Development and Testing of a Near Tank Cesium Removal Process

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Near Tank Cesium Removal (NTCR) Features:

- Skid mounted unit for removing Cs from tank waste liquids
  - Mobile and deployable in the field (e.g., tank farms)
- Uses an efficient, simple process
  - Regenerable ion exchange (IX) resins, fixed lead-lag column configuration
  - Streamlined IX processing cycle
  - In-situ spent resin destruction – minimal secondary waste

NTCR Process Overview

- Batches of 60-m^3 (16 kgal) clarified tank waste at 5M – 7M Na accepted into the NTCR feed tanks
- Processed downflow through two beds (lead-lag) of Spherical Resorcinol-Formaldehyde (SRF) Cs IX resin
- <u>Processing ends when Cs breaks through lead column</u>
- Downflow feed displacement with 0.1 M NaOH
- <u>Upflow elution of lead column with 0.5 M HNO_3 at low temperature</u>
  - Higher density eluate below displacer promotes plug flow
  - Upflow keeps downstream piping, valving, etc. “clean”
  - Low temperature extends resin lifetime

NTCR Overview (con't)

- Upflow regeneration with high density solution: 2M NaOH, 3 M $NaNO_3$
  - Completely flushes lower density loaded eluate from column
  - Matches density of feed for next load cycle
- After multiple cycles spent resin is dissolved in hot HNO_3
- Decontaminated LAW feed delivered to WTP LAW melter or supplemental treatment (such as Bulk Vit)
- Cs-rich eluate neutralized with used process solutions, then stored or delivered back to Hanford tank farm
- Resin dissolution liquor neutralized and added to decontaminated LAW feed stream
- No other significant waste streams

NTCR R&D Plan

- Bench Scale Testing
  - Resin Dissolution/Destruction Testing
  - Small Column IX Testing
- Demonstration Unit Testing (Pilot Plant)
- Deployed Unit Engineering

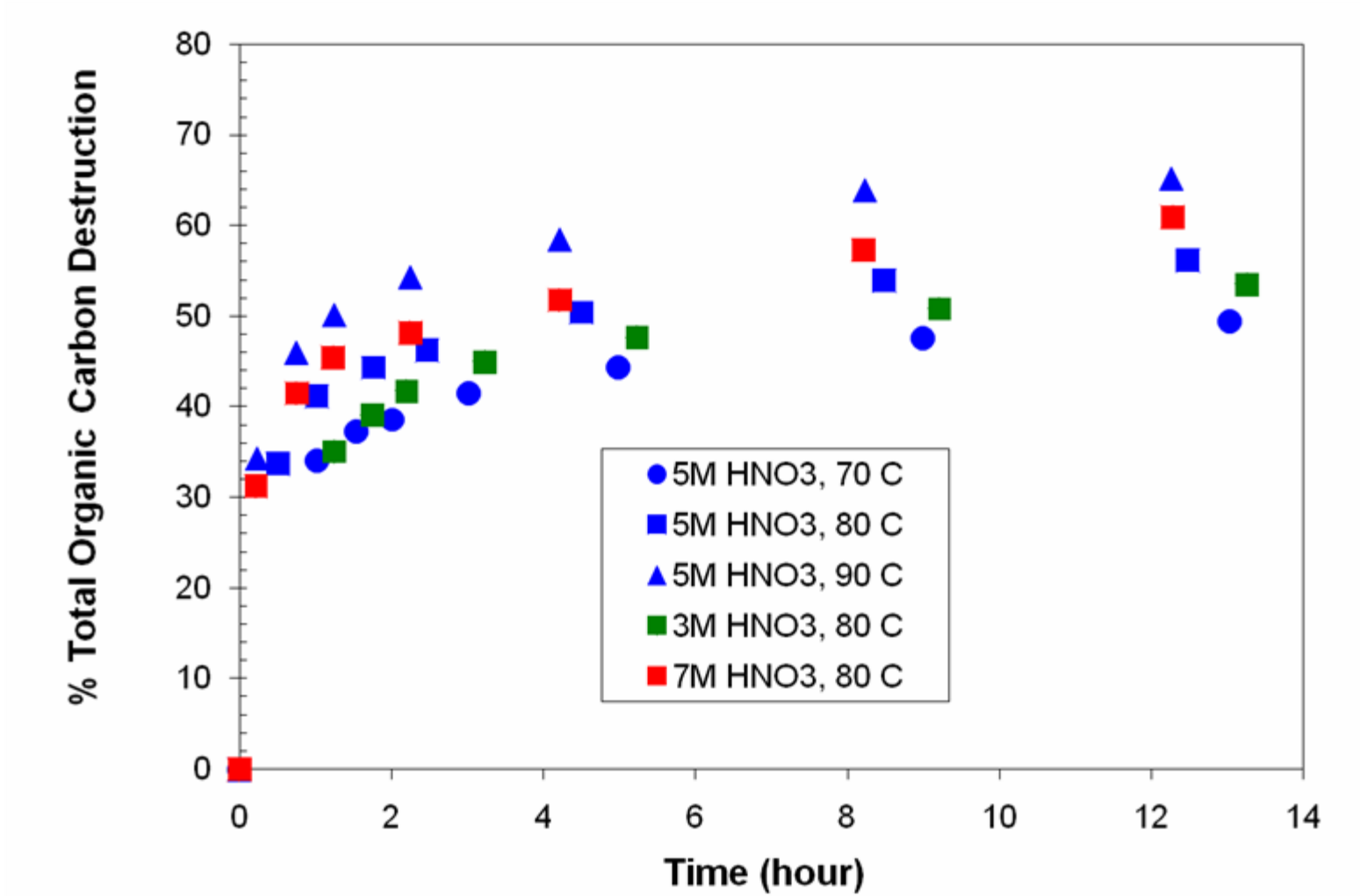
Resin Dissolution/Destruction Test Objectives

- Minimum dissolution conditions
- Kinetics (small batch tests)
- Effect of peroxide (H_2O_2) on residual TOC
- Large batch demonstration
- Dissolved resin liquor neutralization demo
  - With used regeneration solution from IX tests
- Initial characterization of off-gas and aqueous resin destruction residues

Resin Dissolution/Destruction Test Methods

- Add resin to hot acid; monitor bead dissolution and collect liquid and off-gas samples
- Nitric acid concentrations: 3M, 5M, 7M
  - Excess acid (24X – 35X) to keep conc. constant
- Temperatures: 70ºC, 80ºC, 90ºC
- Hydrogen peroxide (H_2O_2) destruction tests:
  - Use solutions from previous tests w residual TOC
  - Heat to 40ºC
  - Add 2X excess of 31.5% H_2O_2
  - React at temperature for 6 hours

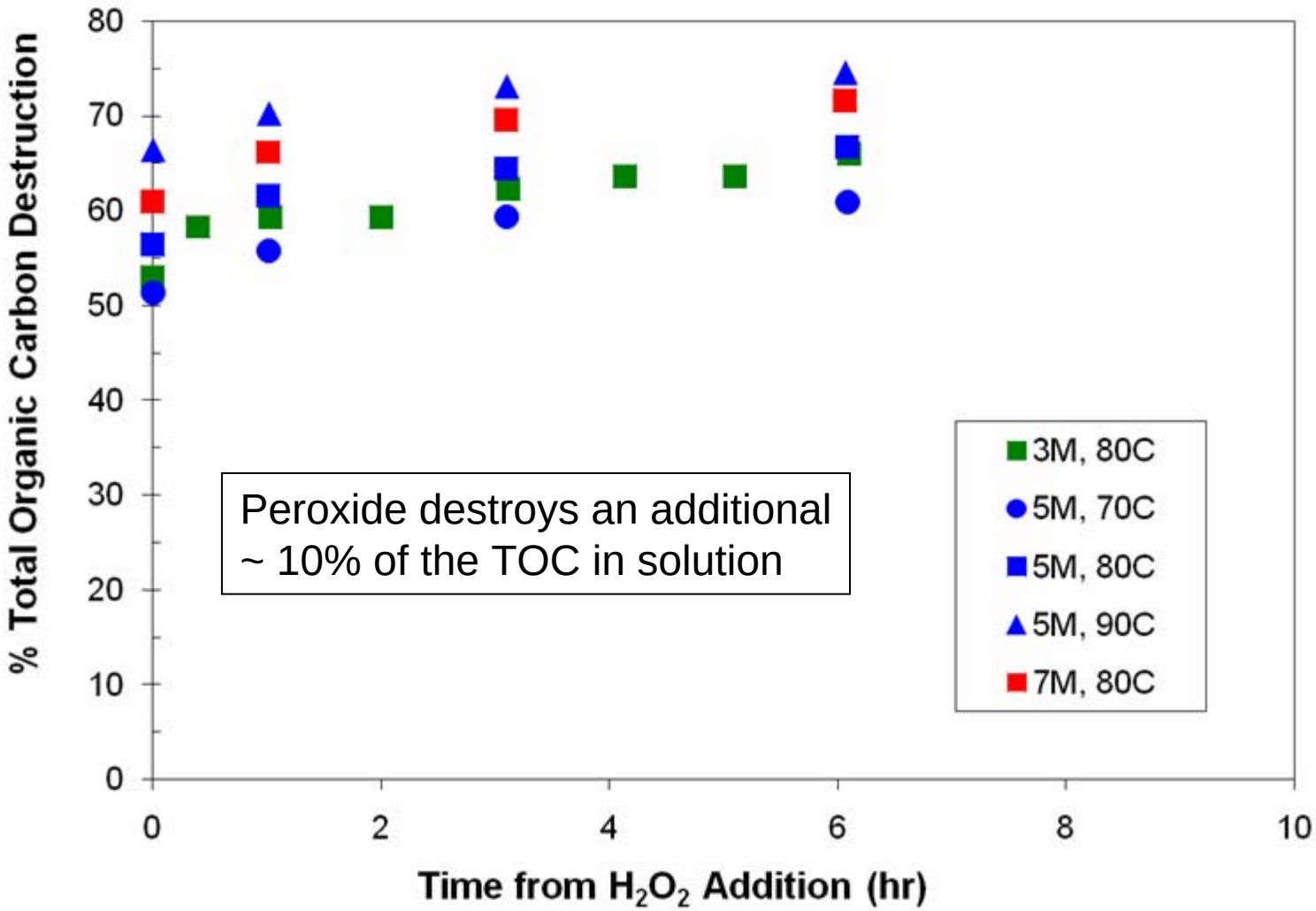
Resin Dissolution/Destruction Kinetics Test Data



