This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818470

NUTRIMAN

Nutrient Management and Nutrient Recovery Thematic Network

Specific presentation: the Struvite (ID:208)
Specific presentation: the Struvite (ID:250)

Sofía Grau MSc – DAM

Francisco Corona PhD – CARTIF

11 june 2021

- **Sofía Grau.**
- **Project manager Innovation department.**

Depuración de Aguas del Mediterráneo

WWTP Management.

PHORWater

LIFE12 ENV/ES/ 000441

Integral Management Model for Phosphorus recovery and reuse from Urban Wastewater

With the contribution of the LIFE finantial instrument of the European Union

NUTRIMAN

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818470

- **Technology ID: 207**
- **Product ID: 208**

NUTRIMAN

PROBLEM

PROBLEM

PROBLEM

CHALLENGE


2
ZERO
HUNGER


11
SUSTAINABLE CITIES
AND COMMUNITIES


12
RESPONSIBLE
CONSUMPTION
AND PRODUCTION


14
LIFE
BELOW WATER

SOLUTION

CONTENT

Why recover struvite?

How do we recover struvite?

What is struvite?

Field test results.

Future.

Why recover struvite?

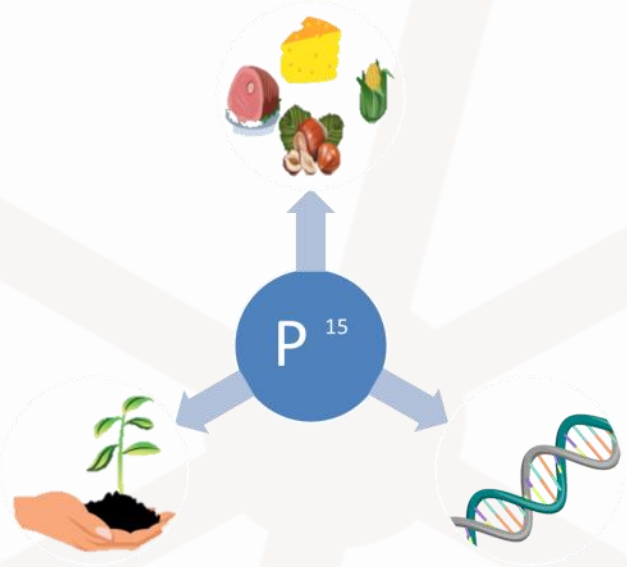
Struvite at WWTP?

Struvite

$P + NH_4 + Mg = NH_4MgPO_4 \cdot 6H_2O$

Why recover struvite?

Why Phosphorous?



1. It is essential for living organisms.

2. It is a limited natural resource.

4. There are no major P deposits in Europe.

5. There is no known substitute.

Why recover struvite?

Phosphorous and environment.

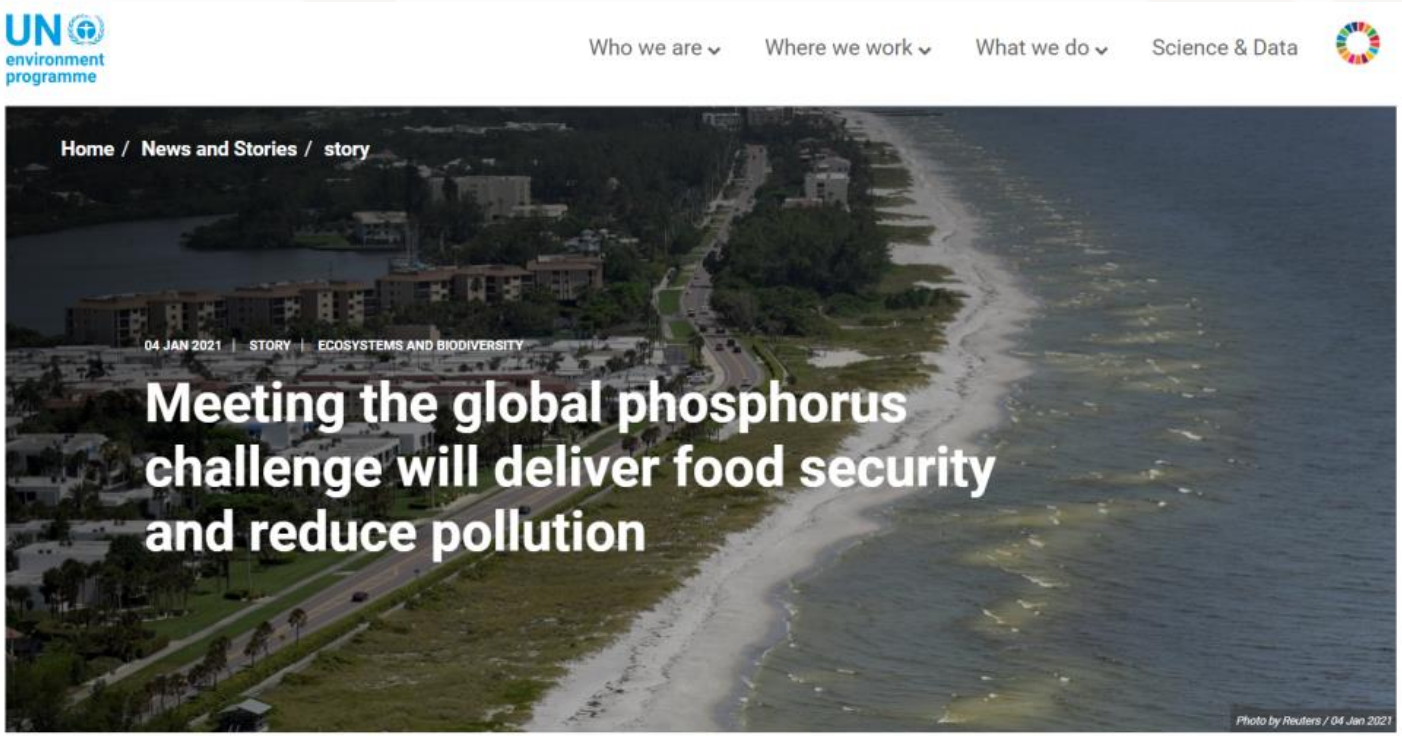
Bayovar P deposit.

(Source: http://infraestructuraperuana.blogspot.com/2014/04/yacimiento-de-fosfatos-de-bayovar.html)

Effects of P discharges.

Why recover struvite?

On 2017 European Commission included phosphorus and phosphates in the Critical Raw Material List.



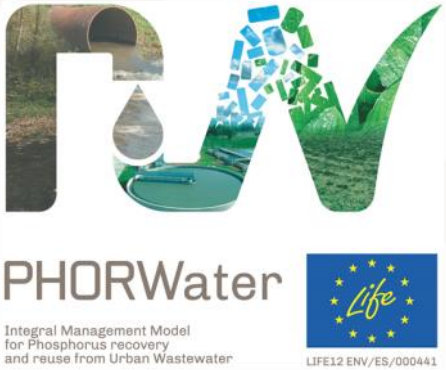
Fuente: https://www.unep.org/

Why recover struvite?

