



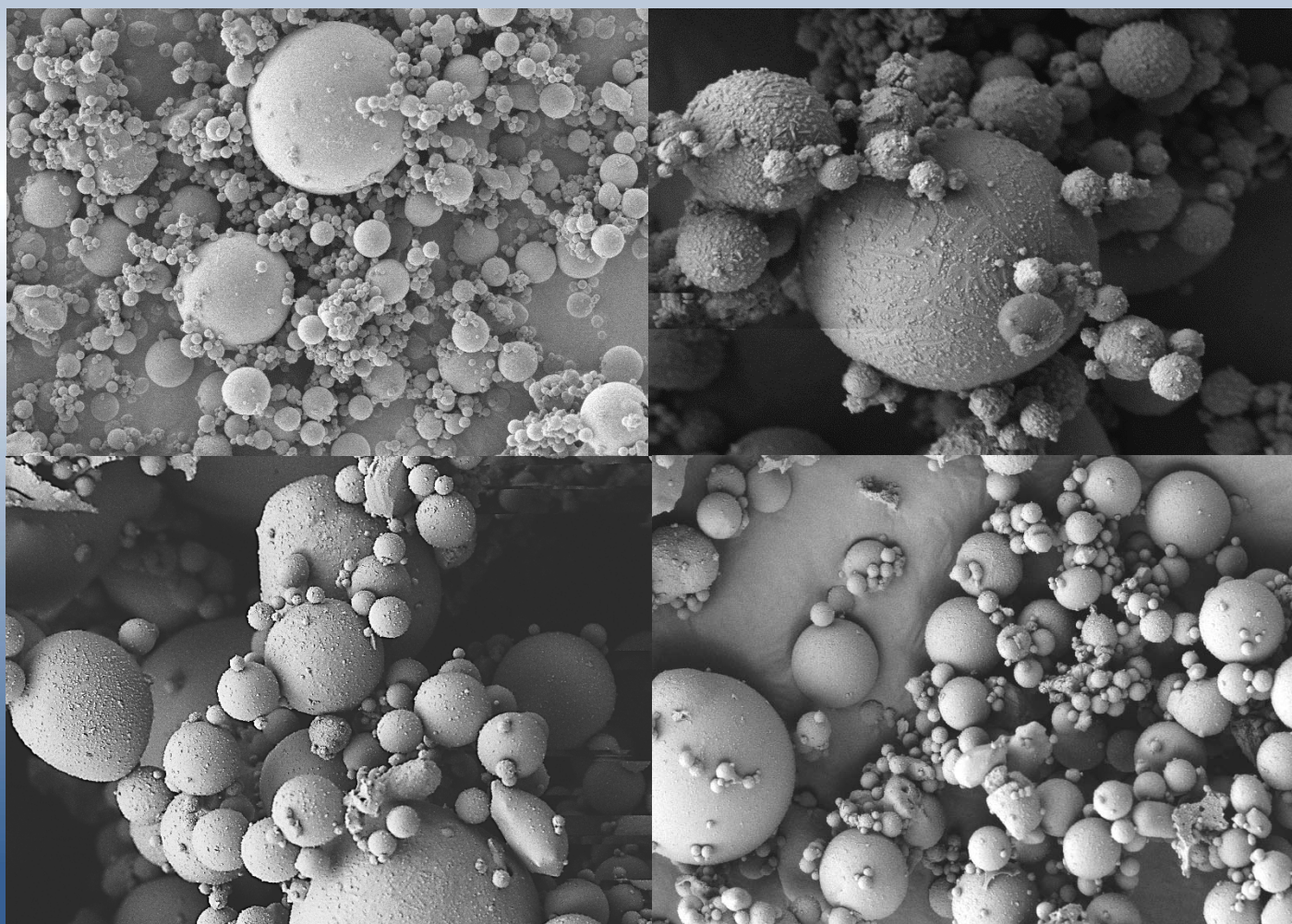
EUROCOALASH 2019



10 - 12 June 2019,
Dundee, Scotland

EUROCOALASH 2019

Proceedings



Organised by:



University
of Dundee



Dundee & Angus
CONVENTION BUREAU
WORKING WITH YOU FOR YOU



Supported by:

ISBN 978-0-9573263-2-3



9 780957 326323



ATRITOR



Investigation of Pore Structure and Properties of Lightweight Geopolymer based on Swelled Na-Bentonite <i>Yang, Y, Jiang, J, Lu, Z Y, Li, J</i>	275
A Novel Mechanically Robust Superhydrophobic Cement Foam <i>Zheng, Z, She, W, Miao, C</i>	287
Optimizing the Dosage of Leca and Fly Ash in Lightweight Concrete To Study the Performance of Steel-Concrete Composite Slab <i>Banupriya, R, Arul Mary, S</i>	295
Study on Structural Grade Lightweight Concrete and Composite Concrete Structure Design <i>Kalathingal, A, Desai, P, Shaikh, M T A</i>	308
Lagoon Fly Ash: A Potential Source of the Precursor for Geopolymer Binders <i>Kwasny, J, McGrath, T, Lawther, S, Correia, R, Soutsos, M, Sha, W, Cox, S, Chen, J F</i>	322
Phase-Transition Conductometry to Study Pore Structure Evolution in Fly Ash Mortar <i>Suryanto, B, Kim, J, McCarter, W J</i>	334
Tailoring the Mechanical Properties of Landfilled Fly Ash Geopolymers by Grinding <i>Ambrus, M, Szabó, R, Csőke, B, Mucsi, G</i>	346
Use of Fly Ash in Concrete: Current Indian Scenario and a Case Study on HVFAC for Shear Wall Construction in India <i>Kulkarni, V</i>	356
Fly Ash as Alumina Resource <i>Marko, M, Opravil, T, Šoukal, F, Pořízka, J</i>	366
Fly Ash Reclamation and Beneficiation Using a Triboelectric Belt Separator <i>Baker, L, Gupta A, Hrach, F</i>	376
Mobility of Arsenic, Chromium and Copper Arising From Soil Application of Stabilised Aggregates Made From Contaminated Wood Ash <i>Mitchell, K, Moreno-Jimenez, E, Jones, M R, Zheng, L, Trakal, L, Hough, R, Beesley, L</i>	386
Influence of Heat and Chemical Activation on Strength and Durability of High Strength High Volume Fly Ash Concrete <i>Nwaubani, S, Hlabangana, M</i>	399
Ca-rich Oil-shale Ash Waste as a Carbon Dioxide Sink: Stable Carbon and Oxygen Isotope Study <i>Leben, K, Mõtlep, R, Kirsimäe, K</i>	414
Examination of Particle Packing in Ternary Blends of Portland Cement, Fly Ash and Silica Fume <i>Dyer, T, Csetenyi, L, Scobbie, K</i>	420

TAILORING THE MECHANICAL PROPERTIES OF LANDFILLED FLY ASH GEOPOLYMERS BY GRINDING

M Ambrus

R Szabó

B Csőke

G Mucsi

University of Miskolc

Hungary

ABSTRACT. Due to the continuous shutdown of coal fired power plants, landfilled fly ash (FA) has become a substantial secondary resource for several branches of industry. The utilisation of FA as a raw material for geopolymerisation is becoming more and more widespread not only because of the appropriate reactivity of the base material, but also the environmentally benefits and good mechanical properties of the final products. Examination of the effect of mechanical activation of landfilled brown coal FA from Tatabánya (Hungary) on the mechanical properties of geopolymers was carried out. The FA was ground in a ball mill for 10, 20, 30, 60 and 120 minutes before geopolymer production. However, fluctuation was observed in the unconfined compressive strength results. Thus, comparison was made with previous data on geopolymers made from “fresh” FA to reveal possible reasons behind the inconsistency. Furthermore, both the raw materials and the geopolymers were examined (particle size analysis, FT-IR analysis, XRF, SEM) to investigate their geopolymerisation behaviour. Important conclusions can be drawn from the results about the effect of mechanical activation on the modification and reactivity of landfilled FA.

Keywords: Compressive strength, Deposited fly ash, Geopolymerisation, Mechanical activation

Mária Ambrus is an environmental engineering MSc student and research engineer at the Faculty of Earth Science and Engineering at the University of Miskolc, Hungary. Her research interests include the utilisation and management of wastes.

Roland Szabó is a PhD candidate of Mikoviny Sámuel Doctoral School of Earth Sciences from 2018 and assistant research fellow at University of Miskolc, Hungary. His current research is into the development of geopolymers with special properties using industrial wastes.

Professor Barnabás Csőke is a Professor Emeritus at the Faculty of Earth Science and Engineering, University of Miskolc, Hungary. He is one of the country's pioneer researchers in waste preparation technologies, and has published extensively on many aspects of processing of secondary raw materials for industrial applications.

Assoc. Professor Gábor Mucsi is the Deputy Dean of the Faculty of Earth Science and Engineering at the University of Miskolc, Hungary. A renowned practitioner in the field of waste recycling technology, he is a member of many technical committees and has published extensively on material processing technology for concrete and cement.

