

## Permanganate In-Situ Chemical Oxidation of TCE in a Fractured Bedrock Aquifer

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**ABSTRACT:** A treatability study of in-situ chemical oxidation (ISCO) using permanganate was conducted in a bedrock aquifer at Site N7, NASA Dryden Flight Research Center, Edwards Air Force Base. The objectives were to achieve contaminant destruction, determine the injection radius of influence, optimize injection methods for bedrock, monitor persistence of permanganate, and evaluate groundwater quality effects. The study area was approximately 100 ft by 50 ft and 100 ft deep. 7,450 gallons of 1.8% potassium permanganate solution were serially injected into 8 screened wells and 2 boreholes over 5 days. Groundwater samples collected periodically for 60 days following treatment were analyzed for permanganate, metals, and volatile organic compound concentrations. Trichloroethylene and cis-1,2-dichloroethylene remained below detection (from a pre-injection cumulative concentration of 7,210 ug/L). Acetone (presumably an oxidation product) was detected at up to 3,000 ug/L following injection and has attenuated to  $\leq 460$  ug/L. Elevated metal concentrations following treatment have decreased to  $\leq 80\%$  of their post-injection maxima, with the exception of chromium and nickel. Permanganate degradation rates yield an average half-life of 19 days, and permanganate should degrade below visible concentrations ( $< 0.5$  mg/L) in approximately 283 days. Permanganate ISCO appears effective and viable for treatment of chlorinated hydrocarbons at Edwards Air Force Base.

### Introduction

NASA Dryden Flight Research Center (Dryden) is located at Edwards Air Force Base, approximately 60 miles north-northeast of Los Angeles, California. Dryden occupies approximately 800 acres on the northwestern edge of Rogers Dry Lake, and consists of administrative, research, laboratory, service, hangar, and storage buildings for support of aeronautical research operations. Site N7 formerly contained two former drum storage areas used by various facility management contractors and a paint shop.

Site N7 has approximately 5 feet of silty sand overlying granitic bedrock. Approximately the first 10 feet of bedrock is moderately weathered with progressively greater competence with increasing depth. Primary fractures strike northwesterly/southeasterly with a southwesterly dip, and secondary fractures strike north-northeasterly/south-southeasterly with a northwesterly dip. The dip magnitudes are typically 60 to 90 degrees. Apertures generally range from 0.08 to 0.77 inches. Depth to groundwater is approximately 10 feet. Groundwater flow is easterly.

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Geophysical and hydraulic tests conducted at Site N7 yielded hydraulic conductivity estimates ranging from  $8.7 \times 10^{-8}$  to  $1.3 \times 10^{-4}$  cm/sec, with no consistent depth trends. Pump tests yielded average transmissivity of 0.004 to 0.035 ft<sup>2</sup>/min. Groundwater quality at Site N7 is alkaline and slightly saline, with groundwater pH ranging from 7.6 to 8.5, total alkalinity ranging from 383 to 552 mg/L, and chloride concentration ranging from 465 to 1,610 mg/L.

Trichloroethylene (TCE) and its natural degradation product cis-1,2-dichloroethylene (CIS) were detected at Site N7 with maximum baseline concentrations of 6,500 ug/L and 710 ug/L, respectively. Packer tests indicated that TCE and CIS concentrations decreased with depth, with maxima of 45 ug/L TCE and 120 ug/L CIS at depths deeper than 100 ft below grade.

### **Treatability Study Approach, Implementation and Monitoring**

Six existing screened wells and 2 new wells were used for injection. The new wells were left as open boreholes (except for shallow overburden casing) to provide maximum injection flexibility. Packer testing and geophysical logging were conducted on each new borehole to evaluate the vertical distribution of contaminants and potential transmissive zones within the bedrock aquifer.

Project design included an injection volume of approximately 1,000 gallons of 2% KMnO<sub>4</sub> solution to each of the 8 locations. This volume was based upon dissolved VOC concentrations and corresponding estimate of VOC mass within the treatment area, plus a conservative excess for inefficiencies. Based upon oxidation stoichiometry and a weighted average ratio of KMnO<sub>4</sub> mass to VOC mass of 2.6:1 (based upon observed TCE and CIS concentrations), the minimum mass of solid KMnO<sub>4</sub> required was estimated at approximately 31.4 lbs. This estimate assumed perfect reaction efficiency and did not allow for natural inefficiencies due to competing reactions and delivery. A ratio of 40:1 was considered a conservative estimate to ensure complete delivery and oxidation, thus a KMnO<sub>4</sub> mass of 1,256 lbs was estimated.

