The simultaneous removal of technetium and iodine from Hanford tank waste

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ABSTRACT

The simultaneous removal of radionuclides technetium-99 and iodine-129 from an actual decontaminated Hanford tank waste sample (a mixture of decontaminated waste from tanks 241-AP-105 and 241-AP-107) was demonstrated for the first time in this work. A series of commercially available ion exchange resins were evaluated in batch contact tests in the tank waste, and all showed removal of both Tc and I. The highest Tc removal from the tank waste was observed for Purolite A530e while the highest iodine removal was observed for ResinTech SIR-110-MP. Isotherm tests in simulated tank waste with these two resins showed that the SIR-110-HP-MP had consistently higher K_d for both pertechnetate and iodide; with much higher K_d than previous works on Tc removal from Hanford waste. As such, the SIR-110-MP was evaluated in a dual-column (lead/lag) test processing 5.2L of the tank waste mixture showing 50 % breakthrough of Tc on the lead column and no significant breakthrough on the lag after 641 bed volumes (BV, 6 mL size) while significant iodine breakthrough (>50 %) occurred after 28 BV. The limited iodine uptake was attributed to the column conditions generating mass transfer limitations. A fraction of the Tc and I was not captured by the resin (<10 %) in either the batch tests or column tests. The iodine fraction is not iodate and is likely organo-iodide. The fraction of the Tc was identified as a non-pertechnetate species which is the first time non-pertechnetate has been identified in AP-105 and AP-107 tanks. This non-pertechnetate fraction contained Tc(I) and for the first time a stable Tc(VI) species in Hanford waste was identified..

1. Introduction

The Hanford site in Washington State (USA) was the home of the world's first full scale nuclear reactors used for plutonium production efforts between the 1940's and 1980's [1]. As a byproduct of these activities a lasting environmental legacy remains in the form of over 56 million gallons of chemically complex and radioactive wastes that are stored in underground tanks at the site [2]. The tanks contain a mixture of sludge (primarily insoluble Al and Fe phases with long-lived actinides) [3], saltcake (primarily precipitated sodium salts) and supernate liquid (primarily alkaline sodium nitrate) [4]. Through leaks from single shell tanks and intentional waste discharges to the subsurface there is significant contamination of the Hanford site by a multitude of contaminants and radionuclides that require monitoring and active management [5,6]. To alleviate the risk of further releases to the subsurface and local environment the tank wastes are slated to be vitrified to a glass waste form for disposal at Hanford's Waste Treatment and Immobilization Plant (WTP)[4]. Upon retrieval from the tanks the wastes will be filtered to remove solids and passed through an ion exchange column to remove Cs (along with Sr and other radionuclides) [7]. The liquid effluent from this process is known as a treated low-activity waste (LAW) feed that is transferred to the LAW vitrification facility at WTP, while the solids are returned to tanks to be treated in the high-level waste (HLW) vitrification facility.

The resulting LAW feed contains technetium-99 (Tc) and iodine-129 (I) as the radionuclides of concern for long-term disposal as both elements primarily exist as soluble forms in the tank waste, are not affected in the filtration and ion exchange processes, have long half-lives and high environmental mobility in their anionic forms [8,9]. It is estimated that there are ~26,600 Ci of Tc-99 and ~29 Ci of I-129 in the Hanford

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tank waste. The majority of the Tc is likely to be present as pertechnetate ($Tc(VII)O_4^-$) while the iodine is likely present as iodide (I^-), although other species of each have been identified previously (e.g. non-pertechnetate species and iodate [10,11]. Tc and I present challenges in vitrification due to their volatility at the melter temperature that can lower their retention in the glass [12–14]. The off-gas volatilized from the melter is treated in an off-gas management system to generate secondary wastes. A portion of these secondary wastes are immobilized as a cementitious waste form or they are recycled back to the melter to enhance retention [15–17]. Upon disposal of these waste forms the release of Tc and I is of concern at disposal facilities that provide a pathway for contaminants to potable groundwater [18,19].

Due to the large scale of the vitrification mission at Hanford it is acknowledged that an additional treatment capacity for LAW will be required to supplement the baseline mission. Recent analyses have highlighted that the use of a cementitious waste form for the immobilization of LAW can provide supplemental capacity for LAW [20,21]. The long-term behavior of Tc and I in cementitious waste forms upon disposal carries uncertainty due to the physical and chemical processes responsible for retention of these species [22–24]. Removing these radionuclides from the primary waste stream prior to immobilization will reduce the long-term disposal uncertainty or reduce inventory moving to secondary wastes. The sequestered radionuclides can be handled in a smaller volume stream and disposed of separately at a favorable disposal site (e.g., no access to potable groundwater).

While the removal of radionuclides from wastewaters have been pursued by a number of methods including modified clays, layered hydroxides, imidazolium-based ion exchange resins [25–29], the extreme conditions of the Hanford tank waste make the applicability limited for many of these techniques. The removal of Tc and I has, however, been previously pursued independently from tank wastes using a select set of approaches. The majority of the work on Tc removal from Hanford tank waste has focused on the use of an elutable ion exchange resin SuperLig 639 [30–38]. In earlier flowsheet designs of the Hanford WTP Tc removal was planned using Superlig® 639, where the Tc could be eluted and moved for processing with the HLW. However, this unit operation was removed in further development of the facility. Other approaches to Tc removal from Hanford LAW (or simulated LAW) have involved other ion exchange resins [25,30,31,39–41], polyethylene glycol treatment [42], iron-based materials [43–45], crown ethers [46], cationic polymers [47], supramolecule receptors [48], electrochemical removal [49], tin-based materials [50,51], and sulfide-based materials [52]. The removal of iodine species is less studied in Hanford tank wastes with the majority of work focusing on the use of Ag-based materials to precipitate the iodine [53–55]. Some prior work with Superlig 639 has investigates iodine removal in LAW simulants [56]. Historical efforts toward iodine removal in the processing of Hanford wastes has focused mainly on vapor phase capture during reprocessing or in the off-gas of vitrification [57].

In the last decade there have been improvements in materials that can capture both Tc and I, including new classes of bifunctional and hybrid resins. These resins have shown success for iodine and technetium removal in a variety of liquid streams such as secondary wastes and groundwater [58–61]; but no testing in Hanford tank waste has been performed to date. Removing both radionuclides with a single resin could provide a simplified route of using a single unit operation to lower the radionuclide content versus needing multiple steps to sequester each radionuclide. Lowering the inventory in the primary waste form would subsequently reduce the long-term performance uncertainty associated with LAW waste forms. This work evaluated, for the first time, the simultaneous removal of Tc and I from real Hanford tank waste samples (a combination of wastes from 241-AP-105 and 241-AP-107) using several commercially available resins in batch contact tests. A column test was also used to assess continuous removal using SIR-110-MP resin in real tank waste. Isotherms were assessed for the resins in simulated LAW. The speciation of Tc and I was also investigated in the tank waste sample for its role in the removal of each.

