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CO_2 SEQUESTRATION EXPERIMENTS BY PRODUCING GEOPOLYMER SPECIMENS FROM LIGNITE FLY ASH

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Abstract: The mineral-based sequestration of CO_2 offers a permanent and safe method to store CO_2 captured from flue gas. In this process, CO_2 reacts with calcium and/or magnesium-bearing materials to form stable, environmentally benign carbonate minerals. In a recent research project, CO_2 sequestration was performed on deposited fly ash from Visonta, Northern Hungary, coupled with mechanical activation. The resultant carbonate phases were analyzed for their suitability as geopolymer-based construction materials. CO_2 sequestration and mechanical activation occurred in a Fritsch Pulverisette 5 planetary ball mill under wet conditions. The samples were dried post-sequestration, and 20x20x20 mm geopolymer specimens were prepared and tested for compressive strength after seven days. It was found that bassanite, the primary calcium source in fly ash, reacts with CO_2 only in the presence of NaOH. Additionally, low NaOH concentrations (0.5 M) during grinding positively impacted the compressive strength of the geopolymer, while higher concentrations reduced it. At 2 M NaOH, the specimen failed to set fully, deforming plastically under pressure. The experiment yielded a maximum compressive strength of 16.1 MPa for the geopolymer using 0.5 M NaOH.

***Keywords**: CO_2 sequestration, fly ash, mechanical activation, geopolymer*

1. INTRODUCTION

Global warming is a critical challenge we face today, primarily driven by the rise in Earth's atmospheric temperature due to increased greenhouse gases. While these gases naturally exist in the atmosphere, anthropogenic greenhouse gases, such as CO_2, have surged, particularly since the Second Industrial Revolution.

One promising approach to mitigate atmospheric CO_2 is mineral sequestration. This process involves reacting CO_2 with non-carbonate minerals that contain alkali metals (e.g., sodium or potassium) and alkaline earth metals (e.g., calcium or magnesium). The reaction leads to the formation of various carbonate minerals, which can be either anhydrous or contain hydroxide (OH^-) or water (H_2O), such as calcite ($CaCO_3$), magnesite ($MgCO_3$), or siderite (Fe_2CO_3) (Turvey et al., 2018).

For effective CO_2 sequestration, the host material should be rich in non-carbonate calcium and/or magnesium minerals. Based on this requirement, natural silicate minerals with high levels of serpentinite, forsterite, or olivine (Romão, 2014), as well as industrial by-products with similar mineralogical properties, such as construction and demolition waste (Ghacham et al., 2017), red mud (Mucsi et al., 2021), steel slag (Bonenfant et al., 2008), and fly ash (Montes-Hernandez et al., 2009), can be utilized for CO_2 sequestration.

This study focuses on fly ash-based CO_2 sequestration enhanced by mechanical activation. The aim is to capture and permanently sequester CO_2 through mineral carbonation, forming stable compounds. Additionally, we explore the potential of using fly ash with newly formed mineral phases as a geopolymer material for construction. We apply a direct carbonation approach to increase the reactivity of the ash through high-energy milling in a wet medium.

2. MATERIAL AND METHODS

2.1. Material

The experiments were carried out on lignite fly ash from MVM Mátra Energia Ltd., Visonta, Northern Hungary. The analysis of the particle size distribution of the sample reveals that the sample primarily comprises particles below 400 µm, with a 66 µm median particle size. The initial moisture content was found to be 24.1 wt%. The fly ash particle density was 1.92 g/cm^3, and the bulk density was 0.58 g/cm^3. Biogon-C CO_2 gas (95.5% purity) was used for carbonate reactions without further purification.

2.2. Methods

2.2.1. Mechanical activation and CCS

The experiment conducted CO_2 sequestration and mechanical activation simultaneously in a Fritch Pulverisette 5 planetary ball mill under wet conditions, using NaOH solution of varying concentrations (0.1, 0.25, 0.5, 1, and 2 M) as the grinding fluid. The milling was carried out using 500 ml steel jars with a gas valve and steel grinding media. The jars were filled with 54.3 g of dry sample, 162,9 g NaOH solution and 543 g of 20 mm diameter grinding balls. The grinding was carried out at 200 rpm for 180 min, and the free grinding chamber was filled with CO_2 gas at up to 5.5 bar pressure and refilled every 15 min to the initial CO_2 pressure.

