



# Ion Exchange Treatment Background

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# Webinar Overview

- Introductions
- Acknowledgements
- Background
- Nitrate Management Options
- Treatment Options and Selection
- California  
Violations, Occurrence, Treatment  
Installations, Costs
- Case Studies
- Conclusions



# Acknowledgements

- Dennis Clifford, Ph.D.
- AWWA Technical & Education Council and Inorganic Contaminants Water Quality and Research Committees (including Susan Brownstein, CDPH!)
- CDPH SWRF Fund, Contract No. 06-55254
- Cal. State Water Resources Control Board, Contract No. 09-122-250



# Associated Research

- *An Assessment of the State of Nitrate Treatment Alternatives* for AWWA (2011)

<http://www.awwa.org/Portals/0/files/resources/resource%20dev%20groups/tech%20and%20educ%20program/documents/TECNitrateReportFinalJan2012.pdf>

- California Nitrate Project, Implementation of Senate Bill X2 1 prepared for the California State Water Resources Control Board (Technical Report 6, 2012)

<http://groundwaternitrate.ucdavis.edu/>

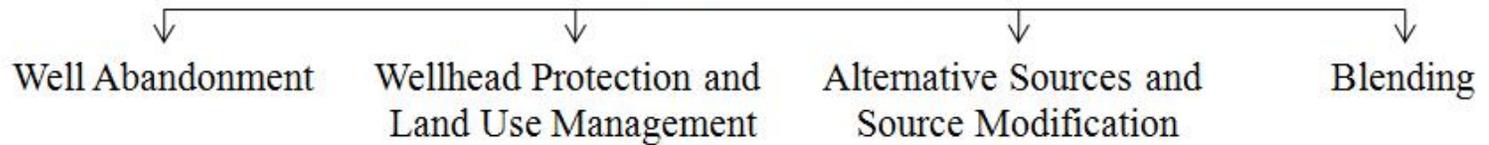
- The Center for Affordable Technology for Small Water Systems (Director: Dr. Jeannie Darby)

<http://smallwatersystems.ucdavis.edu/>

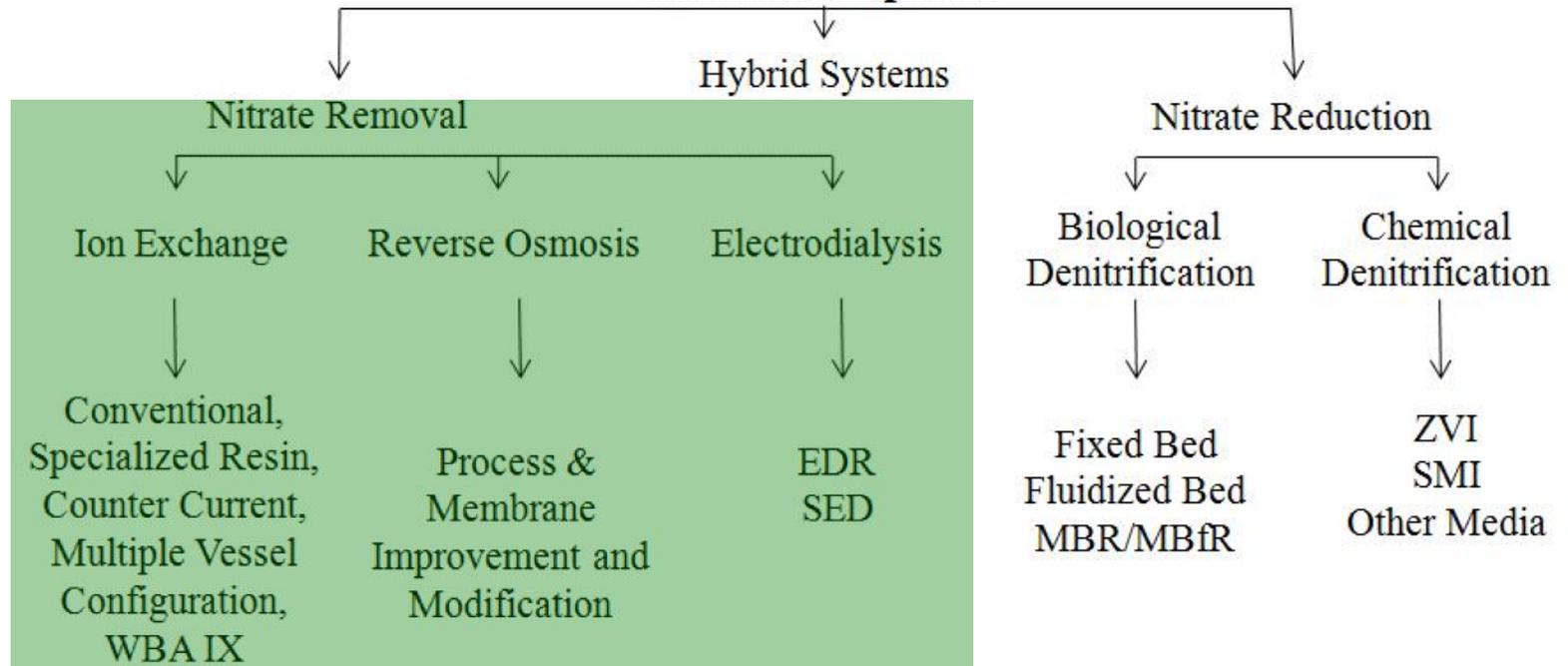
- Jensen et. al., *Drinking Water Treatment for Nitrate*, Critical Reviews in Environmental Science and Technology, Accepted 2013

