

Identification of a Hanford Waste Site for Initial Deployment of the In Situ Gaseous Reduction Approach

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November 2000

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under the Subsurface Contaminants Focus Area

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Richland, Washington 99352

Summary

The U.S. Department of Energy is currently developing In Situ Gaseous Reduction (ISGR), a technology to clean up soil at sites contaminated with hexavalent chromium [Cr(VI)]. This document presents the results of recent characterization activities undertaken at a number of the soil wastes sites at the Hanford Site that are contaminated with Cr(VI) and provides the basis for selecting a specific test location to demonstrate the ISGR approach.

This data was gathered by sampling surface and subsurface soil samples that were analyzed for hexavalent chromium. Previously collected data were also utilized where available. In addition, an early phase of this activity involved analysis of drill cuttings associated with installation of new groundwater wells in the 100-D Area during FY 1999. Soil sampling was conducted at the following specific sites:

- 100-C Pluto Crib
- 183-DR Head House and Filter Plant
- 108-D Site
- 190-D Complex
- 100-D Sodium Dichromate Transfer Station
- 183-H Solar Evaporation Basins
- 183-KE and 183-KW.

The samples collected at the 100-C Pluto Crib were obtained from an excavation pit, whereas subsurface samples collected at the other sites were obtained using a Geoprobe™ and a cone penetrometer. In addition, surface samples were collected for analysis at several sites.

Significant concentrations of Cr(VI) were identified at the 190-D and 183-KW sites, which is consistent with their operational histories. These sites were initially identified as the best candidates for an ISGR demonstration. However, results of field sampling activities suggest that Cr(VI) contamination decreases with depth at 190-D and is not homogeneously distributed. It also appears to decrease with depth at 183-KW, although a hard zone at about 3 m (10 ft) prohibited obtaining deeper samples. In addition, site access is difficult at 183-KW because of utilities and lines.

The results of this study indicate that the 183-DR site is the best location for the first demonstration and deployment of the ISGR technology at the Hanford Site. This recommendation is based primarily on recent groundwater data that indicates a source of Cr(VI) contamination in the vadose zone source at this site. The recommendation is further supported by operational records that indicate Cr(VI) was added as a corrosion inhibitor to water treated at 183-DR. Significant Cr(VI) contamination was not detected in sediment samples collected by Geoprobe™ at the site, but low levels of contamination were present in samples taken at the center of the site at a depth of 4 m (13 ft) by cone penetrometer. An area of high total chromium, primarily in the form of Cr(III), was also identified at the northeastern corner of the head house foundation by track hoe excavation activities, accompanied by trace levels of Cr(VI). An acidic

chromate solution originating in storage tanks in the head house may have been released to the soil in this area, resulting in the reduction and precipitation of a portion of the Cr(VI) and migration of the remainder deeper into the vadose zone. Other potential sources of Cr(VI) contamination also exist at 183-DR, notably chemical lines and a filter plant.

Deeper characterization should be undertaken at the 183-DR site by drilling vadose zone boreholes to groundwater. Groundwater samples and soil core samples will be collected for analysis of Cr(VI) and determination of soil characteristics. If sufficient concentrations of Cr(VI) are found at the 183-DR site as a result of drilling vadose zone boreholes, a demonstration workplan will be developed that provides a detailed description of the activities and resources required to test the ISGR technology at this site. Approval of the workplan by Hanford Site regulators and stakeholders will be the final step in preparing for the demonstration. Subsequent to completion of the test, site data will be collected and an evaluation of treatment effectiveness completed. If the degree of treatment effectiveness meets clean up standards and the technology is determined to be cost effective, consideration will be given to deploying the ISGR technology at 183-DR to complete remediation of the site.

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1.0 Introduction

Laboratory investigations conducted over the last several years indicate that reduction and immobilization of chromium in contaminated soils can be achieved through treatment with a diluted hydrogen sulfide (H_2S) gas mixture. The primary chemical reaction of interest associated with these tests involves the reduction of Cr(VI) to Cr(III), with subsequent precipitation as a nontoxic solid product.

The application of diluted hydrogen sulfide to chromium reduction in the field can be accomplished through the injection of the gas mixture into waste site soils in a central borehole (Figure 1). The gas mixture is then drawn through the waste site by vacuum applied at extraction boreholes located at the site boundary. Monitoring of breakthrough of hydrogen sulfide at the extraction wells provides a basis to assess treatment progress. Verification of treatment effectiveness is subsequently accomplished through comparison of Cr(VI) distribution through site soils before and after treatment.

Initial field testing of the In Situ Gaseous Reduction (ISGR) approach has been completed at White Sands Missile Range in a cooperative effort between the U.S. Department of Energy (DOE) and the Department of Defense (Thornton et al. 1999; see Figure 1). In this pilot-scale test, in situ remediation was undertaken by injecting 200 ppm hydrogen sulfide into chromate-contaminated soils. Final performance assessment findings indicate that 70% of the Cr(VI) present at the site was reduced to Cr(III) during the test, thus verifying the effectiveness of the approach. An even higher degree of effectiveness is anticipated as design improvements to the technology are developed. These improvements will be incorporated into a full-scale demonstration at a DOE site as part of deployment of the technology.

Thornton and Last^(a) presented a strategy to select the initial DOE deployment site for the technology. Their study concluded that the Hanford Site was the facility having the greatest near-term need for this technology after considering several DOE sites.

The primary objective of this document is to utilize existing information and to collect additional field data to determine which Hanford waste sites are suitable for an initial deployment of this technology. Section 2.0 describes the methods and overall approach in the characterization and selection process, while Section 3.0 summarizes the site specific information gathered during this study. Section 4.0 identifies the site(s) chosen for the initial deployment at the Hanford Site and provides recommendations regarding additional characterization needs.

English units are used in this report because they are used by drillers to measure and report depths and well construction details. The conversion to metric can be made by multiplying feet by 0.3048 to obtain meters or by multiplying inches by 2.54 to obtain centimeters.

^(a) Thornton, E. C., and G. V. Last. 1999. *Selection of a DOE Deployment Site for Demonstration of the In Situ Gaseous Reduction Approach (Draft)*. Pacific Northwest National Laboratory, Richland, Washington.

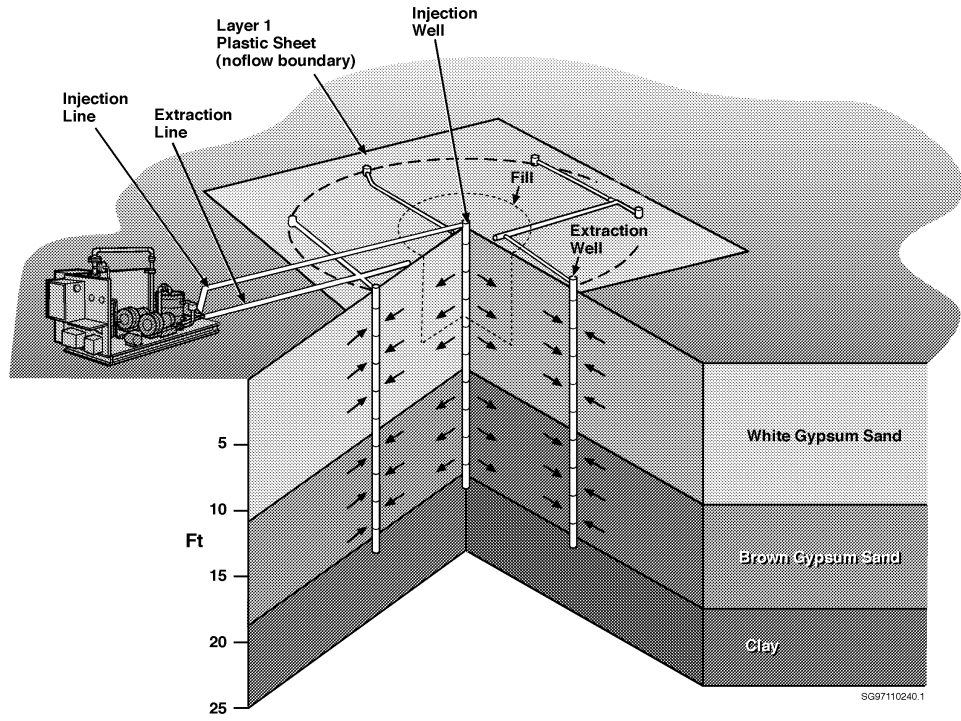


Figure 1. In Situ Gaseous Reduction System and Wellfield Network (White Sands Missile Range Demonstration)

2.0 Approach for Selection of the Deployment Site

Hexavalent chromium is an important contaminant in the 100 Areas at the Hanford Site, as evidenced by major groundwater plumes. However, information related to vadose zone sources is limited. Thus, the objective of this study was to identify Cr(VI) sources using historical information and by collecting additional data. This information will thereby serve as the basis to select the ISGR test site.

