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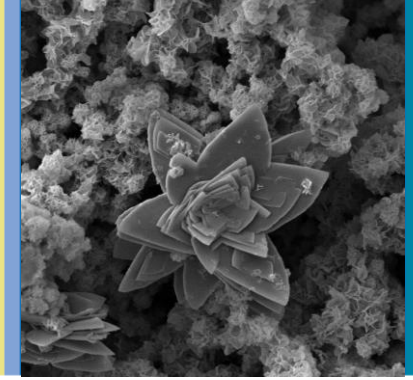


# Phosphorus recovery from iron-coagulated sewage sludge

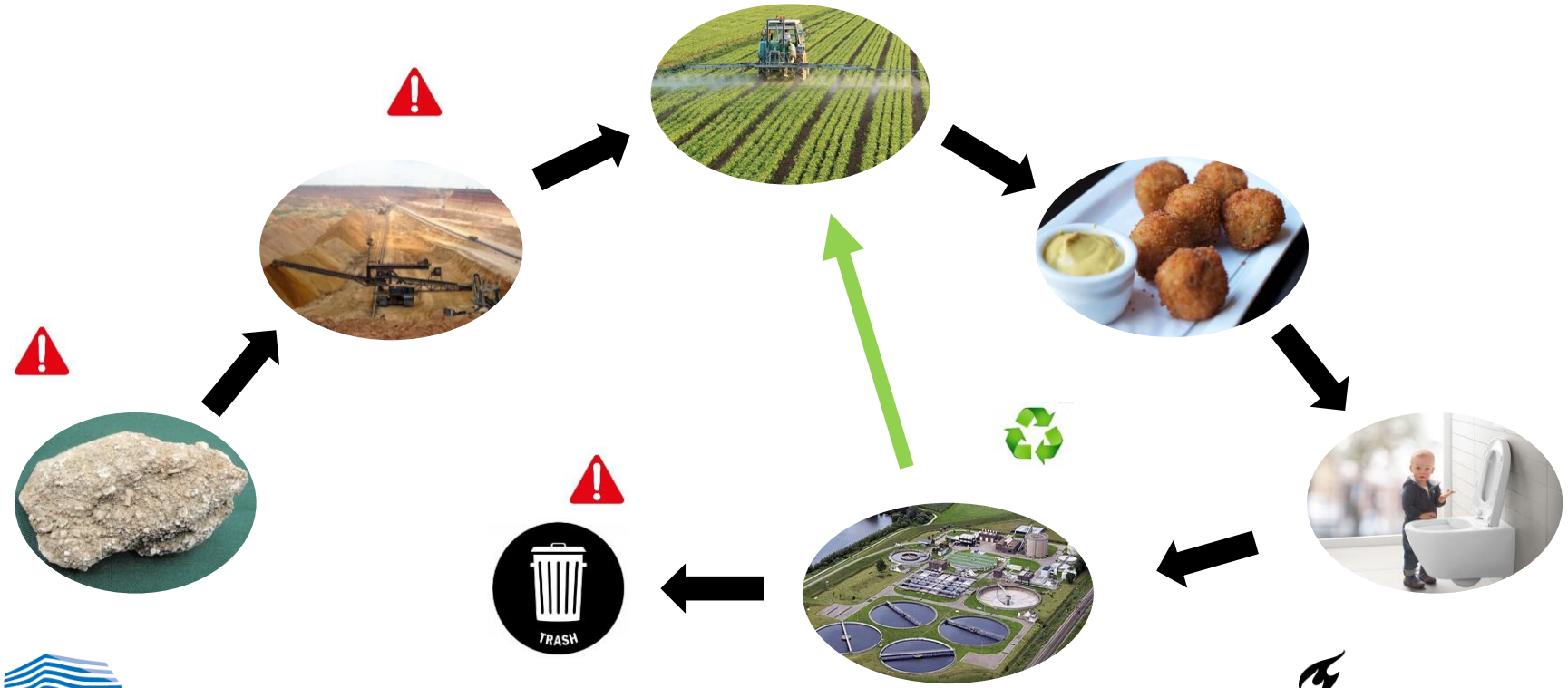
Thomas Prot

April 6th 2023

*MCT Dissertation Award*

TU Delft

# Motivation: closing the phosphorus cycle

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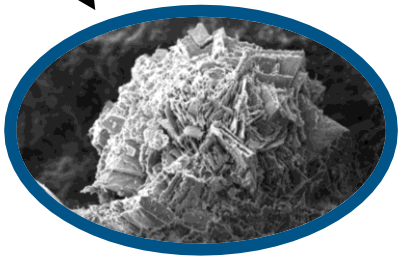
# Vivianite is a major sink of FeP in sewage sludge

