

**American Water Works Association  
2004 Annual Conference**

***Bench and Pilot-Scale  
Investigation of Boron Removal  
for Seawater Membrane  
Desalination***

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**Long Beach Water Department**

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# Presentation Outline

- 💧 **Long Beach Overview**
- 💧 **Long Beach's Approach**
- 💧 **Water Quality Concerns**
- 💧 **Conclusion**

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# Long Beach Water Department

- 💧 California's 5th most populous city (480,000 people)
- 💧 70,000 AF of drinking water per year
- 💧 5,500 AF of reclaimed water per year
- 💧 Operate largest GW treatment plant in US
- 💧 912 miles of drinking water lines
- 💧 763 miles of sewer lines



# Long Beach Water Department

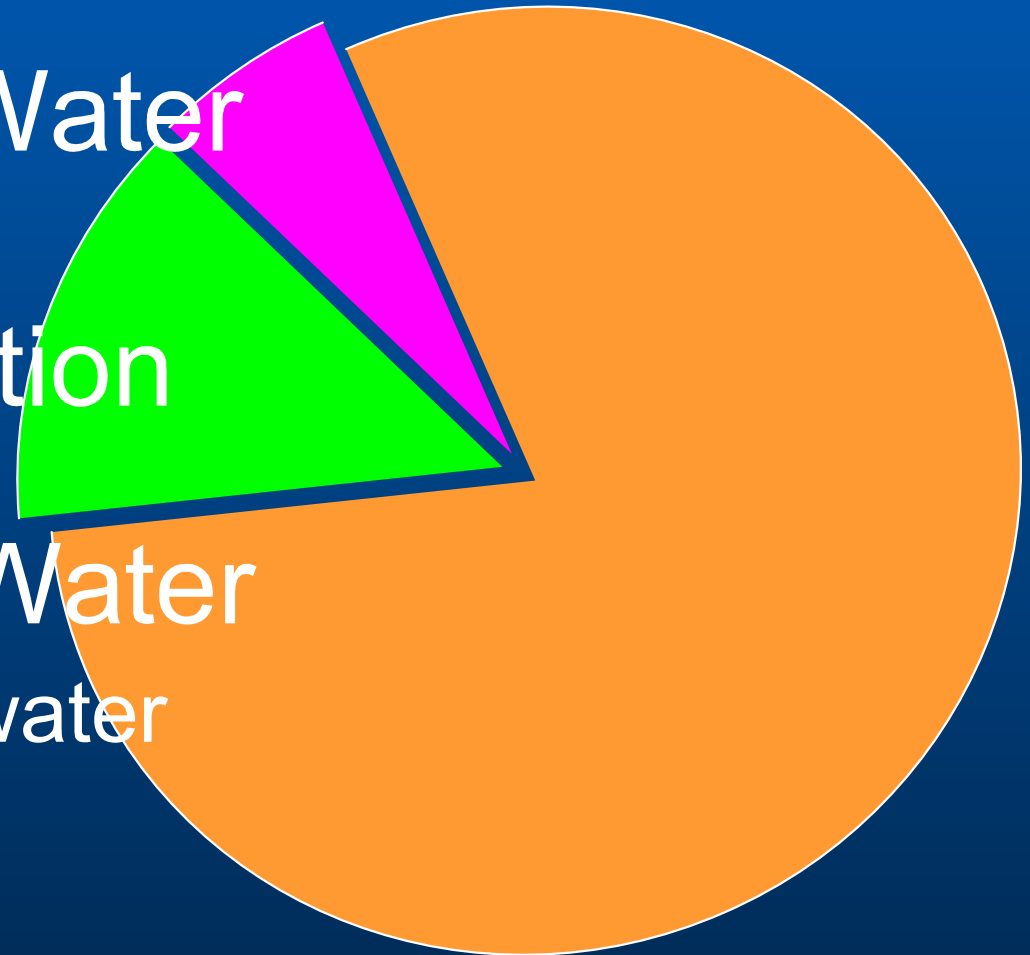
6%: Recycled Water

14%: Conservation

80%: Drinking Water

-46% LB Groundwater

-54% Imported



# Imported Water Supply

A topographic map of California with three colored lines representing major aqueducts: a red line for the California Aqueduct, a light blue line for the Los Angeles Aqueduct, and a dark blue line for the Colorado River Aqueduct. The map shows the state's terrain, with the Central Valley in green and the Sierra Nevada mountains in brown.

**Los Angeles Aqueduct:  
~37% reduction**

**California  
Aqueduct:  
~No Increase**

**Colorado River Aqueduct:  
~50% reduction**

**...communities  
must produce  
more water locally  
to manage new  
limits on imports  
and growth in  
southern  
California's  
population  
and  
economy.**

# Future Reliability

- 💧 Very little population growth
- 💧 Expansion of recycled water and water conservation
- 💧 Seawater desalination necessary ==> supplement City's imported drinking water supply