2.2.2. Measurement of mineral characteristics

The WD-XRF measurement was performed using RIGAKU Supermini 200 type WDXRF. The radiation source was an air-cooled 200 W palladium (Pd) X-ray tube with an excitation voltage of 50 kV and 4.0 mA. Quantitative analysis requires the calibration of the standards for the identified elements. Calibration is performed element-by-element, with 8-12 pcs for main elements and 6-10 pcs for trace elements (the number of standards used is not constant, but is determined by the concentration of each component in the standards). Each element is measured seven times (two background points 10-10, peak position 40 sec), thus the errors can be reduced statistically, and the measurement also gives a better average value.

The mineralogy of the fly ash was determined by X-ray powder diffraction (XRD) with a Bruker D8 Advance diffractometer using Cu K-alpha radiation (40 kV, 40 mA) in parallel beam geometry obtained with Göbel mirror, in the 2°–70° (2θ) range with a 0.007° (2θ) step interval and a 24 s step counting time. The crystalline phases were identified by Bruker DiffracPlus software package in its EVA module ICDD PDF-2 (2005) database for search/matching of phases. The quantitative evaluation was carried out by Rietveld refinement in the TOPAS4 software, where the amorphous content was determined by the amorphous hump method.

The stretching and bending vibrations of the chemical bonds in the samples before and after CO_2 sequestration were detected by a JASCO FT-IR 4200 type Fourier Transformed Infrared Spectrometer in reflection mode with a diamond ATR. The infrared transmission spectra of the samples were recorded between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}. The observed spectra are plotted as a function of wavenumber and transmittance. Observed FTIR bands were interpreted based on the handbook by Chukanov and Chervonny (2014).

The Controls C250Kn uniaxial compression machine was used to measure the compressive strength of the prepared specimens. The test involved placing the specimens between parallel steel plates and subjecting them to axial compression up to the breaking load, with a load increment of 300 N/min.

3. RESULTS

3.1. Chemical and mineral properties of fly ash

According to the XRF measurement (Table 1) the major component of the fly ash is CaO, proving it a suitable material for CCS. The sample contains a total of 15.51 wt% of CaO and MgO, which is relatively low for CO_2 sequestration. The utilization of CO_2-treated fly ash will play an important role.

Table 1

Oxidic components of fly ash (weight percent, error +/- 0.01 relative percent, LOI 0,05 wt%

Al_2O_3	Fe_2O_3	SiO_2	TiO_2	Na_2O	MgO	CaO	P_2O_5	K_2O	MnO	S	F
14	11.2	39.8	0.50	0.54	3.41	12.1	0.35	1.61	0.18	6.5	<0.3

Table 2 shows the mineral composition of fly ash. Among the minerals present in the sample, bassanite, bytownite, and magnesioferrite can react with CO_2. Considering the amount of crystalline calcium and magnesium phases, the amorphous phase also contains 3-3 wt% of calcium and magnesium. Portlandite, lime, brucite, and periclase are the mineral phases typically found in typical fly ashes (Monasterio et al., 2020), and they possess good CO_2 sequestration capacity. However, these minerals are not present in the Visonta lignite fly ash.

