

Fundamentals of Radium and Uranium Removal from Drinking Water Supplies

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Important Radium Isotopes

Radium Isotope	Half Life	Primary Emission	Decay Series
^{226}Ra	1600 y	Alpha	Uranium
^{228}Ra	5.7 y	Beta	Thorium
^{224}Ra	3.64 d	Alpha	Thorium

Important Uranium Isotopes

Isotope, Emission	Natural Abundance %	Half Life yr	Specific Activity pCi/μg	Relative Activity %
$^{238}\text{U}, \alpha$	99.276	4.51×10^9	0.333	47.33
$^{235}\text{U}, \alpha/\gamma$	0.7196	7.1×10^8	2.144	2.21
$^{234}\text{U}, \alpha$	0.0057	2.47×10^5	6189.0	50.51

Natural abundance and half life from Lange's Handbook, 1973, p. 3-108

Specific activity and relative activity calculated from isotope mass, half life and natural abundance.

If present at natural abundance $1\mu\text{g U} = 0.67 \text{ pCi}$

Chemical and Physical-Chemical Behavior of Isotopes

- Although possessing differing decay rates and modes of decay, the chemical and physical-chemical behavior of all isotopes is the same.
- 95% removal of ^{226}Ra is also 95% removal of ^{228}Ra when they are present together regardless of the ratio of their initial activities.
- 95% removal of ^{238}U is also 95% removal of ^{235}U when they are present together regardless of the ratio of their activities.

Radium and Uranium Speciation in Ground Water as a Function of pH

pH Range	Predominant Species	Predominant Species Charge
<i>All</i>	Ra^{2+}	<i>a divalent cation</i>
< 5	UO_2^{2+}	a divalent cation
5 to 6.5	$UO_2CO_3^0$	a neutral molecule
6.5 to 7.6	$UO_2(CO_3)_2^{2-}$	a divalent anion
➤ 7.6	$UO_2(CO_3)_3^{4-}$	<i>a tetravalent anion</i>

$$pCO_2 = 10^{-2} \text{ atm}, C_{T,U} = 2.38 \text{ mg/L}, 25 \text{ }^\circ\text{C}$$

Above pH 10.5, positively charged uranyl hydroxide complexes are dominant.

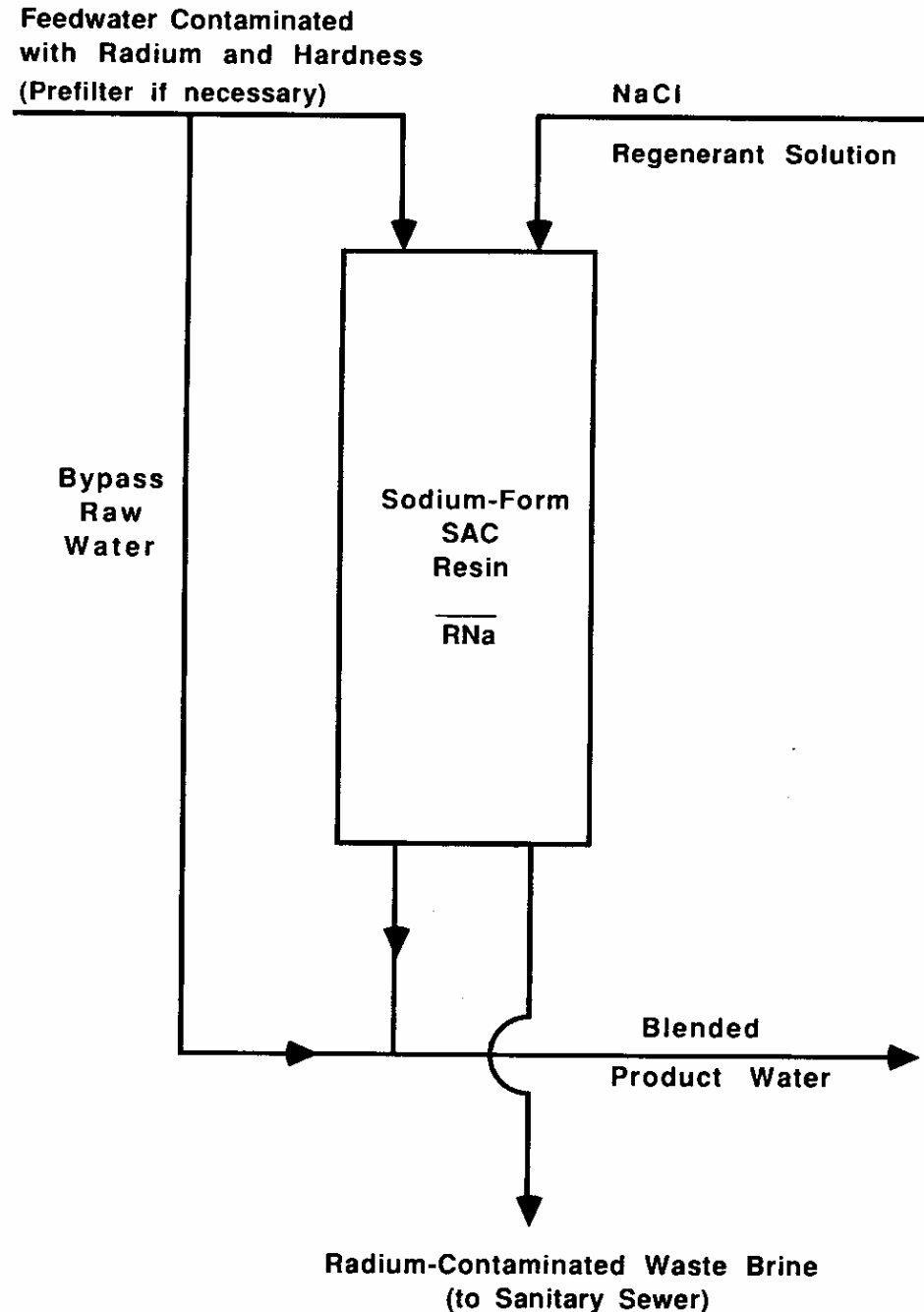
Radium-Removal Methods

- **Cation Exchange Softening (BAT)**
$$2 RNa + Ra^{2+} \rightarrow R_2Ra + 2 Na^+$$
- **Lime Softening (BAT)**
- **Reverse Osmosis (BAT)**
- **Sorption onto MnO₂ (HMO)**
- **Precipitation with BaSO₄ (by adding BaCl₂)**
 - (Excess)Ba²⁺ + (Trace)Ra + SO₄²⁻ = Ba(Ra)SO₄
- **Sorption onto BaSO₄-Impregnated Media**
 - Media•BaSO₄ + Ra²⁺ = Media•Ba(Ra)SO₄ + Ba²⁺
- **Electrodialysis**

