4. Calcium phosphate (CaP) from manure: Creating value for farmers

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Every time we flush our toilets, we end up diluting the nutrients present in human waste. But animal excrete is used directly as manure and has a much higher concentration of nutrients. Legal restrictions mean that farmers have a limit on how much of the manure they can apply on the field. Based on the success of CaP granulation from blackwater, a similar approach is used for P recovery from manure, but the conditions are way more challenging.

***Chris Schott**: "We are happy that our process removes P from the manure because any P we can take out is a win for the farmer. But in terms of recovery, the complex matrix of the manure creates a real challenge."*

Manure is a source with a much higher concentration of P than usual wastewater streams. But when it comes to manure, usually one thinks about its direct application as fertilizer. Why would you want to recover the P from manure instead of directly using it as it is?

Chris: The goal of my project is to recover P specifically from cow and pig manure. Just like us, animals also consume P through their food. The P from human excrete ends up in WWTP, whereas the animal excrete is generally used as manure on the fields. The amount of P in manure produced just from pigs and cows in the Netherlands is about 71 million Kgs annually. This is a huge quantity. Next to P, the manure is very rich in nutrients like nitrogen (N), potassium (K), and organics, all of which are essential for plant growth. But the unfortunate part is that the ratio between the nutrients in manure do not fit the plant demands, and if this is applied directly on the field, often the surplus of P would be washed-off and will result in polluting the surface waters through eutrophication. Thus, there are legal restrictions on the amount of manure that can be applied directly to the fields.

Hence, the farmers whose animals generate the manure, have to find ways to get rid of the excess manure from their farms. This is usually done by sending the manure to incineration plants, or by transporting it to other countries. This results in high costs, both environmentally and economically. Now imagine, if we can specifically separate the P from the manure, the farmers can use the rest of the manure and besides saving on the disposal costs, they can perhaps even generate revenue by selling the recovered P, or use it in a controlled manner on their fields. This is the main motivation for us to recover P from the manure.

Do you use the manure directly from the farm or is does it need some further treatment before the P recovery process?

The manure is basically the excreta from the animals on the farm. There are outlets on the floor where the animals reside, from where all their excrete gathers at a collection point. This total excrete is then passed through a machine that presses it out through a sieve into two different fractions: called the thin and thick fractions. As the names suggest, the thin fraction is the more liquid fraction and consists of particles smaller than 200 µm. The thick fraction is the fraction with more solids and consists of particles larger than 200 microns. This fraction is pressed out into a compact form where the solid content is very high; so it's almost like a dry cake.

In terms of composition, the thick fraction is rich in organic fibers with a long chain of carbon atoms. So, they are valuable in terms of improving the fertility of the soil. Hence, they can directly be applied to enrich the soil quality.

The thin fraction has more than 90 % of the inorganic nutrients, by which we mean the P, N, and K. Hence, this is the fraction that we use in our reactor for recovering the P.

You use a specific reactor for recovering the P. What is it and how does it function?

We use a Upflow Anaerobic Sludge Bed/Blanket (UASB) reactor for this process **(Figure 1).** This work is inspired by the concept of recovering CaP from black water (human excrete) which was a previous PhD project at Wetsus of Ricardo Cunha. We worked together on black water during his PhD and continued working together on manure for my PhD.

The reactor is basically a vertical column, and you introduce the thin fraction of the manure at the bottom of the reactor, and the flow is upwards. Calcium is dosed into the reactor to facilitate the precipitation of soluble P as CaP. As the CaP precipitates, they settle to the bottom of the reactor due to their higher density. An advantage here is that the solid retention time (SRT) is more than the hydraulic retention time (HRT) of the reactor. Therefore, the time the CaP granules spend at the bottom of the reactor is longer than the time the liquid flows through the reactor. This allows the CaP granules to grow in size and can be harvested easily.

Another advantage of this reactor is that the microbial consortia present in the manure anaerobically digest the organics and result in the formation of biogas. The biogas forms in the sludge bed and is collected at the top. As it moves to the top through the reactor, it also causes the mixing of the solution and suspended particles in between. Hence no additional mixing is required in the reactor.

Through means of this process, more than 80 % of the P can be recovered in the UASB reactor. The effluent that comes out at the top is low in P and can be used directly in the field. The concentrated P recovered as CaP can be transported more readily or be used to fertilize crops in a controlled way.