2. Experimental

2.1. Materials

The resins tested in this work are as follows:

1) Purolite ® A530e which is a quaternary amine styrene divinylbenzene copolymer microporous resin in the chloride form that has been used previously for Tc removal from simulated Hanford waste and groundwater [39,62,63]and for iodine removal from secondary wastes [64,65].
2) Purolite® A532e a microporous gel polystyrene crosslinked with divinylbenzene with a complex amino functional group in the chloride form that has been shown to remove I from secondary waste [64].
3) Purolite ® PGW6002e a macroporous polystyrene crosslinked with divinylbenze using a type I quaternary ammonium functional group in the chloride form used for hexavalent chromium removal in wastewater [66].
4) ResinTech ® ASM-10-HP a selective hybrid anion exchange resin with hydrated iron oxide in the resin developed for arsenate removal that has been shown to remove iodine as both iodide and iodate [58,64,67].
5) ResinTech® SIR-110-MP a macroporous polystyrene resin using a tributylamine functional group in the chloride form used for perchlorate removal [68].
6) Superlig ® 639 which uses a crown-ether group to form an ionic complex with the TcO_4^- counter cation is an elutable ion exchange resin tested extensively for Tc removal from Hanford wastes.
7) DOWEX 21K XLT a quaternary amine styrene divinylbenzene copolymer microporous resin in the chloride form used for mineral processing and nitrate removal [69].
8) ABEC 2000 a polystyrene gel that has been shown to remove Tc from alkaline wastes in the past with a polyethylene glycol backbone, in this case one with a molecular weight of 2000. [70].

The resins were rinsed with deionized water to remove colloidal fines and then allowed to air dry. After air drying the rinsed resins, aliquots targeting 1.0 g (dry mass basis relative to 105 °C drying temperature) were collected for batch contacts. Both immediately before and immediately after resin subsamples were collected for batch contacts, a pair of F-factor samples were collected. The set of F-factor samples (one sample collected before the resin subsampling activities, one collected after) was heated to 105 °C to assess the moisture context of each media used. The average F-factors of the resins are shown in Table 1.

2.2. Tank waste sample

The Hanford tank waste media used in batch contact and column

Table 1
Measured F-factors of the resins used in this work.

Resin	F-Factor	RPD
A530e	0.85	0.88 %
A532e	0.94	0.67 %
PGW6002e	0.82	9.1 %
ASM-10-HP	0.91	0.48 %
SIR-110-MP	0.80	2.6 %
Superlig 639	0.94	0.39 %
DOWEX 21 K XLT	0.86	1.3 %
ABEC2000	0.60*	–

RPD = relative percent difference.
*From literature as the ABEC2000 had high variability in measuring the f-factor, and the one tested was ~60 wt% solids [71].

tests was a 4.4:1 vol% mix ratio of liquid waste from Tanks 241-AP-105 and 241-AP-107. Prior to combining the tank waste samples, each individual tank waste was filtered and ion exchanged to generate the decontaminated LAW feed [7]. The individual decontaminated AP-105 and AP-107 were then combined in a single bottle and manually agitated to mix. The composition of the waste sample is given in Table 2. The combined sample had a density of 1.2482 g/mL.

2.3. Simulant

A simplified LAW simulant was used for isotherm tests to prevent competition from the Tc and I nominally present in the waste. The simulant was based on an averaged composition of the Hanford tanks prepared following the recipe given in Table S1. The simulant was prepared with double deionized water (DDI, >18.0 MΩ•cm conforming to ASTM D1193-06(2018) specifications for Type I water). The resulting simulant was more concentrated than the tank waste sample (7.2 M Na compared with 5.4 M Na) to increase competition with other species during the tests (Table 3).

2.4. Batch contact tests

The removal of both Tc and I from the tank waste sample was evaluated using batch contact tests. A nominal 10-mL aliquot of waste was added to the ~1.0 g resin aliquot; exact volume was determined from net solution mass and density. The solution volume-to-resin mass phase ratios averaged 11.6 (range 10.1 to 12.9). Samples were mixed for 48 h at ambient temperature on a Cole-Parmer (Vernon Hills, Illinois) large orbital shaker with a 16-mm orbit set to 240 rpm. These batch contact tests in the actual tank waste sample were performed in triplicate. Following the designated contact time the samples were removed and then phase separated by filtration through a 0.45- μm pore size nylon filter. The concentration of Tc or I (C_f) was measured in the post-contacted solutions using inductively couple mass spectroscopy (ICP-MS), and the measured Tc and I fractionation was used to determine total exchange. The Tc and I reportable detection limits were 37 μg/L and 7.3 μg/L respectively in the tank waste samples, which are higher than traditional ICP methods, but the tank waste samples require a significant dilution due to their high salt content and radioactivity. A full method description of the analysis is included in the SI. From these experiments, a distribution coefficient, K_d, can be determined using equation (1):

$$K_d = \frac{C_f - C_0}{C_o} \times \frac{V_{waste}}{m_{resin} \times F - factor} \tag{1}$$

where:	C_f	concentration of the species after the batch contact (mg/L)
	C_0	initial concentration of the species (mg/L)
	V_{waste}	volume of waste in the batch contact (mL)
	m_{resin}	mass of resin in the batch contact (g)

Table 2
Measured composition of the combined 241-AP-105 and 241-AP-107 tank waste sample used in batch and column testing. The relative percent difference presented is taken from the measurement of three samples of the waste.

Component	Conc (g/L)	Conc (mol/L)	RPD
Al	10.9	0.41	**0.7 %**
B	0.04	3.3×10^{-3}	2.0 %
Cd	1.5×10^{-3}	1.3×10^{-5}	1.1 %
Ca	0.03	8.0×10^{-4}	1.3 %
Cl	3.7	0.11	0.4 %
Cr	0.3	6.0×10^{-3}	0.6 %
F	0.2	0.01	0.0 %
Fe	2.3×10^{-3}	4.2×10^{-5}	0.2 %
Mo	0.04	4.0×10^{-4}	0.3 %
Ni	0.02	3.6×10^{-4}	0.7 %
NO_3	111	1.86	0.4 %
NO_2	56.3	1.22	0.2 %
PO_4	1.3	0.01	0.7 %
K	3.0	0.08	8.6 %
Si	0.09	3.0×10^{-3}	1.4 %
Ag	1.5×10^{-3}	1.5×10^{-5}	1.3 %
Na	124	5.40	2.0 %
SO_4	3.2	0.03	0.5 %
U	4.5×10^{-3}	1.9×10^{-5}	1.7 %
Tc-99	7.4×10^{-3}	7.4×10^{-5}	1.6 %
I-127	2.0×10^{-3}	1.6×10^{-5}	3.7 %
I-129	5.6×10^{-4}	4.3×10^{-6}	16 %

Table 3
Composition of LAW simulant used in the isotherm tests.