Iron addition

20-30 days of digestion



70-90% of the P can be in vivianite

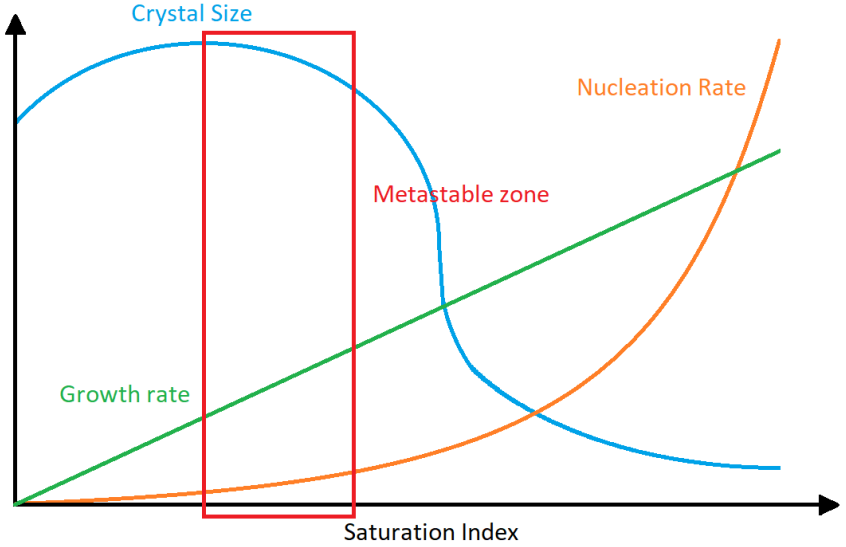
Wilfert, P., Korving, L., Dugulan, I., Goubitz K., Witkamp, G. J., Van Loosdrecht M.C.M. (2018). Vivianite as the main phosphate mineral in digested sewage sludge and its role for phosphate recovery. *Water Research*, 144, 312-321.

# Questions to be answered during my PhD

- What are the factors limiting the growth of vivianite in sludge?
- How can the vivianite be recovered from sludge?
- How to promote vivianite formation in WWTPs?
- Can vivianite crystallization be used for phosphorus recovery from manure?

