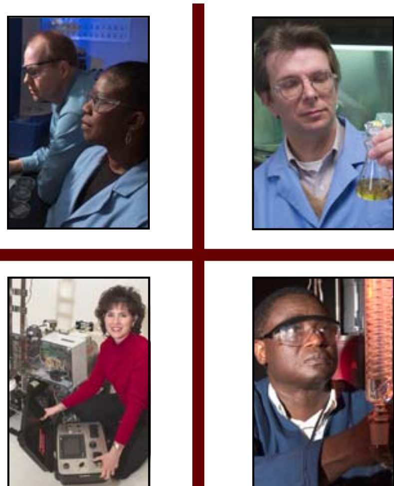
Cesium Removal Performance of Resorcinol-Formaldehyde Resin



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Introduction

- The Hanford River Protection Project Waste Treatment Plant (RPP-WTP) will use ion exchange for cesium removal from high sodium/alkaline liquid nuclear waste.
- Spherical Resorcinol-Formaldehyde (RF) resin is being examined as an alternative to SuperLig™ 644 (IBC Advanced Technologies) for
  - Lower cost
  - Better kinetics and hydraulics
  - Less proprietary issues
- Current task provided much information on the chemical nature of RF resin. Isotherm, kinetics, and column data were obtained on one "gold standard" batch of resin. Results are being used in isotherm and column modeling.

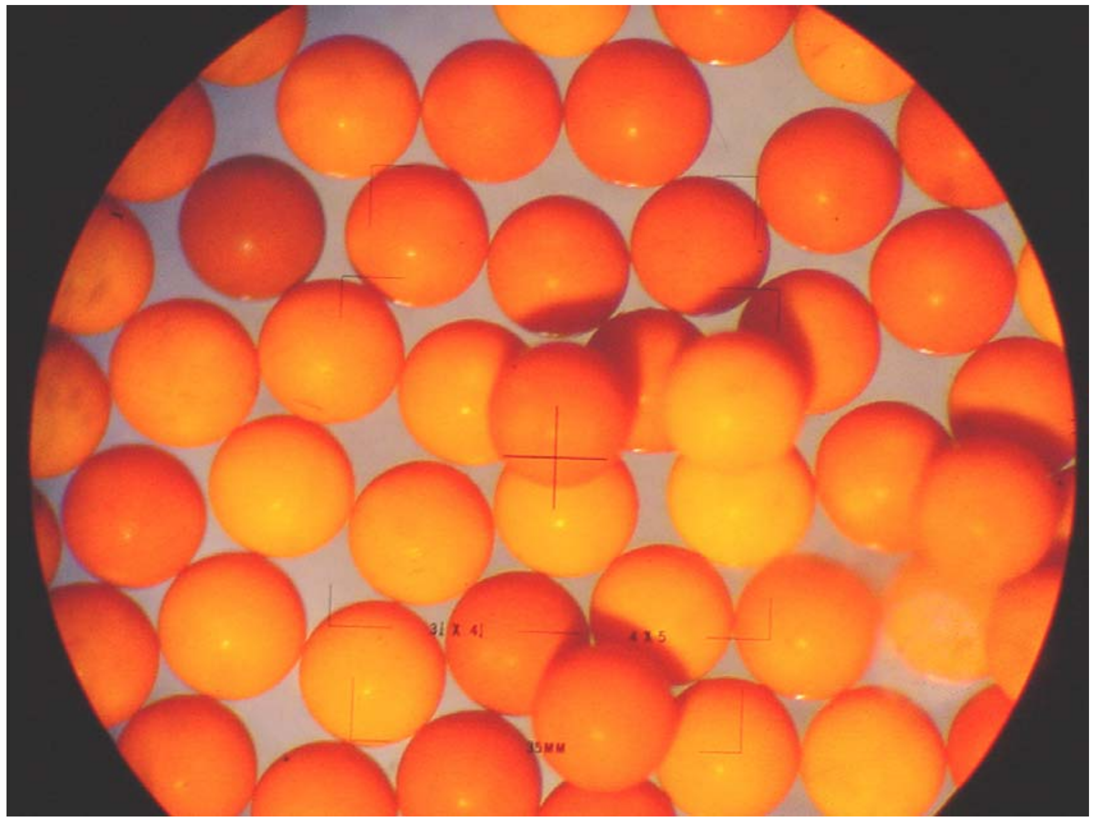
Spherical RF Weak Acid Resin from MicroBeads

