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Mechanical Activation to Enhance the Reactivity of Coal Gangue for Tailoring Geopolymer Properties

Thesis booklet of Doctoral (PhD) dissertation

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1. The scientific background and aims of the dissertation

Mining and mineral processing represent a persistent and growing environmental challenge worldwide. Over the past century, the surge in global demand for metals, minerals, and energy resources has led to a dramatic increase in both active open-pit and underground mining operations [1,2]. Among these resources, coal remains a cornerstone of global power generation. However, its extraction produces substantial quantities of coal gangue, a solid waste by-product that typically accounts for approximately 10 – 25 % of total coal production, or roughly 0.15 tons per ton of coal mined [3]. The Bükkábrány opencast lignite mine in Borsod-Abaúj-Zemplén County, Hungary, produces significant quantities of coal waste as a by-product of mining, as shown in Fig 1 [4]. This waste material consists of sandy, muddy, and clay sediments that lie between the lignite, as well as overburden layers that must be removed. The coal gangue is composed of fine-grained clay and interbedded sediments within the lignite deposits. Large quantities of coal gangue are associated with environmental problems related to disposal, polluting soils and groundwater.

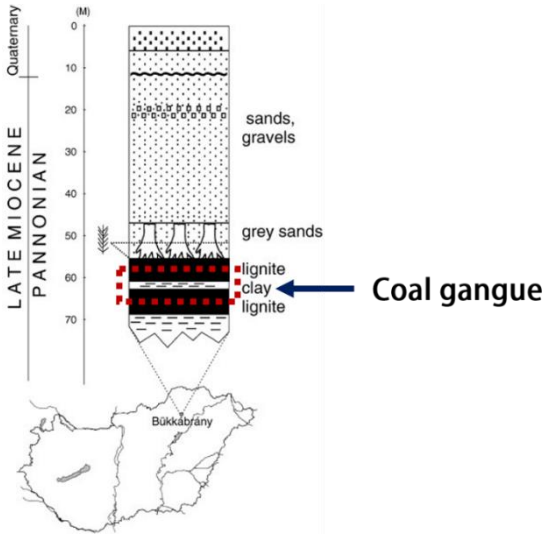


Fig 1: Location and sampling site of coal gangue

In recent years, the transition to a circular economy has emerged as the key sustainable alternative to the traditional linear economic model. This paradigm shift is driven by the need to optimize material recycling and repurpose industrial by-products for new, value-added applications. Unlike primary raw materials, which are increasingly costly and resource-intensive to extract, secondary materials offer a viable solution. However, their heterogeneous composition often poses technical challenges that require innovative processing approaches. This shift directly aligns with the European Commission ambitious 2030 climate target plan,

which aims to reduce greenhouse gas emissions by 2030 and achieve climate neutrality by 2050 [5]. Achieving these targets will require systemic changes in resource management, particularly in high environmental impact sectors such as mining, manufacturing, and energy, where waste recovery and circular economy principles can significantly reduce the carbon footprint. The principles of the circular economy have rapidly been adopted and implemented by most countries, fundamentally changing global economic perspectives and influencing national strategic plans [6]. To maximize the potential of recycling coal gangue and address the associated environmental concerns, it is crucial to explore recent advancements in processing techniques and gain a deeper understanding of the coal gangue properties.

Global research into waste-derived geopolymers as sustainable building materials has increased significantly. This emerging field has attracted great scientific and industrial interest because geopolymers represent a highly promising, environmentally friendly alternative to traditional Portland cement. Geopolymers not only exhibit exceptional mechanical properties, including high compressive strength and durability, but their manufacture also produces significantly lower carbon emissions [7]. These properties make geopolymer technology particularly attractive for sustainable construction applications, aligning with global efforts to reduce the environmental impact of building materials. Nevertheless, a major obstacle to using coal gangue in geopolymerization is its inherently low reactivity. This low reactivity means coal gangue particles frequently fail to achieve complete dissolution before the finalized hardened structure forms. This limitation presents substantial challenges in accurately quantifying reaction progression in coal gangue-based geopolymers [8],[9]. Methods such as mechanical activation [10],[11], calcination activation [12],[13], and chemical activation [14] represent alternative strategies to recycle coal gangue and significantly improve its reactivity for geopolymerization. Calcination activation, despite its effectiveness in enhancing the reactivity of certain materials, presents significant drawbacks that hinder its widespread industrial application. High energy consumption is the primary issue, as the process typically requires maintaining temperatures ranging from 650 - 900 °C extended durations. This energy demand directly contradicts the principles of sustainable resource utilization [15],[16]. In contrast, the mechanical activation process requires specialized high energy mills that employ various working regimens, including compression, shear, and impact forces, to increase the material surface energy by inducing amorphization or defect into crystal lattice [17]. Mechanical activation represents a particularly promising approach as it modifies raw material reactivity through surface property alterations without fundamentally changing the overall

chemical structure. This methodology is increasingly recognized as a pioneering and environmentally friendly processing technique, with applications extending across diverse technological fields, such as cement [18],[19], metal extraction [20], mineralization [21], and the extraction of rare earth elements [22]. Mechanical activation is a recognized strategy to enhance the reactivity of raw materials for geopolymer applications, a fact that has been consistently demonstrated in recent years. The underlying mechanisms include particle size reduction, increased specific surface area, the creation of crystal lattice defects, and higher amorphous content [23-25]. As a result, significant improvements in geopolymer properties for their utilization, such as compressive strength, setting time, and rheology characteristics, are now thoroughly reported [25-28].

2. Research aims and objectives

This research aims to investigate the mechanical activation of coal gangue through a dry grinding process, employing high-energy milling to enhance its reactivity. The primary objective is to determine the optimal grinding parameters to achieve the most favourable reactivity while also identifying limitation of specific grinding energy. Ultimately, this study seeks to establish a comprehensive understanding of both raw and mechanically activated coal gangue and effect on the performance characteristic of resulting geopolymer properties.

- **i.** To investigate a comprehensive analysis and characterization of raw coal gangue.
- **ii.** To systematically optimize the key grinding parameters, grinding media size (d_{GM}), revolution per minute (rpm), and grinding time (t_G) for high-energy milling to achieve mechanically activated coal gangue properties while determine specific grinding energy (E_m) consumption. Furthermore, to critically compare the effectiveness of two distinct high-energy milling techniques (vibratory vs. planetary ball milling) on the resulting coal gangue reactivity
- **iii.** To conduct comprehensive analysis of the mechanically activated coal gangue to specifically examining changes in particle size distribution (PSD), aggregation/ agglomeration and deagglomeration, specific surface area (S_{BET}) and geometric surface area (S_m), powder morphology (SEM), functional groups via (FT-IR) that cause its molecular bonds to vibrate (stretch and bend), and phase composition (XRD).

Characterization and optimization of raw and mechanically activated coal gangue for geopolymer applications.

- **i.** To experimentally synthesize geopolymers using both raw and optimized mechanically activated coal gangue as the primary precursor. This includes systematically optimizing the key geopolymerization parameters (liquid-to-solid ratio, NaOH molarity, sodium silicate percentage, and curing temperature) to evaluate and maximize the resulting mechanical strength and performance characteristics.
- **ii.** To develop a comprehensive matrix and establish a predictive correlation, relationship between the physicochemical properties of the mechanically activated coal gangue and the final geopolymer performance.

3. Description of raw materials, experimental equipment, applied measurement methods

3.1. Raw material and properties

Coal gangue, the primary material for these experiments, was sourced from the Bükkábrány coal mine in Hungary. During the initial exploratory phase of this study, three representative samples were collected from this single mining site. The purpose of analysing these initial samples was to conduct a preliminary characterization of the coal gangue properties before subjecting it to further mechanical activation processes. Additionally, a characterization was performed to assess the coal gangue suitability as a geopolymer precursor. The step-by-step methodological framework of this study is illustrated in the schematic outline in Fig.3.1. As a next step in the sample preparation, the collected coal gangue samples underwent a drying process in an oven at 105 °C for 24 hours until a constant mass was recorded, ensuring the removal of any free water. As an initial step, the coal gangue sample was crushed using a hammer crusher for quantitative sample preparation to approach required particle size. This preliminary crushing was performed to reduce the size of the raw coal gangue, which was deemed too large for direct analysis of particle density and for chemical composition. Furthermore, to ensure effective mechanical activation, the median particle x_{50} feed size was targeted to be less than 1000 μm for further investigations.