POU Radium-Removal Methods

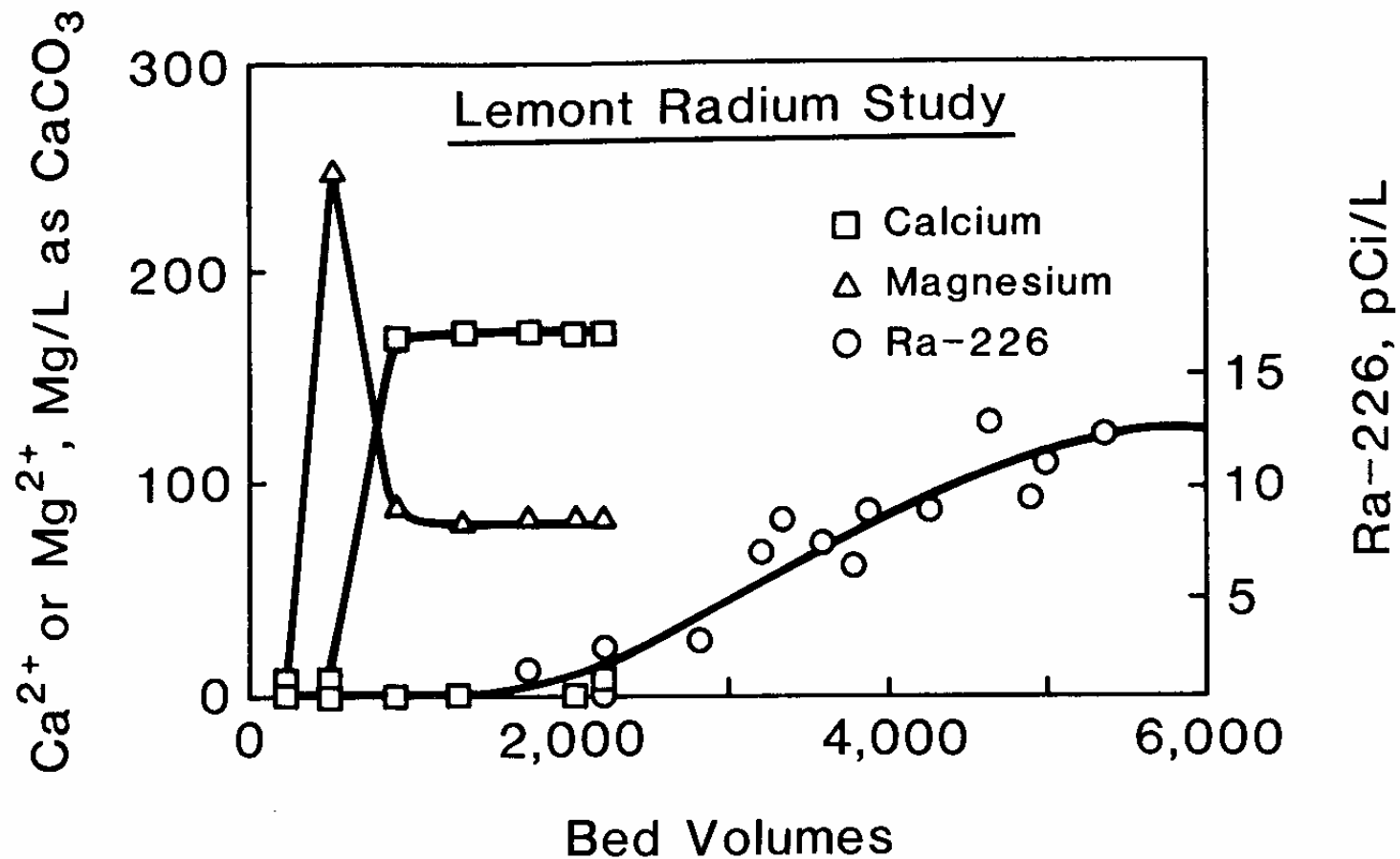
- **Reverse Osmosis (BAT)**
- **Cation Exchange Softening**
$$2 RNa + Ra^{2+} \leftrightarrow R_2Ra + 2 Na^+$$
- **Sorption onto MnO₂-impregnated fibers or filters, e.g., DE or granular media.**
- **Sorption onto BaSO₄-Impregnated Resin or Activated Alumina**

Radium
removal by
ion-
exchange
softening
with
bypass
blending of
raw water.