-**Proprietary process, (Microbeads AS, Skedsmokerset, Norway),**

-**Resin grown on a Dynoseed® substrate.**

-**World Patent WO 93/02112, J. Ugelstad.**

-**Uniform spheres desired because hydraulics are much better than granular shard resin (shrink/swell issue).**



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Batch Testing Conditions

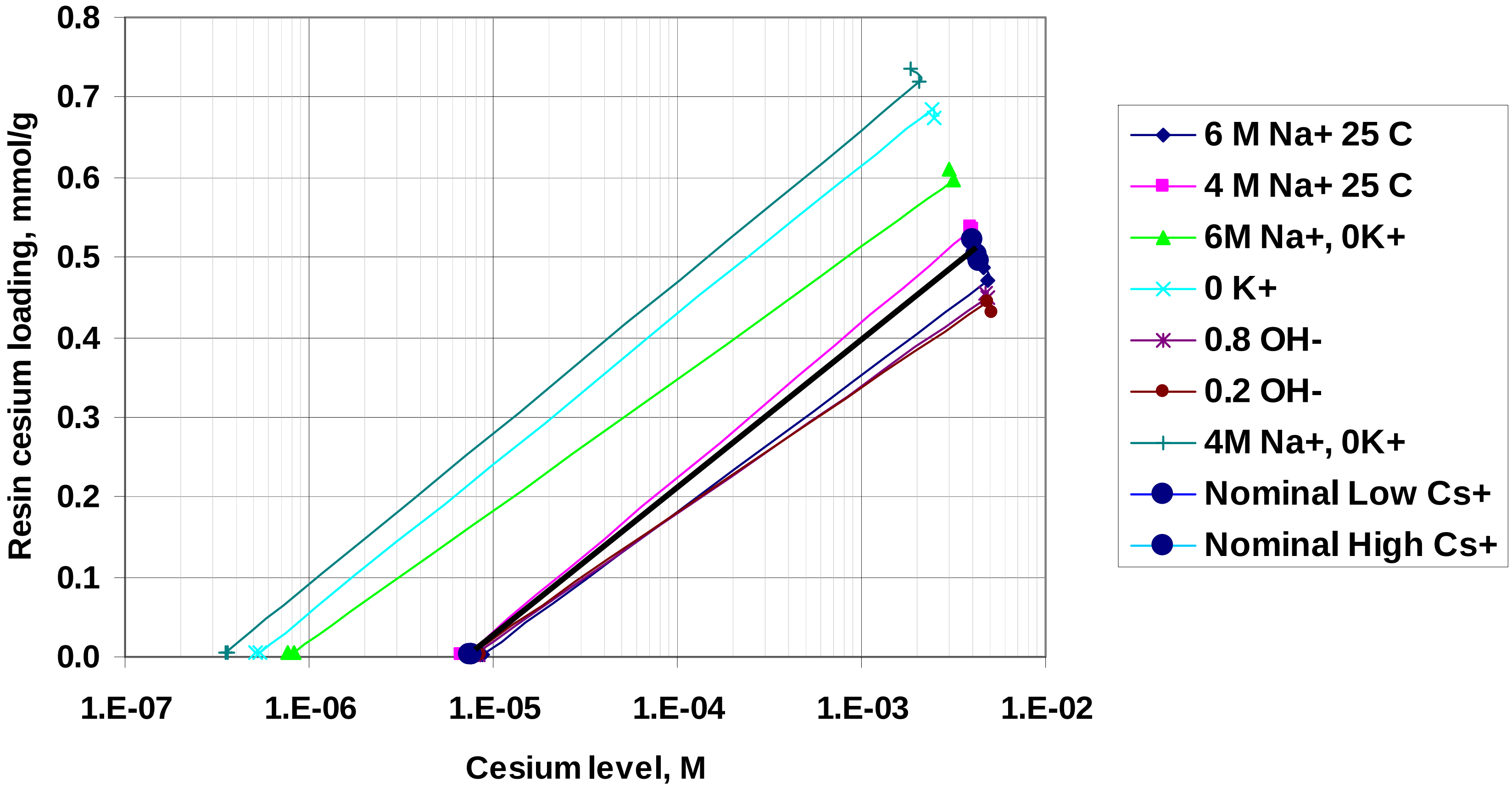
- Simulant makeup for each batch: Hanford Waste Tank AP-101 alkaline simulating solution without toxic metals used in most cases. Aluminate often omitted to avoid precipitation.
- Na^+, K^+, Cs^+, Rb^+, and free OH^- levels were varied to support isotherm modeling.
- A few batches with the full AP-101 simulating solution with toxic metals were included.
- Batch phase ratio: 20 mL solution and 0.2 g resin (phase ratio 100 mL/g) is used.
- Temperature for each batch is shown in the matrix, next slide.

