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Development of efficient sorbents by alkali-treatment of high-calcium-content fly ash from the paper industry

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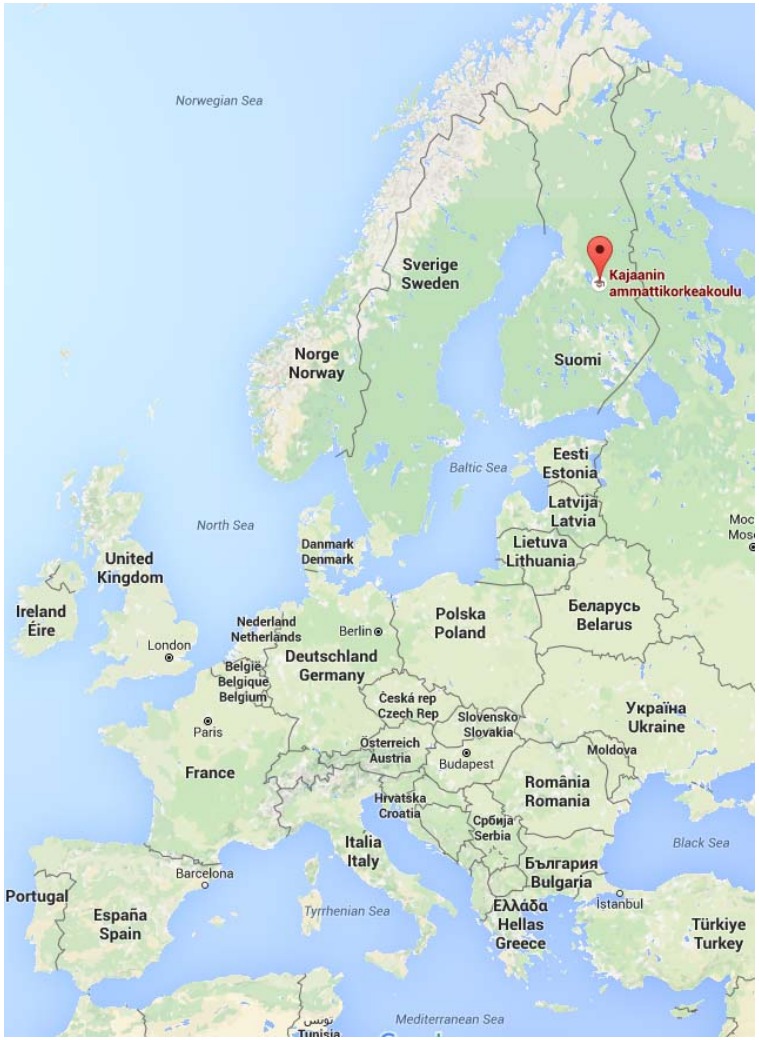
Kajaani University of Applied Sciences?

- Higher education institute offering degrees up to master level:
  - School of Health and Sports
  - School of Business
  - School of Tourism
  - School of Engineering
- Several years of R&D experience in the development of high-added value products from industrial side-products



About the fly ash used in this study

- In this study, the fly ash was obtained from paper industry.
  - Fuel consisted partially of deinking sludge and the $CaCO_3$ mineral filler results the high calcium (119 g/kg) content of fly ash.
- Amount of this specific fly ash is annually 90 000 t and its current main uses are excavation and cement additive.

Waste removal using wastes

Purpose of this research: could this fly ash be refined into higher added-value products such as adsorbent for wastewater treatment.