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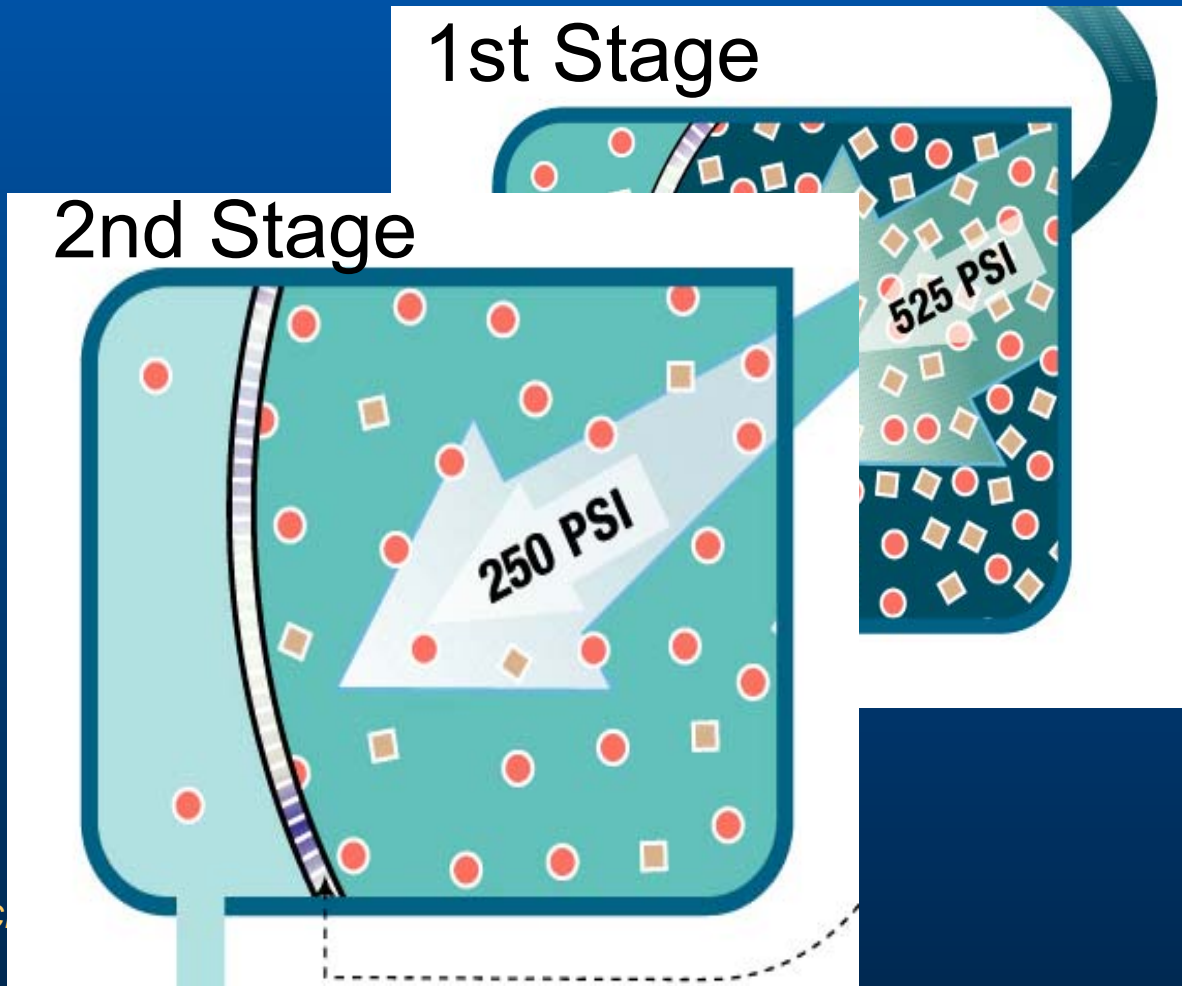


# “Traditional” RO Process

- 💧 Uses pressures in excess of 800 psi
- 💧 Energy intensive
- 💧 High-pressure materials required ⇒ high capital costs
- 💧 “Traditional” seawater desalination method cost prohibitive

# Process Development

- ▶ Patent pending 2-pass Nanofiltration (NF<sup>2</sup>) process



- ▶ Evaluating Energy Consumption
- ▶ Evaluating Quality protection

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# Typical NF<sup>2</sup> Water Quality

## 💧 Water quality

	Unit	Raw Seawater	Stage 1 Permeate	Stage 2 Permeate	LBWD Tap
Mg <sup>2+</sup>	mg/L	1532	28	0.2	13
Ca <sup>2+</sup>	mg/L	546	10.1	0.1	39
SO <sub>4</sub> <sup>2-</sup>	mg/L	2888	33	0.2	100
Na <sup>+</sup>	mg/L	11912	1280	92	75
Cl <sup>-</sup>	mg/L	19737	1806	117	59
TDS	mg/L	37480	3247	218	390
Hardness (as CaCO <sub>3</sub> )	mg/L	7755	140	1.26	151
pH	---	8.01	7.84	7.37	8.16
LSI	---	1.12	-1.93	-4.56	0.34

