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Project Work Plan Chromium Vadose Zone Characterization and Geochemistry

CC Ainsworth

May 2006

Pacific Northwest
NATIONAL LABORATORY

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Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy
Richland, Washington 99352

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1.0 Introduction

Chromate was used throughout the 100 Areas (100-B, 100-C, 100-D/DR, 100-F, 100-H, and 100-K) as a corrosion inhibitor in reactor cooling water at concentrations between 2.0 and 0.7 mg L^{-1}. After passing through the reactor, cooling water was transported through large-diameter underground pipes to retention basins for thermal and radioactive cooling prior to release to the Columbia River. In the 100-D Area, chromate concentrations at >4000 μg L^{-1} have been measured in the groundwater, which demonstrates that the source of chromate is not the cooling water but a more concentrated source. In addition, chromate concentrations upgradient of the in situ redox manipulation (ISRM) have remained high since the plume was discovered in 1999, and suggests that there is a chromate source associated with the vadose zone.

Sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) was used as the chromate cooling water source that was metered into the processed cooling water post-chlorination by a proportioning pump to achieve the desired chromate concentration (~2.0 to 0.7 mgL^{-1}). Until approximately 1953, the sodium dichromate solutions were made up in a batch system using 100-lb bags manually hoppered into large (~3,600 gal) tanks to obtain a final solution concentration of 15% $Na_2Cr_2O_7$ by wt (Whipple 1953). After 1953, 70% by wt $Na_2Cr_2O_7$ solutions were delivered to the site as pure product, stored in large tanks, and diluted as desired (Schroeder 1966). These concentrated solutions were delivered to various water treatment plants in rail cars, tanker trucks, barrels, and local pipelines as stock solutions. These concentrated chromate solutions were inevitably discharged to surface or near surface ground through spills during handling, pipeline leaks, or discarded to cribs. Unfortunately, inadvertent spills and discharges were not routinely reported, hence locating spill sites has been difficult, although discoloration (yellow-orange) of surface and shallow subsurface soils have lead to discovery of multiple small chromate contaminated sites throughout the 100 Areas. While the exact acidity of Hanford chromate stock solutions is not well known, a 10% $Na_2Cr_2O_7$ (0.82 mol L^{-1} Cr) has a pH of 3.5, a 70% $Na_2Cr_2O_7$ (8.96 mol L^{-1} Cr) will be lower (~1.5 to 2), but addition of concentrated sulfuric acid to these stock solutions may have occurred. The pH of these solutions, buffering capacity, and counter ion concentration is critical to $Na_2Cr_2O_7$ solution vadose zone geochemistry.

One such example of Cr(VI) in the vadose zone was discovered in the 100-C Area after removal of the 100-C process water treatment head house. Below the concrete slab, a patch of yellow stained soil was observed at about 15 ft below ground surface (bgs). The sediment was excavated with a backhoe to approximately 32 ft with Cr(VI) analysis at about 1-ft intervals (Figure 1). At this point, a borehole was sunk approximately 10 to 15 ft east of the excavation site and all the way to groundwater (~80 ft below ground surface [bgs]). From the shape of the depth versus Cr(VI) plot in Figure 1, it appears that the borehole missed or just caught the edge of the upper part of the vadose zone plume until about 60 ft (the insert, Figure 1a, is an enlargement of the 40- to 88-ft section of the borehole). Other examples of small vadose zone plumes have been found and remediated. While these small spill sites and associated data clearly indicate that Cr(VI) is being retained in the vadose zone and possibly connected to the groundwater, the mechanism(s) by which Cr(VI) is retained is limited or non-existent.

The Hanford vadose zone material (Hanford and Upper Ringold formations) is characterized by Pleistocene-age, catastrophic flood deposits and riverine and lucustrine deposits, respectively, with very low natural organic matter content. While sediment texture varies with depth (from coarse to silty sand), x-ray diffraction (XRD) and optical microscopic analyses indicate that sediment mineral composition remains relatively constant from the upper to lower Hanford formation. The sand mineralogy is dominated by quartz, plagioclase, hornblende, and mica (muscovite, biotite) with minor magnetite, orthoclase, ilmenite; and the silt and clay mineralogy contains micas, vermiculite, chlorite (clinochlore), and ferrigenous biedellite. The natural pH of these sediments ranges between pH 7.5 to 8.5 in the absence of caliche, which is found occasionally in the Hanford formation. At neutral and alkaline pH, chromate moves nearly unretarded (no adsorptive retardation) through the sediments of the Hanford vadose and saturated zones (Ginder-Vogel et al. 2005; Poston et al. 2001; Fruchter et al. 2000).

