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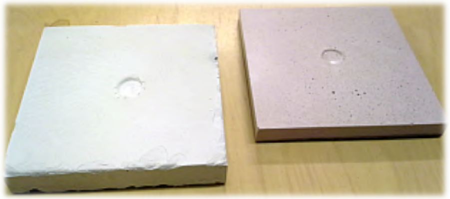
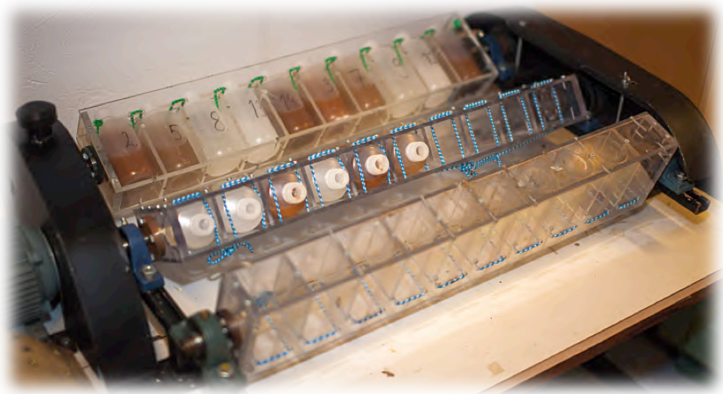


Geopolymers & water treatment

Tero Luukkonen, 9.7.2014, Geopolymer camp, St. Quentin



How can geopolymers be utilized in water treatment (as adsorbents)?

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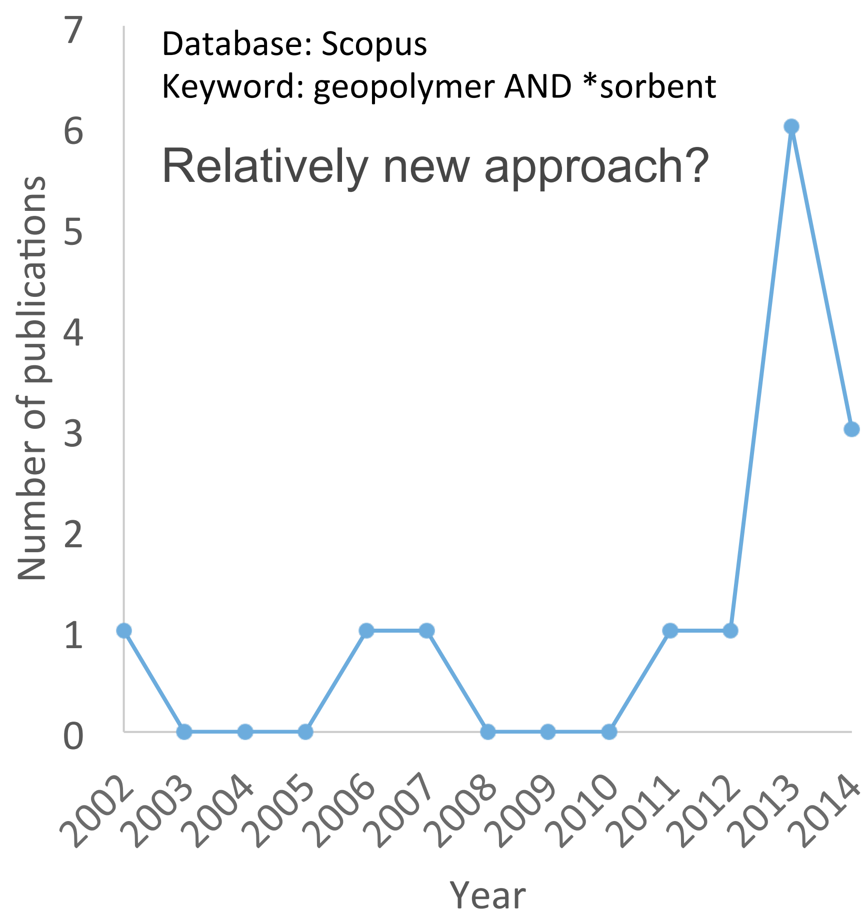
- Adsorbent = material used to attach molecules (in this case) from water to its surface.
- Geopolymers are known to be amorphous analogues of zeolites.
- Zeolites can be used as ion exchangers in various water treatment applications: soluble heavy metal removal, water softening (Ca^{2+}, Mg^{2+}), ammonium removal etc. depending on the pore size distribution.
- Therefore: it could be assumed that geopolymers could have similar properties.