# Vivianite growth is limited by thermodynamics

Struvite: $NH_4MgPO_4 \cdot 6H_2O$

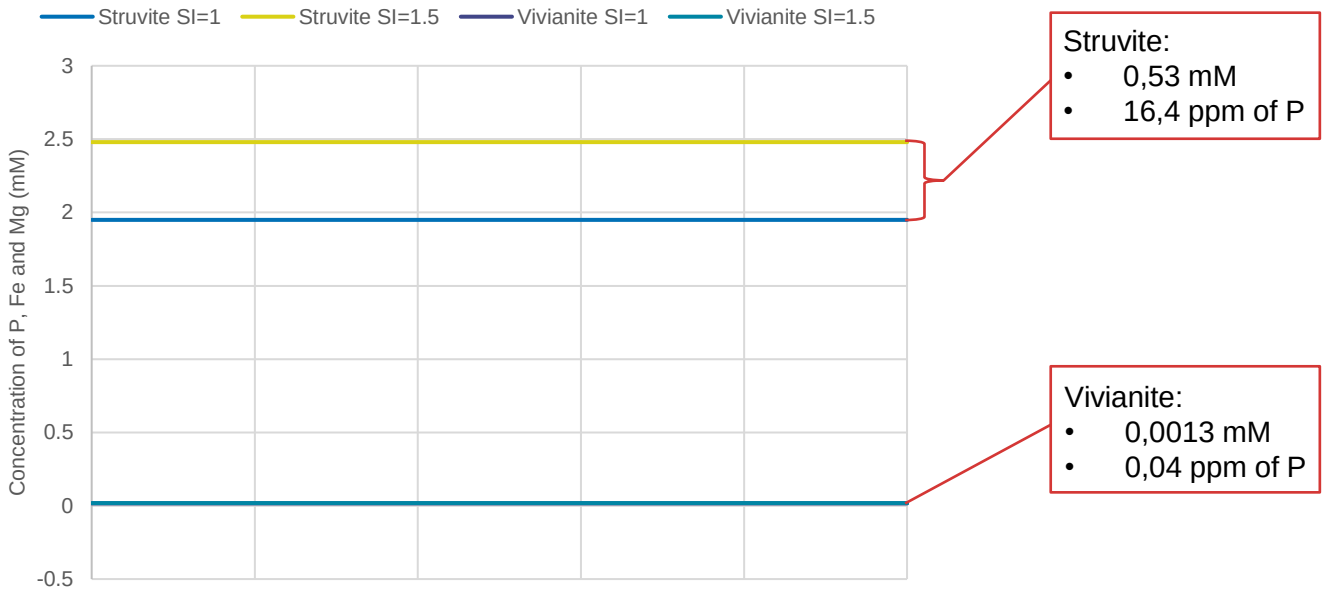



$$SI = \log\left(\frac{IAP}{K_s}\right)$$

# Vivianite growth is limited by thermodynamics

Assumptions:

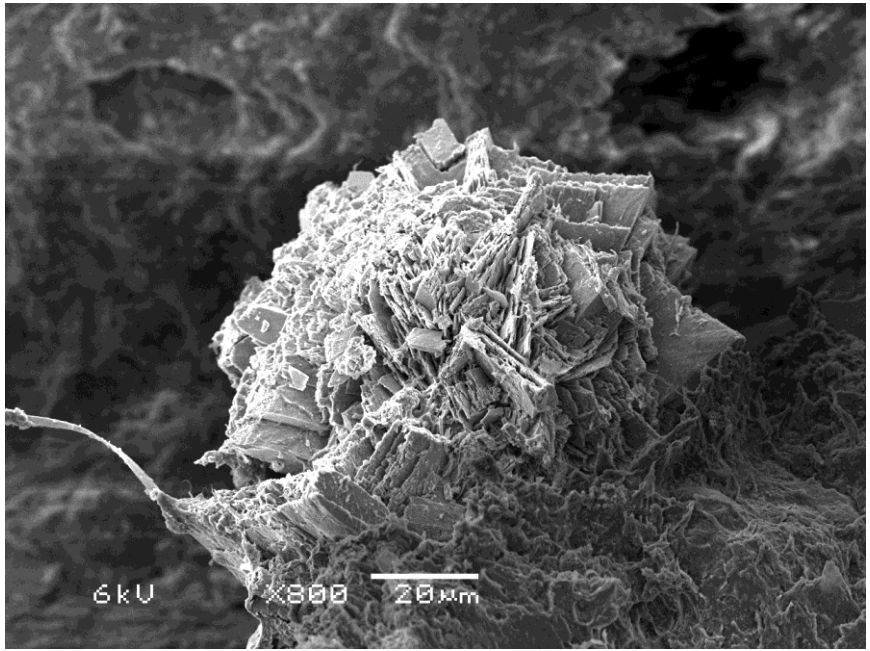
- Metastable zone SI=1 – 1,5
- For struvite, $NH_4^+$ = 700ppm
  P=Mg
- For vivianite, P=Fe




$$IAP_{vivianite} = (a_{Fe^{2+}})^3 \left(a_{PO_4^{3-}}\right)^2 \quad / \quad IAP_{struvite} = \left(a_{NH_4^+}\right)\left(a_{Mg^{2+}}\right)\left(a_{PO_4^{3-}}\right)$$

# Gravity-based separation was not possible

- Vivianite crystal size between 20 and 200 µm
- Morphology: assembly of plates
- Density of 2,7
- Gravity-based separation intented with hydrocyclone and Humphrey spirale…but failed

