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TECHNETIUM-99 REMOVAL FROM PROCESS SOLUTIONS AND CONTAMINATED GROUNDWATER

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ABSTRACT

The predominant form of technetium under oxic conditions is the pertechnetate anion (TcO_4^-), which is highly soluble in water and readily mobile in the environment. Technetium-99 is of particular concern because of its persistence and mobility.

Various equipment decontamination and uranium recovery operations at the Portsmouth Gaseous Diffusion Plant generate a "raffinate" waste stream characterized by toxic heavy metals, high concentration of nitric acid, and low levels of radionuclides (^{235}U and ^{99}Tc). Dilution and adjustment of solution pH to a value of 8.2 to 8.5 precipitates a heavy-metals-sludge and a filtrate. The removal of ^{99}Tc from these waste streams and from contaminated groundwater can be accomplished using anionic ion-exchange resins.

Batch equilibrium and packed column breakthrough and regeneration studies were performed using inorganic sorbents and organic ion-exchange resins (Dowex SRB-OH and Reillex resins). These studies were performed on actual and surrogate raw raffinates, filtrates, and surrogate groundwater samples. The experimental conditions were chosen to closely represent the actual process.

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INTRODUCTION

Technetium-99 (^{99}Tc) undergoes radioactive decay by low-energy (0.29 MeV) beta emission, with a half-life of 213,000 years and a specific activity of 17.0 mCi/g. It is formed with high yield (~ 6%) in the thermal neutron fission of ^{235}U. Typical low enrichment light-water nuclear power reactors may yield 27.5 Kg (467 Ci) of ^{99}Tc per 1000 MW-year of electric energy produced (1). ^{99}Tc from the nuclear fuel cycle may enter the environment as a result of disposal of aqueous wastes or during the separation and recovery of spent nuclear fuels (2). The predominant form of Tc under oxic conditions is the pertechnetate anion [TcO_4^-] (3), which is highly soluble in water and it is of particular concern because of its persistence and mobility (1,2,4). ertain reduced forms of Tc [e.g. hydrolyzed Tc(IV) oxides (5)] have limited solubility.

^{99}Tc entered the gaseous diffusion enrichment plants as an impurity in uranium oxide recovered from spent fuels generated in government owned reactors. The multi-step conversion of the oxide to uranium hexafluoride also produced a volatile technetium fluoride that accompanied the uranium hexafluoride (6). This UF_6 was subsequently fed to the enrichment cascades where the ^{99}Tc remained adsorbed on surfaces. Some ^{99}Tc is periodically removed from these surfaces by wet-chemical decontamination for personnel protection when equipment is removed for maintenance or repair. At the X-705 facility of the Portsmouth (Ohio) Gaseous Diffusion Plant (PORTS) decontamination is achieved with nitric acid, which solubilizes uranium residues and ^{99}Tc. Uranium is recovered by solvent extraction, with the majority of the Tc remaining in the aqueous raffinate waste. Composition of the raffinate waste stream varies, but is generally characterized by toxic heavy metals, high concentration of nitric acid, and relatively low levels of radioactivity (See Table 1). The treatment of the raffinate stream generally consists of i) dilution with an equal volume of water and pH adjustment to about 8.5 to precipitate the hydrolyzable heavy

Table 1. ANALYSIS OF PORTSMOUTH RAFFINATE AND FILTRATE FROM HMS PRECIPITATION OF RAFFINATE

	Concentration (mg/L)		
	Raw raffinate		
Constituent or Characteristic	Typical range[a]	Sample as Tested	Filtrate[b]
Aluminum		11,500	8.5
Barium		13.5	0.47
Cadmium		9.8	< 0.03
Chromium		66	< 0.1
Copper	15 to 360	160	< 0.04
Iron	700 to 7100	5,300	< 0.04
Lead		56.5	< 0.5
Manganese		105	< 0.01
Nickel	80 to 620	635	< 0.1
Uranium	2 to 1450	45	< 0.3
Zinc	15 to 210	150	< 0.01
Mercury		2.32	< 0.92
Nitrate	250,000 to 400,000	250,000	94,500
Sulfate		2,600	330
Technetium	0.1 to 120	34	13
Gross alpha(pCi/L)		410,000 <	< 4500
pH	< 1	0.1	8.5
Specific gravity	1.05 to 1.25	1.20	1.15

[a] Raffinate characteristics reported by Acox (7)

[b] HMS filtrate made from PORTS raffinate sample by dilution, neutralization, and filtration (1.5 L of raw raffinate yields 4.0 L of slurry, before filtration).