# Water Quality Concerns

## 💧 Standard operating conditions:

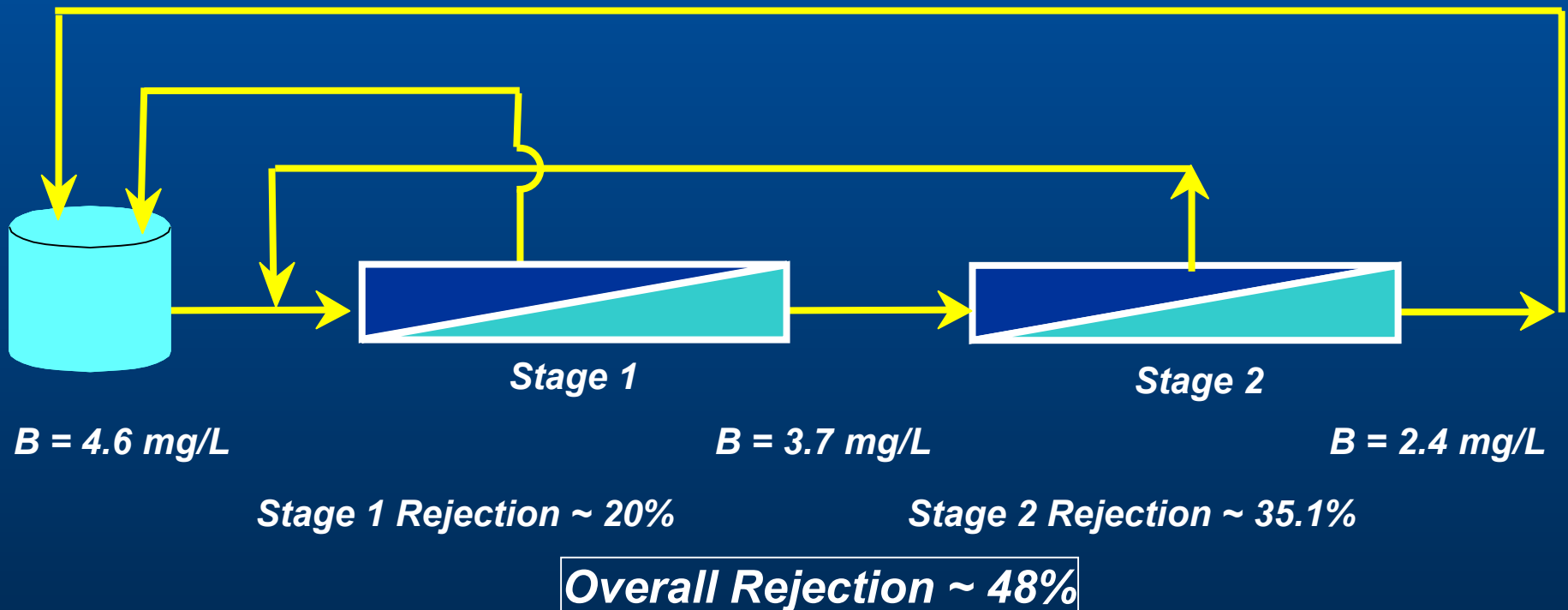
	Raw Seawater	NF <sup>2</sup> Permeate
TDS	~ 34,500 mg/L	< 300 mg/L
Bromide	~ 62 mg/L	0.4 - 0.6 mg/L
Boron	~ 4.5 mg/L	?

# Boron: Background

- 💧 Typically < 1 mg/L in surface waters
- 💧 Naturally occurring in seawater (~4.5 mg/L)
- 💧 Toxic to some common trees (0.3 - 1.0 mg/L)
- 💧 Show reproductive health effect in animals
- 💧 CDHS established Action Level at 1 mg/L
- 💧 No USEPA “MCL” but is on EPA CCL
- 💧 WHO guideline at 0.3 mg/L (original)
- 💧 WHO revised guideline to 0.5 mg/L (treatment limitation)
- 💧 Analytical interferences