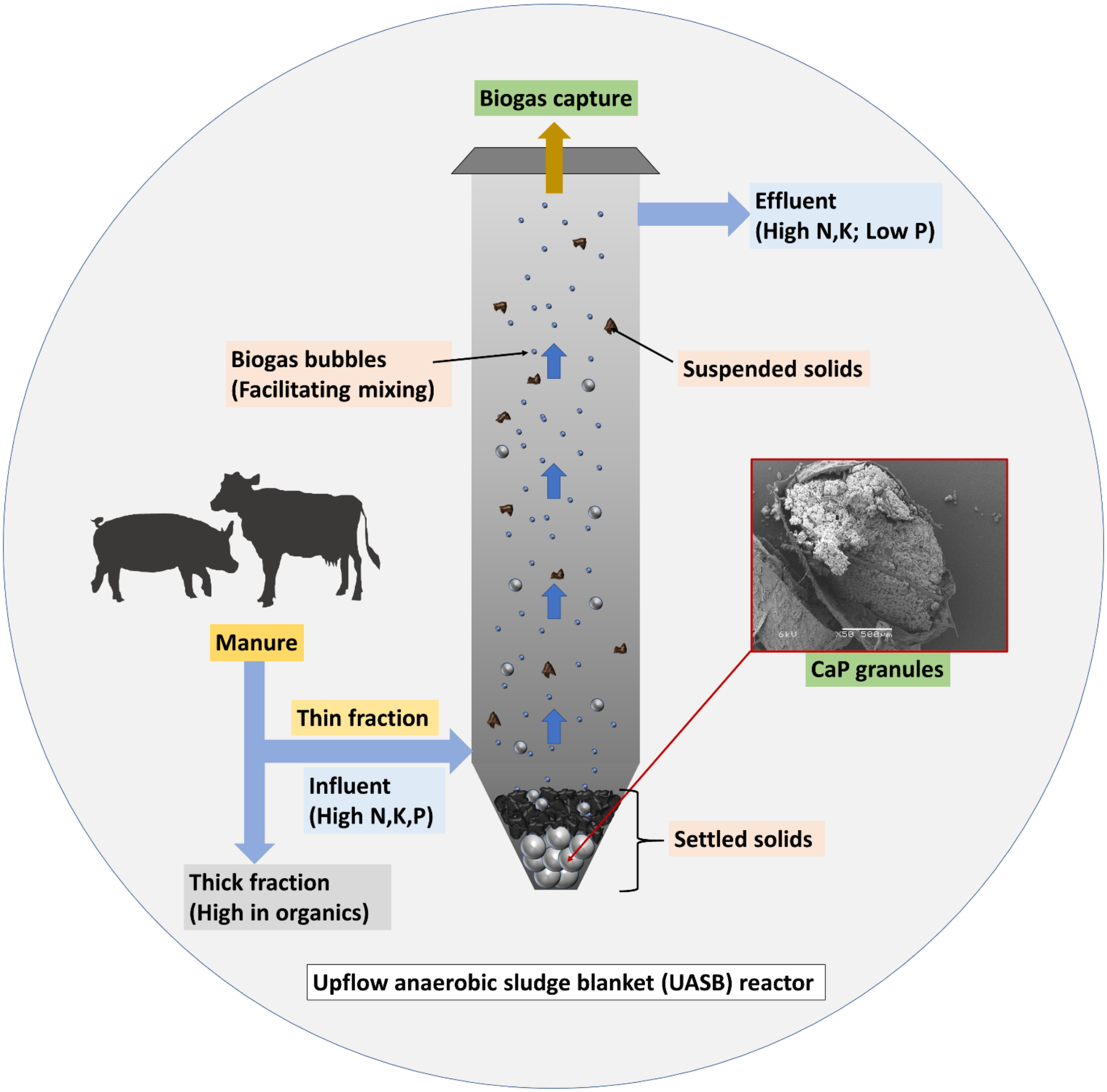

Figure 1: CaP recovery from manure (thin fraction) via a upflow anaerobic sludge blanket (UASB) reactor*. The biogas formed by anaerobic digestion serves the purpose of mixing the liquid phase in the reactor. The inset on the right shows a SEM image of the CaP granules recovered from this reactor. The CaP granules are covered with biofilm formed by the microbial consortia present in the reactor.*

Since your approach works on precipitation, the high concentrations of P in the manure should naturally aid the formation of the CaP. But this also means that there would be high concentrations of other ions. Is this a challenge for the process?

It is a very big challenge. Because even though we achieve high P removal from the manure, it's currently not so much as CaP. The conditions of the thin fraction from the manure are so different from those of blackwater that the whole process changes. On average, the concentration of other ions is at least 10-fold higher in the stream from manure as compared to blackwater. High concentration of ions triggers precipitation and formation of solids. As a result, the phosphate is already bound in the solids and there is very little soluble phosphate available in the reactor, which in turn means the formation of CaP is trickier than in blackwater.

What about the concentration of soluble phosphate in the manure as compared to blackwater?

In blackwater, the soluble phosphate, i.e., inorganic or ortho-phosphate can easily be 90 % of the total P. This allows for easy precipitation as CaP. But for manure, if I consider pig manure, the soluble phosphate is less than 30 % of the total P. If we consider cow manure, the soluble fraction is even less, usually less than 5 % of the total P. The rest of the P is already bound in the solid.

But if P is already bound in the solids, isn't that an advantage? It's anyway what you want to do with your process?

