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Iodine Adsorption on Ion-Exchange Resins and Activated Carbons–Batch Testing

September 2014

1 KE Parker
2 EC Golovich
3 DM Wellman

U.S. DEPARTMENT OF ENERGY

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

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Among radioactive contaminants, iodine-129 (^{129}I) is commonly either the top or among the top risk drivers, along with technetium-99 (^{99}Tc), at radiological waste disposal sites and contaminated groundwater sites where nuclear material fabrication or reprocessing has occurred. Radioactive iodine (^{129}I) is of environmental concern due to its long half-life (1.6×10^7 years), toxicity, and mobility in the environment (Councell et al. 1997). However, there are currently very few approaches that effectively manage risks to human health and the environment.

At the Hanford Site in Washington State, radioactive iodine (^{129}I), a fission product of plutonium, was discharged in 200 West Area disposal cribs. This discharge is responsible for the majority of ^{129}I contamination found in the groundwater (Zhang et al. 2013). The 200 West Area contains two separate plumes covering 1,500 acres where ^{129}I concentrations are ~3.5 pCi/L.

The objective of this study was to evaluate the efficacy of commercial ion exchange resins and granular activated carbon (GAC) materials which will enable direct removal of all iodine species present in Hanford groundwater through treatment at the 200W pump and treat. Iodine sorption onto seven resins and six carbon materials was evaluated using water from well 299-W19-36 on the Hanford Site. These materials were tested using a range of solution-to-solid ratios. The test results are as follows:

- The efficacy of the resin and granular activated carbon materials was less than predicted based on manufacturers' performance data. It is hypothesized that this is due to the differences in speciation previously determined for Hanford groundwater.
- The sorption of iodine is affected by the iodine species in the source water. Iodine loading on resins using source water ranged from 1.47 to 1.70 µg/g with the corresponding K_d values from 189.9 to 227.0 mL/g. The sorption values when the iodine is converted to iodide ranged from 2.75 to 5.90 µg/g with the corresponding K_d values from 536.3 to 2979.6 mL/g. It is recommended that methods to convert iodine to iodide be investigated in fiscal year (FY) 2015.
- The chemicals used to convert iodine to iodate adversely affected the sorption of iodine onto the carbon materials. Using as-received source water, loading and K_d values ranged from 1.47 to 1.70 µg/g and 189.8 to 226.3 mL/g respectively. After treatment, loading and K_d values could not be calculated because there was little change between the initial and final iodine concentration. It is recommended the cause of the decrease in iodine sorption be investigated in FY15.
- In direct support of CH2M HILL Plateau Remediation Company, Pacific Northwest National Laboratory has evaluated samples from within the 200W pump and treat bioreactors. As part of this analysis, pictures taken within the bioreactor reveal a precipitate that, based on physical properties and known aqueous chemistry, is hypothesized to be iron pyrite or chalcopyrite, which could affect iodine adsorption. It is recommended these materials be tested at different solution-to-solid ratios in FY15 to determine their effect on iodine sorption.

Acknowledgement

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Acronyms and Abbreviations

μg	microgram(s)
μg/g	microgram(s) per gram
eq/L	equivalence per liter
DDI	distilled deionized
FY	fiscal year
GAC	granular activated carbon
ICP-MS	inductively coupled plasma mass spectrometer
K_d	distribution coefficient(s)
pCi/L	picocuries per liter

Contents

Figures

Tables

1.0 Introduction

Among radioactive contaminants, iodine-129 (^{129}I) is commonly either the top or among the top risk drivers, along with technetium-99 (^{99}Tc), at radiological waste disposal sites and contaminated groundwater sites where nuclear material fabrication or reprocessing has occurred. Radioactive iodine (^{129}I) is of environmental concern due to its long half-life (1.6×10^7 years), toxicity, and mobility in the environment (Councell et al. 1997). However, there are currently very few approaches that effectively manage risks to human health and the environment.

At the Hanford Site in Washington State, radioactive iodine (^{129}I), a fission product of plutonium, was discharged in 200 West Area disposal cribs. This discharge is responsible for the majority of ^{129}I contamination found in the groundwater (Zhang et al. 2013). The 200 West Area contains two separate plumes covering 1,500 acres (Figure 1.1) where ^{129}I concentrations are ~3.5 pCi/L.