Table 2 . ANALYSIS OF PADUCAH GASEOUS DIFFUSION PLANT CONTAMINATED GROUND WATER (WELL 66)

Constituent or Characteristic	Range	Average	Units
Calcium	27.0-38.0	33.3	mg/L
Sodium	17.7-22.2	20.5	mg/L
Magnesium	6.9-10.6	8.8	mg/L
Total lead		<0.05	mg/L
Total iron	<0.01-1.44	0.019	mg/L
Total chromium		<0.05	mg/L
Total nickel	<0.05-0.185	0.059	mg/L
Total zinc	<0.001-0.06	0.013	mg/L
Total copper		<0.01	mg/L
Total cadmium		<0.01	mg/L
Alkalinity	46-138	98	mg/L
Chloride	20-32	26	mg/L
Sulfate	10.0-25.0	11.0	mg/L
Nitrate	2.3-9.0	6.3	mg/L
Phosphate		<2.0	mg/L
Fluoride	<0.10-0.20	0.14	mg/L
^{99}Tc	544-3670	2803	pCi/L
^{222}Rn	248-307	282	pCi/L
Uranium		<0.001	mg/L
Trichloroethylene	670-6200	3478	µg/L
PCBs		<0.10	µg/L
Color	3-11	5	Std.Unit
Conductivity	304-498	411	µmhos/cm
pH	6.1-7.2	6.5	Std.Unit
Turbidity	0.2-12	2.7	NTU
TDS	178-328	240	mg/L
TOC		<1.0	mg/L

metals, ii) filtration of the precipitation slurry to yield a wet filter cake designated as heavy metal sludge (HMS) and a HMS filtrate, iii) processing of the HMS filtrate with a strong-base anion exchange resin to remove the soluble pertechnetate ion, and potentially: iv) biodenitrification, and v) sewage disposal(7).

Because of its great mobility and accidental releases ^{99}Tc has also been detected in groundwater samples taken from some monitoring wells around uranium enrichment plants. Treatability studies, presently in progress, to remove ^{99}Tc and other contaminants (see Table 2) from on-site and off-site wells envision the use of ion-exchange resins.

MATERIALS TESTED

The inorganic sorbents and organic resins used in the present studies are briefly described in Table 3.

EXPERIMENTAL AND RESULTS

Batch Equilibrium Experiments

Figure 1 illustrates sorption isotherms for removal of soluble ^{99}Tc from HMS filtrate, using several of the more effective sorbents that were identified in testing with surrogate raffinate (8,9).

Dowex SRB-OH removes ^{99}Tc from HMS filtrate, along with a significant amount of nitrate, but was less efficient than Reillex 402. Reillex 402-I, an industrial grade of Reillex 402, was significantly less effective than the purified resin. These PVP resins have pK_a values of ~3 to 4 and thus may act as weak base anion exchangers in acidic media. In the slightly alkaline HMS filtrate, the pyridine moiety is essentially a free base, and the resin demonstrates little uptake of nitrate or other anions. The mechanism for uptake of pertechnetate is thus believed to be predominantly sorptive (10,11). Ferrous sulfides and iron metal are very efficient and inexpensive for the removal of soluble

TABLE 3. SORBENTS AND RESINS TESTED

Material Designation	Manufacturer	Characteristics
Reillex 402	Reilly Industries, Inc.	Poly-4-vinylpyridine (PVP) cross-linked with 2% divinyl-benzene.
Reillex 402-I	Reilly Industries, Inc.	Industrial grade Reillex 402.
Reillex HP	Reilly Industries, Inc.	PVP cross-linked with 25% divinyl-benzene.
Reillex HPQ	Reilly Industries, Inc.	Poly-1-methyl-4-vinylpyridine cross-linked with 25% divinyl-benzene.
Dowex SRB-OH (Dowex 1-X8)	Bio-Rad Laboratories (Dow Chemical)	Quaternary ammonium styrene-divinyl-benzene.
Greigite (8,9)	Prepared-in house	Fe_3S_4 strongly magnetic.
Iron filings(8,9)	Fisher Scientific Co.	Fe^0 degreased filings.