Mechanisms how geopolymers work as sorbents

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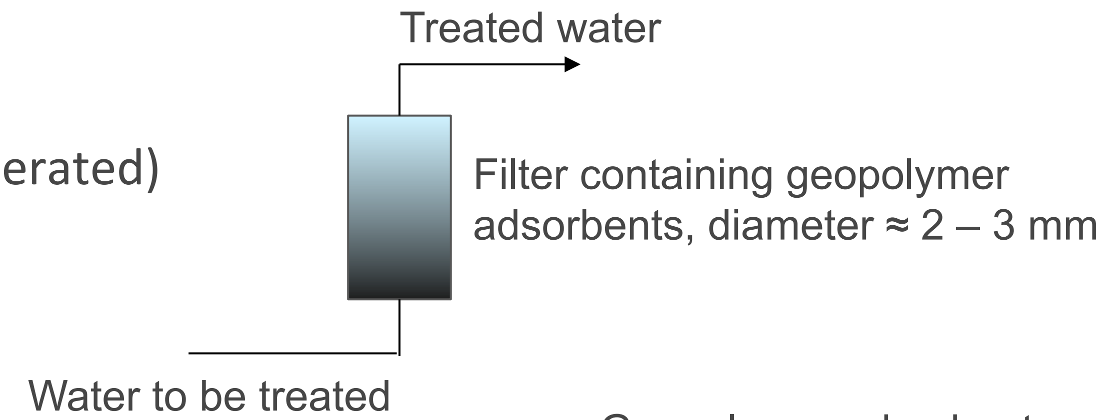
- Geopolymers work similarly to zeolites:
  - Cation exchanger (releasing Na+ or K+ if prepared by geopolymerzation in alkaline medium) → only cations can be removed from water!
  - Adsorbent (chemisorption or physisorption).
  - Increase of pH due to residues of alkalis used in synthesis → precipitation of metal hydroxides. This effect decreases as geopolymer is being washed.

- Smaller particle size / more porous structure → more surface area → more active sorbent.