Hydrothermal processing of fly ash

Mixing of fly ash with 14 M NaOH, L/S = 0.8

10 min mixing

Casting to silicone molds

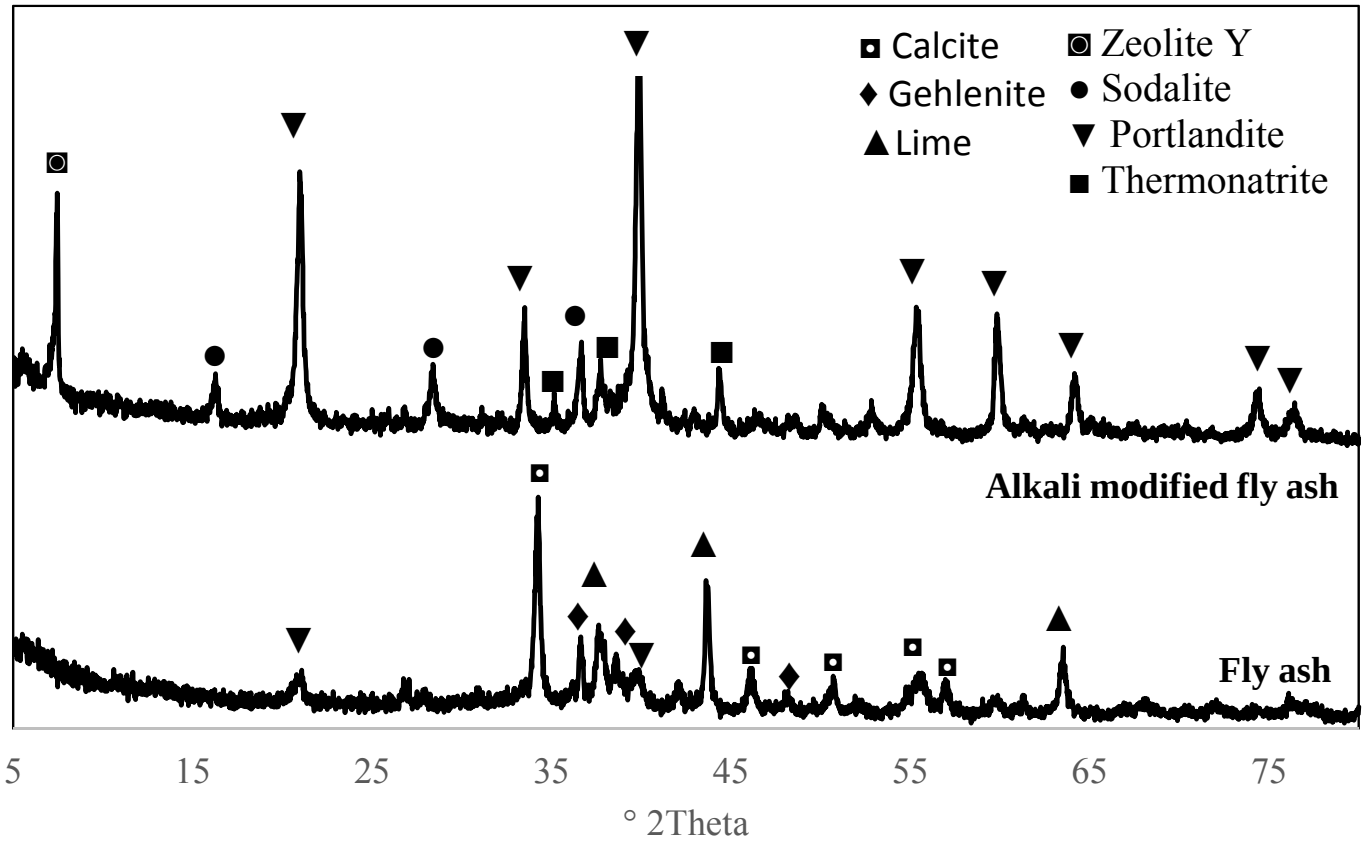
24 h consolidation at 22 °C

24 h consolidation at 105 °C

Grounding to 63–125 µm, washing, drying at 105 °C

Characterization of fly ash and zeolite

X-ray diffraction (XRD):



- Formation of zeolite Y (3 %) and sodalite (13 %) according to the Riedveld analysis.
- Gehlenite, $Ca_2Al[AlSiO_7]$, in fly ash is the phase providing reactive aluminosilicate for synthesis.
- Synthesized material was more porous than fly ash according to BET and BJH analyses.