Resin Dissolution/Destruction Kinetics Test Results

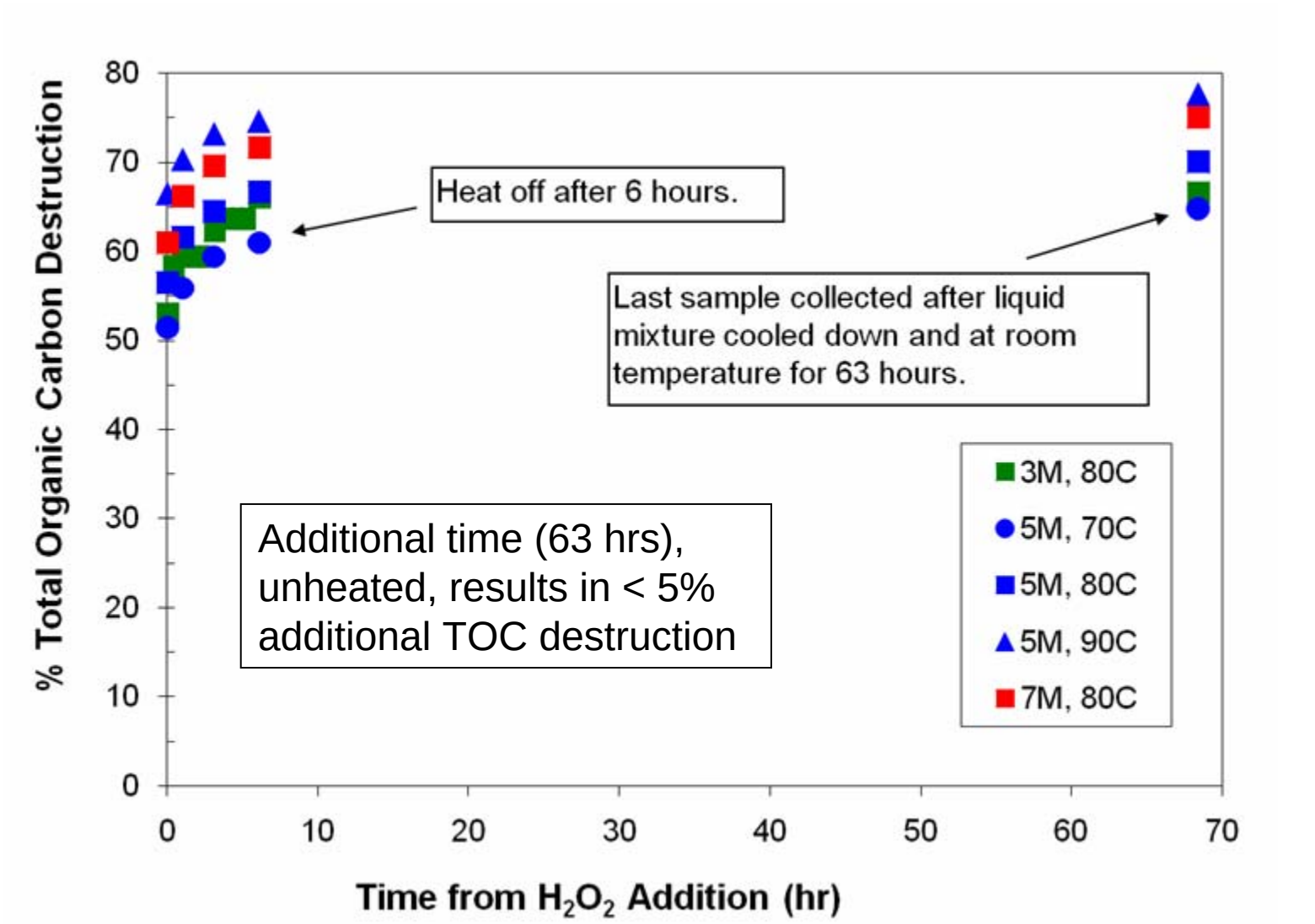
- Resin destruction begins during dissolution
- TOC destruction increases with increasing temperature
- Effect of [HNO_3] in the range tested is relatively small
- Reaction effectively complete at 10 – 12 hours
- Approx. 50% or more of total theoretical TOC destroyed
  - Residual TOC small relative to sugar added at melter
- Large range of reaction orders and rate constants found in fitting the data; attributed to large number of intermediate reactions with different dependences on T and [TOC]

Small Batch Resin Dissolution/ Destruction: Peroxide Tests

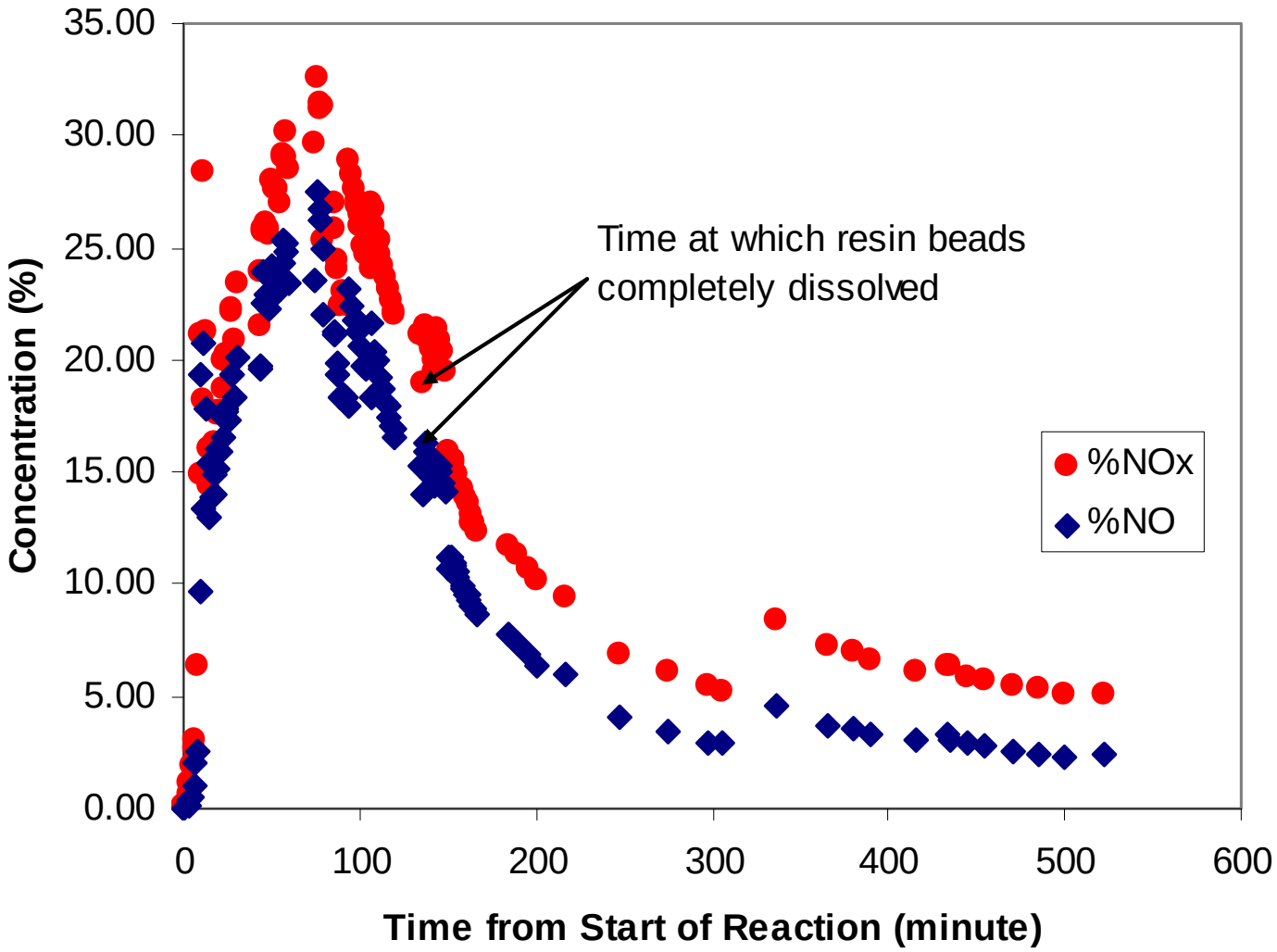


Peroxide destroys an additional ~ 10% of the TOC in solution

Small Batch Resin Dissolution/ Destruction: Peroxide Test Results



Resin Dissolution: Off-Gas NO_x Analysis



Resin Dissolution/Destruction Succesfully Demonstrated

- Minimum dissolution conditions: 3M acid and 60ºC - 70ºC, <u>or</u> 5M acid and 40ºC - 50ºC
- More than 50% of TOC destroyed at higher acid/temp
- H_2O_2 destroys an additional ~ 10% TOC
- No hazardous SVOCs identified in liquids; significant NO_x component in off-gas
- Results support a two phase resin dissolution process:
  - Low T and acid conc to remove resin from column
  - Higher T and acid conc to destroy resin/TOC in separate vessel
- Successful neutralization of resin dissolution liquor with used IX regeneration solution:
  - High pH solution, no precipitates or significant gas generation

