3. Vivianite in sewage sludge: A phosphate with a magnetic charm

Magnets are fascinating in general, not a term one would usually associate with sewage sludge. And yet, Wetsus researchers have found a way to interconnect the two, through a special compound called vivianite.

***Thomas Prot**: "What is fascinating is that you take any digested sewage sludge from wastewater treatment plants using iron as a coagulant and look under the light microscope, you will see vivianite. You will see blue particles all around. It's surprising why no one chose to look at it before".*

Unlike Yang's research which aims to recover P from solution, your research recovers the P once it has been precipitated in the sludge. However, you seem to rely on the fact that the precipitated P in the sludge transforms into a very specific compound, one that gives an exciting property to facilitate its separation. Can you tell us more about this exciting compound?

Thomas: Sure, that exciting compound is vivianite, a paramagnetic compound that eventually turns blue after oxygen exposure **(figure 1).** It is an iron (II) phosphate and has actually been in use for centuries. Johannes Vermeer, the famous Dutch painter from the 17th century, has used it in his paintings. Now you may ask what's a pigment used by painters doing in a sewage sludge? The answer to that lies in the complex chemistry of iron and phosphate in the wastewater treatment plants (WWTPs).

Two methods are usually used to remove the phosphate from the WWTPs: i) Enhanced Biological phosphorus removal (EBPR), which relies on phosphate accumulating microorganisms, and ii) Chemical phosphorus removal (CPR), which involves using metal salts, usually iron to bind the phosphorus. In EBPR plants, the P is recovered as struvite, albeit with a low recovery percentage which is about 25% if things go well). In CPR, the phosphate is left for recovery after incineration, which pertains to high infrastructural costs. Hence there is a need to find an alternative way to recover the P, which is where vivianite fits in.

Figure 1: ***(Left):*** *Vivianite concentrates from sludge getting attracted to a magnet.* ***(Right)*** *Vivianite crystals separated from sludge as viewed under a light microscope (scale bar 500 µm). The darker blue colors (inset B as compared to inset A) indicate a higher extent of oxidized Fe in the sample.*

How exactly is it formed in WWTPs using CPR? Are there other types of Fe-P compounds forming?

The iron is dosed to the WWTP influent, in either of its two common oxidation states, in the form of Fe(II) or Fe(III) salts. This can result in the formation of different types of complexes or precipitates. For instance, Fe(II) or Fe(III) can precipitate directly with phosphate to form Fe(II) phosphate, i.e. vivianite, or Fe(III) phosphate, respectively. But it could also be that iron precipitates with hydroxide ions to form different types of iron (hydr)oxides. The soluble phosphate could then bind to these iron oxides. Hence, we do have different types of Fe-P complexes forming in the WWTP.

But the redox sensitivity of Fe(II) and Fe(III) means that these compounds are subject to further transformation. For instance, after the initial Fe-P complexes form in the sludge, these then make the journey through the different parts of the WWTP. This includes going through clarifiers and aeration tanks. Here the conditions are usually aerobic and thus the Fe(II) gets oxidized to Fe(III), which results in a predominance of Fe(III)P compounds at this stage **(figure 2).** But the final say happens in the anaerobic digestion tank. Here, the conditions facilitate the reduction of Fe(III) to Fe(II). The long residence time of sludge in these tanks, coupled with the fact that Vivianite is thermodynamically stable and has very low solubility in these conditions, results in the formation of…you guessed it, vivianite.

Hence, regardless of whether Fe(III) or Fe(II) salts are added to chemically remove phosphorus, when they end up in the anaerobic digesters, eventually they transform into vivianite. This allows it to be magnetically separated from the digested sewage sludge. Thus, vivianite is an important P sink in these WWTPs.

