Utilization applications for water treatment sludges – WaterPro project

Kokkola Material Week - ReKokkola

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Programme for Sustainable Growth and Jobs

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Background

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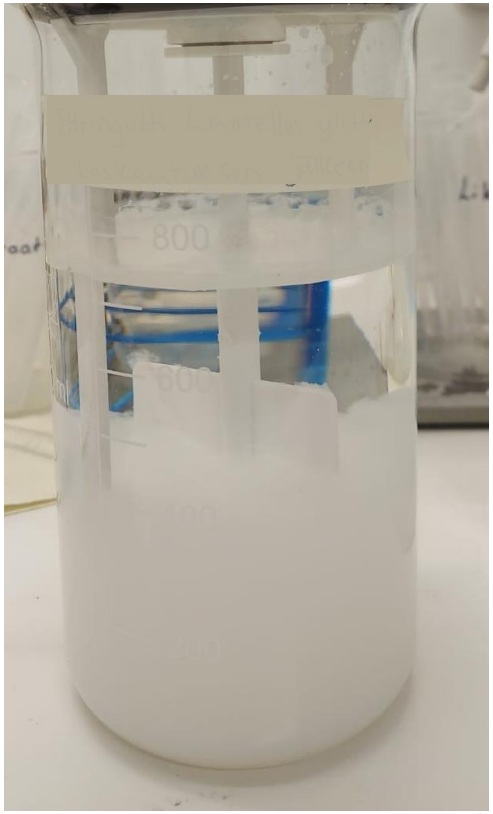
- Chemical and electrochemical water treatment generates sludge that is considered waste
  - Sludge handling and disposal costs
    - Waste tax 70 €/ton
- Sludge contain valuables such as metals and/or nutrients
  - Utilization options
  - Case 1: Struvite
  - Case 2: EC-sludges



Case 1: Struvite

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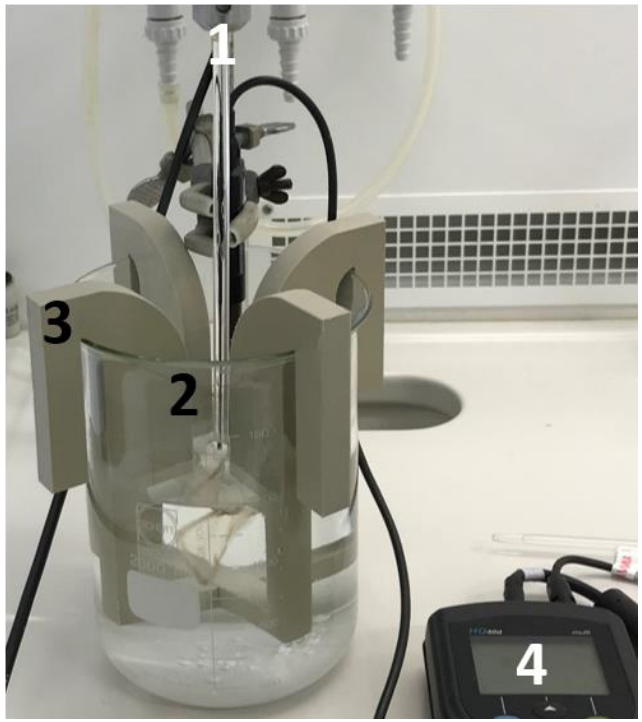
Case 1: Struvite ($NH_4MgPO_4 \cdot 6H_2O$)

Contains:
N 5.7 m%
P 12.6 m%

- Struvite is regarded as a slow-release fertilizer
  - could reduce the eutrophication of waterways caused by commercial water-soluble nitrogen and phosphorus fertilizers
- Struvite fertilizers also reduce the need to use virgin materials such as the declining phosphate rock reserves in fertilizer production
- Large commercial potential in the recycled fertilizer market
  - Estimated market size in Finland alone 500 million € annually [1]
- Struvite fertilizers are 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] Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003 (2019)

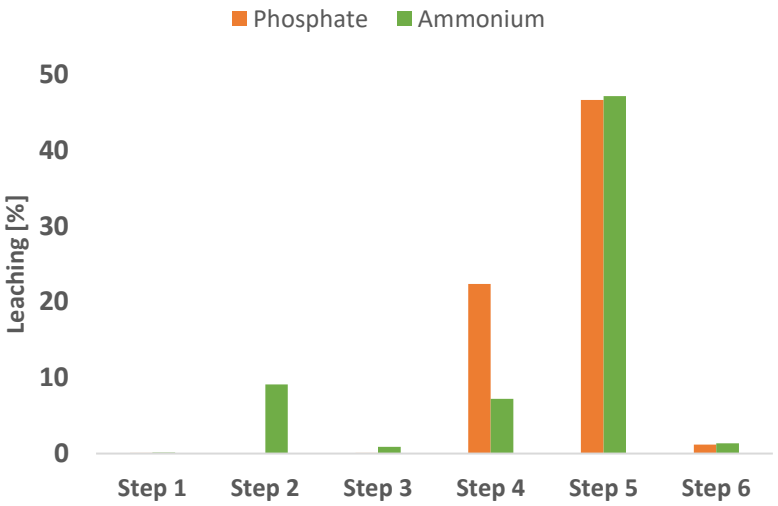
Case 1: Struvite



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)

