Phosphate Removal and Recovery from Anaerobic Digester Effluents Using Dolomite Lime

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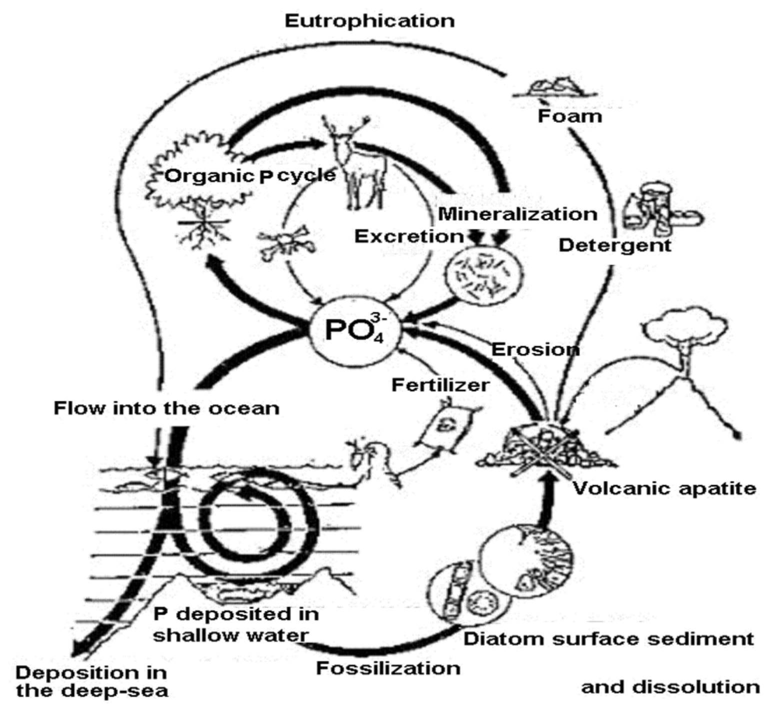
Lake Eutrophication Problems

Elevated concentrations of P and N in the environment has resulted in eutrophication problems worldwide, with more than about 50% of the lakes in North America, Europe and Asia being eutrophic.

Phosphorous: a limited and non-renewable resource

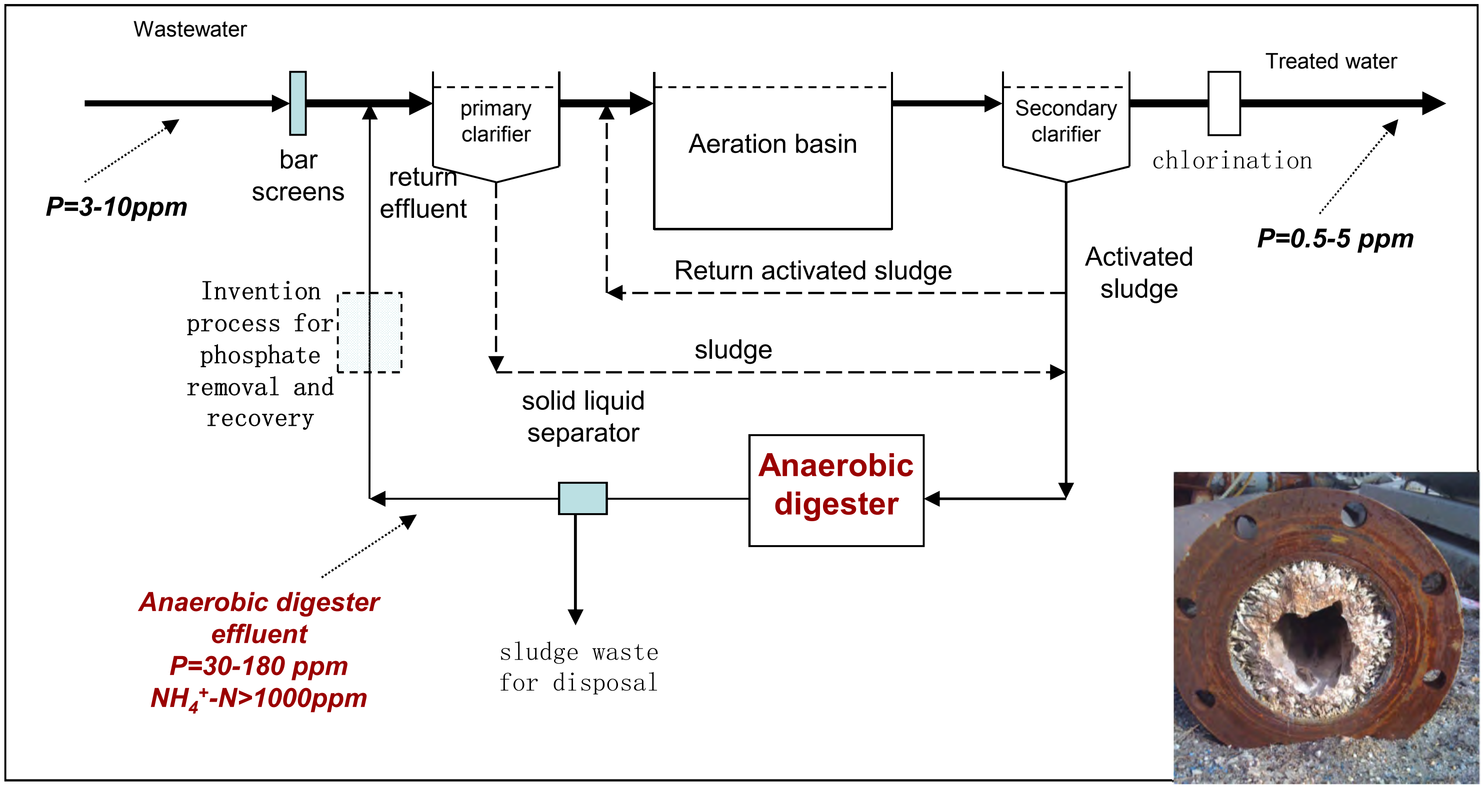
Phosphate mine near Flaming Gorge, Utah, 2008,
http://en.wikipedia.org/wiki/Phosphate



P Geochemical Cycle

- The world's known resources are sufficient for only about 370 years.
- P and N fertilizers are large energy consumers, accounting for about a third of energy consumption in US crop production.

