Utilization of landfilled fly ash by tailoring its reactivity in stirred media mill

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Scientific day

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Problem

Coal combustion products (CCP) – about **780 million tons** yearly (Feuerborn, 2010).
Steel slag - **450 million tons** (280 million t iron- and 170 million t steel industry).
EU regulations, it is crucial to develop **new technologies** that allow the **recycling** of various industrial **by-products** (coal fly ash and steel slag) into **added-value products**.

Another important goal of the European Union is to **reduce** significantly the **CO_2 footprint**.

Two of the biggest CO_2 emission sources beside the **cement plants** (clinker burning, electric energy) are the **solid fired power stations** and the **iron/steel industry**.

Mission

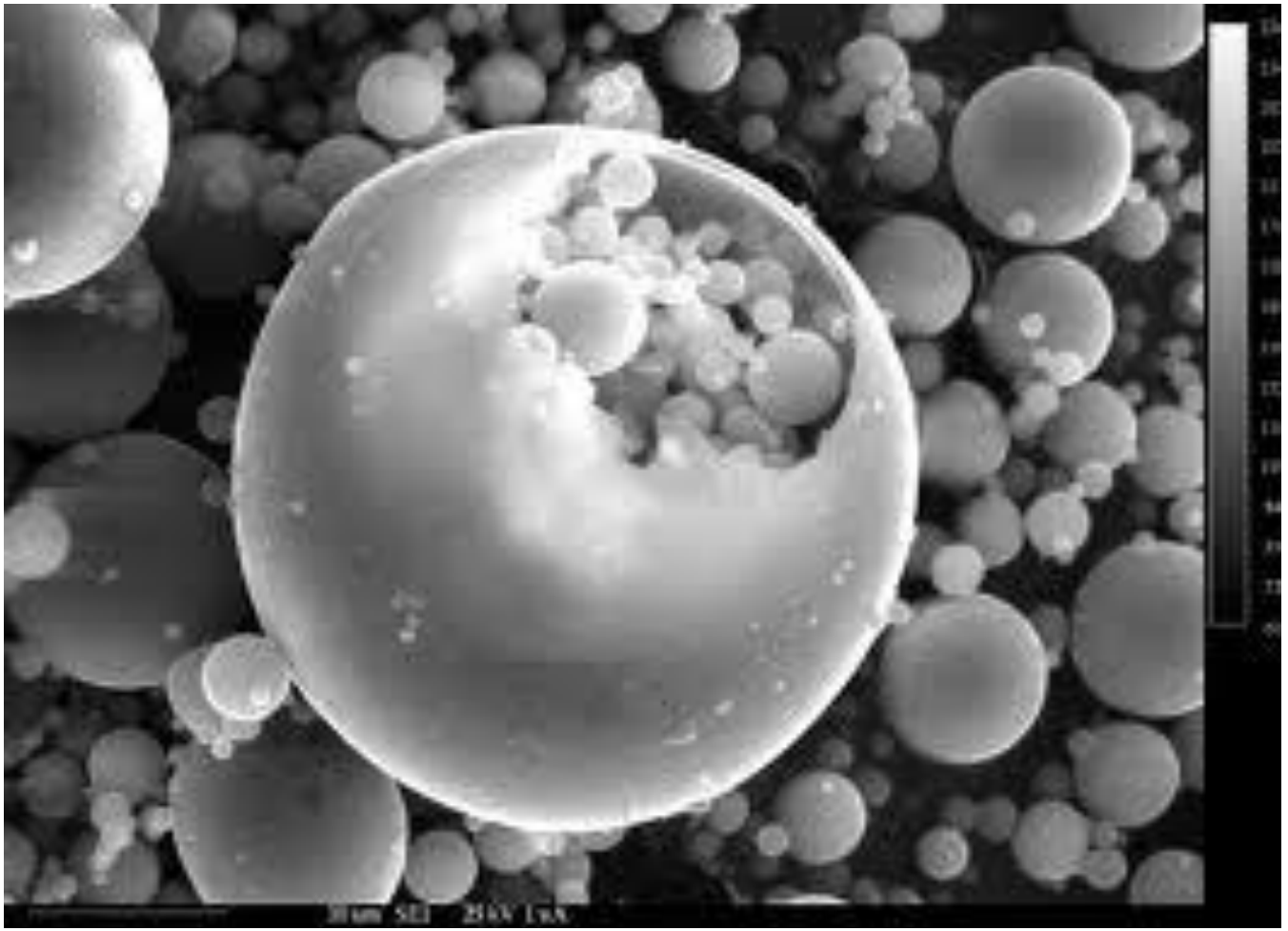
Control the material and product **properties** (and reactions) by mechanical processes - **fine grinding** and **classification**.

Industrial and mining wastes

Silicate bearing wastes:

- Mining gangue (ore and coal gangue)
- Power station waste (slag, fly ash),
- Metallurgical wastes
- Waste incineration slag and fly ash
- Red mud, …

Fly ash



Fly ash

In general hydraulic admixtures modify the properties of cement. The generation of **hydration heat**, **early strength**, **28 days strength** of these kind of cements are **smaller**, **water demand, afterhardening (90 days)** of them are **greater**, **sulphate resistance** is **better** finally the **freezing resistance** is **worse** than that of pure Portland cement.

Pozzolanic reaction:

$$x\ Ca(OH)_2 + SiO_2 + m H_2O = xCaO.SiO_2\ m\ H_2O$$

Landfilled fly ash

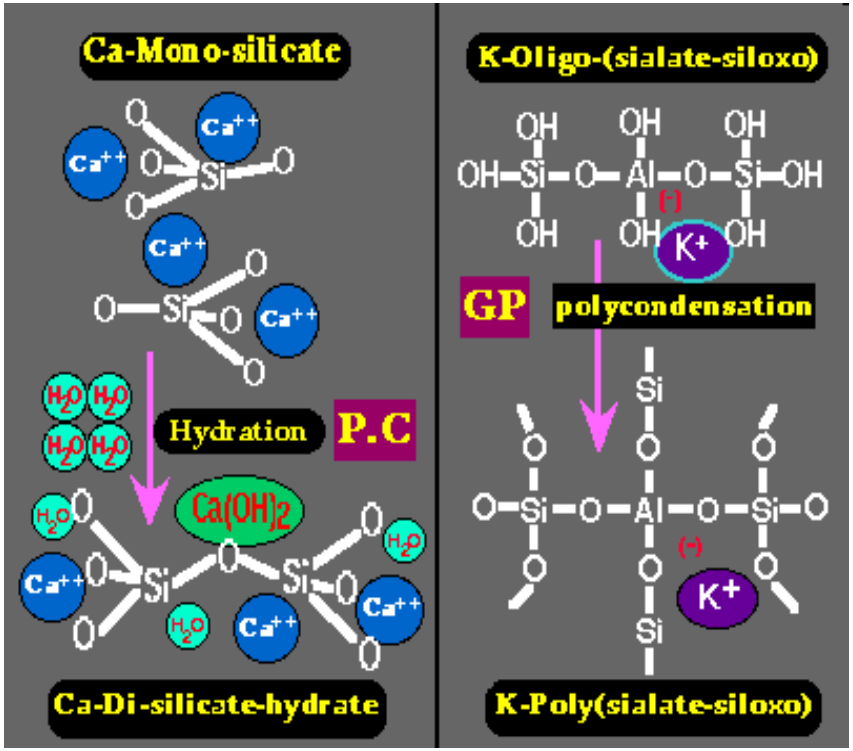
Reactivity of fly ash and other silicate bearing by-products decreases as funtion of time and weathering conditions.

