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“Final Report of Results for the In Situ Chemical Oxidation Field Experiment, Santa Susana Field Laboratory, Ventura County, California”

Submitted to:

California Department of Toxic Substances Control

On Behalf of:

The Boeing Company
5800 Woolsey Canyon Road
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Date:

June 14, 2016

Approved by:

The registered professionals listed below supervised or personally conducted all the work described in this report.



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Final Report of Results for the In Situ
Chemical Oxidation Field Experiment,
Santa Susana Field Laboratory,
Ventura County, California

Prepared for

The Boeing Company

June 14, 2016



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Executive Summary

Overview and Project Objectives

The Boeing Company (Boeing) conducted a rigorous, long-term in situ chemical oxidation (ISCO) field pilot study, with fieldwork and data acquisition occurring between October 2012 and January 2016. The ISCO technology involves delivery of an oxidizing agent to the subsurface to promote transformation of organic compounds into less harmful chemical species (carbon dioxide, chloride, and water). The overall purpose of the ISCO field experiment was to collect data to evaluate its effectiveness in removing chlorinated volatile organic compounds (VOCs) from the saturated Chatsworth Formation. Results from the study will be used to evaluate the effectiveness, implementability, and cost of using ISCO relative to other potential remedial technologies in a forthcoming corrective measures study (CMS) for Santa Susana Field Laboratory (SSFL), conducted as part of the Resource Conservation and Recovery Act (RCRA) corrective action process.

The ISCO field experiment was completed in the northeastern portion of SSFL (Administrative Area I), within the former Instrument and Equipment Laboratories (IEL) RCRA facility investigation (RFI) site (see Figure ES-1). Although the IEL RFI site was selected as the location for the field experiment, results from this study are considered applicable on a site-wide basis.

The scope of work included the following key work elements:

- Modify existing monitoring RD-35A well for use as an injection well.
- Collect rock core and install several new multi-level system (MLS) monitoring wells (C-10, C-18, RD-105, RD-106, and RD-107).
- Conduct groundwater flow system tracer testing (using fluorescein dye and bromide).
- Inject an oxidant (potassium permanganate - KMnO_4) into the injection well over seven individual, week long events.
- Collect groundwater samples before, during, and following the various injection events.
- Drill a post-injection corehole and analyze rock core samples.
- Compile the data to assess overall effectiveness in meeting the project objectives.

The ISCO field experiment was conducted based on several work plan documents approved by the California Environmental Protection Agency, Department of Toxic Substances Control (DTSC). The injection and monitoring elements of the ISCO field experiment were completed under the provisions of a *General Waste Discharge Requirements for the In Situ Chemical Oxidation Pilot Testing for Groundwater Remediation* (General WDR Permit) issued by the Los Angeles Regional Water Quality Control Board (LARWQCB, 2013). The project also included collection of supplemental data (beyond that required in work plans and permits) to: 1) better understand the groundwater flow system and potential influence from the ISCO injection events; 2) obtain data to support the CMS technology evaluation, and; 3) enhance the overall site conceptual model (SCM) through innovative high resolution site characterization (HRSC) data acquisition, with support from University of Guelph (UG) research staff.

The ISCO injection solution for each of the seven injection events was mixed onsite using hydrant water and RemOx[®]S ISCO reagent supplied by Carus Corporation. Each event was completed by injecting the ISCO reagent solution by gravity into RD-35A at an average flow rate of 2 gallons per minute (gpm) for approximately 8 hours each day for five consecutive days, followed by one additional day of rinseate injection during system cleanout. Water levels were measured in RD-35A and nearby MLS wells using pressure transducers. Over 6,000 pounds of ISCO reagent and nearly 37,000 gallons of solution were

injected over the seven injection events. Groundwater samples were collected from a performance monitoring well network consisting of 8 primary wells (43 sample intervals), 4 secondary wells (28 sample intervals), and 3 tertiary wells (3 sample intervals). Samples were analyzed for VOCs, metals, and general water quality parameters in accordance with the General WDR Permit (LARWQCB, 2013). The primary site-related contaminants (which were the primary focus for data evaluation) include trichloroethene (TCE) and daughter products cis-1,2-dichloroethene (cDCE), trans-1,2-dichloroethene (tDCE), and vinyl chloride (VC). Additional VOCs including 1,1-dichloroethene (1,1-DCE), 1,1-dichloroethane (1,1-DCA), carbon tetrachloride (CT), and 1,4-dioxane (1,4-D) are considered secondary site-related contaminants for this study.

