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Sustainable Catalytic Treatment of Waste Ion Exchange Brines for Reuse during Oxyanion Treatment in Drinking Water

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Collaborators:
Calgon Carbon Corporation and Johnson Matthey

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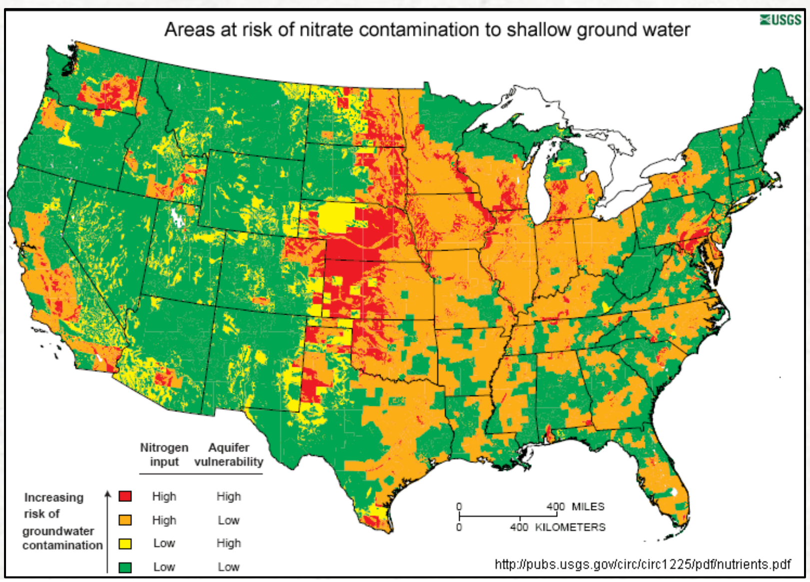
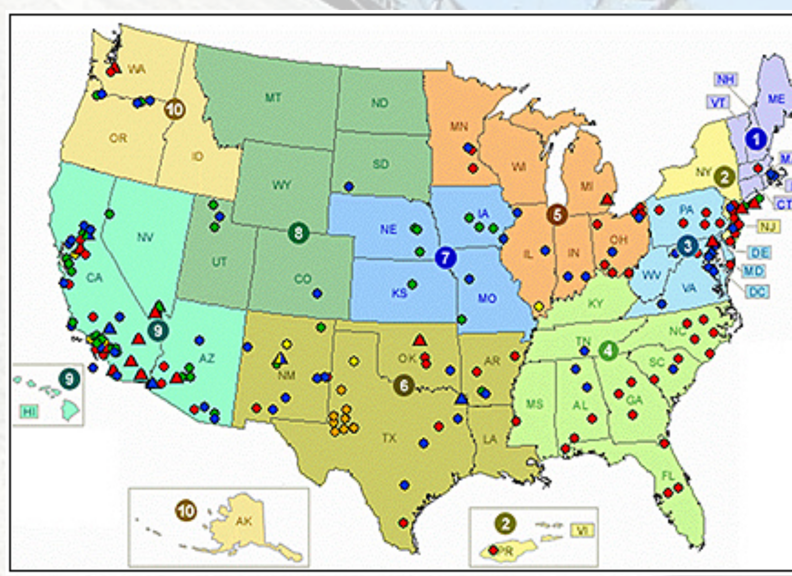
Motivation

- Oxyanion contaminants (e.g., NO_3^-, ClO_4^-) are a challenge for small water systems
- Ion exchange (IX) is the most common approach to treat NO_3^- and ClO_4^-
- Concentrated brines (high concentration of salt and oxyanions) are generated as wastes – high disposal cost and negative environmental impact.





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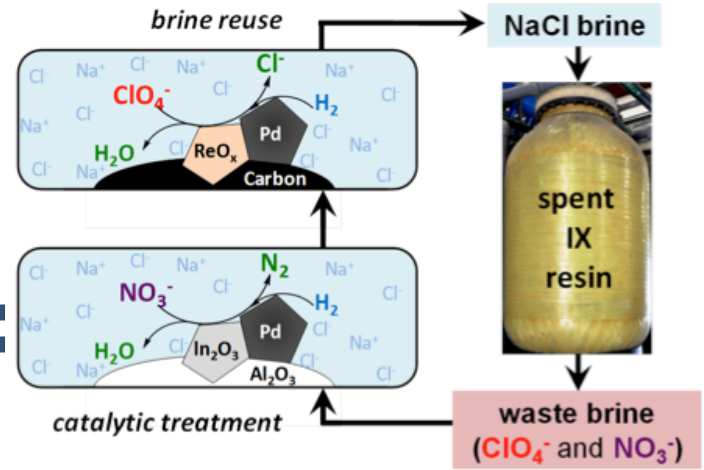
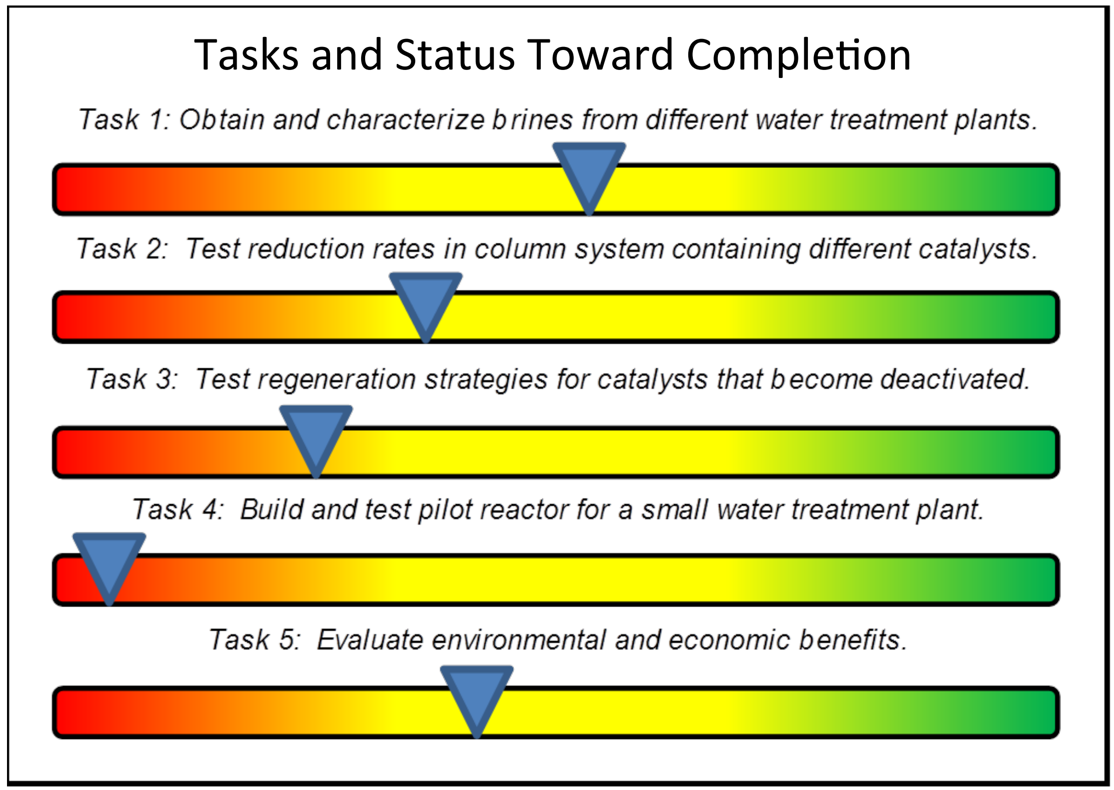
Project Overview