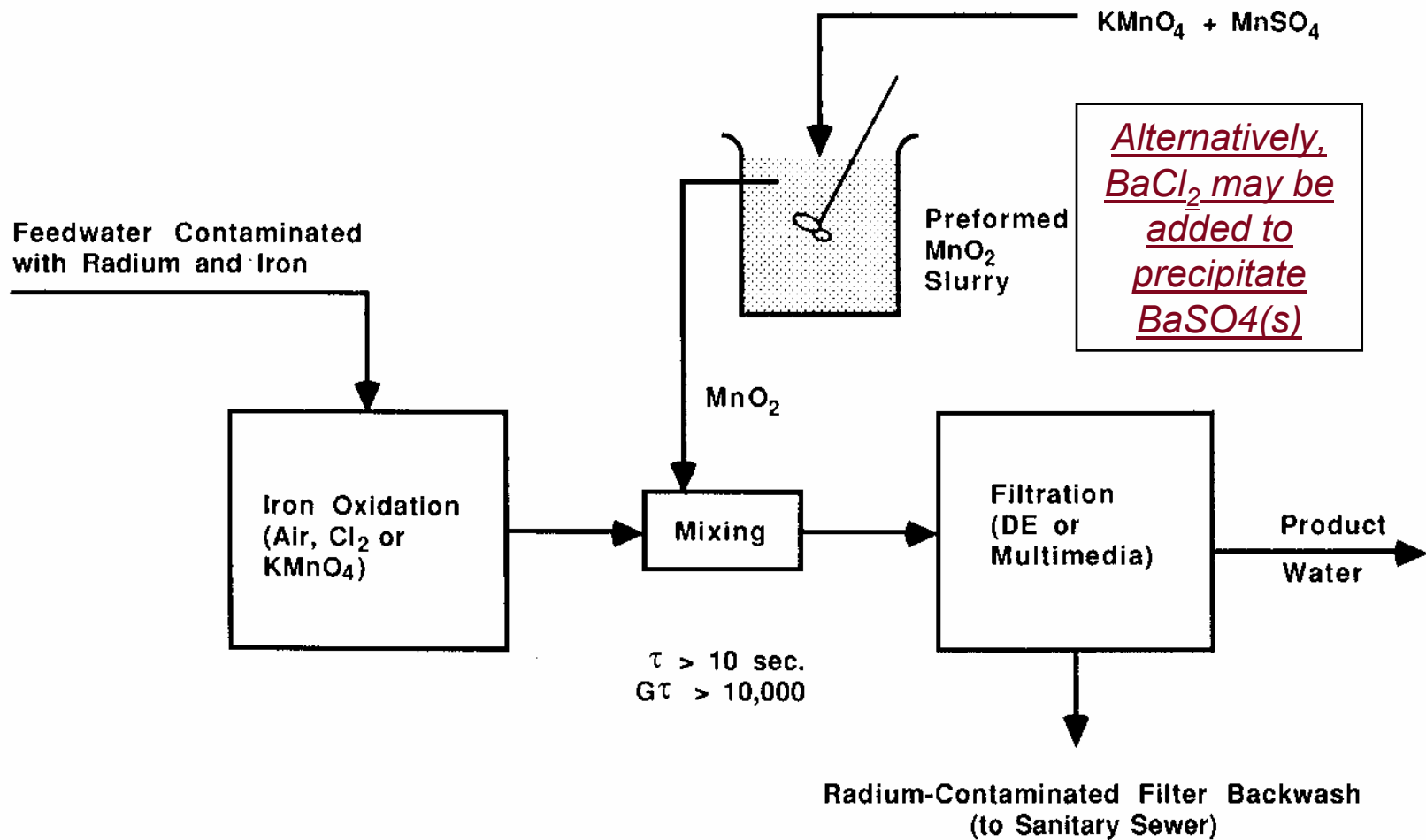
Ion Exchange Resins for Radium Removal

Designation	Resin Description	Ionic Form	Capacity meq/mL
Strong Acid Cation exchange resin for radium removal: Amberlite IR-120+, Duolite C20, Purolite C100, Dowex HCR-S	Standard gel SAC resin, polystyrene-DVB matrix, —SO₃⁻ exchange groups	Na⁺	1.9