INTRODUCTION

Over the past decades, sustainable consumption and production has been recognised as a key political, economic and industrial concept. In 1992, the United Nations Conference on Environment and Development conference was held in Rio de Janeiro where issues such as limited water supply, health problems caused by air pollution and the use of alternative energy sources were addressed [1]. As a result, sustainable consumption and production was included in the 2030 Agenda for Sustainable Development that was adopted by all United Nations Member States in 2015. Among the 17 sustainable development goals proposed by the UN, goal 12 was set to “Ensure sustainable consumption and production patterns”. Some of the main issues that should be resolved until 2030 include the reduction of waste, the efficient use of natural resources and the elimination of ineffective fossil fuel subsidies [2].

Between 2000-2016, almost 10 % decline in the use of solid fossil fuels (e.g. lignite, brown coal, peat etc.) and over 15% increase in the use of renewable energy sources could be observed in the European Union [3]. However, in China and India, over 70% of the total electricity production was from various coal sources in 2015, with an increasing tendency in India [4].

The reduced use of solid fossil fuels for electricity production is a suitable method to reduce greenhouse gas emissions. However, the fly ash produced by fossil fuel power plants is a potential and valuable raw material for the construction industry that also contributes to the decrease of CO₂ emissions through the replacement of Portland cement. Due to the shifting of secondary raw material sources from the EU to Asian countries, the solution to the shortage of domestic fly ash sources can be importing or using previously landfilled fly ash [5, 6].

Geopolymers are synthetic alumino-silicate materials produced through the reaction between solid alumino-silicates and oxides with alkaline media [7, 8]. The effect of the mechanical activation of fly ash on the mechanical properties of geopolymers has been examined using various mill types [8, 9, 10, 11]. However, the effect of grinding on the mechanical properties of landfilled fly ash geopolymers is a less investigated topic.

Kusnierová et al. [12] examined the amorphous content change in black coal fly ash in relation to time (i.e. 5 and 20 years) and determined that the samples underwent significant devitrification. Yeheyis et al. [13] carried out similar investigation, concentrating on the chemical, mineralogical and geochemical properties of landfilled fly ash. The samples were deposited at various times and at various depths. Thus, the effects of weathering were also examined. According to their results, the mineralogy and microstructure of the fly ash was altered and the formation of secondary minerals (e.g. calcite and ettringite) could be observed, mainly due to hydration, carbonation and pozzolanic reactions.

The mechanical activation of deposited fly ash and its effect on geopolymer products was examined by Mucsi et al. [14, 15] and Molnár et al. [16], concluding that the compressive strength of geopolymers can be controlled via milling the deposited fly ash – because of the higher specimen density, the compressive strength was also increased. Szabó et al. examined the effect of milling on geopolymer foam and were able to establish connection between the rheology of geopolymer paste and the decreased particle size [17].

The aim of the research is to examine the potential usage of landfilled fly ash from Tatabánya (Hungary) and to explore the possibility of tailoring the mechanical properties of geopolymer products from landfilled fly ash by grinding.

MATERIALS AND METHODS

Landfilled brown coal fly ash (B-FA) from Tatabánya (Hungary) and fresh lignite fly ash (L-FA) from Mátra Power Station, Visonta (Hungary) were used for the experiments. The chemical composition of the FA samples was measured with Rigaku Supermini 200 type X-ray fluorescence spectrometer. The results of the XRF analysis are summarised in Table 1. The examination of the chemical compositions revealed that both samples are class F fly ash with rather similar SiO₂ content. However, the B-FA contained higher wt.% Al₂O₃ which can have positive effect on the geopolymerisation process, while the L-FA had higher CaO content that can result in pozzolanic reactions beside geopolymerisation.

Table 1 The chemical composition of the FA samples.

	B-FA	L-FA
Chemical composition, wt.%		
SiO ₂	46.40	48.10
Al ₂ O ₃	27.40	14.42
CaO	7.04	11.76
Fe ₂ O ₃	6.96	10.97
MgO	2.23	3.34
K ₂ O	1.65	1.66
TiO ₂	0.941	0.492
Na ₂ O	0.50	0.37
MnO	0.029	0.171
P ₂ O ₅	0.117	0.264
Σ	93.27	91.55

The loss on ignition (LOI) was low for both samples: 0.75% for B-FA and 0.37% for L-FA.

The mechanical activation of the fly ashes was carried out in a Ø305×305 mm size cylindrical ball mill with steel ball grinding media. The filling ratio of the grinding media was 30 V/V%, the material filling ratio was 110 V/V%. The time duration of mechanical activation was 5, 10, 20, 30, 60 and 120 minutes for B-FA and 5, 10, 20, 30 and 60 minutes for L-FA.

The particle size distribution of the samples was examined with a Horiba LA950 V2 type laser particle size analyser. The specific surface areas (SSA) were calculated from the distributions, using shape factor 1.75.

The microstructures of the raw fly ash samples were examined with a Phenom ProX EDX scanning electron microscope (SEM).

