AN EVALUATION OF AN ION-EXCHANGE METHOD FOR THE REMOVAL OF TECHNETIUM-99 FROM GROUNDWATER

By

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The members of the Committee appointed to examine the thesis of WANDA SUE ELLIOTT find it satisfactory and recommend that it be accepted.

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Abstract

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This thesis presents and interprets the results of a treatability test for removing technetium-99 (^{99}Tc) from groundwater extracted by the pump-and-treat system at the 200-ZP-1 Operable Unit (OU) at the Hanford Site in Benton County, Washington. The primary risk driving contaminants within the OU included carbon tetrachloride and ^{99}Tc that resulted from disposal activities associated with nuclear fuel processing. Ten extraction wells and five injection wells removed carbon tetrachloride from the groundwater. Groundwater from two of extraction wells began to show increasing concentrations of ^{99}Tc shortly after they were put online in 2005.

A treatability test was conducted to evaluate the efficiency of ion exchange at removing ^{99}Tc from groundwater. The test involved the installation of Purolite® A-530E ion exchange resin columns on the discharge lines of two of the extraction wells. Groundwater samples were collected from sampling ports twice a week and analyzed for ^{99}Tc and selected anions. Test results showed that the ion exchange resin was effective at removing ^{99}Tc from groundwater to below detection limits even in the presence of competing anions (e.g., nitrate and sulfate) at concentrations 5 to 6 orders of magnitude higher than ^{99}Tc. Sampling results showed that nitrate and sulfate concentrations in the influent and the effluent remained nominally equal and static over the course of the sampling efforts indicating that competition between nitrate and sulfate for ion exchange sites was very low compared to that of ^{99}Tc. Overall, the Purolite® A-530E ion exchange resin is an effective remedial method for ^{99}Tc removal in groundwater.

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PREFACE

Fluor Hanford Inc., (FH) was the prime contractor responsible for the implementation of this treatability test. A number of individual subcontractors were used to implement various components of the test which included: the design and implementation of the treatability test plan in the field, groundwater sample collection, and analyses on the groundwater samples. The author's role was to summarize and interpret analytical data from the treatability test, as well as provide supporting calculations. Analytical values presented are in the units (e.g., pCi/L) that were collected and recorded by field personnel, and were transmitted into metric where applicable.

LIST OF ACRONYMS AND ABBREVIATIONS

^{99}Tc	technetium-99
beq	bequerel
C_{Eff}	concentration of the effluent
C_{In}	concentration of the influent
CRDL	contract required detection limit
USEPA	U.S. Environmental Protection Agency
ETF	Effluent Treatment Facility
FH	Fluor Hanford, Inc.
ft^3	cubic feet
GAC	granular activated carbon
gal	gallon
gpm	gallons per minute
HEIS	Hanford Environmental Information System
ICP/MS	inductively coupled plasma/mass spectrometry
in	inches
L	liter
LERF	Liquid Effluent Treatment Facility
LSC	liquid scintillation counting
M	moles
MCL	maximum contaminant level
mg	milligram
OU	operable unit
pCi	picocurie
PNNL	Pacific Northwest National Laboratory
psi	pounds per square inch
SAI	sampling and analysis instruction
TcO_4^-	pertechnetate anion
WMA	Waste Management Area
WSCF	Waste Sampling and Characterization Facility

1.0 INTRODUCTION

1.1 BACKGROUND

The Hanford Site is a federal facility located in the southeastern portion of Washington State. It was designed to manufacture nuclear materials for the purpose of the nation's defense. From the 1940s to the 1980s, liquid wastes from nuclear material processing (e.g., solvents and fission products) were disposed in underground storage tanks and waste sites known as cribs and trenches [1]. Some of the contaminants (e.g., technetium-99 [^{99}Tc]) migrated through the vadose zone and contaminated the groundwater underlying the waste sites. The depth to groundwater is 67 to 76 m (220 to 250 ft) below ground surface in the area underlying the waste sites [2].

1.1.1 200-ZP-1 Pump-and Treat System

The 200-ZP-1 Groundwater Operable Unit (OU) is one of two groundwater OUs located within the 200 West groundwater aggregate area of the Hanford Site (Figure 1). The 200 West Area is in the middle of Hanford's chemical-separation and disposal areas. The primary risk-driving contaminants associated with the OU include carbon tetrachloride and ^{99}Tc that resulted from disposal activities associated with nuclear fuel processing. A groundwater pump-and-treat system for this OU was implemented in 1995 to control a carbon tetrachloride plume [2]. Ten extraction wells and five injection wells removed carbon tetrachloride from the groundwater. The system processed the groundwater through an evaporative treatment (i.e., air stripping) that volatilized the carbon tetrachloride and subsequently removed it by adsorption onto granular activated carbon (GAC) [2]. The treated groundwater was then returned to the aquifer via injection wells. Technetium-99 was not removed by this treatment system, but remained in the groundwater and was subsequently re-injected into the aquifer.

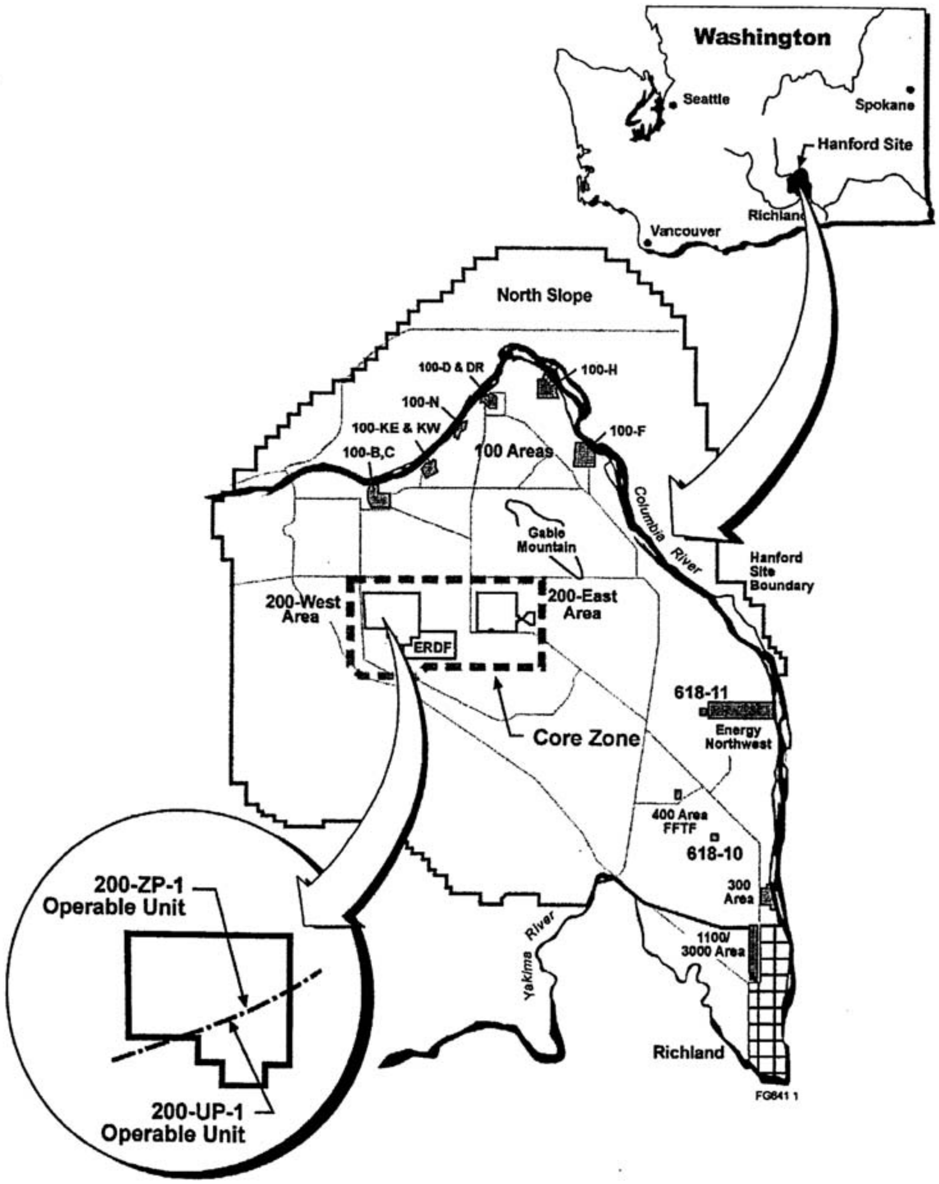

Figure 1. Location of the 200-ZP-1 Operable Unit at the Hanford Site.