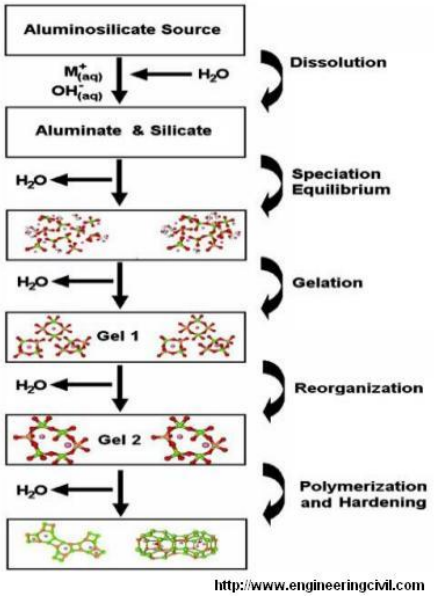
Kusnierová et al. (2005) investigated the change of amorphous content of a black coal fly ash as function of time (5 and 20 years) => significant devitrification.
Muluken et al. (2009) investigated the chemical, mineralogical and geochemical properties of fly ash after landfilling for various durations and at various depths (effects of weathering). Alternation in mineralogy and microstructure of the fly ash, formation of secondary minerals (calcite and ettringite) mainly due to hydration, carbonation and pozzolanic reactions.

Mechanical activation is more important!

Binders

Hardening of Portland cement





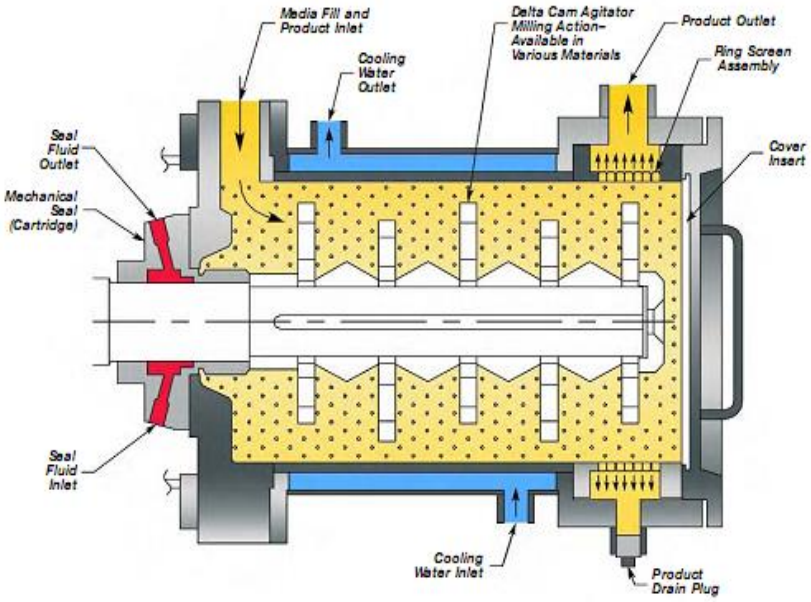
Hardening (setting) of Geopolymer resin
Cross linked network.
CO_2 generation:
10…20% of PC production.

Source: J. Davidovits (www.geopolymer.org)

Apparatus and method

- Mechanical activation – batch ball mill and stirred media mill (various time and energy density).
- PSD – Horiba 950 LA V2.
- FT-IR – Jasco 4200 with diamond ATR.
- XRD, XRF
- SEM
- Geopolymer production technology – cylindrical mould (Ø50x50 mm), heat treatment at 60 and 90 ^{o}C, utilization of NaOH solution (6, 8, 10, 12 and 14 M).
- Analyses – uniaxial compressive strength (7 days), specimen density.

Stirred media mill



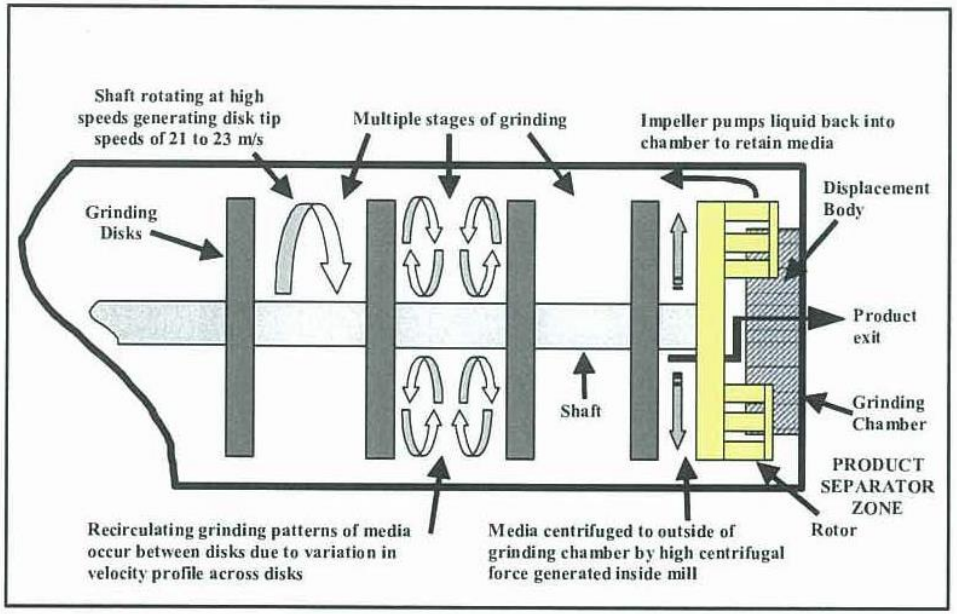
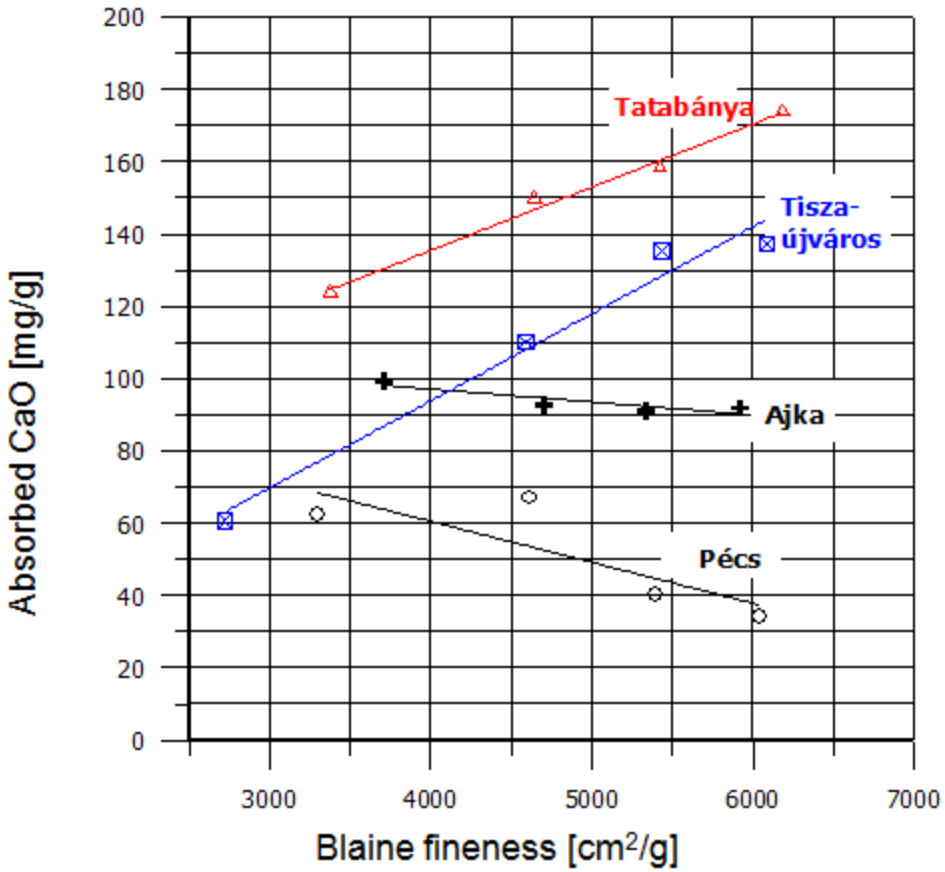