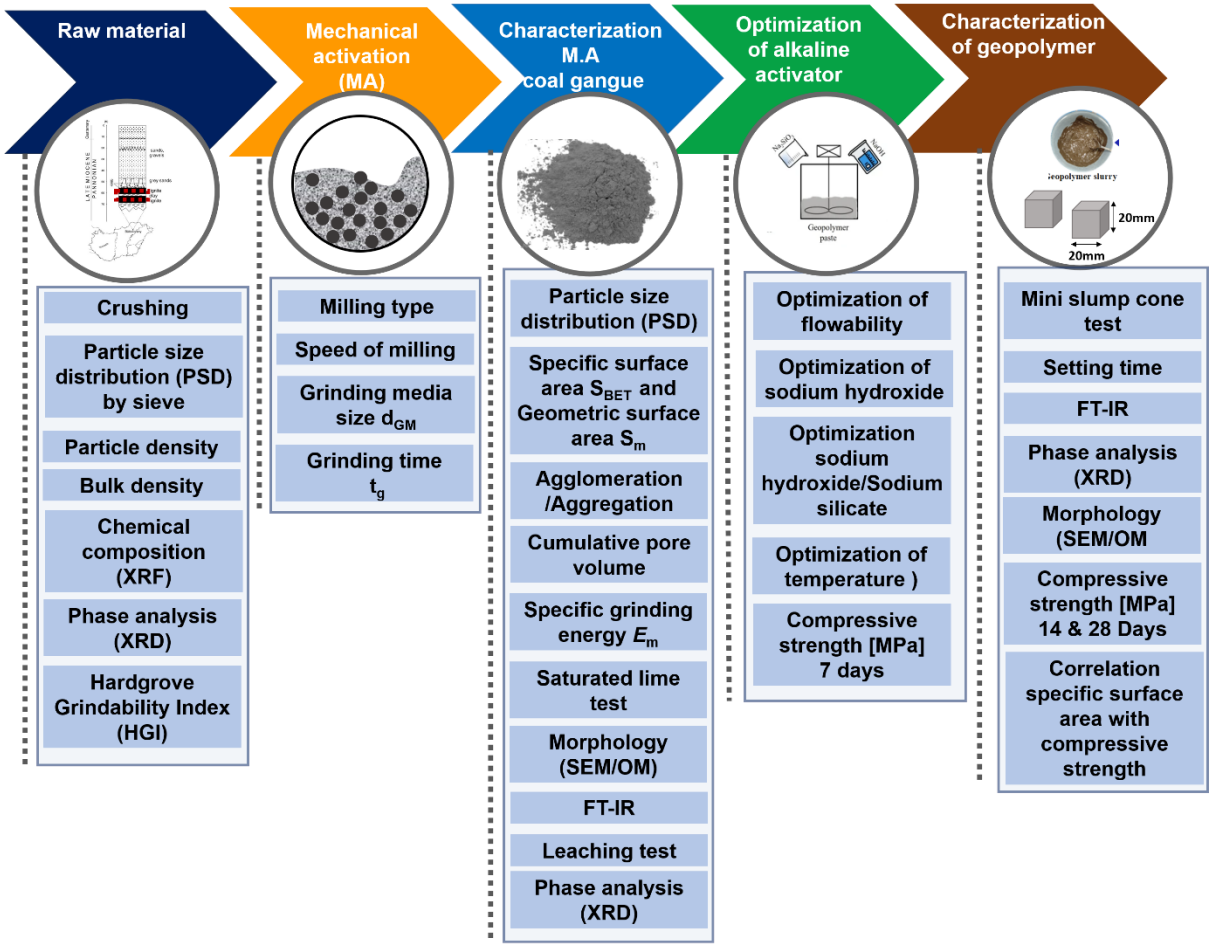


Fig.3.1: Schematic outlining the study methodological approach.

Chemical composition analysis of all coal gangue samples revealed a substantial combined content of SiO_2, Al_2O_3, and Fe_2O_3, ranging from 84.03 % to 89.33 %, as detailed in Table 3.1. This determined value significantly exceeded the minimum requirement of 70 wt% stipulated by ASTM C618 for Class N pozzolans. Trace elements were also detected, including Cu (36 ppm), Zn (127 ppm), Pb (12 ppm), Rb (118 ppm), Sr (102 ppm), Ba (526 ppm), As (12 ppm), Cr (100 ppm), Ni (52 ppm), and Zr (244 ppm). The concentrations of these metals were found to be much smaller than permissible [28]. Consequently, based on the criteria outlined in ASTM C618 [29], the investigated coal gangue samples were determined to possess pozzolanic activity and certain cementitious characteristics. In addition to their favourable oxide composition, all coal gangue samples exhibited relatively low loss on ignition (LOI) values, which ranged from 4.5% to 7.9%. These measurements fell well below the maximum allowable limit of 10% as outlined in ASTM C618 standards. Loss on ignition was identified as a critical parameter in assessing the geopolymerization potential of the samples, as research indicates

that the presence of unburned carbon in such materials can significantly impact performance by absorbing the activator solution during the geopolymerization process [30].

Table 3.1: Chemical composition of raw coal gangue

Component	**Coal gangue 1**	**Coal gangue 2**	**Coal gangue 3**
SiO_2	59.2	61.1	72.1
Al_2O_3	20.8	17.8	13.4
MgO	2.30	1.92	1.07
CaO	0.68	0.67	0.65
Na_2O	0.55	0.69	0.86
K_2O	3.50	2.99	2.20
Fe_2O_3	7.08	5.67	4.33
MnO	0.127	0.104	0.123
TiO_2	1.076	0.959	0.624
P_2O_5	0.093	0.103	0.084
S	0.14	0.13	0.02
F	<0.3	<0.3	<0.3
Total	95.5	92.1	95.5
$SiO_2 + Al_2O_3 + Fe_2O_3$	87.08	84.57	89.33
LOI	4.5	7.9	4.5

Phase analysis of the coal gangue samples (1–3) indicated that the primary mineral components were the 1:1 clay mineral kaolinite and the 2:1 clay mineral illite, with quartz being the dominant phase. Based on this analysis, as detailed in Table 3.2, the amorphous content was determined to be less than 20%.

Table 3.2: Phase analysis of raw coal gangue

Type of minerals	**Coal gangue 1 wt%**	**Coal gangue 2 wt%**	**Coal gangue 3 wt%**
Kaolinite	6.2	4.5	6.3
Illite	22.5	16.2	12.6
Quartz	30.7	45.2	56.3
Muscovite	14.1	9.6	5.6
Albite	4.5	5.7	6.1
Microcline	2.8	2.6	2.1
Amorphous	**16.3**	**13.8**	**8.8**

3.2. Geopolymerization of raw coal gangue and test procedures

The raw coal gangue was investigated to optimize the alkaline solution. The optimization of the alkaline activator in this study is schematically represented in Fig.3.2. The alkaline solution

used in the geopolymerization process was a combination of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3). The molarity of the alkaline activator was crucial for establishing the environment necessary for the dissolution of aluminium (Al) and silicon (Si) species. For the alkaline solution, laboratory-grade sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) were used as activators. An 8-14 M (NaOH) solution was prepared by dissolving sodium hydroxide pellets in double-distilled water. The sodium silicate (Na_2SiO_3) solution used in this stage had a composition of Na_2O (14.2%), SiO_2 (31.12%), and H_2O (54.68%) by mass.

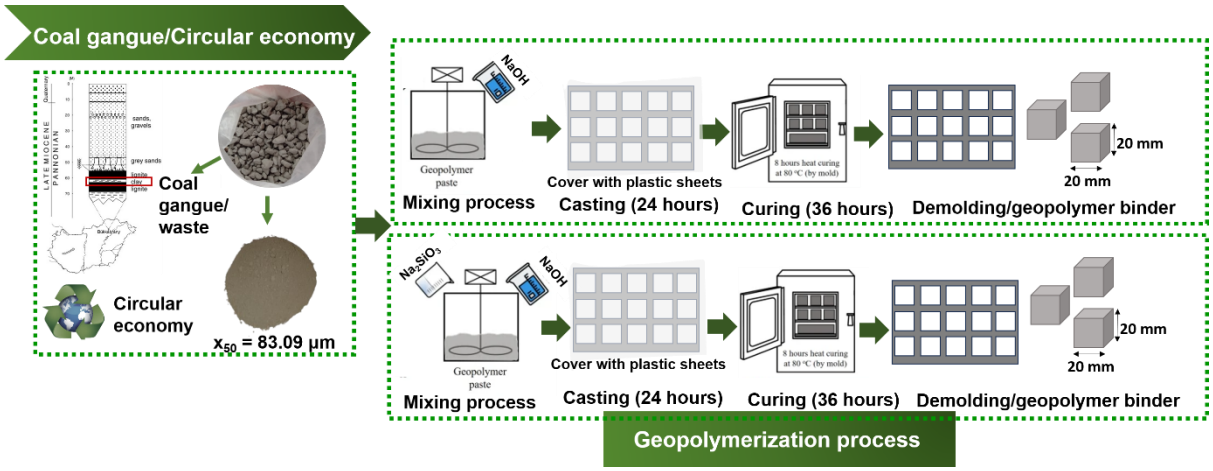


Fig.3.2: A systematic preliminary of geopolymerization of raw coal gangue

3.3. Mechanical activation and geopolymerization

3.3.1. Mechanical activation in vibratory ball mill

Mechanical activation was achieved using a vibratory ball mill operating in parallel mode under dry grinding conditions, as depicted in Fig.3.3. The mill was equipped with two 1000 mL steel bowls; each charged with 2542.5 g of 15 mm diameter steel grinding media. Detailed process parameters are provided in Table 3.3. The grinding media filling ratio was maintained at 70% (v/v), while the material filling ratio relative to the media pore volume was set at 110% (v/v), based on optimized conditions according to the methodology used previous works by Musci et al. [31]. The electrical power consumption was cumulatively recorded using a digital energy meter, enabling the calculation of the specific grinding energy based on the difference between the initial and final meter readings.