Why NUTRIMAN?

1. Reducing external dependency on P supply.
2. Boosting more efficient agriculture.
3. Encouraging P recovery solutions.

How do we recover struvite?



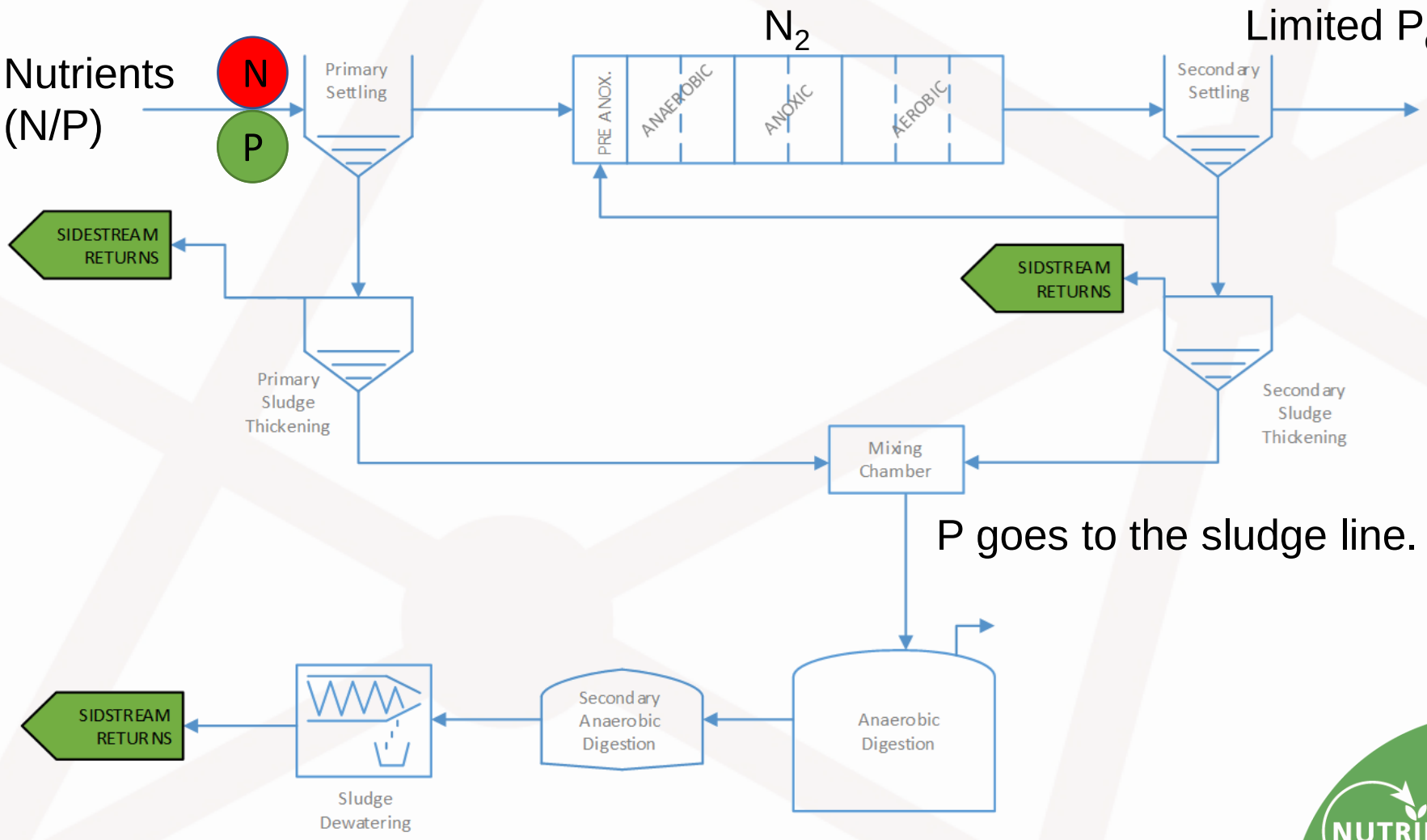
"Integral Management Model for Phosphorus Recovery and reuse from Urban Wastewater"

Sustainable Management of P in WWTPs

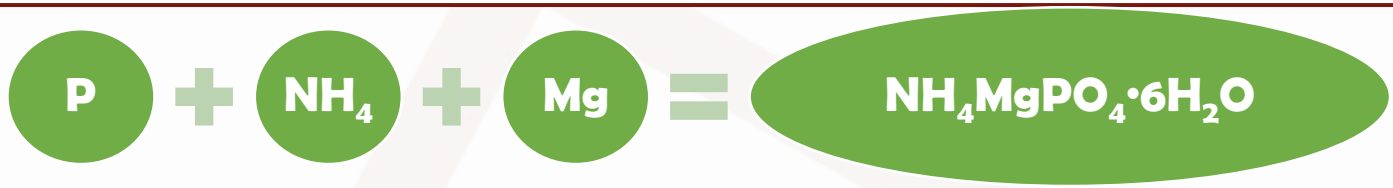
Uncontrolled P precipitation

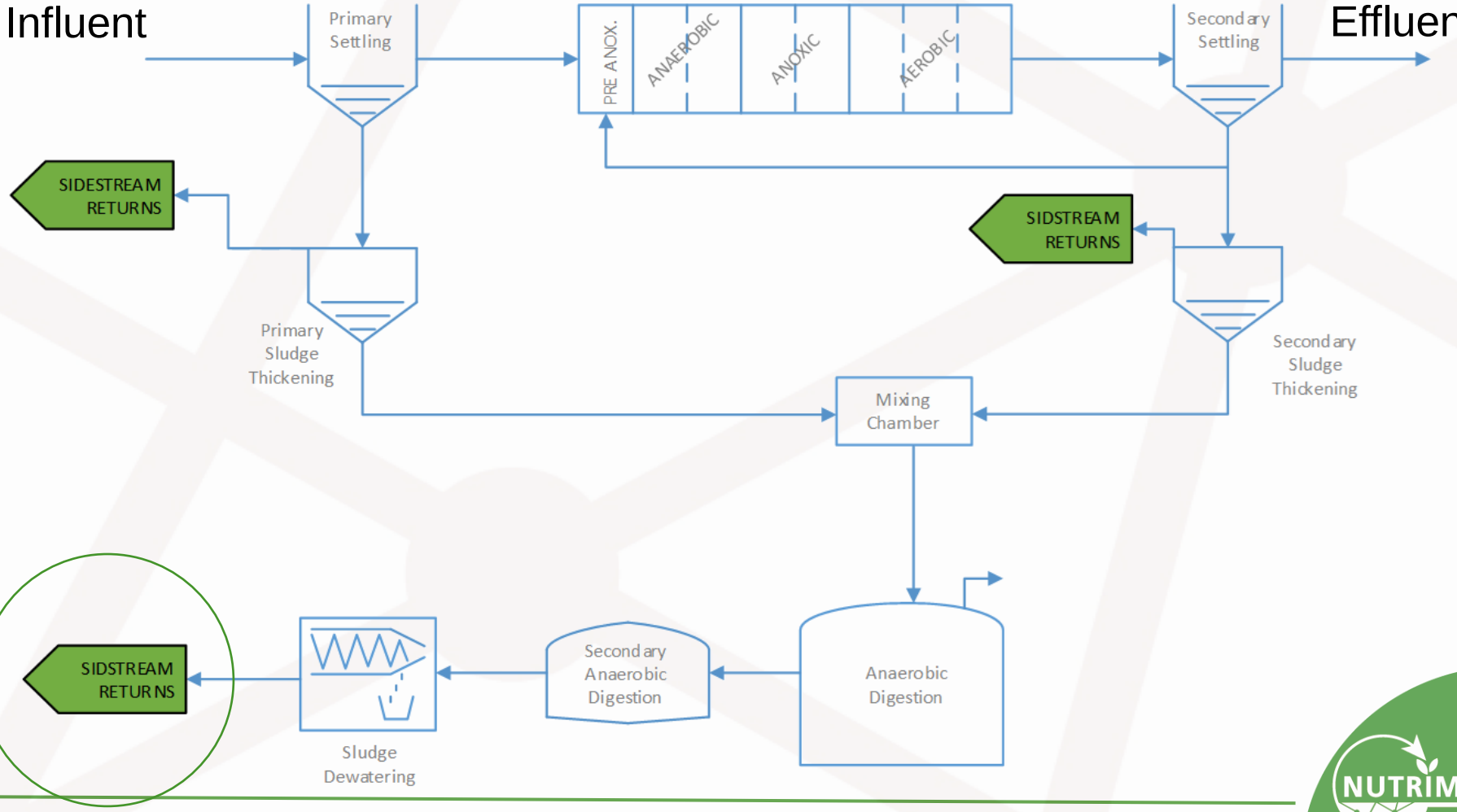
P recovery from sludge line supernatants

