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}U, α	99.276	4.51×10^{9}	0.333	47.33
^{235}U, α/γ	0.7196	7.1×10^{8}	2.144	2.21
^{234}U, α	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 1µg U = 0.67 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
All	*Ra^{2+}*	*a divalent cation*
< 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	*$UO_2(CO_3)_3^{4-}$*	*a tetravalent anion*

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

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

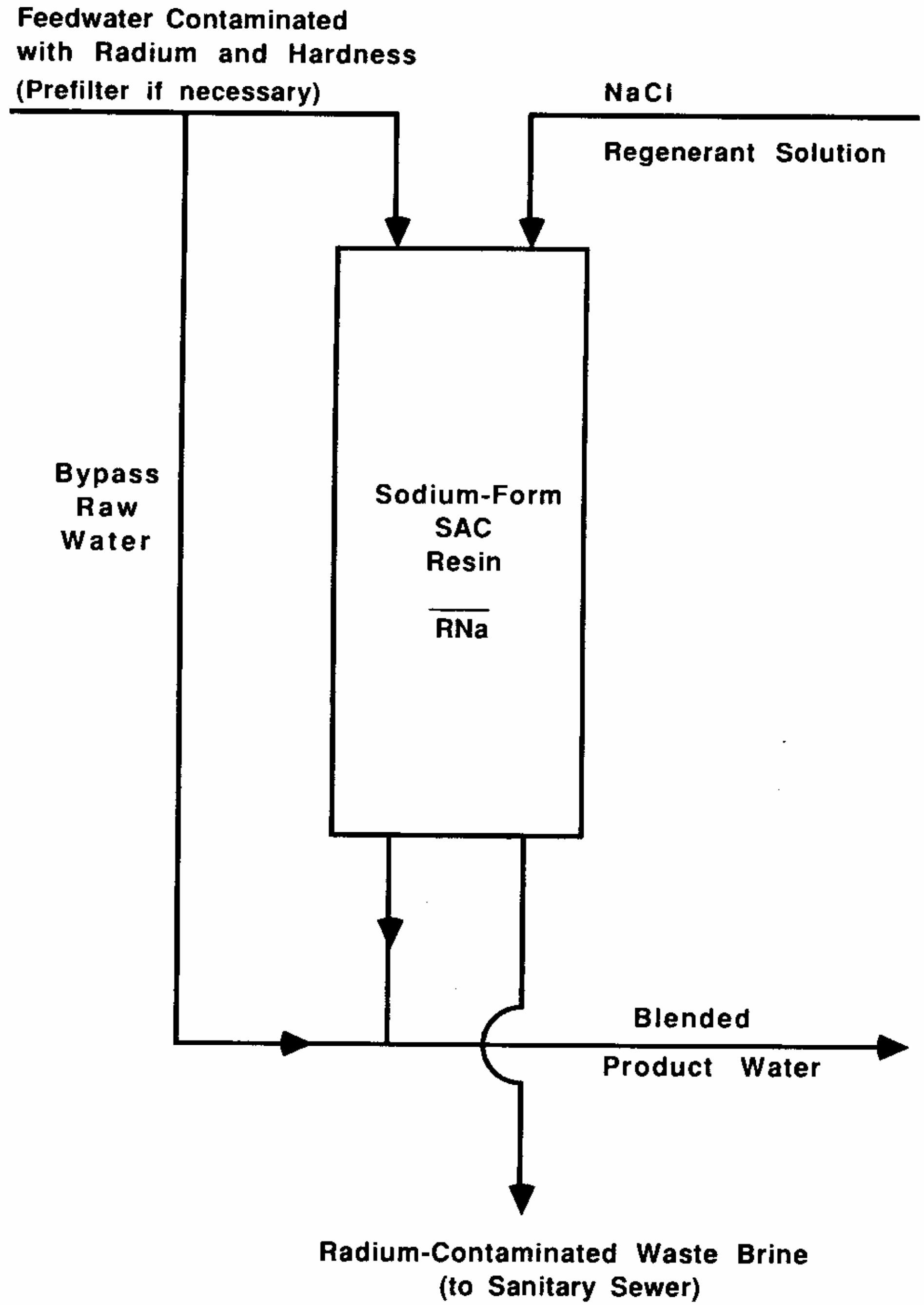
Radium-Removal Methods

- **Cation Exchange Softening (BAT)**
  $2\,RNa + Ra^{2+} \rightarrow R_2Ra + 2\,Na+$
- **Lime Softening (BAT)**
- **Reverse Osmosis (BAT)**
- **Sorption onto MnO_2 (HMO)**
- **Precipitation with $BaSO_4$ (by adding $BaCl_2$)**
  - **(Excess)Ba^{2+} + (Trace)Ra + SO_4^{2-} = Ba(Ra)SO_4**
- **Sorption onto $BaSO_4$-Impregnated Media**
  - **Media•$BaSO_4$ + Ra^{2+} = Media•Ba(Ra)SO_4 + Ba^{2+}**
- **Electrodialysis**