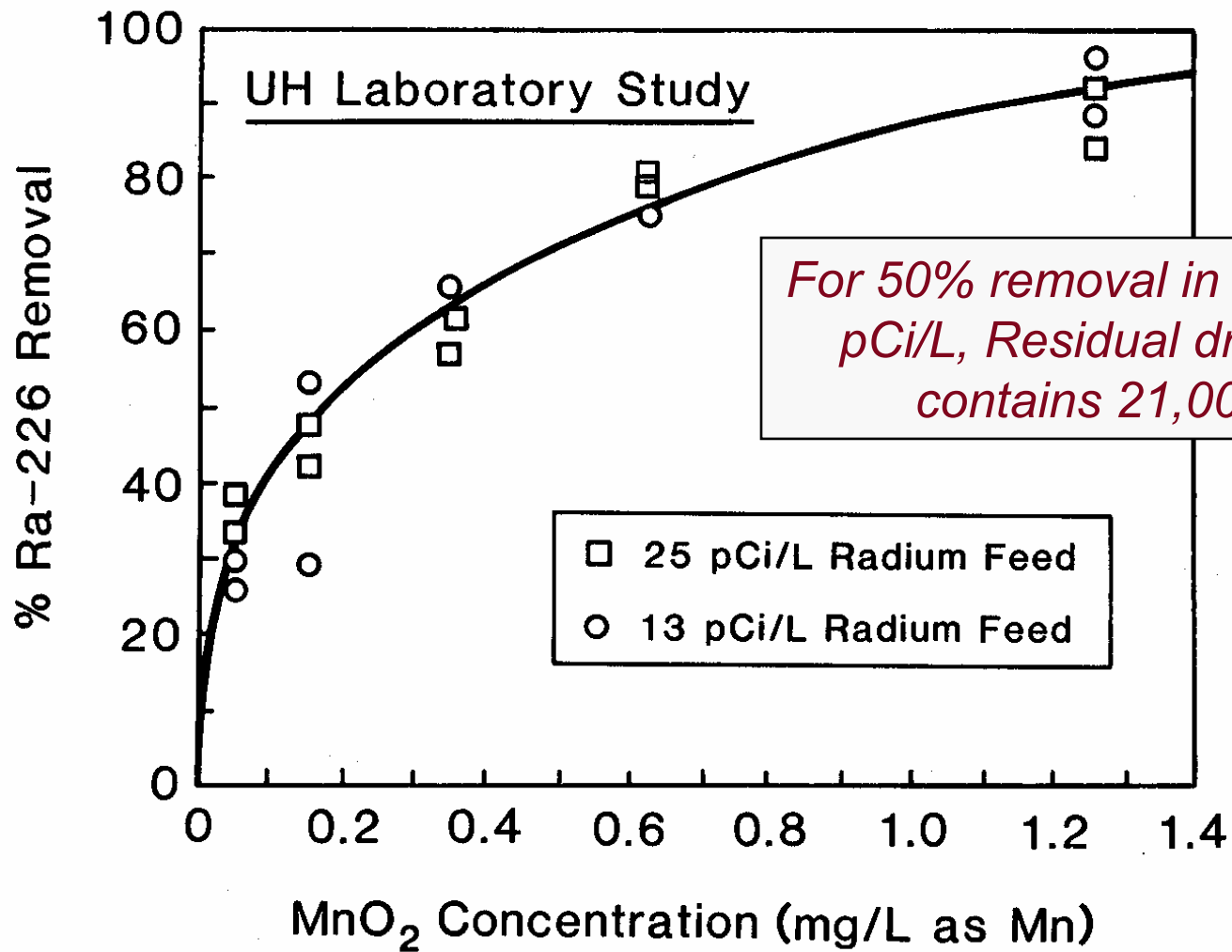


Magnesium, calcium and radium breakthrough curves for ion-exchange softening.

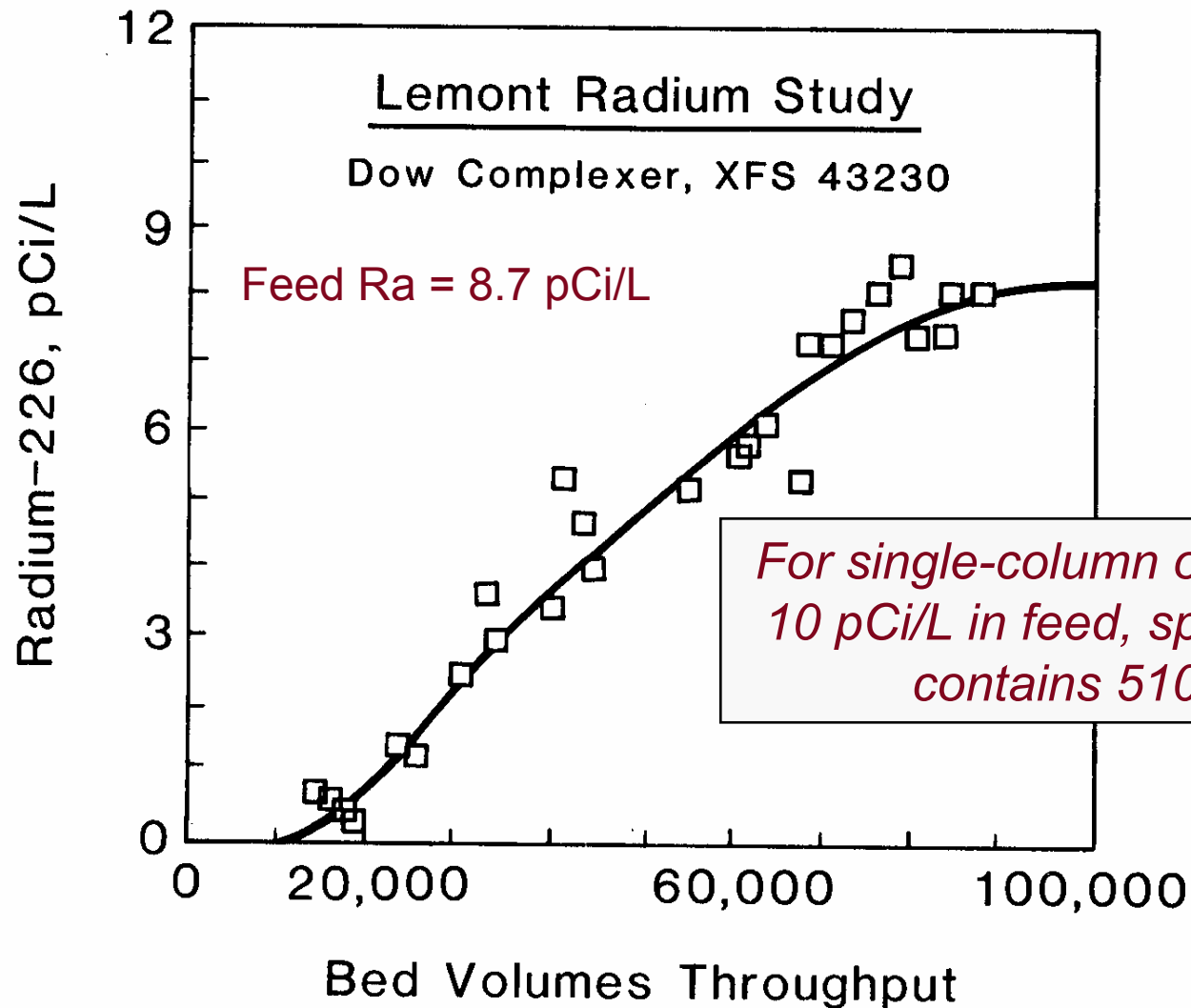
If feed water contains 10 pCi/L, the resin contains ~20 pCi/g at steady state operation. Waste brine contains ~600 pCi/L