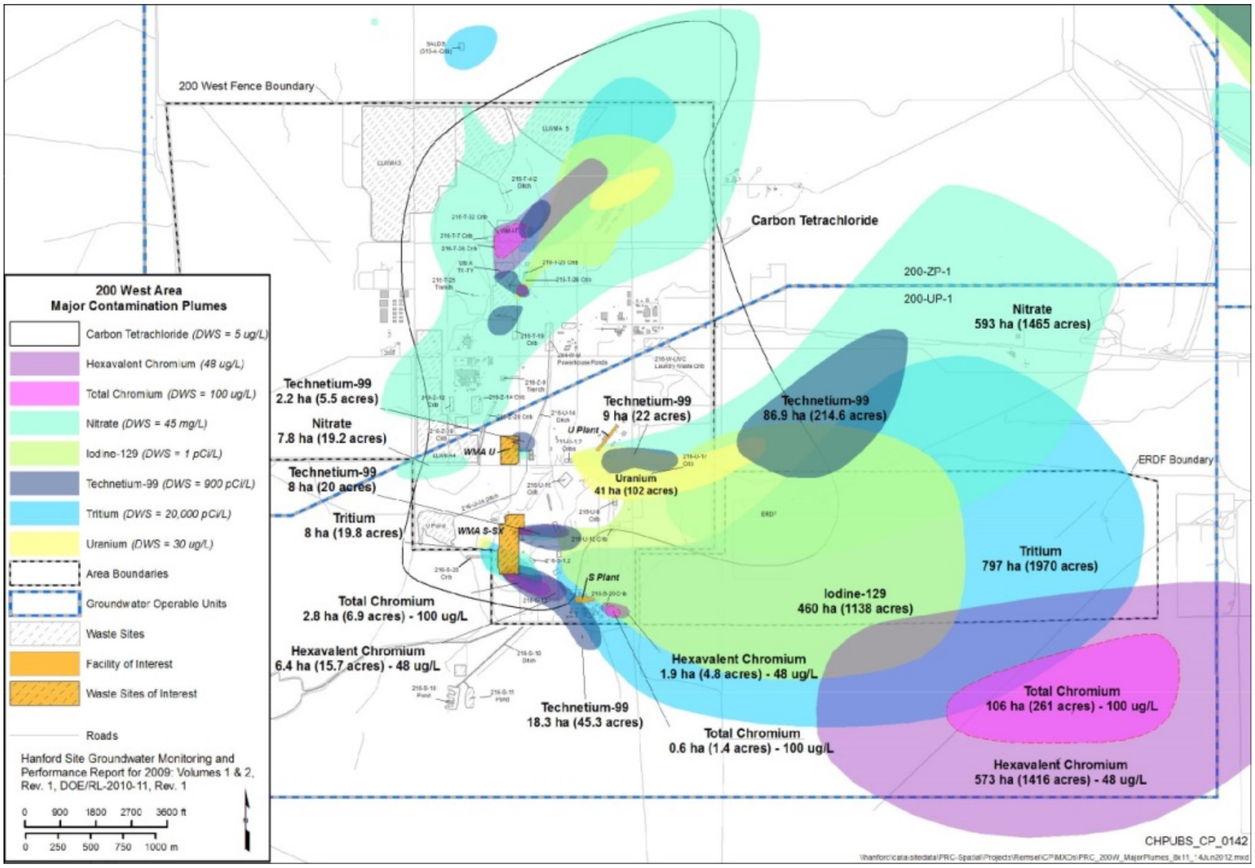

Figure 1.1. 200 West Groundwater Plume Map. ^{129}I is shown in green. (http://www.hanford.gov/files.cfm/CAL_Proposed_Plan_200-UP-1.pdf)

The speciation of iodine in Hanford groundwater has been previously demonstrated to be dominated by the presence of iodate (IO_3^-), ~75%. Unexpectedly, iodide (I^-), which was likely the form of iodine in the source materials and the expected dominant groundwater species based on thermodynamic considerations, only accounted for 1% to 2% of the total iodine concentration (Santschi et al. 2012). Organo-iodine comprised approximately 26% of the iodine speciation in groundwater, which has exceedingly low concentrations of soil organic matter. The predominance of iodate in Hanford groundwater is contrary to chemical thermodynamic predictions and is the subject of ongoing investigations. The objective of this study is to evaluate the efficacy of commercial ion exchange resins and granular activated carbon (GAC) materials which will enable direct removal of all iodine species present in Hanford groundwater through treatment at the 200W pump and treat.

2.0 Quality Assurance

The Pacific Northwest National Laboratory (PNNL) Quality Assurance (QA) Program is based upon the requirements as defined in U.S. Department of Energy (DOE) Order 414.1D, Quality Assurance, and 10 CFR 830, Energy/Nuclear Safety Management, Subpart A, Quality Assurance Requirements (a.k.a. the Quality Rule). PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, Quality Assurance Requirements for Nuclear Facility Applications, Part 1, Requirements for Quality Assurance Programs for Nuclear Facilities.

- ASME NQA-1-2000, Part II, Subpart 2.7, Quality Assurance Requirements for Computer Software for Nuclear Facility Applications, including problem reporting and corrective action.

- ASME NQA-1-2000, Part IV, Subpart 4.2, Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development.

The procedures necessary to implement the requirements are documented through PNNL's "How Do I?" (HDI), a system for managing the delivery of laboratory-level policies, requirements, and procedures.

The DVZ-AFRI Quality Assurance Plan is the minimum applicable QA document for all Deep Vadose Zone – Applied Field Research Initiative (DVZ-AFRI) projects. This QA Plan also conforms to the QA requirements of DOE Order 414.1D, Quality Assurance, and 10 CFR 830, Subpart A, Quality Assurance Requirements. The DVZ-AFRI is subject to the Price Anderson Amendments Act.

The implementation of the DVZ-AFRI QA Program is graded in accordance with NQA-1-2000, Part IV, Subpart 4.2, Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development.

The following technology levels are defined for this DVZ-AFRI QA Program:

- Basic Research consists of research tasks that are conducted to acquire and disseminate new scientific knowledge. During basic research, maximum flexibility is desired to give the researcher the latitude to conduct the research.

- Applied Research consists of research tasks that acquire data and documentation necessary to ensure satisfactory reproducibility of results. The emphasis during this stage of a research task is on achieving adequate documentation and controls necessary to be able to reproduce results.

- Development Work consists of research tasks moving toward technology commercialization. These tasks still require flexibility and there uncertainty still exists in many cases. The role of quality on development work is to make sure that there are adequate controls to support movement into commercialization.

