 9 - Reduction in Benzene Plume Size Following Persulfate Treatment



Hexavalent chromium levels increased immediately following each of the ISCO injections. The hexavalent chromium levels stayed elevated for several weeks in two monitoring wells (over 30 µg/l) but quickly returned to non-detectable levels within several months following ISCO. A temporary conversion of total chromium to hexavalent chromium occurs during oxidizing conditions (ORP levels above 300 mV). Within 60 days following the first ISCO application, the hexavalent chromium levels returned to non-detectable levels as the hexavalent chrome is converted back to trivalent chromium under normal reducing conditions. Figure 10 illustrates the temporary conversion of total chromium to hexavalent chromium during ISCO treatment.

Figure 10. Variation in Hexavalent Chromium Levels Following ISCO Treatments



Field water quality measurements were very useful for tracking the movement and consumption of oxidants in groundwater. The oxidation reduction potential (ORP) levels increased immediately to over 600 mV in wells MW-4 and GTI-14 one week following the second ISCO injection. Sharp increases were also observed in dissolved oxygen and conductivity in these wells immediately following the injection. The field water quality measurements returned to baseline levels within 30 to 75 days following ISCO treatment.

CONCLUSIONS

Based on the success of the ISCO treatment, a full scale treatment using permanganate is currently being planned for the entire TCE plume. Nine injection wells along the east side of the property (including two on Canary Street) are planned where TCE levels are still above groundwater cleanup goals (50 ppb). The injection wells are located so that the expected radius of influence (40 feet each) will cover the entire area to be treated. Seven existing monitoring wells will be used as injection wells in the full scale treatment program to minimize well construction costs.

Quarterly monitoring of the benzene levels in wells GTI-14 and MW-4 will continue to track the progress in cleanup of the benzene plume. We expect that the current benzene levels will continue to decrease by natural attenuation and that cleanup levels can be attained and stabilized by mid 2008. The pump and treat and SVE systems will be operated on an as needed basis until stabilized benzene levels are maintained in these wells.

Approximately 6-12 months following the full scale permanganate treatment (which is scheduled for March 2008), a request for closure of the two groundwater contaminant plumes from the Los Angeles RWQCB will be sought. The efficiency of using chemical oxidation treatment versus continued pump and treat for this site is estimated to save five years of pump and treat operation and over $500,000 in cost savings.

REFERENCES

Groundwater Technology, Inc, 1993. *On-Site Investigation/Feasibility Study and Remedial Selection*, US Gypsum Company, La Mirada, CA, prepared January 15, 1993.

JAG Consulting Group, Inc. 2007a. 4th *Quarterly Progress Report: In- Situ Chemical Oxidation Using Catalyzed Hydrogen Peroxide and Activated Sodium Persulfate*, US Gypsum Company, La Mirada, CA, prepared October 15, 2007.

JAG Consulting Group, Inc. 2007b. *Semi-Annual Groundwater Monitoring and Sampling Report, December 2007.* US Gypsum Company, prepared December 29, 2007**.**

Los Angeles Regional Water Quality Control Board, 2006. *General Waste Discharge Requirements for Interim Treatment Injection, US Gypsum Facility, 14370 Gannet Street, La Mirada, CA,* WDR Order No. R4-2005-0030*,* File No. 2041700, Monitoring and Reporting Program No. CI-9176. Dated September 18, 2006.

Shaw Environmental & Infrastructure, Inc., 2002. *Progress Report: Potassium Permanganate Injection Pilot Test*, US Gypsum Company, prepared September 2002**.**