Use of calcined dolomite as chemical coagulant in the simultaneous removal of nitrogen and phosphorus

6th International Conference on Sustainable Solid Waste Management

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Background

Background

https://pixabay.com/en/canal-water-froth-alga-pier-2643420/

- **Phosphorus (P) and nitrogen (N) are the main nutrients in agricultural wastewaters and sludges**
  - Runoffs to waterways cause eutrophication
  - Nitrogen typically as ammonium (NH_4^+) which evaporates easily as ammonia (NH_3) gas
- **Large commercial potential in the recycled fertilizer market**
  - Estimated market size in Finland alone 0.5 billion € annually [1]
  - Recycled fertilizers will be included in the revised fertilizer legislation of the European Union [2]

[1] Aho, M., Pursula, T., Saario, M., Miller, T., Kumpulainen, A., Päällysaho, M., Autio, M., Hillgren, A., Descombes, L.: Ravinteiden kierron taloudellinen arvo ja mahdollisuudet Suomelle. Sitra, Helsinki (2015)
[2] European Commission: Proposal for a regulation of the European Parliament and of the Council laying down rules on the making available on the market of CE marked fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 (2016)

Background

- **Ammonium and phosphate could be precipitated as a struvite ($NH_4MgPO_4 \cdot 6H_2O$)**
  - Molar ratios Mg:P:N 1:1:1
  - Slow-release fertilizer
  - Typical precipitation reagents are commercial Mg-salts ($MgCl_2$, $MgSO_4$, MgO and $Mg(OH)_2$)
  - Cheaper precipitation reagents should be tested
- **Dolomite is carbonite mineral composed of calcium magnesium carbonate ($CaMg(CO_3)_2$**
  - Used e.g. as a soil improver
  - In this study, dolomite was used as a precipitation reagent

