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100-KW Pump and Treat ResinTech SIR-700 Test Results and Recommendations for Use Across 100-KR-4 Operable Unit

Prepared for the U.S. Department of Energy Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy under Contract DE-AC06-08RL14788



Approved for Public Release; Further Dissemination Unlimited





100-KW Pump and Treat ResinTech SIR-700 Test Results and Recommendations for Use Across 100-KR-4 Operable Unit

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Terms

bgs	below ground surface
CHPRC	CH2M HILL Plateau Remediation Company
gpm	gallons per minute
HEIS	Hanford Environmental Information System
IX	ion exchange
OU	operable unit
RPO	Remedial Process Optimization
TDS	total dissolved solids



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1 Test Overview

CH2M HILL Plateau Remediation Company (CHPRC) conducted a performance test of ResinTech[®] SIR-700 Ion-Exchange Resin (ResinTech, 2009) at the 100-KW groundwater treatment system. This test was intended to demonstrate the successful conversion of an existing treatment system from the previously specified DOWEX[™] 21K resin to the higher-performing SIR-700 resin to remove hexavalent chromium from contaminated groundwater. The test results indicate successful conversion and operation of the 100-KW system.

An important component of Remedial Process Optimization (RPO) at the Hanford Site River Corridor has been to enhance the usage of ion exchange (IX) resin in pump-and-treat systems to remove hexavalent chromium. The goal is to implement high-capacity resin with a longer operation between resin change outs to reduce material costs and provide environmentally sound disposition of spent resin without having to send the resin offsite for regeneration. A comprehensive resin strategy was initiated as part of the RPO and SIR-700 resin was preferred because it performed best for typical Hanford Site groundwater chemistry as a single-use, high-capacity resin (up to 3.2 kg [7 lb] dichromate/ft³) that could ultimately be disposed of on site.

The work culminated in SGW-46621, 100 Area Groundwater Chromium Resin Management Strategy for Ion Exchange Systems, which sets the strategy for resin use in the hexavalent chromium extraction systems at the Hanford Site River Corridor. The SIR-700 resin ultimately was implemented at both the DX and HX pump-and-treat systems in 100-HR-3. The strategy report recommended that the remaining 100 Area pump-and-treat facilities be converted to single-use resin in order to reduce operating costs and eliminate offsite transportation. The 100-KW pump-and-treat system was selected to test the implementation of SIR-700 resin at a mildly acidic pH (5.5 ± 0.5), to determine if the pH would cause any system lining degradation and aquifer effect, and whether there would be any negative effects to the aquifer as a result of injecting lower pH water. Progress of the resin testing at 100-K has been provided at the 100-300 Unit Managers Meeting since January, 2010.

[®] ResinTech is a registered trademark of the ResinTech Inc., West Berlin, New Jersey.

[™] DOWEX is a trademark of The Dow Chemical Company, Midland, Michigan.

2 Scope and Objectives of Test

The SIR-700 IX resin test scope and objectives are described in SGW-48676, *Test Plan to Implement ResinTech SIR-700 in the 100-KW Pump and Treat*. The test scope implements SIR-700 IX resin at the 100-KW pump-and-treat system and tests the resin performance. The test will have the following differences from previous routine operations:

- Replace DOWEX[™] 21K with ResinTech[®] SIR-700 resin in each treatment train.
- Operate each train in a "lead, lag, and polish" configuration in three vessels instead of four, with the influent water first entering the lead vessel where much of the hexavalent chromium is removed, followed by the lag vessel for intermediate treatment, and finally the polish vessel to scrub out any residual mass.
- Load each vessel with 1.8 m³ (63 ft³ or about 9 drums) of SIR-700 resin.
- Control influent pH at 5.5 ± 0.5 units.
- Monitor effluent pH.
- Increased Cr(VI) analysis frequency at the start of the test to monitor the resin performance

The specific test objectives are listed in this section. The data collected to fulfill the following objectives are described in Section 4:

- Objective 1: Demonstrate the installation and performance of SIR-700 resin (relative to DOWEX[™] 21K) in the existing pump-and-treat system by documenting the installation of the new resin and analyzing plant operational data to ensure that flow rates, pressures and hexavalent chromium removal is within specifications.
- **Objective 2:** Demonstrate compatibility of vessel lining material with lower pH groundwater by analyzing the vessel-wall thickness over time with ultrasonic thickness measurements.
- Objective 3: Generate data to establish the groundwater influent operating conditions for the SIR-700 resin by monitoring pH and hexavalent chromium removal data.
- **Objective 4:** Generate data to establish operating limits for effluent pH from the SIR-700 resin by monitoring flow rates and water levels at the injection wells together with an understanding of the groundwater geochemistry.

3 Regulatory Analysis

The 100-KR-4 Operable Unit (OU) pump-and-treat systems were authorized under the Record of Decision (ROD), as amended.

- Record of Decision for the 100-HR-3 and 100-KR-4 Operable Units Interim Remedial Actions, Hanford Site, Benton County, Washington (EPA/ROD/R10-96/134)
- As revised under Explanation of Significant Differences for the 100-HR-3 and 100-KR-4 Operable Units Interim Action Record of Decision, Hanford Site, Benton County, Washington (EPA et al., 2009)

The ROD is implemented under the Remedial Design (RD) and Remedial Action Work Plans (RAWP):

- DOE/RL-96-84, Remedial Design and Remedial Action Work Plan for the 100-HR-3 and 100-KR-4 Groundwater Operable Units Interim Action
- DOE/RL-2006-75, Supplement to the 100-HR-3 and 100-KR-4 Remedial Design Report and Remedial Action Work Plan for the Expansion of the 100-KR-4 Pump and Treat System

The implementing documents state that an alternate resin (other than DOWEX[™] 21K resin) may be used if approved by EPA (DOE/RL-2006-75, Section 3.3.4). Approval for use at 100-KW was received through Unit Managers Meeting (UMM) discussions held between November 2010 and July 2011. Approval will be required before implementation at other 100-KR-4 OU systems.

The ROD specifies a pump-and-treat injection limit specific to hexavalent chromium. Neither the ROD nor the RD/RAWPs have requirements to meet secondary MCLs (WAC 173-200, "Water Quality Standards for Groundwaters of the State of Washington"), which include pH limits.

The use of injection wells for Comprehensive Environmental Response, Compensation, and Liability Act of 1980 remediation is allowed under "Underground Injection Control Program" (WAC 173-218), unless it is considered a dangerous waste (WAC 173-303-090, "Dangerous Waste Regulations," "Dangerous Waste Characteristics"), which includes a pH definition greater than or equal to 12.5 or less than or equal to 2. The injection water at the 100-KR-4 OU is not considered a dangerous waste and, from a regulatory perspective, may be re-injected without adjusting the pH as long as it does not enter the dangerous waste limitations.

4 Test Operating Conditions

The 100-KW pump-and-treat system has a design capacity of 757.1 L/min (200 gallons per minute [gpm]) equally split between two treatment trains housed in the 6004KW process building. The system includes 8 extraction wells focused on the hexavalent chromium plume downgradient of the 105KW Reactor and adjacent waste sites. Three injection wells return the treated groundwater to the aquifer upgradient of the 183-KW Reservoir and Filter Plant. The well network is shown in Figure 1.

The extraction well lines are input to the influent tank. The influent tank includes a pH meter and an acid injection line for pH adjustment before the water enters the two treatment trains. The treatment trains each include four vessels; only three are being used in this test because of the much higher hexavalent chromium removal capacity of the SIR-700 resin. Each vessel holds 1.8 m³ (63 ft³) of resin. At the maximum operating capacity of 378.5 L/min (100 gpm), each train should have a throughput of 305 bed volumes per day (ECF-100KR4-12-0006, *Daily Bed Volume at 100 Gallons Per Minute of Water for K West Resin Train at K West Pump and Treat System*).

The 100-KW pump-and-treat system originally was configured for acid addition. Several small design and structural modifications were conducted for the resin change (GW-11-01570, *KW Resin Test Preparation Work Package*); subsequently a bulk acid storage tank was installed outside the operations building and placed in service. The test period began on August 31, 2011 when the SIR-700 resin was placed in service in the first of two treatment trains (Train A). The second treatment train (Train B) was loaded with SIR-700 and placed in service on September 12, 2011. A leak in the acidification system caused by a failed fitting resulted in the 100-KW system being shut down from September 13 through 21, 2011 to effect repairs. The full system with both trains running at capacity resumed on September 22, 2011 and functioned normally thereafter. The initial groundwater sample at monitoring Well 199-K-173 was collected on September 20, 2011; a second sample was collected February 10, 2012.



Figure 1. 100-KW Pump-and-Treat System Well Network

5 Measurement Data Collected During Test

The test and required measurements were conducted under CHPRC internal work control processes, consistent with the Test Plan. The data collected for each objective are listed in Table 1.

Data Collected	Location	Frequency	Citation ^a	Objectiveb
Flow rate	IX Train	Daily	5.4	1
Flow rate	Injection well	Daily	5.4	4
Water levels	Injection well	Daily	5.4	4
Water temperature	Influent tank	Daily	5.4	1,2
Differential pressure	IX vessel	Daily	5.4	1
рН	Influent tank	Daily	5.4	3
рН	IX Vessel	Daily for first seven days, then as identified in WP	Table 1	2, 3
pH	Effluent tank	Daily	5.4	4
Field Analysis: Cr(VI)	Influent tank	Twice weekly or as identified in the WP	Table 1	1
Lab Analysis: Cr(VI), Cr total	Influent tank	At startup; additional samples case-by-case	Table 1	1
Lab Analysis: Ca, Mg, Nitrate, Sulfate, chloride, Alkalinity, TDS, Sr-90, C-14, H-3, Tc-99, U	Influent tank	At startup; additional samples case-by-case	Table 1	4
Field Analysis: Cr(VI)	IX Vessel	Daily for first seven days, then as identified in WP	Table 1	1
Lab Analysis: Cr(VI), Cr total	IX Vessel	At startup; after both trains have operated for 2 weeks; additional samples case-by-case	Table 1	1
Lab Analysis: Ca, Mg, Nitrate, Sulfate, chloride, Alkalinity, TDS, Sr-90, C-14, H-3, Tc-99, U	IX Vessel	At startup; after both trains have operated for 2 weeks; additional samples case-by-case	Table 1	4
Field Analysis: Cr(VI)	Effluent tank	Twice weekly or as identified in the WP	Table 1	1, 4
Lab Analysis: Cr(VI), Cr total	Effluent tank	At startup; additional samples case-by-case	Table 1	1
Lab Analysis: Ca, Mg, Nitrate, Sulfate, chloride, Alkalinity, TDS, Sr-90, C-14, H-3, Tc-99, U	Effluent tank	At startup; additional samples case-by-case	Table 1	4

Table 1. Data Collection Summary

Data Collected	Location	Frequency	Citation ^a	Objectiveb
Field Analysis: Cr(VI)	Well 199-K-173	Quarterly (If operated as an extraction well)	Table 1	4
Lab Analysis: Cr(VI), Cr total, Ca, Mg, Nitrate, Sulfate, chloride, Alkalinity, TDS, Sr-90, C-14, H-3, Tc-99	Well 199-K-173	Quarterly	Table 1	4
Lab Analysis: Sr-90, Tc-99	Well 199-K-173	Annual	Table 1	4
Ultrasonic wall thickness measurements	Vessel walls	At startup and after 3 – 6 months	5.5	2
See DQO (SGW-48306)	SIR-700 Resin	When removed from the vessel	Table 1	Resin disposal

Table 1. Data Collection Summary

Source: SGW-48306, Waste Management Data Quality Objective Summary Report for the 100-KR-4 Pump and Treat Systems.

a. Citations are from SGW-48676, Test Plan to Implement ResinTech SIR-700 in the 100-KW Pump and Treat.
b. Objectives include the following (per SGW-48676):

- 1. Demonstrate the installation and performance of SIR-700 resin (relative to Dowex 21K) in existing pump-and-treat systems.
- 2. Demonstrate compatibility of vessel lining material with lower pH groundwater.
- Generate data to help establish the groundwater influent pH operating range for the SIR-700 resin in existing pump-and-treat systems.
- 4. Generate data to help establish operating limits for effluent pH form the SIR-700 resin in existing pump-and-treat systems.

TDS = total dissolved solids

6 Observations and Measurements

The data compiled from observations and measurements collected during the test period are summarized and presented in this section. The data are organized by their related objectives.

6.1 Objective 1: Observations and Measurements

Objective 1 states: "Demonstrate the installation and performance of SIR-700 resin (relative to DOWEX[™] 21K) in the existing pump-and-treat system by documenting the installation of the new resin and analyzing plant operational data to ensure that flow rates, pressures and hexavalent chromium removal is within specifications." The observations and measurements associated with this objective are presented in this section.

These data and observations include the installation of the SIR-700, flow rate through the IX trains, resin vessel differential pressure, and the influent water temperature. This information was collected from daily rounds sheets as specified in the test plan. These data were tabulated and plotted (ECF-100KR4-12-0009, *Tabulate and Plot Operational Data for K West Resin Trains at K West Pump and Treat System*). In addition, hexavalent chromium measurements were taken from the influent tank, effluent tank, and following each vessel in both trains. Laboratory data were also collected to confirm the field hexavalent chromium measurements. Bed volumes are measured using the flow rate data.

