

# Electrochemical Nutrient Recovery

\*Disclaimer: This project is likely the bulkiest, least efficient code you have ever seen. I could not wrap my head around putting every desireable variable into a single SV, so I coded each time step to obtain transient information. As such, my high hopes for this model falls now to this very small investigation with an unwieldy amount of lines of code that can run.

## Introduction

With the global population growth accelerating along with the rise in industrialism, farmers primarily rely on mined phosphate rock as a component of fertilizer to grow high yields of crops. However, phosphate rock is a nonrenewable resource, and some estimates have suggested that the world's phosphate reserves will become depleted within the next 100 years. In addition, due to intensive farming practices such as overapplication and inappropriate fertilizer use, high quantities of nutrients are often washed away as runoff. These excess nutrients contribute to eutrophication of surface waters and cost over 2 billion dollars per year in cleanup efforts in the United States alone. With the spatial distribution problem of both nutrient depletion in soils and over-enrichment of surface waters, there exists an opportunity to develop a process where nutrients are recovered from wastewater prior to discharge and sold as a customizable renewable fertilizer.

Phosphorus and nitrogen can be recovered from wastewater in the form of struvite, a phosphate mineral. Generally, struvite precipitation occurs according to Reaction 1:



where n = 0, 1, or 2 depending on solution pH.

Struvite has been known to spontaneously form in the pipes of wastewater treatment plants, causing flow issues. As a result of these flow assurance problems, struvite precipitation has been widely investigated so that preventative action can be taken for pipeline blockages. Over the last two decades, interest in precipitation of struvite as a sustainable phosphorus recovery method has increased due to struvite's utility as a natural slow-release fertilizer. Because struvite is composed of equimolar ratios of magnesium, phosphorus, and nitrogen, practical struvite precipitation requires dosing the low magnesium-containing waste streams with magnesium salts. In addition, pH adjustment is needed as the solubility of struvite is high in acidic and neutral environments. The need for these additional chemicals drive up the price of struvite recovery, accounting for up to 97% of process costs. These costs have hindered the practicality of widespread struvite precipitation as a nutrient recovery method.

Recently, efforts have been made to precipitate struvite electrochemically. Electrochemical struvite precipitation with a sacrificial magnesium anode does not require addition of magnesium salts since magnesium metal, which serves as the anode, participates in the reaction

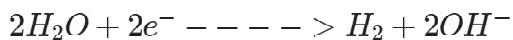
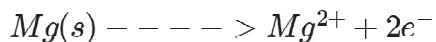
by providing electrons and dissolving to form magnesium ions. With the use of pure magnesium, transportation costs associated with transportation of spectator ions in magnesium salts are no longer necessary, thus improving the economics of the process.

## Model Formulation

The domain includes:

- 1) Solid Magnesium Metal anode
- 2) Aqueous electrolyte, 120mM ammonium dihydrogen phosphate
- 3) 316 Stainless Steel cathode

The relevant reactions are magnesium dissolution at the anode and hydrogen evolution at the cathode:



Magnesium ions then interact with phosphate and ammonium in solution to precipitate struvite  $MgNH_4PO_4 \cdot 6H_2O$  on the magnesium surface. This precipitation occurs when the ion activity product,  $IAP$  becomes greater than the solubility product,  $K_{sp}$  which is reported in the literature as  $10^{-13.26}$

$$IAP = [Mg][NH_4][PO_4]$$

While the low equilibrium potential of Mg means it dissolves spontaneously when in contact with water, applying a potential will enhance this reaction. However, excess Mg dissolution that is unused in the precipitation reaction is wasteful as it means the anode needs to be replaced at a faster rate and drives up energy costs. In addition, formation of the solid on the anode surface reduces the area available for reaction. Thus, this model will explore how applied potential affects struvite formation taking into account the area and concentration effects at the surface. To simplify the system, the cathodic reaction of hydrogen formation was not investigated. The anodic reaction should be limiting the global system because there are much more water molecules available to form hydrogen than there are magnesium ions to form struvite. Of course energy considerations for the cathode will impact the anode, but these are ignored for this study.

