Treating More with Less: Hybrid Ion Exchange Resins for the Remediation of Comingled Groundwater Contaminants

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Background

The US Department of Energy's Hanford Site contains legacy nuclear waste generated during plutonium production. Discharged waste has entered the subsurface and created overlapping contaminant plumes that are challenging to remediate.

Groundwater beneath the Hanford 200 West (200W) Area has comingled plumes of uranium (U), technetium-99 (Tc-99), hexavalent chromium (Cr(VI)), and iodine-129 (I-129).

Pump and treat (P&T) operations in 200W use ion exchange (IX) resins Dowex 21K and Purolite A532E to treat U and Tc-99, respectively. Limited or no Cr(VI) or I-129 is removed. P&T facilities in the 100 Area use SIR-700-HP for Cr(VI) removal.

Hybrid IX resins can remove multiple contaminants through a combination of IX and other mechanisms (redox, precipitation, and sorption reactions) but have not been studied under 200W groundwater conditions.

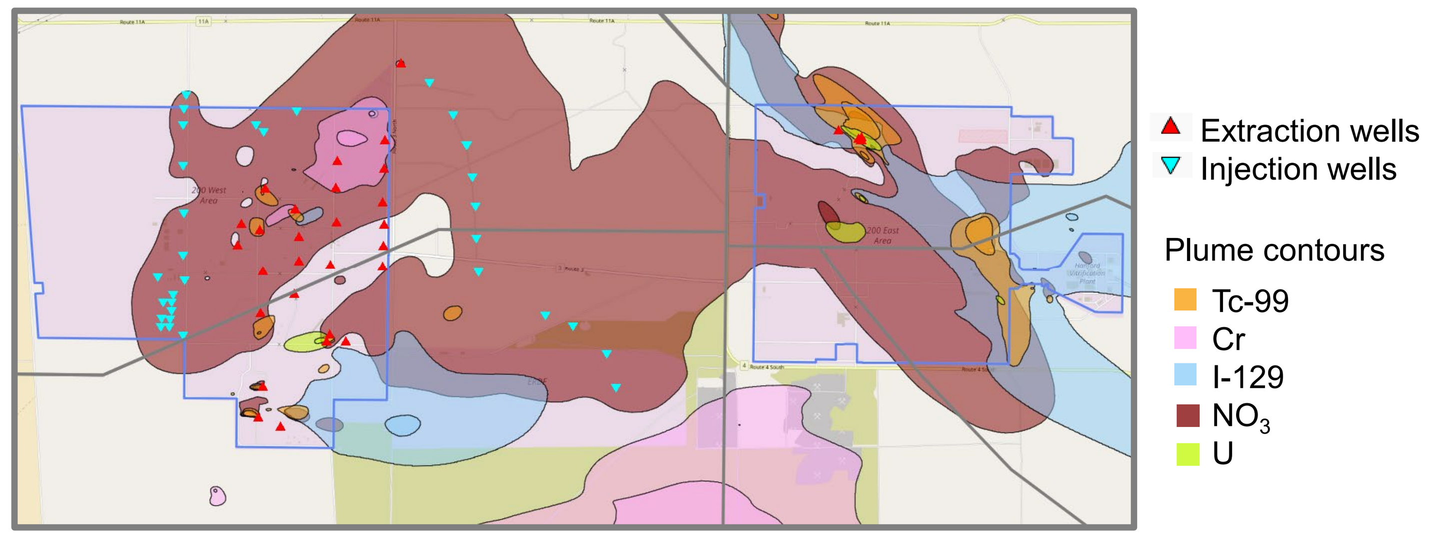


Figure 1. Hanford's 200 area groundwater plume map (as of 2023) from SOCRATES[1]. Expanding P&T operations will include plumes containing Tc-99, I-129, U, Cr(VI).