Municipal Wastewater Treatment System



struvite, $MgNH_4PO_4 \cdot 6(H_2O)$

Large amount of phosphate and ammonium is formed in the anaerobic digester, which may lead to the formation of struvite mineral in the pipes carrying the digestion effluent.

Municipal Wastewater Treatment System

Major chemical composition of the anaerobic digester effluent sample

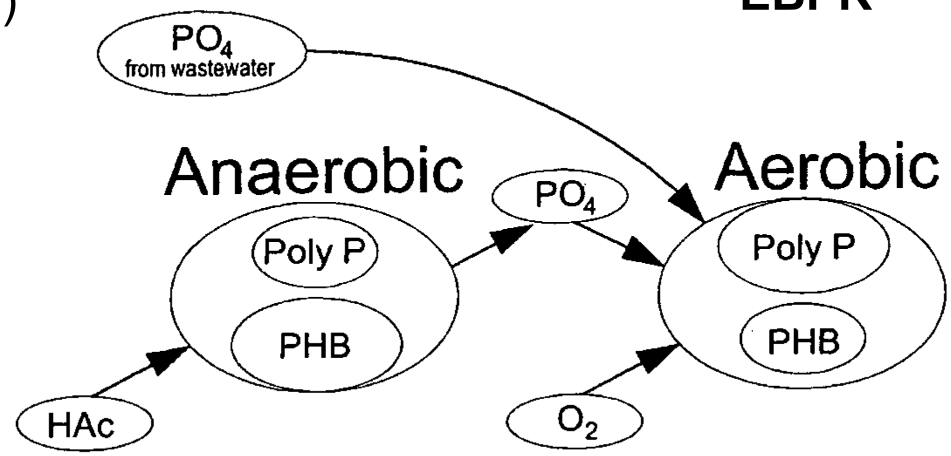
Chemicals	Concentration (mg/L)
PO_4^{3-}-P	87
Ca^{2+}	51
Mg^{2+}	7.2
NH_4^+	1142
CO_3^{2-}	641

Phosphate Removal Technology

Phosphorus **A**ccumulating **O**rganisms(PAOs)

- **Advantages**
  Much lower operating costs
  Less sludge generated
  Sludge recycle using
- **Disadvantages**
  used less
  sensitive to wastewater composition

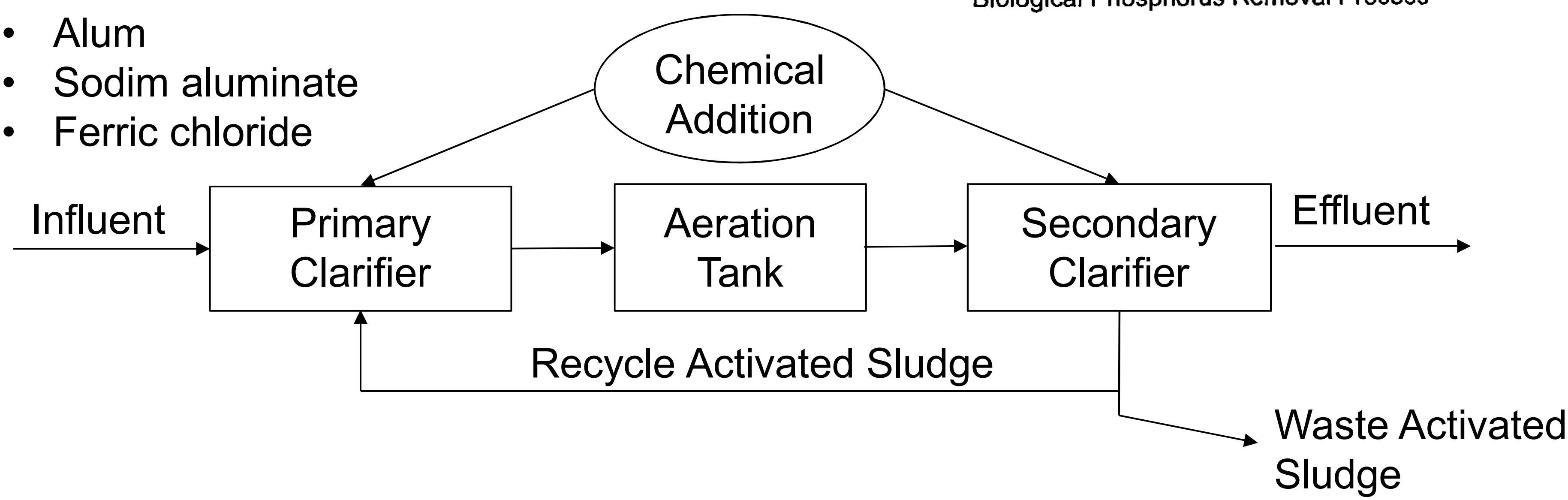
EBPR



Biological Phosphorus Removal Process

Chemical coagulation-precipitation

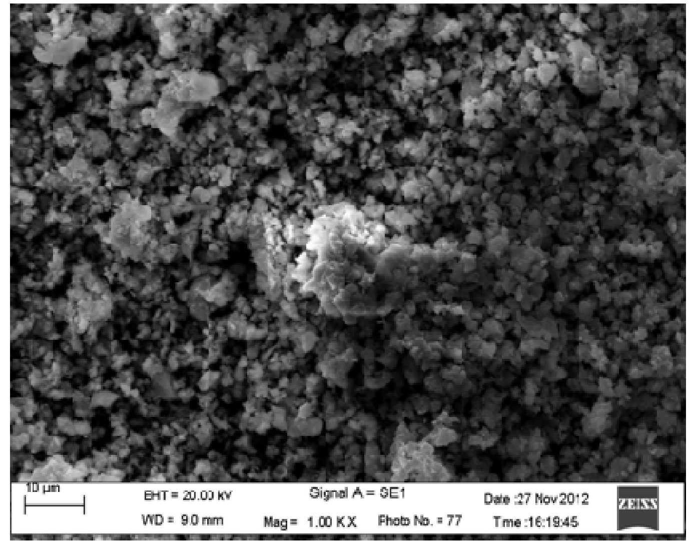
- Alum
- Sodim aluminate
- Ferric chloride