- Goal: Develop a novel catalytic treatment process for removing multiple oxyanion contaminants from waste IX brines to enable brine reuse at small water systems



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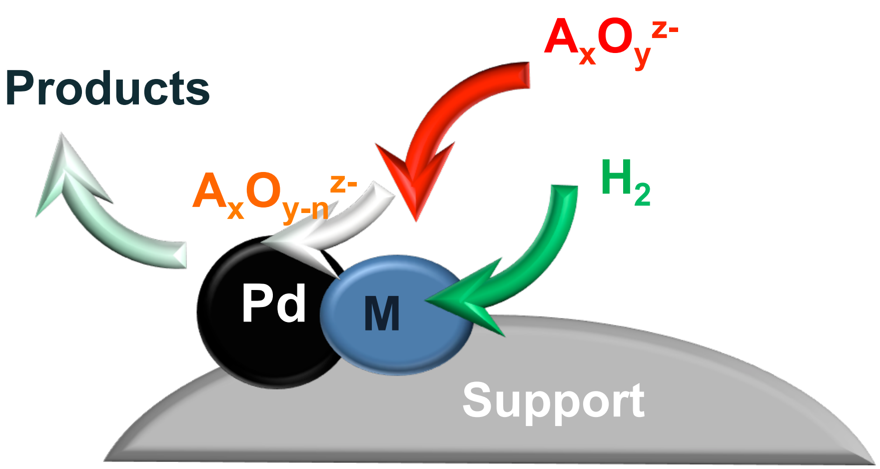
Overview of Catalytic Reduction

- Oxyanion ($A_xO_y^{z-}$) is reduced by H_2 over a Pd or Pd/Me supported catalyst.



Common Oxyanions Treated/Products	Catalyst
$NO_3^- \rightarrow N_2, NH_3, H_2O, OH^-$	Pd/In,Cu,Sn
$NO_2^- \rightarrow N_2, NH_3, H_2O, OH^-$	Pd
$BrO_3^- \rightarrow Br^-, H_2O$	Pd
$ClO_4^- \rightarrow Cl^-, H_2O$	Pd/Re

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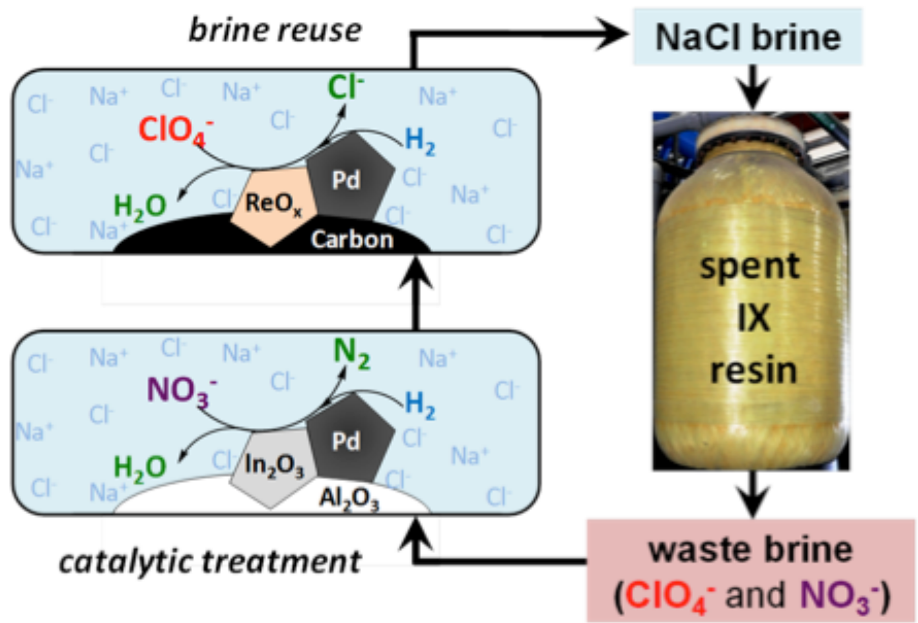
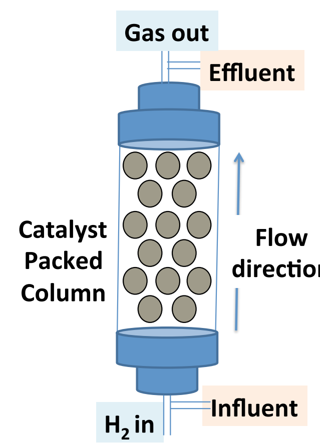
Hybrid IX-Catalytic Treatment

- Oyxanion reduction in brine is measured
  - in a batch reactor
  - In a two phase (brine + H_2/CO_2) flow-through column reactor





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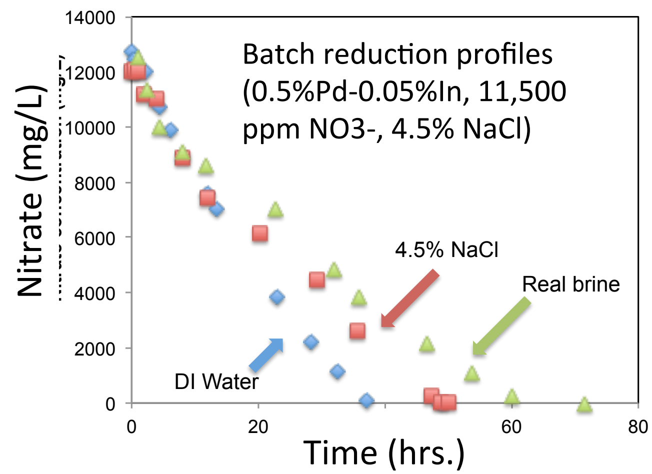
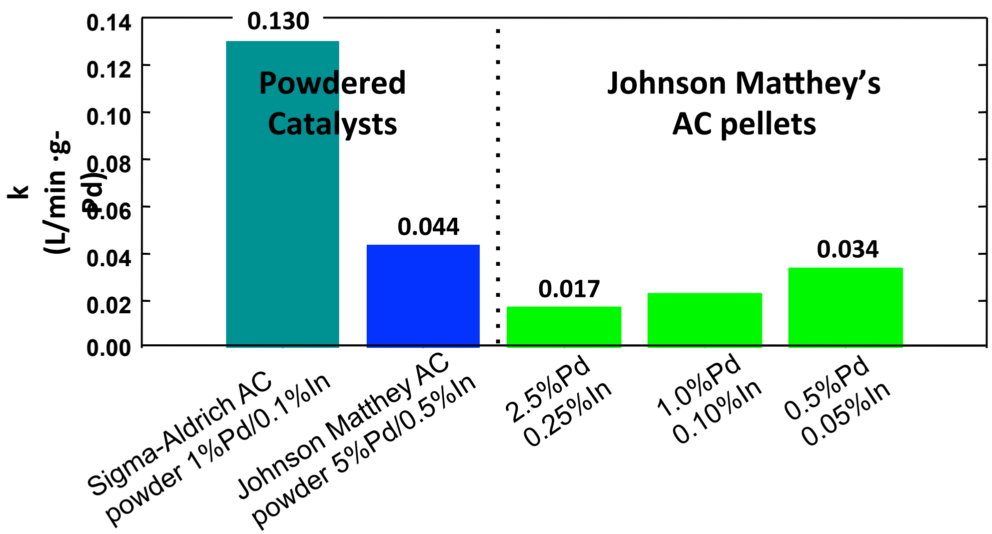
Nitrate Reduction: Effects of Brine and Catalyst Formulation

