PHORWater

Integral Management Model
for Phosphorus recovery
and reuse from Urban Wastewater

LIFE12 ENV/ES/000441

Depuración de Aguas del Mediterráneo

Vniversitat de València

Cal Agua

Université Claude Bernard Lyon 1

LAGEP

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Design and Performances of the Precipitation Reactor

Workshop

P-recovery as struvite

Regulation constraints for its use as a fertilizer

Lyon-Villeurbanne, le 12 Mai 2016

DAM Depuración de Aguas del Mediterráneo

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Struvite Precipitation

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O$$

Solubility product $$K_S = \left(Mg^{2+}\right)_{eq}\left(NH_4^{+}\right)_{eq}\left(PO_4^{3-}\right)_{eq}$$

Supersaturation ratio $$\beta = \left[\frac{\left(Mg^{2+}\right)\left(NH_4^{+}\right)\left(PO_4^{3-}\right)}{K_S}\right]^{1/3}$$

- Primary nucleation
- Secondary nucleation
- Growth
- Agglomeration
- Breakage

Struvite Precipitation

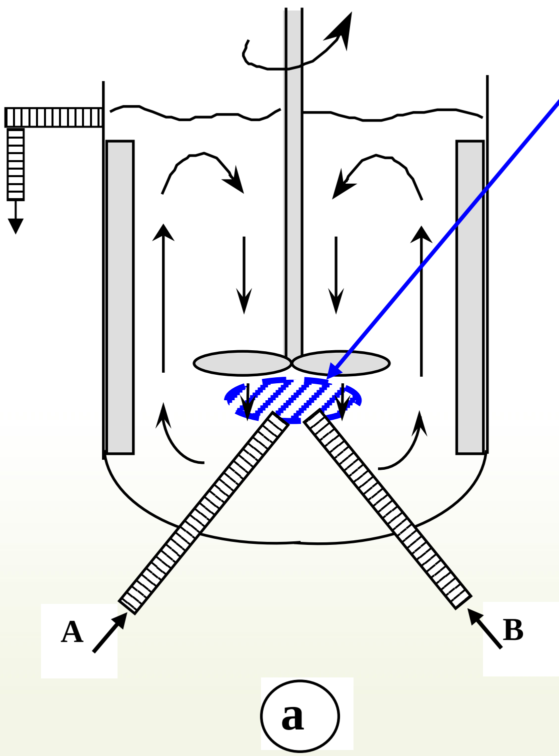
$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O$$

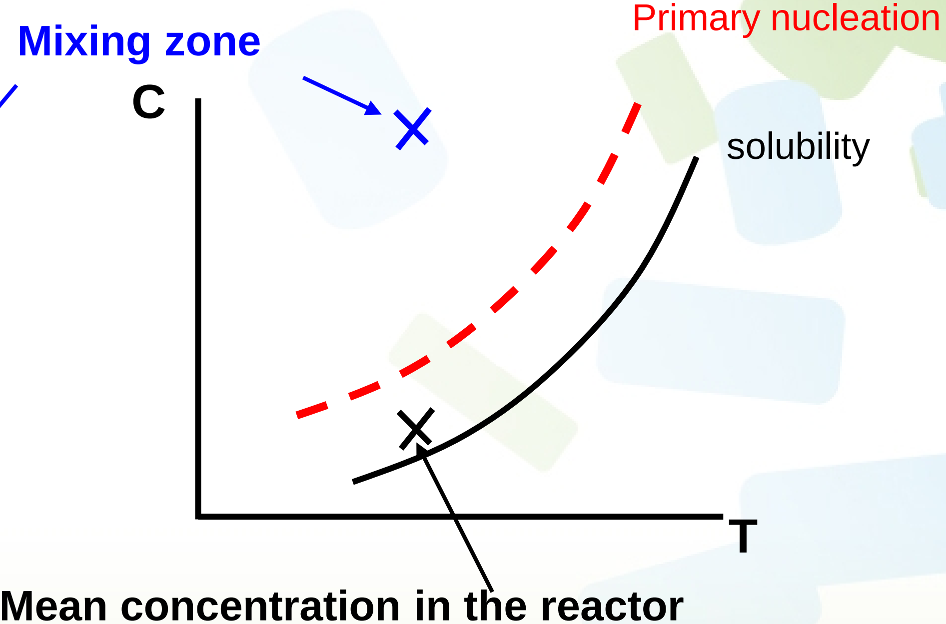
⇒ Control of the supersaturation
Control of the hydrodynamics

The same chemistry, the same reactants, the same working temperature, even the same concentrations,
can lead to **completely different solids** (different sizes, different polymorphs, amorphous or crystalline solids…), **vessel fouling**,
if hydrodynamics is not controlled.

