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ENGINEERING CHANGE NOTICE

Page 1 of 2

1. ECN 163396

Proj. ECN

2. ECN Category (mark one)	3. Originator's Name, Organization, MSIN, and Telephone No.	4. Date
Supplemental [] Direct Revision [x] Change ECN [] Temporary [] Standby [] Supersedure [] Cancel/Void []	E.C. Thornton, Geosciences, H6-06, 376-6107	9-22-93
	5. Project Title/No./Work Order No.: Chromium Speciation	6. Bldg./Sys./Fac. No.: NA
		7. Impact Level: 3Q
	8. Document Numbers Changed by this ECN (includes sheet no. and rev.): WHC-SD-EN-AP-135, Rev. 0	9. Related ECN No(s.): NA
		10. Related PO No.: NA

11a. Modification Work	11b. Work Package No.	11c. Modification Work Complete	11d. Restored to Original Condition (Temp. or Standby ECN only)
[] Yes (fill out Blk. 11b) [X] No (NA Blks. 11b, 11c, 11d)	NA	NA Cog. Engineer Signature & Date	NA Cog. Engineer Signature & Date

12. Description of Change

Document revised per DOE comments.

13a. Justification (mark one)							
As-Found	[X]	Criteria Change	[]	Design Improvement	[]	Environmental	[]
		Facilitate Const.	[]	Const. Error/Omission	[]	Design Error/Omission	[]

13b. Justification Details

Changed technical details of field sampling and laboratory testing activities associated with DOW.

14. Distribution (include name, MSIN, and no. of copies)

E.C. Thornton	H6-06	EPIC (1) FFC(1)	H6-08
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A-7900-013-1 (11/88)

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1. ECN (use no. from pg. 1): 163396

15. Design Verification Required	16. Cost Impact				17. Schedule Impact (days)	
	ENGINEERING		CONSTRUCTION			
[] Yes	Additional	[] $	Additional	[] $	Improvement	[]
[X] No	Savings	[] $	Savings	[] $	Delay	[]

18. Change Impact Review: Indicate the related documents (other than the engineering documents identified on Side 1) that will be affected by the change described in Block 12. Enter the affected document number in Block 19.

SDD/DD	[]	Seismic/Stress Analysis	[]	Tank Calibration Manual	[]
Functional Design Criteria	[]	Stress/Design Report	[]	Health Physics Procedure	[]
Operating Specification	[]	Interface Control Drawing	[]	Spares Multiple Unit Listing	[]
Criticality Specification	[]	Calibration Procedure	[]	Test Procedures/Specification	[]
Conceptual Design Report	[]	Installation Procedure	[]	Component Index	[]
Equipment Spec.	[]	Maintenance Procedure	[]	ASME Coded Item	[]
Const. Spec.	[]	Engineering Procedure	[]	Human Factor Consideration	[]
Procurement Spec.	[]	Operating Instruction	[]	Computer Software	[]
Vendor Information	[]	Operating Procedure	[]	Electric Circuit Schedule	[]
OM Manual	[]	Operational Safety Requirement	[]	ICRS Procedure	[]
FSAR/SAR	[]	IEFD Drawing	[]	Process Control Manual/Plan	[]
Safety Equipment List	[]	Cell Arrangement Drawing	[]	Process Flow Chart	[]
Radiation Work Permit	[]	Essential Material Specification	[]	Purchase Requisition	[]
Environmental Impact Statement	[]	Fac. Proc. Samp. Schedule	[]		[]
Environmental Report	[]	Inspection Plan	[]		[]
Environmental Permit	[]	Inventory Adjustment Request	[]		[]

19. Other Affected Documents: (NOTE: Documents listed below will not be revised by this ECN.) Signatures below indicate that the signing organization has been notified of other affected documents listed below.

