Treatability Testing of an In Situ Biostimulation Barrier for Nitrate and Chromium Treatment - 9126

M. Truex, V. Vermeul, and J. Fruchter
Pacific Northwest National Laboratory
P.O. Box 999, Richland, Washington, USA

ABSTRACT

An ongoing treatability test is evaluating in situ biostimulation at the 100-D Area of the Hanford Site in Richland, Washington. This test is part of a strategy to couple multiple technologies to accelerate cleanup of hexavalent-chromium contaminated groundwater discharging into the Columbia River. A permeable chemical reducing barrier was previously applied as the primary treatment to prevent the chromium plume from reaching the river at concentrations that exceed regulatory standards. In situ biostimulation is intended to provide supplemental treatment upgradient of this chemical treatment barrier by reducing the concentration of the primary oxidizing species in groundwater (i.e., nitrate and dissolved oxygen) and chromium, thereby increasing the longevity of the chemical barrier and helping to diminish the chromium plume.

INTRODUCTION

Pacific Northwest National Laboratory is conducting a treatability test designed to demonstrate that in situ biostimulation can be applied to help meet cleanup goals in the Hanford Site's 100-D Area. The treatability study is examining two commercially available approaches, one using a soluble substrate (molasses) and the other using an immiscible substrate (emulsified vegetable oil). The application of in situ biostimulation at Hanford is targeted at providing supplemental treatment upgradient of a permeable chemical reducing barrier installed to treat chromate. This existing treatment barrier uses the In Situ Redox Manipulation (ISRM) technology [1] where sediment-associated iron is chemically reduced and then remains as a reductant within the barrier [2]. The longevity of the barrier is related to the amount of reduced iron within the barrier and the flux of oxidizing species into the barrier. Chromate is the contaminant of concern and is readily reduced within the existing barrier. However, other oxidizing species such as nitrate and dissolved oxygen in the water are also reduced and decrease the longevity of the barrier by consuming some of the iron [3]. In situ bioremediation installed as a treatment barrier upgradient of the ISRM barrier is intended as an inexpensive method to reduce the concentration of the primary oxidizing species in groundwater (i.e., nitrate and dissolved oxygen) and chromate, thereby increasing the longevity of the ISRM barrier. This paper summarizes the initial results from field testing of an in situ biological treatment zone implemented at Hanford through injection of a soluble substrate (molasses). The results summarized herein are for the first year of a planned 2-year treatability test.

The treatability testing has multiple objectives focused on evaluating the performance of biostimulation as a reducing barrier for nitrate, oxygen, and chromate. The soluble substrate portion of the treatability test is being conducted to evaluate whether an effective biobarrier could be installed using a substrate that is microbially degraded over a relatively short time frame relative to the desired life span of the barrier. Specific objectives to be addressed in the field test include:

- Determine the effective radius of treatment.
- Evaluate the uniformity of substrate distribution.
- Identify operational needs for injection.
- Induce fermentation reactions and reducing conditions, and grow biomass.

- Minimize permeability changes due to the growth of biomass (assessed through comparison of pre- and post-hydraulic test results).
- Quantify the ability to obtain and maintain low oxygen and nitrate/nitrite concentrations (limit primary electron acceptor flux), and determine longevity of treatment.
- Quantify the ability to obtain and maintain low chromium concentrations (augment chromium treatment) and determine longevity of treatment.
- Compile information required for full-scale application at Hanford.

TEST SITE DESCRIPTION

The treatability test site is located in the southwestern portion of the 100-D Area at Hanford within the chromate and nitrate plumes (Fig.1 and Fig. 2, respectively). Fig. 3 shows the well network layout for the field test. The thickness of the aquifer at this location is approximately 5.6 m (18 ft).