The ISCO field experiment performance objectives included the following:

- Objective 1 - Evaluate the effectiveness of delivery and distribution of oxidant in the fractured sandstones of the Chatsworth Formation.
- Objective 2 - Assess the extent of oxidation of TCE and its daughter products in the rock matrix (evaluate the magnitude of contaminant concentration reduction in the rock matrix).
- Objective 3 - Assess the natural oxidant demand (NOD) of the minerals and/or organics present in the rock matrix.
- Objective 4 - Assess the magnitude and extent of reactive minerals (such as pyrite, magnetite, etc.) on the solid surfaces of the rock that may influence the oxidation reaction.
- Objective 5 - Assess the occurrence and effects of the precipitation of oxidation reaction by-products (particularly solid manganese oxides [MnO₂[s]]) in the fracture system, and the occurrence of other by-products (particularly metals) in groundwater.

Tracer Testing Results

Following installation of the MLS wells and before the ISCO injection events, a fluorescein dye tracer test was conducted through a continuous 96-hour injection period. The objective of the fluorescein tracer test was to identify sample intervals hydraulically connected to injection well RD-35A. Groundwater samples were collected from the primary wells at a high frequency during and immediately after the injection period to evaluate dye arrival and concentrations. Fluorescein was detected in a total of 17 sample ports in MLS wells C-18, RD-106, and C-10.

The first KMnO₄ injection event included the addition of bromide as a conservative, non-reactive tracer. The primary objective of the bromide tracer test was to evaluate the influence of NOD on permanganate consumption. Bromide was detected at concentrations greater than baseline levels in a total of 32 sample ports in 5 MLS wells (C-10, C-18, RD-105, RD-106, and RD-107). However, bromide was found at greater than 10 times the laboratory reporting limit (RL) (or greater than 5 milligrams per liter [mg/L]) in only 10 of the 32 ports, indicating significant dilution-dispersion along the flow paths.

The first arrival of fluorescein and bromide occurred in some C-18 and RD-106 sample ports within approximately one day after injection commenced. Both wells are located approximately along bedrock strike relative to RD-35A. These rapid arrival times reveal the relatively rapid groundwater transport velocities in the fractures. By contrast, the tracers were not detected until more than 30 days after the injection period in some C-10 sample ports, likely because of the longer travel distance, variable groundwater flow velocities with distance, and dilution-dispersion of the injected solution down dip relative to RD-35A.

Bromide detection occurred in a greater number of sample ports (32) compared to fluorescein (17) at least partly due to multiple subsequent injection events, which promoted distribution, and because of the significantly longer monitoring period.

Permanganate Distribution

Groundwater samples were collected from the primary wells at a high frequency during and after each injection event to evaluate permanganate arrival and concentrations. Following the seven ISCO injection events, visible permanganate (above 5 mg/L) was observed in MLS wells C-18 (Ports 3 and 5) and RD-106 (Ports 6 to 9), as depicted on Figure ES-1. Only one port, C-18 (Port 5), showed gradually increasing colorimeter concentrations several months after injections were complete, suggesting the fracture at this port is poorly connected to the wider fracture network. Although samples from C-10 did not meet the visibility threshold criteria, sporadic low-level colorimeter concentrations suggest that permanganate may have been present in this well below the visibility threshold.

In general, permanganate detections in C-18 and RD-106 occurred within one week from the start of injection and the permanganate presence was short-lived, approximately 2 to 3 weeks. The relatively short residence time is likely due to permanganate consumption through reaction with NOD and VOCs and elevated groundwater flow velocities in the fractures at some locations. The presence of visible permanganate in fewer sample ports (6) compared to ports with detectable bromide (32) indicates a significant influence of NOD on permanganate consumption along the flow path. Laboratory thin section analysis conducted during the project revealed $MnO_{2(s)}$ precipitates were found in close association with fragments of organic carbon, which was identified as the dominant, naturally-occurring contributor to NOD.

