PNNL-20135

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
Under Contract DE-AC05-76RL01830

Uranium Adsorption on Ion-Exchange Resins – Batch Testing

SV Mattigod
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EA Cordova
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December 2010

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

The uranium adsorption performance of five resins (Dowex 1, Dowex 21K 16-30 [fresh], Dowex 21K 16-30 [regenerated], Purofine PFA600/4740, and ResinTech SIR-1200) were tested using unspiked, nitrate-spiked, and nitrate-spiked/pH adjusted source water from well 299-W19-36. These batch tests were conducted in support of a resin selection process in which the best resin to use for uranium treatment in the 200-West Area groundwater pump-and-treat system will be identified. The results from these tests are as follows:

- The data from the high-nitrate (1331 mg/L) tests indicated that Dowex 1, Dowex 21K 16-30 (fresh), Purofine PFA600/4740, and ResinTech SIR-1200 all adsorbed uranium similarly well with K_d values ranging from ~15,000 to 95,000 ml/g. All four resins would be considered suitable for use in the treatment system based on uranium adsorption characteristics.
- Lowering the pH of the high nitrate test conditions from 8.2 to 7.5 did not significantly change the uranium adsorption isotherms for the four tested resins. The K_d values for these four resins under high nitrate (1338 mg/L), lower pH (7.5) ranged from ~15,000 to 80,000 ml/g.
- Higher nitrate concentrations greatly reduced the uranium adsorption on all four resins. Tests conducted with unspiked (no amendments; nitrate at 337 mg/L and pH at 8.2) source water yielded K_d values for Dowex 1, Dowex 21K 16-30 (fresh), Purofine PFA600/4740, and ResinTech SIR-1200 resins ranging from ~800,000 to >3,000,000 ml/g. These values are about two orders of magnitude higher than the K_d values noted from tests conducted using amended source water.
- Compared to the fresh resin, the regenerated Dowex 21K 16-30 resin exhibited significantly lower uranium-adsorption performance under all test conditions. The calculated K_d values for the regenerated resin were typically an order of magnitude lower than the values calculated for the fresh resin.
- Additional testing using laboratory columns is recommended to better resolve differences between the adsorption abilities of the resins and to develop estimates of uranium loading on the resins. By determining the quantity of uranium that each resin can adsorb and the time required to reach various levels of loading, resin lifetime in the treatment system can be estimated.

Acronyms and Abbreviations

µg	microgram(s)
µg/g	microgram(s) per gram
µm	micrometer(s) or micron(s)
ALARA	as low as reasonably achievable
CERCLA	*Comprehensive Environmental Response, Compensation, and Liability Act of 1980*
CHPRC	CH2M HILL Plateau Remediation Company
DD	deionized distilled
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
g	gram(s)
IX	ion exchange
ICP-MS	inductively coupled plasma-mass spectrometer
OU	operable unit
K_d	distribution coefficient(s)
L	liter(s)
mg	milligram(s)
mg/g	milligram(s) per gram
mg/L	milligram(s) per liter
ml	milliliter(s)
ml/g	milliliters per gram
PNNL	Pacific Northwest National Laboratory
Tri-Party Agreement	*Hanford Federal Facility Agreement and Consent Order*

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1.0 Introduction

CH2M HILL Plateau Remediation Company (CHPRC) is currently developing a 200-West Area groundwater pump-and-treat system to remove radioactive and non-radioactive hazardous constituents from groundwater beneath the area. Pump-and-treat is the remedial action selected under the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA) Record of Decision for the 200-ZP-1 Operable Unit (OU) (*Record of Decision Hanford 200 Area 200-ZP-1 Superfund Site, Benton County, Washington* [EPA et al. 2008]). This action is being performed in accordance with the *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement) (Ecology et al. 1989). The treatment design is based, in part, on the removal of selected contaminants of concern using various sorbent media. CHPRC asked Pacific Northwest National Laboratory (PNNL) to perform treatability testing to quantify the ability of selected ion-exchange (IX) resins to adsorb uranium from groundwater in the Hanford Site's 200-West Area.

Laboratory sorption experiments included batch tests from which the sorption characteristics of each of the IX resins were quantified. Using IX resin samples and groundwater provided by CHPRC, PNNL researchers tested five IX resins using batch techniques. The batch isotherm tests were conducted according to the approved test plan (CHPRC 2010).

The goals of the batch testing were as follows:

- Confirm that the IX process will remove uranium from groundwater at well 299-W19-36 in the 200-UP-1 OU.
- Identify suitable IX resins for possible use in the new 200-West Area pump-and-treat system.
- Determine the uranium-loading capacity of these resins and the potential loading of other radionuclides and non-radionuclide constituents that may affect uranium removal or disposal of spent resin.
- Measure IX resin performance when the pH of the groundwater is lowered by 0.5 standard units.
- Determine the effect of increased nitrate concentration (approximately 1400 mg/L) of uranium adsorption on IX resins.

Batch testing involved preparing the IX resins and groundwater (including adjusting pH and nitrate concentrations in the latter), performing contact tests, analyzing solutions, compiling data, and reporting results. The ensuing sections of this report describe the experiment, summarize the results of batch isotherm tests, and provide related conclusions.

2.0 Experiment

2.1 Material Preparation

2.1.1 Ion Exchange Resin

The as-received ion exchange materials were prepared by first centrifuge washing two times with deionized distilled (DD) water to remove any soluble contaminants accumulated during storage. Next, the resins were soaked in DD water for 2 hours to ensure proper hydration. After hydration, the excess water was decanted, and the resins were stored wet until needed.

2.1.2 Source Water

The source water from well 299-W19-36 was analyzed for pH, alkalinity, sulfate (SO_4), nitrate (NO_3), uranium, and technetium-99. The pH of a portion of well 299-W19-36 source water was lowered by 0.5 standard units using 0.1N HCl for use in batch tests to examine the effect of lowered pH on uranium adsorption. The nitrate concentration of another portion of source water was enhanced to ~1400 mg/L to test the effect of higher nitrate concentrations on adsorption of uranium. Unspiked source water (natural nitrate concentration) was used for another set of batch isotherm tests.