The structure of the geopolymer products was investigated with a JASCO FT-IR 4200 type Fourier Transformed Infrared Spectrometer, equipped with a single-reflection diamond crystal.

RESULTS AND DISCUSSION

For the B-FA geopolymer specimens 75 wt.% Betol SB type water glass (25.3% SiO₂; 13.7% Na₂O; 2.7% K₂O) and 25 wt.% NaOH in 8M concentration was used as activator solution. The liquid-solid ratio of the geopolymers was 0.82. After moulding and a 24-hour holding time, the geopolymers were cured at 50 °C for 6 h, then the specimens were left to cool down. The uniaxial compressive strength tests were carried out after a five-day holding time. The effect of grinding time on the average uniaxial compressive strength and specimen density of landfilled B-FA geopolymers can be observed in Figure 1.

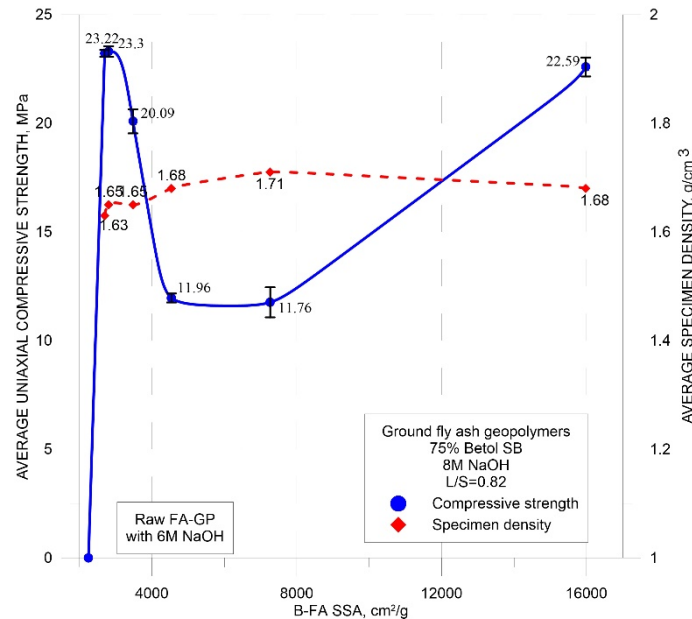


Figure 1 The average compressive strength and specimen density values of B-FA geopolymers.

Milling has been proven to be an appropriate process not only to modify the specific surface area and improve the reactivity of fly ash, but to drastically increase the mechanical strength of the resulted geopolymers as well [8, 10]. However, it has also been observed that the deposited fly ash has an optimal grinding time that can be observed as a maximum point in the compressive strength curve. After reaching the optimum, the compressive strength of the produced geopolymers starts to decrease with a close to linear trend. The occurrence of such decline might be due to the binding strength between the particles being higher than the strength of the particles itself [18]. The initial lack of reactivity is presumably due to the changes in the crystalline structure of fly ash (deamorphisation) during its stay in the deposit, but as it can be observed in Figure 1, the uniaxial compressive strength of the specimens could be improved with grinding the B-FA for 5 and 10 minutes. However, between 20-60 min grinding time, the mechanical activation had a negative effect on the compressive strength, which was reduced by more than half after 30- and 60-min grinding. Then, further mechanical activation had a positive effect on the compressive strength, reaching similar values achieved with shorter grinding time.

The decrease of specimen density can be a potential reason for the decrease of compressive strength [14, 16]. However, as no significant deviation can be observed in the specimen density values between 10-60 minutes grinding (Figure 1), the decreasing compressive strength is not related to changes in the compactness of the specimens.

To reveal the possible cause of the considerable drop in the mechanical properties of geopolymers, first, specimens prepared from B-FA ground for 5, 30 and 120 minutes were used for FT-IR analysis. The obtained spectra can be seen in Figure 2.