Test Matrix for Isotherm

Recipe	$[Na^+]$, M	$[K^+]$, M	$[OH^-]$, M	Cs level	15 ˚C	25 ˚C	45 ˚C
1. Nominal	**5.**	**0.71**	**1.94**	4-pt.	N/A	3 X*	2 X
2. Full Recipe	5.	0.71	1.94	4-pt.	2 X	2 X	2 X
3. No Rubidium	5.	0.71	1.94	4-pt.	N/A	2 X	2 X
4. Modified	6.	0.71	1.94	2-pt.	N/A	2 X	2 X
5. Modified	4.	0.71	1.94	2-pt.	N/A	2 X	2 X
6. Modified	6.	0.0	1.94	2-pt.	N/A	2 X	2 X
7. Modified	5.	0.0	1.94	2-pt.	N/A	2 X	2 X
8. Modified	5.	0.71	0.8	2-pt.	N/A	2 X	2 X
9. Modified	5.	0.71	0.2	2-pt.	N/A	2 X	2 X
10.Modified	4.	0.0	1.94	2-pt.	N/A	2 X	2 X

2 X = duplicate, 3 X = triplicate; *two of four points run in triplicate for better statistics

Chemical Effects on Resin Performance



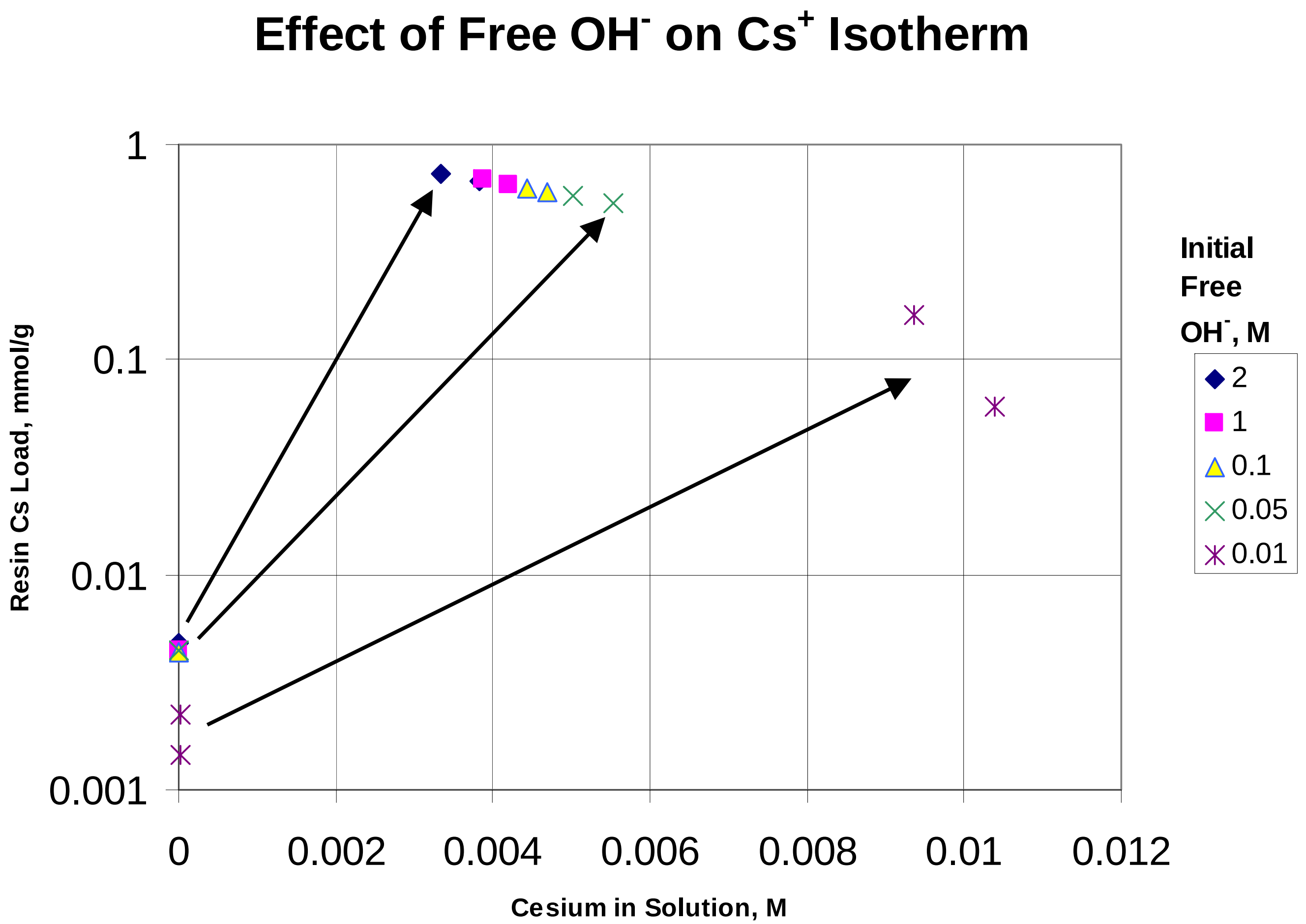
Test Matrix for Effect of Free Hydroxide

