Treatability Test for Removing Technetium-99 from 200-ZP-1 Groundwater, Hanford Site — 8038

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ABSTRACT

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. The primary risk-driving contaminants within the 200-ZP-1 OU include carbon tetrachloride and technetium-99 (Tc-99). A pump-and-treat system for this OU was initially installed in 1995 to control the 0.002 kg /m^3 (2000 µg/L) contour of the carbon tetrachloride plume. Carbon tetrachloride is removed from groundwater with the assistance of an air-stripping tower. Ten extraction wells and three injection wells operate at a combined rate of approximately 0.017m^3/s (17.03 L/s). In 2005, groundwater from two of the extraction wells (299-W15-765 and 299-W15-44) began to show concentrations greater than twice the maximum contaminant level (MCL) of Tc-99 (33,309 beq/m^3 or 900 pCi/L). The Tc-99 groundwater concentrations from all ten of the extraction wells when mixed were more than one-half of the MCL and were slowly increasing. If concentrations continued to rise and the water remained untreated for Tc-99, there was concern that the water re-injected into the aquifer could exceed the MCL standard. Multiple treatment technologies were reviewed for selectively removing Tc-99 from the groundwater. Of the treatment technologies, only ion exchange was determined to be highly selective, commercially available, and relatively low in cost. Through research funded by the U.S. Department of Energy, the ion-exchange resin Purolite® A-530E[1] was found to successfully removeTc-99 from groundwater, even in the presence of competing anions. For this and other reasons, Purolite® A-530E ion exchange resin was selected for treatability testing. The treatability test required installing resin columns on the discharge lines from extraction wells 299-W15-765 and 299-W15-44. Preliminary test results have concluded that the Purolite® A-530E[1] resin is effective at removing Tc-99 from groundwater to below detection limits even in the presence of competing anions (e.g., nitrate and sulfate) at concentrations five to six magnitudes higher than Tc-99.

[1]Purolite® A-530E is a registered trademark of the Purolite Company, Bala Cynwyd, Pennsylvania.

INTRODUCTION

The radionuclide technetium-99 (Tc-99) is a contaminant of concern at a few U.S. Department of Energy (DOE) Sites including the Hanford Site, in southeastern Washington State. In oxygenated groundwater, Tc-99 is highly soluble and exists as the pertechnetate anion (TcO_4^-). The mobility of Tc-99 in groundwater, coupled with its health hazards and long half-life of 214,000 years, makes it a concern at sites where it is present.

Several technologies for selectively treating Tc-99 in groundwater were reviewed [1], including the following: membrane separation, electrocoagulation, selective adsorbents, zero-valent iron, and ion exchange. The review compared (1) the technologies' selectivity for Tc-99, (2) their commercial availability, and (3) their relative cost. Of the technologies evaluated, only ion exchange met all three criteria. Therefore, ion exchange was selected for use in this treatability test.

Based on the technology screening process the product selected for this treatability test is a bi-functional organic resin that is commercially available from Purolite® under the designation of "A-530E." In bench and field tests this resin has been effective in selectively removing pertechnetate anions from groundwater in the presence of ions at higher magnitudes than the target anion [2]. The groundwater in the 200-ZP-1 OU exhibits concentrations of nitrate and sulfate 5 to 6 magnitudes higher than Tc-99.

Tc-99 is present at levels of concern in two extraction wells (299-W15-44 and 299-W15-765) and is not expected to be of concern in the majority of the 200-ZP-1 OU extraction wells. Therefore, it was desirable to minimize the size and cost of a Tc-99 pre-treatment system by implementing the system only at the impacted wells rather than treating the full combined and diluted Tc-99 concentration at the main pump-and-treat influent. The ion-exchange test systems were designed as short-term treatability systems to meet rapid scheduling and low-cost requirements.

Test Objectives

The ion exchange treatability test for the 200-ZP-1 OU had two objectives. First, verify that Purolite® A-530E resin adequately removes Tc-99 from 200-ZP-1 groundwater and determine the site-specific resin usage rate (i.e., verify vendor-provided data indicating treatment of 71,000 and 20,000 bed volumes). Second, confirm that the resin is selective for Tc-99 and does not significantly adsorb other anions (e.g., nitrate and sulfate) present in the groundwater.