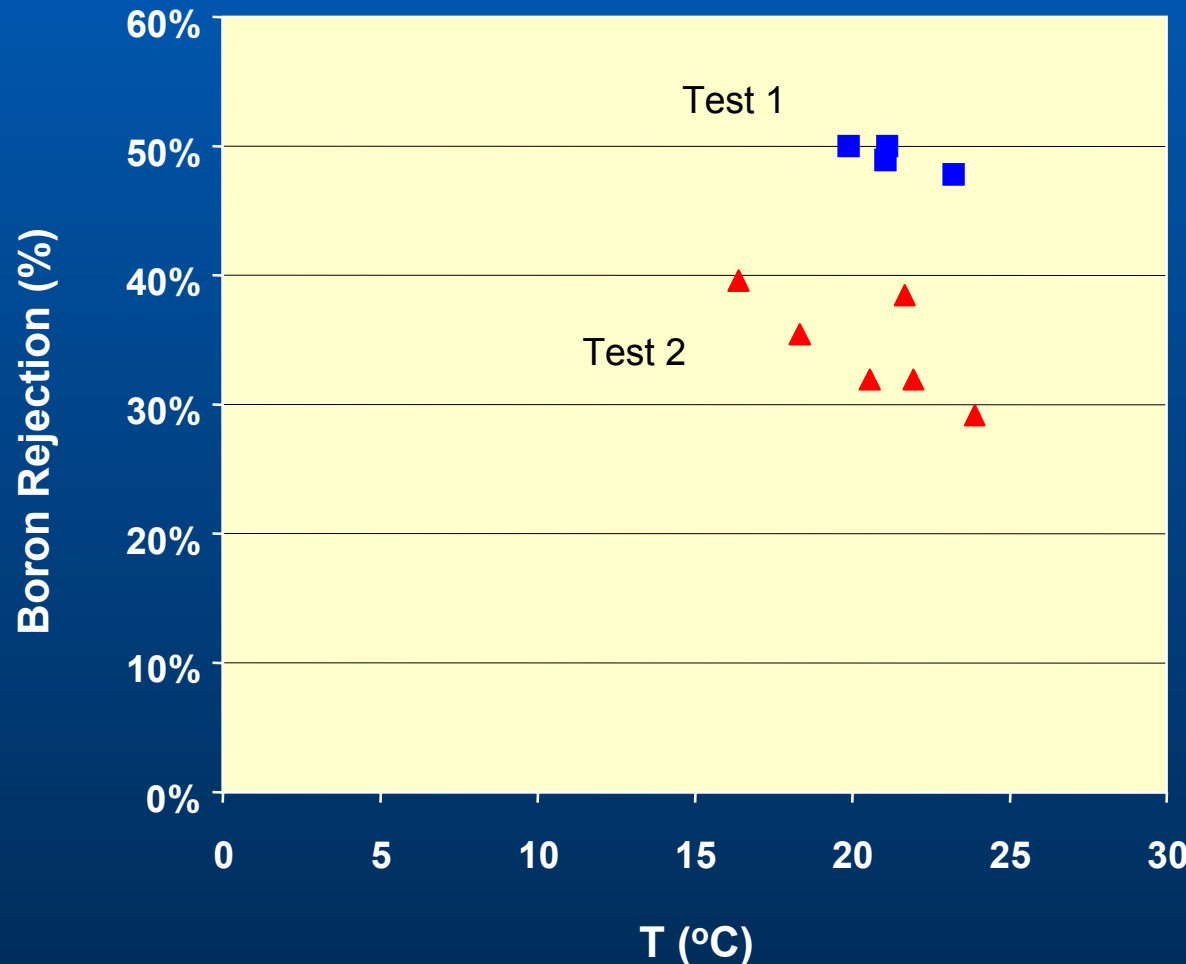
# Boron Removal

- Traditional single-pass SWRO achieves 43% - 78% rejection
- LBWD's NF<sup>2</sup> Process



# Temperature Effects on Rejection

- 🔥 Boron rejection substantially deteriorates with warm water temperatures
- 🔥 Some membranes are less affected by temperature, but selection may be few, limiting market competition
- 🔥 Successful boron control solution must be independent of temperature





# Literature Review

Technology	Water Tested	% Removal	Comments	Reference
Softening	Seawater	Insignificant	Batch tests of calcite precipitation	Kitano et al., (1978)
Coagulation	Drinking Water	<28%	Typical removal < 10%	Borax (1996)
Activated Carbon	Synthetic Water	Up to 90%	High carbon doses needed	Choi et al, (1979)
Reverse Osmosis	Seawater	43 - 78%	Survey of 8 operating RO Plants	Magara (1996)
Ion Specific Resin	RO Permeate	>99%	pH of produced waters <4.5 for 600 bed volumes	Nadav (1999)
2-pass RO with pH adjustment	RO Permeate	40 - 100%	Best removal at pH 10.5	Prats et al (2000)
Boron Chelation	Synthetic Water	>80%	N-methyl-D-glucamine	Smith et al, (1995)
	RO Permeate	>98%	Fluoride	Derwent (1997-1999)

\*Edwards, M (2000)