Groundwater from two installed extraction wells (i.e., 299-W15-44 and 299-W15-765) began to show increasing concentrations of ^{99}Tc shortly after they were put online in 2005 [2]. The 200-ZP-1 pump-and-treat system was not designed to remove ^{99}Tc. If the groundwater continued to remain untreated for ^{99}Tc there was concern that the water re-injected into the aquifer could exceed the maximum contaminant level (MCL) of 900 pCi/L.

Multiple treatment technologies were reviewed for the remediation of ^{99}Tc from groundwater. Of these treatment technologies, only ion exchange was determined to be selective for ^{99}Tc in the presence of competing ions. The resin selected for this treatability test is commercially available from Purolite[1] under the designation of "A-530E." In bench and field tests, this resin has been effective in the selective removal of ^{99}Tc from groundwater in the presence of ions at higher concentrations than the target anion [3].

A treatability test was implemented to assess the ^{99}Tc removal capacity of the Purolite® A-530E. The scope of this thesis was to summarize and interpret data from the treatability test, as well as provide supporting calculations.

1.2 TECHNETIUM-99 PROPERTIES

Technetium-99 is a beta emitting radionuclide that has a half life of 214,000 years. Technetium-99 exists in groundwater at the Hanford Site in a fully oxidized form (+VII), as the pertechnetate anion (TcO_4^-) [4]. Pertechnetate is chemically stable in groundwater over wide ranges of pH [5]. Pertechnetate is highly soluble and exhibits poor adsorption to soil with low organic content [4]. The solubility of ^{99}Tc depends on the chemical state and the surrounding

[1] Purolite is the registered trademark of the Purolite Company of Bala Cynwood, Pennsylvania.

environment. In aqueous solutions, the +IV and +VII oxidation states predominate. However, the lower +IV (TcO_2) oxidation state is prevalent in areas that are absent of oxygen (reducing conditions) and is converted to the +VII state (pertechnetate) in the presence of oxygen [6]. When sediments containing ^{99}Tc are hydrated, it is displaced from sediments, allowing downward migration in the vadose zone. If enough aqueous solution contacts the sediment the ^{99}Tc becomes mobile and enters the groundwater below [7]. The high mobility in groundwater coupled with a long half life make pertechnetate an environmental concern where it is found.

2.0 TEST OBJECTIVES

The objectives of this thesis are shown below:

- Verify that the resin adequately removes ^{99}Tc to below the drinking water MCL from 200-ZP-1 groundwater.
- Determine the resin usage rate, that is, verify the vendor-provided data.
- Verify that the resin is selective for ^{99}Tc and does not remove other anions (e.g., nitrate and sulfate) present in 200-ZP-1 groundwater at much higher concentrations.

3.0 HYPOTHESIS

The hypothesis of this thesis is that the Purolite® A-530E ion exchange resin will remove ^{99}Tc from 200-ZP-1 groundwater to below the maximum contaminant level (MCL) of 900 pCi/L.

4.0 METHODS AND MATERIALS: TREATABILITY TEST APPROACH AND IMPLEMENTATION

Since ^{99}Tc was only present at concentrations of concern in two (299-W15-44 and 299-W15-765) of the ten 200-ZP-1 extraction wells, it was decided by FH to minimize the size and cost of a ^{99}Tc pre-treatment system by employing the treatment at the impacted wells rather than treating the water from all ten extraction wells at the main treatment building. This decision was also made to avoid space constraints within the treatment system building, to take advantage of existing piping at the well heads, and to minimize the radiological exposure to workers.

4.1 DETERMINATION OF TESTING PARAMETERS

Concentrations of the target anion ^{99}Tc and competing anions (e.g., nitrate and sulfate) in the groundwater of wells 299-W15-44 and 299-W15-765 were used by the manufacturer (Purolite) for calculating minimum bed volumes that could be processed. A bed volume is defined as the volume of resin in one column that the groundwater will contact. The resin usage rates are the minimum number of bed volumes that the column can process before 50% breakthrough will occur. The 50% breakthrough is defined as the point at which the effluent concentration equals one-half of the influent concentration:

$$\frac{Concentration\,of\;Effluent}{Concentration\,of\;Influent} = 0.50 \qquad \text{(Eq. 1)}$$

The baseline parameters and concentrations of each anion that were used by Purolite® to determine column sizing are presented in Table 1 for both wells. The bed volume calculations are presented in Appendix A. Descriptions of the testing conditions implemented at extraction wells 299-W15-44 and 299-W15-765 are provided in the following subsections.

Table 1. Testing Parameters and Analyte Concentrations Used for Column Sizing

Well #	**Anion**	**Concentrations**	**Molarity[a]**	**Resin Volume**	**Groundwater Volume to Process[b]**	**Bed Volumes[c]**	**Estimated Minimum Days to Breakthrough[d]**
299-W15-44	Technetium-99	<5,000 pCi/L	<3.0 X 10^{-9}	49.14 L (13 gal)	3,498,170 L (923,000 gal)	71,000	86
	Nitrate	110 mg/L	1.77 X 10^{-3}				
	Sulfate	<50 mg/L	<5.2 X 10^{-4}				
299-W15-765	Technetium-99	<5,000 pCi/L	<3.0 X 10^{-9}	415.8 L (110 gal)	8,338,000 L (2,200,000 gal)	20,000	73
	Nitrate	400 mg/L	6.5 X 10^{-3}				
	Sulfate	<50 mg/L	<5.2 X 10^{-4}				

[a] Molecular concentration calculated into Moles/L.
[b] Groundwater volume to process is the total volume of groundwater that needs to flow through the system to reach the bed volume endpoints.
[c] The number of bed volumes until breakthrough are calculated from the total flow in gallons that needs to pass through the system divided by the resin bed volume.
[d] Estimated days to breakthrough.

4.2 INSTRUMENTATION DESIGN

The test systems were manufactured with simplicity in mind using commercial off-the-shelf materials (e.g., polyvinyl chloride materials, hand valves). The ion exchange columns were designed as short-term treatability systems to meet rapid scheduling and low-cost requirements.

The ion exchange test columns were piped in at the well heads. The systems were installed in a manner to allow continued flow of groundwater from the well to the air-stripper treatment system in the event that the testing equipment needed to be isolated and repaired. Containment skids were installed for both columns to capture minor leaks and drips.

The treatment train in both columns allowed the groundwater to enter the system, pass through initial filters to remove any particulate matter in the groundwater. Water was then passed through a digital flow meter and flow totalizer to monitor the rate of flow and total volume of groundwater that passes through the system. The water entered the top of the ion exchange columns and flowed downward through the ion exchange resin, out through collectors in the bottom of the column, and back up through riser tubes in the center. The water then exited the top of the columns. Once the water exited the resin column it flowed through another particulate filter and then out to the main pump-and-treat system where it joined with groundwater from the other extraction wells. Instrument design diagrams for both columns are shown in Appendix B.

One pressure-indicating gauge and three differential-pressure gauges were installed within the testing equipment to monitor the system and identify possible issues (e.g., plugging of the filter or the ion exchange resin bed). A temperature gauge was installed to monitor the groundwater temperature. Sample ports were installed to allow for the collection of influent and effluent samples from the resin columns.

4.3 COLUMN SETUP

The two treatability test systems were designed and built by MSE Technology Applications, Inc.[2]. The units were intended to discern the true loading capacity of ^{99}Tc (in the presence of competing ions) utilizing the existing flow from the groundwater wells. The following subsections are derived from engineering field logs collected by contracted personnel during column setup.

The test systems were delivered to the site on April 12, 2007 and setup on April 13, 2007. A detailed inspection of the test columns was performed to make sure there was no damage to the column and that any debris or foreign materials were removed. The systems were attached to the well head and the in/out heads of the columns were removed. Approximately 1/3 of the column heights were filled with water from a water truck that was brought to the well locations. Once the columns were filled with water, the resin was transferred to the top of the open columns using plastic containers.