POU Radium-Removal Methods

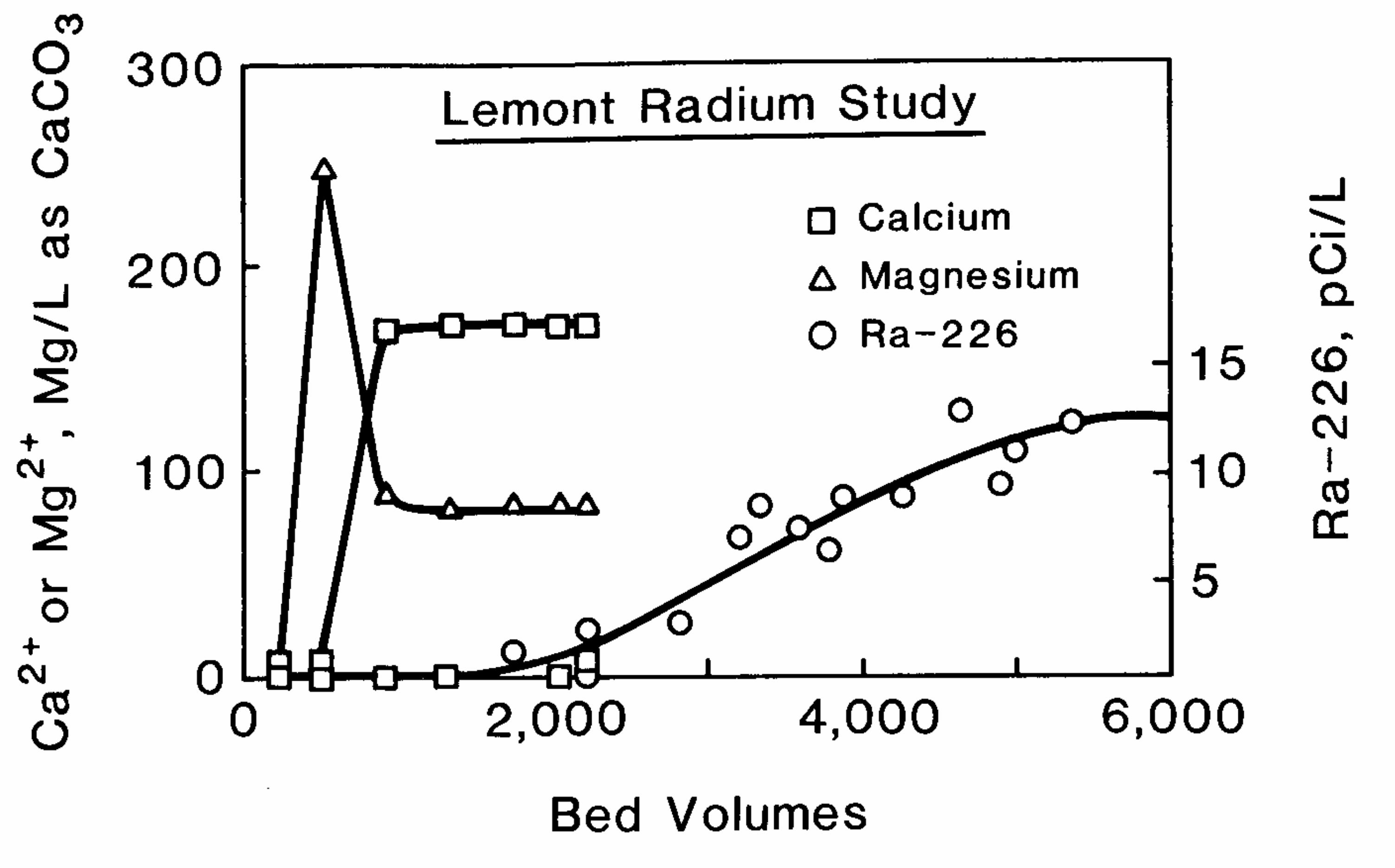
- **Reverse Osmosis (BAT)**
- **Cation Exchange Softening**
  $2\ RNa + Ra^{2+} \leftrightarrow R_2Ra + 2\ Na^+$
- **Sorption onto MnO_2-impregnated fibers or filters, e.g., DE or granular media.**
- **Sorption onto $BaSO_4$-Impregnated Resin or Activated Alumina**