# Treatment Options: Nitrate Removal

## Non-Treatment Options



## Treatment Options





# Ion Exchange Options

- Resin Types
  - Strong-base anion exchange (SBA, pH 6-9.5)
  - Weak-base anion exchange (WBA, pH 3-5)
- Equipment Configurations
  - Fixed bed columns
    - Downflow exhaustion-regeneration (“conventional”)
    - Counterflow exhaustion-regeneration (more efficient)
  - Multiple fixed-bed columns in parallel
  - Continuously mixed flow reactor
- Brine Management
  - Lower NaCl concentration, partial regeneration, brine reuse, brine denitrification

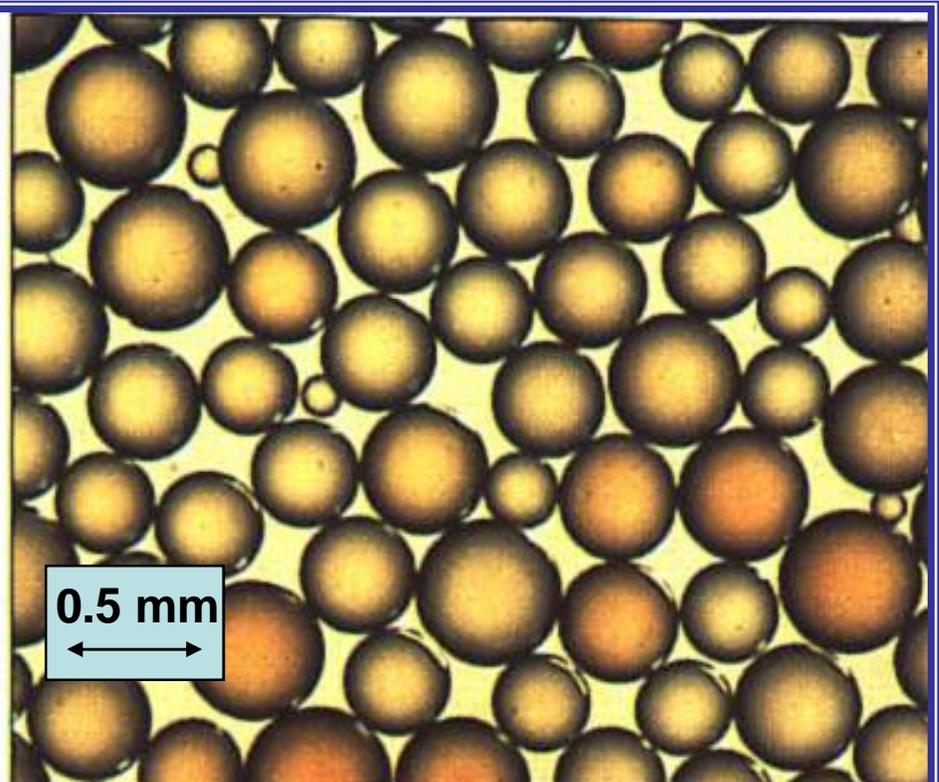
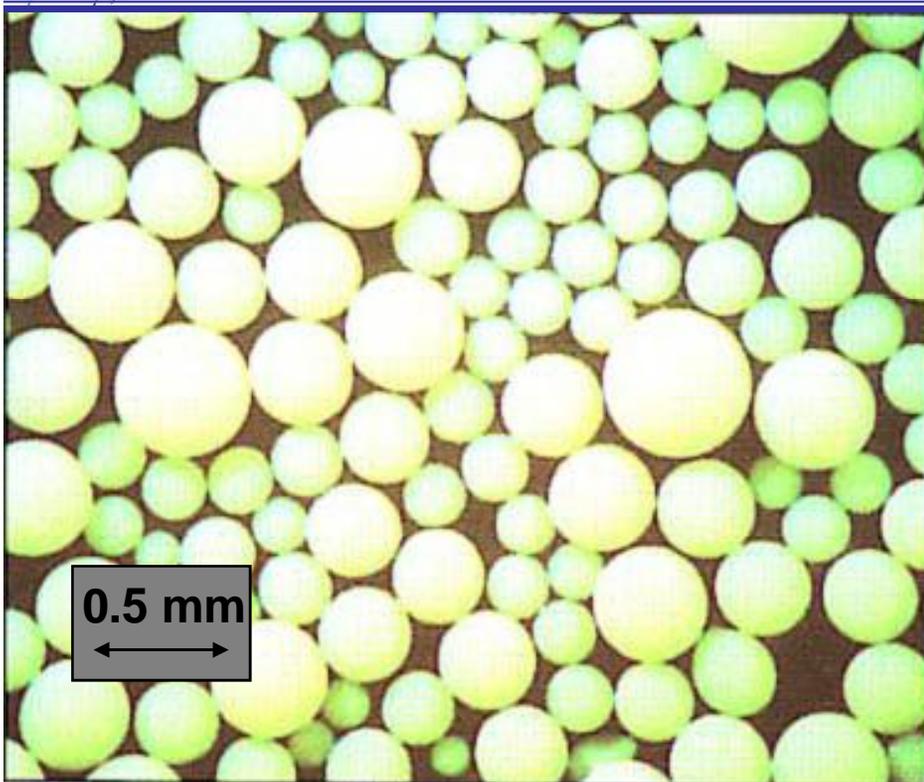


# Strong-Base Ion Exchange

- Ion exchange with Cl-form SB anion resin
  - A “water softener for anions”
    - Exhaustion:  $\text{NO}_3^- + \text{RCl} = \text{RNO}_3 + \text{Cl}^-$
    - Regen:  $\text{RNO}_3 + 4\text{NaCl} = \text{RCl} + 3\text{NaCl} + \text{NaNO}_3$
- Advantages: Simplicity, on-demand operation, relatively low cost
- Disadvantages: Nitrate peaking (dumping) may occur; regeneration is inefficient, high NaCl consumption, produces large volume of nitrate-contaminated salt brine for disposal

