Ion exchange for concentration of phosphorus in wastewater and recovery as struvite

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About Me

- 1st year M.S. at Marquette University in Environmental Engineering
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- Captain Marquette Club Ultimate Team
- Avid Musician

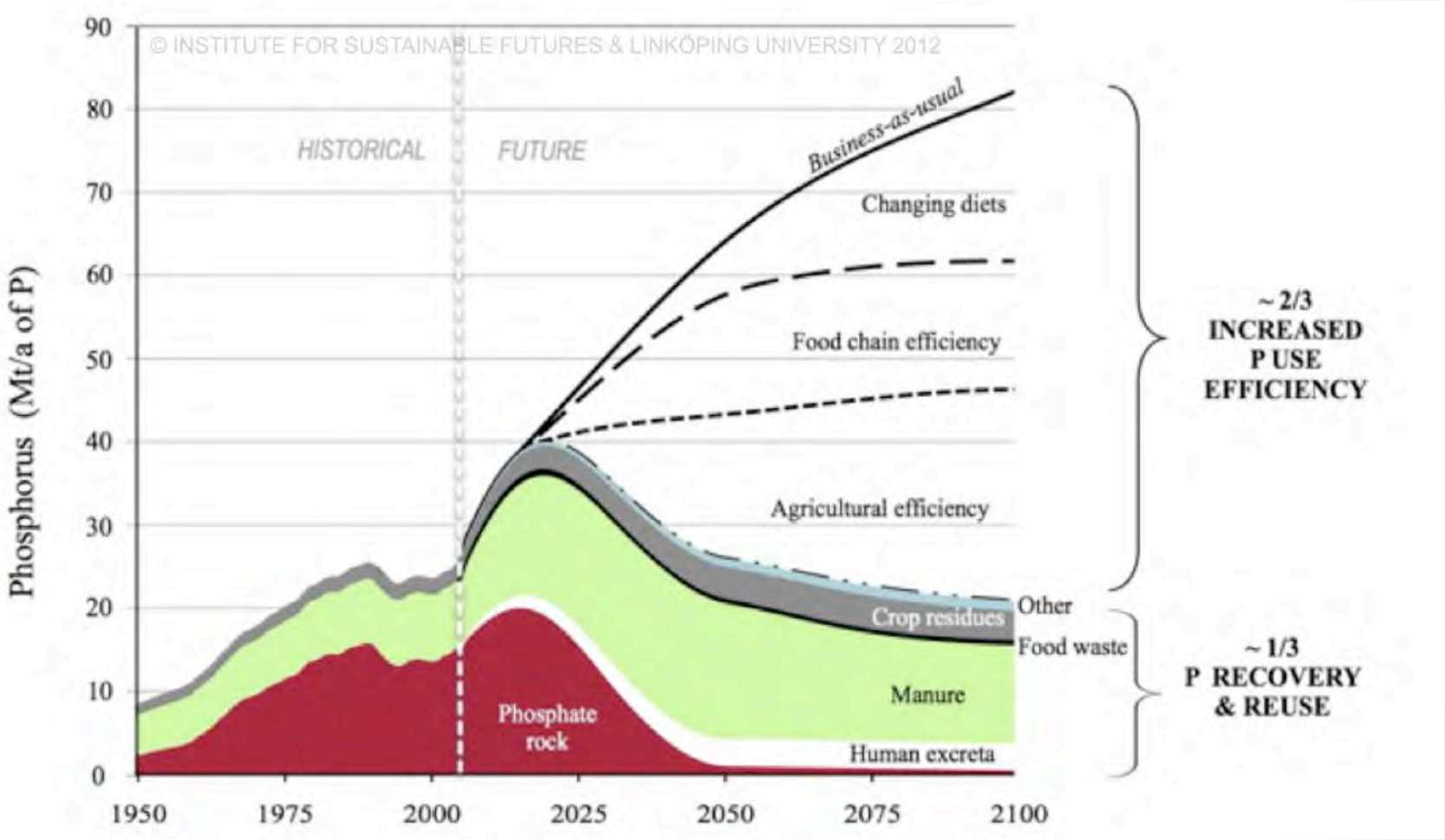
Phosphorus: Nutrient Background

- Essential nutrient for living organisms
  - DNA
  - Cell membranes

- Agricultural use
  - Limiting nutrient for plant growth
  - Fertilizer from mined phosphate rock reserves
    - Finite supply
    - 69-100 years before depletion (Cordell & White, 2011)

- Presence in natural waters
  - High loading rates of phosphorus can cause overgrowth of algae (eutrophication)

Phosphorus Sources



(Cordell, Rosemarin, Schröder, & Smith, 2011)

Wastewater as Phosphorus Source

- Wastewater treatment plants (WWTP) are required to meet low phosphorus levels in effluent
  - Strong wastewaters can have up to 20 mg/L of Total P in influent (Davis & Cornwell, 2008)
- Land application of dried activated sludges from WWTP is a common agricultural practice
  - Land applied biosolids do not always have high N-P-K concentrations
  - Can contain organic micropollutants and heavy metals

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Ion Exchange

- Physical/chemical removal process that can concentrate targeted phosphate anions onto exchange media
- Transfer of ions from solid surface (media) for similarly charged ions in solution (wastewater)
  - Reversible process
- Synthetic and natural ion exchange medias available