6.1.1 Flow Rate

The flow rates through the IX trains are shown in Figure 2. Flow rates are shown from September 22, 2011 after both trains were brought on line. Flow through the system was maintained at, or near, the design capacity of 757.1 L/min (200 gpm) from September 22 onward. Flow at each train is measured before entering the IX vessels.

6.1.2 Differential Pressure

The differential pressure, also shown in Figure 2, is within the specifications for the system (40 psi) and ranges from 20 to 28 psi. This pressure distribution is very similar to that observed at the HX system in 100-HR-3 OU. The lessons learned from DX and HX for loading SIR-700 resin into the vessels were implemented during the loading of the 100-KW resin. This included backflushing of the resin to remove fines before operation. The differential pressure relationship shown in Figure 2 indicates that the 100-KW SIR-700 resin was loaded appropriately.



Figure 2. Flow Rates and Differential Pressures in Trains A and B

6.1.3 Hexavalent Chromium

Hexavalent chromium removal was evaluated weekly by comparing measured concentrations in the influent tank, effluent tank, and the discharge point of each resin vessel using the Hach DR/2010¹ (ECF-100KR4-12-0008, *Tabulate and Plot Hach Kit Hexavalent Chromium Operational Data for K West Resin Trains at K West Pump and Treat System*). The measurements at the influent and effluent tanks are shown in Figure 3. No detectable levels of hexavalent chromium are measured in the effluent tank. The published hexavalent chromium MDL for the Hach instrument is 0.010 mg/L; additional calibration is conducted by operations to reduce the MDL to 0.005 mg/L. The laboratory hexavalent chromium MDL is 0.002 mg/L. The full data set is shown in Table 2. The lead, lag, and polish vessels are W2A1, W2A2, and W2A3 in Train A and W2B1, W2B2, and W2B3 in Train B. Hexavalent chromium enters the system at between 0.063 to 0.110 mg/L and exits at less than 0.003 mg/L. The residual hexavalent chromium value is well below the requirements for injecting water at less than 0.050 mg/L upgradient of the plume as is done at 100-KW. The laboratory measurement for hexavalent chromium taken during the test (HEIS) is consistent with the Hach measurements. Several negative values near zero are reported in the Daily Rounds Sheets; these are within the calibration error of the field instrument and are reduced to zero in Figure 3.



Figure 3. Influent and Effluent Tank Hexavalent Chromium Concentrations

Results for the individual vessels for each train indicate that a large fraction of the hexavalent chromium is removed in the lead vessel. The yellow highlighted values in Table 2 indicate detections of hexavalent chromium above the MDLs for the field and laboratory analyses (that is, 0.010 mg/L and 0.002 mg/L, respectively). These results are summarized in Table 3 for the amount of hexavalent chromium retained by the first vessel. These results indicate that 82 to 95 percent of the hexavalent chromium is removed by the first vessel. Referring to Table 2, the remainder is removed in the lag vessel. The process stream reaching the lag vessel contains nondetectable hexavalent chromium. No detectable quantities are measured after the lag vessel. These results indicate the resin is performing within specifications and that the operational configuration with three vessels in each train at 100-KW is removing the hexavalent chromium efficiently. The results indicate only two vessels are required to treat the groundwater contaminated with hexavalent chromium down to levels that are below the detection levels of both the Hach and laboratory measurement methods.

¹ DR/2010 is a product of Hach Company, Loveland, Colorado.

Hach Kit								
Data	influent							Effluent
Date	Tank	W2A1	W2A2	W2A3	W2B1	W2B2	W2B3	Tank
09/22/11	0.110	-0.002	-0.001	-0.001	-0.001	0.001	-0.002	0.000
09/26/11	0.077	0.000	-0.003	-0.003	0.000	-0.002	-0.003	-0.001
10/04/11	0.073	0.006	-0.001	-0.001	0.008	-0.003	-0.003	-0.002
10/10/11	0.076	0.009	0.002	-0.001	0.011	0.000	-0.002	-0.001
10/17/11	0.072	0.010	0.002	0.005	0.013	0.006	0.003	0.003
10/24/11	0.074	0.007	0.000	0.000	0.008	0.001	0.000	-0.001
10/31/11	0.073	0.007	0.001	0.000	0.008	0.001	0.000	0.000
11/07/11	0.073	0.009	0.000	-0.002	0.008	0.001	0.000	0.000
11/14/11	0.071	0.009	0.002	0.000	0.009	0.002	0.000	-0.001
11/21/11	0.071	0.010	-0.001	-0.001	0.010	0.002	0.000	0.000
11/28/11	0.070	0.008	0.001	0.000	0.007	0.001	0.000	0.000
12/05/11	0.071	0.007	0.002	0.001	0.007	0.003	0.001	0.001
12/12/11	0.070	0.008	0.001	-0.001	0.008	0.001	0.000	0.000
12/19/11	0.070	0.008	0.000	0.000	0.009	0.003	0.000	0.000
12/27/11	0.070	0.009	0.003	0.001	0.010	0.003	0.000	0.000
01/03/12	0.068	0.008	0.000	0.000	0.007	0.003	0.000	0.000
01/09/12	0.067	0.008	0.001	-0.001	0.008	0.003	0.000	0.000
01/16/12	0.068	0.008	0.001	0.001	0.009	0.003	0.001	0.001
01/23/12	0.066	0.010	0.003	0.001	0.008	0.003	0.000	0.000
01/30/12	0.065	0.008	0.002	0.000	0.007	0.002	0.001	0.000
02/06/12	0.064	0.008	0.001	0.001	0.008	0.002	0.001	0.000
02/13/12	0.063	0.006	0.001	0.000	0.005	0.001	0.000	0.000
02/21/12	0.063	0.008	0.001	0.000	0.007	0.002	0.001	0.000

Table 2. Cr(VI) Hach® and Laboratory Analytical Measurements (mg/L) (Above MDL Highlighted)

Lab Sample Collection Date	Influent Tank	W2A1	W2A2	W2A3	W2B1	W2B2	W2B3	Effluent Tank
09/06/11	0.098	0.006	0.002	0.002				0.002
09/29/11	0.075	0.002	0.002	0.002	0.004	0.002	0.002	0.002

Table 3. Train A and B First Vessel Cr(VI) Percent Retained

Date	Method	Vessel	Influent Conc mg/L	Vessel Exit Conc mg/L	% Retained
9/6/2011	Lab	W2A1	0.098	0.006	94
9/29/2011	Lab	W2B1	0.075	0.004	95
10/10/2011	Hach	W2B1	0.076	0.011	86
10/17/2011	Hach	W2A1	0.072	0.01	86
10/17/2011	Hach	W2B1	0.072	0.013	82
11/21/2011	Hach	W2A1	0.071	0.01	86
11/21/2011	Hach	W2B1	0.071	0.01	86
12/27/2011	Hach	W2B1	0.07	0.01	86
1/23/2012	Hach	W2A1	0.066	0.01	85

6.1.4 Bed Volumes

The number of bed volumes treated by SIR-700 is shown in Figure 4 (ECF-100KR4-12-0007, *Cumulative Bed Volumes for K West Resin Trains at K West Pump and Treat System*). As of February 1, 2012, approximately 83,000 vessel volumes had been treated without replacement.

The system will have processed over 50,000 vessel bed volumes per train by the end of February 2012. Each train is processing about 9,000 vessel bed volumes per month. The theoretical maximum capacity for 100-KW with both trains in operation is the removal of approximately 1,200 kg of hexavalent chromium. The removal rate during the test was 2.3 kg/month of hexavalent chromium. Comparison of the rate of hexavalent chromium removal with the available capacity in the vessel indicates that years of operation may be achieved before a resin change is required.



Figure 4. 100-KW Bed Volumes Treated

6.1.5 Influent Water Temperature

The water temperature at the influent tank is shown in Figure 5 (ECF-100KR4-12-0009). Process influent temperature ranged from about 57.5°F to 63°F, substantially below the maximum allowable temperature specified by the resin manufacturer (that is, less than 100°F). The seasonal drop in ambient temperature from September into December is clearly visible.



Figure 5. 100-KW Influent Water Temperature

6.2 Objective 2: Observations and Measurements

Objective 2 states: "Demonstrate compatibility of vessel lining material with lower pH groundwater by analyzing the vessel-wall thickness over time with ultrasonic thickness measurements." The observations and measurements associated with this objective are presented in this section.

The vessel wall thicknesses are monitored as part of the test using an ultrasonic measurement technique to track vessel wall thickness (GW-11-01570). The testing is being conducted by AREVA. Ten locations are monitored on each of the eight vessels in the two treatment trains. The first measurement point is located near the top of the vessel, and the measurements continue in sequence down the side of the vessel to the ninth and tenth locations at the base of the vessel. The vessels are assumed to be axisymmetric and the measurements assumed to be representative of the wall thickness around the tank at that level. The initial measurement was taken on July 6, 2011, and the test measurement was taken on January 25, 2012.

The results are presented in Table 4. In general, the differences in the two measurements are less than 0.005 inch, the tolerance of the ultrasonic instrument for a single measurement. Several locations have a difference between 0.005 inch and 0.01 inch. The expected tolerance for two measurements should be 0.005 inch × 2 or 0.01 inch. The only two measurements that have a difference greater than 0.01 inch are IX-W2A2 at location 9, and IX-W2B2 at location 8. The instrument is calibrated using the same procedure for each set of measurements, but there could be minor variations. Other factors besides the instrument that may affect the measurement include temperature differences at the times of the readings which were within several degrees Fahrenheit, relocation of the measurement probe to the identical location for each measurement, and curvature of the vessel at different locations. The instrument is sensitive to temperature variations and there may be some variation in calibration and operational characteristics between the July and January measurements. For location, a circle is placed on the vessel at each location to return the measurement head to the same position. However, it is nearly impossible to return to the exact same position and there will likely be an offset between measurements. These data indicate that no measurable degradation of the vessel lining has occurred.

6.3 Objective 3: Observation and Measurements

Objective 3 states: "Generate data to establish the groundwater influent operating conditions for the SIR-700 resin by monitoring pH and hexavalent chromium removal data." The observations and measurements associated with this objective are presented in this section.

The field pH readings of the influent and effluent tanks are shown in Figure 6 (ECF-100KR4-12-0009). The pH data measured at the influent tank tend to be highly variable because of the proximity of the pH meter to the acid addition tube. The effluent pH is steady with values of 6.03 to 6.04. The consistent pH values are because of mixing of the acid and groundwater between the influent and effluent tanks. Laboratory measurements of pH in samples of process effluent from each vessel and the effluent accumulation tank are shown in Table 5.

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	UT location											
IX-W2A1	1	2	3	4	5	6	7	8	9	10		
7/6/2011	0.328	0.341	0.272	0.274	0.273	0.276	0.264	0.330	0.332	0.339		
1/25/2012	0.329	0.341	0.271	0.273	0.274	0.268	0.265	0.329	0.332	0.333		
delta	0.001	0.000	-0.001	-0.001	0.001	-0.008	0.001	-0.001	0.000	-0.006		
IX-W2A2	1	2	3	4	5	6	7	8	9	10		
7/6/2011	0.359	0.344	0.277	0.266	0.265	0.267	0.264	0.327	0.341	0.327		
1/25/2012	0.358	0.344	0.269	0.270	0.268	0.270	0.267	0.330	0.353	0.330		
delta	-0.001	0.000	-0.008	0.004	0.003	0.003	0.003	0.003	0.012	0.003		
IX-W2A3	1	2	3	4	5	6	7	8	9	10		
7/6/2011	0.333	0.352	0.276	0.285	0.275	0.270	0.268	0.346	0.342	0.338		
1/25/2012	0.330	0.343	0.274	0.284	0.275	0.270	0.265	0.338	0.335	0.338		
delta	-0.003	-0.009	-0.002	-0.001	0.000	0.000	-0.003	-0.008	-0.007	0.000		
IX-W2A4	1	2	3	4	5	6	7	8	9	10		
7/6/2011	0.332	0.355	0.287	0.306	0.287	0.280	0.281	0.345	0.345	0.351		
1/25/2012	0.332	0.352	0.280	0.305	0.283	0.280	0.282	0.346	0.346	0.352		
delta	0.000	-0.003	-0.007	-0.001	-0.004	0.000	0.001	0.001	0.001	0.001		
IX-W2B1	1	2	3	4	5	6	7	8	9	10		
7/6/2011	0.263	0.266	0.259	0.262	0.259	0.257	0.263	0.269	0.276	0.267		
1/25/2012	0.265	0.268	0.259	0.263	0.262	0.259	0.262	0.270	0.283	0.270		
delta	0.002	0.002	0.000	0.001	0.003	0.002	-0.001	0.001	0.007	0.003		
IX-W2B2	1	2	3	4	5	6	7	8	9	10		
7/6/2011	0.266	0.267	0.265	0.263	0.263	0.266	0.274	0.272	0.266	0.264		
1/25/2012	0.268	0.270	0.258	0.265	0.263	0.267	0.282	0.285	0.274	0.273		
delta	0.002	0.003	-0.007	0.002	0.000	0.001	0.008	0.013	0.008	0.009		
IX-W2B3	1	2	3	4	5	6	7	8	9	10		
7/6/2011	0.287	0.289	0.282	0.259	0.266	0.277	0.258	0.283	0.280	0.275		
1/25/2012	0.289	0.289	0.290	0.262	0.267	0.278	0.258	0.284	0.278	0.283		
delta	0.002	0.000	0.008	0.003	0.001	0.001	0.000	0.001	-0.002	0.008		
IX-W2B4	1	2	3	4	5	6	7	8	9	10		
7/6/2011	0.274	0.278	0.285	0.266	0.265	0.267	0.273	0.271	0.285	0.275		
1/25/2012	0.275	0.278	0.282	0.267	0.265	0.267	0.273	0.274	0.278	0.266		
delta	0.001	0.000	-0.003	0.001	0.000	0.000	0.000	0.003	-0.007	-0.009		
	tole	rance =+	/- 0.005							-		

Table 4. Results of Ultrasonic Thickness Measurements (Inches)



Figure 6. pH in the Influent and Effluent Tanks

Measurement Point	HEIS Number	pH	
INFLUENT T-TW1 (V-WE06C)	B2H374	6.2	
Train A, Lead Vessel	B2H376	6.3	
Train A, Lag Vessel	B2H377	6.3	
Train A, Polish Vessel	B2H378	6.3	
Train B, Lead Vessel	B2H379	6.4	
Train B, Lag Vessel	B2H380	6.3	
Train B, Polish Vessel	B2H381	6.5	
EFFLUENT T-W3 (V-WJ13)	B2H375	6.4	

Table 5. September 29, 2011 Laboratory pH Measurements

6.4 Objective 4: Observations and Measurements

Objective 4 states: "Generate data to establish operating limits for effluent pH from the SIR-700 resin by monitoring flow rates and water levels at the injection wells together with an understanding of the groundwater geochemistry." The observations and measurements associated with this objective are presented in this section.