Component	Conc (g/L)	Conc. (mol/L)
Na^+	165	7.20
Al^{3+}	12.9	0.50
Cl^-	1.80	0.05
Cr	0.9	0.02
F^-	0.38	0.02
NO_3^-	128	2.06
NO_2^-	32.1	0.70
SO_4^{2-}	11	0.11
K^+	2.06	0.05
PO_4^{3-}	2.36	0.02
pH	13.5	–
Density (g/cm^3)	1.31	–

2.5. Isotherm tests

A second set of batch contacts were performed using the LAW simulant and the Purolite A530e and SIR-110-MP resins. In these tests the concentration of Tc or I was individually varied between 1000 mg/L and 0.2 mg/L to assess sorption isotherms. Test solution concentrations were prepared such that the post-contacted equilibrium concentrations would bracket the feed concentrations found in the AP-105 and AP-107 tank waste. The phase ratio of 10 was maintained for these batch contact samples (10 mL liquid and 1.0 g dry resin mass). The tests were performed in duplicate and shaken on an orbital shaker for 48 h. The Tc was added to the LAW simulant from a 10,000 mg/L stock solution of NaTc(VII)O_4 while the I was added from a 10,000 mg/L stock solution of NaI.

Three isotherm models were evaluated: the Langmuir isotherm, the Freundlich isotherm and a hybrid isotherm. An ion exchange isotherm is not considered in this case due to the large excess of competing ions in the Hanford tank waste that will not change in concentration during the process. The ion exchange isotherm, where all available sites are open at the beginning, is simplified to the Langmuir isotherm. The Langmuir model is expressed by Eq. (2) and linearized in Eq. (3) [72].

$$q_e = \frac{q_m C_e}{C_e + \frac{1}{K_L}} \tag{2}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L \bullet q_m} + \frac{1}{q_m} \bullet C_e \tag{3}$$

where:	q_e	equilibrium mass of iodine sorbed per gram of media (mg/g)
	K_L	Langmuir equilibrium constant (L/mg)
	Ce	equilibrium final concentration, mg/L
	q_m	Maximum capacity of iodine (mg/g)

The Freundlich model is defined by Eq. (4) and linearized in Eq. (5) [72]:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{4}$$

$$\log_{10}q_e = \log_{10}K_F + \frac{1}{n}\log_{10}C_e \tag{5}$$

where	K_F	Freundlich constant related to adsorption capacity
	n	Heterogeneity factor

A Freundlich/Langmuir Hybrid equilibrium isotherm model was also evaluated [73] according to Eq. (6). This hybrid isotherm bridges the gap between a Freundlich isotherm behavior at higher concentrations and Langmuir isotherm success at low concentration.

$$\frac{\alpha_i + C_e}{(\beta + C_e)} = q_e \tag{6}$$

where:

α_i	=	isotherm parameter constant (mg/g media)
β	=	isotherm parameter constant (mg/L)

The α_i parameter typically represents the maximum capacity that each exchange media contains, where the β parameter incorporates selectivity coefficients, making it dependent on impacts such as temperature and composition of ionic species in solution; the larger the beta parameter, the less favorable (and lower loadings) an isotherm will be. For the assessments presented in the main body of the report the isotherm parameters were determined using the linear relationships in the Excel Solver function for least squares.

2.6. *Column tests*

SIR-110-MP was used in a column test for the removal of Tc and I from the AP-105/AP-107 mixture. A dual column (lead/lag) column configuration was used and a schematic can be found in Fig. S1. The resin was packed into borosilicate glass columns (9 cm tall with a 1.5 cm ID) each containing a bed volume (BV) of 6 mL SIR-110-MP. The resin bed was supported on the top and bottom by an in-house constructed support consisting of a 200-mesh stainless steel screen tack welded onto a stainless-steel O-ring. The resin was first treated with DDI then 0.1 M NaOH to check for leaks in the system. An automatic, positive displacement pump (Fluid Metering Inc.) with a stroke rate controller was used for the feed delivery. The feed was processed at 1.9 BV/h for the duration of the test based on processing rates at Hanford's Tank Side Cesium Removal (TSCR) system that is used for filtration and cesium ion exchange from the tank waste[7]. It is envisioned that any ion exchange deployment for Tc or I would involve a similar design concept (columns in series) and processing rates. As such, testing conditions and the available test platform based on TSCR were selected for this work. Samples (~5 mL) were collected from three-way valves placed after the lead and lag columns respectively and a bulk effluent jug collected the remaining effluent. At the end of processing the column was treated with 125 mL of 0.1 M NaOH for feed displacement, then 125 mL of DDI for a rinse and a nitrogen fluid flush from the system.

Based on the solution analysis with ICP-MS the lead/lag column data were evaluated to estimate the BVs to 50 % breakthrough. The breakthrough curve can be estimated by the error function, Eq. (7) (Hougen and Marshall 1947; Klinenberg 1994):

$$\frac{c}{c_0} = \frac{1}{2}\left(1 + \mathrm{erf}\left(\sqrt{k_1 t} - \sqrt{k_2 z}\right)\right) \tag{7}$$

where:

k_1, k_2	=	parameters dependent on column conditions and ion exchange media performance
t	=	time
z	=	column length

Where k_1 and k_2 are parameters dependent on column conditions and ion exchange media performance, t is time (or bed volumes processed) and z is the length of the column. Using this model, a fit was generated to the experimental data. The 50 % breakthrough can then be estimated by multiplication of k_1 and k_2. Parameters k_1 and k_2*z were found using an Excel solver to minimize the sum of square error.

