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One Resin to Rule Them All: Hybrid Resins Simultaneously Remove Multiple Contaminants from Groundwater

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U.S. DEPARTMENT OF ENERGY BATTELLE

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Talk Preview

- Lab-scale ion exchange (IX) hybrid resin tests to evaluate co-contaminant remediation performance for pump-and-treat (P&T) facilities
- Challenges for P&T at the Hanford Site (case study)
  - Co-contaminants
  - Variable influent chemistry
- Hybrid resin remediation performance
  - Batch experiments
  - Column experiments
  - Solid phase characterization

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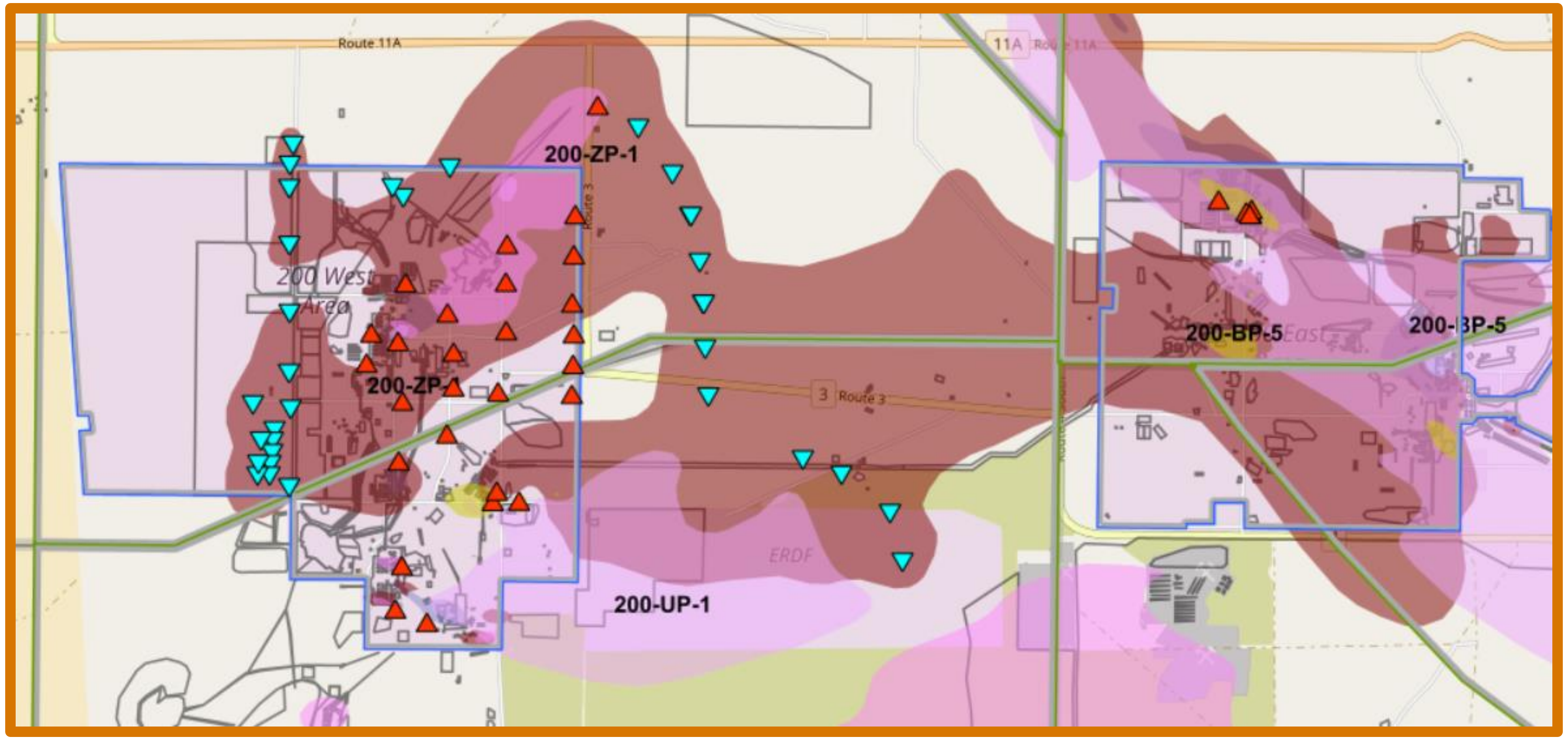
Hanford Site Central Plateau Contaminant Plumes

- Significant overlap of contaminant plumes
- Potential for competition in treatment of contaminants (Tc, U, Cr(VI), and I) and major groundwater ions (e.g. NO_3^-)

▲ Extraction wells
▼ Injection wells

Plume contours

- Tc-99
- I-129
- NO_3
- U
- Cr



Plume Map generated using SOCRATES (pnnl.gov/projects/socrates), a suite of online tools that support remedy decisions, optimization, and exit strategies

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P&T Operations in the Hanford Site Central Plateau

200W P&T Facility

The assumed anion <u>speciation of the CoPCs:</u>

U: $UO_2(CO_3)_x^{2x-2}$

Tc: TcO_4^-

Cr(VI): CrO_4^{2-}

I: IO_3^-

- 200 West (200W) P&T
- Current IX resin treatment by:
  1. Purolite A532E IX resin for Tc
  2. Dowex 21K IX resin for U
- Future 200W P&T Operations
  - Expand to areas where all four contaminants of potential concern (CoPC: U, Tc, Cr(VI), and I) may be present in influent
  - **Current IX resins are designed to be selective for one contaminant**
- Evaluate hybrid resin performance
  - **Remove multiple contaminants** by IX and additional mechanisms
  - Potential to decrease 200W P&T operating costs by decreasing the number of resins needed to remove all CoPCs

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Hybrid Resin Types

Metal oxides dispersed through the polymer

Iron-based materials – removal of IO_3^- and TcO_4^- (doi:10.1016/j.scitotenv.2019.136167)

Bismuth-based materials – high uptake for co-located contaminants; iodine-129 (IO_3^-, I^-), Cr(VI), and U (uranyl carbonates) (doi:10.1016/j.scitotenv.2019.136167)