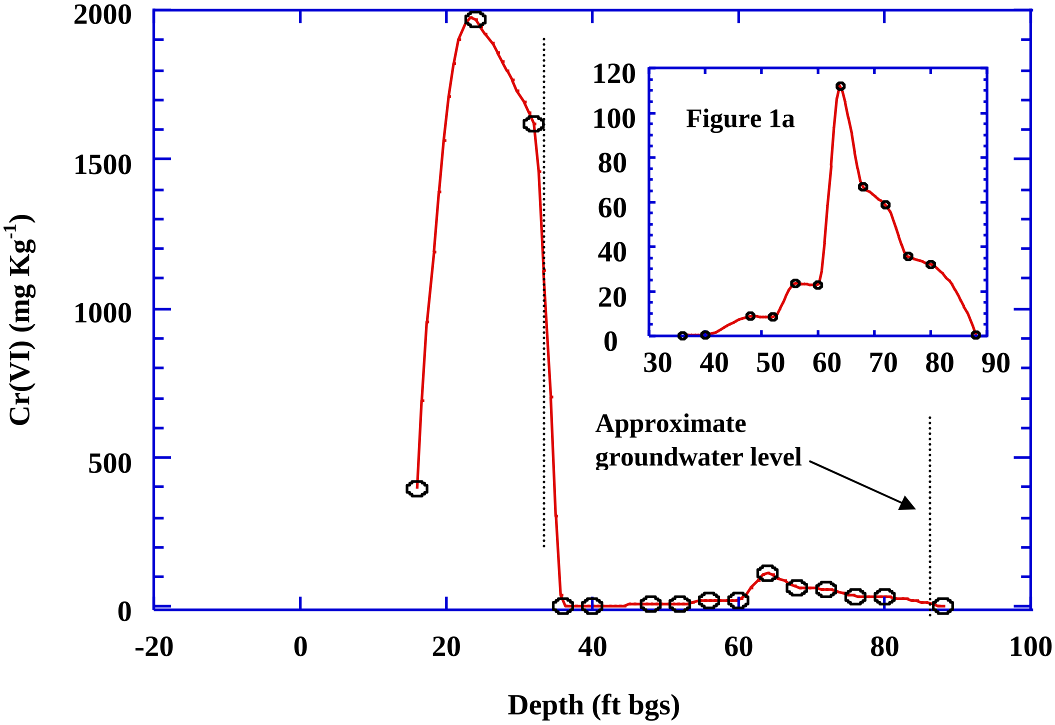

Figure 1. Cr(VI) Concentration Data with Depth from Sediment Beneath the 100-C Process Water Treatment Plant Head House (dashed line denotes shift from backhoe excavation to borehole sample collection; Figure 1a is an expanded view of borehole collected data)

2.0 Technology Description

The reduction of Cr(VI) to Cr(III) can occur in the presence of aqueous and sorbed Fe(II), reduced sulfur compounds, soil organic matter, and via microbial processes (Ginder-Vogel et al. 2005 and references therein; Fendorf and Li 1996; Fendorf et al. 2000). The Hanford vadose zone, however, is an oxic, very low organic carbon content oligotrophic environment, and any substantive microbial reduction of Cr(VI) requires major additions of both NO_3^- and organic carbon (Oliver et al. 2003). While there are Fe(II)-bearing minerals present in the Hanford and Upper Ringold formations, Ginder-Vogel et al. (2005) demonstrated no retardation of Cr(VI) occurred in these sediments except after pretreated with a strong

(0.5 mol L^{-1} HCl) acid. Similar studies with these sediments demonstrated no Cr(VI) retardation in the absence of a strong base (simulating the leaching of highly alkaline, saline underground storage tank leaks) (Zachara et al. 2004; Qafoku et al. 2003). In both of the latter cases, Fe(II) solubilized by mineral dissolution (acid or base) subsequently reduced Cr(VI) to Cr(III). Hence, low pH stock dichromate solutions spilled/discharged to ground could result in solubilization of ferrous iron from dissolution of Fe(II)-bearing mineral phases.

