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* Per telecon with E.C. Thornton

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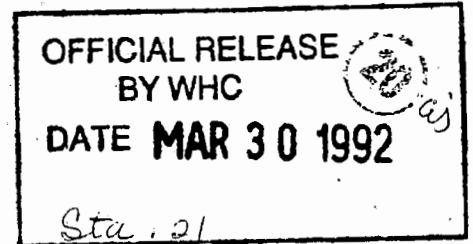
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INTRODUCTION

As part of the Environmental Restoration program being conducted by Westinghouse Hanford Company at the Hanford Site, technical evaluation of contaminant distribution and cleanup options are being conducted for the 100-BC aggregate area. Potential contaminants of concern include radionuclides and chemical hazardous materials including lead, mercury, acids, polychlorinated biphenyls (PCB), asbestos, and sodium fluoride. A specific chemical contaminant of great concern is hexavalent chromium, which has been a hazardous chemical constituent of waste effluent streams associated with production activities.

The objective of this report is to evaluate past disposal practices associated with this contaminant, including waste liquid volumes and chemical inventories for individual disposal facilities, and unplanned releases associated with reactor cooling water systems. Based on this information and known hydrochemical aspects of hexavalent chromium and characteristics of site soils, predictions of the concentrations of chromium in waste site soils and total volumes of contaminated soil can be presented. An assessment also can be made of potential impact to the groundwater in the area. This information is important in the selection of treatment systems and approaches that will be utilized in 100-BC remediation activities.

SUMMARY OF THE OPERATIONAL HISTORY OF THE 100-BC AREA

The 100-BC Area is composed of the 100-BC-1, 100-BC-2, 100-BC-3, and 100-BC-4 source operable units and the 100-BC-5 groundwater operable unit. The 100-BC-1 and 100-BC-2 operable units are of primary importance to this study, since the liquid waste disposal facilities and reactor cooling water systems were associated with these units (DOE-RL 1991a, 1991b). These facilities are assumed to be the predominant sources of hexavalent chromium contamination in vadose zone soils and groundwater system of the 100-BC Area.

The B Reactor was operational from 1944 through 1968 and is associated with the 100-BC-1 operable unit (DOE-RL 1991a). The C Reactor operated from 1952 through 1969 and lies in the 100-BC-2 Operable Unit (DOE-RL 1991b). A schematic flow diagram (Figure 1) is provided to illustrate the configuration of the cooling water system and major liquid waste disposal facilities associated with these two reactors.

REACTOR COOLING WATER SYSTEM

The greatest contributor of hexavalent chromium to the soils and groundwater of 100-BC Area was probably the cooling water effluent system. Thus, a detailed analysis of the reactor cooling water systems is necessary to evaluate the extent of chromium contamination. As illustrated in the flow diagram presented in Figure 1, water obtained from the Columbia River was circulated in a single pass through the reactor systems, retention basins, and then discharged to the river.

Figure 1. Flow Diagram for Reactor Cooling Water System in the 100-BC Area and Major Facilities Associated with Hexavalent Chromium.