## Assumptions

This reaction takes place in a single-cell, constantly stirred batch reactor with 120mM ammonium dihydrogen phosphate as the aqueous electrolyte. Because of this, the following assumptions can be made:

- 1) Bulk concentration is spatially homogeneous except near the electrodes. Convection dominates as the transport mechanism because the reactor is well-mixed.
- 2) Temperature is constant. Water has a high heat capacity and any heat generated by the low applied potentials should not contribute to substantive temperature increases.
- 3) Solution resistance is negligible. The starting concentration of 120mM electrolyte provides sufficiently high conductivity (10mS/cm, measured in the lab) to eliminate solution resistance impacting electrochemical tests.

## Model Structure

The Butler-volmer equation is used to calculate current from user-applied potential. The user cannot apply a potential greater than 1V because that is outside the electrochemical window of the aqueous electrolyte. The current is then translated to  $[Mg^{2+}]$  using Faraday's law, assuming 100% efficiency. Struvite precipitation occurs when the Ion Activity Product of struvite's constituent ions surpass the solubility constant  $K_{sp}$ . Because struvite consists of equimolar constituents ( $[Mg] = [NH_4] = [PO_4] = C$ ), it is easy to find the equilibrium concentration  $C$  at which solids will precipitate:

$K_{sp} = C^3$  Struvite precipitates on the surface of the Mg anode, reducing available surface area.

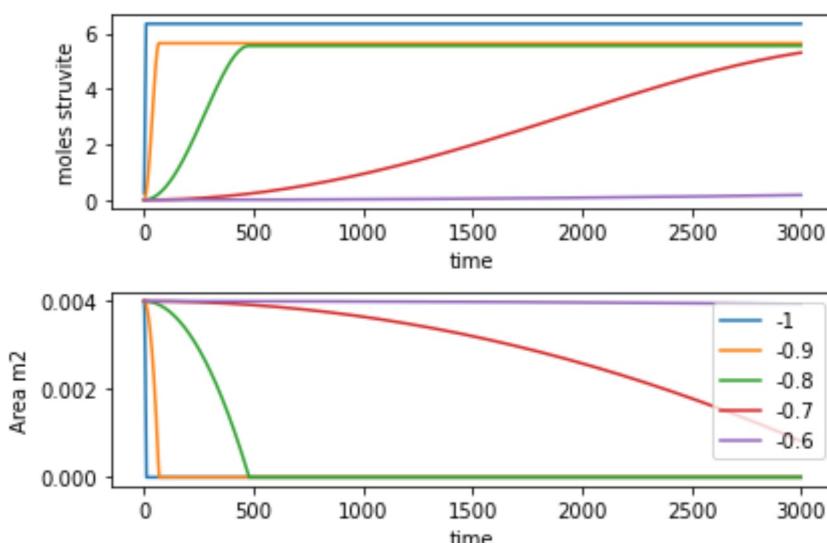
## Results and Discussion

Part 1: First, the model is run at constant potential assuming that 120mM of  $[NH_4]$  and  $[PO_4]$  are readily available at the surface. This investigation simply looks at struvite generation and available surface area change with time at different, constant potentials.

For one constant, user-set potential, let's see how the moles of struvite precipitated and anode area change over time, utilizing Butler-Volmer kinetics.  $\eta = \phi_{an} - \phi_{eq,an}$

$$i_{an} = A * i_0 * \exp\left(\frac{nF\eta}{RT}\right)$$

The thickness  $L$  of precipitate formed on the anode is calculated by:  $L = \frac{MQ}{nF\rho A}$  where M=molar mass, Q=charge,  $\rho$ =density of precipitate, A=area. This is taken from equation 13.4 of the textbook. The equilibrium potential at the anode is -2.357 V, taken out of Appendix 1 in the textbook.



As the above figure shows, application of higher (more negative) potentials lead to faster struvite formation and subsequent loss of available area. At -1V, the maximum quantity of struvite precipitated on the anode is near 6 moles, while at -0.9V, it is slightly less at 5. As the applied potentials decreases (more positive), the amount of struvite generated is slower and surface area changes more slowly. Thus, a more negative applied potential increases amount of Mg released

and struvite formed, as expected.