Sodium chloride/hydroxide solution was used in this testing per F. Helfferich, Ion Exchange.

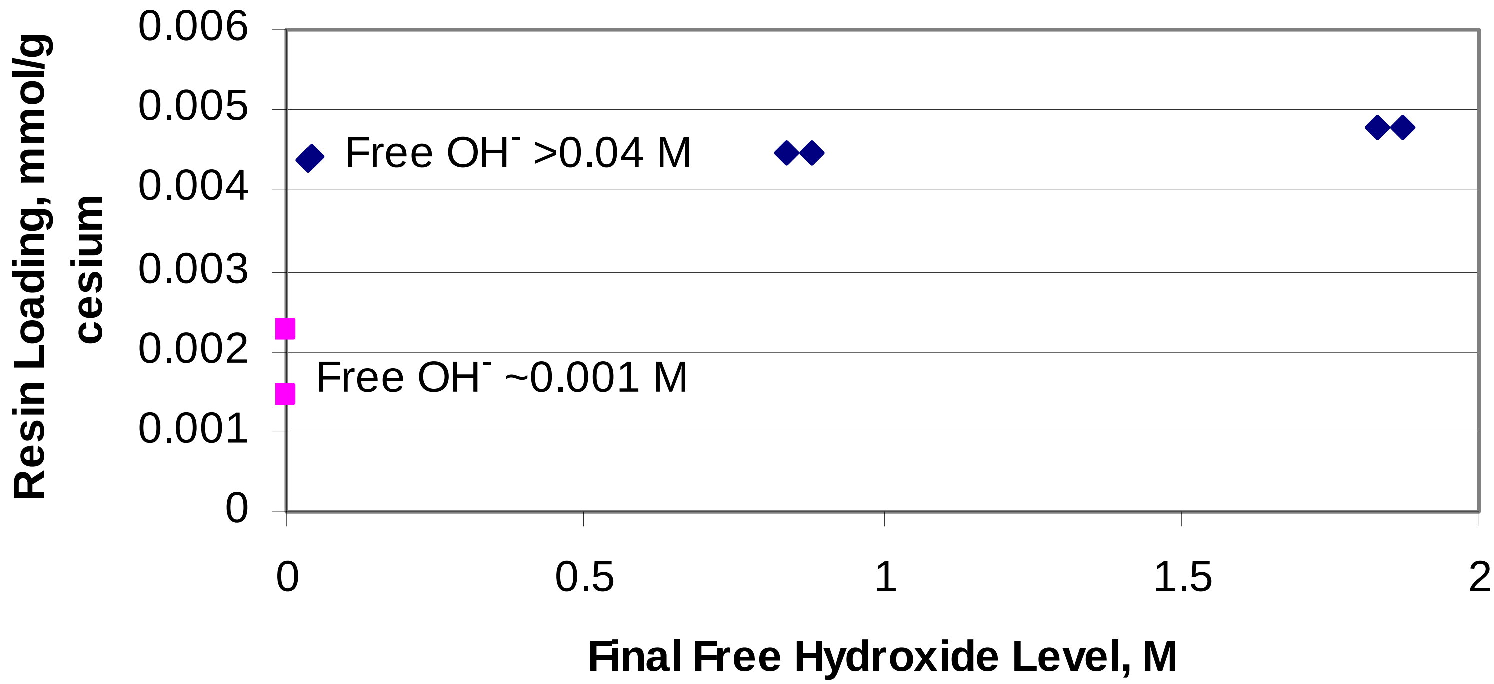
$[Na^+]$, M	$[Cl^-]$, M	$[OH^-]$, M	Cs^+
5.	3	2	3-pt. *
5.	4	1	3-pt.
5.	4.9	0.1	3-pt.
5.	4.99	0.05	2-pt.
5.	4.999	0.01	2-pt.

