Crystal Growth of Sparingly Soluble Salts: Prospects for Sustainable Phosphorus Recovery from Wastewater

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and

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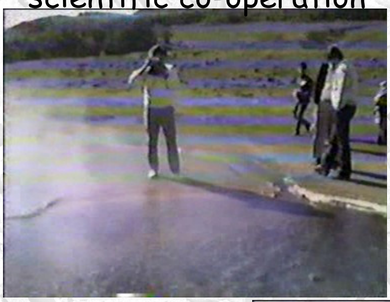
The solid precipitates forming scale deposits from solutions and A. Karabelas: The onset of a friendship and scientific co-operation



20 years after…

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Calcium Carbonate Deposit Formation under Isothermal Conditions

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THE CANADIAN JOURNAL OF CHEMICAL ENGINEERING, VOLUME 74, DECEMBER, 1996

INTERNATIONAL SUMMER SCHOOL
on Direct Application of Geothermal Energy

Under the auspice of the Division of Earth Sciences

SCALE FORMATION IN GEOTHERMAL PLANTS

N. Andritsos[1], A.J. Karabelas[1] and P.G. Koutsoukos[2]

Langmuir **1997**, *13*, 2873−2879

Morphology and Structure of $CaCO_3$ Scale Layers Formed under Isothermal Flow Conditions

N. Andritsos,† A. J. Karabelas,*,† and P. G. Koutsoukos‡

The problem of domestic wastewater due to phosphorus enrichment becomes increasingly acute

The allowable limits of Phosphorus and Nitrogen in natural waters must be low enough in order to avert eutrophication

↓

urgent demand for the optimization of the removal processes. Possibility of Recovery

Phosphorus recovery from wastewater by ***precipitation*** in the form of crystals of ***struvite***, $MgNH_4PO_4 \cdot 6H_2O$

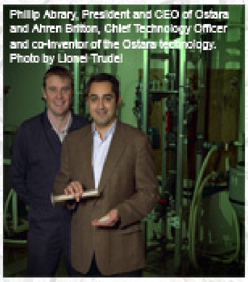
Advantages

1. Efficiency and simultaneous reduction of both Phosphorus and Nitrogen
2. The recovered salt may be utilized as an efficient, slow nutrient release fertilizer
3. Saving raw materials through re-use of recovered phosphorus

Venice

phosphate recovery process at Geestmerambacht municipal waste water treatment plant, Edam, Holland (230,000 p.e.) Process: DHV calcium phosphate Crystalactor®

Struvite recovery from urine in Nepal (STUN)



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Scale formation problems in anaerobic digestion of wastewater for phosphorus removal

Tackling the problem

- Thermodynamics analysis (definition of the potential for precipitation of salts)
- Kinetics measurements: The conditions and the corresponding rates of precipitation from supersaturated solutions

Thermodynamics

- Driving force for the formation of struvite is the ***difference between the chemical potentials*** *of the salt in the supersaturated solution,s, and at equilibrium, Ω*

$$\Delta\mu = \mu_s - \mu_\infty = -\frac{kT}{3}\ln\Omega$$

$$\mu_{MgNH_4PO_4} = \mu^0_{MgNH_4PO_4} + kT\ln\alpha_{MgNH_4PO_4}$$

$$\alpha_{MgNH_4PO_4} = \left(\alpha_{Mg}\alpha_{NH_4}\alpha_{PO_4}\right)^{1/3}$$

$$\Omega = \frac{a_{Mg^{2+}}\cdot a_{NH_4^+}\cdot a_{PO_4^{3-}}}{K_s^0}$$

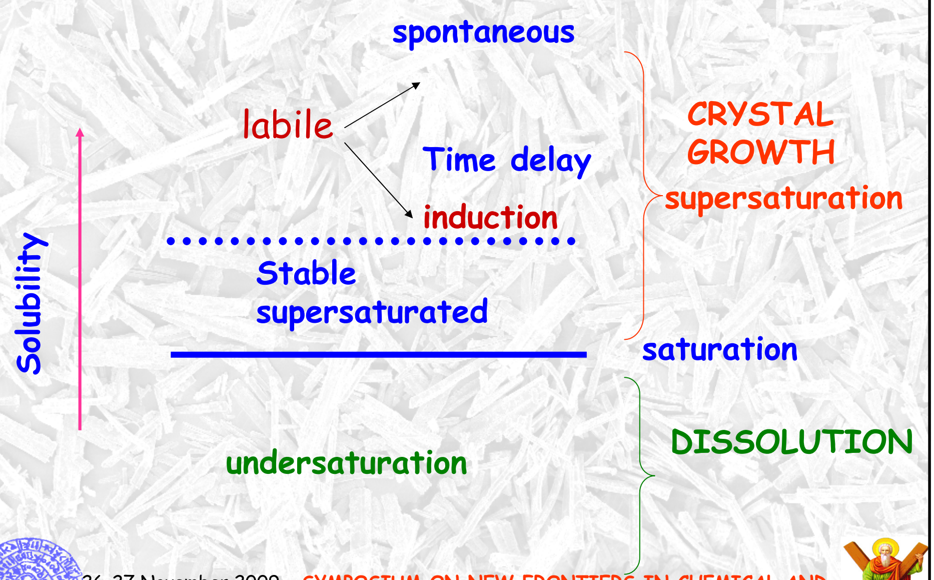
and $\sigma = \Omega^{1/3} - 1$

- The activities of the ionic species in solution were calculated by the **MINEQL+** chemical equilibrium modeling software taking into account all chemical equilibrium together with mass balance and electro neutrality conditions