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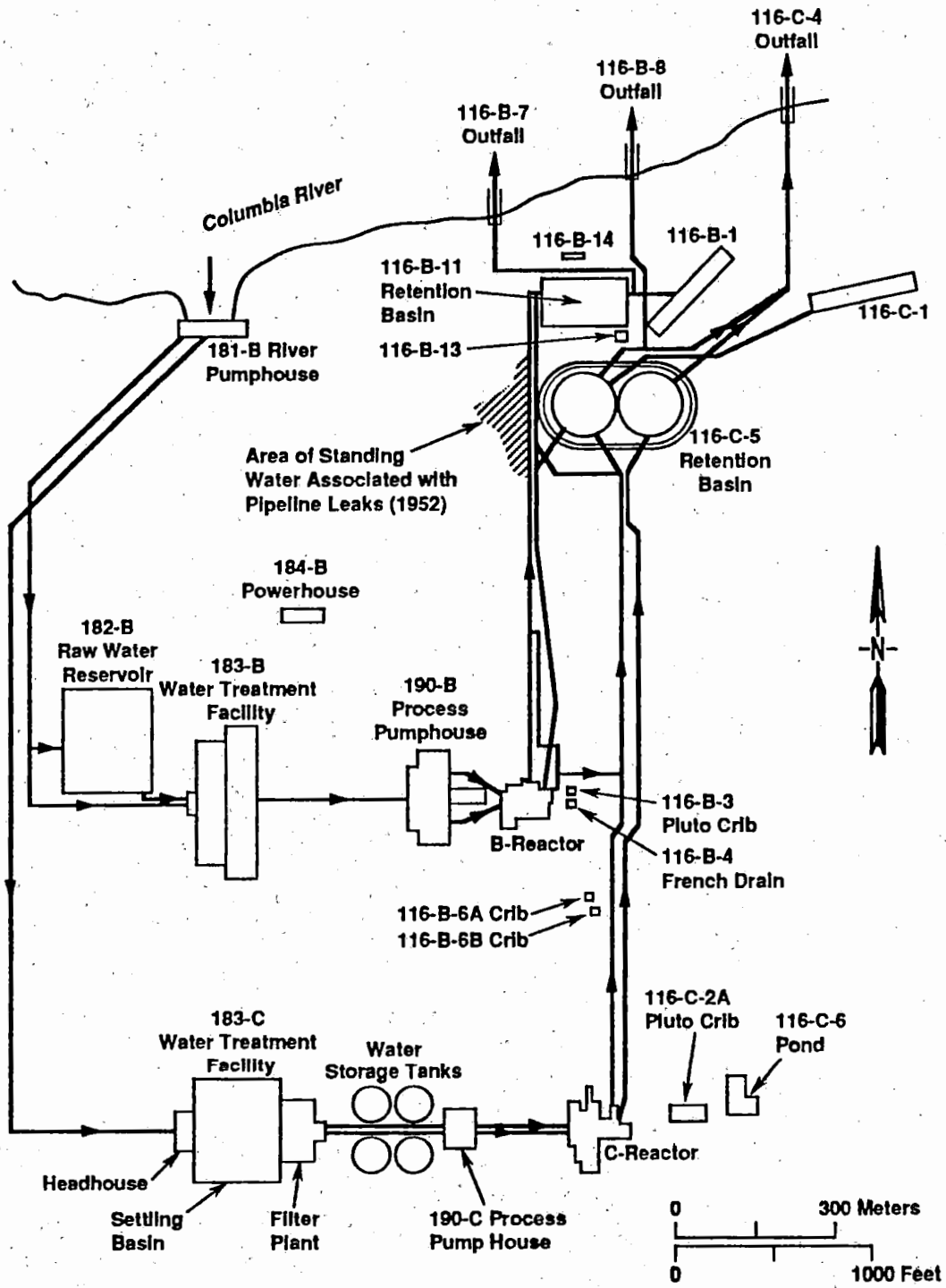


Figure 1. Flow Diagram for the Reactor Cooling Water System in the 100-BC Area and Major Facilities Associated with Hexavalent Chromium.

Water from the river was pumped through the 181-B Pumphouse and passed on to both the B and C reactors. The line to the B Reactor cooling system initially sent water to either the 183-B Water Treatment Facility or to the 182-B Holding Reservoir. The 183-B facility was the main source of cooling water for the B Reactor, while the holding reservoir was predominantly used to supply raw water to other facilities associated with Hanford Site operations.

At 183-B, the river water was treated with chemical additives (alum with excess sulfuric acid, hydrated calcium oxide, and chlorine) and passed through flocculators, settling basins, and filters to remove precipitates and particulate materials (DOE-RL 1991a, Richards 1953). This treated water was then passed to the 190-B building (process pumphouse). Approximately 2 mg/L of sodium dichromate was added at the inlet of storage tanks located in 190-B to inhibit corrosion of aluminum slugs and process tubes in the reactor (Richards 1953). Water then was passed from the storage tanks to the B Reactor building for circulation through the reactor block.

Water also was sent from the river pumphouse to 183-C Water Treatment Facility, which was associated with the C Reactor. The water was treated in 183-C, as described above, and passed on to four water storage tanks, where 2 mg/L of sodium dichromate was added. The water subsequently was passed on to a high-pressure pumping station in the 190-C Building and then to the reactor block of the C Reactor building.

An average daily use of about 300 million liters of cooling water per reactor was required in the 100-BC Area. Total volume of cooling water exiting the B Reactor was originally as high as 174,000 L/min. for the period from 1944 to 1956. In 1956, flow increased to approximately 269,000 L/min., until termination of reactor operations in 1968. Flow through the C Reactor was originally about 246,000 L/min. from 1952 to 1960. In 1960, higher capacity pumps were installed that increased C Reactor flow rates by approximately 34,065 L/min. C Reactor operations ended in 1969.