The primary criteria used as the basis for the selection of the test and initial deployment site at Hanford are as follows:

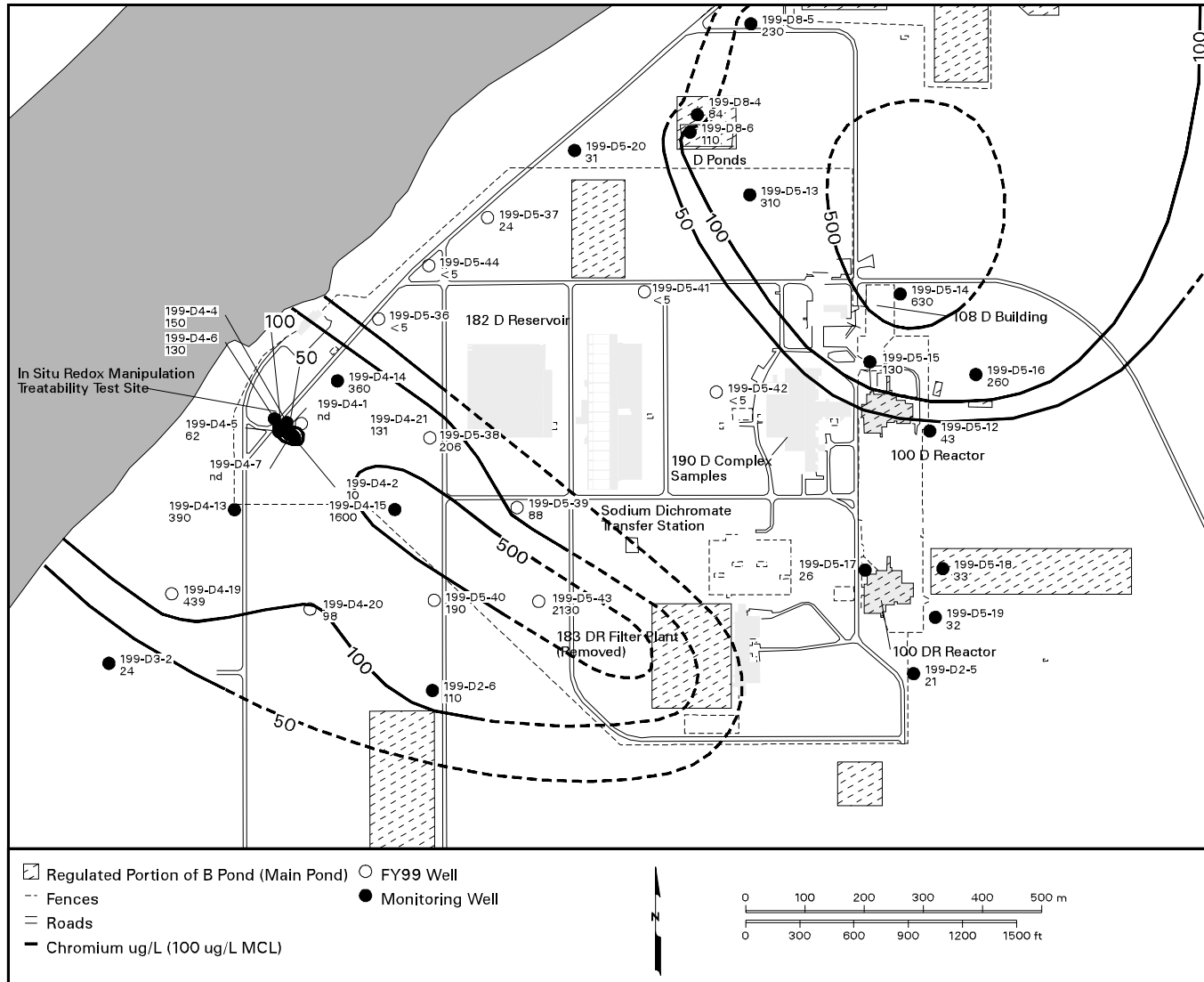
- depth of contamination >15 ft
- concentration of Cr(VI) in soil >2.2 mg/kg
- site should not be near the Columbia River
- site should be identified as a waste site scheduled for remediation
- suspected continuing source of groundwater contamination.

The depth minimum of 15 ft reflects the general feasible limit of typical excavation activities; thus, contamination extending below this depth could potentially be better addressed by an in situ remediation approach. The minimum concentration limit of 2.2 mg/kg (ppm) Cr(VI) is based on river protection standards established for the 100 Areas at the Hanford Site. The demonstration should be far enough from the Columbia River to ensure that soil treatment activities will have no impact on the river environment. A higher priority is also given to sites that are scheduled for remediation in the near term.

In addition, members of the Hanford Site Technology Steering Committee (STCG) have expressed a preference for deployment in the 100-D Area has been expressed by members of the Hanford Site Technology Steering Committee (STCG) because the largest Cr(VI) groundwater plumes are located in that area. Figure 2 identifies major facilities in the 100-D Area and the configuration of the major Cr(VI) groundwater plumes present.

The major objective of this study was to undertake sufficient field sampling and analysis of soil samples to determine which site(s) are viable for testing and deployment of the In Situ Gaseous Reduction approach based on the criteria listed above. The methods and activities associated with obtaining the necessary characterization data for supporting this decision are summarized below.

An early phase of this activity involved analysis of drill cuttings associated with installation of new groundwater wells in the 100-D Area during FY 1999. These and all other soil samples associated with this study were analyzed for Cr(VI) by a colorimetric approach (Appendix A).



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Figure 2. Facilities and Cr(VI) Groundwater Plumes in the 100-D Area

Vadose zone sampling also was conducted at the following specific sites:

- 100-C Pluto Crib
- 183-DR Head House and Filter Plant
- 108-D Site
- 190-D Complex
- 100-D Sodium Dichromate Transfer Station
- 183-H Solar Evaporation Basins
- 183-KE and 183-KW.

The samples collected at the 100-C Pluto Crib and the 100-D Sodium Dichromate Transfer Station were obtained from excavation pits. Subsurface samples collected at the other sites were obtained by Geoprobe™ and a cone penetrometer. In addition, surface samples were collected for analysis at several of the above sites.

3.0 Summary of Characterization Activities

Characterization data collected during this study are summarized below. An evaluation of how well each site meets the selection criteria and recommendations for future characterization efforts are also presented.

3.1 100-D Well Cuttings

Bechtel Hanford, Inc. (BHI) drilled 12 new groundwater monitoring wells at 100-D in FY 1999. Pacific Northwest National Laboratory (PNNL) participated in this effort by analyzing vadose zone samples (cuttings) from seven of these wells for Cr(VI) as described in Appendix A. The objective of this effort was to obtain information regarding Cr(VI) contaminant sources associated with the plume west of the 100-DR reactor (see Figure 1). Sediment analyses were performed on samples from the following wells:

- 199-D4-20
- 199-D5-38
- 199-D5-39
- 199-D5-40
- 199-D5-41
- 199-D5-42
- 199-D5-43.

Approximately 70 samples, collected during April and May 1999 at depths ranging from 5 ft to 80 ft (top of the unconfined aquifer), were analyzed for Cr(VI). All analytical results were non-detects (<0.4 ppm Cr(VI)). The negative results may be related to the fact that the wells were not drilled near the vadose zone source, which appears to be in the vicinity of the 183-DR facility (see Figure 2). However, Cr(VI) may also have been reduced during the drilling process (air rotary). Reduction could be brought about by iron released during abrasion of the drill bit or by exposure of fresh Fe(II)-bearing surfaces of basalt cobbles fractured during drilling (White et al. 1985). Generation of hydrogen during drilling may also have occurred (Bjornstad et al. 1994), thereby potentially reducing Cr(VI).

3.2 100-C Pluto Crib

The 100-C Pluto Crib (116-C-2A) is a facility currently being remediated in the 100-C Area, primarily by excavation. This approach is considered appropriate for removal of radionuclides. However, it was believed that Cr(VI) could be present at depths of >15 ft because it is highly mobile. If so, this site would be a candidate for deployment of the ISGR approach to address the contaminated zone below this excavation limit.

During excavation of surficial material at this site by CH2M HILL Hanford, Inc. (CHI) in June 1999, sediment samples were collected from a pit and submitted to PNNL for analysis of Cr(VI). All samples

were below the limits of detection for Cr(VI) per the approach presented in Appendix A (see data in Table 1). Thus, this site has been eliminated from the list of candidate test sites for deployment of the technology.

3.3 183-DR Head House and Filter Plant

The former location of the 183-DR facility is shown in Figure 2. This appears to be the source of Cr(VI) present in the plume west of the site. This facility was originally used to remove suspended solid material from the cooling water and to add Cr(VI) as a corrosion inhibitor before passing the water into the DR reactor.

During July and August 1999, CHI and PNNL staff drilled a series of Geoprobe™ holes in the vicinity of the former head house and filter plant to obtain sediment samples for analysis of Cr(VI). The locations of these holes are presented in Figure 3. Sampling was restricted to the outer edges of a large concrete slab in the area. In addition, the Geoprobe™ had difficulty obtaining samples at depths of greater than about 15 ft, which appears to be the top of an open-framework gravel. However, in several instances samples were collected to depths of greater than 20 ft (below the gravel bed). Analytical results for the Geoprobe™ sediment samples collected from the 183-DR site are presented in Table 1. Note that essentially no Cr(VI) was detected in any of these samples.