***First two [Cs+] initial concentration points are "high", 1450 mg/L, and "low", 6 mg/L. The third point is "very low", 0.11 mg/L. Also, measured free OH- after resin contact, along with [Cs+].**

Effect of Free OH on Cesium Loading



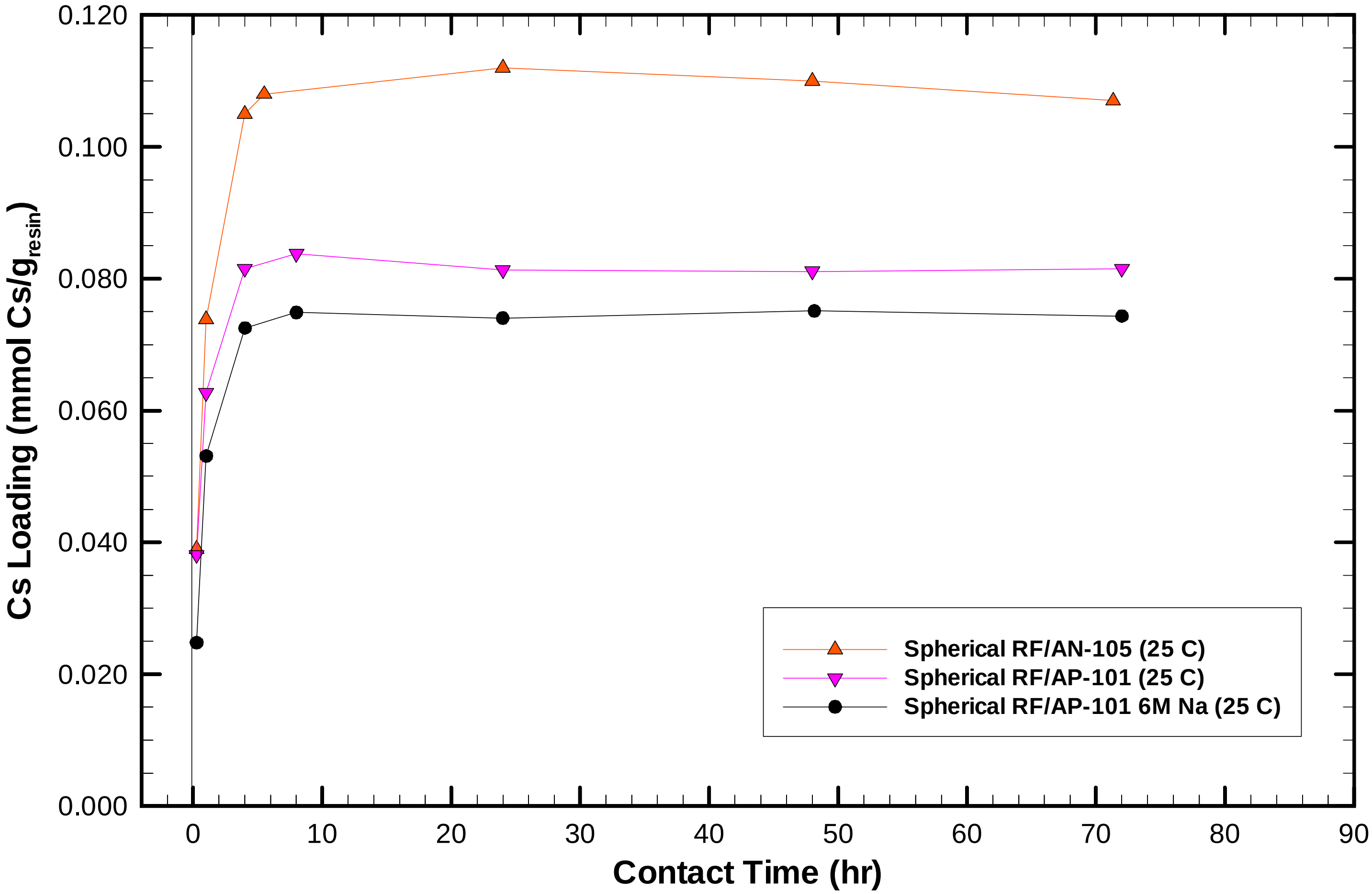
Free Hydroxide Effects on Resin Performance