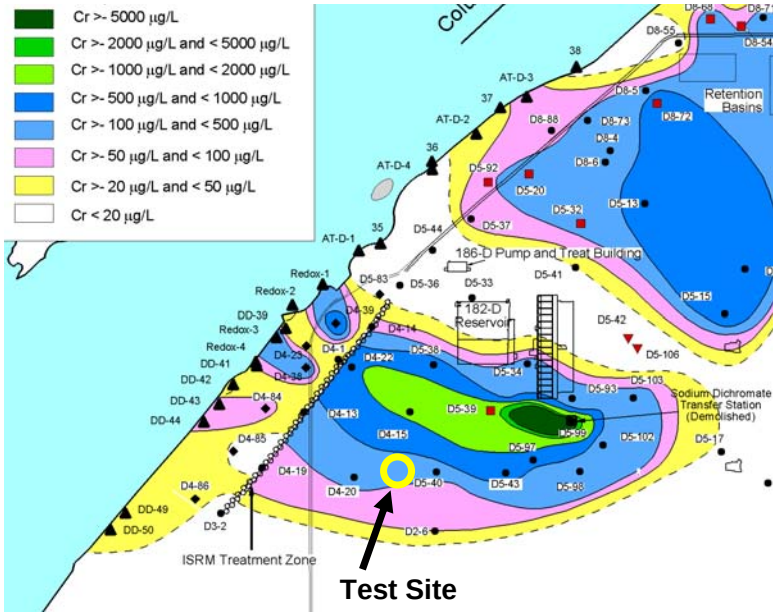

Fig. 1. Test location and recent chromate concentration data for the 100-D Area unconfined aquifer. (Adapted from [4].)

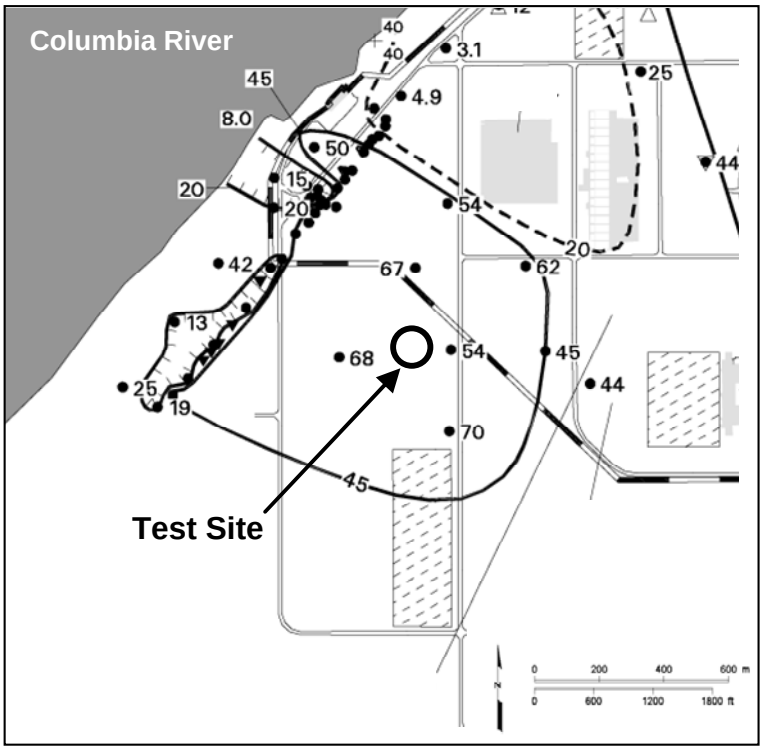

Fig. 2. Test location and nitrate concentration data for the 100-D Area unconfined aquifer.

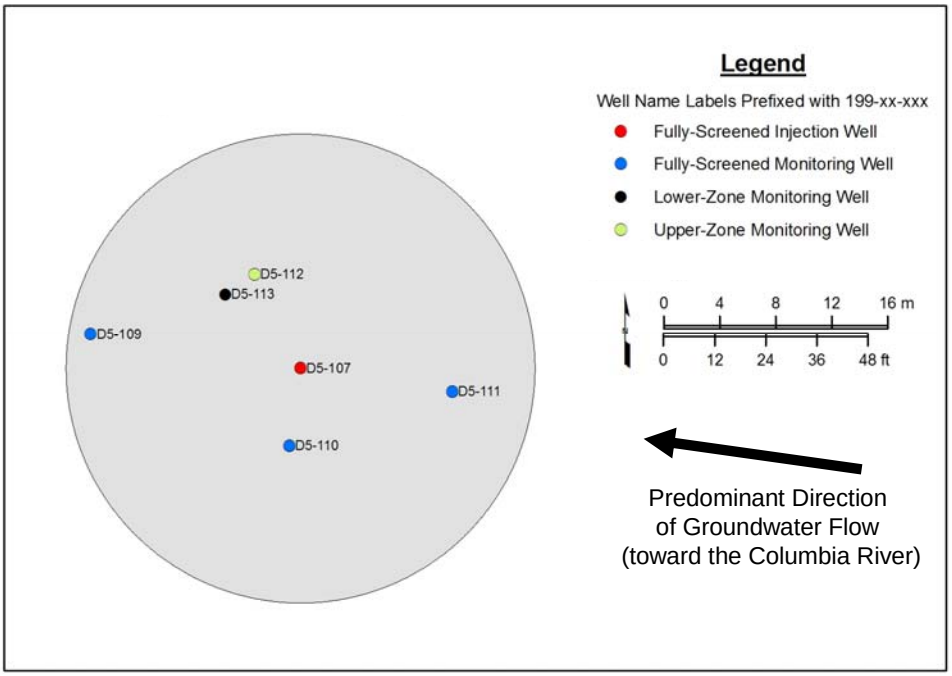

Fig. 3. Well layout for the field test.