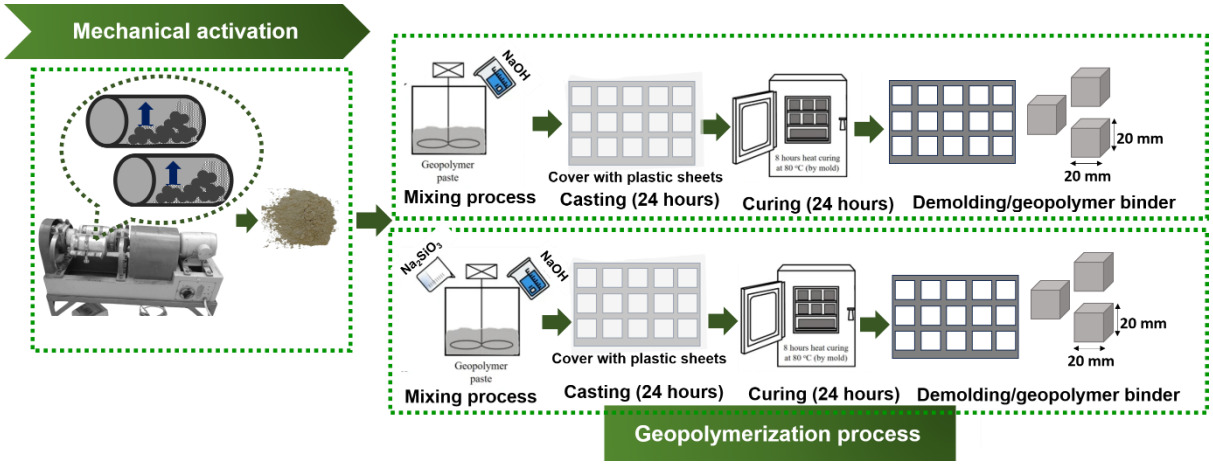


Fig.3.3: Schematic diagram of M.A coal gangue in vibratory ball mill for geopolymerization

Table 3.3: Investigated parameters of mechanical activation

Parameters	**Value**	**Unit**
Frequency	50	Hz
Volume of grinding chamber V_{GC}	1000	mL
Grinding media size (steel) d_{GM}	15	mm
Density grinding media d_{GM} = 15 mm, ρ_{GM}	7.87	g/cm^3
Grinding time	1, 5, 10, 15, 30, 60, 120	min

3.3.2. Mechanical activation in planetary ball mill

The schematic diagram for the mechanical activation of coal gangue in a planetary ball mill for geopolymer applications was illustrated in Fig.3.4. A material to ball ratio of 1:10 was maintained, following the manufacturer technical data. Grinding was performed at 450, 600, 650, and 700 rpm for durations of 1, 5, 10, 15, 30, 60, and 120 min, as shown in Table 3.4. To mitigate the high temperatures generated by long-term grinding, the operation was paused after every 20 min for a 20-min cooling period.

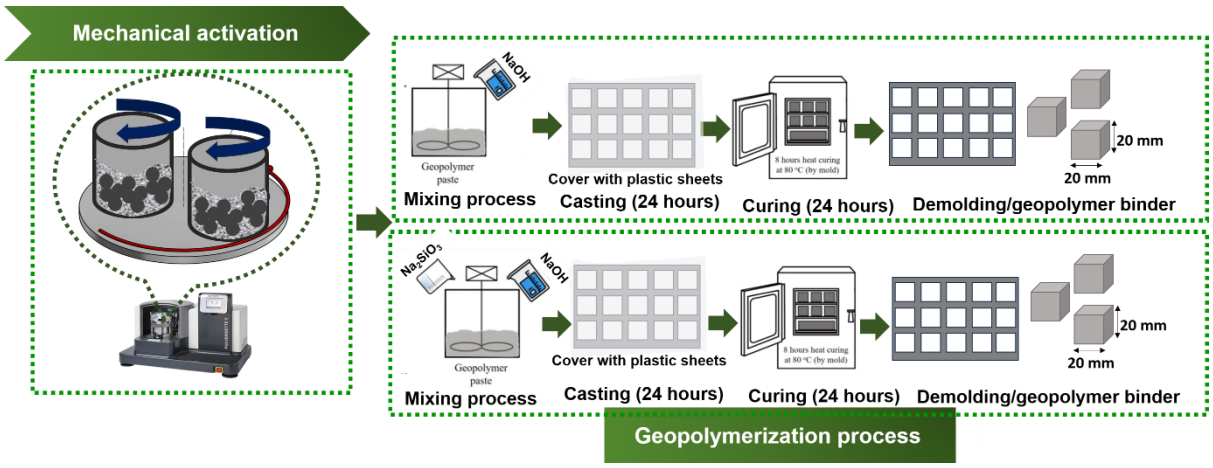


Fig.3.4: Schematic diagram of M.A process coal gangue in planetary ball mill

Table 3.4: Investigated process parameters

Parameters	Value	Unit
Rotational speed	450, 600,650,700	rpm
Grinding media size (steel) d_{GM}	5, 10	mm
Density grinding media d_{GM} = 5 mm, ρ_{GM}	0.956	g/cm^3
Density grinding media d_{GM} = 10 mm, ρ_{GM}	1.332	g/cm^3
Grinding media filling ratio φ_{GM}	2.662, 2.773	-
Grinding media size steel d_{GM}	5, 10	mm

3.4. Test procedures

3.4.1. Particle size distribution and geometric surface area of coal gangue powder

The particle size distribution (PSD) of both the raw and mechanically activated coal gangue was determined using a HORIBA LA-950V2 laser particle size analyser. Deionized water (H_2O) served as the dispersion medium. The PSD was estimated from the measured data using Fraunhofer's approximate method. The geometric surface area, a parameter related to the external or relative surface area, was obtained by software-based calculation from the PSD data, assuming a spherical particle surface (S_m)[32]. To evaluate the potential for particle aggregation or agglomeration, selected samples were tested with sodium pyrophosphate ($Na_4P_2O_7$) as a dispersing medium. This specific test was performed on samples ground for 60 and 120 min.

3.4.2. Morphology of coal gangue powder and geopolymer samples

Powder coal gangue and geopolymer samples morphology was assessed via scanning electron microscopy (SEM) using a JEOL JCM-7000NeoScope^{TM} Benchtop. Secondary electron (SE) imaging was performed at an accelerating voltage of 30 kV. Samples were sputter-coated with a gold layer to facilitate electron conduction and improve signal detection.

3.4.3. Specific surface area S_{BET} of coal gangue powder

For the measurement of the total specific surface area S_{BET}, Tristar 3000 from Micrometrics Corporation was used. Before each measurement, the sample was degassed. From the adsorbed gas, the surface area of the particle is determined. The BET (Brunauer, Emmett, and Teller) method is used to determine the specific surface area of the particles including meso- and micropores. To degas the powder, the samples were dried at 90 °C for 30 min and additionally at 300 °C for 180 min in flowing nitrogen gas in the Micrometrics Smart prep before the adsorption measurements were taken. The gas used for adsorption was nitrogen, and the

adsorption temperature were 190 °C. The complete adsorption isotherms were recorded. The specific surface area was calculated by a five-point BET method. The weight of each sample was approximately 1 g.

3.4.4. Saturated lime test of coal gangue powder

The saturated lime test was conducted to assess the pozzolanic reactivity of both raw and mechanically activated coal gangue. For each material, 2 g was placed into separate plastic bottle containers, followed by the addition of 100 mL of a saturated lime solution $Ca(OH)_2$. The containers were then sealed and thoroughly shaken. To ensure continuous interaction, the containers were manually shaken once daily. At 2-day intervals, a 50 mL of the solution was extracted for titration with a 0.05 mol/L hydrochloric acid solution, using methylene orange as an indicator. Immediately after each sampling, 50 mL of fresh saturated lime solution was added back to the respective plastic container to maintain a consistent. Based on the titration results, the amount of CaO uptake by the 2 g of each material was subsequently calculated to evaluate its pozzolanic activity.

3.4.5. Alkaline leaching test of coal gangue powder

The reactivity of both raw and mechanically activated coal gangue was evaluated by quantifying the release of alumina (Al) and silica (Si) during leaching in 8M sodium hydroxide (NaOH) solution. Specifically, one gram of each material was stirred at 400 rpm in 40 mL of the NaOH solution, maintained at a temperature of 60 °C for a duration of 2 hours. Following leaching, the resulting suspensions were subjected to centrifugation at 5000 rpm for 3 min and subsequently acidified using 37 % HCl. The concentrations of the leached Al and Si were then determined using microwave plasma atomic emission spectrometry (MP-AES).

