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# Enzyme-Induced Carbonate Precipitation (EICP) Using Fresh Urine and Calcium-Rich Zeolites

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## Background

- Traditional cementation methods have high energy usage and fossil fuel production
- An alternative method is EICP, but the environmental impact is a concern:
  - Urea is synthetically created as an input to EICP
  - Ammonium is produced as an output from EICP
- Urine can be used as a novel source of urea for EICP
  - Urine currently accounts for a large majority of nitrogen, potassium, phosphorus, and other nutrients entering wastewater treatment plants
  - However, urine accounts for less than 1% of the volumetric flow; thus, repurposing these nutrients would be beneficial for operation of wastewater treatment plants
  - The use of urine for EICP has not been fully explored
- Zeolites can be used to adsorb the ammonium byproduct
  - Zeolites have been proven as an adsorbent of ions within a multitude of solutions, but have not been fully explored for EICP
  - Calcium-rich zeolites may be more beneficial for EICP because they exchange calcium with ions in solution, promoting calcium carbonate formation

***Urea Hydrolysis***

$$Urea \xrightarrow[\text{urease}]{} Ammonium + CO_2$$

- Process that occurs naturally in urine and synthetically in EICP
  - Presence of urease enzyme catalyzes reaction
  - pH rises due to ammonium formation
  - Carbon dioxide forms into carbonic acid ($H_2CO_3$), which dissociates into carbonate ion ($CO_3^{2-}$)

***Enzyme-Induced Carbonate Precipitation***

$$Ca^{2+} + HCO_3^{-} \longrightarrow CaCO_{3\,(s)} + H^{+}$$

- Through addition of calcium chloride, calcium carbonate precipitates, which bonds together sand particles to create cement
  - Calcium exchanged from calcium-rich zeolites may also be a source of calcium ions
  - pH decrease due to released $H^{+}$ ion

## Objectives

1. Investigate efficacy of calcium-rich zeolites to adsorb ammonium ions.
2. Investigate differences between calcium-rich and natural zeolites to produce calcium carbonate.
3. Investigate efficacy of zeolites to adsorb ammonium within cement.
4. Investigate how the orientation of zeolites affects ammonium adsorption.

**Table 1. Synthetic Fresh Urine Composition**

| Chemical Species | Concentration (M) |
|---|---|
| Urea | 0.250 |
| NaCl | 0.440 |
| $Na_2SO_4$ | 0.015 |
| KCl | 0.050 |
| $MgCl_2{\cdot}6H_2O$ | 0.005 |
| $NaH_2PO_4$ | 0.020 |
| $CaCl_2{\cdot}2H_2O$ | 0.004 |

**Table 2. Zeolite Concentrations**

| Species | Concentration |
|---|---|
| Calcium-rich clinoptilolite | 100, 300, 500 g/L |
| Calcium-rich chabazite | 100, 300, 500 g/L |
| Natural clinoptilolite | 100, 300, 500 g/L |
| Natural chabazite | 100, 300, 500 g/L |

**Table 3. EICP Solution Composition**

| Futu | Concentration |
|---|---|
| $CaCl_2{\cdot}2H_2O$ | 0.200 M |
| Urease Enzyme | 3.000 g/L |
| Zeolite | See Table 2 |

**Figure 1. Preparation of calcium-rich zeolites through 0.45-µm filter.**

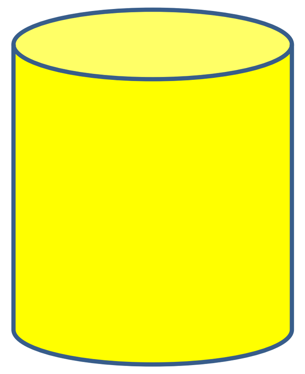
**Figure 2. Prepared calcium-rich clinoptilolite zeolite.**

## Experimental Design

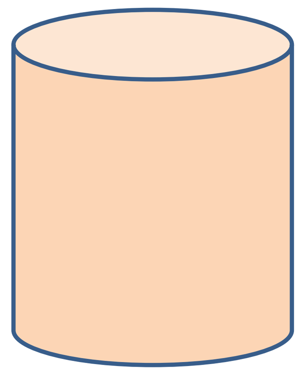
## Progress

### *Objectives 1 and 2: Beaker Experiments*

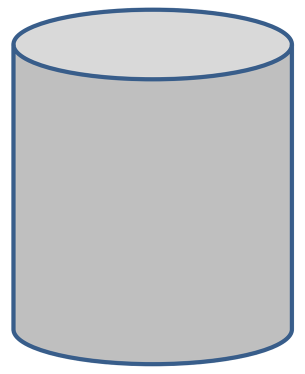
Preparation of three beaker solutions, combine until reaction to completion (24-36 hours):



