Removal of Technetium-99 on Ion Exchange Resin – A Case Study at 200 West Pump and Treat-17303

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ABSTRACT

The 200 West Pump and Treat (P&T), on the U.S. Department of Energy's Hanford Site and operated by CH2M HILL Plateau Remediation Company, has a 9,464 liters per minute capacity designed to capture and treat an 8 km^2 contaminated groundwater plume and reduce the mass of contaminants of concern (COCs) by 95 percent in 25 years. The plume is a complex mix of contaminants including technetium-99 (Tc-99), uranium, carbon tetrachloride, chromium, hexavalent chromium, nitrate, and iodine-129 (I-129). Ion exchange (IX), a common treatment approach for Tc-99 used by many nuclear remediation sites, is used to remove uranium and Tc-99 at 200 West P&T. The IX vessels are arranged in a sequence of three to provide a lead, lag and polish vessel. Tc-99 concentrations are monitored monthly to assure good performance of the system. Performance tracking revealed surprising results. On October 14, 2015, the resin in the lead vessels released Tc-99 at concentrations greater than what was being fed. Although Tc-99 was captured by the downstream lag and polish vessels, the facility staff grabbled with the sudden release of Tc-99 entertaining a variety of scenarios that might result in sudden failure of the IX processes. Subsequent sampling indicated Tc-99 removal began a steady return to normal. The incident raised many questions, chief among them whether the same events could recur and undermine Tc-99 treatment.

INTRODUCTION

The DOE and its contractor, CH2M HILL Plateau Remediation Company, is addressing contamination of groundwater at the Hanford site. In 2008, the *Record of Decision Hanford 200 Area 200-ZP-1 Superfund Site Benton County, Washington* [1] (hereafter referred to as the Record of Decision [ROD]) recommended the installation of a groundwater pump-and-treat system to remediate contaminated groundwater beneath the 200-ZP-1 Operable Unit (OU). The system (designed, constructed and operated by CH2M) has a 9,464 liters per minute capacity designed to capture and treat an 8 km^2 contaminated groundwater plume and reduce the mass of COC by 95 percent in 25 years. Treatable COCs are a complex mix of radionuclides, metals, anions, and volatile organic compounds including carbon tetrachloride, trichloroethene, chromium, hexavalent chromium, nitrate, I-129, and, more importantly for this evaluation, Tc-99.

The contaminant plumes and performance the first three years have been documented previously [2]. The facility treats a complex waste stream from 30 extraction wells in three OUs. Injection wells return treated water to the aquifer providing flow-path control to mitigate migration of contamination toward the Columbia River.

Table I lists the contaminants and the cleanup level. The groundwater treatment approach involves multiple treatment steps to remove the various COCs to below the cleanup levels.

Table I. Final Cleanup Levels for the 200-ZP-1 Groundwater Operating Unit

Contaminant of Concern	Units	Final Cleanup Level	Cleanup Level Basis
Carbon tetrachloride	µg/L	3.4	MTCA, Method B
Chromium (total)	µg/L	100	Federal/State MCL
Hexavalent chromium	µg/L	48	MTCA, Method B
Nitrate-nitrogen	µg/L	10,000	Federal/State MCL
Trichloroethene	µg/L	1	MTCA, Method B
Iodine-129	pCi/L	1	Federal MCL
Technetium-99	pCi/L	900	Federal MCL
Uranium	µg/L	30	Federal MCL

The relationship between each unit process and the targeted COCs is presented in Fig. 1. Groundwater containing radiological contamination is treated first through a uranium IX system followed by two parallel trains for Tc-99 removal.

Tc-99 and U are removed with separate IX systems. This paper presents the experiences with the IX system and provides guidance based on this experience.