During the post-injection rock coring (corehole C-20), visible and detectable permanganate was only present in one zone from 115.8 to 117.3 feet below ground surface (bgs), which confirms the significant NOD influence on the lack of permanganate extent and short residence time.

Contaminant Concentrations

Trend plots for concentrations of the primary site-related contaminants TCE, cDCE, tDCE, and VC were prepared to include the baseline sampling event through 6 months after the final ISCO injection event, with a focus on the six ports in MLS wells C-18 and RD-106, where visible permanganate was found. VOC concentrations in most ports generally increased after the first injection event, suggesting mobilization or movement of VOC mass in the fracture network. At five ports (C-18 [Port 3] and RD-106 [Ports 6 to 9]), VOC concentrations generally decreased immediately following injection events, but rebounded to levels near or above baseline levels shortly thereafter. The VOC concentrations in these five ports generally remained at or above baseline levels at the end of the monitoring period, and were well above MCLs for these constituents. The only exception was at C-18 (Port 5), where permanganate concentrations increased for several months following the final two injection events, and VOC concentrations decreased to levels near or below maximum contaminant levels (MCLs). However, it was not possible to evaluate potential rebound in C-18 (Port 5) because permanganate was still present at the end of the experiment.

The relatively short permanganate residence time in most ports where it was present above the visibility threshold (except C-18, Port 5) suggest there was likely insufficient time for significant diffusion of permanganate into the rock matrix, where most of the VOC mass is stored. In addition, following dissipation of the permanganate, back diffusion of VOCs from the rock matrix to groundwater in the adjacent fractures occurred, resulting in contaminant rebound. In addition, several secondary site-related contaminants including 1,1-DCE, 1,1-DCA, CT, and 1,4-D were not amenable to treatment by permanganate, consistent with other similar studies (U.S. Environmental Protection Agency [USEPA], 2006).

At C-10, trace colorimeter concentrations (below the visibility threshold) were detected in several ports. Relatively stable concentrations of TCE, cDCE, and tDCE were observed in most ports through the end of the monitoring period, with a distinct increase in VC, suggesting that existing reductive dechlorination

processes were accelerated by the ISCO injections, likely from mobilized organic matter in the aquifer system. This soluble carbon supports microbial growth, which can promote reductive dechlorination of VOCs.

The concentrations of redox-sensitive metals, especially chromium, increased in some ports following the start of injection, but concentrations generally returned to, at, or near baseline levels by the end of the monitoring period as natural aquifer conditions were restored. For C-18 (Port 5), concentrations of potassium, manganese, chromium, and selenium continued to increase through the end of the monitoring period, consistent with the extended permanganate residence time, but these levels are also expected to decline as natural aquifer conditions are restored. However, manganese concentrations remained at elevated levels at the end of the monitoring period, particularly at RD-106. There were no significant long-term increases in VOC by-products 2-methyl ethyl ketone (MEK) and acetone, and concentrations remained low throughout the monitoring period.

Evaluation of Project Performance Objectives

The field and laboratory data were evaluated against the performance objectives, to assess the overall viability of the ISCO technology in reducing VOC concentrations in groundwater. A brief summary of the evaluation of each performance objective is included herein (Section 10 provides a more detailed evaluation).

Objective 1: Evaluate the effectiveness of delivery and distribution of oxidant in the fractured sandstones of the Chatsworth Formation.

Delivery of the oxidant over seven week-long injection events was considered sufficient for evaluating the influence from permanganate on VOC concentrations. The distribution of bromide tracer (added to the first oxidant injection) was modest for a fractured rock system (with many detections at trace levels), while the overall distribution of the oxidant was considerably less because of its reactive nature with NOD and chlorinated ethenes.

Objective 2: Assess the extent of oxidation of TCE and its daughter products in the rock matrix (evaluate the magnitude of contaminant concentration reduction in the rock matrix).

The overall extent of oxidation of TCE and its daughter products in the rock matrix was very limited.

Objective 3: Assess the NOD of the minerals and/or organics present in the rock matrix.

The NOD of the minerals and/or organic carbon content in the Chatsworth Formation rock matrix is significant, and resulted in elevated oxidant consumption and limited diffusion into the rock matrix.