- Calgon Carbon helped obtain waste brine from small treatment plants
- Synthetic brines created to match (4.5-7 wt% NaCl, 5000-11,500 ppm NO_3^-)
- Initially used powdered activated carbon (AC) catalysts
- Johnson Matthey provided pelletized AC catalysts with variable Pd/In





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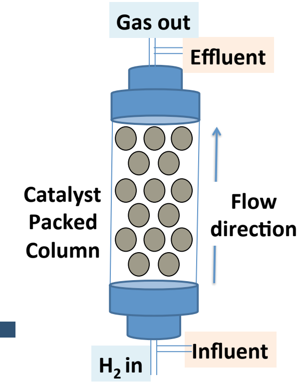
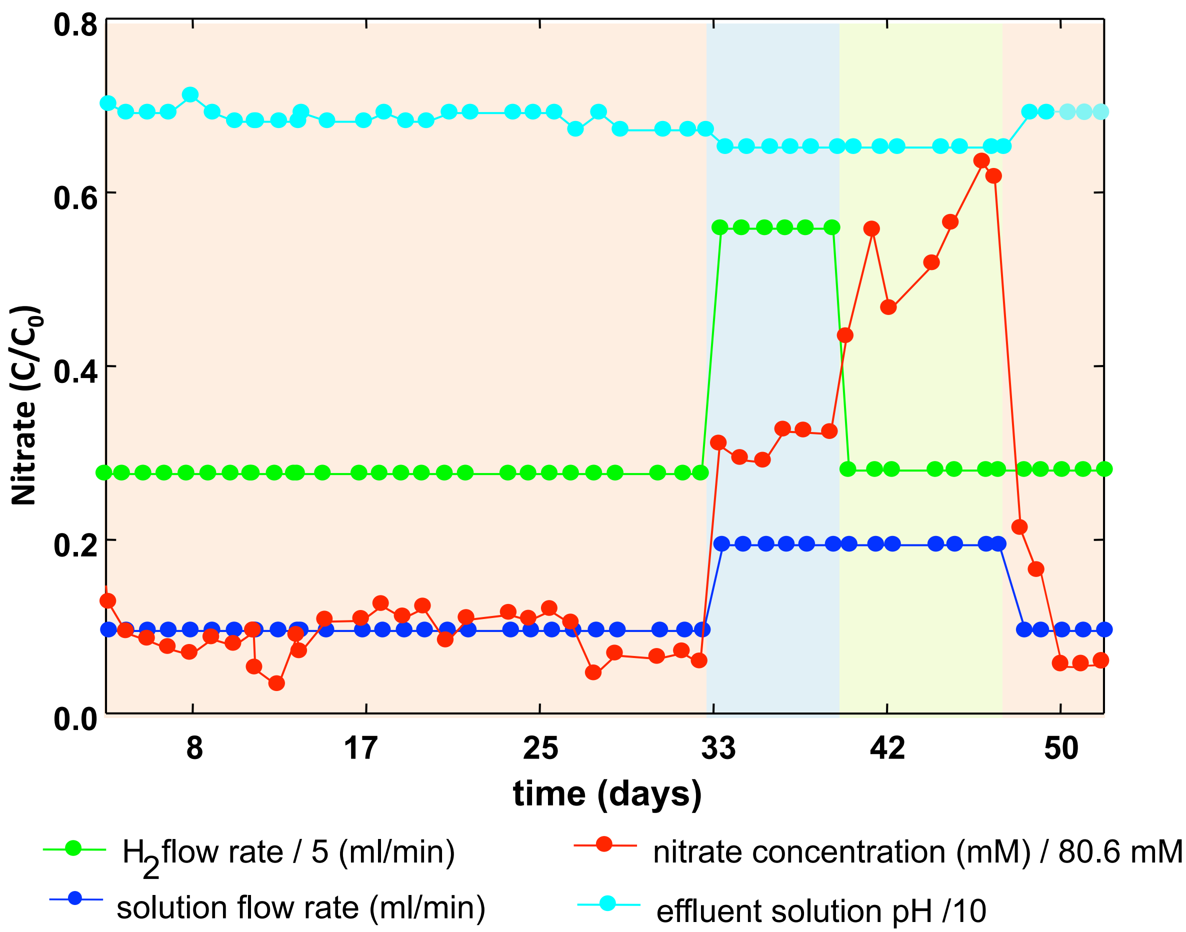
Nitrate Reduction Activity Sustained for >50 Days in Synthetic Brine





- Nitrate reduction rate constant with column 3X less than with batch

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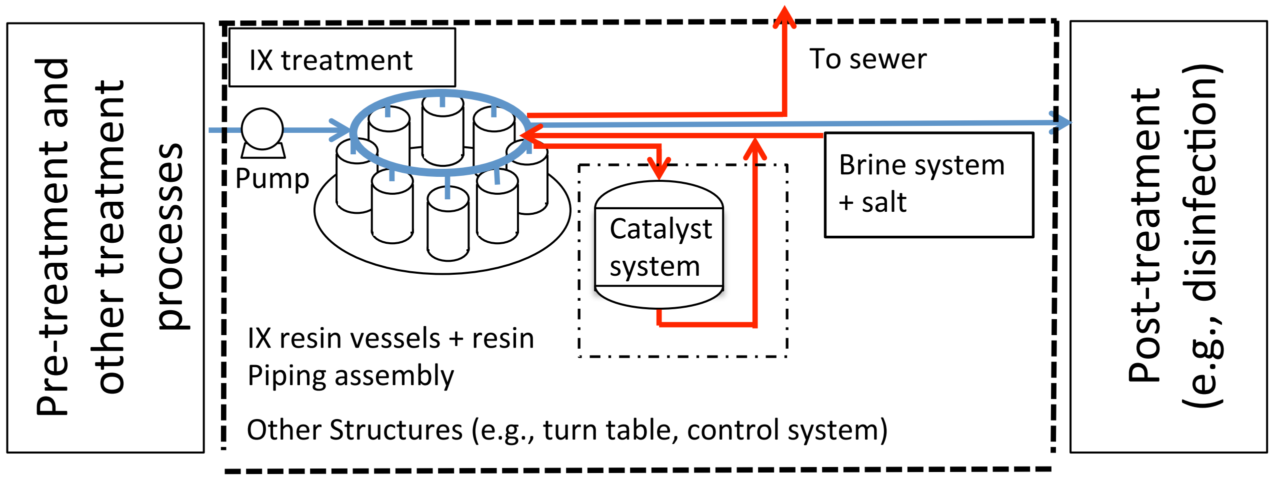
Life Cycle Assessment of Hybrid IX-Catalyst System for Nitrate