Geopolymers in water treatment: some process options

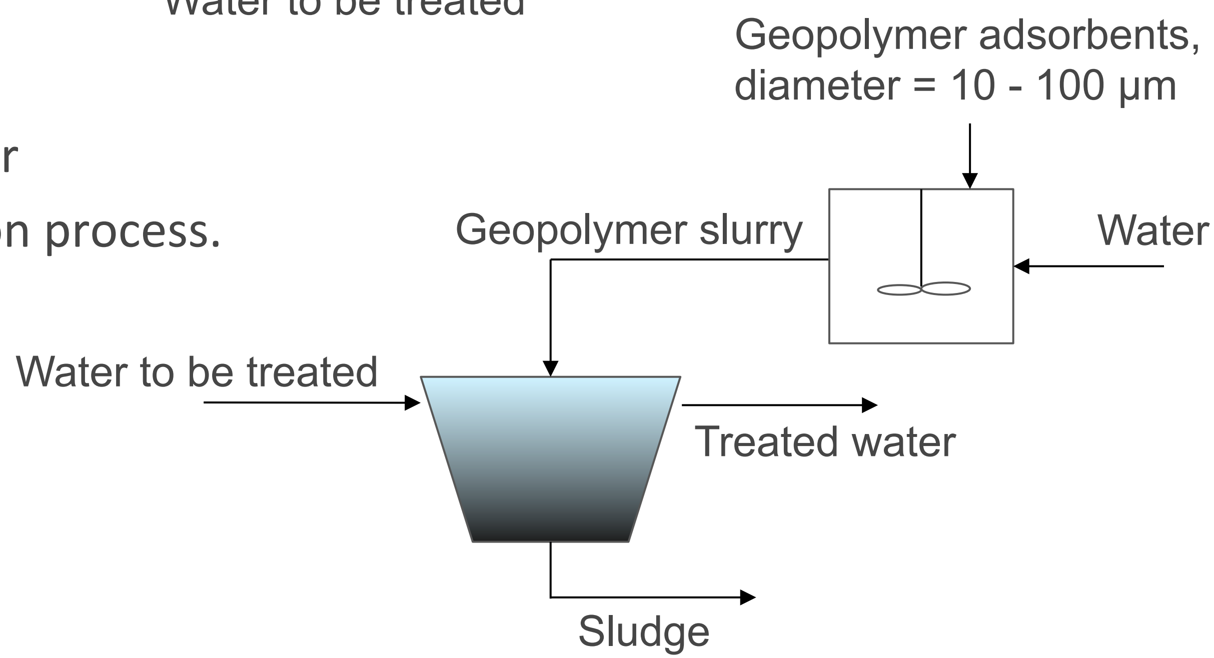
1. As an active filter medium

- Geopolymer can be re-used (regenerated)



2. As a slurry made from powder

- To be dosed to sedimentation process.
- Geopolymer not re-usable.



How to prepare geopolymer adsorbents (some examples)?

- Dissolution of **rice husk ash** and **NaOH** pellets (97% purity) in distilled water. **Metakaolin** was added after the dissolution of silica. (Chem. Lett. 2014, 43, 128–130)

- The **zeolitic tuff** and **kaolinitic soil** were mixed in different ratios, and then the **sodium hydroxide solution** was added. After molding, compacting, **curing at 80ºC**, the samples were ground and sieved into aggregate size between 250-500 µm. Then the product was washed with excess amount of distilled water (to remove unreacted alkali), dried at 100ºC and kept in a desiccator. (Advances in Materials Physics and Chemistry, 2012, 2, 119-125)

- **Fly ash** was mixed with 14M **NaOH** solution using a mass ratio of 1.25. Geopolymer paste then started to form, which was mixed for 5–10 min to give complete homogenization. Vibration with ultrasonification to de-foam and enhance the dissolution of Al–Si material (fly ash) in the alkaline solution. The mixtures were then procured for 24 h at room temperature. The paste was then poured in a cylindrical container which was closed for **curing at a temperature of 105 ◦C** for 24 h in an oven. (Journal of Hazardous Materials 188 (2011) 414–421)

- How we did it: mixing of **metakaolin** with alkaline solution (**10 M NaOH + Na-silicate**). Curing at room temperature for 48 h. Crushing to required particle size. Washing with distilled water. Drying at 105 C.


d > 1 mm
50 µm < d < 1 mm
d < 50 µm

What geopolymer adsorbents have been used to remove (examples)

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- **Cs^{+}** (Chem. Lett. 2014, 43, 128–130)
- **Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}** (Advances in Materials Physics and Chemistry, 2012, 2, 119-125)
- **Pb^{2+}** (Journal of Hazardous Materials 188 (2011) 414–421)
- **Pb^{2+}, Cu^{2+}, Cr^{3+}, and Cd^{2+}** (Applied Clay Science 56 (2012) 90–96)
- **Cs^{+}** (Applied Clay Science 87 (2014) 205–211)
- **Cu^{2+}, Ni^{2+} and Pb^{2+}** (Chemical Papers 67 (5) 497–508 (2013))
- **Cu^{2+}** (Journal of Hazardous Materials B139 (2007) 254–259)

- Our research: **Ni, As and Sb** in real mine wastewater matrix.

