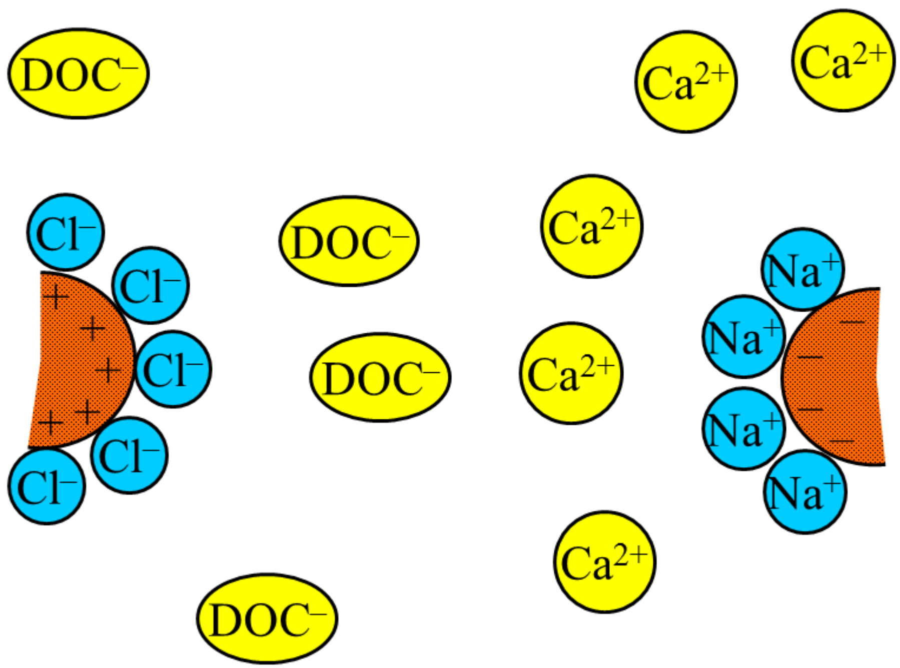
Combined Ion Exchange for Removal of Dissolved Organic Carbon and Hardness

Treavor Boyer

30 August 2016



EPA's Small Drinking Water Systems Webinar Series

Removal of Multiple Contaminants: Biological Treatment and Ion Exchange

Acknowledgements

Small, Safe, Sustainable (S3) Public Water Systems through Innovative Ion Exchange (R835334)

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WINSSS
Water Innovation Network for Sustainable Small Systems
A National Center for Innovative Small Drinking Water Systems

Many great students – Jennifer Apell, Katie Indarawis, Sarah Comstock, Gabe Maul, Jerrine Foster, Yue Hu, Alysse Ness

Dr. Qiong (Jane) Zhang

Cedar Key Water & Sewer District

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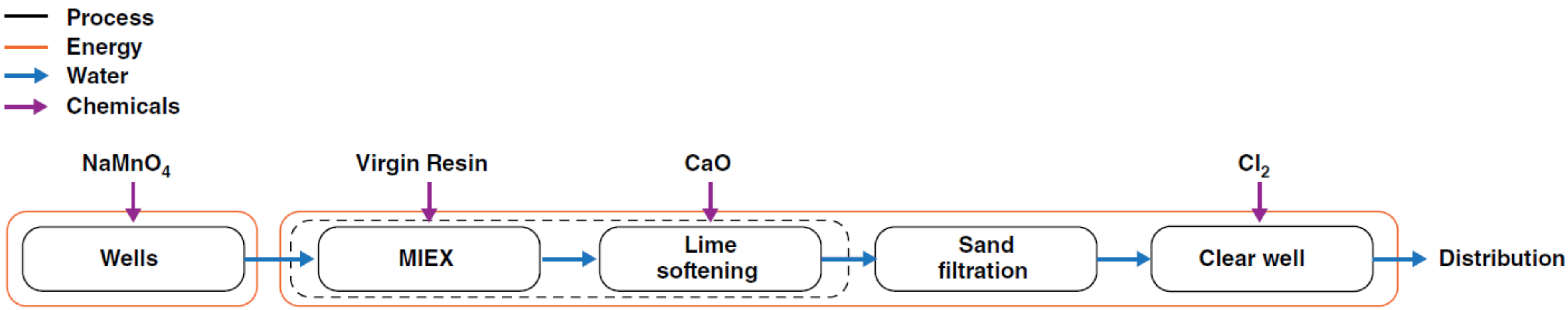
Trusted systems. Resourceful thinking.

Challenges faced by small water systems

Oxenford & Barrett, 2016. Understanding Small Water System Violations and Deficiencies. *Journal AWWA*, 108(3), 31–37.

- Management and operations
- Source water
- Security
- Pumps
- Compliance
- Data verification
- Treatment
- Finished water storage
- Distribution
- Financial