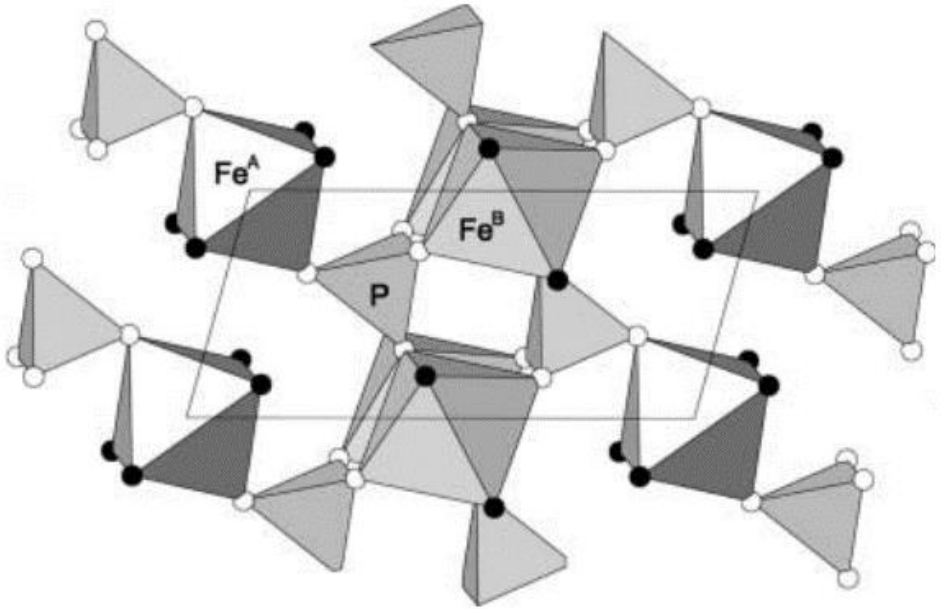


# A new hope: paramagnetic properties of vivianite

- Vivianite presents a crystalline structure in sludge
- $Fe(II)_3(PO_4)_2*8H_2O$
- Electronic configuration: $[Ar]3d^6\ 4s^2$

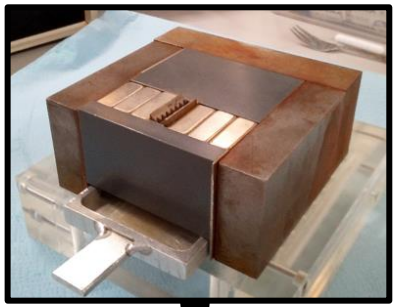
$\Rightarrow$ 4 unpaired electron

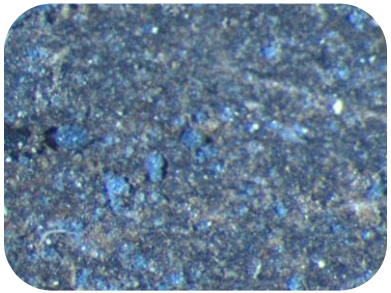
- Vivianite is paramagnetic!

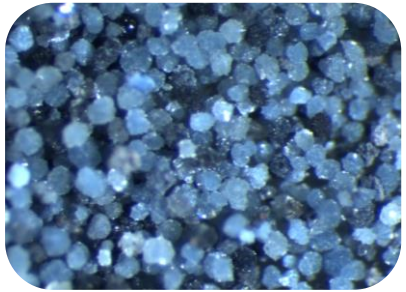



Grodzicki, M., Amthauer. G. (2000). Electronic and magnetic structure of vivianite : cluster molecular orbital calculations. Physics and Chemistry of the minerals, 27(10), 694–702.

# Vivianite can be recovered magnetically and splited







Alkaline treatment

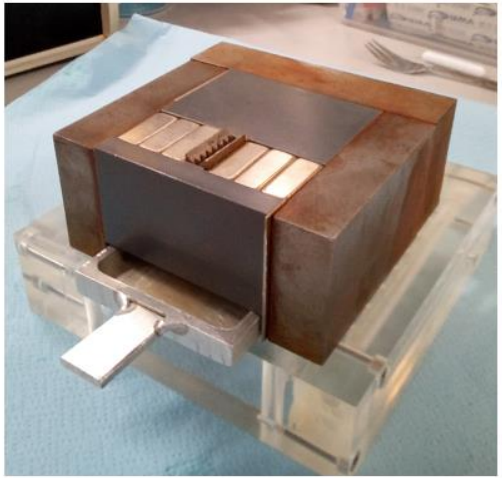
P solution

Fe hydroxide

Prot, T., Nguyen, V. H., Wilfert, P., Dugulan, A. I., Goubitz, K., De Ridder, D. J., … van Loosdrecht, M. C. M. (2019). Magnetic separation and characterization of vivianite from digested sewage sludge. Separation and Purification Technology. doi:10.1016/j.seppur.2019.05.057