Determination of Testing Parameters and Constituents for Monitoring

Concentrations of the target anion (e.g., Tc-99) and competing anions (e.g., nitrate and sulfate) in the groundwater of well 299-W15-44 and 299-W15-765 were utilized by the manufacturer for calculating minimum bed volumes that could be processed. Details of the anion concentrations for both test columns are presented in Table I.

The primary constituents that were monitored include Tc-99, nitrate, sulfate, and chloride. Secondary parameters collected were carbon tetrachloride, phosphate, alkalinity and pH. Groundwater samples were taken from the influent and effluent sampling ports of each test system twice per week (when accessible) and analyzed for the parameters listed in Table I.

Table I. Anion Groundwater Concentrations.

Well #	Anion	Average Influent Concentration[a]	Units	Molarity[b], M
299-W15-44	Technetium-99	75,870 (2,050 ± 133.70)	beq/m^3 pCi/L	1.22×10^{-9}
	Nitrate	0.1437 (143.70 ± 2.69)	kg/m^3 mg/L	2.32×10^{-3}
	Sulfate	0.05124 (51.24 ± 1.28)	kg/m^3 mg/L	5.33×10^{-4}
	Chloride	0.02625 (26.25 ± 0.77)	kg/m^3 mg/L	7.40×10^{-4}
299-W15-765	Technetium-99	89,563 (2,420 ± 192.79)	beq/m^3 pCi/L	1.44×10^{-9}
	Nitrate	0.4146 (414.63 ± 10.34)	kg/m^3 mg/L	6.69×10^{-3}
	Sulfate	0.04897 (48.97 ± 2.73)	kg/m^3 mg/L	5.10×10^{-4}
	Chloride	0.02159 (21.59 ± 1.27)	kg/m^3 mg/L	6.09×10^{-4}

[a] Average influent concentrations for radiological constituents are presented in bequerels per cubic meter and picocuries per liter. Non-radiological constituents are presented in kilograms per cubic meter and milligrams per liter and associated standard deviations.
[b] Concentrations in molarity reflect the concentration in Moles/L.

Criteria for Termination of Testing

The criteria for terminating the ion exchange treatability test were when 50% breakthrough of Tc-99 had been measured at the effluent of both of the test columns and the analytical result of a second sample confirmed the breakthrough.

The number of bed volumes, or resin usage rates are the minimum number of bed volumes that the test 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, as shown below:

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

MATERIALS AND METHODS

The test systems were manufactured with simplicity in mind using commercial off-the-shelf materials (i.e., polyvinyl chloride materials and hand valving). Fiberglass-reinforced plastic vessels were used for both test columns. The test columns were piped in at the well heads and were installed with a bypass that allows continued flow of the groundwater from the wells to the main carbon tetrachloride treatment system in the event that the equipment had to be isolated and repaired. Containment skids were installed to capture minor leaks and drips.

The groundwater enters the test system, passes through an initial filter, through a flow totalizer, and then into the test column. In each test column, water enters the top and flows downward through the resin, out through collectors in the bottom and back up through riser tubes in the center, and exits the top. Once the water exits the test column it flows through another filter and then out into the main pump-and-treat system where it joins with the groundwater from the other extraction wells.

Sample ports were installed to allow influent and effluent samples to be collected from the test systems. One pressure-indicating gauge and three differential pressure gauges were installed to monitor system pressure. Digital turbine flow meters, flow totalizers, and temperature gauges were installed to monitor operational parameters during the test. Testing parameters for both columns are listed in Table II.

Table II. Testing Parameters for Resin Columns on Both Wells.

Well Number	**Column Height, m**	**Column Diameter, m**	**Resin Bed Depth, m**	**Resin Bed Volume[a], m^3 (L)**	**Volume to Process[b], m^3 (L)**	**Resin Usage Rate or Bed Volumes[c]**
299-W15-44	1.37	0.254	0.965	0.049 m^3 (49.14 L)	3,493.9 (3,488,940)	~71,000
299-W15-765	1.83	0.762	0.914	0.418 (415.8)	8,327.9 (8,316,000)	~20,000

[a] Resin volumes are in cubic meters and liters.
[b] The number of cubic meters (liters) of groundwater that are needed to be processed to achieve the manufacturer specified bed volumes.
[c] The resin usage rates, or number of bed volumes are calculated from the total flow in cubic meters (liters) that needs to pass through the system divided by the resin bed volume.