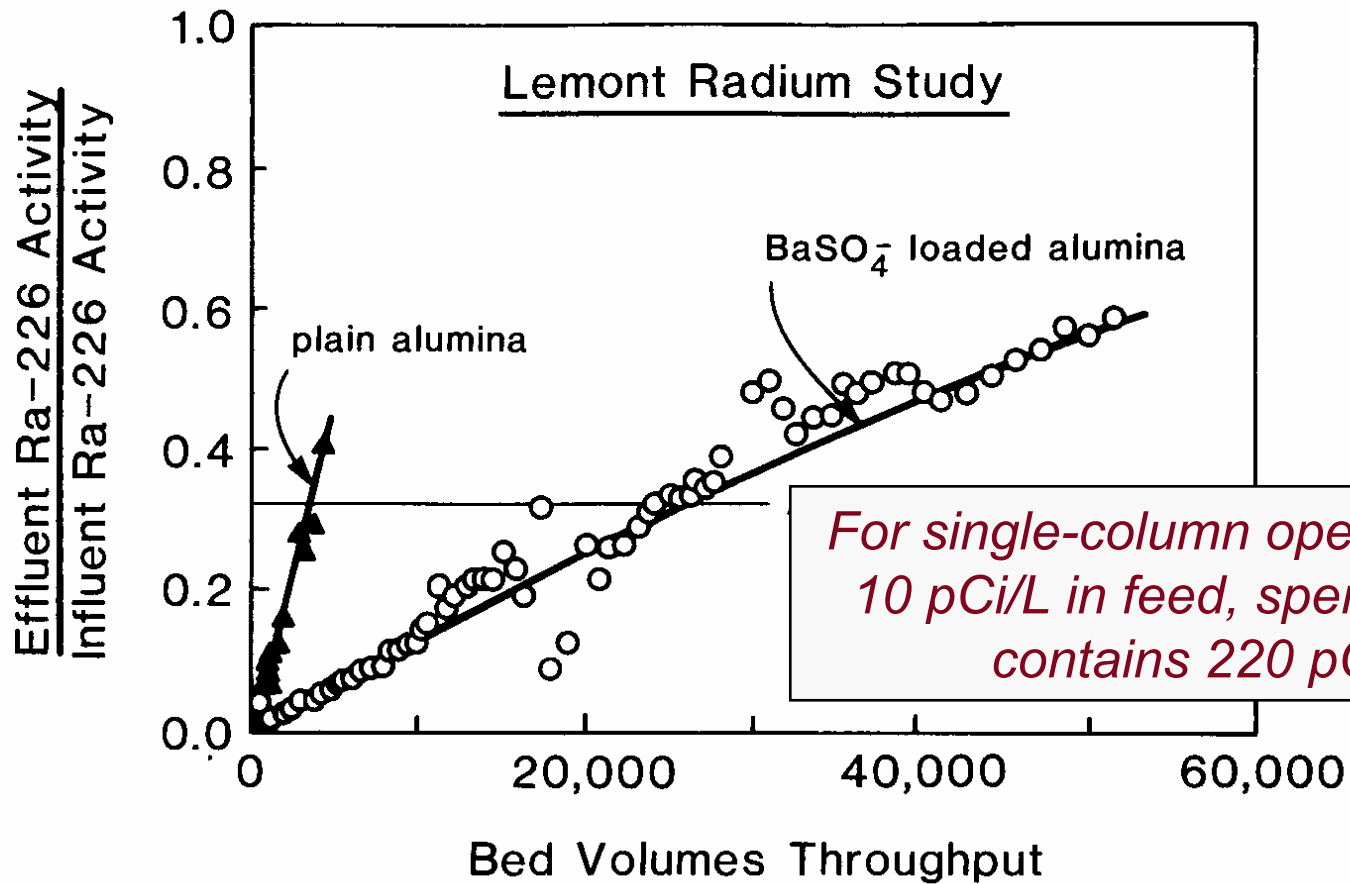
Process flow schematic for radium removal by adsorption onto preformed MnO₂



Radium Removal as a function of MnO_2 dose.
Houston GW with 120 mg/L hardness and pH = 7.5



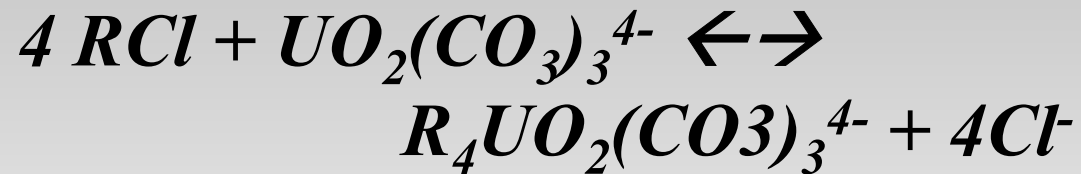
Radium breakthrough curve for Dow Radium Selective Complexer (RSC), a BaSO₄(s) loaded cation resin.



Radium breakthrough curves for plain and BaSO_4 -loaded activated alumina. EBCT = 3 min. Feed Ra = 8.7-11.3 pCi/L