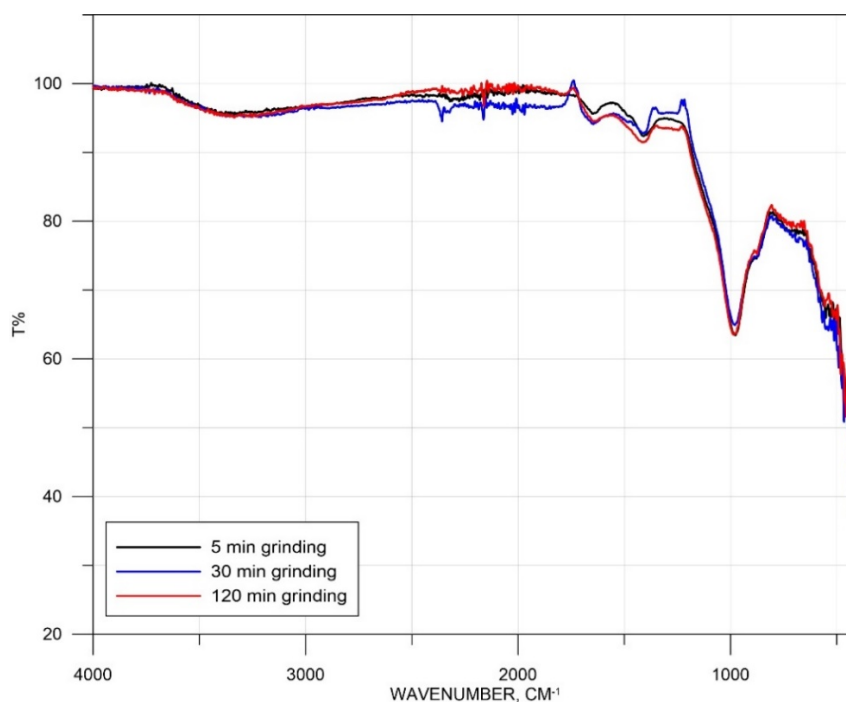


Figure 2 The FT-IR spectra of the B-FA geopolymers with 5-, 30- and 120-minute grinding.

The stretching vibrations of -OH and HOH between are represented by a broad band, centred at $\sim 3400\text{ cm}^{-1}$ and the bending vibrations between 1650 and 1630 cm^{-1} . These bands are attributed to the absorbed water on the surface and the water in the cavities. The peaks around 1400 cm^{-1} indicate the stretching vibrations of the O-C-O bond due to atmospheric carbonation. The sharp peak around 990 cm^{-1} is the result of the asymmetric stretching vibrations of Si-O-Si and Si-O-Al bonds, which is the indication of the geopolymerisation reaction [8, 19, 20]. The analysis revealed that no significant deviation can be found in case of the main peaks related to the geopolymerisation process.

Experiments with fresh L-FA showed similar results that can be found in literature: the higher the milling time of fly ash is, the higher the mechanical properties of geopolymers will be [19, 20]. The L-FA geopolymer specimens were prepared with 6 M concentration NaOH solution as alkaline activator, with 0.67 L/S ratio. The comparison of the effect of grinding of landfilled and fresh FA geopolymers on their compressive strength is illustrated in Figure 3. In contrast to the B-FA samples, a clearly increasing trend can be observed in the compressive strength of the L-FA specimens as longer grinding time was used for the preparation of fly ash.

The morphology of the base materials was investigated to reveal possible differences in the used base materials. The SEM images of the raw fly ashes can be observed in Figure 4.

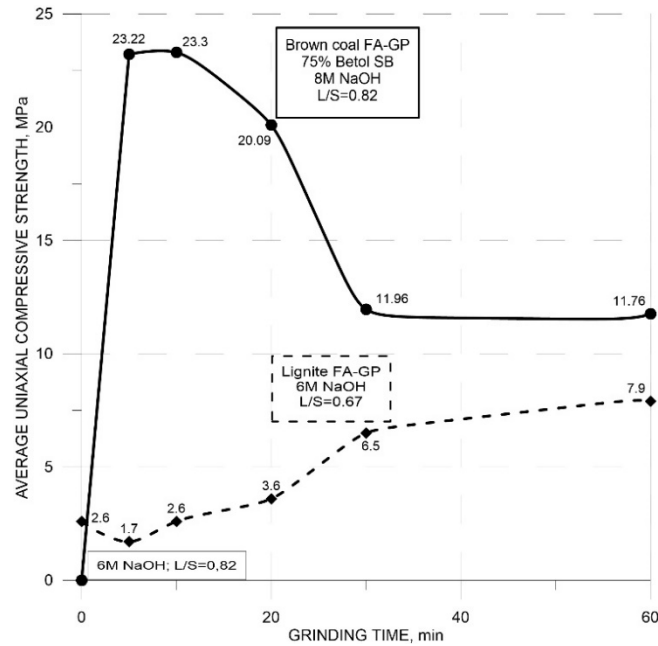


Figure 3 The average compressive strength of ground B-FA and L-FA geopolymers.

The SEM images with 310-320x magnification (Figure 4 a and d) show mostly irregular shaped particles, both B-FA and L-FA samples containing a low amount of spherical cenospheres. Similar, irregular shaped agglomerates could be found in both samples at higher magnification (Figure 4 b and e), and the spherical particles only appeared at approximately $<10\ \mu\text{m}$ size (Figure 4 c and f). The porosity of the particles could also be observed, especially in case of the L-FA sample.