Small Column IX Test Objectives

- Assess impact of proposed process conditions on Cs IX performance
  - Abbreviated LAW displacement
  - Short upflow elution
  - Upflow resin conversion to Na form with high density solution
- Evaluate impact of feed variability on resin performance
- Evaluate low temperature Cs elution
  - Extends resin lifetime

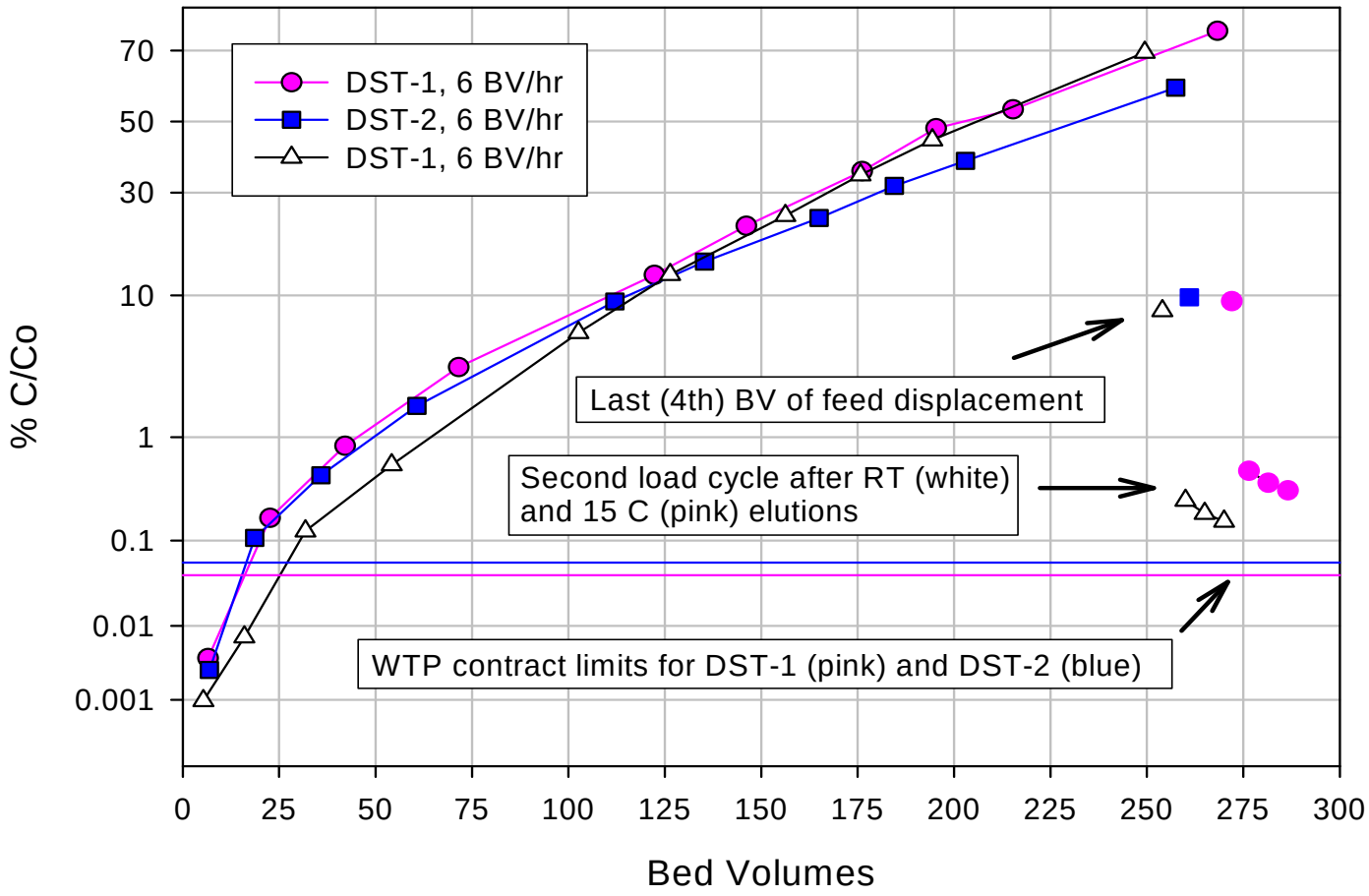
Small Column IX Test Methods

- Small columns (10 mL resin beds) to minimize waste generation; one jacketed for low T elution
- Four simulants; three that bracket compositions of the likely first four double shell tank supernates, and one of a dissolved saltcake
  - Target 6 M Na and 5 M Na feed concentrations
  - Bracket Cs and K concentrations expected in tanks
  - Simple compositions, but include components that test for efficiency of feed displacement and resin conversion: $Al(OH)^-_4$, NO_2^-, CO_3^{-2}

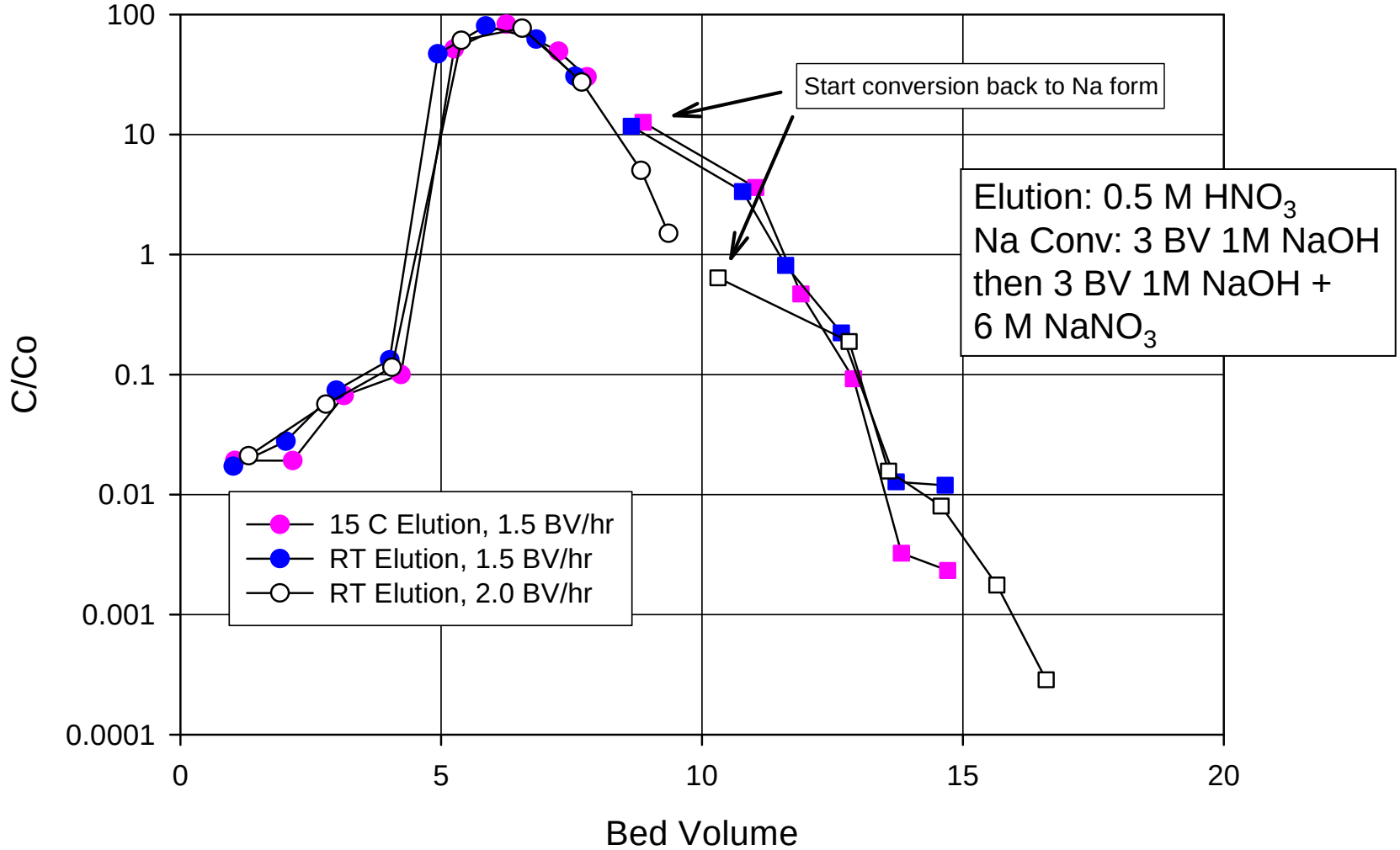
Small Column IX Test Systems

Small Column Ion Exchange Tests: High Conc (~6M Na) and Flow (6 BV/hr)