# Strong-Base Ion Exchange Resin

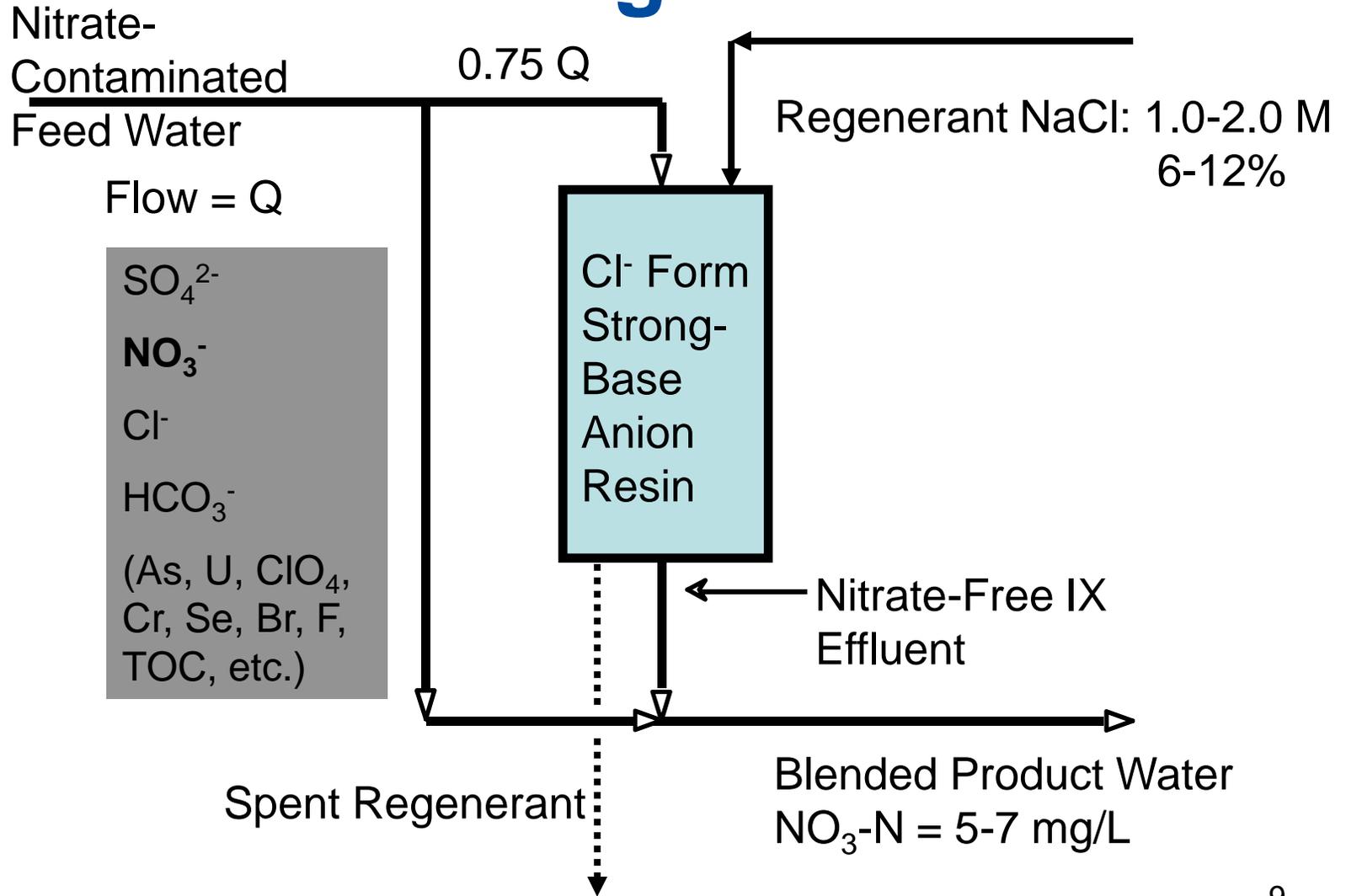
Polystyrene-DVB polymers, quaternary amine groups.  
Typical particle size range 0.3-1.2 mm (16x50mesh)