Adsorption studies

Preparation of model solutions (”synthetic wastewater”) from metal salts

The effects of
- metal or anion concentration,
- sorbent dose, and
- contact time

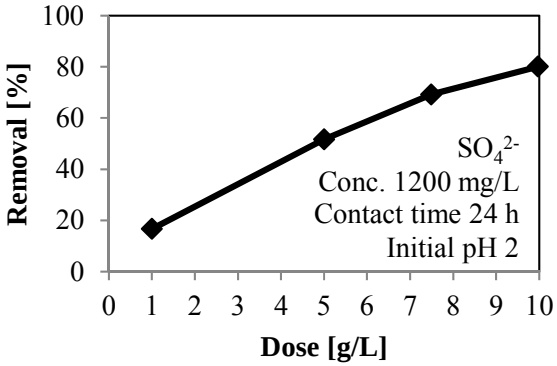
were tested using batch tests.

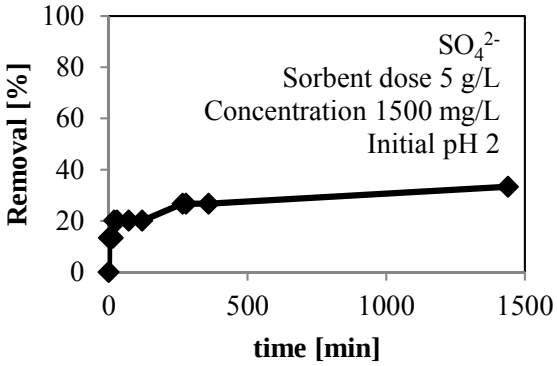
Isotherm and kinetics modelling

Utilization as adsorbent

- Sulphate
  - Low concentrations could be readily achieved.
  - Most of removal occured already during 1 min.
  - Possible mechanism: adsorption / surface precipitation on Ca-containing surface sites.
  - Maximum capacity 151.62 mg/g.
- Phosphate:
  - Efficient removal of low concentration of phosphate using low dose of sorbent.
  - Contact time to reach near equilibrium approx. 250 min.
  - Possible mechanism adsorption / surface precipitation on Ca-containing surface sites.
- Removal of Cd, Co, and Cu
  - High removal when dose > 1 g/L.
  - Required contact time about 1min for Co and Cu, 120 min for Cd.
  - Removal was partly due to precipitation of metal hydroxides or oxides.
- Removal of Zn and Ni
  - Low efficiency over whole dosing range.

Sulphate removal as an example:





Leaching of impurities

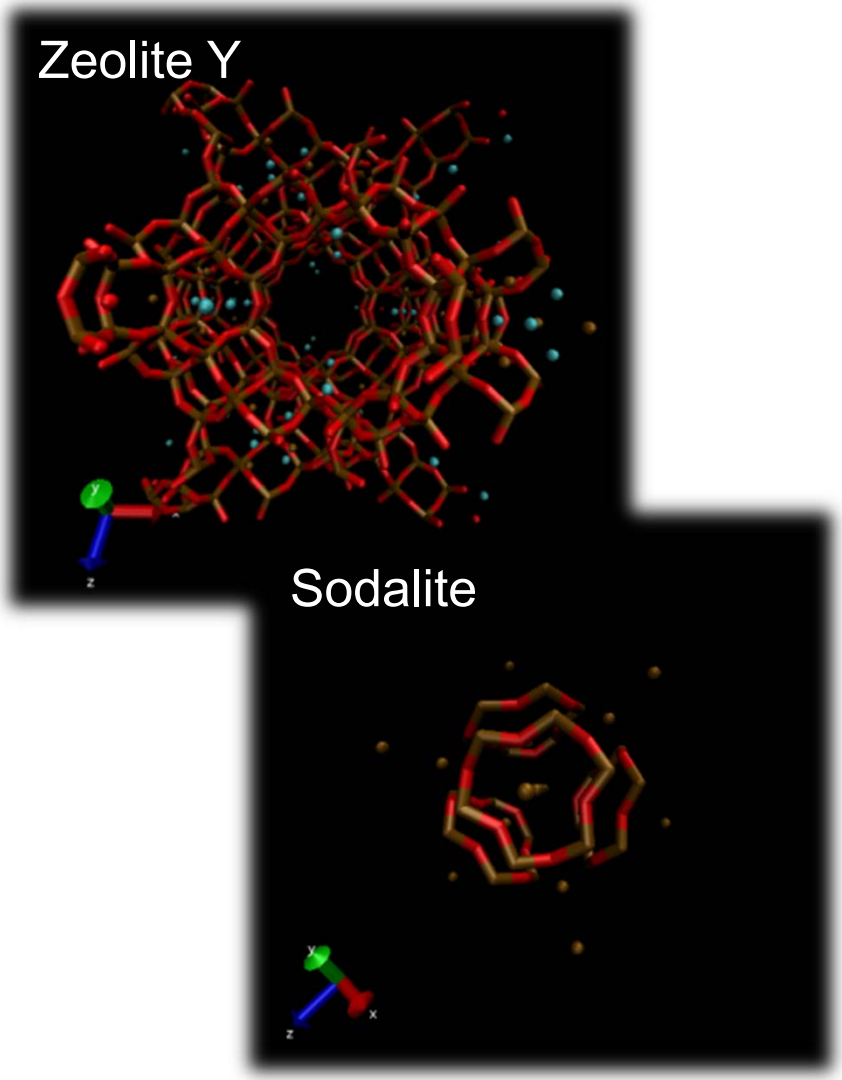
- Fly ash and the prepared sorbent were tested according to SFS-EN 12457-3 which is a two stage test to evaluate waste material stability.

[mg/kg]	Fly ash		Alkali modified fly ash	
	1st step (L/S = 4)	2nd step (L/S = 14)	1st step (L/S = 4)	2nd step (L/S = 14)
Al	6.80	7.73	9.74	26.2
As	< 0.03	< 0.17	< 0.03	< 0.17
B	0.07	0.47	0.54	1.89
Ba	17.34	53.86	0.17	2.07
Ca	1396	7535	28.80	555.2
Cd	< 0.004	< 0.022	< 0.004	< 0.022
Co	< 0.006	< 0.033	< 0.006	< 0.033
Cr	< 0.02	< 0.1	0.60	2.04
Cu	0.04	0.06	0.11	0.24
Fe	0.20	0.09	0.09	0.07
K	228	448	312	944
Mg	0.86	0.73	0.26	0.26
Na	80.4	236	9400	28284
Ni	< 0.01	< 0.06	0.01	0.06
P	< 0.10	< 0.50	0.42	0.90
Pb	< 0.03	< 0.17	< 0.03	< 0.17
S	2.36	5.79	120	257
Sb	< 0.030	< 0.166	< 0.030	< 0.166
Zn	0.03	0.01	0.16	0.15

- Leaching of some elements increased as a result of alkali-modification.
- Possible solutions:
  - More effiecient washing?
  - Development of modification to more stabilizing?

Summary

- Unconventional hydrothermal processing (high NaOH concentration, low L/S ratio, and open reactor in the synthesis) for high calcium-content fly ash was applied.
- Zeolite Y and sodalite were obtained in the amounts of 3% and 13% (weight-%), respectively.
- The alkali-treated material proved to a suitable sorbent, especially for sulphate and phosphate.
- However, the ways to prevent leaching of harmful elements needs further studying.



Thank you for your attention!

Question and comments?