LCA boundaries drawn around oxyanion specific processes



Environmental Impact Characterization Procedure

List of all materials in the system	e.g., 7wt% NaCl Brine 5000 ppm NO_3^- 2.5wt%Pd-0.25wt%In/C
Inventory of resource & emissions to environment	Input: MJ energy Emission: kg CO_2 & CH_4 to air
Environmental Impacts in different categories	Global warming potential: kg CO_2 equivalent

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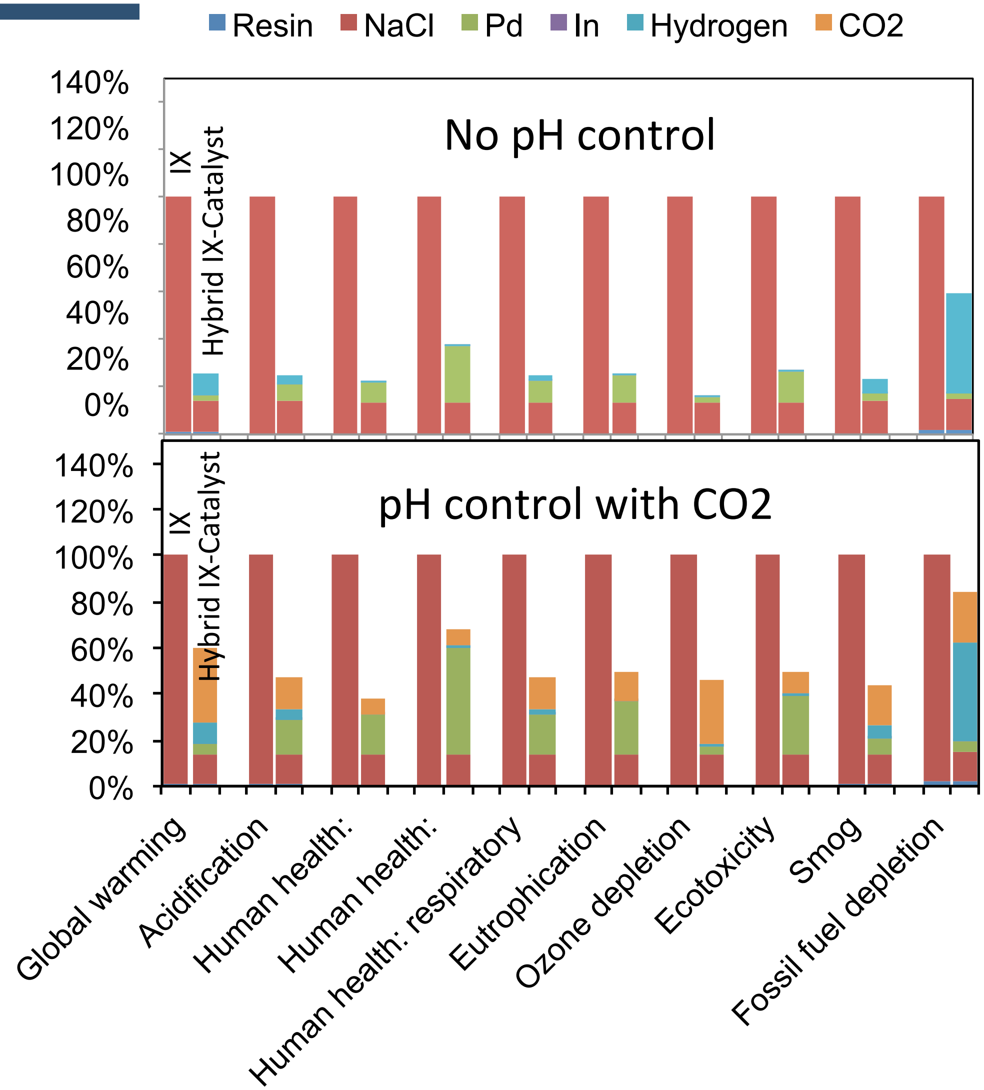
Life Cycle Impacts of IX versus the Hybrid IX-Catalyst System

- 6% salt make-up assumed for each treatment cycle, and complete brine replacement assumed after 15 treatment cycles
- CO_2 amendment during catalytic treatment has been used for pH control, but the need for this is not yet clear
- The hybrid IX-catalyst technology has a lower environmental impact in all categories



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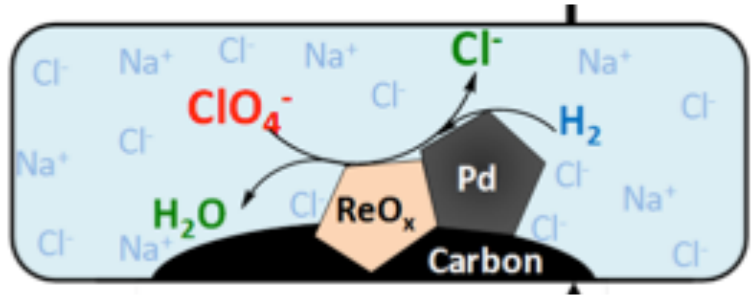
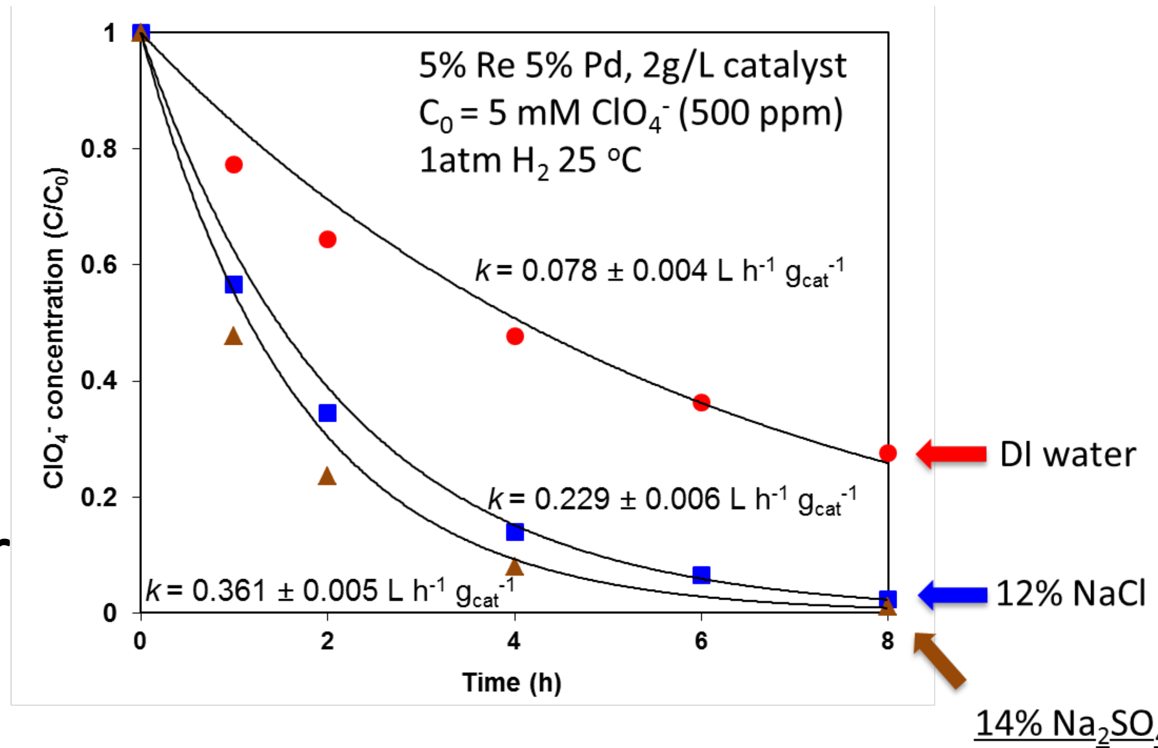
Perchlorate Reduction: Effect of Brine

