Presented at The Third International Conference on Oxidation and Reduction Technologies for In-Situ Treatment of Soil and Groundwater, San Diego, October 2004.

IN SITU REDOX MANIPULATION AND FIXATION OF Cr(VI) IN VADOSE ZONE SOILS

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ABSTRACT

To test the applicability of In-Situ Redox Manipulation for treating 2,700 mg/Kg of Cr(VI) in unsaturated alluvium at a former metal plating facility, a series of bench-scale experiments were completed. Bottle tests were performed to select an appropriate reductant (e.g., sodium metabisulfite {SMB}) and treatment dosage. Flow-through column microcosms were then prepared with site soil to evaluate the effectiveness of controlled SMB treatment by gravity driven infiltration through the alluvium. The column data indicated that three pore volumes of a 5,000 mg/L solution of SMB were sufficient to reduce leachable chromium levels to below 10 µg/L. Mass balances developed from soluble chromium levels measured in the effluent from the treated and control columns indicate that ISRM reduced and "fixed" approximately 840 mg of Cr (VI). The mass of solute removed per unit mass of soil was approximately 6,000 mg-Cr(VI)/Kg-soil. Treated columns were then flushed with oxygenated groundwater to evaluate the potential for re-oxidation of Cr(III) to and mobilization of Cr(VI). After each flushing event, soluble Cr(VI) levels remained below 10 µg/L.

INTRODUCTION

The Manistee Plating facility is a former metals finishing and plating operation located on the banks of the Manistee River in Manistee, Michigan. Environmental impacts consisting primarily of hexavalent chromium- and nickel-contaminated soil and groundwater have been documented at the facility since the early 1990s. Hexavalent chromium (Cr(VI)) concentrations as high as 140,000 µg/L have been measured in samples from monitoring wells located in the vicinity of the source. The U.S. Environmental Protection Agency (EPA) and the Michigan Department of Environmental Quality (MDEQ) have been engaged in a series of actions directed at remediating source materials and groundwater at the site.

To date, the groundwater treatment activities appear to have been effective in reducing the masses of soluble Cr(VI) and nickel from the affected water-table aquifer beneath and downgradient of the source. Between January 1998 and May 2002, the concentration of Cr(VI) in groundwater was reduced from 140,000 µg/L to 370 µg/L.

However, the results from the analyses of vadose zone soil samples collected from beneath the source reveal that a significant mass of chromium and nickel remains in the unsaturated sediments. Cr(VI) levels as high as 160,000 µg/Kg have been measured in these soils as recent as February of 2002. Leach testing (via the SPLP) of the impacted soils revealed that infiltration through the impacted unsaturated soils could result in hexavalent chromium releases in excess of 650 µg/L to the groundwater. The current cleanup criteria for Cr(VI) is 29 µg/L, based on a mixing zone determination.