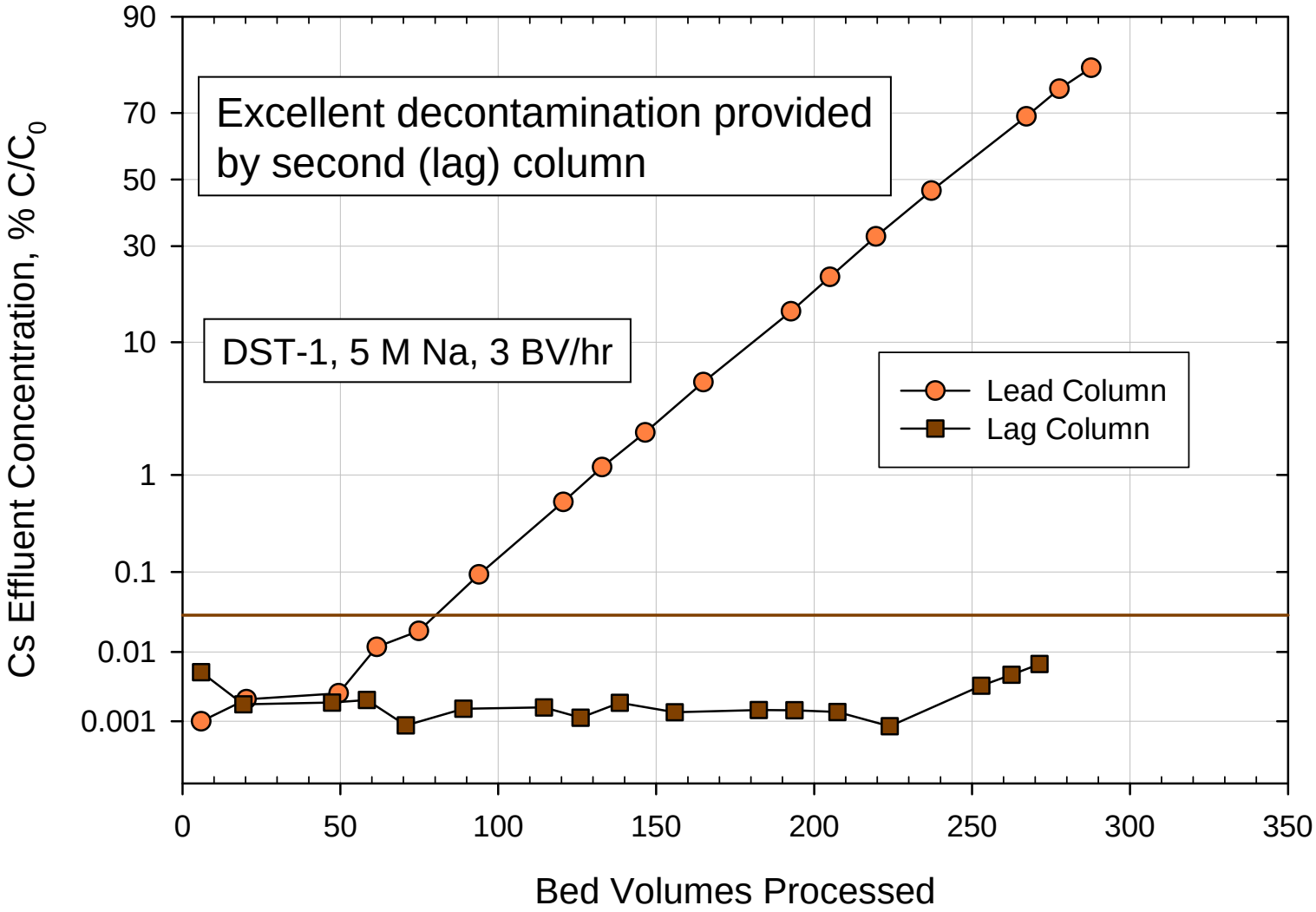
Probability Y-Axis



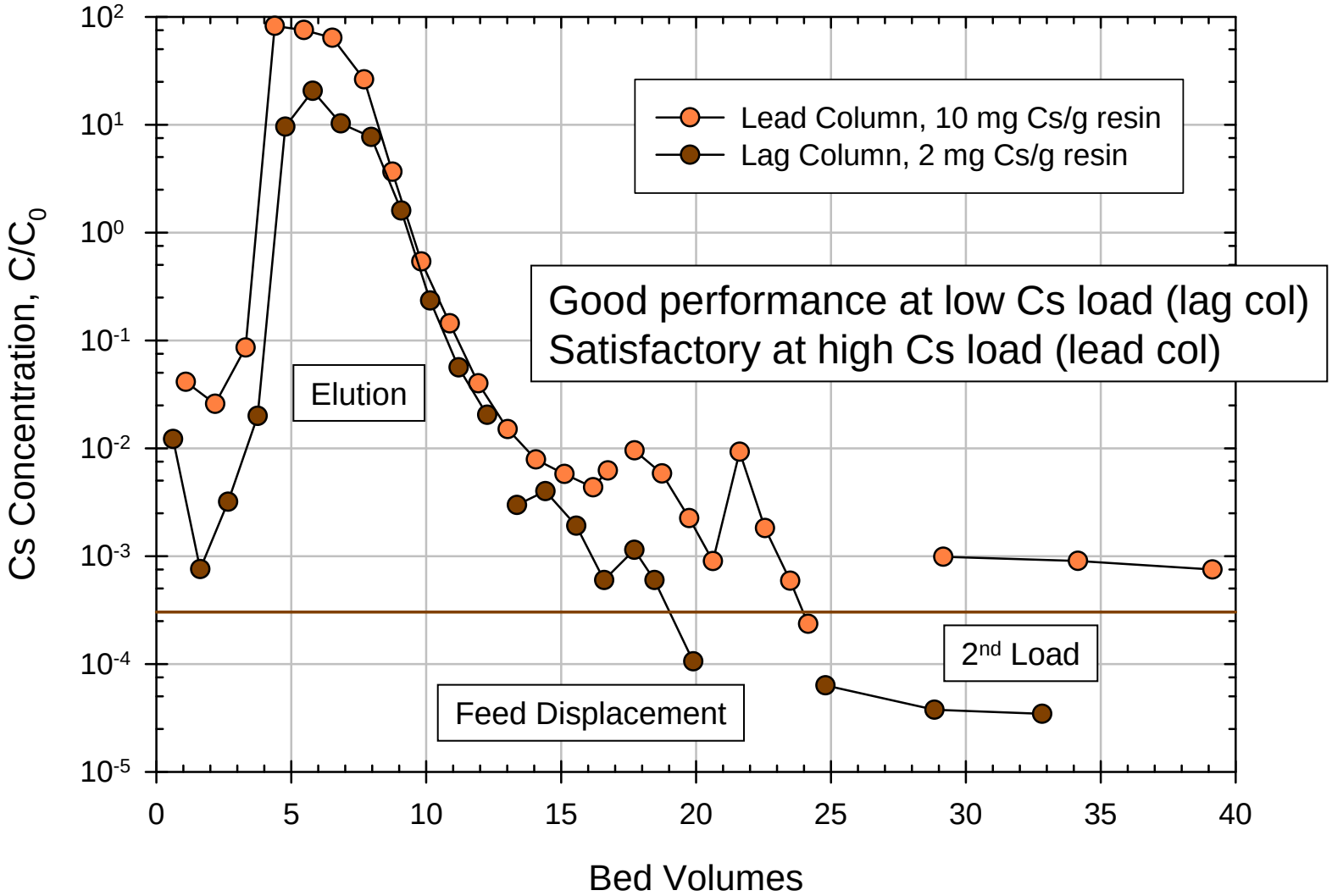
Small Column Ion Exchange Tests: Upflow Elution and Na Conversion



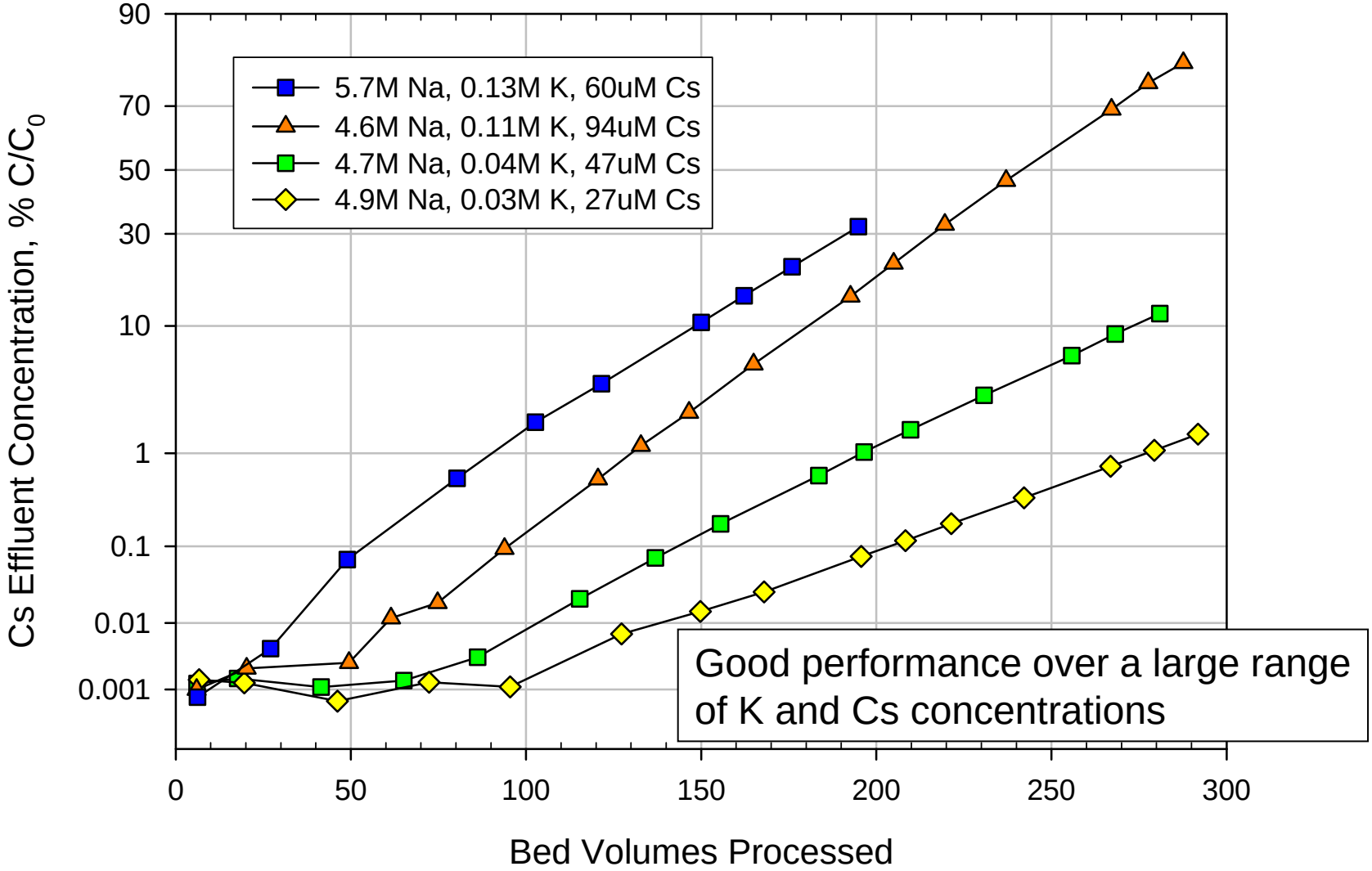
Small Column Ion Exchange Tests: Two Column Performance