3.4.6. Phase composition analysis of coal gangue powder

The crystalline phases of both raw and mechanically activated coal gangue samples were identified using X-ray diffraction (XRD) with a Rigaku Mini flex II diffractometer with CuKα radiation and a monochromator, scanned at 1°/min and matched against the ICDD database.

3.4.7. Fourier transform-infrared spectroscopy (FT-IR)

The vibrational characteristics of chemical bonds (stretching and bending) in the coal gangue powder and geopolymer samples were determined by Fourier transform - infrared spectroscopy (FT-IR) using a JASCO FTIR 4200 system equipped with a diamond ATR for reflection

measurements. To ensure reproducibility, three parallel measurements were carried out for each sample with each spectrum were recorded in the absorbance range of 4000 - 400 cm^{-1} at a resolution of 4 cm^{-1}.

3.4.8. Setting time of geopolymer paste

The setting time of the fresh geopolymer paste was determined in accordance with ASTM C191 [33]. The initial setting time was identified using a Vicat apparatus, where a penetration depth of 25 mm was taken as the benchmark. The penetration depth was recorded over time for geopolymer pastes produced with mechanically activated coal gangue that was subjected to varying grinding times. The results were then plotted to illustrate the relationship between penetration depth and grinding time.

4. New scientific results (NSR) of the PhD thesis

NSR 1: Influence of grinding parameters for optimization mechanically activated coal gangue, comparison the results obtained by vibratory and planetary ball mill

The optimization of mechanically activated coal gangue was investigated by examining the effects of different high-energy milling devices and their respective grinding parameters. Two distinct milling devices a vibratory ball mill and a planetary ball mill were used to represent batch and laboratory-scale operations, in order to address the selection of a suitable device for activation. My research establish correlation between median particle size x_{50}, specific surface area SSA as function specific grinding energy. In addition, the relationship among particle characteristics x_{10}, x_{50}, x_{90} and the relative span (RS) was examined. For the planetary ball mill with design of experiment (DoE) was conducted at rotational speeds ranging from 600 to 700 rpm and a grinding media size of 10 mm.

I experimentally proved that initial grinding proportionally increases the specific surface area (SSA) and reduces the median particle size x_{50}. However, this trend reverses beyond a distinct inflection point. Extending the specific grinding energy beyond this point leads to a decrease in SSA due to aggregation/agglomeration, followed by subsequent deagglomeration. This finding is based on a comprehensive evaluation of mechanically activated coal gangue, including an assessment of the grinding kinetics limit and a Design of Experiments (DoE) approach. In addition, the effect of grinding time on the specific surface area S_{BET} includes the area contributed by all surface features, such as internal porosity (pores, cracks, and surface roughness) and geometric surface area S_m which is calculated based on an assumed spherical particle size distribution also highlighted

- *Grinding kinetic limit*:

The mechanically activated coal gangue reached its grinding limit after 30 min in the vibratory ball mill, resulting in particle aggregation. At this point, the mechanically activated coal gangue had a geometric surface area of 3690 cm^2/g. Its particle characteristic of x_{10} (3.93 μm), x_{50} (4.20 μm), x_{90} (13.79 μm) with a relative span (RS = 0.9) and a specific grinding energy of 2.97E+02 J g^{-1}. In the planetary ball mill operated at 450 rpm, particle aggregation/agglomeration of the mechanically activated coal gangue was observed after 10 min of grinding. At this point, the geometric surface area was 15341 cm^2/g with particle sizes of x_{10} (0.49 μm), x_{50} (4.86 μm), x_{90} (11.09 μm), relative span (RS = 2.17) and a specific grinding energy that reached 4.63 E+05 J g^{-1}. **It was revealed that based on characteristic median particle size and specific surface area as function of specific grinding energy correlation was determined using exponential**

function (Table 1, Table 2). **I experimentally proved that that for coal gangue grinding, the grinding limit strongly depends on the energy used and the type of mechanical stress. Specifically, the lowest the stress intensity, the higher the grinding limit (higher specific surface area achieved) within a specific grinding interval** (Fig 1a-b).

Table 1: Fitting correlation median particle size as function specific grinding energy

Type of grinding device	Equation	R^2
Vibratory ball mill	$y = 7.62 + 75.46e^{-0.17308x}$	0.99
Planetary ball mill	$y = 7.62 + 75.46e^{-8.5637E-5x}$	0.99

Table 2: Fitting correlation geometric surface area as function specific grinding energy

Type of grinding device	Equation	R^2
Vibratory ball mill	$y = 3640.26 - 1951.09e^{-0.0052x}$	0.83
Planetary ball mill	$y = 16659.21 - 15143.6e^{-9.761E-5x}$	0.61

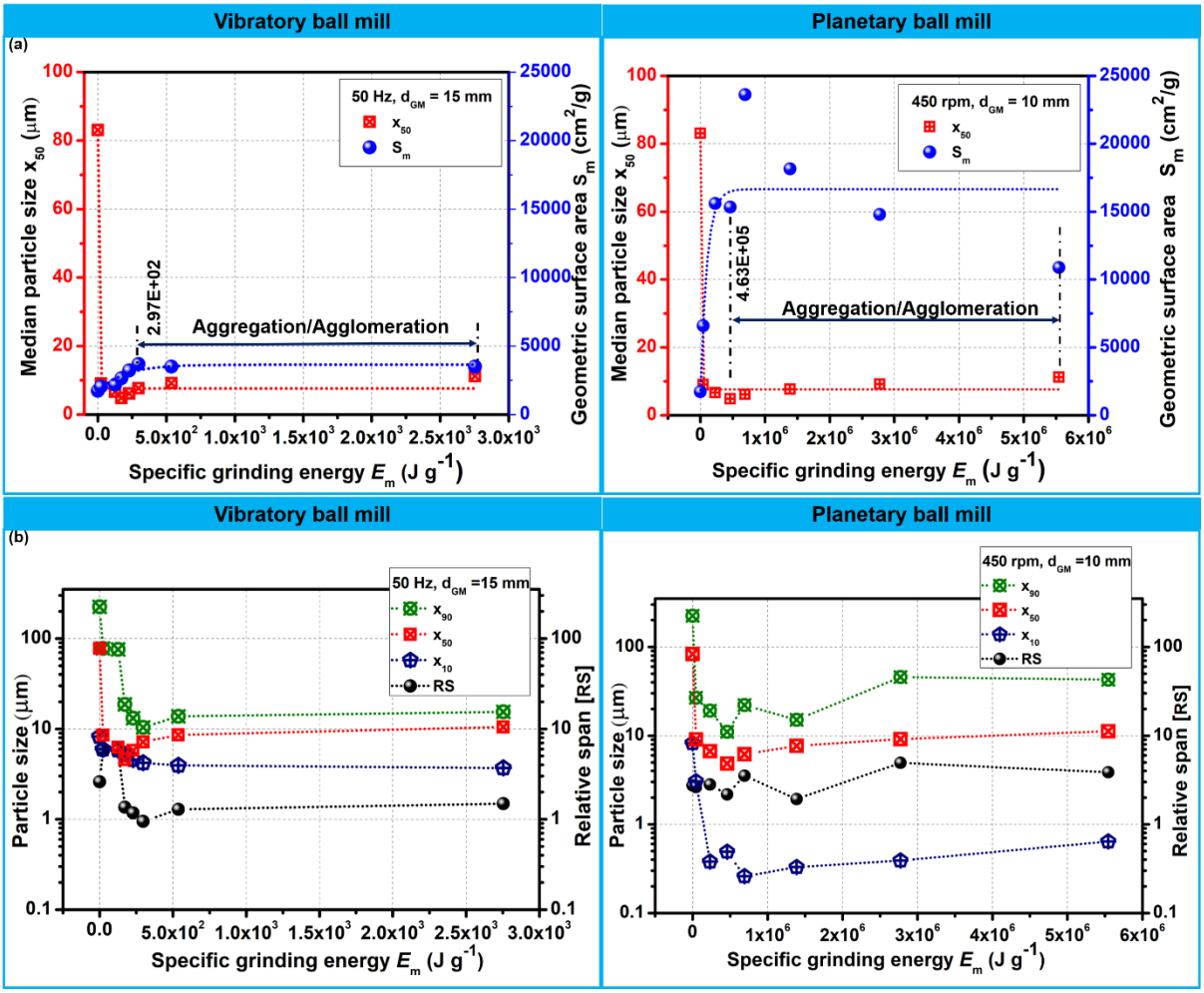


Fig. 1: (a) Grinding kinetics (b) Characteristic particle size of raw and mechanically activated coal gangue

- *Design of Experiment (DoE)*:

The experimental analysis revealed a relationship between geometric surface area as a function of grinding time, specific grinding energy, stress intensity *SI*, and active mass (estimated by quantifying the mass of powder adhering to the grinding media). This establishes a comprehensive framework for predicting mechanically activated coal gangue above 600 rpm thereby providing a quantitative basis for grinding process optimization. The Design of Experiment (DoE) showed maximum specific grinding energy between 4.79E+06 -7.71E+06 kJ g^{-1} where the mechanically activated coal gangue shifted to deagglomeration (120 min grinding time) (Fig. 2a-d).