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



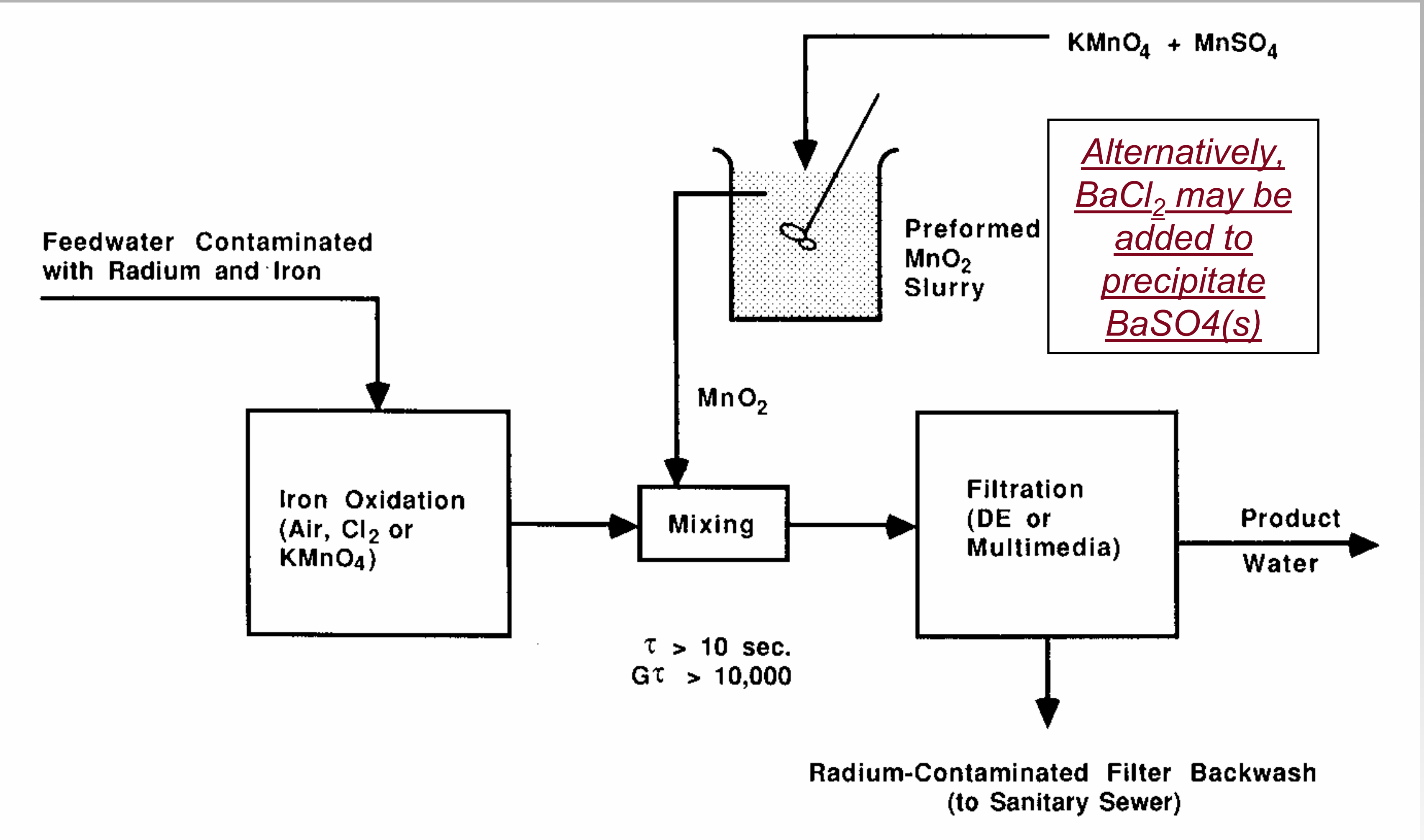
Ion Exchange Resins for Radium Removal

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, —SO_3^- exchange groups	Na^+	1.9