Research and development support activities are those that are conventional and secondary in nature to the advancement of knowledge or development of technology, but allow the primary purpose of the work to be accomplished in a credible manner. An example of a support activity is controlling and maintaining documents and records. The level of quality for these activities is the same as for developmental work.

Within each technology level, the application process for QA controls is graded such that the level of analysis, extent of documentation, and degree of rigor of process control are applied commensurate with their significance, importance to safety, life-cycle state of a facility or work, or programmatic mission. The work for this report was performed under the technology level of Applied Research.

The project used PNNL's Environmental Sciences Laboratory (ESL) for chemical analyses required as part of laboratory and field experiments and testing. The ESL operates under a dedicated QA plan that complies with the Hanford Analytical Services Quality Assurance Requirements Document (HASQARD) (DOE/RL-96-68). ESL implements HASQARD through Conducting Analytical Work in Support of Regulatory Programs (CAWSRP). Data quality objectives established in CAWSRP were generated in accordance with HASQARD requirements. Chemical analyses of testing samples and materials were conducted under the ESL QA plan.

3.0 Experiment

3.1 Material Preparation

3.1.1 Source Water

Water used for the batch experiments was sourced from well 299-W19-36 on the Hanford Site. The analysis (Mattigod et al. 2010) is shown in Table 3.1.

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

Constituent	Concentration (µg/L)	Constituent	Unsparged Conc (µg/L)	Sparged Conc (µg/L)
Barium	113	Acetone	<0.0028	<0.0028
Calcium	122,000	1,1-Dichloroethene	0.01	0.01
Chloride	181,000	Methylene Chloride	0.15	0.15
Total Cr	<17.3	cis1,2-dichloroethene	<0.001	<0.001
Cr(VI)	<0.05	Chloroform	0.25	0.01
Magnesium	36,400	1,2 dichloroethane	0.1	<0.002
Molybdenum	65.9	1,1,1 trichloroethane	<0.002	<0.002
Nitrate	317,000	Benzene	0.01	0.01
Potassium	7,020	Carbon tetrachloride	4.99	0.03
Sodium	118,000	Trichloroethene	0.09	0.02
Sulfate(a)	50,000	Toluene	0.02	0.03
Strontium	618	Dibromochloromethane	0.01	0.01
Tin(b)	216	Tetrachloroethene	<0.001	<0.001
Alkalinity (as $CaCO_3$)(c)	116,000	Ethyl benzene (d)	0.03	0.06
Uranium(a)	174	p/m xylene (d)	0.08	0.19
Total Suspended Solids	607	o-xylene (d)	0.04	0.09
Total Organic Carbon	<5			
pH	8.2 (SU)			

(a) Average of four measurements
(b) The source of these constituents in the groundwater is unknown
(c) Average of duplicate measurements
(d) Results are at the lower limits of instrument detection

Treatments to the water were completed prior to the sorption test and are summarized in Table 3.2. To convert the oxidize iodine to iodate and reduce to iodide, a procedure described by Korkisch (1988) was used.

Table 3.2. Source Water Treatments

Treatment ID	Amount of Water (L)	Treatment and Amounts Added	Reason For Treatment
A	40	As received	NA
B	1.2	1.78 g sodium nitrate	Increase nitrate level from 317 to 1400 mg/L
C	2	2.5 mL of 5% sodium hypochlorite-mixed at 600 rpm for 3 min	Convert iodine to iodate
D	4	5 mL of 5% sodium hypochlorite-mixed at 600 rpm for 3 min, 25 mL of 1 M hydroxylamine hydrochloride, 10 mL of 1M sodium bisulfide, mixed at 600 rpm for 45 min. Adjust pH to 6.5 with sodium hydroxide.	Convert iodine to iodide

Sodium hypochlorite and hydroxylamine hydrochloride-Sigma Aldrich, Dallas, TX
Sodium nitrate, sodium hydroxide and sodium bisulfite -Fisher Scientific, Pittsburgh, PA

3.1.2 Ion Exchange Resin

The ion exchange resin materials were cleaned to remove residual metals left over from the manufacturing process by centrifuge washing two times for 1 hour with distilled deionized (DDI) water at a solution-to-solid ratio of 3:1, followed by centrifugation at 1700 rpm for 5 minutes. After decanting the second wash water, the resins were soaked in DDI water for 24 hours. The excess water was decanted, and the resins were stored at room temperature until needed. The ion exchange resins used in this study are shown in Table 3.3.

Table 3.3. Resins Used in Batch Sorption Tests

Product Name	Vendor
Dowex 1	The Dow Chemical Company, Midland, Michigan
Dowex-21K	The Dow Chemical Company, Midland, Michigan
Purolite PFA600	The Purolite Company, Bala Cynwyd, Pennsylvania
Resin Tech SIR-700	ResinTech, Inc, West Berlin, New Jersey
Resin Tech SIR-1200	ResinTech, Inc, West Berlin, New Jersey
Purolite A530E	The Purolite Company, Bala Cynwyd, Pennsylvania
Purolite A-532E	The Purolite Company, Bala Cynwyd, Pennsylvania

Due to the various amounts of water in the resins, the decision was made to use the dry weight of the solids as the basis to determine the solution-to-solid ratios, and to calculate the loading and sorption capacity. Thus, the dry weights of the resins used in the tests are reported along with the test results in section 3.