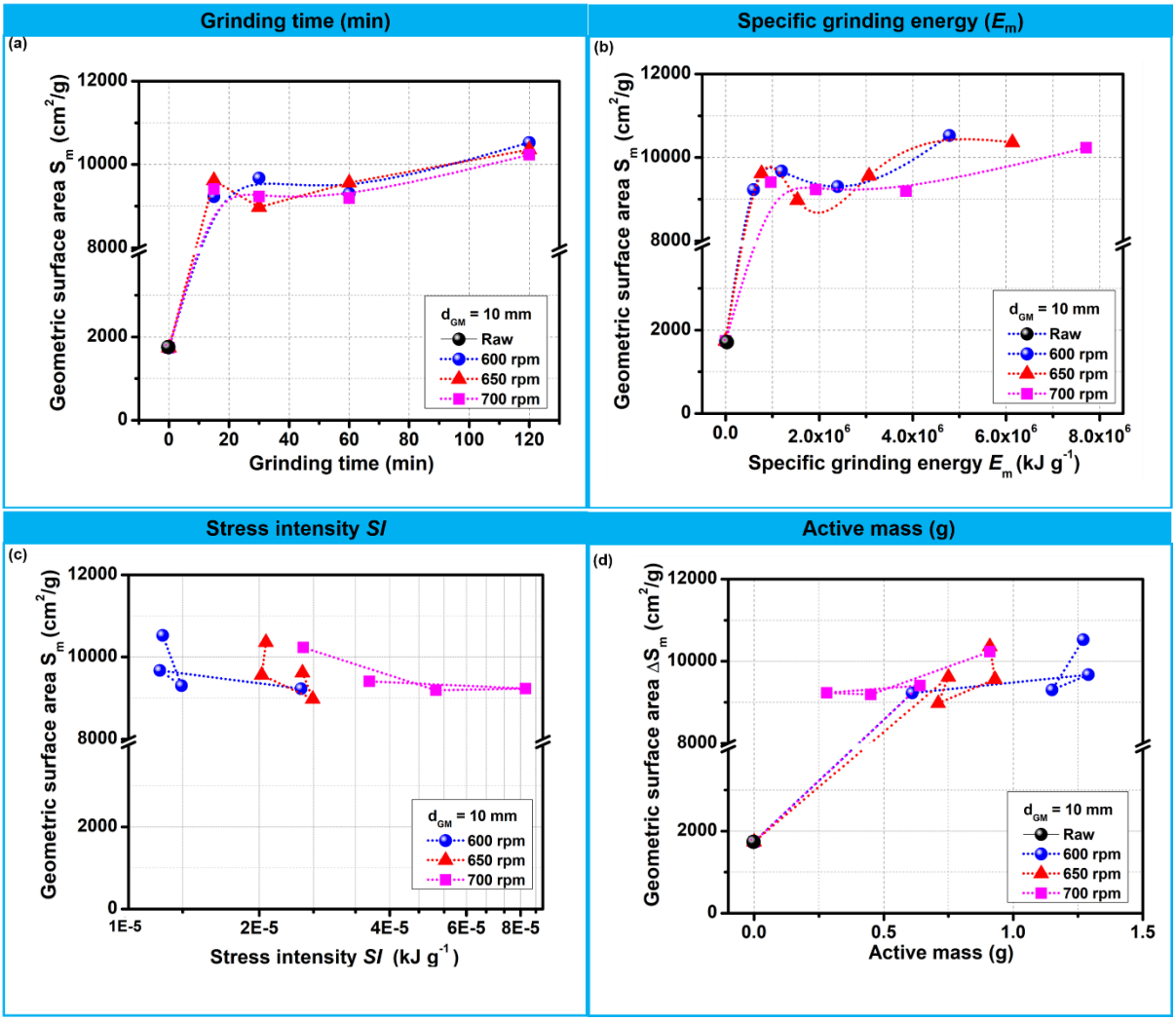


Fig.2: Geometric surface area as a function of (a) grinding time (min) (b) specific grinding energy (c) stress intensity *SI* (d) active mass

- *Specific surface area (SSA):*

Experimental results showed that the S_{BET} values for the mechanically activated coal gangue ranged from 7.67-12.47 m^2/g when processed by a vibratory ball mill, and from 8.52 to 18.06 m^2/g when processed by a planetary ball mill. The results are relatively close, particularly at the 120 min of grinding, where the specific surface area was 11.50 m^2/g for the vibratory mill and 12.45 m^2/g for the planetary ball mill, respectively. Meanwhile, the geometric surface area S_m was 0.34 m^2/g for the vibratory ball mill and 1.08 m^2/g for the planetary ball mill at 120 of grinding. The dissolution reaction occurs on the external and readily accessible surfaces of the particle when it is mixed in the alkaline activator. For this reason, the S_m values (which focus on the outer particle size) can be more directly relevant affecting the reactivity of mechanically activated coal gangue (Fig 3). As the result, compressive strength of geopolymer is higher with geometric surface area 1.08 m^2/g.

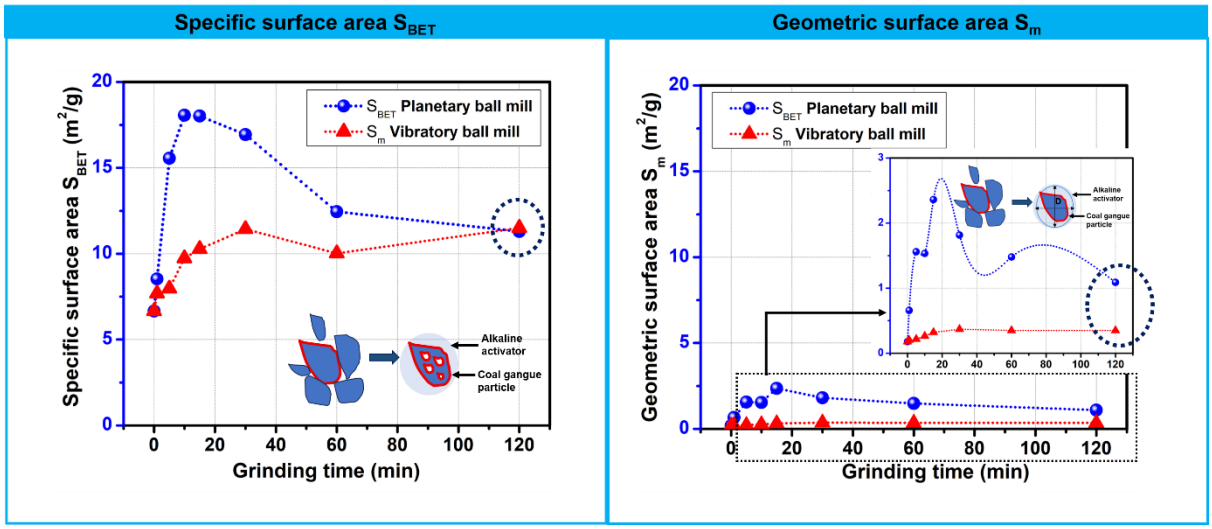


Fig. 3: Comparison of specific surface area and geometric surface area coal gangue as function of grinding time

NSR 2: Influence of aggregation/agglomeration and deagglomeration of mechanically activated coal gangue on geopolymer compressive strength

To study and investigate the influence of particle rearrangement mechanisms (aggregation/ agglomeration, and deagglomeration) on the resulting compressive strength of geopolymer.

I experimentally demonstrated that the aggregation/agglomeration and subsequent deagglomeration of mechanically activated coal gangue significantly affect the geopolymer compressive strength. This finding is based on a correlation of geometric

surface area and compressive strength as a function of the specific grinding energy which can be written by exponential function (Fig. 4).

- *Vibratory ball mill:*

The highest compressive strength of 1.25 MPa (14 days of curing) was using mechanically activated coal gangue 30 min, which also exhibited the highest geometric surface area of 3690 cm^2/g and specific grinding energy 2.97E+02 J g^{-1}. As expected, the increase in specific surface area contributed positively to the particle reactivity of mechanically activated coal gangue and dissolution kinetics during geopolymerization. However, beyond the optimal specific grinding energy, particularly after 30 min, the compressive strength began to decline to between 0.92 - 0.96 MPa (26.4 %) despite further specific grinding energy 2.754 E +03 J g^{-1}, as aggregation had a negative effect on the compressive strength.

- *Planetary ball mill:*

The coal gangue mechanically activated for 120 min exhibited the performance in highest compressive strength (46.7 MPa) after 14 days, despite possessing a decreasing of geometric surface area of 10,882 cm^2/g. The compressive strength of geopolymer exhibited suggesting that the aggregation/agglomeration of mechanically activated coal gangue particles does not affect the final compressive strength for grinding process 450 rpm, 10 mm grinding size. Design of Experiment (DoE) of 600 - 700 rpm and similar a grinding media size, the analysis revealed that the condition of deagglomeration was indicated by highest geometric surface 8978 to 10,360 cm^2/g and the maximum specific grinding energy between 4.79E+06 - 7.71E+06 kJ g^{-1}. The analysis indicated that compressive strength in this DoE was not negatively affected by aggregation/agglomeration and deagglomeration. This providing a crucial mechanistic link between mechanically activated coal gangue particle characteristics and final geopolymer mechanical performance.