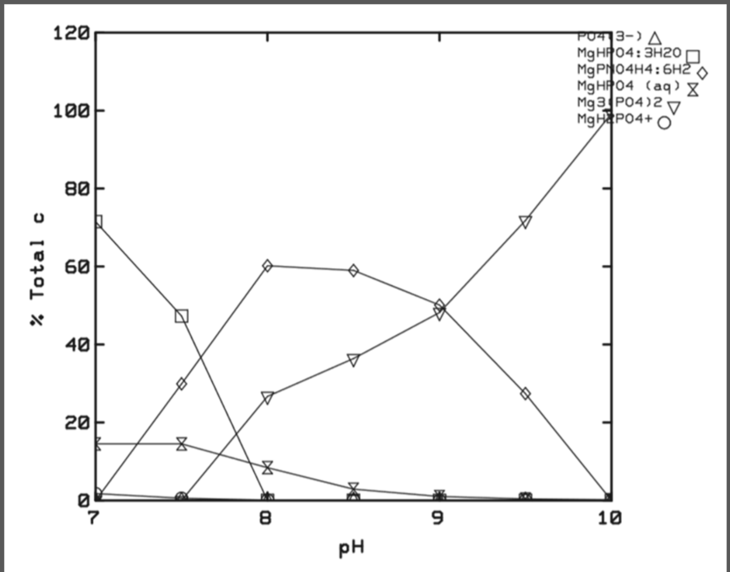
Materials and methods

Materials and methods

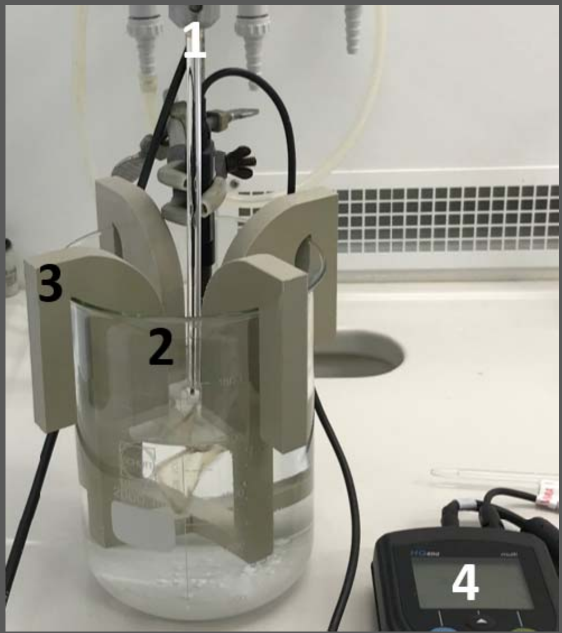
- Dolomite was first calcined at 750 °C or at 950 °C

$$(CaMg(CO_3)_2 \xrightarrow{\text{Heat}} CaO + MgO + 2\ CO_2\ (g)$$

- Commercial MgO was used as a comparison
- Mine QL program was used to calculate optimal conditions for the precipitation
  - Molar ratios Mg:P:N of 1.1-1.6:2:2 for dolomite and Mg:P:N of 1.1-1.6:1:2 for MgO
  - pH 8.5 (MgO and dolomite 750 °C) or 9.0 (dolomite 950 °C)
  - Room temperature (20 °C)



Materials and methods



Precipitation reactor consists of a curved blade (1) connected to a rotor; a 2 L decanter glass (2); stators (3); and a pH-meter (4)

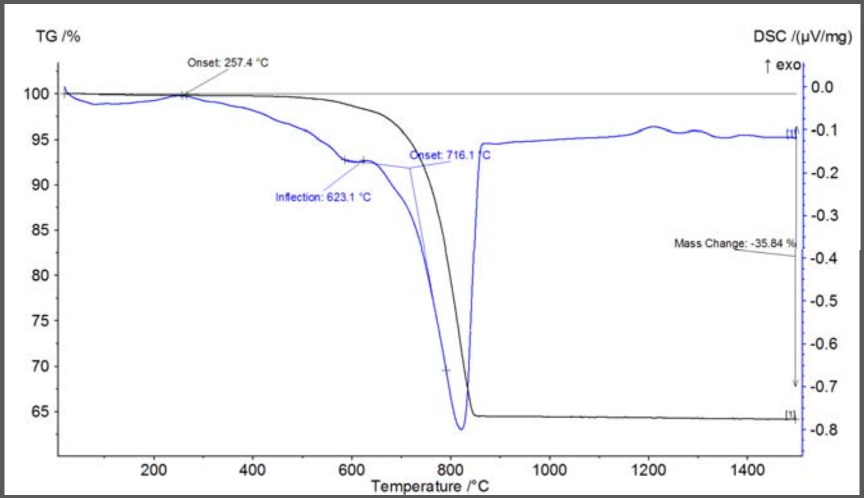
- **Solutions:**
  - Coagulant: 0.5 – 2.3 g of (dolomite or MgO) coagulant in 10 mL of de-ionized water
  - Ammonium phosphate $(NH_4)_2HPO_4$: ammonium chloride (NH_4Cl) and potassium hydrogen phosphate (KH_2PO_4) salts (200 mg/L NH_4^+ and 100-200 mg/L PO_4^{3-}) in de-ionized water
- **Precipitation:**
  - Coagulant solution added to $(NH_4)_2HPO_4$ solution while stirring the solution at 450 rpm (1 minute)
  - Constant stirring during experiments (50 rpm)
  - Small amount of seed crystals added (10 mg struvite; 4 h experiments only)
  - Water samples taken every half an hour
  - Reaction time 4 h or 24 h
- **Analyzes:**
  - Water samples: NH_4-concentration measured with NH_4-selective electrode
  - Precipitate: CHNS-analyzer, XRD and SEM
  - Dolomite: SEM, XRF and TG-DSC