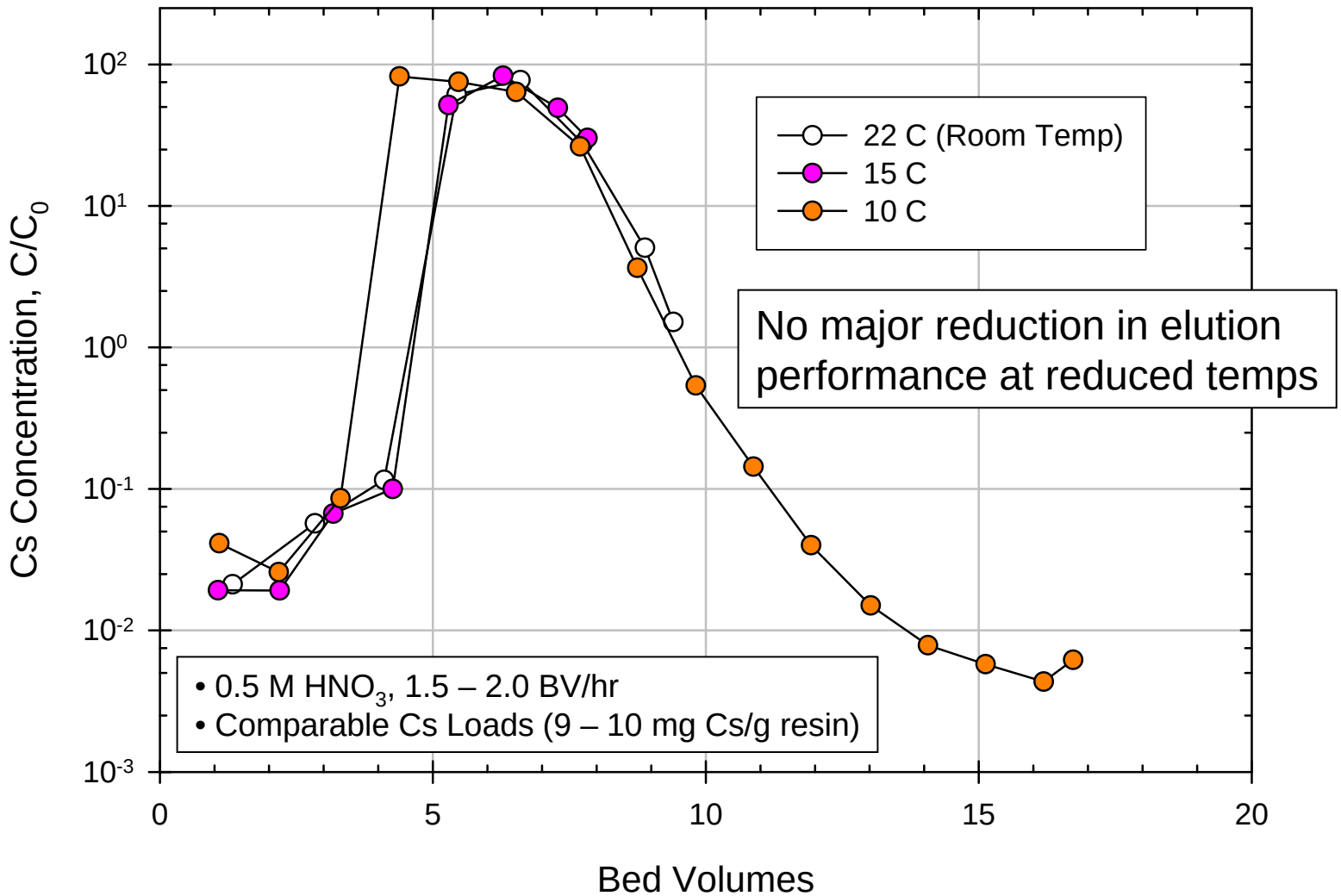
Small Column Ion Exchange Tests: Assessment of Process Conditions



Small Column IX Tests: Affect of Feed Variability at 3BV/hr



Small Column IX Tests: Affect of Temperature on Elution



Small Column Ion Exchange Tests: Recommended Process Steps

Operation	Process Solution	Volume (BV)	Flow (BV/h)	Duration (h)	Direction
LAW Processing	LAW @ 5 M Na	100+	3	33+	Down
LAW Displacement	0.1M NaOH	4	3	1.3	Down
Elution (Lead Col)	0.5M HNO_3	8	1.5	5.3	Up
Regeneration	a) 1 M NaOH b) 2M NaOH + 3M $NaNO_3$	a) 3 b) 3	3	2	Up

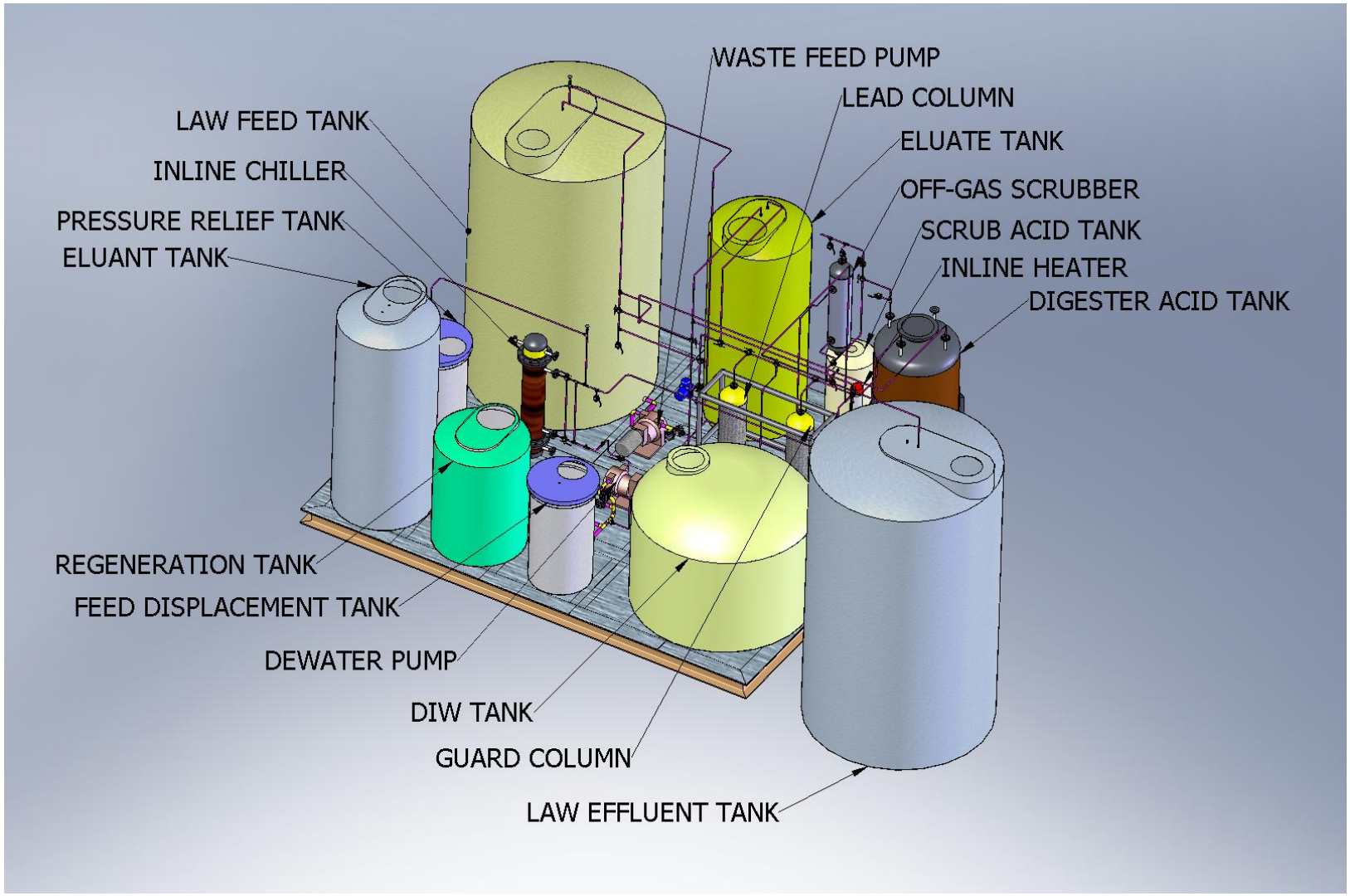
Small Column IX Test Results

- Successfully demonstrated abbreviated process conditions
- Assessed impact of feed variability – good performance for all target feeds
- Successfully demonstrated reduced temperature elution