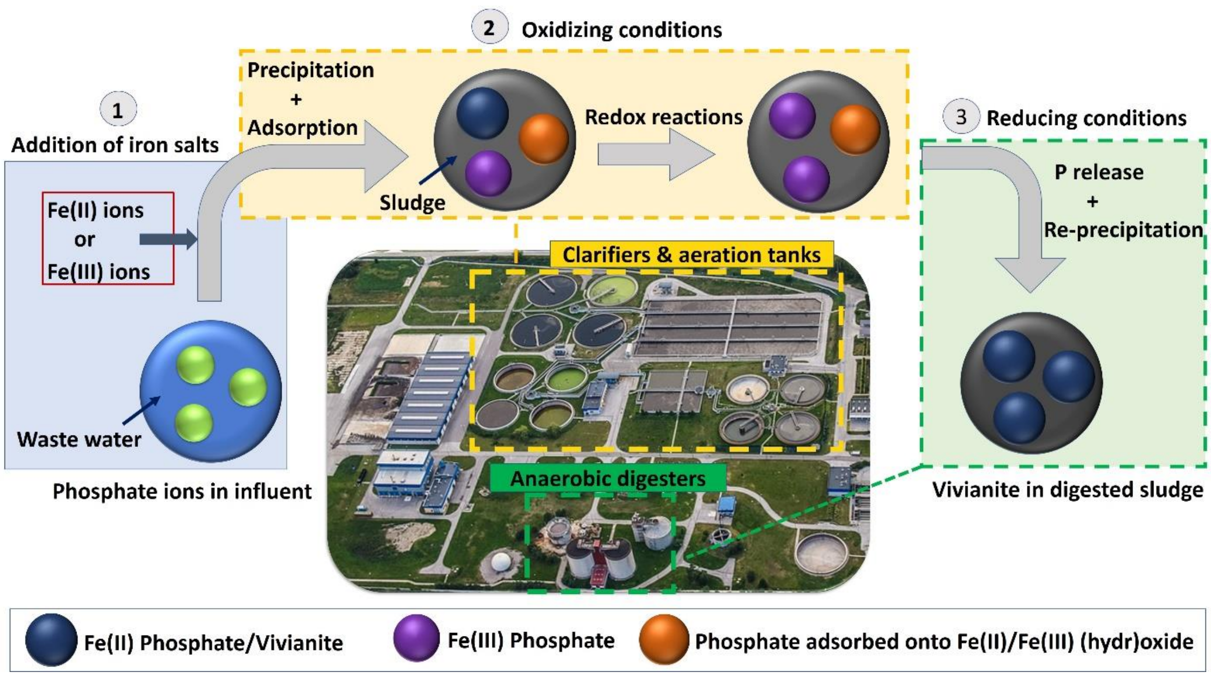

Figure 2: Vivianite as an important P sink - *The picture shows a wastewater treatment plant (WWTP) and the insets show the type of interactions between Fe and P at different stages of the WWTP. Regardless of whether Fe(II) or Fe(III) ions are added, most of the P bound to Fe is transformed into vivianite in the anaerobic digestion tanks.*

If vivianite is formed naturally in these WWTPs, why has it only gotten focus recently?

Well, what is fascinating is that you take any digested sewage sludge from wastewater treatment plants using iron as a coagulant and look under the light microscope, you will see vivianite. You will see blue particles all around. It's surprising why no one chose to look at it before.

I understand that the blue color comes from the partial oxidation of Fe(II) to Fe(III). Is there a proper definition of vivianite based on its oxidation state? And how can you be so sure that the blue is from vivianite?

When you look at sludge under a light microscope, there are not so many colored substances to look at. In that sense, it is sad to look at. You will see some organics and some iron particles in brown color, but otherwise, it's pretty black. So, the blue from the vivianite stands out, except for microplastics which can also have a blue color but they have a very different appearance. Vivianite particles are pretty spherical, which makes them easier to spot. And we do always confirm the presence of vivianite particles in the sludge by using techniques like Mössbauer spectroscopy and X-Ray diffraction. But there is no fixed rule regarding the definition of vivianite, as compounds containing different oxidation degrees of the Fe have different names.

The color of these vivianite particles also varies with the extent to which the Fe(II) is oxidized in the presence of oxygen. The darker the blue color, the more the sample has been oxidized **(figure 1).** The vivianite particles in these samples can be between 20 to 200 µm.

How did you go about your research once you discovered the presence of vivianite? Can you walk us through the thought process?