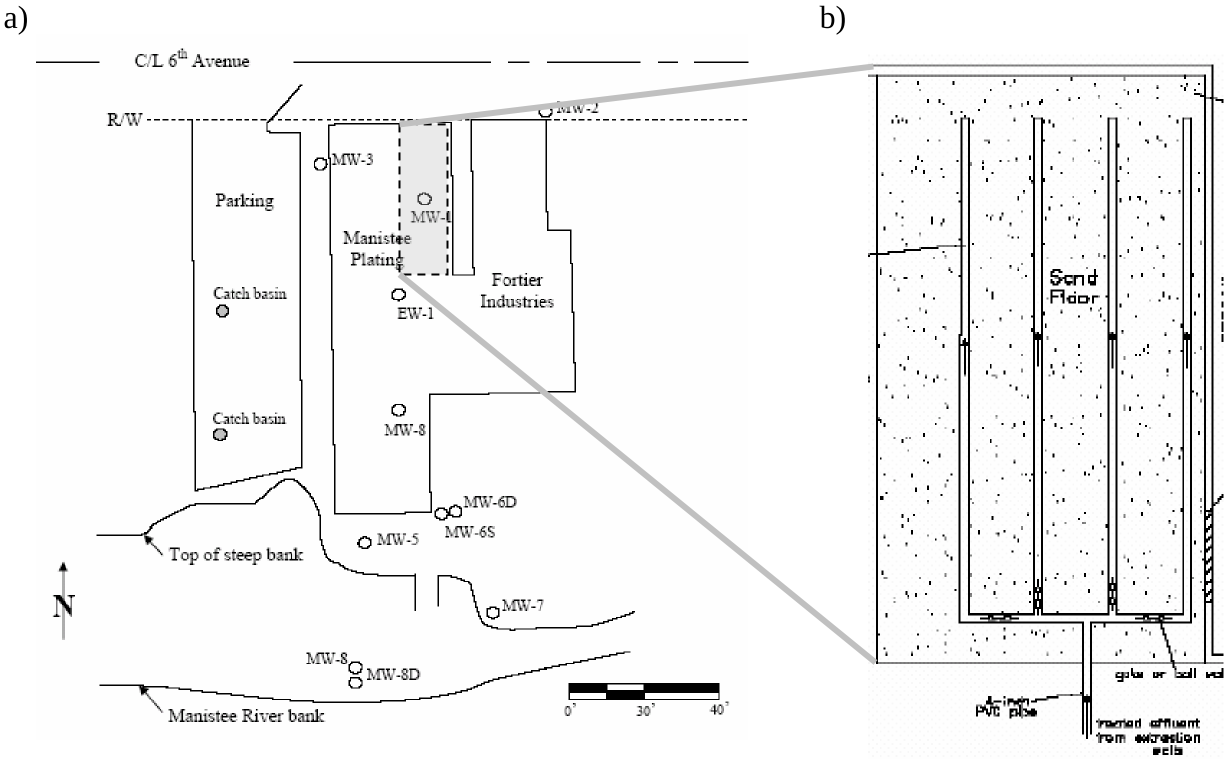

Figure 1 – Site layout (a) and infiltration gallery (b)

In anticipation of attaining cleanup standards in groundwater as a result of the on-going collection and treatment efforts described above, the MDEQ has been seeking a more direct treatment method for the impacted unsaturated soils to limit the potential for additional loadings of Cr(VI) to the water table. An option that is currently under consideration is in-situ redox manipulation (ISRM). This process entails the controlled introduction into saturated and unsaturated soils reagents that are capable of reducing metal oxidants, such as ferric iron and Cr(VI) [Fruchter, et al (1)]. By saturating the affected unsaturated sediments at the Manistee Plating facility, it may be possible to reduce Cr(VI) to less toxic and less soluble trivalent chromium (Cr(III)).

To explore the applicability of ISRM and develop preliminary engineering and operating parameters for full-scale implementation, the MDEQ requested that Weston Solutions, Inc. coordinate bench-scale treatability studies of the process. Accordingly, Weston commissioned Dr. Timothy Mayotte to design a bench-scale experimental program to simulate ISRM at the site.

Objectives

The objectives for the ISRM bench study were to identify an aqueous reducing agent and associated application dosage that is effective for reducing Cr(VI) in the site soils to less soluble and less toxic Cr(III), and is also both safe to handle and of limited cost compared to other applicable commercially available reductant solutions. An additional goal was to verify that the re-oxidation and mobilization of chromium in ISRM-treated site soils is unlikely.

EXPERIMENTAL PLAN

To accomplish the objectives for the ISRM bench study, an experimental plan consisting of the following three distinct tasks was designed:

Task 1 – Reductant Selection and Dosage Testing
Task 2 – Column Experiments
    Subtask 2.1 – Chromium Saturation
    Subtask 2.2 – In-Situ Redox Manipulation
    Subtask 2.3 – Post-Treatment Leaching Evaluation
Task 3 – Reductant Dose Optimization Testing

Task 1 – Reductant Selection and Dosage Testing

Bottle tests were performed to evaluate the effectiveness of a variety of reagents for reducing Cr(VI) to Cr(III) in untreated groundwater from the Manistee Plating site. A total of five reductants were tested. The following reagents were evaluated at five distinct dosage levels: sodium dithionite ($Na_2S_2O_4$); sodium metabisulfite ($Na_2S_2O_5$); sodium sulfite (Na_2SO_3); calcium sulfide (Ca_2S); and ammonium sulfide ($(NH_4)_2S$). Reagent concentrations were 100 millimolar (mM). The reagent dosage concentrations evaluated included: 50 mg/L; 250 mg/L; 500 mg/L; 1,000 mg/L; and 2,000 mg/L.