- Pd/Re on activated carbon catalyst
- Perchlorate reduction in synthetic brine actually faster than in DI water





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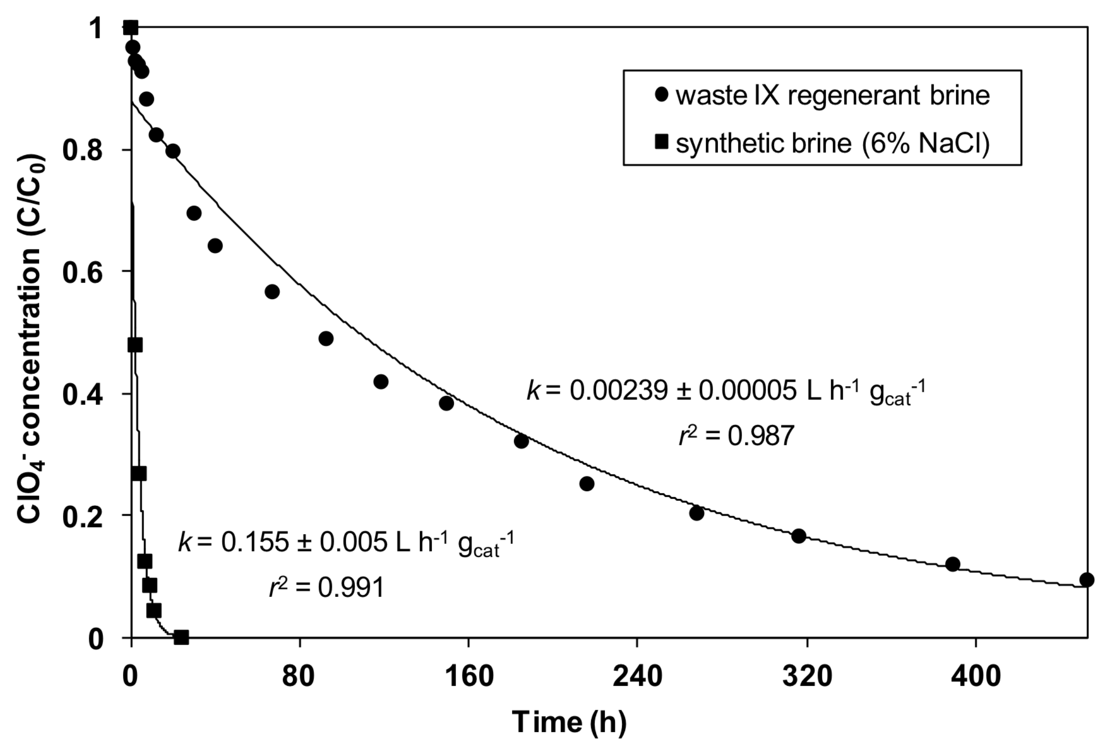
Perchlorate Reduction is Much Slower in a Real IX Waste Brine

Waste IX Brine Composition

Component	Concentration
Chloride	32.3 g/L as Cl^- (~5 wt% NaCl)
Perchlorate	2 mg/L as ClO_4^-
Nitrate	2.36 g/L as NO_3^-
Sulfate	4.70 g/L as SO_4^{2-}
Bicarbonate	7 g/L as $CaCO_3$
Phosphate	20.9 mg/L as PO_4^{3-}
Nitrite	ND[a]
Chlorate	ND[a]
Bromide	ND[a]
Sulfite	ND[a]
Sulfide	ND[a]
Calcium	40 mg/L
Magnesium	0.96 mg/L
Iron	0.4 mg/L
Manganese	ND[a]
pH	7.4

[a]Not detected.



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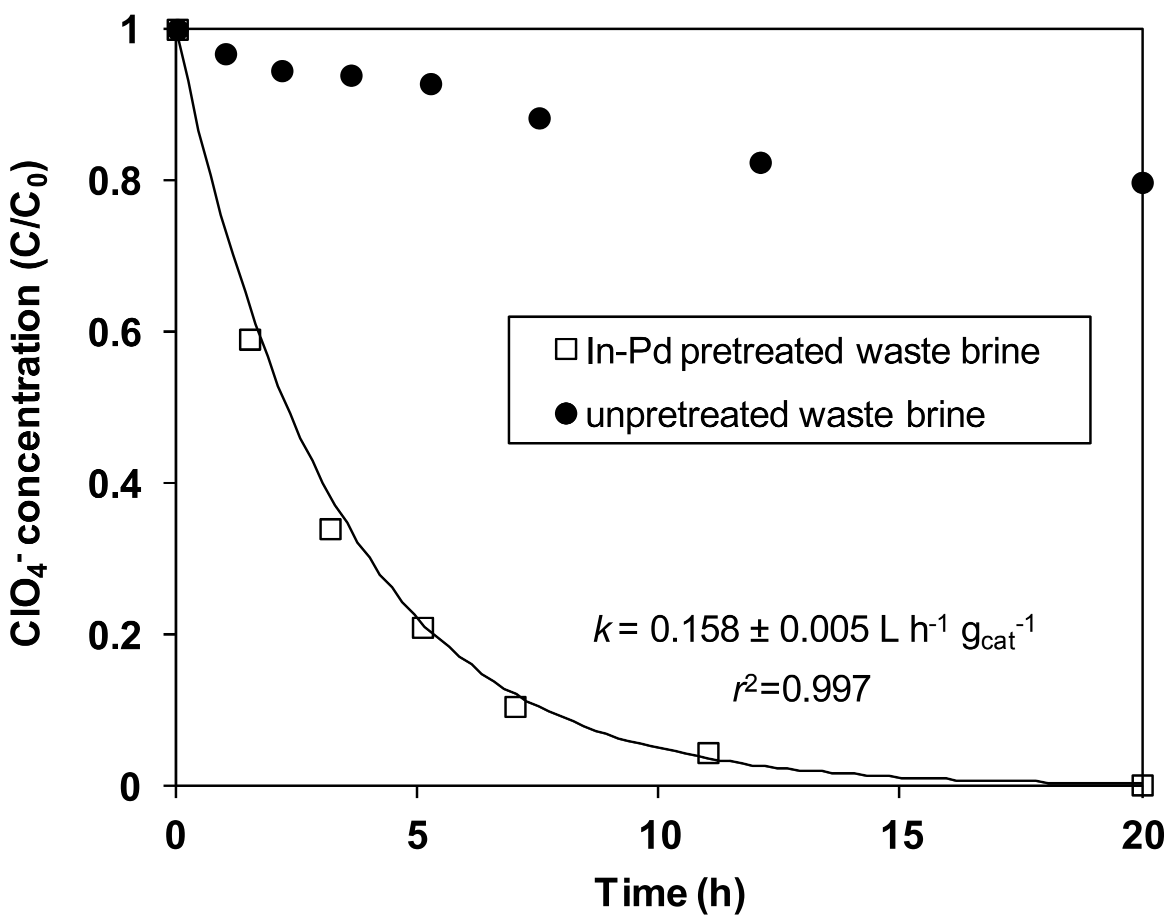
Pretreatment of Real IX Waste Brine to Remove NO_3^- Recovers ClO_4^- Activity