Challenges faced by small water systems



Fe oxidation

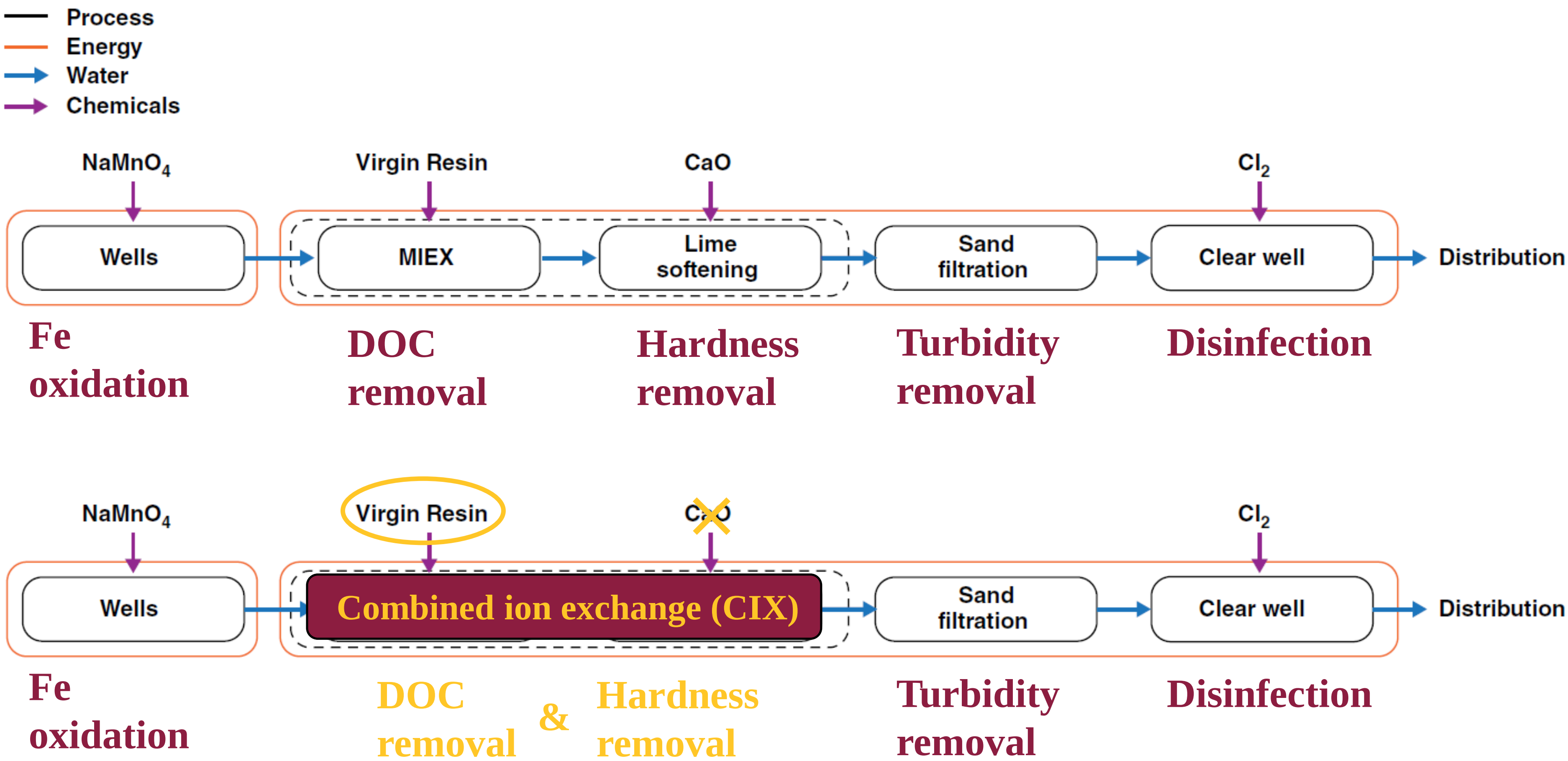
DOC removal

Hardness removal

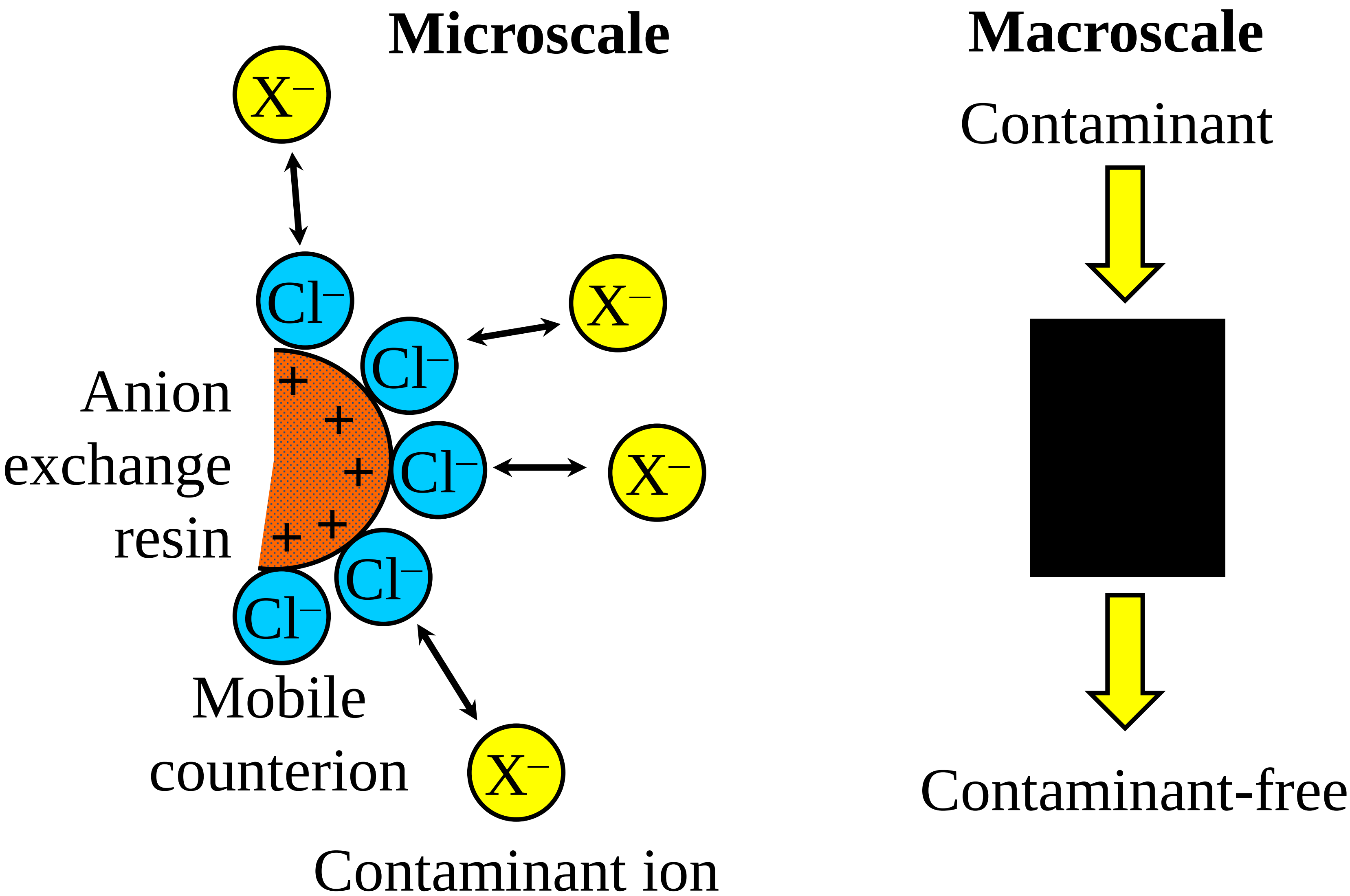
Turbidity removal

Disinfection

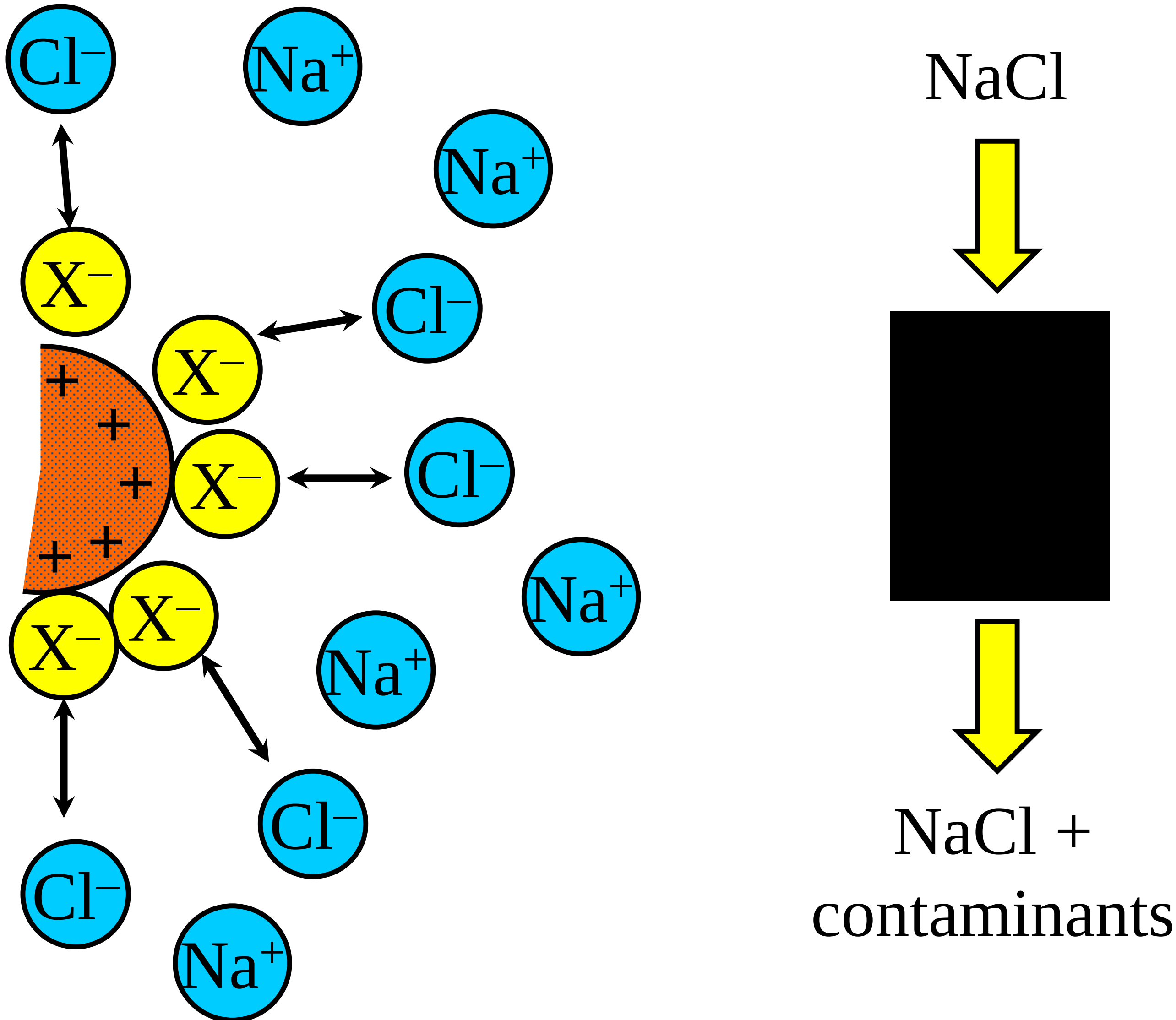