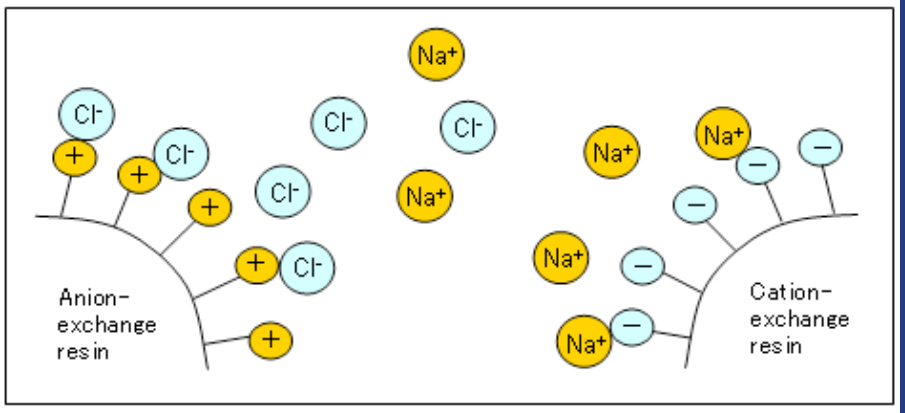

Figure 1. Pattern diagram illustrating ion exchange mode

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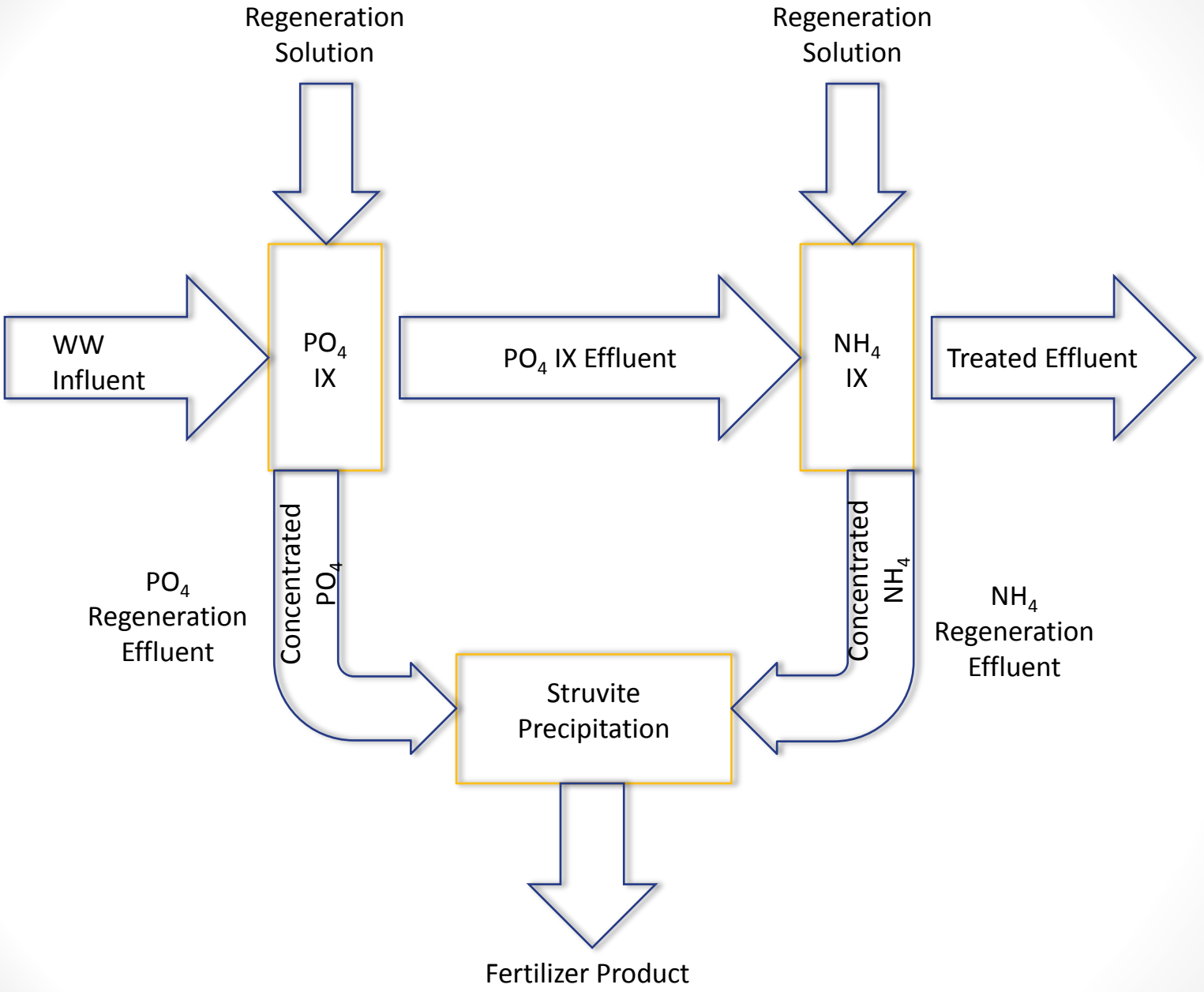
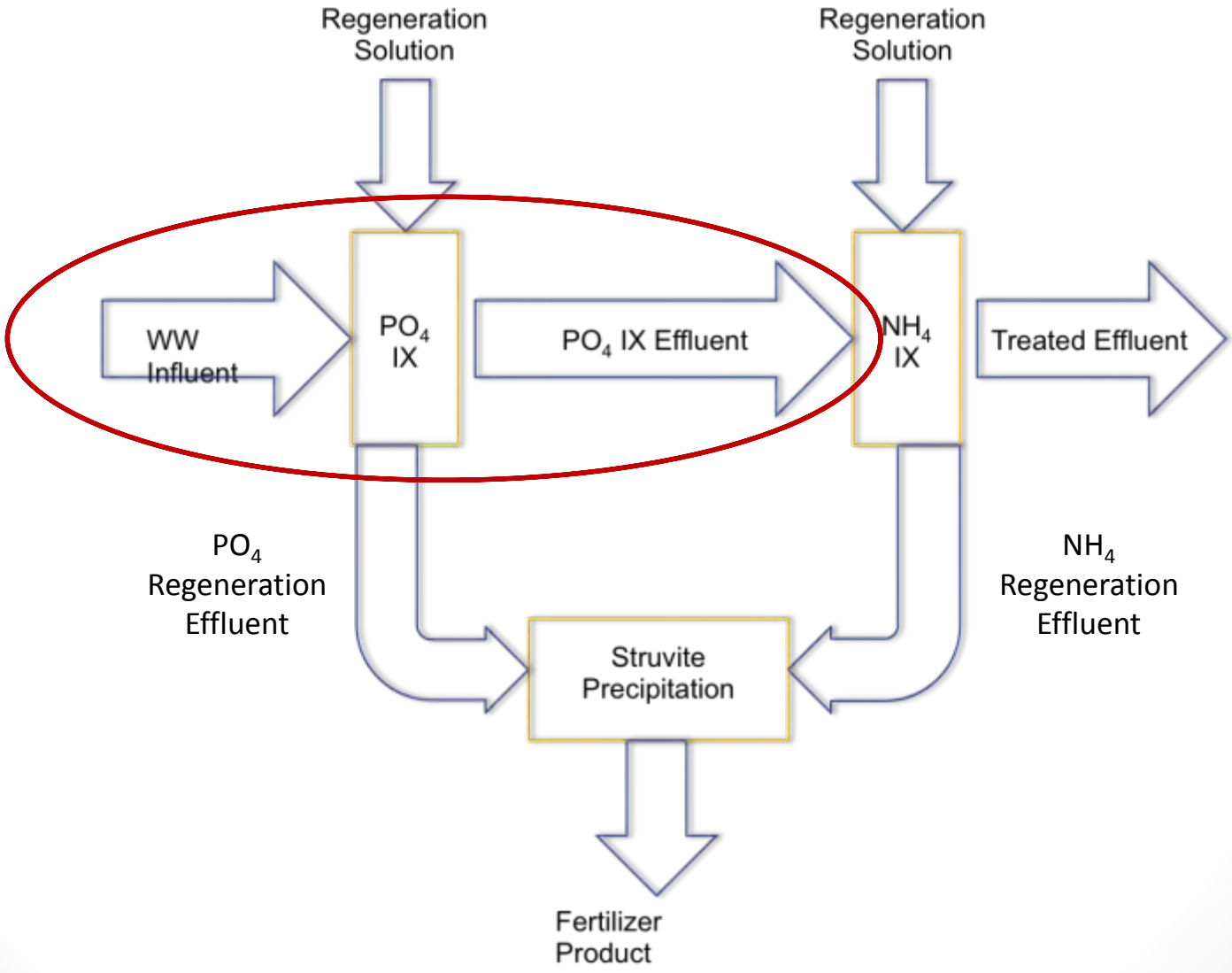

Regeneration Solution
Regeneration Solution
WW Influent
PO4 IX
PO4 IX Effluent
NH4 IX
Treated Effluent
Concentrated PO4
Concentrated NH4
PO4 Regeneration Effluent
NH4 Regeneration Effluent
Struvite Precipitation
Fertilizer Product

Nutrient Removal/Recovery Questions

1. How can we selectively capture influent phosphorus from wastewater?

Q1: How can we selectively capture influent phosphorus from wastewater?