Chromium-51 was one of the radionuclide species generated in the reactor blocks by high neutron fluxes. The amount of chromium generated by this process is assumed to be insignificant relative to the hexavalent chromium added to inhibit corrosion. Furthermore, the half life of ^{51}Cr is only 27.7 d and, thus, decayed rapidly. Diatomaceous slurry used to scour reactor piping was also combined with cooling water effluent. This slurry constituted the bulk of sludge that accumulated in the cooling water effluent system.

The cooling water was transferred from the B and C reactor buildings at near boiling temperatures through effluent lines to the 116-B-11 and 116-C-5 retention basins, respectively, for thermal cooling and decay of short-lived radionuclides. Retention time was about 2.8 h in 116-B-11 and 3.2 h in 116-C-5. The 116-B-11 Retention Basin was used from 1944 until the mid-1950s, when cracking of concrete became a serious problem. Cooling water from the B Reactor subsequently was diverted to 116-C-5. The 116-C-5 Retention Basin was in service from 1952 to 1969.

From the retention basins, the cooling water was transferred through the 116-B-7, 116-B-8, and 116-C-4 outfall structures to pipes that discharged at the center bottom of the Columbia River. Outflow from the basins also was discharged directly to the shore of the river through spillways located near the outfall structures when the river was at high levels.

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During reactor operation, ruptures of the fuel element cladding frequently occurred while the fuel elements were in the process tubes. When failures occurred, contamination levels increased in the bulk cooling water exiting the reactor, and the cooling water in the affected process tube, of course, became highly contaminated.

Segregated contaminated cooling water associated with cladding ruptures was diverted from the retention basins to 116-B-1 or 116-C-1 overflow trenches. This practice continued until the mid-1950s when segregation in the basins was no longer possible.

Highly contaminated water flushed directly from the process tube was disposed to the vadose zone via "pluto cribs" (116-B-3 and 116-C-2A). Pluto crib 116-B-3 was used for only 2 yr; after that time, contaminated cooling water from the B Reactor was no longer segregated from the bulk cooling water effluent. Pluto crib 116-C-2A was in service for the entire period that C Reactor was in operation.

During both reactor operations and shutdowns, large quantities of decontamination solutions routinely were used to remove radionuclides from facility equipment and surfaces. Chromic acid was known to be one of the agents present in these decontamination solutions. Decontamination solutions were generally disposed of in cribs, trenches, and french drains. Pluto crib 116-C-2A may have been utilized for disposal of decontamination solutions from the C Reactor. Occasionally, these solutions were combined with the cooling water and discharged to the river.

It is well documented that extensive leakage was associated with the retention basins and effluent lines (DOE 1991a, 1991b, Dorian and Richards 1978). This resulted in the release of cooling water to the area in and around the basins, lines, and shore at a rate as high as several thousand gallons per minute (3 million gal/d or 10 million L/d). Evidence of leakage includes observations of water pooling over large areas of the ground adjacent to the 116-B-11 Retention Basin and over the effluent lines. Leakage from the 116-B-11 Retention Basin in some cases moved west into the 181-B forebay, causing the inlet water at the 181-B Pumphouse to become contaminated. Several warm springs with elevated beta activity initially were observed along the Columbia River shoreline below the 116-B-11 Retention Basin in the late 1940s. Stenner et al. (1988) indicated that 116-C-5 and associated effluent lines also leaked, possibly at rates as high as 5,000 to 10,000 gal/min. Radionuclide contamination is known to exist to depths of at least of 20 ft below the basin.

The effluent lines from the reactors to the retention basins were generally about 20 ft below grade. The first indications of gross leaks were observed in early 1952 for a distance of about 800 ft just south of 116-B-11, where the soil surface was covered with water and liquid was observed to be bubbling up from the subsurface (Figure 1). Two additional leaks were observed in late 1952. These were located at a diversion box for a crosstie from the B to C Reactor lines and at a site northeast of B Reactor.

RADIOACTIVE SLUDGE

Several thousand tons of radioactive sludge were generated during reactor operations, and accumulated in pipes in the cooling water effluent system, in 116-B-11 and 116-C-5 retention basins, and in reactor fuel storage basins. A portion of the sludge in the 100-BC-2 Operable Unit also accumulated in the 116-C-2A Pluto Crib system. The sludge consisted primarily of the diatomaceous earth used to scour reactor process tubes, but also included radionuclides and various chemical contaminants such as hexavalent chromium.