A 100 mL volume of groundwater and reagent was added to each test bottle in proportions necessary to achieve the requisite reagent concentrations. Reagent dilutions were made using pretreated groundwater from the site. The hexavalent chromium concentration in the untreated groundwater used for testing was approximately 600 µg/L.

After thoroughly mixing reagent with groundwater by shaking and a subsequent holding period of approximately one hour, the solutions in each test bottle were observed to note changes in turbidity and coloration. Further, the pH and Cr(VI) concentration of each solution were measured using a standard electrode and colorimeter cell, respectively.

Additional considerations during the evaluation of reductant reagents included cost, toxicity and ease of handling. Accordingly, due to their toxic nature and the associated care necessary to store and handle these reagents, there was a bias against further testing of sodium dithionite, and the two sulfide reagents.

The results of the bottle tests revealed that treatment objectives could be achieved with a minimal reagent dosage using sodium metabisulfite. Therefore, a final bottle test was performed to more accurately assess the dosage requirements on aqueous Cr(VI) concentrations that are consistent with those measured in the source area at the site (e.g. 50 – 100 mg/L). During this test, sodium metabisulfite was provided to untreated groundwater spiked with potassium dichromate (24 mL of 5,000 mg/L KCr_20_4 stock to 576 mL of water) in dosages of 50 mg/L, 500 mg/L and 5,000 mg/L. Changes in color and turbidity were noted in these mixtures. Cr(VI) and pH measurements were performed as described previously.

The results from the two sets of batch experiments suggest that treated groundwater amended with 5,000 mg/L of 100 mM sodium metabisulfite provided in a volume sufficient to inundate the impacted unsaturated soils will reduce soluble chromium levels to below cleanup concentrations. Therefore, subsequent experimental tasks were conducted using sodium metabisulfite exclusively.

Task 2 – Column Experiments

ISRM was simulated using column systems packed with impacted site soils. Although a total of four column systems were prepared, only two columns were used to facilitate the requisite ISRM simulations. To accomplish the simulations and achieve the objectives of the study, three experimental stages (Subtasks 2.1, 2.2 and 2.3) were conducted. The initial stage entailed the addition of untreated site groundwater spiked with elevated doses of hexavalent chromium until the solid- and liquid-phase solute concentrations were near equilibrium. The second stage involved the addition of reductant-amended untreated site groundwater to the chromium-saturated soils to simulate ISRM. Stage three entailed passing treated and clarified site groundwater through the ISRM-treated soils to evaluate the potential for re-oxidation and mobilization of chromium. A control column was maintained during Subtasks 2.2 and 2.3 to verify and assess the magnitude of the affects of ISRM.

Column Preparation

Soil for column preparation was collected by Weston personnel from the unsaturated zone beneath the infiltration gallery. Sampling was accomplished in February 2002 and soil was transported to Dr. Mayotte's laboratory in Lansing in mid-March. The soil was then processed by first selecting for materials with the highest measured quantities of chromium and then sieving the composite soil mass through No. 8- and No. 5-mesh sieves to produce a poorly graded sample with hydraulic characteristics favorable for routine pore fluid exchange. The processed soils were then packed into a total of four glass columns, 30 cm in length with 2.5 cm inside diameters.

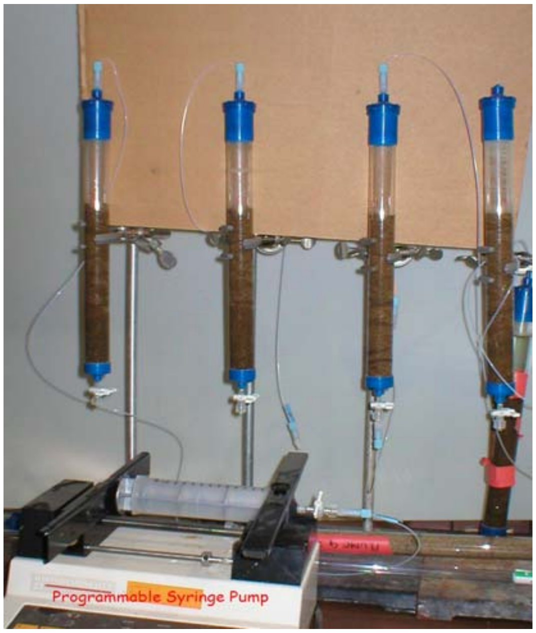

Figure 1 – Soil columns used for ISRM experiments.