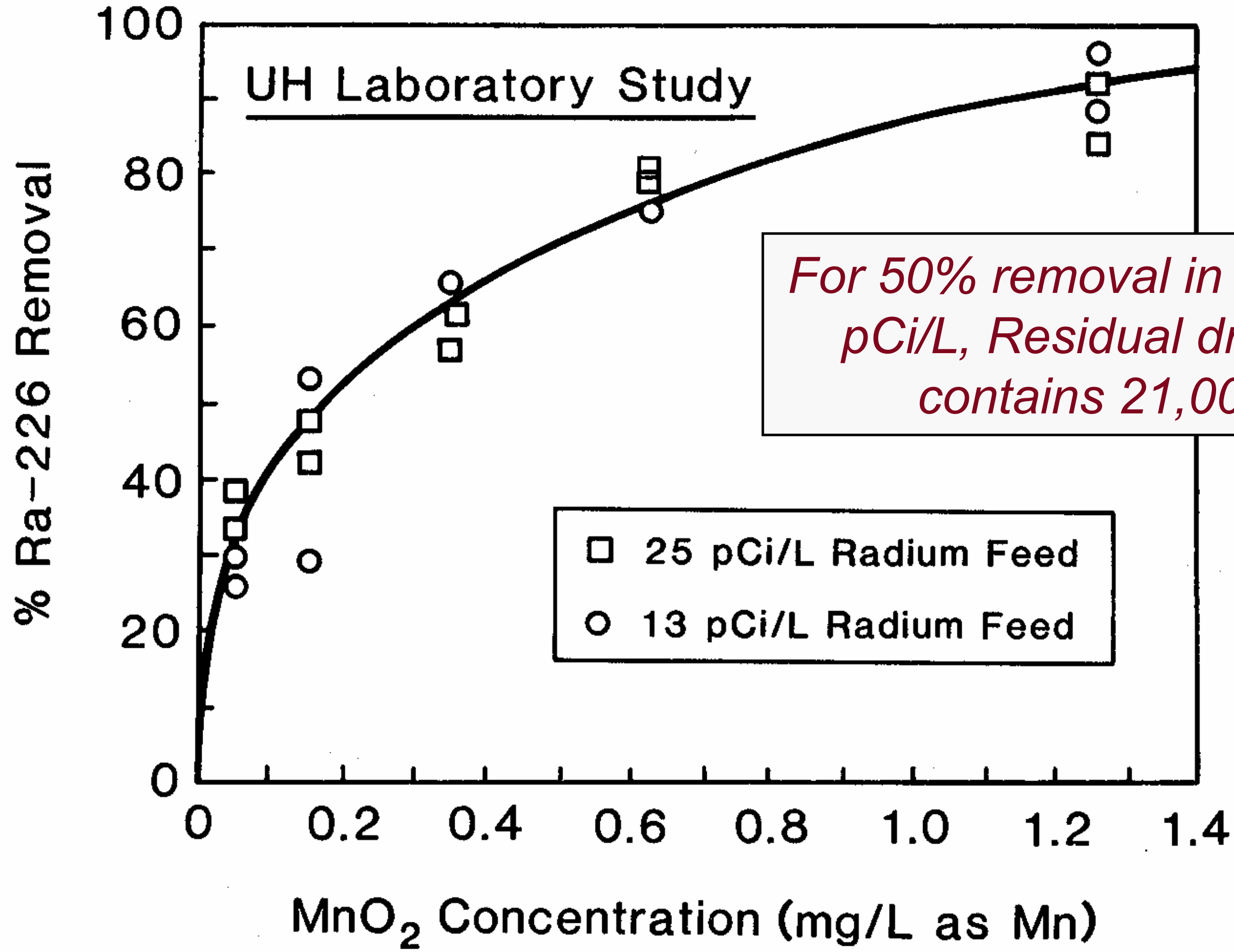


Magnesium, calcium and radium breakthrough curves for ion-exchange softening.