Materials and methods

- **Also one test with agricultural sludge**
  - Sludge filtered before precipitation
  - Phosphate concentration 25 mg/L; ammonium concentration 137 mg/L; pH 8.95
  - Potassium hydrogen phosphate (KH_2PO_4) added to obtain a molar ratio Mg:N:P 1.3:1:1
  - Precipitation agent dolomite 750 °C (pH 9; reaction time 24 h)

Results

Dolomite characterization



– XRF:

- Main components CaO, MgO and SiO_2 (calcined at 950 °C)
- Molar ratio MgO:CaO 1:1.3

	Na_2O (%)	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	P_2O_5 (%)	S (%)	K_2O (%)	CaO (%)	TiO_2 (%)	FeO (%)	MnO (%)
Dolomite	0.16	27.4	1.34	15.27	0.31	0.07	0.22	50.59	0.05	0.96	0.02

– TG-DSC:

- Complete decomposition at 850 °C
  - Calcination at 950 °C: all $MgCO_3$ and $CaCO_3$ transformed to oxides (MgO and CaO)
  - Calcination at 750 °C: most of the $MgCO_3$ decomposed to MgO, $CaCO_3$ mostly in the carbonate form [3]

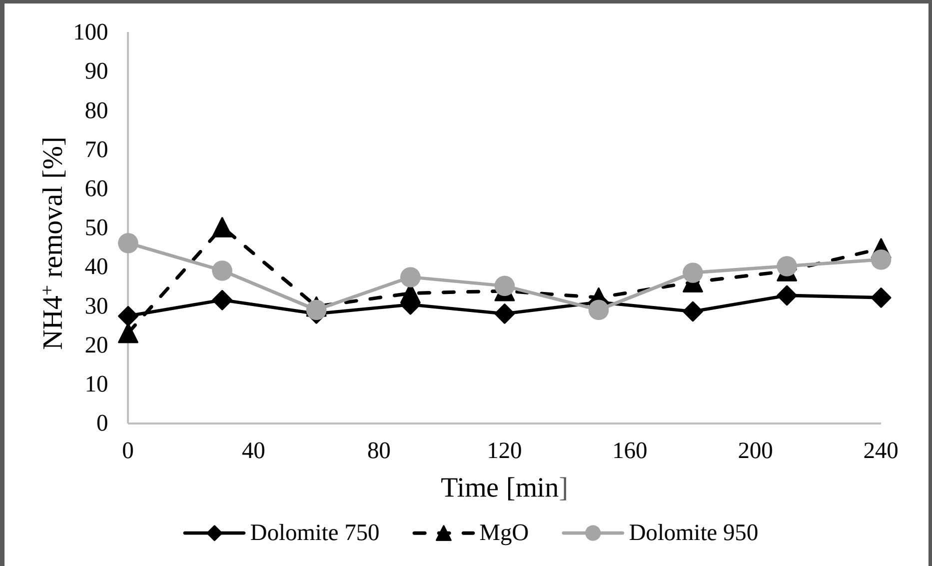
$$(CaMg(CO_3)_2 \longrightarrow CaCO_3 + MgO + CO_2\ (g)$$

Heat

$$(CaMg(CO_3)_2 \longrightarrow CaO + MgO + 2\ CO_2\ (g)$$

[3] Olszak-Humienik, M., Jablonski, M.: Thermal behavior of natural dolomite. J Therm. Anal. Calorim. 119. 2239-2248 (2015)