# The upscaling of the separation was possible

Lab-scale



0.001 m3/h

Bench-scale

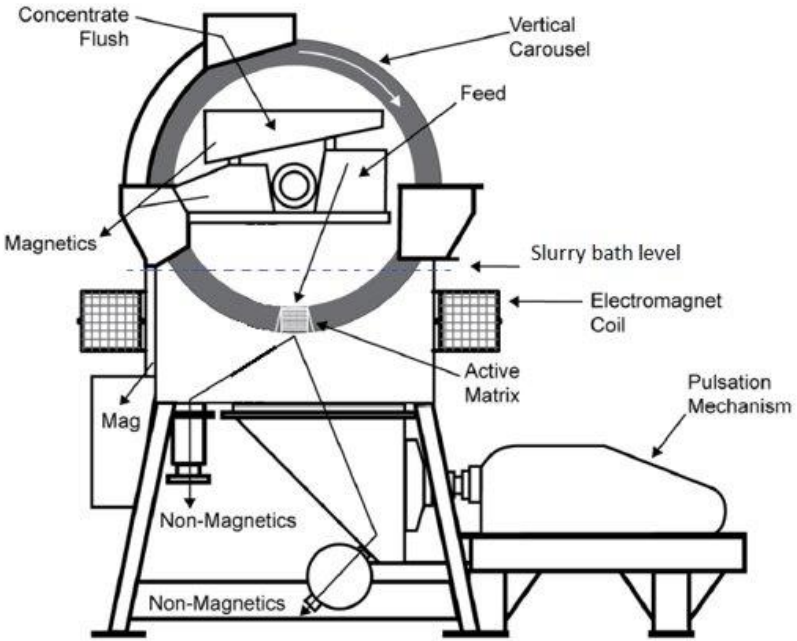

0.01 m3/h

Pilot-scale

1.0 m3/h

Wijdeveld, W. K., Prot, T., Sudintas, G., Kuntke, P., Korving, L., & van Loosdrecht, M. C. M. (2022). Pilot-scale magnetic recovery of vivianite from digested sewage sludge. Water Research, 212, [118131]. https://doi.org/10.1016/j.watres.2022.118131

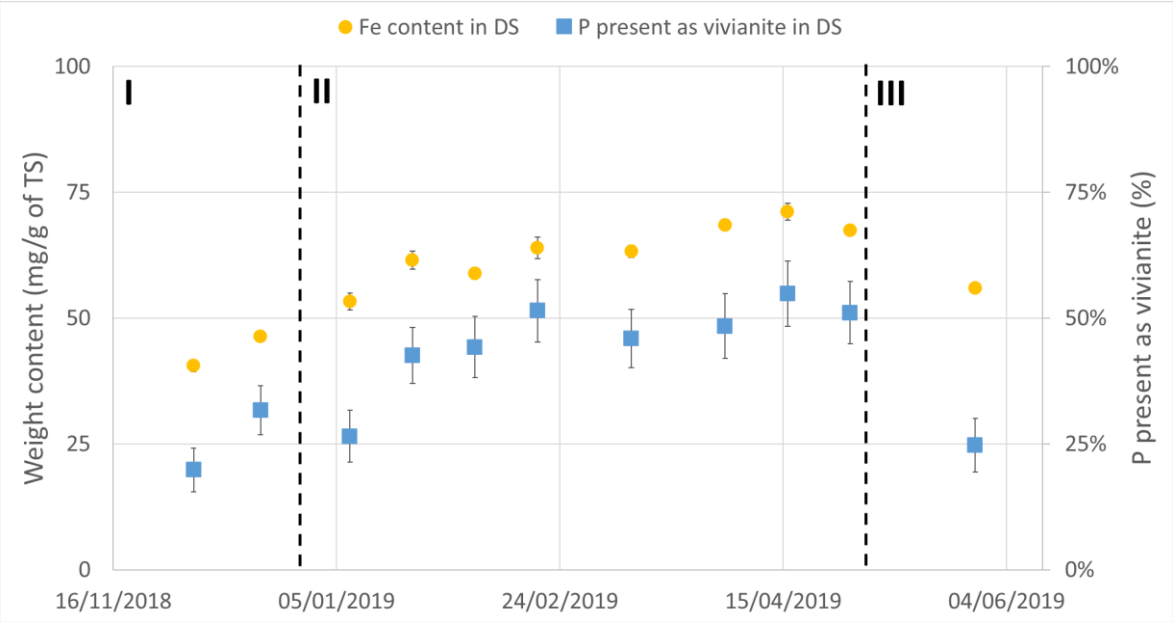
# The upscaling of the separation was possible