## Part 2. Incorporate concentration gradients near surface of electrode

The previous figures are incredibly simplistic as they assume that [NH<sub>4</sub>] and [PO<sub>4</sub>] are readily available as soon as a Mg ion is released. In reality, a double layer and a diffusion layer exist near the electrode which lowers the concentration near the Mg anode. To take this concentration gradient into account, the Poisson-Boltzmann equation was implemented to calculate the concentration at the surface and the potential drop.

$$C_{surface} = C_{bulk} \exp\left(\frac{-ze\phi_{surf}}{k_b T}\right)$$

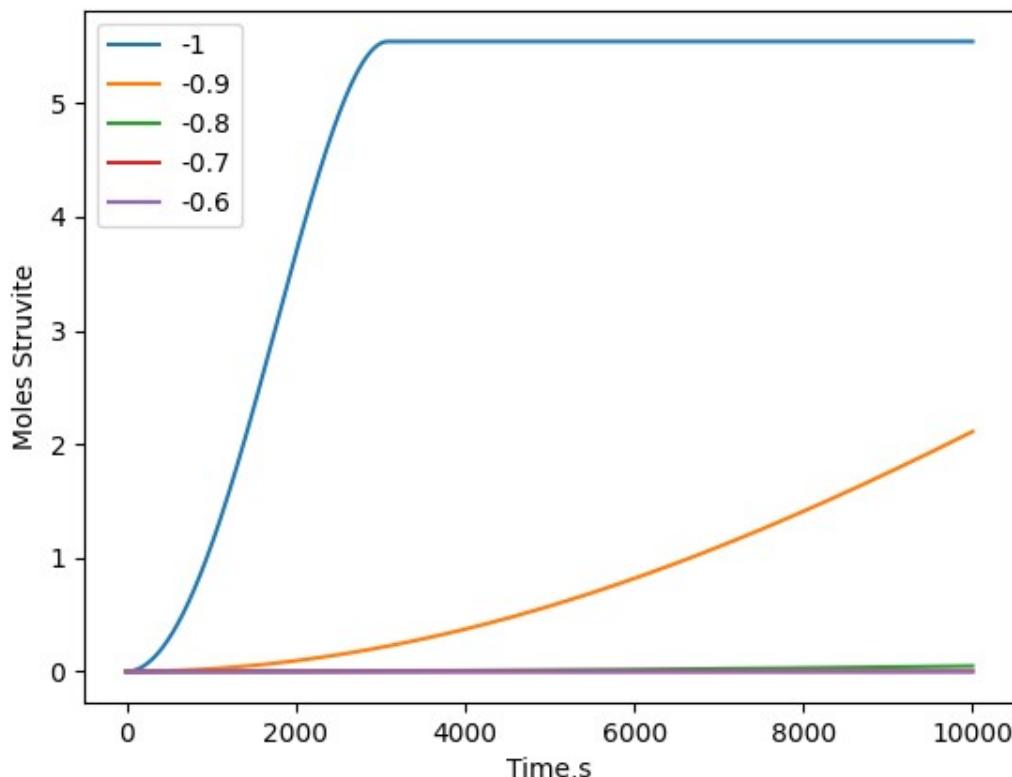
Boltzmann's Law where z=charge, e=electron charge,  $k_b$ =Boltzmann constant.

$$\phi = \phi_{surf} e^{(-\kappa x)}$$

Solution to the linearized Poisson-Boltzmann equation for a charged plane where x=distance from electrode,  $\phi$  = potential