Dolomite Lime ($CaMg(OH)_4$)

DL is provided by Graymount Lime Inc.

Ca and **Mg** content in DL were 39.9% and 22.4%, respectively.



Calcined

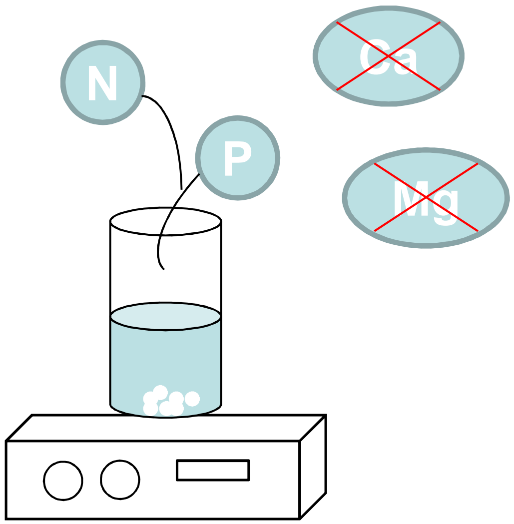
$$CaMg(CO_3)_2 \rightarrow MgO + CaO + 2CO_2 \uparrow$$

DL Components	phase	Molecular formula	Wt. %
	Periclase	MgO	28.3
	Portlandite	$Ca(OH)_2$	58.4
	Brucite	$Mg(OH)_2$	12.3
	Calcite	$CaCO_3$	1.0

Removal of Phosphate Using a Dolomite Lime ($CaMg(OH)_4$) in a Complete Mix Reactor

Kinetic Tests

- Synthetic solution
  1). PO_4^{3-}+NH_4^+ 2). PO_4^{3-}
  both solutions were without Ca and Mg.
  Initial pH was adjusted to 7.5



