Waste Recycling – Sludge based fertilizers (Waste Recycling and WaterPro projects)

Kokkola Material Week - ReKokkola

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Vipuvoimaa EU:lta 2014–2020

Euroopan unioni
Euroopan aluekehitysrahasto

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WaterPro – Chemical precipitation of nutrients as struvite

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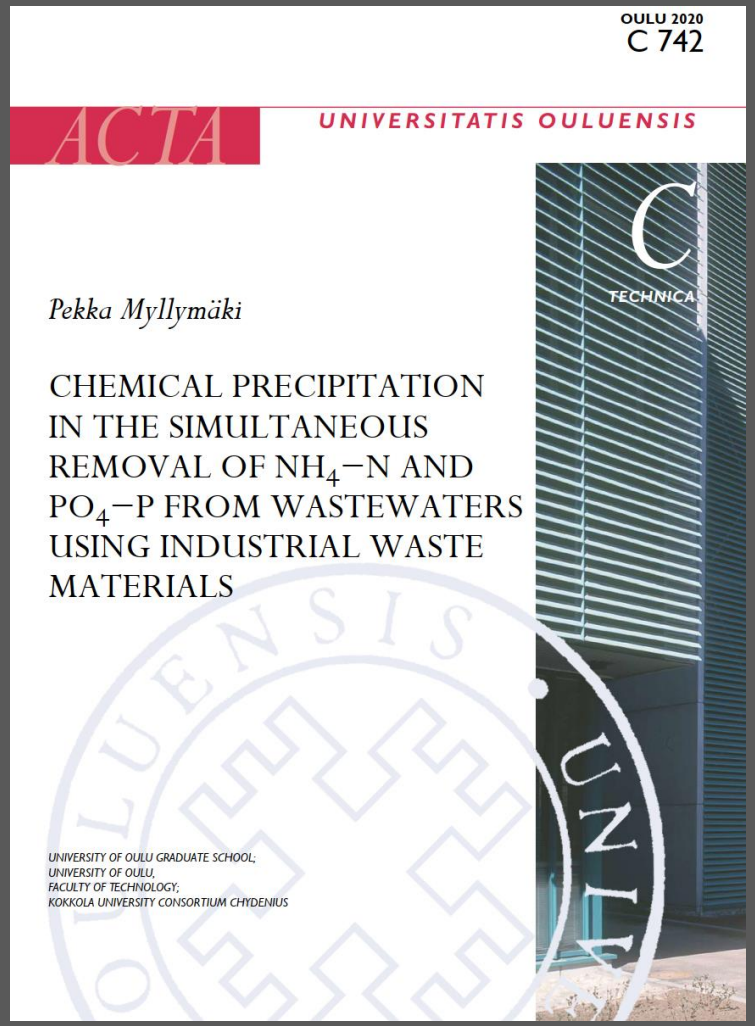
Papers so far...



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- Myllymäki, Pekka; Pesonen, Janne; Tynjälä Pekka; Hu, Tao; Lassi, Ulla: The Use of Ca- and Mg-rich Fly Ash as a Chemical Precipitant in the Simultaneous Removal of Nitrogen and Phosphorus − Recycling and Reuse, Recycling, 2019(4)2: 14.
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- Myllymäki, Pekka; Pesonen, Janne; Tynjälä Pekka; Hu, Tao; Lassi, Ulla: Use of paper mill sludge as chemical coagulant in the simultaneous removal of nitrogen and phosphorus, Desalination and Water Treatment, 2020(194)459-467.
- Pesonen, Janne; Sauvola, Emilia; Hu, Tao; Tuomikoski, Sari: Use of sidestream based MgSO4 as chemical coagulant in the simultaneous removal of nitrogen and phosphorus from wastewaters, Desalination and Water Treatment, 2020(194)389-395).

Materials

Dolomite is a carbonite mineral composed of calcium magnesium carbonate ($CaMg(CO_3)_2$)

Used e.g. as a soil improver

Fly ash is fine-grained, inorganic residue that is left behind after combustion at a thermal power plant

Contains mostly Ca, Mg, Al, and Si oxides in varying proportions (depending on the fuel used)
Can be used as a fertilizer

Struvite ($NH_4MgPO_4 \cdot 6H_2O$)
Molar ratios Mg:P:N 1:1:1
Slow-release fertilizer

- **Ca precipitates phosphate as hydroxylapatite -> the more Ca there is, the less struvite is formed**
- **Dolomite and fly ash was treated with H_2SO_4 to prepare $MgSO_4$ solution**