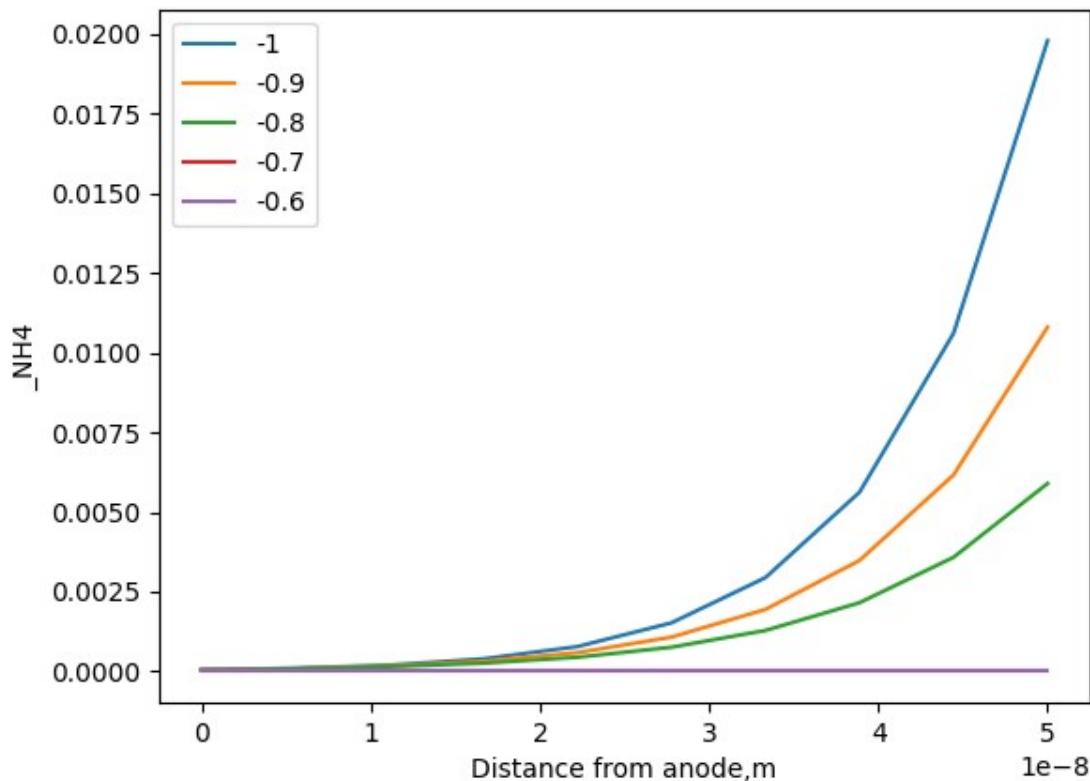
$$\kappa^2 = \frac{2z^2 e F C_{bulk}}{k_b T \epsilon} \text{ and}$$

$1/\kappa$  = Debye Length,  $\epsilon$ =permittivity of medium (water in this case)



The figure above shows moles of struvite generated with time for different applied potentials from -1V to -0.6V. We see that the response time is much slower compared to the first figure now that concentration gradients near the electrode are taken into account. This result makes

sense because there is some resistance associated with bringing ions near a charged surface due to charge neutrality. At -1V, the maximum amount of struvite (for the provided surface area of anode) is reached within 1h. For potentials lower than -1V, (more positive), there is not enough energy for significant struvite generation within 2 hours. We can see why this behavior occurs by looking at the concentration change with distance.