Document Number/Revision	Document Number/Revision	Document Number Revision

20. Approvals

Signature	Date	Signature	Date
OPERATIONS AND ENGINEERING		ARCHITECT-ENGINEER	
Cog Engineer E.C. Thornton E.C. Thornton	9-27-93	PE	
Cog. Mgr. R.P. Henckel R P Henckel	9-27-93	QA	
QA G.S. Corrigan Gary Corrigan	10-1-93	Safety	
Safety		Design	
Security		Environ.	
Environ.		Other	
Projects/Programs			
Tank Waste Remediation System			
Facilities Operations		DEPARTMENT OF ENERGY E.D. Goller	
Restoration & Remediation		Signature or Letter No.	10/12/93
Operations & Support Services			
IRM		ADDITIONAL	
Other R.L. Biggerstaff R L Biggerstaff	9/27/93		
J.E. Amonette	10/1/93		

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Date Received: 11/10/93

INFORMATION RELEASE REQUEST

Reference: WHC-CM-3-4

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- [ ] Thesis or Dissertation
- [ ] Manual
- [ ] Brochure/Flier
- [ ] Software/Database
- [ ] Controlled Document
- [ ] Other

ID Number (include revision, volume, etc.): WHC-SD-EN-AP-135, Rev. 1

List attachments: ECN 163396

Date Release Required: 9/29/94

Title: Description of Work for the Evaluation of Chromium Speciation in the Hanford Unconfined Aquifer and the Columbia River

Unclassified Category: UC-NA

Impact Level: 3Q

New or novel (patentable) subject matter? [X] No [ ] Yes
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Date(s) of Conference or Meeting: NA

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Will proceedings be published? [ ] Yes [X] No
Will material be handed out? [ ] Yes [X] No

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CHECKLIST FOR SIGNATORIES

Review Required per WHC-CM-3-4	Yes	No	Reviewer - Signature Indicates Approval: Name (printed) / Signature / Date
Classification/Unclassified Controlled Nuclear Information	[ ]	[X]	
Patent - General Counsel	[X]	[ ]	not req'd per OGC memo 2-4-93 GJ 9-23-93
Legal - General Counsel	[X]	[ ]	
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Information conforms to all applicable requirements. The above information is certified to be correct.

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Transmit to DOE-HQ/Office of Scientific and Technical Information	[ ]	[X]

Author/Requestor (Printed/Signature) Date: E.C. Thornton E.C. Thornton 9/23/93

Intended Audience: [ ] Internal [ ] Sponsor [X] External

Responsible Manager (Printed/Signature) Date: R.L. Jackson R L Jackson 9/23/93

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SUPPORTING DOCUMENT

1. Total Pages 8

2. Title	3. Number	4. Rev No.
Description of Work for the Evaluation of Chromium Speciation in the Hanford Unconfined Aquifer and the Columbia River	WHC-SD-EN-AP-135	1

5. Key Words

100-D Area, 100-H Area, speciation, colorimetric, reservoirs

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6. Author

Name: E.C. Thornton

E.C. Thornton 11/9/93
Signature

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7. Abstract

Thornton, E. C., 1993, *Description of Work for the Evaluation of Chromium Speciation in the Hanford Unconfined Aquifer and the Columbia River*, WHC-SD-EN-AP-135, Westinghouse Hanford Company, Richland, Washington.

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9. Impact Level 3Q

10. RELEASE STAMP

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RECORD OF REVISION	(1) Document Number WHC-SD-EN-AP-135	Page 1

(2) Title

Description of Work for the Evaluation of Chromium Speciation in the Hanford Unconfined Aquifer and the Columbia River

CHANGE CONTROL RECORD

(3) Revision	(4) Description of Change - Replace, Add, and Delete Pages	Authorized for Release	
		(5) Cog. Engr.	(6) Cog. Mgr. Date
0	(7) Release document (EDT 142073)		
1 RS	Changed technical details of field sampling and laboratory testing activities (ECN 163396)	E.C. Thornton E.C. Thornton 11/9/93	R.L. Jackson [signature] 11/5/93 for RLJ

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CONTENTS

1.0 INTRODUCTION

This document describes laboratory activities that will be conducted to provide information regarding the probable fate of hexavalent chromium that flows through the Hanford unconfined aquifer and discharges into the Columbia River. The speciation of the chromium in the groundwater and the river is not presently known in detail, nor are the changes in speciation or concentration of chromium that may occur as a result of mixing of groundwater with river water. Activities described in the following sections will provide information needed to characterize chromium speciation in groundwater, and predict changes in chromium speciation and subsequent transport characteristics of chromium after entering the Columbia River.