3.1.3 Granulated Activated Carbon

The GAC was used “as-received.” The GAC materials are shown in Table 3.4.

Table 3.4. Activated Carbon Used in Batch Sorption Tests

Product Name	Source Material	Vendor
Calgon Filtrasorb 400	Bituminous coal	Calgon Carbon Corporation, Pittsburgh, PA
Carbon Resources 1240A	Sub-bituminous coal	Carbon Resources, Oceanside, California
General Carbon GC20X50	Bituminous coal	General Carbon Corporation, Paterson, New Jersey
Siemens[a] AC1230AWC	Coconut shell	Siemens Corporation, Warrendale, Pennsylvania
Norit GAC830 M1871	Coconut shell	Norit Americas, Inc, Marshall, Texas
Norit GCA830 M1917	Bituminous coal	Norit Americas, Inc, Marshall, Texas

(a) As of August 2014, this material is no longer sold by Siemens. This material is now known as AquaCarb 1230AWC and is available from Evoqua Water Technologies, Alpharetta, GA.

3.2 Determination of Resin Moisture Content

The resin moisture content was determined using EPA Method 1314. The moisture content of each resin was determined by weighing, nominally, 1 to 3 g of wet resin in individually tarred aluminum weighing boats and the resin dried in an oven for 24 hours at 105±2°C. The dried resin was weighed and returned to the oven for 2 hours. This step was repeated until a constant weight was obtained.

3.3 Batch Sorption Tests

Batch sorption tests were conducted where a mass of resin or carbon and the appropriate amount of water were placed into a poly bottle of the appropriate size for a given solution-to-solid ratio. The poly bottles were sealed and placed on a shaker table set at 60 rpm to ensure the sorption materials and groundwater remained well mixed for the required 24-hour period. All sorption tests were conducted at room temperature. After the 24-hour contact time, the poly bottles were removed from the shaker table and the sorption materials were allowed to settle for 30 minutes. A 0.45 µm syringe filter was then used to separate the aqueous matrix from the sorbent. A 5 mL aliquot was analyzed for total iodine by inductively coupled plasma mass spectrometry. See Appendix A for description of analysis procedure.

The resin exchange capacities (Table 3.5), carbon loading capacity (Table 3.6), and iodine concentration of 11.0 µg/L based on previous source water analysis (Mattigod et al. 2010) was used to calculate a starting solution-to-solid ratio. It was calculated that ratio #2 should remove all of the iodine in 1 L of source water. Ratio #1, which increases the amount of test material in 1 L, was added to the matrix to ensure that iodine sorption was not affected by the sorption of other ionic species. Based on initial batch test results, additional solution-to-solid ratios were included in the test matrix for use in subsequent sorption tests. The solution-to-solid ratios used in the batch sorption tests are listed in Table 3.7. Actual material masses and solution volumes used in the batch tests are reported with the test results in section 4.0.

Table 3.5. Resin Exchange Capacity

Resin	Total Exchange Capacity (eq/L Cl^- form)
Dowex 1	0.7
Dowex-21K	1.2
Purolite PFA600	1.4
Resin Tech SIR-700	2.7
Resin Tech SIR-1200	1.4
Purolite A530E	0.6
Purolite A-532E	0.85

Table 3.6. Carbon Material Loading Capacity

Carbon Material	mg Iodine/g Material
Calgon Filtrasorb 400	1000
Carbon Resources 1240A	1000
General Carbon GC20X50	950
Siemens AC1230AWC	1100
Norit GAC830 M1871	920
Norit GCA830 M1917	920

Table 3.7. Sorption Test Solution-to-Solid Ratios

Ratio #	Nominal Dry Solid Material (g)	Nominal Solution Volume (mL)	Nominal Solution-to-Solid Ratio
1	0.1	1000	10,000
2	0.02	1000	50,000
3	0.1	10	100
4	0.04	10	250
5	0.2	100	500
6	0.1	100	1,000
7	0.04	100	2,500
8	0.05	250	5,000

The test matrix for this study is shown in Table 3.8. The table shows materials, solution-to-solid ratios, and water treatments used in the sorption tests. Batch sorption tests were completed in six sets. Sorption tests using ratios #1 and #2, sparged source water, and the getters were conducted together. Sorption tests using Resin Tech SIR-1200, Carbon Resources 1240A, and two nitrate levels were also conducted together. All other tests were conducted separately.

Table 3.8. Sorption Test Matrix

	Solution-to-Solid Ratios							
Materials	Ratio 1	Ratio 2	Ratio 3	Ratio 4	Ratio 5	Ratio 6	Ratio 7	Ratio 8
Dowex 1	A	A	A			C, D		
Dowex-21K	A	A	A			C, D		
Purolite PFA600	A	A	A			C, D		
Resin Tech SIR-700	A	A	A			C, D		
Resin Tech SIR-1200	A	A	A, B	A, B	A, B	C, D	A, B	A, B
Purolite A530E	A	A	A			C, D		
Purolite A-532E	A	A	A			C, D		
Calgon Filtrasorb 400	A	A	A			C, D		
Carbon Resources 1240A	A	A	A, B	A, B	A, B	C, D	A, B	A, B
General Carbon GC20X50	A	A	A			C, D		
Siemens AC1230AWC	A	A	A			C, D		
Norit GAC830 M1871	A	A	A			C, D		
Norit GCA830 M1917	A	A	A			C, D		

A - As received water
B - High nitrate water
C - As received water treated to iodate
D - As received water treated to iodide

4.0 Results

4.1 Moisture Content of Resins

The moisture content of each resin was measured and the results are presented in Table 4.1. To obtain a similar amount of dry material for each sorption test and maintain the solution-to-solid ratios given in Table 3.5, different amounts of wet resin had to be used in the sorption tests shown in Table 3.8. These amounts are presented in Table 4.2.