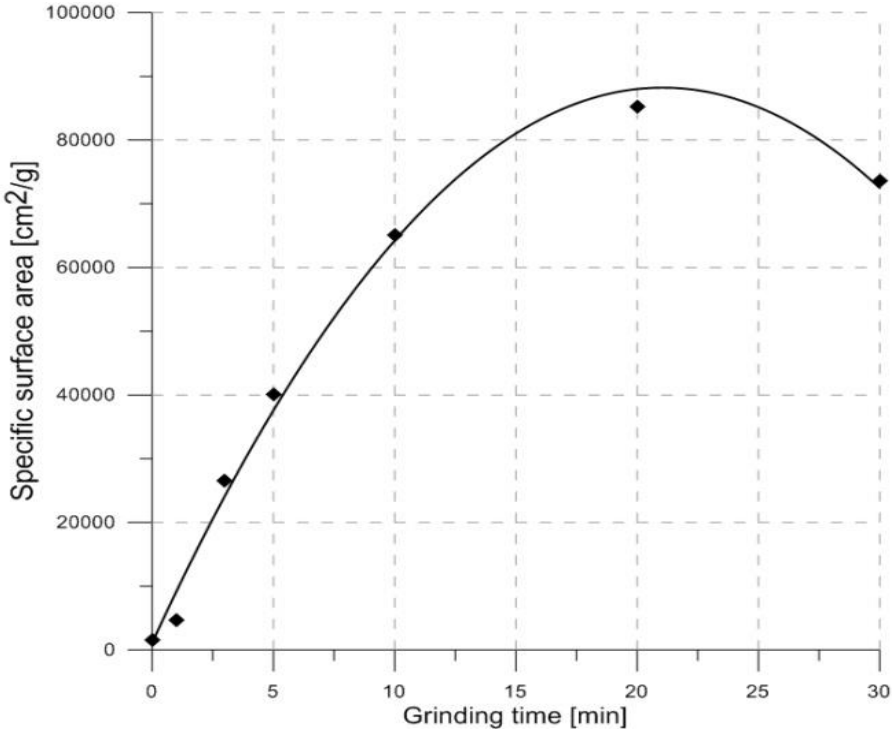
Figure 2: IsaMill™ Grinding Mechanism

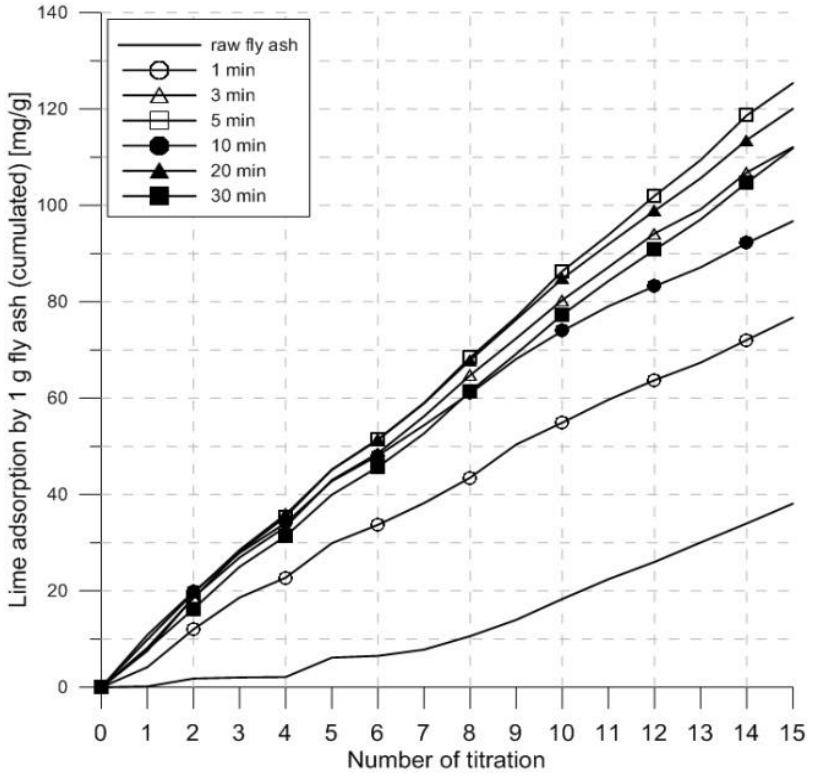
Hydraulic binder



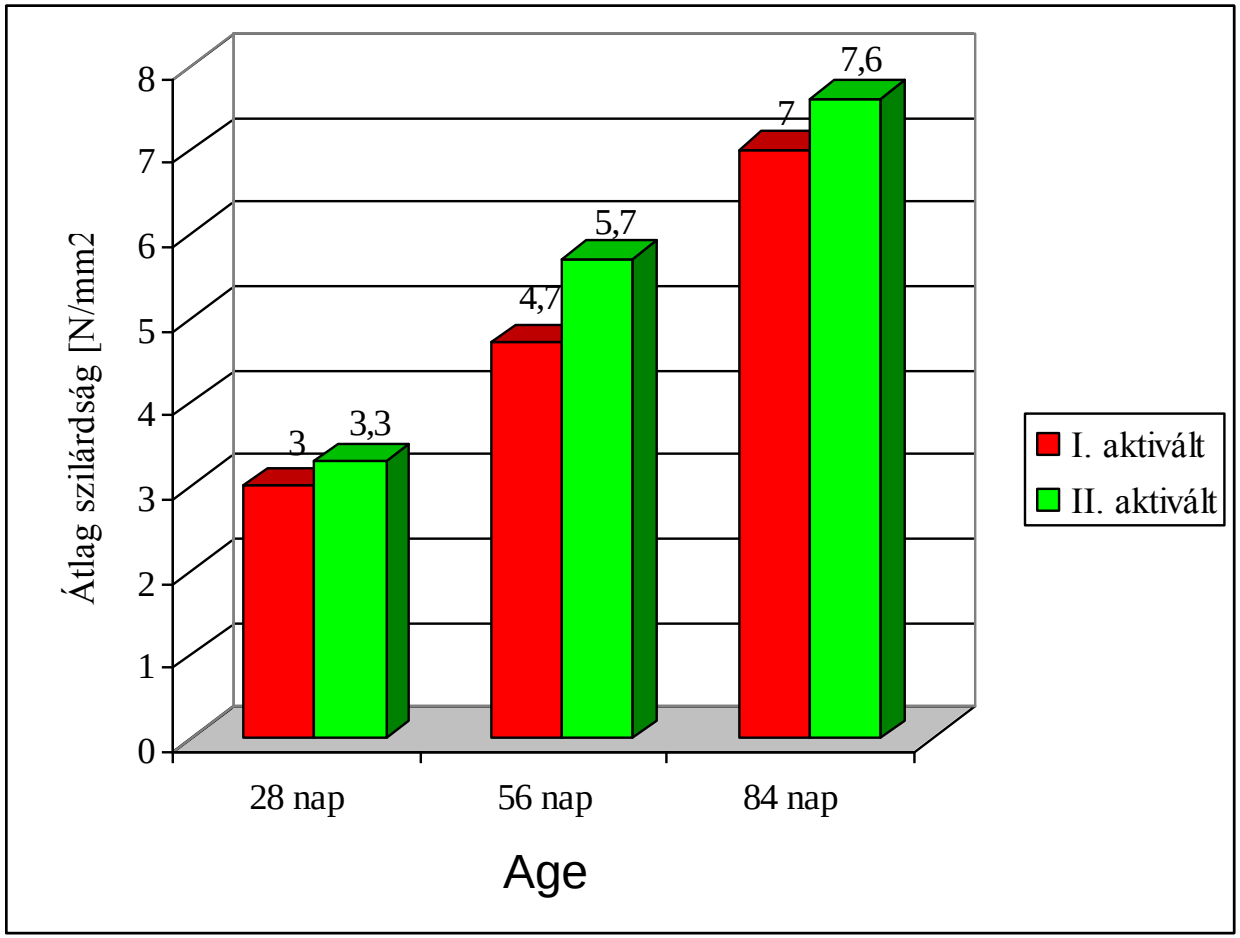
Cumulative value of the quantity of CaO absorbed from the saturated lime solution by 1 g of fly ash sample under investigation as a function of the specific surface area of the ground material