How do we recover struvite?

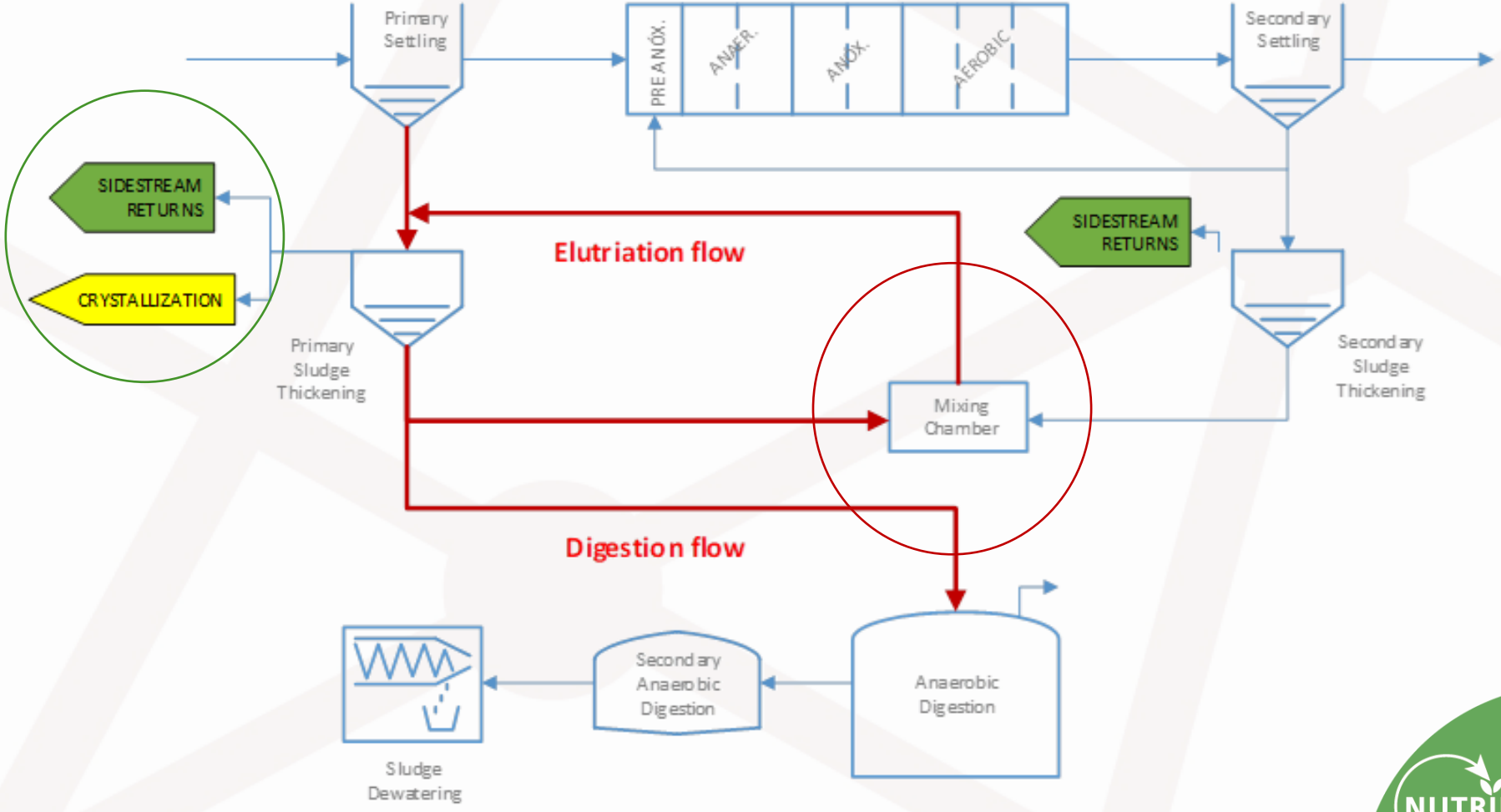


How do we recover struvite?