In October 1999, Applied Research Associates Inc (ARA) used a cone penetrometer to obtain sediment samples at 13 ft depth near the center of the site (Figure 3). Possible Cr(VI) contamination is indicated by the results (≤ 0.5 ppm; Table 1). Deeper sampling was not possible owing to the presence of a concrete structure or cobble bed at a depth of 13 ft.

Additional sampling was undertaken in FY 2000 (January 26-27, 2000) at the 183-DR site. This task involved digging two trenches on the east and west sides of the head house foundation using a track hoe (Figure 3). In addition, a pit was excavated on the south side of the head house where a former drain field was located. The trenches were excavated to the concrete floor or foundation of the head house (a depth of several ft to 15 ft) over most of their lengths and the pit was excavated to a depth of about 25 ft.

The trench located on the east side of the head house was also extended to the north side of the head house and beyond the concrete slab. Plant drawings indicate that chromate storage tanks were originally located in this part of the head house and also indicate that a drainage line exited from the north end of the head house. A slight reddish orange discoloration of the soil was noted in the eastern trench just beyond the northern end of the head house foundation. This was most noticeable at a depth of about 3 ft and extended over a moderately large area (perhaps 15 ft in diameter). A vitreous clay drainage pipe was located at a depth of about 15 ft and was also associated with soil discoloration. Sampling was conducted at this location to a depth of about 25 ft.

A total of 50 samples (including duplicates) were collected during excavation of the trenches and pit. All were analyzed by PNNL for Cr(VI) with generally no significant concentrations detected. The discolored soil from the northern end of the head house contained a trace of Cr(VI) in one sample, however. Ten of the excavated soil samples from the two trenches were selected for further analysis of metals by

Table 1. Chromium(VI) Analytical Results from 100-C, 100-D, 100-H, and 100-K Area Sediment Samples

Location ID	Depth	Sample Location	Sediment [Cr+6] (ppm)	Easting (m)	Northing (m)
A1-03	>15'	100-C Pluto Crib	0.1		
A1-04	>15'	100-C Pluto Crib	0.1		
A1-10	>15'	100-C Pluto Crib	0.0		
A1-16	>15'	100-C Pluto Crib	0.0		
A2-03	>15'	100-C Pluto Crib	0.0		
A2-06	>15'	100-C Pluto Crib	0.0		
A2-07	>15'	100-C Pluto Crib	0.0		
A2-15	>15'	100-C Pluto Crib	0.0		
A3-01	>15'	100-C Pluto Crib	0.1		
A3-02	>15'	100-C Pluto Crib	0.0		
A3-04	>15'	100-C Pluto Crib	0.0		
A3-11	>15'	100-C Pluto Crib	0.0		
GPD1	0.5'	183-DR	0.0	573243.8	151193.7
GPD2	0-2.5'	183-DR	0.0	573242.6	151193.8
GPD2	4-4.5'	183-DR	0.0	573242.6	151193.8
GPD2	6-6.5'	183-DR	0.0	573242.6	151193.8
GPD2	8-8.75'	183-DR	0.0	573242.6	151193.8
GPD2	10-12'	183-DR	0.0	573242.6	151193.8
GPD2	20-22'	183-DR	0.0	573242.6	151193.8
GPD3	1-1.5'	183-DR	0.0	573249.6	151209.7
GPD3	2-3'	183-DR	0.0	573249.6	151209.7
GPD4	2-2.4'	183-DR	0.0	573242.5	151201.3
GPD4	4-4.5'	183-DR	0.0	573242.5	151201.3
GPD8	6-8'	183-DR	0.0	573219.3	151211.9
GPD9	14-14.3'	183-DR	0.0	573217.0	151211.6
GPD9	16-18'	183-DR	0.0	573217.0	151211.6
GPD9	18-20'	183-DR	0.0	573217.0	151211.6
GPD10	17-19'	183-DR	0.0	573215.7	151211.4
GPD11	15-17'	183-DR	0.0	573240.5	151222.2
GPD12	4-6'	183-DR	0.0	573356.1	151190.0
GPD12	6-8'	183-DR	0.0	573356.1	151190.0
GPD12	8-10'	183-DR	0.0	573356.1	151190.0
GPD12	12-13'	183-DR	0.0	573356.1	151190.0
GPD15	5-7'	183-DR	0.0	573367.1	151187.2

Table 1. (contd)

Location ID	Depth	Sample Location	Sediment [Cr+6] (ppm)	Easting (m)	Northing (m)
GPD15	11.5-12'	183-DR	0.0	573367.1	151187.2
GPD15	15-17'	183-DR	0.0	573367.1	151187.2
GPD15	17-19'	183-DR	0.0	573367.1	151187.2
GPD15	19.5-21.5'	183-DR	0.0	573367.1	151187.2
GPD15	21.5-23.5'	183-DR	0.0	573367.1	151187.2
GPD18	3.5' TOE	183-DR	0.1*	573236.9	151217.2
GPD20	6-8' TOE	183-DR	0.0	573236.8	151212.8
GPD20	8-10'	183-DR	0.0	573236.8	151212.8
GPD20	8-10' TOE	183-DR	0.0	573236.8	151212.8
GPD20	10-12'	183-DR	0.1	573236.8	151212.8
GPD20	10-12' TOE	183-DR	0.0	573236.8	151212.8
GPD21	4-6'	183-DR	0.2	573238.7	151178.4
GPD21	6-8' TOP	183-DR	0.0	573238.7	151178.4
GPD21	6-8' BOS	183-DR	0.1	573238.7	151178.4
GPD21	12-14'	183-DR	0.0	573238.7	151178.4
GPD21	12-14' D	183-DR	0.0	573238.7	151178.4
GPD21	14-16'	183-DR	0.1	573238.7	151178.4
GPD21	14-16' D	183-DR	0.0	573238.7	151178.4
GPD21	16-18'	183-DR	0.0	573238.7	151178.4
GPD21	18-20'	183-DR	0.0	573238.7	151178.4
GPD21	20-22'	183-DR	0.0	573238.7	151178.4
183DR-CPT-2	13'	183-DR	0.4		
183DR-CPT-2	13' D	183-DR	0.3		
183DR-CPT-2	13' D	183-DR	0.5		
GPD16	4-6'	108-D	0.1	573730.9	151784.5
GPD16	6-8'	108-D	0.1	573730.9	151784.5
GPD16	8-10'	108-D	0.0	573730.9	151784.5
GPD16	10-12'	108-D	0.0	573730.9	151784.5
GPD16	12-14'	108-D	0.0	573730.9	151784.5
GPD16	14-16'	108-D	0.1	573730.9	151784.5
GPD16	14-16' D	108-D	0.0	573730.9	151784.5
GPD16B	17-19'	108-D	0.0	573731.8	151784.4
GPD16B	20.5-22.5'	108-D	0.0	573731.8	151784.4

Table 1. (contd)

Location ID	Depth	Sample Location	Sediment [Cr+6] (ppm)	Easting (m)	Northing (m)
GPD17	4-6'	190-D	1.1	573596.6	151549.6
GPD17	4-6' D	190-D	1.1	573596.6	151549.6
GPD17	6-8'	190-D	1.2	573596.6	151549.6
GPD17	6-8' D	190-D	0.8	573596.6	151549.6
GPD17	8-10'	190-D	1.0	573596.6	151549.6
GPD17	8-10' D	190-D	1.2	573596.6	151549.6
GPD17	10-12'	190-D	2.2	573596.6	151549.6
GPD17	10-12' D	190-D	2.3	573596.6	151549.6
GPD17	12-14'	190-D	0.6	573596.6	151549.6
GPD17	12-14' D	190-D	0.4	573596.6	151549.6
GPD17	12-14' D	190-D	0.9	573596.6	151549.6
GPD17	14-15.5'	190-D	0.1	573596.6	151549.6
GPD17	14-15.5' D	190-D	0.5	573596.6	151549.6
GPD22	4-6'	190-D	1.6	573596.4	151556.7
GPD22	4-6' D	190-D	1.2	573596.4	151556.7
GPD22	6-8'	190-D	1.9	573596.4	151556.7
GPD22	6-8' D	190-D	1.8	573596.4	151556.7
GPD22	8-10'	190-D	0.1	573596.4	151556.7
GPD22	8-10' D	190-D	0.1	573596.4	151556.7
GPD22	10'	190-D	1.4	573596.4	151556.7
GPD22	10-12' TOE	190-D	2.0	573596.4	151556.7
GPD22	10-12' TOE D	190-D	1.6	573596.4	151556.7
GPD22	12-14'	190-D	1.1	573596.4	151556.7
GPD22	12-14' D	190-D	1.3	573596.4	151556.7
GPD23	20-22' #1	190-D	2.1	573595.3	151556.9
GPD23	20-22' #1 D	190-D	2.5	573595.3	151556.9
GPD23	20-22' #2	190-D	0.6	573595.3	151556.9
GPD23	20-22' #2 D	190-D	1.0	573595.3	151556.9
GPD23	22-24'	190-D	0.9	573595.3	151556.9
GPD23	22-24' D	190-D	0.8	573595.3	151556.9
GPD24	2-4'	190-D	0.1	573596.8	151559.6
GPD25	2-4'	190-D	3.2	573599.5	151556.4
GPD25	2-4' D	190-D	3.1	573599.5	151556.4
GPD25	4-6'	190-D	1.1	573599.5	151556.4
GPD25	4-6' D	190-D	0.5	573599.5	151556.4