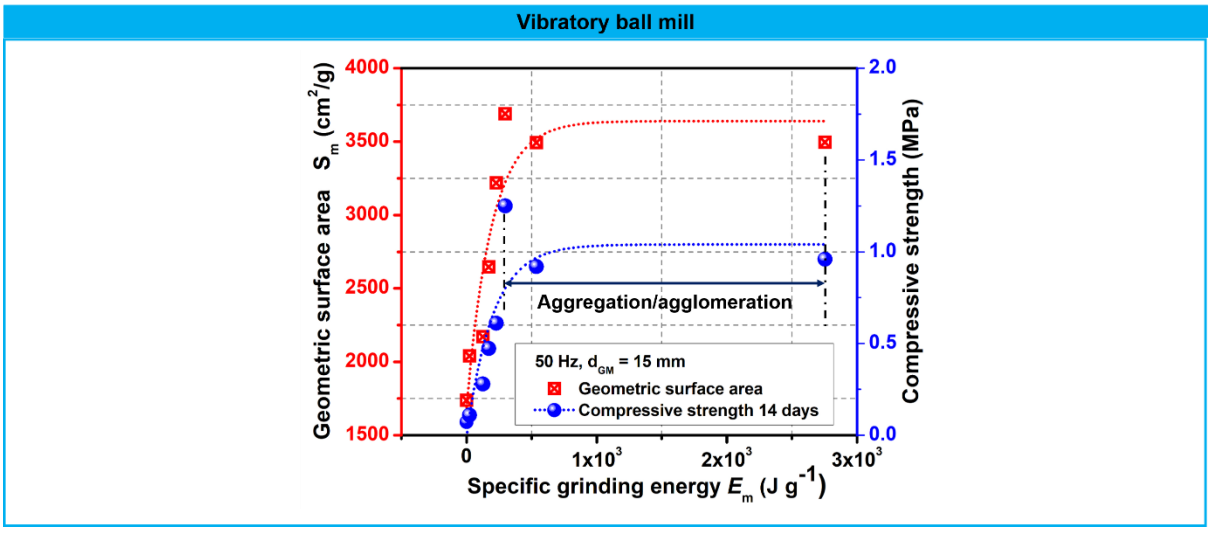
It was found that an exponential function can accurately describe the geometric surface area as a function of specific grinding energy. A very high R^2 value 0.8 proves the goodness-of-fit of this model. For compressive strength as a function of specific grinding energy, the relationship can be modelled using an exponential function for the vibratory ball mill and a linear function for the planetary ball mill (Table 3 and Table 4).

Table 3: Fitting correlation of geometric surface area as function specific grinding energy

Type of grinding device	Equation	R^2
Vibratory ball mill	$y = 3640.26 - 1951.09e^{-0.0052x}$	0.82
Planetary ball mill	$y = 7.62 + 75.46e^{-8.56E-5x}$	0.99
	$y = 9858.92 - 8119e^{-4.20E-6x}$	0.96
	$y = 9634.81 - 7896e^{-1.01E-5x}$	0.97
	$y = 9557.78 - 7819.64e^{-4.01E-6x}$	0.96

Table 4: Fitting correlation of compressive strength as function specific grinding energy

Type of grinding device	Equation	R^2
Vibratory ball mill	$y = 1.04 - 1.051e^{-0.00497x}$	0.69
Planetary ball mill	$y = 8.77E-6 - 1.16x$	0.96
	$y = 6.67E-7 + 1.24x$	0.75
	$y = 7.63E-7 + 1.42x$	0.75
	$y = 5.85E-7 + 1.58x$	0.67



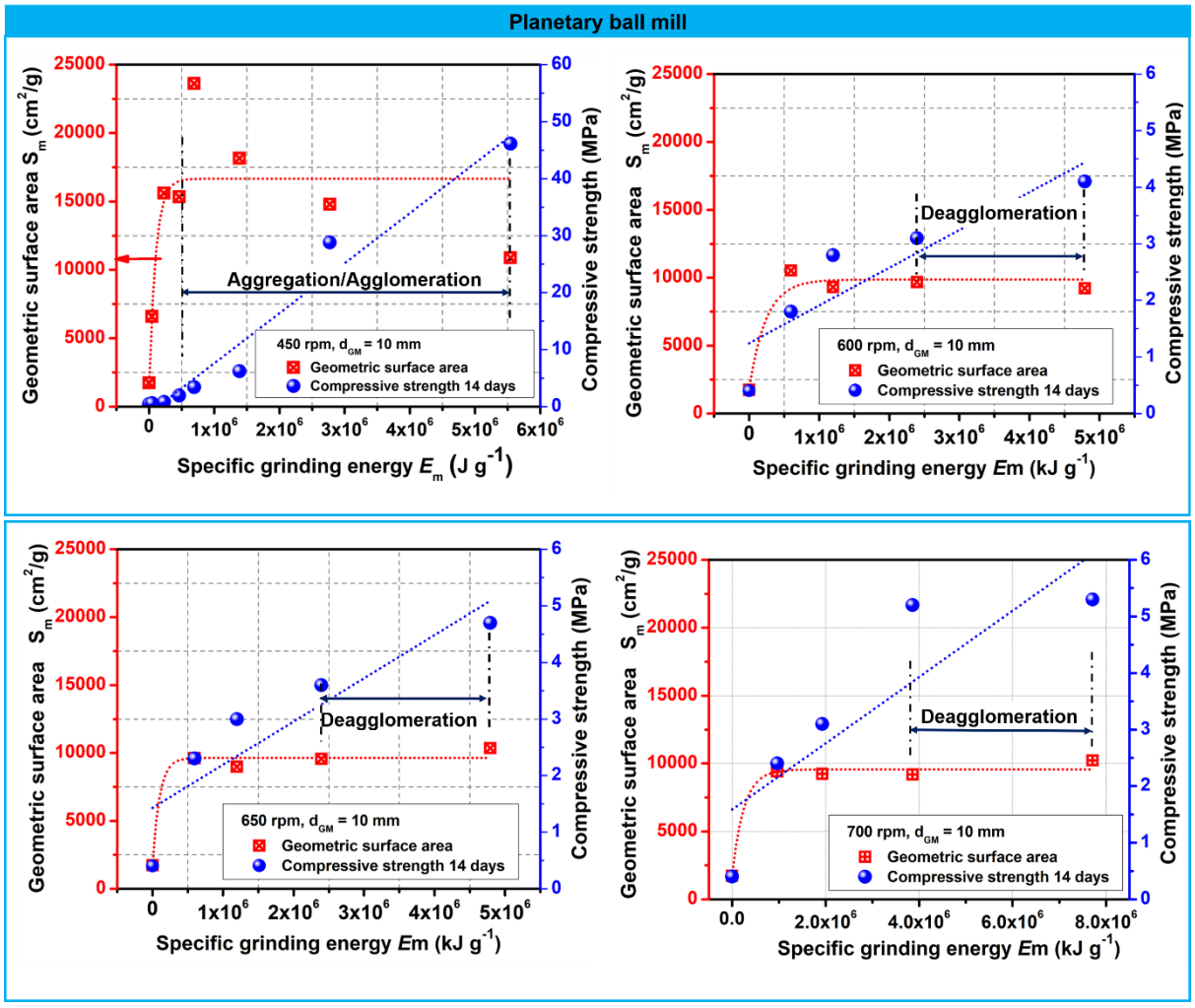


Fig 4: Correlation geometric surface area with compressive strength as function of specific grinding energy

NSR 3: The effect agglomeration of mechanically activated coal gangue on the leaching test, setting time of geopolymer paste, and compressive strength of geopolymer.

To study the effects of agglomeration on mechanically activated coal gangue, samples were selected from the planetary ball mill processed at 450 rpm, using 10 mm grinding media size, with grinding times ranging from 1 to 120 min.

I experimentally demonstrated the relationship by which particle agglomeration of mechanically activated coal gangue influences the geopolymerization process. This finding is based on a comprehensive evaluation of the leaching test results, the setting time of the geopolymer paste, and the final compressive strength of geopolymer samples (Fig. 5a-c).

- *Leaching test:*

Mechanical activation enhances the reactivity of coal gangue by increasing its geometric surface area S_m and inducing structural defect and disordered at particle surfaces, which generally accelerate the leaching process. However, as shown in Figure 5(a), prolonged grinding of 120 min leads to particle agglomeration of the mechanically activated coal gangue. As the result, significantly affects the release of silica (Si) and alumina (Al). The concentrations of Si and Al in the leachate decrease from 93.96 mg/L to 73.52 mg/L (Si) and from 101.48 mg/L to 75.6 mg/L (Al) representing a proportional decrease between 21 % and 26 % after 120 min of grinding time

- *Setting time of geopolymer paste:*

Mechanically activated coal gangue for 120 min was observed to significantly slow the geopolymerization process. This effect was evident in increase in setting times of geopolymer paste, with the initial setting time rising from 106 min to 171 min and the final setting time increasing from 165 min to 238 min.

