

# Technology Assessment for Radioiodine at the Hanford Site

Vicky Freedman, Mike Truex, Jim Szecsody, Carolyn Pearce, Guohui Wang, and Hilary Emerson



PNNL is operated by Battelle for the U.S. Department of Energy





## **200-UP-1 Interim ROD Context**

- Feasibility study for <sup>129</sup>I determined no existing treatment technologies to achieve the federal drinking waster standard of < 1 pCi/L in the 200-UP-1 Operable Unit at the Hanford Site
  - Current remedy is hydraulic control
  - Current <sup>129</sup>I conditions in groundwater are relatively dilute: 1 to ~23 pCi/L
- Interim Record of Decision (ROD) dictated three elements be investigated
  - Close conceptual model data gaps for <sup>129</sup>I
  - Investigate potential remedies for iodine (in situ and ex situ)
  - Consider whether an Applicable or Relevant and Appropriate Requirements (ARAR) Technical Impracticability (TI) waiver for <sup>129</sup>I is appropriate





## **Plume Location**

- Plume core located below the Environmental Restoration Disposal Facility (ERDF)
  - ERDF expansion coincides with plume trajectory
- Plume characteristics
  - Full plume: 3 km<sup>2</sup> area, 1.2 km wide, 45 m thick





## **Presence of Stable Iodine (127I)**

- Natural stable iodine (<sup>127</sup>I) is also present in the aquifer at much greater concentrations than <sup>129</sup>I
  - Remedies are not specific for a particular iodine isotope
  - Recent resin analysis at pump-and-treat (P&T) facility identified concentrations of <sup>127</sup>I:<sup>129</sup>I as 1000:1
  - Concentration ratio (<sup>127</sup>I / <sup>129</sup>I) is not constant within aquifer
- Source of <sup>127</sup>I is unknown, but iodine commonly exists as a trace constituent of nitric acid
  - Large volumes of nitric acid used during operations likely contribute to its high concentrations in groundwater
  - Presence of high <sup>127</sup>I concentrations must be considered because they exhibit the same geochemical behavior



## **Iodine Speciation**

- Iodate is the predominant species in Hanford groundwater
  - Iodate (IO<sub>3</sub><sup>-</sup>) is the prevalent form of iodine, ~70%
  - lodide (l<sup>-</sup>), ~5%
  - Organo-iodine, ~25%
- Predominant species previously thought to be iodide
  - More mobile
  - Consideration for treatment technology





## **Technology Identification**

- Literature review to identify promising technologies
- Laboratory scoping tests where further evaluation was needed
- Extended evaluation/scale-up to evaluate whether treatability testing was needed
  - Evaluation based on ability to meet the maximum contaminant level of 1 pCi/L in groundwater

# d testing was of 1 pCi/L in



## **Technology Approaches**

- Technologies for further screening organized into three categories
  - In situ sequestration
    - ✓ Calcite co-precipitation
    - ✓ Apatite sorption and co-precipitation
    - $\checkmark$  Organic sorption (chitin, lignin, humic acid)
    - ✓ Iron oxide sorption and co-precipitation
  - In situ mobilization to enhance P&T extraction efficiency
    - ✓ Dithionite

## Ex situ extraction within P&T system

- ✓ Ferrihydrite, bismuth oxyhydroxide, bismuth-cobalt-aluminum
- ✓ Commercially available resins
- No microbial-based technologies selected for evaluation
  - Demonstrated to be insignificant process in the conceptual model evaluation
  - Operational difficulties associated with ex situ treatment (P&T)



## In Situ Sequestration Technology Screening

- Calcite co-precipitation
  - 70% removal of iodate only
- Apatite sorption/co-precipitation
  - Minimal removal

- Organic sorption (chitin, lignin, humic acid)
  - Only chitin effective for iodide
- Iron oxide sorption/co-precipitation
  - ~98% removal of iodate
  - ~70% removal of iodide
  - Iodate sorbs
  - Iodate and iodide can be incorporated during ferrihydrite precipitation
  - Possible treatability candidate