Table 1. (contd)

Location ID	Depth	Sample Location	Sediment [Cr+6] (ppm)	Easting (m)	Northing (m)
GPD26	8-10'	190-D	0.1	573593.1	151557.7
GPD26	10-12'	190-D	0.6	573593.1	151557.7
GPD26	10-12' D	190-D	0.7	573593.1	151557.7
GPD26	12-14'	190-D	0.1	573593.1	151557.7
GPD-26A	14-16'	190-D	0.1		
GPD27	10-12'	190-D	1.1	573590.4	151557.6
GPD28	4-6'	190-D	≤0.1	573588.1	151558.3
GPD28	6-8'	190-D	0.5	573588.1	151558.3
GPD28	8-10'	190-D	≤0.2	573588.1	151558.3
GPD28	10-12'	190-D	≤0.1	573588.1	151558.3
GPD28	12-14'	190-D	≤0.1	573588.1	151558.3
190D-CPT-1	8-8.5'	190-D	2.6		
190D-CPT-1	10-10.5'	190-D	0.1		
190D-CPT-1	12-12.5'	190-D	0.1		
190D-CPT-1	14-15'	190-D	0.1		
190D-CPT-1	14-15' D	190-D	1.0		
190D-CPT-1	19-19.5'	190-D	1.7		
190D-CPT-1	21-24'	190-D	0.1		
190D-CPT-1	30-32'	190-D	0.1		
190D-CPT-2	30-32'	190-D	0.1		
190D-CPT-2	30-32' TOE	190-D	0.1		
1A#1	10'	100-D CTS	0.0		
1B#2	13'	100-D CTS	0.1		
1C#3	16'	100-D CTS	0.0		
2A#4	3'	100-D CTS	0.0		
2B#5	6'	100-D CTS	0.1		
2C#6	9'	100-D CTS	0.0		
2D#7	12'	100-D CTS	0.0		
2E#8	15'	100-D CTS	0.0		
3A#9	3'	100-D CTS	0.0		
3B#10	6'	100-D CTS	0.0		
3B#10	6' D	100-D CTS	0.0		
3C#11	9'	100-D CTS	0.0		

Table 1. (contd)

Location ID	Depth	Sample Location	Sediment [Cr+6] (ppm)	Easting (m)	Northing (m)
3D#12	12'	100-D CTS	0.0		
3E#13	15'	100-D CTS	0.0		
4A#14	3'	100-D CTS	0.0		
4B#15	6'	100-D CTS	0.0		
4C#16	9'	100-D CTS	0.0		
183H GP1	6-8'	183H Basin	≤0.3	577915.2	152858.9
183H GP1	6-8' TOE	183H Basin	≤0.2	577915.2	152858.9
183H GP1	8-10'	183H Basin	≤0.2	577915.2	152858.9
183H GP1	8-10' TOE	183H Basin	≤0.3	577915.2	152858.9
183H GP1	10-12'	183H Basin	≤0.3	577915.2	152858.9
183H GP1	10-12' TOE	183H Basin	≤0.1	577915.2	152858.9
183H GP1	12-13' TOE	183H Basin	≤0.1	577915.2	152858.9
183H GP2	6-8'	183H Basin	≤0.2	577916.2	152857.0
183H GP2	6-8' TOE	183H Basin	≤0.1	577916.2	152857.0
183H GP2	8-10'	183H Basin	≤0.2	577916.2	152857.0
183H GP2	8-10' TOE	183H Basin	≤0.1	577916.2	152857.0
183H GP3	6-8'	183H Basin	≤0.3	577915.7	152862.8
183H GP3	6-8' TOE	183H Basin	≤0.1	577915.7	152862.8
183H GP3	10-12' TOE	183H Basin	0.0	577915.7	152862.8
183H GP3B	10-12+' TOE	183H Basin	≤0.1		
183H GP4	6-8' TOE	183H Basin	≤0.2	577912.3	152860.3
183H GP4	8-10' TOE	183H Basin	0.1	577912.3	152860.3
183H GP4	10-12'	183H Basin	≤0.1	577912.3	152860.3
100H-CPT-1	12-14'	183H Basin	0.1	577904.7	152838.9
100H-CPT-1	22.2-24.9'	183H Basin	0.1	577904.7	152838.9
100H-CPT-1	22.2-24.9' TOE	183H Basin	0.1	577904.7	152838.9
100H-CPT-2	15-19.1'	183H Basin	0.1	577904.2	152831.4
100H-CPT-2	15-19.1' D	183H Basin	0.1	577904.2	152831.4
100H-CPT-3	15.2-18.7'	183H Basin	0.1	577905.9	152846.9
100H-CPT-3	15.2-18.7' TOE	183H Basin	0.1	577905.9	152846.9
GPKE1	4-6'	K-East CTS	0.0		
GPKE1	6-7'	K-East CTS	0.0		

Table 1. (contd)

Location ID	Depth	Sample Location	Sediment [Cr+6] (ppm)	Easting (m)	Northing (m)
GPKE1	6-7' D	K-East CTS	0.0		
GPKE1	7-7.5'	K-East CTS	0.0		
KW1	Surface	K-West CTS	185		
KW2	Surface	K-West CTS	0.4		
KW3	Surface	K-West CTS	1.2		
KW4	Surface	K-West CTS	0.3		
KW5	Surface	K-West CTS	0.6		
KW6	Surface	K-West CTS	0.9		
KW7	Surface	K-West CTS	0.4		
KW8	3"	K-West CTS	0.2		
KW9	9"	K-West CTS	0.2		
GPKW1	4-4.5'	K-West CTS	0.0	568850.4	146090.6
GPKW1B	8.6'	K-West CTS	0.0		
GPKW1B	8.7'	K-West CTS	0.0		
GPKW1B	8.8'	K-West CTS	0.0		
GPKW1B	8.9'	K-West CTS	0.0		
GPKW1B	9.0'	K-West CTS	0.0		
GPKW1B	9.1'	K-West CTS	0.0		
GPKW1B	9.2'	K-West CTS	0.0		
GPKW2A	2-3.6'	K-West CTS	0.0	568854.6	146088.5
GPKW2A	2-3.6' TOE	K-West CTS	0.2	568854.6	146088.5
GPKW2A	4-6'	K-West CTS	0.6	568854.6	146088.5
GPKW2A	4-6' TOE	K-West CTS	57.0	568854.6	146088.5
GPKW2A	6-8' TOE	K-West CTS	0.1	568854.6	146088.5
GPKW2C	8-9'	K-West CTS	420		
GPKW3	2-4'	K-West CTS	11.0		
GPKW3	4-6'	K-West CTS	3.0		
GPKW3	4-6' D	K-West CTS	3.0		
GPKW6	6-8' TOE	K-West CTS	0.7		
GPKW6	6-8' TOE D	K-West CTS	0.9		
GPKW6	7'	K-West CTS	1.3		
GPKW6	7' D	K-West CTS	0.7		
GPKW6	8'	K-West CTS	0.2		

Table 1. (contd)

Location ID	Depth	Sample Location	Sediment [Cr+6] (ppm)	Easting (m)	Northing (m)
GPKW6	8' D	K-West CTS	0.8		
GPKW6	9-10'	K-West CTS	1.5		
GPKW6	9-10' BOS	K-West CTS	0.5		
GPKW6	9-10' BOS D	K-West CTS	0.5		
GPKW6	9-10' TOE	K-West CTS	0.2		
GPKW6	9-11' TOP	K-West CTS	0.8		
GPKW6	9-11' TOP D	K-West CTS	1.0		
GPKW8	2-4'	K-West CTS	0.0		
GPKW8	2-4' TOE	K-West CTS	0.0		
GPKW8	4-6' TOE	K-West CTS	0.0		
GPKW8	6-7'	K-West CTS	0.1*		
GPKW8	6-7' TOE	K-West CTS	0.1*		
KW-CPT-1	9.5'	K-West CTS	0.7		
KW-CPT-2	3-9' TOP	K-West CTS	0.2		
KW-CPT-2	3-9'	K-West CTS	0.3		
KW-CPT-2	3-9' TOE	K-West CTS	0.2		

BOS = Base of cored interval.

CPT = Cone penetrometer sample.

CTS = Chromate Transfer Station.

D = Duplicate.

GP = Geoprobe sample.

TOE = Sample collected from toe or shoe of sampler.

TOP = Top of cored interval.

Northing/Easting data (NAD 1983) obtained by GPS.