Challenges faced by small water systems



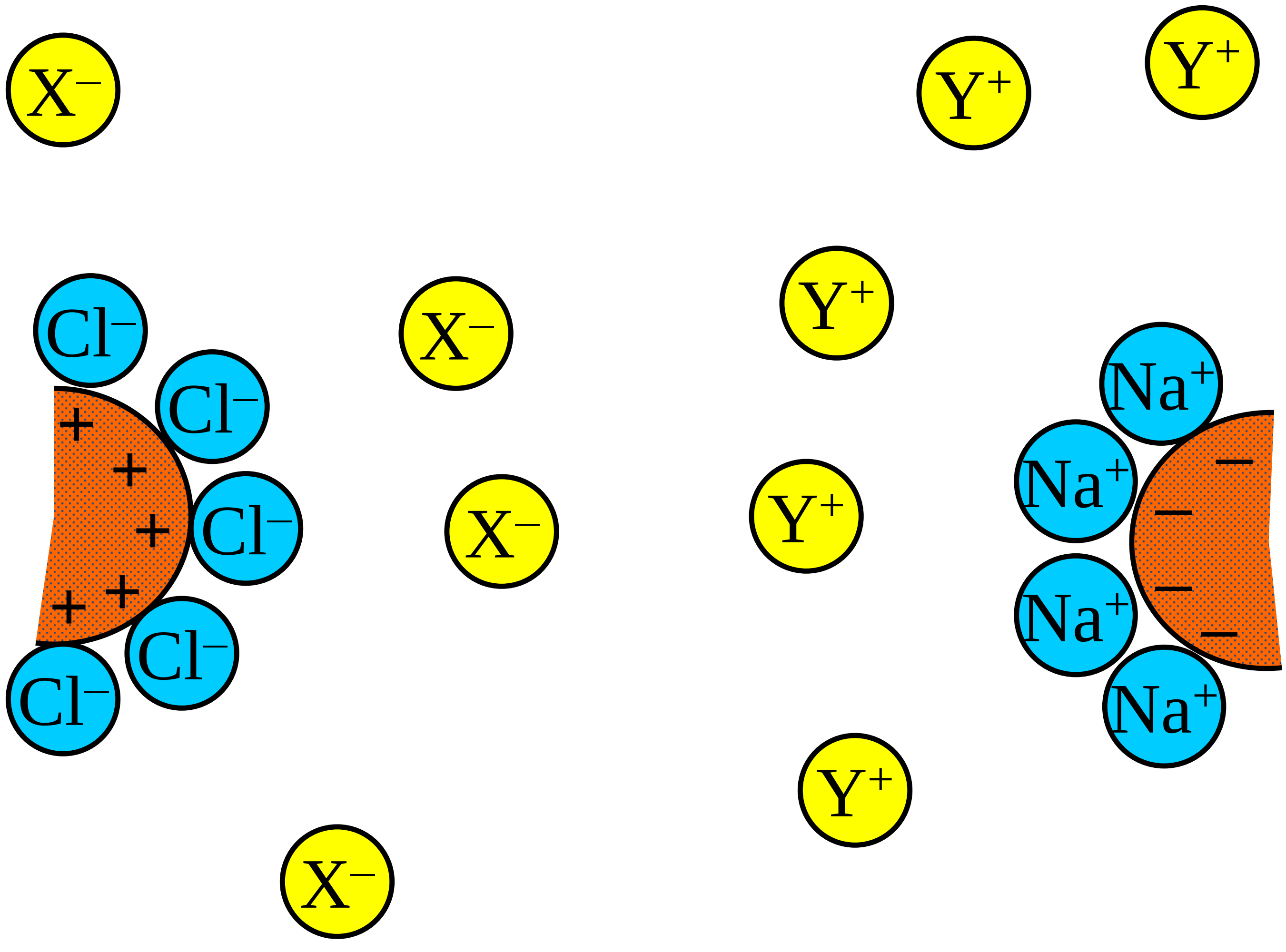
Ion exchange



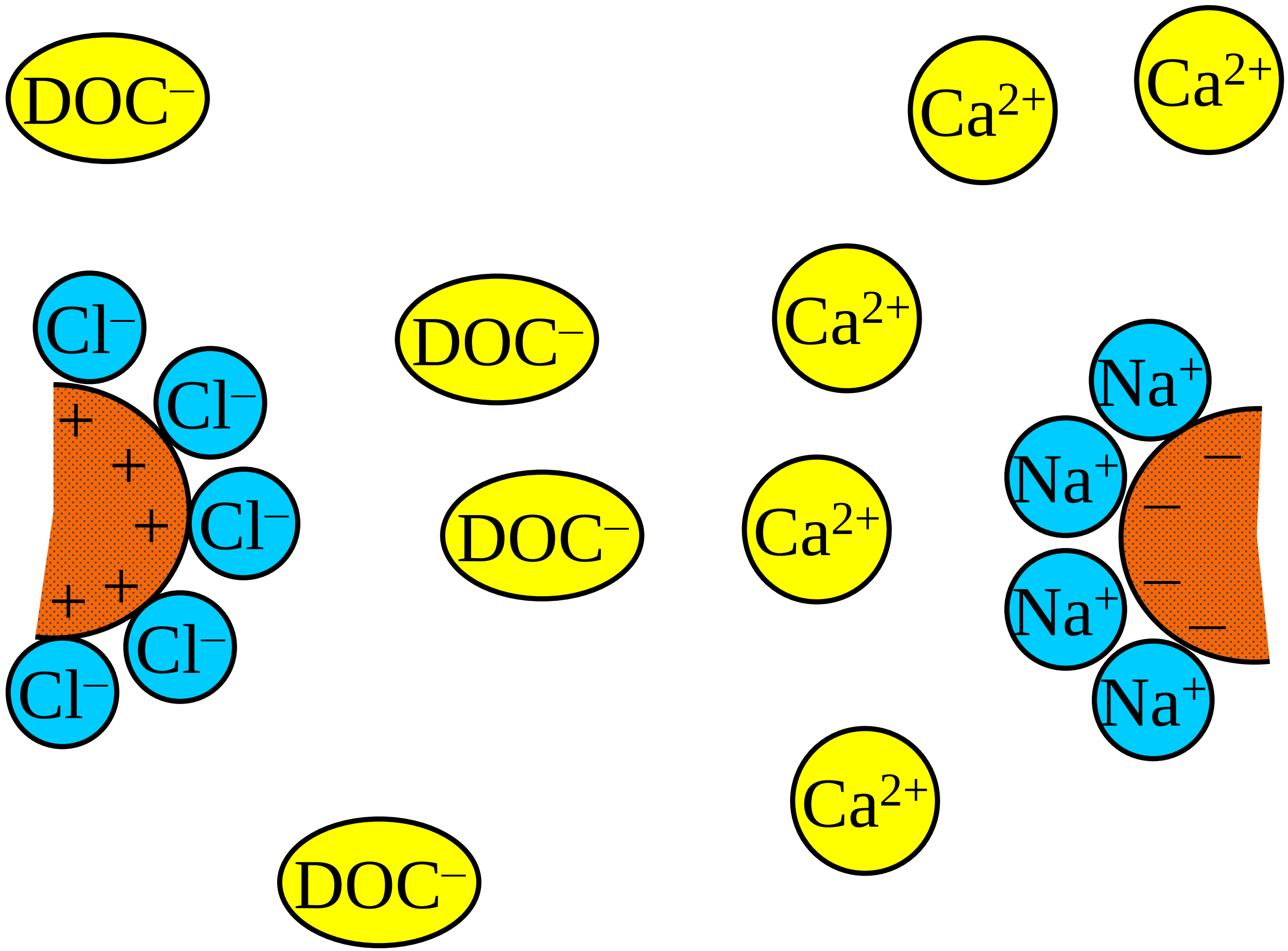
Regeneration



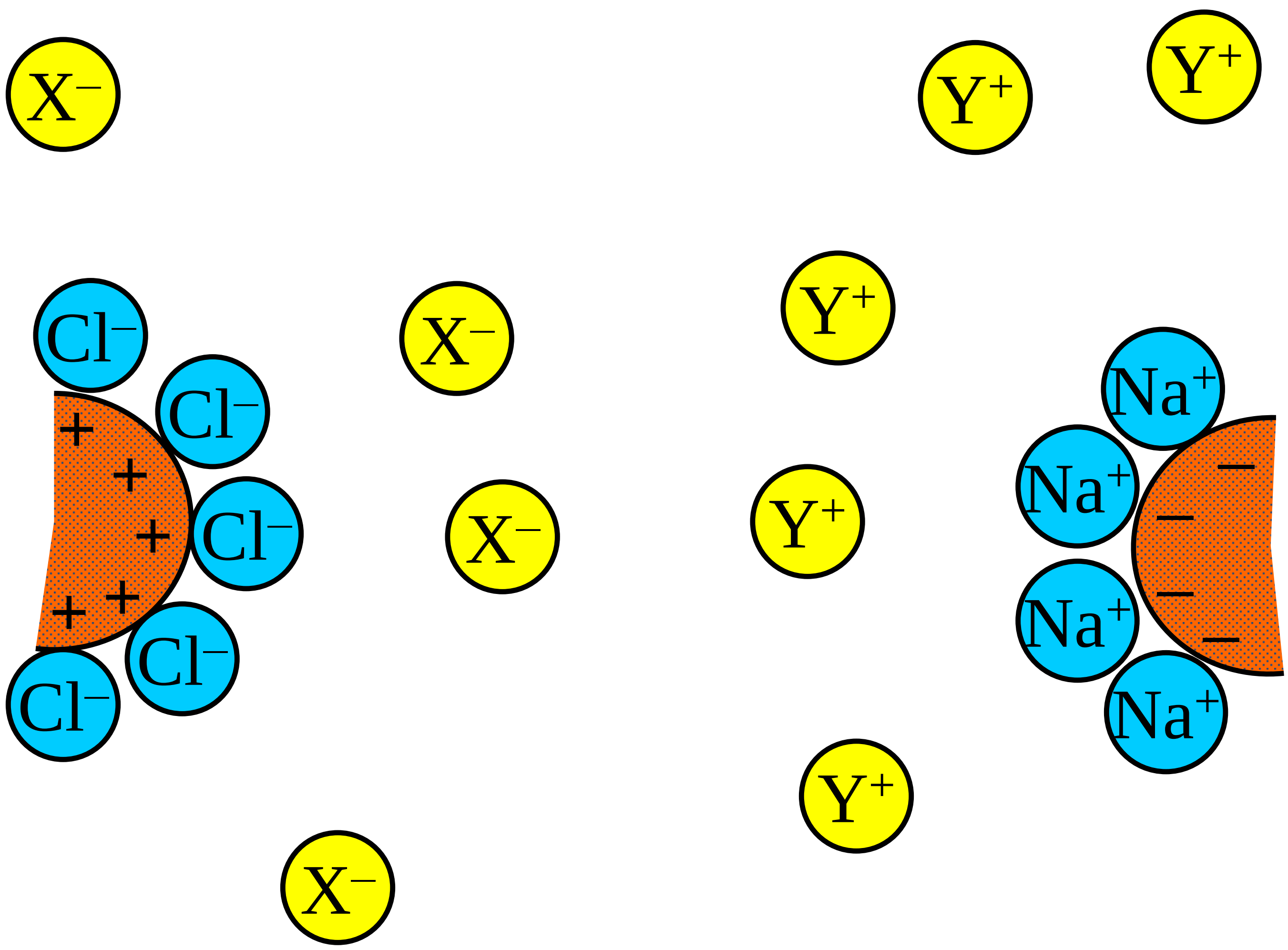
Combined ion exchange (CIX)



