 doi:10.20944/preprints202106.0394.v1

Communications

X-ray Diffraction of Alkali-Activated Materials with CBPD

Barbara Vojvodíková[1,*], Lukáš Procházka[1] and Jana Boháčová[1]

[1] Faculty of Civil Engineering, Technical University of Ostrava, L. Podeste 1875, Ostrava - Poruba Czech Republic;
* Correspondence: barbara.vojvodikova@vsb.cz

Abstract: Alkali-activated materials are alternative building binders, where secondary raw materials are processed. Possibility to use landfilled waste materials in their preparation, increases their potential application in construction practice, and therefore they are subject to extensive research, especially in recent years. This paper briefly summarizes interesting results of an experiment aimed at verifying the possibility of applying cement by-pass dust (CBPD) in the preparation of alkali-activated materials. The research work was focused on the possibilities of using these wastes for the preparation of small elements of garden architecture. The paper briefly evaluates in particular the results of X-ray diffraction, which were subjected to three types of binder pastes differing in the amount of used activator. In the experiment, a mixture of blast furnace granulated slag, fly ash and cement by-pass dust was alkali activated with sodium metasilicate.

Keywords: Cement By-Pass Dust; Blast Furnace Granulated Slag; Silica Fly Ash; Alkali-Activated Materials.

1. Introduction

In the current construction industry, Portland cement and materials based on it still play a major role in the field of binders. [1, 2] However, due to the limited reserves of limestone as well as suitable aggregates, there are already concerns about the long-term development and possibilities of using the raw materials needed for its production. Therefore, many producers of concrete are already looking for alternative binder systems that could replace Portland cement-based materials, or that Portland cement could be used at minimum. Thus, various hybrid cements, ternary binders, alkali-activated systems and others are slowly beginning to be used. [3, 4, 5]

In these alternative binders, the cement is partially or completely replaced by other binders. Hybrid cements are a type of binder that combines the use of small amounts of Portland cement, mineral admixtures and alkaline activation. [3] Ternary binders are materials based on gypsum binder with pozzolan and exciter (calcium hydroxide, Portland cement). [6, 7] Alkaline activated systems are based on alkaline activation of latently hydraulic or pozzolanic materials. In the preparation of these materials, secondary raw materials are used, most often fly ashes and slags. [4, 5, 8]

In the preparation of alkali-activated materials, probably the best required properties are achieved in systems based on alkali-activated blast furnace finely ground granular slag. However, as this is widely used in blast furnace cements, this formerly waste raw material is now becoming scarce. [9, 10] The effort of many research works is therefore the partial replacement of slag by other raw materials of a waste nature. A partial replacement of the fly ash seems possible. [11, 12, 13] At present, the application of fly ash is focused on fly ash after denitrification. Requirements for nitrogen reduction lead to the introduction of denitrification methods. [14] Denitrification processes causes the nitrogen compounds to remain bound in the fly ash in various forms. This phenomenon has a positive effect on the air, but in the field of the application of fly ash to building materials, it brings new research topics, as this modification also changes some properties of the original material. [15, 16]

Another potential additive usable in alkali activated systems is a cement by-pass dust (CBPD). It is a fine material arising in various stages of cement production. These fine particles are trapped so that they do not escape into the air and do not burden the environment. Installing a by-pass causes, that the kiln gases are sucked out and, with rapid cooling, undesired gases condense on the surface of the dust particles. It is therefore a question of how to use these trapped particles, given their diverse composition and properties. One of possible application that is widely tested is in alkali activated systems. [17-23]

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 June 2021 doi:10.20944/preprints202106.0394.v1

2. Materials and Methods

2.1. Blast-furnace granulated slag (BFS)

For the experiment, finely ground granulated blast furnace slag was used. This slag has latent hydraulic properties and a surface area of 400 m^2/kg. [24] The percentages of individual oxides obtained by a fluorescence spectrometer measurement are shown in Table 1. Mineralogical composition of BFS in Figure 1 shows that Akermanite, Merwinite and Calcit are present in this slag. [25]

Table 1. Content of selected oxides in input raw materials.