Equilibrium	log k	Equilibrium	log k
$H^+ + PO_4^{3-} \Leftrightarrow HPO_4^{2-}$	12.375	$Mg^{+2} + CO_3^{2-} \Leftrightarrow MgCO_3$	2.92
$H^+ + HPO_4^{2-} \Leftrightarrow H_2PO_4^-$	7.198	$NH_3 + H^+ \Leftrightarrow NH_4^+$	9.244
$H^+ + H_2PO_4^- \Leftrightarrow H_3PO_4$	2.148	$NH_3 + Mg^{+2} \Leftrightarrow MgNH_3^{+2}$	0.24
$Na^+ + PO_4^{3-} \Leftrightarrow NaPO_4^{2-}$	1.43	$2NH_3 + Mg^{+2} \Leftrightarrow Mg(NH_3)_2^{+2}$	0.2
$Na^+ + HPO_4^{2-} \Leftrightarrow NaHPO_4^-$	1.07	$3NH_3 + Mg^{+2} \Leftrightarrow Mg(NH_3)_3^{+2}$	-0.3(I=2)
$Na^+ + H_2PO_4^- \Leftrightarrow NaH_2PO_4$	0.3	$Mg^{+2} + PO_4^{3-} \Leftrightarrow MgPO_4^-$	4.8
$Na^+ + NaPO_4^{2-} \Leftrightarrow Na_2PO_4^-$	1.16	$Mg^{+2} + HPO_4^{2-} \Leftrightarrow MgHPO_4^-$	2.80
$H^+ + Na_2PO_4^- \Leftrightarrow Na_2HPO_4$	10.73	$Mg^{+2} + H_2PO_4^- \Leftrightarrow MgH_2PO_4$	0.45
$H^+ + CO_3^{2-} \Leftrightarrow HCO_3^-$	10.329	$H^+ + OH^- \Leftrightarrow H_2O$	13.997
$H^+ + HCO_3^- \Leftrightarrow H_2CO_3$	6.352	$Na^+ + OH^- \Leftrightarrow NaOH$	0.1
$H_2O + CO_2 \Leftrightarrow H_2CO_3$	-1.466	$Mg^{+2} + OH^- \Leftrightarrow MgOH^+$	2.6
$Na^+ + CO_3^{2-} \Leftrightarrow NaCO_3^-$	1.27	$Na^+ + Cl^- \Leftrightarrow NaCl$	-0.5
$Na^+ + HCO_3^- \Leftrightarrow NaHCO_3$	-0.25	$Mg^{+2} + Cl^- \Leftrightarrow MgCl^+$	0.6
$H^+ + SO_4^{2-} \Leftrightarrow HSO_4^-$	1.99	$Na^+ + SO_4^{2-} \Leftrightarrow NaSO_4^-$	0.73
$NH_4^+ + SO_4^{2-} \Leftrightarrow NH_4SO_4^-$	1.03	$Mg^{+2} + SO_4^{2-} \Leftrightarrow MgSO_4$	2.26
$Mg^{+2} + HCO_3^- \Leftrightarrow MgHCO_3^+$	1.01	$Mg^{+2} + PO_4^{-3} + NH_4 + 6H_2O \Leftrightarrow MgNH_4(PO_4)_3 \cdot 6H_2O$	13.26
$Na^+ + NO_3^- \Leftrightarrow NaNO_3$	-0.55		

Thermodynamics calculations

- Ω>1 or σ >0 : A solid phase is a potential precipitate from the respective solution (supersaturated)
- Measure of deviation from saturation (equilibrium)
- Different solution compositions correspond to different driving force



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Investigation of the kinetics of the spontaneous precipitation of struvite in a complex aqueous system such as the synthetic wastewater

- *pH stat experiments 8.50 - 9.50*
- *Experiments at Constant Supersaturation*

Morphology of struvite crystals-Transformation

- *$MgNH_4PO_4 6H_2O$*
- *$MgNH_4PO_4 1H_2O$*

Experimental Procedure

Stock solutions

$MgSO_4 \cdot 7H_2O$ $NH_4H_2PO_4$

Synthetic wastewater solution

Table 1: Chemical composition for **pH stat experiments**

Component	Concentration
Glucose	Equal to100COD
$NaHCO_3$	17.86 mM
NaCl	10 mM
$NaNO_3$	0.59 mM

Table 2: Chemical composition for experiments at **constant supersaturation**

Component	Concentration
Glucose	Equal to100COD
$NaHCO_3$	17.86 mM
NaCl	10 mM
$NaNO_3$	0.59 mM
Na_2SO_4	12 mM

