## 2. Electrochemical Calcium Phosphate: An electrifying way to recover P

Calcium phosphate (CaP) precipitation is not something unusual for us. Our bones and teeth comprise mostly of CaP, a testimony of the preference of these ions for each other. But recovering P from wastewater in the form of CaP presents some challenges, mostly in the form of the pH requirements. And overcoming these challenges requires a new approach, an electrochemical one.

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Phosphorus from wastewater treatment plants (WWTPs) is commonly removed by chemical precipitation. That implies removing the soluble P using another soluble substance, resulting in a solid precipitate. In your case, this is calcium phosphate, formed in a novel way. Before we get to your process, could you tell us why you chose to recover P as calcium phosphate in the first place? Why not as struvite?

**Yang:** My research focuses on P recovery from wastewater. This can include municipal wastewater, but also other sources like wastewater from the food industry. When it comes to P recovery from WWTP, struvite is often seen as a popular product. Struvite is magnesium ammonium phosphate (MgNH<sub>4</sub>PO<sub>4</sub>.6H<sub>2</sub>O), and a slow-release fertilizer. It ideally requires a Mg:NH<sub>4</sub>:PO<sub>4</sub> ratio of 1:1:1. But if you consider most waste streams, the concentration of Mg is low compared to the concentration of ammonium and phosphate. So quite often there is the need to dose additional Mg.

But calcium (Ca<sup>2+</sup>) is an abundant ion in most waste streams. Therefore, the addition of calcium ions is most likely not necessary to precipitate calcium phosphate (CaP). Even if there is a case where additional calcium is required, the cost of dosing calcium is cheaper than dosing magnesium. Moreover, calcium phosphate is the key component of mined phosphate rock. Hence it can readily be used as a raw material for fertilizer production.

## You however don't conventionally recover CaP, but rather focus on an electrochemical approach. Could you tell us why?

There are certain drawbacks to the conventional method of recovering CaP. As is common with precipitation reactions, you need a high pH to create supersaturation conditions and trigger the formation of CaP. This is done by dosing a strong alkali like sodium hydroxide (NaOH). The wastewater however has a high buffering capacity due to the presence of organics and bicarbonate ions, and as a result, high amounts of NaOH are required to increase the pH. This results in a significant cost. Moreover, the high pH required to facilitate CaP precipitation would need to be reduced again before discharging the treated water stream. This would require acid, and would be an additional cost. Hence,

to overcome these drawbacks, we opted for an electrochemical approach of recovering the P as CaP (figure 1).



**Figure 1:** Setup for electrochemical recovery of calcium phosphate (CaP). The setup has a wastewater solution that already contains calcium and phosphate ions. The before and after images are of the cathode, and the white color highlights the deposition of CaP from the electrochemical process.

### How does the electrochemical P recovery work?

It involves an electrochemical cell which includes a cathode and an anode **(figure 2).** The cell consists of wastewater that already has phosphate and calcium ions. A current is passed through the cell and leads to water electrolysis, i.e., splitting of water molecules, at both the electrodes. Let's look at them one by one. Let's start with the cathode because that's where our desired reaction happens. At the cathode, there is a supply of electrons, and the water molecule gets reduced, producing hydroxide ions. Now, these hydroxide ions increase local pH, i.e., the pH near the cathode becomes high. This high pH provides a driving force for the precipitation of the calcium and phosphate ions, and CaP precipitates and deposits on the cathode.

At the anode, there is a loss of electrons, and the water molecule gets oxidized, producing protons. The number of protons and hydroxide ions produced from the electrolysis reactions are the same. But the buffering capacity of the wastewater ensures that the pH of the bulk solution does not change much. In addition, hydrogen and oxygen gas are formed at the cathode and anode respectively. These can either be recovered or can be used in combination with other treatment processes in the WWTP.

On the whole, by just creating a local pH increase near the cathode, we make use of the existing calcium ions and form CaP without any need for additional chemical dosing.



# **Figure 2:** Mechanism of electrochemical calcium phosphate (CaP) recovery – The illustration of the electrochemical cell shows the pH increase near the cathode that results in the CaP formation on its surface. The pictures to the right show the cathode covered with the CaP precipitates. The bottom picture shows a scanning electron microscopy (SEM) image of the same (scale bar 200 $\mu$ m). The pores in the image are formed due to the escape of H<sub>2</sub> gas from the reaction at the cathode.

## But instead of generating high pH by the addition of chemicals, you use electricity. Isn't this also an added cost to the process? Or do the advantages offset this cost?

Electricity is indeed consumed during the generation of hydroxide ions, but certain advantages are exclusive to this process. A key factor here is the advantage of creating a local pH increase. This means the precipitation does not depend on the bulk pH and as a result, we can recover P from even acidic waste streams. For instance, waste streams from cheese factories tend to be acidic, and increasing the pH at the bulk would require very high dosing of NaOH. But this process offsets that. Thus, this process can work over a wide range of pH.