Types of Hybrid IX Resins	
Incorporated with Metal (Oxy)hydroxides	Contain Redox-Active Functional Groups
• Metal (oxy)hydroxide dispersed throughout the polymer • Cerium, iron, bismuth, and manganese-based hybrid resins	• Secondary alcohol group for redox sensitive contaminants

Goals:

1. **Determine if hybrid IX resins improve treatment of comingled contaminants in simulated 200W groundwater (i.e., U, Tc-99, Cr(VI), and incidental removal of I-129) by removing more mass and/or multiple contaminants.**
2. **Determine the secondary mechanisms driving iodine removal to aid predictive modeling of incidental iodine uptake.**

Methods

Strong base anion (SBA), weak base anion (WBA), and hybrid resins listed in Table 1 were used in the batch and column tests described below. Simulated groundwater (SGW) was used in all tests.

- Multi-contaminant column test in SGW + NO_3^- (**MCCN**): Establish breakthrough curves for U, Tc-99, Cr(VI), iodine (as IO_3^-).
- Concentrated U and Cr(VI) column test in SGW + NO_3^- (**UCrC**): Establish Cr(VI) and U breakthrough curves for SIR-700 resin only.
- Iodine-only batch test in SGW + NO_3^- (**IBSN**): Evaluate I removal mechanism in the presence of NO_3^-.
- Iodine-only column test in SGW (**IOC**): Evaluate Tc, U, and Cr(VI)'s impact on I removal without NO_3^-.

Solid phase characterization techniques: X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Raman, X-ray Absorption Near Edge Structure (XANES), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS)

Table 1. IX resins used during MCCN, UCrC, IBSN, and IOC testing.

SBA Resin	Type	Functional Group(s)	Tests
A532E	I, Gel	Trihexylamine, Triethylamine	MCCN
SBG1	I, Gel	Trimethylamine	IBSN
SIR-110-MP	I, Macroporous	Tributylamine	MCCN, IBSN, IOC

WBA Resin	Type	Functional Group(s)	Tests
SIR-700-HP	Weak Base, Gel	Tetraethylenepentamines	UCrC, IBSN

Hybrid Resin	Parent Resin	Hybrid Metal	Tests
SIR-110-MP-Ce	SIR-110-MP	Ce	MCCN, IBSN, IOC
SBG1-Ce	SBG1	Ce	MCCN, IBSN, IOC
CHM-110-A	SIR-110-MP	Ce	MCCN, IBSN, IOC
SIR-110-MP-Fe	SIR-110-MP	Fe	MCCN, IBSN, IOC