Hydraulic binder



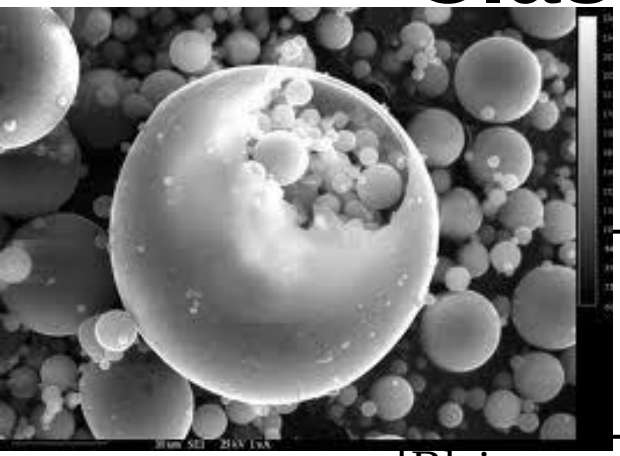


Hydraulic binder



Compressive strength of specimens as function of consolidation time

Classification of fly ash

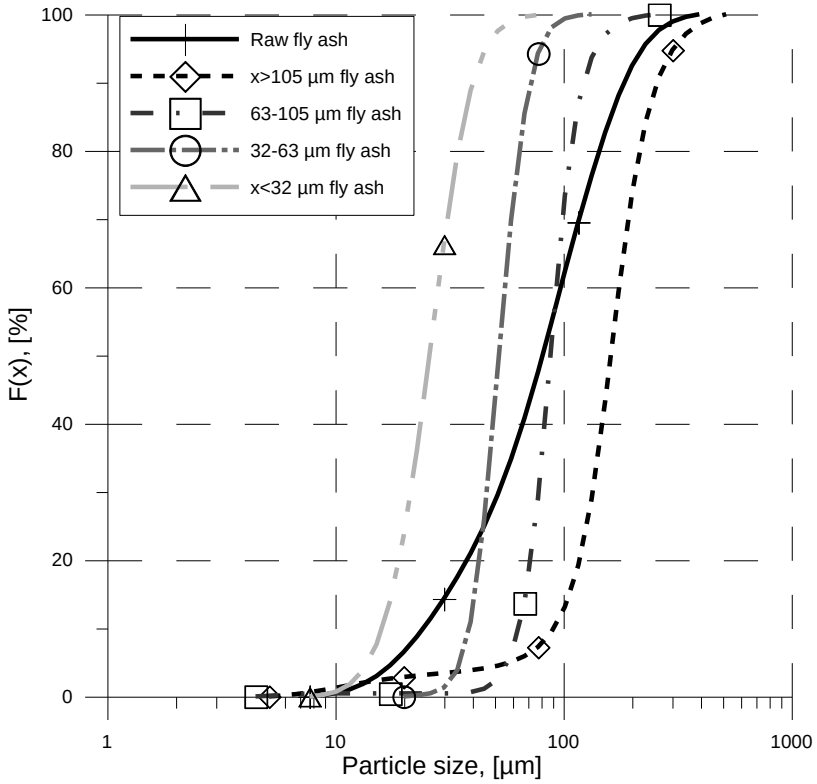


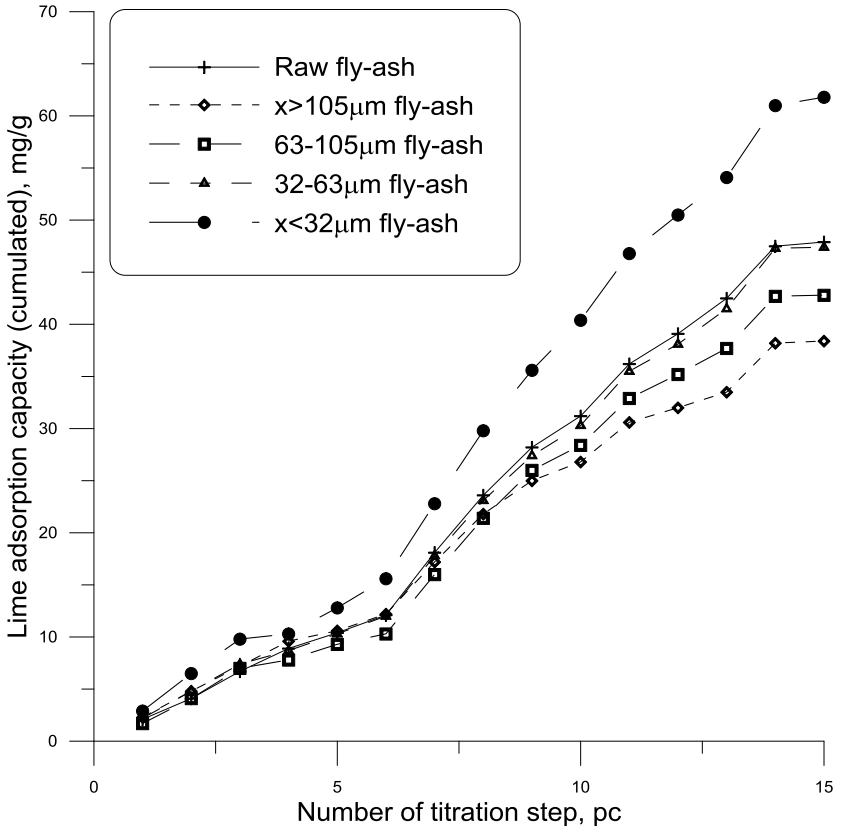
	‘Fine’ (< 30 μm)	‘Coarse’ (> 30 μm)
	fraction	
Blaine specific surface [cm^2/g]	14000	3600
Significant components [m/m%]		
Loss on ignition	4.00	2.04
SiO_2	35.19	50.27
Reactive SiO_2	***26.13***	***33.89***
CaO	18.89	9.77
Reactive CaO	***4.10***	***7.03***
Al_2O_3	***13.91***	***18.04***