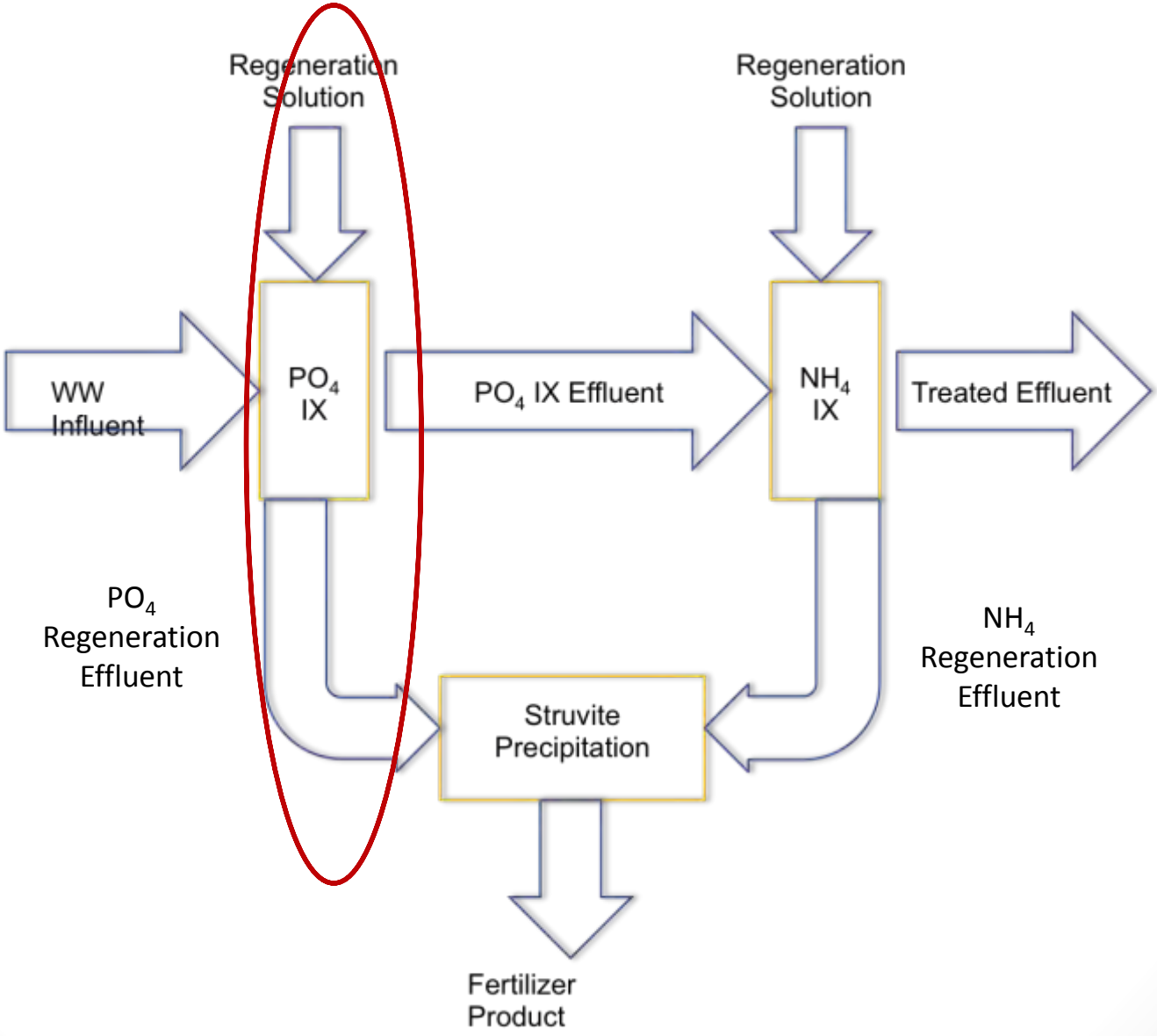


Nutrient Removal/Recovery Questions

1. How can we selectively capture influent phosphorus from wastewater?

2. How do we recover the captured phosphate?

Q2: How do we recover the captured phosphate?