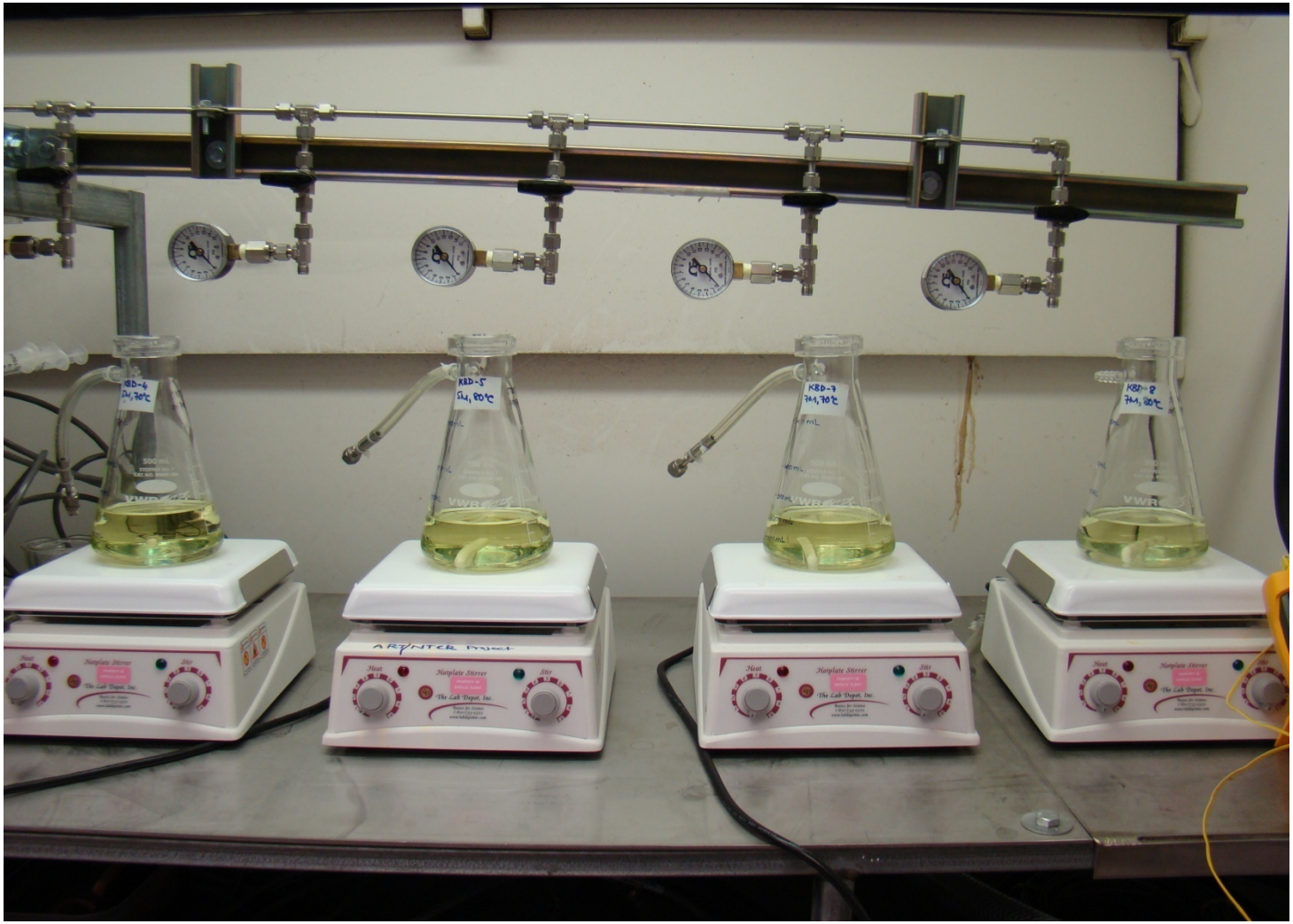
NTCR Bench Scale Testing Conclusions

- Bench scale testing objectives met, providing the foundation for pilot plant testing
- More details can be found at:
  - Tran, DN, DE Kurath, DL Blanchard, JM Peterson, and TL Sams. Near Tank Cesium Removal – Phase II Resin Dissolution and Destruction. September 2008, PNWD-4011, Battelle—Pacific Northwest Division, Richland, WA
  - Blanchard Jr, DL, SK Fiskum, JM Peterson, AF Farawila, and DE Kurath. Small Column Ion Exchange Testing for the Near Tank Cesium Removal Project. September 2008, PNWD-3985, Battelle—Pacific Northwest Division, Richland, WA
  - WM09 Symposia Proceedings, Paper #9222 (Blanchard et al., in press)
  - WM09 Symposia Proceedings, Paper #9143 (Sams et al., in press)

Backup Slides



Resin Dissolution/Destruction Experimental Setup



Small Batch Resin Dissolution/ Destruction: SVOC Analyses

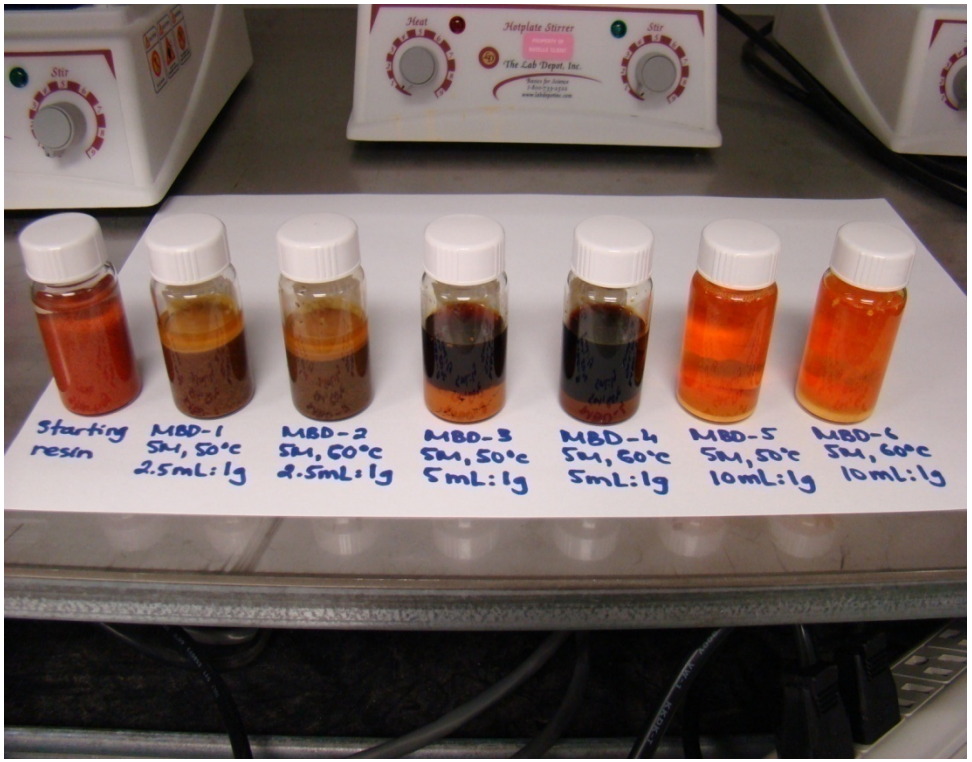
- Five liquid samples from kinetics batch destruction tests and five liquid samples from peroxide destruction tests analyzed for semi-volatile organic compounds
  - EPA Method 8270C modified for small sample size
  - 66 target compounds; any tentatively identified compounds (TICs) also requested
  - None of the 66 compounds found
  - Small amounts of acetone and fluorinated nitrophenols tentatively identified.

Small Batch Resin Dissolution/ Destruction: Minimum Dissolution Conditions

Acid Conc (M)	Acid Vol per 1 g Resin (mL:g)	Temp (°C)	Observations	Solid Residue (~ Vol% of Original)
5M	2.7 mL : 1 g	50	Very vigorous bubbling; Most beads didn't dissolve	80%
5M	2.7 mL : 1 g	60	Very vigorous bubbling; Most resin beads didn't dissolve	80%
5M	5.3 mL: 1 g	50	Very vigorous bubbling; Fine powder residue	35%
5M	5.3 mL : 1 g	60	Very vigorous bubbling; Fine powder residue	30%
5M	10.6 mL : 1 g	50	Slow bubbling; Fine powder residue	10%
5M	10.6 mL : 1 g	60	Very vigorous bubbling; Fine powder residue	10%
5M	10.6 mL : 1 g	40	No bubbling; Fine powder residue	40%
5M	10.6 mL : 1 g	45	No bubbling; Fine powder residue	30%
3M	10.6 mL : 1 g	60	Slow bubbling; Fine powder residue	15%
3M	10.6 mL : 1 g	70	Vigorous bubbling; Fine powder residue	10%
3M	14.5 mL : 1 g	60	Slow bubbling; Fine powder residue	10%
3M	14.5 mL : 1 g	70	Slow bubbling; Fine powder residue	5%

Green text indicates viable conditions

Small Batch Resin Dissolution/Destruction: Minimum Dissolution Condition Final Solutions



Final mixtures

Small Batch Resin Dissolution/ Destruction: Conclusions

- Resin destruction starts during dissolution
- TOC reaction is largely complete after 10 hours
- TOC destruction increases with increasing temperature at each acid strength:
  - Up to ~ 7% for 3M and 5M acids
  - Up to ~ 14% for 7M acid
  - High initial rate for 5 M acid at 80 C appears anomalous – rerun indicates 5 M acid at 90 C goes faster
- TOC destruction increases slightly (~ 3% - 5%) with increasing acid strength at each temperature

Small Batch Resin Dissolution/ Destruction: Conclusions (con't)

- Repeatability generally good; trends consistent despite some variability
- Hydrogen peroxide with heating destroys an additional ~ 10% of the TOC
  - Aging without heat for 63 hrs results in < 5% additional TOC destruction.
- Minimum condition tests successfully dissolved resin beads
  - 3 M nitric acid at 60-70 ^{o}C
  - 5 M nitric acid at 40-50 ^{o}C
- Results support a two phase resin dissolution process
  - Low temperature and acid concentration to remove resin from column
  - Higher temperature and acid concentration to destroy TOC in separate vessel