Somewhere below [OH^-] <0.04 M resin capacity "falls off a cliff"

Kinetics Column and Flow System

Chemical Effects on Resin Performance



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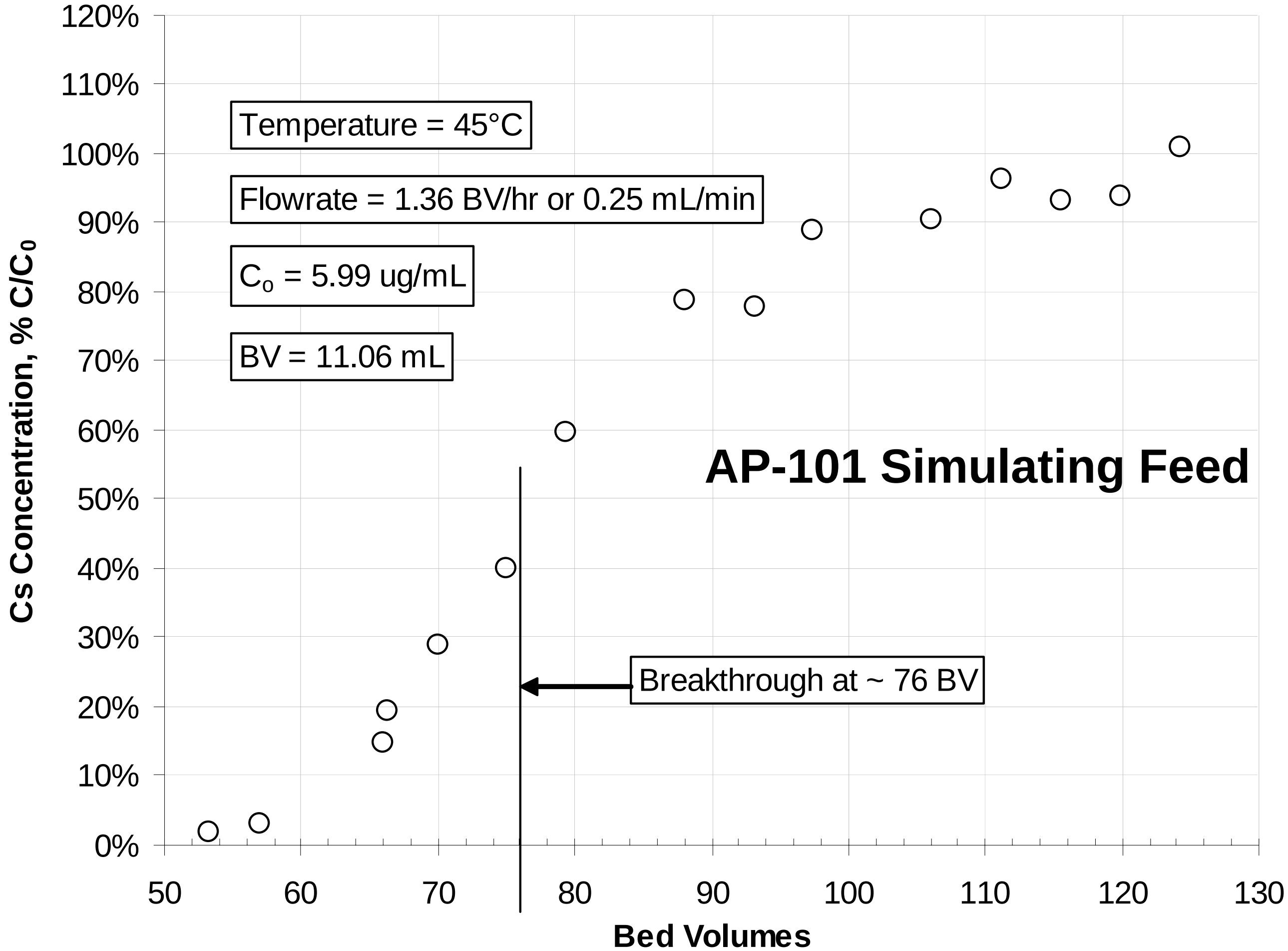
Ion Exchange Column