2.2 Batch Isotherm Tests

Batch isotherm tests were conducted using the standard practice for determining adsorption isotherms for IX resins (as suggested in *Application Information – DOWEX Ion Exchange Resins; Equilibrium Isotherm Testing for Liquid Phase Applications* (DOW 1997) as a guide with modifications to comply with the U.S. Department of Energy (DOE) principle of limiting radiation dose to as low as reasonably achievable (ALARA). Therefore, the mass of resin and solution volume used in each batch contact was reduced to minimize waste volume. The following resin-to-solution ratios were used in most of the batch isotherm tests:

- Ratio #1 – 0.25 g resin/50 ml solution
- Ratio #2 – 0.50 g resin/50 ml solution
- Ratio #3 – 0.75 g resin/50 ml solution
- Ratio #4 – 1.00 g resin/50 ml solution.

The test matrix is shown below in Table 2.1.

All batch adsorption tests were conducted for 18 hours. During that time, the centrifuge tubes were agitated continuously so the IX resin and groundwater remain well mixed. This was done in a SHEL Lab shaking incubator at 250 RPM and 18°C. After the required contact time of 18 hours, the tubes were centrifuged in a Thermo Centra GP8R centrifuge for 15 minutes at 2500 RPM. A 0.45-µm syringe filter was then used to separate the groundwater from the IX resin, and a 10-ml aliquot was taken for uranium analysis. See Appendix for description of analysis procedure. The batch-testing procedure was repeated for each IX resin sample, as described in Table 2.1.

Table 2.1. Test Matrix for Uranium Resin Batch Tests

Isotherm	Ion Exchange Resin	Resin/Solution Ratio			
		Test #1	Test #2	Test #3	Test #4
1	Dowex 1	Ratio #1	Ratio #2	Ratio #3	Ratio #4
2	Dowex 21 K (fresh)	Ratio #1	Ratio #2	Ratio #3	Ratio #4
3	Dowex 21 K (regenerated from 100 Area tests)	Ratio #1	Ratio #2	Ratio #3	Ratio #4
4	Purofine PFA600/4740	Ratio #1	Ratio #2	Ratio #3	Ratio #4
5	ResinTech SIR-1200	Ratio #1	Ratio #2	Ratio #3	Ratio #4

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Purofine® and Purolite® are the registered trademarks of The Purolite Company, Bala Cynwyd, Pennsylvania.
ResinTech® is a registered trademark of ResinTech, Inc, West Berlin, New Jersey.

2.2.1 High Nitrate Tests

The high nitrate batch isotherm tests were conducted by measuring appropriate quantities of IX resin products into a set of labeled centrifuge tubes. The required volume (50 ml) of nitrate-spiked (~1400 mg/L) source water from well 299-W19-36 was added to achieve the appropriate resin and solution ratios as specified in Table 2.1. The adsorption tests were conducted as specified in Section 2.2.

2.2.2 High Nitrate-Low pH Tests

The high nitrate-low pH batch isotherm tests were conducted by measuring appropriate quantities of IX resin products into a set of labeled centrifuge tubes. The required volume of nitrate-spiked (~1400 mg/L), pH-adjusted (lowered by 0.5 pH units) source water from well 299-W19-36 was added to achieve the appropriate resin and solution ratios as specified in Table 2.1. The adsorption tests were conducted as specified in Section 2.2.

2.2.3 Low-Nitrate Tests

The low-nitrate (as received) batch isotherm tests were conducted by measuring appropriate quantities of IX resin products into a set of labeled centrifuge tubes. The required volume of source water (without any nitrate spiking and pH adjustment) from well 299-W19-36 was added to achieve the appropriate resin and solution ratios as specified in Table 2.1. The adsorption tests were conducted as specified in Section 2.2.

2.2.4 Duplicate Tests

After the initial test sets were complete, CHPRC reviewed the data and selected isotherms for duplicate runs.

2.2.4.1 ResinTech SIR-1200 – Low Nitrate

The duplicate batch isotherm tests for ResinTech SIR-1200 were conducted by measuring appropriate quantities of IX resin products into a set of labeled centrifuge tubes. The required volume of source water (without any nitrate spiking and pH adjustment) from well 299-W19-36 was added to achieve the appropriate resin and solution ratios as specified in Table 2.1. The adsorption tests were conducted in accordance with Section 2.2.

2.2.4.2 Dowex 21K Regenerated – High Nitrate

The duplicate batch isotherm tests for Dowex 21K (regenerated from 100 Area tests) were conducted by measuring appropriate quantities of IX resin products into a set of labeled centrifuge tubes. The required volume of nitrate-spiked (~1400 mg/L) source water from well 299-W19-36 was added to achieve the following resin and solution combinations:

- Ratio #1 – 0.01 g resin/50 ml solution
- Ratio #2 – 0.50 g resin/50 ml solution
- Ratio #3 – 1.00 g resin/50 ml solution
- Ratio #4 – 2.00 g resin/50 ml solution.

The adsorption tests were conducted in accordance with Section 2.2.

3.0 Results

3.1 Source Water

The results of the initial analyses of source water from 299-W19-36 used in the batch isotherm experiments are listed in Table 3.1.

Table 3.1. Concentrations of Specified Constituents in 299-W19-36 Source Water

Constituent	Units	Low Nitrate, As Received[(a)]	High Nitrate	High Nitrate, Low pH
pH	SU	8.20	8.19	7.50
Alkalinity (as $CaCO_3$)	mg/L	116	112	100
Sulfate	mg/L	50	49	45
Nitrate	mg/L	317	1331	1338
Uranium	µg/L	171.61	179.99	170.95
Technetium-99	µg/L	0.385	0.383	0.384

(a) Average of duplicate measurements.

Spiking with nitrate and pH adjustments did not significantly change the technetium-99 concentrations.

3.2 High-Nitrate Tests

The results of the batch isotherm tests for all five ion-exchange resins are listed in Tables 3.2–3.6 and displayed graphically in Figures 3.1–3.6. The parameters derived from Langmuir isotherm fit to these data are listed in Table 3.7.