Adsorption studies @ Kajaani University of Applied Sciences

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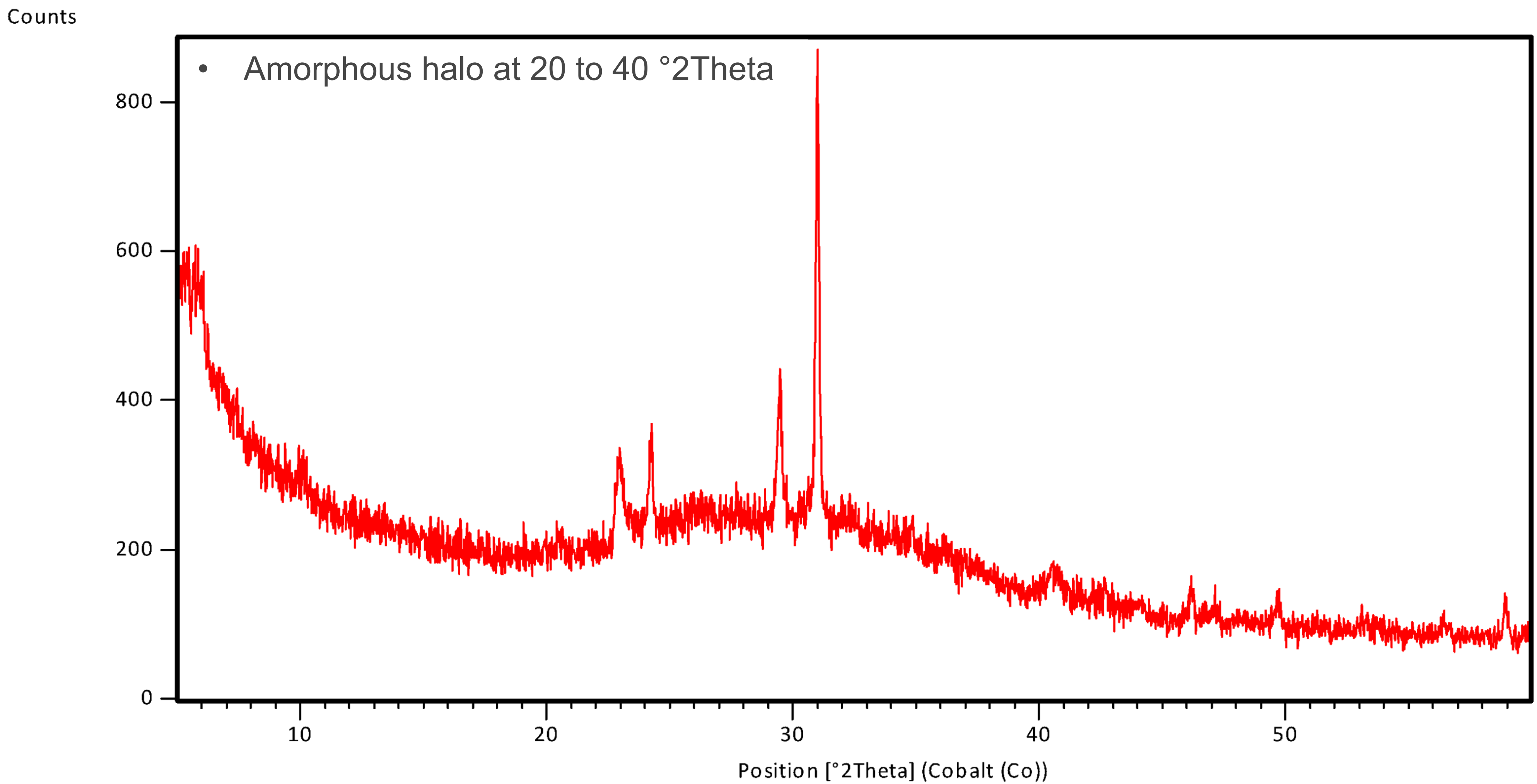
- Preparation of fly ash, **metakaolin** and **blast furnace slag** based geopolymer adsorbents.
- Batch and continuous sorption tests with **(real) mine wastewaters**:
  - Adsorption capasities, q [mg/g]
  - Adsorption isotherms (Langmuir, Freundlich, etc.)
  - Kinetics (reaction kinetics equations)
  - Regeneration
- Characterization of geopolymers:
  - XRD (identification of crystalline phases)
  - XRF (elemental composition)
  - SEM-EDS (surface morphology, elemental composition)
  - BET (surface area, pore volumes)
  - IR (identification of surface chemical groups)
  - Total surface charge