# Fluoride Addition

- Two fluoride sources added



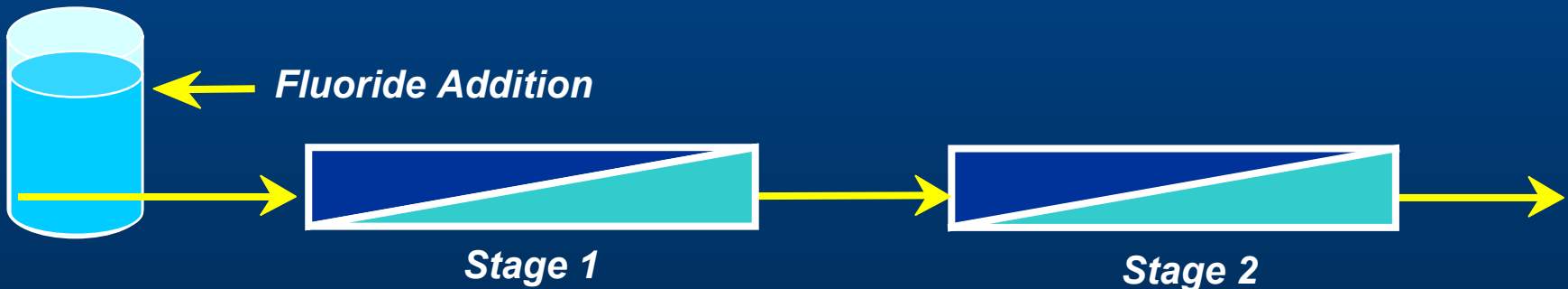




    - Adjust pH

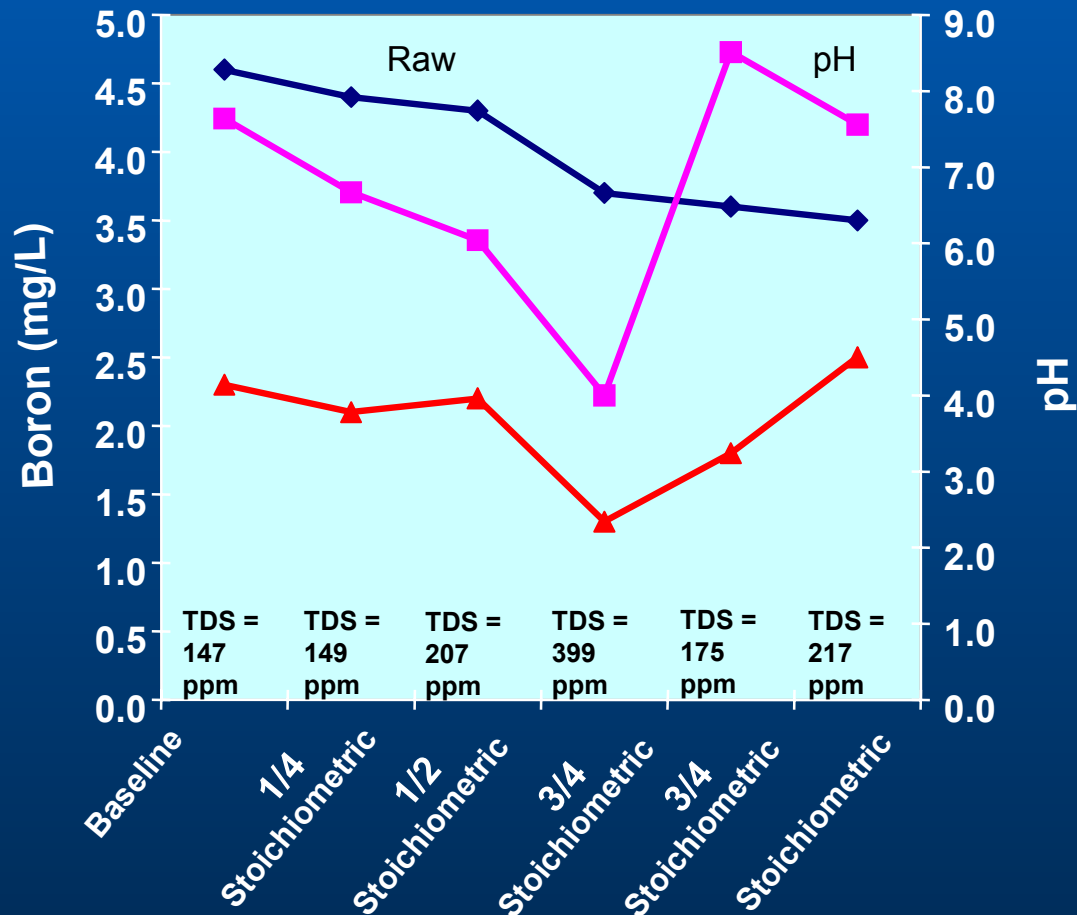


- Fluoride added in stoichiometric ratio increments ( $\frac{1}{4}$ ,  $\frac{1}{2}$ ,  $\frac{3}{4}$ , 1)