As the pH of an infiltrating $Na_2Cr_2O_7$ solution is neutralized the potential for Fe(II) solubilization and CrO_4^{-2} reduction becomes limited, and retention of CrO_4^{-2} in the vadose zone would require other physico-chemical processes. While there is little or no mechanistic data related to Cr(VI) retardation in the oxic vadose zone or aquifer sediments in the 100 Areas of the Hanford Site, we posit that vadose zone retention of CrO_4^{-2} in the 100 Areas of the Hanford Site probably results from physical matrix potential effects holding CrO_4^{-2} contaminated pore water against gravimetric force, and with time (up to 40 or 50 years) water content reduces to more typical vadose zone conditions (~15% by wt) creating conditions under which normally very soluble and slightly soluble CrO_4^{-2} phases form. These soluble forms could then act as continual sources of groundwater CrO_4^{-2} contamination.

Recent investigations of CrO_4^{-2} contamination in the Hanford vadose zone sediment beneath the SX Tank Farm found evidence that suggests formation of soluble CrO_4^{-2} salts that would not normally form in an aqueous environment (Zachara et al. 2004). These sediments were exposed to Cr(VI) waste solutions for decades, and when leached with a 0.5 mol L^{-1} solution showed that a fraction of the Cr(VI) present (between 15% and 43%) was either adsorbed or precipitated, and resistant to leaching (Zachara et al. 2004). Previous studies from the same author demonstrated that CrO_4^{2-} formed a relatively weak outer sphere surface complex and adsorption of this anion was suppressed by other electrolyte anions, mainly NO_3^-, HCO_3^-, SO_4^{2-} (Zachara et al. 1987; Zachara et al. 1988). For this reason, Cr(VI) retardation via adsorption is unlikely to occur under the conditions of the Hanford vadose zone. On the other hand, high concentrations of CrO_4^{2-} may induce precipitation of a moderately soluble mineral (hashemite: $BaCrO_4$) and/or the formation of the less soluble solid solution of $BaCrO_4$-$BaSO_4$. These phases may control Cr(VI) solubility and mobility in aged contaminated sediments. A single SX-108 sediment leached with a 0.5 mol L^{-1} solution, exhibited a CrO_4^{2-} release profile that could be fit to a non-reactive transport model suggesting that all the CrO_4^{2-} associated with this particular sediment was freely soluble and unretarded; possibly held in the sediment by matrix forces or as a very soluble salt not unlike sodium chromate whose precipitation was induced by low water potential and high Na and CrO_4^{2-} concentration. The conditions under which the sediments at the SX Tank Farm and the 100 Areas were exposed to CrO_4^{2-} contamination are substantially different, yet retention of CrO_4^{2-} in the vadose zone does occur and the mechanism(s) associate with the 100 area CrO_4^{2-} retention may very well be of a similar nature as those observed in the aforementioned study.

3.0 Work Plan Objectives

The major objectives of the proposed study are to (1) determine the leaching characteristics of Cr(VI) from contaminated sediments collected from 100 Area spill sites, (2) elucidate possible Cr(VI) mineral and/or chemical associations that may be responsible for Cr(VI) retention in the Hanford Site 100 Areas through the use of (i) macroscopic solubility studies and (ii) microscale characterization of contaminated sediments, and (3) from these data construct a conceptual model of Cr(VI) geochemistry in the Hanford 100 Area vadose zone. These objectives are based on locating and obtaining contaminated sediment with depth and at varying Cr(VI) concentrations as we hypothesize that mineral/chemical-Cr(VI) associations should be related to the total Cr concentration and other master geochemical variables (e.g., pH, counter-cation type and concentration, and water content). In addressing these objectives, additional benefits accrued will be (1) a fuller understanding of Cr(VI) entrained in the vadose zone that will that can be utilized in modeling potential Cr(VI) source terms, and (2) accelerating the Columbia River 100 Area corridor cleanup by developing remedial action based on a fundamental understanding of Cr(VI) vadose zone geochemistry.

4.0 Project Scope

The following six work elements, outlined below, form the scientific basis for this proposed project, and will work closely with the proposed drilling campaign in the 100-D Area to obtain sediment samples when available. The science investigations of these work elements (Tasks 2-5) are structured on recent successful investigations of Cr, Cs, and U geochemistry that the scientific leads performed and which are documented in the attached resumes. In addition, these tasks are integrated so that resources are maximized. That is, sediments used by a given task will be based on preliminary characterization results, and as the project unfolds, findings from other tasks will help direct study to/of particular sediments.