Primary nucleation and mixing effects

nucleation occurs before complete reactant mixing is achieved

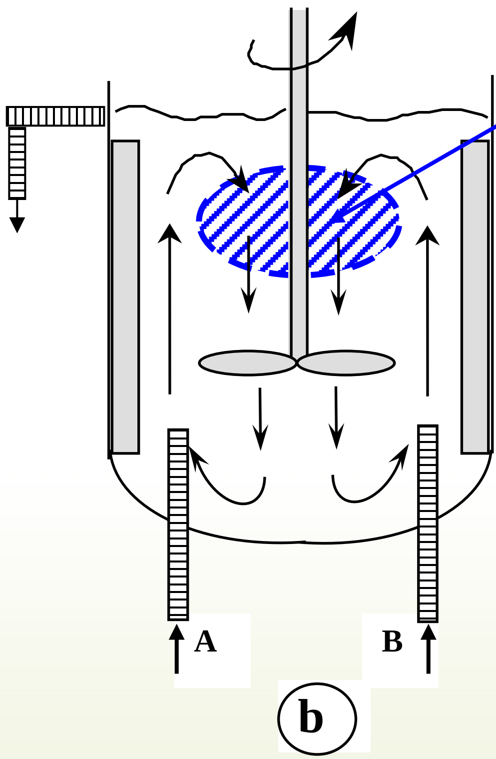


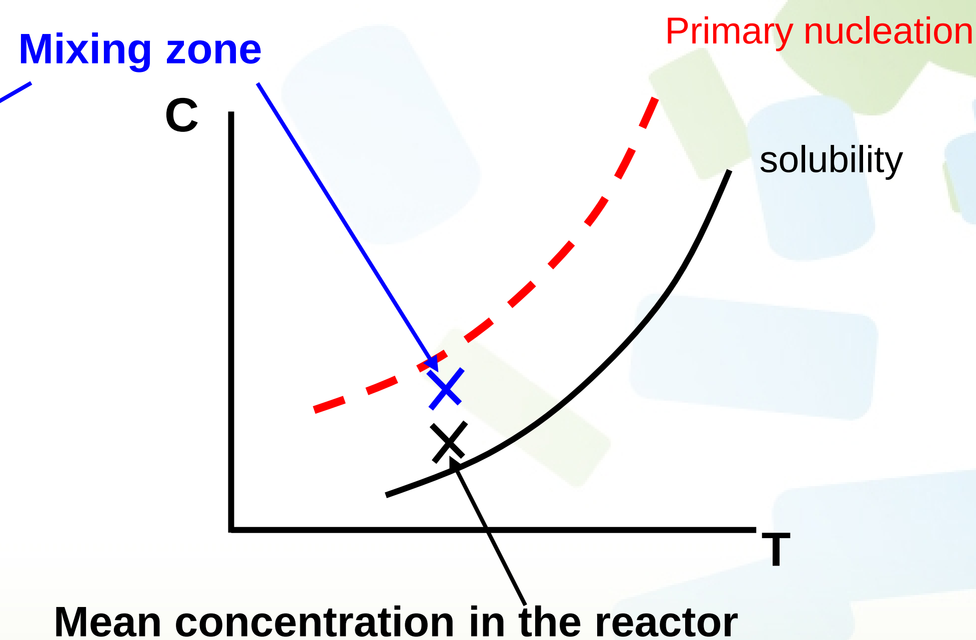


Early mixing :
⇒ High local supersaturation
⇒ Elevated rates of nucleation (locally)
⇒ « Small » particles

Primary nucleation and mixing effects

Primary nucleation can be avoided provided the inlet concentrations are not too high





Late mixing:
⇒ Dilution of both reactants with the bulk
⇒ Suppression or diminution of local nucleation
⇒ « Large » particles