The particle size distributions of the fly ashes after mechanical activation (Figure 5) clearly demonstrate the decrease in particle size as the grinding time became longer. In case of the B-FA sample with 120 min grinding, increased number of fine particles can be observed, which may have contributed to the high compressive strength observed in Figure 1.

The characteristic particle sizes and the calculated specific surface area values are summarised in Table 2. It can be seen, that the x_{50} of B-FA were lower at all but one examined sample and the x_{80} values were lower in every sample. The SSA of both fly ashes continuously increased with the longer milling time. The SSA of B-FA were higher than the L-FA values until reaching 30 minutes. Then the SSA of L-FA nearly tripled from $3375.57\ \text{cm}^2/\text{g}$ at 30 min to $9494.71\ \text{cm}^2/\text{g}$ at 60 min.

CONCLUSIONS

The effect of mechanical activation of deposited brown coal fly ash in a ball mill was examined. As the compressive strength results were different from the literature data, the structure of the geopolymers was examined and the base material was compared to a previously successfully utilised lignite type fly ash. Based on the FT-IR, XRF, particle size, specific surface area, and SEM test, no clear reason for the compressive strength decrease can be stated. Thus, further examinations should be carried out to reveal the reason for the behaviour of the specimens using X-ray Diffractometry (XRD) of the fly ash as well as the resulted geopolymers.

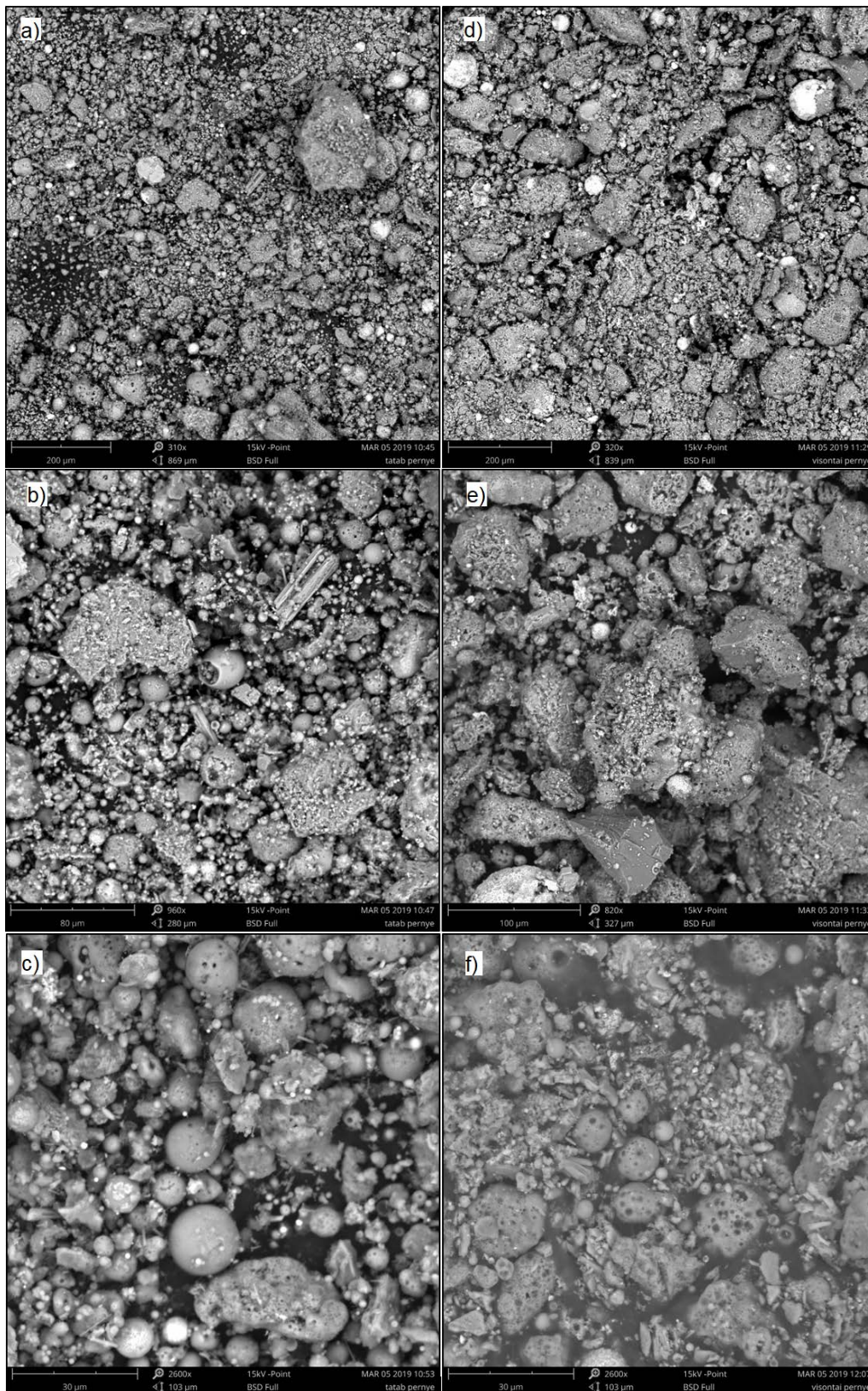


Figure 4 The SEM images of raw B-FA with M=310x (a), M=960x (b), and M=2600x (c) and raw L-FA with M=320x (d), M=820x (e) and M=2600x (f).