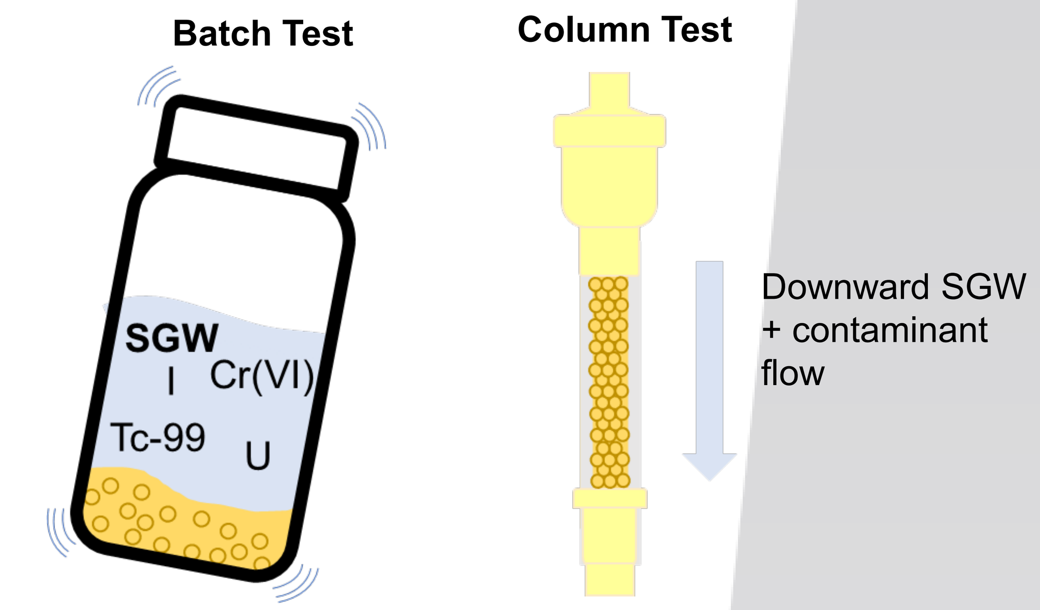
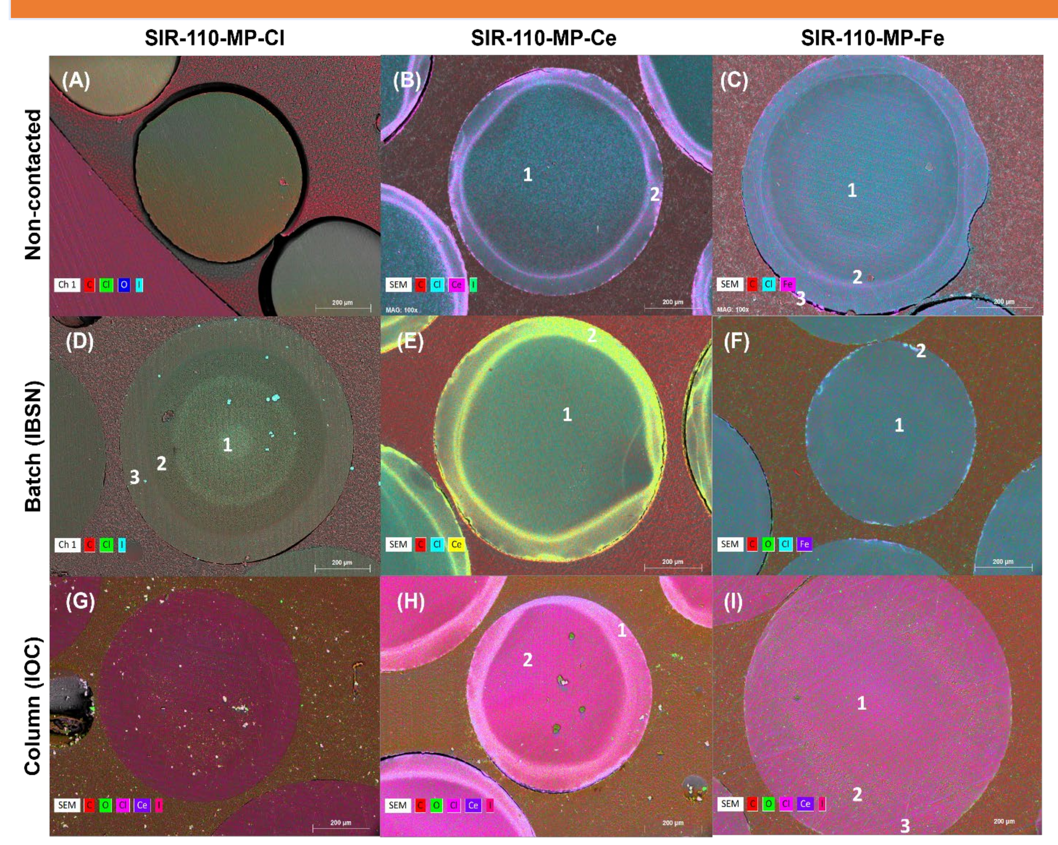


Figure 2. Schematic of typical setups for batch (*left*) and column (*right*) tests. The batch tests are placed on a shaker for 72 hours while the column tests have a constant 45 mL/hr flow rate.

Results – Iodine Uptake Mechanism



Key results from IBSN and IOC tests:

- No significant alteration of resins observed during iodine uptake.
  - Backbone and functional groups unaltered (FTIR/Raman).
  - Metal phases unchanged, including oxidation state (XRD, XANES).
- No I^- was detected, so IO_3^- reduction is not a removal mechanism (XPS).
- Iodine uptake greater with Ce and Fe metal hybrids (SEM-EDS), suggesting iodine adsorption on these phases.