- Operated at 1m$^3$/h of sludge being to 20,000 people
- Determining parameters:
  - Pulsation frequency
  - Rod diameter
- Vivianite recovery: 80%
- Grade: 70-80%

Wijdeveld, W. K., Prot, T., Sudintas, G., Kuntke, P., Korving, L., & van Loosdrecht, M. C. M. (2022). Pilot-scale magnetic recovery of vivianite from digested sewage sludge. Water Research, 212, [118131]. https://doi.org/10.1016/j.watres.2022.118131

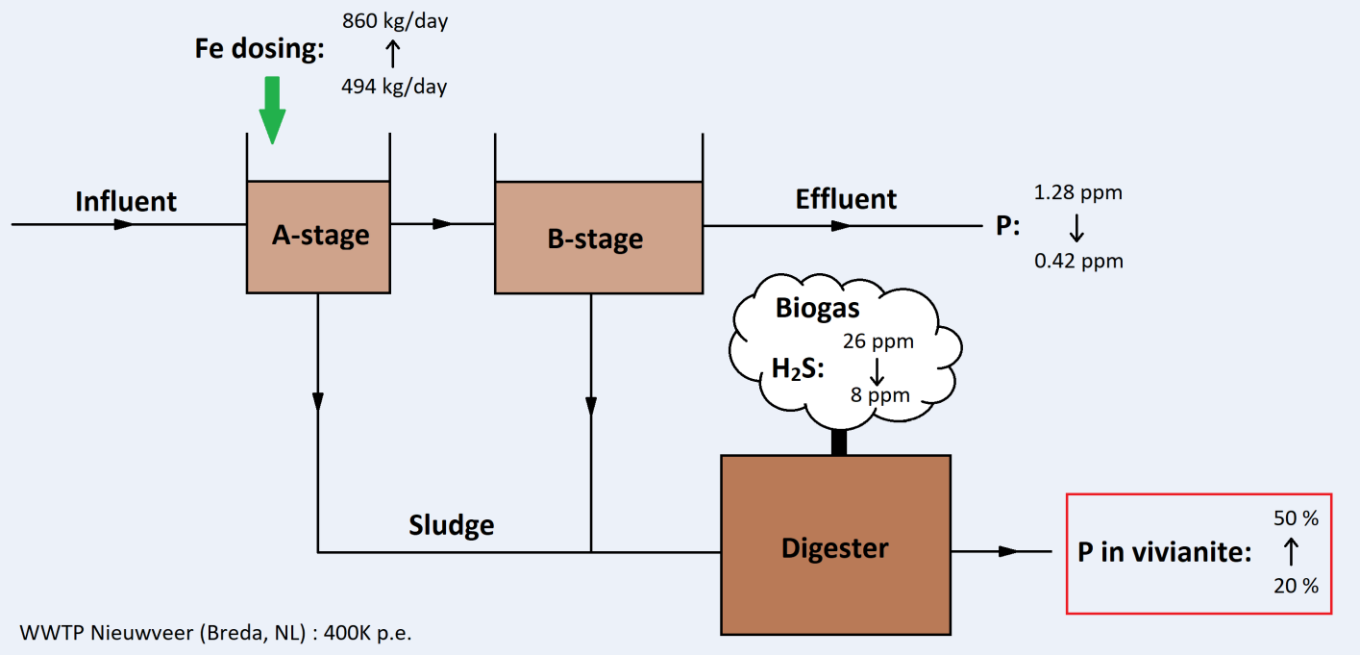
# Vivianite formation can be promoted by increased Fe dosing