Data from the high-nitrate (1331 mg/L) tests indicated that the uranium adsorption performance of Dowex 1, Dowex 21K 16-30 (fresh), Purofine PFA600/4740, and ResinTech SIR-1200 were similar (Tables 3.2, 3.3, 3.5 and 3.6). At the lowest resin-to-solution ratio, the uranium adsorption for these four resins typically ranged from 32.00 to 33.75 µg/g, and at the highest resin-to-solution ratio, it ranged from 8.24 to 8.49 µg/g, respectively. The calculated distribution coefficients (K_d) for these four resin ranged from ~15,000 to 94,000 ml/g. The adsorption isotherms for these exchange resins fit the Langmuir equation with predicted maxima of 84.87, 57.3, 44.41 and 44.57 µg/g for Dowex 1, Dowex 21K 16-30 (fresh), Purofine PFA600/4740, and ResinTech SIR-1200, respectively (Table 3.7).

Compared to the Dowex 21K 16-30 (fresh resin), the regenerated form of this resin exhibited diminished uranium-adsorption performance. Depending on the resin-to-solution ratio, the final uranium concentrations in contact with the regenerated resin were 5 to 30 times higher than the concentrations measured in solutions in contact with the fresh resin (Tables 3.3 and 3.4) because of differences in adsorption capability. The adsorption isotherm for the regenerated resin was linear within the tested range of resin-to-solution ratios (Figure 3.3) and the K_d ranged from ~2,000 to 4,000 ml/g (Table 3.4), reflecting its attenuated performance characteristics compared to the fresh resin.

Table 3.2. Uranium-Adsorption Data for Dowex 1 Resin

Sample #	U Initial Conc. (µg /L)	U Final Conc. (µg /L)	Resin Mass (g)	Soln. Vol. (ml)	U Ads. (µg /g)	K_d (ml/g)
Nitrate: 1331 mg/L						
DOW1-S1-R1-1	179.99	2.0693	0.273	49.10	32.00	15,460
DOW1-S1-R2-1	179.99	0.6968	0.492	49.10	17.89	25,680
DOW1-S1-R3-1	179.99	0.2567	0.777	49.06	11.35	44,200
DOW1-S1-R4-1	179.99	0.1346	1.072	49.14	8.24	61,240
Nitrate: 1338 mg/L, pH: 7.5						
DOW1-S2-R1-1	170.95	2.1458	0.259	49.06	31.98	14,900
DOW1-S2-R2-1	170.95	0.5447	0.555	49.18	15.10	27,720
DOW1-S2-R3-1	170.95	0.2771	0.756	49.08	11.08	39,980
DOW1-S2-R4-1	170.95	0.1532	1.008	49.17	8.33	54,380
Nitrate: 317 mg/L						
DOW1-S3-R1-1	171.61	0.0270	0.261	49.26	32.38	1,200,000
DOW1-S3-R2-1	171.61	0.0114	0.512	49.80	16.69	1,464,000
DOW1-S3-R3-1	171.61	<0.0110	0.772	49.85	>11.08	>1,007,000
DOW1-S3-R4-1	171.61	<0.0110	1.016	49.53	>8.36	>760,000

Table 3.3. Uranium Adsorption Data for Dowex 21K 16-30 (Fresh) Resin

Sample #	U Initial Conc. (µg /L)	U Final Conc. (µg /L)	Resin Mass (g)	Soln. Vol. (ml)	U Ads (µg /g)	K_d (ml/g)
Nitrate: 1331 mg/L						
DOWF-S1-R1-1	179.99	1.6257	0.266	49.06	32.90	20,240
DOWF-S1-R2-1	179.99	0.5862	0.518	49.14	17.02	29,030
DOWF-S1-R3-1	179.99	0.2983	0.777	49.13	11.36	38,080
DOWF-S1-R4-1	179.99	0.1652	1.063	49.69	8.41	50,870
Nitrate: 1338 mg/L, pH: 7.5						
DOWF-S2-R1-1	170.95	1.7537	0.265	49.09	31.34	17,870
DOWF-S2-R2-1	170.95	0.5992	0.511	49.05	16.35	27,290
DOWF-S2-R3-1	170.95	0.2588	0.778	49.09	10.77	41,620
DOWF-S2-R4-1	170.95	0.1613	1.003	49.36	8.40	52,110
Nitrate: 317 mg/L						
DOWF-S3-R1-1	171.61	0.0405	0.262	49.43	32.37	799,000
DOWF-S3-R2-1	171.61	<0.1100	0.509	49.29	>16.62	>1,511,000
DOWF-S3-R3-1	171.61	<0.0110	0.766	49.69	>11.13	>1,012,000
DOWF-S3-R4-1	171.61	<0.0110	1.037	49.22	>8.14	>740,000

Table 3.4. Uranium Adsorption Data for Dowex 21K 16-30 (Regenerated) Resin

Sample #	U Initial Conc. (µg /L)	U Final Conc. (µg /L)	Resin Mass (g)	Soln. Vol. (ml)	U Ads (µg /g)	K_d (ml/g)
Nitrate: 1331 mg/L						
DOWR-S1-R1-1	179.99	8.1055	0.275	49.12	30.70	3,800
DOWR-S1-R2-1	179.99	6.7722	0.527	49.11	16.14	2,400
DOWR-S1-R3-1	179.99	5.5457	0.775	49.36	11.11	2,000
DOWR-S1-R4-1	179.99	4.8251	1.067	49.11	8.06	1,700
Nitrate: 1338 mg/L, pH: 7.5						
DOWR-S2-R1-1	170.95	7.9473	0.268	49.02	29.81	3,750
DOWR-S2-R2-1	170.95	5.7684	0.516	49.14	15.73	2,700
DOWR-S2-R3-1	170.95	5.3539	0.759	49.14	10.72	2,000
DOWR-S2-R4-1	170.95	4.5287	1.025	49.56	8.05	1,800
Nitrate: 317 mg/L						
DOWR-S3-R1-1	171.61	0.9002	0.274	49.22	30.67	34,060
DOWR-S3-R2-1	171.61	0.6850	0.526	49.38	16.05	23,420
DOWR-S3-R3-1	171.61	0.6355	0.772	49.08	10.87	17,110
DOWR-S3-R4-1	171.61	0.5557	1.017	49.42	8.31	14,960
Nitrate: 1331 mg/L – Duplicate						
DOWR-S4-R1-1	182.88	76.265	0.014	45.881	349.40	4,580
DOWR-S4-R2-1	182.88	7.170	0.432	45.524	18.52	2,580
DOWR-S4-R3-1	182.88	5.140	0.902	45.241	8.91	1,730
DOWR-S4-R4-1	182.88	4.155	1.814	45.971	4.53	1,090