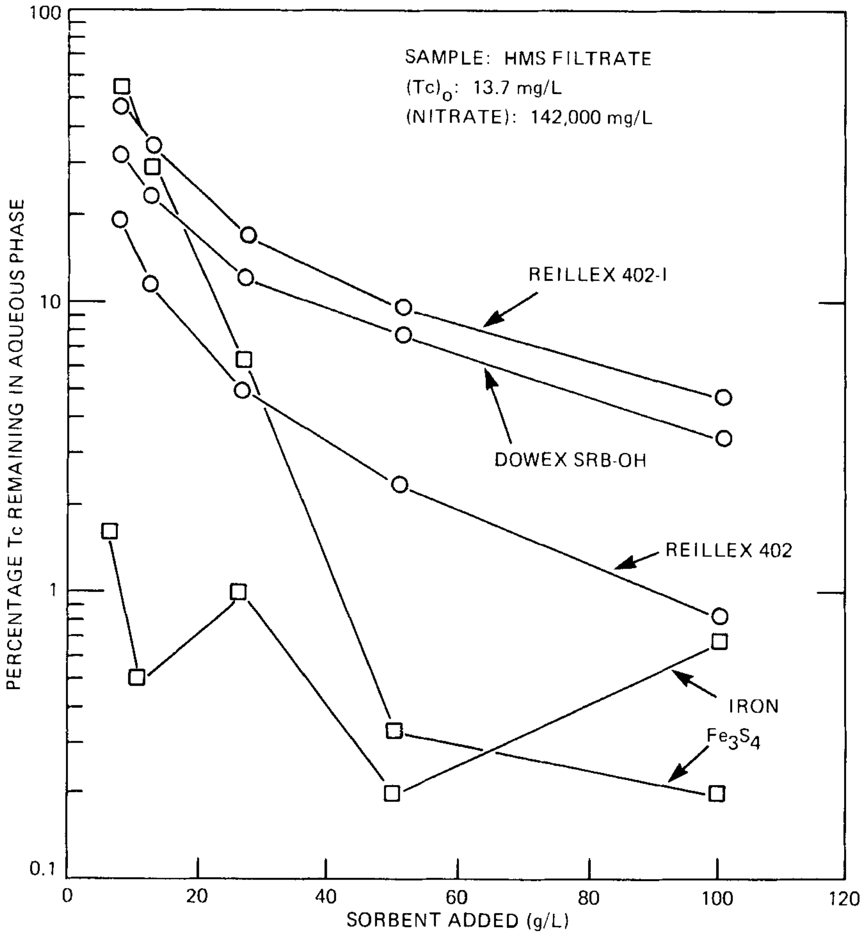

FIGURE 1. Technetium removal from HMS filtrate by selected sorbents (24-h equilibration time).

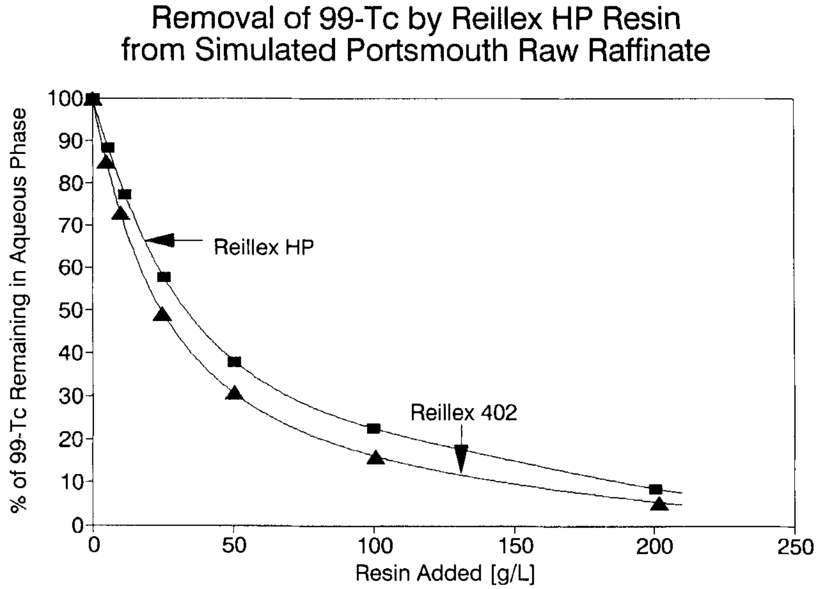

FIGURE 2. Technetium removal from raw HMS raffinate by Reillex HP and 402 resins (72-h equilibration time).