Uranium-Removal Methods

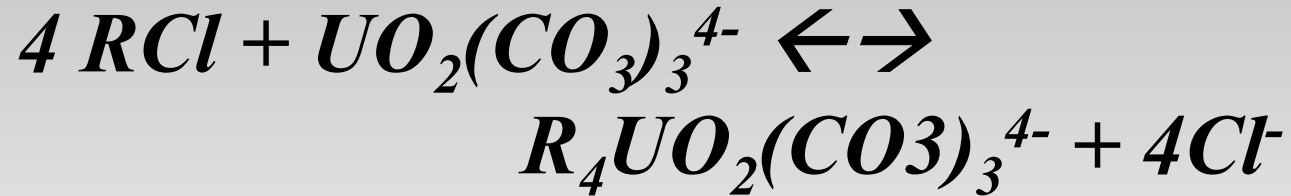
- **Anion Exchange (BAT)**



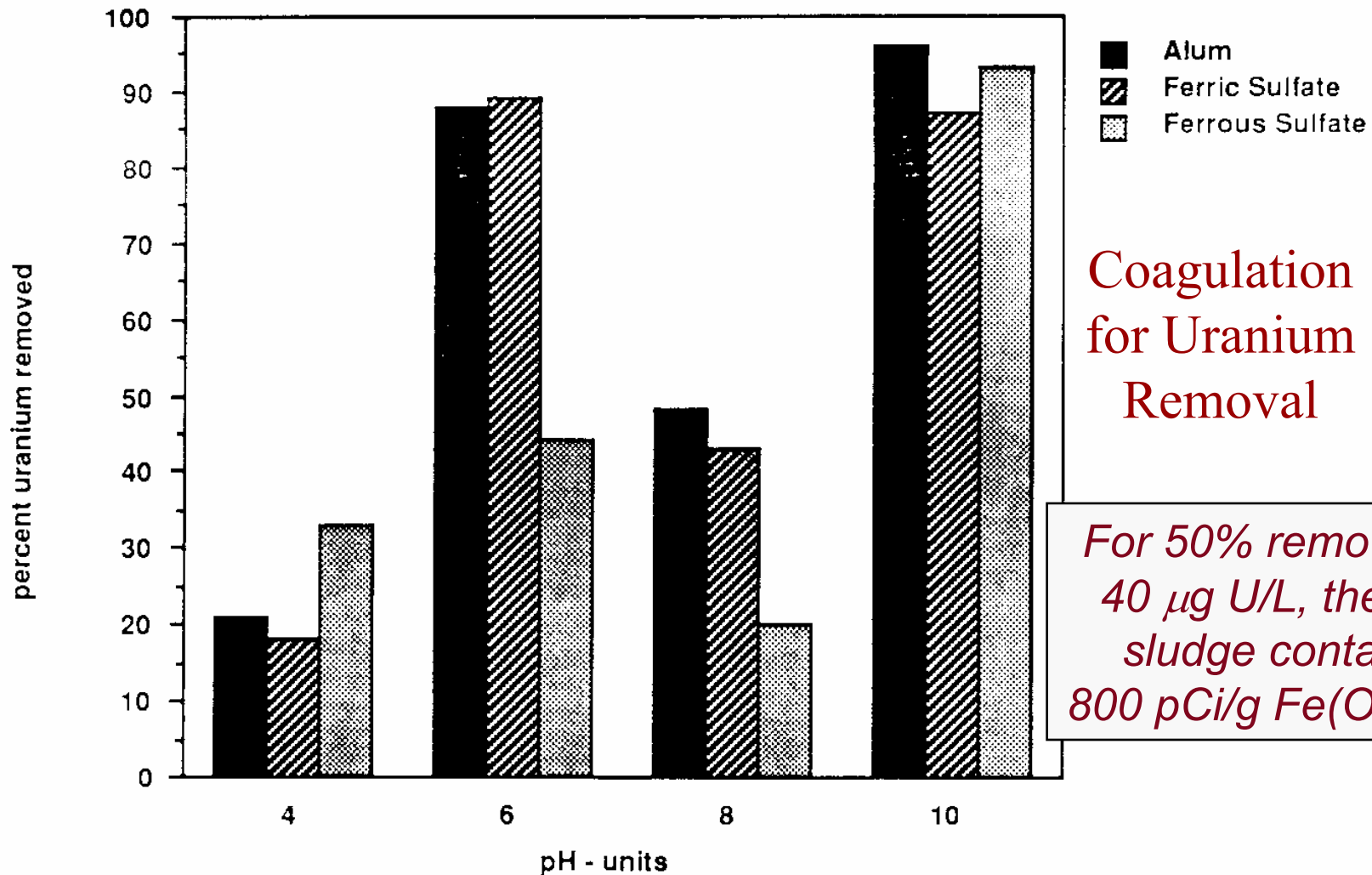
- **Lime Softening (BAT)**
- **Enhanced Coagulation /Filtration (BAT)**
- **Reverse Osmosis (BAT)**
- **Activated Alumina Adsorption**
- **Electrodialysis**