METHODS

The treatability test was implemented in the following phases.

Pretest Monitoring

Before the test injection, hydraulic testing and baseline aqueous sampling were conducted. Hydraulic testing included slug interference and recovery testing, electronic borehole flow meter testing in each fully screened well, and a geophysical survey. Additional baseline monitoring included water level measurements at test cell monitoring and injection wells as well as other selected locations to determine the hydraulic gradient. Baseline sample analyses included total organic carbon (TOC), organic acids, nitrate, nitrite, sulfate, chromium, major cations and anions, metals covered by the Resource Conservation and Recovery Act of 1976, and dissolved oxygen concentration at the test cell monitoring and injection wells and at well 199-D5-40, which is the upgradient monitoring well.

Substrate Injection

The substrate injection was conducted using process water injected at approximately 132.5 Lpm (35 gpm) amended with approximately 40 g/L molasses, 100 mg/L ammonium chloride, and 70 mg/L potassium bromide. Samples of the injected solution at the test cell monitoring wells were collected periodically during injection and were analyzed for bromide, TOC, organic acids, nitrate, nitrite, sulfate, and chromium. At the end of the substrate injection, process water was injected for approximately 1 hour to clear the injection system of substrate. The decline in hydraulic head at the monitoring locations was monitored after injection flow was terminated to evaluate hydraulic properties of the test zone. After the injection was completed, the injection system was disconnected and the injection well was converted to a monitoring location.

Process Monitoring

Process monitoring was conducted after injection to assess the formation of a reducing barrier. Samples were collected at each well in the test cell weekly for 8 weeks and analyzed for TOC, organic acids, nitrate, nitrite, sulfate, chromium, oxygen, oxidation reduction potential, bromide, and pH. To assess the impact of the injected solutions, slug tests and additional geophysical surveys were conducted at the end of the process monitoring phase.

Performance Monitoring

Performance monitoring is being conducted to evaluate the conditions within the reducing zone and to determine when nitrate, chromate, and oxygen breakthrough occurs as an indication of barrier longevity. This paper includes data for approximately 10 months of the planned 2-year monitoring period. Samples were collected periodically at each well in the test cell and at the upgradient monitoring well (199-D5-40). Samples were analyzed for TOC, organic acids, bromide, nitrate, nitrite, sulfate, chromium, oxygen, oxidation reduction potential, and pH. Additionally, major cations and anions, metals covered by the Resource Conservation and Recovery Act of 1976, and methane were monitored for comparison to the baseline water quality determined in the pretest monitoring.

RESULTS

Results are presented for each phase of the treatability test operations and then summarized with respect to the treatability test objectives.

Pre-test Monitoring

The pre-test monitoring quantified initial conditions in the test zone. Generally, the aquifer had near-saturation concentrations of oxygen, positive oxidation-reduction potential, nearly neutral pH, chromium concentrations near 150 ppb, and nitrate concentrations around 50 ppm. Pre-test hydraulic analyses, including slug tests, electronic borehole flow meter tests, geophysical surveys, and hydraulic gradient/groundwater flow assessments were conducted to provide a baseline for determining the impact of the substrate injection and biological processes on groundwater flow.

Substrate Injection

Approximately 19,300 L (5100 gal) of molasses (ca. 44 g/L or 11 g/L as TOC) were injected with an average injection flow rate (water and all solutes) of approximately 125 Lpm (33 gpm) over a 3.25-day period for a total injection volume of about 594,000 L (157,000 gal). Based on the injected volume, estimated aquifer properties (5.6 m [18 ft] thick at the time of injection with a porosity of 0.15), and an idealized radial geometry, the nominal injection radius was 15 m (50 ft). Injection pressure was variable throughout the injection, but was typically about 1.758 kg/cm (25 psi). Table I shows the distribution of molasses at the end of the injection period as measured by TOC at each monitoring location.