*Turbidity interference; no colorimetric reaction observed (possible false positive).

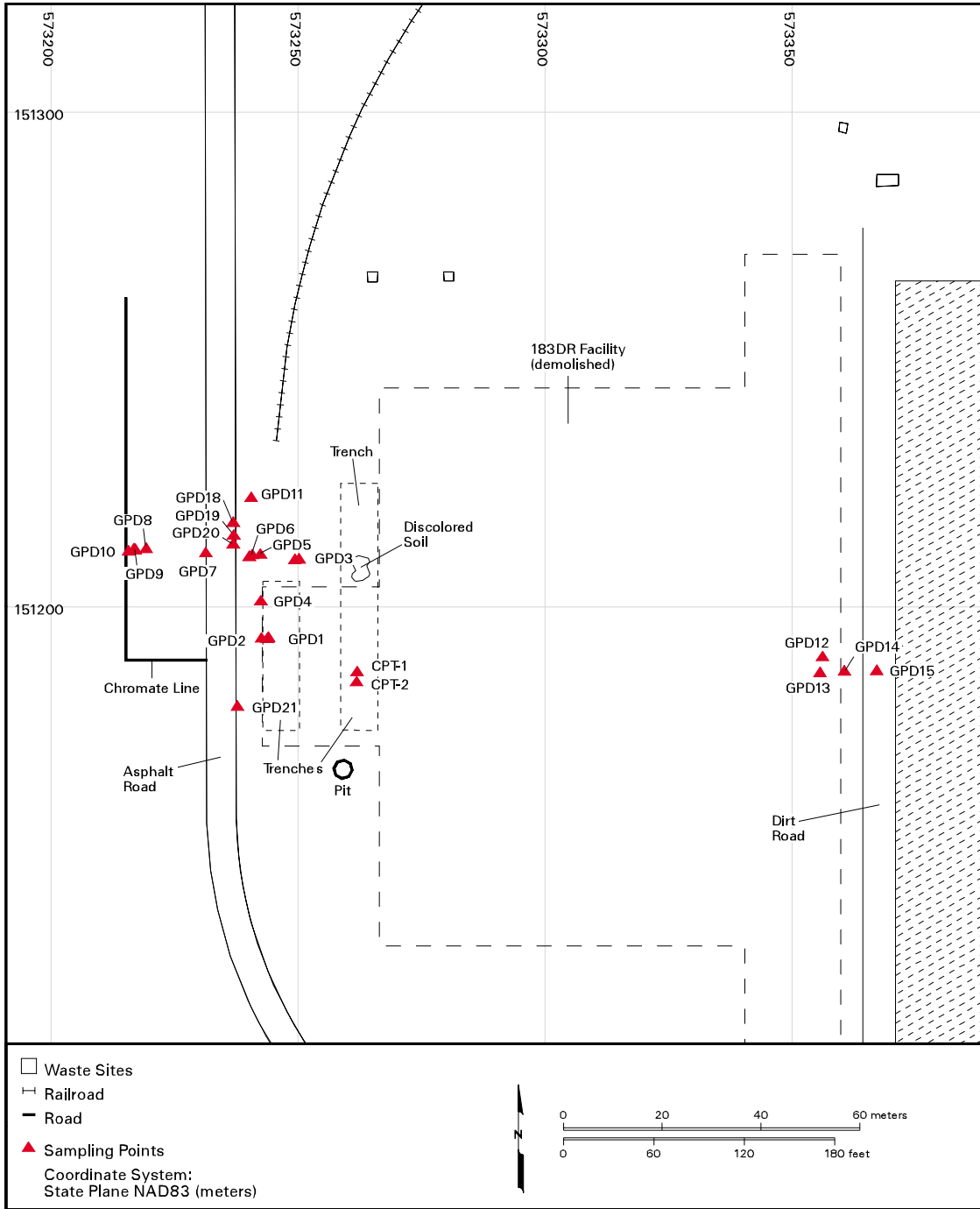


Figure 3. 183-DR Head House and Filter Plant Site

x-ray fluorescence (XRF). Most were uncontaminated with a total chromium concentration of about 20 to 30 ppm (i.e., background levels). However, a discolored soil sample collected at the northern end of the head house at a depth of 3 ft contained about 650 ppm total chromium (analyzed in duplicate). This sample was depleted in iron, manganese, and calcium and slightly enriched in lead. Another sample collected north of the head house at a depth of 15 ft had similar chemical characteristics, with a total chromium content of 43 ppm.

A Cr(VI)-bearing solution may have been released in the area north of the head house that resulted in the reduction and precipitation of chromium as Cr(III) oxides. If this solution was acidic in character, it may have released reduced iron from the soil which lead to the reduction of Cr(VI) to Cr(III) by the oxidation of Fe(II) to Fe(III). It is likely that the faint orange color of the soil is due to the oxidation of iron. Alternatively, the reduction of chromium may have resulted from the presence of organic material (a layer of asphalt was observed above the discolored soil zone). Excess Cr(VI) may have subsequently been leached deeper into the vadose zone by water draining into this area.

It is possible that Cr(VI) has migrated deeper than can be reached by Geoprobe™, cone penetrometer, or by trenching (i.e., greater than 20 ft depth). However, groundwater monitoring data strongly suggests that this facility was the source of contamination responsible for the Cr(VI) groundwater plume present in this area (see Figure 2). The area of discolored soil discovered north of the head house also appears to be a potential point source of contamination. It is recommended that a vadose zone borehole be drilled at this location and sediments sampled and analyzed to determine if Cr(VI) exists at depth, and, if so, the vertical distribution of contamination at the 183-DR site.

3.4 108-D Site

This facility was formerly located north of the D Reactor, as shown in Figure 2. This facility appears to have been the source of the Cr(VI) groundwater plume located north of the reactor and may originally have been a chromate transfer station. Access to this site is difficult owing to the presence of underground radionuclide contamination. However, a Geoprobe™ sampling location was set up a short distance to the west of a fence surrounding the area associated with subsurface radioactivity. Soil samples were collected in August 1999, and Cr(VI) was detected at low concentrations (≤ 1 ppm; Table 1).

The 108-D site is not suitable for a demonstration both because of underground radionuclide contamination, which would increase the cost and complexity of conducting a demonstration, and the low levels of Cr(VI) contamination detected. Future excavation activity in the area may be an opportunity to obtain more information about this site, however.

3.5 190-D Complex

This site was the location of a facility, now demolished, situated west of the D Reactor. Hexavalent chromium was added to cooling water at the 190-D complex before entering the reactor, and fairly widespread contamination is present in this area. Trenching was undertaken several years ago by BHI

staff and sediment samples were collected and analyzed for Cr(VI) (Lerch 1998). Hexavalent chromium staining of soil and concrete debris is also visible in surficial materials, commonly reaching levels of several hundred to greater than 1000 ppm.

The location of eight Geoprobe™ and two cone penetrometer holes associated with this study are presented in Figure 4. Geoprobe™ sampling at 190-D was undertaken in November 1999 and cone penetrometer sampling in October 1999. The samples collected for this study were analyzed for Cr(VI) and the results are presented in Table 1. The highest value obtained was 6.3 ppm, associated with a sample collected in the depth interval from 3 to 3.6 m (10 to 12 ft) at location GPD26. This is the same location where a value of 6.96 ppm was reported by Lerch (1998) for a sample collected at a depth of 4 m (10 ft). The two cone penetrometer holes drilled at this location both reached a total depth of 9.6 m (32 ft). Samples from these holes suggest that the depth of contamination does not exceed 6 m (20 ft) (Table 1).

Significant levels of Cr(VI) contamination exist in soil at the 190-D site. However, the contamination appears to be rather localized and possibly restricted to a shallow depth. Cr(VI) may be present deeper in the vadose zone at the site, however, if mobilization by water infiltration has occurred.

3.6 100-D Sodium Dichromate Transfer Station

Chromate stock solutions were unloaded from rail cars at the 100-D Sodium Dichromate Transfer Station (100-D-12) and transferred by pipelines to the 190-D and 183-DR facilities (see Figure 2). A previous study at this location indicated nil-to-low concentrations of Cr(VI) in the soil (≤ 0.4 ppm; Lerch 1998). On March 2, 2000, a pit was excavated by CHI at the site and sample splits were provided to PNNL for analysis. The analyses performed by PNNL (see Table 1) indicate that the samples did not contain Cr(VI). CHI staff have since indicated a contract laboratory reported no significant concentrations of Cr(VI) were detected during analysis of the corresponding splits.

3.7 183-H Solar Evaporation Basins

The 183-H Solar Evaporation Basins site is a former waste storage facility in the 100-H Area of Hanford associated with contaminated soil and groundwater. A total of four Geoprobe™ and three cone penetrometer holes were driven at this site in November and October 1999, respectively, and sediment samples collected for Cr(VI) analysis (Figure 5 and Table 1). Levels of Cr(VI) in all samples were at or below the limits of detection (≤ 0.4 ppm).