**Macroporous  
(Opaque)**

**Microporous or Gel  
(Translucent)**

# Simplified Process Flow Diagram



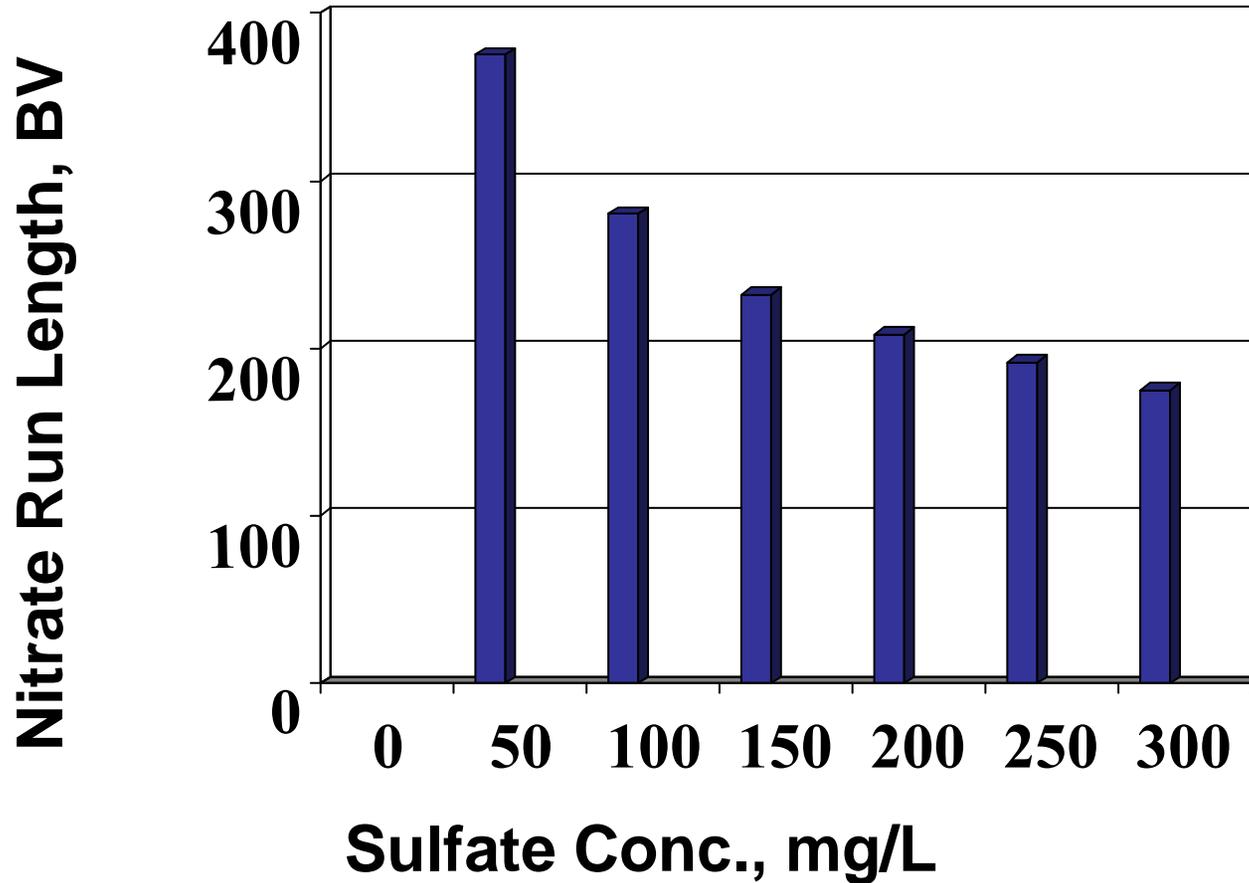


# Typical Nitrate-Contaminated Water Example Glendale, Arizona

<i>Species</i>	<i>mg/L</i>	<i>meq/L</i>
NO <sub>3</sub> -N	21	1.5
SO <sub>4</sub> <sup>2-</sup>	48	1.0
Cl <sup>-</sup>	106	3.0
HCO <sub>3</sub> <sup>-</sup>	122	2.0
<b>TDS</b>	<b>530</b>	<b>7.5</b>

All background ions, especially sulfate, compete with nitrate for sites on the anion-exchange resin; higher TDS and SO<sub>4</sub> = fewer bed volumes (BV) (shorter run length).