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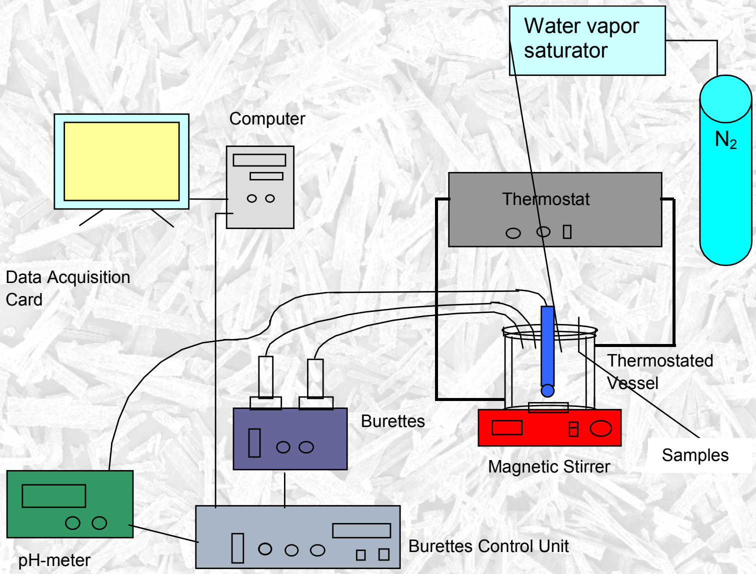

Struvite precipitation

$$Mg^{2+}:PO_4^{3-}:NH_4^{+} = 1:1:1$$

$$\theta = 25^{o}C$$

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$Mg^{2+} + NH_4^+ + H_2PO_4^- \Leftrightarrow MgNH_4PO_4 \cdot 6H_2O + 2H^+$

protons released into the solution

Drop of pH

A drop of pH exceeding 0.005 pH units triggers the addition of titrant solution(s) from the burette(s) of the computerized automatic titrator

- pH stat experiments

  Addition of standard ***NaOH solution (one titrant)***

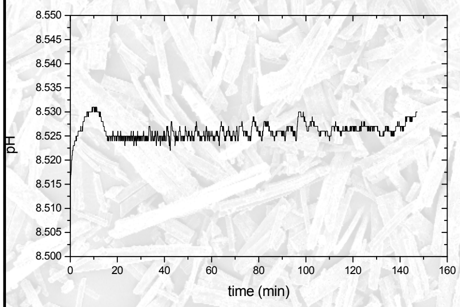
- Experiments at constant supersaturation

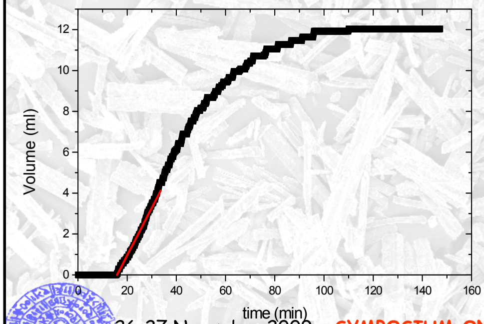
  Simultaneous addition of ***two titrant solutions***

Titrant 1: **$(2x_1+c)$M $MgSO_4 \cdot 7H_2O$ + $(2x_4 - 2c)$M synthetic wastewater**

Titrant 2: **$(2x_2+c)$M $NH_4H_2PO_4$ + $(2x_3 + 2c)$M NaOH+ $(2x_4 - 2c)$M** synt.wastewater

Steady state- constant composition of solutions





induction time

The time lapsed between the preparation of supersaturation solution and the first addition of titrants.

Initial rate of precipitation

Calculated by the slope of the curve

Several samples withdrawn and filtered

- Filtrates:

  magnesium (atomic absorption spectrometry)

  phosphate (Vanado-molybdae complex, spectrophotometrically)

- Solid phase :

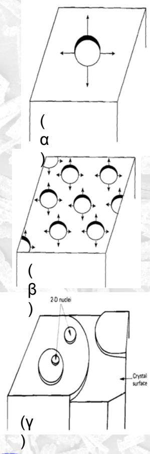
  Powder X-ray diffraction (XRD)

  Scanning electron microscopy (SEM)

  Thermogravimetric analysis (TGA)

  BET surface area

Kinetics of Precipitation-Crystal Growth



(α) Mononuclear

$$R_M^{2D} = A \cdot h_N C_1^{2D} (\ln S)^{1/2} \exp\left(-\frac{\pi \cdot h_N \cdot \gamma_s{}^2 V_m}{k_B^2 T^2 \ln S}\right)$$