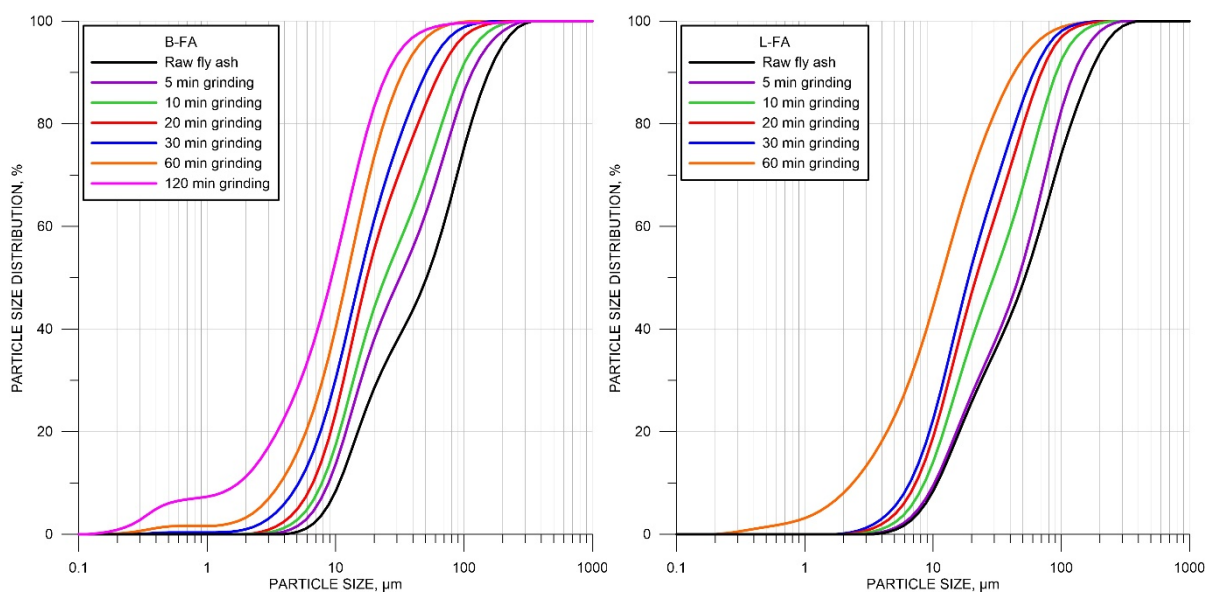


Figure 5 The particle size distribution of B-FA (left) and L-FA (right).

Table 2 The characteristic particle size and SSA values of the FA samples.

	B-FA			L-FA		
Grinding time, min	x ₅₀ , μm	x ₈₀ , μm	SSA, cm ² /g	x ₅₀ , μm	x ₈₀ , μm	SSA, cm ² /g
0	51.12	113.35	2246.72	52.04	119.32	2016.12
5	31.62	82.78	2693.65	43.82	91.72	2133.77
10	24.28	67.17	2805.6	29.84	69.67	2625.51
20	17.50	43.82	3475.73	21.29	49.09	3042.25
30	15.40	34.58	4540.29	18.94	43.58	3375.57
60	12.21	23.66	7263.95	11.60	27.09	9494.71
120	9.29	18.26	15981.23	-	-	-

ACKNOWLEDGEMENTS

The described work/article was carried out as part of the „Sustainable Raw Material Management Thematic Network – RING 2017”, EFOP-3.6.2-16-2017-00010 project in the framework of the Széchenyi 2020 Program. The realization of this project is supported by the European Union, co-financed by the European Social Fund.

The authors are grateful for Nóra Pappné Halyag for the SEM and Ferenc Móricz for the XRF analysis.