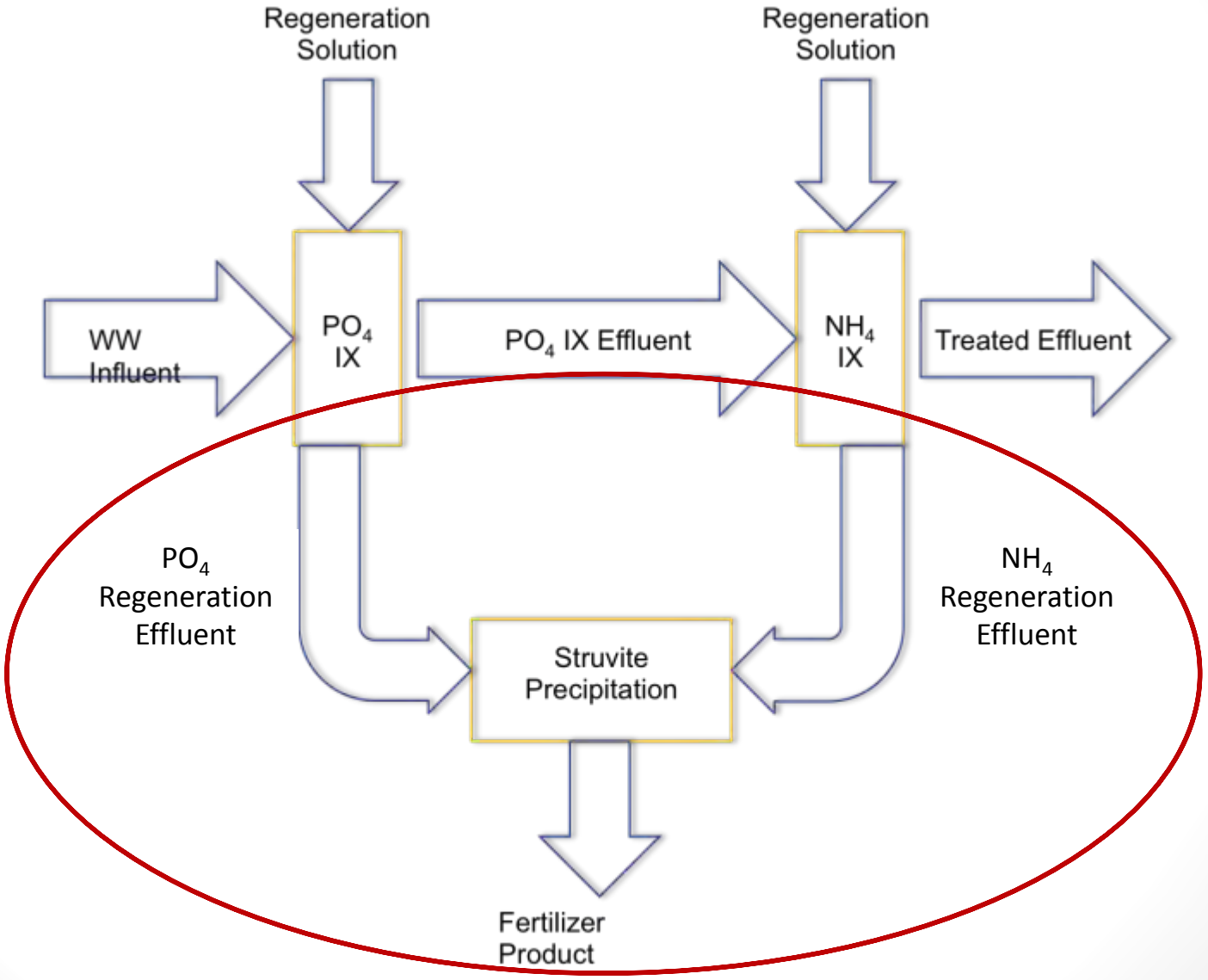
Nutrient Removal/Recovery Questions

1. How can we selectively capture influent phosphorus from wastewater?

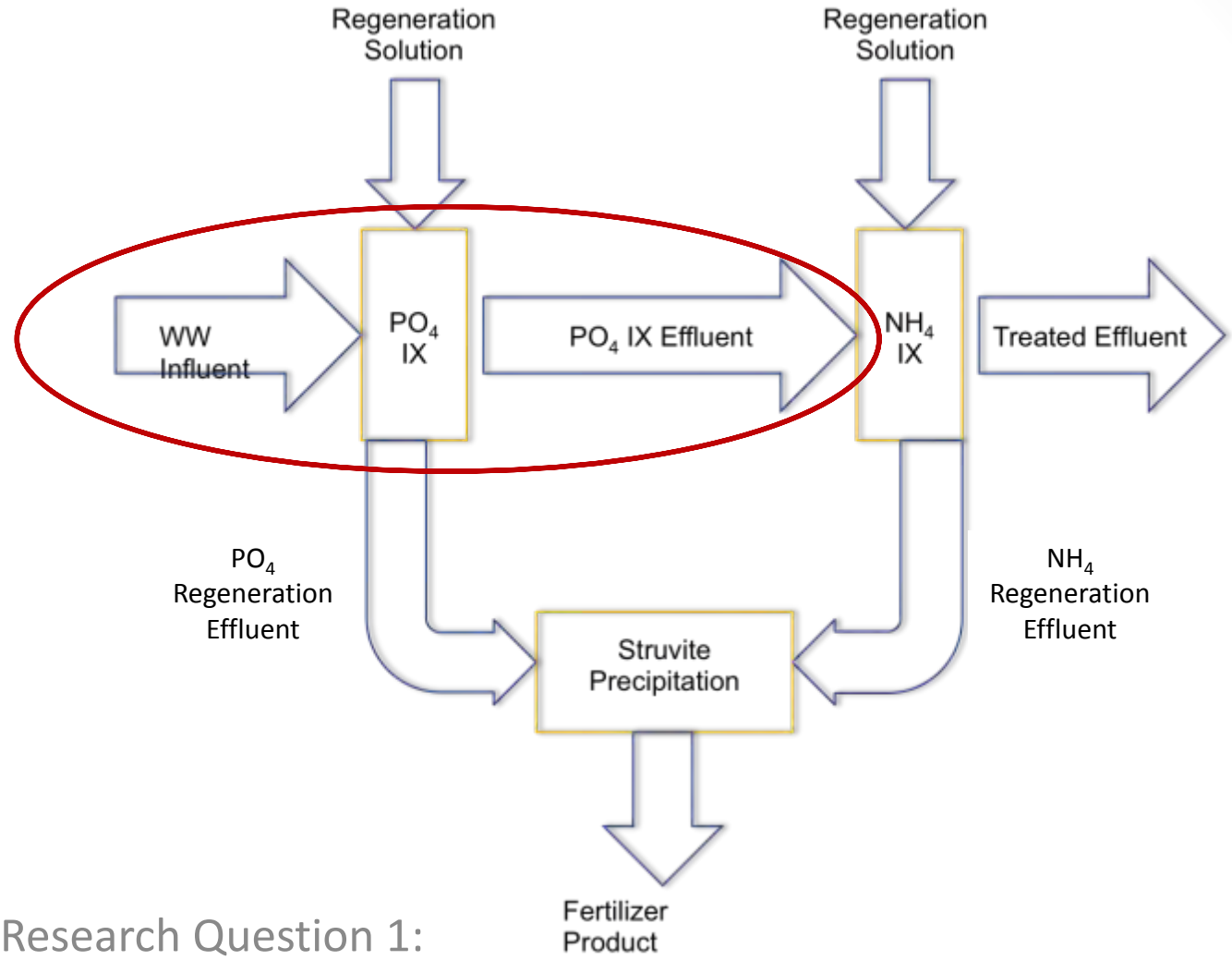
2. How do we recover the captured phosphate?

3. How can we use the nutrient-rich regeneration solution in an agricultural setting?

Q3: How can we use the nutrient-rich regeneration solution in an agricultural setting?



Research Objectives

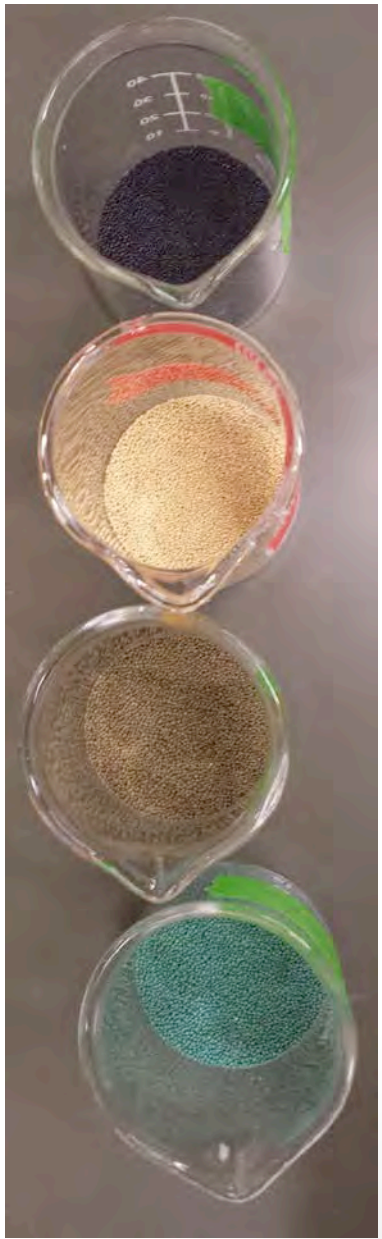


Research Question 1:

WHAT IS THE REMOVAL EFFICIENCY OF DOW-HFO-CU?