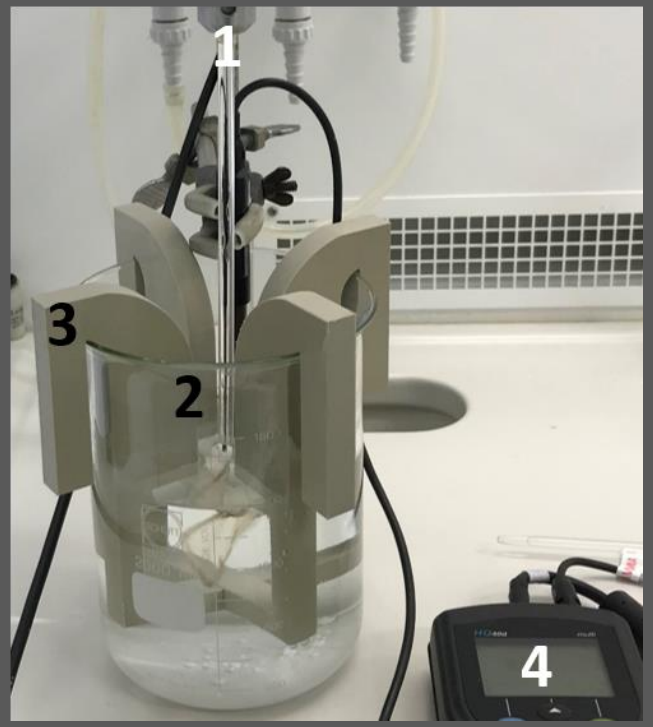
Main components (XRF) of the dolomite and fly ash

	CaO (%)	MgO (%)	SiO_2 (%)	Al_2O_3 (%)	FeO (%)	P_2O_5 (%)	K_2O (%)	Na_2O (%)	TiO_2 (%)	MnO (%)	Others (%)
Dolomite	**37.9**	**16.5**	10.4	3.1	3.5	0.1	1.1	0.2	0.3	0.1	26.8
Fly ash	**36.9**	**14.2**	17.7	8.1	8.9	1.6	0.5	0.5	0.3	0.3	11.0

Mg, Ca and harmful element concentrations (ICP) of the $MgSO_4$ solutions

Sample	Ca (mg/L)	Mg (mg/L)	As (mg/L)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Ni (mg/L)	Pb (mg/L)	Zn (mg/L)
DOL based $MgSO_4$	**494**	**9430**	3.94	0.10	0.97	3.41	1.81	0.14	2.79
FA based $MgSO_4$	**483**	**14500**	0.08	0.01	0.64	0.59	1.21	0.04	1.32

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)

– Precipitation of struvite:

- Molar ratios Mg:P:N of 1.1-2:1-2:1-2
- pH 9.0
- Room temperature (20 °C)
- Time 4-24 h

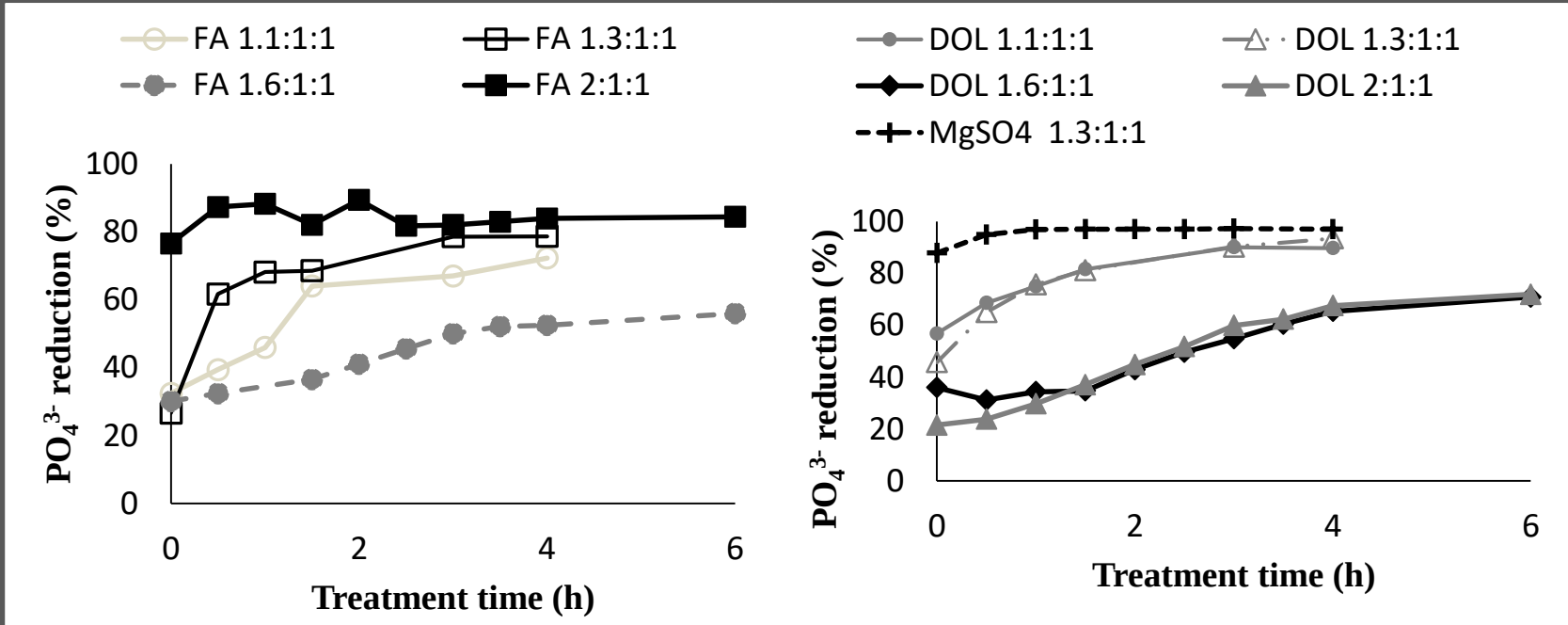
- Coagulant solution added to $(NH_4)_2HPO_4$ solution while stirring the solution at 450 rpm (1 minute)
- Constant stirring during experiments (50 rpm)
- Water samples taken every half an hour