2.7. *Solution analysis*

Major cations were analyzed quantitatively using inductively coupled plasma optical emission spectroscopy (ICP-OES) with a PerkinElmer Optima 8300 dual view and a PerkinElmer S-10 auto-sampler interface. Total Tc-99 and I-127 was measured quantitatively at mass 99 and 127, respectively, using a *Thermo Scientific X-Series* quadrupole ICP-MS and an Elemental Scientific SC4 DX *FAST* auto-sampler interface. The tank waste sample was also measured for I-129, however analyses focused on I-127 for ease of measurement. The I-129 has an interference with Mo which is present in high amounts in the tank waste. The amount of I-129 was ~25 % of the total iodine in the sample as measured via ICP-MS [74]. There is no expected difference in behavior between the I-127 and I-129. Samples were analyzed quantitatively for anions using a Dionex Reagent Free IC System (RFICS) 2000 with an AS-1 auto-sampler interface or a Dionex RFICS 5000 with an AS-AP auto-sampler interface. Full analytical details are presented in the Supplemental information. Samples were analyzed for iodine speciation and isotopic ratios (total I-129) by ion chromatography coupled to inductively coupled plasma mass spectrometry (IC-ICP-MS) [74]. The method utilizes collision cell technology to suppress an isobaric interference from ^{129}Xe, which is present in the argon supplied to the ICP. Iodate and iodide detection limits in this method in de-ionized water for ^{127}I were approximately 24 ng/L, while the corresponding values for ^{129}I were approximately 3 ng/L. However, the reportable detection limits in the tank waste matrix were ~100 μg/L due to required dilutions of the tank waste sample.

2.8. *Nuclear magnetic resonance (NMR) spectroscopy*

Procedures for ^{99}Tc NMR experiments on liquid samples have been described previously [75]. Solutions (volume = 2.5 mL) were doubly contained for radiological safety in capped PTFE/FEP copolymer sleeves (Wilmad) inserted in 10 mm glass NMR tubes. Technetium-99 NMR data were collected at 67.553 MHz on a Tecmag Redstone spectrometer equipped with a 10 mm broadband Nalorac probe. The chemical shift scale was referenced to 0.050 M NH_4TcO_4(aq) [76]. The temperature was regulated at 21 °C with dry nitrogen gas flow. Scans were acquired once every two seconds, which ensured complete recovery of the magnetization.

2.9. *Electron paramagnetic resonance (EPR) spectroscopy*

EPR spectra were acquired on a Bruker EMX Spectrometer equipped with an ER4102ST resonator and an Oxford ESR900 cryostat. Samples were doubly contained by employing unbreakable 3.15 mm ID liners FEP tube liners (Wilmad Lab Glass, Vineland, NJ) inside traditional quartz 5 mm EPR tubes.

2.10. *Fluorescence spectroscopy*

Excitation and emission spectra from the tank waste samples were recorded using a Horiba Jobin Yvon FluoroMax Plus-C spectrofluorometer equipped with a 150 W ozone-free xenon lamp, single Czerny Turner excitation spectrometer blazed ed at 330 nm, and a single Czerny Turner emission spectrometer blazed at 500 nm. Incremental excitations (1 nm) were performed between 200 nm and 700 nm wavelengths at 0.1

s integration times. Excitation parks of 465 nm and 505 nm were selected based on the excitation scan.

3. Results and discussion

3.1. Batch tests

All resins were able to capture both Tc and I simultaneously during the batch contact tests, Table 4. The highest K_d for Tc was the Purolite ® A530e at 158 mL/g while the highest for I was ResinTech SIR-110-MP at 154 mL/g. Analysis of the contacted tank waste did not show any significant change in the concentration of nitrate, nitrite, chromium, fluoride, phosphate, sulphate, potassium, aluminum, cadmium, calcium, molybdenum, nickel, or sodium. Some resins released iron and calcium. Minor (<40 %) removal of boron, and silicon was observed for all resins. The ASM-10-HP was the only resin observed to remove uranium (~23 %). This data can be found in the Supplemental information Table S3.

The fraction of Tc and I observed to breakthrough in the batch tests was not due to reaching capacity at the 1 g to 10 mL contact ratio but instead a likely result of alternate speciation of the Tc and I within the tank waste. Two additional batch contacts were performed by taking the decanted liquid from the original test and adding in fresh SIR-110-MP or Superlig 639 and repeating the process. By the third contact the concentrations had steadied with the SIR-110-MP lowering the concentration of Tc to 351 μg/L from 7353 μg/L in the waste, while the Superlig 639 reduced the concentration to 521 μg/L. The I concentration decreased from 1838 μg/L to 33 μg/L for the SIR-110-MP and 219 for the Superlig 639. It is hypothesized that the SIR-110-MP may have some capacity for the alternate Tc and I species in the absence of the primary pertechnetate and iodide that are initially removed in the first contacts. However, as the exact species of Tc and I in the waste is not fully identified, further studies would be required to demonstrate any such affinity for non-pertechnetate or non-iodide species. These batch contact samples were also analyzed for I-129. The initial concentration of I-129 was 560 μg/L and after contact with the Superlig 639 the concentration was 202 μg/L (equal to a 63 % removal) while the SIR-110-MP test had concentration below the detection limit of 140 μg/L.

To account for this alternate speciation inventory that is not removed, adjusted K_d values were calculated where the excess Tc or I attributed to alternate species was subtracted from the measured total. These adjusted K_d can be considered approximates for the K_d of pertechnetate and iodide. The highest Tc and I K_d were calculated for the SIR-110-MP at 17864 mg/L and 2349 mL/g, respectively. The A530e had concentrations of Tc less than the subtracted amount and only one of the triplicate runs had a reportable value. Upon adjustment the value of Superlig 639 is similar to those reported from tests in an adjusted Tank 50 waste sample from the Savannah River Site where K_d of 582 mL/g for Tc and 49 mL/g for I was reported following testing at a 100 mL to 1 g ratio [56], from tests with tank 241-AW-101 waste with a maximum of 500 mL/g reported in batch tests and 839 mL/g in column tests [39]. The ABEC2000 had the lowest K_d for Tc at 35 mL/g where in prior testing using a simulant of tank SY-101 waste measured a K_d of 410 mL/g [39], and for iodine, with prior work suggesting additives would be needed or a possible conversion to I_3 [77]. Prior work with Purolite A520e measured a Tc K_d of 620 mL/g in simulated tank 241-SY-102 waste while work with Reillex HPQ in simulated tank 241-SY-102 and 241-AW-101 waste measured K_d as high as 370 mL/g for Tc [78]. The resins tested in this work exceeded the removal of Tc compared with these prior works using resins previously considered for use at Hanford. Although most of the resins in this work are not elutable and would require immobilization for disposal. The SIR-110-MP shows promise for the removal of both Tc and I from Hanford wastes, including alternate species (See Table 5).

Table 4

Summary of the K_d's measured during batch contact tests of the resins in a mixture of AP-105/AP-107 Hanford Tank Waste and the RPD for the triplicate tests.