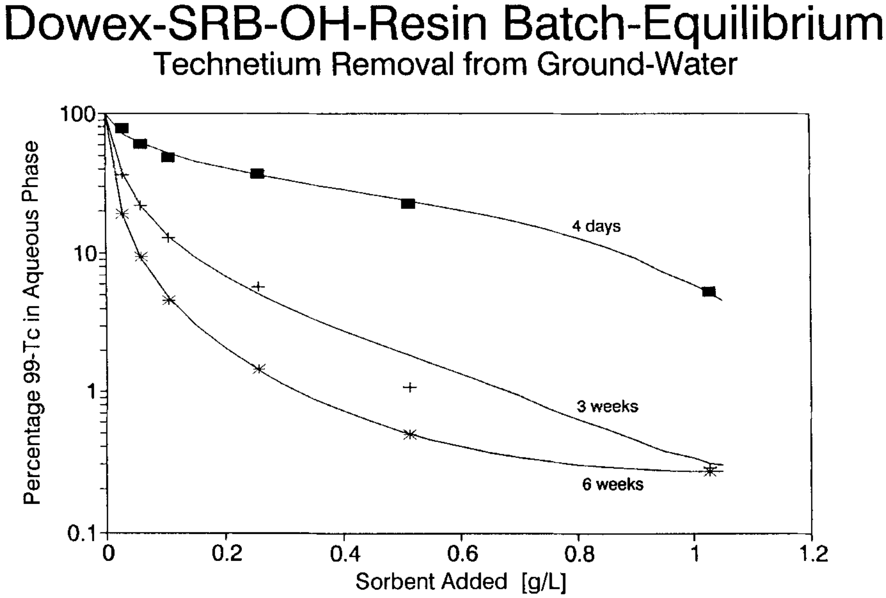

FIGURE 3. Technetium removal from simulated Paducah ground water by Dowex SRB-OH resin.

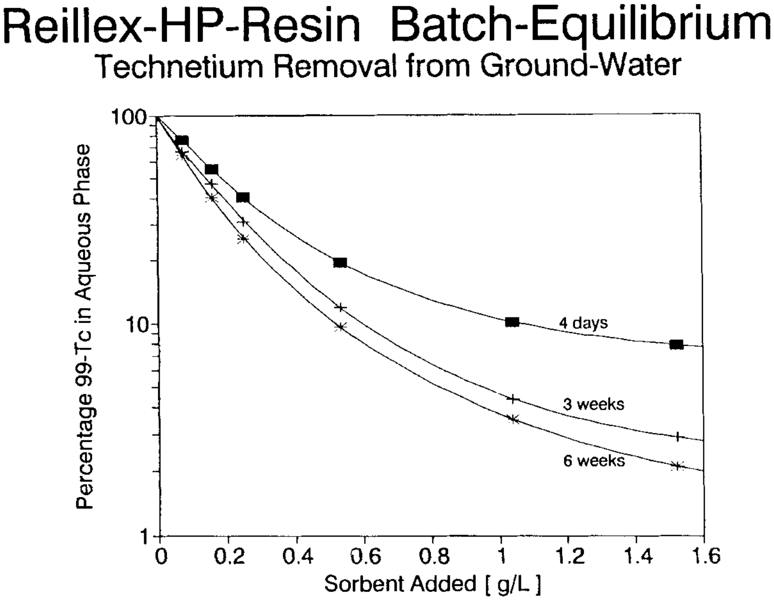

FIGURE 4. Technetium removal from simulated Paducah ground water by Reillex HP resin.

pertechnetate by sorption and reduction to less soluble forms of Tc. Several ferrous sulfides were previously tested for removal of soluble ^{99}Tc (predominantly by reduction to insoluble Tc(IV) and Tc_2S_7) (8,9). The removal efficiency correlated with the redox potential (Eh) of the solution, with Greigite (Fe_3S_4) being the best sorbent. The use of iron or ferrous sulfide for ^{99}Tc removal is advantageous in terms of economy and waste minimization, however the relatively slow kinetics may be a disadvantage for the continuous treatment of relatively large volumes of slightly contaminated water.