Table I. Total Organic Carbon Concentrations at the End of the Substrate Injection Period

Well	Total Organic Carbon (g/L)
199-D5-107 (Injection well)	11
199-D5-109	3.2
199-D5-110	11
199-D5-111	11
199-D5-112	6
199-D5-113	0.1 (Rising to 1.5 shortly after injection terminated)

Based on the estimated injection radius of 15 m (50 ft), monitoring wells 199-D5-110, -111, -112, and -113 should have had a TOC concentration comparable to the injected concentration by the end of the injection. Well 199-D5-109 should have been near the edge of the substrate injection. As shown in Table 1, TOC data at monitoring wells 199-D5-110, -111, and -109 are consistent with what would be expected for the substrate injection. TOC values are lower than expected at monitoring wells 199-D5-112 (upper-zone monitoring) and 199-D5-113 (lower-zone monitoring). Characterization data showed that the hydraulic conductivity over the screened interval for well 199-D5-112 was higher than what was observed at other locations. Substrate arrival data indicate that transport in the direction of wells 199-D5-112 and -113 moved predominantly through the upper, more-permeable zone and was diluted or otherwise diverted by this high conductivity layer (as indicated by the early tracer arrival that never reached full concentration). Very little substrate appeared in the lower interval at well 199-D5-113, which is located in a relatively low permeability zone, although the TOC concentration did increase by a factor of 10 within 1 week after injection. This information suggests that heterogeneities in the direction of wells 199-D5-112 and -113 impacted the initial distribution of substrate.

Process Monitoring

The goal of the process monitoring phase was 1) to assess the anticipated fermentation process induced by the injection of substrate, and 2) to evaluate the “drift” of the substrate and fermentation products

downgradient because of the natural groundwater flow. Results from process monitoring indicate that fermentation was rapidly induced through injection of the substrate and continued for about 10 months (into the performance monitoring phase of the test). While the substrate distribution was lower than expected at wells 199-D5-112 and -113, fermentation activity occurred at these locations and additional substrate continued to redistribute into these monitoring locations. As expected, substrate and fermentation products drifted downgradient to well 199-D5-109. The concentration of nitrate, oxygen, and chromium remained low during the initial fermentation processes, partially due to displacement during the injection of molasses/process water solution. Laboratory experiments had been used to evaluate whether additional buffering capacity would be needed during substrate injection. Based on these results, no additional buffering was added during substrate injection because the buffering available in the sediment was sufficient. However, the pH drop observed in the field was larger than expected and generally lowered the pH by 2 pH units—from about pH 7 to about pH 5—during fermentation. It is likely the presence of carbonate minerals as buffering materials may be heterogeneously distributed, and the overall buffering capacity may be different than what was observed in the laboratory buffer tests. The pH remained low during the process monitoring phase, although fermentation continued and the pH increased again so that 10 months after injection the pH was above pH 6.5.

Performance Monitoring

Fig. 4 depicts the difference between the concentration of primary treatment constituents upgradient and within the treatability test zone. The test zone has maintained reducing conditions for at least 1 year since substrate injection with dissolved oxygen concentrations below 0.5 mg/L and negative oxidation-reduction potential. As observed in a laboratory test with Hanford Site sediment, nitrate is reduced without buildup of nitrite as an intermediate. The nitrate concentrations upgradient of the test zone were generally about 50 ppm during the test operations but nitrate and nitrite concentrations have generally been maintained below 2 ppm during the first year of monitoring. Total chromium concentrations upgradient of the test zone were generally about 150 ppb during the test operations but have been maintained below 40 ppb during the first year of monitoring. Good performance of the reducing zone has occurred and been sustained at all of the monitoring locations despite the initially uneven substrate injection. Thus, over time substrate and reducing activity has redistributed and been able to create a relatively uniform treatment zone. Test zone monitoring is being continued to evaluate the longevity of the treatment zone reducing activity.