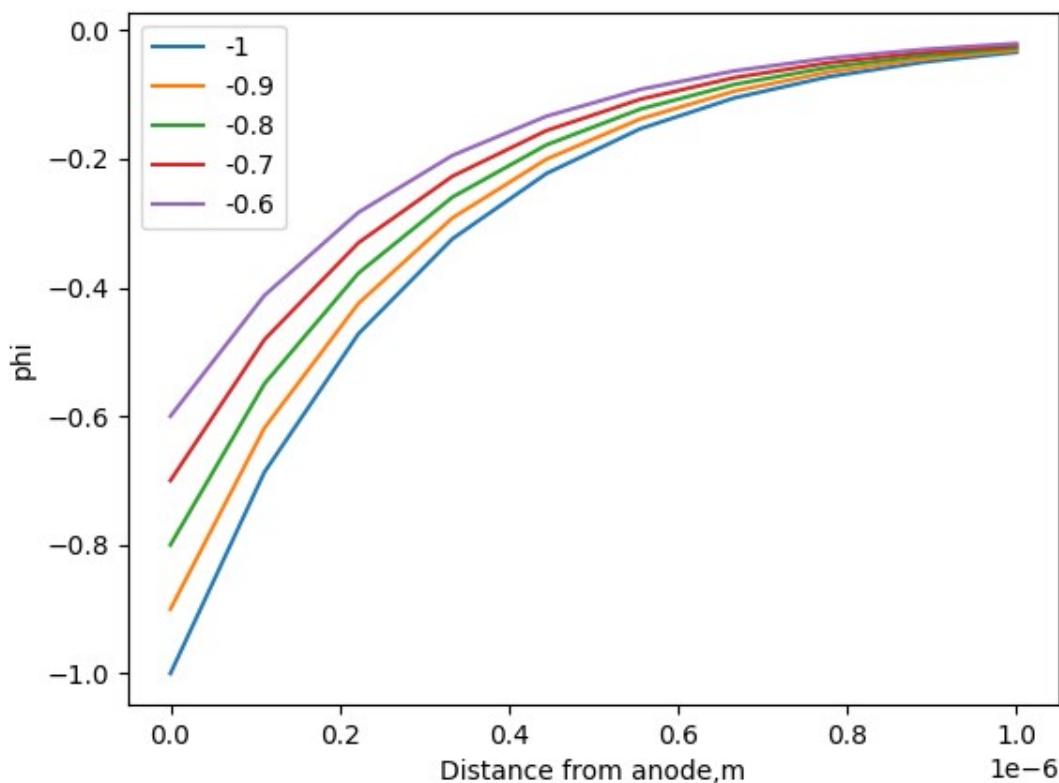
This figure shows the concentration of ammonium (moles/m<sup>3</sup>) with distance from the anode. It is assumed that the concentration of ammonium is the same as the concentration of phosphate in this model since both start at the same value and are only consumed by struvite generation. (Negligible side reactions). At x=0, or the surface of the electrode, the concentration is the solubility equilibrium concentration since struvite starts precipitating immediately in all cases ( $C = 4 \times 10^{-5}$ ). Application of higher potentials leads to a more severe concentration difference per distance, and subsequently a shorter distance to reach the bulk concentration.

We can see why potential decreases thickness by recognizing that the Debye length,  $\lambda^2$ , is inversely proportional to  $z^2C$ :

$$\lambda^2 = \frac{eRT}{F^2 \Sigma z^2 C}$$

Rearranged Poisson's equation:  $\Sigma z^2 C = \Delta^2 \phi \frac{\epsilon}{-F}$

Thus, for a higher  $\phi$ ,  $z^2C$  is higher, leading to smaller  $\lambda$ . We can also look at the change in  $\phi$  with distance.



The phi value at the surface of the electrode is equal to the user-set value. The potential then becomes more positive as distance from the surface increases due to double layer. The range of potentials investigated in this study all collapse onto one another far away from the anode.

## Conclusions

In conclusion, the operating conditions for electrochemical struvite precipitation play a major role in overall success. Application of high potentials increase the quantity of struvite formed per second and reduces the thickness of the double layer at the anode. Of course, operating at high voltages come at higher costs, so balancing the budget for the process with the time necessary for the desired production rate is necessary. This model has many shortcomings that need to be addressed to form a more robust model. It was assumed that the concentrations of ammonium and phosphate only change with struvite precipitation. In reality, phosphate and ammonium both react in water to form  $HPO_4^{2-}$ ,  $H_2PO_4^-$ ,  $H_3PO_4$ , and  $NH_3$ . In addition, taking the cathode reaction into account produces hydroxides which will change pH and corresponding speciation of these species. Furthermore, it was assumed that no oxide layer forms on the solid magnesium anode, but in reality a thin layer of magnesium oxide is present. This layer easily dissolves in water but will alter the surface area available. It has also been reported that magnesium metal form local cathodes and anodes when immersed in water, which once again alters the ability for Mg ion release. In summary, there are a number of complicating phenomena which work to reduce the total moles of struvite formed as predicted in this study, but as a first