None of the inorganic sorbents, nor the strong-base Dowex-SRB resin are suitable to remove ^{99}Tc from the acidic raw raffinate. Batch equilibrium tests (see Figure 2) using PVP resins (Reillex 402 and Reillex HP) and surrogate raw raffinate indicate that PVP resins

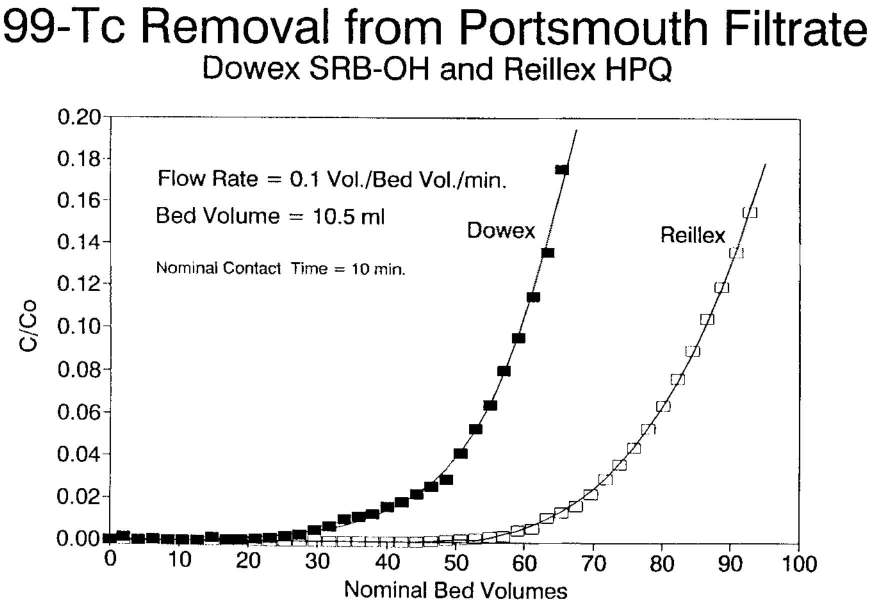

FIGURE 5. Technetium removal from simulated Portsmouth filtrate by Reillex HPQ and Dowex SRB-OH resins.

can remove ^{99}Tc from acidic solutions. However, by omparison with the results for HMS filtrate (Figure 1), it can be concluded that the efficiency is significantly diminished.

Sorption isotherms,for removal of ^{99}Tc from surrogate Paducah groundwater using small amounts of resins (Dowex SRB-OH and Reillex HP), display an unexpected long-term sorption behavior. As shown in Figures 3 and 4, the ^{99}Tc in solution is noticeably diminished after prolonged contact intervals. This behavior has no significance for the relatively short contact times involved in column-type operations. Nevertheless, it may have practical consequences for prolonged or intermittent decontamination treatments.

^{99}Tc Breakthrough in Resin Columns

Consistent with the batch equilibrium results for the HMS filtrate the PVP resins were more efficient than the Dowex resin

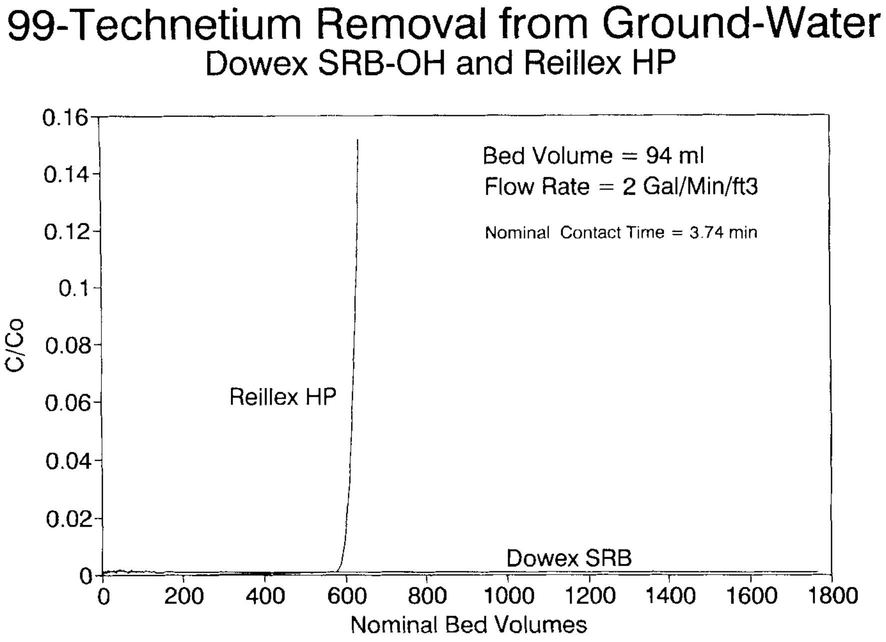

FIGURE 6. Technetium removal from simulated Paducah ground water by Reillex HP and Dowex SRB-OH resins.