Blaine specific surface and chemical composition of fly ash

Gável, 2014

Hydraulic binder





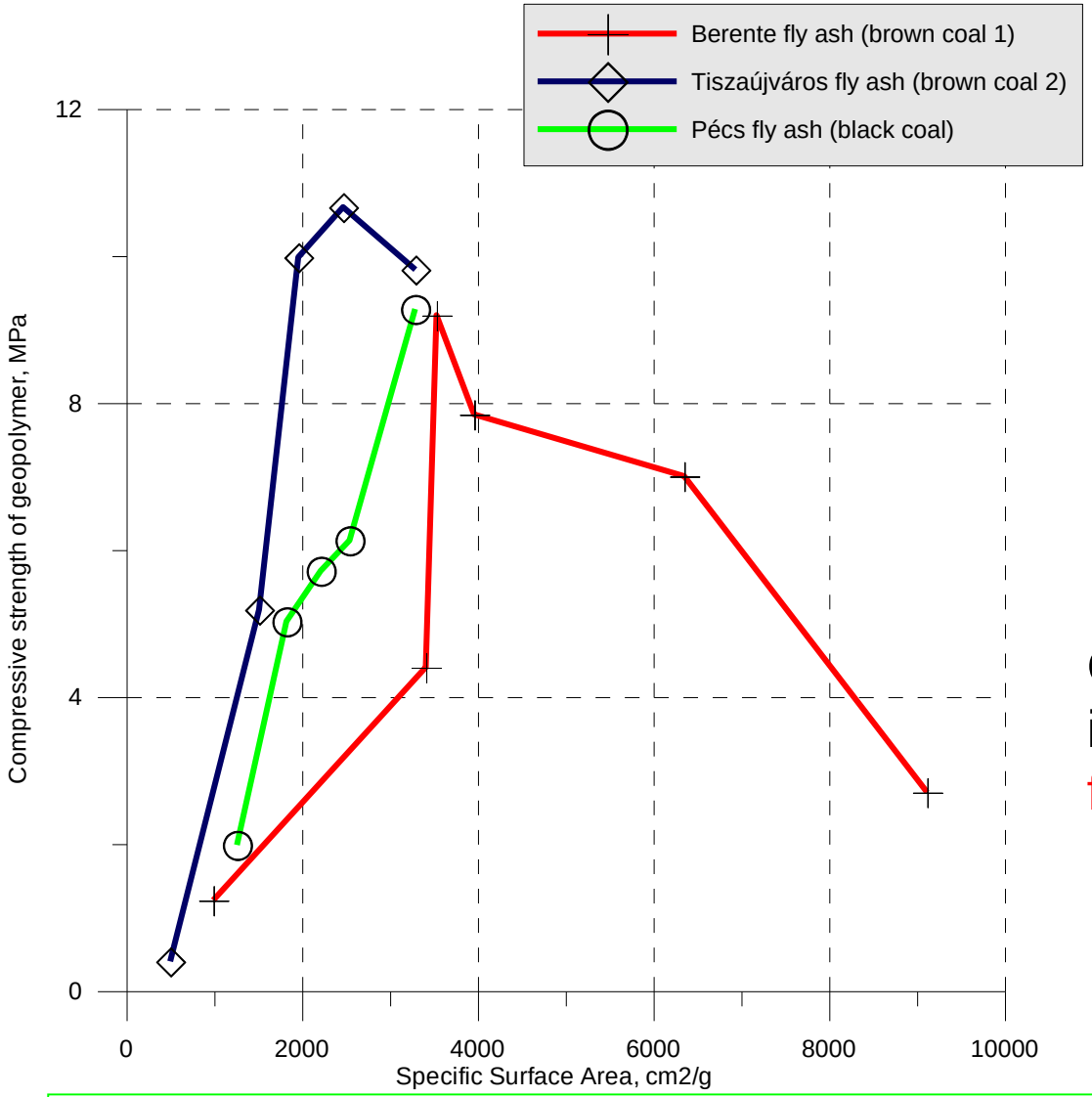
Geopolymer

Special properties of geopolymers:
- excellent durability,
- high compressive strength,
- low shrinkage,
- fast hardening,
- acid, fire and heat resistance,
- low greenhouse emission, ….

Some application:
- geopolymer cement,
- geopolymer bricks, and ceramics,
- foam geopolymer,
- advanced toolings,
- radioactive and toxic waste encapsulation, …