## **Enhanced Pump-and-Treat Technology Screening**

- Dithionite
  - Up to 4X more and 3X faster leaching of iodine
- Possible treatability candidate



127 Extractions			
	C9510 114'		
	untreated	dithionite treatment	
	extract phase:		
l	part Fe oxides		
r	aqueous		
	adsorbed		
	partial CaCO3		
2.3	all CaCO3		
	Fe oxides		
5C	not shown		



## Ex Situ Treatment Technology Screening

- Non-commercial materials
  - Ferrihydrite, bismuth oxy(hydroxide), and bismuth-cobalt-aluminum
  - High affinity for iodate
  - Effective even in the presence of <sup>127</sup>I (1000 times higher than <sup>129</sup>I)
  - Possible treatability candidates
- Commercial resins
  - CHM-20: Hybrid Type 2 dimethylethanolamine strong base anion resin containing CeO<sub>2</sub>-like phase
  - ASM-10-HP: Hybrid Type 2 dimethylethanolamine strong base anion resin containing ferrihydrite-like phase
  - Possible treatability candidates

Material Tested	Measured Kd (mL/g)
Ferrihydrite	3230
Bismuth (oxy)hydroxide	200,000
Bi-Co-Al	13,000
12 other compounds tested	zero - 680

Batch test Kd values measured after 24 hr





## **Treatability Test Decision Factors**

- ROD requirements
  - If one or more viable technologies are identified, treatability tests will be conducted for those technologies
- EIC evaluation based on scale-up (e.g., batch to column)
  - Effectiveness
    - $\checkmark$  Removal from aqueous phase, rate of removal, and stability
  - Implementability
    - $\checkmark$  Effort type, potential hurdles, similarity to known processes
  - Cost
    - ✓ Relative to P&T
  - Maturity
    - ✓ Deployment timeline for FS readiness





## In Situ: Iron Oxide Precipitation



# Conclusion in situ approach

No demonstrated



## **Enhanced P&T: Dithionite**



## **Conclusion**

 Poor performance and implementability and no demonstrated in situ approach



## **Non-Commercial Resins: Ex Situ Pump-and-Treat**



## Conclusion

 Significant uncertainties associated with technology development [poor column performance for custom (PAN) beads]



## **Commercial Resins: CHM-20 and ASM-10-HP**

- Column testing scale up
  - 200W groundwater supplemented with iodate (100 ppb) – same order of magnitude as field concentrations of <sup>127</sup>
  - Flow rate = 25 mL/h
- Capacity determined at 3% breakthrough
  - Based on reaching 1 pCi/L standard





## **Commercial Resin Column Test Results**

- 3% breakthrough occurred at ~125 pore volumes for both resins
- Pulse of iodate in effluent (C/C<sub>o</sub> > 1) shows some likely interaction of the resin and the groundwater constituents (possibly nitrate or carbonate)
- Loading: Column ~10 µg-iodine/g-resin; Batch ~200 µg-iodine/g-resin
- Performance is marginal due to low capacity
  - Iodine: ~1L-treated/g-resin
  - Uranium: ~100L-treated/g-resin
  - 99Tc: ~10,000L-treated/g-resin
- Groundwater constituent interactions would need to be addressed





## **Commercial Ex-Situ: Pump-and-Treat**



## Conclusion

- Poor technical practicability
- Resin performance is marginal
  - Low capacity
  - Sensitivity to groundwater constituents
- Plume core beneath ERDF



## **Technology Evaluation Conclusions**

- Practicability of all candidate technologies was low, driven by site and contaminant properties that hinder effectiveness and/or implementability of the technologies
- Effectiveness-Implementability-Cost evaluation included technology maturity
  - CERCLA process requires treatability testing for existing technologies that can be adapted for site-specific needs
- Technology evaluation results can be used to support consideration of a TI waiver