for the removal of ^{99}Tc from a high nitrate solution, such as HMS filtrate (8,9). Figure 5 shows the comparison between Reillex HP and Dowex SRB-OH breakthrough behavior using a surrogate HMS filtrate.

On the other hand, for relatively diluted solutions without any significant concentration of competing anions, as in the case of the Paducah groundwater, the observed behavior reversed. As shown in Figure 6, the Dowex SRB-OH is noticeably more efficient for ^{99}Tc removal than the PVP resin.

One significant aspect of the ^{99}Tc sorption on organic ion-exchange resins is the great difficulty of its subsequent desorption. Only the strongest reagents such as perchloric acid can remove a sizable fraction of the Tc. Figure 7 shows the displacement of ^{99}Tc from Reillex HP resin by 1 M sulfuric acid. Other reagents

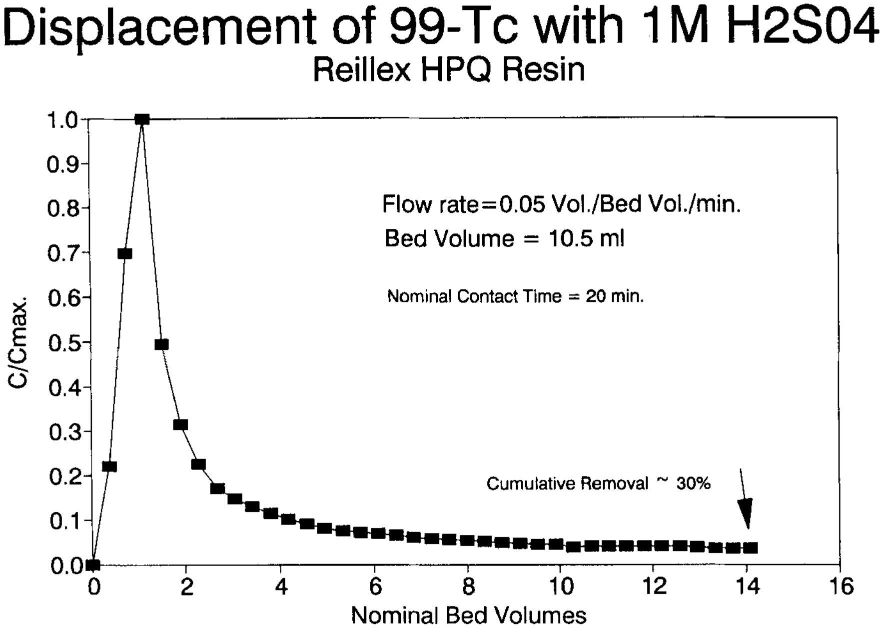

FIGURE 7. Displacement of ^{99}Tc with 1 M sulfuric acid from Reillex HPQ resin.

such as sodium citrate, sodium hydroxide, and ammonium hydroxide are even less effective (12). As a result, it appears there is no practical way to regenerate and reuse the laden resins and they must be discarded after they reach the maximum capacity. Among the treatment options for the spent resins, the most commonly used are grout solidification (12,13) and dewatering (14).

CONCLUSIONS

Several sorbents were investigated for their ability to remove soluble ^{99}Tc from process solutions and contaminated groundwater. Polyvinylpyridine resins were found to be more effective than standard quaternary ammonium resins for removing TcO_4^- in the presence of competing anions. Inorganic sorbents such as iron filings or powder and Fe_3S_4 offer a great potential as an inexpensive and effective means to remove soluble ^{99}Tc. Development is necessary to prepare materials with higher surface area and larger particle size to allow their use in continuous operations. Strong quaternary ammonium resins were found to be more effective to remove TcO_4^- from relatively soft contaminated groundwater.

A slow sorption process of TcO_4^- by the organic ion exchange resins was observed in addition to a relatively fast sorption mechanism. This behavior has practical consequences for prolonged or intermittent operations.

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