Figure 3. SEM-EDS imaging of select resins from IBSN and IOC tests. Visible hybrid precipitation ring is present in SIR-110-MP(-Ce, Fe).

Conclusions

1. SIR-700 and SIR-110-MP-Ce could achieve effective removal of Cr(VI), U, and Tc-99 at the Hanford Site. Incidental iodine removal is also possible using SIR-110-MP-Ce.[3]

2. This study suggests that IO_3^- is removed by adsorption processes and that the efficacy of this removal mechanism is influenced by the distribution of the metal (oxy)hydroxide phase throughout the resin.[3]

- Removal of IO_3^- by IX sites in all the resins was only efficient in DDI, highlighting anions outcompeting IO_3^- for IX sites.
- Metal (oxy)hydroxide phases can remove IO_3^- by a different mechanism when IX is not favorable.
  - No change in resin backbone structure or metal oxidation state occurs, suggesting the removal of IO_3^- does not occur via chemical transformation and is likely removed via adsorption to the metal (oxy)hydroxide phase.

Results – Comingled Contaminant Uptake

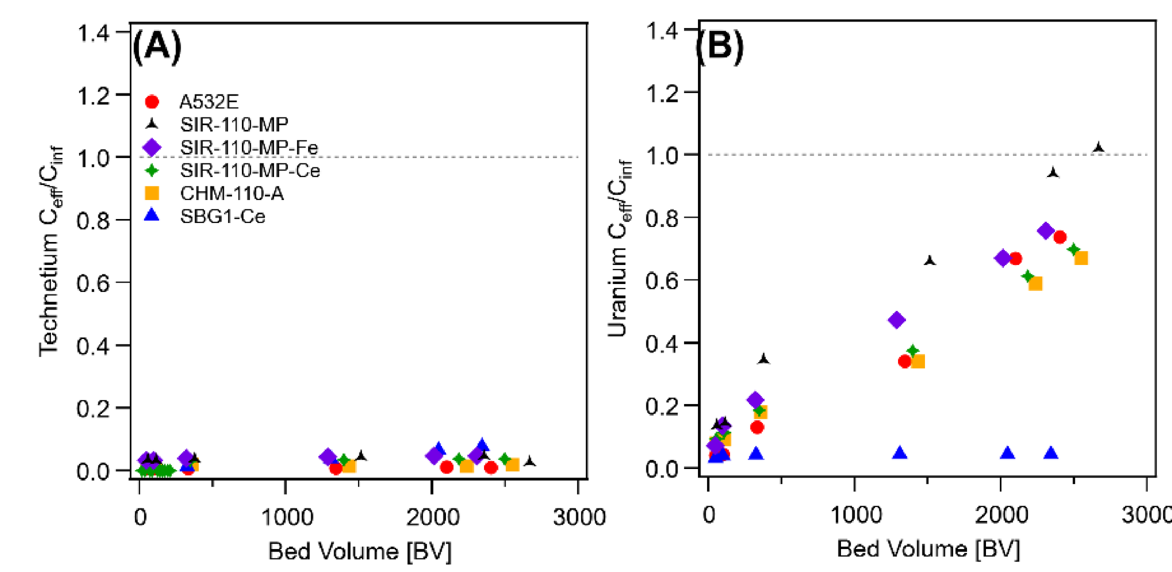
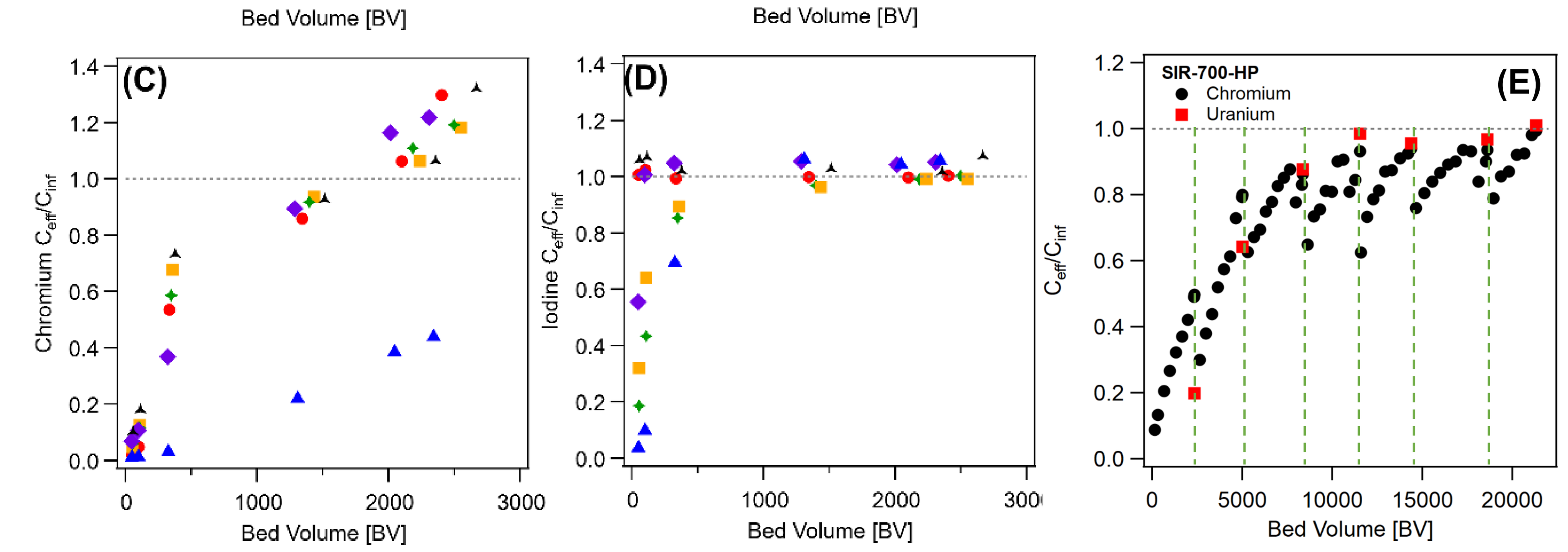