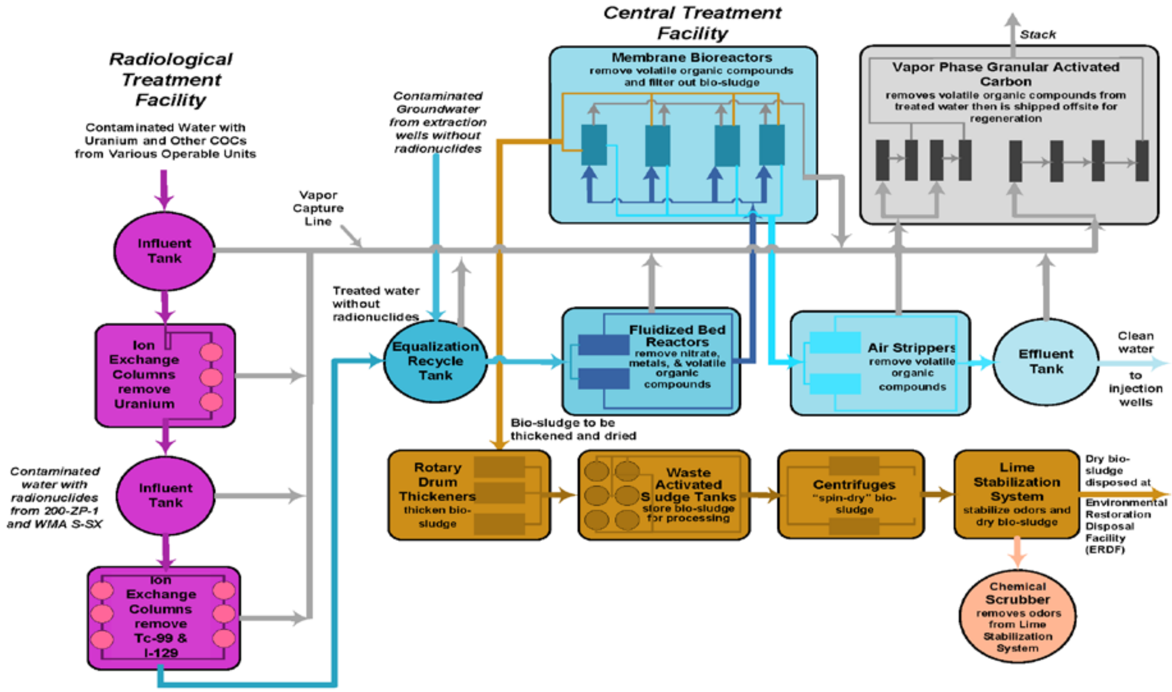


Fig. 1. 200 West Pump and Treat Process Flow

Ion Exchange system

The IX system is composed of two parts as shown in Fig. 2. The uranium IX system (U-IX) is comprised of one train and precedes the Technetium-99 IX system (Tc-99-IX), which is composed of two trains.