Small Column IX Tests: Technical Strategy/Approach

- Three simulants that bracket compositions of the likely first four double shell tank supernates, and one simulant for a dissolved saltcake
  - Target 6 M Na in feed; some reduced to 5 M Na based on initial set of tests
  - Bracket Cs and K concentrations
  - Simple compositions, but include components that test for efficiency of feed displacement and resin conversion: $Al(OH)^-_4$, NO_2^-, CO_3^{-2}

Small Column IX Tests: Technical Strategy/Approach

- Spherical RF resin
- Six single- and one dual-column systems
- Test all process steps: load, feed displacement, elution, conversion back to Na form
- Second short (15 BV) load cycle in some tests to assess efficacy of regeneration (elution + reconversion to Na form)
- Two “waves” of testing – 3 tests in first, 4 in second
  - Allows adjustment of test conditions for second wave

Small Column Ion Exchange Tests: Jacketed Column System

Small Column Ion Exchange Tests: Test Plan Summary

Wave	Test	Simulant	Loading Flow Rate (BV/hr)	Elution Temperature	Simulant Conc (Total [Na])
1	E1	DST-1	6	15°C	6
1	IX1	DST-1	6	RT	6
1	IX2	DST-2	6	RT	6
2	E2	DST-1 (Lead-Lag)	3	Lead: 10°C Lag: RT	5
2	IX3	DST-3	3	RT	5
2	IX4	DS	3	RT	5
2	IX5	DST-2	3	RT	6

E2 Lag column and IX5 added based on Wave 1 results.

Small Column Ion Exchange Tests: Method

- Three simulants that bracket compositions of the likely first four double shell tank supernates, and one simulant for a dissolved saltcake
  - Target 6 M Na; some reduced to 5 M Na based on Wave 1 (green highlight in next slide)
  - Bracket Cs and K concentrations (blue highlight)
  - Simple compositions, but include components that test for efficiency of feed displacement and resin conversion: $Al(OH)^-_4$, NO_2^-, CO_3^{-2} (yellow highlight)
- Based on Wave 1 the DST-1, DST-3 and DS target concentrations changed to 5 M Na for Wave 2.

Small Column Ion Exchange Tests: DST Simulants

	Tank Compositions (M)				Target Simulant Compositions (M)		
Species	AP-108	AP-104	AN-101	AN-104	DST-1	DST-2	DST-3
Na	6	6	6	6	6	6	6
K	0.08	0.05	0.06	0.13	0.13	0.13	0.05
Total [Cs] (X 10-5)	5.3	5.8	4.3	11.7	12	6	6
Al	0.5	0.8	0.5	0.6	0.3	0.3	0.3
nitrite	1.5	1.6	1.6	1.2	1.6	1.6	1.6
nitrate	1.8	1.9	1.6	1.6	2	2	2
free OH	1.3	1.4	1.0	1.7	1.5	1.5	1.5
TIC--C	0.09	0.08	0.03	0.07	0.1	0.1	0.1

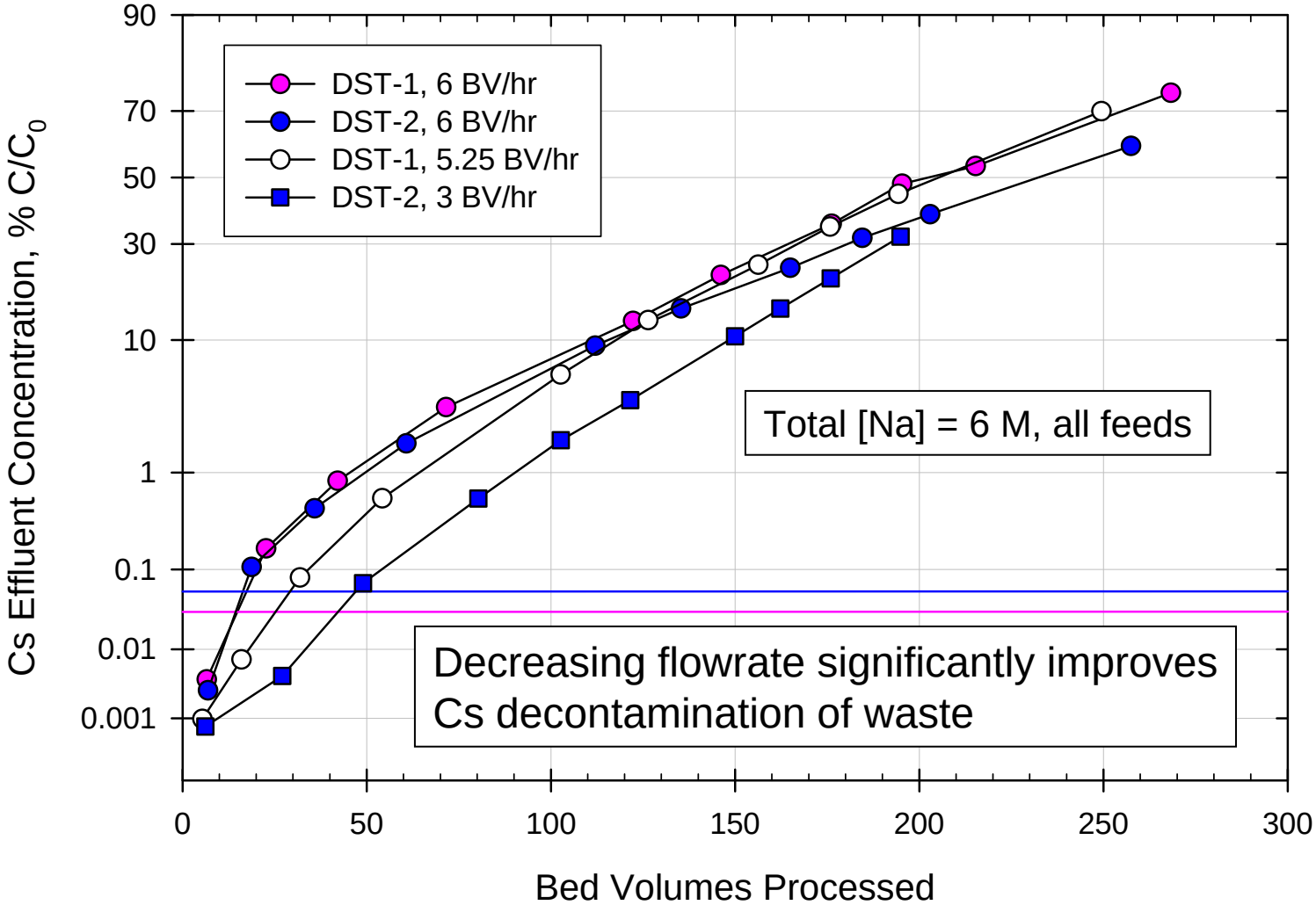
- **Tank compositions from TWINS data, adjusted to 6 M Na**
- **DST-1 and DST-3 conc's reduced to 5 M Na for Wave 2**

Small Column Ion Exchange Tests: Simulants Adjusted to 5 M Na for 2nd Wave

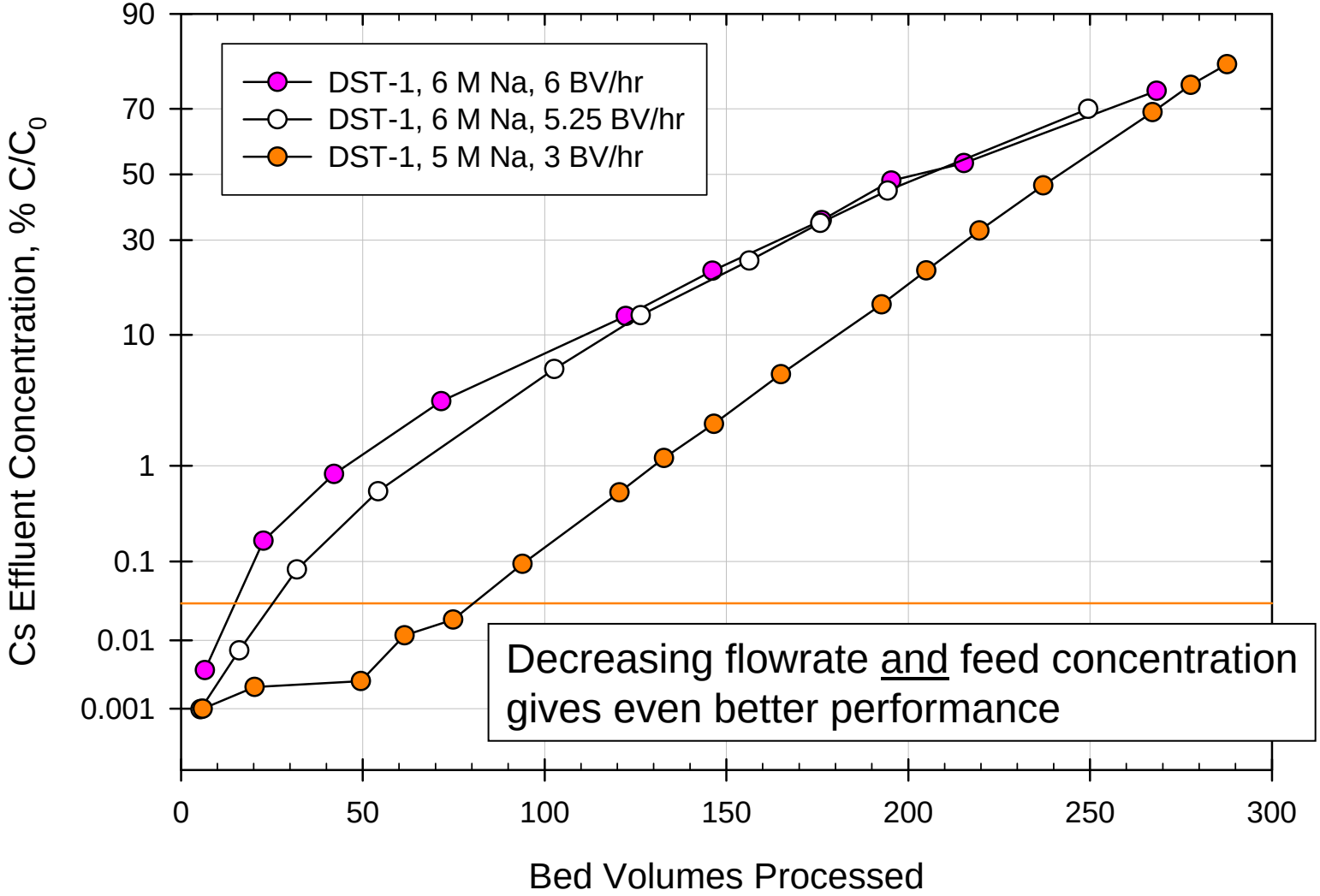
	S-Tank Dissolved Saltcake Composite	S-Tank Simulant "DS" Target
Analyte	M	M
Na	5	5
K	0.025	0.025
Total Cs ($X\ 10^{-5}$)	2.75	2.75
Cs/K ($X\ 10^{-5}$)	92	92
Al	0.275	0.275
nitrite	0.80	0.8
nitrate	1.88	1.9
free OH	0.7	0.7
TIC--C	0.5	0.5