(β) polynuclear

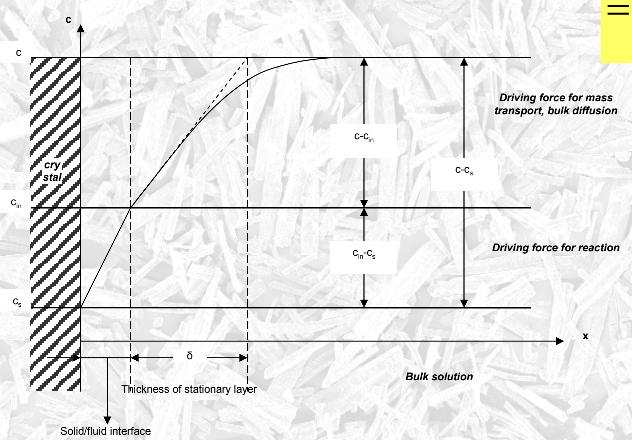
$$R_P^{2D} = C_2^{2D} \cdot f(S) \cdot \exp\left[-\frac{\beta \cdot \gamma_s{}^2 \cdot V_m^{4/3}}{3 \cdot (k \cdot T)^2 \cdot \ln S}\right]$$

$$f(S) = S^{7/6} \cdot (S-1)^{2/3} \cdot (\ln S)^{1/6}$$

(γ) Polynuclear-Birth and Spread

$$R_{BS}^{2D} = C_1^{2D} C_3^{2D} \cdot (\ln S)^{5/6} \cdot \exp\left[-\frac{h_N \pi \cdot \gamma_s{}^2 V_m}{3 \cdot (kT)^2 \cdot \ln S}\right]$$

$$R = k_D \sigma = \frac{D\upsilon}{\delta}\sigma$$



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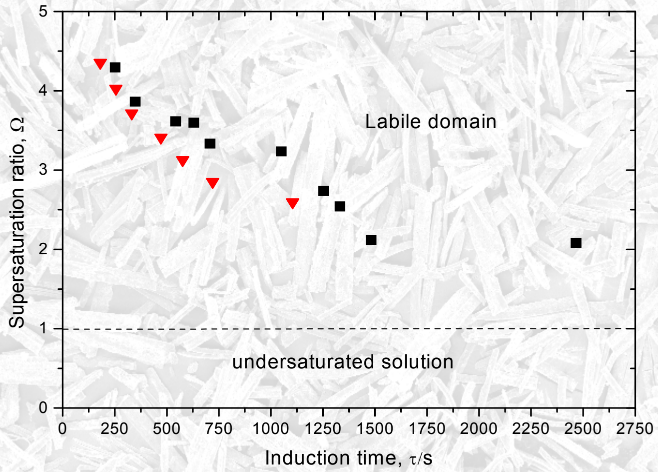
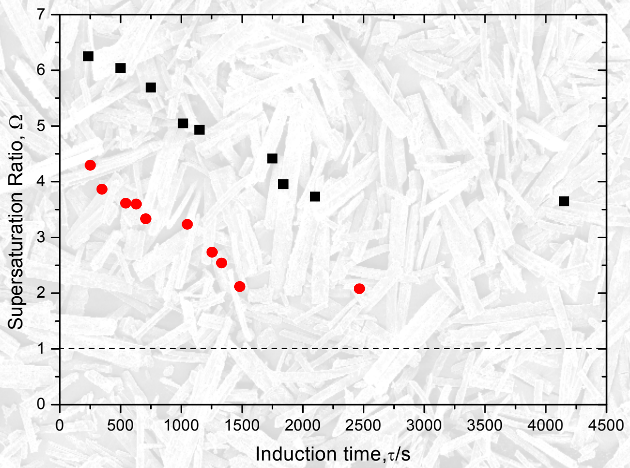


Stability diagram for the precipitation of Struvite in synthetic wastewater, determined from pH stat experiments. Variation of the induction times preceding precipitation on the supersaturation ratio with respect to struvite; 25ºC; (■) pH 8.50; (▼) pH 9.00.



Stability diagram for the precipitation of Struvite in synthetic wastewater, determined from pH stat (●) and from experiments at constant solution composition (■). Variation of the induction times preceding precipitation on the supersaturation ratio with respect to struvite; 25ºC; pH 8.50

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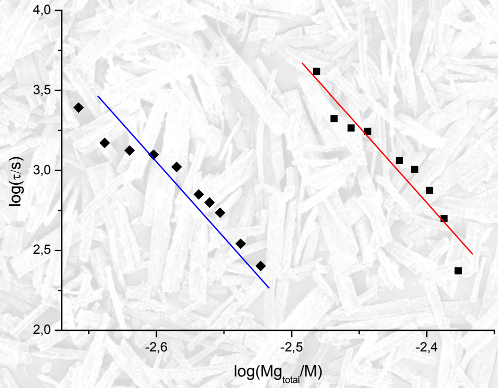
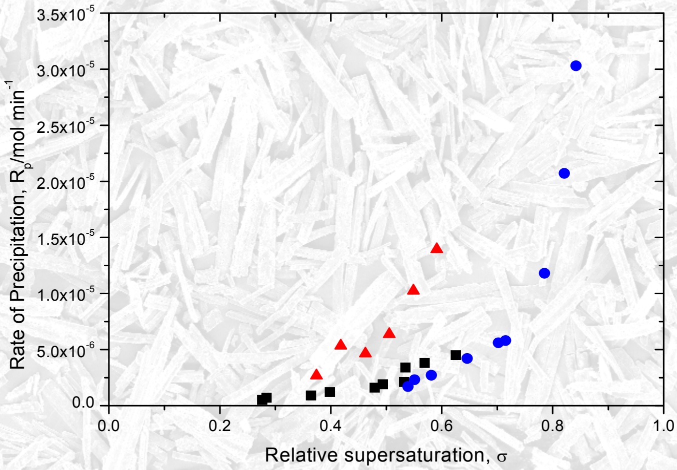
$$\tau = k_p [Mg]_0^{1-p}$$