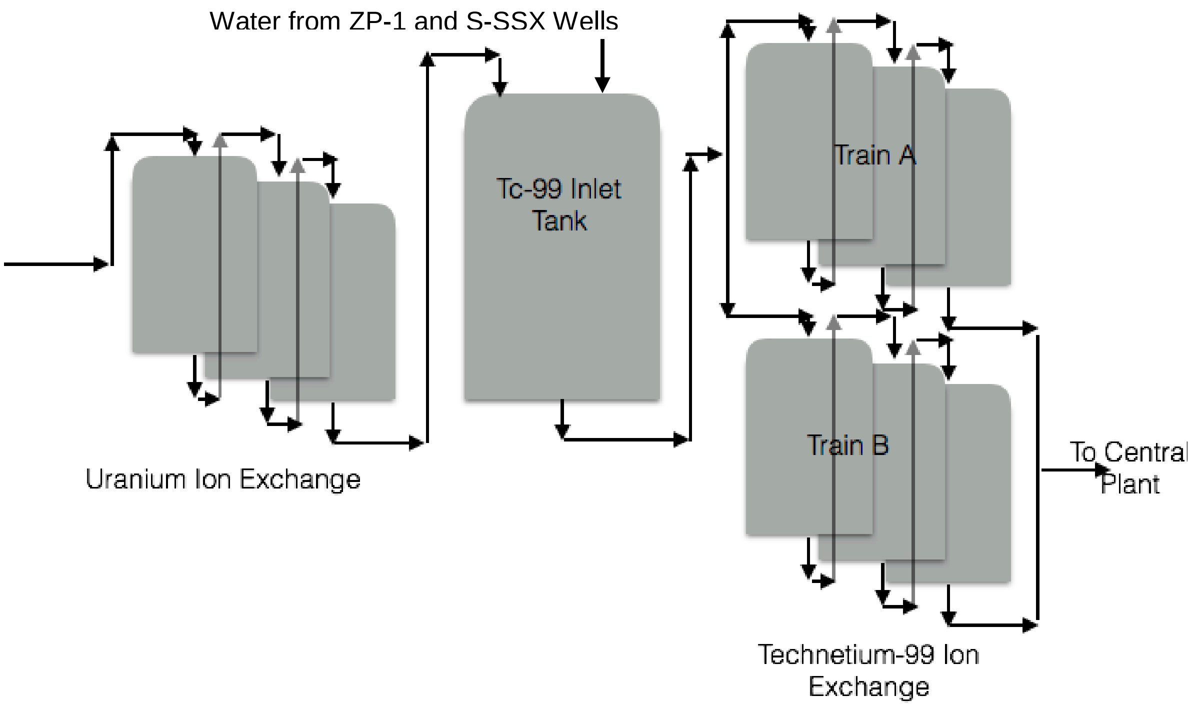


Fig. 2.IIIon Exchange System Schematic

Information on both of the IX systems are summarized in Table II. The resin vessels themselves are identical in their dimensions. However the resin is different. Tc-99 is removed using a Purolite A530E®[1] resin and uranium is removed with Dowex 21K®[2].

[1] Purolite is a registered trademark of BROTECH CORP., Bala Cynwyd, Pennsylvania
[2] Dowex is a registered trademark of Dow Chemical Company Midland, Michigan

Table II. Ion Exchange System Summary

Parameter	Uranium Ion Exchange System	Technetium-99 Ion Exchange System
Vessels in a Train	3	3
Trains	1	2
Flow Range per Train (lpm; gpm[a])	568 – 1,514; 150 - 400	568 – 1,514; 150 - 400
Vessel Surface Area (per Vessel) (M^2; ft^2)[b]	4.42; 47.5	4.42; 47.5
Loading Rate (lpm/M^2; gpm/ft^2)[c]	135 – 359; 3.3 – 8.8	135 – 359; 3.3 – 8.8
Empty Bed Contact Time (min)[d]	5.6 – 15	5.6 - 15
Resin Type	Dowex 21K®[e]	Purolite A530E®[f]
Quantity of Resin per Vessel (L; ft^3)[g]	8,495; 300	8,495; 300
Total Resin Capacity (Theoretical) (eq/L; eq/ft^3)[h]	1.2; 34	0.6; 17

[a]lpm = liters per minute; gpm = gallons per minute
[b]M^2 = square meters; ft^2 = square feet
[c]lpm/M^2 = liters per minute per square meter; gpm/ft^2 = gallons per minute per square feet
[d]min = minutes
[e] Dowex is a registered trademark of Dow Chemical Company Midland, Michigan
[f] Purolite is a registered trademark of BROTECH CORP., Bala Cynwyd, Pennsylvania
[g]L = liters; ft^3 = cubic feet
[h]eq/L = equivalents per L of resin; eq/ft^3= equivalents/cubic feet of resin

Ion Exchange Chemistry

Both resins are considered strong base anion exchange resins. The theoretical capacity is the total capacity for all anions. The resin is manufactured to preferentially adsorb the target compounds. But other anions will bind to sites on the resin and displace uranium or technetium, especially if the other anions are present at higher concentrations. The effective capacity is that part of the total capacity that can be used for the target compounds. The effective capacity is dependent on site specific conditions such as water chemistry and operating conditions and can be as low as 10 percent of the theoretical capacity.

Water pH is one of the key water quality variables impacting effective capacity for Uranium and Tc-99 removal. The pH of the water may need to be adjusted to assure that the target compound is in the correct form. For uranium the IX resin removes $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$. Each water quality condition is different and at 200 West uranium is in these preferred forms at pHs 7.0 and greater. However, at pH values greater than 8.0 water quality modeling indicated the potential for calcium carbonate to precipitate and poison the resin. A target pH of 7.4 was selected as a compromise. For Tc-99 the preferred form is pertechnetate (TcO_4^-) which is present at a wider pH band in our water so target pH of 6.8 was chosen to reduce the potential for precipitation and enhance resin performance. The natural pH of the water is 7.5 and sulfuric acid is added to reduce the pH.

Resin selectivity for Strong Base Anion (SBA) resins were obtained from published data[2] for SBA resin as shown in Table III for select anions. The selectivity coefficient, α_{i/Cl^-}, describes the relative affinity for each anion compared to chloride. Anions with greater selectivity values are adsorbed preferentially to those with lower values. However, the concentration of the anion will play a strong role and that is why the effective capacity is less than the total capacity.