That's the ironic thing. When we analyzed the manure fractions, we found that a lot of the bound P is as struvite, i.e., magnesium ammonium phosphate. But the struvite is distributed as small particles throughout the solids. That makes is hard to harvest and recover P from manure efficiently without forming dense CaP granules. Thus, we are anyway not able to refine and use the P bound in the solids of manure.

Yes, we are happy that our process removes P from the manure because any P we can take out is a win for the farmer. The effluent discharged from the UASB reactor is something that the farmers can directly use. So, in that sense, it is already a benefit. But in terms of recovery, the complex matrix of the manure creates a real challenge. We would need to find ways to separate the P bound in the solids as a more concentrated and refined product. We still believe the formation of CaP granules would lead to a more concentrated product that can be recovered.

So how do you handle this challenge and how does this shape your subsequent research direction?

As a first step, we have to understand the exact differences between the waste stream from blackwater and manure. Can we do something to change the manure properties so that it behaves more like blackwater? Do some treatment to have a lower concentration of solids, get more orthophosphate, and make the P more available for the calcium and thus enhance CaP formation **(figure 2)**. For instance, increasing the dosage of Ca in the reactor could shift the reaction thermodynamics and the bound P can be released and reprecipitated as CaP. But this would also imply more chemical consumption. Another idea could be to increase the temperature of the reactor, and this would increase the activity of thermophilic bacteria. Thus, the anaerobic digestion will go faster. Higher temperatures also help to hydrolyze organic substances through hydraulic stress, which in turn would result in better digestion, higher production of biogas, and could facilitate more CaP formation.

We also thought about the acidification of the reactor to solubilize the bound P. This could be done via adding acid, but we could also engineer it in such a way that the microorganisms make the acid for us. For example, acetic acid is one of the metabolic products of the microbes, and we could stimulate conditions so that microbes produce more of this acid. But to be able to do this effectively, we would need a better understanding of the microbial communities that are there in the manure. We are currently doing DNA extraction and sequencing of the microbial communities. This should help us understand the difference in microbial communities between the blackwater and the manure. Thus, if we want to form CaP granules it would help to get closer to the conditions in blackwater.

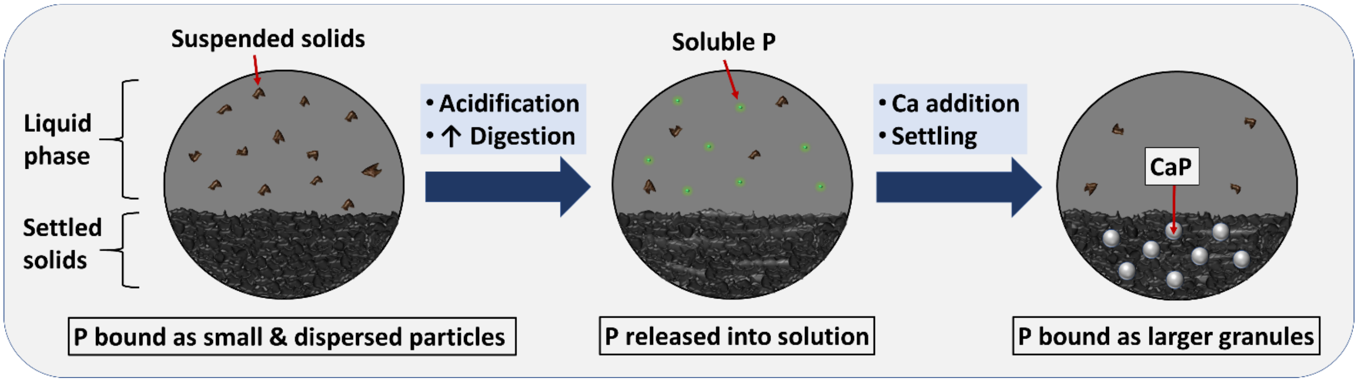

Figure 2: Inducing CaP granulation in manure - *The P initially bound in the solid fraction is too small and dispersed to be directly extracted. Mobilizing the bound P and recrystallizing them as larger CaP granules would facilitate easier extraction.*

It's incredible that you work with such challenging conditions and try to make a fist of it. This feels fascinating by itself and I guess the challenge spurs the research further. Is there something else that you find fascinating about your research?

What I absolutely love about the project is the combination of different scientific disciplines. If you only look at the USAB reactor you have the fluid dynamics and how the flow affects the CaP granules formation and their settleability. Then you have the biology which is playing a big role in making biogas by anaerobic digestion, and we do some DNA extraction to check the differences between the microbial communities. Then you have the actual chemistry of the CaP precipitation. This kind of combination facilitates cooperation with other PhDs.

Also, throughout the project, I interact with different stakeholders like the farmers in this case. I go out to the field and understand the interaction between livestock and the nutrition distribution in the soil. I find these sorts of connections fascinating and this also motivates you further to understand the science and help bring an improvement.