Oxide	Content [%]		
	FAD	BFS	CBPD
SiO_2	50.89	33.81	5.32
Al_2O_3	21,34	8.14	1.46
Fe_2O_3	9.49	0.32	1.22
CaO	4.48	46.16	34.08
SO_3	0.58	1.46	5.16
K_2O	3.14	0.42	18.62
MgO	1,67	7.86	0.48
LOI	6.27	0.00	21.90

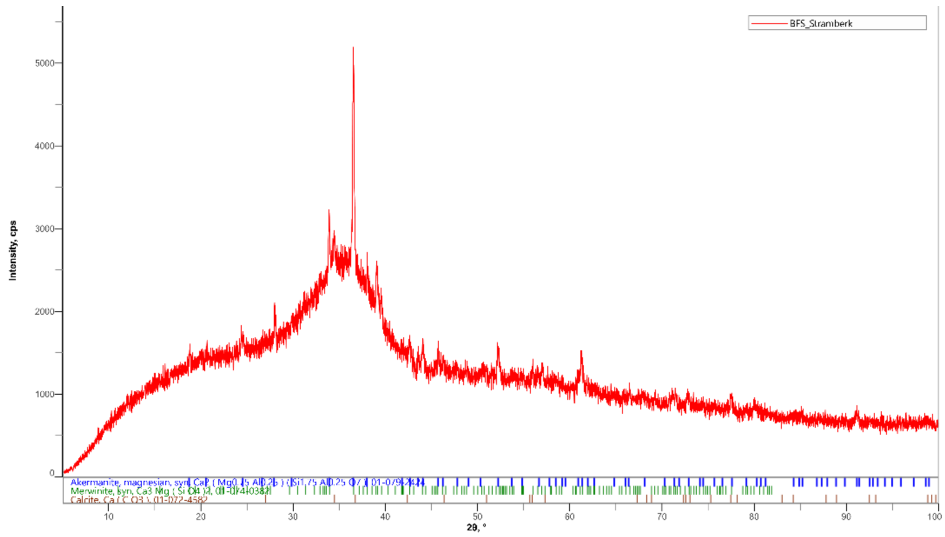

Figure 1. Mineralogical composition of BFS determined by X-ray diffraction (XRD).

2.2. Silica fly ash (FA)

In the experiment, a siliceous fly ash after denitrification by the SNCR method and ground fly ash with the surface area of 500 m^2/kg was used. This fly ash is produced by the power plant in Ostrava-Třebovice. The content of ammonia released from the aqueous extract is 22.8 mg/kg. The chemical composition is shown in Table 1. The mineralogical composition of the fly ash was determined by X-ray diffraction. SiO2 is present in the fly ash in the form of α-quartz (Figure 2). Other minerals represented in this fly ash include Mulite, Magnetite, free lime and Hematite. The content of the soluble amorphous phase determined by cooking in a 4 M solution of potassium hydroxide was only 4.17%, so it can be assessed that it is a low reactive fly ash. [25, 26]

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 June 2021 doi:10.20944/preprints202106.0394.v1