Resin	Tc K_d (mL/g)	RPD	I K_d (mL/g)	RPD
Purolite A530e	158	2	48	2
Purolite A532e	137	3	41	7
Purolite PGW6002e	132	3	46	7
ResinTech ASM-10-HP	100	2	27	8
ResinTech SIR-110-MP	132	4	154	1
SuperLig 639	107	0	12	10
DOWEX 21K XLT	123	1	52	3
ABEC2000	55	1.3	9	13

3.2. Isotherm tests

Based on the batch tests in the tank waste sample, additional batch tests with varying concentrations of Tc (as pertechnetate, TcO_4^-) and I (as iodide, I^-) were performed in LAW simulant. Purolite A530e was selected as it measured the highest K_d for Tc and SIR-110-MP for the high K_d for both Tc and I in the original tank waste tests. The K_d values from these measurements (compared with the final equilibrium concentration in the test, C_e) are presented on a log–log scale in Fig. 1; the AP-105/AP-107 Tc and I feed concentrations are shown in vertical dashed lines. Between 0.005 and 5 mg/L, the K_d values were essentially constant (flattened portion of the curve). The SIR-110-MP measured larger K_d's than the A530e across the tests, with the difference being larger at lower concentrations. The expected concentrations of Tc and I in the tank waste are < 10 mg/L and < 1 mg/L, respectively and it can be expected that the SIR-110-MP would have better performance of the two resins. When coupled with the observation of the SIR-110-MP possibly removing some of the non-iodide fraction of the iodine the SIR-110-MP shows the most promise for the removal of Tc and I. These results also highlight the selectivity for Tc and I as the resins retained capacity for increasing concentrations of these elements in the high ionic strength of the LAW simulant.

Isotherm fits were also performed on the varied concentration batch test data, Fig. 2. The fitting parameters for the Freundlich and hybrid isotherms are given in Table 6, the Langmuir isotherm poorly fit the data ($R^2 < 0.5$). From the hybrid isotherm maximum capacities of 24 mg_{Tc}/g_{resin} (Tc) and 76 mg_I/g_{resin} (I) were calculated for the A530e while the SIR-110-MP data calculated 40 mg_{Tc}/g_{resin} (Tc) and 127 mg_I/g_{resin} (I). Based on these fits the Tc K_d at the feed concentration would be 656 mL/g for the A530e and 1504 mL/g for the SIR-110-MP, while the iodine would be 22 mL/g for the A530e and 36 mL/g for the SIR-110-MP The dataset may be limited in a lack of high concentration values, that would be well beyond projected tank waste concentrations of both Tc and I. Performing higher concentration tests of Tc would skew the chemistry of the simulant as the preparation of the solution occurs with a concentrated Tc solution that caused a 10 % dilution at the highest test concentration used.

Table 5

Summary of the adjusted K_d's measured during batch contact tests of the resins in a mixture of AP-105/AP-107 Hanford Tank Waste. The concentrations were adjusted to subtract the inventory of alternate species of Tc and I present in the tank waste.

Resin	Tc K_d (mL/g)	RPD	I K_d (mL/g)	RPD
Purolite A530e	>5857	–	65	2
Purolite A532e	1404	15	52	10
Purolite PGW6002e	863	36	61	6
ResinTech ASM-10-HP	306	4	31	11
ResinTech SIR-110-MP	17,864	119	2349	43
SuperLig 639	489	10	12	11
DOWEX 21K XLT	532	3	70	5
ABEC2000	35	1	4	17

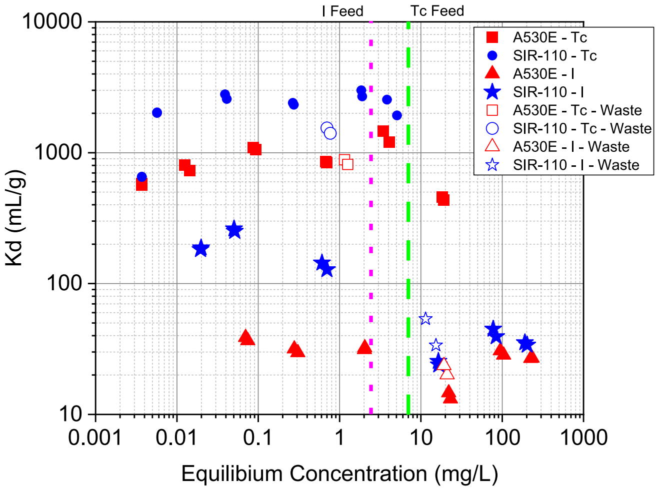

Fig. 1. Comparison of the Tc and I K_d measured in batch tests in LAW simulant (full symbols) or the AP-105/AP-107 mixture (hollow symbols). The vertical dashed lines are the concentration of Tc (green) and I (magenta) in the AP-105/AP-107 mixture. All replicate samples are shown on the plot. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.3. Column tests

A column test using SIR-110-MP and 5.2 L of AP-105/AP-107 was performed with a BV of 6 mL and processing rate of 1.9 BV/h based on the processing rate of the TSCR system at Hanford. The column effluent samples were measured for Tc and I against the BV of AP-105/AP-107 tank waste processed, Fig. 1. Fitting parameters for the column are given in Table 6. After 713 BV had been processed the AP-105/AP-107 mixture was exhausted and the column test was terminated. In the early samplings of the column, <50 BV, the effluent concentrations are <the base concentration of I, indicating some removal of iodine is occurring. Based on the batch contact tests iodide was the likely species removed with an alternate species of iodine remaining in the waste sample, and a similar process likely occurred in these early samplings.. Fitting of the effluent data predicted 50 % breakthrough after 28 BV for the lead column and 50 BV for the lag column. This breakthrough represents 77 % of the predicted capacity based on the fitting of the hybrid isotherm data. However, the SIR-110-MP was able to remove Tc at the conditions

Table 6
Isotherm fitting parameters from the varying concentration batch contact tests. "Linear" values were determined from fits of the Freundlich isotherms while "Solver" values were determined using the Excel solver function.

Freundlich	Technetium (TcO_4^-)			Iodide		
	n	***K_F (mg/g) (L/mg)$^{1/n}$***	***Error***	***n***	***K_F (mg/g) (L/mg)$^{1/n}$***	***Error***
A530E – Linear	1.05	1.22	R^2 = 0.980	1.05	0.0300	R^2 = 0.990
SIR-110 Linear	0.983	2.48	R^2 = 0.997	1.36	0.106	R^2 = 0.975
Hybrid	***a_i (mg/g)***	***β (mol/L)***	***Error***	***a_i (mg/g)***	***β (mol/L)***	***Error***
A530E – Solver	24.0	3.04×10^{-4}	SQSS = 0.971	76.0	2.71×10^{-2}	SQSS = 1.29
SIR-110 Solver	40.0	2.15×10^{-5}	SQSS = 2.95	127	2.85×10^{-2}	SQSS = 2.11

SQSS = square root of the sum of squares.