Queensland, AUS, 2013

Results

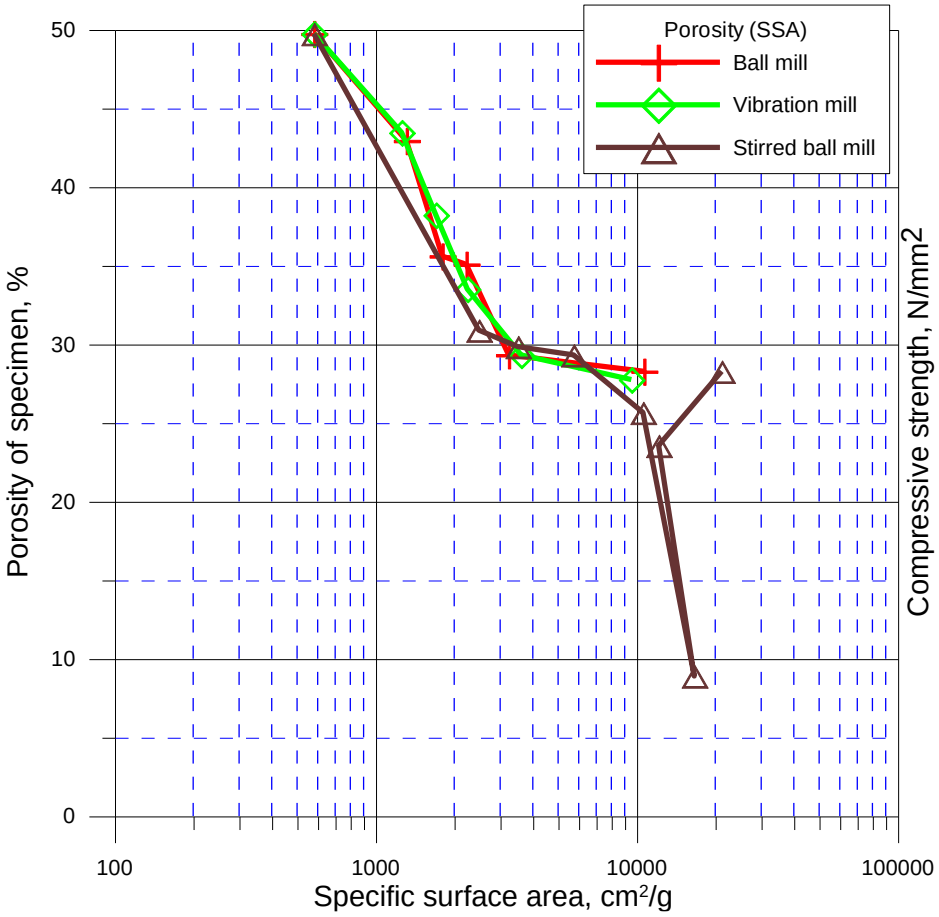


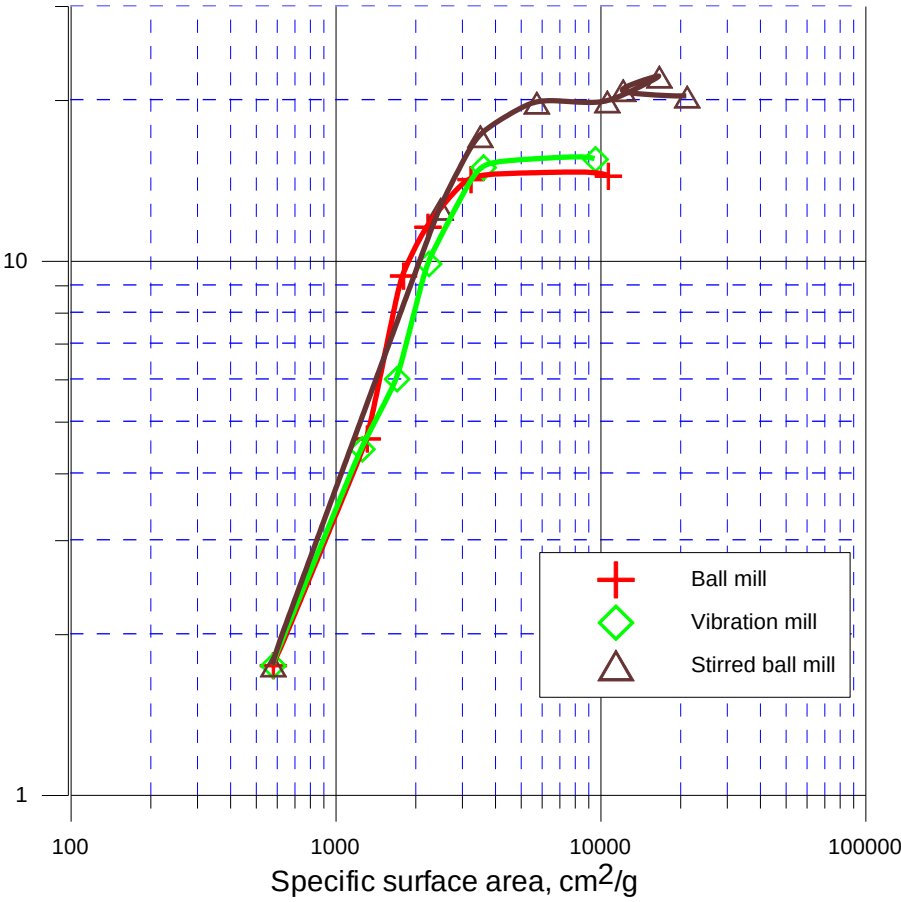
Higher specific surface area does not indicate obviously higher mechanical stability!

Optimal grinding fineness is different depending on fly ash type!

Compressive strength and specific surface area of fly ash as function of fly ash SSA

Tailoring of fly ash geopolymer properties by **mechanical activation**. Indo-Hungarian TéT project, 2012-2014

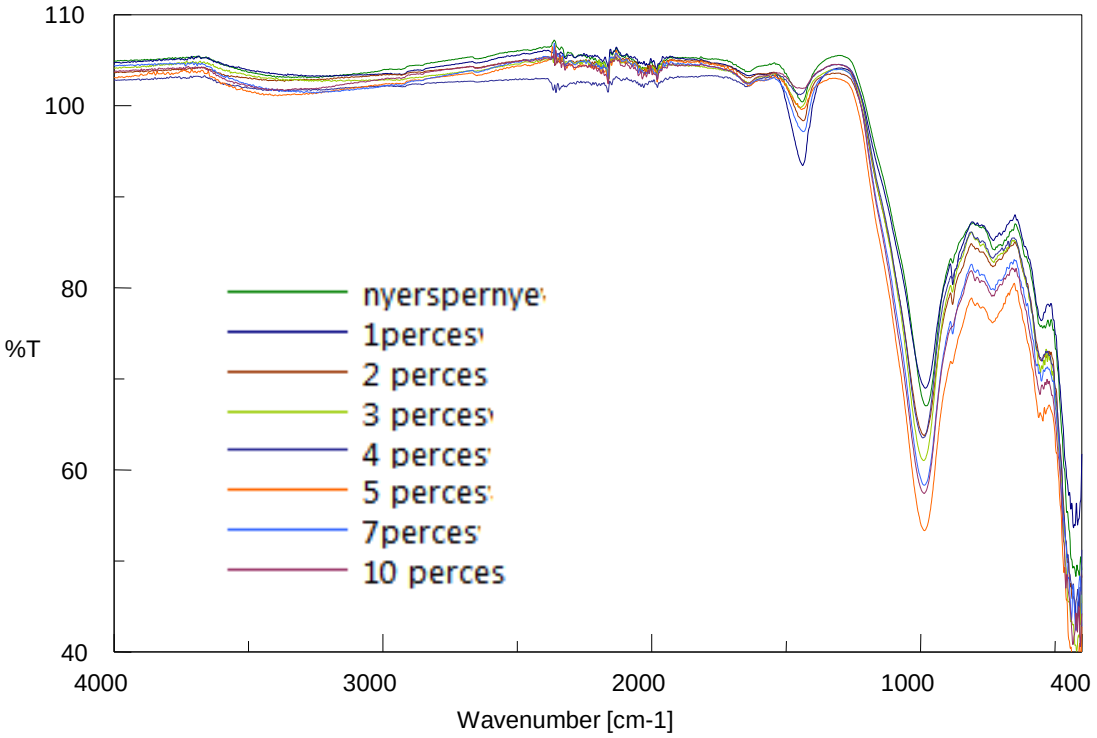


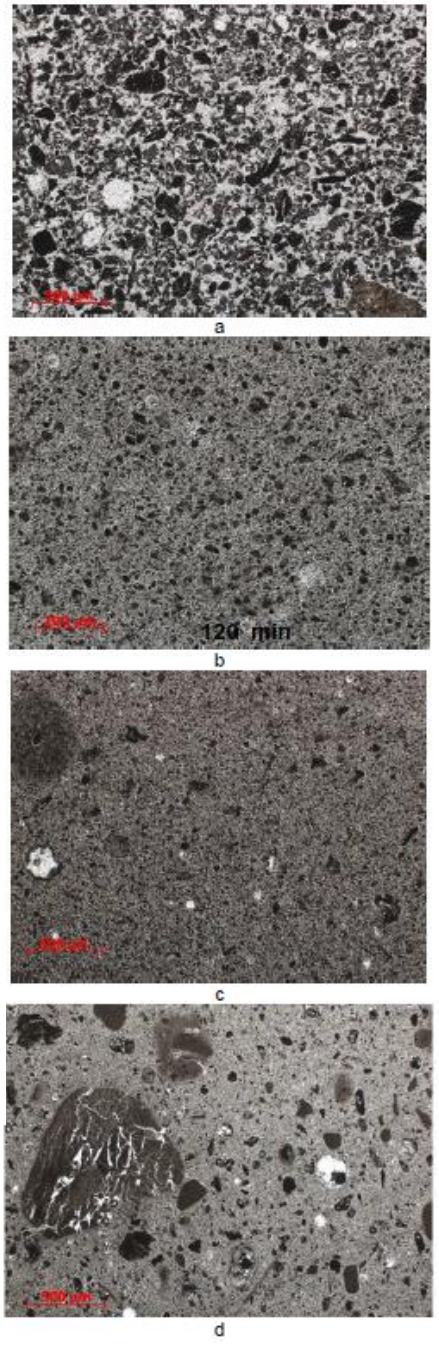


Porosity and compr. strength of geopolymer as function of fly ash SSA

Tailoring of **fly ash** geopolymer properties by mechanical activation.