Cerium-based hybrid resin – removal of IO_3^- removal from Hanford groundwater (doi.org/10.1021/acsami.0c01527)

Redox active functional groups (SIR-700)

Weak anion base resin

Two sites on the backbone that work differently:

- **IX** for anions
- **Secondary alcohol group** for redox sensitive contaminants

For these tests, we used:

Backbone: SIR-110-MP (ResinTech)

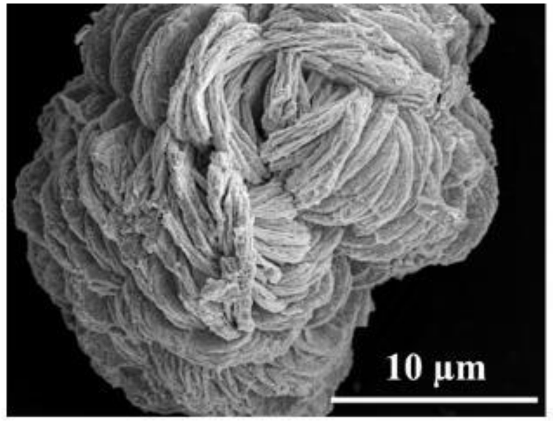
- Similar functionality as A532E
- Used for TcO_4^-, I^-, NO_3^- removal (https://www.resintech.com/product/sir-110-mp-hp/)

Hybrid metals: Fe, Bi, and Ce

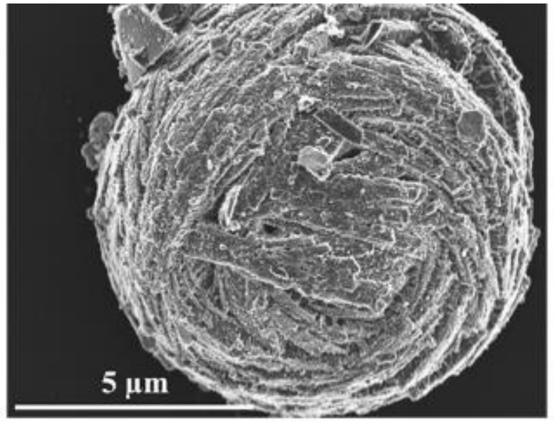
For these tests, we used:

SIR-700 (ResinTech)

- Designed to remove Cr(VI), used in 100 area P&T
- Demonstrated removal of U, less extent Tc and I (doi:10.1016/j.jhazmat.2023.132165)

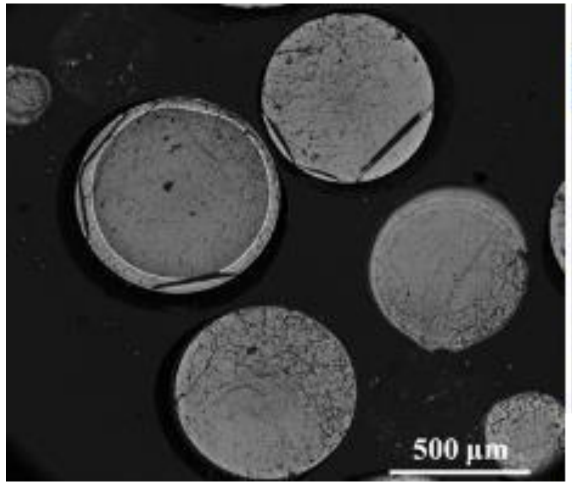


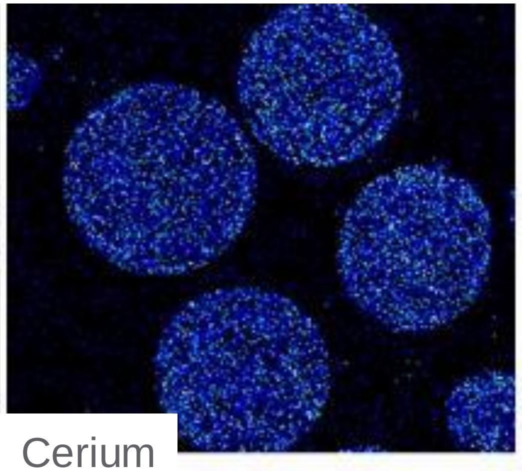
Bismuth oxy(hydroxide)



Bismuth subnitrate

ResinTech, Inc SIR-110-HP
Strong Base Anion Exchange Resin





Cerium

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Objectives and Approach

Compare the performance of currently used resins at Hanford P&T to hybrid resins for removal of co-located contaminants in 200W groundwater conditions.

Phase 1: Initial Batch Experiments

- Compare relative selectivity of current P&T resins with hybrid resins to remove: U, Tc, Cr(VI), I

Phase 3: Iodine Batch Experiments

- IO_3^- uptake in 200W simulated groundwater (200W SGW) for best performing Ce-hybrids
- IO_3^- uptake in DDI for different hybrid types

Phase 2: Column Experiments

- Account for thermodynamic & kinetic contaminant removal processes
- Compare relative contaminant selectivity for each resin under 1D flow conditions

Phase 4: Solid Phase Characterization

- Determine IO_3^- removal mechanism(s) using:
  - X-ray diffraction (XRD)
  - Scanning electron microscopy (SEM)
  - Fourier transform infrared (FTIR) spectroscopy
  - X-ray photoelectron spectroscopy (XPS)
  - X-ray absorption near edge structure (XANES) spectroscopy

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Summary of Resins

Strong Base Anion Exchange Resins		
Resin	*Type*	*Functional Group(s)*
A532E **(✓)**	I	trihexylamine, triethylamine
DOWEX **(✓)**	I	trimethylammonium
SIR-110-MP	I	Tributylamine
SIR-110	I	Tributylamine
SBG1	I	Trimethylamine
SBG2	II	Dimethylethanolamine
Weak Base Hybrid Resins		
Resin	*Type*	*Functional Group(s)*
SIR700 **(✓)**	Weak Base	tetraethylenepentamines
Hybrid Resins		
Resin	*Parent Resin*	*Hybrid Metal*
SIR-110-MP-Ce	SIR-110-MP	Ce
SIR-110-MP-Bi	SIR-110-MP	Bi
SIR-110-MP-Fe	SIR-110-MP	Fe
SIR-110-Ce	SIR-110	Ce
CHM20 (2020)	SBG2	Ce
CHM20 (2021)	SBG2	Ce
SIR1300	SBG1	Mn