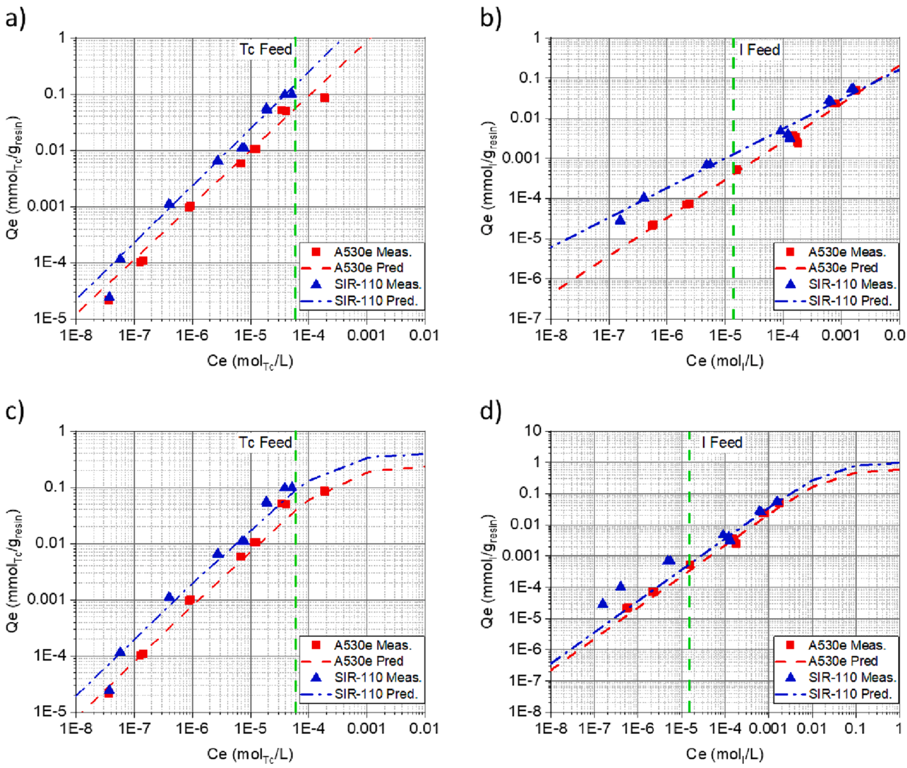

Fig. 2. Comparison of the Freundlich isotherm fit for a) Tc and b) I and the hybrid isotherm for c) Tc and d) I from batch contact tests of the A530e and SIR-110-MP resins in LAW simulant. The green dotted line in each plot shows the concentration of Tc or I in the AP-105/AP-107 mixture. All replicate samples are shown on the plots and the RPD between the replicates was < 1% in all samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

evaluated. The lead column was fit to show 50 % breakthrough after 641 BV were processed, while the breakthrough on the lag column only initiated at the final sampling limiting the predictive power for the lag column analysis. Lag breakthrough would be expected to be close to ~1280 BV based on the lead column data, but the prediction on the limited lag column dataset was 2417 BV. Prior work on Superlig 639 processing Hanford waste samples would measure 50 % breakthrough at ~200 – 300 BV processing [73,79]. It is likely that the flow rate selected did not allow for adequate residence time in the column due to mass transfer limitations for the exchange sites in the SIR-110-MP. Future studies to evaluate the impact of changing flow rate and concentrations in the column influent are planned when opportunistic tank waste samples are made available (See Fig. 3 and Table 7).

Following processing of the AP-105/AP-107 waste the NaOH displacement collection measured 1630 μg/L I and 490 μg/L Tc. The DDI displacement collection measured 58.7 μg//L I and 6.0 μg/L Tc suggesting that the I on the resin can be displaced while the Tc remains. The final flush collection measured 29.8 μg/L I and 4.6 μg/L Tc. This retention of Tc upon flushing indicates the resin stability during the two-week column test. Photos of the resin beads following contact in LAW simulant and after the column test can be found in Figs. S2 and S3 in the Supplemental information. The only visible change in the resin was a color change, likely due to minor Cr uptake. The effluent concentrations of other species of interest form the lead column are shown in Fig. 2 and full column effluent concentrations are presented in Table S4. Just as in the batch contact tests there was no measurable change in nitrate, nitrite, chromium, and sulphate concentrations (due to the concentrated nature of the waste these values ranged ± 10 % which is within the presumed analytical experimental error). While boron and silicon saw minor removal during the test. In this work the SIR-110-MP showed better performance for Tc removal than prior tests and was able to sustain Tc removal in the presence of competitors that hinder other removal processes (nitrate, nitrite, chromium) (See Fig. 4).

Table 7
Fitting parameters for the column test of SIR-110-MP using the AP-105/AP-107 mixture.

Column	k_1	$k_2 \times z$	BV to 50 % C/C$_0$
Tc Lead	105	6.1	641
Tc Lag	357	6.8	2417*
I Lead	26	1.1	28
I Lag	34	1.5	50

* There may not have been sufficient data on the lag column to reasonably predict breakthrough.

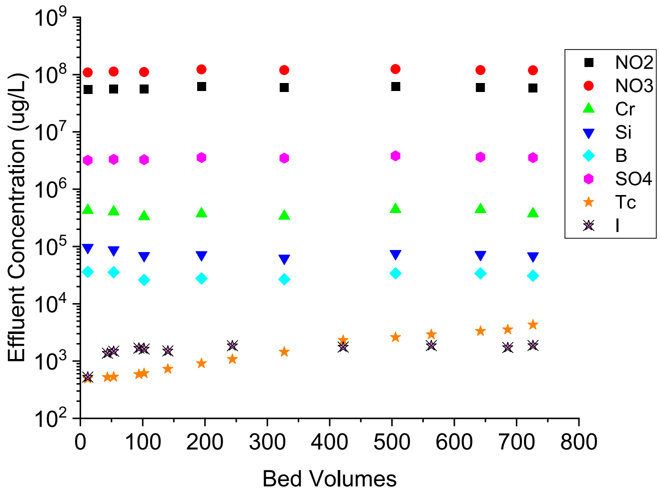

Fig. 4. Effluent concentrations of other possible competing species for Tc and I anions during the column test of SIR-110-MP.

3.4. *Column effluent characterization*

The effluent from the column test was characterized to identify the species of Tc and I that are not removed by the resins. NMR was used to detect the presence of Tc in odd-oxidation states [80]. The resulting ^{99}Tc spectra of the column feed and effluent are shown in Fig. 5. The feed spectrum contained a strong signal for Tc(VII)O_4^- at − 5.0 ppm which was absent in the effluent. No species with odd Tc oxidation states lower than +7 were observed in the unaltered feed or effluent solutions. These results indicate that TcO_4^- was removed in the column test leaving only Tc in the form of non-pertechnetate species in the decontaminated waste sample.