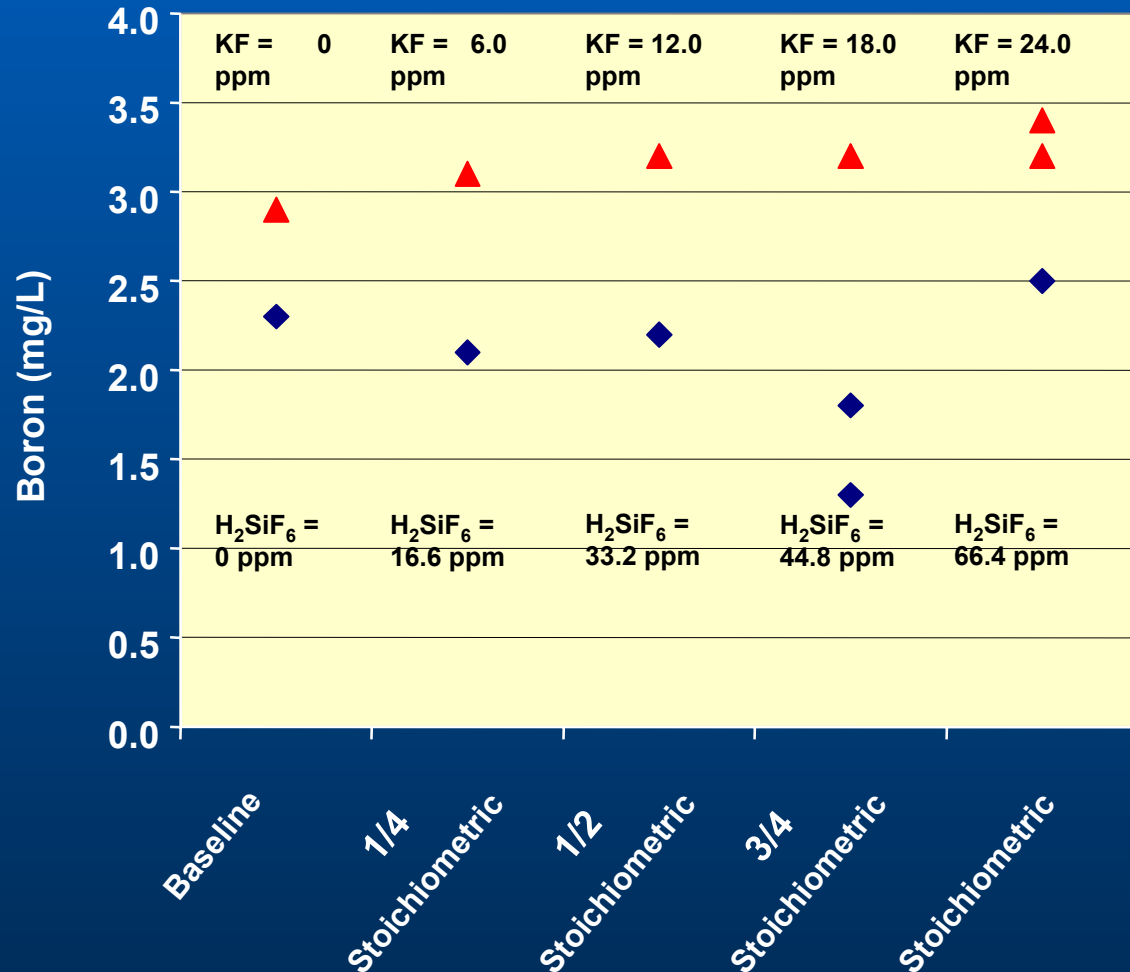
# Fluoride Addition

- Initially,  $H_2SiF_6$  addition appear to improve boron rejection.
- Improvement appears to be correlated to pH, not fluoride.
- Although lower pH improved boron rejection, lower pH deteriorated TDS quality.
- $H_2SiF_6$  addition appeared to reduce raw water boron levels.
- Increase in boron rejection may be associated with co-precipitation of boron.



# Fluoride Addition

- Isolating pH effect by adding KF, fluoride did not appear to improve boron rejection compared to  $H_2SiF_6$ .
- Fluoride dose required to reach stoichiometric ratio with raw water boron was an order magnitude greater than typical water treatment doses.

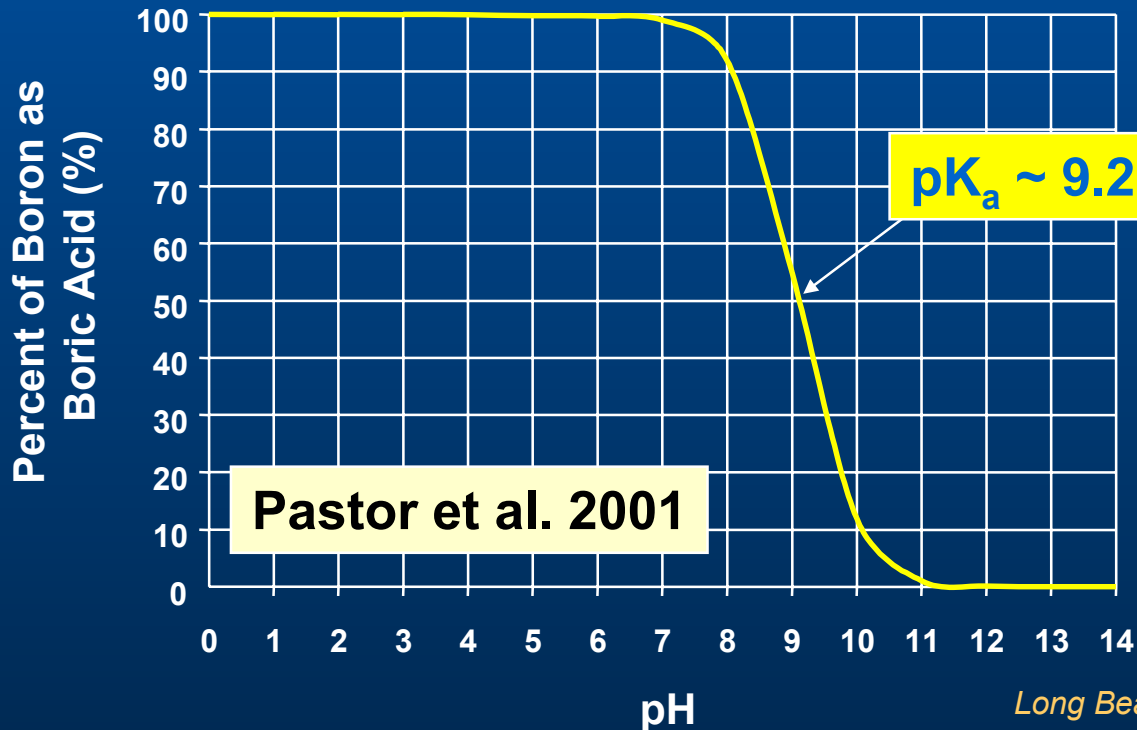


# Fluoride Evaluation Summary

- ✦ Reduction in pH appears to improve boron rejection, while inversely affecting TDS.
- ✦  $\text{H}_2\text{SiF}_6$  addition appears to improve boron rejection, but benefits appear to be associated with boron reduction in raw water, possibly due to co-precipitation.
- ✦  $\text{H}_2\text{SiF}_6$  doses necessary to achieve potential boron regulatory targets may be impractical.
- ✦ Fluoride alone does not appear to improve boron rejection, as illustrated by KF addition.