(✓) Currently used at Hanford P&T

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Initial Batch Experiments

Objectives:

- Compare relative selectivity of current P&T resins with hybrid resins to remove: U, Tc, I, and Cr(VI)

Methods:

- Solution:solid ratios: 200 & 1000 (mL/g)
- Solution: 200W SGW
- Shaking: 125 rpm
- Duration: 72 hours
- Measure:
  - Initial & final pH
  - Tc, U, Cr(VI), I

Strong Base Anion Exchange Resins		
Resin	*Type*	*Functional Group(s)*
A532E (✓)	I	trihexylamine, triethylamine
DOWEX (✓)	I	trimethylammonium
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SIR-110-MP-Bi	SIR-110-MP	Bi
SIR-110-MP-Fe	SIR-110-MP	Fe
SIR-110-Ce	SIR-110	Ce
CHM20 (2020)	SBG2	Ce
CHM20 (2021)	SBG2	Ce
SIR1300	SBG1	Mn

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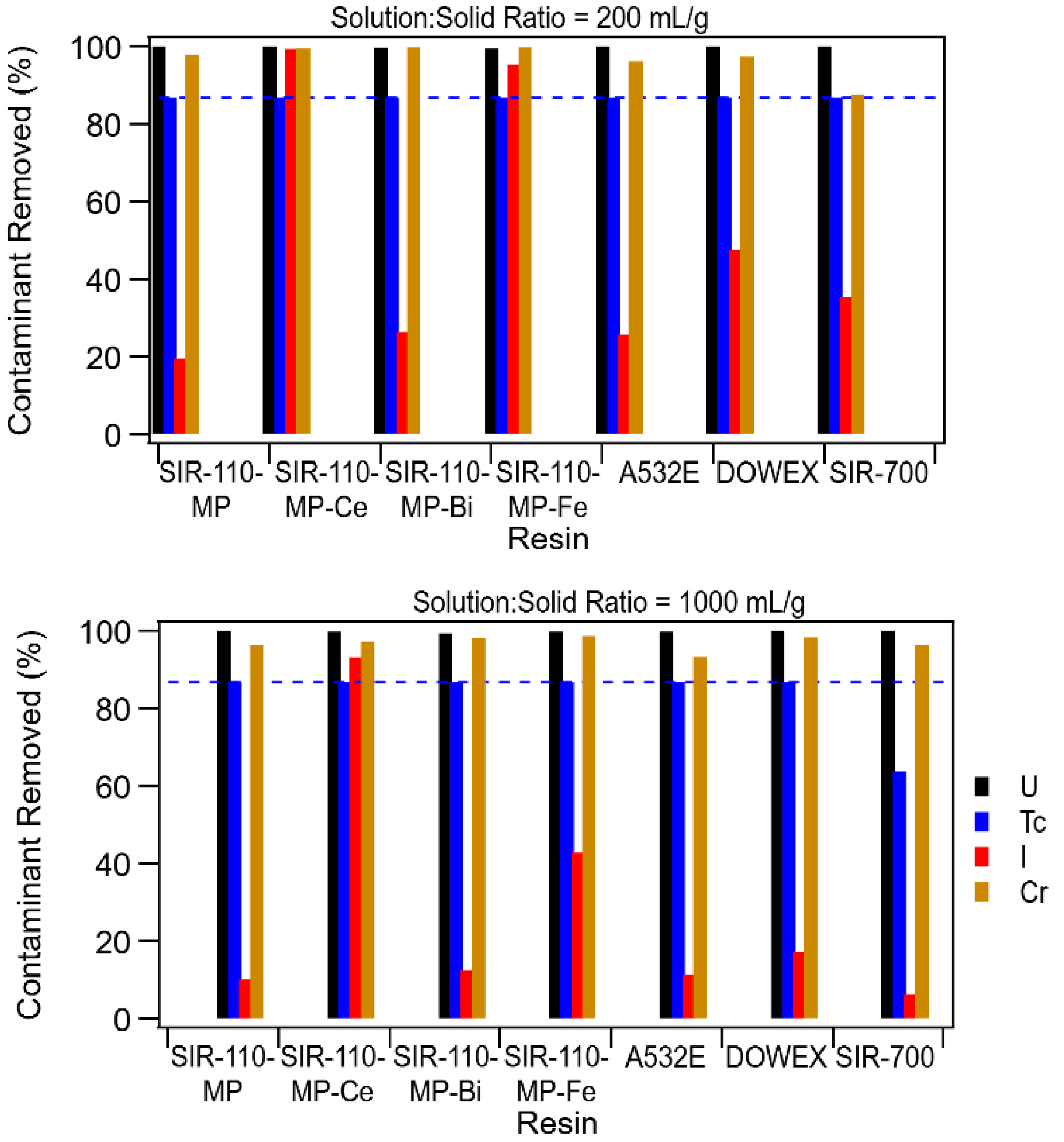
Initial Batch Experiments

- **U** [43,800 µg/L]$_0$
  - Complete removal by all resins
- **Tc** [2.87 µg/L]$_0$
  - Removal was 87% (limit of detection)
  - Complete removal by all resins (except SIR-700 at 1000 mL/g)
- **Cr(VI)** [258 µg/L]$_0$
  - Removal by all resins was ≥ 87%
- **I** [128 µg/L]$_0$
  - Generally: ↑ mL/g ratio = ↓ uptake
  - SIR-110-MP-Ce, -Fe most effective
- **<u>All resins removed most of the contaminants (except I)</u>**



Contaminant removal by hybrid IX resins. The blue dashed line indicates the limit of detection for ^{99}Tc, 0.37 µg/L, where removal above 87% Tc cannot be determined.