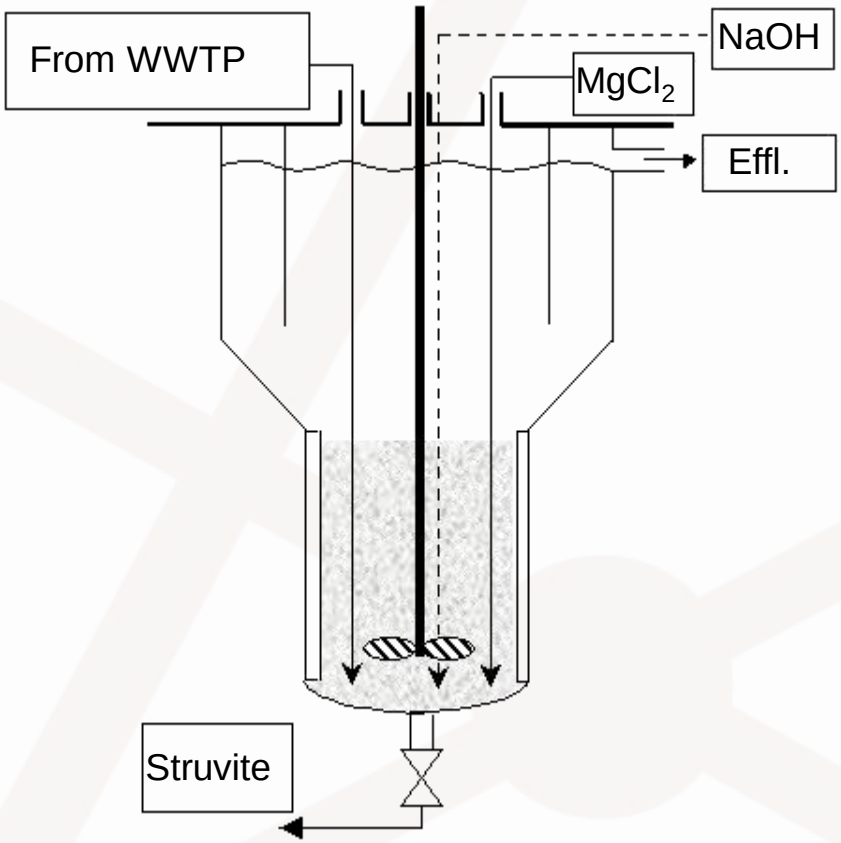


STRUVITE RECOVERY



How do we recover struvite?

- CSTR(reaction)+Settling

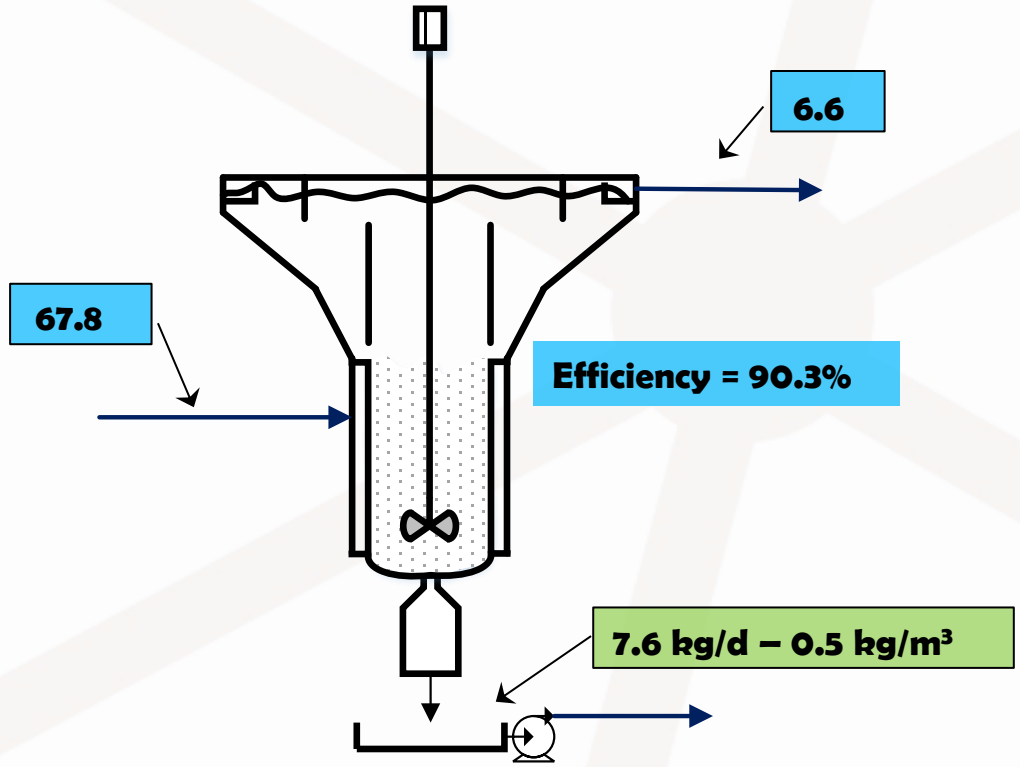


- Prototype: 20L ⟶ 5m^3.
- Flow: 20 m^3/d.
- Two areas:
  - Mixed, where the reaction takes place.
  - Settling, to separate struvite from liquid fraction.
- The P-rich flow from the WWTP is **continuously fed** to the reactor while struvite is **recovered in batches**.

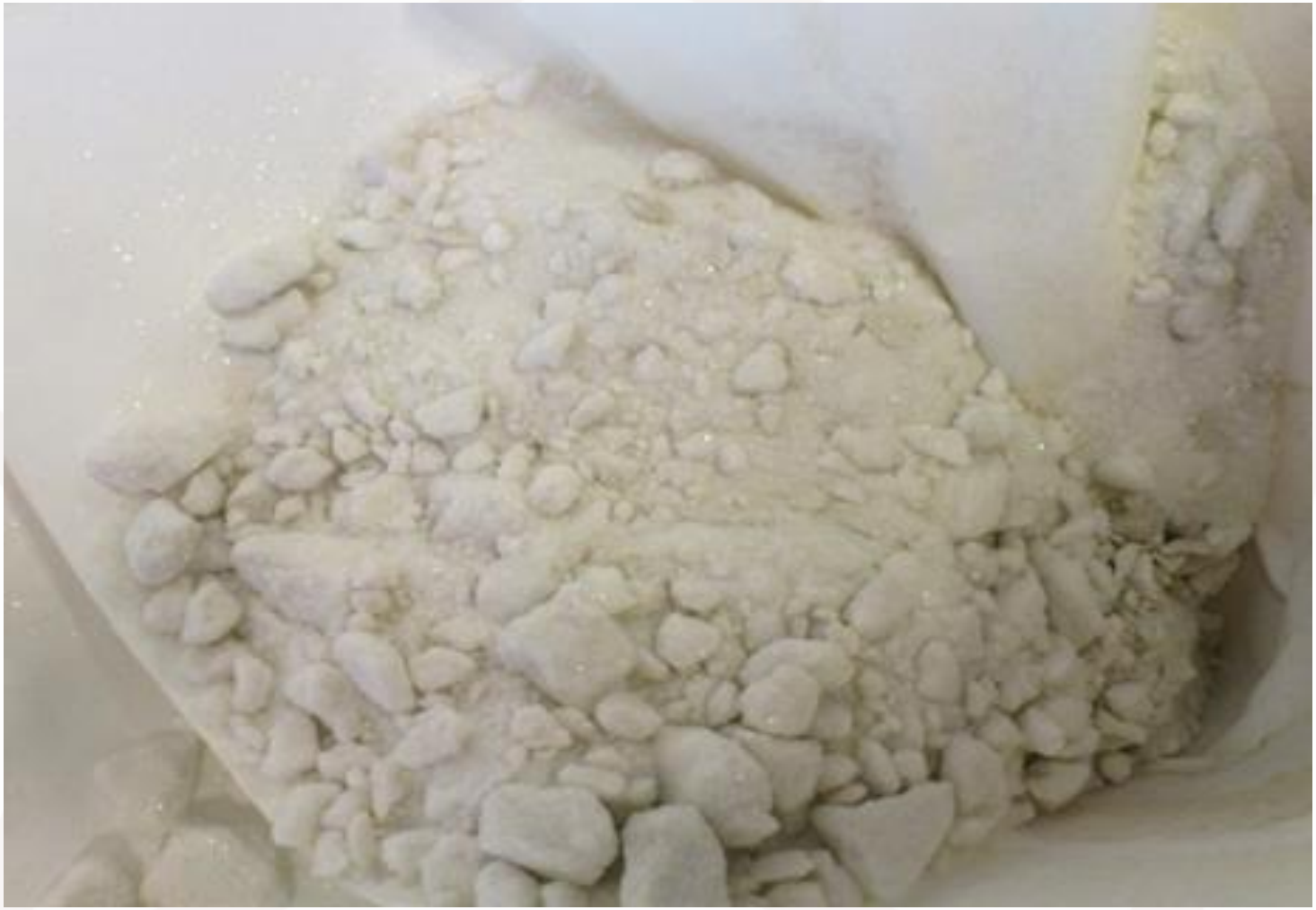
How do we recover struvite?