XRD: metakaolin geopolymer

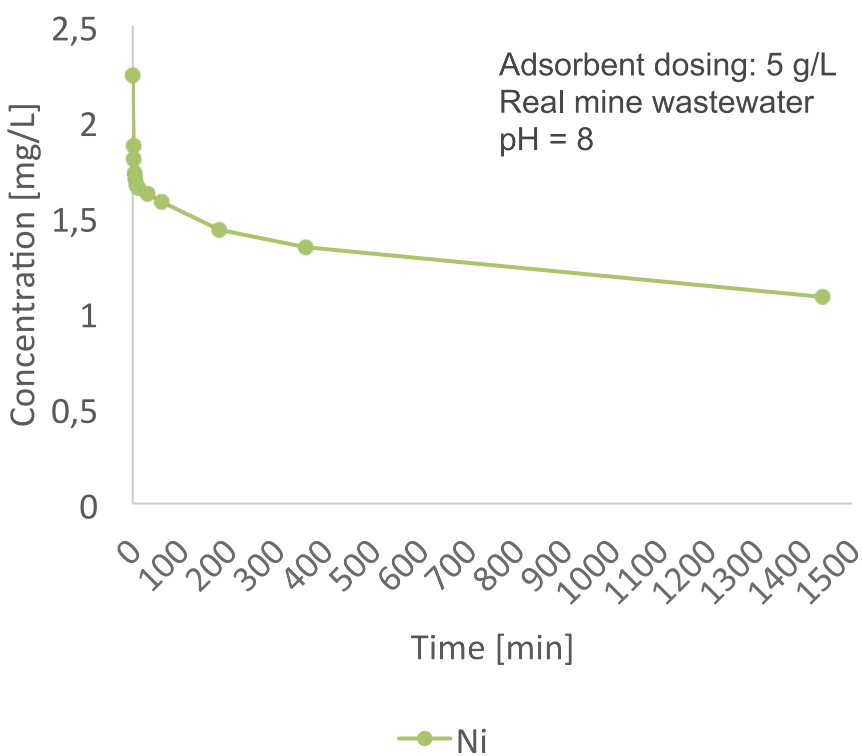


BET: surface area

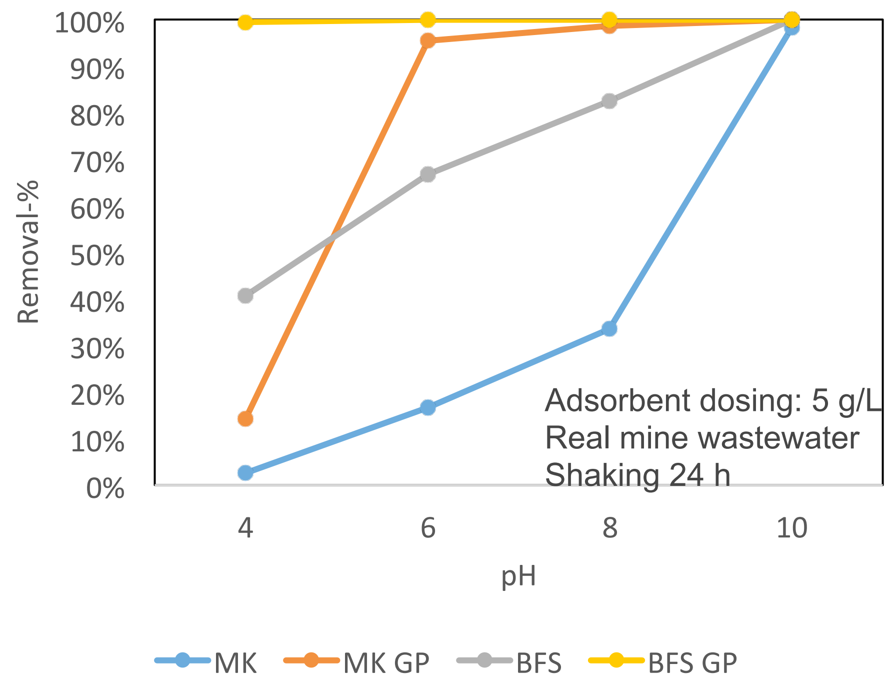
- Specific surface area:
  - Metakaolin 11,50 m^2/g
  - Metakaolin GP 22,42 m^2/g.
  - (For comparison: activated carbon typically 1000 m^2/g).