Prior to packing, each column was filled partially with non-treated groundwater collected from the site. A wad of fused-silica wool was then saturated in the standing water and placed at the base of each column to provide a permeable support for the soil. The silica wool was then gently compacted with an aluminum rod to remove residual air bubbles. With the permeable base emplaced, processed soils were then added to each column by spooning small quantities into the top of the standing water column and permitting the mass to settle under gravity. The 30 cm long columns were packed to a bed depth of approximately 20 cm. Once packed, each column was fitted with feed and effluent plumbing and appurtenances. Plumbing consisted of 1/8-inch I.D. Teflon tubing and ETFE and Tefzel fittings, including two-way stopcocks and joints.

The six columns assembled for the bench study were categorized as follows:

- Column A (30 cm) – used for ISRM
- Column B (30 cm) – used for ISRM testing with alkalinity addition.
- Column D (30 cm) – Control (chromium saturated; leached but no ISRM)

Pore Fluid Exchange and Sampling

Columns were operated in a semi-batch mode. Specifically, this entailed discrete pore fluid exchanges of a constant volume. Each exchange involved the rapid transfer of a specific volume of pore fluids {site groundwater (treated or untreated) spiked with reductant amendments, as necessary} in each column followed by an incubation period of a few days to a few weeks. After incubation, the pore fluids were exchanged again. Theoretically, the average concentration of the target analytes in the triplicate samples obtained from the initial 10 mL of groundwater exiting each column represented the solute concentrations of the pore fluids during an incubation period. Conversely, the average solute concentrations measured in triplicate samples of the final 10 mL of groundwater exiting each column at the conclusion of an exchange represented the initial conditions of the subsequent incubation period. By comparing the initial conditions of an exchange with the post-incubation concentrations measured during the following exchange, the change in solute mass during the incubation period could be estimated. From the comparison of each exchange event, mass balances for soluble chromium were developed.

Pore fluid exchanges were accomplished in each column by conveying fluids from large plastic syringes compressed at a constant rate of 5-10 mL/min using a programmable Harvard syringe pump. Fluids were delivered to the top of each column and allowed to infiltrate the contained soils under the influence of gravity. Delivered fluids were removed by gravity drainage through the base of each column.

Sampling of pore fluids was accomplished by collecting discrete volumes (typically 2 mL) of draining fluids in 15 mL centrifuge tubes for temporary storage prior to analyses or additional processing. Sample processing was dependent on the analyses performed. Typically, samples for ion chromatography (standard ions) or atomic absorption (soluble chromium and iron) were filtered through 20-micron syringe filters and decanted in appropriate sample containers. Samples for soluble metals analysis were also preserved with 1 M nitric acid (2 µL per 1 mL sample volume). All processed samples were stored at 4^0C prior to analyses.

Subtask 2.1 – Chromium Saturation

A total of four pore volume exchanges (140 mL each exchange) were conducted in Columns A, B, C and D using untreated site groundwater spiked with potassium dichromate (18-24 mL of 5,000 mg/L KCr_20_4 stock to 576-582 mL of water) in order to saturate each column with hexavalent chromium. During the initial exchange, 100 mg/L of sodium bromide was also added to the exchange fluids as a conservative tracer. Each column was maintained completely saturated during the incubation periods between each exchange. This was done to ensure that the open surface area of the soils contained within each column was completely exposed to the chromium-spiked groundwater, thereby maximizing the potential for sorption. Evaluation of the initial and final pore fluid concentrations associated with these exchanges revealed that only four events were necessary to establish equilibrium between the solid and liquid phase concentrations of Cr(VI) fed to each column.

Note that during the initial exchange, discrete volumetric samples were taken throughout the exchange in order to measure bromide concentrations and, in turn, develop breakthrough profiles for the tracer to estimate the internal porosity of the packed soils, as required for mass balance calculations.

A fifth and final exchange was carried out without the introduction of spiked groundwater. During this exchange, the groundwater retained in each column was allowed to drain under the influence of gravity without replacement. The Cr(VI) concentration within the pore fluids exiting each column during this event represented the equilibrium saturation concentration.