6.4.1 Injection Well Operational Data

Operational data on the injection wells was monitored for the test (ECF-100KR4-12-0009). The pH of the effluent water was slightly acidic for the entire period of the test to date. Most of the pH data collected was generated by the in-line pH electrodes that automatically monitor the process stream pH at the inlet and outlet. The outlet pH trend generated from the in-line monitoring system is shown in Figure 6, previously. On three occasions, additional process stream samples were analyzed for pH either in the field, or in the laboratory. The comparison of these measurements is shown in Table 6.

Measurement Date	Laboratory Measurement (pH Units)	Field Measurement (pH Units)	Automated In-Line Measurement (pH Units)
9/6/2011	7.9	-NA-	6.4 to 6.8
9/13/2011	-NA-	6.72	6.0
9/29/2011	6.4	-NA-	6.1 to 6.2

Table 6. Comparison of Process Effluent pH Measurements from Various Sources.

Where comparable data are available, the automated in-line measurements were generally lower than other measurements; the difference ranged from 0.2 to 1.5 pH units. The large differences appear to be the result of transient conditions during the early startup of the system using the SIR-700 resin. The source of this variation is not identified. Since late September 2011, the indicated effluent pH has been very stable between 6.0 and 6.1 pH units.

The injection well flow rates are shown in Figure 7 and the injection well water levels are shown in Figure 8. The flow rates and head levels within the injection wells have remained constant over the duration of the test. This is a favorable condition because it indicates that flow from the injection well into the aquifer is not being negatively affected by well or aquifer fouling that would reduce the porosity of the aquifer matrix and cause reduced pumping rates and/or increased water levels (hydraulic head). Injection Well 199-K-158 (WJ1) is operating at rate of approximately 321.8 L/min (85 gpm) with a water level of 26 m (85 ft) below ground surface (bgs). Injection Well 199-K-174 (WJ3) is operating at a rate of approximately 287.7 L/min (76 gpm) and a water level of 22.25 m (73 ft) bgs. Injection Well 199-K-175 (WJ4) is operating at a rate of approximately 147.6 (39 gpm) and a water level of 31.4 m (103 ft) bgs. Flow rates remained steady within 5.7 L/min (1.5 gpm) over the duration of the test. Most of this variation in flow rate is due to adjustments in the flow routed to each well by the plant operators.

These flow rate and water level data indicate that addition of the pH 6.0-6.5 water into the approximately 8.0 pH groundwater has not negatively affected either injection well flow rates or water levels. This indicates that no observable effect to the hydraulic conductivity of the aquifer or efficiency of the wells has occurred as a result of the test. Sufficient time has passed and sufficient flow has passed through the injection wells into the aquifer to indicate that no acute effects to the aquifer have occurred as a result of operating 100-KW with effluent at the reduced pH. Routine well maintenance (that is, periodic inspection and re-development as needed) should be sufficient to maintain well performance. Monitoring of the injection well flow rates and water levels should be continued, with drops in pump rates and/or increases in water level taken as the primary indicators of any problems.

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Figure 7. 100-KW Injection Well Flow Rates



Figure 8. 100-KW Injection Well Water Levels (ft bgs)

The potential for long-term accumulation of precipitates or scale is an issue at injection wells. The act of accelerating water through a well screen can cause enough chemical imbalances to initiate chemical precipitation along the screen. Given the geochemical composition of the Ringold Formation Unit E aquifer matrix within the 100-KW capture area and the ambient groundwater chemical composition, no significant precipitates would be expected to form based on geochemical analyses. The 100-K groundwater is characterized as calcium carbonate-type water with minor amounts of magnesium, sodium, potassium, chloride and sulfate. The ambient groundwater and soil chemistry at 100-K is documented extensively in DOE/RL-2010-97, *Remedial Investigation/Feasibility Study for the 100-KR-1, 100-KR-2, and 100-KR-4 Operable Units.* Injecting water at a pH below neutral (that is, pH<7.0) might cause some redistribution of calcium carbonate within the aquifer matrix, but the effects are expected to be minimal. Much of this redistribution in the immediate vicinity of the injection wells likely has already occurred during the early portion of the test and there do not appear to be any effects on flow rates or water levels in the injection wells.

However, well plugging incidents occur at Hanford and they provide important lessons learned to mitigate these problems in the future. A significant instance of injection well plugging was observed and documented at Well 199-D5-42 at the DR-5 pump-and-treat system in 2009.

The exacerbating circumstance at this location was the periodic metering of resin regeneration wastes into the effluent stream of the pump-and-treat system. Degradation in the ability to inject water at the injection well was observed through increases in water level and drop off in injection pumping rates. Well maintenance concluded the well was becoming plugged up. Extensive analysis of the chemistry of the groundwater and the regeneration waste indicated the presence of phosphate in the injection stream resulted in the formation of fluorapatite, hydroxylapatite, and calcite (PNNL-18797, *Precipitate Formation Potential of Resin Regeneration Effluent in the 100-HR-3 Operable Unit*). Precipitation of fluorapatite was relatively insensitive to pH, but the other minerals exhibited increased precipitation with increasing pH.

The groundwater at 100-K contains very little phosphate either naturally or as a result of Hanford operations. No phosphate is added as a result of the use of SIR-700 in the pump-and-treat system. Consequently, the likelihood of forming the significant chemical precipitates fluorapatite or hydroxylapatite is small because there is little available phosphate for their formation.

6.4.2 Monitoring at 199-K-173

Monitoring Well 199-K-173 is between the 100-KW extraction and injection wells and has been routinely monitored, including measurement of groundwater pH, since it was constructed in 2008. Samples collected during drilling were used to prepare a depth profile of pH within the aquifer. The depth profile is shown in Figure 9. The conditions at this well location exhibited increasing pH with depth, pH about 7.0 near the water table and increasing to about 8.1 near the bottom of the aquifer. Figure 10 presents the time series of pH measurements in Well 199-K-173 since the well was completed. The pH at this location has varied between 7.6 and 8.0 with no clear trend indicated. Well 199-K-173 was identified as an observation well to monitoring changing conditions in the vicinity of the 100-KW system extraction and injection wells. No identifiable change in groundwater pH has been observed in this well.

Groundwater was sampled at Well 199-K-173 on September 20, 2011 in the early stages of the test. The pH in the aquifer at that time was 7.99. The most recent sample was collected February 10, 2012 with a pH measurement of 8.04. Over the course of the test to date, injected effluent water may not have reached monitoring Well 199-K-173 yet. Calculation of groundwater travel time between the three injection wells and Well 199-K-173 indicates that travel times of 105 – 461 days at low river stage to 187 – 923 days at high river stage are likely (ECF-100KR4-12-0015, *Cooper Jacob Equation to Estimate Radius of Influence of Injection at K West Pump and Treat and Groundwater Velocity and Travel Time for K West Area*).



Figure 9. Vertical Profile of Measured pH in the Aquifer at Well 199-K-173





Injection of the slightly-acidic effluent water has not effected observable changes in either the hydraulic performance of the injection wells and surrounding aquifer or in the measured pH of the nearest downgradient monitoring well (that is, 199-K-173).

6.4.3 Evaluation of Geochemical Effects on the Aquifer Resulting from Lower pH

The focus of the pH operational objective is directed at determining whether the injection of the slightly-acidic effluent water generated by the 100-KW pump-and-treat process will result in a negative effect on the aquifer and/or the hydraulic or contaminant removal efficacy of the remedial action system. The potential effects of returning treated groundwater to the aquifer at a pH different from the original, near background, pH level presents potential complications for operation of the system as well as the continued ability to meet remedial action objectives under continued system operation. The project team identified the following problem statement to provide focus to the assessment of potential effects on aquifer conditions:

- Will direct injection of the pump-and-treat effluent water from Hanford 100 Area plants using ResinTech® SIR-700 resin, without alkaline pH adjustment, result in any of the following difficulties:
 - Will groundwater contaminants of concern (that is, total and/or hexavalent chromium, strontium-90, carbon-14, tritium, nitrate, or TCE) or other selected metallic constituents (that is, calcium, magnesium, sodium, iron, manganese, aluminum, arsenic, and mercury) be mobilized (dissolved and/or displaced) from the periodically-rewetted zone to increase the contaminant mass and/or concentration in groundwater?
 - Will groundwater contaminants of concern (that is, total and/or hexavalent chromium, strontium-90, carbon-14, tritium, nitrate, or TCE) or other selected metallic constituents (that is, calcium, magnesium, sodium, iron, manganese, aluminum, arsenic, and mercury) that are presently sorbed to aquifer solids or otherwise exhibiting reduced mobility become displaced and/or more mobile, increasing the contaminant mass and/or concentration in groundwater?
 - Will the injection wells and/or their surrounding filter pack and/or aquifer formation become less transmissive (that is, become fouled) because of accumulation of mineral solids within the interstitial spaces of the system?
 - Will the injection wells and their components (for example, screens) exhibit accelerated corrosion and correspondingly shortened service life?
 - Will the discharged effluent continue to meet drinking water standards (for example, MCLs) for the contaminants of concern under the anticipated aquifer conditions as modified by injection of non-alkaline adjusted effluent water?

These considerations can be addressed qualitatively to greater or lesser extent based on historical experience and existing measurement data. The nature and expected duration of the remedial activities in the Hanford 100 Areas, however, introduces the need to provide quantitative estimates of aquifer effects where possible. This discussion includes the following assessment elements and three types of evidence:

 Assessment and interpretation of empirical measurements and observations collected at the 100-KW remediation area

- Assessment and interpretation of measurements and observations collected at similar sites at other locations, including literature search
- Assessment and interpretation of geochemical simulations to prepare estimates of groundwater, contaminant, and aquifer matrix behavior

A summary evaluation of the constituents of interest for this assessment and the potential effects of injection of slightly-acidic effluent water on their relative solubility and mobility is presented in Table 7.

The information collected for incorporation into this analysis includes the following:

- Operating data collected from the 100-KW pump-and-treat system, which includes the geochemical content of the effluent water, the measured pH of the effluent water, the operating water levels within the injection and extraction wells, and the well configurations
- Applicable literature information based on review of common reference materials and industry publications (sources are cited)
- Geochemical modeling used to estimate the aquifer behavior following injection of the slightly acidic effluent water

The geochemical evaluation includes the assessment of the potential effects of addition of the slightly-acidic remediation process effluent water to the aquifer at 100-KW. This evaluation included the following elements:

- Measurements and observations collected during operation of the 100-KW pump-and-treat system
- Measurements and observations of groundwater and aquifer conditions at other Hanford sites
- Expected changes in constituent ionic conditions and phase changes based on published relationships of pH and REDOX potential (that is, eH/pH diagrams)
- Potential for the effluent water to contact the periodically-rewetted zone
- Potential changes in aquifer pH and reaction with residual calcium carbonate in the aquifer matrix using industry-standard computational tools
- Potential changes in contaminant distribution coefficients (K_d) using published computational methods

The results of this evaluation for the identified constituents of interest are presented in the following subsections.