- *Compressive strength:*

Mechanically activated coal gangue with a grinding time of 30 min, the compressive strength at 28 days was 15.01 MPa. Increasing the grinding time to 60 min led to a substantial increase in compressive strength, reaching 42.1 MPa which represent a 64.3 %. Subsequently, increasing the grinding time between 60 and 120 min resulted in compressive strength further increasing from 42.1 MPa to 55.7 MPa corresponding to a 24.4 % with improvement at 28 days. The maximum compressive strength of 46.12 MPa at 14 days and 55.7 MPa at 28 days was achieved at a grinding time 120 min despite the observed agglomeration of mechanically activated coal gangue, which had a geometric surface area of 10,882 cm^2/g.

The key finding is that while excess energy stored in the lattice enhances the dissolution of silica (Si) and alumina (Al), agglomeration counteracts this effect, which ultimately slows the geopolymerization process.

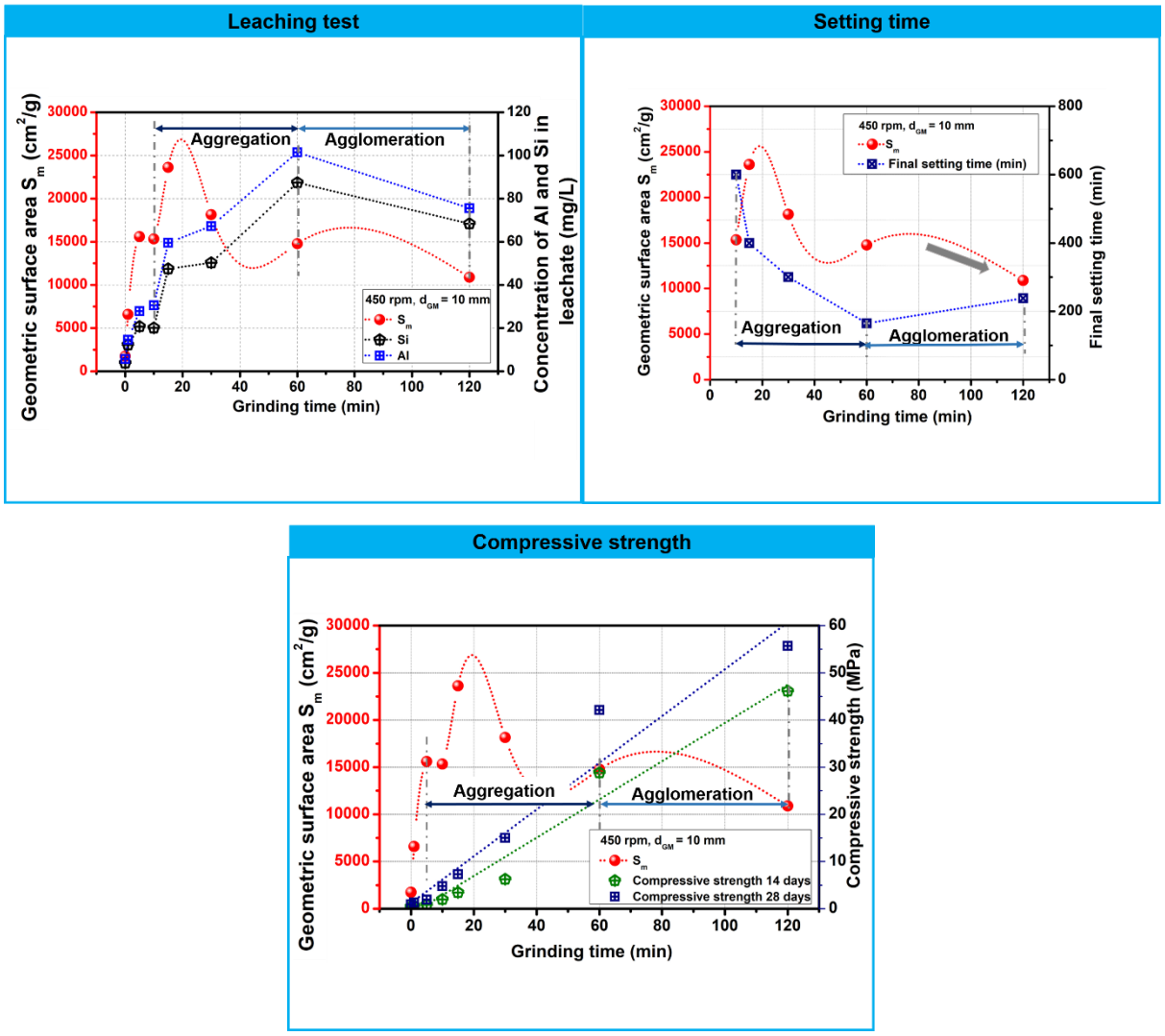


Fig 5: Geometric surface area as function of (a) concentration of Al and Si (b) final setting time (c) compressive strength

NSR 4: Influence of mechanical stress on structural disorder of mechanically activated coal gangue.

This research establishes a mechanistic framework that links specific grinding energy consumption to the formation of structural disorder mechanisms that govern the transition from mechanical dispersion to surface activation.

I experimentally demonstrate that the mechanical activation of coal gangue is profoundly influenced by mechanical stress and specific grinding energy consumption, leads to structural disorder and defects. The corresponding shifts in vibrational modes fundamentally revealing that the asymmetric stretching vibration of Si-O-T, (T= Si or Al) is the most important factor governing its reaction in geopolymerization (Fig 6).

- *Vibratory ball mill:*

With a maximum specific grinding energy of 2.754E+03 J g^{-1}, the grinding process primarily imparts mechanical stress (compression, impact, friction, shear) leading to mechanical dispersion with only minimal surface activation. This is confirmed by the limited shift in the molecular bond to vibrate, asymmetric stretching vibration Si-O-T, (T= Si or Al) from 997 - 993 cm^{-1} which indicates minimal structural defect formation. This establishes that, below this specific grinding energy, limited increase in activation is governed solely by mechanical dispersion

- *Planetary ball mill:*

By varying the rotational speed (rpm) and grinding media size, the coal gangue is agitated at a high speed over a wide specific grinding energy range of 4.6E+04 - 9E+09 J g^{-1}. This process significantly increases the activation energy that stored in non-equilibrium and disordered crystal lattice of coal gangue. The resulting surface activation of mechanically activated coal gangue is confirmed by prominent shifts in the vibrational modes of key functional groups, particularly in shifts asymmetric stretching vibrations Si-O-T (T= Si or Al) which shift to range 998 cm^{-1} and 1071 cm^{-1}

The observation is that the vibratory ball mill $R^2 = 0.85$, exhibit a significant strong correlation to logarithmic function compared to planetary ball mill ($R^2 = 0.39$). From mechanical activation point of view, this study can differentiate the structural defects according to energy regime.

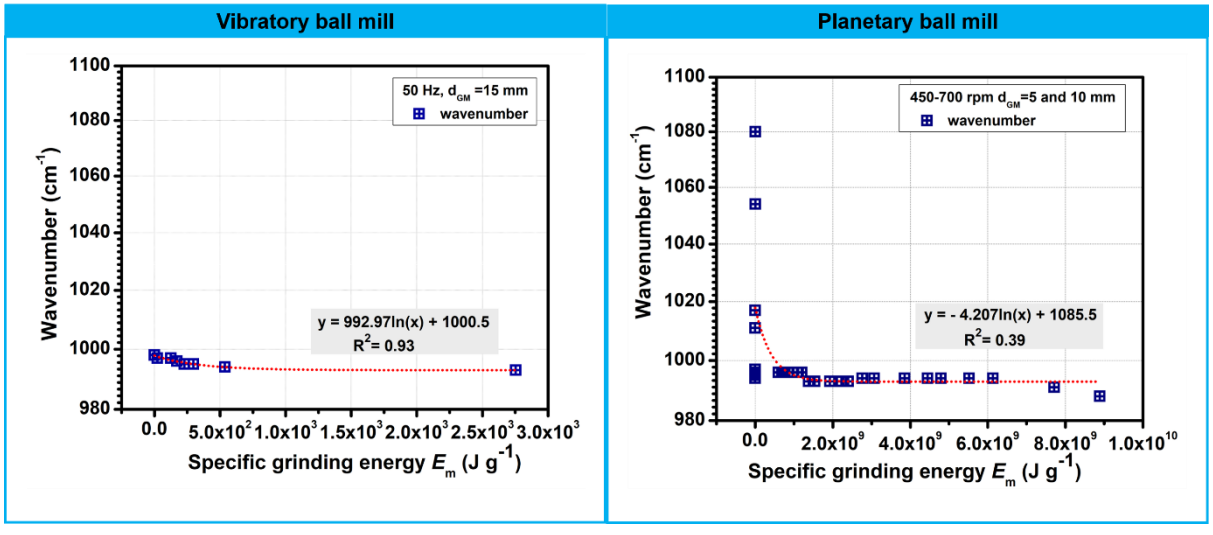


Fig.6: Wavenumber as function of specific grinding energy

NSR 5: Effects of geometric surface area and pozzolanic reactivity

My research establishes the relationship between grinding process parameters and the pozzolanic reactivity of coal gangue.