principles "ideas" situation this model runs

## References

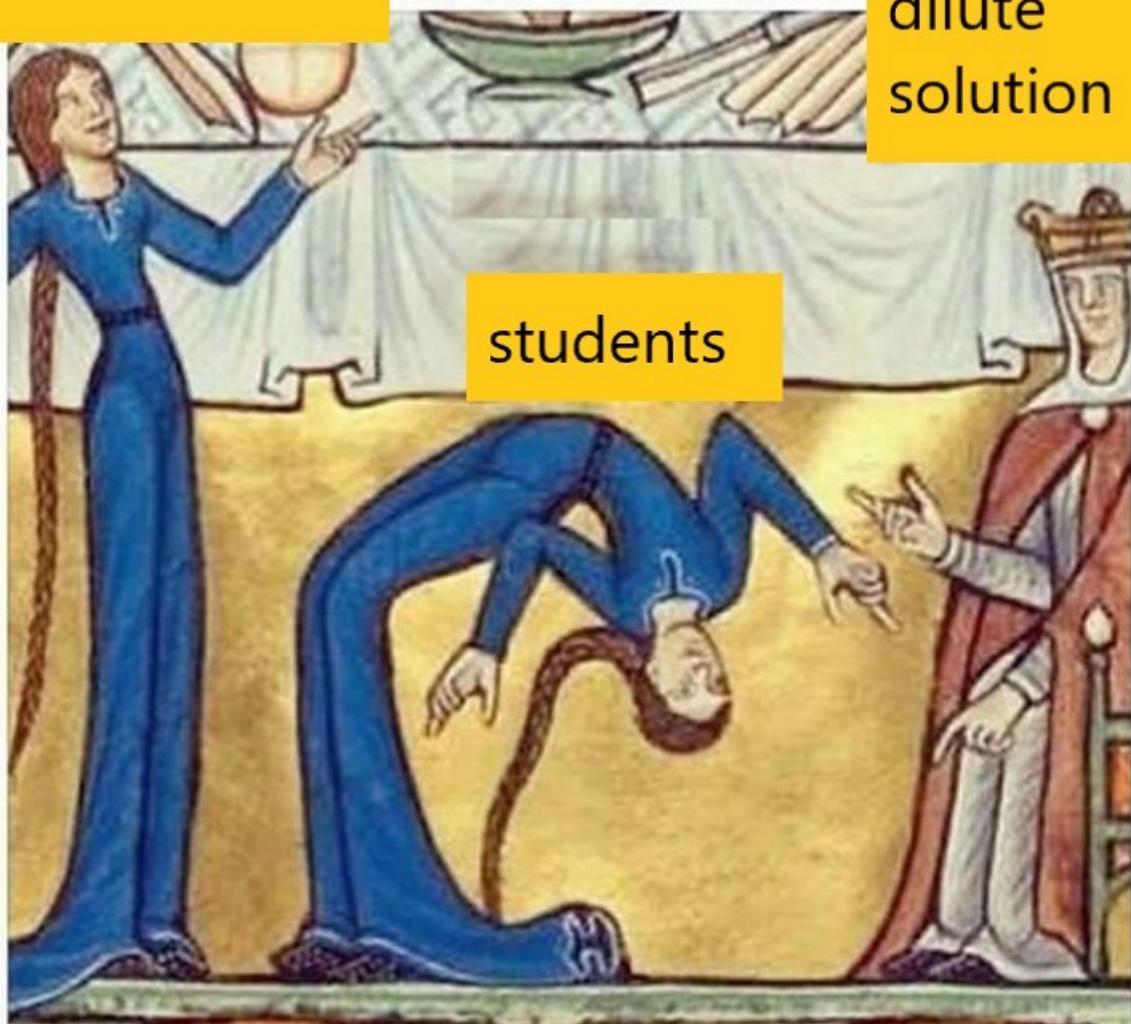
### Memes



Estimate  
activity  
coefficients

Assume  
infinitely  
dilute  
solution

students



## Memes not related to learning

Every Office Hours:





When you write one line of code and  
get 6 errors already

In [1]:

```
C:\Users\Ivy\anaconda3\envs\echem\lib\site-packages\IPython\html.py:12: ShimWarning: The `IPython.html` package has been deprecated since IPython 4.0. You should import from `notebook` instead. `IPython.html.widgets` has moved to `ipywidgets`.
```

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    warn("The `IPython.html` package has been deprecated since IPython 4.0. ")
```

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