- Average pore width
  - Metakaolin 18,16 nm
  - Metakaolin GP 30,97 nm

Some preliminary results: removal of Ni



Removal of Ni with BFS geopolymer: kinetics



Removal of Ni with BFS and MK geopolymers: effect of pH and comparison with starting material

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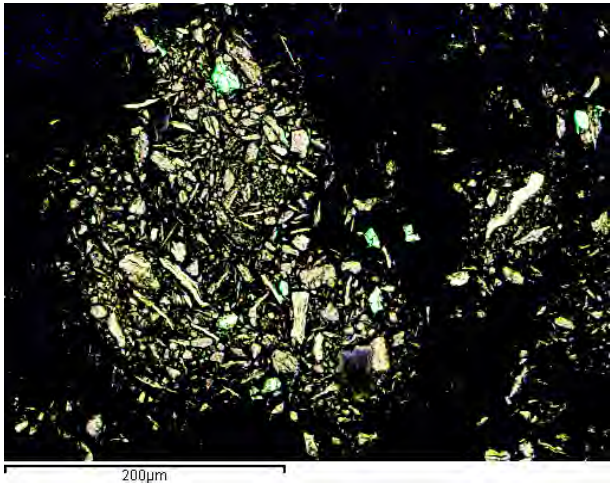
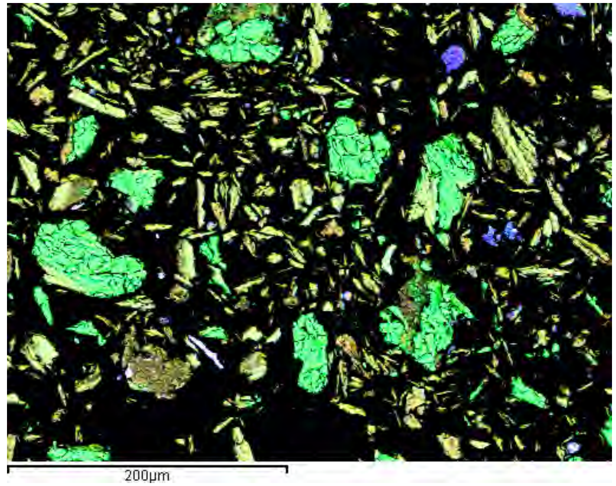
Conclusions and remarks at this point

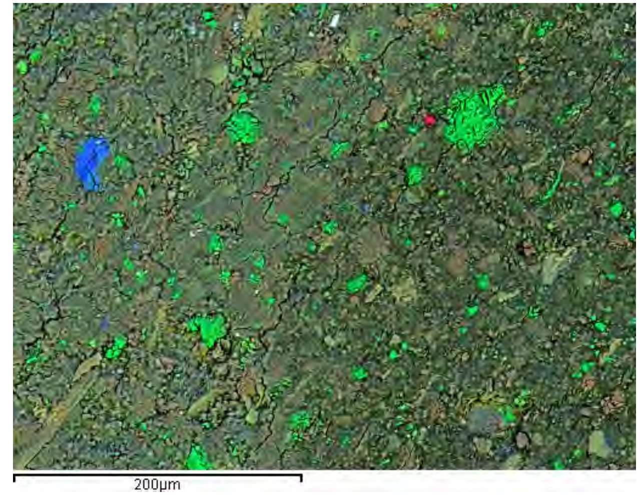
- Geopolymerization as a process to produce efficient adsorbents (cation exchangers) seems promising.
- Possible to reuse via regeneration (for example concentrated NaCl solution).
- Geopolymerization increases adsorption capacity, specific surface area and average pore width.
- Some further research questions:
  - Na vs K hydroxide / silicate in alkaline geopolymerization?
  - Applicability of acidic medium geopolymers?
  - Optimization of geopolymer synthesis in terms of specific surface area?



Kaolinite



Metakaolin



Metakaolin geopolymer

SEM-EDS, x700, red=Al, green=Si, blue=O

THANKS FOR YOUR ATTENTION!