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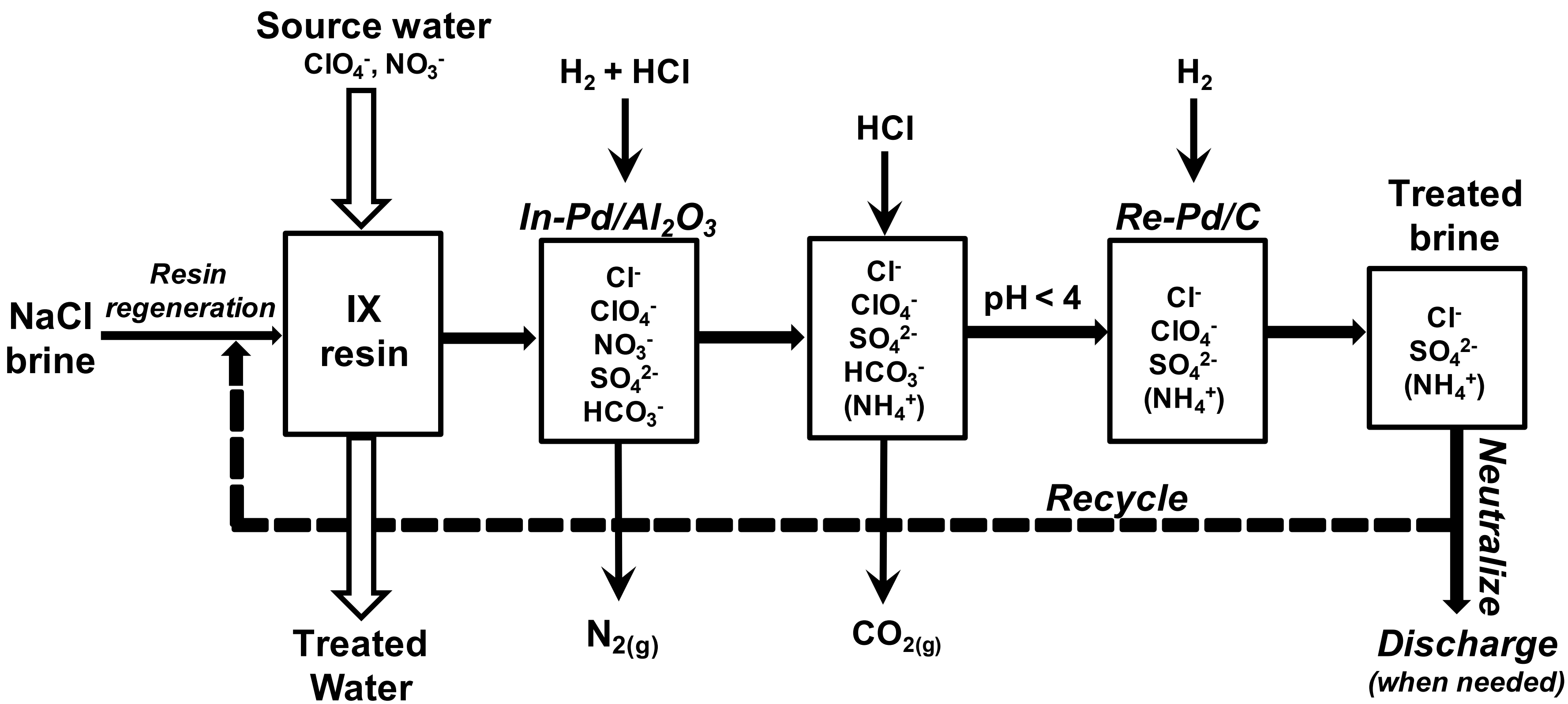
A Sequential Treatment Process for NO_3^- and ClO_4^- Is Required When Both Oxyanions are Present Above Regulatory Levels



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Conclusions and Future Work

- The hybrid-IX catalyst system can effectively treat NO_3^- in synthetic brine with lower life cycle impacts than IX alone
  - The effects of real waste brines on catalyst activity and longevity are being explored
- The hybrid-IX catalyst system can effectively treat ClO_4^- in synthetic and real brine
  - Catalyst longevity/life cycle impacts require further study

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Questions?

- Publications
  - 1) J. Liu, J. Choe, C. J. Werth, and T. J. Strathmann. Application of a Re-Pd Bimetallic Catalyst for Treatment of Perchlorate in Waste Ion-Exchange Regenerant Brine. *Water Res*. **2013**, *47*, 91-101.
  - 2) R. Zhang, D. Shuai, K. A. Guy, J. R. Shapley, T. J. Strathmann, C. J. Werth. Elucidation of Nitrate Reduction Mechanisms on a Pd-In Bimetallic Catalyst using Isotope Labeled Nitrogen Species. *ChemCatChem*. **2013**, *5*, 313-321.
  - 3) J. Choe, M. H. Mehnert, J. S. Guest, T. J. Strathmann and C. J. Werth. Comparative Assessment of the Environmental Sustainability of Existing and Emerging Perchlorate Treatment Technologies for Drinking Water. *Environ. Sci. Technol*. **2013**, *47*, 4644-4652.