Figure 4. (A) Tc, (B) U, (C) Cr(VI), and (D) iodine (as IO_3^-) breakthrough for resins during MCCN test. (E) Cr(VI) and U breakthrough curve for UCrC test. Gray dashed lines are positioned at $C_{eff}/C_{inf} = 1$ where complete breakthrough occurs. Green dashed lines represent stop flow (soak) events in the UCrC test.



MCCN:

- Overall, the Ce resins performed well for all contaminants (Tc, U, Cr(VI), iodine).
- Iodine breakthrough occurred in all resins, SBG1-Ce, SIR-110-MP-Ce performed best.
- Tc-99 breakthrough did not occur in any resins.
- U and Cr(VI) breakthrough occurred for all resins except for SBG1-Ce.

UCrC:

- Cr(VI) is reduced to $Cr(III)(OH)_3$, U is removed by surface complexation with sulfate at IX sites = no competition between U and Cr(VI).[2]
- Cr(VI) removal is kinetically hindered at this flow rate and requires a "soak" step for complete reduction.
- Cr(VI) and U breakthrough occurs at similar bed volumes.

Citations:

1. Johnson C.D., D. Appriou, T.P. Franklin, J.L. Fanning, P.D. Royer, P.K. Tran, and S.N. Baur, et al. 2024. "SOCRATES Software Release 5.0." PNNL-SA-202633.
2. Saslow S. A., et al. "Accumulation mechanisms for contaminants on weak-base hybrid ion exchange resins" *Journal of Hazardous Materials*, Vol. 459, 2023, DOI 10.1016/j.jhazmat.2023.132165.
3. Saslow S. A., et al. "Hybrid resins for simultaneous removal of multiple groundwater contaminants" *Journal of Environmental Chemical Engineering*, Vol. 13, 2025, DOI 10.1016/j.jece.2025.116721.

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