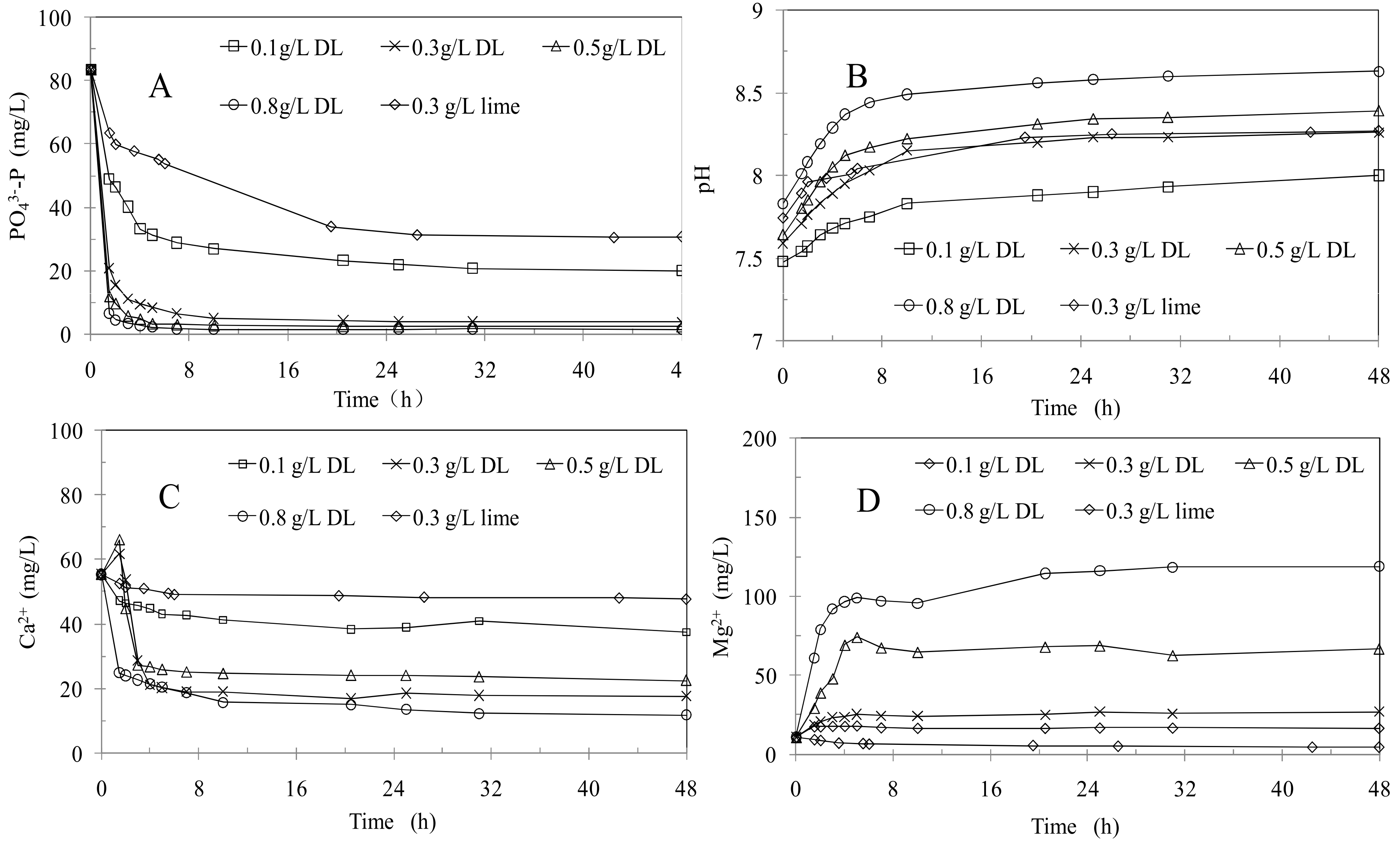
- Real wastewater

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

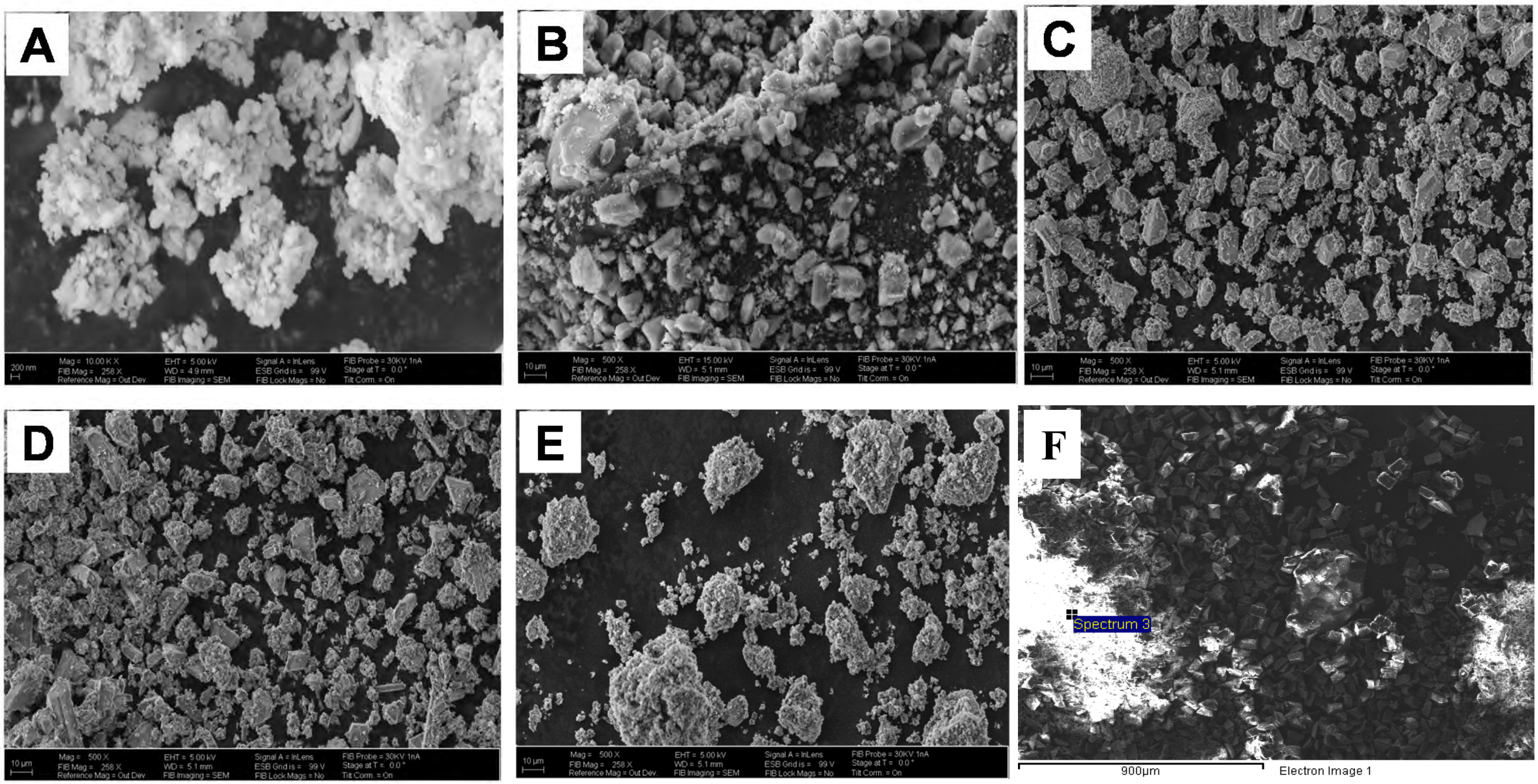
$$Ca^{2+} + PO_4^{3-} + OH^- \rightarrow Ca_5(PO_4)_3OH$$

P in the effluent water = 98 ppm

Removal of Phosphate Using a Dolomite Lime ($CaMg(OH)_4$) in a Complete Mix Reactor