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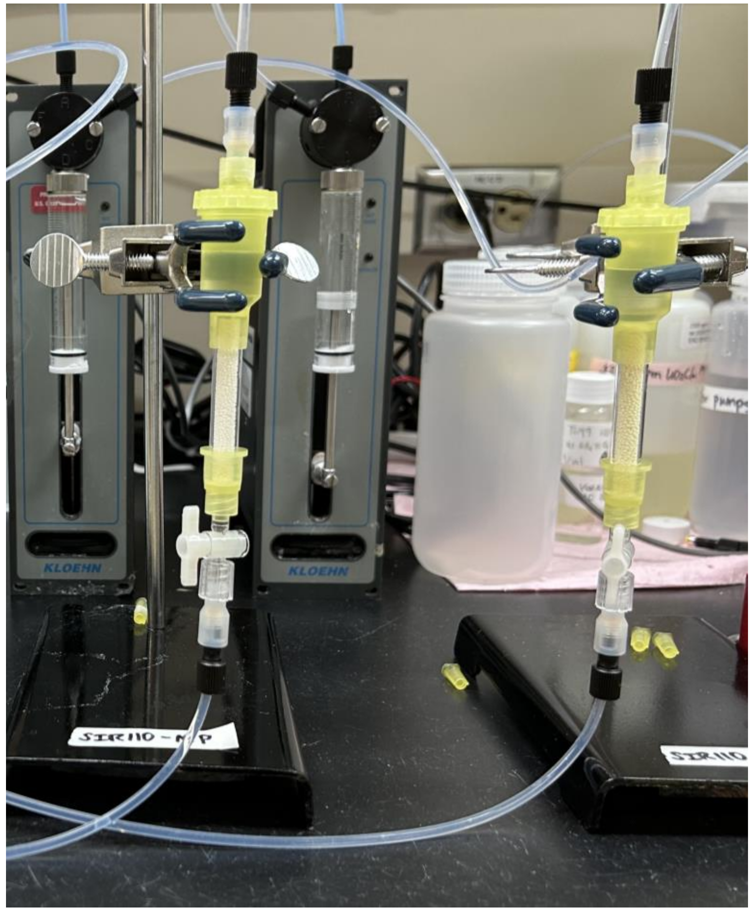
Column Experiments

Objectives:

- Account for thermodynamic & kinetic contaminant removal processes
- Compare relative contaminant selectivity for each resin under 1D flow conditions

Methods:

- Top to bottom flow
- Flow rate: 45 mL/hr
- Solution: 200W SGW
- Duration: 72 hours
- U, Tc, Cr(VI), & I concentrations: 1000 ppb
- Measure:
  - Initial & final pH
  - Tc, U, Cr(VI), I



Strong Base Anion Exchange Resins		
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Weak Base Hybrid Resins		
Resin	*Type*	*Functional Group(s)*
SIR700 (✓)	Weak Base	tetraethylenepentamines
Hybrid Resins		
Resin	*Parent Resin*	*Hybrid Metal*
SIR-110-MP-Ce	SIR-110-MP	Ce
SIR-110-MP-Bi	SIR-110-MP	Bi
SIR-110-MP-Fe	SIR-110-MP	Fe
SIR-110-Ce	SIR-110	Ce
CHM20 (2020)	SBG2	Ce
CHM20 (2021)	SBG2	Ce
SIR1300	SBG1	Mn

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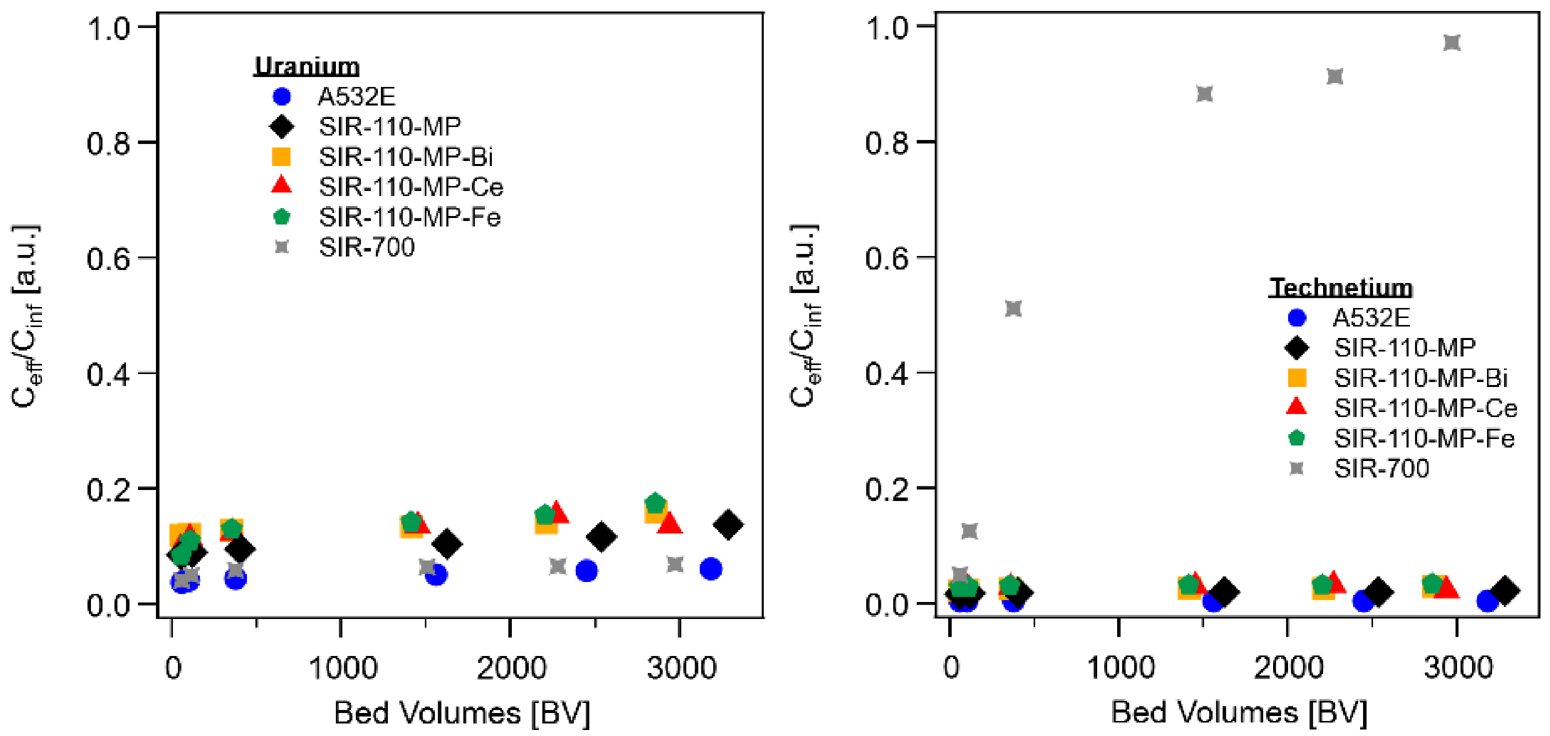
Column Experiments – U & Tc-99