Table 4.1. Moisture Content of Resins

Resin	Initial Wet Resin Mass (g)	Final Dry Resin Mass (g)	Calculated Moisture Content (%)
Dowex 1	1.799	0.698	61.20
Dowex-21K	1.864	0.554	70.28
Purolite PFA600	2.173	0.836	61.53
Resin Tech SIR700	2.586	1.285	50.31
Resin Tech SIR1200	3.183	0.800	74.87
Purolite A530E	1.906	0.650	65.90
Purolite A532E	2.566	1.074	58.14

Table 4.2. Amounts of Wet Resin Required for a Constant Solid to Solution Ratio

	Amount (g) of Wet Resin Needed for:				
Resin	0.02 g Dry	0.04 g Dry	0.05 g Dry	0.1 g Dry	0.2 g Dry
Dowex 1	0.033	0.065	0.082	0.163	0.327
Dowex-21K	0.028	0.057	0.071	0.142	0.285
Purolite PFA600	0.033	0.065	0.081	0.163	0.325
Resin Tech SIR700	0.040	0.080	0.099	0.199	0.398
Resin Tech SIR1200	0.027	0.053	0.067	0.134	0.267
Purolite A530E	0.030	0.061	0.076	0.152	0.304
Purolite A532E	0.034	0.069	0.086	0.172	0.344

4.2 Sorption Tests Using Source Water

Loading and K_d values from ratio #1 and #2 sorption tests could not be determined because the difference in measured concentration of the starting groundwater and that after treatment with the material of interest was less than 15%, which is within analytical error. This suggests that the materials of interest do not perform as well as specified by the manufacturers. This could be a result of the differences in determined versus predicted values based on chemical thermodynamics.

4.3 Sorption Tests: Two Materials, Two Nitrate Levels, and Six Ratios

Because the differences in measured iodine concentrations within the initial and treated groundwater were within analytical error, a series of sorption tests using lower solution-to-solid ratios were conducted to determine the optimum solution-to-solid ratio. Tests were conducted using ratios #3 through #8. Sorption test results were using source water with as-received nitrate concentrations of 317 mg/L (Mattigod et al. 2010) or increased to a nominal 1400 mg/L nitrate using ResinTech-SIR 1200 and Carbon Resources 1240A.

The results from the sorption tests using as-received source water with no change to nitrate levels are shown in Table 4.3 and Table 4.4. The results from the high nitrate tests are shown in Table 4.5 and Table 4.6.

Table 4.3. Sorption Results for ResinTech-SIR 1200 Using As-Received Source Water, 317 mg/L Nitrate

Ratio #	Iodine Initial Concentration (µg/L)	Iodine Final Concentration (µg/L)	Mass of Material - Dry (g)	Soln. Vol. (mL)	Iodine Adsorption (µg/g)	K_d (mL/g)
3	9.77	5.75	0.10	10.2	0.40	69.8
4	9.77	6.86	0.04	10.1	0.73	105.9
5	9.77	7.29	0.20	100.7	1.24	169.8
6	9.77	7.62	0.10	101.9	2.15	281.6
7	9.77	7.86	0.04	102.9	4.76	605.9
8	9.77	8.11	0.05	247.0	8.27	1020.1

Data from sorption tests using ratios #3 through #8 and ResinTech-SIR 1200 resin show that total iodine loading ranged from of 0.40 µg/g at ratio #3 to 8.27 µg/g at ratio #8. The K_d values were 69.8 to 1020.1 mL/g over the same range.

Table 4.4. Sorption Results for Carbon Resources 1240A Using As-Received Source Water, 317 mg/L Nitrate

Ratio #	Iodine Initial Concentration (µg/L)	Iodine Final Concentration (µg/L)	Mass of Material - Dry (g)	Soln. Vol. (mL)	Iodine Adsorption (µg/g)	K_d (mL/g)
3	9.77	7.45	0.10	10.1	0.23	31.2
4	9.77	7.53	0.04	10.0	0.56	74.5
5	9.77	7.56	0.20	100.0	1.10	145.9
6	9.77	7.64	0.10	100.1	2.13	278.4
7	9.77	7.97	0.04	100.0	4.49	563.3
8	9.77	8.48	0.05	250.0	6.43	757.7

Data from the Carbon Resources 1240A sorption tests for ratios #3 through #8 indicate the iodine loading ranged from of 0.23 µg/g at ratio #3 to 6.43 µg/g at ratio #8. The K_d values ranged from 31.2 to 757.7 mL/g over the same solution-to-solid ratios. Both loading and K_d values are lower for Carbon Resources 1240A than for ResinTech-SIR1200.