Plot of the logarithm of the induction times measured as a function of the initial magnesium concentration in solution; pH stat (♦); constant solution composition (■); 25ºC; pH 8.50.

$$R_p = k_{sp} \sigma^n$$



Plot of the rates of struvite precipitation as a function of the solution supersaturation, pH 8.5,25ºC;(■) constant solution pH; (●)constant solution supersaturation; (▲) pH 9.50, constant solution pH

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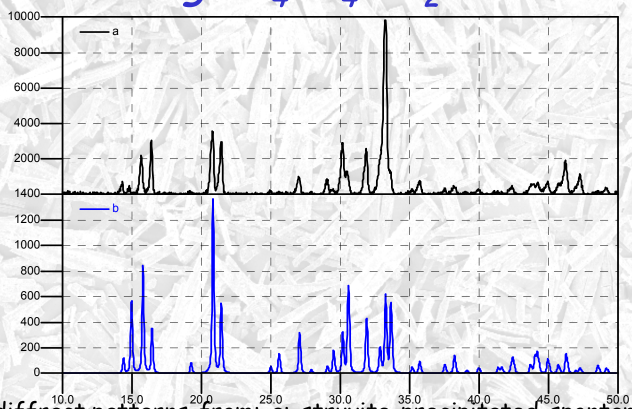
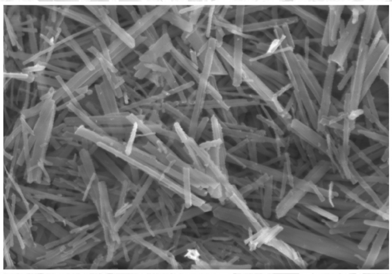
In all cases the mineral phase precipitated was struvite $MgNH_4PO_4 \cdot 6H_2O$

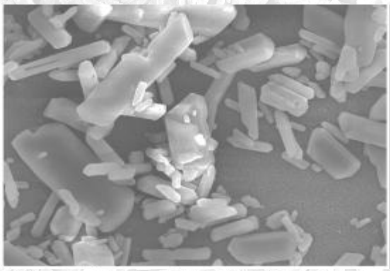


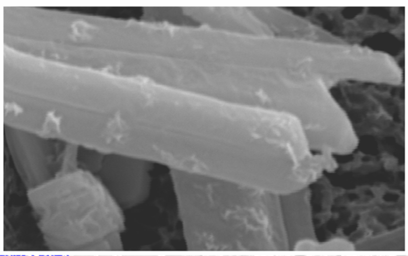
Powder X-ray diffractipatterns from: a: struvite precipitated spontaneously from SWW at constant pH/constant supersaturation; b: Reference pattern file no. 15-762 for synthetic struvite (reference JCPDS)

pH-stat experiment

pH 8.50







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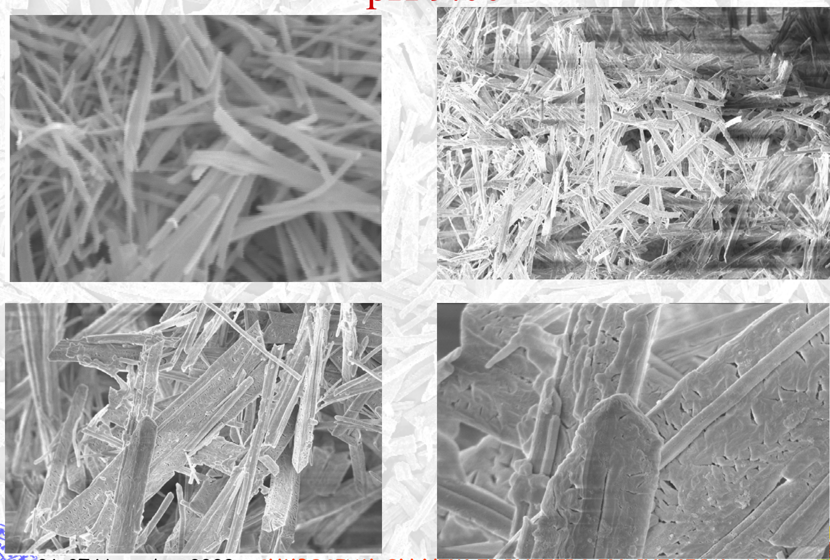
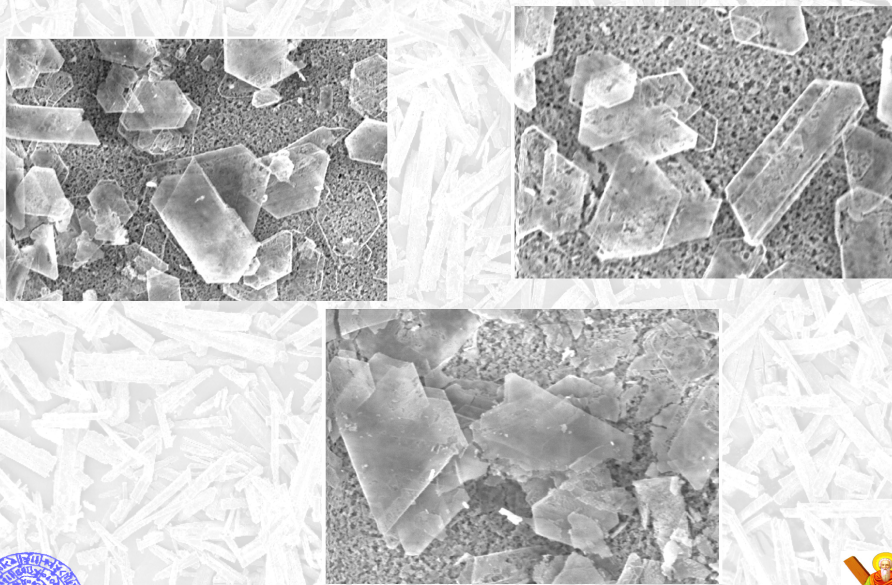
pH-stat experiment