An unknown quantity of sludge that had accumulated in the 116-B-11 Retention Basin was removed and placed in two unlined trenches, 116-B-13 and 116-B-14, near the basin. No record of a similar cleanout of the 116-C-5 Retention Basin exists. Approximately 1,500,000 kg of sludge is estimated to remain in 116-B-11 and 500,000 kg in 116-C-5.

NONRADIOACTIVE LIQUID WASTES

Water treatment chemicals, including sodium dichromate, were used and stored near the 183-B, 183-C, 190-B, and 190-C buildings. Releases could have resulted from leakage, spillage, or disposal. Chromates and other chemicals also were used for boiler water treatment and ended up in boiler sludge, such as in the 184-B Powerhouse. Disposal methods for this sludge are not known.

WASTE VOLUMES AND CR(VI) INVENTORIES OF THE 100-BC AREA

Information is provided in Stenner et al. (1988) and the Waste Information Data System (WIDS) database (WHC 1991) concerning waste facilities and associated waste volumes and chemical inventories for the 100-BC Area. Liquid waste volumes and hexavalent chromium inventories disposed to the vadose zone are summarized in Table 1. This information can be utilized in determining the concentration of hexavalent chromium that may be present in the vadose zone. The following discussion does not include potential concentrations of hexavalent chromium associated with solid wastes sites or with sludge in trenches since chemical analytical data for these wastes are not available.

Only eight facilities of the 100-BC Area were intended to be used in the disposal of liquids containing hexavalent chromium to the vadose zone (Figure 1). These included the 116-B-1 and 116-C-1 overflow trenches, which received contaminated cooling water from the retention basins. The 116-B-3 and 116-C-2A pluto cribs received contaminated cooling water from the process tubes after cladding ruptures. The 116-B-4 French Drain and the 116-B-6A and 116-B-6B cribs were utilized in the disposal of liquid waste containing hexavalent chromium that was associated with decontamination activities. The 116-C-2A crib may also have received decontamination solutions containing hexavalent chromium. The 116-C-6 Pit or pond received processed water associated with cleanout of the C Reactor fuel storage basin. Radionuclide contaminants were removed from this water by ion exchange to concentrations below release criteria prior to disposal. It is unknown if hexavalent chromium was present in these fluids. It will be assumed here that the fluids contained 2 mg/L of sodium dichromate, the standard concentration of chromium added to reactor system cooling water.

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Table 1. Summary of Liquid Waste Volumes and Hexavalent Chromium Inventories of 100-BC Area Sites
(Liquid wastes sites only; septic tanks and solid waste or sludge disposal sites not included).

<u>Waste Site</u>	<u>Type</u>	<u>Volume, L</u>	<u>Cr(VI), kg*</u>	<u>Cr(VI), mg/L</u>	<u>mg Cr(VI)/kg soil</u>	<u>m³ soil</u>
116-B-1	trench	60,000,000	60	1	0.072	600,000
116-B-2	trench	4,000,000	0	0	0	0
116-B-3	pluto crib	4,000	0.004	1	72	40
116-B-4	french drain	300,000	1,000	3,300	239	3,000
116-B-5	crib	10,000,000	0	0	0	0
116-B-6A	crib	5,000	50	10,000	725	50
116-B-6B	crib	5,000	50	10,000	725	50
116-B-7	outfall str.	--	--	2**	0.14	--
116-B-8	outfall str.	--	--	2**	0.14	--
116-B-9	french drain	40,000	0	0	0	0
116-B-10	french drain	5,000,000	0	0	0	0
116-B-11	ret. basin	--	--	2**	0.14	--
116-B-12	crib	420,000	0	0	0	--
116-C-1	trench	100,000,000	100	1	0.072	1,000,000
116-C-2A	pluto crib	7,500,000	990	132	9.6	75,000
116-C-4	outfall str.	--	--	2**	0.14	--
116-C-5	ret. basin	--	--	2**	0.14	--
116-C-6	pit	2,157,450	--	2**	0.14	21,575

* Total inventory of hexavalent chromium disposed to the vadose zone, reported as sodium dichromate.

** Leakage associated with reactor cooling water is assumed to contain 2 mg/l sodium dichromate.

-- Information not available.