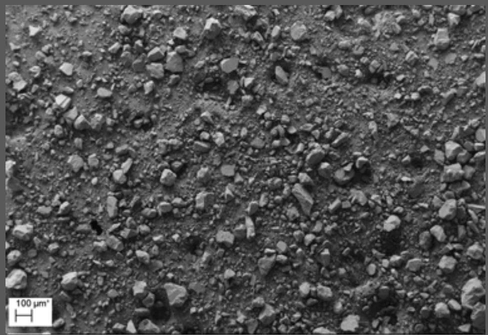
Ammonium removal, 4 h experiment

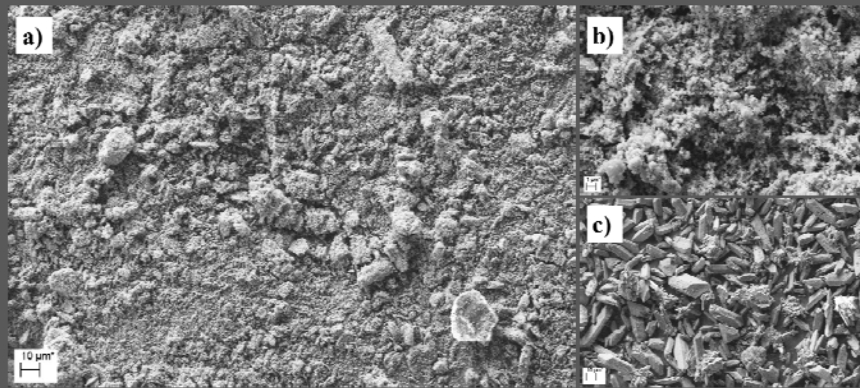


- Ammonium removal: 32 % for dolomite 750 °C, 41 % for dolomite 950 °C and 44 % for MgO
- Removal percentage was roughly the same throughout the experiment when dolomite was used, indicating a poor precipitation
  - Longer contact times should be used

Precipitate characterization, SEM (4 hours)

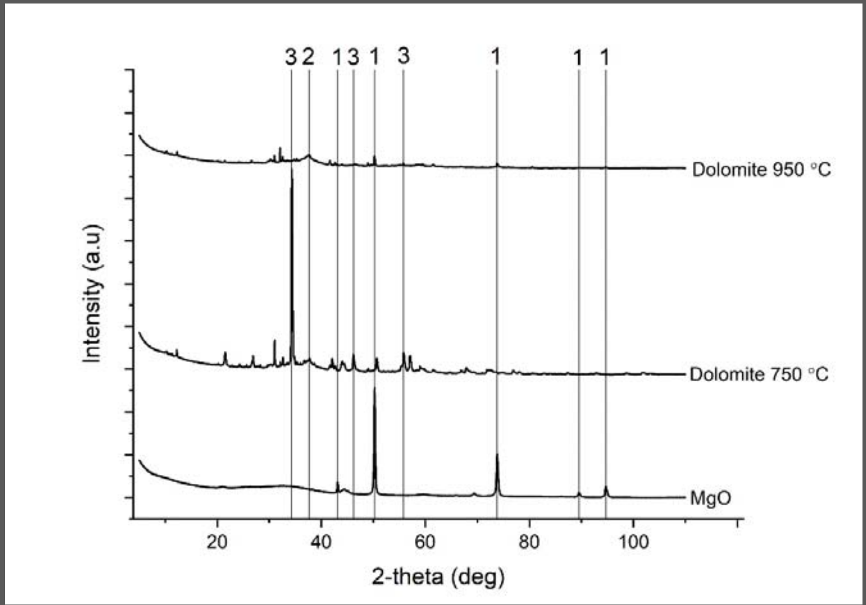
– **Dolomite particles are covered with very fine precipitate particles in Figs a) and b)**


SEM-image of the dolomite



SEM-images of the precipitates (Mg:P:N 1.1:1:2 for MgO and 1.1:2:2 for dolomite): a) and b) calcined dolomite 950 °C; c) MgO. The bars at a) and c) indicate 10 µm length and at b) 1 µm length