Table III. Selectivity of Anions for Strong Base Anion Resins from Published Data

Anion	**Formula**	**Selectivity Value (α_i/Cl$^-$)[a]**	**Molecular Weight**	**Valence**	**Equivalent Weight (mg/mM)**
Technetium	TcO_4^-	384	162	1	162
Chromate	CrO_4^{2-}	100	116	2	58
Divalent Sulfate	SO_4^{2-}	9.1	96	2	48
Nitrate	NO_3^-	3.2	62	1	62
Chloride	Cl^-	1	35	1	35
Bicarbonate	HCO_3^-	0.27	61	1	61

[a] α_i/Cl$^-$ = Selectivity of strong base anion resin for given ion relative to chloride

DISCUSSION

The benefits of tracking performance is first discussed, followed by unexpected results of the monitoring program. The information gathered during the monitoring program provided the basis for understanding the reason resin was performing poorly. The insights gained are being used to assure good resin performance in the future.

Tracking Resin Performance

The concentration of the target compounds (uranium and technetium) are monitored regularly to track resin performance. Fig. 3 shows the following key features of a good monitoring program.

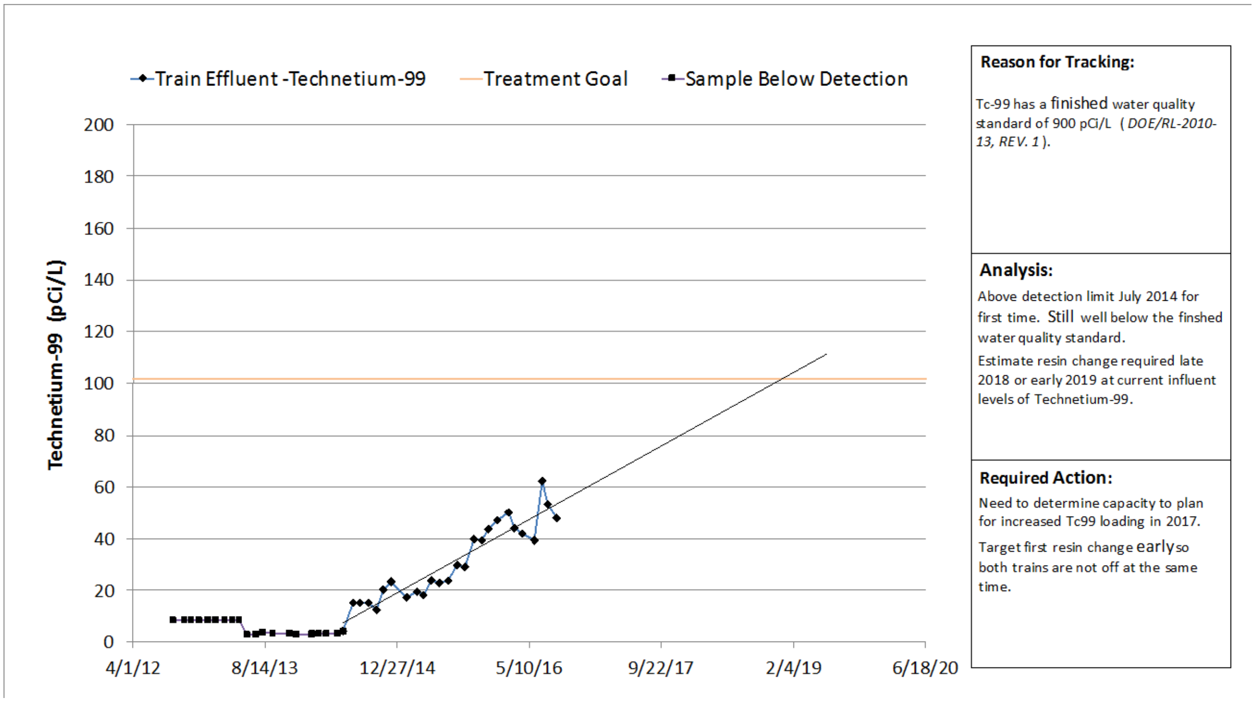


Figure 3.IIITechnetium Concentration with Time in the Effluent from the Technetium Ion Exchange System.