The process can furthermore be combined with bio-electrochemical systems where organics can be degraded at the anode. This will reduce the level of chemical oxygen demand (COD). Additionally, electrochemical cells can also recover P from non-reactive forms of phosphorus. For instance, organic P like phosphonates is used as antiscalants. These can be oxidized at the anode and be converted into inorganic/reactive phosphate that can be recovered as CaP. Thus, oxidation and precipitation can be combined in a single reactor and used to recover P from non-reactive forms of P.

Also, it's good to note that the CaP formed is already deposited on the cathode. So, it is enough to take this electrode and get the CaP from it, instead of having a separate extraction step from the liquid phase. For instance, if the CaP precipitates in the bulk solution, then a separate step like filtration or sedimentation might be required, which is avoided in this case.

#### So, would you say the process is already cost-effective on the real scale?

The majority of the costs are associated with energy consumption in the form of electricity. The overall economic feasibility also depends on the wastewater streams to be treated. The cost of electrochemically recovered P is comparable to the cost of phosphate rock when the influent P concentration is about 100 mg P/L. But for lower P concentrations, the cost could be several factors higher and would need further optimization to make it more energy-efficient. We have steadily been improving on this aspect.

#### Could you give examples of how you have been optimizing the process to make it further efficient?

Throughout the research, we have been constantly looking at ways to improve the process. We have evaluated several options and monitored the pros and cons. For instance, depending on the composition of the wastewater, there could be other types of precipitates formed during this process. These precipitates could consume calcium, e.g., by forming calcium carbonate (CaCO<sub>3</sub>), and hydroxide ions, e.g. as magnesium hydroxide (Mg(OH)<sub>2</sub>), and thereby lower the recovery of P. We found out that the current density is crucial in selectively precipitating CaP among other minerals like CaCO<sub>3</sub> and Mg(OH)<sub>2</sub>. This selective precipitation is possible because the local pH can be adjusted by the applied current density and conditions can make CaP thermodynamically more favorable than CaCO<sub>3</sub> and Mg(OH)<sub>2</sub>.

In a different approach, we have combined the existing system with bio-electrochemical systems. Apart from the additional removal of COD, the reduction of oxidation potential in such a system significantly reduces the energy consumed. The use of a bioanode in such a system also avoids the formation of chlorine which can oxidize into toxic compounds.

We found that we can further lower energy consumption by varying the electrode material. Using graphite felt as the cathode, we could increase the precipitation area and also limit the diffusion of hydroxide ions from the cathode towards the bulk, thereby maintaining a higher pH near the cathode. This resulted in a decrease in energy consumption of almost 2 orders of magnitude. This substantially reduced energy consumption was an important step in taking the process towards a realistic application.

Another approach was to use an electrochemical cell filled with  $CaCO_3$  particles. These  $CaCO_3$  particles would consume the protons formed at the anode, releasing  $Ca^{2+}$  ions in the process **(figure 3)**. The consumption of protons means that in addition to the usual increase in pH at the cathode, the bulk pH would also be higher. Moreover, the  $CaCO_3$  particles would provide additional  $Ca^{2+}$  ions, as well as act as seed particles for CaP precipitation in the bulk.

The above approach could however make the collection of CaP particles difficult since they are not just on the electrode anymore. But since  $CaCO_3$  is in general more soluble than CaP, over time it could be possible to convert all the  $CaCO_3$  into CaP. This way all the solids from the column can be collected as CaP and be replaced with new  $CaCO_3$  particles. This process also enabled a more efficient recovery.



**Figure 3: Electrochemical P recovery in a column packed with calcium carbonate (CaCO<sub>3</sub>) particles**. The inset to the right shows that just like in the usual electrochemical cell, hydroxide ions are produced at the cathode, causing a local pH increase and CaP precipitation. However, in this column, the proton produced at the anode is consumed to release calcium ions. Thus, these protons cannot neutralize hydroxide ions and there is also a pH increase in the bulk. The CaCO<sub>3</sub> particles act as seed particles for the CaP formation in the bulk. The numbers in the inset highlight the sequence of events.

## It seems there are so many ways that you can work around to further improve the process. Would you say there is still further room for improvement?

I do think so. I would just like to add one further piece of information, which many people may not be aware of. If you consider how NaOH is produced commercially, it is already done via an electrolysis approach. This means the electrochemical production of hydroxide ions in our process could be economically competitive to the commercial approach of producing it. Moreover, this approach avoids the transport and storage of corrosive chemicals. The challenge is how we can make the electrochemical production and the subsequent use of these hydroxide ions as efficient as possible.

So yes, I can imagine our research just lays the foundation and I hope it encourages more research to follow in the area of electrochemical P recovery, thereby further improving the efficiency of the process.