Outfall structures, cooling water lines, and retention basins also must be considered as significant sources of hexavalent chromium to the vadose zone, even though these facilities were not intended for disposal. Their locations are identified in Figure 1. It is known, as discussed above, that major leakage of reactor cooling water occurred from these structures during production operations. Although it is not possible to accurately assess the volume of this leakage, it is reasonable to assume that the average chromium concentration of these solutions was 2 mg/L as sodium dichromate. The outfall structures include 116-B-7, 116-B-8, and 116-C-4, and retention basins 116-B-11 and 116-C-5.

Several other structures present in the 100-BC-2 Operable Unit should be mentioned. The 116-C-3 Chemical Storage Tank is located north of the C Reactor. WIDS indicates, however, that this facility was never used. The 116-C-2B Pump Station and 116-C-2C Sand Filter were also associated with the 116-C-2A Pluto Crib. Possible leakage of chromium-containing decontamination solutions from the latter two facilities is possible, although it is not considered to be a major source of hexavalent chromium to the vadose zone. The three structures discussed above are not included in Table 1 or Figure 1 and will not be considered further in this study.

Other facilities are listed in Table 1 that received liquid waste not containing chromium (these facilities are not included in Figure 1). Sites of this type include 116-B-2, 116-B-5, 116-B-9, 116-B-10, and 116-B-12. Although hexavalent chromium probably is not associated with these sites, other hazardous chemicals and radionuclides were. A number of septic tanks also are present in the 100-BC Area, but no known chemical hazardous or radionuclide constituents were disposed of in these structures. It should be pointed out that Table 1 does not include any solid waste disposal sites. Information provided by WIDS and the operable unit work plans (DOE-RL 1991a, 1991b) suggest that little or no hexavalent chromium is associated with these sites. The primary waste of concern associated with the solid waste sites appears to be radioactive metallic waste. Chemical hazards include lead, mercury, and cadmium.

ANTICIPATED CONCENTRATION OF CR(VI) IN VADOSE ZONE SOILS

The information provided in Table 1 can be utilized to calculate the average concentration of hexavalent chromium in the liquid waste streams disposed to the vadose zone in the 100-BC-1 and 100-BC-2 operable units. Note that only seven sites are indicated to have received hexavalent chromium, plus 116-C-6, which is presumed to have received hexavalent chromium. Approximate volumes of disposed liquid associated with these sites are known. Thus, as is shown below, it is possible to estimate both the concentration of chromium in contaminated soils and to estimate the maximum volume of contaminated soil.

Other major sources of chromium introduced to the vadose zone include leakage of reactor cooling water associated with the retention basins, outfall structures, and cooling water lines. It is assumed that the concentration of hexavalent chromium associated with these leaks is 2 mg/L sodium dichromate, the amount added prior to circulation through the reactor blocks. It is also

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possible to estimate the concentration of chromium in soils contaminated by the leaks, but it is not possible to accurately estimate the total volume of contaminated soil since the volume of leakage is not known.

Transport of hexavalent chromium through the vadose zone is dependent on the movement of the waste solution and the degree to which Cr(VI) is adsorbed to soil particles. Hexavalent chromium exists primarily in the anionic form in solution ($\text{Cr}_2\text{O}_7^{2-}$ or CrO_4^{2-}). Since anions are not, in general, adsorbed to any significant degree the sorption coefficient of hexavalent chromium may be assumed to be zero; this is substantiated by data presented in Serne and Wood (1989). Thus, Cr(VI) distribution and transport through the soil should be dependent solely on hydrologic considerations.

The vertical movement of the waste solution through the vadose zone will be determined by hydraulic head and conductivity characteristics. Of greatest significance to this report, however, is the specific retention of the soil for the waste solution. As a generalization, it is reasonable to assume that the specific retention of the soil for the waste water is 10% by volume immediately following drainage (Bear and Verruijt 1987). If we assume a porosity of 40% for the soil, and a density of 2.3 g/cm^3 for the soil particles and 1.0 g/cm^3 for the waste solution, 1 cm^3 of soil will contain 1.38 g of soil particles and 0.1 g of waste solution. Thus, the mass in milligrams of hexavalent chromium present in 1 cm^3 of soil is equal to:

$$0.1 \text{ g solution} \times [\text{mg Cr(VI)/L solution}] \times 1 \text{ L}/1,000 \text{ g solution}$$

and the amount of Cr(VI) in the soil (expressed as milligrams Cr(VI) per kilograms of soil) is, on a dry basis,

$$\text{mg Cr(VI)/cm}^3 \times (1 \text{ cm}^3 \text{ soil}/1.38 \text{ g soil}) \times (1,000 \text{ g/kg}).$$