EPR spectra where collected at near liquid helium temperatures (7–8 K) in order to detect both S = 1/2 (Tc(II) and Tc(VI)) as well as S = 3/2 (Tc(IV)) species, Fig. 6. A spectrum was also collected at a higher temperature (80 K) where only S = 1/2 species would have a signal (due to the fast relaxation of S > 1/2 species). A standard sample (strong pitch) was run with the same parameters for quantitation. This spectrum was compared with known spin concentration standards and a conversion factor to compute Tc concentration from the area of the integrated spectrum.

Overall, spectra of the two samples were similar with only subtle differences, these are shown in a zoomed in view in Fig. 6 B and Fig. 6C. A peak in the low field region (1600 G) is commonly associated with Fe (III), while free radicals and most metals appear in the g = 2 region and this peak decreased in the effluent. A second signal at ~2900 G also disappeared in the effluent.

Tc(IV) oxides tend to be insoluble, their spectrum is very broad (2000 G). Soluble Tc(IV) molecular species have been reported, however

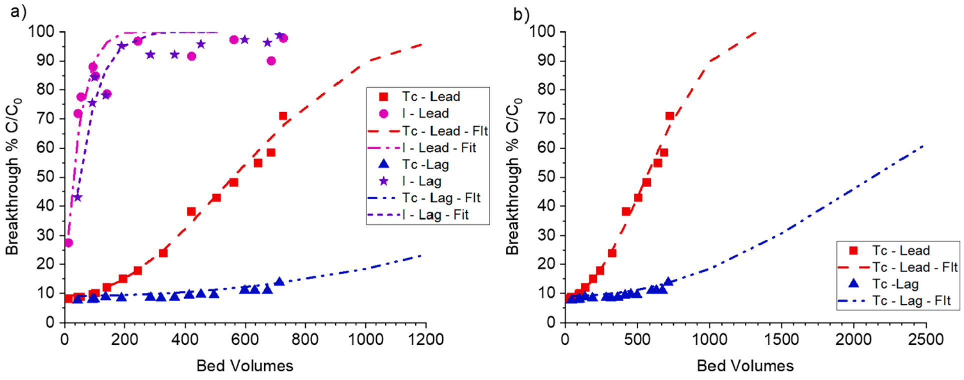

Fig. 3. a) Tc and I effluent concentrations as a function of bed volumes passed for SIR-110-MP processing the mixture of AP-105 and AP-107 tank waste at a rate of 1.9 BV/h (6 mL BV). The lines are the column fits, b) Tc only plot extended out to show the projected lag column behavior.

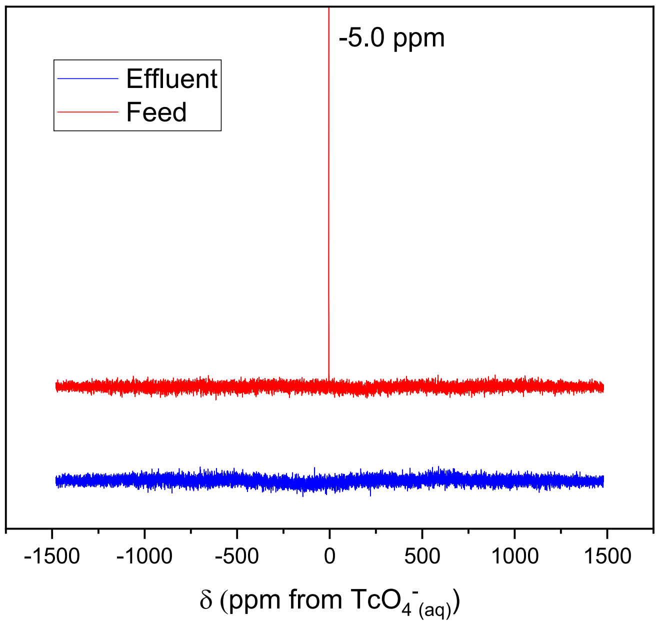

Fig. 5. ^{99}Tc NMR spectra from the SIR-110-MP column test feed (top) and effluent (bottom).

only at temperatures below 10 K [10]. Since the major features of the samples' spectrum are unchanged at 80 K, Tc(IV) is likely not their origin. Both $S = 1/2$ Tc oxidation states display a spectrum with a characteristic patterns of 10 equally spaced lines as a result of hyperfine coupling to the $I = 9/2$ ^{99}Tc nucleus [81]. These patterns are not apparent in the spectra. However, these lines could be obscured by a dispersion of Tc molecular species (each with a slightly different spectrum) or by overlapping spectra from other EPR active paramagnetics in the sample. If we assume the most generous case – that all of the EPR spectrum between 3000 and 3500 G is due to Tc – then the samples contain at most 0.9 +/- 0.5 ppm EPR active Tc (probably Tc(VI) oxidation state), close to the measured effluent Tc concentrations. With the decreasing signal seen at 1600 G and 2900 G being removed in the effluent sample it is likely that the resin can remove some this Tc(VI) species, and the breakthrough Tc is attributed to a separate species.

The feed and effluent waste samples were analyzed with fluorescence spectroscopy and the resulting excitation and emission scans are shown in Fig. 7. The signal in the feed sample in both the excitation and emission scans was higher than that in the effluent, suggesting removal of a species. The excitation max was at 465 nm. A weaker emission response was seen at 500 nm by exciting the tank waste at 275 nm and 365 nm. The excitation of a Tc(I)-gluconate has been previously observed at 506 nm and a Tc(V) gluconate has shown at 535 nm [82]. In these scans the emission max was at 505 nm. Suggesting a possible Tc(I) species present as the breakthrough.

This analysis is the first identification of a non-pertechnetate fraction of Tc from the waste in tanks AP-105 and AP-107. Based on the breakthrough in the column tests the non-pertechnetate form accounts for ~8 % of the Tc inventory. Previously non-pertechnetate has only been identified in 8 of the 177 tanks at Hanford (with two tanks investigated but showed only pertechnetate) with the amount of non-pertechnetate ranging from 8 % and 80 % in individual tanks (the highest being in tanks 241-AN-102, 241-AN-107 and 241-SY-103). The identification of the non-pertechnetate species has only been made on samples from tanks SY-101 [83]for a Tc(I) carbonyl species and in AN-102 [10]where both Tc(I) and Tc(IV) species were identified along with Tc(VII). The non-pertechnetate behaves differently than pertechnetate for resin uptake but may also have different behavior in grout waste forms. Further work is planned to positively identify the non-pertechnetate species, both the species that appears to interact with the resin (possibly Tc(VI) based on the EPR) and the species that are not removed (a combination of Tc(VI) based on EPR and Tc(I) from fluorescence measurements).