Reactor design - requirements

- Low level of phosphate concentration in wastewater

⇨ Process intensification by increasing solid phase concentration

- Fluctuations in wastewater flowrates and composition

⇨ Flexibility ; easy to operate

- Little vessel fouling

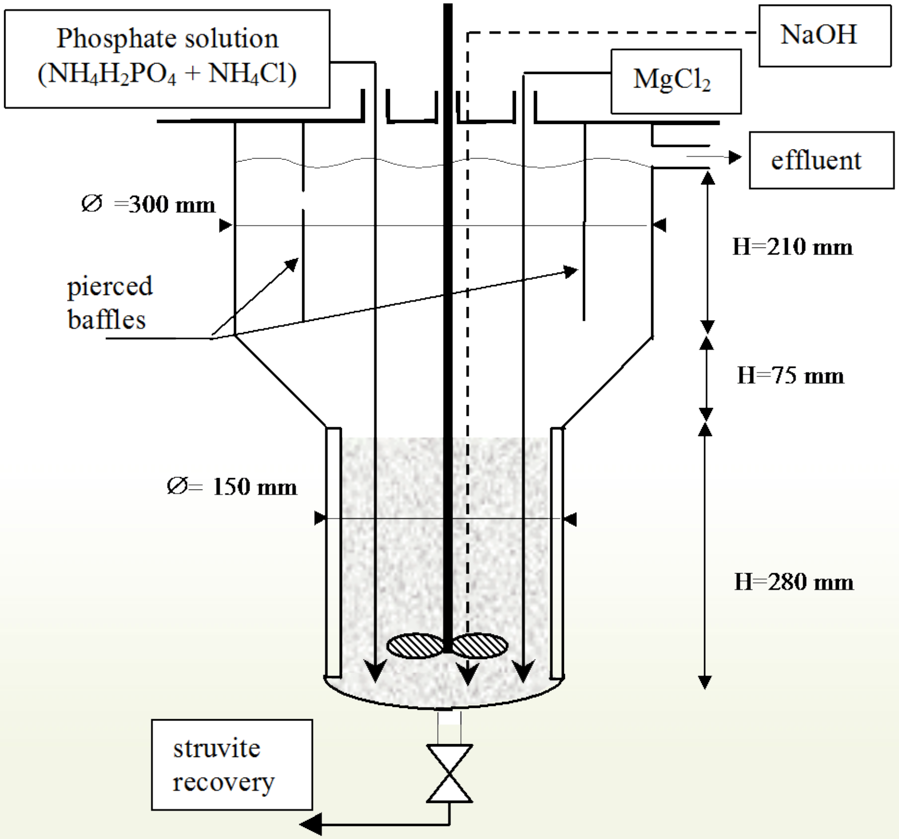
⇨ Control of the local supersaturation (hydrodynamics)

- Large particles of size over 200µm

⇨ Control of the crystallization mechanisms (Supersaturation, hydrodynamics)
Optimization of the solid withdrawal frequency

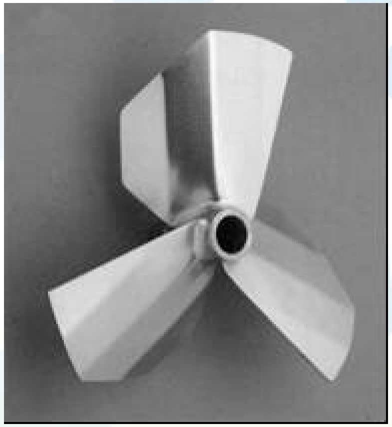
Lab-scale precipitator

Continuous reactor for the liquid phase
Batch reactor for the solid phase



Settling zone

Reaction zone

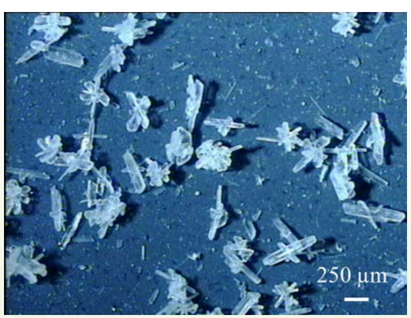


Lab-scale precipitator

Encourageous results : CEEP study, Pastor's phD, PHORWater

$$Eff_{precipitation} = \frac{P_{Total\ inlet} - P_{disolved\ effluent}}{P_{total\ inlet}} = \textit{Thermodynamic efficiency}$$

$$Eff_{recovery} = \frac{P_{Total\ inlet} - P_{Total\ effluent}}{P_{Total\ inlet}} \approx Eff_{precipitation}$$