Prior to flowing well water through the ion exchange system, a classification procedure, or back-flow of fresh water is necessary to expand the resin, increase resin void volume, and bring resin fines to the top of the bed where they can be flushed out. The water from a truck was attached to the column in/out head. Water was allowed to flow through the system until a portion of the beads floated out of the top of the column and clogged the outlet filters. The operation was stopped, and the in/out lines to the column were reversed and the water then

[2] MSE Technology Applications, Inc., of Butte Montana.

flushed the system in a top-down fashion to clear the lines of resin. The outlet filters were removed, cleared of resin, replaced, and put back into service. The tests systems were put online for an in-process leak check. Once flow was established, the systems were checked for leaks and put into bypass mode until the sampling schedule and personnel could be established. Both test systems began operation on April 26, 2007.

4.3.1 Well 299-W15-44 Column Setup and Commissioning

It was determined by the manufacturer that a flow rate of 0.0005 m^3s^{-1} (8 gpm), and a resin bed volume of 49.14 L (13.0 gallons), would achieve 50% breakthrough after processing 71,000 resin bed volumes of groundwater. A 25.40 cm (10 in.) diameter, fiberglass-reinforced plastic test vessel was used for the test column for well 299-W15-44. The column had a resin bed depth of 95.52 cm (38 in.), and a height of approximately 137.16 cm (54 in.) to accommodate the volume of resin.

4.3.2 Well 299-W15-765 Column Setup and Commissioning

It was determined by the manufacturer that a flow rate of 0.0019 m^3s^{-1} (30 gpm) from this well and a resin bed volume of 415.8 L (110.0 gal) would achieve 50% breakthrough after processing 20,000 resin bed volumes of groundwater. A 76.2 cm (30 in.) diameter, fiberglass-reinforced plastic test vessel was used. The column had a resin bed depth of 91.44 cm (36 in.), and a height of approximately 182.88 cm (72 in.) to accommodate the volume of resin.

4.3.2.1 Column Failure

On May 25, 2007 the in/out head piping failed on well 299-W15-765, the system shut down. The containment skid holding the column had collapsed into the substrate approximately 1.27 cm (1.5 in.), the same side of the piping failure on the column head. The stress of the collapse led the in/out head pipe to rupture at the threaded joint that attached to the fiberglass column.

Approximately 378 to 567 L (100 to 150 gal) of water leaked from the column when the piping failed. Prior to any stabilization activities, the substrate surrounding the column foundation was completely removed and transferred to 207.0 L (55 gal) drums for disposal. All loose or disturbed soil was removed. After the removal of substrate, the excavated area was replaced with backfill and then compacted.

4.3.2.2 New Column Setup and Commissioning

After the construction and compaction activities were complete, it was determined by FH the column would be fully replaced and moved onto the same containment skid as the piping apparatus. Flexible hoses were installed on the inlet and outlet lines, with piping supports added to ensure proper stability with added flexibility.

On July 19, 2007 the system was loaded again with 415.8 L (110.0 gal) of resin, which gave a resin depth of 91.44 cm (36 in.). Classification was not performed. The system was put into service on July 19, 2007.

4.4 OPERATION AND MAINTENANCE PROCEDURES

Normal operation and maintenance procedures included daily examination of the groundwater extraction well and associated piping. As part of this daily routine, a contracted operator examined the test systems and recorded relevant operational data (Table 2) during the testing period. An operation log was completed once each day for each well throughout the duration of the test.

Table 2. Operational Data Collected Daily at Both Wells

Operational Data	Log	
Time of Reading	AM/PM	
System on Line	Yes/No	
Inlet Filter Differential Pressure	PDI-1	
System Temperature	TI (°F)	
System Flow	FI-1(gpm)	
Totalized Flow in gallons	FI-2	
System Pressure	PI (psi)	
Resin Column Differential Pressure	PDI-2	
Outlet Filter Differential Pressure	PDI-3	
Leak Inspection (Yes response shall include note in "Comments" indicating condition found and the action taken)	Yes/No	
Liquid in Secondary Containment (Yes response shall include note in "Comments" indicating source of liquid and the action taken)	Yes/No	
Water Sample (s) Scheduled for Today	Yes/No	
Comments:		

PDI= pressure differential indicator gauge.
TI= temperature indicator in degrees fahrenheit (°F).
FI= flow indicator
gpm= gallons per minute.
PI= Pressure indicator.
psi= pounds per square inch.

4.5 SAMPLING AND ANALYSIS SCHEDULE

This section provides the background on the sampling and analysis that was conducted throughout the ion exchange treatability test. A list of the sample collection frequency, and the parameters used for laboratory analysis is provided in Table 3. This section refers to the sampling and analysis instruction (SAI), which is presented in Appendix D of the *Treatability Test Plan for Using Purolite Resin to Remove Technetium-99 from 200-ZP-1 Groundwater* [8].

4.6 CONSTITUENTS FOR MONITORING

The primary constituents that were monitored related to this study include ^{99}Tc, nitrate, sulfate, and chloride (Table 3). Secondary constituents and water quality parameters that were collected for design purposes were: carbon tetrachloride, phosphate, alkalinity, and pH. The secondary constituents and parameters are not presented here.

4.7 SAMPLING LOCATIONS AND FREQUENCY

Groundwater samples were collected from sampling ports placed in line with the extraction water from wells 299-W15-44 and 299-W15-765. Samples were taken from the influents and effluents of each well on Mondays and Thursdays (when accessible) and analyzed for the parameters specified in Table 3.

Table 3. Sampling Parameters and Frequency

	Anions			Technetium-99[a]
	Nitrate	Sulfate	Chloride	
Baseline				
299-W15-44	X	X	X	X
299-W15-765	X	X	X	X
299-W15-44				
Influent (two times per week)	X			X
Effluent (two times per week)	X			X
Influent (weekly)		X	X	
Effluent (weekly)		X	X	
A-530E resin post-study samples[b]	X	X	X	X
299-W15-765				
Influent (two times per week)	X			X
Effluent (two times per week)	X			X
Influent (weekly)		X	X	
Effluent (weekly)		X	X	
A-530E resin post-study samples[b]	X	X	X	X

[a] A set of samples consisting of an influent and an effluent were collected twice each week (typically on Monday and Thursday). Both sets of samples were analyzed by ICP/MS screening (quick turn-around). One quarter of the influent and effluent samples were analyzed by the fixed lab using LSC.

[b] Resin will need to be sampled for waste-designation purposes at end of test.

ICP/MS= inductively coupled plasma mass spectrometry

LSC = liquid scintillation counting.

4.8 SAMPLING PROCEDURES AND DATA ACQUISITION

The following subsections present the procedures and requirements for sampling methods, analytical methods, and field and laboratory quality control (QC). The requirements for sampling and analysis, instrument calibration and maintenance, and data management are also addressed in [8].

4.9 ANALYTICAL METHODS

The procedures implemented in the field and the laboratory were conducted in accordance with those outlined in the SAI [8]. Analytical parameters and methods are listed in Table 4.

Table 4. Analytical Performance Requirements

Constituents/Parameters		Survey or Analytical Method[a]	CRDL[b]	Precision Required	Accuracy Required
Nonradiological Constituents					
Non-metals	Nitrate	EPA 300.0	75 µg/L	[c]	[c]
	Sulfate	EPA 300.0	500 µg/L	[c]	[c]
	Chloride	EPA 300.0	200 µg/L	[c]	[c]
Radiological Constituents					
Beta emitters	^{99}Tc	Liquid scintillation	20 pCi/L	±30%	70-130%
	^{99}Tc	EPA 6020 ICP/MS[d]	100 pCi/L	±30%	70-130%

[a] Analytical method selection is based on available methods by laboratories currently contracted to the Hanford Site. Equivalent methods may be substituted in future sampling and analysis instructions or other documents.
[b] Typical CRDL or minimum detectable concentrations are based on current Hanford laboratory contracts.
[c] Precision and accuracy in accordance with cited procedure.
[d] ICP/MS analytical method was used for field screening (quick turnaround).
CRDL= contract-required detection limit
ICP/MS = inductively coupled plasma mass spectrometry

4.10 QUALITY CONTROL REQUIREMENTS

Table 5 lists the field QC requirements for sampling.