Objective 4: Assess the magnitude and extent of reactive minerals (such as pyrite and magnetite) on the solid surfaces of the rock that may influence the oxidation reaction.

The Chatsworth Formation rock core contains reactive minerals including pyrite, but pyrite does not appear to significantly influence the oxidation reaction. Other reactive minerals may contribute to oxidant consumption.

Objective 5: Assess the occurrence and effects of the precipitation of oxidation reaction by-products (particularly $MnO_{2(s)}$) in the fracture system, and the occurrence of other by-products (particularly metals) in groundwater.

The multiple ISCO injection events resulted in relatively limited $MnO_{2(s)}$ precipitates, with a modest decrease in permeability, within the fracture dominated flow system. The concentration of manganese in groundwater remained elevated at some locations by the end of the monitoring period.

Overall Conclusions

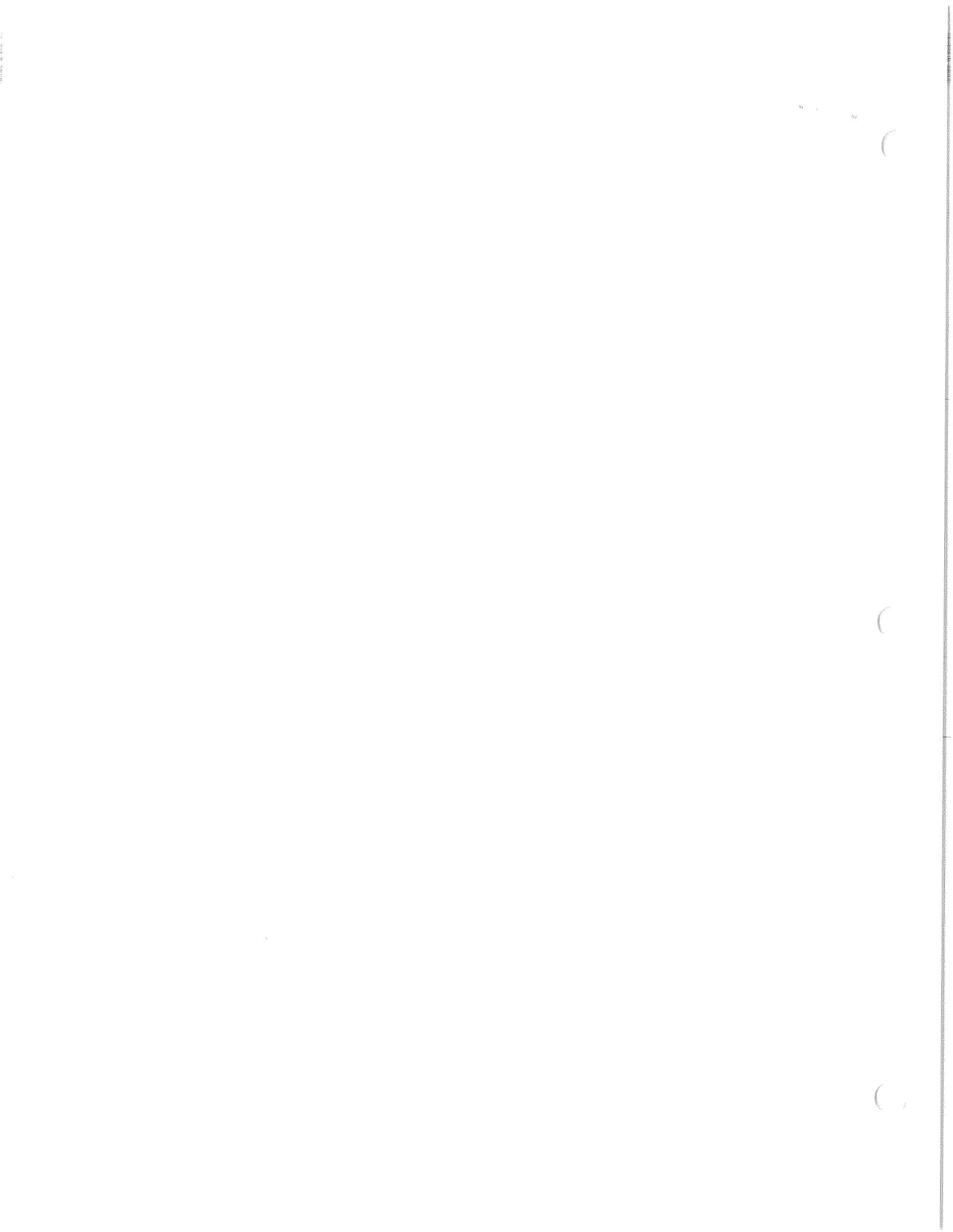
The ISCO field experiment achieved the overall scope of injecting KMnO_4 over multiple events, combined with groundwater performance monitoring and post-injection rock coring. However, the presence of permanganate above the visibility threshold concentration was limited to six ports in two MLS wells. The limited distribution of permanganate reflects the influence of NOD, which consumed the permanganate before it could create a larger target treatment zone (TTZ) and result in a longer residence time for diffusion into the rock matrix.