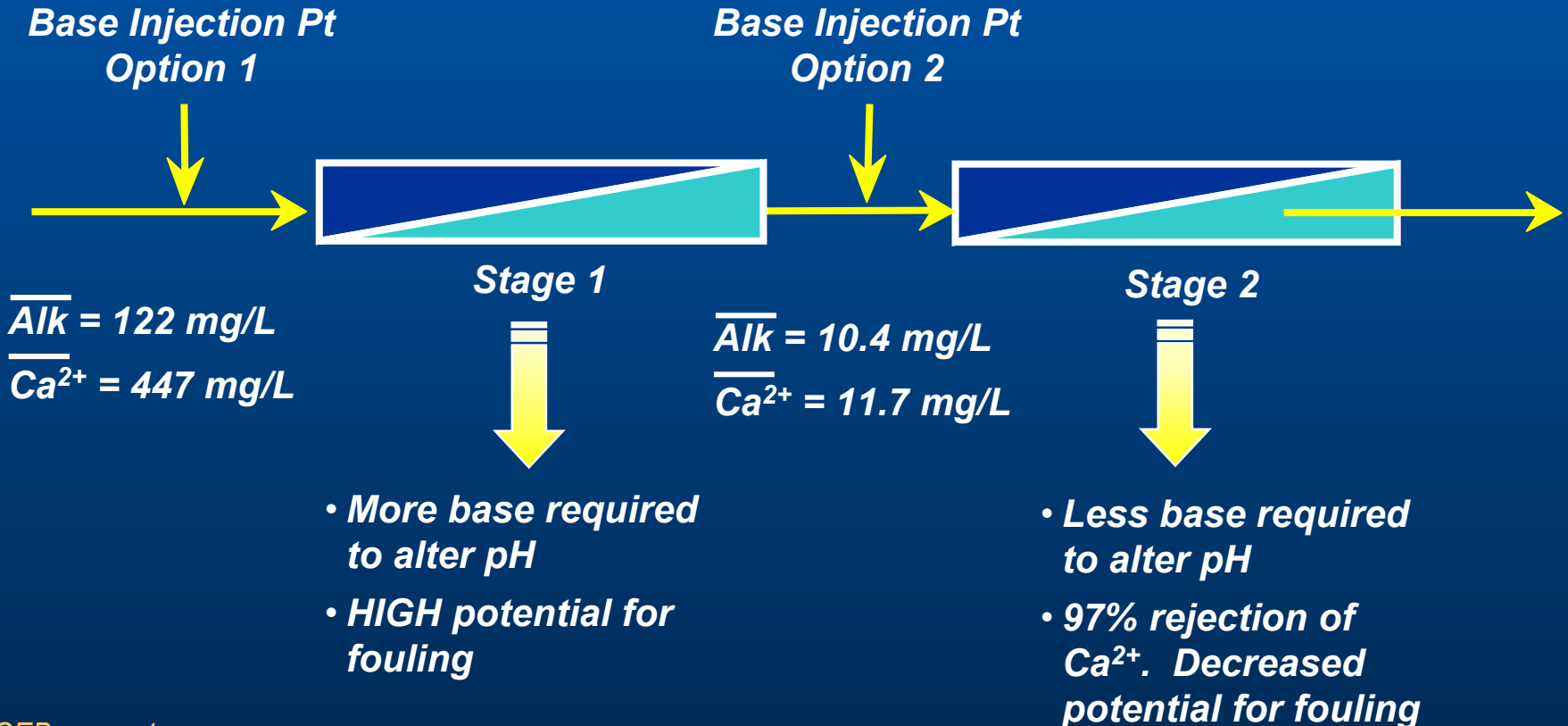
# Base Addition

- 🔥  $B(OH)_3 + OH^- \rightarrow B(OH)_4^-$
- 🔥 Boron rejection can be improved by increasing pH