- Demonstration plant.

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



What is struvite?

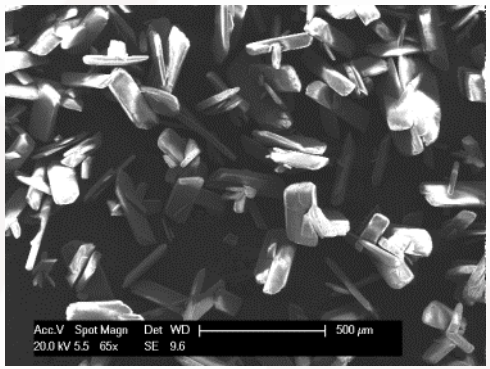


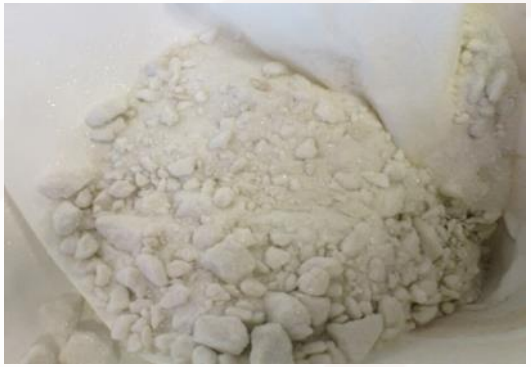
What is struvite?

$$MgNH_4PO_4 \cdot 6H_2O$$

Struvite recovery reaction:

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





The low water solubility and the high solubility in acidic solution bring ideal properties as a slow-release fertilizer

What is struvite?

- Nutrients:

5 N%, 29 P_2O_5%, <1,0 K_2O%

- Characteristics:
- Size: >200 µm
- TOC: <0,5 %
- Purity: 81%
- No presence of heavy metals.

What is struvite?

- Nutrients:

5 N%, 29 P_2O_5%, <1,0 K_2O%

Micropollutant	Unit (µg/kg)	Micropollutant	Unit (µg/kg)
Octylphenol	<0.1	Hexachlorobenzene	1.1
t-Nonylphenol	<0.5	Hexachlorobutadiene	2.6
4-Nonylphenol	<0.05	Pentachlorobenzene	3.4
Alachlor	<3	Trifluralin	<0.3
Chlorfenvinphos	<5	123-Trichlorobenzene	<0.5
Aldrin	<0.1	124-Trichlorobenzene	3.4
Dieldrin	<0.1	135-Trichlorobenzene	<0.5
Isodrine	<0.1	Quinoxyfen	<0.1
Endrin	<0.1	Aclonifen	<1
Endosulfan 1	<0.5	Irgarol	<1
Brominated diphenylethers	<10	Terbutryn	<0.6
Chloroalkanes	<60	Di(2-ethylhexyl)-phthalate	<1.5
Anthracene	<1	Naphthalene	32.7
Benzo(a)pyrene	2.5	Fluoranthene	3.8
Benzo(b)fluor-anthene	3.2	Benzo(g,h,i)-perylene	0.8
Benzo(k)fluor-anthene	1.8	Indeno(1,2,3-cd)-pyrene	1.3
Diclofenac	<0.5	Paracetamol	<50
Acetylsalicylic acid	<10	Ibuprofen	<1

Summary

- Struvite was first described on 1845, found at the Hamburg sewage system.
- The WWTP problems due to uncontrolled struvite precipitation are known since 1970s.
- Its uncontrolled precipitation damages severely pipes and equipment.
- It is considered a promising fertilizer due to its slow release properties.



Field test results

- Field test.

  Potato

Field test results

- Field test.

Corn

Field test results

Potato

Corn

- Results with conventional fertilization and struvite fertilization were similar.
- **Number of plants**: no significant difference.
- P-availability from **soil**: bigger on struvite fertilized crops.
- **Leaf** analysis: No significant difference.
- No **phytotoxicity** neither **any handling problem** with the struvite.

FUTURE – What's missing?

- STRUVITE

5 N%, 29 P_2O_5%, <1,0 K_2O%

- CONVENTIONAL FERTILIZERS

NPK

- Combination of struvite with other fertilizers.

THE NEW COMBINATION

- Scarole

- Persimmon

CONCLUSIONES

- Struvite obtained is a high-quality product.
- The lack of N and K is not a problem.
- It can be combined with other mineral fertilizers.
- It can be applied with organic fertilizers (compost).

Struvite meets all the requirements to be consider as a safe slow release fertilizer.

- The new Regulation1009/2019 opens the way for using struvite as fertilizer in the whole European Union.

CONTACTO

SOFÍA GRAU GONZÁLEZ

sofia.grau@dam-aguas.es

https://www.linkedin.com/in/sofia-grau/

https://nutriman.net/farmer-platform/technology/id_207

https://nutriman.net/farmer-platform/product/id_208

https://www.dam-aguas.es/

DAM Depuración de Aguas del Mediterráneo

Avda. Benjamin Franklin, 21
Parque Tecnológico
46980 Paterna (Valencia)
SPAIN

Thank you

For Your Attention

Special thanks to CEBAS-CSIC for sharing pictures from the field test.

STRUVITE RECOVERED FROM LIVESTOCK WASTE

- Francisco Corona, Ph.D.
- Researcher of Circular Economy Area from Fundación Cartif.

CENTRO TECNOLÓGICO CARTIF

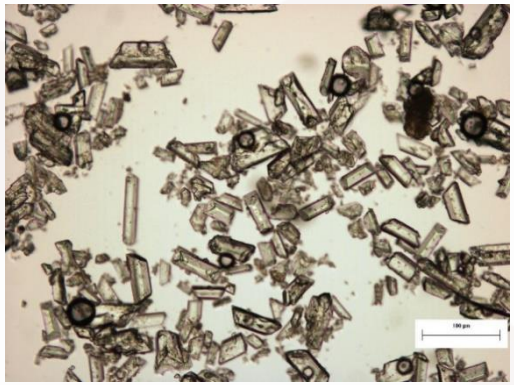
Research & Technology Organisation

STRUVITE

- Ammonium (N) and phosphate (P) can be removed from the wastewater or livestock waste by precipitating a salt of phosphate and ammonium called struvite.