pH 9.00

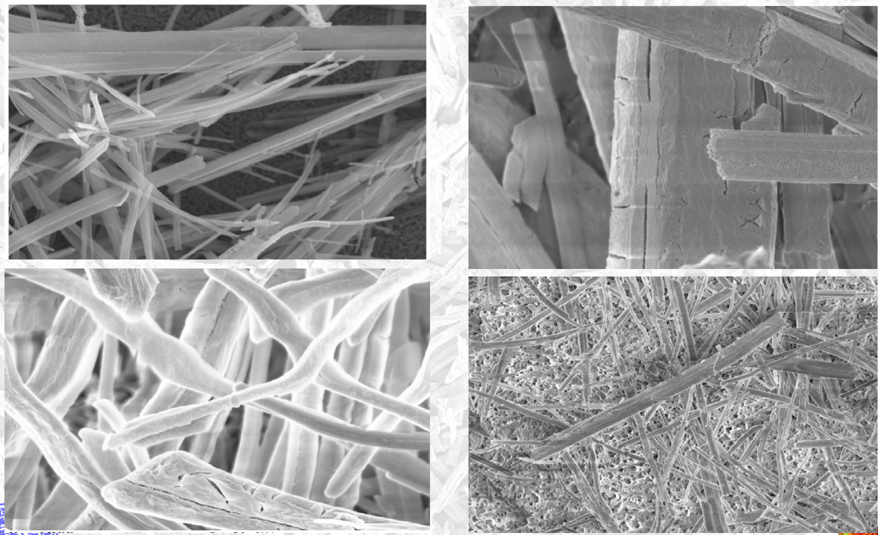


pH-stat experiment pH 9.50

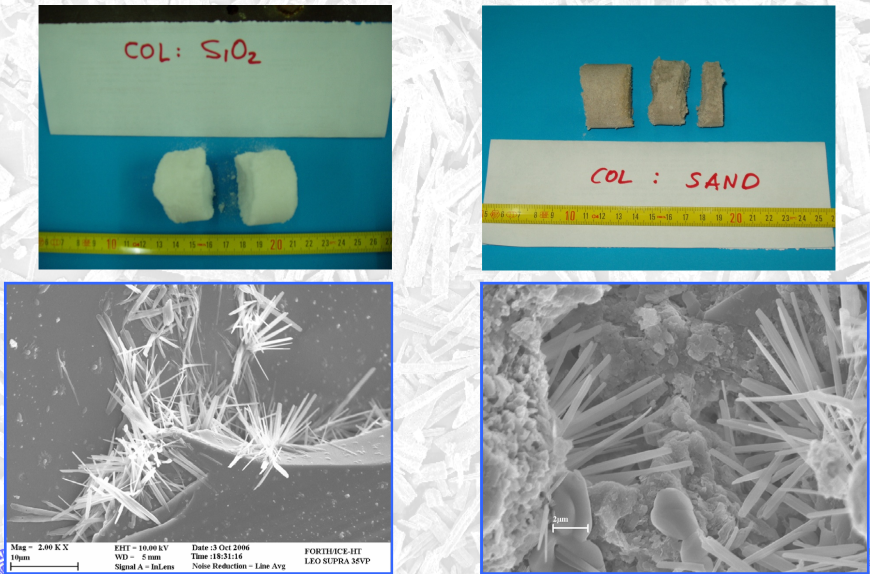


Constant Supersaturation Experiments

pH 8.50 and 9.00



Consolidation tests by struvite deposition



ENZYME CATALYZED STRUVITE PRECIPITATION

substrate
(phosphate source)

Enzyme
(for the hydrolytic decomposition of phosphoesters)