Constituent	Form in Primary Source	Form as Present in Soil/GW	Relative Solubility	Subject to REDOX changes	Change in Solubility w/ pH Decrease	Potential Effect on COC concentration in GW	Potential Effect on Scaling/Fouling of Wells or Aquifer
				C	DCs		
Chromium	Sodium Dichromate Dihydrate	Cr(VI) as Chromate ions Cr(III) as Chromic hydroxide or chromic oxide	Chromate = High Chromic Hydroxide/ Oxide= Low	Yes	Chromate = minimal effect not sensitive to pH change Chromic hydroxide = slight increased solubility similar to amorphous iron hydroxide	Cr(VI) = minimal effect Total Chrome = slight increase in dissolved Cr(III)	No anticipated effect
Strontium-9 0	Metallic Sr and Sr ⁺⁺ cations	Sr ⁺⁺ cations	Moderate	No	Minimal Effect	Slight increase in concentration in portion of aquifer affected by increased dissolved calcium	No anticipated effect
Carbon-14	Carbonate and cyanide anions	Carbonate and Bicarbonate anions; solid calcium carbonate	Low at background pH	Yes (as carbonate and bicarbonate)	To the extent that some C-14 is present as solid-phase calcium carbonate, solubility will increase	A small increase in C-14 concentration may be expected.	No anticipated effect
Tritium	Diatomic tritium and tritiated water	tritiated water	High	No (not within stability of water)	No change	No effect	No effect
Nitrate	Nitrate oxyanion and ammonia	nitrate oxyanion	high	yes	Minimal Effect	No effect	No effect
TCE	TCE	TCE	Low	Yes	Minimal Effect	No effect	No effect

Table 7. Overview of Features of Constituents of Interest at 100-KW Pump-and-Treat Area

Constituent	Form in Primary Source	Form as Present in Soil/GW	Relative Solubility	Subject to REDOX changes	Change in Solubility w/ pH Decrease	Potential Effect on COC concentration in GW	Potential Effect on Scaling/Fouling of Wells or Aquifer
				Other Constitu	ients of Interest		
Calcium	Ca ⁺⁺ cation, calcium oxide and hydroxide complexes, and solid calcium carbonate	Calcium Carbonate = Low	No	Increased dissolution of calcium carbonate by acidic water.	Not a COC, concentration may increase	No anticipated effect	Ca ⁺⁺ cation, calcium oxide and hydroxide complexes, and solid calcium carbonate
Magnesium	Mg ⁺⁺ cation, oxide and hydroxide complexes, and solid phase compounds	As carbonate = Low	No	Increased dissolution of magnesium carbonate by acidic water.	Not a COC, concentration may increase	No anticipated effect	Mg ⁺⁺ cation, oxide and hydroxide complexes, and solid phase compounds
Sodium	Na^+ cation	Moderate to high	No	Minimal Effect	No effect	No effect	Na^+ cation
Iron	Iron complexes and solid ferric hydroxide	Low	Yes	Slight increased solubility of ferric hydroxide and oxide	No effect	No effect	Iron complexes and solid ferric hydroxide
Manganese	Anionic, cationic, and solid phases	variable	Yes	Increased solubility with decreasing pH	Minimal effect	Minimal effect	Anionic, cationic, and solid phases

Table 7. Overview of Features of Constituents of Interest at 100-KW Pump-and-Treat Area

Constituent	Form in Primary Source	Form as Present in Soil/GW	Relative Solubility	Subject to REDOX changes	Change in Solubility w/ pH Decrease	Potential Effect on COC concentration in GW	Potential Effect on Scaling/Fouling of Wells or Aquifer
Aluminum	Anionic and cationic hydroxide ions and solid phases	Moderate	No	Minimal effect	No effect	No effect	Anionic and cationic hydroxide ions and solid phases
Arsenic	Variously- hydrated oxyanions	Moderate	Yes	Minimal effect over expected pH range	No effect	No effect	variously-hydrated oxyanions
Mercury	Mercuric or mercurous salts and ions	Mercurous sulfate = Low; mercuric sulfate = decomposed. Mercurous oxide = insoluble	No	Degree of water solubility is strongly compound-dep endent.	Minimal effect. Residual mercury may exist higher in the vadose zone in the vicinity of the 183-KW head house. Not expected to be affected by effluent injection. Not historically detected in groundwater at this location.	No effect	Mercuric or mercurous salts and ions

Table 7. Overview of Features of Constituents of Interest at 100-KW Pump-and-Treat Area

6.4.3.1 Evaluation of Potential for pH Change and Calcium Carbonate Solubility Effects

The potential for changes in solubility and mobility of numerous constituents of interest at 100-KW pump-and-treat system is largely determined by the groundwater equilibrium with calcium carbonate. The pH of natural water systems is controlled by reactions involving the carbonate system (Drever, 1982, *The Geochemistry of Natural Waters*) and an anthropogenic disturbance such as the injection of treated water will result in geochemical reactions to re-establish equilibrium. This evaluation identified a residual buffering capacity of the aquifer, based on estimated calcium carbonate content, which ranges from 19 to 52 years, after which the affected portion of the aquifer would begin to exhibit alteration to a slightly-acidic pH consistent with the pH of the injected effluent.

Groundwater at the Hanford 100 Areas is generally at, or near, equilibrium with calcium carbonate and solid-phase calcium carbonate in the aquifer matrix provides most of the pH buffering capacity in the aquifer. Injection of slightly-acidic effluent water generated from the treatment of contaminated groundwater by the SIR-700 ion exchange resin system will affect the aquifer's calcium carbonate equilibrium. The net aquifer response to the injection of the acidic water will be dissolution of residual calcium carbonate from the aquifer matrix in a neutralization reaction, re-establishing the system equilibrium in an alkaline, calcium carbonate-buffered, condition as long as sufficient calcium carbonate remains in the aquifer system.

Ultimately, the continued addition of acidic water will consume the residual calcium carbonate in the aquifer matrix and at that point, the aquifer will establish a new equilibrium, not based on calcium carbonate buffering. This new equilibrium will most likely exhibit slightly acidic conditions consistent with the pH of the injected water. When injection of the acidic effluent water is discontinued, the aquifer would be expected to gradually become alkaline once again as alkaline, calcium-carbonate-based groundwater again enters the affected aquifer from up gradient.

To evaluate this effect quantitatively, equilibrium simulations were performed using the computer code PHREEQC (Parkhurst and Appelo, 1999, User's Guide to PHREEQC (Version 2)—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations). The application of this computational tool is described in a calculation brief (ECF-100KR4-12-0016, Geochemical Analysis of Speciation and Buffering Capacity in the Aquifer at the 100-KR-4 Pump and Treat Systems). The PRHEEQC code (Parkhurst and Appelo, 1999) uses initial water quality conditions to calculate equilibrium conditions based on pH and specific chemical constituents. For this analysis, the initial conditions were derived from the chemical analysis of 100-KW effluent water extracted from the HEIS database. The relative equilibrium status of the water is then used to identify the quantity of solid-phase minerals that would need to be dissolved to establish equilibrium between dissolved and solid phases in the system.

Estimates of the residual calcium carbonate content of the Ringold E Formation aquifer were derived from various sources, including quantitative analysis of calcium carbonate in the Ringold E collected from a borehole in 100-BC Area. The residual calcium carbonate content of the Ringold E is not extremely large; an estimated content of 0.01 weight percent calcium carbonate was used for these calculations. The estimated calcium carbonate content of the aquifer and the relative equilibrium status of the discharged water were then used to calculate the buffering capacity (in years) of the aquifer matrix.

The effluent water was found to be substantially under-saturated with respect to calcium carbonate; residual calcium carbonate in the aquifer matrix will, therefore, be consumed by neutralization reactions with the water. The calculated buffering capacity of the aquifer under these conditions ranges from 19 to 52 years, varying largely on the stability of the carbon dioxide partial pressure of the groundwater, and the contributing reaction effects of other amorphous compounds in the aquifer (for example, SiO₂,

Al(OH)₃, and Fe(OH)₃). There is considerable uncertainty in the quantification of calcium carbonate content in the Ringold E Formation aquifer matrix at 100-KW. The actual calcium carbonate content may be locally greater or lesser than the estimated 0.01 weight percent, with some likelihood that it may be lower based on sediment analyses at 100-B/C. The estimated reporting limit for quantitative measurements of calcium carbonate content of the Ringold E Formation in samples collected from Well 199-B3-2 (which all exhibited non-detectable calcium carbonate) were used to represent conditions at 100-K. These results are presented in Hanford's Virtual Library Function "ROCSAN" database module.

6.4.3.2 Potential Effects on Solubility and Mobility of Chromium

Chromium (trivalent and hexavalent) may be mobilized by contact with the effluent water; however, this effect is not expected to be dramatic. Evaluation of the results of water leach testing of soil samples collected from Well 199-K-195, located in the midst of the former chemical storage tank farm adjacent to 183-KW head house indicates that only a relatively small fraction of the chromium, both hexavalent and trivalent, was extractable in a slightly-acidic (that is, $pH \sim 5.0$) water extractant. By comparison, this indicates that the treatment effluent at pH = 6.0 would not be expected to mobilize a substantial fraction of the chromium from the periodically-rewetted zone. Figure 11 illustrates the relative leachability of the chromium from soil samples at this location.





As seen in Figure 11, the deepest portion of the vadose zone (that is, below a depth of about 70 ft bgs) did not exhibit substantial leachable chromium, even at intervals where hexavalent chromium was detected in the soil (for example, the interval at about 91 ft bgs). Within the pH range evaluated here (that is, pH = 8to pH = 6) the oxidation state of chromium ions is not affected, therefore, interaction with the slightly-acidic effluent water is not expected to produce substantial changes in either the solubility or the mobility of the chromium within the aquifer.

6.4.3.3 Potential Effects on Solubility and Mobility of Carbon-14

Carbon-14 is expected to occur in a variety of physical states, depending on the aquifer pH and general geochemistry of the system. The net effect of injection of slightly-acidic effluent water into the aquifer on the observed carbon-14 concentration in groundwater is expected to be small. The environmental chemistry of carbon-14 is identical to that of common carbon. The fate and transport characteristics of carbon-14 as carbon dioxide in the vadose zone at 100-K will reflect a range of factors, including unsaturated water content, extent of microbial respiration, biomass production, temperature, diffusion rates, sorption processes, and carbonate equilibria. These same processes will also control the fate and transport of carbon-14.

Carbon (including carbon-14) in the groundwater at 100-K is subject to retardation and sequestration processes similar to those that occur in the vadose zone. Given the organic-poor nature of the Ringold E in the saturated zone, microbial processes are likely less important than in the shallow vadose zone, and carbon mobility in the aquifer is primarily controlled by solid/gas/water exchange processes governed by carbonate equilibria. For example depending on the pH, carbon-14 in 100-K groundwater may be present primarily as carbonic acid, bicarbonate, or carbonate; each of these carbonate species would be subject to somewhat different retardation factors in the aquifer. Any change to the 100-K aquifer that perturbs the distribution of the various carbonate species or the solubility of carbonate phases, will have some effect on the mobility of carbon-14 in the aquifer. Carbon-14 is present in the aquifer and in the periodically-rewetted zone in very small mass concentrations and, therefore, constitutes only a very small fraction of the overall inorganic carbon in the system.

On a qualitative basis, the injection of acidified effluent into the 100-K aquifer should increase the overall dissolved concentration of carbon-14. The extent of this increased mobility will depend, in large part, on the extent that carbon-14 has been sequestered in calcite or other carbonate phases that may be present in the portion of the aquifer that is affected by the acidic effluent. Given the small amounts of calcite that will be required to neutralize the acidity of the effluent, relative to the total amount present in the potentially affected aquifer volume, the potential for substantial long-term increases in carbon-14 activities in the aquifer are believed to be unlikely.

There is some uncertainty in this analysis, primarily because of the lack of site-specific measurement of the calcium carbonate content of the Ringold E Formation in the vicinity of 100-KW pump-and-treat system. Measurement of calcium carbonate content in the Ringold E at 100-BC Area indicates very low content. In order to better define the extent that carbon-14 mobility could be increased by the long-term injection of acidified effluent, the collection of additional information for the aquifer system is suggested. This may include:

- The distribution and abundance of calcite or other solid phases in the aquifer matrix that may represent a significant sink for carbon-14.
- The carbon-14 activity for the various carbon phases or species going into or out of the solution: (for example, the activity of C-14 in calcite, in CO₂, in HCO₃⁻ etc.).

6.4.3.4 Potential Effects on Solubility and Mobility of Strontium-90

Strontium-90 may potentially exhibit slightly increased mobility because of interaction of the acidic treatment effluent water with the aquifer. This change is related to the potential for release of additional calcium into the aquifer system as the slightly-acidic effluent water reacts with residual calcium carbonate, releasing some calcium into solution. Calcium is a strong competitor with strontium-90 for exchange sites in vadose soil and aquifer systems. This condition has been well described at Hanford (HW-56582, *The Influence of Limestone Neutralization on the Soil Uptake of Sr-90 from a Radioactive Waste*) as well as other sites (Baker et al., 1966, *Adsorption Equilibria Between Earth Materials and Radionuclides*) since the 1950s. A modest amount of calcium and/or magnesium will be released during the alkaline buffering reaction between the effluent and the aquifer matrix; a net change in the effective distribution coefficient (K_d) of strontium-90 from about 24 ml/g to a value ranging from about 7 to 11 ml/g could be expected. The modified K_d for strontium-90 of 10 ml/g is still relatively high and a substantial increase in the overall mobility of strontium-90 in the aquifer system is not expected. This effect is described in detail in this section.