- Analyzes:

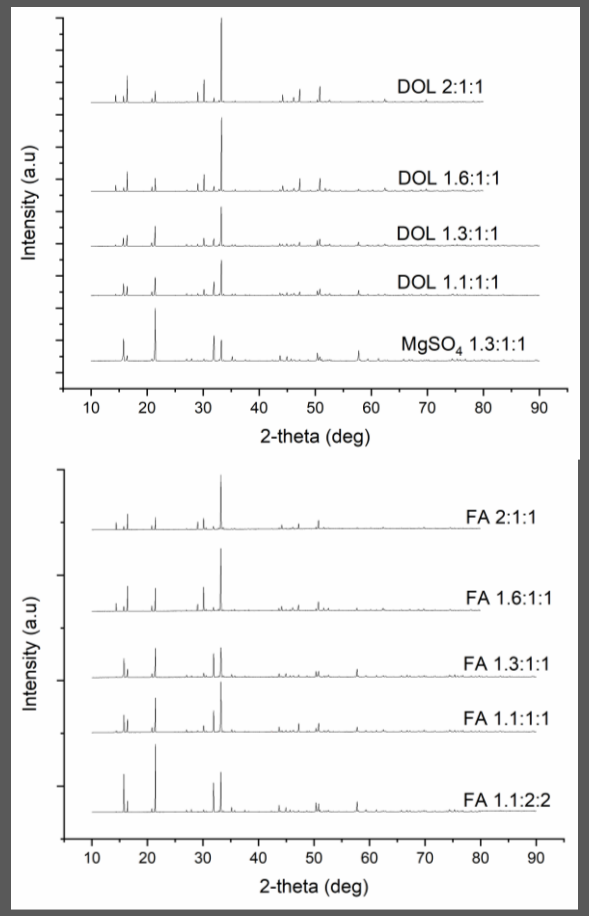
- Water samples: ICP, IC, and NH_4-selective electrode
- Precipitate: XRD and SEM
- Dolomite: SEM, XRF and TG-DSC
- Fly-ash: SEM, XRF

Results: Phosphate removal

- Best phosphate removal was achieved with commercial $MgSO_4$ (97 %)
- Very good phosphate removal also with DOL 1.3:1:1 (93.3 %) and DOL 1.1:1:1 (89.8 %)
- For FA the best removals were 84.5 % for FA 2:1:1, 82.5% for FA 1.1:2:2, and 78.7 % for FA 1.3:1:1



Precipitate characterization, XRD and yield



- **All peaks associated with struvite**
- **The best yield was obtained with commercial $MgSO_4$ salt (90.4 %).**
- **The best yields for both DOL and FA were obtained with molar ratio 1.3:1:1, 77.5 % for DOL and 71.3 % for FA**

Yields of the formed struvite for the corresponding molar ratios

Sample	Yield (%)
FA 1.1:2:2	**70.2**
FA 1.1:1:1	58.3
FA 1.3:1:1	**71.3**
FA 1.6:1:1	46.5
FA 2:1:1	55.2
DOL 1.1:1:1	**73.8**
DOL 1.3:1:1	**77.5**
DOL 1.6:1:1	54.1
DOL 2:1:1	45.7
$MgSO_4$ 1.3:1:1	**90.4**

Yield = (total mass of the precipitate / theoretical mass of struvite formed) x 100

Summary – WaterPro

- **$MgSO_4$ solution prepared from dolomite and fly ash and tested for struvite precipitation**
  - Pure struvite obtained
  - The best struvite yields for both DOL and FA were obtained with molar ratio Mg:P:N 1.3:1:1
- **Fly ash and dolomite based $MgSO_4$ solutions have great potential in the ammonium and phosphate precipitation**
- **Tests with authentic wastewaters, solubility tests and growth tests in greenhouses and fields should be conducted**