After 5 days

- Few fines are lost with the effluent
- More phosphorous is lost in the effluent with real inlet supernatant (due to the presence of organic matter)
- $Eff_{recovery} \rangle$ 80% to 90%
- Low vessel fouling
- Influence of [Ca2+] : Competition between precipitation of amorphous calcium phosphate and struvite

Design, construction and start-up of the crystallization process

Lab-scale crystallization assays

Crystallizing process results for the three experiments

	Exp. 1	Exp. 2	Exp. 3
HRT (h)	4.35	2.05	1.05
pH	8.7±0.1	8.7±0.1	8.7±0.1
Molar ratio Mg/P	1.5±0.3	1.6±0.1	1.6±0.1
Molar ratio N/P	2.3±0.2	2.6±0.1	2.4±0.2
PO_4-$P_{influent}$	150±26	134±6	132±9
Total $P_{effluent}$	13.8±5.4	24.1±2.3	35.9±11.2
PO_4-$P_{effluent}$	5.9±0.8	4.7±0.5	5.5±0.9
Precipitation Efficiency (%)	95.8±1.3	96.4±0.3	95.8±0.9
Recovery Efficiency (%)	89.7±5.9	82.1±1.7	72±10
Struvite production (g struvite/L supernatant treated)	1.1±0.3	1.00±0.04	0.96±0.08
Average particle size (µm)	183±59	207±8	213±19

PHORWater reactor design

Extrapolation – Modelling

Scale-up : 20 L => 5 m^3

1) Extrapolation criteria (same mixing input power)

2) CFD (Computational Fluid Dynamics)