Table 5. Field Quality Control Requirements

Sample Type	Frequency	Purpose
Duplicate	5% (1 sample in 20)	To check the precision of the laboratory analyses.
Field Blanks	One per trip	To check the effectiveness of the field sampling.

4.11 DATA MANAGEMENT

Analytical results from this study were stored in the Hanford Environmental Information System (HEIS) database. The database houses all of the environmental data generated on the Hanford Site. All reports and supporting analytical data packages were transmitted either in hard copy or electronic formats. The analytical data were manually transferred into spreadsheets. All of the analytical data was subjected to technical quality assurance review before submittal or inclusion.

5.0 RESULTS AND DISCUSSION

The following subsections present the results from the ion exchange treatability test up to the point that the test objectives presented in Section 2.0 and hypothesis were fulfilled. The test was not complete at the time this thesis was written, and continued until the 50% breakthrough mark has been fulfilled.

5.1 TECHNETIUM-99 REMOVAL

5.1.1 Technetium-99 Removal at Extraction Well 299-W15-44

The system at extraction well 299-W15-44 ran for a total of 92 operational days to meet the manufacturer's suggested 71,000 treatment bed volumes. The operational days were not continuous days. From April 26th to September 13th the system was down 49 out of 141 days. Eighteen of the days the system was offline due to either 1) the 200-ZP-1 main treatment facility being offline or 2) water levels in the well were too low to support pumping. From May 25th to June 26th the system was offline to evaluate the possibility of a failure similar to what occurred to column 299-W15-765. After the addition of support beams to the testing apparatus the system was placed back online.

Figure 2 shows concentrations present in both the influent and effluent for all sampling dates. The levels of ^{99}Tc in the effluent are below the MCL of 900 pCi/L. The effluent concentrations were nominally non-detects in the effluent throughout the duration of the test. Note that the break in time between May and July for column modifications is denoted in Figure 2 as "Break – System Modifications."

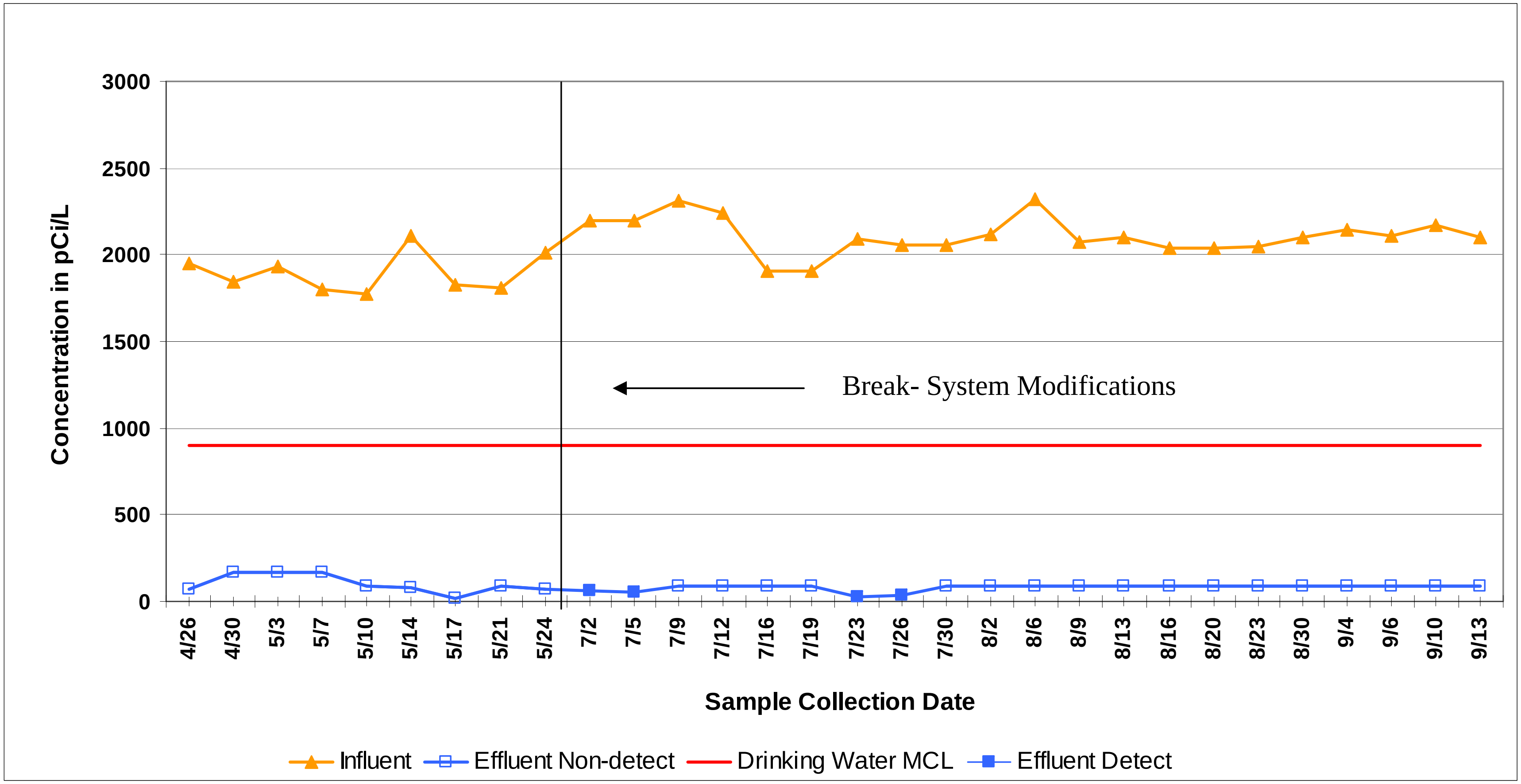

Figure 2. Techetium-99 data from extraction well 299-W15-44.

5.1.2 Technetium-99 Removal at Extraction Well 299-W15-765

The first system at extraction well 299-W15-765 ran a total of 31 operational days before the rupture occurred shutting it down while a new system was set up. Results from the first run will not be presented here due to the system failure and subsequent total system replacement, except where the data helps elucidate other test results.

The second column ran a total of 67 operational days to meet the manufacturer's suggested 20,000 treatment bed volumes. The operational days were not continuous days. From July 23rd to September 27th the system was down 3 out of 70 operational days due to the offline conditions at the main treatment facility.

Figure 3 shows concentrations present in both the influent and effluent for all sampling dates. The data show that the ^{99}Tc in the effluent of this column are below the MCL of 900 pCi/L. The effluent concentrations were nominally non-detects throughout the duration of the test.