Indo-Hungarian TéT project, 2012-2014

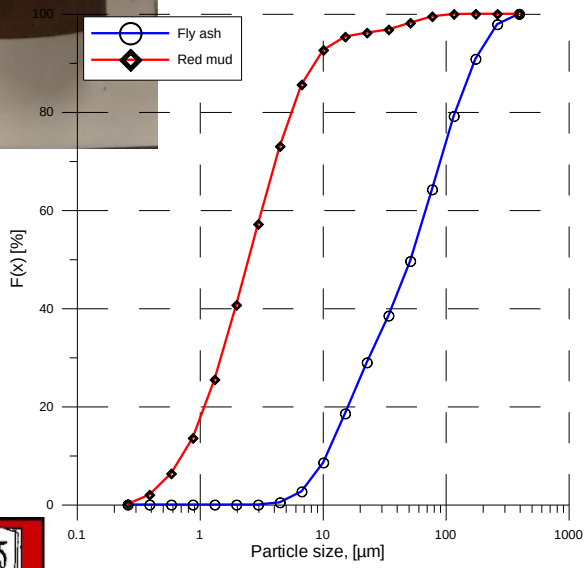


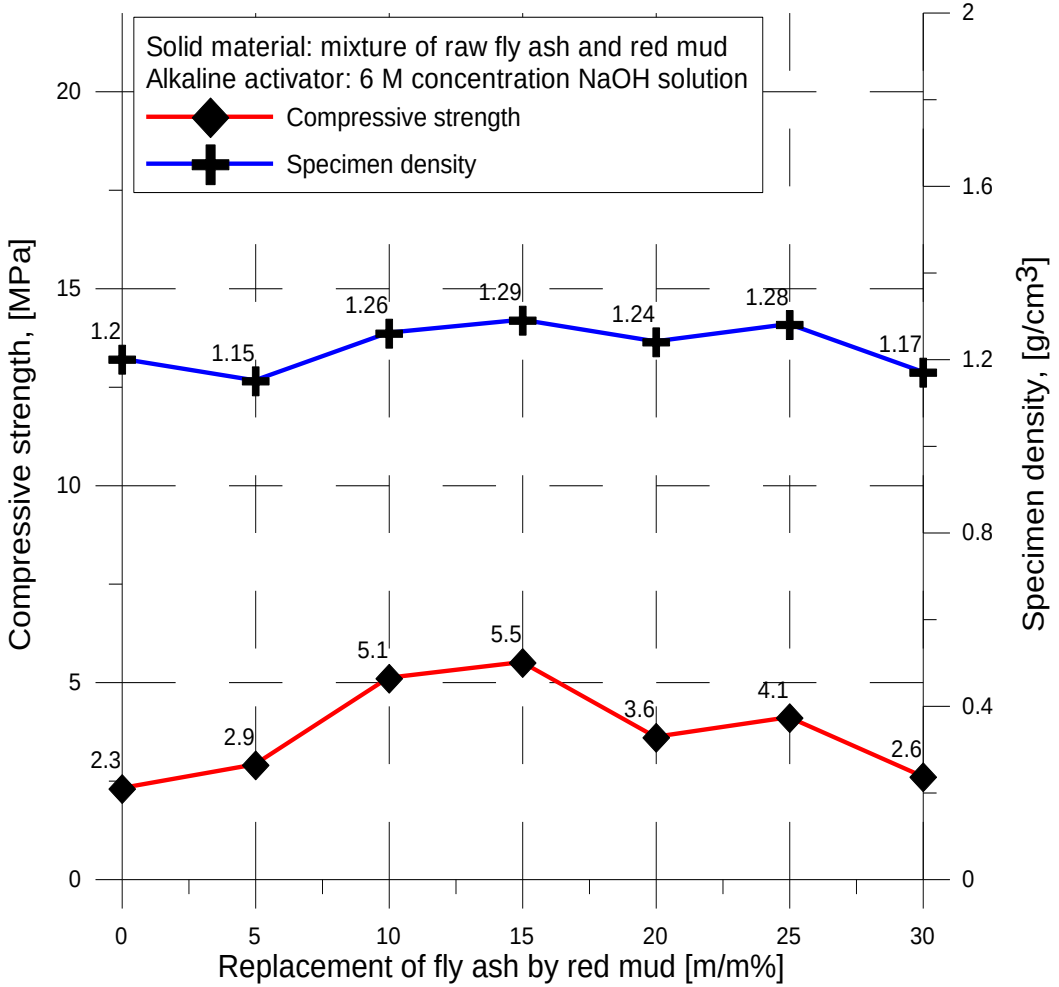


FT-IR and SEM

Furthermore: XRD, ICC, ICP - OES

Red mud bearing geopolymer



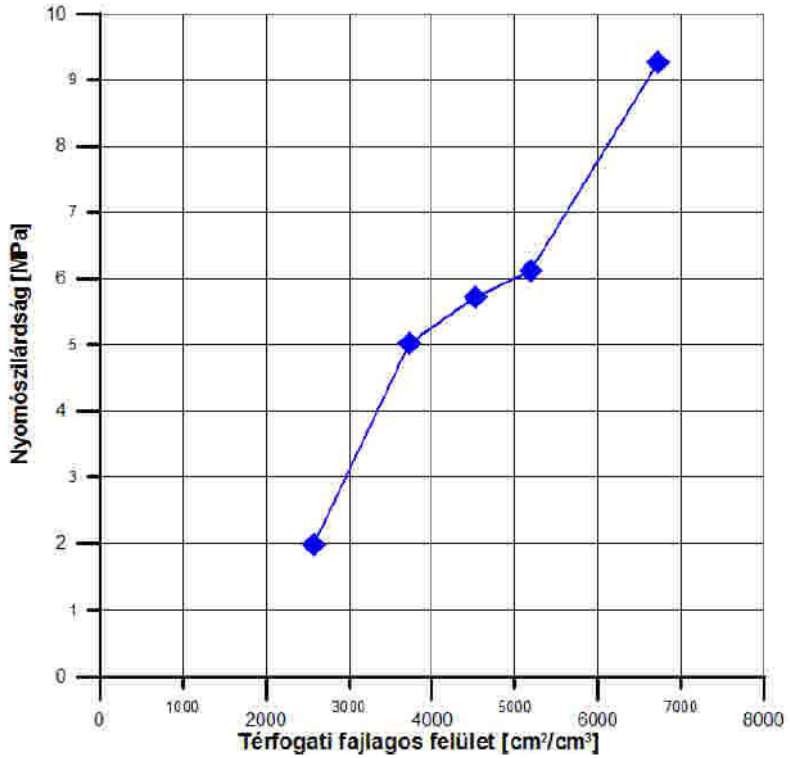


Effect of red mud content on the geopolymer strength and density of specimen, Geopolymer specimen containing red mud (80 % fly ash and 20 % red mud)