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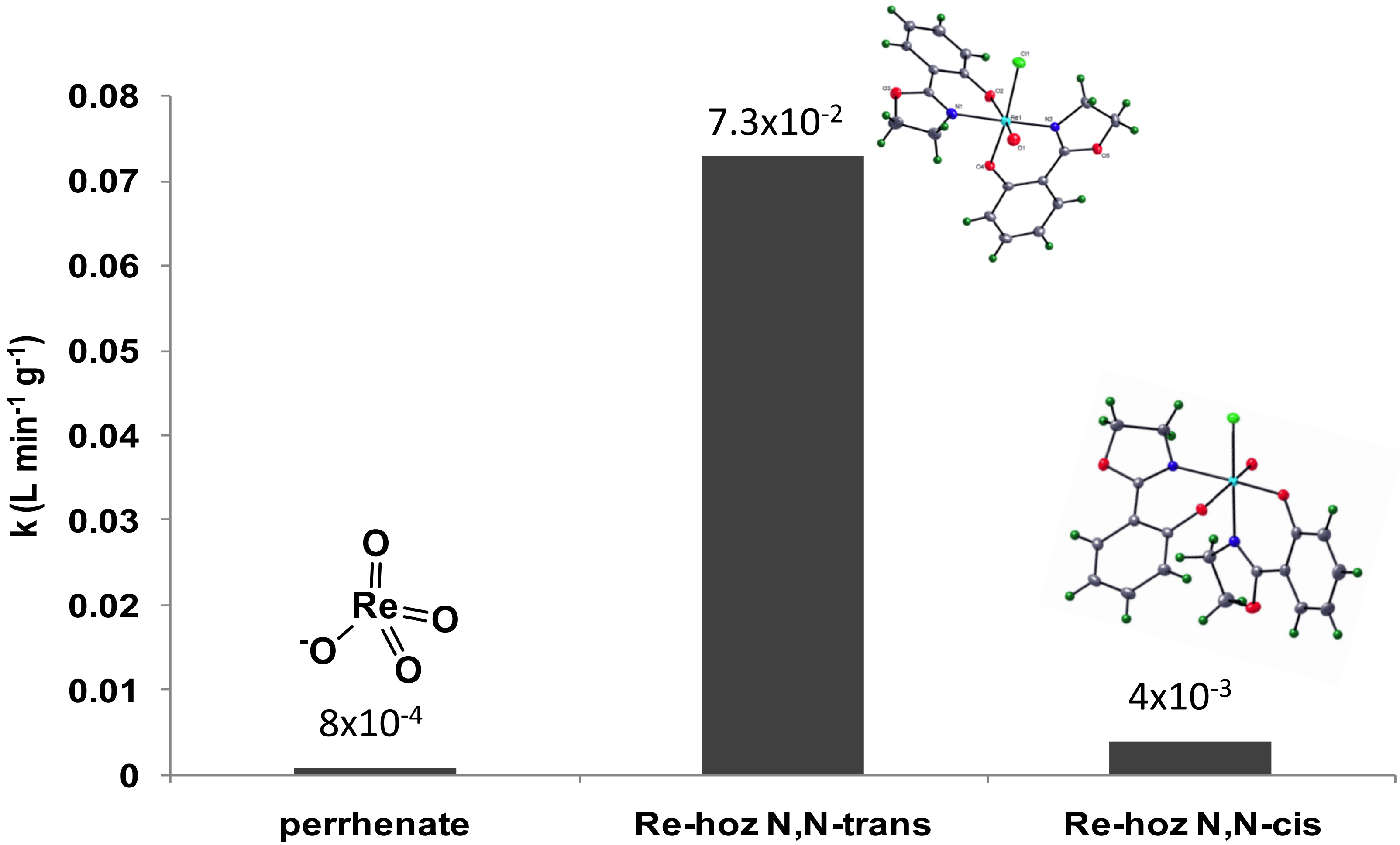
We Also Explored Direct Treatment of ClO_4^- in Drinking Water (i.e., no IX)



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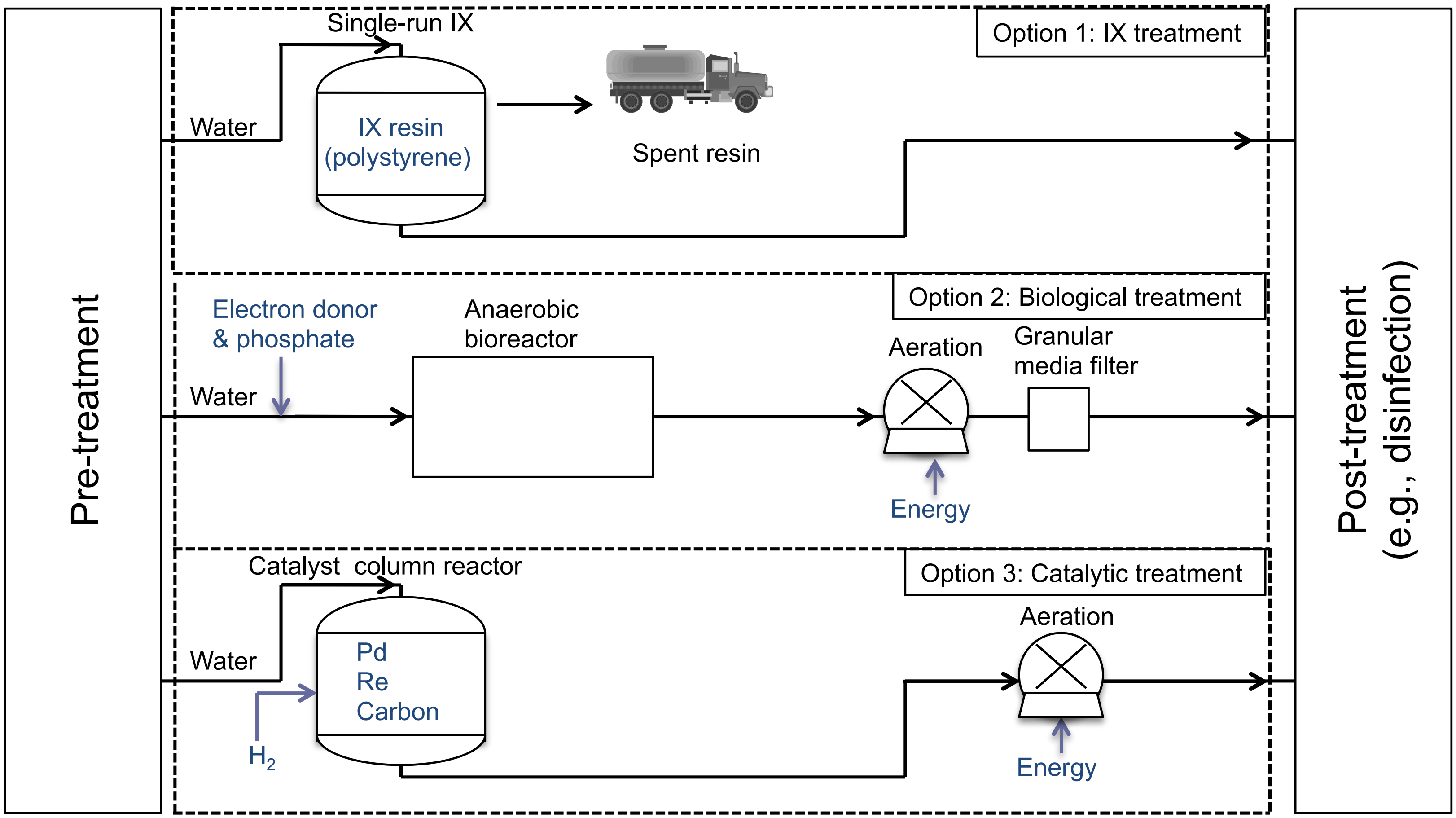
A Life Cycle Assessment Was Performed to Compare Direct Catalytic Treatment to Competing Technologies



IX: Tripp & Clifford J. AWWA (2006) 98, 105-114.
Catalytic: Choe et al. ES&T (2010) 44, 4716-4721.
Bio: Neremberg et al. Water Res. (2008) 42, 1151-1159.
Brown et al. J. AWWA. (2005) 9, 70-81.