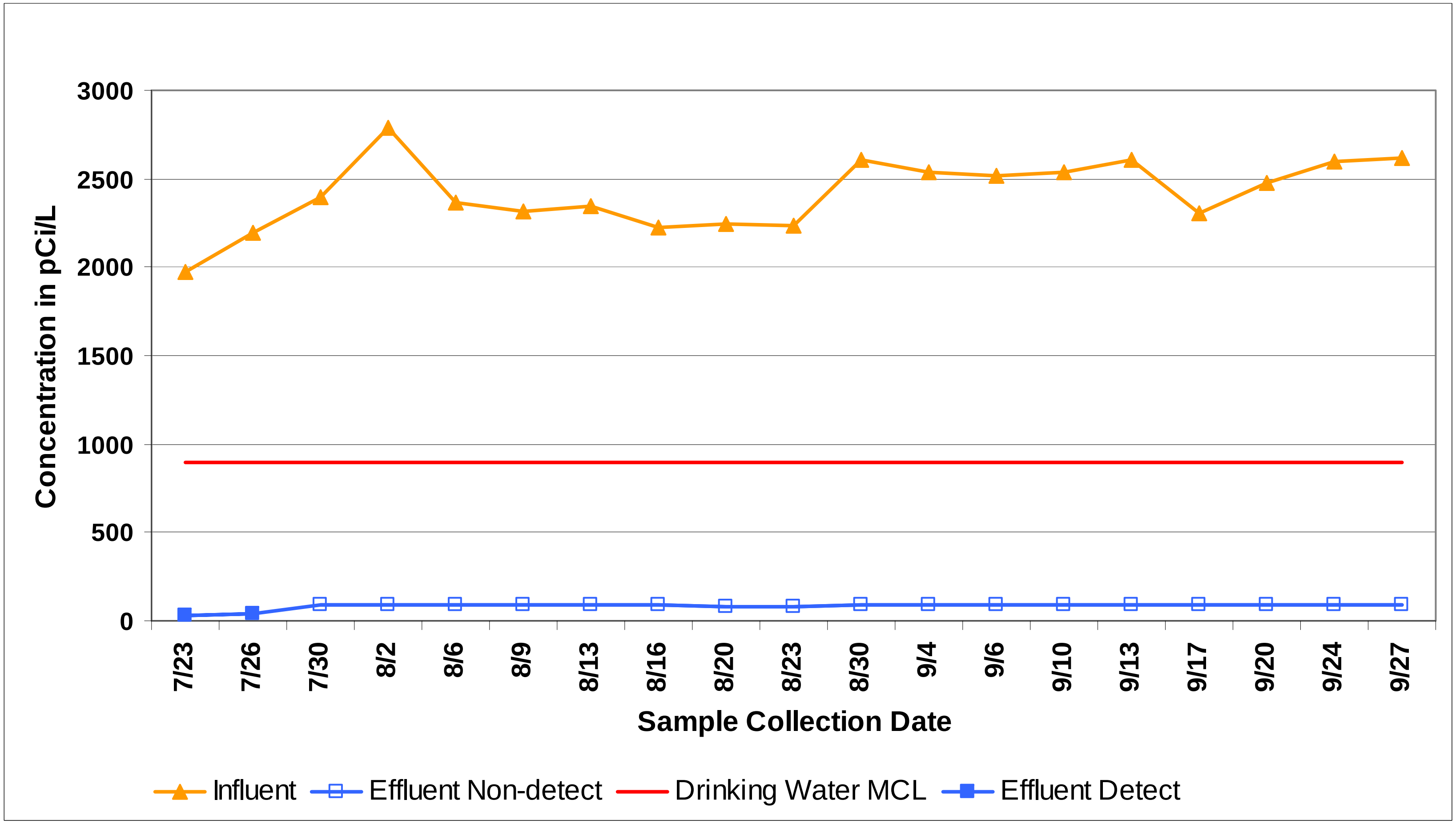

Figure 3. Technetium-99 data from extraction well 299-W-15-765.

5.2 RESIN USAGE RATE

Both columns surpassed the manufacturer's suggested resin usage rates that indicated the minimum number of days that the columns would run before the 50% breakthrough occurred. The 50% breakthrough endpoint was not achieved in the timeframe of this thesis.

As shown in the preceding sections, ^{99}Tc was removed from the groundwater to below detection limits. The mass of ^{99}Tc removed was calculated using the average influent values and the number of gallons that were treated (See Appendix A). Table 6 presents the amount of ^{99}Tc, in grams, and curies that was bound in both columns. The assumption was that all of the ^{99}Tc entering the column was bound, and therefore the average influent values were used to calculate the amount of ^{99}Tc bound in both columns.

Table 6. Amount of Technetium-99 Bound During Study

Well #	Average Influent Concentration	Volume of Groundwater Treated	Amount of Technetium-99 Bound[a]	
299-W15-44	2,050 pCi/L	3,549,864 L (937,164 gal)	0.43 g	0.007 Ci
299-W15-765	2,420 pCi/L	8,745,894 L (2,308916 gal)	1.25 g	0.02 Ci

[a] The values shown are the total ^{99}Tc that was bound in each column in grams and curies.

5.2.1 Resin Usage Rate at Extraction Wells

The system installed on extraction well 299-W15-44 contained a volume of 49.14 L (13.0 gal) of resin. The system operated at an average flow of 0.00046 m^3s^{-1} (7.3 gpm) and treated 3,549,864 L (937,164 gal) of groundwater, thus reaching the minimum 71,000 bed volumes in approximately 92 days. Table 7 presents the final operational parameters for the column installed on extraction well 299-W15-44.

The system installed on extraction well 299-W15-765 contained a volume of 415.8 L (110.0 gal) of resin. The system operated at an average flow of 0.0014 m^3s^{-1} (22.3 gpm) and treated 8,745,894 L (2,308,916 gal) of groundwater, thus reaching the minimum 20,000 bed volumes in approximately 67 days. Table 7 presents the final operational parameters for the column installed on extraction well 299-W15-765.

Table 7. Final Operational Parameters for Wells 299-W15-44 and 299-W15-765

Well #	Resin Bed Volume[a]	Number of Operational Days[b]	Average Flow Rate[c]	Total Gallons Processed[d]	Bed Volumes[e]
299-W15-44	49.14 L (13.0 gal)	92	0.0014 m^3s^{-1} (7.3 gpm)	3,549,864 L (937,164 gal)	72,090
299-W15-765	415.8 L (110.0 gal)	67	0.00046 m^3s^{-1} (22.3 gpm)	8,745,894 L (2,308,916 gal)	20,990

[a] Resin bed volumes are the total reactive volume of media present in each column.
[b] Number of operational days are the days the system was actually online.
[c] Flow rates are in gallons-per-minute and cubic-meters-per-second.
[d] The total gallons and liters that flowed through the columns are presented.
[e] The number of bed volumes that passed through the system. Bed volumes are calculated from the total flow in gallons that needed to pass through the system divided by the resin bed volume.

5.3 RESIN SELECTIVITY FOR TECHNETIUM-99 OVER COMPETING ANIONS

The average influent concentrations of anions in the groundwater of both wells are presented in Table 8. The molarity values shown in Table 8 are derived from calculations presented in Appendix A.

Table 8. Anion Groundwater Concentrations

Well #	Anion	Average Influent Concentrations[a]	Molarity[b]
299-W15-44	Technetium-99	2,050 ± 133.70 pCi/L	1.22×10^{-9}
	Nitrate	143.70 ± 2.69 mg/L	2.32×10^{-3}
	Sulfate	51.24 ± 1.28 mg/L	5.33×10^{-4}
	Chloride	26.25 ± 0.77 mg/L	7.40×10^{-4}
299-W15-765	Technetium-99	2,420 ± 192.79 pCi/L	1.44×10^{-9}
	Nitrate	414.63 ± 10.34 mg/L	6.69×10^{-3}
	Sulfate	48.97 ± 2.73 mg/L	5.10×10^{-4}
	Chloride	21.59 ± 1.27 mg/L	6.09×10^{-4}

[a] Average influent concentrations are shown with ± one standard deviation.
[b] Concentrations are shown in Moles/L.

5.4 ANION CONCENTRATIONS

The primary anions of concern in this study are nitrate (NO_3^-), sulfate (SO_4^{2-}), and pertechnetate (TcO_4^-), with chloride (Cl^-) a secondary concern. The averages and standard deviations for the influent and effluent anion concentrations in the groundwater of both columns are presented below in Table 9. The anion exchange resin utilized in the treatability tests was generated with chloride as the fixed anion embedded in the matrices. Therefore, it was expected that the chloride concentrations in the effluents would consistently be higher than the influents as the chloride was exchanged for the anions in solution.

Table 9. Average Influent and Effluent Concentrations for Both Columns

Well #	Analyte	Average Influent Concentrations[a]	Units[b]	Average Effluent Concentrations[a]	Units[b]
299-W-15-44	Technetium-99	2,050 ± 133.70	pCi/L	92.3 ± 27.97	pCi/L
	Nitrate	143.70 ± 2.69	mg/L	143.74 ± 2.62	mg/L
	Sulfate	51.24 ± 1.28	mg/L	51.71 ± 1.33	mg/L
	Chloride	26.25 ± 0.77	mg/L	29.35 ± 14.43	mg/L
299-W15-765	Technetium-99	2,420 ± 192.79	pCi/L	85.6 ± 0.29	pCi/L
	Nitrate	414.63 ± 10.34	mg/L	415.39 ± 11.42	mg/L
	Sulfate	48.97 ± 2.73	mg/L	49.71 ± 1.89	mg/L
	Chloride	21.59 ± 1.27	mg/L	21.64 ± 1.05	mg/L

[a] Average concentrations are shown with ± one standard deviation.
[b] Units shown are either in pCi/L for radionuclides, or mg/L for non-radionuclides.