- **All work is in downflow. One load/elute cycle per column was run.**
- **0.5 M nitric acid used for elution.**
- **Weak acid resin changes color on hydrogen/sodium conversion.**
- **Shrink/swell significant (8.5 to 11.1 mL range for this bed, Na+ form = expanded).**
- **Bead diameter relatively monodisperse, 460 +/- 28 micron when expanded.**

Chemical Effects on Resin Performance



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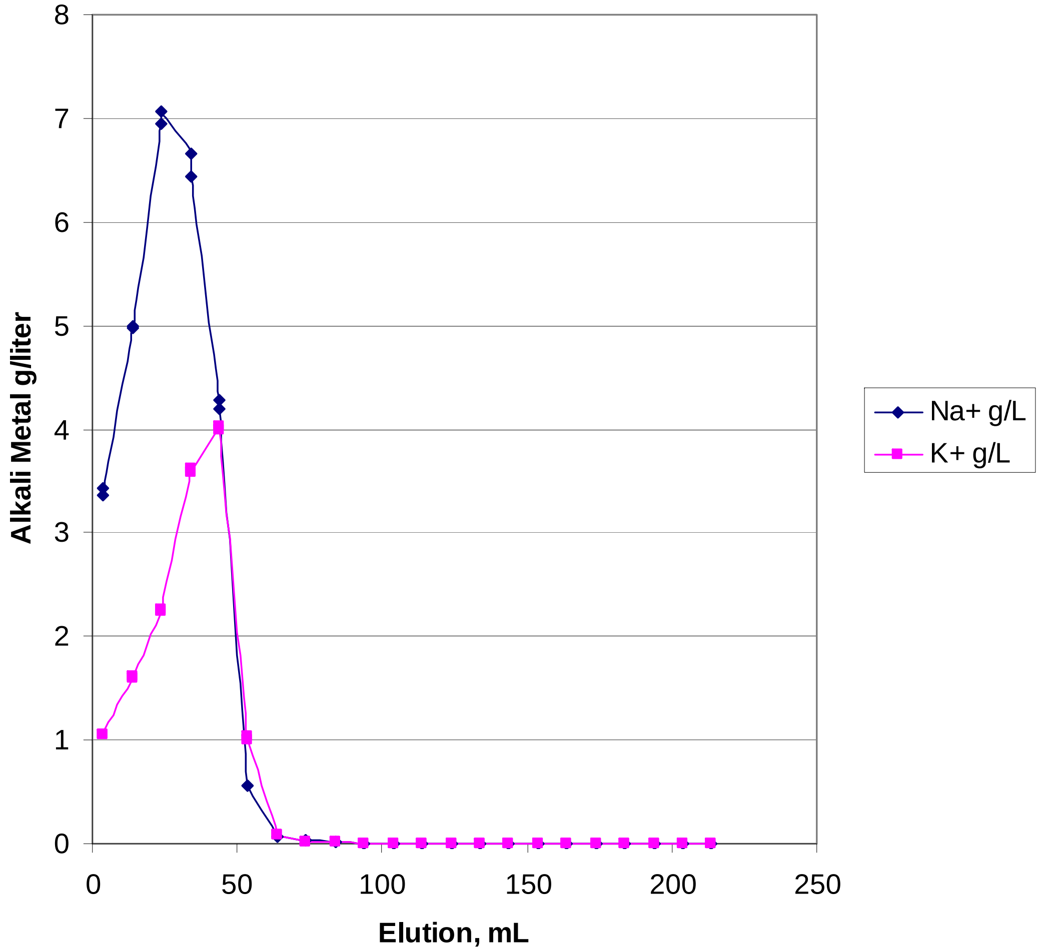
Elution Profiles from the AP-101 Column Run