Subtask 2.2 – In-Situ Redox Manipulation

To simulate ISRM in unsaturated soils, drained Column A received 50 mL pulses of treated groundwater spiked with 5,000 mg/L of sodium metabisulfite. Column D received 50 mL pulses of non-spiked treated groundwater. These fluid exchanges were conducted until Column A consistently yielded effluent Cr(VI) below 100 µg/L. Six exchange events were completed during this subtask.

Subtask 2.3 – Post-Treatment Leaching Evaluation

A series of three exchanges were performed in Columns A and D (control) using non-amended (e.g. no reductant added) clarified effluent from the treatment facility at the site. These tests were performed to evaluate the potential for re-oxidation and remobilization of the reduced and fixed Cr(III) mass. Each exchange was performed as previously described. Cr(VI) measurements were conducted using field colorimetry procedures with a detection limit of 10 µg/L.

Task 3 – Reductant Dose Optimization Testing

In an effort to explore means for potentially reducing the dosage of sodium metabisulfite necessary for full-scale treatment, a follow-up set of batch treatment tests (bottle tests) were performed. Other researchers have postulated that Cr(VI) reduction is maximized in the presence of both soluble and solid forms of reduced (ferrous) iron [Anderson et al. (2)]. Therefore during the dosage optimization batch tests, the effect on reductant treatment performance by measured addition of a soluble ferric iron source to impacted site groundwater was examined.

The batch tests consisted of adding ferric chloride (100 mM) to a total of three sets (Sets A, B, and C) of four bottles containing untreated site groundwater spiked with potassium dichromate (18 mL of 5,000 mg/L KCr_2O_4 stock in 582 mL of water). Each set of four bottles received a distinct dosage of ferric chloride, as follows: Set A - 100 mg/L; Set B - 250 mg/L; Set C - 500 mg/L. Bottles were numbered 1-4 in each set. The reductant dosages evaluated in each bottle included: Bottle 1 - 100 mg/L; Bottle 2 - 250 mg/L; Bottle 3 - 500 mg/L; Bottle 4 - 1,000 mg/L. Measurements and observations were performed as described for the batch tests conducted during Task 1. Select bottles were sampled for more precise analysis by atomic adsorption. These samples were processed, handled and stored as previously described.

RESULTS AND DISCUSSION

The breakthrough profile and associated data for a representative column is provided on Figure 3. These data reveal that the internal effective porosities of the processed site soil in the packed columns averaged approximately 38%. Saturation exchange data (Figures 3) reveal that approximately four exchanges was necessary to establish near chemical equilibrium between the packed soil mass and untreated groundwater spiked with 50-70 mg/L of soluble chromium. A mass balance was produced using the initial and final concentration data from the saturation exchanges, an assumed soil bulk density of 1.4 g/mL (ref), and the measured effective porosity of the site soils. These calculations reveal that approximately 440-880 mg of chromium was retained in the soil columns prior to the subsequent treatment exchanges.