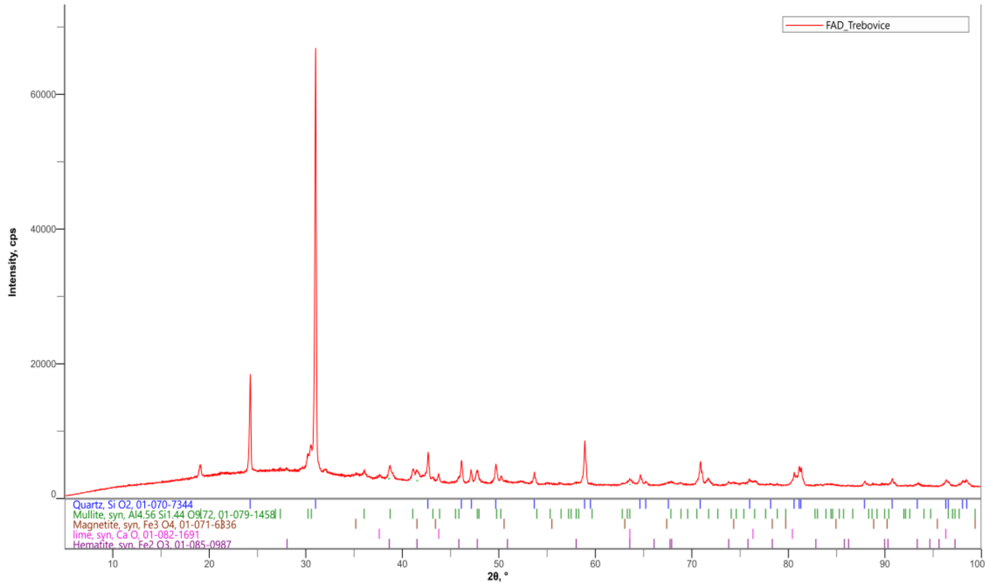

Figure 2. Mineralogical composition of fly ash determined by X-ray diffraction (XRD).

2.3. Cement by-pass dust (CBPD)

Cement by-pass dust from the cement plant in Horné Srnie was utilized in the experiment. The percentages of individual oxides obtained by a fluorescence spectrometer measurement are shown in Table 1. The chlorine content in CBPD is 10.49%. The phase composition of CBPD is given in Figure 3 and Table 2. The LOI is 21.9% for CBPD.

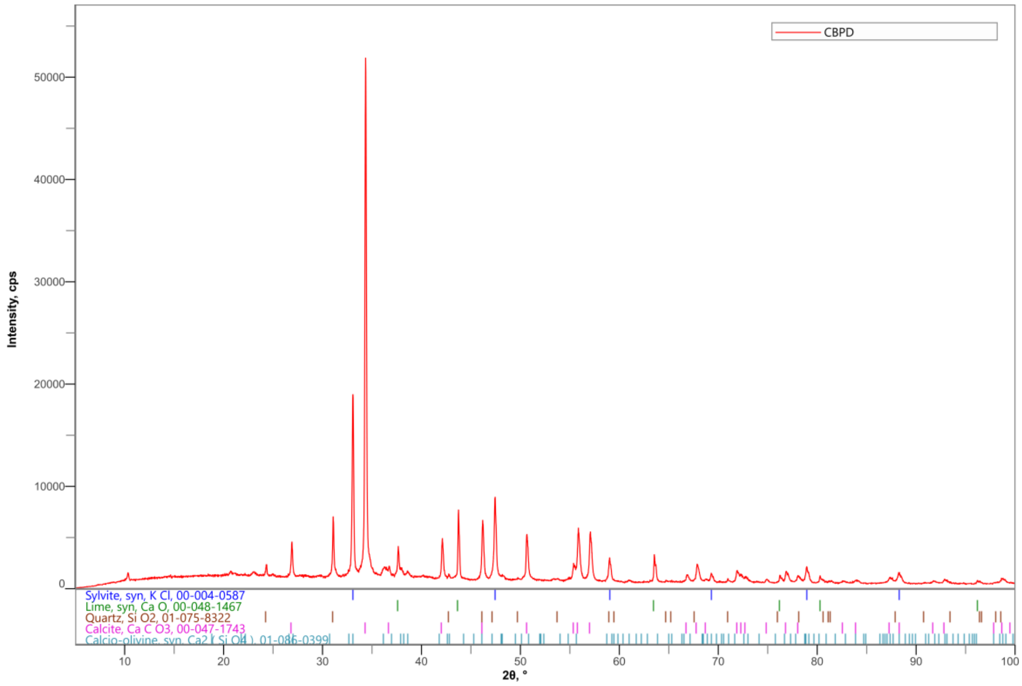

Figure 3. Mineralogical composition of CBPD determined by X-ray diffraction (XRD).

Table 2. Cement by-pass dust composition (in wt. %) measured by XRD.

Participant	Content [%]
Sylvite	21.9
Free CaO	22.4
Portlandite	15.0
Arcanite	14.4
Quartz	4.02
Larnite/Belite	19.2
Alunite	–
Hatrurite/Alite	–
Ferrite	–
Mayenite	–
Calcite	1.36
Dolomite	1.67

2.4. Activator - Anhydrous disodium metasilicate (A)

Anhydrous disodium metasilicate (MSS) contains min. 44% SiO_2 it is produced by Penta Chemicals. [27] This activator has a silicate modulus of 1. The basic chemical properties are given in Table 3.

Table 3. Composition of anhydrous disodium metasilicate [27].