Table 3.5. Uranium Adsorption Data for Purofine PFA600/4740 Resin

Sample #	U Initial Conc. (µg /L)	U Final Conc. (µg /L)	Resin Mass (g)	Soln. Vol. (ml)	U Ads. (µg /g)	K_d (ml/g)
Nitrate: 1331 mg/L						
PPFA-S1-R1-1	179.99	1.7678	0.259	49.05	33.75	19,090
PPFA-S1-R2-1	179.99	0.4384	0.521	49.07	16.91	38,570
PPFA-S1-R3-1	179.99	0.1868	0.797	49.58	11.19	59,890
PPFA-S1-R4-1	179.99	0.0881	1.069	49.07	8.26	93,770
Nitrate: 1338 mg/L, pH: 7.5						
PPFA-S2-R1-1	170.95	1.8153	0.259	49.04	32.02	17,640
PPFA-S2-R2-1	170.95	0.8396	0.557	49.34	15.07	17,950
PPFA-S2-R3-1	170.95	0.1937	0.750	49.59	11.29	58,290
PPFA-S2-R4-1	170.95	0.0992	1.021	49.12	8.22	82,850
Nitrate: 317 mg/L						
PPFA-S3-R1-1	171.61	0.0139	0.270	49.48	31.44	2,259,000
PPFA-S3-R2-1	171.61	<0.0110	0.552	49.36	>15.34	>1,395,000
PPFA-S3-R3-1	171.61	<0.0110	0.762	49.77	>11.21	>1,019,000
PPFA-S3-R4-1	171.61	<0.0110	1.021	49.15	>8.26	>751,000

Table 3.6. Uranium Adsorption Data for ResinTech SIR-1200 Resin.

Sample #	U Initial Conc. (µg /L)	U Final Conc. (µg /L)	Resin Mass (g)	Soln. Vol. (ml)	U Ads. (µg /g)	K_d (ml/g)
			Nitrate: 1331 mg/L			
RTSI-S1-R1-1	179.99	1.8394	0.260	49.08	33.63	18,280
RTSI-S1-R2-1	179.99	0.4380	0.543	49.14	16.25	37,100
RTSI-S1-R3-1	179.99	0.2029	0.757	49.05	11.65	57,420
RTSI-S1-R4-1	179.99	0.1066	1.047	49.39	8.49	79,630
			Nitrate: 1338 mg/L, pH: 7.5			
RTSI-S2-R1-1	170.95	1.5566	0.256	49.10	32.49	20,870
RTSI-S2-R2-1	170.95	0.3873	0.551	49.17	15.22	39,300
RTSI-S2-R3-1	170.95	0.2117	0.743	49.21	11.31	53,420
RTSI-S2-R4-1	170.95	0.1137	0.995	49.10	8.43	74,130
			Nitrate: 317 mg/L			
RTSI-S3-R1-1	171.61	<0.0110	0.297	49.52	>28.61	>2,601,000
RTSI-S3-R2-1	171.61	<0.0110	0.553	49.72	>15.43	>1,406,000
RTSI-S3-R3-1	171.61	<0.0110	0.762	49.65	>11.18	>1,016,000
RTSI-S3-R4-1	171.61	<0.0110	1.045	49.28	>8.09	>736,000
			Nitrate 317 mg/L – Duplicate			
RTSI-S4-R1-1	182.32	<0.0110	0.231	46.764	>36.91	>3,482,000
RTSI-S4-R2-1	182.32	<0.0110	0.473	45.852	>17.67	>1,667,000
RTSI-S4-R3-1	182.32	<0.0110	0.676	46.171	>12.45	>1,175,000
RTSI-S4-R4-1	182.32	<0.0110	0.913	46.214	>9.23	>871,000