A treatment goal is established that is less than the clean-up level. At P&T the cleanup level is 900 pCi/L and the treatment goal is 102 pCi/L. The clean-up level of 900 pCi/L is based on the drinking water standard for technetium. The treatment goal was established using the results of an integrated mass balance developed when the plant was first designed (SGW-45097 Integrated Mass Balance for the 200 West Pump and Treat Facility). The calculation indicated that ion exchange resin should decrease the technetium-99 to 102 pCi/L and was recommended by the Environmental Control Organization on site as a treatment goal. The benefit of a treatment goal less than the regulatory limit is that it spurs a resin change in advance of exceeding the regulatory limit.

The data is collected on a regular basis to allow a trend to form. This trend provides information on the rate that the resin is being saturated and the amount of variability to expect. In Fig. 3 a linear trend is projected forward to indicate that at the current rate the effluent will exceed the treatment goal in late 2018 or early 2019. This projection provides information needed to develop initial plans for resin change including the scheduling of staff and appropriate budget planning.

The resin in both Tc-99 trains was placed on line at the same time in 2012. If allowed to run to exhaustion both trains can be expected to need to be replaced at the same time resulting in a cessation of treatment while the resin is changed out. By replacing the resin in one train early a staggered replacement schedule can be developed. Staggered replacement allows one of the two resin trains to remain in service and spaces out the effort so it is less disruptive.

It is important to recognize that if influent should change, then trend will change. In general, if influent increases, then slope of line increases and vice versa. Changes in general water quality can have surprising impacts on the effective capacity. Increases in the concentration of competing anions such as sulfate and nitrate will decrease adsorption of Tc-99. In particular, the ratio of Tc-99 to anion concentrations will change the equilibrium conditions between the bulk solution and the resin surface.

Unexpected Impacts

Fig. 4 shows the Tc-99 activity in the influent and effluent from the lead and lag vessels. From start-up in 2012 through September 2015 the influent Tc-99 activity ranged from 1,000 to 2,210 with an average of 1484 pCi/L. On October 14, 2015 the Tc-99 activity decreased unexpectedly to only 768 pCi/L and remained low for four months. At this time the effluent from the lead vessel increased to greater than the influent. The effluent from the lag vessel also increased during this period.