Column Setup on Well 299-W15-44

It was determined by the manufacturer that a flow rate of 0.0005 m^3/s and a resin bed volume of 0.049 m^3 (49.14 L) would take at least 60 days to achieve the 50% breakthrough in a 60 day minimum timeframe after processing 71,000 resin-bed volumes of the groundwater. A test vessel with a 10-in. (0.254 m) diameter was used. The column had a resin bed depth of 38 in. (0.965 m), and a height of approximately 24 in. (1.37 m) to accommodate the resin.

Column Setup on Well 299-W15-765

It was determined by the manufacturer that a flow rate of 0.00189 m^3/s from this well and a resin bed volume of 0.416 m^3 (415.8 L) would achieve the 50% breakthrough after processing 20,000 resin bed volumes of the groundwater. A test vessel with a 30-in. diameter (0.762 m) was used. The column had a resin bed depth of 63 in. (0.914 m) and a height of approximately 72 in (1.83 m) to accommodate the resin.

PRELIMINARY RESULTS

The primary anions of concern in this study are Tc-99 (TcO_4^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}), with chloride (Cl^-) a secondary concern. Chloride is shown because it is the fixed anion in the exchange resin. The effluent concentrations for competing anions were nominally static across the sampling efforts for both columns with exceptions noted in the following subsections. The effluents on both test columns had just begun showing breakthrough at the time this paper was written, approximately four months after the test began.

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

The manufacturer-calculated number of bed volumes to meet 50% breakthrough at extraction well 299-W15-44 was 92 operational days. The operational days were not continuous days. From April 26 to September 13 the system was down 49 out of 141 days. Eighteen of the “down” days were due to either the 200-ZP-1 main treatment facility’s being offline, or the water level in the well being too low to support pumping. Thirty-one of the “down” days were due to system modifications, including well piping reinforcements.

Figure 1 graphically represents the effectiveness of the test column in removing Tc-99 at extraction well 299-W15-44. The sample collection dates shown are plotted against concentrations present in both the influent and effluent for all sampling dates. The drinking water MCL and the break in time for system modifications are also outlined. Concentrations in the effluent began to rise on November 8 signaling the beginning of breakthrough.

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

At extraction well 299-W15-765, the manufacturer calculated that 50% breakthrough would occur in 67 days of operation. Again, the operational days were not continuous days. From July 23 to September 27 the system was down three out of 70 days due to the off-line conditions at the 200-ZP-1 main treatment facility.

Figure 2 plots the data showing the efficiency of the test column in removing Tc-99 at extraction well 299-W15-765. The sample collection dates are plotted against concentrations present in both the influent and effluent for all sampling dates. The drinking water MCL is also outlined. Concentrations in the effluent began to rise on October 4, signaling the beginning of breakthrough.

Anion Concentrations

The anions of concern in this study are nitrate (NO_3^-), sulfate (SO_4^{2-}), Tc-99 (TcO_4^-), and chloride (Cl^-). The average influent and effluent anion concentrations in the groundwater of both columns are presented below in Table III.