The anticipated concentrations of hexavalent chromium present in 100-BC waste sites is presented in Table 1, based on the above relationships. This information, together with regulatory criteria or risk assessment considerations, provides a basis for evaluating whether or not a cleanup action may be necessary at any of the waste sites. One basis that may be utilized as a cleanup standard for hexavalent chromium is the Model Toxics Control Act (WAC 173-340), which proposes a soil cleanup level of 100 mg/kg (total chromium) as a conservative (stringent) goal. This corresponds to 252 mg/kg of sodium dichromate. If we accept this as a cleanup standard, waste sites 116-B-6A and 116-B-6B, and possibly 116-B-3 and 116-B-4, appear to be the only facilities in the 100-BC Area that may require a cleanup action (ignoring other chemical or radionuclide contaminant constituents). Note that we are also assuming that the only significant source of chromium in the soil is the hexavalent chromium associated with the disposed liquids, thus ignoring any occurrences of chromium in the soil that may be of natural origin.

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Finally, we can obtain an estimate of the total volume of contaminated soil in cubic meters associated with a facility based on the relationship:

$$\text{mass} = \frac{(\text{volume of waste liquid, L}) \times (0.001 \text{ m}^3/\text{L})}{(\text{specific retention})}$$

Table 1 contains the estimated contaminated soil volumes based on this approach. It should be recognized that this represents the maximum potential mass of contaminated soil, since a portion of a vadose zone plume could have intercepted the groundwater table and subsequently been removed from the site by groundwater transport (the groundwater table is only about 50 ft below the surface in the 100-BC Area). Other factors that must be considered on a site-by-site basis in assessing contaminated soil volumes include the drainage area of a facility and anticipated amount of lateral dispersion or advective transport that could occur within the vadose zone. Engineering design considerations such as excavation slopes also must be included in calculating the anticipated total volume of soil to be excavated at a site.

It should be emphasized that total volumes of contaminated soil associated with leakage of reactor cooling water are not included in Table 1 because leakage volumes are unknown. The leakage that occurred is clearly substantial, as discussed above. The estimated concentration of hexavalent chromium retained in the soil, however, is only 0.14 mg of sodium dichromate per 1 kg soil. Thus, it is anticipated that soil contaminated by this leakage will not require cleanup actions based on regulatory guidelines for hexavalent chromium. Actions may be required, however, to meet cleanup criteria associated with radionuclide contamination introduced by leakage of the cooling water from the retention basins and lines. Potential contamination of the soil is further indicated by the observation that cooling water was frequently contaminated with radionuclides associated with cladding ruptures.

Groundwater monitoring activities indicate that present contamination of the unconfined aquifer in the 100-BC Area by hexavalent chromium is negligible. Thus Evans et al. (1990) report that of four monitoring wells sampled in the 100-BC area during 1989, the maximum chromium concentration was only 18 ppb. This is well below regulatory drinking water standards for chromium (50 ppb per 40 CFR 100-149 and WAC 248-54). It can be concluded from this that while contamination of vadose zone soils by hexavalent chromium is probably widespread in the 100-BC Area, groundwater quality does not appear to be significantly impacted at present.

CONCLUSIONS

A review of production operations in the 100-BC Area indicate that the major sources for introduction of solutions containing hexavalent chromium to the vadose zone include:

- Leakage of reactor cooling water from lines and retention basins
- disposal of radionuclide-contaminated cooling water to the vadose zone in the 116-B-1 and 116-C-1 overflow trenches

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- disposal of radionuclide-contaminated cooling water and decontamination solutions in the pluto cribs and similar structures.

It is concluded that vadose zone cleanup activities may be required for the 116-B-6A and 116-B-6B cribs and possibly for the pluto cribs and the 116-B-4 French Drain. Possible volumes of contaminated soil are presented in Table 1, assuming all contaminated fluids remained in the vadose zone.

Though leakage of reactor cooling water was extensive in the 100-BC Area, the concentration of hexavalent chromium in these fluids was so low that cleanup of the vadose zone is unlikely to be necessary (ignoring potential associated radionuclide contamination). It is suggested that this leakage was a major source of groundwater contamination in the past. Presently, however, the minor concentrations of hexavalent chromium retained in the vadose zone do not appear to pose a major threat to groundwater quality.

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