CIX: DOC and hardness removal

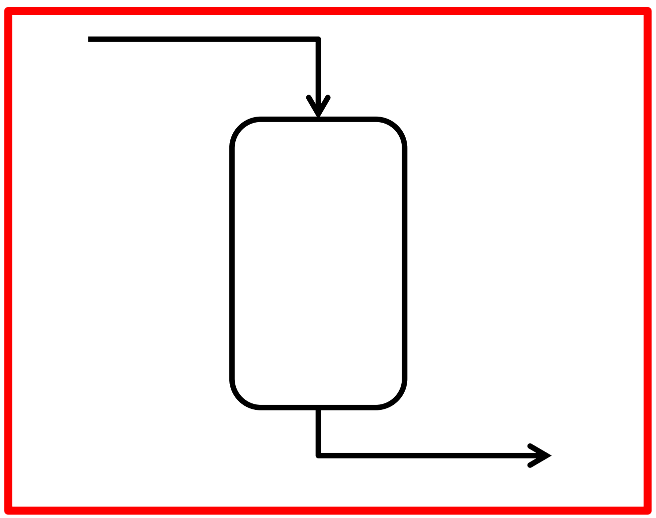


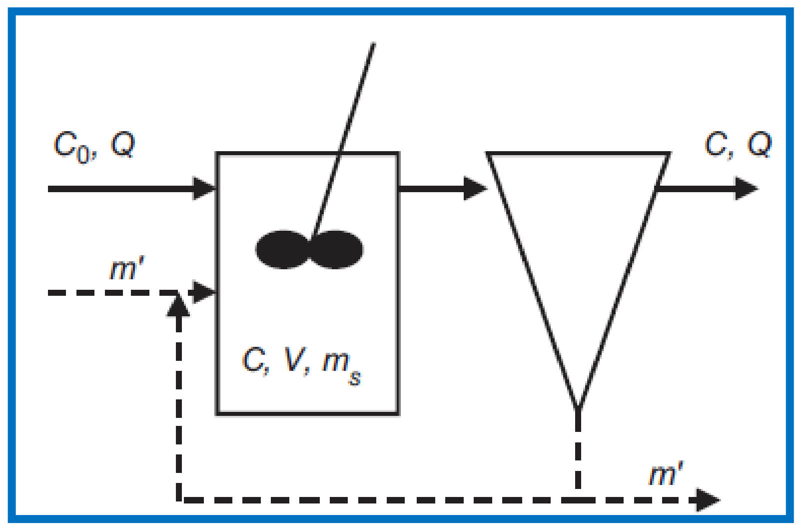
CIX & multi-contaminant removal



Ion exchange reactors

- Fixed bed reactor
- Completely mixed reactor with resin recycle





Proof of concept

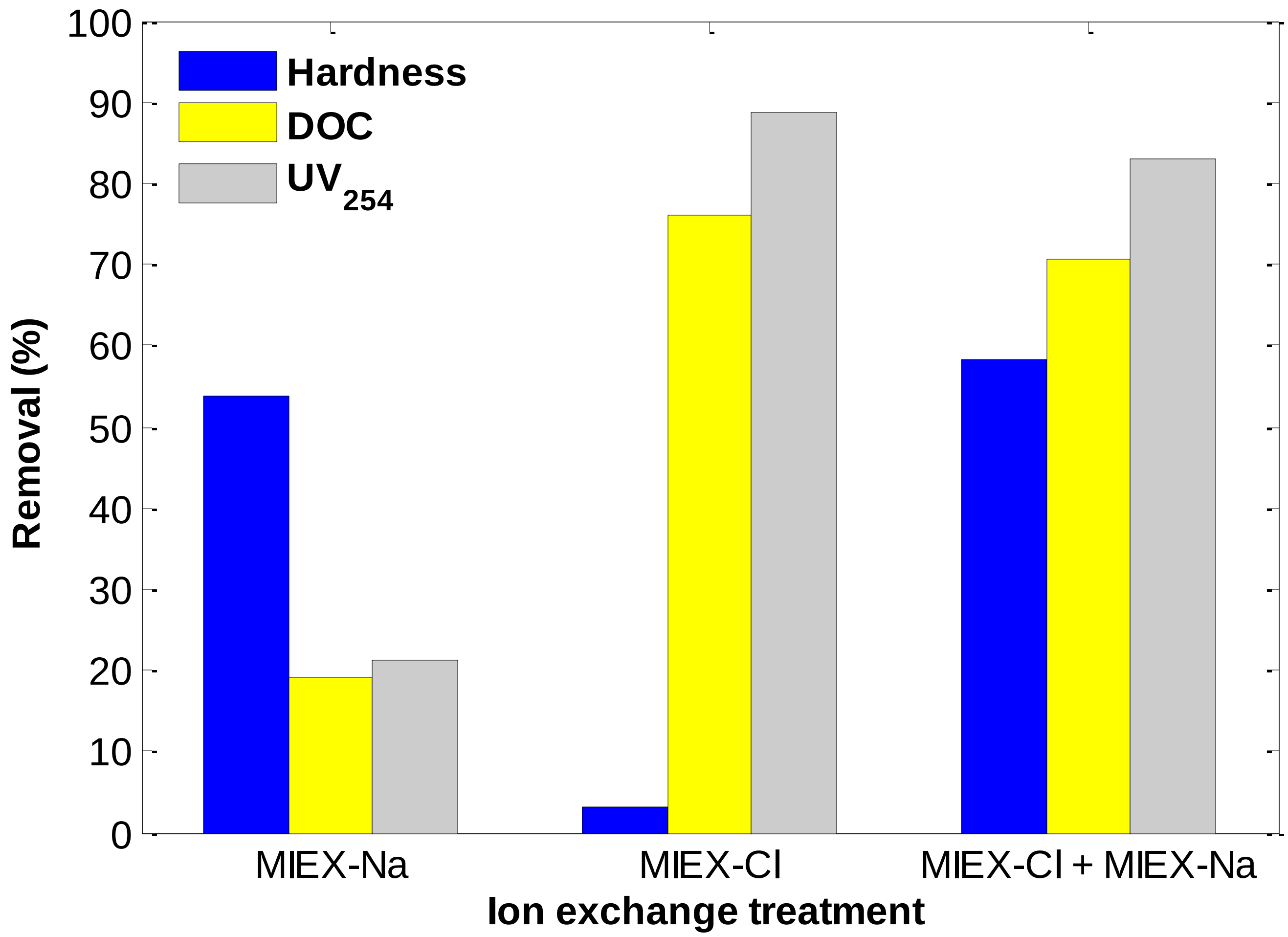
- Apell, J.N., Boyer, T.H., 2009. Simultaneous removal of dissolved organic matter and hardness by combined ion exchange. *AWWA Water Quality Technology Conference and Exposition* Seattle, Washington, 15–18 November 2009, 8 p.
- Apell, J.N., Boyer, T.H., 2010. Combined ion exchange treatment for removal of dissolved organic matter and hardness. *Water Research* 44, 2419–2430.