Table 4.5. Sorption Results for ResinTech-SIR 1200 Using High Nitrate Source Water, 1400 mg/L Nitrate

Ratio #	Iodine Initial Concentration (µg/L)	Iodine Final Concentration (µg/L)	Mass of Material - Dry (g)	Soln. Vol. (mL)	Iodine Adsorption (µg/g)	K_d (mL/g)
3	9.83	6.88	0.10	10.0	0.3	43.1
4	9.83	7.44	0.04	10.0	0.6	80.8
5	9.83	7.65	0.20	99.6	1.1	142.5
6	9.83	7.92	0.10	98.8	1.9	241.2
7	9.83	8.20	0.04	101.0	4.1	496.8
8	9.83	8.37	0.05	250.8	7.3	872.2

The sorption of total iodine from source water with a nominal 1400 mg/L nitrate onto ResinTech-SIR1200 exhibits loading values of 0.3 to 7.3 µg/g and K_d values of 43.1 to 872.2 mL/g over the selected solution-to-solid range. The iodine sorption values are lower in the high nitrate water than in the as-received water, suggesting that nitrate could compete with iodine species for active sorption sites on ResinTech-SIR1200.

Table 4.6. Sorption Results for Carbon Resources 1240A Using High Nitrate Source Water, 1400 mg/L Nitrate

Ratio	Iodine Initial Conc. (µg/L)	Iodine Final Conc. (µg/L)	Mass of Material - Dry (g)	Soln. Vol. (mL)	Iodine Adsorption (µg/g)	K_d (mL/g)
3	9.83	7.79	0.10	10.1	0.2	26.4
4	9.83	7.99	0.04	10.1	0.5	58.0
5	9.83	7.92	0.20	100.1	1.0	120.6
6	9.83	8.18	0.10	100.0	1.7	201.7
7	9.83	8.25	0.04	100.1	4.0	479.2
8	9.83	8.97	0.05	250.3	4.3	479.9

The sorption of total iodine from source water with a nominal 1400 mg/L nitrate onto Carbon Resources 1240A shows loading values of 0.2 to 4.33 µg/g and K_d values of 26.4 to 479.9 mL/g over the selected solution-to-solid range. As observed in the ResinTech-SIR1200 sorption results, the total iodine sorption values are lower in the high nitrate water than in the as-received water, again suggesting potential competition for active sorption sites. For ratio #8, there was a negligible increase in the loading and K_d values for iodine when compared to ratio #7. This was not observed in any other sorption test.

After reviewing the loading and sorption data shown in Table 4.3 to Table 4.6, ratio #6 was chosen for use in all future sorption tests. Ratio #6 demonstrated the highest loading and sorption values when compared to ratios #3 through #5, but also minimized the amount of used effluent generated when compared to ratios #7 and #8.

4.4 Sorption Tests: All Materials

Using ratio #6, all seven resins and six carbon materials were tested using the as-received source water. Results are shown in Table 4.7. Loading and K_d data indicate the amount of total iodine being removed is less than 2 g/L.

Table 4.7. Sorption Test Results Using all Resin and Carbon Materials

Material Tested	Iodine Initial Concentration (µg/L)	Iodine Final Concentration (µg/L)	Mass of Material - Dry (g)	Soln. Vol. (mL)	Iodine Adsorption (µg/g)	K_d (mL/g)
Dowex 1	9.19	7.49	0.100	100.1	1.70	227.0
Dowex-21K	9.19	7.52	0.100	100.0	1.67	221.9
Purolite PFA600 Resin	9.19	7.72	0.100	99.8	1.47	189.9
Resin Tech SIR-700	9.19	7.35	0.100	99.7	1.84	249.8
Resin Tech SIR-1200	9.19	7.63	0.101	101.1	1.56	203.9
Purolite A530E	9.19	7.56	0.100	99.5	1.63	215.0
Purolite A-532E	9.19	8.05	0.099	98.9	-	-
Calgon Filtrasorb 400	9.19	7.49	0.100	100.0	1.70	226.3
Carbon Resources 1240A	9.19	7.72	0.100	100.0	1.47	189.8
General Carbon GC20X50	9.19	7.51	0.100	100.0	1.68	223.1
Siemens AC1230AWC	9.19	7.91	0.100	100.0	-	-
Norit GAC830 M1871	9.19	7.55	0.100	100.0	1.64	216.6
Norit GCA830 M1917	9.19	8.24	0.100	100.0	-	-

Loading values ranged from 1.47 to 1.84 µg/g. K_d values ranged from 189.8 to 249.8 mL/g. Using a 15% instrument error, the difference between the initial and final iodine concentration for Purolite A-532E resin, Siemens AC1230AWC, and Norit GCA830 M1917 was not significant and no loading or K_d values were reported. As previously noted, Zhang et al. (2013) measured stable iodine in water samples from different wells on the Hanford Site, and values ranged from 11.7 to 84.6 µg/L. Iodine was found to exist as three species, iodide (0.4% to 10.8%), iodate (60.5% to 86.7%) and organo-iodine (12.3% to 28.7%). To determine if the various resin and carbon materials were removing iodine based on species, two sorption tests (C and D in Table 3.8) were proposed. For the first test (C in Table 3.8), 2 L of as-received source water was treated to convert iodine to iodate (C in Table 3.2) and sorption tests were conducted using the treated water. Results are shown in Table 4.8.