The identification of vivianite started with a previous PhD project involving former Wetsus PhD Philipp Wilfert. When I started working on it, we knew vivianite was paramagnetic and preliminary experiments showed that magnetic separation could work. The next step was to understand how efficiently we can harvest the P from the sewage sludge via vivianite. So, there were two key things to find out:

i) How much of the total P is bound as vivianite in the sewage sludge?
ii) How much of the vivianite can be separated from the sewage sludge?

To answer the first question, we measured the vivianite content in the digested sludge of the WWTPs that dose iron salts. By correlating the Fe and P content in the sludges from different WWTPs, Philipp had found that if the molar ratio of Fe:P was as high as 2.5, up to 90 % of the incoming P can be bound in the form of vivianite. My studies further confirmed this positive correlation between iron and vivianite by increasing the iron dosing in the Nieuwveer WWTP present in the Netherlands. All the additional iron was transformed into vivianite without impairing the functioning of the WWTP!

To answer the second question, we did experiments on the digested sewage sludge using a magnetic separator. We initially saw that 50 to 60 % of the magnetically separated content contained vivianite. The rest of the fractions consisted mostly of organics, and some amount of minerals like quartz and carbonates. However, fellow researcher Wokke Wijdeveld tested the magnetic separation at the pilot scale, and it was found that depending on the sludge composition up to 80 % of the vivianite could be extracted.

Thus, to further improve our efforts in P recovery via vivianite, we need to find out how to improve the separation efficiency. This also includes studying other routes of vivianite extraction. For instance, if we can induce the formation of larger crystals of vivianite, then gravity-based separation could be an alternative to magnetic separation.

Besides the ability to separate magnetically, are there other benefits to using this process compared to recovering P as a struvite or some other form like CaP?

Vivianite already occurs in existing wastewater plants as part of the usual treatment process, so you do not force nature something new but just encourage the existing process. In some cases, additional Fe dosing might be required to increase the recovery, but this can be done easily without needing a separate infrastructure. However, countries that face strict discharge regulations already dose enough Fe, and they are already optimized in terms of vivianite production.

Moreover, when vivianite formation was stimulated by increasing the Fe dosing in the Nieuwveer WWTP as part of the research, we noted other advantages. Namely, a decrease in H_2S formation in biogas, which resulted in cleaner biogas; and a decrease in the P concentration in the effluent, which helps combat eutrophication. In the case of Nieuwveer, the lower P concentration in the effluent meant that they could discharge in a more sensitive water stream that is closer to the WWTP.

What about the economics of the process? Is it cost-effective?

Saving cost by reducing sludge volume is already a business model; the vivianite can be for free. Normally, the digested sludge contains about 3 % of P by weight, and if all the P is in the form of vivianite, then it will amount to more than 20 % of the sludge.

In the Netherlands, it costs on average about 300 Euros to treat 1 ton of dry solid from WWTP. About 10 to 15 % reduction in costs can be achieved by recovering the vivianite magnetically. The technology is ready to be put into practice even in its current form and can be accelerated soon enough.

As good as everything feels with this technology, there surely must be some challenges?

There are. The theory behind vivianite formation is quite complicated as it is very sensitive to factors like oxygen, light and salts added. These factors can influence the crystallinity and degree of Fe oxidation in vivianite. These variations are challenging already from a detection point of view since the signals can often overlap. Moreover, these variations in types of vivianite formed could affect the magnetic separation, but it has not been studied yet.

There is also the challenge of how to handle the recovered vivianite. We have seen that alkaline treatment of vivianite releases most of the P into solution. This could also lead to the release of arsenic, which has similar chemical properties to phosphorus but is more toxic. Moreover, the iron could have bound other unwanted impurities like heavy metals and micropollutants which would need to be considered while recycling the iron.

But I feel these challenges are important as they shape the future research direction and will in turn give a better understanding of the process and improve the technology. It's important to state here that the success of this project is thanks to the good team spirit of the phosphate recovery theme. This not only includes the fellow researchers, but also the theme members who are actively involved in the discussions and give relevant feedback. This team spirit will be crucial as we go ahead in addressing the upcoming challenges.