4.1 Task 1: Project Management

(Leads: Fruchter/Ainsworth)

This task will plan, organize, and provide top-level guidance and direction for overall project performance. Also, it will provide project-level cost and schedule control, tracking, and reporting. Coordinate the Columbia River Protection Supplemental Technologies Project work scope with DOE, Richland Operations, the Groundwater Remediation and Closure Assessment Project, and the Office of River Protection, including participation in planning, peer reviews, and periodic project meetings.

4.2 Task 2: Identification/Collection/Characterization

(Lead: Ainsworth)

This work element consists of identifying potential locations of Cr contaminated sediment, sampling those locations, preliminary characterization, sample storage, and distribution of sampled materials to other work elements.

As previously noted, several Cr contamination sites were located in the 100-B/C Area, and while these sites have been remediated by Washington Closure Hanford, LLC, several other location have been identified (Figure 2). Currently, we have collected a grab sample (site A, Figure 2) whose estimated Cr concentration is about 1,200 mg Kg^{-1} Cr and is proximal to the previously excavated Cr site (data shown in Figure 1) below the water treatment head house. Two additional sites have been located within the 100-B/C Area (site B and C; Figure 2) that are outside the current Washington Closure Hanford, LLC scope of work but will be proposed for their 2007 work scope. Site B has been excavated to 3 ft and the surface of this excavation is estimated to contain 3,500 mg Kg^{-1} Cr (estimates were made by field portable x-ray fluorescence spectroscopy [XRF]). Site C is located below a concrete monolith that supported