A	MJ	Value
SiO_2 content	%	min. 44
pH	-	12.5
Molar weight	kg/mol	122.06
Relative density	g/cm³	2.6

2.5. Standardized sand

Standard sand CEN, ČSN EN 196-1 was used as a filler in the experiment. It is a natural quartz sand, which is formed by rounded particles and the silica content is min. 98%, 0/2 mm fraction and less than 0.2% moisture content [28].

2.6. Mixture preparation

As a basic mixture, previously verified and tested mixture from the previous works was used [29, 30]. This basic mixture was then in experimental work modified, cement by-pass dust and fly ash were added. These mixtures were then tested, physical-mechanical properties were verified. For REC 1, the amount of activator was calculated from the total binder amount. For REC 2, the dose was reduced by 15% and for REC 3, the dose was reduced by 30%. The composition of the mixtures is shown in Table 4. The pH of the solution prepared by dissolving anhydrous disodium metasilicate in water ranged from 13.95 to 14.00 for all monitored mixtures.

Table 4. Reception of the raw material values is given in [g].

Mixture	BFS	FA	CBPD	A	W	Sand
REC 1	315	67.5	67.5	89.00	215	1350
REC 2	315	67.5	67.5	75.65	215	1350
REC 3	315	67.5	67.5	62.30	215	1350

2.7. X-ray diffraction

X-ray diffraction was performed on a Rigaku MinyFlex instrument in the range of 5 - 100° 2theta at a speed of 3°/min. X-ray diffraction was determined on pastes. The ratio between the binder components and the activator remained the same according to the Table. 4. Only the water coefficient has changed to 0.42.

2.8. Strength

To determine the basic strengths, the specimens were stored in a humidity cabinet until testing. The strengths were determined with a hydraulic press. The determination of the flexural strength was carried out by uniform loading at speeds of (50 ± 10) N/s. The compressive strength was determined by uniform loading at a rate of (2400 ± 200) N/s. [28].

3. Results

The X-ray diffraction results on alkali-activated pastes are shown in Figure 2.

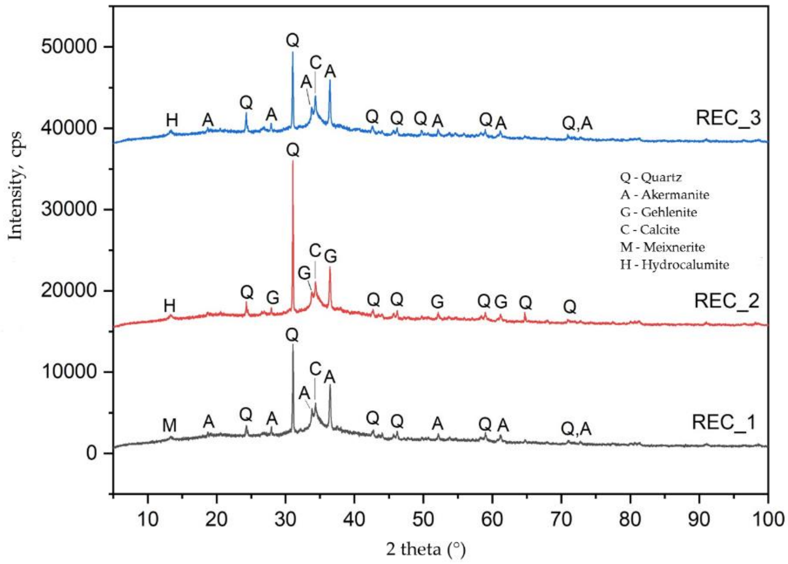

Figure 2. Mineralogical composition determined by X-ray diffraction (XRD) of prepared alkali activated pastes.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 June 2021 doi:10.20944/preprints202106.0394.v1