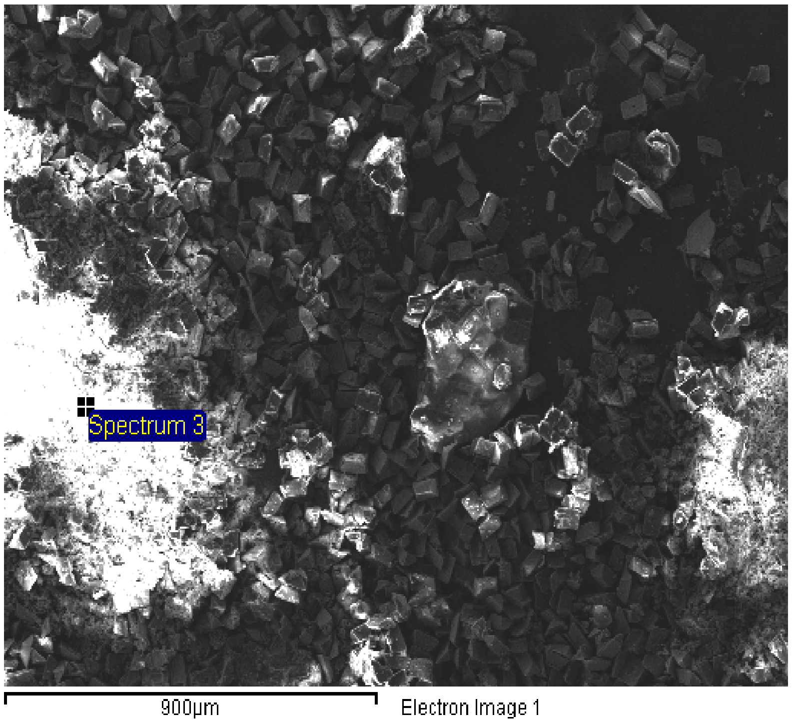


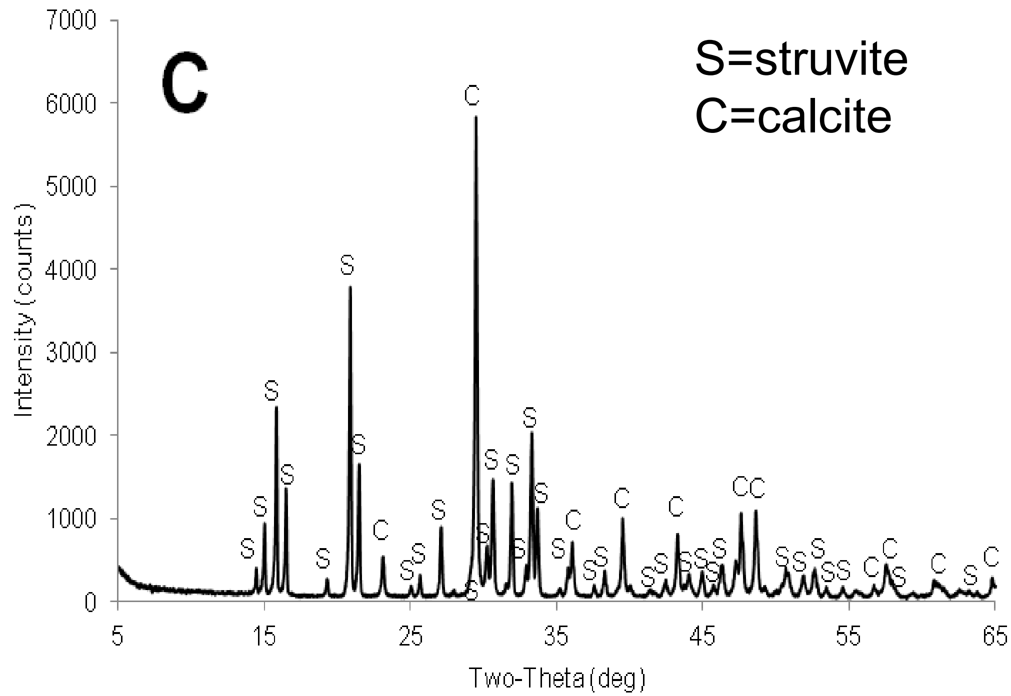
SEM Images of the Processed Mineral and Solid Products



A: processed mineral, B-F: solid products formed under different conditions
Chemical analysis of the solids: 23% P, 11% N, 4% K

SEM Images and XRD Spectra of the Solid Products





Chemical analysis of the solids: 23% P, 11% N, 4% K. The product contains high contents of the nutrients.