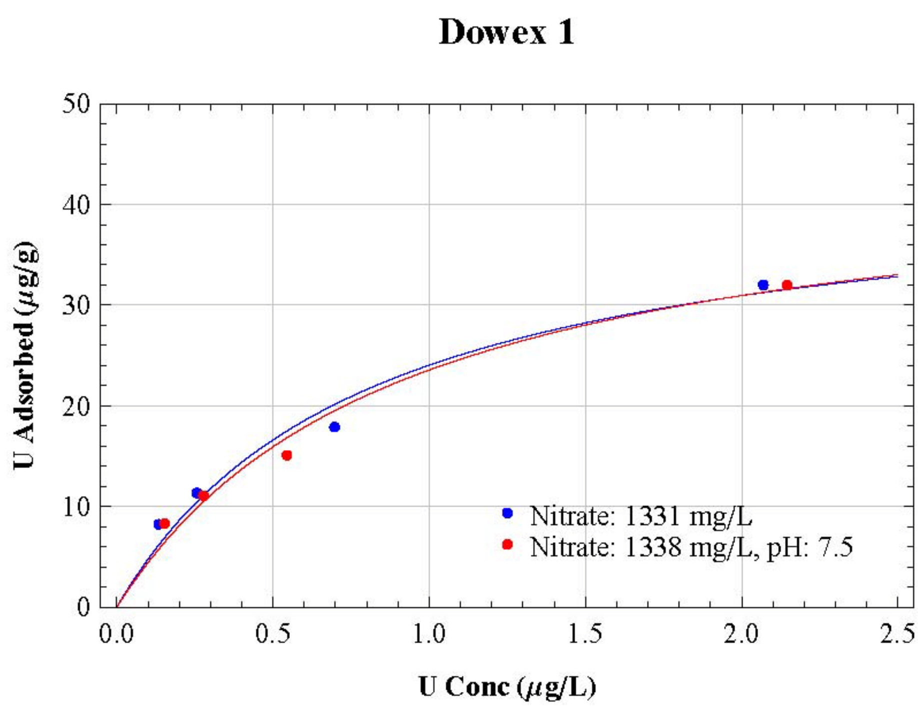

Figure 3.1. Langmuir Adsorption Isotherms for Uranium on Dowex 1 Resin

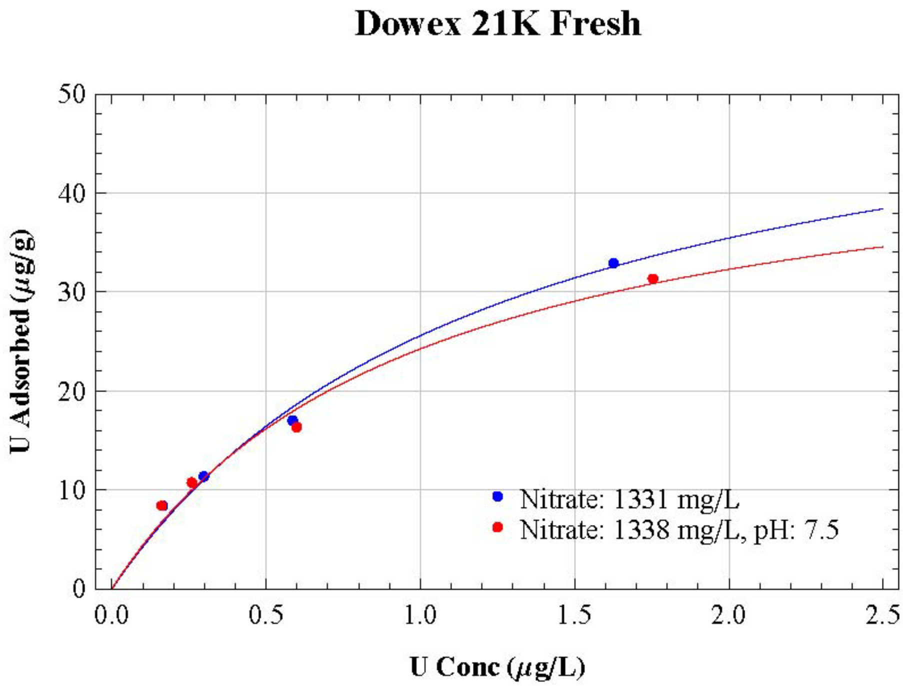

Figure 3.2. Langmuir Adsorption Isotherms for Uranium on Dowex 21K (Fresh) Resin

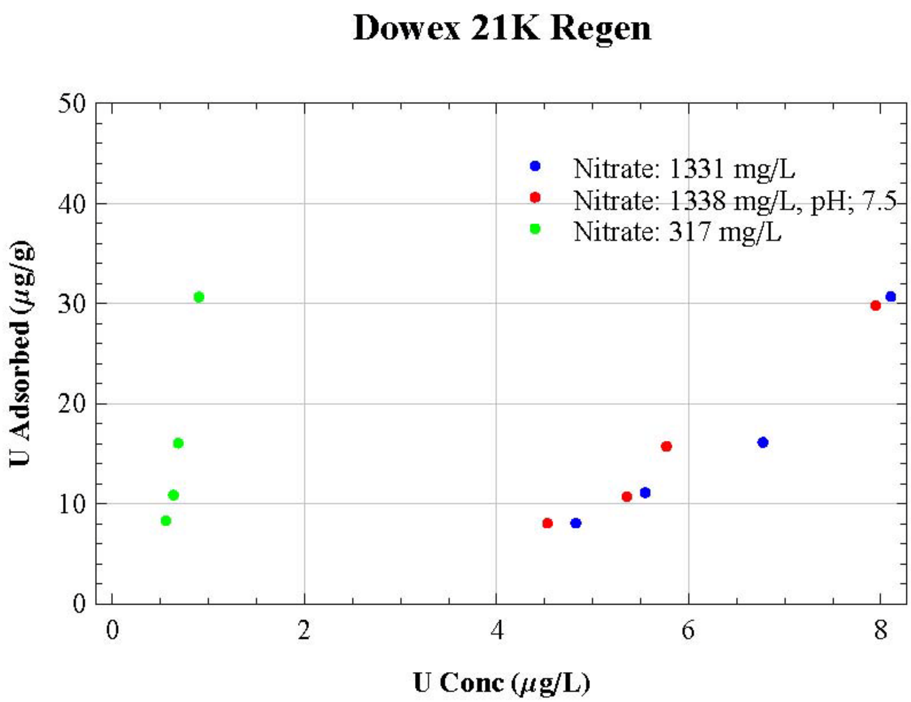

Figure 3.3. Langmuir Adsorption Isotherms for Uranium on Dowex 21K (Regenerated) Resin

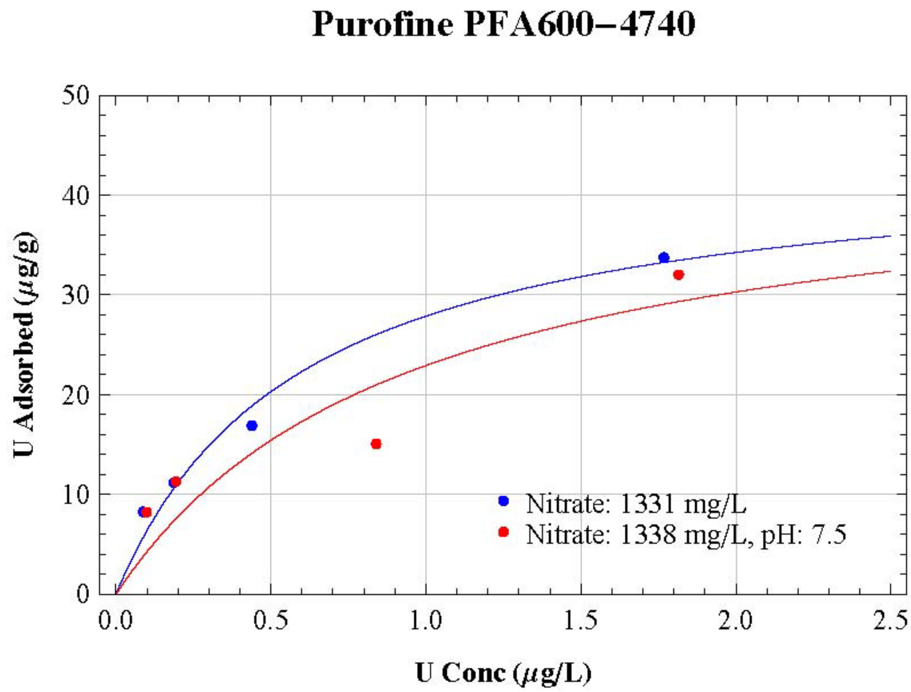

Figure 3.4. Langmuir Adsorption Isotherms for Uranium on Puroline PFA600-4740 Resin