- Kerisit SN, FN Smith, S Saslow, M Hoover, A Lawter, and N Qafoku. 2018. "Incorporation Modes of Iodate in Calcite." *Environmental* • Science & Technology. 52.10.1021/acs.est.8b00339.
- Lawter AR, WL Garcia, RK Kukkadapu, O Qafoku, ME Bowden, SA Saslow, and NP Qafoku. 2018. "Technetium and iodine aqueous species immobilization and transformations in the presence of strong reductants and calcite-forming solutions: Remedial action implications." Science of the Total Environment 636:588-595.
- Neeway JJ, DI Kaplan, CE. Bagwell, ML Rockhold, JE Szecsody, MJ Truex, and NP Qafoku. 2019. "A review of the behavior of radioiodine in the subsurface at two DOE sites." Science of the Total Environment. https://doi.org/10.1016/j.scitotenv.2019.07.146.
- Moore, RC, CI Pearce, JW Morad, S Chatterjee, TG Levitskaia, R M Asmussen, AR Lawter, JJ Neeway, NP Qafoku, MJ Rigali, SA Saslow, JE Szecsody, PK Thallapally, G Wang, and VL Freedman. 2019. "Iodine immobilization by materials through sorption and redox-driven processes: A literature review." Science of The Total Environment. https://doi.org/10.1016/j.scitotenv.2019.06.166.
- Pearce CI, EA Cordova, WL Garcia, SA Saslow, KJ Cantrell, JW Morad, O Qafoku, J Matyàš, AE Plymale, S Chatterjee, J Kang, FC Colon, TG Levitskaia, MJ Rigali, JE Szecsody, S Heald, M Balasubramanian, G Wang, DT Sun, WL Queen, R Bontchev, RC Moore, and VL Freedman. "Evaluation of materials for iodine and technetium immobilization through sorption and redox-driven processes." Science of The Total Environment. Accepted
- Saslow SA, SN Kerisit, T Varga, KC Johnson, NM Avalos, AR Lawter, and NP Qafoku. 2019. "Chromate effects on iodate incorporation ٠ into calcite." ACS Earth and Space Chemistry 3(8):1624-1630.
- Strickland CE, CD Johnson, BD Lee, N Qafoku, JE Szecsody, MJ Truex, and VR Vermeul. 2017. Identification of Promising ٠ Remediation Technologies for Iodine in the UP-1 Operable Unit. PNNL-26934, Pacific Northwest National Laboratory, Richland, WA.



- Szecsody JE, BD Lee, AR Lawter, N Qafoku, CT Resch, SR Baum, II Leavy, and VL Freedman. 2017. Effect of Co-Contaminants • Uranium and Nitrate on Iodine Remediation. PNNL-26955, Pacific Northwest National Laboratory, Richland, WA.
- Szecsody JE, HP Emerson, CI Pearce, CT Resch, and S Di Pietro. "Use of An Aqueous Reductant, Na-Dithionite, to Enhance Iodine Mobility from Aquifer Sediments." Journal of Environmental Radioactivity. Accepted.
- Szecsody JE, G Wang, CI Pearce, AR Lawter, KJ Cantrell, EA Cordova, CF Brown, NP Qafoku, HP Emerson, EC Gillispie, BN Gartman, SR Kimming, and V Garayburu-Caruso. 2019. Evaluation of In Situ and Ex Situ Remediation Technologies for Iodine-129: Final Bench Scale Results. PNNL-28064, Rev. 1, Pacific Northwest National Laboratory, Richland, WA.
- Wang G, NP Qafoku, JE Szecsody, CE Strickland, CF Brown, and VL Freedman. 2019. "Time-Dependent lodate and lodide Adsorption" • to Fe Oxides." ACS Earth and Space Chemistry. doi:10.1021/acsearthspacechem.9b00145.
- Wang, G, JE Szecsody, NM Avalos, NP Qafoku, and VL Freedman. "In situ precipitation of hydrous ferric oxide (HFO) for remediation • of subsurface iodine contamination." Journal of Contaminant Hydrology.



# Thank you