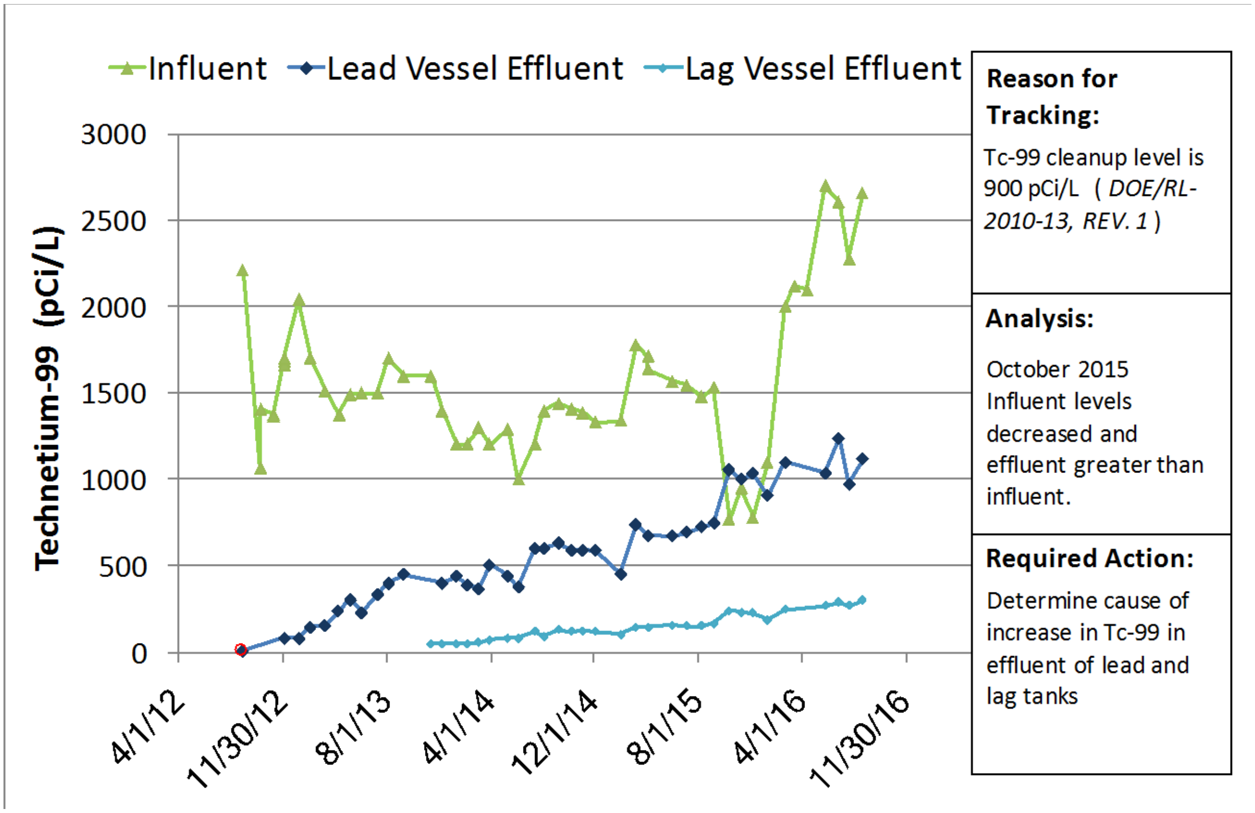
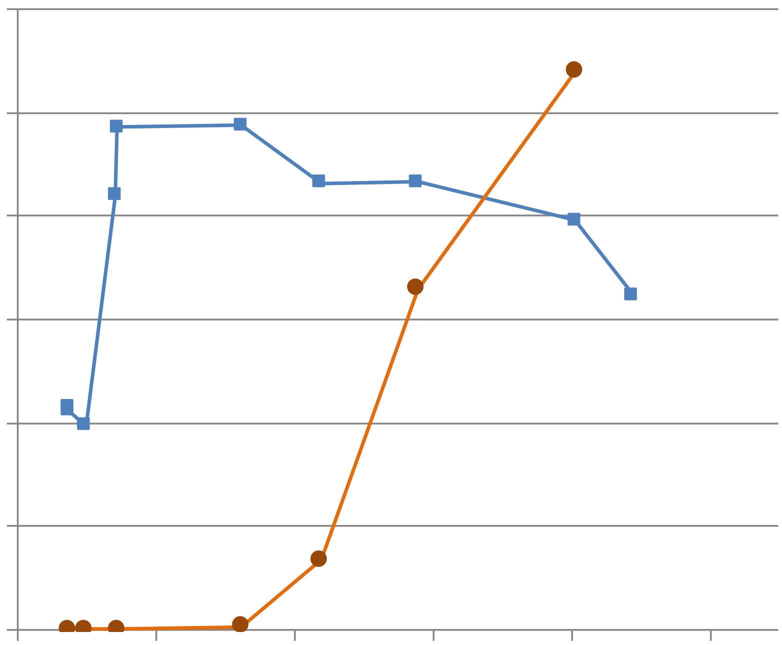


Fig. 4. Technetium-99 Activity in the Influent, and Effluent from the Lead and Lag Vessels

The uranium IX system was brought on line October 12, 2015 and successfully removed uranium to below detection. However, this train also removed Tc-99 (Fig. 5) resulting in low Tc-99 activity in the feed stream to the Tc-99 IX resin for a number of months.



er impacts of Tc-99 release from UIX on downstream Tc-99 IX.

Fig. 5. Removal of Techecium-99 (Tc-99) on Uranium Ion Exchange (UIX) Resin

The period under scrutiny (October 2015 through January 2016) is shown in more dramatic fashion when the concentration of Tc-99 in the effluent is expressed as a fraction of the influent (Ce/Co) as shown in Fig. 6.