- **U** [1,000 µg/L]$_0$
  - No breakthrough for any resins
  - A532E & SIR-700 slightly more effective (0.061-0.066) vs SIR-110-MP hybrid resins (0.138)

- **Tc** [1,000 µg/L]$_0$
  - Breakthrough only observed for SIR-700
  - A532E better (0.005) vs SIR-110-MP hybrid resins (0.022-0.035)



Contaminant breakthrough curves. Removal is represented as the effluent concentration (C_{eff}) normalized by influent concentration (C_{inf}) vs bed volumes.

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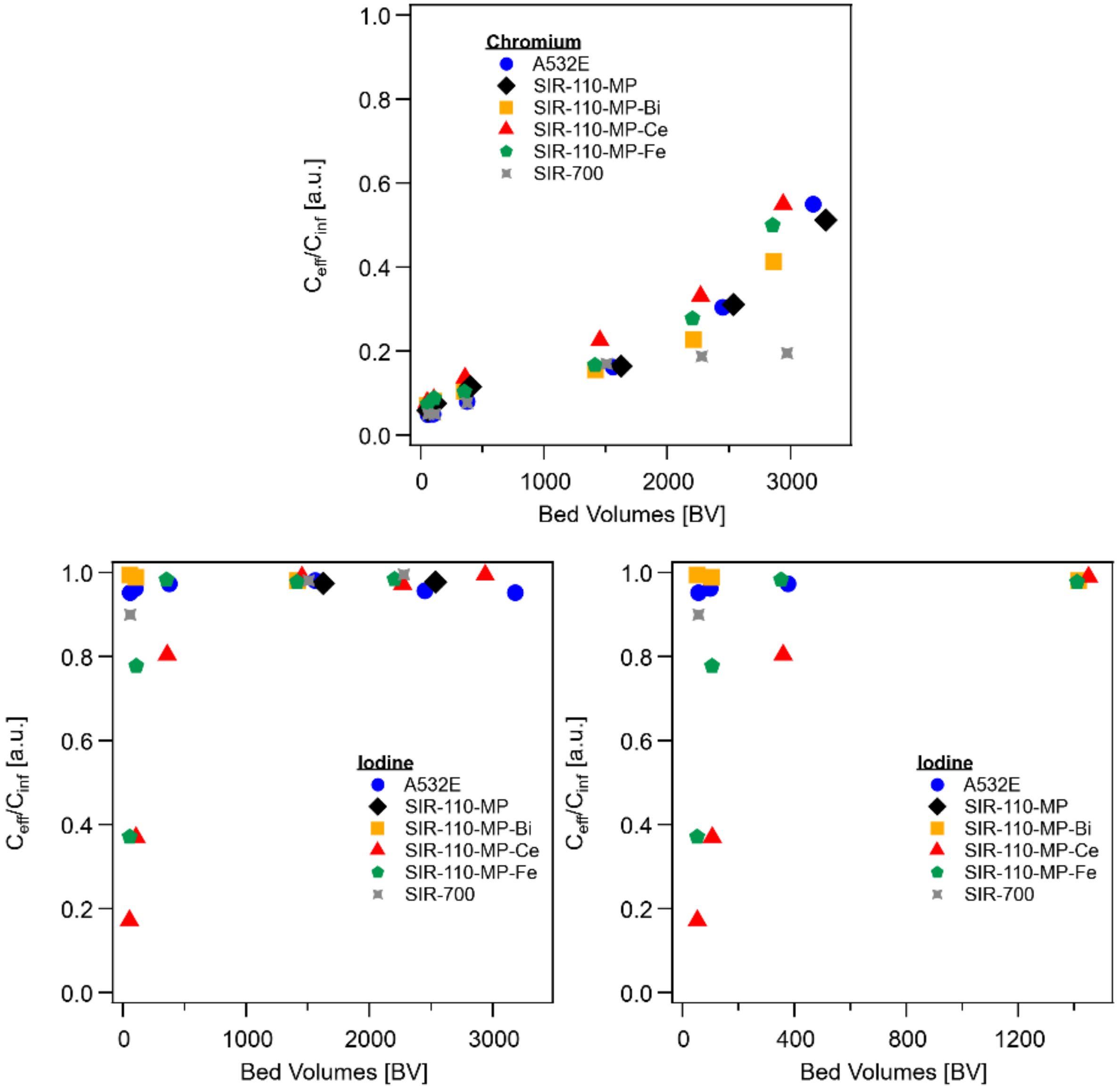
Column Experiments – Cr(VI) & I

- **Cr(VI)** [1,000 µg/L]$_0$
  - All resins show the start of breakthrough
  - SIR-700 performed the best (0.188) vs other resins (0.413-0.550)
- **I** [1,000 µg/L]$_0$
  - All resins reach complete breakthrough
  - SIR-110-MP-Ce, -Fe performed the best (greater BV to reach breakthrough)
    - ✓ Agrees with batch results
  - Need knowledge of I removal mechanism to improve performance



Contaminant breakthrough curves. Removal is represented as the effluent concentration (C_{eff}) normalized by influent concentration (C_{inf}) vs bed volumes. In (E) the first 1500 BVs are shown to differentiate the I breakthrough curves.