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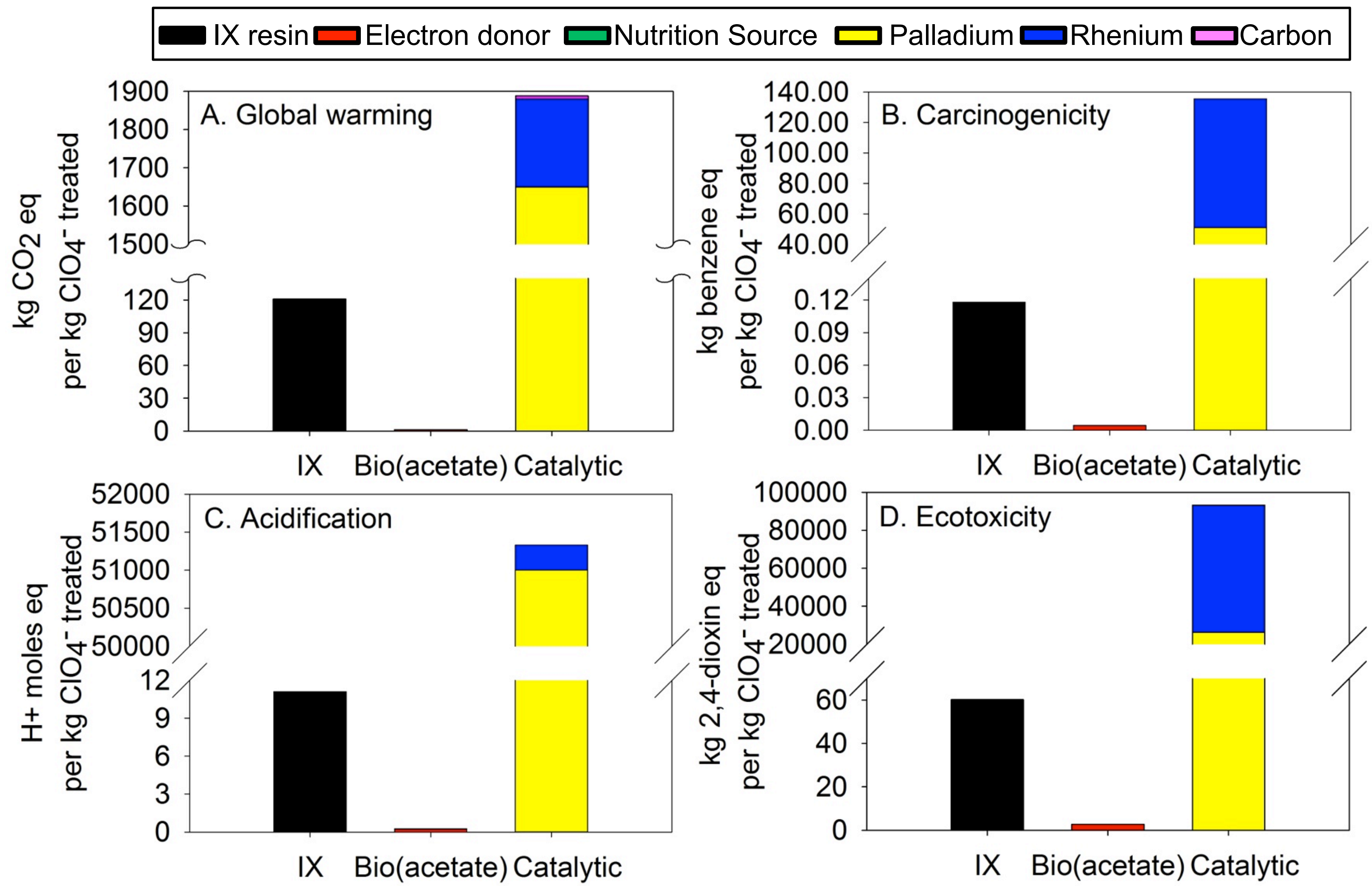
In Water Containing only ClO_4^-, Biological Treatment is Superior to IX and Catalytic Treatment



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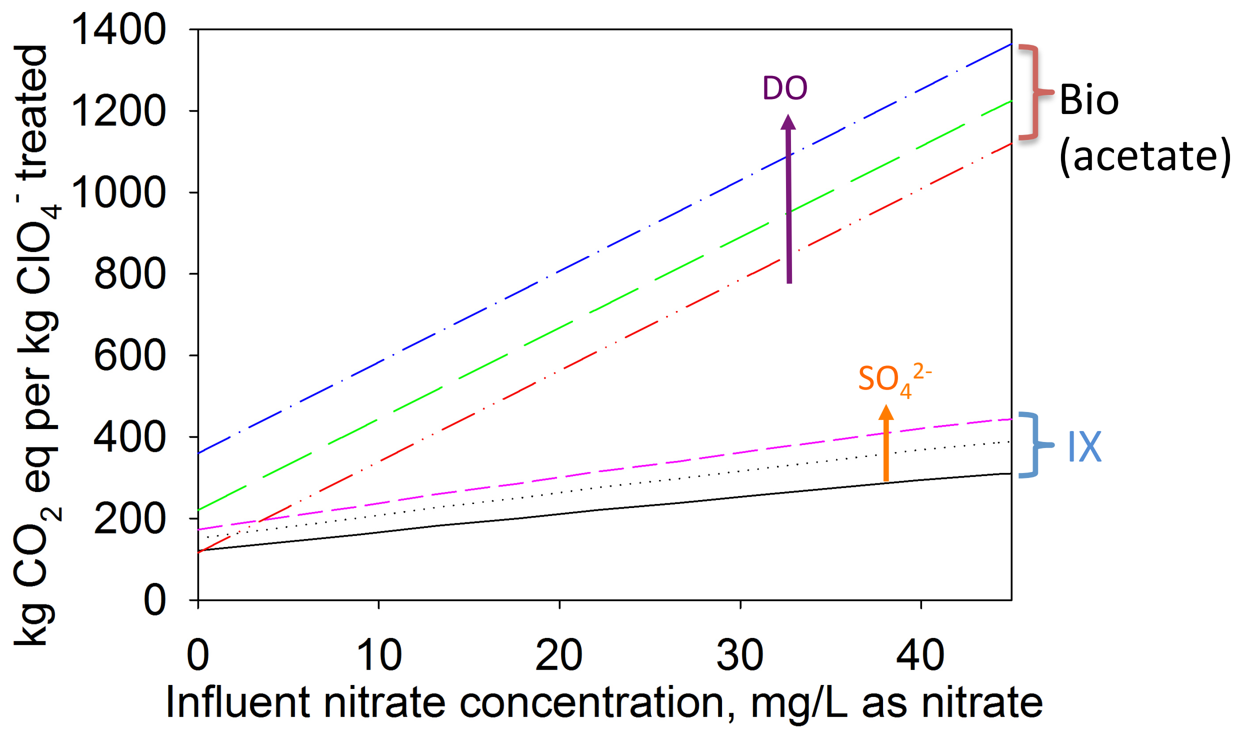
Biological Treatment is Very Sensitive to the Presence of Other Water Constituents

Consumable inputs required to treat 1 kg of ClO_4^- from influent with 50 ppb ClO_4^- (to below 6 ppb)

Impact on global warming



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New Methods For Preparing the Pd-Re Catalyst Are Yielding Major Improvements in Activity