University of Miskolc

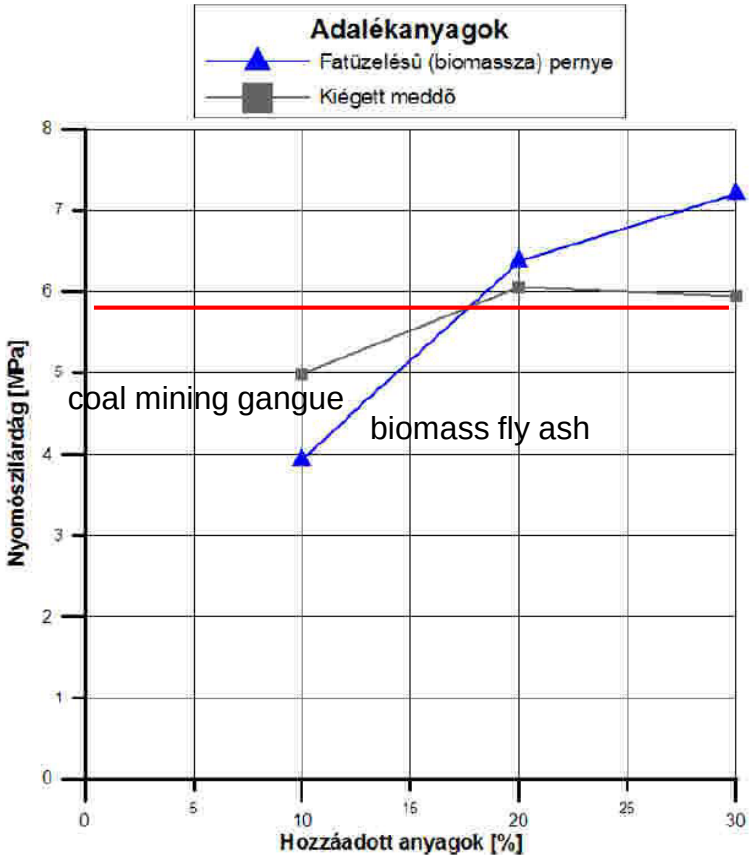
Institute of Raw Materials Preparation and Environmental Processing

Elaboration of technology for treatment of **coal mining gangue**



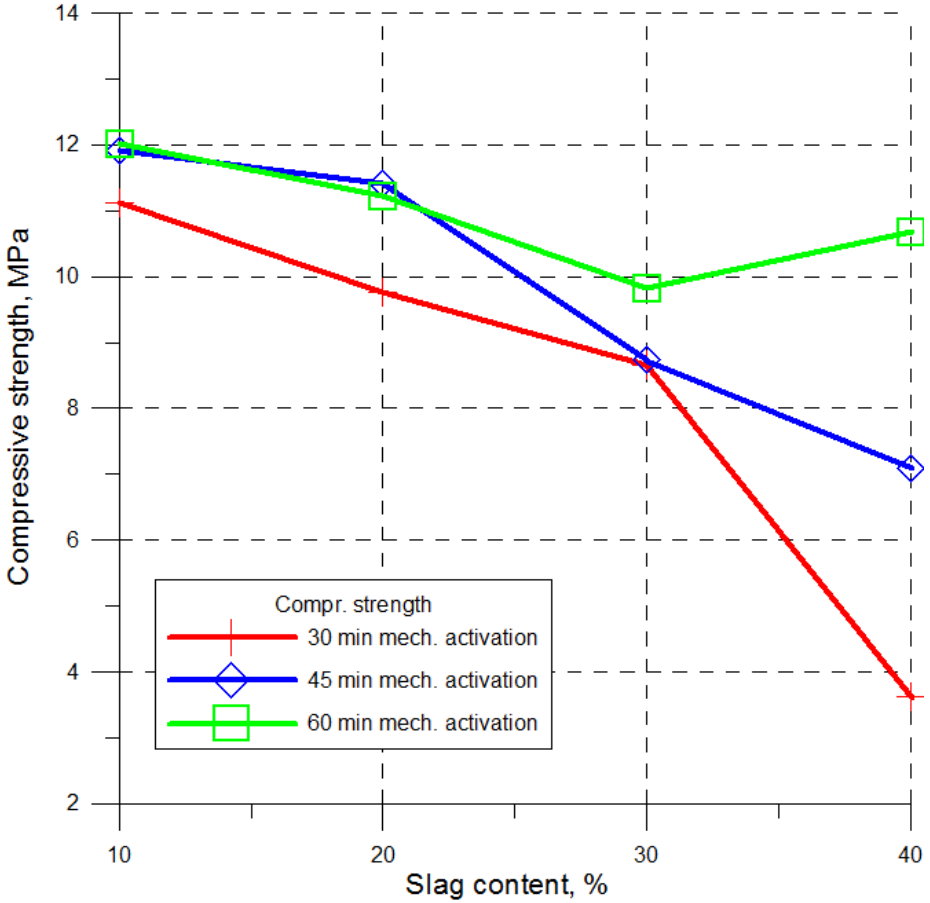
Compr. strength of geopolymer as function of fly ash SSA

Black coal fly ash + biomass fly ash + coal mining gangue



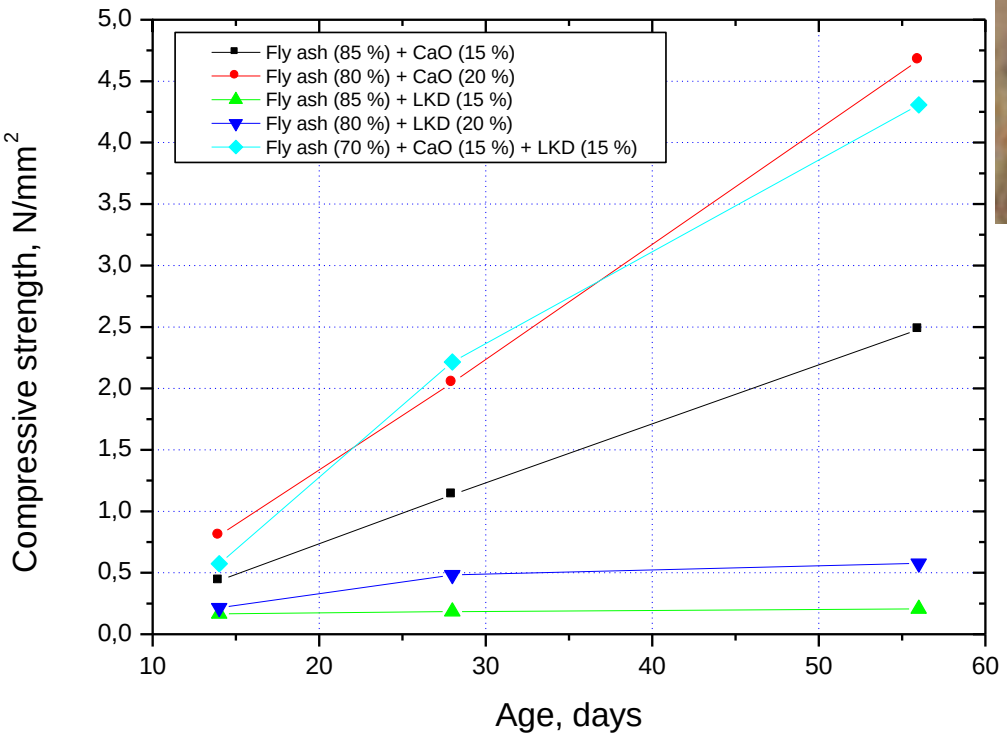
Granulated Blast Furnace Slag

Dunaferr PLC



	FA, 30 min őrlés	GBFS, 30 min őrlés	GBFS, 45 min őrlés	GBFS, 60 min őrlés
SSA cm^2/cm^3	5402,6	5274,9	6523,5	7801,2
Median, um	14,80	46,42	41,97	24,94

Applicability of **LKD** as an additive in fly ash based binder Carmeuse Ltd



Hydraulic binder

Feeding of fly ash

↓

Screening at 6 mm

↓

Drying
(down to 3 % moisture cont.)

↓

Grinding with vibration mill,
Q=75 t/h, W=14,6 kWh/t

↓

Mixing of activated fly ash (75 kg/h) and lime (25 kg/h) with turbo-mixer

↓

Bagging (100 kg/h)

Development of a technological system producing quality guaranteed fly-ash based binder. (2007)
GVOP-3.1.1-2004-05-0113/3.0 project

GOP project

Acknowledgements

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