5.4.1 Nitrate, Sulfate, and Chloride Concentrations in Extraction Well 299-W15-44

The first sampling event of the influent and effluent was conducted three hours after the system was operational. Figure 4 shows an initial release of chloride from the resin column on 299-W15-44, then a return to influent concentrations. When the chloride effluent data are compared to the nitrate effluent results (Figure 4) for the same sampling event, it appears that nitrate was originally taken up and chloride was released. The quick return of nitrate and chloride to that of the influent in subsequent sampling leads to the understanding that the nitrate within the first few hours of contact with the resin became saturated, and reached equilibrium.

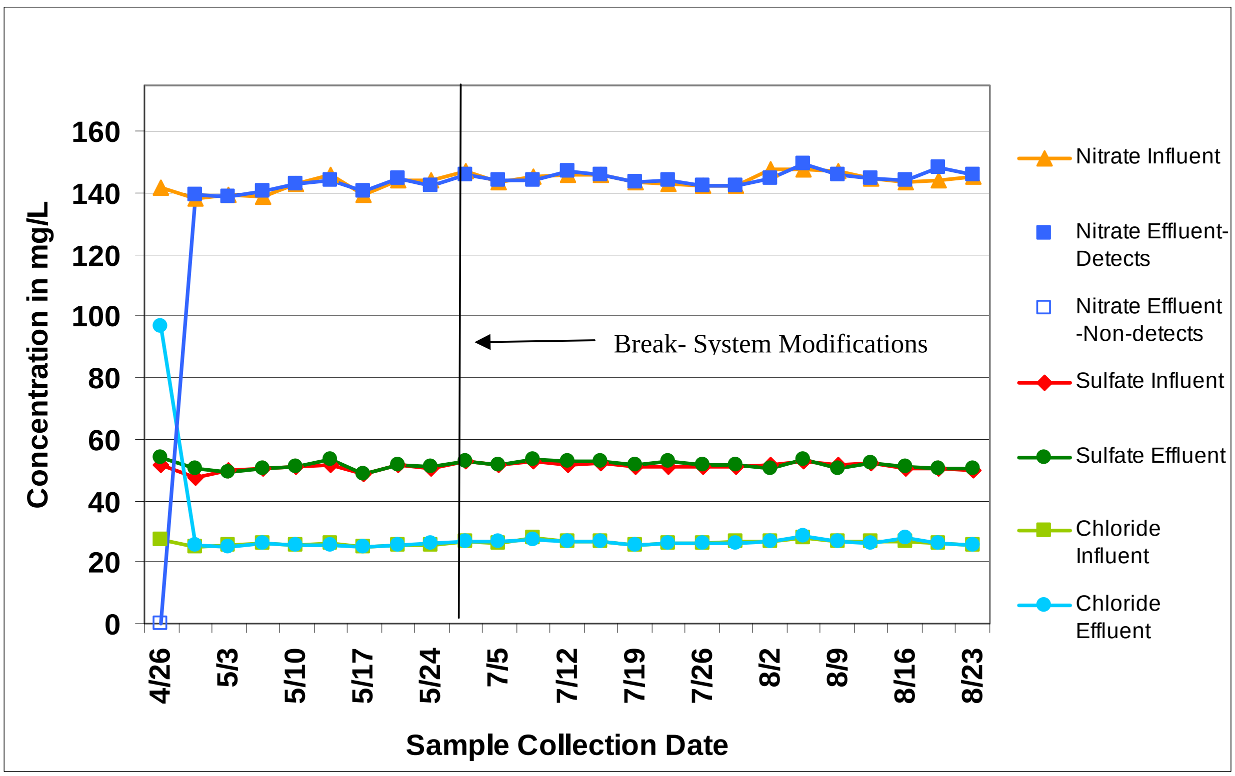

Figure 4. Competing anion data from extraction well 299-W15-44.

5.4.2 Nitrate, Sulfate, and Chloride Concentrations in Extraction Well 299-W15-765

The first sampling event of the influent and effluent was conducted four days after the system was operational. Results presented in Figure 5 for all three constituents indicate that the influents and effluents remained static throughout the sampling period. The same phenomena noted for chloride and nitrate in well 299-W15-44 are not noted for the system on 299-W15-765 (Figure 5) due to a delay in the first sampling event. However, the first resin column on well 299-W15-765 that ruptured did exhibit the same nitrate/chloride phenomenon in the first sampling event. The first sampling event on the first column was conducted within three hours the system was operational. Had the first sampling event on the second column been performed within the first few hours of operation, it is presumed that the same phenomenon would have been captured.

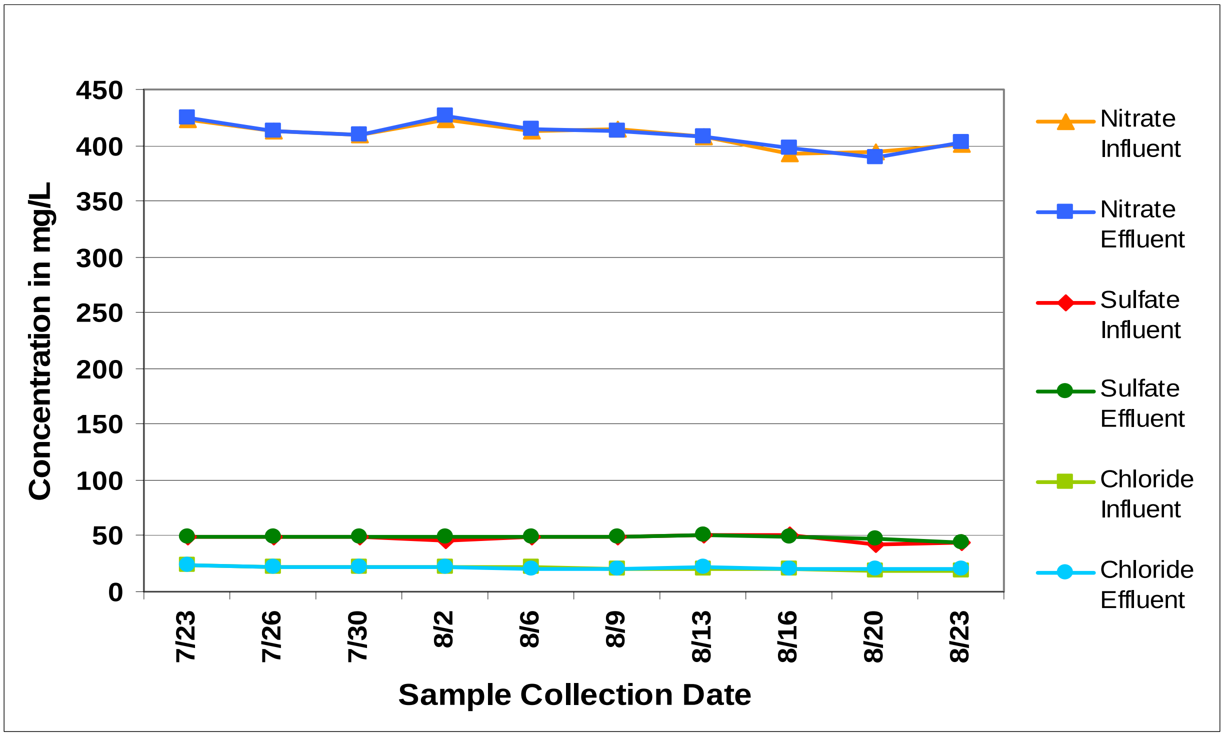

Figure 5. Competing anion data from extraction well 299-W15-765.

6.0 CONCLUSIONS

- The results presented in this thesis support the hypothesis that the resin removes ^{99}Tc to below the maximum contaminant level of 900 pCi/L.

- The results exceeded the manufacturer's suggested treatment volumes of 71,000 and 20,000, concluding that this resin is more effective at removing ^{99}Tc from groundwater than the manufacturer indicated.