# Effect of Sulfate on Ion Exchange Run Length

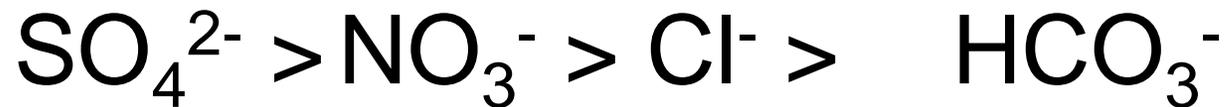


Based on Glendale, AZ GW



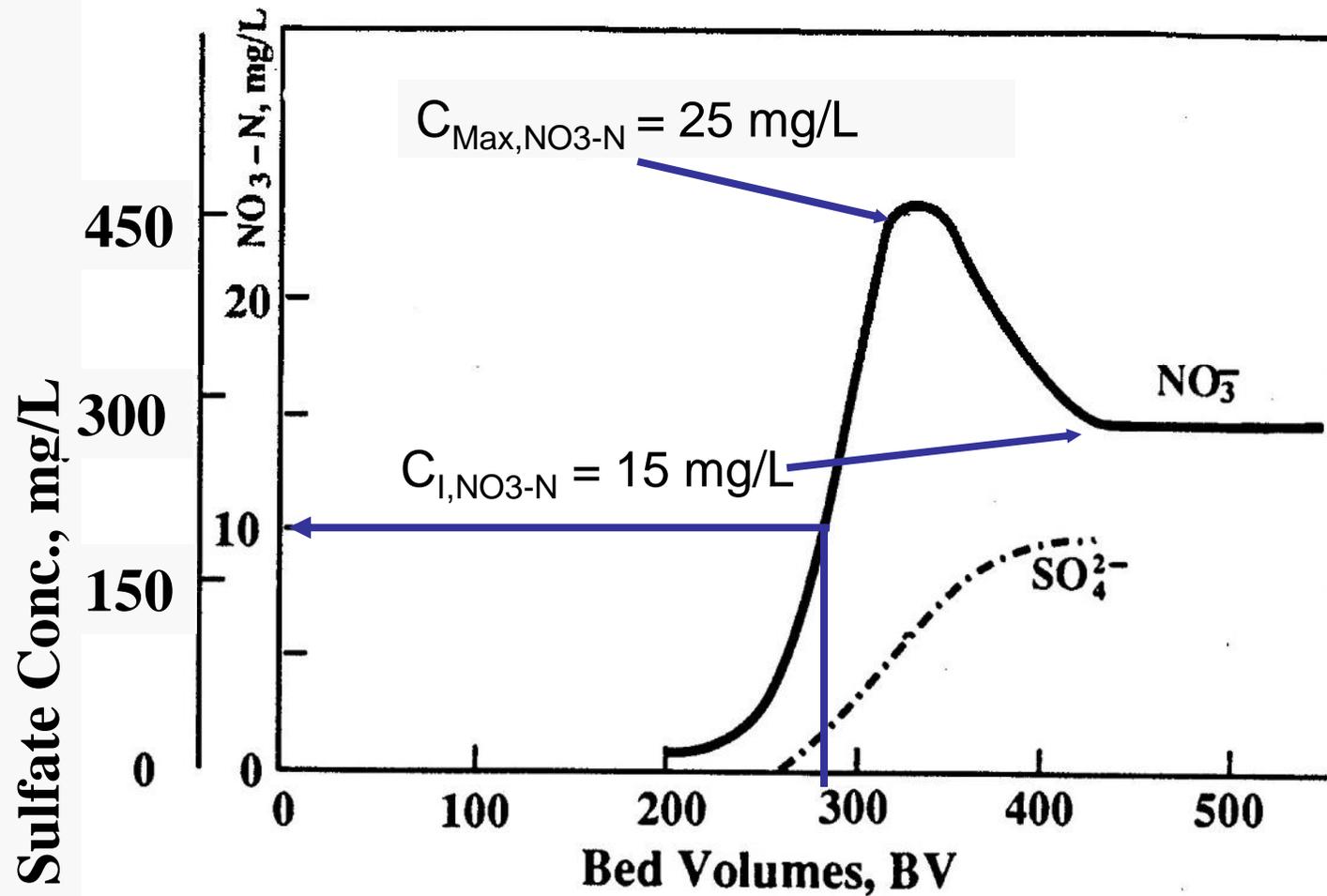


## Anion Selectivity Sequence for Typical Strong-Base Anion Resins



- Problem: Less preferred ions will “peak”. Nitrate is less preferred than sulfate and therefore effluent nitrate concentration will be higher than influent nitrate concentration if the column is run beyond nitrate breakthrough.

# Nitrate Peaking with Typical (Type 1 or Type 2) Sulfate-Selective SBA Resin



Based on Cox et. al. 1987



# Three Ways to Eliminate Nitrate Peaking

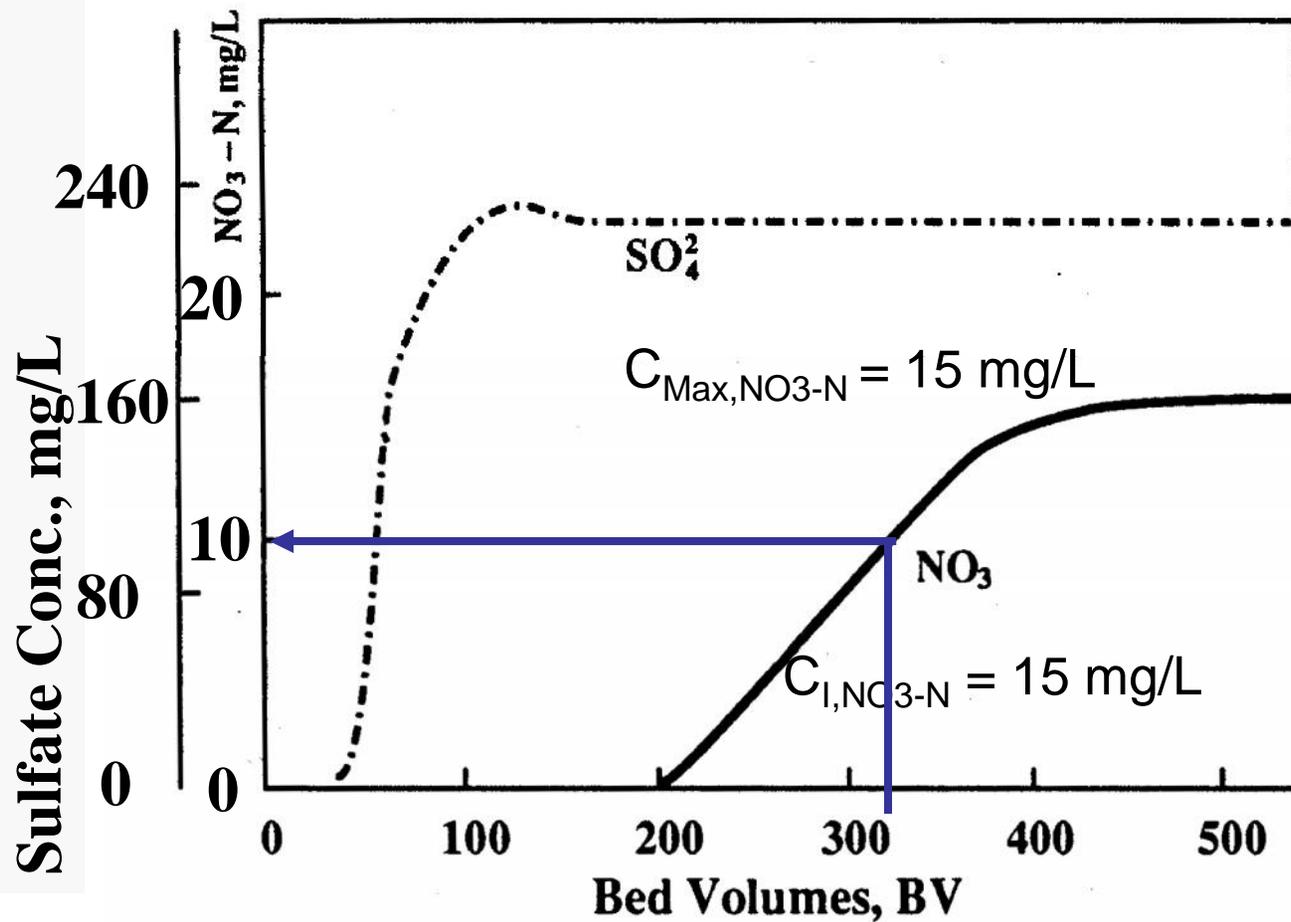
- Use a nitrate-selective (NS) resin
- Operate multiple columns in parallel at different stages of exhaustion
- Use a completely mixed flow reactor



# Nitrate Selective (NS) Resins

- In NS resins, sulfate affinity is decreased by increasing the charge-separation distance between exchange sites
- Nitrate affinity is increased by making the resins more hydrophobic in nature