Choosing an ion exchange media

- Metal oxides
  - Iron oxides
  - Often lack mechanical strength needed for prolonged use
- Polymeric materials
  - Have mechanical strength but lack phosphate selectivity
- Polymeric ligand exchangers (PLEs)
  - Combination of metal oxide phosphate selectivity with mechanical strength of polymeric media



Choosing an ion exchange media

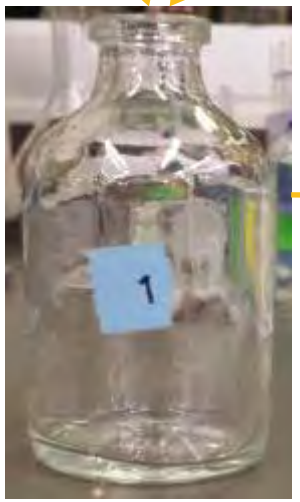
- The use of hydrated ferric oxide (HFO) in conjunction with copper (Cu^{+2}) increase media selectivity towards phosphate ions
- At neutral pH, $H_2PO_4^-$ and HPO_4^{2-} are the most common phosphate species
- Polymeric material has potential for prolonged use (multiple IX cycles)
- How do we test its performance?

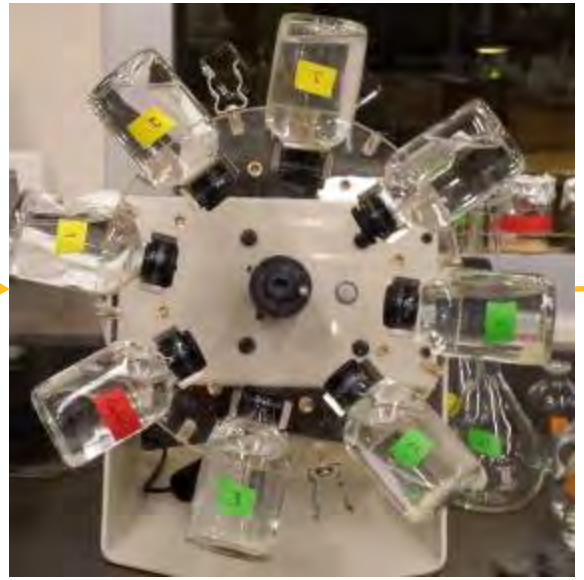
Removal Batch Testing for Dow-HFO-Cu

10 g media per L of solution

50 mL phosphate solution

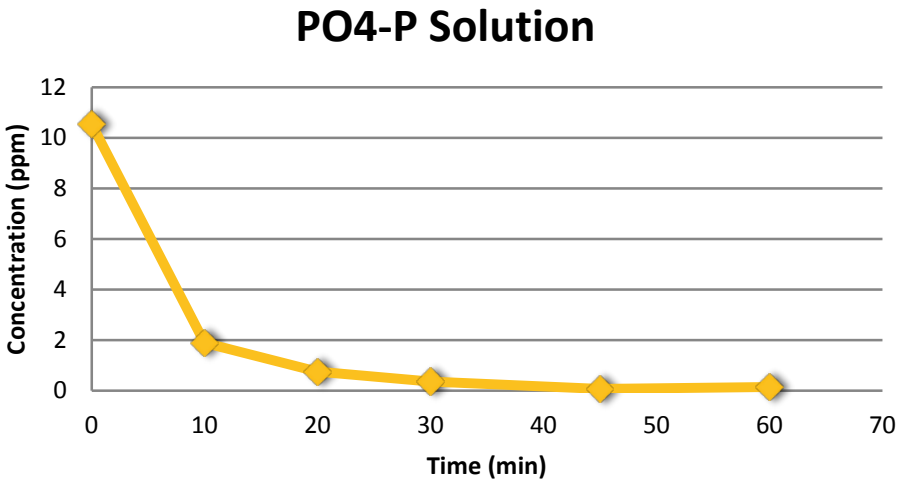
60 mL serum vial





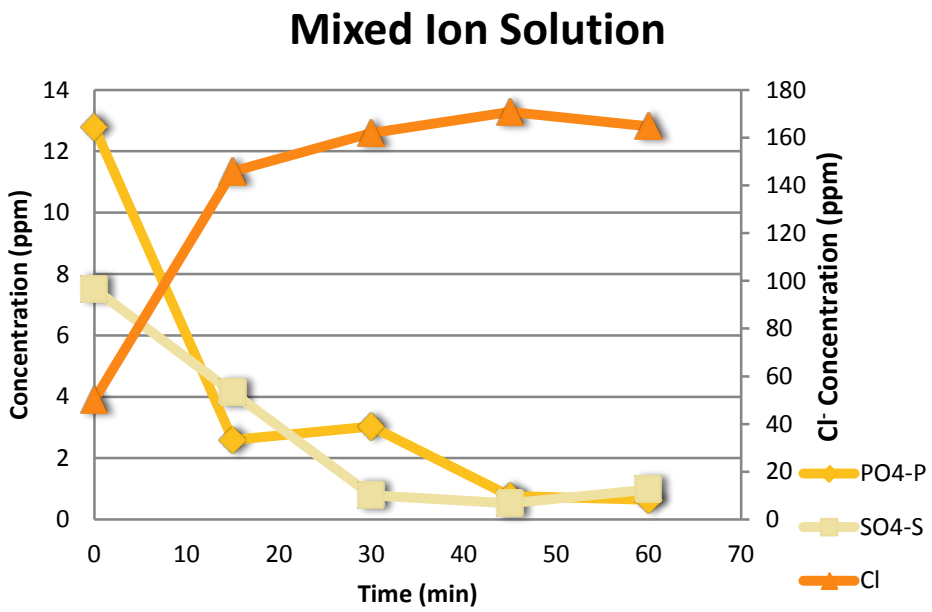
Decant and Analyze effluent

Batch Testing of Dow-HFO-Cu



- Phosphate-only solution containing 10 mg/L PO_4-P (~30 mg/L PO_4)
- Complete removal is achieved within 45 minutes