I experimentally demonstrated the factors governing CaO uptake in mechanically activated coal gangue. Through investigation, the results indicate that CaO uptake measurement is influent not only by geometric surface area (numerous asperities and surface roughness) but also structure defects of mechanically activated coal gangue. Nevertheless, Design of Experiment (DoE) of 600 - 700 rpm demonstrate the overall performance of CaO uptake (Fig 7). While pozzolanic reactivity is typically assessed for cement industry, this study is establishing the direct applicability of mechanically activated coal gangue reactivity to geopolymer system, leveraging a method that is easy and reliable.

- *Vibratory ball mill:*

The CaO uptake of the mechanically activated coal gangue, measured over 30 days (15th titration), varied with the geometric surface area. The highest geometric surface area 3690 cm^2/g of mechanically activated coal gangue was achieved after 30 min of grinding, corresponding to a peak CaO uptake of 75.2 mg/g. Nevertheless, a subsequent decrease in CaO uptake, ranging from 66.2 - 69.2 mg/g was observed at 60 and 120 min. This decline resulted from a reduction in geometric surface area due to particle aggregation (3493 - 3496 cm^2/g). Furthermore, the surface activation validates by functional group of mechanically activated coal gangue that cause molecular bond to vibrate (stretch and bend) structural particularly the asymmetric stretching vibrations of Si-O-T (T= Si or Al) 993 cm^{-1} did not change significant.

- *Planetary ball mill*:

The coal gangue mechanically activated for 120 min yielded a dramatically lower geometric surface area S_m of 10,882 cm^2/g compared to the 15 min activated coal gangue, which measured 23,616 cm^2/g. This result suggests that the change specific surface over extended grinding time demonstrates that the resulting structural disorder, rather than the specific surface area alone, plays the dominant role in enhancing pozzolanic reactivity. For the Design of Experiment (DoE), the maximum geometric surface area of 10,235 - 10,360 cm^2/g for mechanically activated coal gangue (120 min) did not yield the maximum CaO uptake range 121.7 - 132.4 mg/g (30 days reaction time). The maximum geometric surface area resulted in declined CaO uptake compared to grinding times of 30 and 60 min despite the significant structural disorder or defects present in the mechanically activated coal gangue particularly the asymmetric

stretching vibrations of Si-O-T (T= Si or Al) towards 990 - 998 cm^{-1} at 650 - 700 rpm with grinding time 120 min. The 600 rpm yielded the highest CaO uptake of 118 mg/g of mechanically activated coal gangue 120 min (30 days reaction time). Thus, the experimental results demonstrated that the CaO uptake from the Design of Experiments (DoE) for mechanically activated coal gangue exhibited a different trend in the planetary ball mill when the rotational speed exceeded 600 rpm.

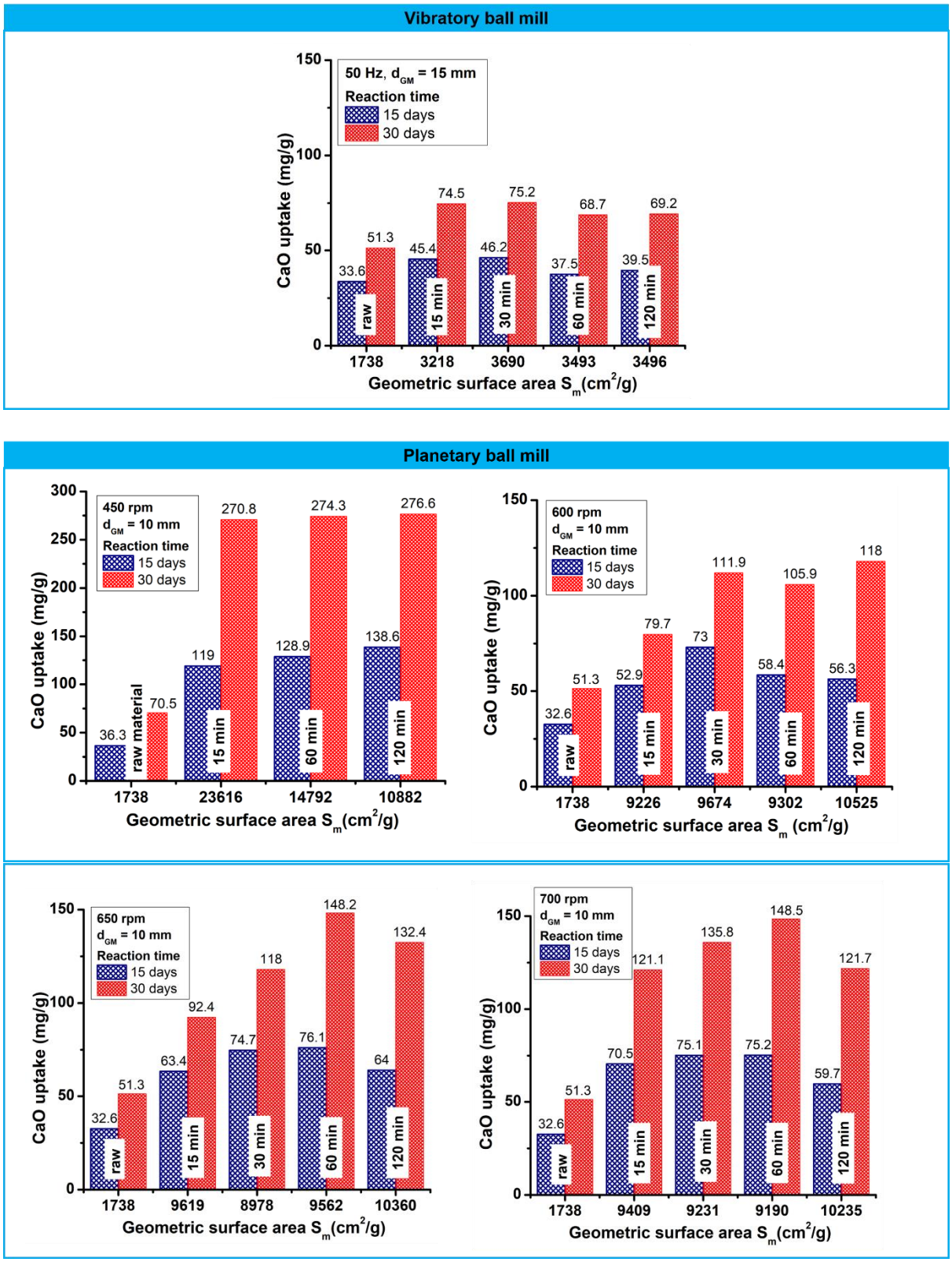


Fig. 7: Relationship CaO uptake as function of geometric surface area

5. List of publications

Journal publications:

1. S.N.A. Bakil, Marton Toth, Jamal-Eldin F.M. Ibrahim, Gábor Mucsi. Influence of mechanical activation of coal gangue on the strength and microstructure of geopolymer. Construction and Building Material. 2025 https://authors.elsevier.com/sd/article/S0950-0618(25)02128-2.

2. S.N.A. Bakil, Sofiia Dibrova, Sandra Breitung-Faes, Gábor Mucsi. Optimizing coal gangue reactivity for geopolymer applications: A comprehensive study on high-energy grinding parameters. Powder Technology. 2025 https://doi.org/10.1016/j.powtec.2025.121441.

3. S.N. Abd Bakil, Mucsi Gabor, Investigation Mechanical Activation Coal Gangue for Geopolymer. No. 66 Proceedings of the 15th *fib* International PhD Symposium in Civil Engineering - 28-30 August 2024.Page 883

4. S.N. Abd Bakil, Mucsi Gabor, Low grade clay as raw material for geopolymer. University of Miskolc. Hungary.16 Nov 2022. https://doi.org/10.33030/geosciences.2023.01.006

5. Siti Natrah Abd Bakil*, Ference Kristaly, Gábor Mucsi. Preliminary study of low-grade clay as secondary raw material for geopolymer. https://ojs.uni-miskolc.hu/index.php/geosciences/article/view/2287/1784

List of conferences:

1. Annual Meeting of the DECHEMA/VDI Specialist Groups 2025, Tu Clausthal, Germany

2. S.N. Abd Bakil, Mucsi Gabor, Investigation Mechanical Activation Coal Gangue for Geopolymer. No. 66 Proceedings of the 15th *fib* International PhD Symposium in Civil Engineering - 28-30 August 2024.Page 883

3. S.N. Abd Bakil, Mucsi Gabor, Low grade clay as raw material for geopolymer. MicroCAD, University of Miskolc. Hungary.16 Nov 2022.

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