Strontium occurs naturally in only the divalent cation state (2+) and the geochemical controls on the mobility of Strontium-90 in aquifers are essentially identical to those that control the solubility and mobility of common strontium. Strontium forms weak complexes with most inorganic anions (for example, carbonate, sulfate, chloride, and nitrate) (EPA 402-R-99-004B, *Understanding Variation in Partition Coefficient, K_d Values: Volume II: Review of Geochemistry and Available K_d Values for Cadmium, Cesium, Chromium, Lead, Plutonium, Radon, Strontium, Thorium, Tritium (³H), and Uranium) and the uncomplexed Sr²⁺ ion typically predominates in groundwater over a wide range of pH conditions. In high pH, carbonate are solubility of strontium carbonate may serve as an upper limit on the strontium concentrations in groundwater. However, in aquifers such as the Ringold E and the Hanford formation that typically have a circumneutral pH and contain a small, but notable clay mineral component, the concentrations of strontium may be limited by cation exchange reactions, to values that are below the solubility limit of strontium carbonate.*

The Ringold E unit at 100-K is lithologically similar to the Ringold Formation unit E that comprises the 100-N aquifer, although there may be a larger component of Hanford formation in the aquifer at 100-N, particularly closer to the River. However, the lithologic and geochemical similarities between the two aquifer units are sufficient to allow studies of contaminant mobility in one unit to be used as a general indicator of contaminant behavior in the other. The effects of cation exchange processes on the mobility of strontium-90 in groundwater from the 100-N Area, were investigated as part of a larger effort to evaluate the use of an apatite barrier to sequester Sr-90 from 100-N groundwater. Test results indicated that cation exchange reactions between groundwater and untreated aquifer sediment resulted in a soil/water distribution coefficient (K_d) for Sr (including Sr-90) of 25 cm3/g (25 ml/g). Based on the cation exchange-based K_d for Sr, groundwater flow rates and other aquifer properties, a retardation factor of approximately 100 was calculated for Sr in the 100-N area (PNNL-16891, *Hanford 100-N Area Apatite Emplacement: Laboratory Results of Ca-Citrate-PO4 Solution Injection and Sr-90 Immobilization in 100-N Sediments*).

The clay assemblage in the Ringold E generally appears to be dominated by Montmorillonite and illite (PNNL-13757-1, *Characterization of Vadose Zone Sediment: Uncontaminated RCRA Borehole Core Samples and Composite Samples*). These clays typically have a much stronger affinity for divalent cations (such as calcium, magnesium, and strontium) than for sodium, the most abundant monovalent cation in 100-K groundwater. Consequently, in aquifer systems such as the 100-K Ringold E, where the groundwater typically contains substantially higher concentrations of calcium and magnesium than either

sodium or potassium (Table 8), the cation exchange sites in the clays should be disproportionately filled with calcium, magnesium, and, to a lesser extent, strontium.

Parameters	Values	Reference
CEC (meq/100 g) for Sandy Ringold E Sediments	5.2 +/- 0.2	Table 5.11 in PNNL-13757-1
CEC (meq/100 g) for Gravelly Ringold E Sediments	3.28 +/- 3.3	Table 11 in PNNL-15502
Ca/Sr Exchange Coefficient	0.77	Appelo and Postma, 2005
Mg/Sr Exchange Coefficient	0.49	Appelo and Postma, 2005

Table 8. Data Used to Calculate the Estimated Change in the Cation Exchange Based Kds for Strontium

Sources: Appelo and Postma, 2005, Geochemistry, Groundwater and Pollution.

PNNL-13757-1, Characterization of Vadose Zone Sediment: Uncontaminated RCRA Borehole Core Samples and Composite Samples.

PNNL-15502, Characterization of 200-UP-1 Aquifer Sediments and Results of Sorption-Desorption Tests Using Spiked Uncontaminated Groundwater.

The mobility of strontium in the aquifer is not primarily controlled by the precipitation of strontium carbonate or by the co-precipitation of strontium with calcite. Rather, cation exchange of strontium onto clays in Ringold E is assumed to be the primary process that limits the solubility and mobility of strontium in the 100-K aquifer.

The mobility of strontium (including Sr-90) will be primarily limited by competition with calcium and magnesium for the cation exchange sites in the aquifer matrix (Appelo and Postma, 2005, *Geochemistry*, *Groundwater and Pollution*). Consequently, at a given concentration of strontium in a system, an increase in the dissolved concentrations of calcium or magnesium should decrease the number of exchange sites available for strontium. This relationship suggests that the increased calcium concentrations that will result from the dissolution of calcite in the aquifer by the injection of acidified effluent may lead to a lower K_d for strontium in those parts of the 100-K aquifer that will equilibrate with the neutralized effluent. Derivation of estimated effective K_d for strontium under differing aquifer solution conditions is described in a calculation brief (ECF-100KR4-12-0030, *Evaluation of Potential Changes in the K_d of Strontium-90 in the 100-K Aquifer in Response to the Injection of pH 6.0 Treated Effluent at 100-KW*). Two conditions were evaluated, one under which the effluent water was not neutralized and remained at the discharged pH (solution 1), and one in which the slightly acidic effluent water was allowed to be neutralized by residual calcium carbonate in the aquifer (solution 2). The derived K_d under these conditions are shown in Table 9.

As shown in Table 9, there may be a measureable reduction in the strontium K_d in the affected portion of the aquifer. This could result in a higher observed concentration of strontium in the groundwater in that aquifer volume. Overall, the general mobility of strontium should not be dramatically affected; the residual K_d would remain 7 mL/g or greater.

Ringold E Cation Exchange Capacity (meq/100 g)	Initial K _d (mL/g)	Derived K _d Under Alternative Conditions (mL/g) ^a
5.2 +/- 0.2	25	24 (Solution 1 ^b)
	25	11 (Solution 2°)
3.28 +/- 3.3	25	15 (Solution 1 ^b)
	25	7 (Solution 2°)

Table 9. Estimated Change in Strontium Distribution Coefficient (Kd) Under Two Aquifer Solution Conditions

a. Indicated K_d values are average of four derived values based on a range of solution strontium concentrations.

b. Solution 1 = Acidic effluent does not react with calcium carbonate in aquifer and remains at discharged pH.

c. Solution 2 = Acidic effluent is neutralized to pH = 7.1 by reaction with calcium carbonate in aquifer.

6.4.3.5 Potential Effects on Solubility and Mobility of Tritium

Tritium is expected to be present in groundwater at 100-KW as tritiated water and will not be affected by addition of slightly-acidic water to the aquifer. The chemistry of tritium (with the exception of its being radioactive) is essentially identical to common hydrogen, and it can migrate in soils as a gas and readily reacts with oxygen to form what is known as heavy water (H3O, or TTO), or it may replace only one hydrogen atom in a water molecule, forming tritiated water (HTO). Once tritium atoms have been incorporated into water molecules, they will be subject to the same dispersive, advective, and other transport processes as common water and will migrate at the same average velocity (EPA 402-R-99-004B).

The fate and transport of tritium in the subsurface at the Hanford Site is primarily controlled by radioactive decay and by the hydrologic characteristics of the affected vadose or groundwater systems. No sorption or precipitation processes are known to significantly retard the movement of tritiated water in the environment, although the fixation of tritiated water on clays and other hydrated soil minerals can have a small effect. The stability of water is not affected by pH over a wide range of conditions and tritiated water in the affected area would remain as stable water in the aquifer. The injection of acidified effluent at 100-K is not expected to produce any geochemical effect that may increase or decrease either the concentration or the mobility of tritium at this site.

6.4.3.6 Potential effects on Solubility and Mobility of Arsenic and Mercury

The solubility and mobility of arsenic and mercury are not expected to be affected by the discharge of slightly-acidic pump-and-treat effluent water to the aquifer. Arsenic and mercury were identified as constituents of interest for this evaluation because they both exhibit relatively high acute toxicity and they are present in groundwater and/or vadose zone soil in the vicinity of 100-KW pump-and-treat system. Arsenic is present at concentrations consistent with background conditions; mercury has exhibited only a single detection in groundwater in this vicinity (a single detection below the reporting level in Well 199-K-35 in 1992). Arsenic may be present in vadose zone soil near the river at 100-K as a result of historical use of arsenical pesticides in orchard lands that predate Hanford Site operations in that area. Mercury was detected in vadose zone soil in the vicinity of the 183-KW Headhouse tank farm resulting from historical releases of mercury-contaminated sulfuric acid residues to an acid neutralization pit in that area. Soil found to be contaminated above remedial action objectives was excavated and removed; mercury has not been identified as a groundwater contaminant at 100-KW area.

Evaluation of the speciation of arsenic indicates that within the expected Eh and pH ranges for groundwater in this area, arsenic will be present as one of the complex oxyanions as shown in Figure 12. Mercury is expected to remain as the Hg+ cation or as a complexed salt under the same conditions as shown in Figure 13.



Figure 12. Arsenic Speciation as a Function of Eh and pH (P=1.0 Atm, DO=8.0 mg/L, Arsenic=0.015 mg/L)





The mobility of both arsenic and mercury in groundwater at near-neutral pH is strongly influenced by the adsorption of these constituents onto iron oxides in the aquifer matrix (Raven et al., 1998, "Arsenite and Arsenate Adsorption on Ferrihydrite: Kinetics, Equilibrium, and Adsorption Envelopes;" Tiffreau et al., 1995, "Modeling the Adsorption of Mercury(II) on (Hydr)Oxides .1. Amorphous Iron-Oxide and -Quartz"). Because the Ringold E Formation that comprises most of the aquifer volume in the area of interest is known to contain about one weight percent amorphous ferric hydroxide, the interaction of arsenic and mercury with the ferric hydroxide in the aquifer matrix will control the mobility of these contaminants. A computational analysis of this interaction was performed using a geochemical modeling software called Geochemists Workbench (Bethke, 1996, *Geochemical Reaction Modeling*). The results of this specific modeling activity are described in a separate calculation (ECF-100KR4-12-0029, *Model-Simulation of Adsorption of Arsenic and Mercury in Response to the Injection of pH 6.0 Treated Effluent at 100-KW*).

The modeling indicates that arsenic and mercury remain relatively immobile over the expected pH range of the aquifer ranging from an anticipated high of about pH = 7.1 (for effluent water equilibrated by neutralization with residual calcium carbonate in the aquifer) down to the discharge pH of 6.0 (for conditions beyond the point where the slightly-acidic water has consumed the residual calcium carbonate in the formation). Sorption to ferric hydroxide in the formation is likely the major controlling factor and no change in measured concentration of arsenic or mercury in groundwater in the area is expected as a result of discharge of the slightly-acidic effluent water.

6.4.3.7 Potential Effects on Solubility and Mobility of Nitrate

Nitrate is a soluble oxyanion of nitrogen and is stable in water over a wide range of pH. Nitrate will remain present as the soluble anion and its solubility or mobility will not be affected by addition of the slightly-acidic effluent water from the 100-KW pump-and-treat system.

6.4.3.8 Potential Effects on Solubility and Mobility of Trichloroethene

Trichloroethene is relatively stable chlorinated organic compound with generally low water solubility. Neither the solubility nor the relative mobility of trichloroethene will be affected by the addition of the slightly-acidic effluent water from the 100-KW pump-and-treat system.

6.4.3.9 Potential Effects on Solubility and Mobility of Other Selected Constituents of Interest

Additional constituents of interest were identified for evaluation. These are calcium, magnesium, sodium, iron, manganese, aluminum, arsenic, and mercury and the potential effects on their solubility and/or mobility are discussed in this section.

Calcium is present in the groundwater system as the divalent cation (Ca^{+2}) , as various soluble oxide and hydroxide complexes, and as solid-phase calcium carbonate. The quantity of calcium in solution in groundwater is a function of the equilibrium between dissolved and solid-phase calcium carbonate. Calcium is the dominant cation in the groundwater at 100-KW. The reaction of slightly-acidic effluent water with residual calcium carbonate in the aquifer matrix will result in dissolution of some amount of the calcium carbonate in a simple neutralization reaction; some calcium will be put into solution by that reaction, resulting in an increase in the observed calcium concentration in groundwater. The increase in calcium content can affect the ion exchange of other constituents as discussed above for strontium-90.

Magnesium is the second-most abundant cation in the groundwater system and is present in conditions and soluble and solid forms similar to calcium. As with calcium, the net concentration of magnesium is expected to increase as the slightly-acidic effluent water reacts with solid phase magnesium compounds in the aquifer matrix. **Iron and Aluminum** are present in the Ringold E Formation primarily as amorphous oxide and hydroxide compounds, with iron being substantially more abundant that aluminum. The concentration of dissolved iron and aluminum are not expected to increase substantially as the slightly-acidic effluent water is neutralized by reaction with residual calcium carbonate in the aquifer. The addition of the effluent water should not affect the oxidation-reduction potential of the aquifer with resultant modification of solubility of these metals. The net effect within the expected pH range will be very little change in the amount of dissolved iron and aluminum.

Manganese is expected to be present in groundwater as either the Mn^{+2} cation or as solid-phase minerals such as pyrolusite (under moderate to highly-oxidizing conditions) in the natural aquifer condition (Takeno, 2005, *Atlas of Eh-pH Diagrams Intercomparison of Thermodynamic Databases*). Within a relatively wide range of pH conditions (for example, between pH = 0 to pH = 9), these two phases will constitute most of the manganese content in the aquifer. The change in pH resulting from addition of the slightly-acidic effluent water may result in an increase in soluble Mn^{+2} .