- **Actual S-tank composite data adjusted to 5 M Na**
- **Simulant conc. target reduced to 5 M Na based on Wave 1**

Small Column Ion Exchange Tests: Affect of Flow Rate

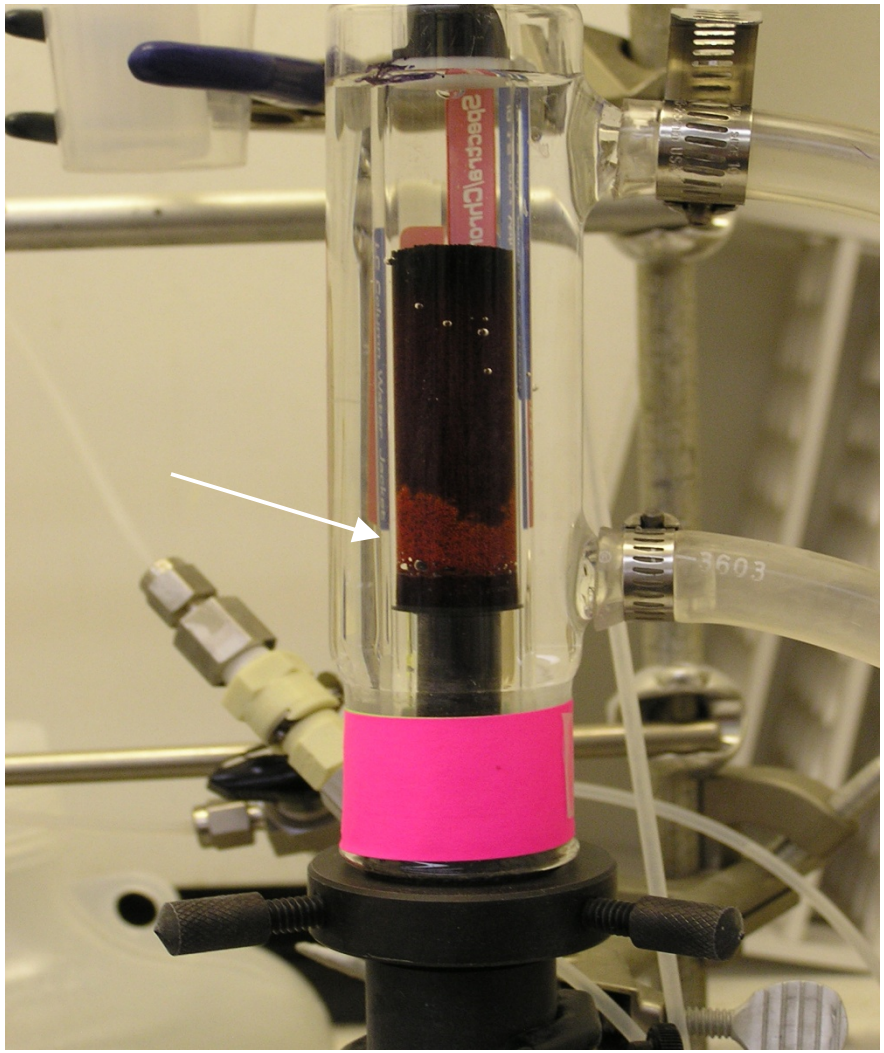


Small Column Ion Exchange Tests: Affect of Feed Concentration and Flow Rate

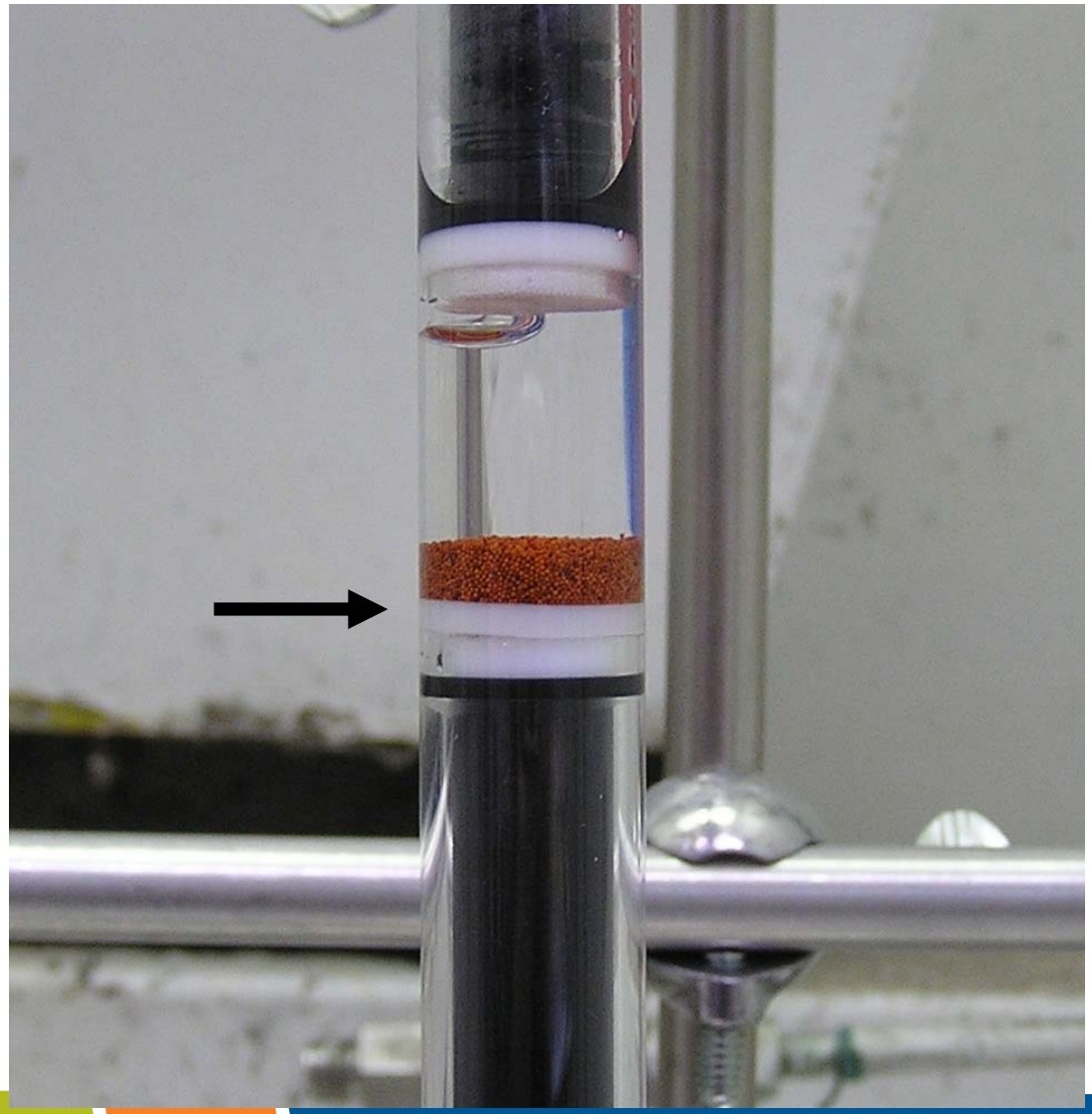


Wave 1 Small Column Ion Exchange Tests: Gas Bubbles Form on Start of Elution

- Incomplete feed displacement at bottom of bed – note dark Na-form resin below orange H-form resin
- Fingering – no apparent impact on elution



Small Column Ion Exchange Tests: Teflon Ring to Eliminate Gap



Small Column Ion Exchange Tests: Conclusions

- Effective process conditions identified:
  - "Dense regenerant" reformulated to prevent NO_x generation in beds
  - Data on impact of feed concentration and flow rate collected; modeling using this data in FY09 will identify optimum operating conditions
  - Elimination of water rinses after feed displacement and elution demonstrated; feed displacement and regeneration volumes increased to compensate
- Feed variability impact assessed – performance good at 5 M Na feed, 3 BV/hr
  - Performance may be optimum at higher feed concentrations and/or faster flow rate – trade-offs modeled in Task 2.
- Reduced temperature elution demonstrated – no major reduction in performance