Proof of concept

Experimental design

- Groundwater from Cedar Key
  - DOC: 5.6 mg/L
  - Hardness: 275 mg/L as $CaCO_3$
- Anion exchange resin: 2 mL/L MIEX-Cl
- Cation exchange resin: 16 mL/L MIEX-Na
- Single-loading jar tests
  - Simultaneous: MIEX-Cl + MIEX-Na
  - Sequence 1: MIEX-Cl → MIEX-Na
  - Sequence 2: MIEX-Na → MIEX-Cl
- NaCl regeneration

Proof of concept



- 70% DOC removal and 55% hardness removal

Apell & Boyer, 2010. *Water Res.*

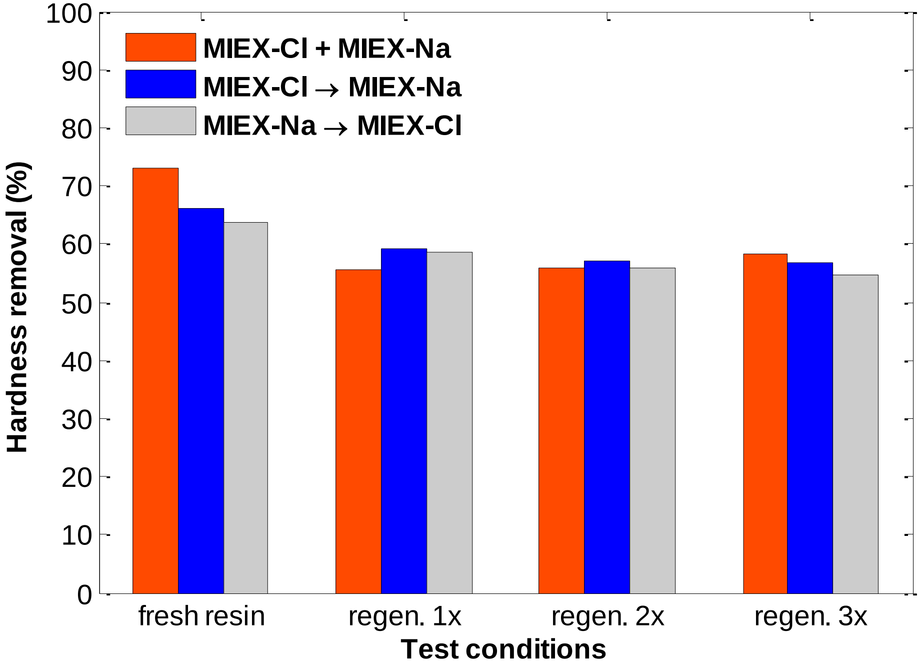
Proof of concept

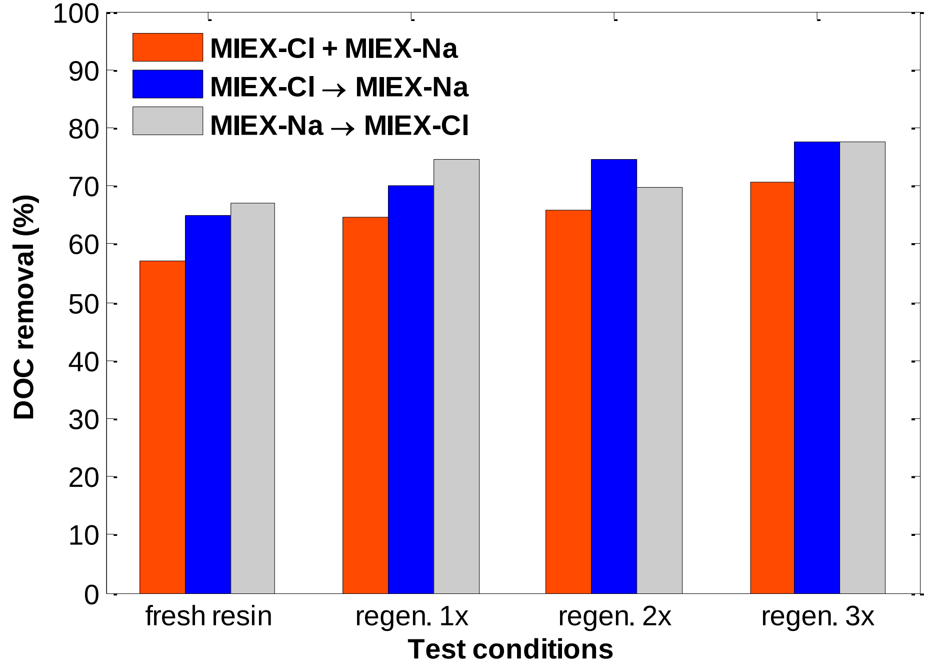
Parameter	MIEX-Cl + MIEX-Na	Finished drinking water[a]
pH	7.7	8.1
DOC (mg C/L)	1.7	1.1
Hardness (mg/L as $CaCO_3$)	112	173
Chloride (mg/L)	49	60
Sulfate (mg/L)	3.1	1.1

[a] Cedar Key Water & Sewer District; August 2009.

Apell & Boyer, 2010. *Water Res.*

Proof of concept





- Decrease in hardness removal and increase in DOC removal after 3 regeneration cycles
- Simultaneous and sequential ion exchange showed similar removals after 3 regeneration cycles

Apell & Boyer, 2010. *Water Res.*

Proof of concept

Conclusions

- MIEX-Cl and MIEX-Na can be used in a single completely mixed vessel to simultaneously remove DOC and hardness
- MIEX-DOC and MIEX-Ca can be effectively regenerated using NaCl in a single completely mixed vessel
- Simultaneous and sequential ion exchange showed approximately equal removal after three regeneration cycles
- NaCl regeneration solution prepared using tap water (i.e., containing hardness and alkalinity) provided the same regeneration efficiency as NaCl regeneration solution prepared using hardness-free, deionized water

Proof of concept

Observations

- MIEX-Na removed DOC in addition to hardness. This was unexpected because DOC is negatively charged.
- Combined ion exchange is expected to be an effective pretreatment to reduce membrane fouling, i.e., decrease organic fouling by DOC and inorganic scaling by calcium minerals

Focus on cation exchange

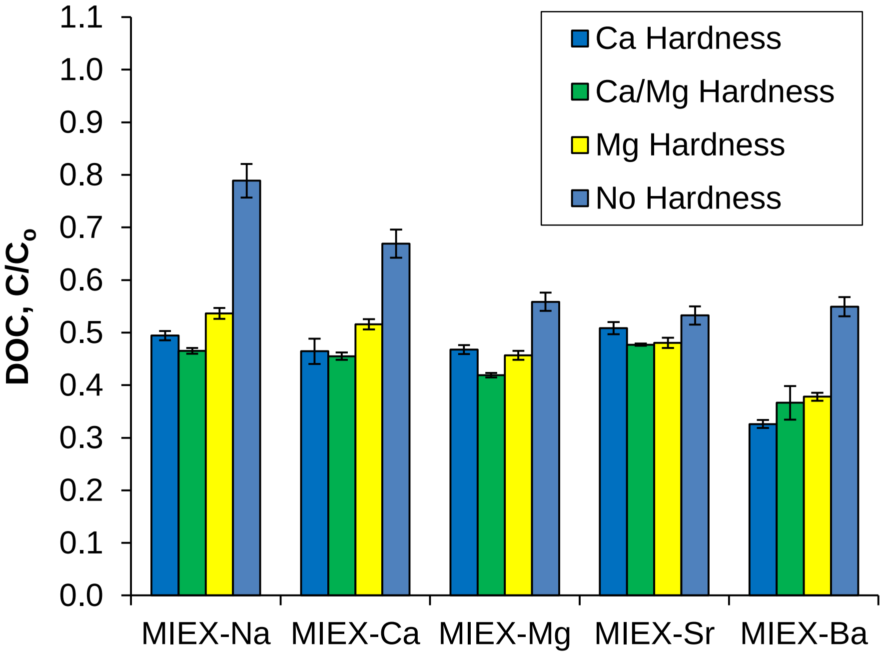
- Indarawis, K.A., Boyer, T.H., 2012. Alkaline earth metal cation exchange: Effect of mobile counterion and dissolved organic matter. *Environmental Science & Technology* 46, 4591–4598.
- Indarawis, K.A., Boyer, T.H., 2013. Superposition of anion and cation exchange for removal of natural water ions. *Separation and Purification Technology*, 118, 112–119.
- Indarawis, K.A., Boyer, T.H., 2014. Evaluation of ion exchange pretreatment options to decrease fouling of a reverse osmosis membrane. *Desalination and Water Treatment*, 52(25–27), 4603–4611.