3.8 183-KE and 183-KW Chromate Transfer Stations

These two facilities are located in the 100-K Area at Hanford. They are sites where Cr(VI) stock solutions were unloaded from rail cars near the head house of water treatment basins. As at 183-DR and 190-D, Cr(VI) was added to reactor cooling water as a corrosion inhibitor. Surficial staining of soil by Cr(VI) is particularly noticeable at 183-KW. Chromium contamination of groundwater at 183-KE has also been identified in the past several years (PNNL-11793). The appearance of Cr(VI) in groundwater

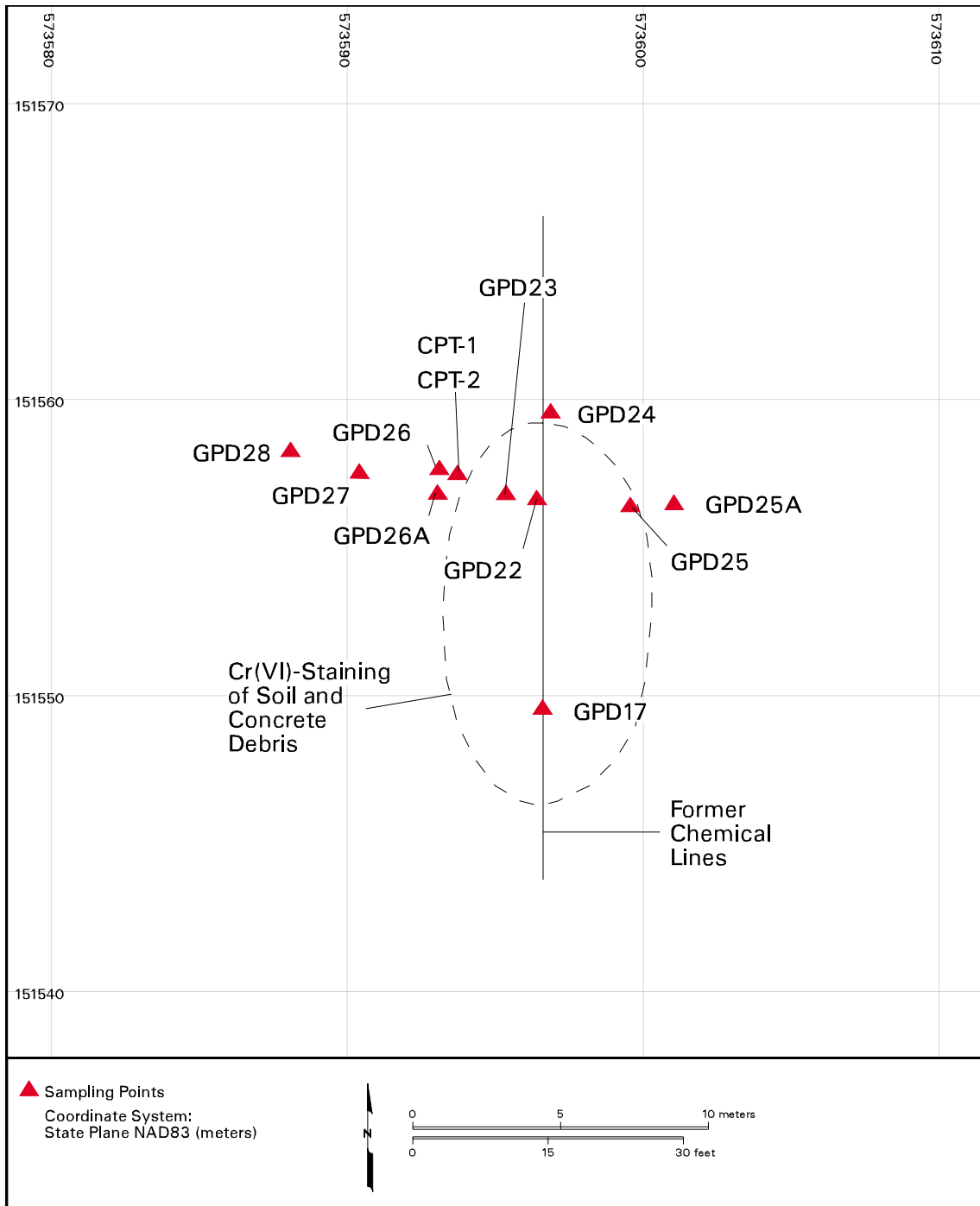
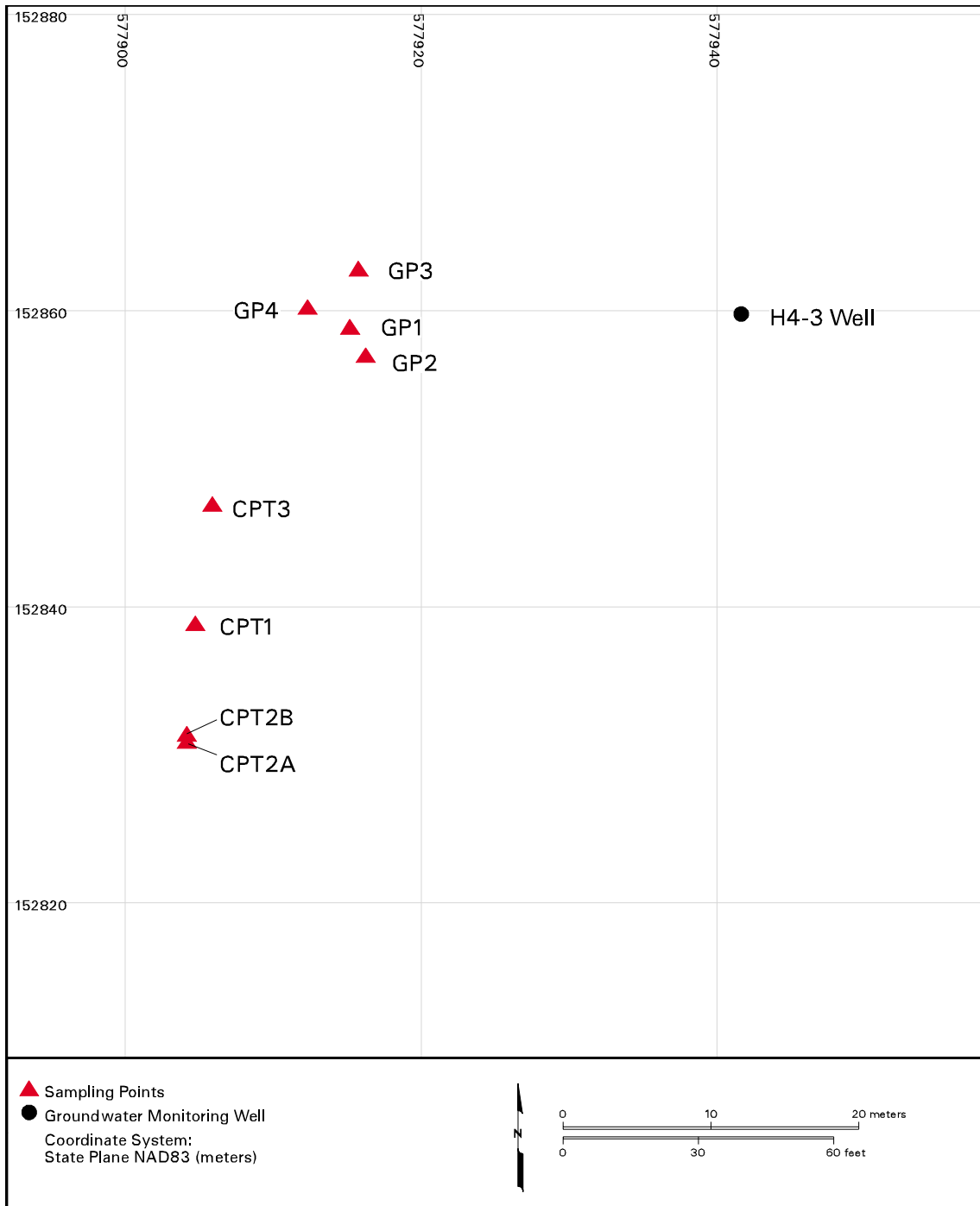