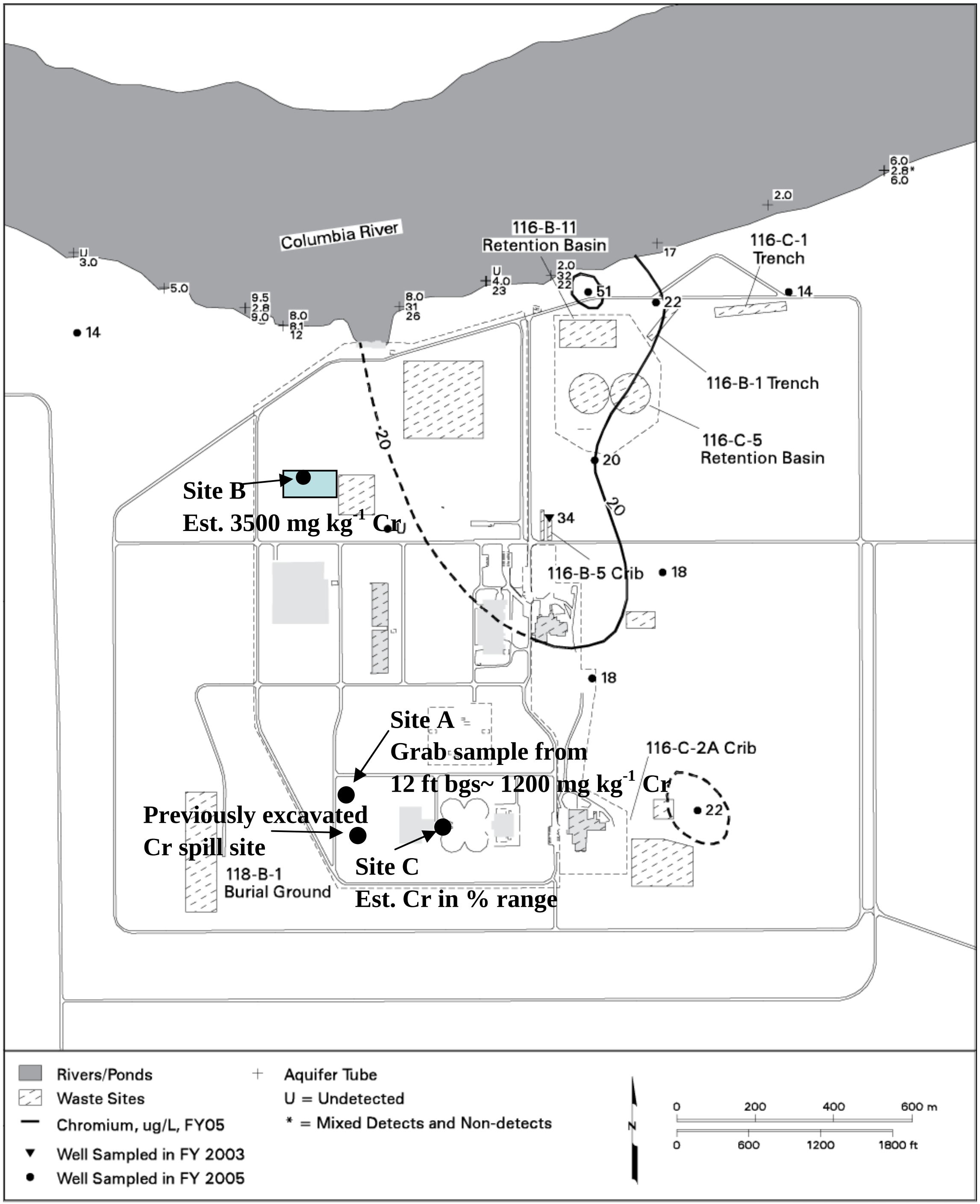

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Figure 2. Average Dissolved Chromium Concentrations in 100-B/C Area, Top of Unconfined Aquifer, and Potential Cr Sampling Sites

pumps and chlorination equipment associated with the process water treatment plant; the site has been excavated to approximately 15 ft, but the estimated Cr level is still in the percent range. The depth of Cr contamination at either site is not known. From preliminary discussions with Washington Closure Hanford, LLC, it is believed that excavation of both sites is possible and may be performed in a cooperative venture. The grab sample currently available will allow initial preliminary characterization, but the focus will be on fresh samples that incorporate a spatial (depth) component to the investigation.

These two sites offer an opportunity to collect Cr contaminated samples with depth and varying Cr concentration that have been in ground for at least 30 years (possibly 40 years). Sites would be sampled below ground surface and, therefore, would not be greatly influenced by surface environmental fluctuations of temperature, organic carbon from detritus, or near surface caliche deposits. In addition, samples can be excavated in the short term. Future sites are anticipated in the 100-D Area as a result of the proposed coring campaign; sediment samples retrieved from this effort will be selectively incorporated into the proposed Cr vadose zone geochemistry efforts as they become available. All collected samples will be collected in plastic buckets, sealed and stored at 4°C.

Preliminary characterization will be performed on sampled sediments as quickly as possible after collection. Characterization will include pH, total Cr (by XRF), 1:1 water/sediment extraction, complete anion/cation analysis, and Cr(VI) extraction and analysis (SW-846 Method 3060A, *Alkaline Digestion for Hexavalent Chromium*; SW-846 Method 7196A, *Chromium, Hexavalent (Colorimetric)*. Ideally, 10 to 20 sediments contaminated with varying concentrations of Cr(VI), from varying depths, geologic units (upper and lower Hanford formation, Upper Ringold Formation), and from different areas within the 100 Areas will constitute a library of sediments and preliminary characterization data that can be used for detailed leaching, macroscopic and microscale characterization.

4.3 Task 3: Column Leaching Studies

(Leads: Ainsworth/Qafoku)

This task will investigate Cr(VI) advective transport under saturated conditions from contaminated sediments from the Hanford 100 Area. While the transport of chromate through uncontaminated sediments is not expected to exhibit retardation, Cr(VI) release from aged contaminated sediments are expected to (1) be kinetically controlled and the release rate will be a function of the pore water velocity (fluid residence time); (2) Cr(VI) concentration will rebound during the stop-flow events, but it will decrease quickly to concentration values observed before the stop-flow (if observed, rebounded concentrations will most likely be limited by the solubility of Cr(VI) solid phases); and (3) the rate of rebounding will decrease with leaching time.

One-dimensional saturated miscible-displacement experiments will be conducted as part of this investigation with at least five uncontaminated sediments and five contaminated sediments. Polyvinyl chloride (PVC) columns with a 3.2-cm inner diameter and 15-cm length will be packed uniformly with each of the sediment. The sediment will be poured into the columns in 10-g increments which will then tamped by hand with a plastic dowel to as high a density as possible. Before adding the next increment, the surface of the tamped portion will be lightly scratched to minimize layering inside columns. Porous plates (0.25 cm thick and 10 μm pore diameter) will be used at the top and bottom of each column to assist in uniform distribution of the leaching solution at the column inlet, and to prevent sediments from being removed from, or blocking the column outlet and tubing that connected the column outlet with syringe pumps. A high performance liquid chromatography (HPLC) pump will be connected to the column inlet. Effluent samples of about 2 to 3 ml will be collected in a fraction collector about every 0.5 pore volumes (more frequently, depending on the total pore volume of the column). Chromate and pH will be determined in each fraction collected and cation and anion suites determined periodically; and before and after each stop-flow event.