Precipitate characterization (4 h experiments), XRD and CHNS

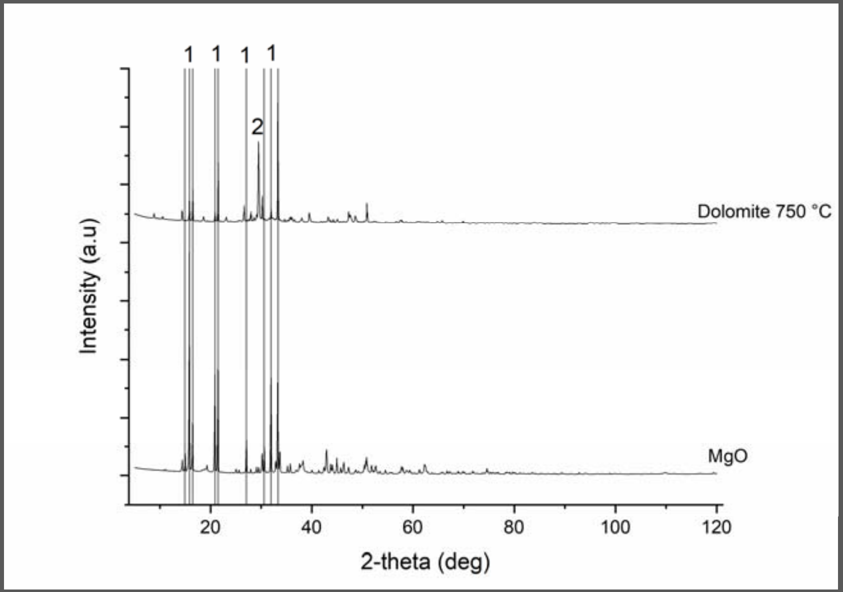


XRD diffractograms of the precipitates (Mg:P:N 1.1:1:2 for MgO and 1.1:2:2 for dolomite): 1 = MgO; 2 = $Ca_5(PO_4)_3(OH)$; 3 = $CaCO_3$

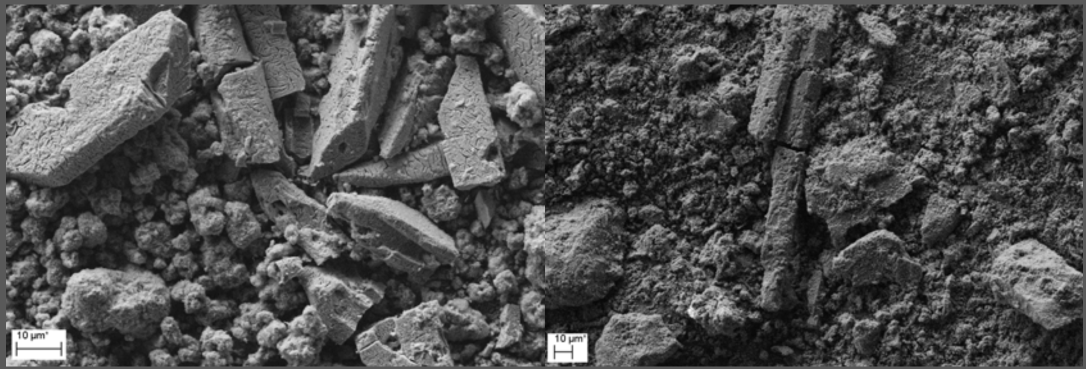
- **Broad amorphous hump was detected below 40 degrees (MgO)**
  - Struvite spikes should be between 10 and 40 degrees
  - One m% of nitrogen present in the precipitate (CHNS analysis) -> some struvite was formed
- **Small amount of Magnesium ammonium phosphate compound was found (dolomite 750 °C)**
- **$CaCO_3$ spike was found, confirming that the decomposition of dolomite was not complete (dolomite 750 °C)**
- **Only hydroxylapatite ($Ca_5(PO_4)_3(OH)$) found (dolomite 950 °C)**
  - CaO precipitates the phosphate as hydroxylapatite before struvite begins to form
  - Calcination at a lower temperature should be preferred

Precipitate characterization (24 h experiments), XRD

- **All main spikes were associated with struvite**
  - Dolomite precipitate contained also some $CaCO_3$
- **24 hour reaction time needed for struvite precipitation when using dolomite**