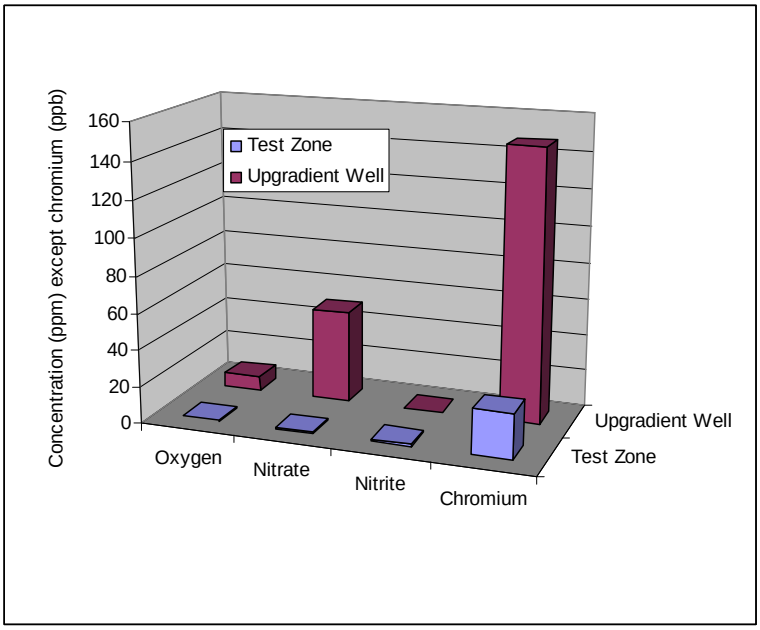

Fig. 4. Comparison of constituent concentrations upgradient and within the treatability test zone. Plotted test zone concentrations are the average concentration at all test zone wells 1 year after substrate injection.

Assessment of Results Relative to Test Objectives

The following is a brief interim summary of the field test results with respect to the test's objectives. These results will be updated with data being collected to evaluate the longevity of the treatment zone.

- Determine the effective radius of treatment.
  Result: A radius of injection of about 15 m (50 ft) from the injection well for a labile substrate is obtainable. However, there was rapid initiation of microbial reactions, and associated biomass buildup near the injection well would need to be addressed for longer duration substrate injection.
- Evaluate the uniformity of substrate distribution.
  Result: Uniformity of substrate injection was, as expected, dependent on formational heterogeneities within and beyond the targeted treatment zone. However, the field test injection was able to distribute substrate to all of the monitoring locations, though at different concentrations. Subsequent microbial activity and maintenance of reducing conditions for at least 1 year has been observed at all monitoring locations.
- Identify operational needs for injection.
  Result: Relatively simple operations with the use of process water and substrate supplied in a tanker truck were demonstrated during the injection. A mitigation approach with pulsing of the molasses was needed during the injection process to manage the injection pressure.
- Induce fermentation reactions and reducing conditions, and grow biomass.
  Result: Process monitoring data showed that fermentation reactions and associated reducing conditions occurred at all of the monitoring locations and persisted for up to 10 months.
- Minimize permeability changes due to the growth of biomass.

Result: Semi-quantitative estimates of permeability reduction based on single-well slug testing in site monitoring wells indicate an average decrease in hydraulic conductivity of only about 20%.

- Quantify the ability to obtain and maintain low oxygen and nitrate/nitrite concentrations, and determine longevity of treatment.
  Result: Low oxygen, nitrate, and nitrite concentrations have been maintained for the first year of monitoring.
- Quantify the ability to obtain and maintain low chromium concentrations, and determine longevity of treatment.
  Result: Chromium concentrations have been maintained below 40 ppb during the first year of monitoring
- Compile information required for full-scale application at Hanford.
  Result: An assessment of full-scale design considerations will be conducted at the end of the treatability test.

CONCLUSIONS

Treatability test results to date have demonstrated that the soluble substrate process is an effective means for developing an in situ treatment barrier at Hanford 100 Areas. Reduced conditions and treatment of nitrate and chromium have been maintained over a 1-year period with indications that these conditions will continue longer. Additional monitoring of the treatability test will be conducted to quantify the longevity of treatment.

REFERENCES

1. M.D. WILLIAMS, V.R. VERMEUL, J.E. SZECSODY, AND J.S. FRUCHTER, “100-D Area In Situ Redox Treatability Test for Chromate-Contaminated Water,” PNNL-13349, Pacific Northwest National Laboratory (2000).

2. U.S. Environmental Protection Agency (EPA), “EPA Superfund Record of Decision Amendment,” EPA/AMD/R10-99/122, EPA ID WA3890090076 (2000).

3. J.E. SZECSODY, V.R. VERMEUL, J.S. FRUCHTER, M.D. WILLIAMS, B.J. DEVARY, J.L. PHILLIPS, M.L. ROCKHOLD, and Y. LIU, “Effect of Geochemical and Physical Heterogeneity on the Hanford 100D Area In Situ Redox Manipulation Barrier Longevity,” PNNL-15499, Pacific Northwest National Laboratory (2005).

4. FLUOR HANFORD, “Calendar Year 2008 Semi-Annual Technical Memorandum for the 100-HR-3 100-KR-4 and 100-NR-2 Pump-and-Treat Operations,” SGW-38942, Rev 0. Fluor Hanford (2008).