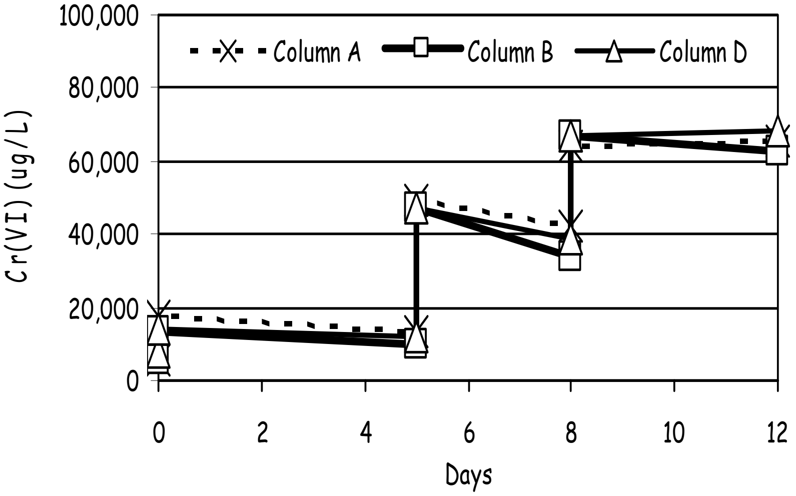

Figure 2 – Chromium mass loading data

The treatment exchange data (attached) indicated that a minimum three pore volumes of treated groundwater spiked with 5,000 mg/L of sodium metabisulfite was necessary to reduce soluble chromium levels exiting the soil mass during infiltration to below 100 µg/L. Mass balance calculations developed from soluble chromium levels measured in the effluent from the treated (Column A) and control column (Column D) suggest that the ISRM process reduced and "fixed" approximately 840 mg of the solute. With an estimated soil mass within each column of 137.4 mg, the unit mass of solute removed per unit mass of soil is 6,084 mg solute/Kg soil.

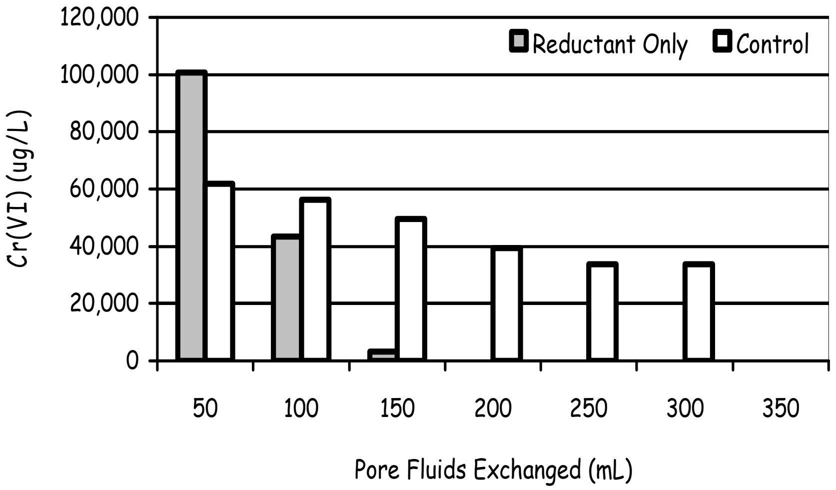

Figure 3 – Chromium Mass Removal

Follow-up reductant dosage optimization efforts revealed that it might be possible to reduce dosage levels from 5,000 mg/L to 2,000 mg/L. However, the optimization will require the addition of approximately 250 mg/L of ferric chloride. Doing so may produce excess levels of iron precipitates and could eventually adversely affect the flow-through properties of the source soil and the ability to deliver additional pore volumes of reductant solution that may be required for treatment.

On three occasions following the conclusion of ISRM simulation, Columns A and D were flushed with treated and aerated site groundwater to evaluate the potential for oxidation of residual Cr(III) and mobilization of Cr(VI). The soluble chromium concentrations measured in the Column A effluent during the flushing events were consistently below an analytical quantitation limit of 10 µg/L. Conversely, Column D effluent measured approximately 40,000 µg/L during the flushing test.

The dimensions of the source area at the Manistee Plating site include a footprint 60 feet in length and 30 feet wide. The depth to the water table is approximately 25 feet. Therefore, the resulting vadose zone treatment volume is approximately 45,000 ft^3 (1,275 m^3). Using the porosity measured in source area soils processed for the bench study (37.7%), the pore volume requiring treatment is conservatively estimated to be 472,000 L. Assuming an application rate of 25 gal/minute (the capacity of the ex-situ treatment system), the duration to deliver one pore volume of reductant solution to source soil is approximately 6 days. Given that an estimated 4.5 pore volumes (e.g. 3 pore volumes + 50% safety factor) will be necessary to complete treatment, and assuming that at least three 10-day long incubation (no infiltration) periods are exercised between delivery periods, the total estimated duration of treatment will be 50 – 60 days. A reductant mass of nearly 1,000 Kg will be conveyed through the soils in the process.

REFERENCES

(1) Fruchter, J.S., Cole, C.R., Williams, M.D., Vermeul, V.R., Amonette, J.E., Szecsody, J.E., Istok, J.D., Humphrey, M.D, *Ground Water Monitoring and Remediation* **2000**, *Spring*, 66-77.
(2) Davis Anderson, L., Kent, D.B., Davis, J.A. *Environ. Sci. Technol.* **1994**, *28*, 1, 178-185.