Batch Testing of Dow-HFO-Cu

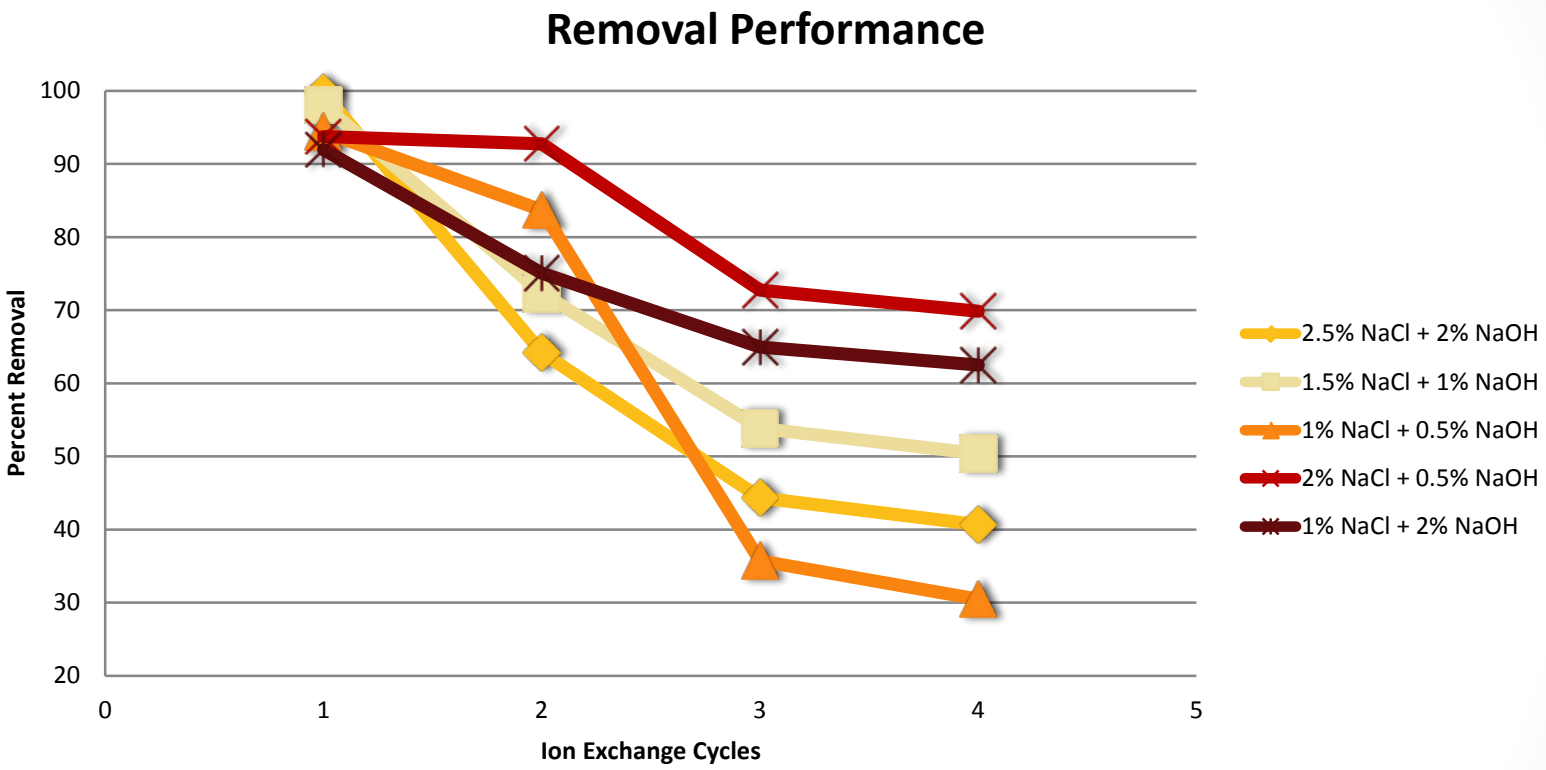


- Mixed ion solution mimics that of secondary wastewater effluent
- Near complete removal of PO_4-P and SO_4-S in 1 hour (<1 ppm)
- High release of Cl^- into solution

Extended Performance of Dow-HFO-Cu

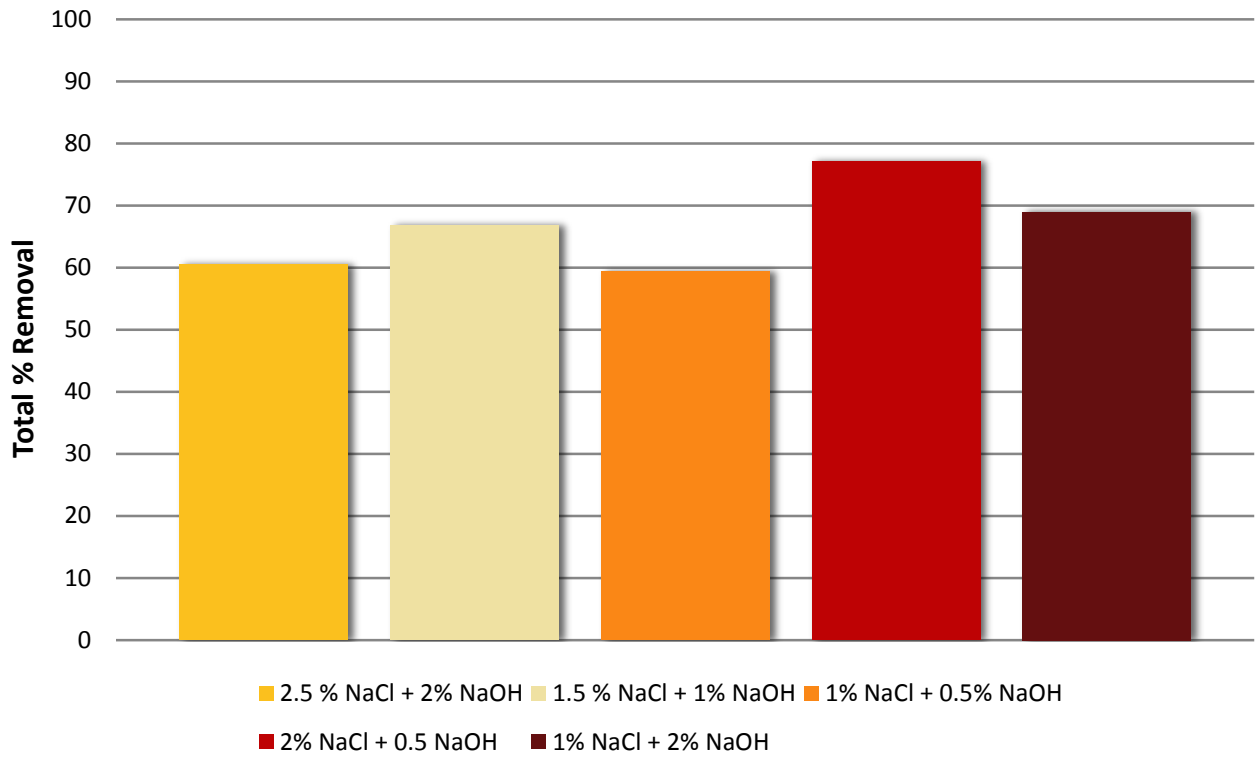
- High concentration PO_4-P solution (~100 mg/L PO_4-P)
  - Ensure that resin will reach capacity with each cycle
  - Similar to breakthrough in column studies
- 4 Ion exchange cycles (1 cycle = removal + regeneration)