Thermodynamic prediction of phosphate precipitates

System: PO_4^{3-}-Ca^{2+}-Mg^{2+}-NH_4^+-CO_3^{2-}

$Ca_5(PO_4)_3OH$ (hydroxyapatite)=$5Ca^{2+} + 3PO_4^{3-} + OH^-$ pKsp=44.33

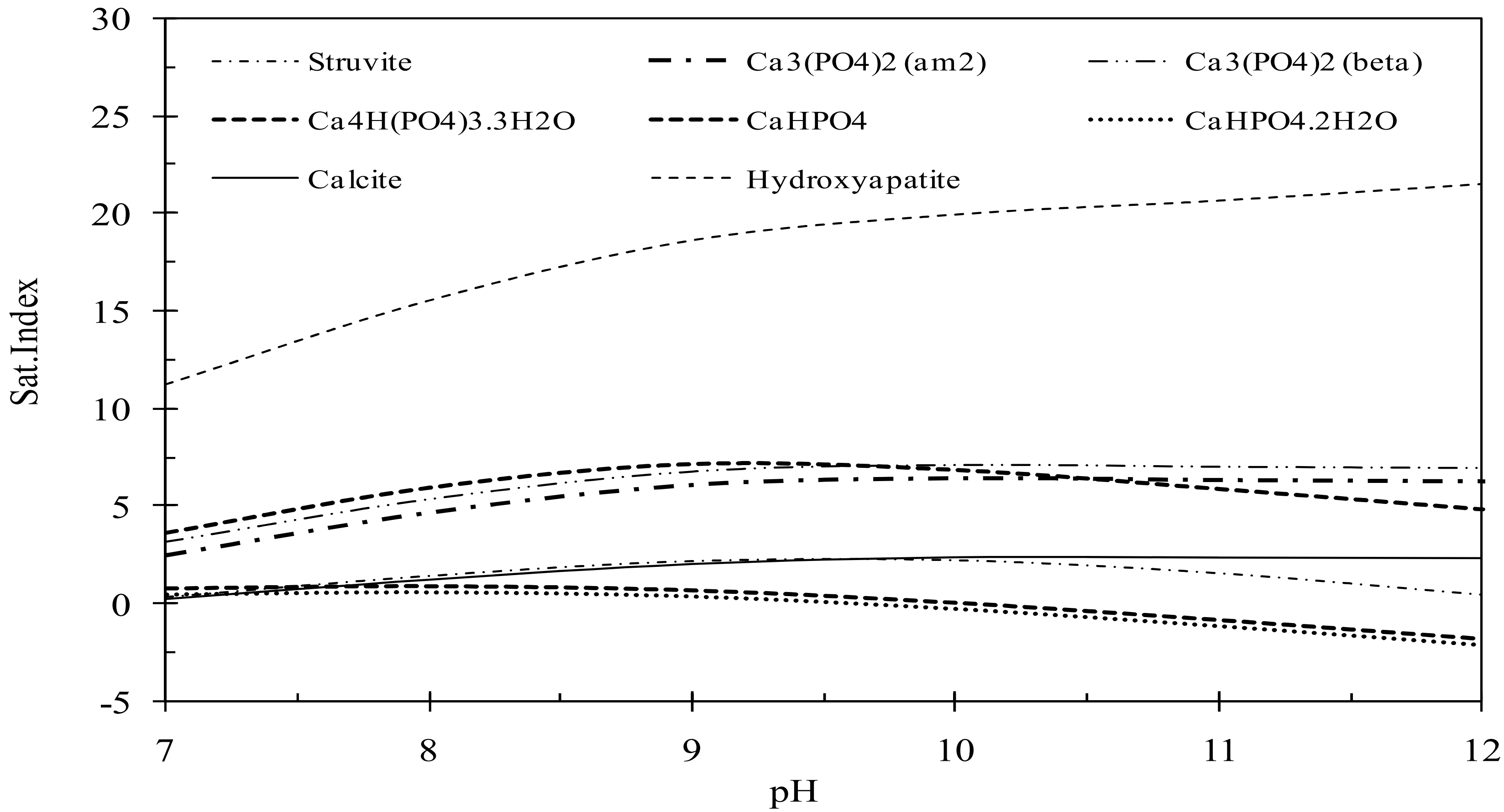
$Ca_4H(PO_4)_3 \cdot 3H_2O = 4Ca^{2+} + H^+ + 3PO_4^{3-} + 3H_2O$ pKsp=47.95

$Ca_3(PO_4)_2$(beta)=$3Ca^{2+} + 2PO_4^{3-}$ pKsp=28.92

$Ca_3(PO_4)_2$(am2)=$3Ca^{2+} + 2PO_4^{3-}$ pKsp=28.25

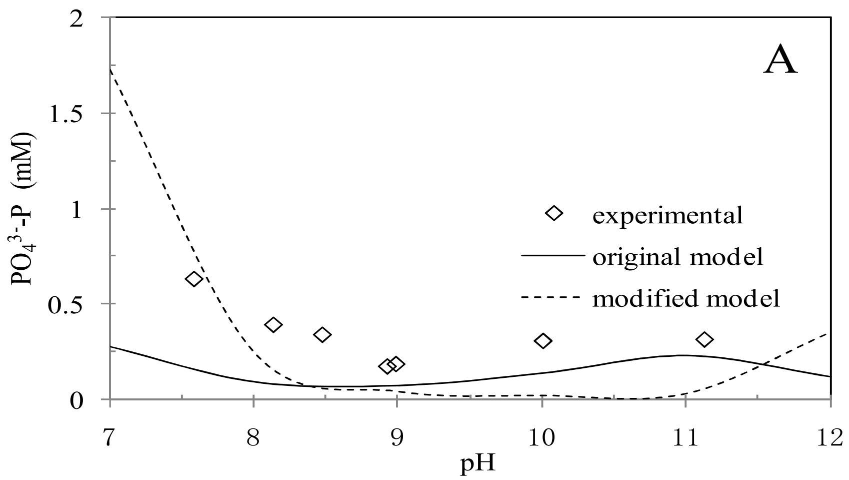
$MgNH_4PO_4 \cdot 6H_2O$ (struvite) = $Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O$ pKsp=13.26