Phosphatase

$$\textbf{polyphosphate} \xrightarrow{\text{Phosphatase}} PO_4^{3-}$$

$$PO_4^{3-} + NH_4^+ + Mg^{2+} \longrightarrow MgNH_4PO_4$$

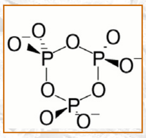
- *Enzymes*

  Acid phosphatase (**pH 5.50**)

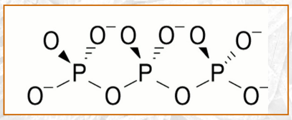
  Alkaline phosphatase (**pH 9.80**)

- *Polyphosphate solutions*

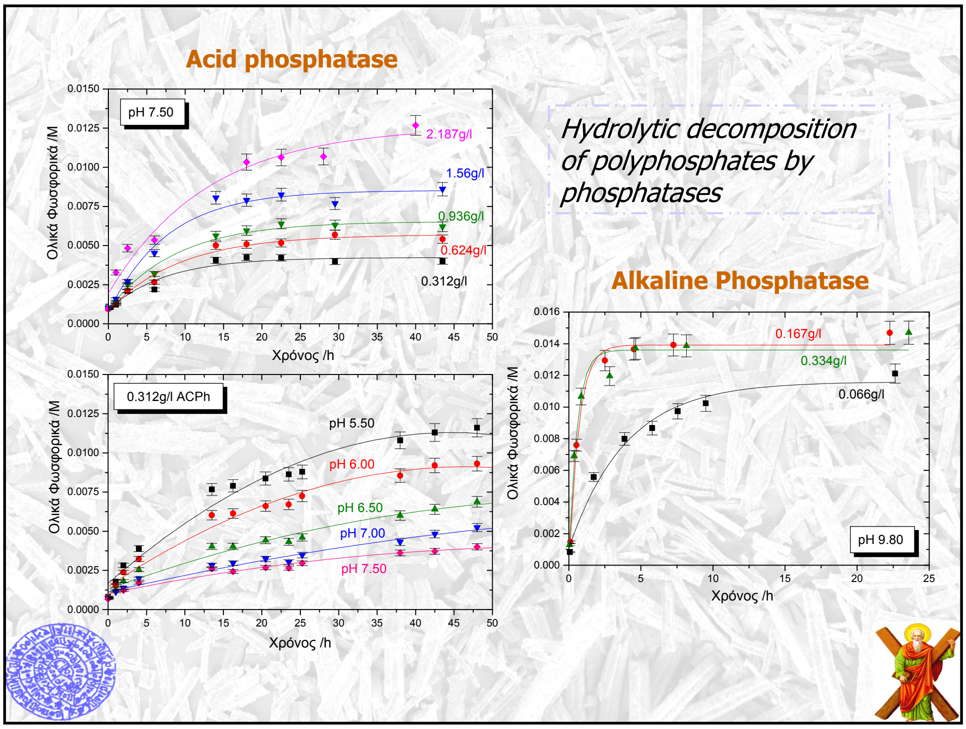
  $Na_3P_3O_9$ for acid phosphatase

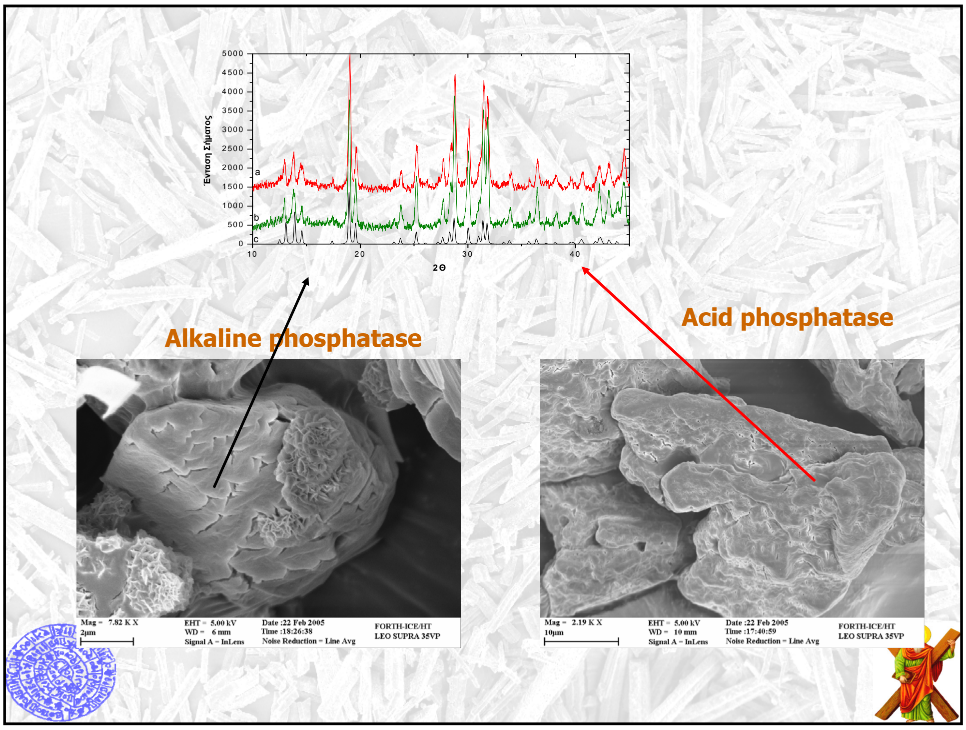
  

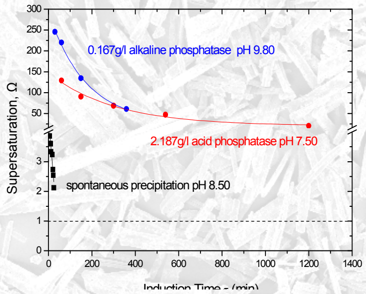
  $Na_5P_3O_{10}$ for alkaline phosphatase

- *$MgCl_2$ $2H_2O$*
- *NH_4Cl*

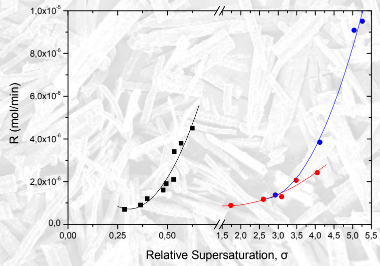

Acid phosphatase
pH 7.50
2.187g/l
1.56g/l
0.936g/l
0.624g/l
0.312g/l
Ολικά Φωσφορικά /M
Χρόνος /h
0.312g/l ACPh
pH 5.50
pH 6.00
pH 6.50
pH 7.00
pH 7.50
Hydrolytic decomposition of polyphosphates by phosphatases
Alkaline Phosphatase
0.167g/l
0.334g/l
0.066g/l
pH 9.80


Ένταση Σήματος
2Θ
Alkaline phosphatase
Acid phosphatase
FORTH-ICE/HT
LEO SUPRA 35VP

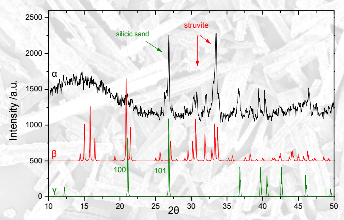


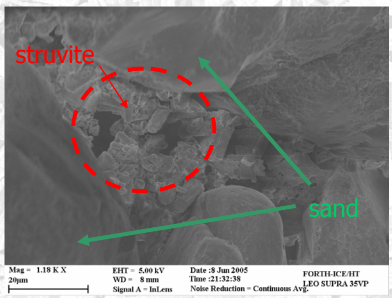
Advantage:

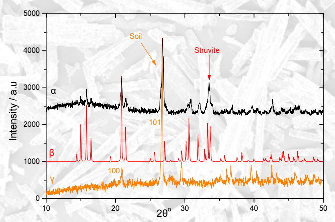
At high supersaturations precipitation is gradual and controlled

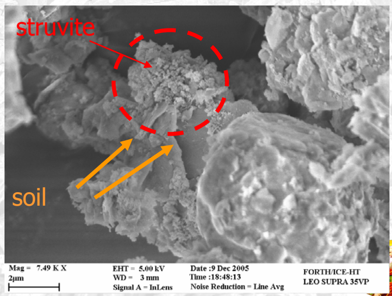


Struvite precipitation on sand and soil grains





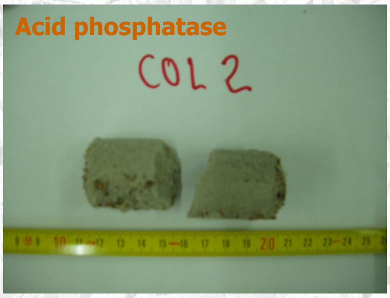




Sand consolidation by struvite precipitation

Alkaline Phosphatase

Acid phosphatase



Soil consolidation tests

Conclusions