3) Particle population balance

PHORWater reactor design

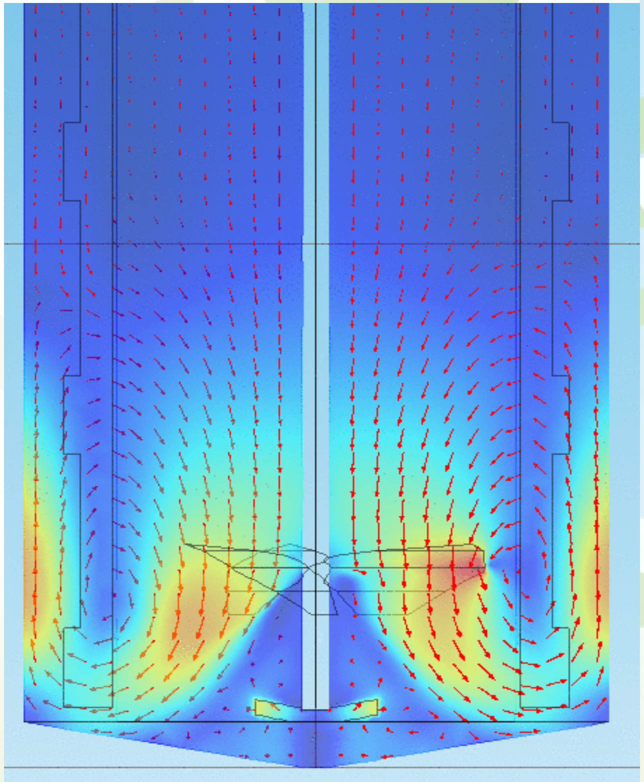
CFD – Modelling

1) Fluid velocity maps

A first step to position the inlet pipes

A tool to estimate the solid sedimentation in the reaction zone

Done with Comsol® multiphysics



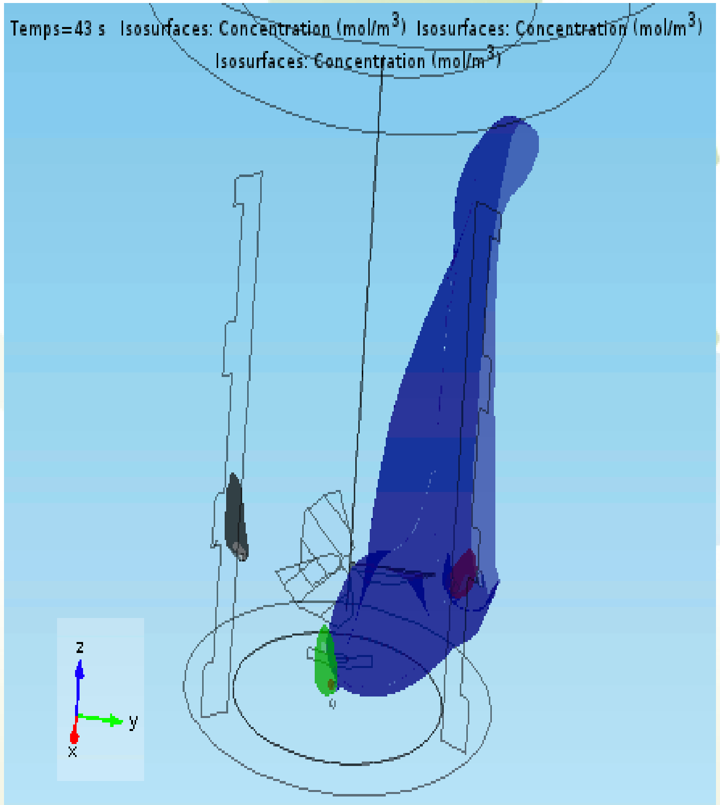
PHORWater reactor design

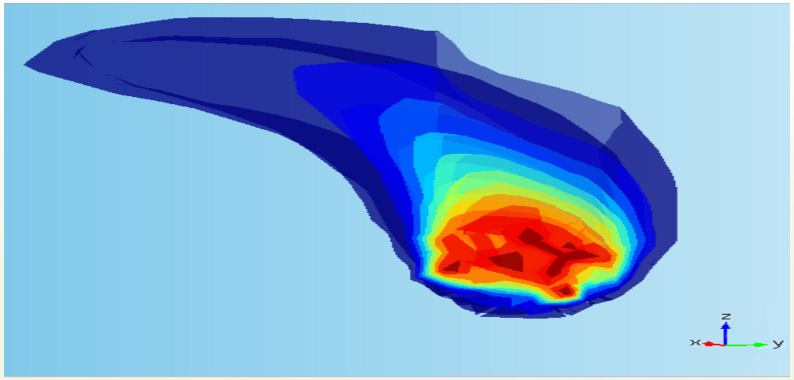
CFD – Modelling

2) Visualization of the reactant dilution

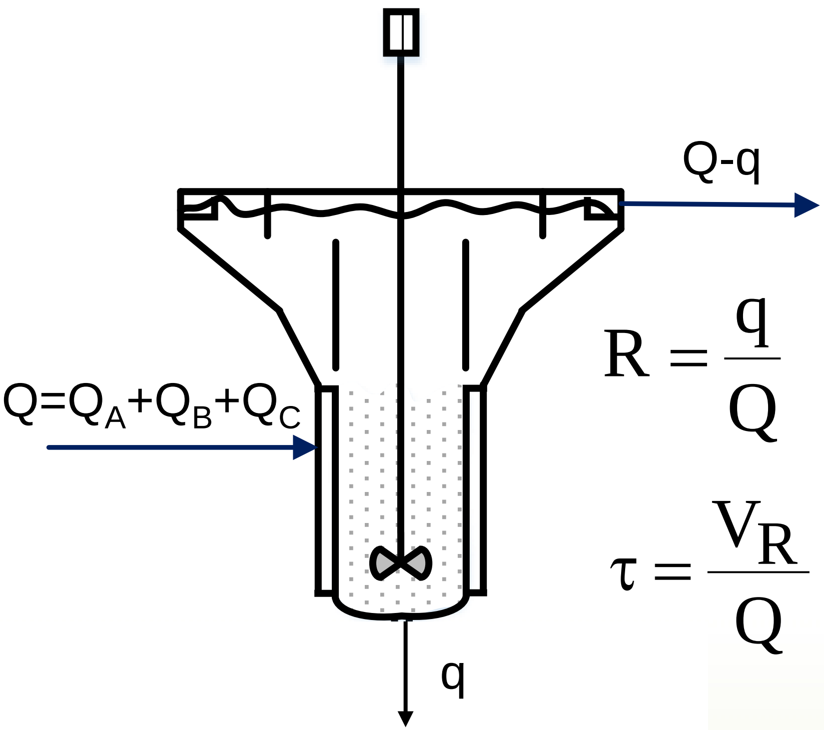
A second step to position the inlet pipes