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

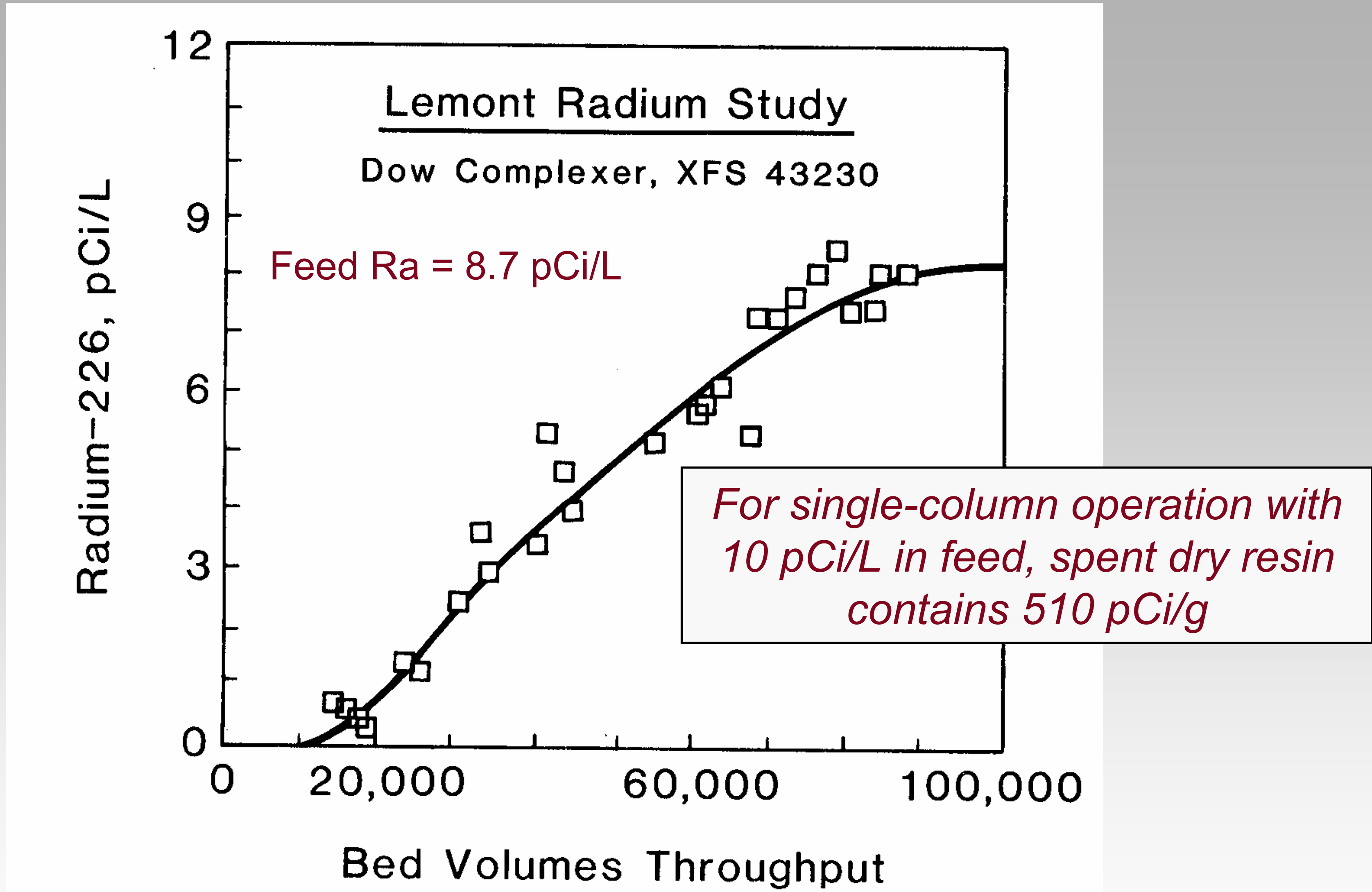


Process flow schematic for radium removal by adsorption onto preformed MnO_2

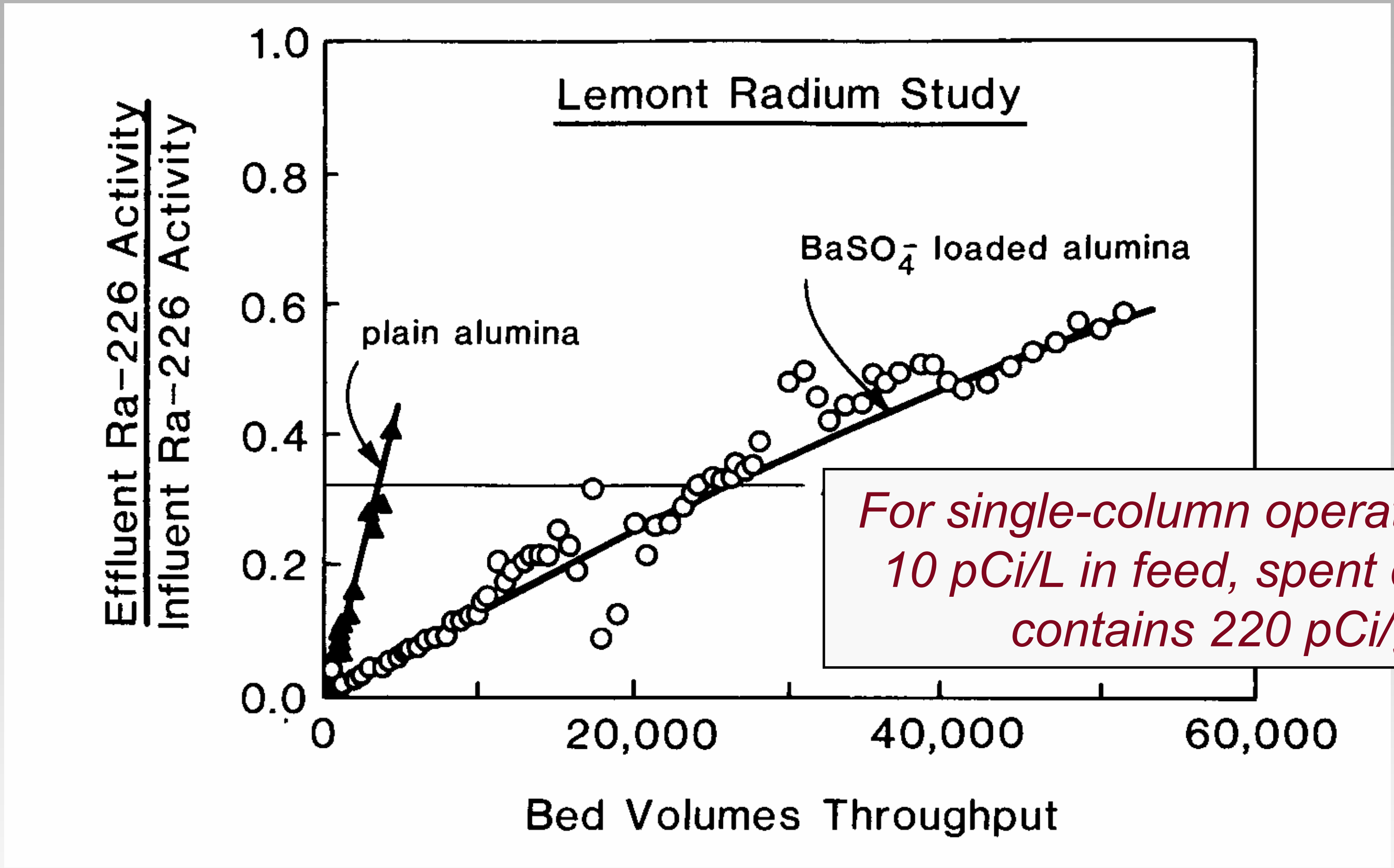


For 50% removal in water with 10 pCi/L, Residual dry MnO_2 (s) contains 21,000 pCi/g

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.



For single-column operation with 10 pCi/L in feed, spent dry AAl contains 220 pCi/g