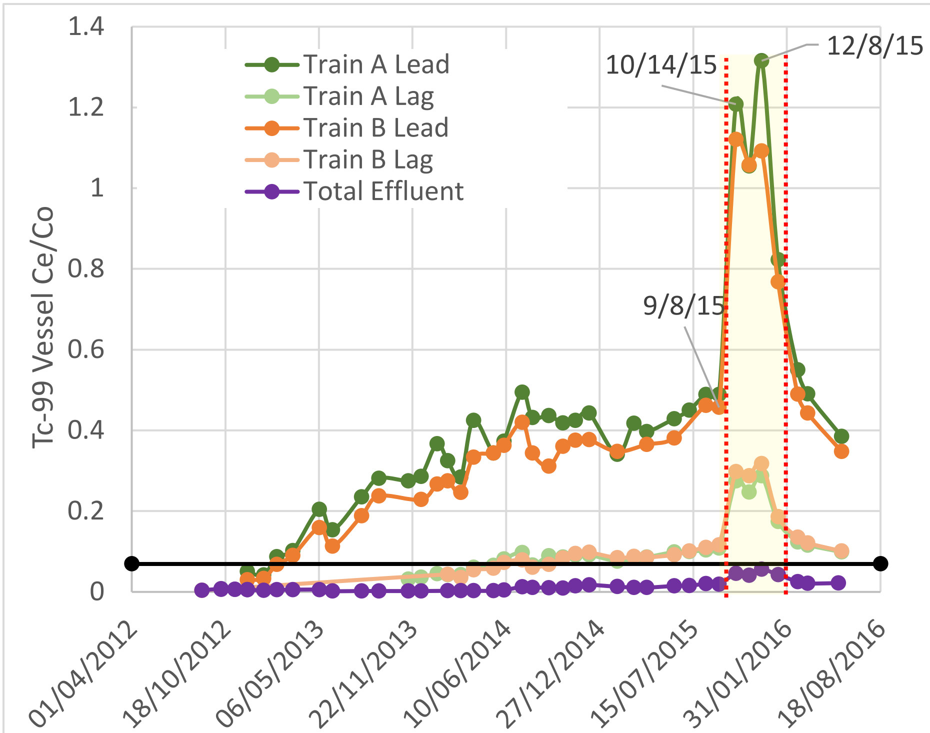


Fig. 6. Technetium-99 in Influent and Effluent from Technetium-99 Ion Exchange Vessels Expressed as Effluent as a Fraction of the Influent (Ce/Co)

The concentration of selected ions was checked to determine whether an increase in one or more anions could have temporarily reduced the effective capacity of the resin for Tc-99. The results, summarized in Table IV, show that the concentrations of mainly sulfate, but also nitrate increased while the concentrations of Tc-99 and chromate were reduced. When expressed in terms of milli-equivalents per liter (meq/L), the Tc-99 concentrations are a small fraction of sulfate and nitrate.

The uranium resin, like the Tc-99 resin, is an SBA resin. When the uranium resin was put online it adsorbed technetium-99. Also the concentrations of sulfate and nitrate increased because the new stream treated by the uranium resin was high in sulfate and nitrate. The combination was enough to displace some of the Tc-99 that had previously adsorbed to the Tc-99 resin. This effect was observed mostly in the lead vessel, but also in the lag and polish vessels. Note that although Tc-99 is more strongly adsorbing, it is present at concentrations that are only a fraction of that of anions such as sulfate. That is why its adsorption and release from the resin can be impacted by changes to the more weakly adsorbing anions, especially sulfate.

Table IV. Concentration of Select Anions Before and After Period of Technetium-99 Release

Anion	Formula	Selectivity Coefficient (α_i/Cl$^-$)a	Equivalent Weight (meq/mg)b	Concentration June through September 2015 (meq/L)[c]	Concentration October 14, 2015 through Jan 12, 2016 (meq/L)[c]	Percent Change
Technetium	TcO_4^-	384	162	5.5E-07	3.3E-07	-41%
Chromate	CrO_4^{2-}	100	58	9.3E-04	4.4E-07	-53%
Sulfate	SO_4^{2-}	9.1	48	0.83	1.33	60%
Nitrate	NO_3^-	3.2	62	0.62	0.85	37%
Chloride	Cl^-	1	35	0.50	0.51	2%
Bicarbonate	HCO_3^-	0.27	61	1.8	1.9	3%

[a] α_i/Cl$^-$ = Selectivity of given anion relative to chloride on strong base anion resin
[b]meq/mg = milli-equivalent per milligram
[c]meq/L = milli-equivalent per liter

CONCLUSIONS

After a careful consideration of the information provided the following conclusions can be drawn:

- IX is a very useful process for cleanup of technetium and uranium.
- The chemistry of IX resin is complex and site specific.
- Tracking resin performance has many advantages including providing an educated estimate of vessel life.
- When one resin is used in front of another the chemical dynamics in the upstream resin can have a detrimental impact on the performance of the downstream resin.
- Understanding the water chemistry helps establish a monitoring program that can reveal the impacts and provide an opportunity for compensatory measures to assure good performance.
- In the future, the state of the resin in the Tc-99 IX system will be evaluated to avoid replacing uranium resin or introducing high sulfate waste streams if the Tc-99 IX resin is nearing exhaustion.

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