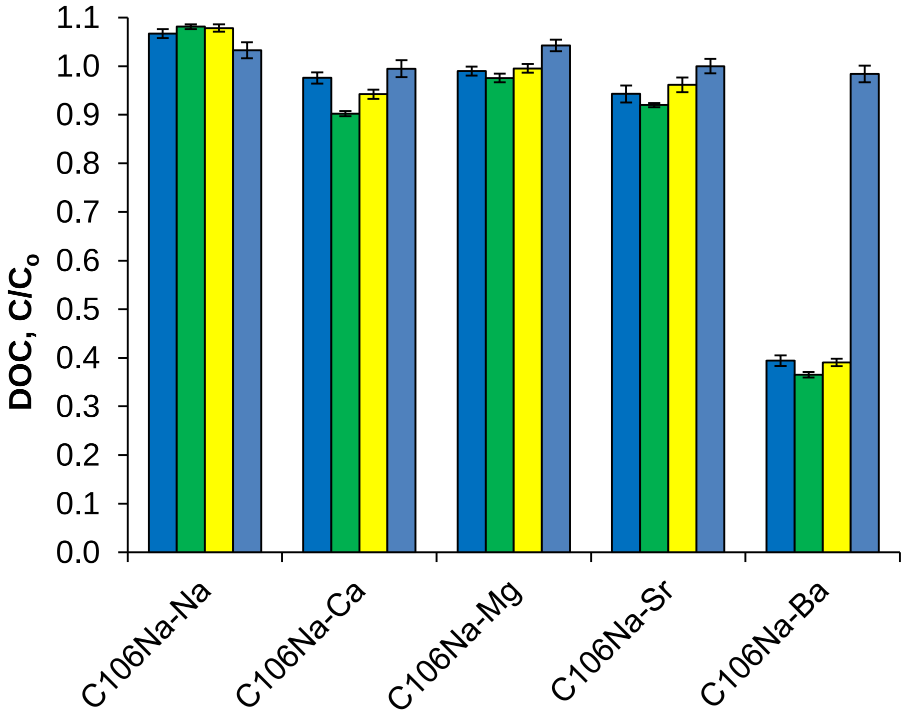
Focus on cation exchange

Experimental design

- Synthetic water to mimic Cedar Key groundwater
  - Suwannee River NOM (~5 mg/L DOC)
  - Hardness as Ca^{2+}, Mg^{2+}, and Ca^{2+}/Mg^{2+} (~250 mg/L as $CaCO_3$)
- Cation exchange resin
  - 16 mL/L MIEX-Na
  - 3.1 mL/L Purolite C106-Na
  - Resin-Na, -Ca, -Mg, -Sr, and -Ba
- Batch equilibrium experiments

Focus on cation exchange

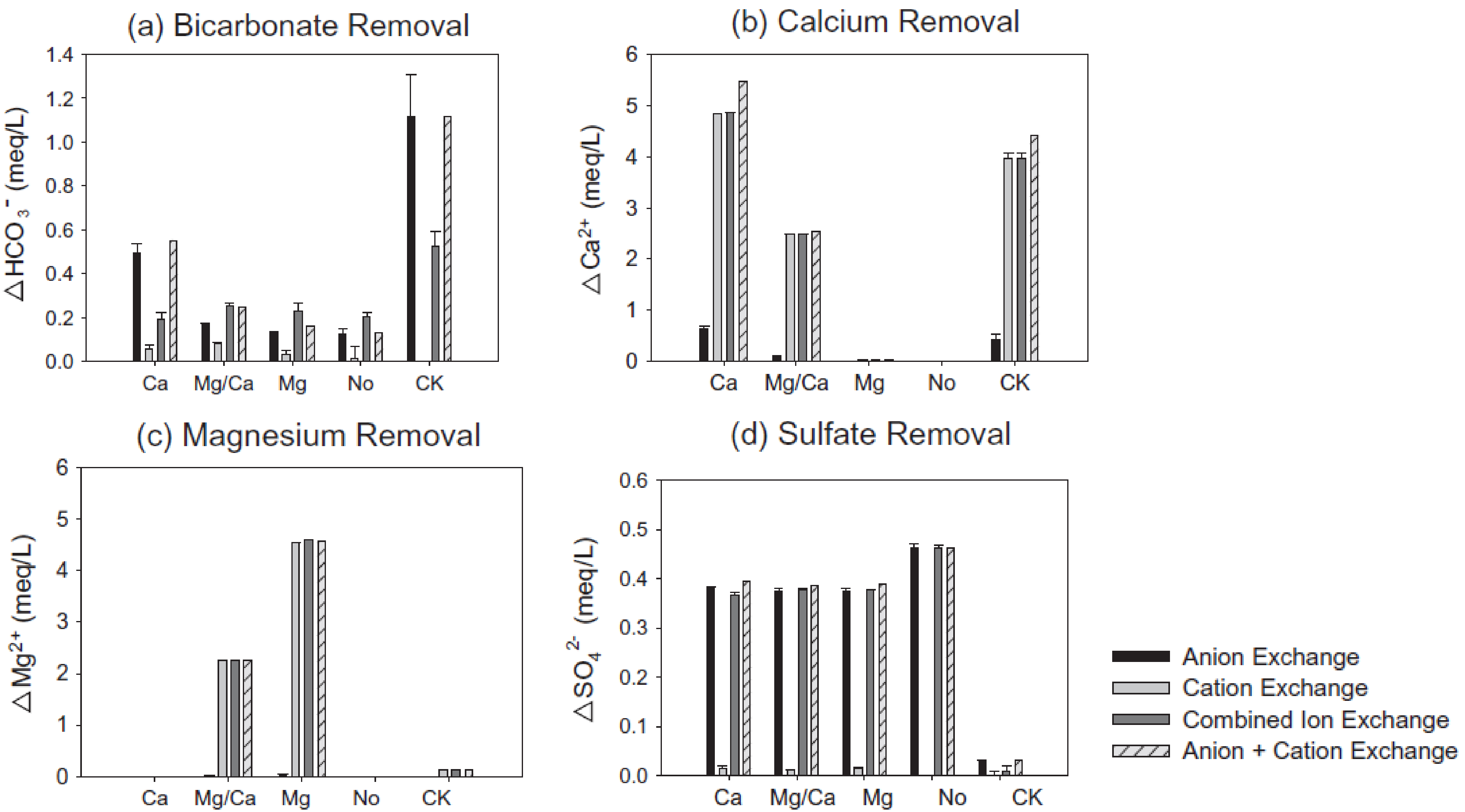




- DOC removal by magnetic cation exchange resin
- No DOC removal by non-magnetic cation exchange resin

Indarawis & Boyer, 2012. *Environ. Sci. Technol.*

Combined ion exchange, revisited



- Combined ion exchange is additive

Indarawis & Boyer, 2013. *Separation and Purification Technology*

Focus on cation exchange

Conclusions

- DOC removal was approximately 20% for MIEX-Na resin with no hardness cations in solution
- DOC removal by MIEX resin increased when the presaturant ion was a divalent metal cation or divalent metal cation was present in solution or both
- There was no measureable DOC removal by the non-magnetic cation exchange resin for all conditions of presaturant ion and metal cations in solution, with the exception of barium as the presaturant ion
- Combined ion exchange is additive

Combined ion exchange (CIX)