- *Nucleation and crystal growth of struvite* from wastewater is feasible and a promising prospective for **Phosphorus recovery**
- Model synthetic wastewater results suggested that it is possible to crystallize struvite , a white *crystalline solid*, which may be used as a **fertilizer**
- In *pH stat experiments* a phosphorus recovery corresponding to **60 %** of the initially phosphorus concentrations was achieved while at *constant supersaturation experiments* phosphorus removal was **continuous**.

- The measured *induction times* as a function of the solution supersaturation were found to reduce rapidly suggesting **narrow limits of stability regime**
- The presence of *additional* SO_4^{2-} ions in the supersaturated solutions results in **threshold inhibition**.
- The *initial rates* showed parabolic dependence on the solution supersaturation with respect to struvite, suggesting **a surface diffusion controlled mechanism**

- The *morphology* of the crystals forming was affected mainly from the **solution pH**
- Enzymically catalyzed struvite precipitation is feasible and may be used for **soil consolidation**

Crystallization not only helps to save raw materials, but also…

BRINGS RESEARCHERS CLOSER!!

BEST WISHES TO TASOS AND STAVROS!!

Acknowledgments

GSRT for support of this work through the PENED program and Bilateral Greece-Albania S&T Cooperation

CEEP for partial support

All of you, for your attention !

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