A tool to estimate supersaturation at the pipe exits





Particle Population Balance



$$R = \frac{q}{Q}$$

$$\tau = \frac{V_R}{Q}$$

$$\frac{d[G(L)n(L)]}{dL} + \frac{n(L)}{R\tau} = r_N \delta(L)$$

<u>Same supersaturation</u>

R ↘ ⇨ τ ↘ ⇨ V_R ↘

⇨ intensification

<u>Supersaturation is let « free »</u>

R ↘, τ → ⇨ Supersaturation ↘, Solid concentration ↗, Mass mean size ↗

However, the trends depend on the kinetics of the different crystallization mechanisms

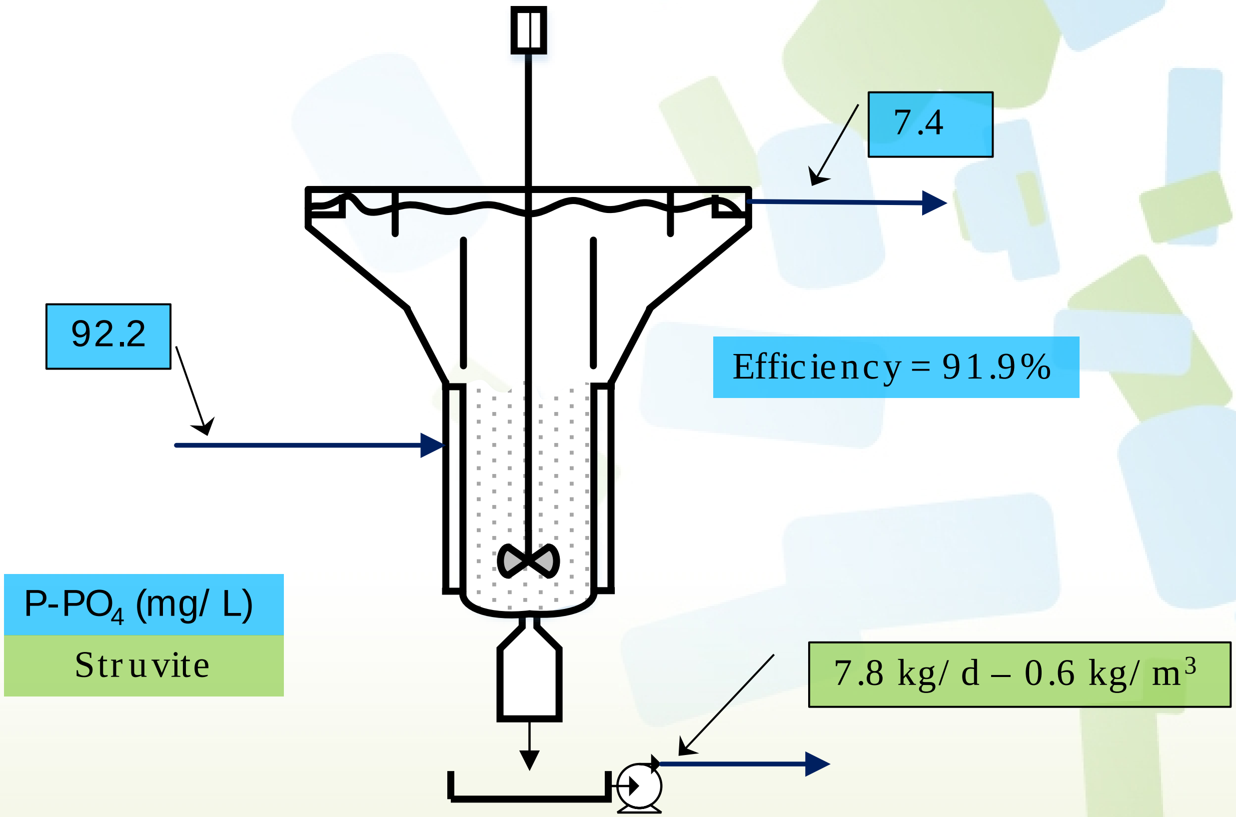
Plasari and Muhr ICheaP8 2007 White and Randolph Ind. Eng. Chem. Res. 1989