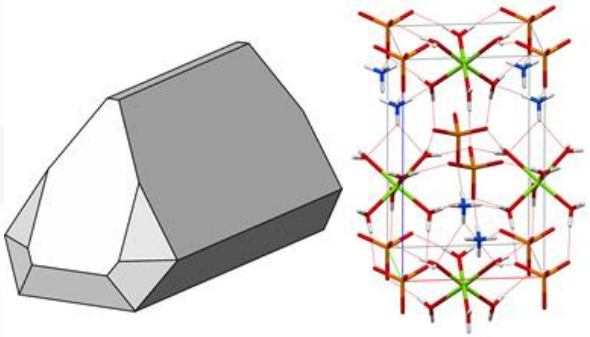
The reaction that takes place is:

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



STRUVITE PROPERTIES

Parameter	*Características*	*Reference*
Nature	Mineral salt	
Chemical name	Magnesium ammonium phosphate hexahydrate	
Formula	$MgNH_4PO_4 \cdot 6H_2O$	
Aspect	White glowing crystal	Bassett & Bedwell, 1933
Structure	Orthorhombic: regular PO_4^{3-} octahedra, distorted $Mg(H_2O)_6^{2+}$ octahedral, and NH_4^+ groups all held together by hydrogen bonding	Abbona & Boistelle, 1979
Molecular weight	245,43 g/mol	
Density	1,711 g/cm^3	Borgerding, 1972
Solubility	Low in water: 0,018 g/100 mL at 25 °C in water High in acids: 0,033 g/100 mL at 25 °C in 0,001 N HCl 0,178 g/100 mL at 25 °C en 0,01 N HCl	Bridger *et al.*, 1961
Solubility constant	10E-13,26	Ohlinger *et al.*, 1998



The low water solubility and the high solubility in acidic media gives it ideal properties as a slow-release fertiliser

STRUVITE INDUSTRIAL SCALE

- Nowadays there are large scale struvite crystallisation facilities with the potential to obtain a commercial product.

- This struvite could be used as a biofertiliser and replace phosphate fertilisers, in which the P comes from the extraction from the phosphate rock.

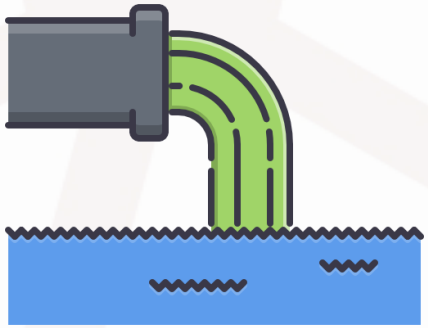
Technology / *Parameter*	*Phospaq™*	*Anphos*	*NuReSys©*	*Unitika Phosnix©*	*Ostara Pearl®*	*Crystalactor©*
Kind of reactor	CSTR with air diffusion	BSTR	CSTR	FBR	FBR	FBR
Product name	Struvite	Struvite	BioStru®	Struvite	Crystal Green®	Struvite, CaP, MgP
Recovery yield (%)	10-40 %N 80 %P	80-90 %P	5-20 %N >85 %P	80-85 %P	10-40 %N 80-90 %P	10-40 %N 70-80 % P (e struvite) >90 %P (CaP)
Large scale facilities (Nº)	11	3	7	2	8	4

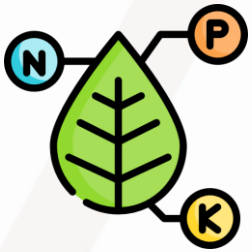
STRUVITE PRODUCTION

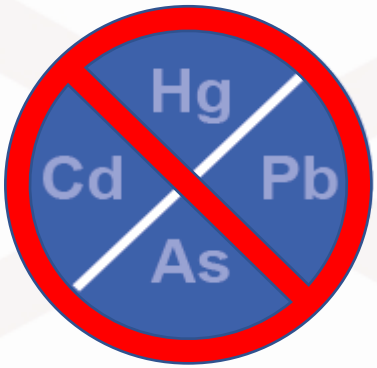
- Nowadays there are large scale struvite crystallisation facilities with the potential to obtain a commercial product. Struvite can mainly be obtained by recovering N and P from two types of effluent:

  1) Wastewater from treatment plants.

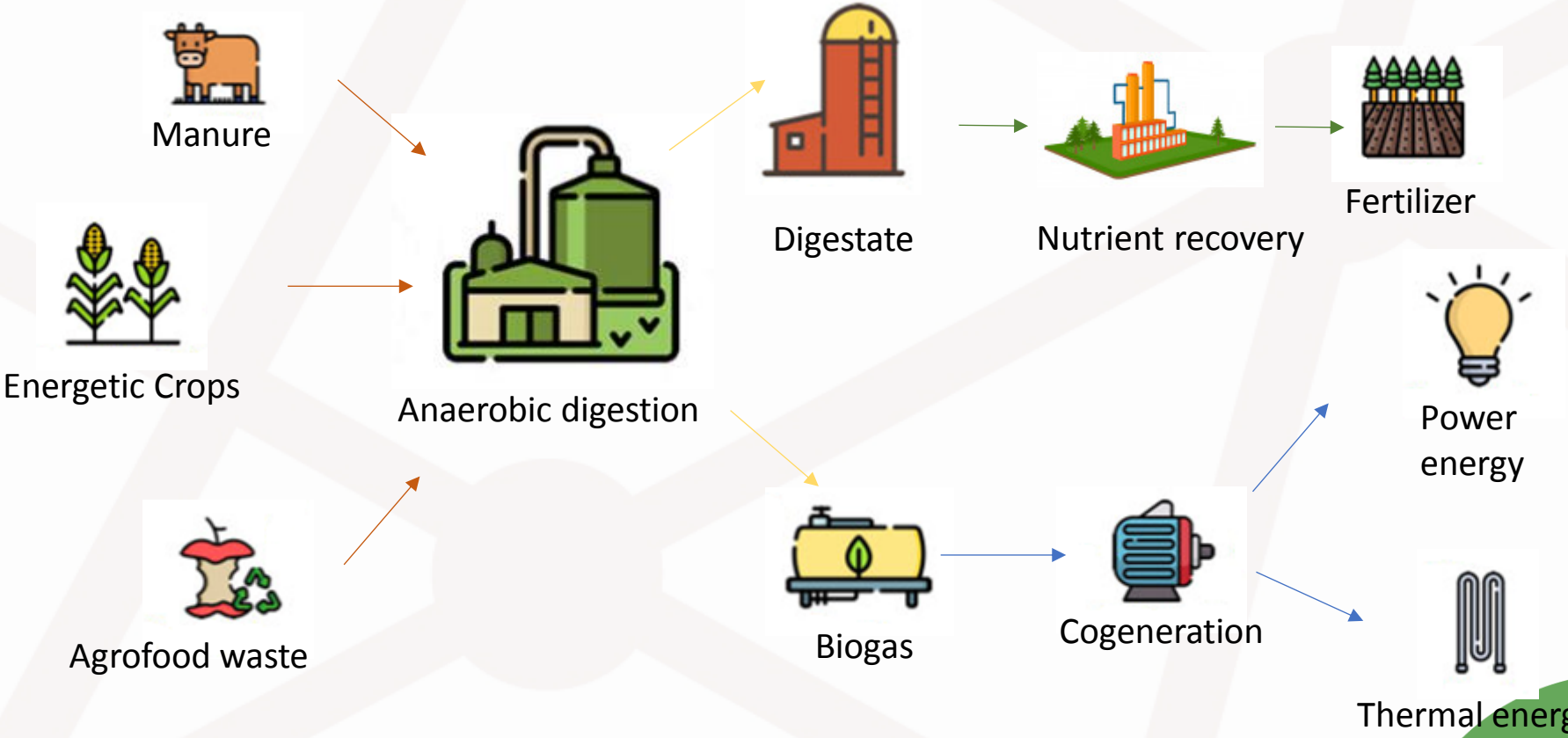
  2) Livestock waste.