Figure 4. 190-D Complex Site



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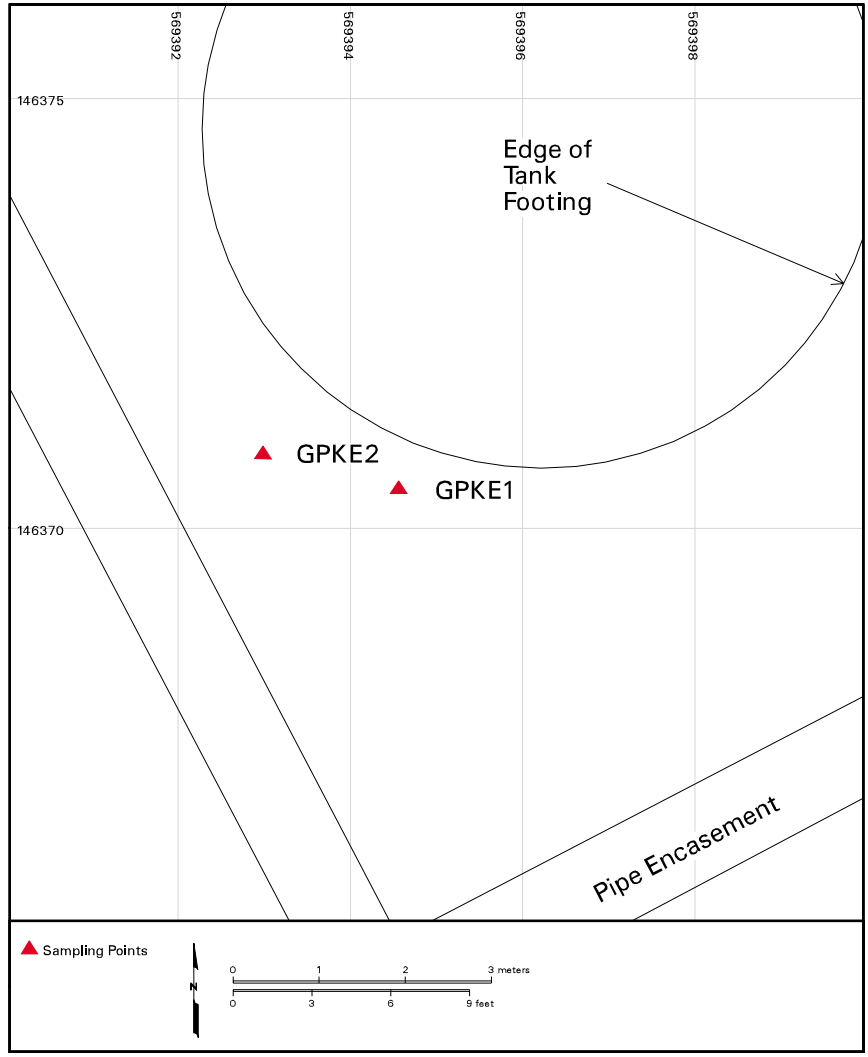
Figure 5. 183-H Solar Evaporation Basin Site

at 183-KE occurred at about the time water was added to a nearby basin, suggesting that water infiltration may have mobilized Cr(VI) existing in the deeper vadose zone.

Geoprobe™ sampling was undertaken at 183-KE and 183-KW in August and September of 1999 (Figures 6 and 7). Samples collected to a depth of about 7.5 ft at 183-KE did not contain detectable Cr(VI), as indicated in Table 1. Deeper sampling could not be achieved at this site, apparently because of gravel or cobble beds. Cr(VI) contamination may exist at depth at the 183-KE site in light of the groundwater contamination that has been reported, but is apparently deeper than 3m (10 ft) and would require drilling to obtain samples for further evaluation. Moreover, a field demonstration would be difficult to undertake at this site since the facility is still being utilized for operations and access is limited because of utilities.

Abundant Cr(VI) staining of soil can be observed at 183-KW. An area containing about 185 ppm was identified during surface soil sampling conducted in May 1999 (see KW1 of Table 1 and Figure 7). Significant concentrations of Cr(VI) were also detected in sediment samples obtained from several Geoprobe™ holes at 183-KW (see Table 1). Geoprobe™ hole GPKW2 had especially high concentrations, up to 420 ppm in the 8 to 9 ft interval. Significant concentrations were also detected in samples collected from Geoprobe™ hole GPKW3, which was driven in the area of surface Cr(VI)-contaminated soil mentioned above. A concentration of 11 ppm Cr(VI) was measured in a sample collected in the 2 to 4 ft depth interval, but decreased to 3 ppm in the 4 to 6 ft interval. Two cone penetrometer holes were also driven at 183-KW in October 1999, but analysis of samples collected indicated that Cr(VI) concentrations were relatively low (<1 ppm; Table 1). It appears that reduction of Cr(VI) to Cr(III) may be occurring at 183-KW. Recent analysis of soil sample KW1 by x-ray adsorption spectroscopy, in particular, suggests that Cr(III)/Cr(VI) ratio of the sample is roughly 20. The reduction of Cr(VI) appears to have resulted from reaction with an unspecified organic fraction of the soil observed during sediment analytical activities.

The 183-KW site was originally considered a potential test site, owing to the presence of elevated levels of Cr(VI) in the soil. In addition, the site has been identified for remediation in the near future. However, advancement of the Geoprobe™ and cone penetrometer equipment was commonly limited to a depth of about 10 ft, apparently because of a gravel or cobble layer, and no samples could be collected below this. Contamination at 183-KW appears to be sporadic and may be largely surficial, although the occurrence of Cr(VI) at depth cannot be ruled out. However, access is presently limited by utilities associated with the site, and performance of a demonstration could be difficult.



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Figure 6. 183-KE Chromate Transfer Station

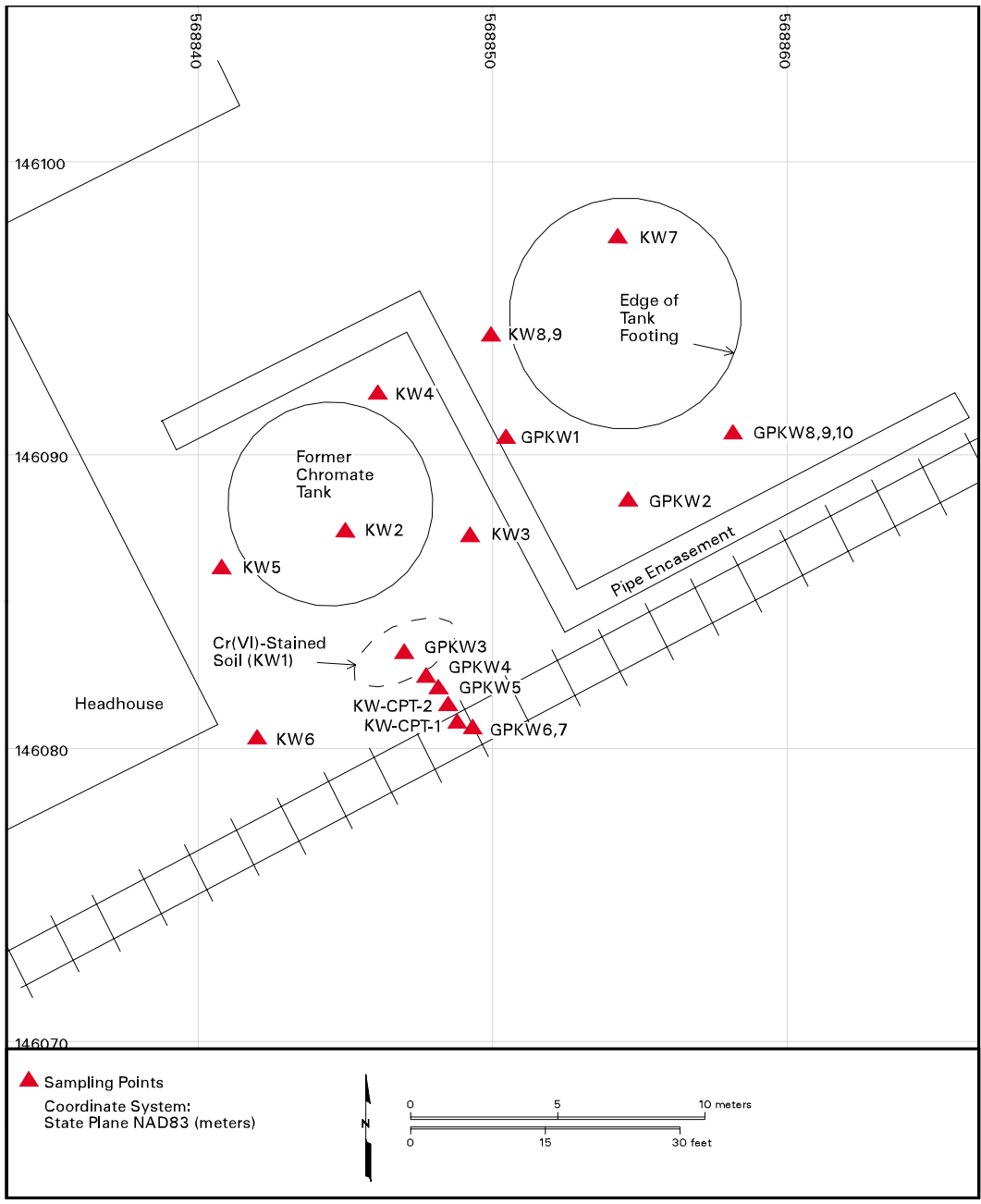


Figure 7. 183-KW Chromate Transfer Station

4.0 Recommendations

A field investigation was undertaken to identify one or two Hanford waste sites where the ISGR technology can be demonstrated and deployed. Sediment characterization data collected during this study were utilized to supporting this determination, together with site operational history and groundwater monitoring data.

The 190-D site has significant concentrations of Cr(VI) in the soil (as high as 7 ppm). However, it appears that contamination is limited to depths shallower than 6 m (20 ft) and is localized in nature.