The columns packed with uncontaminated sediments will be leached with a Na_2CrO_4 solution and the Cr(VI) concentration measured at the column outlet will be used to plot Cr(VI) breakthrough curve (BTC) in different sediments. These columns while yield a set of baseline Cr(VI) BTC to which other contaminated column BTC may be compared. Cr(VI) transport will be followed initially at two input solutions Cr(VI) concentrations (1 and 50 mg L^{-1}); if higher initial Cr(VI) concentrations are required additional BTCs can be initiated. A tracer (such as Br) will be simultaneously injected with the leaching solution. The CXTFIT code will be used to calculate transport parameters based on the Br BTC (Parker and van Genuchten 1984; Toride et al. 1999). The experimental water flux will be calculated as the average flow rate divided by the area of the column. Mean pore water velocity V will be calculated as the experimental water flux divided by the volumetric water content (θ), and the equilibrium adsorption model will be used to calculate D (dispersion coefficient) and R (retardation coefficient). This model assumes that the column is at physical equilibrium. In several columns, we will fit the two–region, physical non-equilibrium model to the Br BTC data using R as a known parameter and D, β (the mobile water fraction), and ω (the mobile-immobile region exchange term) as unknown parameters (Leij and Dane 1992). This is necessary to show that all water is mobile and that physical non-equilibrium will play no significant role in Br (and Cr) transport. The dispersivity values ($\lambda = D/V$) and the values of the Peclet number ($P_N = L/\lambda$, where L is the column length) will be calculated for each column. All parameters calculated from the Br BTC will be used to fit Cr BTC and calculate the Cr retardation coefficient in each experiment (Qafoku et al. 2003).

Columns packed with the contaminated sediments will be leached with a solution that will be equilibrated with uncontaminated sediments packed in a large column, or a simulated pore water determined from uncontaminated column effluent. If the former influent solution is utilized, contact time will be sufficiently large so that quasi-equilibrium conditions may be established between the solid and the aqueous phases. This solution will be used to leach the small columns packed with contaminated sediments to investigate Cr(VI) release extent and rate from these sediments.

Stop-flow (SF) events (Brusseau et al. 1997), where the inflow of the leaching solution is stopped for various time periods, will be used to assess whether Cr concentration in the effluent solutions is in equilibrium with sorbed (adsorbed or precipitated) Cr in the sediment. The SF events may be also used to study the direction and extent of a time-dependent reaction that may control Cr release in the contaminated sediments.

One flow regime that will yield a fluid residence time of 1 hour will be used in all experiments. Although the total number of the SF events that will be applied in each experiment will be decided based on measurements performed during these experiments, the initial plan is to apply at least three SFs in each experiment, as follows:

- First SF: 48 hours (2 days) at 20 pore volume (PV)
- Second SF: 72 hours (3 days) at 40 PV
- Third SF: 72 hours (7 days) at 60 PV

Cr(VI) concentration is expected to strongly rebound during the SF events. Rebounded concentrations will be controlled by the solubility of Cr(VI) mineral(s) during the first SF, and by diffusion during the second and third SF events. Cr(VI) rebounding concentration is expected to decrease with leaching time after Cr(VI) is removed from fast diffusion regions.

Cr release from the sediments may be a mechanistically complex process and the rate limiting step may involve chemical process (such as dissolution or desorption), or a physical process such as diffusion of a reactant to, or a product from a surface or particle interstices. The effect of temperature on rates of such processes can be used to distinguish diffusion control from chemical (surface) control (Brezonik 1993). The former are characterized by low activation energies (2 to 5 kcal mol^{-1}) and relatively small temperature effects (rate increases of ~1.3 to 1.5-fold for a 10°C increase in temperature, and the latter have larger E_{act} values (>7 kcal mol^{-1}). We propose to conduct temperature controlled column experiments in some contaminated sediments to calculate the activation energy of the main reaction that will control Cr release into the aqueous phase. In these experiments, the columns will be oriented vertically inside a water-bath at different temperatures (e.g., 20°C, 35°C, and 50°C).