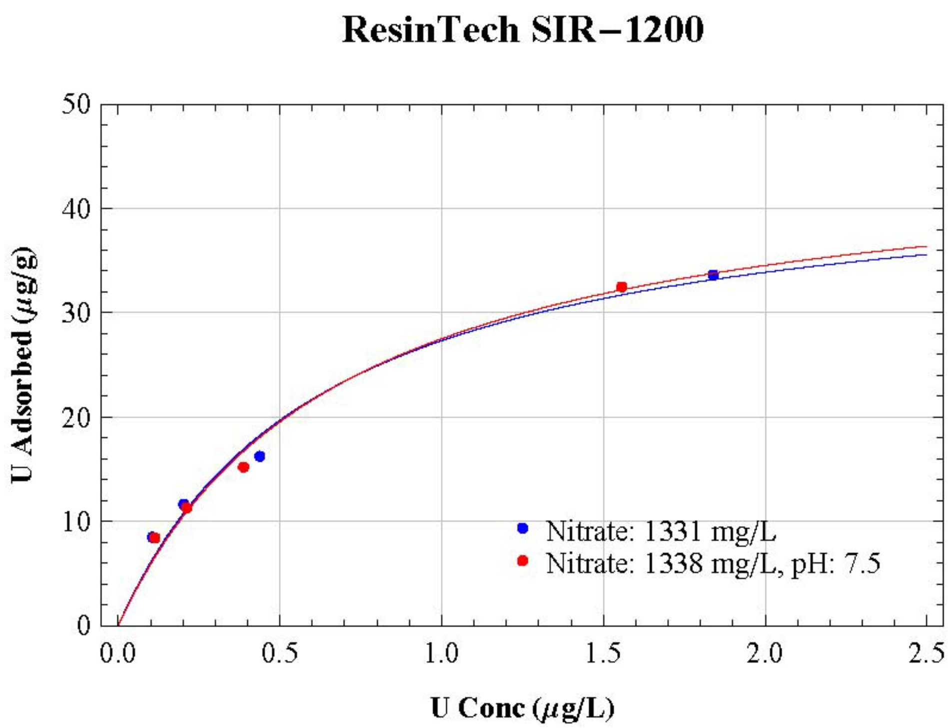

Figure 3.5. Langmuir Adsorption Isotherms for Uranium on ResinTech SIR-1200 Resin

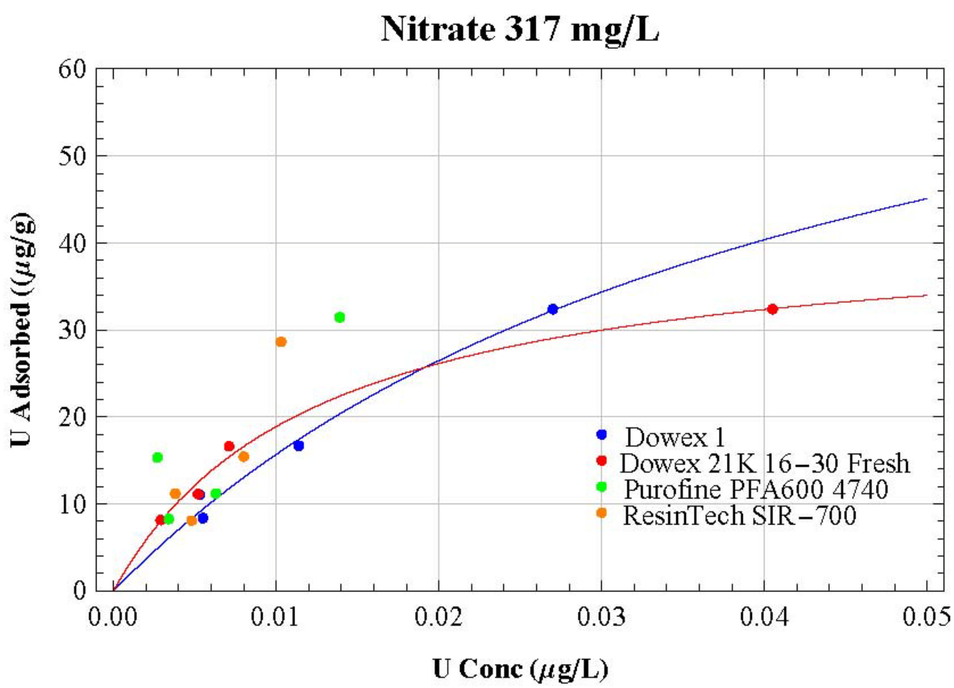

Figure 3.6. Uranium Adsorption Performance of Four of the Five IX-Resins Under Low Nitrate Concentration

Table 3.7. Langmuir Constants for Uranium Adsorption on Selected Ion-Exchange Resins

Resin[a]	Nitrate Conc. (mg/L) pH (SU)	Langmuir Constant K_L (l/µg)	Predicted Ads Maxima M (µg/g)	R^2	Predicted[b] ~K_d (ml/g) at Ads Maximum
Dowex 1	1331	1.24	43.40	0.9932	31,530
Dowex 1	1338, 7.5	1.09	45.11	0.9952	30,330
Dowex 1	317	22.68	84.87	0.9963	138,200
Dowex 21K 16-30 Fresh	1331	0.80	57.63	0.9969	31,670
Dowex 21K 16-30 Fresh	1338, 7.5	1.01	48.27	0.9952	30,940
Dowex 21K 16-30 Fresh	317	80.36	42.42	0.9978	72,830
Dowex 21K 16-30 Regen.	1331				
Dowex 21K 16-30 Regen.	1338, 7.5			(c)	
Dowex 21K 16-30 Regen.	317				
Purofine PFA600/4740	1331	1.69	44.41	0.9934	38,230
Purofine PFA600/4740	1338, 7.5	1.06	44.61	0.9504	29,480
Purofine PFA600/4740	317			(c)	
ResinTech SIR-1200	1331	1.59	44.57	0.9943	37,180
ResinTech SIR-1200	1338, 7.5	1.46	44.37	0.9960	35,360
ResinTech SIR-1200	317			(c)	

(a) Styrene-DVB gel type, strong base anion exchangers.
(b) Based on design U concentration of 570 µg/L.
(c) Adsorption data do not fit Langmuir isotherm.
$Q = MK_LC/(1 + K_LC)$, Q: U adsorbed/unit mass of Resin; C = Equilibrium U Concentration.