- **3 bed volumes 0.1 M NaOH fluid displaces feed**
- **3 bed volumes water displacement**
- **0.5 M Nitric acid elution**



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Estimating Total Resin Capacity

Method	Sodium mass	Potassium mass	Resin mass, average	Total capacity, mmol/g
AP-101 elution	0.268 g	0.137 g	2.8860 g	5.25
AN-107 elution	0.437 g	0.024 g	2.8916 g	6.78
Neutralization of free NaOH*	0.0214 g OH-	N/A	0.205 g	6.16 ± 0.16
Weight percent Sodium in dry resin	0.0159 g	N/A	0.1055 g of sodium form resin	8.1**

*Average of 8 values where initial free hydroxide was 0.1 M.

** Back-calculated to the dry hydrogen form basis.

Summary: Total capacity 6 ± 0.8 meq/gram

Affinity for Elements outside of Cesium

- **Affinities for elements other than Cs can affect spent resin disposal plans.**
- **Elemental data in the table are for post-elution resin, hydrogen form.**
- **Resin mass loss in one cycle is insignificant.**
- **Trace Cd and Pb also adsorbed in loading cycles, but were completely eluted.**

Measurement	AP-101	AN-107	Units
Resin Bed Mass before cycle	2.8865	2.8860	g H^+ form
Resin Bed Mass after cycle	2.8853	2.8971	g H^+ form
- All values below are from resin bed samples AFTER respective cycles -			
Resin Bed Al	54.	<46.5	µg/g H^+ form
Resin Bed Cr	1660.	7.74	µg/g H^+ form
Resin Bed Fe	26.2	70.7	µg/g H^+ form
Resin Bed Na	<51.5	169.	µg/g H^+ form
Resin Bed K	<350.	<319.	µg/g H^+ form
Resin Bed S	1350.	1110.	µg/g H^+ form
Resin Bed Sr	<0.86	2.99	µg/g H^+ form
Resin Bed Zn	<5.15	16.8	µg/g H^+ form
Resin Bed Cs^+ (1)	0.239	0.681	µg/g H^+ form
Resin Bed Cs^+ (2)	0.235	0.664	µg/g H^+ form

Modeling of RF Resin

- Competitors for ion exchange: Cs^+, Rb^+, K^+, Na^+ and H^+
- 2-Site ionic model for monovalent exchange
- 2 pKa dissociation model
- Ionic strength term for neutral species sorption
- Pitzer model for aqueous phase activities
- Wilson model for solid phase activities
- van Hoff temperature dependence for equilibrium constants

Conclusions

- RF resin is very selective for cesium, but major competitors in waste feed challenge performance in the order K^+ > Na^+ > [H^+ when free OH^- exceeds ~ 0.04 M]. H^+ competes strongly at low pH, providing elution of Cs+.
- Total resin capacity is 6 +/- 0.8 meq/g. Under practical conditions (5 M sodium, 1 E-4 M cesium) order of magnitude 1 meq/g of capacity is loaded with cesium.
- Resin also selects other waste components; chromium (chromate in the waste) is especially notable but is not likely a competitor to cesium.
- Shrink and swell characteristics are a significant consideration for large scale design.