2.0 SCOPE AND OBJECTIVES

The sampling, characterization, and testing activities described in this description of work (DOW) are those identified in Activity 1A-4 (Chromium Speciation) of DOE-RL (1992a). Activity 1A-4 addresses the need to determine if hexavalent chromium present in groundwater will remain in the hexavalent state upon entering the river column or if it will be reduced to the much less toxic trivalent state. This DOW also addresses the need identified in Activity 1A-4 to develop sampling techniques and analytical methods for chromium speciation of groundwater in the 100 Area.

The activities to be undertaken under this DOW include collection of a representative composite sample of Columbia River water and characterization of chromium in this sample. Groundwater samples will also be collected from wells in the 100-D and 100-H Areas for analysis and determination of chromium speciation.

Laboratory testing activities will be conducted with the Columbia River sample. Groundwater that is contaminated with chromium (>100 ppb) will be added to the river water sample at several ratios, and aliquots will be taken over time for characterization. The primary objective of the test will be to assess the changes in concentration and speciation of dissolved chromium in the river water following mixing and the extent of subsequent partitioning into the suspended particulate fraction or removal by precipitation.

3.0 GENERAL REQUIREMENTS

3.1 HEALTH AND SAFETY

Sampling of groundwater for chromium speciation determination will be performed by qualified Westinghouse Hanford Company (WHC) personnel in accordance with health and safety requirements as identified in environmental investigation instruction (EII) 5.8, Groundwater Sampling (WHC 1988). This activity will be undertaken in conjunction with routine groundwater monitoring activities taking place in 100-D and 100-H Areas. All sampling activities

shall comply with the applicable safety documents, Hazardous Waste Operations Permit, or Job Safety Analysis defining access control, monitoring, or radioactive and environmental hazards and personnel protective equipment associated with the groundwater monitoring plans for these areas. Specific safety recommendations for collection of near-shore river water samples are provided by DOE-RL (1992b).

Laboratory personnel will follow Pacific Northwest Laboratory's (PNL) guidelines for safe and responsible handling and disposal of possible carcinogenic materials, such as chromate, while conducting testing activities. As much work as possible will be conducted inside a hood when handling chemical reagents containing hexavalent chromium (protective rubber gloves will be worn). Protective rubber gloves will be worn by WHC and PNL personnel working with chromate solutions in the field, and liquid waste will be stored in bottles until proper disposal is possible.

3.2 QUALITY ASSURANCE/QUALITY CONTROL AND DATA RECORDING REQUIREMENTS

Sampling activities shall be performed by WHC personnel in accordance with the following procedures (WHC 1988):

- EII 1.5, Field Logbooks
- EII 5.1, Chain of Custody
- EII 5.8, Groundwater Sampling.

Internal quality control samples associated with groundwater analysis shall also be collected as described in the appropriate groundwater monitoring plans.

PNL will perform the chromium speciation analyses and laboratory testing activities. Precautions shall be considered to prevent contamination of the river water sample since only trace concentrations of chromium are anticipated to be present (possibly <1 ppb). Cranston and Murray (1978 and 1980) provide guidance in the special sampling requirements associated with characterization of chromium speciation at trace concentrations.

Data and sample control activities associated with laboratory testing activities will follow PNL's Quality Assurance Manual (PNL-MA-70). Permanent written records will be kept of all significant information and data generated during these activities. Laboratory Record Books will be the principal documents used to record test results and details of research activities. Other permanent written or visual records of research (log books, computer printouts, etc.) will be referenced in the Laboratory Record Books to provide a clear and complete record of: (1) what was done, (2) why it was done, (3) who did it, (4) when it was done, and (5) results.