POU Uranium-Removal Methods

- **Anion Exchange**



- **Reverse Osmosis**
- **Activated Alumina Adsorption**

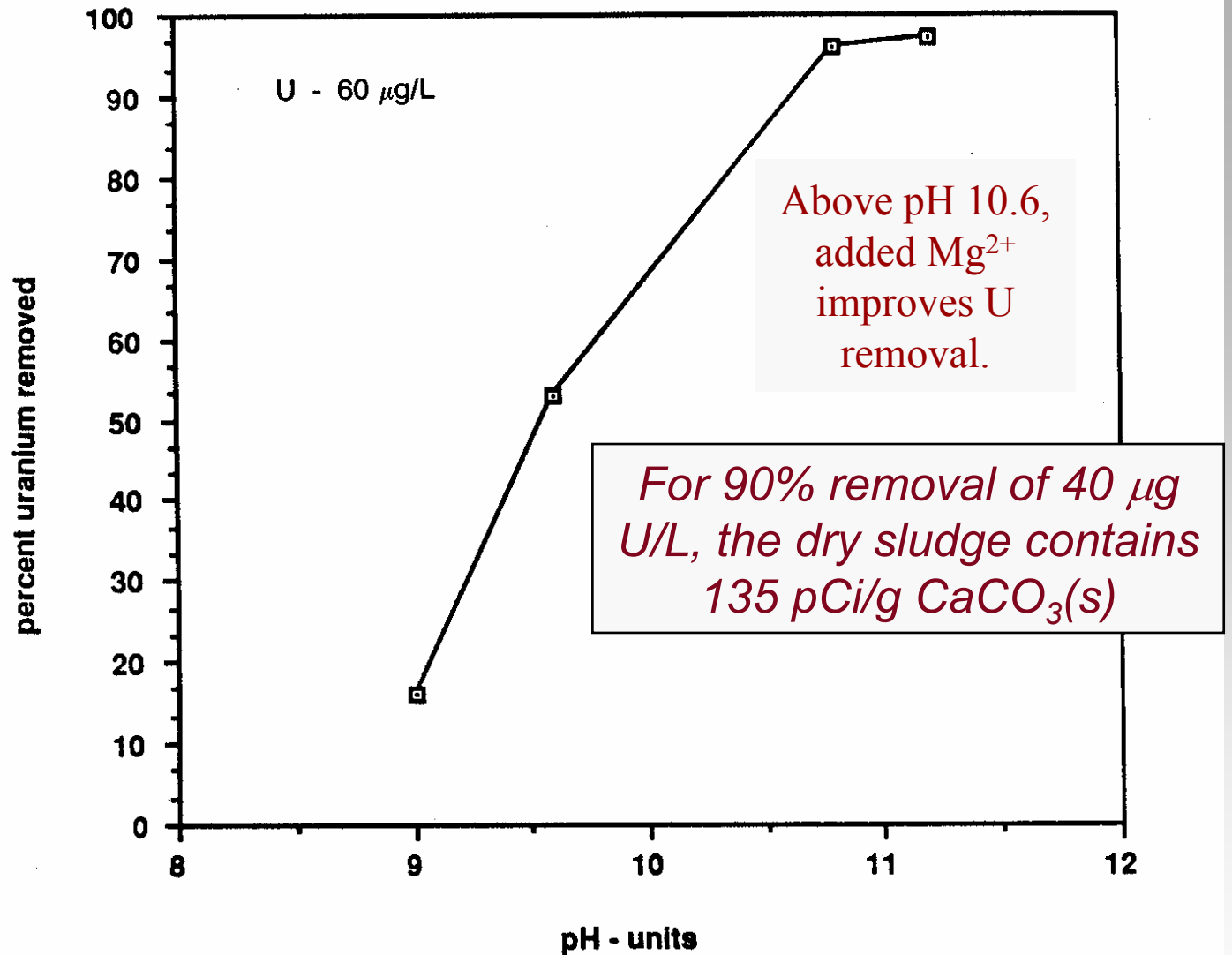


Coagulation for Uranium Removal

For 50% removal of 40 $\mu\text{g U/L}$, the dry sludge contains 800 $\text{pCi/g Fe(OH)}_3(\text{s})$

Effect of pH and coagulant on uranium removal by coagulation with 25 mg/L dose.
(Sorg 1990; Lee & Bondietti, 1983)

Lime Softening for Uranium Removal

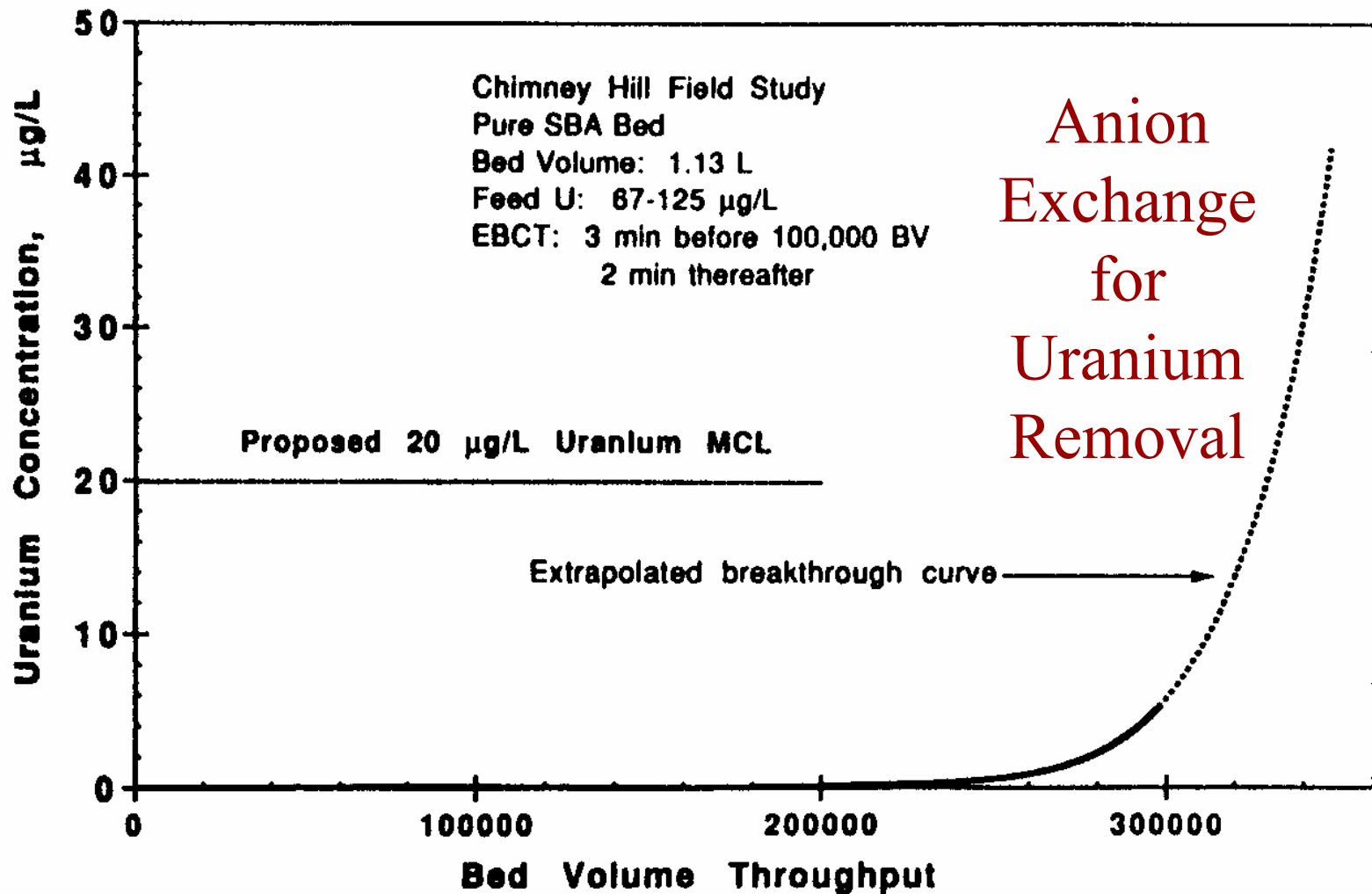


Effect of pH (and lime dose) on uranium removal by lime softening.