Table 2

Mineral components of fly ash (weight percent, error +/- 0.01 relative percent)

Mineral phase	Formula	Weight percent
Calcite	$CaCO_3$	6.2
Quartz	SiO_2	17.6
Bassanite	$Ca[SO_4]\cdot 0,5\ H_2O$	9.5
Hematite	$Fe^{3+}_2O_3$	4.1
Maghemite	$Fe^{3+}_2O_3$	4.9
Bytownite	$Na_{0.2}Ca_{0.8}Al_{1.8}Si_{2.2}O_8$	6.7
Galenite	PbS	3.9
Albite	$NaAlSi_3O_8$	7.6
Mg-Ferrite	$MgFe_2O_4$	1.9
Amorf	-	38

3.2. Change of dispersity

Figure 1 shows the changes in dispersion occurring during grinding. After the grinding in NaOH solution, the samples have almost the same geometric surface area (2,5-3 m^2/g), with a slight increase in coarsening from 3.43 µm to 4.79 µm for the d_{50} particle size with increasing NaOH concentration. A significant difference is observed in the measurement in deionized water, where an increase in the proportion of fine grains is observed, resulting in a decrease in the median grain size from ~3-4 µm to ~0.57 µm compared to the other measurements.

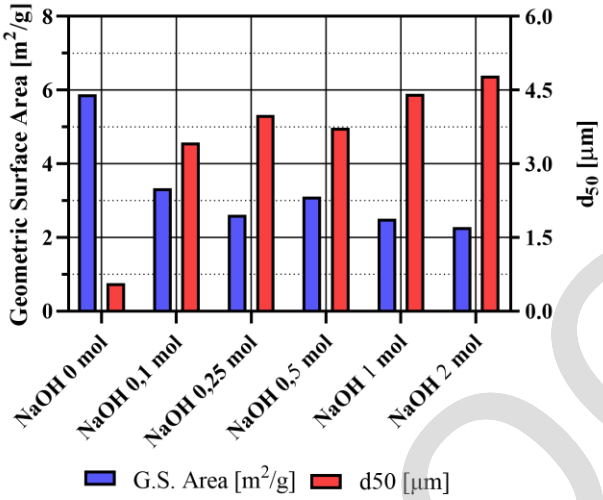

Figure 1

Changes in geometric specific surface area and particle size d_{50}

Fly ash treated with CO_2 was used to create geopolymer specimens in the size of 20x20x20 mm. To achieve the ideal Al_2O_3/Na_2O ratio of 1, various concentrations of NaOH were used as an activating solution. The mixtures were prepared with a liquid-to-solid ratio of 1, with half of the liquid being Betol93 sodium silicate. The oxide composition and mixing ratios of grounded fly ash are shown in Table 3.

The geopolymer poured into the mold was stored at ambient temperature in an isolated from air for 24 hours, followed by heat treatment at 60°C for 6 hours.

Table 3

Oxide components of grounded fly ash and their mixing ratios.

Oxidic components [w%]	Raw	0.1	0.25	5	1	2
Al_2O_3	15.14	16.07	16.24	15.62	14.27	13.11
Fe_2O_3	10.32	11.7	11.5	11.2	10.7	10.0
SiO_2	45.9	50.0	50.3	49.3	45.1	42.3
TiO_2	0.564	0.556	0.549	0.534	0.507	0.492
Na_2O	0.51	1.02	1.48	2.64	4.99	7.42
MgO	2.81	2.78	2.78	2.78	2.52	2,23
CaO	11.42	8.98	9.11	9.00	8.52	8.10
P_2O_5	0.282	0.250	0.257	0.248	0.233	0.217
K_2O	1.64	1.56	1.56	1.55	1.48	1.39
MnO	0.139	0.157	0.156	0.150	0.145	0.139
SO3	11.0	1.95	1.24	1.29	1.31	1.07

	Mixture data					
Concentration of NaOH solution [M]	10	10	10	8	5	3
Total Na_2O [g]	4.60	4.76	4.89	4.57	4.09	3.89
Al_2O_3 [g]	4.54	4.82	4.87	4.69	4.28	3.93
SiO_2 [g]	13.77	15.00	15.09	14.79	13.53	12.69
Al_2O_3/Na_2O	0.99	1.01	1.00	1.03	1.05	1.01
SiO_2/Na_2O	2.99	3.15	3.08	3.24	3.31	3.26
l [g]	30.0	30.0	30.0	30.0	30.0	30.0
s [g]	30.0	30.0	30.0	30.0	30.0	30.0
l/s ratio	1	1	1	1	1	1