All aspects of the data development and reduction associated with the chromium speciation and laboratory testing activities will be carefully documented and recorded in step-wise fashion to show how the instrumental response of each measurement is converted into actual concentration data. Particular attention will be given in describing and quantifying the uncertainties associated with each measurement. This will involve determining the precision, accuracy, and detection limits of the chromium speciation

analyses using NIST-certified reference samples. Precision will be estimated using the standard deviation of replicate determinations. Accuracy will be determined from a comparison of the means of the actual analytical results with the expected results based on the certified values. Detection limits will be determined from a comparison of blanks with diluted standards. The detection limit will be defined as twice the lowest statistically significant concentration. Statistical significance for the accuracy and detection-limit determinations will be as defined by the t test at the 0.05 level.

3.3 SCHEDULE AND DELIVERABLES

Groundwater and river water sampling activities, evaluation of chromium speciation, and all associated laboratory testing activities will be completed within 240 calendar days following regulatory approval of the DOW. A supporting document summarizing the results of laboratory and field activities will be prepared by WHC and PNL technical staff within 60 calendar days following completion of laboratory and field activities.

4.0 SAMPLE COLLECTION AND CHARACTERIZATION

A sample of water from the Columbia River shall be collected by WHC and PNL staff. This sample shall be 40 L in volume and will be composited from a series of near-shore river water samples collected from 10 locations between the 100-D and 100-H Areas. Collection of these samples shall be conducted by the direct sampling method as described in DOE-RL (1992b). Two samples shall be collected at each location: a 2-L sample in about 6 in. of water and a 2-L sample taken further from shore in about 3 ft of water. The second sample shall be collected about 6 in. off bottom. Sampling locations shall be recorded in a WHC field notebook. The composited sample will be transported to the PNL testing laboratory where it will undergo characterization to assess chromium speciation and be used in the mixing tests (Section 5.0).

The composited water sample from the Columbia River will be analyzed per SW-846 (EPA 1986) or approved U.S. Environmental Protection Agency (EPA) Contract Laboratory Program protocol in a laboratory designated by WHC. Analytical data shall include determination of cations and metals by inductively coupled plasma-atomic emission spectroscopy on filtered and unfiltered portions. Anion concentrations of unfiltered river water will be obtained by ion chromatography. Total organic carbon, alkalinity, and pH shall also be determined. Appropriate sampling and analytical protocol will be defined in a task order prepared by WHC Environmental Restoration Engineering and WHC Hanford Analytical Services Management, as indicated by EII 14.1, Analytical Laboratory Data Management (WHC 1988).

Chromium speciation of the Columbia River water shall be performed by PNL by the method presented in Cranston and Murray (1978). This approach provides detection limits in the nanomolar range for total dissolved chromium, dissolved Cr(III), and particulate chromium. Dissolved Cr(VI) is determined by difference. Cranston and Murray (1978 and 1980) reported that water from the lower Columbia River contains a total of about 5 nM (0.26 ppb) chromium. Of this, about 65% is dissolved Cr(VI) and about 35% is chromium associated

with particulate matter. Less than several percent of the chromium was determined to be dissolved Cr(III).

In addition, the concentration of dissolved hexavalent chromium and total dissolved chromium of the composited river sample will be determined colorimetrically using diphenylcarbazide indicator (Skougstad et al. 1979). (It is anticipated that these constituents will be below the limits of detection by this method.) A determination of hexavalent chromium shall also be performed in the field in order to meet the 6-hr holding time limitation associated with this analyte.

A 5-L sample of the river water will be taken from the composite for measurement of the suspended particulate fraction concentration (mg/L). This may be determined by filtering through a 0.45-μm pore-diameter membrane filter.

Samples of groundwater shall be collected from D5-15 (2020 ppb chromium) and H4-14 (410 ppb chromium), since these wells have the maximum concentrations of chromium in the 100-D and 100-H Areas. These samples will be obtained in conjunction with routine groundwater monitoring activities, if possible.