P recovery demonstration plant

Phosphorus recovery process assessment

May to Oct 2015

Operational parameter	Set Value
pH	8.7
Molar ratio (Mg/P)	1.6
Inlet flow (m^3/d)	12.5
Reaction zone HRT (h)	4.0
Total HRT (h)	9.8
Agitator speed (rpm)	83
[Mg^{2+}] (mg Mg/L)	4800



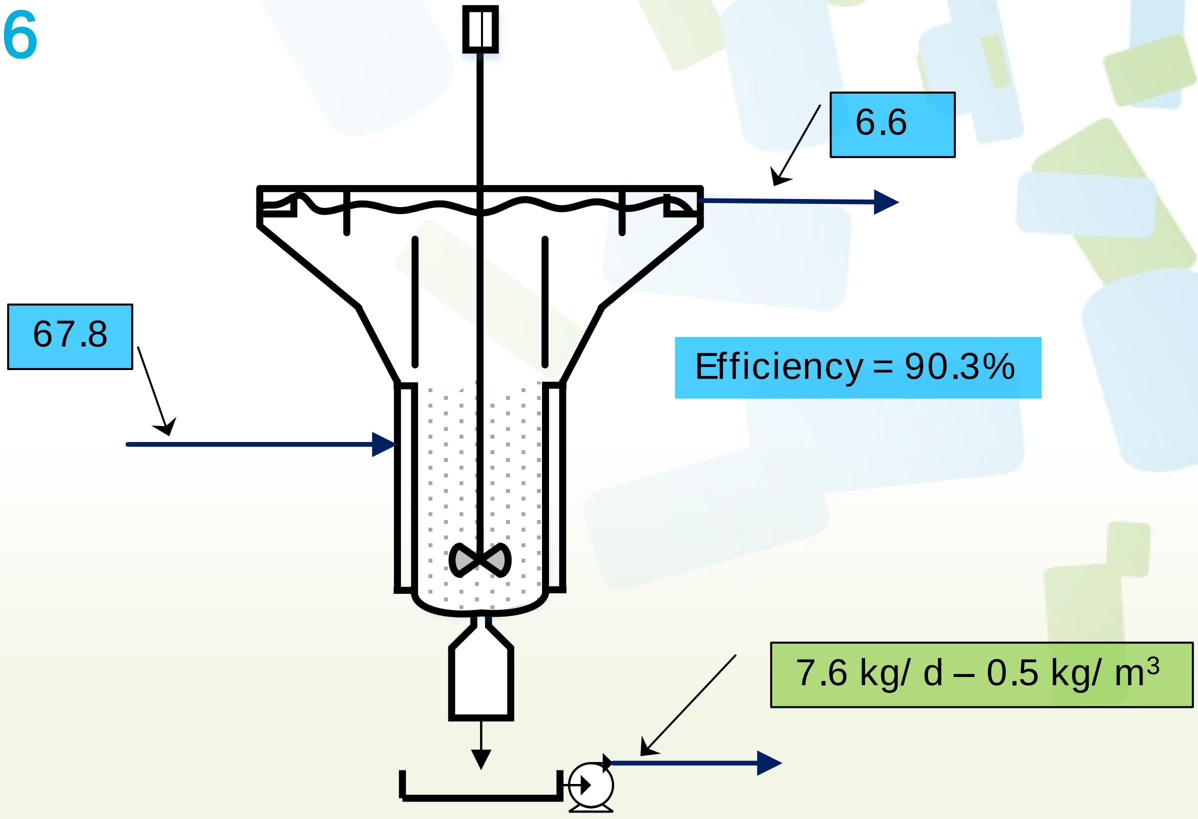
High calcium concentration in the solid produced in september and october (formation of amorphous calcium phosphate or organic matter?)

P recovery demonstration plant

Phosphorus recovery process assessment

Nov 2015 to Apr 2016

Operational parameter	Set Value
pH	8.7
Molar ratio (Mg/P)	1.3
Inlet flow (m^3/d)	20,0
Reaction zone HRT (h)	2.5
Total HRT (h)	6.1
Agitator speed (rpm)	69
$[Mg^{2+}]$ (mg Mg/L)	4800



P-PO$_4$ (mg/ L)
Struvite

Conclusions

- The precipitator has been working well for almost 1 year
  - It gives good P precipitation and recovery efficiencies.
  - It gives large particles
  - No significant fouling is observed

Next steps

- Assess the calcium influence
- Improve struvite washing

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THANK YOU FOR YOUR ATTENTION!

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