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Iodine Batch Experiments - SGW

Objectives:

- I uptake in simulated GW (SGW) for Ce-hybrids

Methods:

- Solution:solid ratio: 200 (mL/g)
- Solution: **200W SGW**
- I concentration: **9.77 mg/L**
- Shaking: 125 rpm
- Duration: **24 hours**
- Measure:
  - Initial & final pH
  - I

Strong Base Anion Exchange Resins		
Resin	*Type*	*Functional Group(s)*
A532E (✓)	I	trihexylamine, triethylamine
DOWEX (✓)	I	trimethylammonium
SIR-110-MP	I	Tributylamine
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Weak Base Hybrid Resins		
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SIR700 (✓)	Weak Base	tetraethylenepentamines
Hybrid Resins		
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SIR-110-MP-Bi	SIR-110-MP	Bi
SIR-110-MP-Fe	SIR-110-MP	Fe
SIR-110-Ce	SIR-110	Ce
CHM20 (2020)	SBG2	Ce
CHM20 (2021)	SBG2	Ce
SIR1300	SBG1	Mn

Iodine Batch Experiments - DDI

Objectives:

- I uptake in DDI for different hybrid types
  - Want to reach max loading capacity

Methods:

- Solution:solid ratio: 200 (mL/g)
- Solution: **DDI**
- I concentration: **4,880 mg/L**
- Shaking: 125 rpm
- Duration: **72 hours**
- Measure: Initial & final pH
- Measure: I and Cl

Strong Base Anion Exchange Resins		
Resin	*Type*	*Functional Group(s)*
A532E (✓)	I	trihexylamine, triethylamine
DOWEX (✓)	I	trimethylammonium
SIR-110-MP	I	Tributylamine
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SIR-110-Ce	SIR-110	Ce
CHM20 (2020)	SBG2	Ce
CHM20 (2021)	SBG2	Ce
SIR1300	SBG1	Mn

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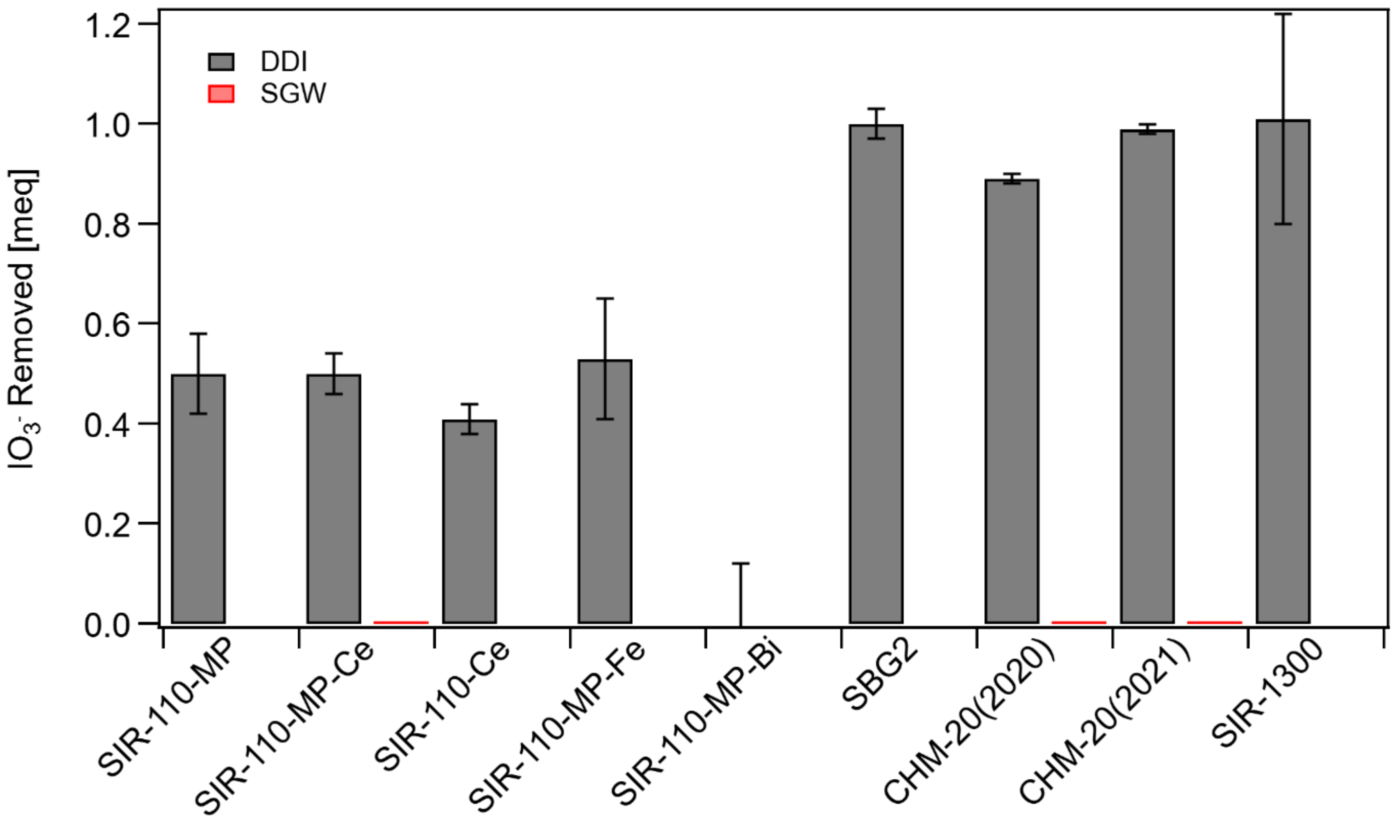
Iodine Batch Experiments

- Ce hybrids: IX more effective in DDI; in SGW there is anion competition
  - DDI: [9.77 mg/L]$_0$
  - SGW: [4,880 mg/L]$_0$

- In DDI:
  - SBG2 removed 2x more I than SIR-110-MP (0.99 meq vs 0.50 meq)
  - SIR-110-MP hybrids performed similarly (removed 0.50-0.53 meq)
  - SIR-110-MP-Bi: No uptake measured
    - ✓ Suggests Bi inhibits I removal



Aqueous removal of I from batch tests performed using KIO_3 in DDI (grey) and SGW (red). Average milliequivalents (meq) of I removed are shown (error bars indicate the standard deviation). Uptake of I in SGW was 0.0014 meq for SIR-110-MP-Ce and 0.0015 meq for CHM-20 resins.