Thermodynamic prediction of phosphate precipitates

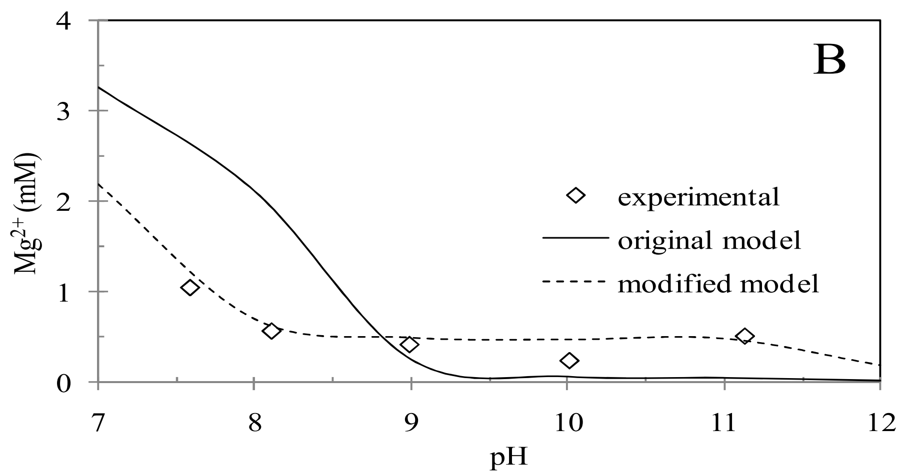


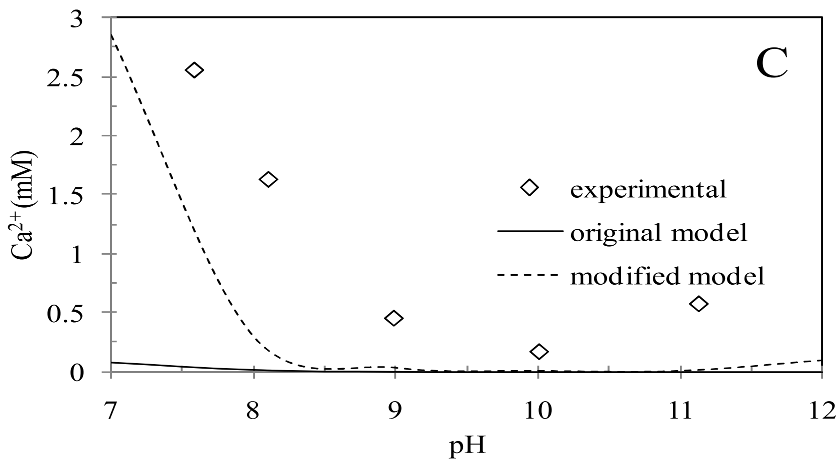
Chemical equilibrium model prediction of saturation index of phosphate precipitates as a function of pH for effluent water treated with 0.3 g/L of DL

Thermodynamic prediction of phosphate precipitates



Initial total concentrations 2.80 mM PO_4^{3-}-P, 3.25 mM Mg^{2+}, and 4.28 mM Ca^{2+}

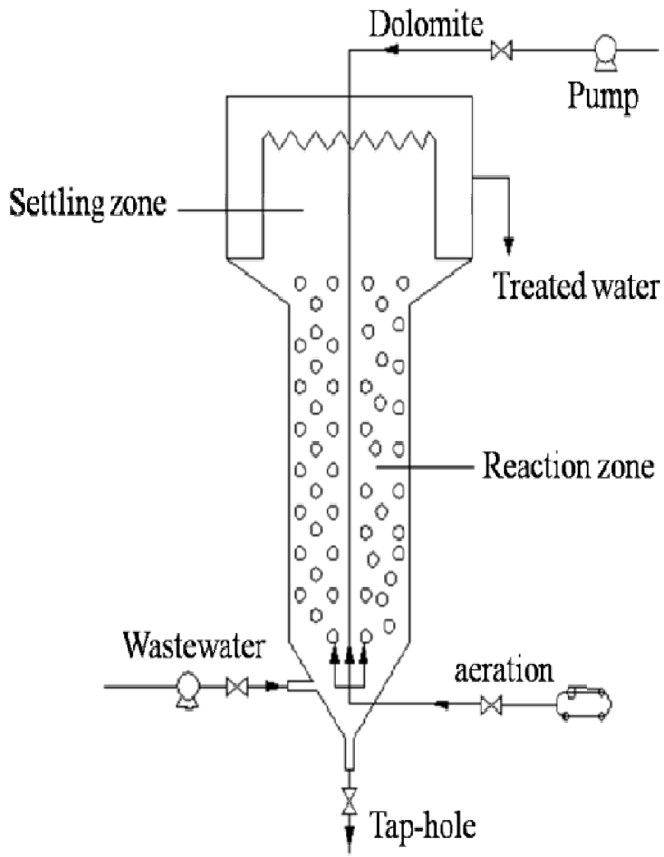




Modified model - only struvite and calcite precipitates were allowed to precipitate

Original model - all solids were allowed to precipitate.

Fluidized Bed Crystallizer



P removal efficiencies could reach up to 86%

- Natural DL (Single-factor investigation)

  dolomite dosage 650mg/L
  hydraulic retention time (HRT) 5.0h
  aeration rate 50ml/min

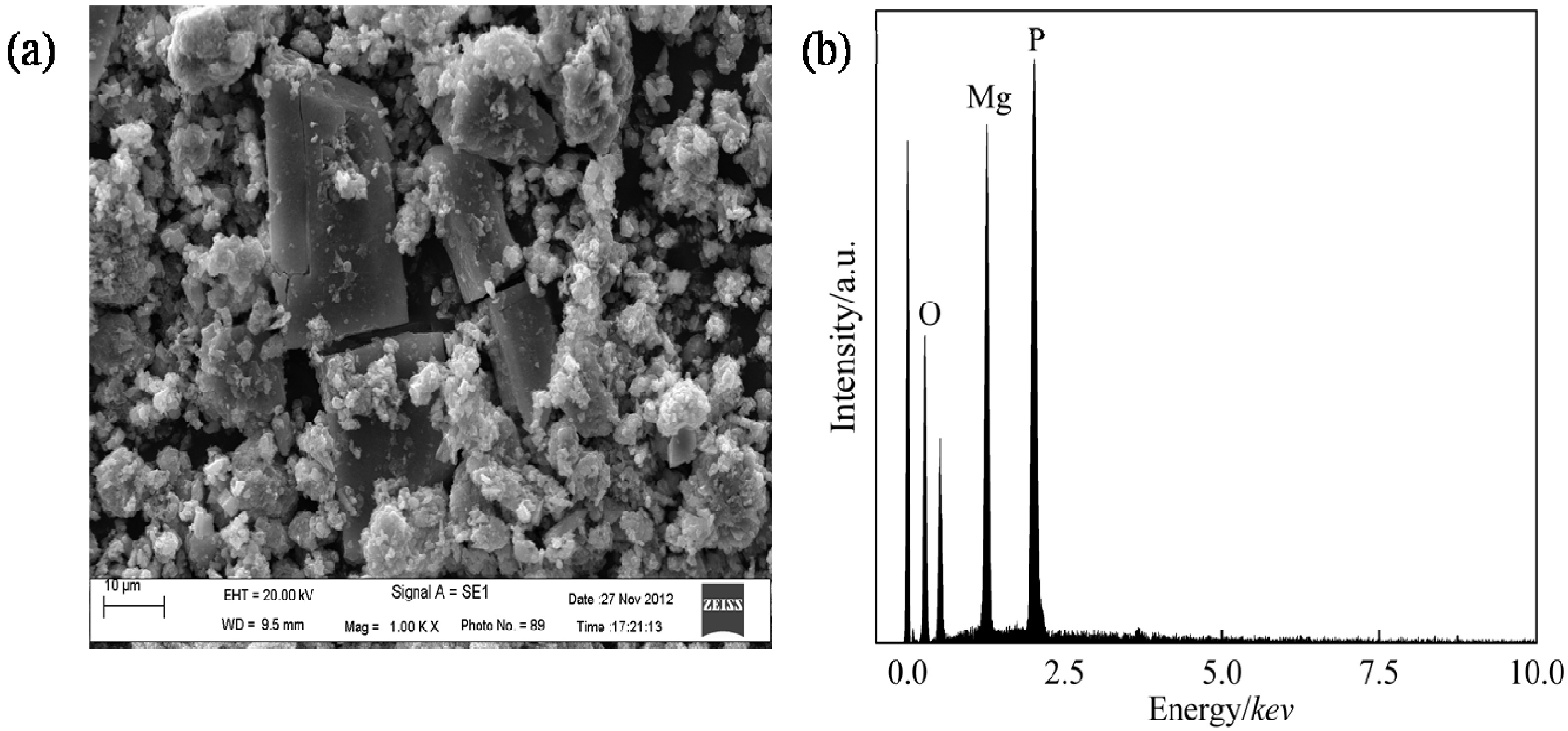
- Acid-treated DL (Response Surface Methodology)