VALORIZATION OF AGRO AND LIVESTOCK WASTE BY ANAEROBIC DIGESTION

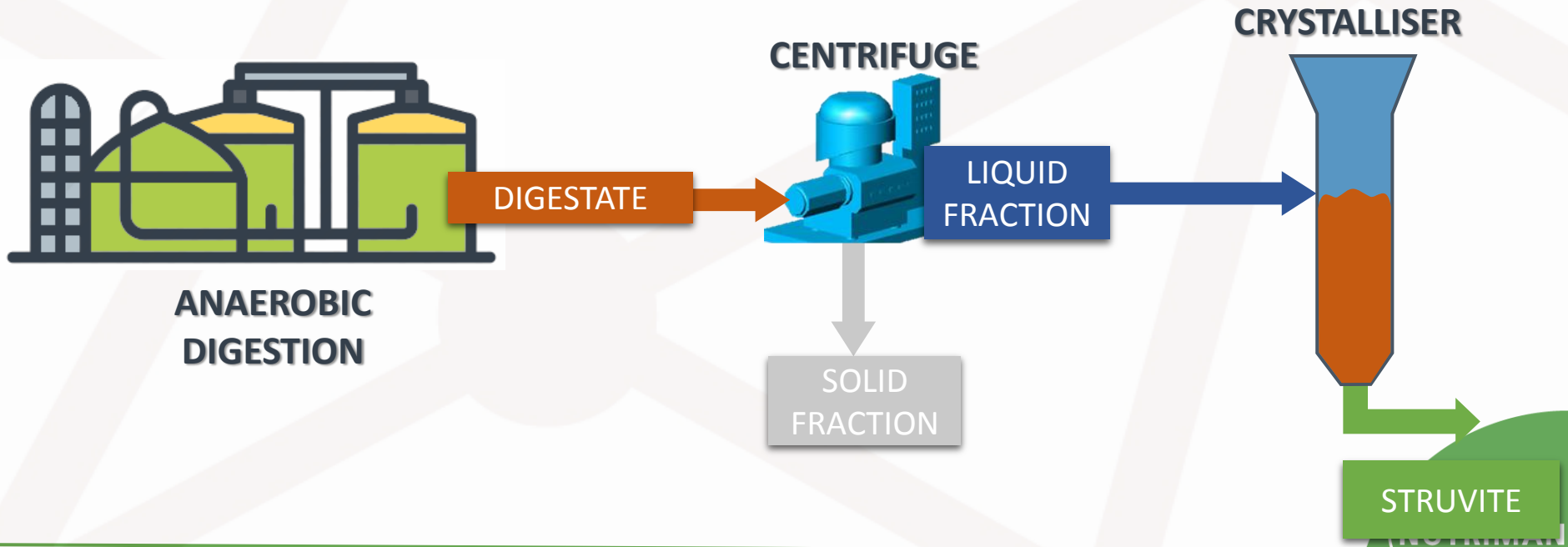


Adapted from: www.cleancoastresources.com

STRUVITE PRODUCTION FROM CARTIF

- Cartif produces the struvite from the digestate coming from the anaerobic digestion of the pig slurry.

- Digestate is the liquid by-product obtained from the anaerobic digestion process.



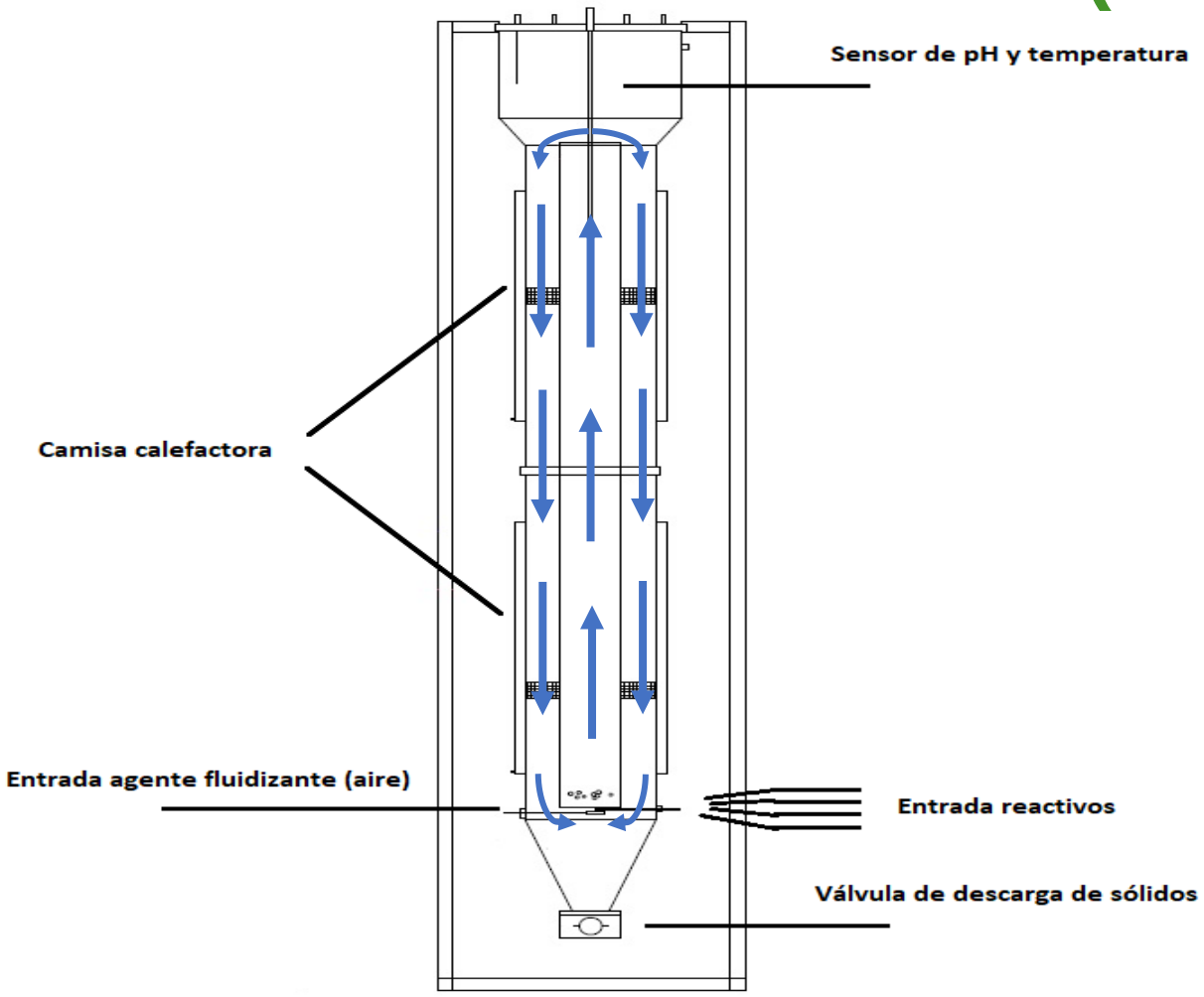
CRYSTALLISATION REACTOR (ID 256)

- The pilot plant for struvite production is composed by a 50 L reactor made of borosilicate glass with a cylindrical shape.