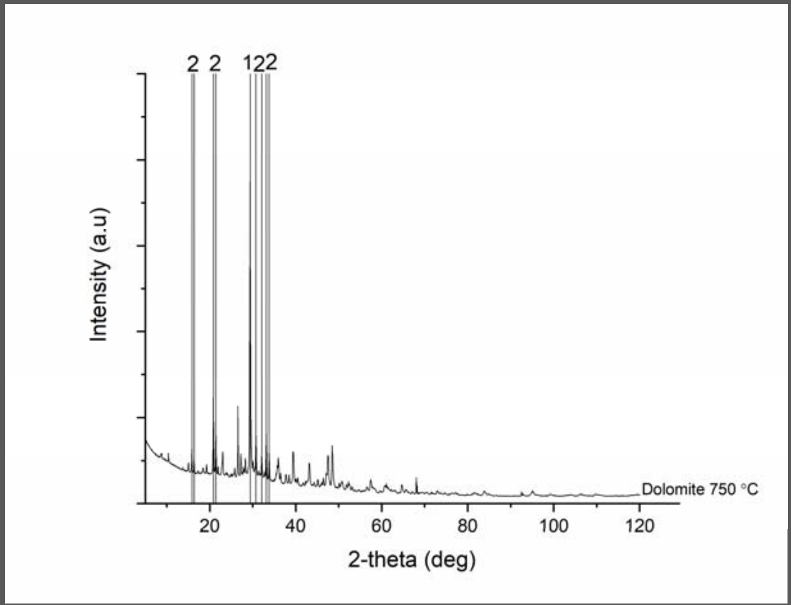


XRD diffractograms of the precipitates (Mg:P:N 1.1:1:2 for MgO and 1.1:2:2 for dolomite): 1 = ($NH_4MgPO_4 \cdot 6H_2O$); 2 = $CaCO_3$



SEM-images of the precipitates. Left MgO and right dolomite 750 °C

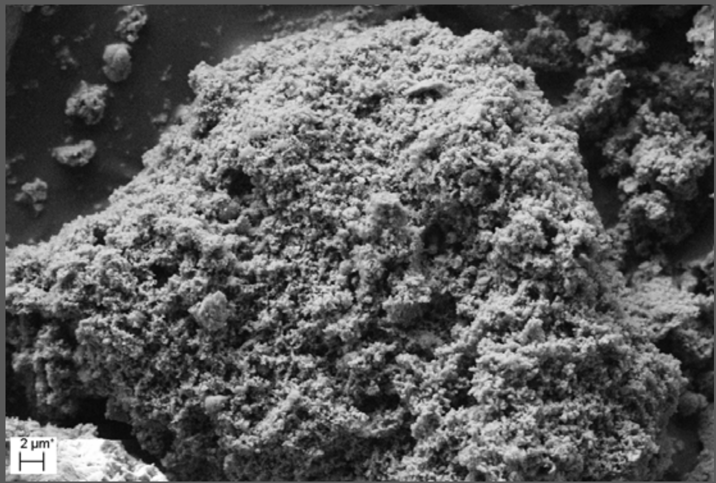
Agricultural sludge



XRD diffractograms of the precipitate (Mg:P:N 1.3:1:1):

1 = $CaCO_3$; 2 = ($NH_4MgPO_4 \cdot 6H_2O$)

– **Main spikes $CaCO_3$ and struvite**
  - Dolomite can be used as precipitation reagent for authentic agricultural sludge
  - Phosphate concentration has to adjusted for optimal precipitation or excess ammonium has to be removed with e.g. adsorption



Summary

Summary

- **Calcined dolomite can be used as inexpensive precipitation reagent in struvite precipitation**
- Calcination temperature 750 °C or lower
- 24 hour precipitation time needed
- **Further studies needed to optimize precipitation**

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