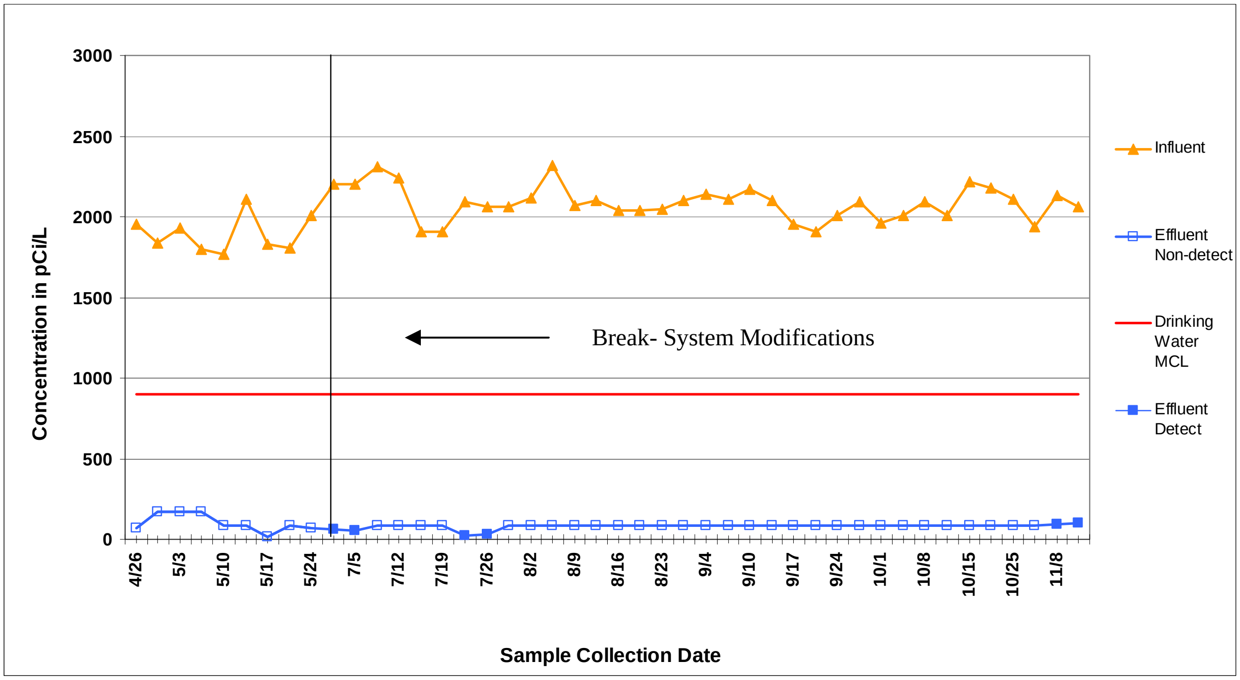

Fig. 1. Technetium-99 data is presented from the resin column on extraction well 299-W15-44.

