

Pilot-Scale Remediation of Dissolved TCE and Vinyl Chloride Plumes Using Different Approaches to *In Situ* Chemical Oxidation

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Abstract: Pilot-scale remediation of volatile organic compounds (VOCs) using Fenton-based *in situ* chemical oxidation processes has been conducted at two sites at Naval Air Station North Island. A traditional process requiring acidification of the aquifer to generate hydroxyl radicals successfully reduced contaminant mass in groundwater and in water-saturated soil at a former liquid waste disposal site, Installation Restoration (IR) Site 5. A modified approach, using an iron-chelate catalyst under neutral pH conditions exhibited similar success at reducing dissolved-phase VOC concentrations at Operable Unit (OU) 20. Unique conditions at each site facilitated use of the different processes. Given the exothermic nature of the Fenton reaction, process selection for each site was made within the context of site-specific criteria including site location and development, as well as hydrogeologic condition, geochemistry, and nature of aquifer contamination. The traditional process requiring an acidified environment has the potential to be highly exothermic, capable of producing mud boils and even explosions given ignition sources within the reaction area. Aquifer buffering capacity is also an important consideration in determining feasibility of aquifer acidification, and acidification has the potential to mobilize metals. The modified process applied under neutral conditions reduces concerns about potential highly exothermic reactions and mobilization of metals.

IR Site 5

Installation Restoration (IR) Site 5, Unit 2, located in the southern portion of the Naval Air Station North Island, lies within the final approach to an airfield runway in an otherwise undeveloped area. Contamination at the site results from operation of two former waste disposal pits and affects a shallow, unconfined aquifer composed of dredged fill materials from the San Diego Bay. Groundwater occurs at approximately 5 feet below grade in loose and permeable sand and silty sand. Bay floor muds occur at 10 feet below grade and provide a vertical barrier to contaminant migration. Primary contaminants (i.e., concentrations greater than 100 parts per million) include *cis*-1,2 dichloroethene (DCE), vinyl chloride, and aromatic hydrocarbons in site soil and groundwater, as well as naphthalene and trichloropropane in site soil. The majority of the contaminant mass resides in soil at and below the groundwater table. Geochemical site conditions include high alkalinity, neutral pH, and redox potential indicative of reducing environments.

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Naval Facilities Southwest Division (SWDIV) and IT Corp. selected the traditional Fenton chemistry for pilot testing at the site. Given the site location in an unindustrialized area, potential surface expressions of exothermic reaction associated with this process were considered manageable from a health and safety standpoint. Site conditions allowed evaluation of aquifer acidification feasibility, given the high site alkalinity, for full-scale application. Also, the effect of *in situ* oxidation on the strongly reducing environment would be evaluated for full-scale remediation.

Observations during the 4-month pilot test indicated no surface expression of the exothermic reaction in the subsurface. Background groundwater temperature measured during baseline sampling ranged between approximately 21°C and 22°C. Peak temperature measured during the pilot study was 70°C in the injection well. Aquifer buffering capacity was temporarily overcome through acidification sufficiently to obtain pH levels conducive to Fenton's reaction. The distribution of conditioning fluids evaluated during the test also suggests economic feasibility of acidification. Test results indicated that the effects of the injected fluids on the geochemistry of the aquifer are temporary. Rebound of pH and alkalinity to near baseline condition was observed during the test, as was the return to anaerobic redox conditions in the vicinity of the injection well where high redox conditions had been obtained. VOC mass reduction within the study area attests to the effectiveness of the technology for the site conditions. Contaminant mass calculations for combined soil, groundwater and soil vapor indicate that vinyl chloride and *cis*-1,2-DCE were reduced by 62% and 46%, respectively, within a 15-ft radius of the injection well. Aromatic hydrocarbons were reduced by 76% within this radius. Full-scale application of the technology is scheduled to begin in Summer 2001.

OU 20

Operable Unit (OU) 20 at Naval Air Station (NAS) North Island is a dissolved-phase trichloroethene (TCE) groundwater plume associated with past aircraft maintenance and repair activities conducted at the site since 1945. The groundwater plume occurs at approximately 20 feet below grade and extends to about 80 feet below grade in a sandy aquifer.

In December 2000, SWDIV and IT Corp. successfully completed a pilot-scale remediation at the OU20 site using a modified *in situ* Fenton's chemistry, which creates the hydroxyl radical under neutral conditions. SWDIV and IT Corp. selected the modified process because the site is located in a highly industrialized area of the base, with nearby potential ignition sources. This modified process is less exothermic than traditional Fenton chemistry, and thus reduces safety concerns regarding explosions or other surface manifestations of the oxidation reaction. The process also eliminates concerns regarding the mobilization of metals or other inorganics, which could result from acidifying the aquifer.

Nested injection wells were used to address three adjacent zones within the vertical extent of the TCE plume. Results of the pilot test indicate mass reductions of up to 98% at 6 feet distant from injection wells, and up to 31% at 28 feet distant from injection wells. These results indicate that *in situ* chemical oxidation using a modified (non-acidified) Fenton reaction may be a fast, cost-effective, and safe *in situ* cleanup method for the OU 20 dissolved plume. Full-scale application of the technology is being evaluated for potential implementation in 2001.

Conclusions

At IR Site 5, the Fenton's reaction was achieved using traditional Fenton's chemistry despite the buffering capacity of the contaminated aquifer. A destruction ratio of approximately 70 to

100 grams hydrogen peroxide to 1 gram of VOC was determined during the pilot test. Through careful application of the conditioning agents and the oxidants, manifestations of the exothermic reaction (e.g., mud boils, explosions, etc.) were not observed. The mass of VOC within the treatment zone was reduced by approximately 50% to 90%. Much of this reduction was observed in saturated soil where the bulk of the contamination at the site resides. Since the total mass of the VOCs throughout the site is unknown, full-scale source treatment will be planned in phases with several interim sampling events to monitor the progress of the remediation.

At OU 20, *in situ* chemical oxidation of VOCs was accomplished at neutral pH and at ambient temperature conditions. This is important when considering the use of this technology in areas where possible detonation sources (e.g., underground storage tanks) may exist and occupant safety is a concern. Since the majority of the VOC mass exists as dissolved phase contamination, the variation of *in situ* chemical oxidation used at OU 20 was slightly more efficient than the technique used at IR Site 5 in that approximately 50 to 70 grams hydrogen peroxide were required to destroy each gram of VOC. The mass of VOCs within the treatment zone was reduced by approximately 50% to 90%. The IT Corp. is currently evaluating the effects of the treatment on the geochemistry and microbiology.

The results of the pilot studies conducted at NAS North Island indicate that the two variations of the *in situ* chemical oxidation processes tested are capable of destroying source VOC groundwater contamination. This technology warrants further consideration for full-scale source treatment for the following reasons:

Complete oxidation of VOCs is achieved and the innocuous end products produced by this technology are water, carbon dioxide, and chloride ions

In contrast to mass transfer technologies (e.g., pump and treat, air sparging and soil vapor extraction, etc.) which are time consuming, costly, and generate waste, *in situ* chemical oxidation is cost-effective, requires relatively short treatment duration (a few weeks) and minimal site disruption, and does not generate significant waste.