6.4.3.10 Potential for Mobilization of Constituents of Interest from the Periodically-rewetted Zone

The potential for mobilization of constituents from the periodically-rewetted zone by the injected effluent water depends on two factors -(1) the water entering the rewetted zone and contacting geological materials in that zone, and (2) the specific interaction of the water with those materials. These factors are discussed in this section.

Groundwater contact with the periodically-rewetted zone. Based on observation of the operating water levels, the frequency or magnitude of contact of the groundwater with the materials within the rewetted zone will not change substantially. In the groundwater extraction areas, there is a small to moderate depression in the groundwater surface elevation. This reduces contact between the groundwater and the former periodically-rewetted zone. Alternatively, the recharge areas exhibit a small increase in the relative groundwater surface elevation in the vicinity of the injection wells. This elevation increase places more groundwater in contact with the periodically-rewetted zone. The operational measurements recorded to data for the 100-KW pump-and-treat system indicate that only one of the three injection wells (that is, 199-K-174) exhibits a dynamic water level substantially above the approximate static water level. This well exhibits a dynamic water level about 4.6 m (15 ft) above the static water level; the other two injection wells (that is, 199-K-158 and 199-K-175) do not exhibit dynamic water levels above the static level.

All of these wells are located some distance from the historical release points that have contributed to the plumes at 100-KW. The nearest location of an injection well to a known release point is Well 199-K-175, located about 92 m (301 ft) upgradient of the former chemical storage tank farm at 183-KW headhouse. As a result of the well placement, the injected treatment effluent water is not expected to contact contaminated soil in the periodically-rewetted zone to any greater degree than would be expected under naturally-occurring seasonal and diurnal water level fluctuations. An example of the effects of contact of groundwater under the local injection well effects is shown in Figure 14.



Figure 14. Illustration of Dynamic Water Level and Groundwater Chromium Concentration Transients in Well 199-K-35 (Measured Values from HEIS)

Well 199-K-35 was used as an injection well for a period of time in 2007 and 2008. During this time, the water level (as indicated by the "Head" measurement in Figure 14) increased about 4.8 m (15.6 ft); the water table declined after injection at that location was discontinued. The chromium concentration in groundwater at that well increased from about 11 μ g/L in October 2005 to about 180 μ g/L in December 2009 (after the water table recovered to normal) and then exhibited a subsequent substantial increase to a maximum of about 750 μ g/L in early 2010, declining subsequently to about 250 μ g/L over the course of the year. The exact cause of this transient has not been determined and it may stem from either of two possible causes: (1) the elevated dynamic water level during the period of injection to this well may have mobilized soluble chromium from the deep vadose zone overlying the aquifer, or (2) water added to control dust during surface demolition and soil excavation work in the vicinity may have mobilized chromium within the vadose to the underlying aquifer. Whichever condition effected the change, it apparently resulted from contact of water with soluble/mobile contaminants in the vadose or the periodically-rewetted zone.

Interaction of remedial system effluent water with the periodically-rewetted zone. Based on geochemical simulations performed for this assessment, the slightly-acidic effluent water would be expected to exert the same influence on the rewetted zone soil as it would in the aquifer matrix. That is, the effluent water would cause some degree of dissolution of variably-soluble mineral species, resulting in a temporary increase in the concentration of natural and contaminant-related metallic constituents. This condition will continue until the aquifer matrix/injected water re-establish equilibrium. The net effect for most constituents will be negligible for the duration of the aquifer matrix buffering capacity.

6.4.3.11 Potential for Increased Mobility of Sorbed Constituents of Interest within the Aquifer

Specific constituents present in the aquifer will exhibit the effects described above and summarized in Table 10. These effects are expected to exhibit the same effects as previously described for the periodically-rewetted zone, with the difference that the aquifer will not be subject to any uncertainty of whether or not the effluent water will contact the aquifer matrix. As discussed previously, the aquifer is expected to provide some residual buffering capacity that will resist pH change following addition of the slightly-acidic effluent water for some time. Concentrations of Sr-90 and C-14 are expected to increase in affected portions of the aquifer. If addition of the effluent water continues to the point where the buffering capacity of the aquifer is exhausted, then a new equilibrium will be established.

6.4.3.12 Potential for Fouling of Injection Wells and/or Aquifer Matrix

The primary well fouling process experienced in the Hanford 100 Areas (including 100-KW pump-and-treat vicinity) is the formation of precipitated calcium carbonate within the treatment system components, water conveyance components, well screens and well filter pack. The injection of slightly-acidic effluent water into the aquifer is not expected to cause precipitation that would result in fouling of injection wells or the formation surrounding those wells.

Most groundwater at the Hanford site exists at a condition that is in, or near, equilibrium with calcium carbonate. The precipitation of calcium carbonate from the treated groundwater is typically caused by specific conditions that alter the calcium carbonate saturation index (that is, the pH_s) of the water. The most common of these modifying conditions encountered in 100 Area pump-and-treat systems are:

- Reduction of the partial pressure of dissolved carbon dioxide (this may occur as a result of aeration or agitation of the water)
- Raising the pH of the water above the saturation pH (this may occur as a result of alkaline pH adjustment)
- Raising the temperature of the water (this may occur because of heating during the treatment process, or heat gain during conveyance of the water through surface mounted pipe during summer months)

These conditions modify the equilibrium between dissolved and solid-phase calcium carbonate and all of the three conditions described above can result in precipitation of solid phase calcium carbonate from the water.

The effluent under evaluation at pH ~6.0 is substantially below the saturation pH for calcium carbonate (that is, this condition is not conducive to precipitation and resultant fouling). Injection of slightly acidic pump-and-treat effluent water (for example, pH ~ 6.0 to 6.1) actually substantially reduces the potential for calcium carbonate fouling within the treatment, conveyance, and injection well system. As the injected effluent reacts with the residual calcium carbonate within the aquifer matrix, it will tend to return to a condition similar to the initially-extracted water and is not expected to cause reduction of the hydraulic conductivity of the aquifer. If the processing continues to the point where residual calcium carbonate buffering capacity is consumed, the aquifer should still maintain good hydraulic conductivity. Over the course of the test at 100-KW to date, the water levels in the injection wells have remained stable, indicating that the injected water has not dramatically affected the ability of either the wells or the surrounding aquifer to transmit water.

The relative uncertainty in this qualitative evaluation is low.

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Constituent	Form as Present in Soil/GW	Relative Solubility	Subject to REDOX changes	Change in Solubility w/ pH Decrease	Potential Effect on COC concentration in GW	Potential Effect on Scaling/Fouling of Wells or Aquifer
Chromium	Cr(VI) as Chromate ions Cr(III) as Chromic hydroxide or chromic oxide	Chromate = High Chromic Hydroxide/Oxi de= Low	Yes	Chromate = minimal effect not sensitive to pH change Chromic hydroxide = slight increased solubility similar to amorphous iron hydroxide	Cr(VI) = minimal effect Total Chrome = slight increase in dissolved Cr(III)	No anticipated effect
Strontium-90	Sr ⁺⁺ cations	Moderate	No	Minimal Effect	Slight increase in concentration in portion of aquifer affected by increased dissolved calcium	No anticipated effect
Carbon-14	Carbonate and Bicarbonate anions; solid calcium carbonate	Low at background pH	Yes (as carbonate and bicarbonate)	To the extent that some C-14 is present as solid-phase calcium carbonate, solubility will increase	A small increase in C-14 concentration may be expected.	No anticipated effect
Tritium	tritiated water	High	No (not within stability of water)	No change	No effect	No effect
Nitrate	Nitrate oxyanion	High	Yes	Minimal Effect	No effect	No effect
TCE	TCE	Low	Yes	Minimal Effect	No effect	No effect

Table 10. Summary of Potential Effects on Constituents of Interest in the Aquifer Because of Injection of Slightly-Acidic Effluent Water at 100-KW Pump-and-Treat System

Constituent	Form as Present in Soil/GW	Relative Solubility	Subject to REDOX changes	Change in Solubility w/ pH Decrease	Potential Effect on COC concentration in GW	Potential Effect on Scaling/Fouling of Wells or Aquifer
Calcium	Ca ⁺⁺ cation, calcium oxide and hydroxide complexes, and solid calcium carbonate	Calcium Carbonate = Low	No	Increased dissolution of calcium carbonate by acidic water.	Not a COC, concentration may increase	No anticipated effect
Magnesium	Mg ⁺⁺ cation, oxide and hydroxide complexes, and solid phase compounds	As carbonate = Low	No	Increased dissolution of magnesium carbonate by acidic water.	Not a COC, concentration may increase	No anticipated effect
Sodium	Na^+ cation	Moderate to high	No	Minimal Effect	No effect	No effect
Iron	Iron complexes and solid ferric hydroxide	Low	Yes	Slight increased solubility of ferric hydroxide and oxide	No effect	No effect
Manganese	Anionic, cationic, and solid phases	Variable	Yes	Increased solubility with decreasing pH	Minimal effect	Minimal effect

Table 10. Summary of Potential Effects on Constituents of Interest in the Aquifer Because of Injection of Slightly-Acidic Effluent Water at 100-KW Pump-and-Treat System

Constituent	Form as Present in Soil/GW	Relative Solubility	Subject to REDOX changes	Change in Solubility w/ pH Decrease	Potential Effect on COC concentration in GW	Potential Effect on Scaling/Fouling of Wells or Aquifer
Aluminum	Anionic and cationic hydroxide ions and solid phases	Moderate	No	Minimal Effect	No effect	No effect
Arsenic	variously-hyd rated oxyanions	Moderate	Yes	Minimal effect over expected pH range	No effect	No effect
Mercury	Mercuric or mercurous salts and ions	Mercurous sulfate = Low; mercuric sulfate = decomposed. Mercurous oxide = insoluble	No	Degree of water solubility is strongly compound-dependent.	Minimal effect. Residual mercury may exist higher in the vadose zone in the vicinity of the 183-KW head house. Not expected to be affected by effluent injection. Not historically detected in groundwater at this location.	No effect

 Table 10. Summary of Potential Effects on Constituents of Interest in the Aquifer Because of Injection of Slightly-Acidic Effluent Water at 100-KW Pump-and-Treat System

6.4.3.13 Potential for Accelerated Corrosion of Injection Well Components

Injection of slightly-acidic treatment process effluent water does not appear to provide a means for accelerated corrosion of injection well components. The well casings and wire-wrapped screens used in construction of the three injection wells at 100-KW are fabricated from Type 304 (Well 199-K-158) and Type 316L (Wells 199-K-174 and K-175) stainless steel. These alloys are known to be substantially resistant to ordinary corrosion in the in-ground applications at Hanford. The vadose zone and groundwater is low in chloride and the operating pH range (that is, from the native pH ~ 7.8 to the treated effluent water at pH~6.0) is well above the range of pH that may cause accelerated corrosion (that is, less than pH = 4.5).

6.4.3.14 Potential for Increased Concentrations of Constituents of Interest in the Treatment Process Effluent

The potential for changes in the observed concentration of constituents of interest in the process effluent is directly related to the change in concentration of those constituents in the extracted groundwater that forms the influent to the treatment process. The SIR-700 resin has not shown an affinity for sorption of the other constituents of concern at 100-KW area (that is, strontium-90, tritium, carbon-14, nitrate, trichloroethene); such affinity was not expected because the resin has a strong, discrete, affinity for sorption of hexavalent chromium ions.

The concentrations of other constituents in the effluent stream represent a volume-weighted average concentration of the contributions from each individual extraction well operating at any particular time. A substantial increase in the influent concentration would produce an equivalent increase in the effluent concentration and vice versa. As discussed above, concentration effects on constituents of interest caused by discharge of slightly-acidic treatment effluent may be seen in the extracted groundwater processed through the 100-KW pump-and-treat system. This may include some increases in strontium-90 and carbon-14. There remains some uncertainty in what the magnitude of those changes may be. The actual changes that are related to pH effects in the aquifer may be less than the effects of migration and capture of localized highly-concentrated plume segments that are known to exist in the vicinity of the 100-KW extraction wells.

Groundwater extracted and treated to date at 100-KW has not exhibited concentrations of either strontium-90 or carbon-14 that indicate the maximum historically-observed concentrations in groundwater near the primary release points at 116-KW-1 and 116-KW-2 Cribs. This may be because of the expected dilution of extracted groundwater that occurs as a result of radial capture of water at extraction wells; it may also indicate that the extraction well capture zones have not yet intercepted those known areas of elevated concentrations. In the future, it will be difficult to assess whether potential increases in influent/effluent concentrations have resulted from the normal variations in groundwater plume capture, or from the effects of return of the slightly-acidic effluent water to the aquifer.

7 Conclusions and Recommendations

The test requirements have been met and the objectives have been realized. The treatment system and re-injection system are all functioning normally and hexavalent chromium is being removed from the process stream nearly completely. The conclusions for the specific objectives are as follows.