4.4 Task 4: Macroscale Characterization

(Leads: Ainsworth/Mattigod)

This task is designed to determine the (1) chemical composition of pore water associated with Cr(VI) contaminated sediments collected from the 100 Area vadose zone, (2) potential solid phases controlling Cr(VI) solubility through geochemical modeling, and (3) the extent to which Cr(VI) can be supplied by sediment to equilibrating solutions. While column studies will investigate the leaching characteristics of Cr(VI) from contaminated sediments, long-term studies that probe pore water chemical composition changes with equilibration time, at relevant water content, and variable sediment parameters [e.g., total Cr(VI)] are required to fully understand Cr vadose zone geochemistry.

Gravimetric water content in these sediments averages about 15%, which should allow sufficient pore water to be extracted by ultracentrifugation. Depending on volume of pore water extracted, analysis of pore water will include pH, oxidation/reduction potential, electrical conductivity, and aqueous chemical composition [anion, cation, dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC) analysis]. Extraction will be performed under an inert gas atmosphere, and stored in a glovebox during sample analysis preparation.

In combination with the above extraction, three time dependent equilibrations studies will be performed at three different water contents: field moisture capacity (approximately 45% gravimetric water content), 95% gravimetric water content (near-saturation), and 1:1 sediment to water ratio. Well mixed contaminated sediment will be equilibrated with deionized water at these three water contents in a batch mode. Samples will be sacrificed at intervals of one or two months over a period of up to 12 months. Pore water from sacrificed samples will be extracted by centrifugation and analyzed as discussed above.

Geochemical data generated from all pore water analyses will be analyzed using several geochemical equilibrium codes depending on the ionic strength (IS) of the solution. For data that are nominally close to 0.5 mol L^{-1}, IS will be analyzed using either MINTEQA2 or MINEQL+. Higher IS solution data may require a free energy minimization code (i.e., GMIN) that include the Pitzer equations and the Davies equation (Felmy 1995 and references therein).

4.5 Task 5: Microscale Characterization

We will combine several analytical methods to determine the distribution and mineral associations of chromate in contaminated sediments. At the Hanford Site 100 Areas, chromate occurs at nominally trace concentrations within the saturated zone, but recent analyses of vadose zone materials from the 100-B/C Area (Figure 1) suggests Cr(VI) may be locally concentrated and only slightly mobile. This behavior is anomalous, since the chromate ion is anionic and does not normally sorb to the solid phase. We hypothesize that chromate in these sediments arises from spills and ground discharges of concentrated $Na_2Cr_2O_7$ solutions (between 15% to 70% $Na_2Cr_2O_7$ by wt), and is currently immobilized in the vadose zone by physical and geochemical processes. These solutions were naturally acidic and may have had additional H_2SO_4 added to maintain solubility. Since the chromate originated within a reactive, high ionic strength solution, the immobilizing process or processes may have included the production of insoluble Cr(III) through reductive interaction with Fe(II) in the sediment column. Alternatively, chromate may have precipitated, either as a coprecipitate within a mineral phase, or as a relatively insoluble chromate phase such as barium chromate. The latter mode of removal would likely result from the introduction of solute cations from ion exchange reactions between sodium and mineral surfaces within the sediment column. In any of these immobilization processes, the insoluble chromium would likely have been concentrated in microscopic mineral domains or as trace-level coprecipitates not readily observed macroscopically nor deduced by bulk chemical manipulations. We have had some success using a combination of electron microscopy and x-ray microprobe methods, in combination, to determine the mode of contaminant occurrence and its process-related mineral associations.

Samples will first be screened according to depth-resolved bulk compositional measurements to identify sediments containing relevant chromate concentrations within the lithological intervals present at the study sites. These include the Hanford and Upper Ringold formations, consisting of unconsolidated clastic materials of fine to coarse grain size. We will screen the sediments to remove the greater than 2-mm-size fraction, representative of relatively non-reactive materials on a volume basis. We will then choose a representative set of five sediment samples for detailed analysis, including a control of low or background chromate concentration from within the set of candidates. For comparison across samples, the samples will be described mineralogically in hand sample and analyzed for bulk mineralogy using XRD, and compositionally using XRF. XRD analysis is sufficiently precise to provide a qualitative determination of major mineral phases. XRF analysis will provide bulk compositional information for major and trace elements.