# Nitrate Peaking Eliminated with Nitrate-Selective Resin



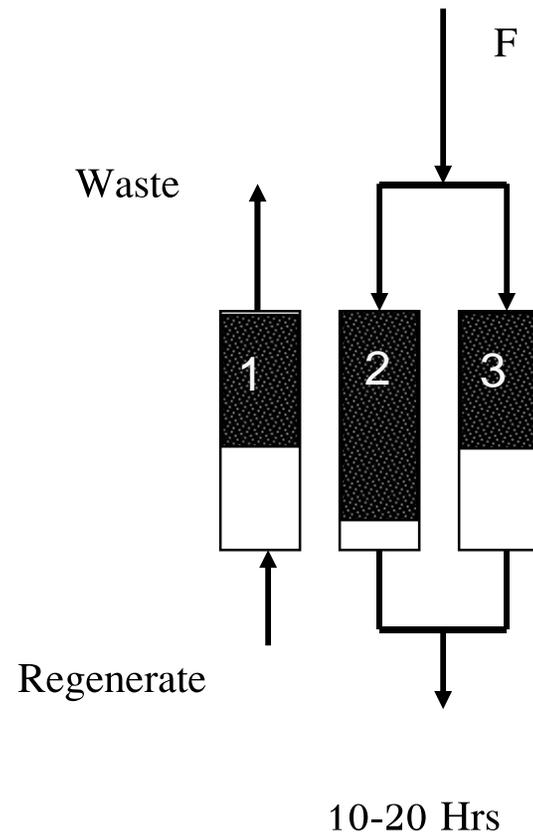
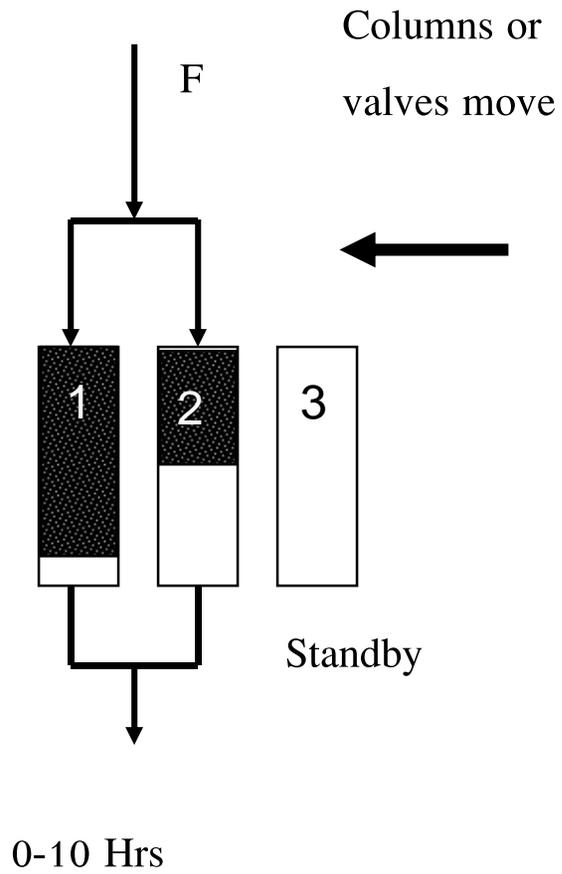
Based on Cox et. al. 1987



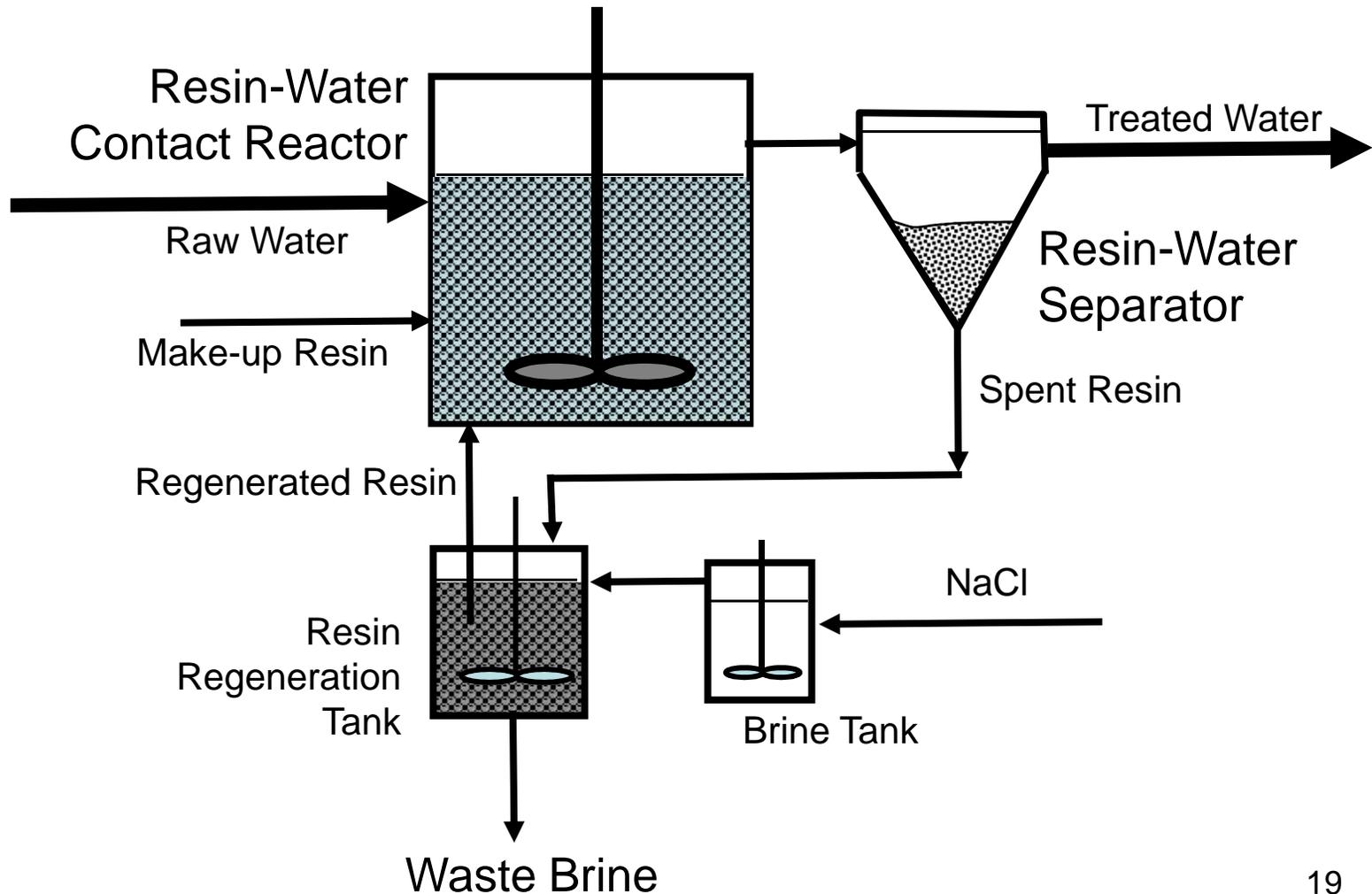
# Multiple Parallel Columns Eliminate Peaking