7.1 Installation and Performance of SIR-700 (Objective 1)

The SIR-700 met target installation and performance objectives relative to DOWEXTM 21K. The test results indicate that the SIR-700 was able to replace the DOWEXTM 21K effectively in the treatment trains at 100-KW. No resin replacement has been required, and the initial installment of SIR-700 continues to operate after treating over 100,000 bed volumes. The pH adjustment system was found to be implementable and adequate to provide mildly acidic water into the treatment train to allow the SIR-700 resin to operate under design conditions.

7.2 Demonstrate Compatibility of Vessel Lining Material (Objective 2)

Each of the four resin vessels in each treatment train was measured at 10 locations for a total of 80 measurements on July 6, 2011, and again on January 25, 2012, using the ultrasonic measurement technique. No significant changes in vessel wall thickness were measured.

7.3 Generate Data to Establish Influent pH Operating Range (Objective 3)

Operator and laboratory data on influent pH indicate the influent water pH is being reduced within the range of 5.5 to 6.3, within the test range, and no significant hexavalent chromium concentrations were observed in the effluent after processing 50,000 resin bed volumes per train.

7.4 Generate Data to Establish Effluent pH Operating Range (Objective 4)

Data collected for the test indicate the treated water exited the trains at a pH of approximately 6.0 and was injected back into the aquifer. The test confirmed the expected conditions in the aquifer. The test data indicates that no decrease in the apparent specific injection capacity in the injection wells occurred. A decrease in the specific capacity would have suggested fouling of either the wells or the Ringold Formation Unit E sediments that constitute the aquifer matrix as a result of the test. The injection of reduced pH water has not produced any measureable negative effects to the aquifer over the course of operation to date. There does not appear to be any leaching of contaminants of concern from the periodically-rewetted zone; nor does there appear to be measureable mobilization of other contaminants of interest within the aquifer to date. The geochemical analysis of the aquifer system indicates that expected residual buffering capacity in the aquifer will neutralize the slightly acidic effluent water for a period of up to 20 years, after which the affected portion of the aquifer may start to exhibit an altered pH.

The treatment does not add or remove metals from the groundwater other than the treatment target: hexavalent chromium. There is limited potential to mobilize any metals adsorbed on the sediment in the periodically-rewetted zone based on the low potential for the effluent water to contact that region. There is a potential for slight increases in strontium-90 and carbon-14 content in groundwater as the effluent/aquifer reactions progress; at some point, the effects of increasing dissolution of calcium carbonate from within the aquifer is expected to slightly reduce the K_d of strontium-90 in the aquifer. To the extent that carbon-14 is present in an insoluble solid phase as calcium carbonate, dissolution of calcium carbonate in the affected regions will result in an increase in carbon-14 concentration in groundwater. The carbon-14 plume is reasonably far downgradient from the injection wells so the long flow path distance should minimize these effects. Other constituents in the aquifer are not expected to be substantially affected by the effluent injection. Specific uncertainties in this evaluation were identified and selected recommended actions for more fully understanding site conditions and monitoring changes in the aquifer are presented in Section 7.7.

7.5 Applicability of 100-KW Pump-and-Treat SIR-700 Resin Test Information to 100-KR4 and 100-KX Systems

The evaluation of the potential effects of discharge of acidic pump-and-treat process effluent water on aquifer conditions at the 100-KW system can be extrapolated to both the 100-KR4 and 100-KX systems based on similarities in the aquifer geochemistry and the contaminants present and their historical release scenarios. The basis for comparison of the 100-KW assessment to 100-KR4 and 100-KX is described in this section.

7.5.1 Aquifer Contaminant Chemistry

The groundwater contaminants of concern at the three 100-K Area pump-and-treat systems are summarized in Table 11. Chromium (total and hexavalent), nitrate, tritium, strontium-90, carbon-14, and trichloroethene are the contaminants of concern in 100-K Area groundwater. The primary sources of these contaminants, as well as their principal release points have been identified and are shown in Table 11. These six contaminants all exhibit the same chemical properties in all three pump-and-treat system capture areas.

A composite map illustrating all of the 100-K groundwater contaminant of concern plumes exceeding the MCL is shown in Figure 15. The highest concentration plumes of strontium-90 and carbon-14 are clearly located near the KE and KW reactor buildings. Lower concentrations of strontium-90 (although still exceeding the 8 pCi/L MCL) are found along the length of the 116-K-2 Trench. The highest concentrations of Cr(VI) in groundwater are found associated with the reactor areas, within, and downgradient of, the Head House areas. Lower concentrations of Cr(VI) are found associated with the 116-K-1 Crib and 116-K-2 Trench. The large volume of cooling water historically discharged to those facilities resulted in a wide-spread groundwater plume of relatively dilute Cr(VI). Based on the assessment of contaminants presented above, the contaminants of concern for 100-K Area are expected to behave similarly in all of the three affected aquifer areas that are being remediated by the three pump-and-treat systems.

7.5.2 Aquifer Geochemistry

A detailed analysis of aquifer geochemistry effects from discharge of acidic process effluent water at 100-KW pump-and-treat area was presented in Section 6.4.3 of this report. Additional evaluation of aquifer geochemistry was previously performed as part of the 100-K Remedial Investigation/Feasibility Study (RI/FS) and presented in the RI/FS report (DOE/RL-2010-97). Although some variability in basic geochemistry of the aquifer at 100-K has been observed, the groundwater in each of the three pump-and-treat system areas is fundamentally the same. The groundwater generally exhibits low to moderate levels of dissolved solids and is dominated by calcium and carbonate/bicarbonate ions in solution. Figure 16 illustrates the distribution of these groundwater geochemical types using a six-axis plot to display the relative equivalent concentrations of major ions in selected wells at 100-K.

Contaminant	Pump-and-Treat Systems with Plumes >MCL	Chemical Form (dissolved)	Chemical Form (sorbed)	Primary Source	Principal Release Point
Cr(VI)	100-KW 100-KX 100-KR4	Chromate or dichromate ions	Same. Not readily sorbed. Under reducing conditions may be reduced to trivalent chromium compounds.	Sodium dichromate used as reactor cooling water corrosion inhibitor.	Concentrated solutions released in vicinity of 183-KE and –KW Head Houses. Treated cooling water released at 116-K-1 Crib and 116-K-2 Trench.
Nitrate	100-KW	Nitrate ion (NO ₃ ⁻)	Same (not readily sorbed)	Dissolved ammonia in reactor gas dryer condensate. Potential for some contribution from sanitary waste systems.	116-KE-1 and 116-KW-2 Gas Condensate Cribs. Highest concentrations near 116-KW-1 Crib.
Tritium	100-KX 100-KR4	Tritiated water (HTO)	Same (not readily sorbed)	Tritium in reactor gas condensate and contaminated cooling water. Possibly tritium associated with solid waste from reactor operations.	116-KE-1 and 116-KW-2 Gas Condensate Cribs. Highest concentrations near 116-KE-1 Crib. Possible release from 118-K-1 Burial Ground.
Strontium-90	100-KW 100-KX 100-KR4	Strontium divalent cation (Sr ⁺²)	Same. Exchangeable divalent cation.	Fission products released from failed fuel elements during reactor operation and/or fuel storage	116-KE-3 and 116-KW-2 Fuel Storage Basin Cribs. 116-K-1 Crib and 116-K-2 Trench.
Carbon-14	100-KW 100-KX 100-KR4	Bicarbonate ion (HCO ₃ ⁻) and/or dissolved carbon dioxide (CO ₂)	Precipitated calcium carbonate (CaCO ₃).	Reactor gas dryer condensate	116-KE-1 and 116-KW-2 Gas Condensate Cribs. Highest concentrations near the cribs.
Trichloroethene	100-KW	Dissolved organic molecule	Same	Source not clearly identified. Most likely residue from machinery cleaning and maintenance.	No specific release point identified.

Table 11. Summary of Groundwater Contaminants of Concern at 100-K Area

Three groups of similar water quality conditions were identified within the 100-K Area shallow, unconfined, aquifer. All are dominated by calcium and carbonate/bicarbonate; however, they do differ somewhat in relative concentrations of magnesium, sodium, potassium, chloride and sulfate. The most dramatic differences are observed in locations that are considered to be geochemically modified, most likely as a result of historical Hanford reactor operations. This condition is exemplified by Wells 199-K-108A, 199-K-36, and 199-K-106A in the 100-K reactor operations area, Well 199-K-157 near the head end of the 116-K-2 Trench, and 199-K-135, Well 199-K-135, located northeast of the distal end of 116-K-2 Trench, shows the geochemical effects of injection of calcium polysulfide into the aquifer during a treatability test of in situ reduction of hexavalent chromium. This well exhibits extremely high calcium and carbonate/bicarbonate equivalent concentrations in the years following the 2005 test. Because of the relatively small injection volume of the test, this condition is not expected to extend very far from the 30-m test area radius. In general, the aquifer to the east and northeast of the reactor area exhibits a major ion pattern similar to that of the Columbia River, although with substantially-higher equivalent ion concentrations. The Columbia River, presented for comparison, is also dominated by calcium and carbonate/bicarbonate, but contains very low dissolved ion concentrations (that is, less than 1 meq/L of calcium and carbonate/bicarbonate, and almost no sodium, potassium, or chloride).

The groundwater at 100-K Area that is subject to the pump-and-treat remedy for treatment of hexavalent chromium exhibits variable concentrations of major ions; however, it remains a calcium carbonate dominated water at all locations. This indicates the detailed geochemical evaluation of potential effects to the aquifer performed for the 100-KW system should be sufficiently representative to describe potential effects at the two remaining systems (that is, 100-KX and 100-KR4). The same uncertainties identified for the aquifer at 100-KW (that is, unspecified calcium carbonate content of the Ringold Unit E and unspecified overall alkaline buffering capacity of the aquifer) also apply to the remaining areas of 100-K.

7.5.3 Treatment System Materials and Configuration

The groundwater treatment systems at 100-KR4 and 100-KX pump-and-treat operations are functionally the same as that at 100-KW; the differences being primarily piping configuration, sizing, and the number of vessels in each plant. All three plants are designed and operated for single-pass treatment for removal of hexavalent chromium from contaminated groundwater. The comparability of the KR and KX systems to KW are described in this section with respect to materials and system configuration.

7.5.4 Objective 1: Installation and Performance of SIR-700

SIR-700 resin was placed in service at all ion exchange treatment trains in 100-KR4 and 100-KX pump-and-treat systems between March and June 2012. Each treatment train was operated at 50 percent flow capacity for several days after resin loading before increasing the flow to 100 percent capacity. The SIR-700 startup time-line for the KR and KX systems is shown in Table 12. The removal efficiency of the SIR-700 resin for hexavalent chromium will continue to be monitored regularly at all systems.



Figure 15. Composite Map of Groundwater Plumes Exceeding MCLs (Fall 2011)







System	Train	Date Started at 50% Capacity	Date Changed to 100% Capacity
100-KR4	A	5/30/2012	6/4/2012
	В	5/31/2012	6/4/2012
	С	6/5/2012	6/12/2012
100-KX	A	3/27/2012	3/29/2012
	В	4/12/2012	4/19/2012
	С	4/4/2012	4/9/2012
	D	4/9/2012	4/12/2012
	E	4/2/2012	4/9/2012
	F	4/19/2012	4/23/2012

Table 12. SIR-700 Resin Startup Time Line for 100-KR4 and 100-KX Treatment Systems

7.5.5 Objective 2: Compatibility of Vessel Lining Material

The ion exchange resin vessels at 100-KR4 and 100-KX treatment systems are identical to those at 100-KW, with the exception of variations in location of the service entry access ports. Some of the vessels have top-mounted ports; others have side-mounted ports. The vessels are, therefore, directly comparable and the observations and measurements of vessel lining effects made at 100-KW pump-and-treat system are directly applicable to the treatment systems at 100-KR4 and 100-KX. No negative effects were observed during the test period at 100-KW pump-and-treat.

7.5.6 Objective 3: Establishment of Influent pH Range

The treatment influent pH range was established for 100-KR4 and 100-KX pump-and-treat systems based on the initial experience with SIR-700 resin operation at 100-KW system. The SIR-700 resin performs most efficiently for hexavalent chromium removal at an influent pH of less than 6.0 pH units. An influent pH range of 5.5 to 6.0 pH units was selected for 100-KR4 and 100-KX based on the operational experience with the SIR-700 resin at 100-KW during the test period and resin vendor data.

7.5.7 Objective 4: Establishment of Effluent pH Range

The effluent pH at the systems operating with SIR-700 is a function of the influent pH and the small alkaline buffering that occurs as water passes through the resin. No adjustment to the pH of effluent water is anticipated. The initial treatment effluent pH for 100-KR4 and 100-KX pump-and-treat systems was established based on the test experience with SIR-700 resin at 100-KW pump-and-treat. An initial effluent pH of 6.5 pH units was selected based on the influent pH. The systems are subsequently being evaluated to reduce the influent pH to 5.5 units, which is expected to reduce the effluent pH to about 6.0 pH units. This is expected to be consistent with the operational conditions at 100-KW.