Table 4.8. Sorption Test Results Using Water Treated to Convert Iodine to Iodate

Material Tested	Iodine Initial Concentration (µg/L)	Iodine Final Concentration (µg/L)	Mass of Material-Dry (g)	Soln. Vol. (mL)	Iodine Adsorption (µg/g)	K_d (mL/g)
Dowex 1	8.41	7.99	0.100	99.8	-	-
Dowex-21K	8.41	8.68	0.100	99.8	-	-
Purolite PFA600	8.41	7.49	0.101	100.9	-	-
Resin Tech SIR-700	8.41	8.22	0.100	99.6	-	-
Resin Tech SIR-1200	8.41	7.72	0.100	100.3	-	-
Purolite A-530E	8.41	8.79	0.100	99.5	-	-
Purolite A-532E	8.41	8.34	0.101	100.6	-	-
Calgon Filtrasorb 400	8.41	7.35	0.100	100.0	-	-
Carbon Resources 1240A	8.41	8.2	0.100	100.0	-	-
General Carbon GC20X50	8.41	7.34	0.100	100.0	-	-
Siemens AC1230AWC	8.41	8.04	0.100	100.0	-	-
Norit GAC830 M1871	8.41	8.24	0.100	100.0	-	-
Norit GCA830 M1917	8.41	7.46	0.100	100.1	-	-

To determine if the total iodine concentration changed during treatment, samples of the source water before and after treatment were obtained and analyzed. The iodine concentration in the source water was 8.27 ± 0.04 µg/L before treatment and 8.41 ± 0.05 µg/L after. Thus, the concentration of iodine did not change during the oxidation treatment.

Loading and K_d values could not be calculated for any of the 13 materials tested because iodine concentrations measured in as-received and treated groundwater were within the analytical error of 15%. This indicates that little if any sorption of iodate occurred.

For the second sorption test (D in Table 3.8), 4 L of as-received source water was treated to convert iodine to iodide (D in Table 3.2). Sorption tests were conducted using seven resins, six carbon materials, and the reduced iodine water solution at ratio #6. The results are shown in Table 4.9.

Table 4.9. Sorption Test Results Using Water Treated to Convert Iodine to Iodide

Material	Iodine Initial Concentration (µg/L)	Iodine Final Concentration (µg/L)	Mass of Material-Dry (g)	Soln. Vol. (mL)	Iodine Adsorption (µg/g)	K_d (mL/g)
Dowex 1	7.88	3.38	0.099	99.20	4.50	1332.1
Dowex-21K	7.88	5.13	0.100	99.84	2.75	536.3
Purolite PFA600	7.88	3.47	0.100	99.66	4.41	1270.7
Resin Tech SIR-700	7.88	6.75	0.101	100.65	1.13	167.5
Resin Tech SIR-1200	7.88	4.00	0.100	100.35	3.88	970.2
Purolite A530E	7.88	2.85	0.100	100.16	5.03	1764.8
Purolite A-532E	7.88	1.98	0.101	100.59	5.90	2979.6
Calgon Filtrasorb 400	7.88	6.97	0.100	100.06	-	-
Carbon Resources	7.88	7.39	0.100	100.01	-	-
General Carbon GC20X50	7.88	7.40	0.100	100.06	-	-
Siemens AC1230AWC	7.88	7.66	0.100	100.01	-	-
Norit GAC830 M1871	7.88	7.12	0.100	100.07	-	-
Norit GCA830 M1917-	7.88	7.49	0.100	100.04	-	-

The resin loading values ranged from 1.13 to 5.90 µg/g and the K_d ranged from 167.5 to 2979.6 mL/g. The loading and K_d values for the carbon materials could not be reported because the iodine concentrations measured in groundwater before and after treatment were within the 15% analytical error.

Samples of the source water before and after treatment were obtained and analyzed. The total iodine concentration in the source water was 8.12 ± 0.08 µg/L before treatment and 7.88 ± 0.24 µg/L after.

The results of the sorption tests using untreated source water (Table 4.7), treated water to oxidize the iodine to iodate (Table 4.8), and the treated water to convert iodine to iodide (Table 4.9) are summarized in Table 4.10. The loading and sorption of iodine data in Table 4.10 clearly show that iodine speciation plays an important role in the sorption of iodine onto the resins. Oxidizing the iodine to iodate resulted in little if any iodine sorption onto the resins and carbon materials when compared to the as-received source water.

When the as-received source water was treated such that the iodine was oxidized to iodate and then reduced to iodide, the loading and K_d values increased for six of the seven resins. The largest loading and K_d values were observed in Purolite A-532E. It should be noted that only the Purolite A532E resin reduced the final iodine concentration to less than 2 µg/L in the source water when treated to convert iodine to iodide (Table 4.9). Loading did decrease for ResinTech SIR700. Since iodate is the dominant species in Hanford groundwater (60.5% to 86.7%), additional work should be conducted to determine the most effective methods of reducing iodine to iodide in order to effectively remove iodine within the 200W pump and treat system.

The loading and K_d values for Siemens AC1230AWC and Norit GAC830 M1917 could not be calculated from any sorption test or for any carbon materials that came into contact with the treated source water. It is not known what effect, if any, the treatment chemicals are having on the carbon materials. The effect of the chemicals on resins and carbon materials should be investigated in fiscal year (FY) 2015.