- The results indicate that the resin is selective for ^{99}Tc over competing anions such as nitrate and sulfate even when they are at 5 to 6 orders of magnitude higher in concentration than ^{99}Tc. Results of the sampling efforts show that nitrate and sulfate concentrations in the influent and the effluent remained nominally equal and static over the course of the sampling efforts. This suggests that competition between nitrate and sulfate for ion exchange sites is very low compared to that of ^{99}Tc.

- The results also suggest that the Purolite® A-530E ion exchange resin is overall an effective method to remediate ^{99}Tc from groundwater.

7.0 REFERENCES

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APPENDICES

APPENDIX A

CALCULATIONS

A.1.0 CALCULATIONS

Numerous calculations were performed in support this thesis and are presented in the following subsections.

A.1.1 BED VOLUMES

The bed volume is defined as the volume of resin that the groundwater will contact within each column. The manufacturer estimated that 1.75 and 14.75 ft^3 of resin would be needed to support 60 days of column operation, for wells 299-W15-44 and 299-W15-765, respectively. The calculations presented in this section support the values presented in Table 1.

A.1.1.1 Bed Volumes for Both Wells

The bed volumes calculated below are from the volume of material used in the test.

$$\text{Bed Volume Well 44} = 1.75\ \text{ft}^3 \times \frac{1728\ \text{in}^3}{1\ \text{ft}^3} \times \frac{16.39\ \text{mL}}{1\ \text{in}^3} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times \frac{0.264\ \text{gal}}{1\ \text{L}} = 13.08\ \text{gal or} \sim 13.0\ \text{gal}$$

$$\text{Bed Volume Well 765} = 14.75\ \text{ft}^3 \times \frac{1728\ \text{in}^3}{1\ \text{ft}^3} \times \frac{16.39\ \text{mL}}{1\ \text{in}^3} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times \frac{0.264\ \text{gal}}{1\ \text{L}} = 110.3\ \text{gal or} \sim 110.0\ \text{gal}$$

A.1.1.2 Total Number of Bed Volumes Treated

The total number of bed volumes that were treated in both systems were derived from the total number of gallons that were treated in each system divided by the gallons in one bed volume. The calculations presented in this section support the values presented in Table 7.

$$\text{Total Treated Bed Volume 44} = 937{,}164\ \text{gal} \times \frac{1\ \text{bed volume}}{13.0\ \text{gal}} = 72{,}089.5\ \text{or}\ 72{,}090\ \text{bed volumes}$$

$$\text{Total Treated Bed Volume 765} = 2{,}308{,}916\ \text{gal} \times \frac{1\ \text{bed volume}}{110.0\ \text{gal}} = 20{,}990.1\ \text{or}\ 20{,}990\ \text{bed volumes}$$

A.1.3 MOLARITY

The molarity of a solution is defined as the number of moles of solute per liter of solution. The resin manufacturer utilized a baseline set of water quality parameters for both wells. Baseline concentrations of 99Tc, nitrate, and sulfate utilized by the manufacturer to calculate the number of bed volumes for both wells are shown below in molarity. The calculations presented in this section support the values presented in Table 1.

$$\text{Molarity Tc-99 Well 44 and 765} = \frac{5000\ \text{pCi Tc}}{1\text{L}} \times \frac{1\ \text{Ci Tc}}{1.0 \times 10^{12}\ \text{pCi Tc}} \times \frac{1\ \text{g Tc}}{0.0169\ \text{Ci Tc}} \times \frac{1\ \text{mole Tc}}{99\ \text{g Tc}}$$

$$= \frac{2.97 \times 10^{-9}\ \text{moles Tc}}{1\text{L}} \quad \text{or}\ 2.97 \times 10^{-9}\ \text{M Tc}$$

$$\text{Molarity NO}_3^-\ \text{Well 44 and 765} = \frac{110\ \text{mg NO}_3^-}{1\ \text{L}} \times \frac{1\ \text{g NO}_3^-}{1000\ \text{mg NO}_3^-} \times \frac{1\ \text{mole NO}_3^-}{62\ \text{g NO}_3^-} = \frac{1.77 \times 10^{-3}\ \text{moles NO}_3^-}{1\ \text{L}}$$

$$\text{or}\ 1.77 \times 10^{-3}\ \text{M}\ \ \text{NO}_3^-$$

$$\text{Molarity } SO_4^{2-} \text{ Well 44 and 765} = \frac{50\,\text{mg } SO_4^{2-}}{1\,\text{L}} \times \frac{1\,\text{g } SO_4^{2-}}{1000\,\text{mg } SO_4^{2-}} \times \frac{1\,\text{mole } SO_4^{2-}}{96\,\text{g } SO_4^{2-}} = \frac{= 5.20\times10^{-4}\text{ moles } SO_4^{2-}}{1\,\text{L}}$$

$$\text{or } 5.20\times10^{-4}\text{ M } SO_4^{2-}$$

A.1.3.1 Molarity Well 299-W15-44

The average concentrations of 99Tc, nitrate, sulfate, and chloride measured in groundwater water from well 299-W15-44 are shown below in molarity. The calculations presented in this section support the values presented in Table 8.

$$\text{Molarity Tc-99 Well 44} = \frac{2050\text{ pCi Tc}}{1\,\text{L}} \times \frac{1\text{ Ci Tc}}{1.0\times10^{12}\text{ pCi Tc}} \times \frac{1\text{ g Tc}}{0.0169\text{ Ci Tc}} \times \frac{1\text{ mole Tc}}{99\text{ g Tc}} = \frac{1.22\times10^{-9}\text{ moles Tc}}{1\,\text{L}}$$

$$\text{or } 1.22\times10^{-9}\text{ M Tc}$$

$$\text{Molarity } NO_3^{-} \text{ Well 44} = \frac{143.7\text{ mg } NO_3^{-}}{1\text{L}} \times \frac{1\text{ g } NO_3^{-}}{1000\text{ mg } NO_3^{-}} \times \frac{1\text{ mole } NO_3^{-}}{62\text{ g } NO_3^{-}} = \frac{2.32\times10^{-3}\text{ moles } NO_3^{-}}{1\text{L}}$$

$$\text{or } 2.32\times10^{-3}\text{ M } NO_3^{-}$$

$$\text{Molarity } SO_4^{2-} \text{ Well 44} = \frac{51.24\text{ mg } SO_4^{2-}}{1\text{L}} \times \frac{1\text{g } SO_4^{2-}}{1000\text{ mg } SO_4^{2-}} \times \frac{1\text{ mole } SO_4^{2-}}{96\text{ g } SO_4^{2-}} = \frac{5.33\times10^{-4}\text{ moles } SO_4^{2-}}{1\text{L}}$$

$$\text{or } 5.33\times10^{-4}\text{ M } SO_4^{2-}$$

$$\text{Molarity } Cl^{-} \text{ Well 44} = \frac{26.25\text{ mg } Cl^{-}}{1\,\text{L}} \times \frac{1\text{ g } Cl^{-}}{1000\text{ mg } Cl^{-}} \times \frac{1\text{ moles } Cl^{-}}{35.5\text{ g } Cl^{-}} = \frac{7.40\times10^{-4}\text{ moles } Cl^{-}}{1\,\text{L}}$$

$$\text{or } 7.40\times10^{-4}\text{ M } Cl^{-}$$

A.1.3.2 Molarity Well 299-W15-765

The average concentrations of 99Tc, nitrate, sulfate, and chloride in well 299-W15-765 are shown below in molarity. The calculations presented in this section support the values presented in Table 8.