7.6 Waste Sites Potentially-Affected by Discharge of Acidic Effluent

Existing environmental contamination in the vadose zone at some waste sites may potentially be affected by the treatment plant discharges. The potentially-affected contaminants fall into both of the following specific conditions:

- Contaminants that are subject to changes in solubility (that is, changes in relative solution concentration) or mobility (that is, changes in either ionic state or degree of interaction with vadose or aquifer solids) under the slightly acidic pH of the effluent water
- Contaminants residing in vadose locations that may be contacted by the treatment effluent-affected water (that is, the deep vadose within the periodically-rewetted zone and/or within the area of water table elevation associated with injection well recharge mounds)

The groundwater contaminant plumes located within the 100-KR-4 OU have originated from a relatively-small number of waste sites. These source waste sites, their associated contaminants, and related pump-and-treat systems are summarized in Table 13. The net effects on contaminant concentrations and mobility at 100-KR4 and 100-KX systems is expected to be the same as at 100-KW. A water table contour map of the 100-K Area, including inferred groundwater flow directions is presented in Figure 17.

Pump-and-Treat System	Waste Site	Contaminants	Contaminant Situation	Type of Potential Contact	Potential Effect on Contaminant
100-KW ^a	183-KW Head House Area	Cr(VI)	Deep vadose	Injection well mounding	No expected effect.
	116-KW-1 Crib	Nitrate	Deep vadose	Seasonal water table elevation	No expected effect
		C-14	Deep vadose	Seasonal water table elevation	Some increased solubility
		Tritium	Deep vadose	Seasonal water table elevation	No expected effect
	116-KW-2 Crib/Reverse Well	Sr-90	Deep vadose	Seasonal water table elevation	Some decrease in K_d (i.e., increased mobility)
		Tritium	Deep vadose	Seasonal water table elevation	No expected effect
100-KR4	116-K-1 Crib	Sr-90	Deep vadose	Seasonal water table elevation	Some decrease in K_d (i.e., increased mobility)
		Cr(VI)	Deep vadose	Injection well mounding	No expected effect.
		Tritium	Deep vadose	Seasonal water table elevation	No expected effect
	116-K-2 Trench	Sr-90	Deep vadose	Seasonal water table elevation	Some decrease in K_d (i.e., increased mobility)
		Cr(VI)	Deep vadose	Injection well mounding	No expected effect.

Table 13. Relationship of Contaminant Source Waste Sites to Potential Treatment Effluent Effects

Pump-and-Treat System	Waste Site	Contaminants	Contaminant Situation	Type of Potential Contact	Potential Effect on Contaminant
		Tritium	Deep vadose	Seasonal water table elevation	No expected effect
	118-K-1 Burial Ground	Tritium	Deep vadose	Seasonal water table elevation	No expected effect
100-KX ^b	183-KE Head House Area	Cr(VI)	Deep vadose	Injection well mounding	No expected effect.
	116-KE-1 Crib	Nitrate	Deep vadose	Seasonal water table elevation	No expected effect
		C-14	Deep vadose	Seasonal water table elevation	Some increased solubility
		Tritium	Deep vadose	Seasonal water table elevation	No expected effect
	116-KE-3 Crib/Reverse Well	Sr-90	Deep vadose	Seasonal water table elevation	Some decrease in K _d (i.e., increased mobility)
		Tritium	Deep vadose	Seasonal water table elevation	No expected effect
	118-K-1 Burial Ground	Tritium	Deep vadose	Seasonal water table elevation	No expected effect
	100-K-42 KE FSB Leak	Sr-90	Deep vadose	Seasonal water table elevation	Some decrease in K _d (i.e., increased mobility)
		Tritium	Deep vadose	Seasonal water table elevation	No expected effect
	116-K-2 Trench	Sr-90	Deep vadose	Seasonal water table elevation	Some decrease in K_d (i.e., increased mobility)
		Cr(VI)	Deep vadose	Injection well mounding	No expected effect.
		Tritium	Deep vadose	Seasonal water table elevation	No expected effect

Table 13. Relationship of Contaminant Source Waste Sites to Potential Treatment Effluent Effects

Notes:

a. The 100-KW treatment area also includes a localized plume of trichloroethene for which no source has been identified. This COC is not expected to be affected by acidic treatment system effluent water.

b. The 100-KX treatment area also includes the upstream portion of 100-N Area and three KX injection wells are located within the 100-N Area footprint. No apparent sources of groundwater contamination at 100-N are located within 800 m of these injection wells and, therefore, no effects of injection of acidic treatment system effluent water are expected for 100-N Area waste sites.

7.7 Recommendations

It is recommended that SIR-700 be implemented full time at the 100-KW pump-and-treat system without alkaline adjustment to raise the pH in the effluent stream. The operational implementation is straight forward. It is recommended that pH continue to be monitored in Well 199-K-173 as part of regularly scheduled monitoring activities.

Additionally, it is recommended that the application of SIR-700 be implemented at the KR-4 and KX pump-and-treat systems at 100-K. The SIR-700 can be implemented with only minor plant modifications at the KX and KR-4 systems to provide for more acid capacity. These systems have the same resin vessels as the 100-KW system and the operational steps to use SIR-700 can be implemented without any significant modifications to treatment plant configuration.

Because of the uncertainty in the geochemical conditions within the affected aquifer, specific recommendations for focused supplemental characterization and groundwater monitoring have been identified and are described in the following subsections.

7.7.1 Specific Characterization and Monitoring Recommendations

Although no major effects are expected because of the reduced pH operating conditions, there remains considerable uncertainty regarding aquifer-specific conditions and the potential exists for changes in the behavior and groundwater concentration of some constituents in the aquifer (for example, Sr-90 and C-14). Monitoring of pH and selected contaminants of concern (that is, Sr-90, C-14, hexavalent chromium, nitrate, and metals) should continue to be conducted as part of regularly scheduled monitoring activities. Injection well hydraulics will continue to be monitored and routine maintenance will be conducted as needed.

Specific recommendations for monitoring approaches and supplemental characterization include the activities shown in Table 14 for 100-KW, and in Table 15 for 100-KR4, and 100-KX pump-and-treat systems, respectively. Recommendations for 100-KR4 and 100-KX are combined because the extraction and injection wells for those systems are closely placed and, in some cases, interspersed with each other.

Implementation of the recommended monitoring approaches at the 100-K pump-and-treat systems will also require definition of appropriate responses to observed changes in groundwater chemistry. The responses should be defined through revision of operating procedures and should include a graded response to observed changes. Responses could include a range of actions from increasing frequency of measurement of specific parameters to changing operating conditions to prevent or mitigate undesirable effects on system performance.

7.7.2 Proposed Schedule for Implementation of Recommended Characterization and Monitoring

The recommended monitoring activities should be integrated directly into the pump-and-treat system operational monitoring activities. The supplemental characterization activities should commence early in fiscal year 2013. A proposed schedule is presented in Table 16.



Figure 17. Inferred Groundwater Elevation Contours and Groundwater Flow Direction at 100-K (Fall 2011)

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Category	Data Need	Specific Uncertainty	Recommended Data Collection Activity	Data Collection Location	Data Collection Frequency	Comment
Characterization	Quantitative geochemical analysis of aquifer media at 100-KW	Extrapolation of calcium carbonate content from other locations may over- or under-estimate aquifer buffering capacity	Measure calcium carbonate content in samples collected from the aquifer at 100-KW injection wells	Analyze archived samples collected from Wells 199-K-158, 199-K-174, and 199-K-175	Analyze one time	Archive samples should provide representative samples for this analysis
		Extrapolation of amorphous iron, aluminum, and silicon compounds may over-or-underestimate the reactivity with acidic effluent.	Measure content of iron, aluminum, and silicon oxides and hydroxides in samples collected at 100-KW injection wells	Analyze archived samples collected from Wells 199-K-158, 199-K-174, and 199-K-175	Analyze one time	Archive samples should provide representative samples for this analysis
		Calculated buffering capacity may over- or under-estimate actual aquifer buffering capacity.	Determine aquifer matrix buffering capacity by observing pH during acid titration.	Analyze archived samples collected from Wells 199-K-158, 199-K-174, and 199-K-175	Analyze one time	Archive samples should provide representative samples for this analysis

Table 14. Summary of Recommended Monitoring and Characterization to Reduce Uncertainty and Detect Changes in Aquifer Conditio

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Category	Data Need	Specific Uncertainty	Recommended Data Collection Activity	Data Collection Location	Data Collection Frequency	Comment	
Monitoring Remedial system performanc monitoring verify geochemica effects	Remedial system performance monitoring to verify geochemical	Remedial system performance monitoring to verify geochemical The estimated rate and spatial anisotropy of pH change within the aquife is at this site is not clearl predictable	The estimated rate and spatial anisotropy of pH change within the aquifer is at this site is not clearly predictable	Monitor groundwater pH for changes that may be related to effluent injection.	Monitoring Wells 199-K-173, 199-K-106A, 199-K-107A, 199-K-108A, and 199-K-34.	Four times per year on a quarterly basis	Measurements may be made using field instruments, laboratory measurements, or using in situ data logging instruments.
	effects			All operating extraction wells	pH measurement monthly	Define appropriate responses to future changes in aquifer conditions.	
		Concentration trends for constituents of interest and specific geochemical parameters are not yet well defined under the revised operating conditions.	Analyze groundwater samples for pH, ORP, Sr-90, C-14, ICP metals, hexavalent chromium, and nitrate.	Monitoring Wells 199-K-173, 199-K-106A, 199-K-107A, 199-K-108A, and 199-K-34. All operating extraction wells.	Four times per year on a quarterly basis	Establish trend analysis to statistically evaluate changes. Note that concentrations may change because of geochemical response, or simply because of relocation of existing plumes during pumping. Define appropriate responses to future changes in aquifer conditions.	

Table 14. Summary of Recommended Monitoring and Characterization to Reduce Uncertainty and Detect Changes in Aquifer Conditions at 100-KW

Category	Data Need	Specific Uncertainty	Recommended Data Collection Activity	Data Collection Location	Data Collection Frequency	Comment
Characterization Quan geoc analy aqui 100- 100-	Quantitative geochemical analysis of aquifer media at 100-KR4 and 100-KX	Extrapolation of calcium carbonate content from other locations may over- or under-estimate aquifer buffering capacity	Measure calcium carbonate content in samples collected from the aquifer at 100-KR4 and 100-KX injection wells	Analyze archived samples collected from Wells 199-K-128, 199-K-156, 199-K-160.	Analyze one time	Archive samples should provide representative samples for this analysis
		Extrapolation of amorphous iron, aluminum, and silicon compounds may over-or-underestimate the reactivity with acidic effluent.	Measure content of iron, aluminum, and silicon oxides and hydroxides in samples collected at 100-KR4 and 100-KX injection wells	Analyze archived samples collected from Wells 199-K-128, 199-K-156, 199-K-160	Analyze one time	Archive samples should provide representative samples for this analysis
		Calculated buffering capacity may over- or under-estimate actual aquifer buffering capacity.	Determine aquifer matrix buffering capacity by observing pH during acid titration.	Analyze archived samples collected from Wells 199-K-128, 199-K-156, 199-K-160	Analyze one time	Archive samples should provide representative samples for this analysis

Table 15. Summary of Recommended Monitoring and Characterization to Reduce Uncertainty and Detect Changes in Aquifer Conditions at 100-KR4 and 100-KX

Category	Data Need	Specific Uncertainty	Recommended Data Collection Activity	Data Collection Location	Data Collection Frequency	Comment
Monitoring Remedia system perform monitor verify geocher effects	Remedial system performance monitoring to verify	The estimated rate M and spatial anisotropy p of pH change within m the aquifer is at this site is not clearly	Monitor groundwater pH for changes that may be related to effluent injection.	Monitoring Wells 199-K-124A, 199-K-111A, 199-K-119A, and 199-K-151.	Four times per year	Measurements may be made using field instruments, laboratory measurements, or using in situ data logging
	geochemical effects	predictable	predictable	All operating extraction wells.	pH measurement monthly	instruments. Define appropriate responses to future changes in aquifer conditions.
		Concentration trends for constituents of interest and specific geochemical parameters are not yet well defined under the revised operating conditions.	Analyze groundwater samples for pH, ORP, Sr-90, C-14, ICP metals, hexavalent chromium, and nitrate.	Monitoring Wells 199-K-124A, 199-K-111A, 199-K-119A, and 199-K-151. All operating extraction wells.	Four times per year	Establish trend analysis to statistically evaluate changes. Note that concentrations may change because of geochemical response, or simply because of relocation of existing plumes during pumping. Define appropriate responses to future changes in aquifer conditions.+

Table 15. Summary of Recommended Monitoring and Characterization to Reduce Uncertainty and Detect Changes in Aquifer Conditions at 100-KR4 and 100-KX

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Activity	Start	Finish	Comment
Revise Operational Monitoring Plan to Include Recommended Sampling and Analysis and Response to Change of Conditions.	15 September 2012	30 October 2012	Modification of existing documentation.
Prepare Test Plan for Supplemental Characterization	15 September 2012	15 October 2012	Using internal technical test plan format.
Select Archive Samples for Analysis	15 October 2012	20 October 2012	Existing archive samples only, not new sample collection.
Perform Recommended Characterization of Archive Samples	20 October 2012	10 January 2013	Analysis to be conducted by PNNL.
Report Results of Supplemental Characterization	11 January 2013	20 February 2013	Presented in technical memorandum format.

Table 16. Proposed Characterization and Monitoring Implementation Schedule for 100-K Area

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