Removal Performance of Dow-HFO-Cu



- Phosphate removal capacity decreases with each ion exchange cycle

Removal Performance of Dow-HFO-Cu

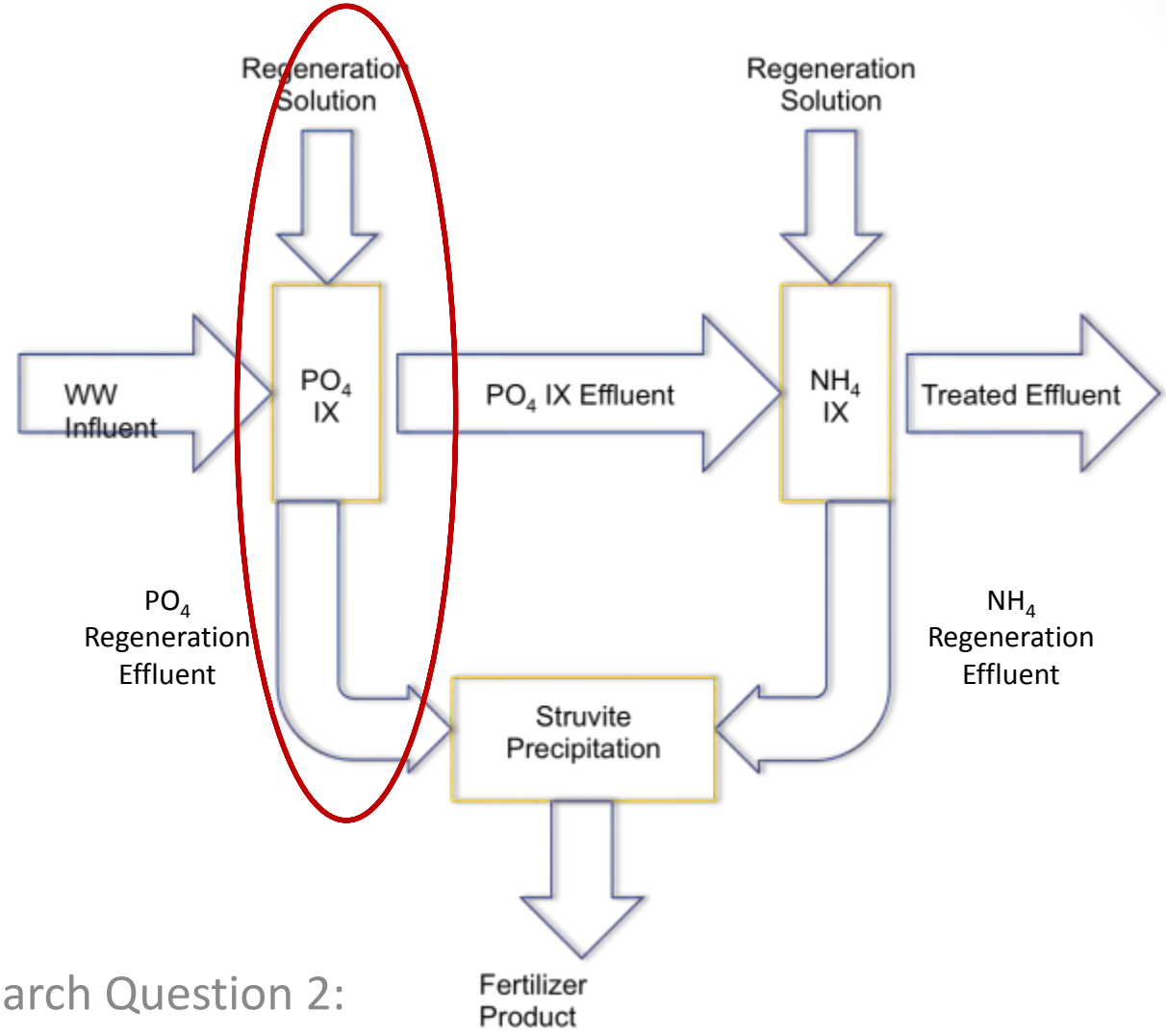


Total % Removal = Total Adsorbed PO_4-P / Total Influent PO_4-P

4 total ion exchange cycles

Removal Performance of Dow-HFO-Cu

- Significant decrease in ion exchange capacity from cycle to cycle (1 cycle = removal and regeneration)
- Leaching of Cu^{+2} from media in first removal step
- However, there is still captured PO_4 on media with each cycle



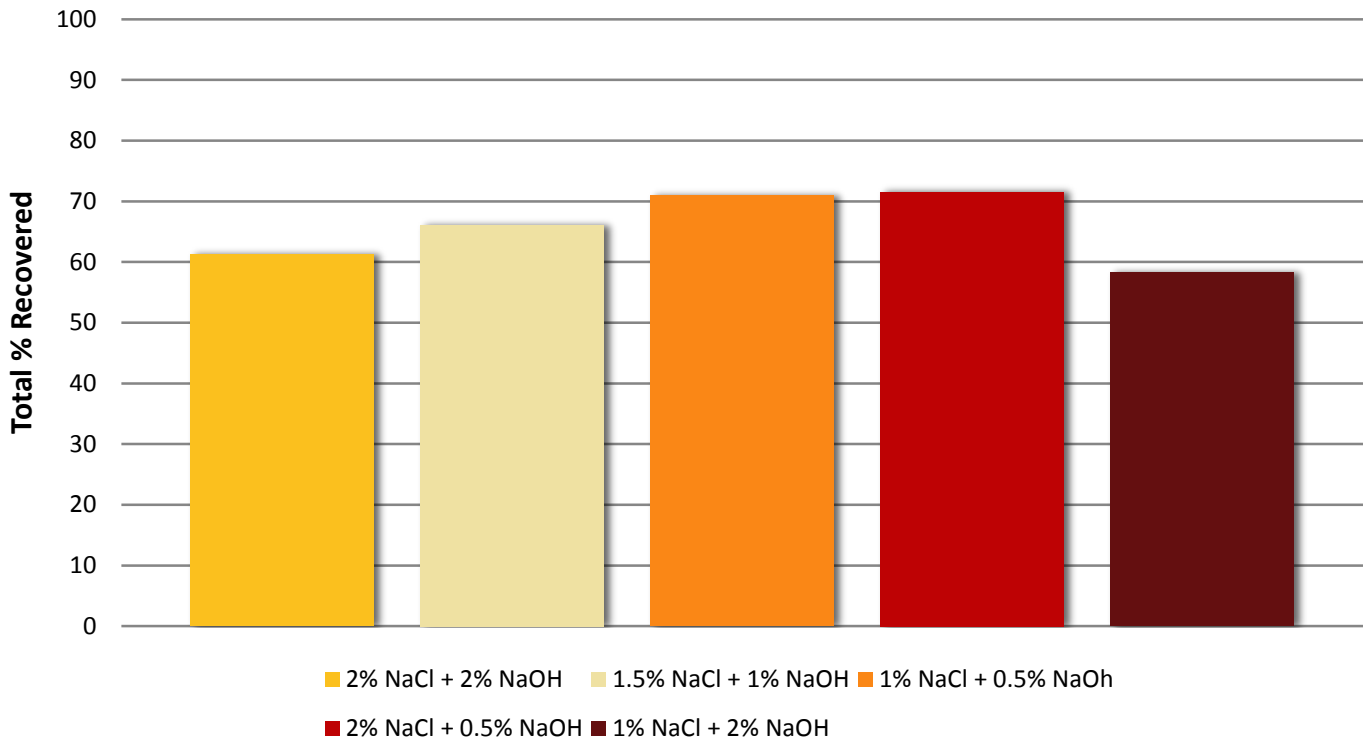
Research Question 2:

WHAT IS THE RECOVERY EFFICIENCY OF THE CAPTURED PHOSPHATE FROM DOW-HFO-CU MEDIA?