3.3. Structural changes during carbonation and geopolymerization

In Figure 2, the spectral images of FTIR measurements on CO2-treated samples can be seen. Measurements on dried samples were carried out one day after milling. After CO_2 sequestration, significant differences can be observed in the -C=O peaks at 1460 cm^{-1} and the C-O peaks at 880 cm^{-1} for calcite. Both peaks increase with NaOH concentration up to a concentration of 1 M and then remain constant. A slight change is observed in the Al-O-Si peak at 1010 cm^{-1}, which decreases slightly in intensity and shifts towards 980 cm^{-1}, indicating that geopolymerization has already started during grinding.

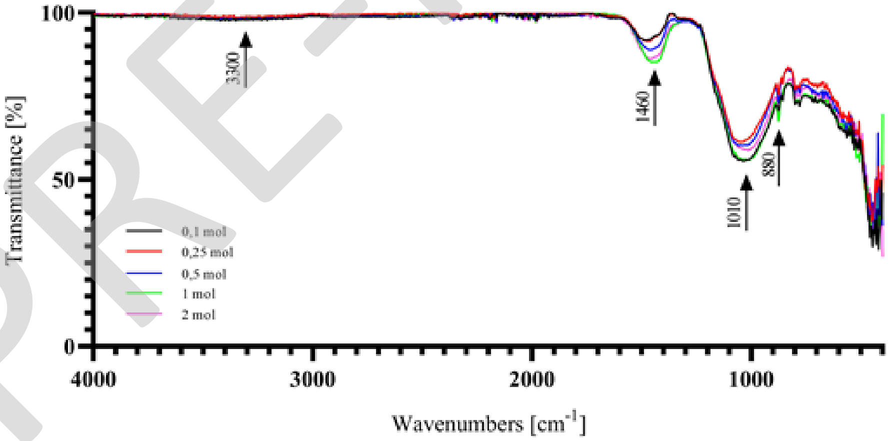

Figure 2
FTIR spectrum of the CO2-treated sample

The mineral composition after milling and CO_2 sequestration is shown in Table 4. Among the three crystalline phases in the fly ash capable of binding carbonates, bassanite and magnesioferrite fully reacted during the process, while the mass fraction of bytownite was reduced by half. From the reacted phases, two types of carbonate minerals were formed: calcite and thermonatrite. However, only calcite is suitable for long-term CO_2 storage. By the end of the process, the sample contained 14.2 wt% calcite, representing an increase of 8.3 wt% compared to the initial state. The remaining bytownite in the sample, if fully reacted, could result in an additional ~1% improvement. Therefore, the amorphous material in the fly ash must still contain a significant Ca source.

Table 4

Mineral components of CO_2 treated (2M) fly ash

Mineral phase	Formula	Volume percent
Calcite	$CaCO_3$	14.23
Quartz	SiO_2	8.47
Bassanite	$Ca[SO_4]\cdot 0,5\ H_2O$	0.00
Hematite	$Fe^{3+}{}_2O_3$	7.98
Maghemite	$Fe^{3+}\ {}_2O_3$	6.00
Bytownite	$Na_{0.2}Ca_{0.8}Al_{1.8}Si_{2.2}O_8$	4.26
Galenite	PbS	1.24
Albite	$NaAlSi_3O_8$	5.65
Mg-Ferrite	$MgFe_2O_4$	0.00
Thermonatritis	$Na_2(CO_3)\bullet(H_2O)$	1.27
Anhydrite	$CaSO_4$	0.16
Amorf	-	50.20

The FTIR spectra show the changes in band intensities that reflect the effects of with NaOH concentration on the geopolymerization process (Figure 3). The FTIR data reveals that up to 0.5 M NaOH, there is a slight decrease in peak intensities, while at 1 M and 2 M NaOH, a significant decrease is observed. The most prominent changes are in the OH-HOH bond (3300 cm^{-1}) and the bound water peak (1645 cm^{-1}), as well as in the silicate band around 980 cm^{-1}, which is a critical indicator of geopolymerization. The relative increase in the silicate band intensity suggests a higher degree of polymerization (Rattanasak and Chindaprasirt, 2009), although this observation does not align with the strength study results. This inconsistency indicates the possible formation of clay-like hydrosilicates in a non-bonded state. Furthermore, the -C=O peak at 1390 cm^{-1} and the C-O peak at 880 cm^{-1} show relative decreases, pointing to carbonate reactions occurring in parallel with polymerization.