At the time of collection of these samples, the temperature, pH, concentration of dissolved oxygen (by oxygen electrode), and Cr(VI) concentration (by colorimetric method of Skougstad et al. 1979) will be determined in the field for later comparison with laboratory results. The groundwater samples will also be analyzed for cations, anions, TOC, alkalinity, and pH per the task order prepared by Environmental Restoration Engineering and Hanford Analytical Services Management personnel.

Chromium speciation of the groundwater samples will be determined by several approaches. The concentration of dissolved hexavalent chromium in the groundwater samples will be determined colorimetrically using diphenylcarbazide indicator (Skougstad et al. 1979). Total dissolved chromium for filtered and unfiltered samples will be determined by ICP and also by a colorimetric approach (Skougstad et al. 1979). The chromium content of the suspended particulate fraction will be measured and will also be calculated by determining the difference between the chromium content of the filtered and unfiltered aliquots. The dissolved Cr(III) content of the groundwater samples will be calculated as the difference between the total chromium and hexavalent chromium contents of the filtered samples. In addition, determination of chromium speciation of these samples will be performed by the method of Cranston and Murray (1978).

At least 5 L of groundwater will be collected from D5-15 for laboratory testing (Section 5.0). This sample will be obtained from the well at the time samples are collected for water analysis and chromium speciation.

5.0 LABORATORY MIXING STUDY

A series of laboratory tests will be conducted in which groundwater and river water are mixed and the resulting changes in chromium speciation determined. These tests will be performed in 10 reservoirs, as described below.

Portions of the composite sample of Columbia River water will be transferred to seven reservoirs for evaluation of mixing of groundwater with river water (2 L of river water per reservoir). Each of these reservoirs will be stirred at a rate similar to that of flow in the Columbia River and will be maintained at river temperature. One of these reservoirs will be used as a control. Portions of groundwater containing chromium will be added to each of the next five reservoirs. The ratio of river water to groundwater shall be 1, 10, 100, and 500 in four of these reservoirs. This range of ratios is intended to represent the range of mixing ratios that can exist in the natural environment. That is, a ratio of 1 represents mixing processes in the bed of the river while a ratio of 500 is more representative of the situation where dilution occurs relatively quickly such that river water greatly dominates the groundwater component. Information gained by comparing the data over this range should clarify the fate of chromium following its entry into the fluvial environment and provide a model for predicting spatial variations in the distribution and speciation of chromium.

A ratio of 10 shall also be used in the sixth reservoir, but this reservoir will be exposed to ultraviolet light during the test to evaluate photo-reductive or photo-oxidative effects. A 2000 ppb Cr(VI) standard solution (prepared from sodium dichromate) shall be added to the river water in the seventh reservoir, also at a ratio of 10. The objective of the last test is to provide a basis for determining if specific matrix effects associated with the groundwater sample materially effect the fate of chromium subsequent to mixing with river water.

An eighth 2-L volume reservoir shall contain only groundwater and be stirred at the same rate as the other reservoirs. This reservoir will serve as a control to determine if chromium speciation changes occur in the groundwater sample over the duration of the testing activities.

Two additional reservoirs shall contain mixtures of filtered groundwater and river water, and shall be stirred at the same rate as the other reservoirs. The ratio of river water to groundwater shall be 10 and 500 for reservoirs 9 and 10, respectively. The objective of these tests is to determine the effect of suspended particulate matter by comparison with the other tests.

Aliquots of water will be taken from each reservoir for determination of changes in chromium speciation by the method of Cranston and Murray (1978). These samples shall be collected at the beginning of each test (after mixing occurs) and at 4 hr, 1 day, 3 days, 7 days, and 21 days. Each sample shall be at least 125 mls (see Cranston and Murray, 1978). The data collected from these tests shall be utilized to determine if the oxidation state of chromium changes during mixing and whether or not any chromium is precipitated. Other data shall also be collected prior to and during the mixing experiments that are related to primary variables controlling the speciation of chromium.

These parameters shall include the concentration of suspended particulates, pH, redox potential (Eh), temperature, total chromium concentration, and the concentration of major oxidants and reductants (primarily dissolved oxygen and total organic carbon).

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