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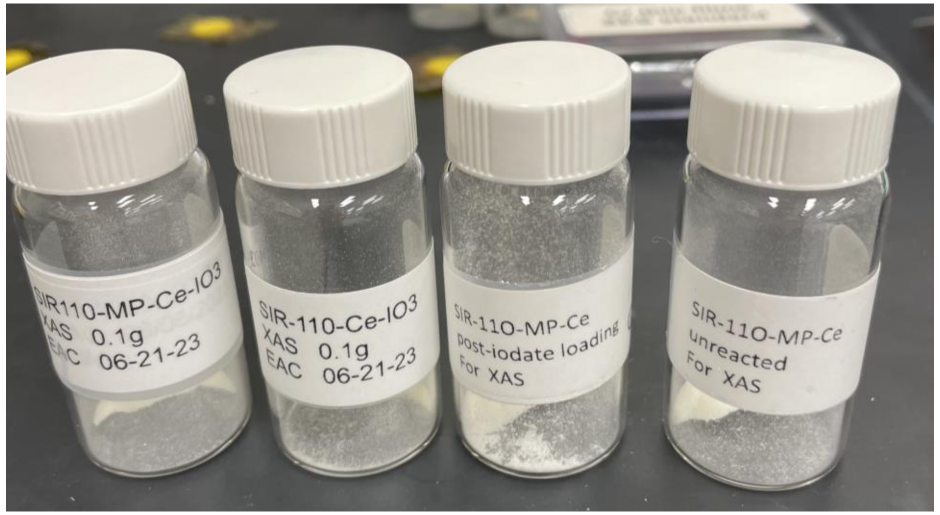
Iodine Batch Experiments - DDI

Solid Phase Characterization

- Determine I removal mechanism(s) using:
  - X-ray diffraction (XRD)
  - Scanning electron microscopy (SEM)
  - Fourier transform infrared (FTIR) spectroscopy
  - X-ray photoelectron spectroscopy (XPS)
  - X-ray absorption near edge structure (XANES) spectroscopy



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SIR-110-Ce	SIR-110	Ce
CHM20 (2020)	SBG2	Ce
CHM20 (2021)	SBG2	Ce
SIR1300	SBG1	Mn

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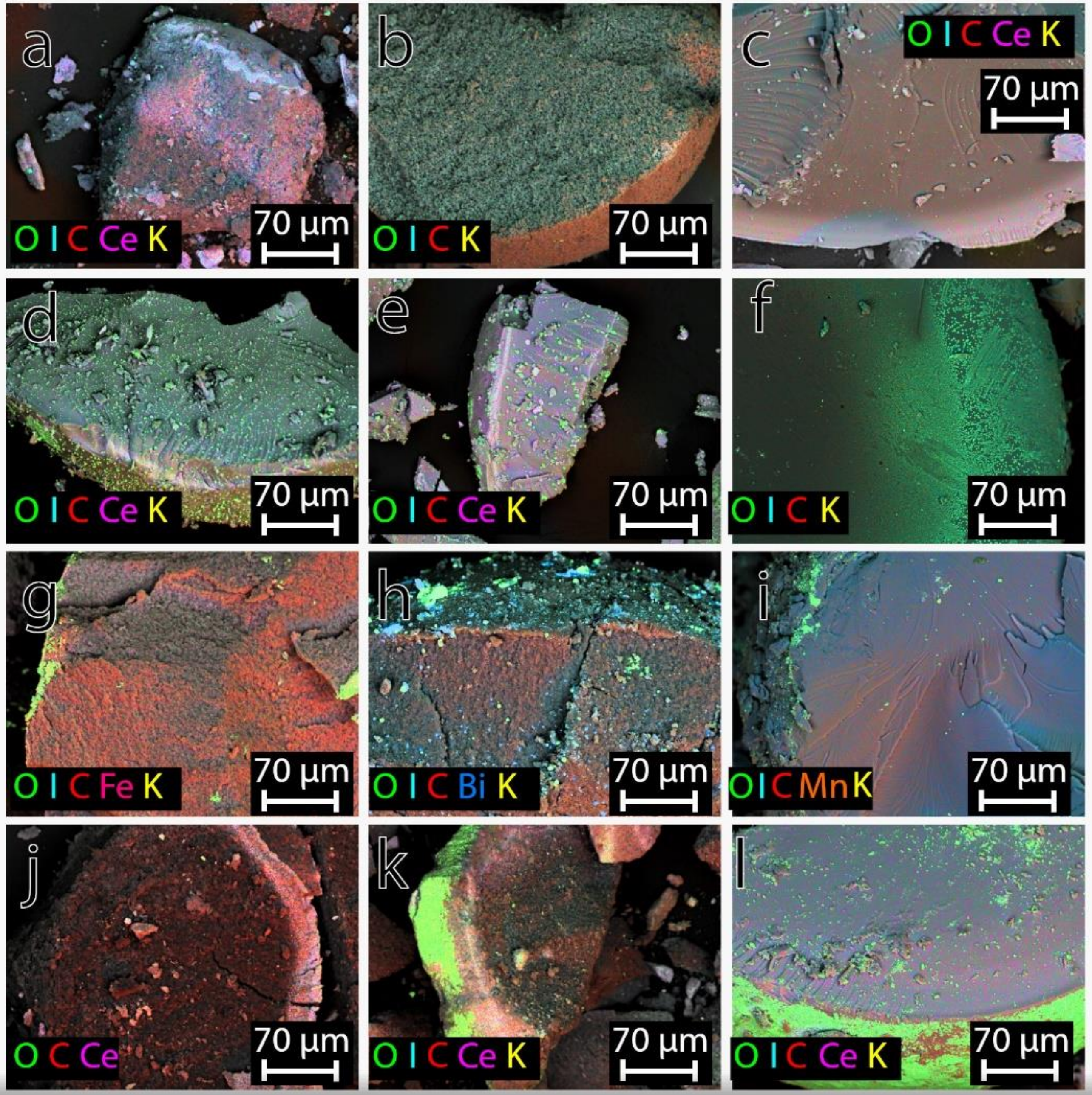
Mechanisms for Iodine Removal