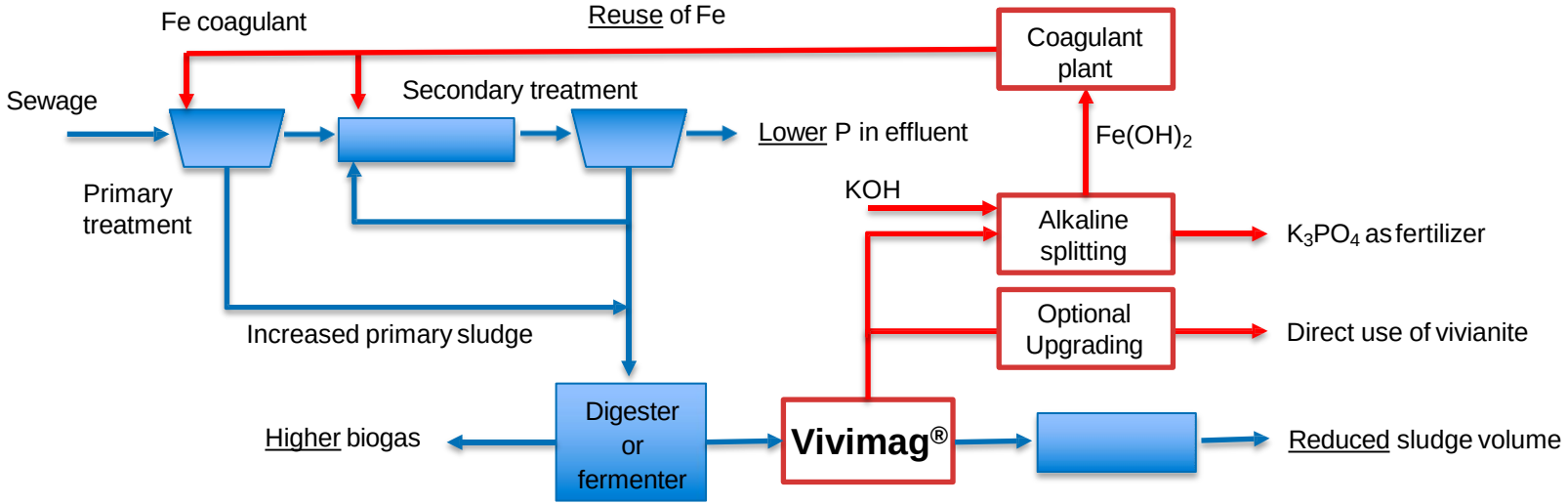

- All the extra Fe dosed turned into vivianite
- S consumes Fe before vivianite can form

T. Prot, W. Wijdeveld, L. Ekua Eshun, A.I. Dugulan, K. Goubitz, L. Korving, M.C.M. Van Loosdrecht. (2020). Full-scale increased iron dosage to stimulate the formation of vivianite and its recovery from digested sewage sludge, *Water Research*, 182, 115911, https://doi.org/10.1016/j.watres.2020.115911.

# Additional Fe dosing had other benefits for the WWTP



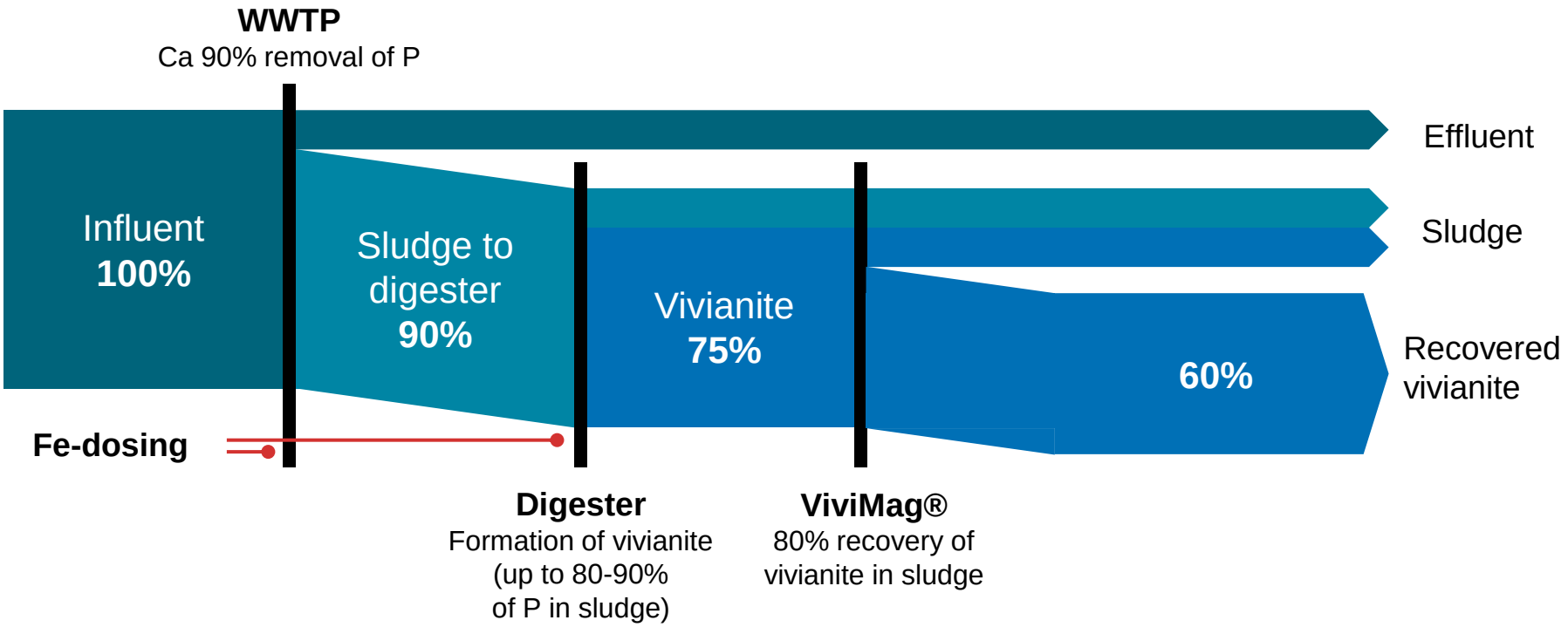
# Overall concept of vivianite recovery for WWTP