- Operation of several (2-20) columns in parallel at different stages of exhaustion
  - A carousel or multiple stationary columns may be employed for multiple parallel columns
  - “Smooths out” the effluent history
  - Minimizes or eliminates peaking
  - Upflow regeneration and partial brine/rinse reuse can conserve salt and reduce brine disposal volume

# Operate Columns (2-20) in Parallel



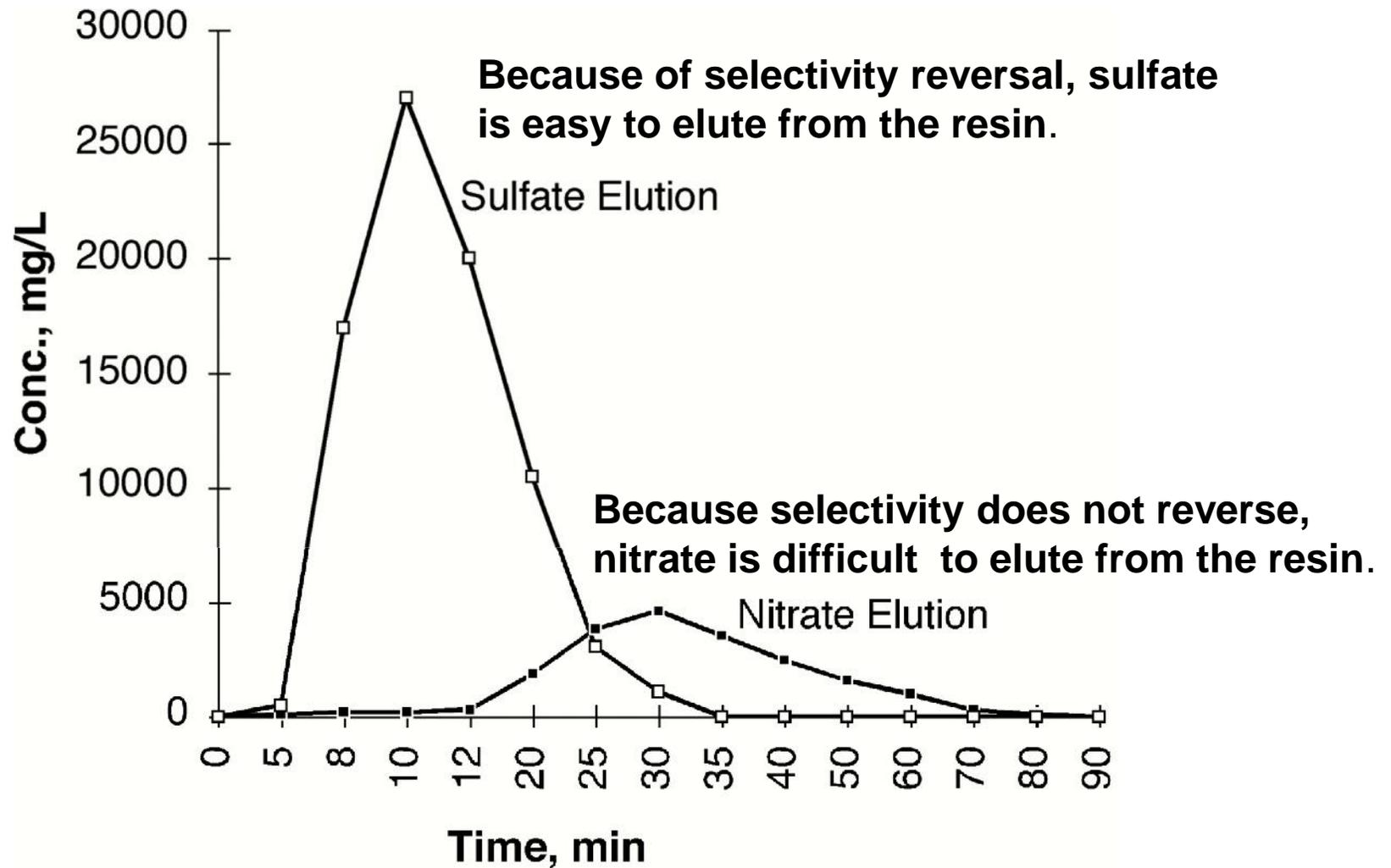
# Completely Mixed IX Flow Reactor





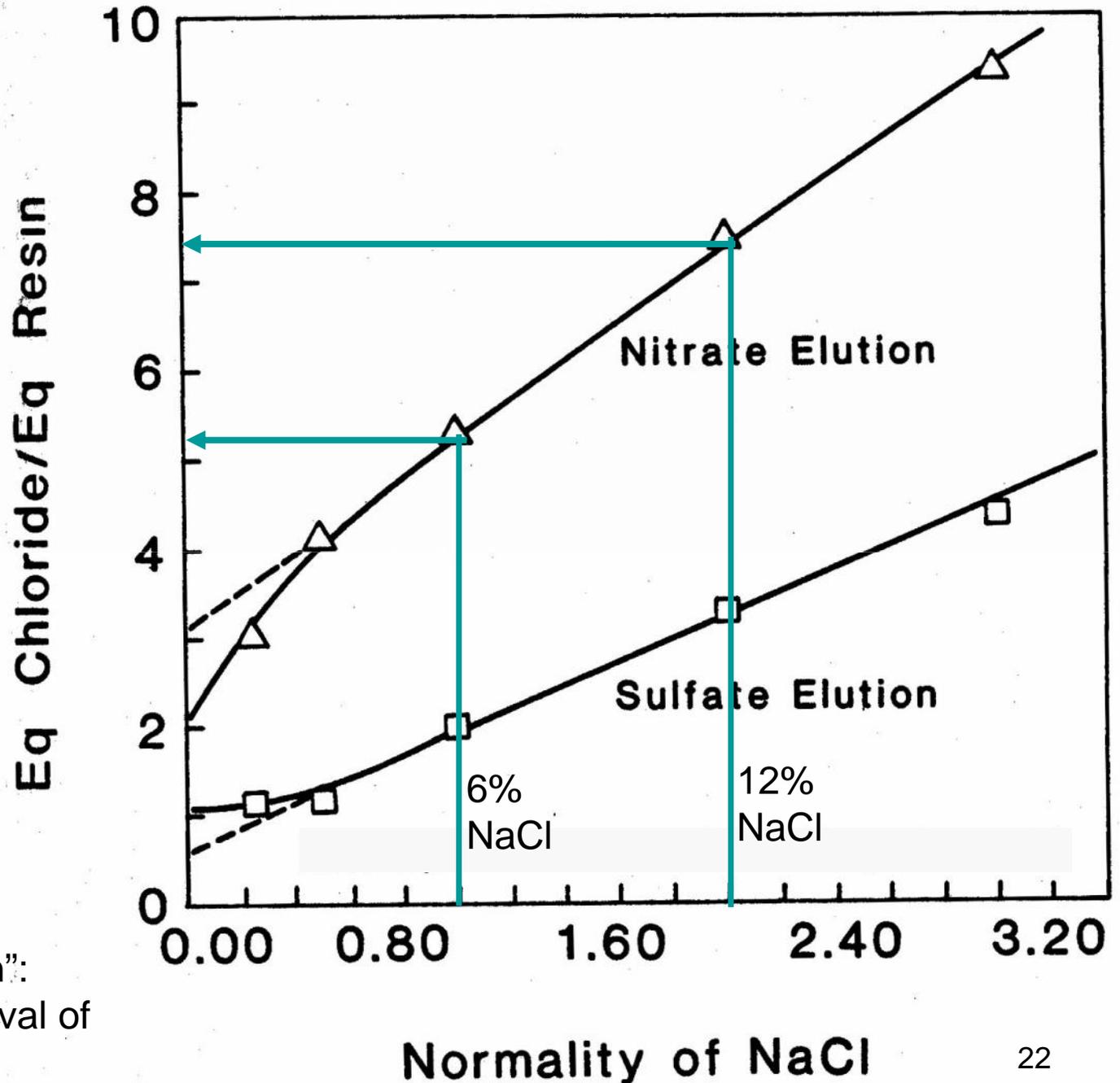
## Regeneration of Spent Resin

- Divalent  $\text{SO}_4^{2-}$  is easy to regenerate because of the “selectivity reversal” for  $\text{SO}_4^{2-}/\text{Cl}^-$  exchange.
- Monovalent nitrate ion does not undergo selectivity reversal during  $(\text{NO}_3^-/\text{Cl}^-)$  exchange; therefore, regeneration is more difficult
- The higher the  $\text{NO}_3^-/\text{Cl}^-$  selectivity, the harder the resin is to regenerate



Typical sulfate and nitrate elution curves during regeneration of a standard SBA resin with 6% NaCl.

Higher  
Conc.  
NaCl  
Wastes  
Salt



“Complete regeneration”:  
> 95% removal of  
nitrate.