Table 4.10. Summary of Loading and Sorption Data for As-Received and Treated Waters

	As Received		Treated to Oxidize Iodine to Iodate		Treated to Reduce Iodine to Iodide	
Material	Iodine Adsorption (µg/g)	K_d (mL/g)	Iodine Adsorption (µg/g)	K_d (mL/g)	Iodine Adsorption (µg/g)	K_d (mL/g)
Dowex 1	1.70	227.0	-	-	4.50	1332.1
Dowex-21K	1.67	221.9	-	-	2.75	536.3
Purolite PFA600	1.47	189.9	-	-	4.41	1270.7
Resin Tech SIR-700	1.84	249.8	-	-	1.13	167.5
Resin Tech SIR-1200	1.56	203.9	-	-	3.88	970.2
Purolite A530E	1.63	215.0	-	-	5.03	1764.8
Purolite A-532E	-	-	-	-	5.90	2979.6
Calgon Filtrasorb 400	1.70	226.3	-	-	-	-
Carbon Resources	1.47	189.8	-	-	-	-
General Carbon GC20X50	1.68	223.1	-	-	-	-
Siemens AC1230AWC	-	-	-	-	-	-
Norit GAC830 M1871	1.64	216.6	-	-	-	-
Norit GCA830 M1917	-	-	-	-	-	-

5.0 Conclusions

Iodine sorption onto seven resins and six carbon materials was evaluated using water from well 299-W19-36 on the Hanford Site. These materials were tested using a range of solution-to-solid ratios. The results of these tests are as follows:

- The efficacy of the resin and GAC materials was less than predicted based on manufacturers' performance data. It is hypothesized that this is due to the differences in speciation previously determined for Hanford groundwater.
- The sorption of iodine is affected by the iodine species in the source water. Iodine loading on resins using source water ranged from 1.47 to 1.70 µg/g with the corresponding K_d values from 189.9 to 227.0 mL/g. The sorption values when the iodine is converted to iodide ranged from 2.75 to 5.90 µg/g with the corresponding K_d values from 536.3 to 2979.6 mL/g. It is recommended that methods to convert iodine to iodide be investigated in FY15.
- The chemicals used to convert iodine to iodate adversely affected the sorption of iodine onto the carbon materials. Using as-received source water, loading and K_d values ranged from 1.47 to 1.70 µg/g and 189.8 to 226.3 mL/g respectively. After treatment, loading and K_d values could not be calculated because there was little change between the initial and final iodine concentration. It is recommended the cause of the decrease in iodine sorption be investigated in FY15.
- In direct support of CH2M HILL Plateau Remediation Company, Pacific Northwest National Laboratory has evaluated samples from within the 200W pump and treat bioreactors. As part of this analysis, pictures taken within the bioreactor reveal a precipitate that based on physical properties and known aqueous chemistry, is hypothesized to be iron pyrite or chalcopyrite, which could affect iodine adsorption. It is recommended these materials be tested at different solution-to-solid ratios in FY15 to determine their effect on iodine sorption.

6.0 References

10 CFR 830, *Energy/Nuclear Safety Management.* Code of Federal Regulations.

ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications.* ASME International, New York, NY.

CAWSRP – Conducting Analytical Work in Support of Regulatory Programs. 2006. Pacific Northwest National Laboratory.

Councell TB, ER Landa, and DR Lovely. 1997. "Microbial Reduction of Iodate." *Water, Air, and Soil Pollution* 100:99‑106.

DOE Order 414.1D, *Quality Assurance*. U.S. Department of Energy, Washington, DC. Hanford

DOE/RL-96-68, *Hanford Analytical Services Quality Assurance Requirements Document*. U.S. Department of Energy, Richland Operations Office, Richland, WA.

EPA Method 1314, *Liquid-Solid Partitioning as a Function of Liquid-Solid Ratio For Constituents in Solid Materials Using an Up-Flow Percolation Column*, Draft. EPA SW-846, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

Korkisch J. 1988. *CRC Handbook of Ion Exchange Resin: Their Application to Inorganic Analytical Chemistry,* Volume VI. CRC Press, Boca Raton, Florida, pp. 315‑316.

Mattigod SV, EC Golovich, DM Wellman, EA Codova, and RM Smith. 2010. *Tc-99 Adsorption on Selected Activated Carbons-Batch Testing Results*. PNNL-20136, Pacific Northwest National Laboratory, Richland, Washington.

Santschi PH, C Xu, S Zhang, Y Ho, HP Li, KA Schwehr, and DI Kaplin. 2012. *Laboratory Report on Iodine (129I and 127I) Speciation, Transformation and Mobility in Hanford Groundwater, Suspended Particles and Sediments*. SRNL-STI-2012-00592, Savannah River National Laboratory, Aiken, South Carolina.

Zhang S, C Xu, D Creeley, Y Ho, H Li, R Grandbois, KA Schwehr, DI Kaplin, CM Yeager, DM Wellman, and PH Santschi. 2013. "Iodine-129 and Iodine-127 Speciation in Groundwater at the Hanford Site, US.: Iodate Incorporation into Calcite." *Environmental Science & Technology* 47:9635‑9642.

Appendix A

Analytical Methods

Appendix A

Analytical Methods

A.1 Iodine Analysis

Iodine analyses of the groundwater/test solution were performed using an inductively coupled plasma mass spectrometer (ICP-MS) following procedure PNNL-AGG-415,[1] which is similar to EPA SW-846, Method 6020A (EPA 1996). High-purity 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. Instrument detection limits for iodine on the ICP-MS are 0.5 µg/L.

A.2 References

EPA. 1996. "Method 6020A, Inductively Coupled Plasma – Mass Spectrometry," Rev. 1. In *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. EPA SW-846, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

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[1] Clayton ET. 2008. *Inductively Coupled Plasma Mass Spectrophotometry (ICP-MS)*. PNNL-AGG-415, unpublished PNNL Technical Procedure, Pacific Northwest National Laboratory, Richland, Washington.

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