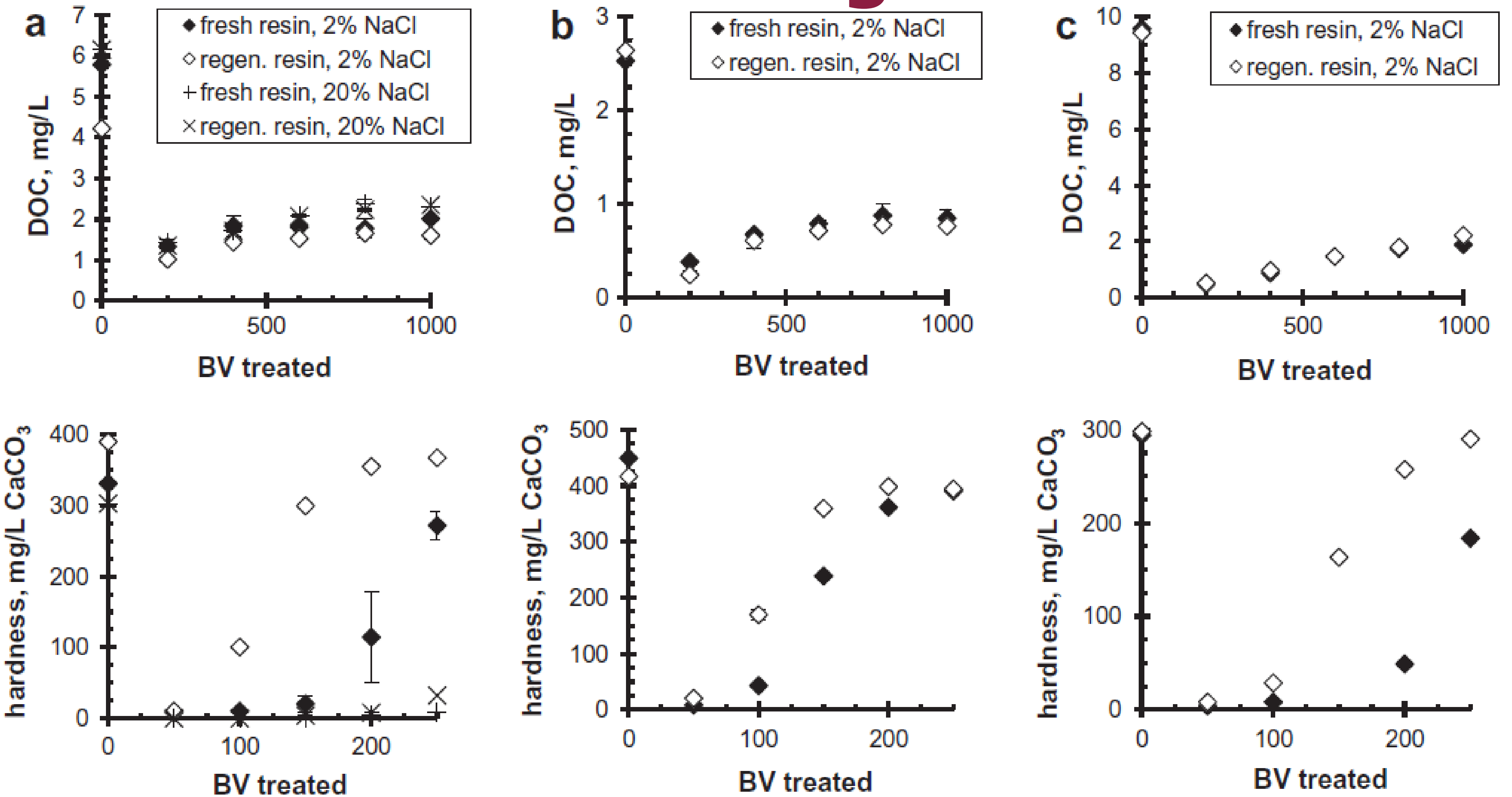
- Comstock, S.E.H., Boyer, T.H., 2014. Combined magnetic ion exchange and cation exchange for removal of DOC and hardness. *Chemical Engineering Journal*, 241, 366–375.

CIX treatment of groundwater

Experimental design

- Cedar Key, Yankeetown, Palm Springs groundwater
  - DOC: 3–10 mg/L
  - Hardness: 300–440 mg/L as $CaCO_3$
- Anion exchange resin: MIEX-Cl
- Cation exchange resin: Amberlite 200C-Na
- Multiple-loading jar tests
  - Bed volumes (BVs)
  - 1000 BVs MIEX-Cl
  - 250 BVs A200C-Na
- NaCl regeneration (2%, 20%)

CIX treatment of groundwater



- 67–85% DOC removal, 1000 BV anion exchange (composite)
- ~50% hardness removal, 250 BV cation exchange (composite)

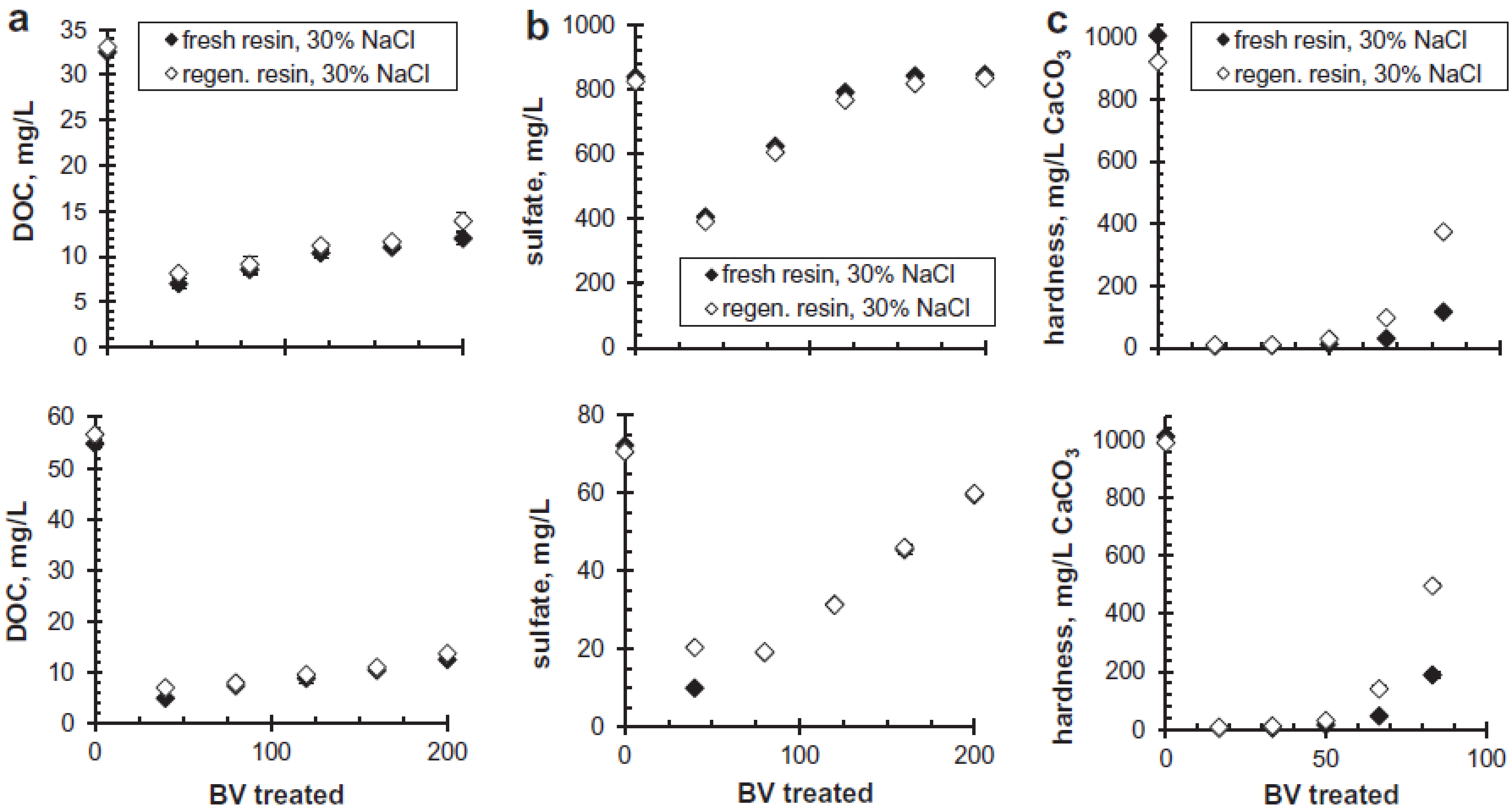
Comstock & Boyer, 2014. *Chem. Eng. J.*

CIX treatment of NF concentrate

Experimental design

- NF concentrate from 2 membrane plants in FL
  - DOC: 33, 56 mg/L
  - Hardness: 960, 1000 mg/L as $CaCO_3$
  - Sulfate: 830, 71 mg/L
- Anion exchange resin: MIEX-Cl
- Cation exchange resin: Amberlite 200C-Na
- Multiple-loading jar tests
  - 200 BVs MIEX-Cl
  - 83 BVs A200C-Na
- NaCl regeneration (30%)