3.3 High Nitrate-Low pH Tests

The results of testing with high nitrate (1338 mg/L) and lowered pH (7.5) adjusted source water are listed in Tables 3.2–3.6 and graphically displayed in Figures 3.1–3.6. The Langmuir parameters for the isotherms are tabulated in Table 3.7.

The data resulting from these set of tests did not differ significantly from the high-nitrate isotherm test (previous section). At all four resin-to-solution ratios, the observed uranium adsorption for Dowex 1, Dowex 21K 16-30 (fresh), Purofine PFA600/4740, and ResinTech SIR-1200 resin were similar (Tables 3.2, 3.3, 3.5 and 3.6). The K_d for these four resins ranged from ~15,000 to 82,000 ml/g. The adsorption maxima predicted from Langmuir equation fits to the data for Dowex 1, Dowex 21K 16-30 (fresh), Purofine PFA600/4740, and ResinTech SIR-1200 resins were 45.11, 48.27, 44.61, and 44.37 µg/g, respectively (Table 3.7).

Also in these tests, the uranium-adsorption performance of regenerated Dowex 21K 16-30 resin was noticeably different than the performance of the fresh resin. First, depending on the resin-to-solution ratio, the final uranium concentrations in solutions contacting the regenerated resin were 5 to 30 times higher than the concentrations measured in solutions in contact with the fresh resin (Tables 3.3 and 3.4). Within the tested range of resin-to-solution ratios, the regenerated resin exhibited a relatively linear relationship between the mass of uranium adsorbed per unit mass of resin and the final uranium concentrations in the contact solution (Figure 3.3). The K_d for this regenerated Dowex 21K 16-30 resin ranged from ~1,800 to 3,800 ml/g (Table 3.4), which are an order of magnitude lower than the K_d values for the fresh resin.

3.4 Low-Nitrate Tests

The results of testing with as received source water (nitrate concentration 317 mg/L) are listed in Tables 3.2–3.6 and graphically displayed in Figures 3.1–3.6. The Langmuir parameters for the isotherms are listed in Table 3.7.

The data resulting from these tests indicated that the uranium-adsorption performance of all resins was significantly better than the results obtained from the high-nitrate concentration source water. The K_d for Dowex 1, Dowex 21K 16-30 (fresh), Purofine PFA600/4740, and ResinTech SIR-1200 resins ranged from ~800,000 to 5,600,000 ml/g. These K_d values are one to two orders of magnitude higher than the values observed when the source water contained high-nitrate concentrations, indicating that enhanced concentrations of nitrate in the source water has an inimical effect on the uranium-adsorption performance of these resins. The adsorption maxima predicted from Langmuir equation fits to the data for Dowex 1, and Dowex 21K 16-30 (fresh) resins were, 84.9 and 42.4 µg/g, respectively (Table 3.7). The uranium-adsorption data for Purofine PFA600/4740 and ResinTech SIR-1200 could not be fit due to lack of data points in the non-linear parts of isotherms.

Compared to the fresh resin, the regenerated Dowex 21K 16-30 resin exhibited attenuated uranium-adsorption performance with K_d values ranging from 15,000 to 34,000 mg/g. which are about an order of magnitude lower than the values calculated for the fresh resin. The adsorption isotherm for the regenerated Dowex 21K 16-30 resin was linear, so its adsorption maximum could not be ascertained (Figure 3.3).

4.0 Conclusions

The uranium adsorption performance of five resins (Dowex 1, Dowex 21K 16-30 [fresh], Dowex 21K 16-30 [regenerated], Purofine PFA600/4740, and ResinTech SIR-1200) were tested using unspiked, nitrate-spiked, and nitrate-spiked/pH adjusted source water from well 299-W19-36. The results from these tests are as follows:

- The data from the high-nitrate (1331 mg/L) tests indicated that the uranium-adsorption performance of Dowex 1, Dowex 21K 16-30 (fresh), Purofine PFA600/4740, and ResinTech SIR-1200 all adsorbed uranium similarly well with K_d values ranging from ~15,000 to 95,000 ml/g. The predicted uranium maxima for Dowex 1, Dowex 21K 16-30 (fresh), Purofine PFA600/4740, and ResinTech SIR-1200 using the Langmuir equation were 43.40, 57.3, 44.41 and 44.57 µg/g, respectively, and would be considered suitable for use in the treatment system based on uranium adsorption characteristics.

- Lowering the pH of the high nitrate test conditions from 8.2 to 7.5 had no significant affect on uranium adsorption for the four tested resins. The K_d values for the four resin ranged from ~15,000 to 80,000 ml/g. The predicted uranium maxima for Dowex 1, Dowex 21K 16-30 (fresh), Purofine PFA600/4740, and ResinTech SIR-1200 using the Langmuir equation were 45.11, 48.27, 44.61, and 44.37 µg/g, respectively.

- Higher nitrate concentrations greatly reduced uranium adsorption on all four resins. Tests conducted with unspiked (no amendments; nitrate at 337 mg/L and pH at 8.2) source water yielded K_d values for Dowex 1, Dowex 21K 16-30 (fresh), Purofine PFA600/4740, and ResinTech SIR-1200 resins ranging from ~800,000 to 3,000,000 ml/g. These values are about two orders of magnitude higher than the K_d values noted from tests conducted using amended source water. The adsorption maxima predicted from the Langmuir equation fits to the data for Dowex 1, and Dowex 21K 16-30 (fresh) resins were, 84.9 and 42.4 µg/g, respectively. The uranium-adsorption data for Purofine PFA600/4740 and ResinTech SIR-1200 could not be fit due to lack of data points in the non-linear parts of the isotherms.