  pH value 9.5
  Mg/P molar ratio 2.2
  HRT 3.0h

$$Y\text{（P removal\%）}=72.74+13.25X_1+2.37X_2+2.64X_3-1.15X_1X_2-3.57X_1X_3-0.83X_2X_3-6.08X_1^2+3.89X_2^2-1.67X_3^2$$

F-statistic: 210.26 value of P_r>F below 0.0001 R^2=0.9963

Fluidized Bed Crystallizer



$$Mg^{2+} + HPO_4^{2-} + NH_4^+ \rightleftarrows NH_4MgPO_4$$

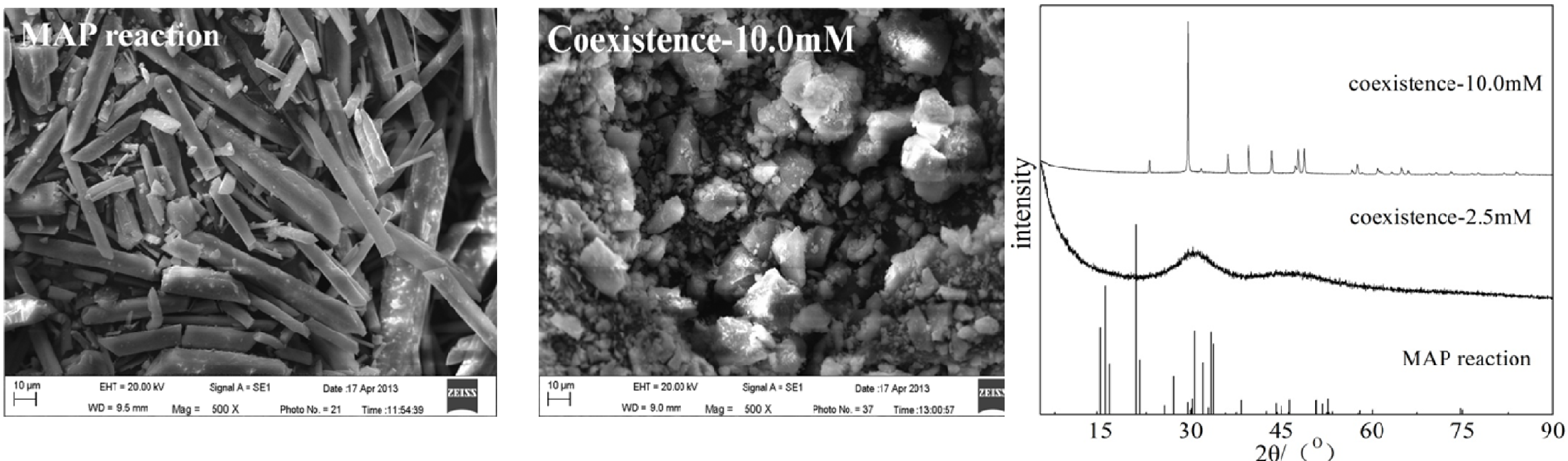
$$3Ca^{2+} + 2PO_4^{3-} \rightleftarrows Ca_3(PO_4)_2$$

$$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3 \qquad K_{sp}=3.36\times10^{-9}$$

$$Mg^{2+} + CO_3^{2-} \rightleftarrows MgCO_3 \qquad K_{sp}=3.5\times10^{-3}$$

Influence of Ca^{2+} and CO_3^{2-} on the MAP reaction

Mg/P=6:1



(a) (b) (c)

With the increasing Ca/Mg molar ratio, MAP appeared in the products.

In the high alkalinity system, calcium was mainly participated in forming $CaCO_3$, and phosphate was mainly removed in the form of MAP.

FBR Power Consumption

The power of devices used in research

Devices	peristaltic pumps1	peristaltic pumps2	aeration pump	Stirrer(×2)	Chrome pH automatic dosing machine
Power/(W)	50	40	2.5	100(×2)	50

The cost of dolomite lime and electricity were \$32.64/t and \$0.082/kW·h (according to the electricity charges in Beijing, China), respectively.

calcium chloride (about \$127.30/t)
magnesium hydroxide (about \$620.16/t)
magnesium chloride (about \$195.84/t)
polyaluminium chloride (about \$228.48/t)

Acid-treated DL process cost:

- DL acidification accounting for 12.73%
- pH adjusted solution 50.93% at maximum
- electricity fee of 36.34%.

Thanks for your attention