The key performance metric of long-term reduction in concentrations of TCE, cDCE, tDCE, and VC was not achieved. At ports with visible permanganate, there was a short-term decrease in VOC concentrations, followed by an increase in VOC concentrations as the permanganate was depleted. The permanganate was not persistent for long in the fracture network, and the concentrations in the fractures were relatively low, limiting the opportunity for diffusion to occur. As confirmed by the laboratory analysis of thin sections, relatively abundant organic carbon is present within the rock matrix, such that permanganate diffusing into the rock matrix was likely depleted by NOD.

Based on the data evaluation conducted as part of the project, the following factors contributed to the lack of overall effectiveness of ISCO as a remedial technology for impacted groundwater in the Chatsworth Formation:

- Elevated NOD in the aquifer, including the fracture zones and rock matrix.
- Variable but locally rapid groundwater flow velocity within portions of the fracture network, reducing the permanganate residence time to 3 weeks or less, and reducing potential for matrix diffusion.
- Fair but limited hydraulic connection between the injection well and many of the sample locations because of the random nature of fracture connections, and the presence of a fault trace within the TTZ.
- Relatively rapid rebound in VOC concentrations, resulting from back diffusion of VOCs from the rock matrix into the monitored fracture zone after permanganate was no longer present.
- Accumulation of VC in several ports following the permanganate injections, likely resulting from an increase in the existing reductive dechlorination process from the mobilization of soluble organic carbon.
- Presence of site-related contaminants (for example, CT, 1,1-DCA, and 1,4-D) that are not amenable to effective treatment by permanganate.
- Potential long-term water quality implications from manganese, which remained at elevated concentrations in some locations at the end of the monitoring period.

Although the IEL RFI site was selected as the location for the field experiment, results from this study are considered applicable on a site-wide basis. The results of this study will be used in the CMS phase of the SSFL project to further assess the effectiveness, implementability, and cost of ISCO as a long-term remedial technology.





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Via FedEx

Electronic Submittal June 14, 2016

June 14, 2016

In reply, refer to SHEA-115501

Mr. Mark Malinowski, P.G.
DTSC Performance Manager – SSFL
California Department of Toxic Substances Control
8800 Cal Center Drive
Sacramento, CA 95826-3200

Subject: *Final Report of Results, In Situ Chemical Oxidation Field Experiment,
Santa Susana Field Laboratory, Ventura County, California*

Dear Mr. Malinowski:

The Boeing Company (Boeing) is pleased to present the attached report entitled, *Final Report of Results, In Situ Chemical Oxidation Field Experiment, Santa Susana Field Laboratory, Ventura County, California*. This report presents the final summary and evaluation of results from the *in situ* chemical oxidation (ISCO) field experiment, conducted from 2012 through 2016 by The Boeing Company, at the Santa Susana Field Laboratory (SSFL).

The overall purpose of the ISCO field experiment project was to evaluate the effectiveness, implementability, and cost of using ISCO as a groundwater remedial technology for removing volatile organic compounds from the saturated bedrock of the Chatsworth Formation underlying the site. Results from the ISCO field experiment will be used in the forthcoming groundwater corrective measures study for SSFL, conducted as part of the RCRA corrective action process.

If you have any questions regarding this submittal, please contact Mike Bower at (818) 466-8776.

I certify under penalty of law that these documents and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

Sincerely,

David W. Dassler, P.E.
Southwest Remediation Manager
The Boeing Company



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