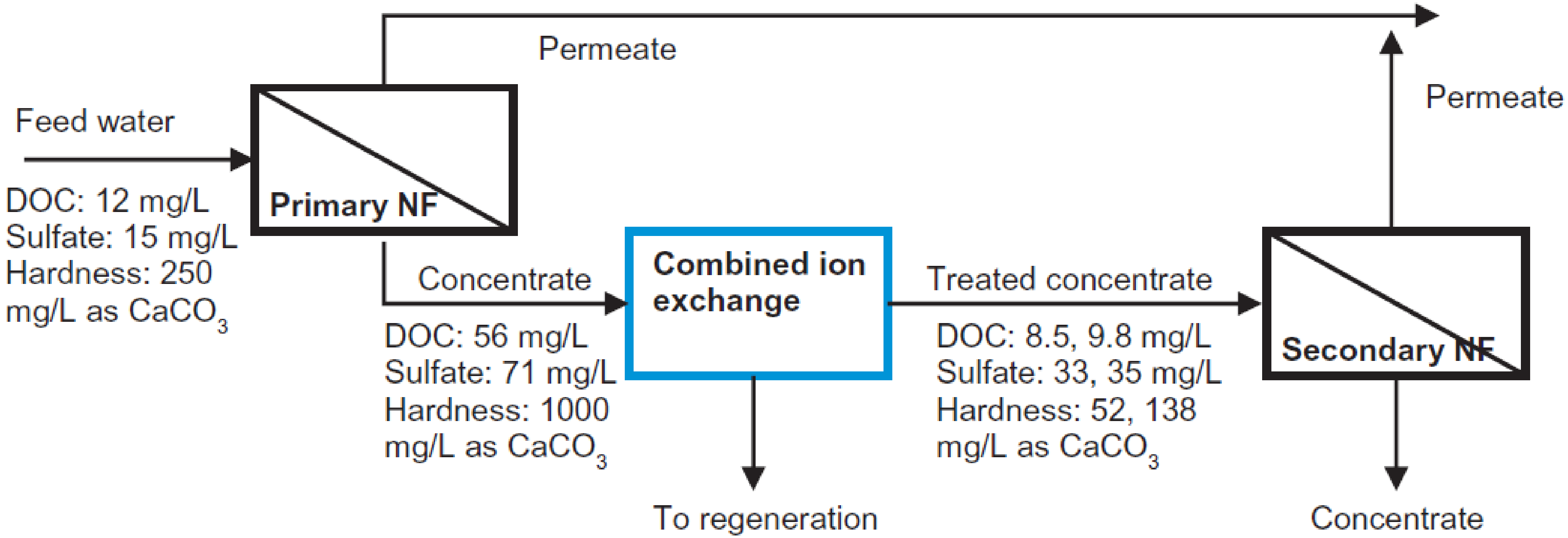
CIX treatment of NF concentrate



- 70–80% DOC removal, 50% sulfate removal, 90% hardness removal

Comstock & Boyer, 2014. *Chem. Eng. J.*

Primary NF – CIX – Secondary NF



- CIX produced similar water composition as NF feed water

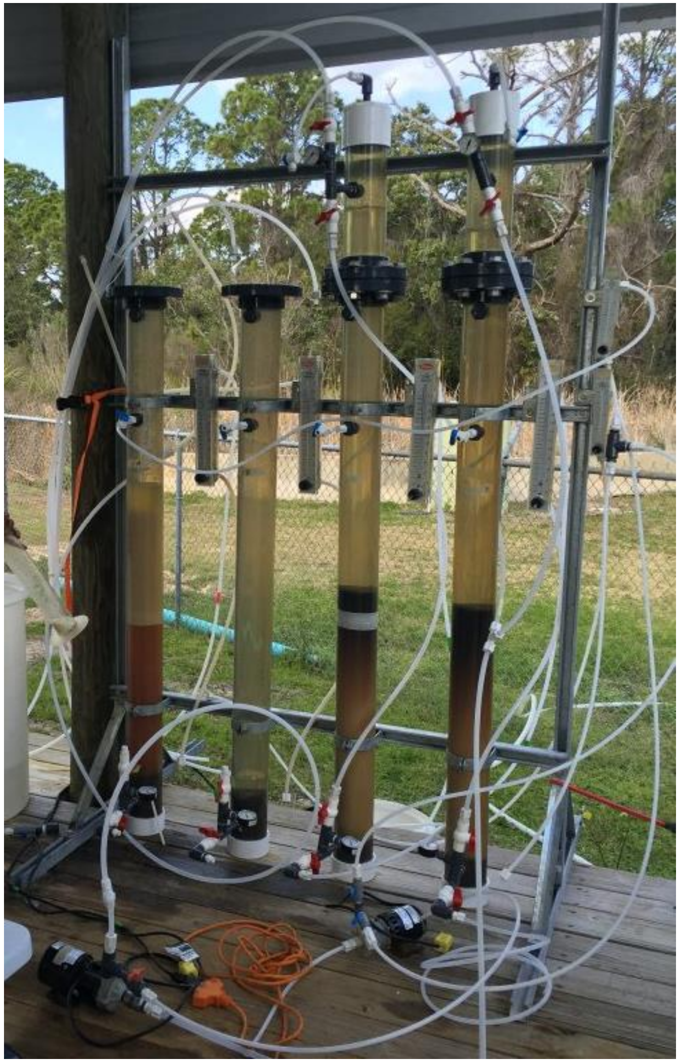
Comstock & Boyer, 2014. *Chem. Eng. J.*

CIX

Conclusions

- CIX treatment of groundwater achieved >70% DOC removal (MIEX-Cl resin) and >50% hardness removal (A200C-Na resin) in composite samples corresponding to 1000 BVs of anion exchange and 250 BVs of cation exchange depending on 2% or 20% NaCl regeneration solution
- CIX removed DOC, sulfate, and hardness from NF concentrate to produce treated concentrate with similar characteristics as NF feed water

Combined ion exchange (CIX) pilot plant



CIX pilot plant

Experimental design

- Cedar Key
    - DOC: ~5 mg/L
    - Hardness: ~300 mg/L as $CaCO_3$
- Anion exchange resin (AER): A-72 Thermax
- Cation exchange resin (CER): T-42 Thermax
- Pilot plant operation
    - Down flow columns
    - <u>Resin ratio: 4 L AER-to-4 L CER</u>
    - 0.5 gpm
- <u>Regeneration: NaCl vs KCl regeneration (12% m/v)</u>

CIX pilot plant, ongoing work

- Regeneration operation, e.g., precipitation
- Effectiveness of NaCl vs. KCl regeneration; disposal
- Lead–lag column operation
- Completely mixed CIX
- NaCl vs. $NaHCO_3$ regeneration (anion exchange only)
- Process modeling (w/ USF, WINSSS)
- Life cycle assessment (w/ USF, WINSSS)
- Decision support tool (w/ USF, WINSSS)

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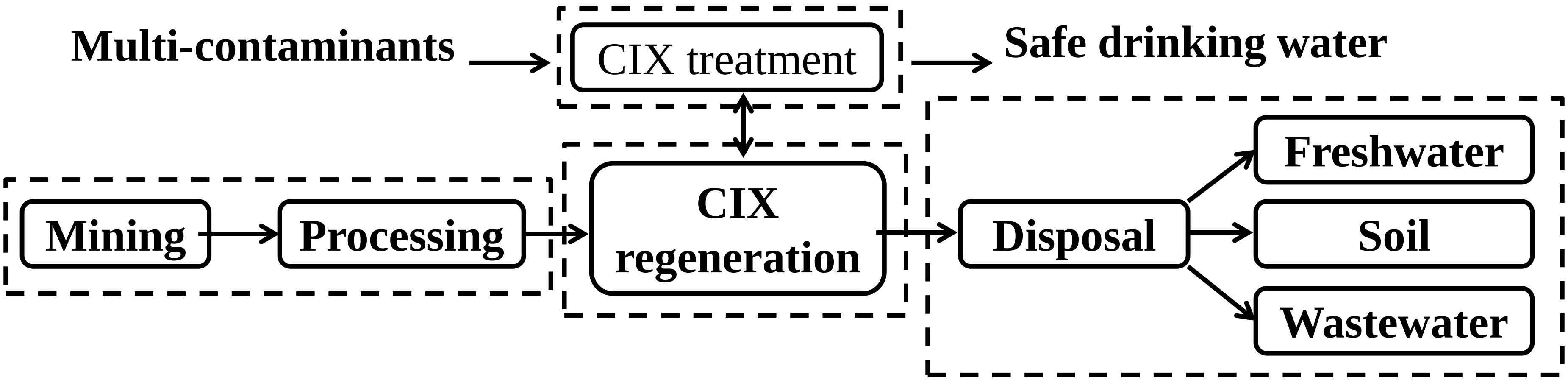

Thank you

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Other resource on Ion Exchange and CIX

- Hu, Y., Foster, J., Boyer, T.H., 2016. Selectivity of bicarbonate-form anion exchange for drinking water contaminants: Influence of resin properties. *Separation and Purification Technology*, 163, 128–139.
- Boyer, T.H., 2015. Removal of dissolved organic matter by magnetic ion exchange resin. *Current Pollution Reports*, 1(3), 142–154.
- Zhang, J., Amini, A., O'Neal, J.A., Boyer, T.H., Zhang, Q., 2015. Development and validation of a novel modeling framework integrating ion exchange and resin regeneration for water treatment. *Water Research*, 84, 255–265.
- Maul, G.A., Kim, Y., Amini, A., Zhang, Q., Boyer, T.H., 2014. Efficiency and life cycle environmental impacts of ion-exchange regeneration using sodium, potassium, chloride, and bicarbonate salts. *Chemical Engineering Journal*, 254, 198–209.