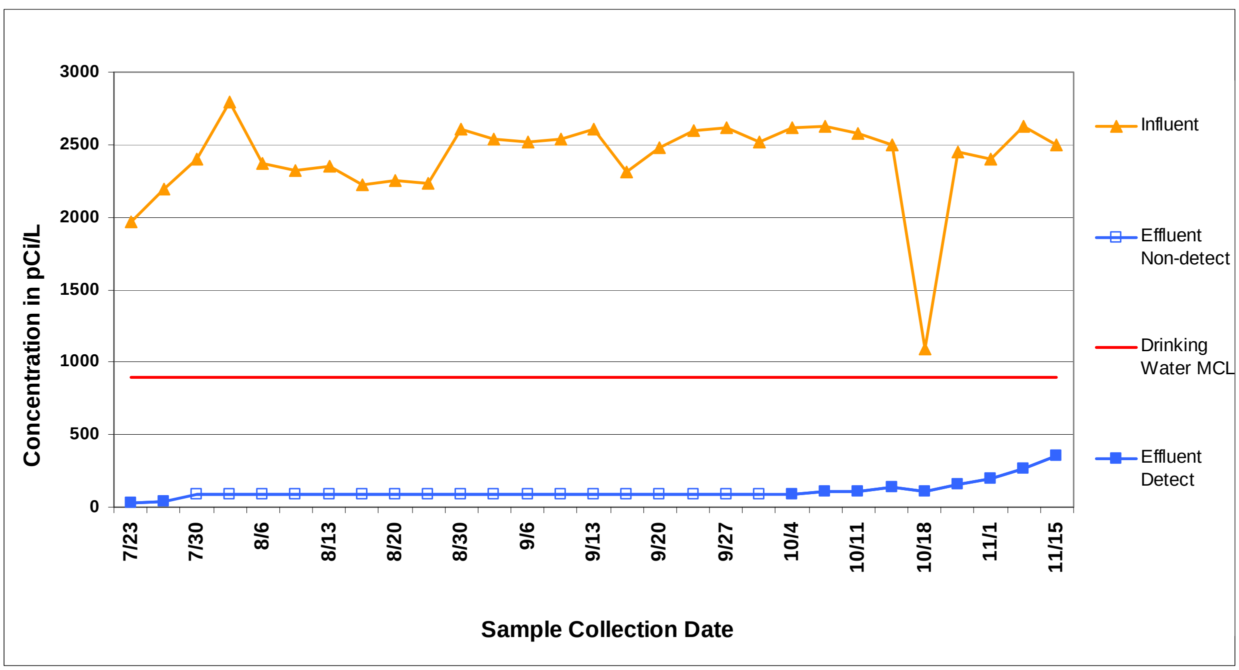

Fig. 2. Techetium-99 data is presented from the resin column on extraction well 299-W15-765.

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

The average concentrations and standard deviations of nitrate, sulfate, and chloride in the influent and effluent of this resin column are presented above in Table III. The data for all 3 constituents are presented in Fig. 3. The first sampling event of the influent and effluent was conducted 3 hours after the system was operational. An initial uptake of nitrate and a release of chloride by the resin in the first effluent sampling event can be seen in Fig. 3. By the next effluent sampling event nitrate increased and the chloride decreased to the same concentrations as their respective influents.

Table III. Average Influent and Effluent Concentrations for Both Test Columns.

Well #	Analyte	Average Influent Concentrations[a]	Units	Average Effluent Concentrations[a]	Units
299-W-15-44	Technetium-99	75,870 (2,050 ± 133.70)	beq/m^3 pCi/L	3,416 (92.3 ± 27.97)	beq/m^3 pCi/L
	Nitrate	0.1437 (143.70 ± 2.69)	kg/m^3 mg/L	0.1437 (143.74 ± 2.62)	kg/m^3 mg/L
	Sulfate	0.05124 (51.24 ± 1.28)	kg/m^3 mg/L	0.05171 (51.71 ± 1.33)	kg/m^3 mg/L
	Chloride	0.02625 (26.25 ± 0.77)	kg/m^3 mg/L	0.02935 (29.35 ± 14.43)	kg/m^3 mg/L
299-W15-765	Technetium-99	89,563 (2,420 ± 192.79)	beq/m^3 pCi/L	3,168 (85.6 ± 0.29)	beq/m^3 pCi/L
	Nitrate	0.4146 (414.63 ± 10.34)	kg/m^3 mg/L	0.4153 (415.39 ± 11.42)	kg/m^3 mg/L
	Sulfate	0.0489 (48.97 ± 2.73)	kg/m^3 mg/L	0.04971 (49.71 ± 1.89)	kg/m^3 mg/L
	Chloride	0.02159 (21.59 ± 1.27)	kg/m^3 mg/L	0.02164 (21.64 ± 1.05)	kg/m^3 mg/L

[a] Average influent and effluent concentrations for radiological constituents are presented in bequerels per cubic meter and picocuries per liter. Non-radiological constituents are presented in kilograms per cubic meter and milligrams per liter and associated standard deviations.

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

The average influent and effluent concentrations of nitrate, sulfate, and chloride are presented above in Table III. The first sampling event of the influent and effluent was conducted 4 days after the system was operational. Results for all 3 constituents (Fig. 4) show that the influents and effluents remained static throughout the sampling period.