Patent owner: kemira

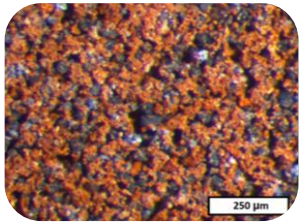
T. Prot, W. Pannekoek, C. Belloni, A.I. Dugulan, R. Hendrikx, L. Korving, M.C.M. van Loosdrecht (2022). Efficient formation of vivianite without anaerobic digester: Study in excess activated sludge, Journal of Environmental Chemical Engineering, Volume 10, Issue 3, https://doi.org/10.1016/j.jece.2022.107473.

# Phosphorus mass balance using Vivimag



# Research projects not discussed today

- Efficient formation of vivianite without anaerobic digester: Study in excess activated sludge
- Formation of vivianite in iron-amended pig manure and its subsequent magnetic recovery
- Vivianite scaling in wastewater treatment plants: Occurrence, formation mechanisms and mitigation solutions




T. Prot, L. Korving, A.I. Dugulan, K. Goubitz, M.C.M. van Loosdrecht. (2021). Vivianite scaling in wastewater treatment plants: Occurrence, formation mechanisms and mitigation solutions, Water Research, Volume 197, https://doi.org/10.1016/j.watres.2021.117045.
T. Prot, W. Pannekoek, C. Belloni, A.I. Dugulan, R. Hendrikx, L. Korving, M.C.M. van Loosdrecht (2022). Efficient formation of vivianite without anaerobic digester: Study in excess activated sludge, Journal of Environmental Chemical Engineering, Volume 10, Issue 3, https://doi.org/10.1016/j.jece.2022.107473.
Thesis chapter: Prot, T. and Schott, C., Fleury, E., Dugulan, A.I., Hendrikx, R., van der Weijden, R.D., Cunha, J.R., Korving, L., Buisman, C., van Loosdrecht, M.C.M. Formation of vivianite in iron-amended pig manure and its subsequent magnetic recovery

# Follow-up research after my PhD

- Deeper understanding of the magnetic separation at pilot-scale: oxidation of vivianite, crystal size, sludge viscosity
- Demonstration installation in 2024 in Breda
- Finding uses for vivianite: Fe-fertilizer, pigment, LiFeP batteries…
- Applying what we have learned about vivianite to phosphorus recovery from animal manure and lake sediment

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# Thank you for your attention!

Any question?

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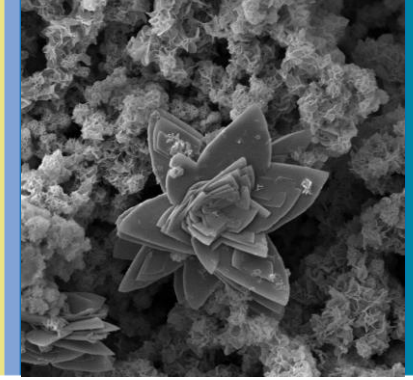

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