REFERENCES

1. UN GENERAL ASSEMBLY. Report of the United Nations Conference on Environment and Development, 3-14 June 1992, A/CONF.151/26 (Vol. I). Available at: <https://www.un.org/documents/ga/conf151/aconf15126-1annex1.htm> [accessed 21 February 2019].
2. UN GENERAL ASSEMBLY. Transforming our world: the 2030 Agenda for Sustainable Development, 21 October 2015, A/RES/70/1, pp 22-23. Available at: <https://www.refworld.org/docid/57b6e3e44.html> [accessed 18 February 2019].
3. EUROSTAT. Gross electricity production by fuel, GWh, EU-28, 2000-2016. Available at: https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Electricity_and_heat_statistics [accessed 09 March 2019]
4. THE WORLD BANK GROUP. Electricity production from coal sources (% of total). Available at: <https://data.worldbank.org/indicator/EG.ELC.COAL.ZS?locations=IN-CN&view=chart> [accessed 02 March 2019]
5. UN Environment. Emissions Gap Report 2018. Available at: http://wedocs.unep.org/bitstream/handle/20.500.11822/26895/EGR2018_FullReport_EN.pdf [accessed 06 March 2019]
6. MILLWARD-HOPKINS, J, BUSCH, J, PURNELL, P, ZWIMER, O, VELIS, C A, BROWN, A, HAHADAKIS, J, IACOVIDU, E. Fully integrated modelling for sustainability assessment of resource recovery from waste, *Science of the Total Environment*, Vol. 612, 2018, pp 613–624.
7. DAVIDOVITS, J. Geopolymers: Inorganic polymeric new materials, *Journal of Thermal Analysis*, Vol 37., 1991, pp. 1633-1656.
8. KUMAR, S, KUMAR, R. Mechanical activation of fly ash: Effect on reaction, structure and properties of resulting geopolymer, *Ceramics International*, Vol. 37, 2011, pp 533–541.
9. KUMAR, S, KUMAR, R, ALEX, T C, BANDOPADHYAY, A, MEHROTRA, S P. Influence of reactivity of fly ash on geopolymerisation, *Adv. Appl. Ceram.*, Vol. 106, 2007, pp 120–127.
10. TEMUJIN, J, WILLIAMS, R P, VAN RIESSEN, A. Effect of mechanical activation of fly ash on the properties of geopolymer cured at ambient temperature, *J. Mater. Process. Technol.*, Vol. 209, 2009, pp 5276–5280.
11. RYU, G S, LEE, Y B, KOH, K T, CHUNG, Y S. The mechanical properties of fly ash-based geopolymer concrete with alkaline activators, *Construction and Building Materials*, Vol. 47, 2013, pp. 409–418.
12. KUSNIEROVÁ, M, SLESÁROVÁ, A, PRASCÁKOVÁ, M. The significance of fly ash for their processing and utilization. In. *Proc. Waste Recycling – IX*. Krakow, 17-19. November 2005.
13. YEHEYIS, M B, SHANG, J Q, YANFUL, E K. Chemical and Mineralogical Transformations of Coal Fly Ash after Landfilling, presentation, World of Coal Ash Conference (WOCA), May 4-7, 2009. Lexington, Kentucky, USA

14. MUCSI, G, GOMBKÖTŐ, I, MOLNÁR, Z, OSVÁTH, I, KUMAR, S. Effect of mechanical activation of fly ash on geopolymer properties, IMPC 2016: XXVIII International Mineral Processing Congress Proceedings, Eds. J Finch, C O'Connor, D Leroux, N Stubina and G Poling 2016, pp. 1-9.
15. MUCSI, G., KUMAR, S., CSŐKE, B., KUMAR, R., MOLNÁR, Z., RÁCZ, Á., MÁDAI F., DEBRECZENI, Á. Control of geopolymer properties by grinding of land filled fly ash. International Journal of Mineral Processing, Vol. 143, 2009, pp. 50 –58.
16. MOLNÁR, Z, KRISTÁLY, F, MUCSI, G. Mechanical activation of deposited brown coal fly ash in stirred media mill, Acta Physica Polonica A, Vol. 126, No. 4, 2014, pp. 988-993.
17. SZABÓ, R, GOMBKÖTŐ, I, SVÉDA, M, MUCSI, G. Effect of grinding fineness of fly ash on the properties of geopolymer foam, Arch. Metall. Mater, Vol. 62, No. 2B, 2017, pp. 1257-1231.
18. MUCSI, G, CSŐKE, B. Power Plant Fly Ash as a Valuable Raw Material, Geosciences and Engineering, Vol. 1, No. 1, 2012, 223-236.
19. HAMDİ, N, MESSAOUD, B I, SRASRA, E. Production of geopolymer binders using clay minerals and industrial wastes. Comptes Rendus Chimie. 2018. doi:10.1016/j.crci.2018.11.010
20. YASERI, S, HAJIAGHAEI, G, MOHAMMADI, F, MAHDIKHANI, M, FAROKHZAD, R. The role of synthesis parameters on the workability, setting and strength properties of binary binder based geopolymer paste, Construction and Building Materials, 157, 2017, pp 534–545.