# Possible Solutions to the Regeneration Problem

- Partial regeneration: 50-60%  $\text{NO}_3^-$  removal
  - Saves salt and reduces waste brine volume
  - High nitrate leakage on next run, may preclude blending
- Upflow regeneration, multiple parallel columns, mixed countercurrent ion exchange
- Denitrification (biological or chemical) and reuse
  - Brine reused more than thirty times
  - >90% reduction in brine waste
  - ~50% savings in NaCl consumption



## Complete vs Partial Regeneration Glendale, AZ Well Water

Description	Complete	Partial
NaCl Concentration, N (%)	0.25 (1.5%)	1.0 (6.0%)
eq Cl/eq resin, (lbs NaCl/ft <sup>3</sup> resin)	3.0 (15.3)	1.2 (6.1)
Wastewater volume as % of blended product water	3.0	1.1
NaCl consumed for 1 Mgd blended product water, lb/day	3250	2360



# Ion Exchange Summary

- SBA with Cl-form IX resin is effective for  $\text{NO}_3$  (and U, As, Cr, TOC,  $\text{ClO}_4$ ) removal
- Nitrate-selective resins, parallel columns, and continuous flow mixed reactor ion exchange smooth out peaks, improve run length, and conserve salt
- Brine disposal is primary challenge
- Partial regeneration (e.g.  $\leq 6\%$  NaCl) and denitrification and reuse can minimize brine disposal and salt consumption