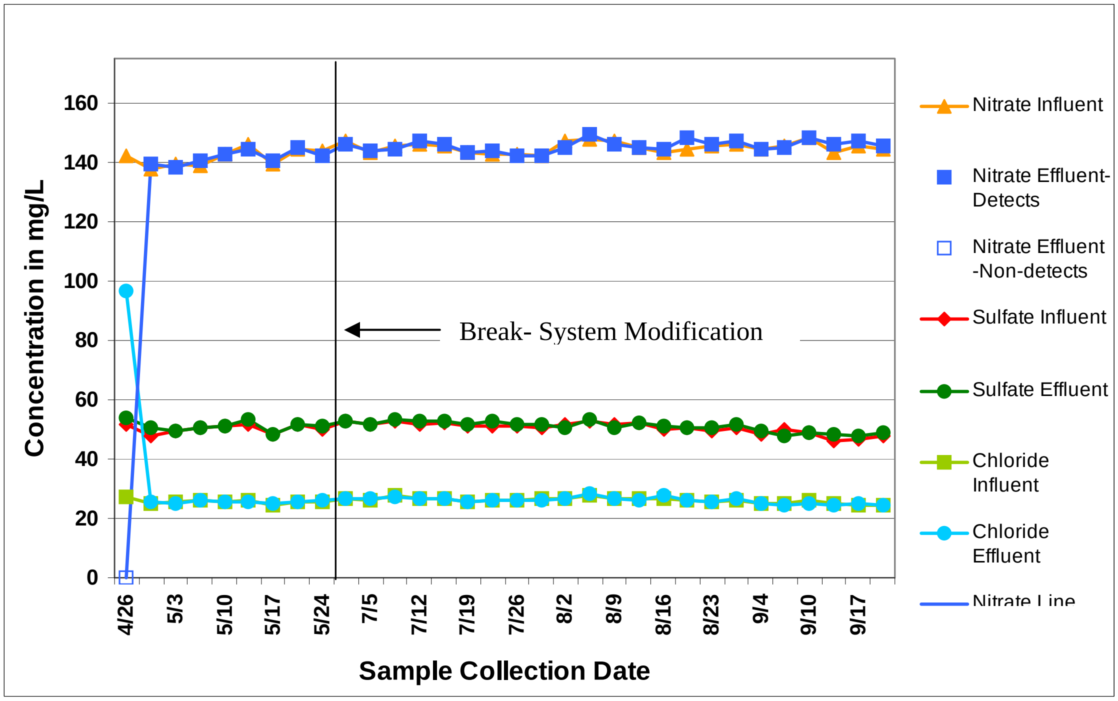

Fig. 3. Competing anion data is presented from the test column on extraction well 299-W15-44.

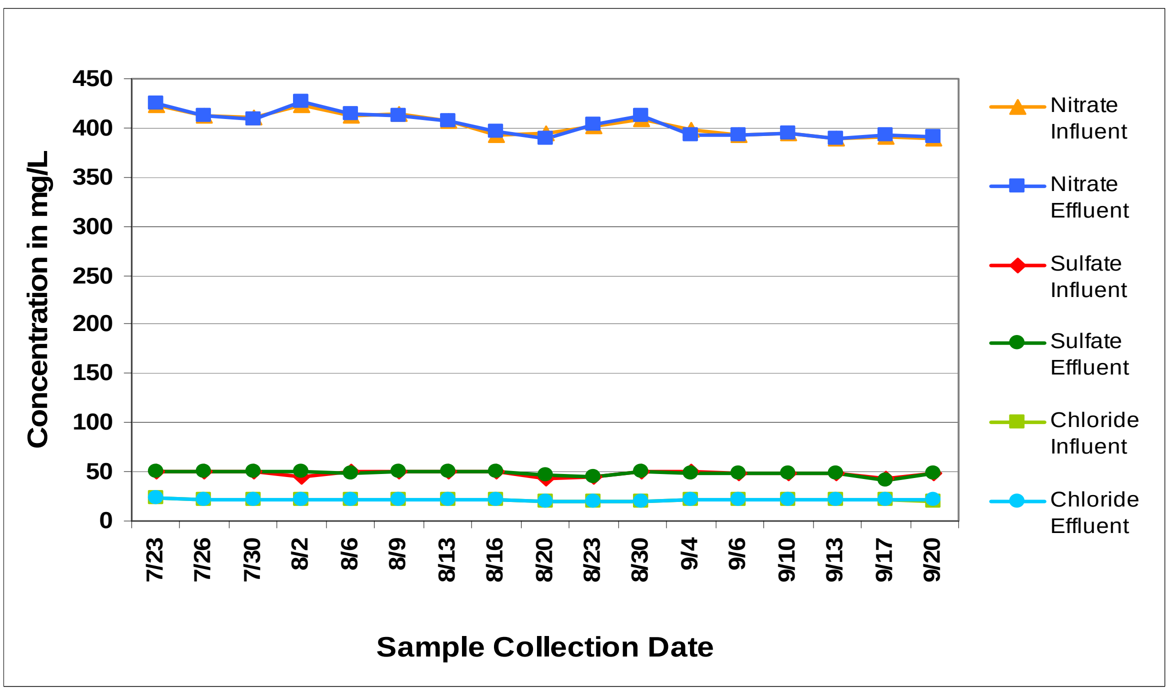

Fig. 4. Competing anion data is presented from the test column on extraction well 299-W15-765.