Significant concentrations of Cr(VI) also occurs in sediment at the 183-KW site, but the distribution appears to be sporadic in nature and decreases with depth. However, operation of the Geoprobe™ and cone penetrometer was limited to shallow sampling activities at 183-KE and 183-KW owing to drilling refusal at depths of 3 m (10 ft) or less. The presence of utilities at both 183-KE and 183-KW would also present problems in conducting an ISGR demonstration at these sites.

The 183-DR site is judged to be the best site currently available to undertake an initial deployment of the ISGR approach at Hanford. Geoprobe™ and cone penetrometer sampling at this site was severely hampered by the presence of concrete and construction debris and fill, but traces of Cr(VI) were reported. Recent groundwater monitoring data also strongly indicates that a deep vadose zone source exists at this site, which is consistent with the operational history of the 183-DR facility. In addition, trenching activities indicate a possible point source of contamination at the northern end of the head house foundation, where an area of high total chromium concentrations was identified. It is recommended that several vadose zone boreholes be drilled to groundwater at 183-DR, and sediment and groundwater samples collected and analyzed to determine if this site is the source for the groundwater plume.

A demonstration test plan will be prepared based on the selection of 183-DR as the test site if borehole sediment samples indicate the presence of significant levels of Cr(VI) in the vadose zone. One of these boreholes will become the gas treatment injection borehole for the demonstration. Installation of the remainder of the wellfield network and completion of a tracer test will then also be performed. The gas treatment test will then be undertaken and final post-treatment assessment activities will subsequently be completed.

5.0 References

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Appendix A

PNNL Procedure – Extraction and Analysis of Cr(VI) in Soil Samples

Appendix A

PNNL Procedure – Extraction and Analysis of Cr(VI) in Soil Samples

This job-specific procedure/workplan will be used by Pacific Northwest National Laboratory (PNNL) for the analysis of Cr(VI) in vadose zone soil samples associated with drilling of groundwater monitoring wells by Bechtel Hanford, Inc.(BHI) at 100-D (BHI-01237). Included in this document is guidance regarding sampling methods and intervals, analysis of soil samples for Cr(VI), and waste management.

Soil analysis involves extraction of the Cr(VI) from the soil sample using either microwave assisted or stirred water leaching. Microwave assisted extraction allows soil samples to be processed at a faster rate, but has a slightly higher detection limit compared to the stir plate extraction.

Following extraction, the leachate is analyzed for Cr(VI) using the diphenylcarbazide colorimetric method and a spectrophotometer. This procedure assumes that the all or most of the Cr(VI) is in readily soluble form, which is true for many Cr(VI)-contaminated soil samples. This procedure is meant for field-screening applications, but quantitative data can be produced if a minimum level of quality control is observed. The detection limit of Cr(VI) in soils by this method is approximately 0.1 mg/kg.

A.1 Equipment

A top loading balance shall be used to weigh soil samples and water during the leaching step. The balance must have a readability 0.1 g or better, with a capacity of at least 150 g.

Hexavalent chromium may be hot water-leached using either beakers on a stir plate or in a microwave digester (e.g., CEM Corporation MDS 2000).

Leachate solutions require filtering before analysis. Plastic syringes (10 ml) with disposable inline filters (0.45 μ) are used for this purpose. Disposable 150 mL filter units are more time efficient, however, a vacuum source (e.g., small electrical or hand-operated vacuum pump) is required.

A Hach DR/2000 spectrophotometer or equivalent should be used for analysis of the leachate samples. The user is referred to the equipment manual for specific instructions in the use of the spectrophotometer (DR/2000 Spectrophotometer Procedures Manual).

A.2 Reagents

Hach powder pillows (Chroma Ver 3) are employed in this procedure. These pillows contain the pre-mixed reagents needed for colorimetric determination of Cr(VI) in the leachate samples. Leaching of soil samples shall be performed using deionized or distilled water.

A.3 Procedure

A.3.1 Sample Collection

PNNL will provide bottles to a BHI geologist to collect samples. Wide-mouth glass sample bottles of suitable size (e.g., 2 ounces or 60 ml) shall be used during sample collection. Sample size should be at least 50 g (about 1/2 bottle). Do not size sediment samples, but discard particles larger than 4 mm (pebble size), if possible. Bottles shall be labeled and marked with information regarding sample location, time, and name of sampler/geologist.

A description of work for the drilling activities and well locations are presented in BHI-01237. The objective of this procedure to obtain information regarding levels and distribution of Cr(VI) in the vadose zone at 100 D in the locations where BHI will be drilling. In particular, concentrations of Cr(VI) in sediment samples in the vicinity of the sodium dichromate transfer station and associated facilities near the reactor are of interest. A total of 12 wells are planned (BHI-01237). The following 7 wells are in the area of interest:

Well Number	Sampling Interval	Total Number of Samples (~80' to groundwater)
4	10'	8
5	5'	16
6	10'	8
7	10'	8
8	10'	8
9	5'	16
10	5'	16

Thus, a total of about 80 samples is anticipated. Actual sampling intervals can be adjusted depending on drilling conditions or data needs.

A.3.2 Microwave Extraction and Analysis

A CEM Corporation MDS 2000 microwave digestion apparatus, rated at 800°W will be used to extract Cr(VI) from the sediment samples. Microwave assisted extraction can be conducted in sets of up to 12 samples. Weigh 3.0 g of soil sample in a Teflon microwave digestion vessel and add 30 mL of

deionized or distilled water. Soil samples are then heated for 2.5 min at 100% power and 10 min at 80% power. Filter sample leachate into a graduated container or beaker. Dilute filtered leachate samples to a total volume of 50 mL with DI or distilled water.

Set up the Hach DR/2000 for analysis of Cr(VI) as described in the user's manual (use stored program 90 and set the wavelength to 540 nm per Hach Method 8023). Transfer filtered leachate solution to two cuvettes (25 mL each). One of these cuvettes is used as a blank. A Chroma Ver 3 powder pillow is added to the other cuvette and allowed to react for 5 minutes before analysis. (See the Hach manual for specific directions.) Record the results in mg/L Cr(VI).

The Cr(VI) concentration of the leachate samples may be converted to the Cr(VI) concentration of the soil as follows:

$$(\text{Cr(VI) conc of solution, mg/L}) \times 16.7 = \text{Cr(VI) conc of soil, mg/kg.}$$

Note: If Cr(VI) content of the soil sample is >10 mg/kg, dilute leachate 10:1 and reanalyze. Modify the above equation in an appropriate manner.

A.3.3 Stir Plate Extraction and Analysis

Alternatively, weigh out 6.0 g of soil into a 100 ml glass beaker. Water (60 mL) is then added and a stir bar is placed in the beaker. Cover the beaker, place on a stir plate, and stir for 1 hour (unheated). The resulting solution is then filtered and analyzed as described below.

Set up the Hach DR/2000 for analysis of Cr(VI) as described in the user's manual (use stored program 90 and set the wavelength to 540 nm per Hach Method 8023). Transfer filtered leachate solution to two cuvettes (25 ml each). One of these cuvettes is used as a blank. A Chroma Ver 3 powder pillow is added to the other cuvette and allowed to react for 5 minutes before analysis. (See the Hach manual for specific directions.) Record the results in mg/L Cr(VI).

The Cr(VI) concentration of the leachate samples may be converted to the Cr(VI) concentration of the soil as follows:

$$(\text{Cr(VI) conc of solution, mg/L}) \times 10 = \text{Cr(VI) conc of soil, mg/kg.}$$

Note: If Cr(VI) content of the soil sample is >6 mg/kg, dilute leachate 10:1 and reanalyze. Modify the above equation in an appropriate manner.

A.4 Quality Control

A Hach DR/2000 spectrophotometer programmed for determination of Cr(VI) at the wavelength of 540 nm is used in this procedure. The program permits the instrument to provide a direct readout of

solution concentrations in mg/L of Cr(VI). The instrument allows analysis of solutions in the range from 0 to 0.60 mg/L Cr(VI). A 0.5 mg/L Cr(VI) check standard shall be used prior to running samples to verify that the instrument is functioning correctly.

At least one duplicate sample shall be run within a 10-sample batch. A blank sample (deionized or distilled water) shall also be carried through the analysis.

A.5 Waste Management

All liquid waste from analysis of leachate samples or Cr(VI) standards shall be placed in a carboy, accompanied by a detailed waste inventory, and turned over to BHI for disposal (waste stream W10 of WMI-HR3-001, Rev 1). All residual soil samples shall also be returned to BHI for disposal with other drilling wastes per the BHI wasteplan.

A.6 References

BHI-01237, Rev. 0. 1998. *Description of Work for Fiscal Year 1999 Drilling Within the Chromium Plume West of the 100-D/DR Reactors*. Bechtel Hanford, Inc., Richland, Washington.

DR/2000 Spectrophotometer Procedures Manual, Hach Company, Loveland, Colorado.

WMI-HR3-001, Rev 1, Draft. *Site Specific Waste Management Instruction 100-HR-3 Well Installations*. Bechtel Hanford, Inc., Richland, Washington.

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