- Compared to the fresh resin, the regenerated Dowex 21K 16-30 resin exhibited significantly lower uranium-adsorption performance under all test conditions. The calculated K_d values for the regenerated resin were typically an order of magnitude lower than the values calculated for the fresh resin. All isotherms for the regenerated resin did not conform to a Langmuir-type adsorption model.

- Additional testing using laboratory columns is recommended to better resolve differences between the adsorption abilities of the resins and to develop estimates of uranium loading on the resins. By determining the quantity of uranium that each resin can adsorb and the time required to reach various levels of loading, resin lifetime in the treatment system can be estimated.

5.0 References

CHPRC. 2010. *Test Plan for Uranium Ion-Exchange Resins*. SGW-47531, Rev. 0. CH2MHill Plateau Remediation Contractor, Richland, Washington.

Comprehensive Environmental Response, Compensation, and Liability Act of 1980. 1980. Public Law 96-150, as amended, 42 USC 9601, et seq. Accessed January 10, 2011, at http://uscode.house.gov/download/pls/42C103.txt.

DOW. 1997. *Application Information – DOWEX Ion Exchange Resins; Equilibrium Isotherm Testing for Liquid Phase Applications*. The DOW Chemical Company, Midland, MI.

Ecology – Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy. 1989. *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement). Document 89-10, as amended, Olympia, Washington. Accessed January 10, 2011, at http://www.hanford.gov/?page=81.

EPA – U.S. Environmental Protection Agency, Washington State Department of Ecology, and U.S. Department of Energy. 2008. *Record of Decision Hanford 200 Area 200-ZP-1 Superfund Site, Benton County, Washington* (transmitted via letter 09-AMCP-0003), Olympia, Washington.

Appendix

Analytes and Analytical Methods

Appendix

Analytes and Analytical Methods

The analytes and analytical methods for the testing are described below.

A.1 Analyte List

Influent water was analyzed for uranium, technetium-99, sulfate, nitrate, pH, and alkalinity. Batch contact solutions were analyzed for uranium only.

A.2 pH Analysis

Approximately 3-ml aliquots of the unfiltered groundwater/test solution were used for pH measurement following Pacific Northwest National Laboratory's (PNNL's) procedure AGG-pH-001, "pH Measurements,"[1] which is similar to the U.S. Environmental Protection Agency's (EPA's) SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, Third Edition; Final Update IV-B, Method 9040C (EPA 2004). Solution pH values were measured with a glass calomel pH electrode and a pH meter calibrated with appropriate buffers at 4, 7, and 10.

A.3 Trace Metals Analysis

Uranium and technetium-99 analyses of the groundwater/test solution were performed using an inductively coupled plasma-mass spectrometer (ICP-MS) following procedure PNNL-AGG-415, "Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Analysis,"[2] which is similar to SW-846, Method 6020A (EPA 1996). High-purity traceable single element standards traceable to the National Institute of Standards and technology (Ultra Scientific [(Kingston, RI] and Inorganic Ventures [Lakewood, New Jersey]) were used to generate calibration curves and to verify continuing calibration during the analytical run. A serial dilution was made of select samples to investigate and correct for matrix interferences. Typical instrument detection limits for the ICP-MS are in the range of parts per trillion.

A.4 Alkalinity

Alkalinity of the groundwater was measured by titrimetry in accordance with Standard Methods for the Examination of Water and Wastewater, Method 2320B (AWWA et al. 1998).

[1] Valenta MM. 2009. "pH Measurements." AGG-pH-00 1, unpublished PNNL Technical Procedure, Pacific Northwest National Laboratory, Richland, Washington.
[2] Clayton ET. 2008. "Inductively Coupled Plasma Mass Spectrophotometry (ICP-MS)," PNNL-AGG-415, unpublished PNNL Technical Procedure, Pacific Northwest National Laboratory, Richland, Washington.

A.5 Nitrate and Sulfate Analysis

Nitrate and sulfate analyses of the groundwater/test solution was performed using PNNL's procedure AGG-IC-001, "Determinations by Ion Chromatography (IC),"[1] which is similar to EPA SW-846, Method 9056A (EPA 2007). Nitrate was separated on a Dionex AS18 column with a sodium hydroxide gradient elution and measured using a conductivity detector. The only modification to the EPA ion-chromatography method was the use of sodium hydroxide for gradient elution. High-purity calibration standards were used to generate calibration curves and to verify continuing calibration during the analytical run.

A.6 References

AWWA, APHA, and WEF. 1998. *Standard Methods for the Examination of Water and Wastewater*. 20th edition, American Water Well Association, Denver, Colorado; American Public Health Association, Washington, D.C.; and Water Environment Federation, Alexandria, Virginia.

U.S. Environmental Protection Agency (EPA). 1996. "Method 6020A, Inductively Coupled Plasma – Mass Spectrometry," Rev. 1. In *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. EPA SW 846, EPA Office of Solid Waste and Emergency Response, Washington, D.C. Accessed June 1, 2010, at http://www.ppa.izov/epawaste/hazard/testrnethods/sw846/pdfs/6020a.pd.

U.S. Environmental Protection Agency (EPA). 2004. "Method 9040C, pH Electrometric Measurement," Rev. 3. In *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. EPA SW 846, EPA Office of Solid Waste and Emergency Response, Washington, D.C. Accessed June 1, 2010, at httl2://www.epa.gov/epawaste/hazard/testrnethods/sw846/pdfs/9040c.pdf.

U.S. Environmental Protection Agency (EPA). 2007. "Method 9056A, Determination of Inorganic Anions by Ion Chromatography," Rev. 1. In *Test Methods for Evaluating Solid Waste: Physical/ Chemical Methods*. EPA SW 846, EPA Office of Solid Waste and Emergency Response, Washington, D.C. Accessed January 11, 2011, at http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/9056a.pdf.

[1] Lindberg MJ. 2004. "Determinations by Ion Chromatography (IC)," AGG-IC-001, unpublished PNNL Technical Procedure, Pacific Northwest National Laboratory, Richland, Washington.

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