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

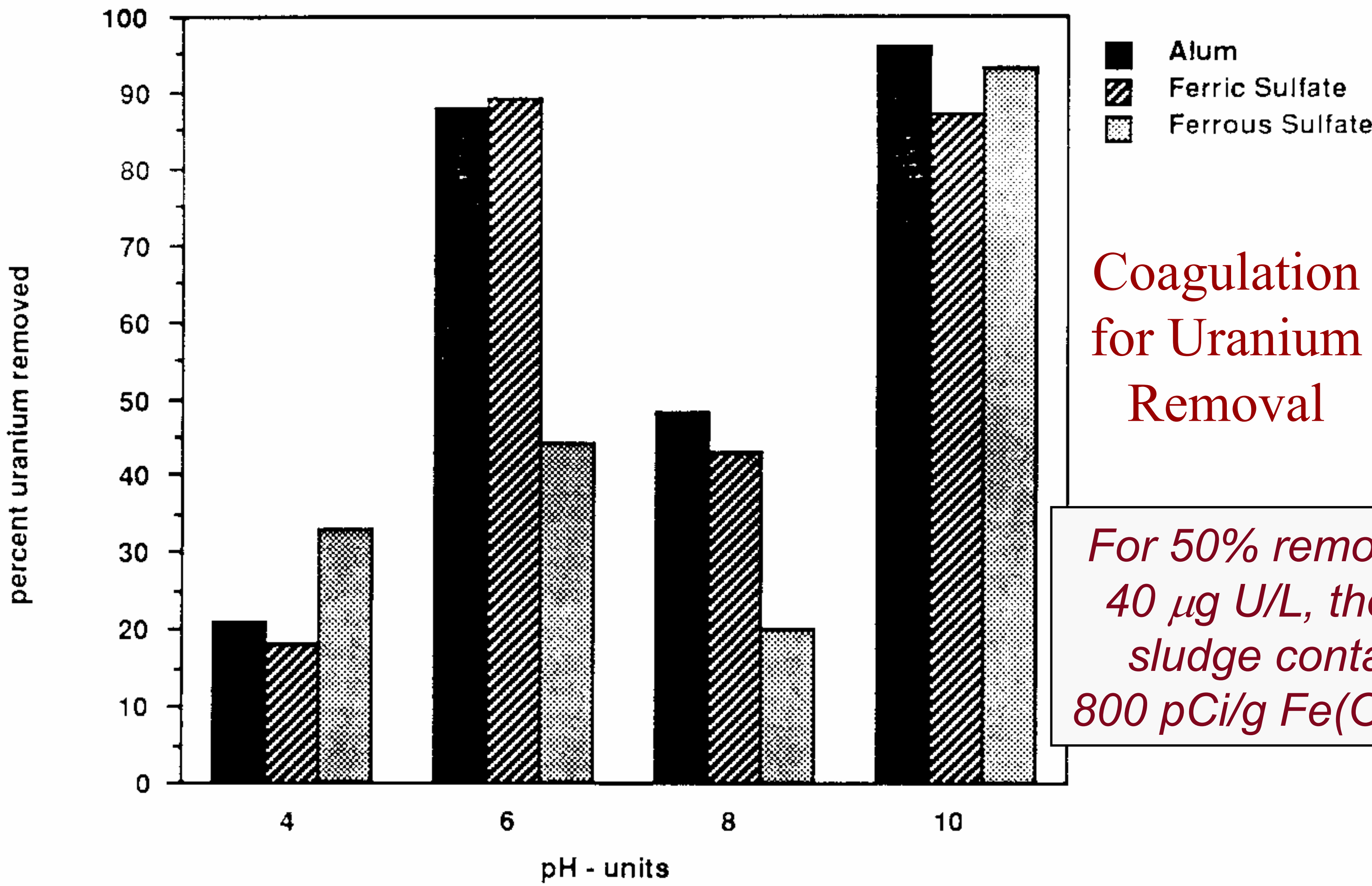
- **Anion Exchange (BAT)**

$$4\ RCl + UO_2(CO_3)_3^{4-} \leftrightarrow R_4UO_2(CO3)_3^{4-} + 4Cl^-$$

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

POU Uranium-Removal Methods

- **Anion Exchange**
  $4\ RCl + UO_2(CO_3)_3^{4-} \leftrightarrow$
  $R_4UO_2(CO3)_3^{4-} + 4Cl^-$
- **Reverse Osmosis**
- **Activated Alumina Adsorption**