Synthetic/real fresh urine solution (See Table 1)

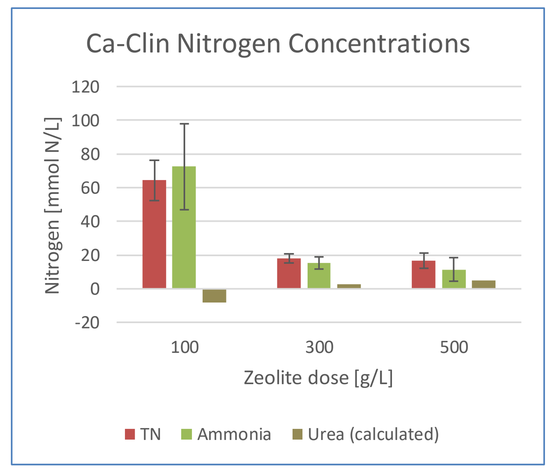


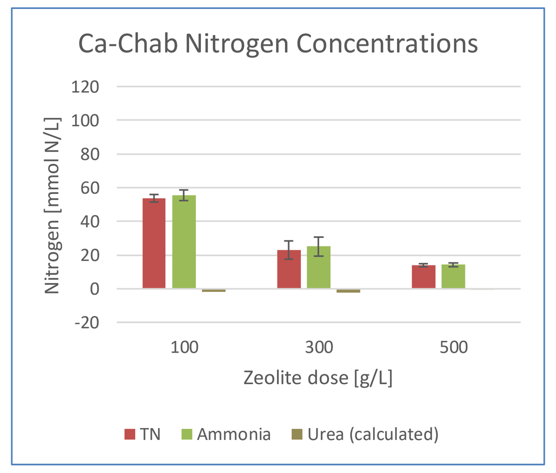
Zeolite (see Table 2) and calcium chloride solution (see Table 3)

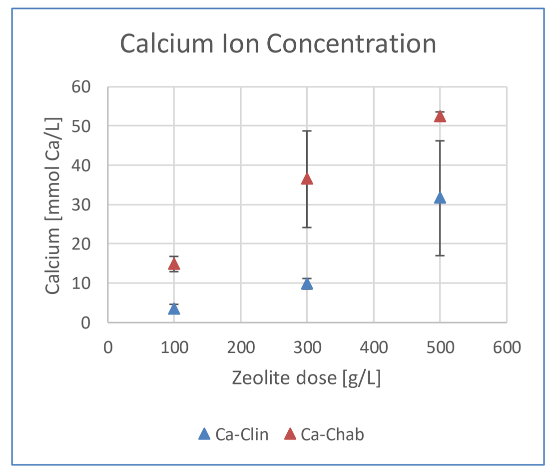


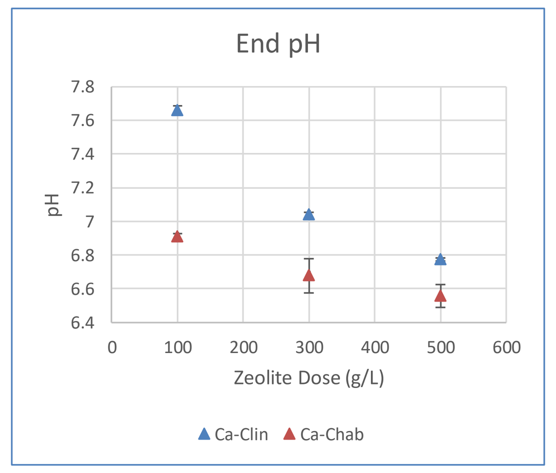
Urease enzyme solution (see Table 3)

*Objective 1:*




*Objective 2:*
Unexplored

### *Objectives 3 and 4: Sand Column Experiments*

Preparation of urine, calcium chloride, and urease solutions; combine and pump through column filled with sand and zeolites.

*Objectives 3 and 4:*
Unexplored

## Future Work

- Finish work on Objectives 1 and 2
- Finalize procedure for Objectives 3 and 4
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- If time permits, conduct studies on the effects of proteins within urine on EICP

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