Speciation analysis of the feed, early column effluent sample and post-batch contact solutions (Superlig 639) showed the waste to only contain iodide and no iodate was measured (<20 μg/L). This finding suggests that the fraction of iodine not captured by the resins in batch contact tests is an organo-iodide species, which has been suggested to comprise a fraction of the Hanford iodine inventory [84]. The SIR-110-MP was able to remove a portion of this organo-iodide in successive batch tests, indicating that the resin can uptake some of the organo-

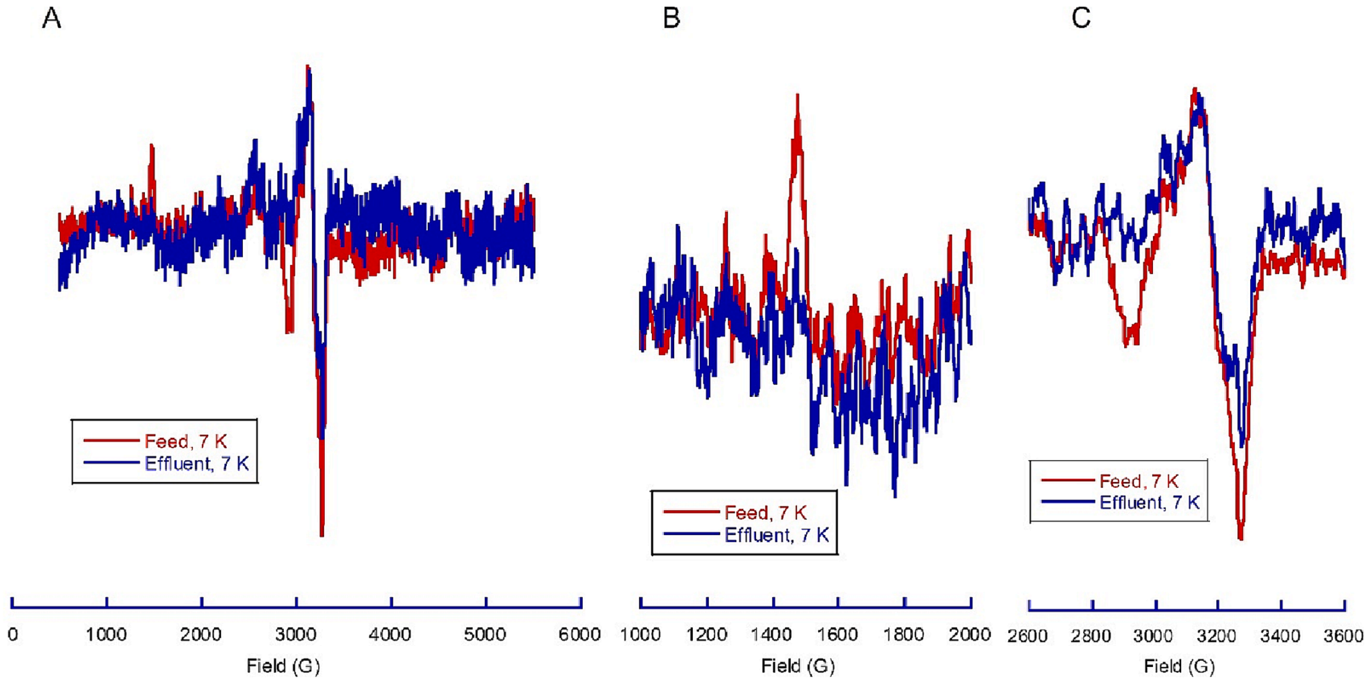

Fig. 6. EPR spectra collected at 7 K. A) Full field sweep. B) Low field region. C) g = 2 region.

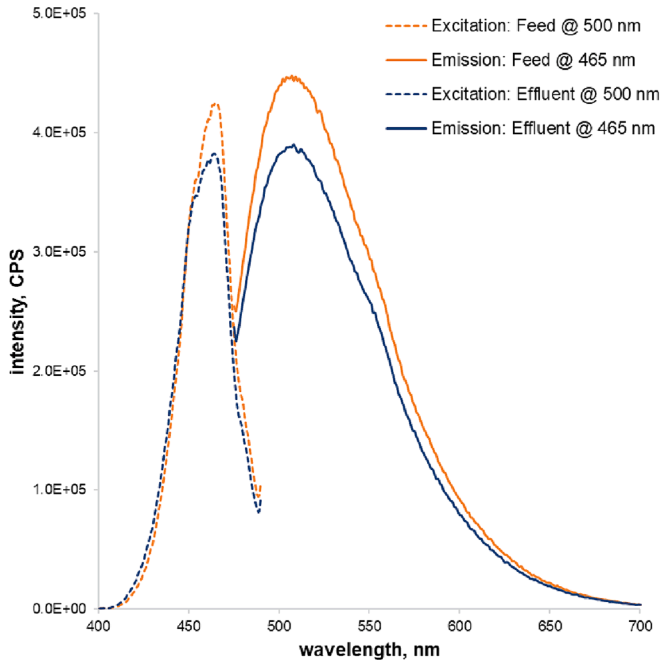

Fig. 7. Excitation and emission scans for the AP-105/AP-107 tank waste mixture prior to column testing (feed) and the column effluent.

iodide but multiple organo-iodine species may be present.

4. Conclusions

In conclusion, the simultaneous removal of both Tc and I from actual Hanford tank waste was demonstrated for the first time using a series of commercially available ion exchange resins. The best performance was observed for the SIR-110-MP resin, and further effort to optimize the resin performance in column deployment is needed and testing is planned for other tank waste samples. The work also showed that a fraction of the I in the tank waste was a not discrete iodide or iodate and is likely an organo-iodide species that does not interact with the resin. A non-pertechnetate component of tanks AP-105 and AP-107 was identified for the first time as well and some of the non-pertechnetate species were not captured by the resin in testing, with evidence of a Tc(VI) species in the wastes for the first time. Further work is planned to positively identify these alternate species. This work highlights that radionuclide removal can be employed in Hanford tank waste to lessen inventories prior to treatment and disposal as long as the loaded resins also have a pathway to disposal.

Credit authorship contribution statement

R. Matthew Asmussen: Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Amy M. Westesen:** Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Christian Alvarez:** Investigation, Data curation. **Reid A. Peterson:** Writing – review & editing, Formal analysis, Conceptualization. **Elsa Cordova:** Investigation, Data curation. **Herman Cho:** Investigation, Data curation. **Shirmir D. Branch:** Investigation, Data curation. **Eric D. Walter:** . **Gabriel B. Hall:** Investigation, Data curation. **Andrew M. Carney:** Investigation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: R. Matthew Asmussen reports financial support was provided by US Department of Energy Office of Environmental Management. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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