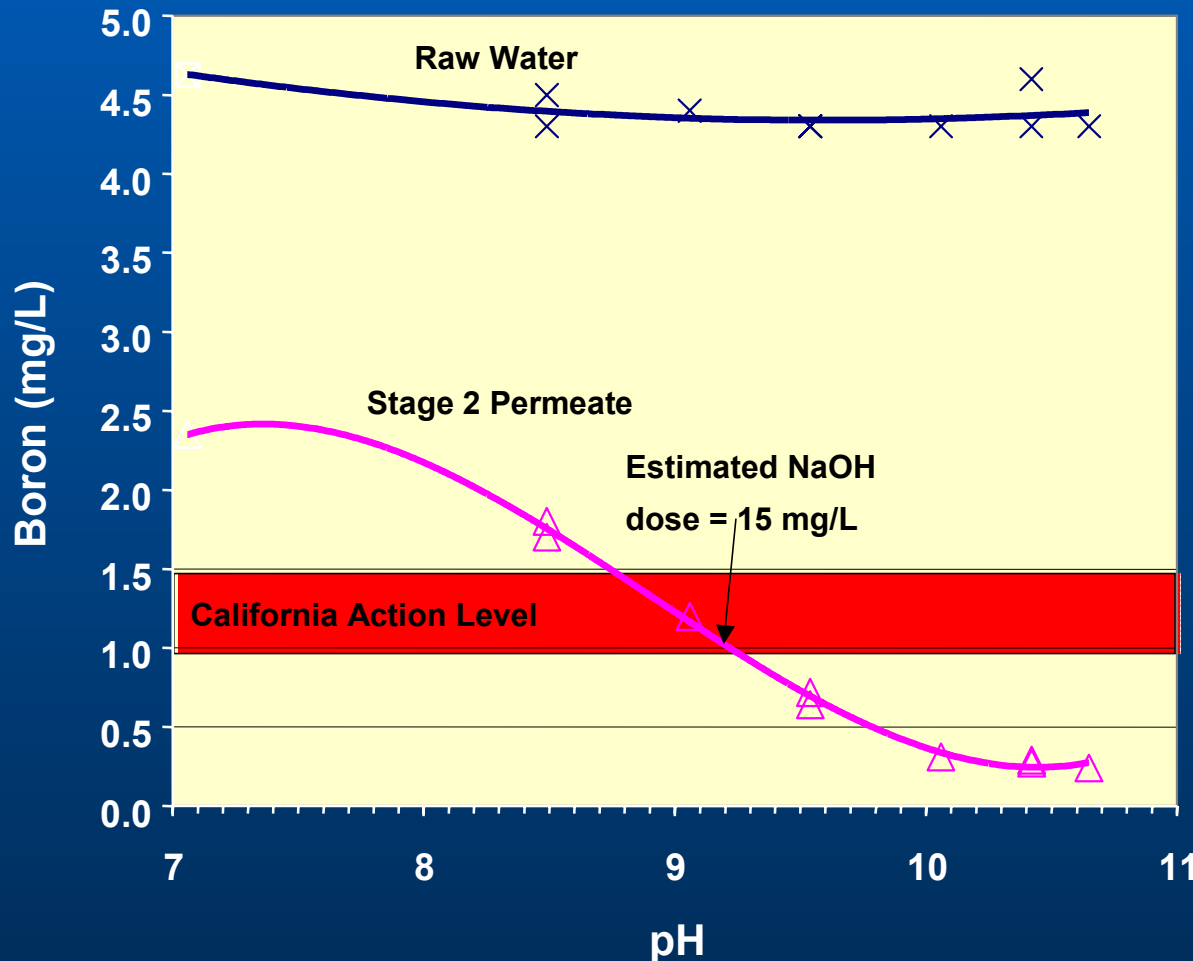
# Base Addition Strategy

- Selecting appropriate base addition location is critical



# Boron Addition Results

- California Action Level for boron is 1 mg/L.
- 1.49 mg/L would comply with action level.
- LBWD's boron goal is < 1.0 mg/L to minimize "significant digit" confusion to customers.
- Results show 15 mg/L NaOH (estimated) required for permeate boron to be < 1.0 mg/L.





# Base Evaluation Summary

- 🔥 Base can be added at the pass 2 feed to prevent inorganic precipitation.
- 🔥 For membranes and water tested, pH 9.2 improves boron in permeate to  $< 1.0$  mg/L.
- 🔥 Increasing pH to 9.8 would meet WHO limit of 0.5 mg/L.
- 🔥 Estimated cost (caustic only):
  - ❄  $< 1.0$  mg/L boron = \$0.02/1000 gallons
  - ❄  $< 0.5$  mg/L boron = \$0.04/1000 gallons

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# Conclusions

- ◆ **General WQ parameters consistent with single-pass SWRO.**
- ◆ **Preliminary results suggest boron rejection with fluoride is not practical.**
- ◆ **Base addition can be used with NF<sup>2</sup> process for boron control, with minimal capital cost.**
- ◆ **Additional chemical cost (caustic soda only) for meeting regulatory guidelines is estimated at \$0.02 to \$0.04 per 1000 gallons.**

# References

- ◆ Borax Consolidated Limited, “Report on Sampling at Selected Water Treatment Works to Determine the Extent of Boron Removal by Conventional Water Treatment”, Feb. 1996.
- ◆ Choi Won-Wook et al., “Evaluation of Boron Removal by Adsorption on Solids”, *Env. Sci and Tech*, Vol. 13(2), 189-198, 1979.
- ◆ Derwent, Machine Assisted Translation of Japanese Patents, JP10-80684, 9-220564, 9-8128325.
- ◆ Edwards, M., “Boron Removal From Drinking Water: Options and Feasibility”, Presented at the AWWA Inorganic Contaminants Workshop. San Diego, CA. February 2002.
- ◆ Kitano, “Co-Precipitation of Borate-Boron with Calcium Carbonate”, *Geochemical Journal*, Vol. 12, 183-189, 1978.
- ◆ Magara, Y., et al., “The Behavior of Inorganic Constituents and Disinfection By-Products in Reverse Osmosis Water Desalination Processes”, *Water Sci. Tech.*, Vol. 34, No. 9, pp 141-148, 1996.
- ◆ Nadav, N., “Boron Removal From Seawater Reverse Osmosis Permeate Utilizing Selective Ion Exchange Resin”, *Desalination* 124, pp 131-135, 1999.
- ◆ Pastor, M.R., “Influence of pH in the Elimination of Boron By Means of Reverse Osmosis”, *Desalination* 140, pp 145-152, 2001
- ◆ Prats, D., et al., “Analysis of the influence of pH and pressure on the elimination of boron in reverse osmosis”, *Desalination* 128, pp 269-273, 2000.
- ◆ Smith, BM., et al., “Boron Removal by Polymer-Assisted Ultrafiltration”, *Separ. Sci. Tech.*, Vol. 30, pp 3849-3859, 1995.