Representative subsamples will be prepared into lithologic thin sections on fused quartz slides for micro-analysis. The sections will be prepared in a water-free process to avoid chromate leaching during preparation. Initial observations will be by electron microprobe (EMP) and scanning electron microscope (SEM). These methods will produce large, low-magnification backscattered electron images of the whole sample surface for the purpose of orientation and individual clast location. In addition, the surfaces will be mapped using EMP with respect to the relative abundance of chromate, using wavelength-dispersive x-ray spectroscopy, to locate small (greater than approximately 10 μm) domains of chromate concentration. If such domains are present, more detailed abundance mapping and SEM imaging of chromate distributions will be undertaken. The detection limit for chromate by EMP is approximately 150 mg Kg^{-1}; smaller microscale abundances will be detected using x-ray microprobe analysis (XMP) at the Advanced Photon Source (APS).

Time at the APS is scheduled on a competitive basis, quarterly, and optimal information recovery is dependent on careful preparation. The XMP configuration consists of a fixed-energy x-ray beam focused on the sample surface at a spot size of approximately 5 μm diameter, with the x-ray fluorescence signal detected by energy or wavelength-dispersibe spectrometers. The sample is moved under the x-ray beam to produce two-dimensional maps of relative elemental abundance. Chromate and other elements of interest will be mapped, with a detection limit of approximately 1 mg kg^{-1} over pre-chosen areas of 1 mm x 1 mm, requiring care in choosing the analysis area. Areas on thin sections for XMP analysis will be selected based on SEM imaging results. In the absence of detectible chromate, this screening assures that XMP analysis will target areas on the thin section where clasts are present and representative of potentially reactive mineral components. The quartz slide provides an impurity-free background. When sediment domains containing chromium are identified, the chromium valence will be determined using microscale x-ray absorption near-edge structure (XANES) analysis. Potential mineral associations with concentrations of chromium will be investigated by imaging the high-chromate areas in detail by SEM, followed by superposition of the XMP and SEM images using Photoshop. This method provides an unambiguous, high-resolution association of trace element and mineral components within the sediment sample.

Our methodology has the advantage that it assays the sample at high resolution only at areas of most interest, and can focus efficiently on contaminant occurrences over a large range in concentration, i.e., from 1 mg kg^{-1} to 100 wt.%, using technologies whose complexity and accessibility are variable according to the contaminant abundance. We will identify whether the non-mobile chromium in 100 Area sediments is present in discrete phases of whatever size, disseminated in physically inaccessible mineral domains, or coprecipitated in secondary minerals, so long as it's in situ microscale concentration is higher than approximately 1 mg kg^{-1}.

4.6 Task 6: Reporting

This work element consists of managing, compiling, and evaluating all of the data generated during these studies and preparing a final report. The final report will cover all activities outlined in the above tasks and integrate with the reporting from the proposed coring campaign.

5.0 Assumptions

The following assumptions pertain to this scope of work:

- No project specific Quality Assurance Plan (QAP) will be required; work under Task 2 will be conducted under the Groundwater Performance Assessment Project QAP (PNNL 2006), and all other laboratory studies will be conducted under PNNL Good Laboratory Practices Standards.
- Cr contaminated sediment samples can be collected in a timely manner from the 100 Area vadose zone.
- Scheduling of beam time at the APS, Argonne National Laboratory moves forward as anticipated.

- The schedule shown in this proposal will be approved by DOE and the appropriate regulatory agencies.
- The project will start on or before August 15, 2006.

6.0 Schedule

A detailed schedule for the Cr Vadose Zone Geochemistry Project is provided in Table 1. The project is scheduled for completion within 18 months after initiation. While this project is not dependent on the success of the proposed drilling campaign, it will coordinate collection and sampling of contaminated sediments identified by coring in the 100-D Area.

7.0 Budget

The total budget for this plan is estimated to be approximately $500,000.

Table 1. Schedule for the Chromium Vadose Zone Geochemistry Project

Phytoremediation Treatability Study Activities	**Start Date**	**Finish Date**	**FY 2006**		**FY 2007**												**FY 2008**					
			2006					**2007**												**2008**		
			Aug	**Sept**	**Oct**	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sept**	**Oct**	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**
Project Management	5/15/2006	2/31/2008	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Sample Identification/Collection/ Characterization	5/15/2006	7/31/2006-	—	—	—	—	—	—	—													
Column Leaching Studies	12/1/2006	12/30/2007					—	—	—	—	—	—	—	—	—	—	—	—	—			
Marcoscale Characterization	10/1/2006	5/31/2008			—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
Microscale Characterization	10/1/2006				—	—	—	—	—	—	—	—	—	—	—	—	—	—	—			
Reporting (* = monthly report)			*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	—	Final report —	—	—	—

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