$$\text{Molarity Tc-99 Well 765} = \frac{2420\text{ pCi Tc}}{1\text{L}} \times \frac{1\text{ Ci Tc}}{1.0\times10^{12}\text{ pCi Tc}} \times \frac{1\text{ g Tc}}{0.0169\text{ Ci Tc}} \times \frac{1\text{ mole Tc}}{99\text{ g Tc}} = \frac{1.44\times10^{-9}\text{ moles Tc}}{1\text{L}}$$

$$\text{or } 1.44\times10^{-9}\text{ M Tc}$$

$$\text{Molarity } NO_3^{-} \text{ Well 44} = \frac{414.63\text{ mg } NO_3^{-}}{1\text{L}} \times \frac{1\text{ g } NO_3^{-}}{1000\text{ mg } NO_3^{-}} \times \frac{1\text{ mole } NO_3^{-}}{62\text{ g } NO_3^{-}} = \frac{6.69\times10^{-3}\text{ moles } NO_3^{-}}{1\text{L}}$$

$$\text{or } 6.69\times10^{-3}\text{ M } NO_3^{-}$$

$$\text{Molarity } SO_4^{2-} \text{ Well 44} = \frac{48.97\text{ mg } SO_4^{2-}}{1\text{L}} \times \frac{1\text{g } SO_4^{2-}}{1000\text{ mg } SO_4^{2-}} \times \frac{1\text{ mole } SO_4^{2-}}{96\text{ g } SO_4^{2-}} = \frac{5.10\times10^{-4}\text{ moles } SO_4^{2-}}{1\text{L}}$$

$$\text{or } 5.10\times10^{-4}\text{ M } SO_4^{2-}$$

$$\text{Molarity } Cl^{-} \text{ Well 765} = \frac{21.59\text{ mg } Cl^{-}}{1\text{L}} \times \frac{1\text{ g } Cl^{-}}{1000\text{ mg } Cl^{-}} \times \frac{1\text{ mole } Cl^{-}}{35.5\text{ g } Cl^{-}} = \frac{6.09\times10^{-4}\text{ moles } Cl^{-}}{1\text{L}}$$

$$\text{or } 6.09\times10^{-4}\text{ M } Cl^{-}$$

A.1.4 AMOUNT OF TECHNETIUM-99 BOUND IN THE RESIN

The amount of 99Tc that is bound in the resin is defined as the mass of 99Tc in grams and curies that the resin has removed from the groundwater. It was assumed that all of the incoming 99Tc was bound in the resin. The calculations presented in this section support the values presented in Table 6.

A.1.4.1 Amount of Technetium-99 Bound in Well 299-W15-44

$$\text{Tc/Liter Well 44} = \frac{2050\,\text{pCi Tc}}{1\,\text{L}} \times \frac{1\,\text{Ci Tc}}{1.0\times10^{12}\ \text{pCi Tc}} \times \frac{1\,\text{g Tc}}{0.0169\,\text{Ci Tc}} = \frac{1.21\times10^{-7}\,\text{g Tc}}{1\text{L}}$$

$$\text{Liters Well 44} = 937{,}164\,\text{gal} \times \frac{1\,\text{L}}{0.264\,\text{gal}} = 3{,}549{,}864\,\text{L}$$

$$\text{Total Tc bound Well 44} = \frac{1.21\times10^{-7}\,\text{g Tc}}{1\,\text{L}} \times 3{,}549{,}864\,\text{L} = 0.43\,\text{g Tc bound}$$

$$\text{Total Curies of Tc bound Well 44} = \frac{2050\,\text{pCi Tc}}{1\,\text{L}} \times \frac{1\,\text{Ci Tc}}{1.0\times10^{12}\ \text{pCi}} \times 3{,}549{,}864\,\text{L} = 0.007\,\text{Ci Tc bound}$$

A.1.4.2 Amount of Technetium-99 Bound in Well 299-W15-765

$$\text{Tc/Liter Well 765} = \frac{2420\,\text{pCi Tc}}{1\,\text{L}} \times \frac{1\,\text{Ci Tc}}{1.0\times10^{12}\ \text{pCi Tc}} \times \frac{1\,\text{g Tc}}{0.0169\,\text{Ci Tc}} = \frac{1.43\times10^{-7}\,\text{g Tc}}{1\,\text{L}}$$

$$\text{Liters Well 765} = 2{,}308{,}916\,\text{gal} \times \frac{1\,\text{L}}{0.264\,\text{gal}} = 8{,}745{,}894\,\text{L}$$

$$\text{Total Tc bound Well 765} = \frac{1.43\times10^{-7}\,\text{g Tc}}{1\,\text{L}} \times 8{,}745{,}894\,\text{L} = 1.25\,\text{g Tc bound}$$

$$\text{Total Curies of Tc bound Well 765} = \frac{2420\,\text{pCi Tc}}{1\,\text{L}} \times \frac{1\,\text{Ci Tc}}{1.0\times10^{12}\ \text{pCi Tc}} \times 8{,}745{,}894\,\text{L} = 0.02\,\text{Ci Tc bound}$$

APPENDIX B

RESIN COLUMN INSTRUMENT DESIGN

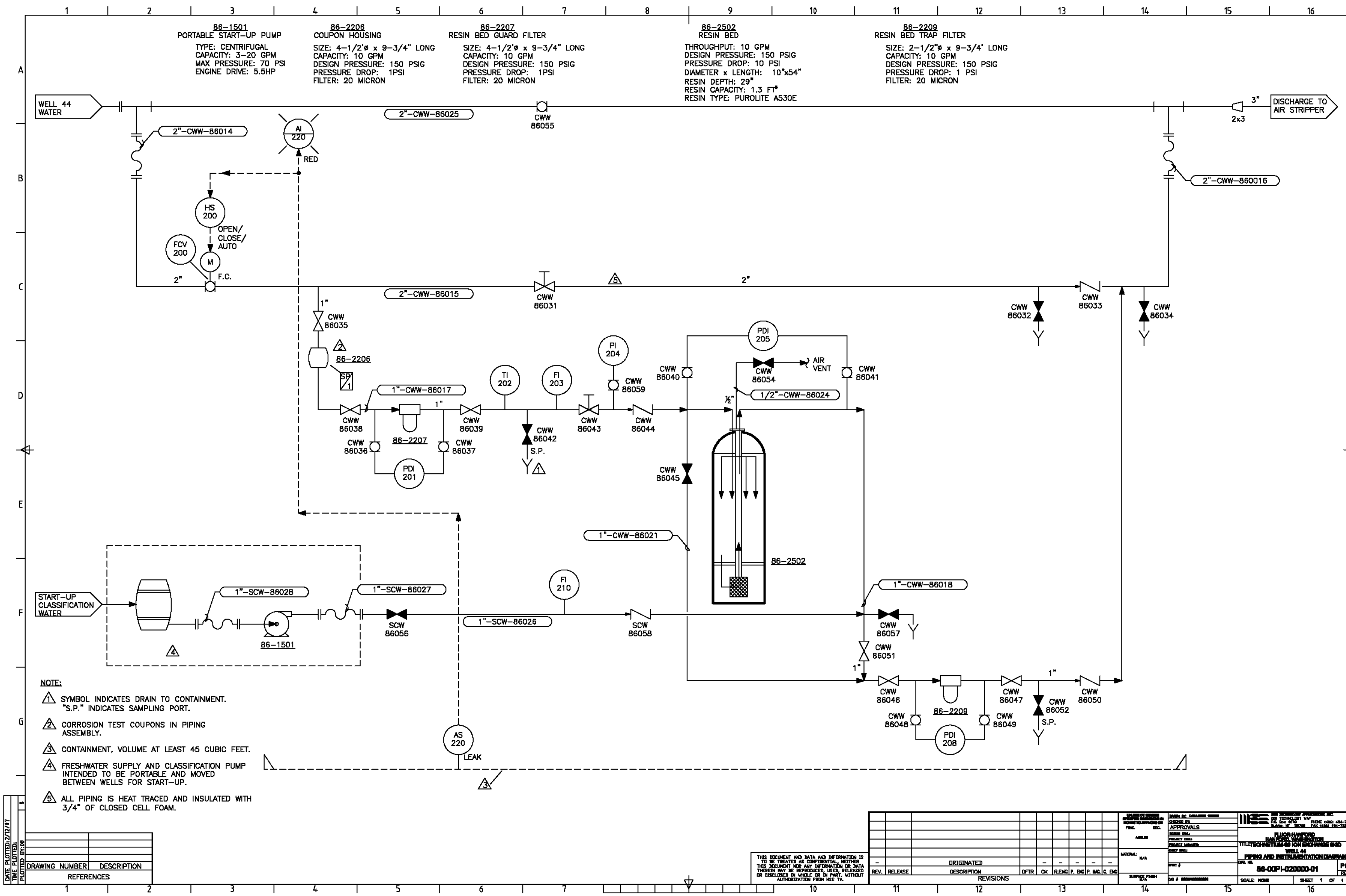

Figure B-1. Instrumentation Design for Resin Columns on Well 299-W15-44 and 299-W15-765.