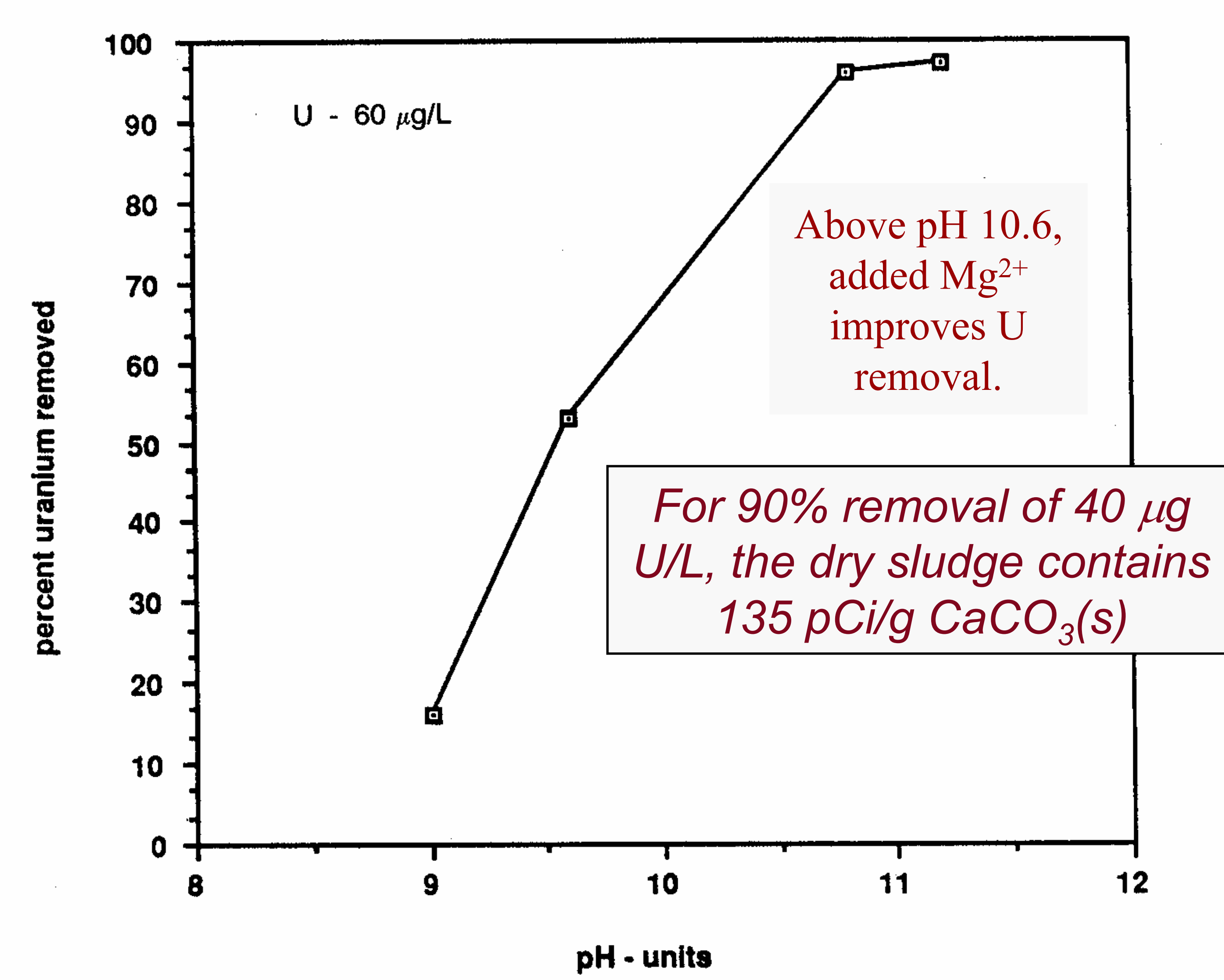


Coagulation for Uranium Removal

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

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

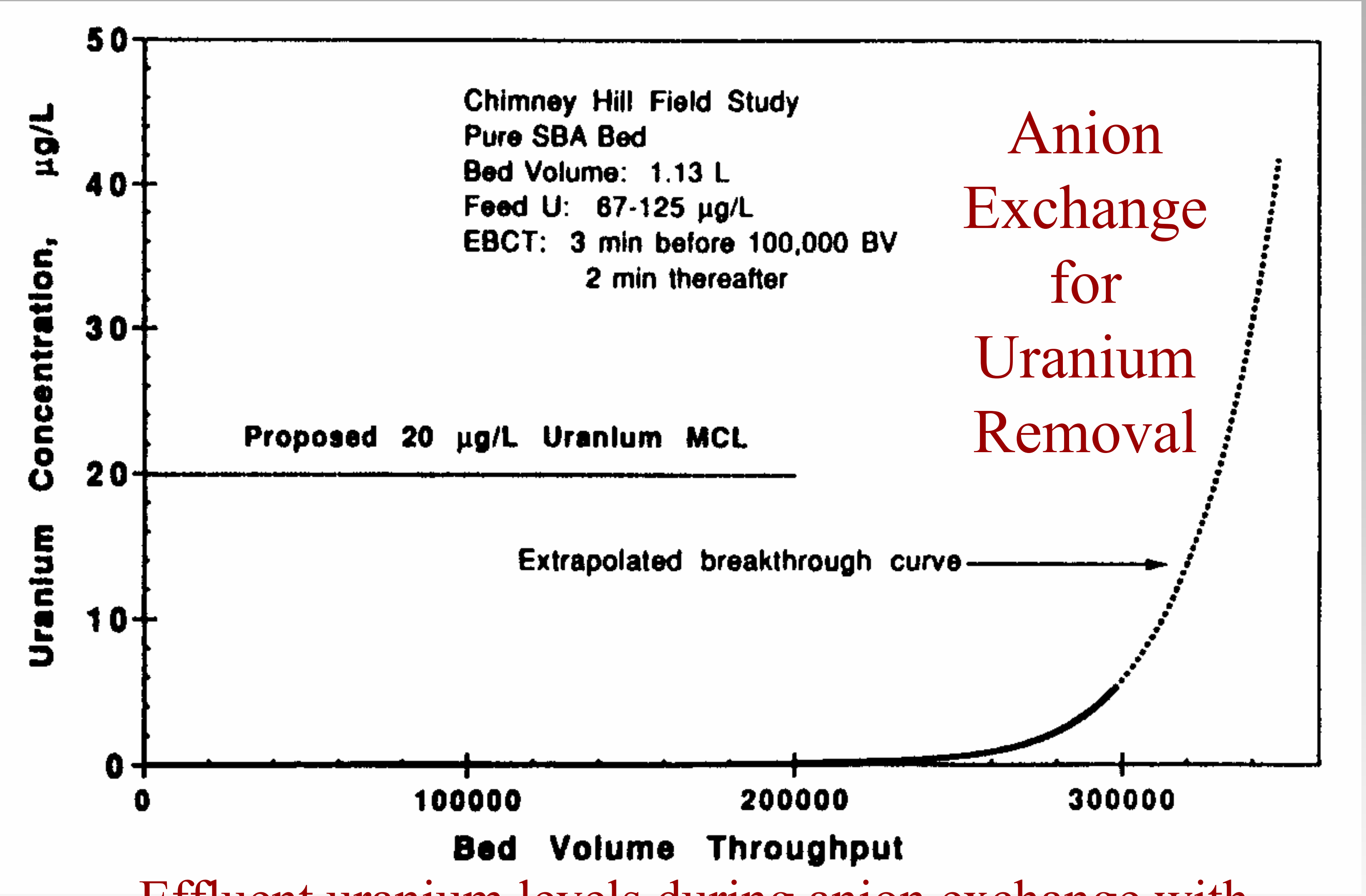


Effect of pH (and lime dose) on uranium removal by lime softening.

(Sorg 1990; Lee & Bondietti, 1983)

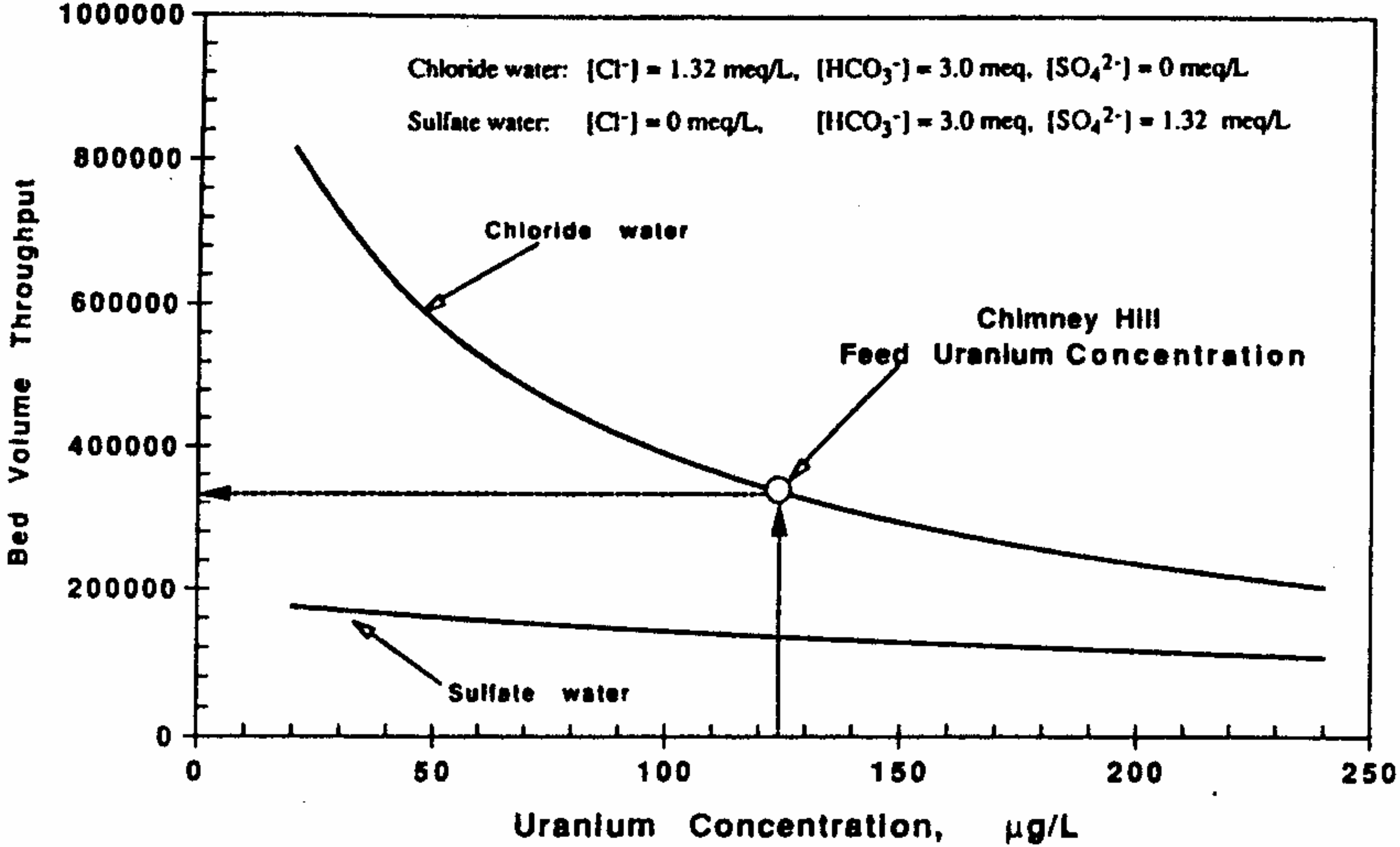
Ion-Exchange Resins for Uranium Removal

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, —$N(CH_3)_3^+$ 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 MnO_2(s) for Radium Removal	21,000 pCi/g dry MnO_2(s)
Fe(III) Coag-Filtration for Uranium Removal	800 pCi/g $Fe(OH)_3$(s)
Anion Exchange for Uranium Removal	80,000 pCi/L spent brine (30,000 BV run length)