(Sorg 1990; Lee & Bondiotti, 1983)

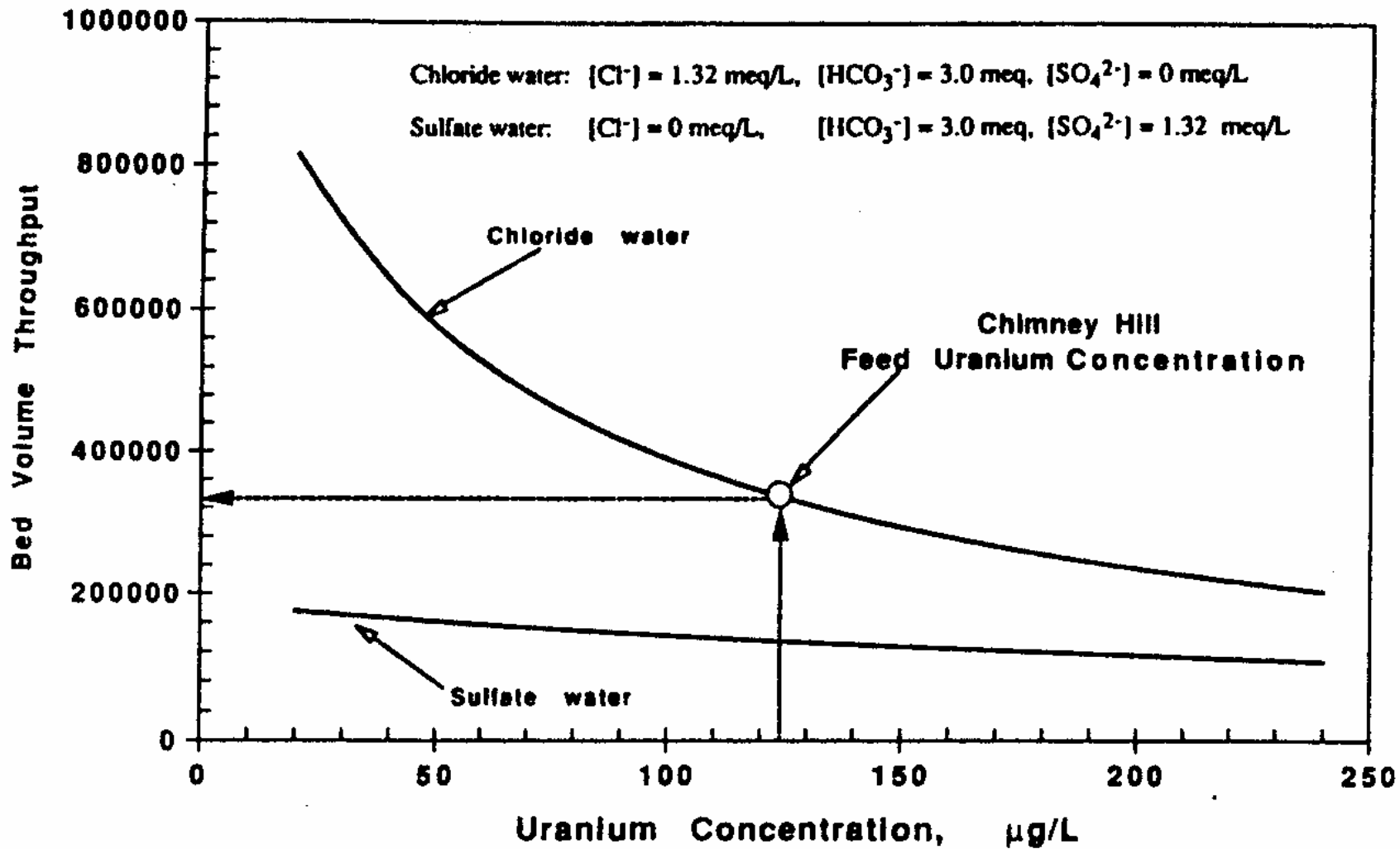
Ion-Exchange Resins for Uranium Removal

Designation	Resin Description	Ionic Form	Capacity meq/mL
Strong-Base Anion exchange resin for uranium removal Ionac A-642 Purolite A-500 Amberlite IRA 900	Type 1, macroporous, SBA resin, polystyrene-DVB matrix, $-\text{N}(\text{CH}_3)_3^+$ exchange groups	Cl⁻	1.0



Effluent uranium levels during anion exchange with macroporous SBA resin at pH 8.

If feed water contains 40 µg U/L, Waste brine contains ~80,000 pCi/L for a 30,000 BV run length.



Effect of uranium, sulfate, and chloride concentrations on BV to uranium exhaustion.

Processes for Radium Removal

Treatment Method	Removal	Comment
IX Softening (Na ⁺ , SAC)	>95%	Operate to hardness breakthrough, NaCl Regen.
Ba(Ra)SO ₄ Precipitation	50-95%	Add BaCl ₂ to feed water before filtration.
MnO ₂ Adsorption	50-95%	Use preformed MnO ₂ or MnO ₂ -coated filter media.
RO	>99%	Effective but expensive

Processes for Uranium Removal

Treatment Method	Removal	Comment
Coagulation w Fe/Al	50-90%	Effective at pH near 6 and 10
Lime Softening	80-99%	Higher pH = greater removal. Mg ²⁺ helps at pH > 10.6.
Anion Exchange	>95%	Regenerate with 2-4 M NaCl after 10,000-50,000 BV
RO	>99%	Effective but expensive

Residuals

- The more effective the coagulant or adsorbent, the higher is the radioactivity in the residuals.

Ion Exchange Softening for Radium Removal	600 pCi/L spent brine 20 pCi/g dry resin
Coag-Filt w $\text{MnO}_2(\text{s})$ for Radium Removal	21,000 pCi/g dry $\text{MnO}_2(\text{s})$
Fe(III) Coag-Filtration for Uranium Removal	800 pCi/g $\text{Fe}(\text{OH})_3(\text{s})$
Anion Exchange for Uranium Removal	80,000 pCi/L spent brine (30,000 BV run length)