- FTIR:
  - I spectral feature similar for most resins (except Bi hybrid & SIR-1300)
- XRD
  - No change in mineralogy (except Bi hybrid)
- XANES:
  - Iodate doesn't impact Ce(IV) oxidation state
- XPS:
  - I present as IO_3^- ; Ce remains Ce(IV)
- SEM-EDS:
  - Homogeneous I distribution in bulk interior of the resin → IO_3^- removed at IX sites and metal phase



SEM-EDS of the post-reacted resins (one image for each resin).

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Conclusions

- Relative selectivity of resins from batch/column tests:
  - All resins (except SIR-700) removed Tc and U
  - SIR-700 not effective for Tc when co-mingled with Cr(VI), great for U with Cr(VI)
  - SIR-110-MP-Ce (& -Fe) removed the most I

- For future 200W P&T operations:
  - Could use a combination of SIR-700 & SIR-110-MP-Ce for removal of U, Tc, Cr(VI), and I
    - ✓ Conduct intermediate scale testing to confirm scalability

- Future Work (Iodine):
  - Determine removal mechanism to improve hybrid resin loading capacity for I

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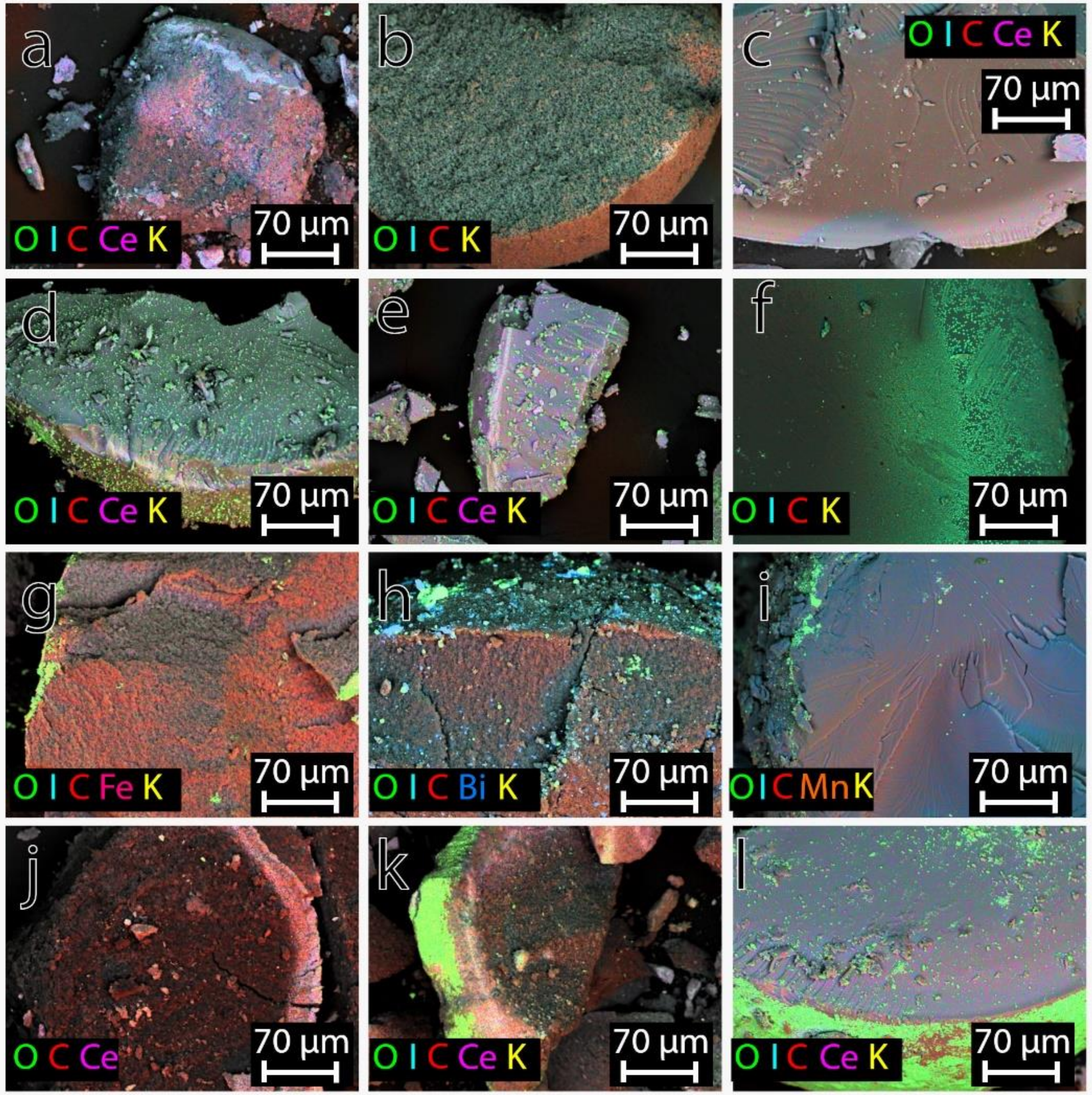
Supplemental Slides

Mechanisms for Iodine Removal



SEM-EDS of:

a) SIR-110-MP-Ce-IO_3
b) SIR-110-MP-IO_3
c) SIR-110-Ce-IO_3
d) CHM-20(2020)-IO_3
e) CHM-20(2021)-IO_3
f) SBG2-IO_3
g) SIR-110-MP-Fe-IO_3
h) SIR-110-MP-Bi-IO_3
i) SIR-1300-IO_3
j) SIR-110-MP-Ce
k) SIR-110-MP-Ce-IO_3 in SGW
l) CHM-20(2020)-IO_3 in SGW

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