- Both electrochemical and chemical struvite precipitation studied
- Sequential leaching of nutrients from struvite
- Granulation with fly ash
  - Chemical composition

6-step sequential leaching*



- Serial extraction in which the sample is treated successively with different reagents and the intensity of the reagents gradually increases
- Sequential leaching divides elements into different fractions in order to assess bioavailability and environmental risk

- Leaching occurred mainly in step 5
- Around 70% of the phosphate and ammonium were dissolved in the extraction
  - Nutrients are released only over a long period of time

Step 1 (water soluble): water
Step 2 (ion-exchangeable): $MgCl_2$, 1M
Step 3 (bound to carbonates): Sodium acetate, 1M
Step 4 (bound to humic acid): Na_4PO_7 (0.1M, pH = 7)
Step 5 (bound to Fe-Mn oxides): $NH_2OH{\cdot}HCl$ (0.25 M) + HCl (0.25 M)
Step 6 (bound to organics): HNO_3 (0.02 M) + 30% hydrogen peroxide; and CH_3COONa (3.2M) + HNO_3 (3.2 M)

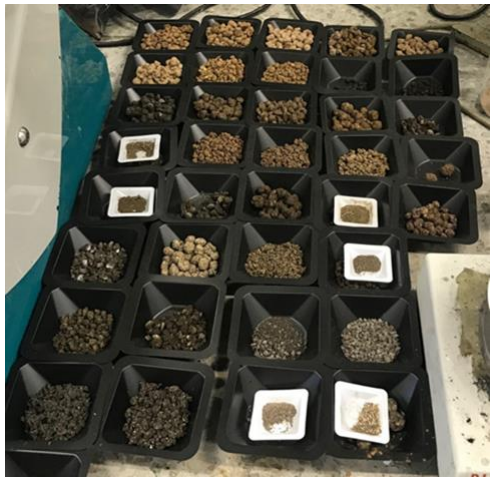
1 g sample, L/S = 50

*doi: 10.1016/j.envpol.2017.12.106

Granulation of struvite with fly ash

- Struvite was granulated with fly ash in a laboratory mixer
  - fly ash-struvite ratio 4:1
  - 28 % water
- Mixer was stopped after the average granule size of around 5 mm was achieved.
- Granules were dried at room temperature for 28 days
  - Elemental analysis

Element concentrations



- Harmful element concentrations were below the Finnish limit values for both field and forest fertilizers
- The addition of struvite caused both P and Mg concentrations to double compared to the fly ash only
  - Minimum requirement for K + P exceeded
- Liming capacity of the granules was 23.7 % Ca whereas the limit value for field fertilizers is ≥10 % Ca
- Therefore, these granules could be suitable for fertilizer use

Concentrations of nutrients and harmful elements of fly ash and granules and limit values of Finnish fertilizer degree. All concentrations are as mg/kg.

	Ca	K	P	Mg	As	Cd	Cr	Cu	Ni	Pb	Zn
Fly ash	103000	7950	9920	19000	25	1.9	69	87	51	31	284
Granule	89900	6075	21945	35724	21	1.1	70	76	65	35	240
Field / Forest	- / ≥ 60000	•/ K + P ≥ 20000			25 / 40	2.5 / 25	300	600 / 700	100 / 150	100 / 150	1500 / 4500

Case 2: EC-sludges

Utilization options for EC-sludges – literature survey

- EC-sludges contain high amounts of Fe, Al, or Mg dissolved from the electrode
- Sludge contains metals and nutrients removed from waste water

- Potential utilization applications for EC-sludges
  - Fertilizers (Mg)
  - Adsorbents (Al)
  - Catalysts (Fe, Ti)
  - Pigments (Fe)
  - Construction (Al, Fe)

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- Fertilizer granules prepared from struvite and fly ash
  - Releases nutrients gradually over a long time period
  - Struvite addition improve phosphorus concentration of granules
- Potential utilization applications for EC-sludges
  - Fertilizers (Mg)
  - Adsorbents (Al)
  - Catalysts (Fe, Ti)
  - Pigments (Fe)
  - Construction (Al, Fe)