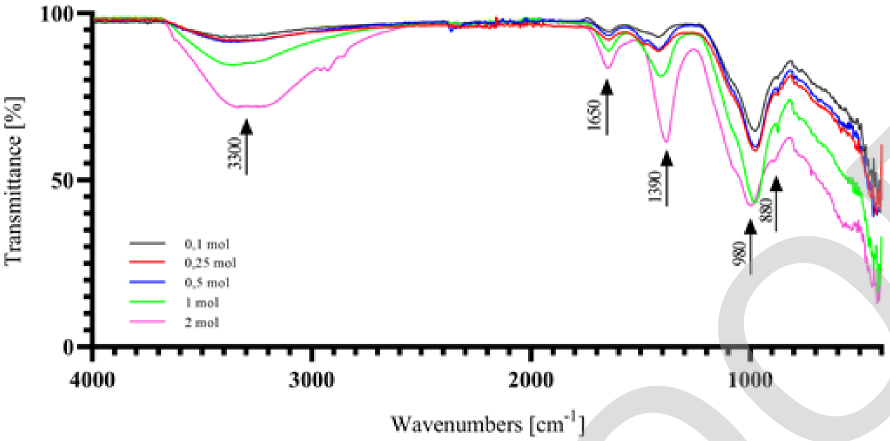

Figure 3
FTIR spectrum of the geopolymer samples

3.4. Result of the axial load test

The compressive strength of the geopolymer specimens (Figure 4) improved as the concentration of the added NaOH solution during grinding increased up to 0.5 M. The compressive strength of the specimens increased from 9.5 MPa to 16.1 MPa. However, a significant loss of strength was observed when the NaOH concentration was further increased to 1 and 2 M. At a concentration of 1 M, the strength of the specimens was only 5.68 MPa, which is approx. 60 % of the reference sample. At 2 M, the specimen did not fully solidify, leading to plastic deformation during measurement.

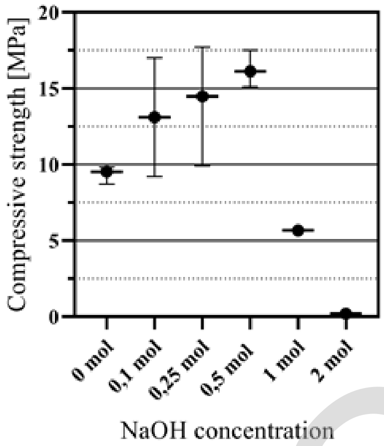

Figure 4
Compressive strength of the test specimens

4. CONCLUSIONS

By increasing the concentration of added NaOH, we can enhance the CO_2 absorption capacity of the sample material. This can be explained by the fact that the primary source of Ca in the fly ash, bassanite, decomposes into sodium sulphate, calcium hydroxide, and water after reacting with NaOH. Only then it can react with CO_2 in the system. Furthermore, adding low concentrations of NaOH (up to 0.5 M) during grinding positively affects the compressive strength of the specimens. Geopolymers prepared this way achieve 40.1% higher strength than specimens subjected only to mechanical activation. This is presumably due to the strength-increasing effect of the resulting microcrystalline calcite (Kamal et al., 2020). However, it is observed that high NaOH concentration (1, 2 M) added during grinding already causes strength loss. At 2 M solution, the specimens still need to be fully solidified. The sample prepared in 0.5 M NaOH meets the 7-day strength requirement for 32.5 strength class standard batch cements. In the next phase of the research, we will extend the strength testing to 2 and 28 days and investigate the role of different bonds (carbonate and geopolymeric bonds) in the setting process.

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