DISCUSSION

Initial Nitrate and Chloride Exchange

The anion exchange resin utilized in the treatability tests was shipped with chloride as the fixed anion embedded in the matrices. It was expected that the chloride concentrations in the effluents would be higher than the influents as the chloride is exchanged for the anions in solution. This, however, was clearly not the case, and after the first sampling event in column 299-W15-44, the chloride concentrations in the effluents and influents remained nominally equivalent.

When the chloride effluent data are compared to the nitrate effluent data as in Fig. 3 for the first sampling event (April 26), it shows that nitrate was originally taken up and chloride was released. In subsequent sampling events, nitrate and chloride effluent concentrations return to that of the influent. The data suggest that the nitrate saturated the resin within the first few hours of contact, releasing an equivalent amount of chloride from the resin. Once the resin became saturated, the resin's relative affinity for nitrate decreased and the effluent concentrations returned to influent concentrations.

The same phenomena are not noted for the system on 299-W15-765. The first sampling of this system was performed 4 days after the system was operational. Had the first sampling event been performed within the first few hours of operation the same phenomena may have been captured.

Selectivity Factors in Ion Exchange Systems

Many contemporary ion exchange systems, such as the one implemented in this test, is composed of a spherical resin-type exchange media that consists of an insoluble polystyrene backbone that carries a fixed amount of exchangeable anions. The frame work, or backbone of the resin is a flexible, hydrophobic matrix, consisting of a three-dimensional macromolecular network of hydrocarbon chains [2]. The overall insoluble properties are due to compounds that crosslink, or interconnect the hydrocarbon chains such as divinylbenzene. The degree of crosslinking determines the rigidity and width of matrix which affects the ability of the resin to swell when immersed in water or other polar solvents [2]. A higher degree of crosslinking, leads to a resins that are stronger and more resistant to breakdown than lesser crosslinked resins, but their ability to swell is reduced. Swelling of the resin is attributable to two factors: 1) unfolding of the hydrocarbon chains to make room for the solvent (the chains swell but do not separate due to the interconnecting crosslinks), and 2) spreading of the matrix due to the electrostatic interactions of neighboring fixed ionic groups repelling one another [2].

Swelling by the resin determines the mobility of the fixed counter ions, and to a certain degree the selectivity, or preference, of the resin to select one anion over another [2]. If the resin swells too far, the pore spaces, or interstices of the resin are no longer available for the movement of ions into or out of the matrices. Increasing the crosslinking increases the rigidity of the matrix, which in turn reduces the ability of the ionic groups to gather in hydrated domains [2]. This aspect adds to the overall enhanced selectivity for less hydrated ions over more hydrated ones. Pertechnetate is a weakly hydrated ion and has a lower hydration energy than either nitrate or sulfate, which lends a bias toward the A-530E resin to select Tc-99 (pertechnetate) over nitrate and sulfate [3].

CONCLUSIONS

- The Purolite A-530E resin columns removed Tc-99 to below the MCL throughout the timeframe presented here.
- The Purolite A-530E resin exceeded the manufacturer's estimated resin loading capacity of 71,000 and 20,000 bed volumes, concluding that this resin is indeed more effective at removing Tc-99 from groundwater than the manufacturer believed.
- The Purolite A-530E resin is selective for Tc-99 over competing anions nitrate and sulfate even when these anions are at five to six orders of magnitude higher than Tc-99. Results of the sampling show that nitrate and sulfate concentrations in the influent and the effluent remained nominally equal and static. This suggests that competition of nitrate and sulfate with Tc-99 for ion-exchange sites is very low, and thus, the resin is more selective for Tc-99 than for nitrate and sulfate.

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