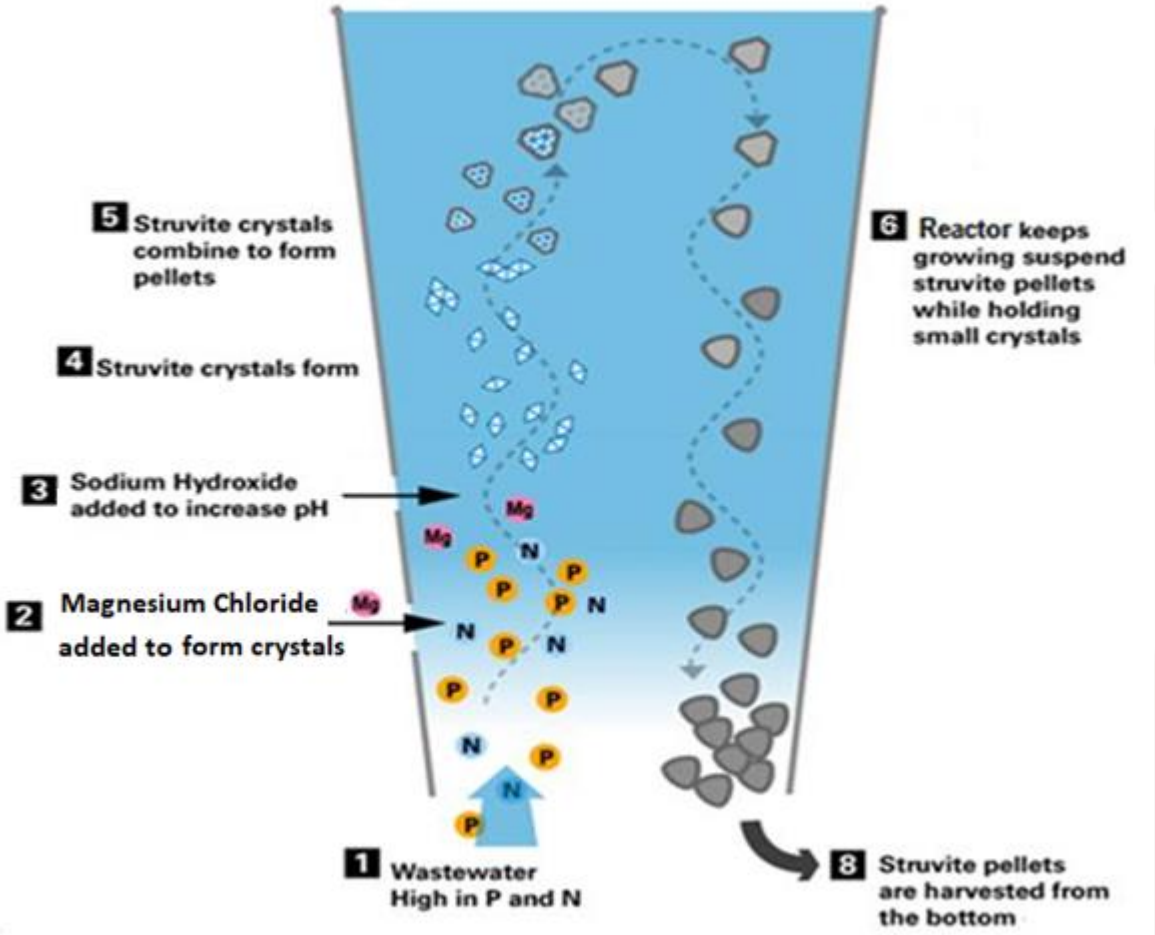
- Magnesium chloride ($MgCl_2 \cdot 6H_2O$) was used as Mg source.

- The pH of the samples was 8.5, so it was necessary to add a concentrated alkali (50% NaOH solution) to raise the pH value to 9.0.

CRYSTALLISATION REACTOR (ID 256)



CRYSTALLISATION REACTOR (ID 256)



CRYSTALLISATION REACTION

- Scanning Electron Microscope (SEM) image of the struvite crystals obtained in this study.

- As can be seen, the crystals obtained have the characteristic shape of struvite crystals (needle-shaped crystals).

STRUVITE COMPOSITION (ID 250)

Parameter	Struvite from CARTIF
C (%w)	3,0
H (%w)	6,9
N (%w)	4,74
Al (%w)	n.d.
Ca (%w)	0,165
Fe (%w)	0,001
Mg (%w)	8,918
P (%w)	11,211
K (%w)	0,561
Si (%w)	n.d.
Na (%w)	0,817
Ti (%w)	n.d.

Parámetros	Struvite from CARTIF
Ba (mg/kg)	n.d.
Cd (mg/kg)	n.d.
Co (mg/kg)	n.d.
Cr (mg/kg)	n.d.
Cu (mg/kg)	n.d.
Mn (mg/kg)	n.d.
Mo (mg/kg)	n.d.
Ni (mg/kg)	n.d.
Pb (mg/kg)	n.d.
Sb (mg/kg)	n.d.
Sr (mg/kg)	n.d.
V (mg/kg)	n.d.
Zn (mg/kg)	0,001

n.d.: not detected

CONCLUSIONS

- Nutrient composition and characteristics of struvite from are very similar than commercial struvite.
- Struvite has no significant content of PTEs or other contaminants that would prevent its use as a biofertiliser.
- Organic matter (carbon content) of struvite can give it undesirable organoleptic properties (bad odour or dark colour), causing it to be rejected by the final user.
- Organic matter could be removed from the struvite by a scrubber.

Struvite obtained by Cartif meets all the requirements to be used as a slow release biofertiliser

CONTACT

DOLORES HIDALGO BARRIO (project manager)

dolhid@cartif.es

FRANCISCO CORONA ENCINAS

fraenc@cartif.es

www.cartif.es

Parque Tecnológico de Boecillo
Parcela 205. 47151. Boecillo, Valladolid
SPAIN
+34 983 546504
+34 983 548911

Nutrient Management and Nutrient Recovery Thematic Network

www.nutriman.net

@NUTRIMANnetwork

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818470.