Regeneration of Dow-HFO-Cu

- Ion exchange process can be reversed
  - Ions collected on solid media released into regeneration solution
- Regeneration solution is often saline
  - Sodium chloride (NaCl) places both positively (Na^+) and negatively (Cl^-) charged ions back onto exchange media
  - How do different concentrations affect resin performance?
- Regeneration effluent can provide a highly concentrated nutrient stream
  - Potential for nutrient reuse

Recovery Performance of Dow-HFO-Cu

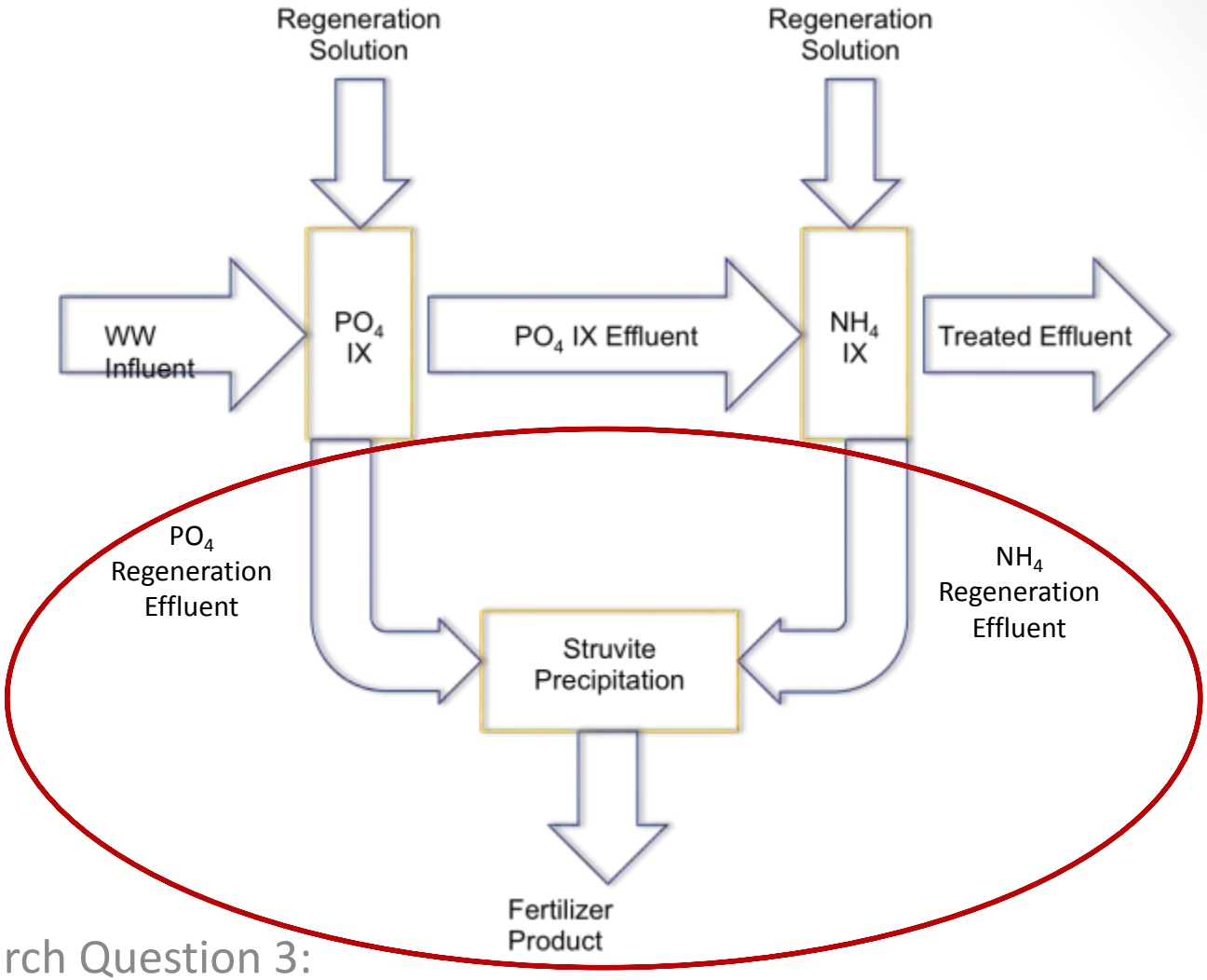


Total % Recovered = Total Recovered PO_4-P / Total Influent PO_4-P
4 total ion exchange cycles

- Regeneration solutions with high sodium hydroxide concentrations (NaOH=2%) recover less of the total influent PO_4-P

Recovery Performance of Dow-HFO-Cu

- Decreased removal capacity caused a decrease in recovery potential
- High concentration of sodium hydroxide (NaOH) may be stripping the media of loaded Cu^{+2}
- Noticeable decrease in exchange capacity after first IX cycle
  - Change in color of media upon addition of regeneration solution



Research Question 3:

WHAT IS THE COMPOSITION OF THE RECOVERED STRUVITE PRODUCT?

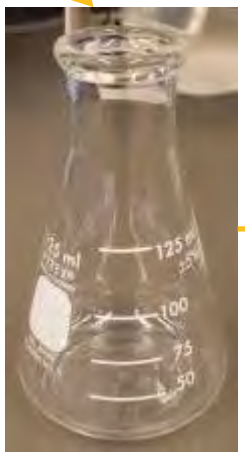
Precipitation of solid struvite with IX regeneration solutions

- Struvite ($MgNH_4PO_4$) is a solid formed by magnesium, ammonium, and phosphate
- Addition of Mg solution to low-volume, PO_4-rich and NH_4^+-rich regeneration solutions (from IX exchange processes) along with pH adjustment can precipitate solid
- Struvite has the potential to be used as a slow-release land applied fertilizer

Precipitation of solid struvite with IX regeneration solutions

- PO_4 regeneration solution
- NH_4 regeneration solution

- $MgCl_2$ solution addition



pH adjustment ~12

Solids settling

Analysis Of Supernatant

Precipitation of solid struvite with IX regeneration solutions

Ion	% Removal
PO_4-P	72.5
NH_4^+-N	10.9
Mg^+	62.5
Cu^{+2}	<1

- Limited results
- Some batch kinetics may limit removal percentages
- Presence of other metals such as calcium may be precipitating with phosphate
- Better pH for precipitation?
- Seed precipitation reactions with crystalized struvite?

CONCLUSIONS & FUTURE WORK

Conclusions

- Dow-HFO-Cu media exhibits complete removal and high selectivity of PO_4 in the presence of competing anions (such as SO_4) in equilibrium batch tests
- Both removal and regeneration exchange capacities decrease significantly with each exchange cycle
  - <75% total influent PO_4-P removal and recovery for each tested regeneration solution
- 73% removal of PO_4-P in struvite precipitation
  - Some removal may be in different phosphate salt forms

Future Work

- Improve Dow-HFO-Cu media preparation
  - Significant leaching of Cu^{+2} was observed during first exchange cycle
- Improve media regeneration step
  - 2% NaOH regeneration solutions showed lowest removal/recover capacities
  - Improved media preparation may improve regeneration step
- Lab-scale column tests of Dow-HFO-Cu media
  - Better models municipal wastewater streams
  - Difference in kinetic flow of tests may help improve media performance

Acknowledgments

- Allen Williams
- Marquette University Water Quality Center

Thank You!

Questions?

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