A mobile treatment unit was staged at the site, with tanks, pumps, gauges and flow control valves to prepare and deliver reagents safely and effectively. Specially designed mixing heads were attached to the riser pipe of packers installed in injection wells and open boreholes. The injection process was dynamic and variables including injection rate, pressure, and use of air to enhance reagent dispersion were modified to evaluate optimal injection conditions. Injection rate ranged from <0.25 to > 2 gpm, injection pressure (at which liquid reagents are delivered) ranged from 5 to 70 psi, and air was also introduced at pressures up to 70 psi and flow rates up to 4 cfm.

### **Treatment Operations and Results**

Field injection operations were conducted from August 21-25, 2000. A total of 7,450 gallons of 1.8% potassium permanganate solution (equivalent to 1,102 lbs of solid KMnO<sub>4</sub>) were injected. Field monitoring during injection indicated offgases were not produced in measurable quantities, and thus offgas monitoring for CO<sub>2</sub>, O<sub>2</sub>, volatile organics, and LEL was discontinued. Groundwater samples collected each morning were analyzed for manganese, chloride, pH, and permanganate, of which only permanganate concentrations were found to be useful field indicators of reaction or reagent distribution. Groundwater samples for VOC and metals analyses were collected at 3 stages during the treatability study: during packer testing to evaluate the vertical distribution of VOCs, prior to injection to establish baseline conditions, and 3 post-injection rounds (at 5 days, 30 days, and 60 days) to evaluate performance.

Destruction of the TCE and CIS in the treatment zone was complete, and TCE and CIS have remained below detection for at least 60 days. Acetone, however, appeared at up to 3,000 ug/L following injection, suggesting formation as an oxidation product. Acetone has not been reported as a permanganate oxidation product of chlorinated ethenes and was not detected in pre-injection bench scale studies of TCE oxidation in groundwater from other sites at Edwards AFB.

Determination of the radius of influence (ROI) was a primary objective. The best ROI indicator was presence or absence of permanganate, which is readily detected in nearby wells. The second indicator is groundwater mounding, indicating connectivity between an injection well and nearby monitoring wells. During the treatability study, the first evidence of groundwater mounding was followed within a few hours by the appearance of permanganate in the well. Monitoring results indicated a horizontal ROI between 30 and 55 feet and a vertical ROI of at least 28 feet.

The permanganate concentration data were utilized to determine the rate of permanganate degradation at the site. An initial rates method was utilized to calculate an average rate constant ( $k$ ) of  $0.036 \text{ day}^{-1}$  (assuming a pseudo-first-order reaction), with a corresponding average half-life of approximately 19 days. The long-term persistence of permanganate was estimated from the rate constant using a first-order decay law. The point at which permanganate is no longer visible (approximately 0.5 mg/L) was taken as the final concentration, and the average maximum permanganate concentration (13,509 mg/L) was taken as the initial concentration, yielding an estimate of 283 days until permanganate is no longer visible.

Concentrations of most metals were elevated following treatment, but all except chromium and nickel have decreased significantly (>80%) over the 60-day sampling interval relative to the post-injection maximum concentrations. Chromium concentrations in the injection wells doubled from averages of 14,300 to 29,320 ug/L between the 5-day and 30-day post-injection sampling rounds, but then subsequently decreased by 29% to 20,804 ug/L in the 60-day round. Nickel, in contrast, has been variable but has remained elevated. Regardless of the mechanism that resulted in the elevated metals (colloidal materials associated with the permanganate or liberated from the formation), the heavy metal concentrations within the treatment area are only anticipated to remain elevated above background concentrations as long as the permanganate persists. Chromium in particular, which may exist in the most soluble hexavalent state, will reduce and precipitate when the treatment zone returns to the ambient alkaline groundwater conditions.

### **Overall Conclusions**

After a 5-day injection period, TCE and CIS have remained non-detectable (reduced from 7,210 ug/L) for 60 days after injection in the treatment zone. Temporary acetone and metals increases observed in groundwater following treatment attenuated rapidly. Only chromium and nickel have remained elevated 60 days after treatment, however neither are stable in alkaline aquifers and are anticipated to attenuate as the permanganate degrades. The purple color imparted to groundwater by permanganate will persist as long as permanganate concentrations remain >0.5 mg/L, which is anticipated to be approximately 283 days based upon permanganate degradation measurements. Overall, permanganate treatment appears to offer an effective and viable remedial alternative for chlorinated solvents dissolved in the fractured bedrock aquifer at Edwards AFB.