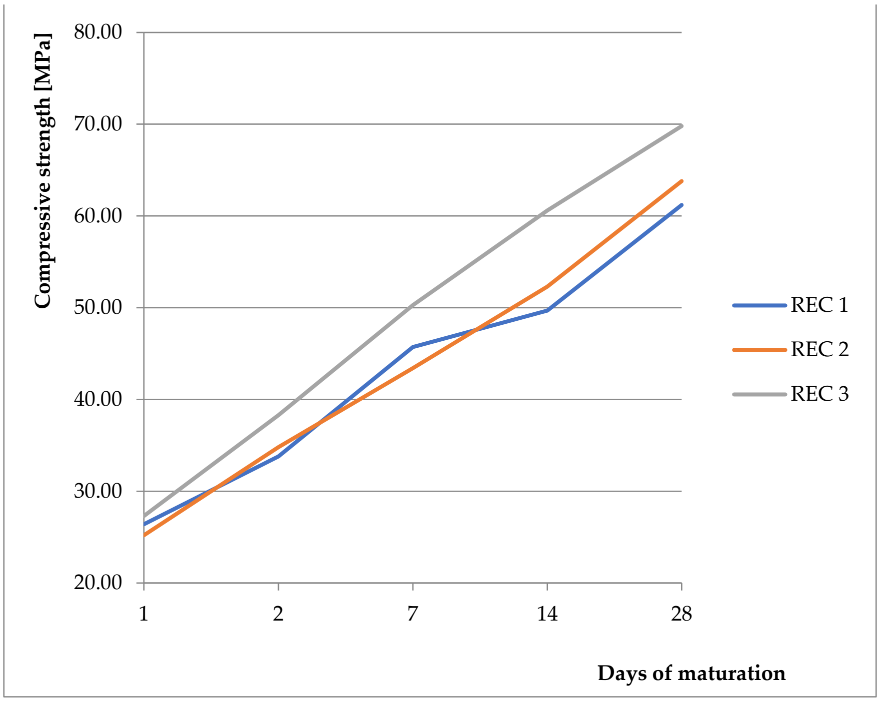

Figure 3. Compressive strength of prepared mixtures.

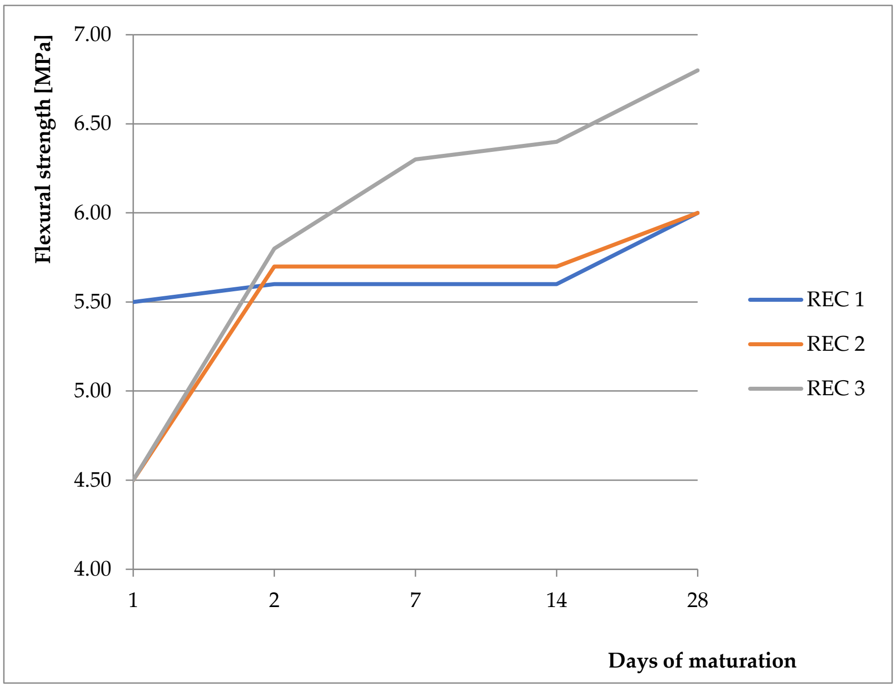

Figure 3. Flexural strength of prepared mixtures.

4. Discussion

According to [31] choosing a suitable type of activator according to the slag properties before starting the experiment is important. Most often, the slag is activated by sodium and potassium water glasses. These are often treated with hydroxide solutions so that the silicate modulus of the water glass is reduced and the workability of the prepared composite is extended. However, one of the most common complaints preventing wider use of alkali-activated systems in construction is the concern that the handling of these liquid strong alkalies is dangerous due to the low professionalism of construction personnel and it is an attempt to avoid handling these substances on the construction site. Therefore, the research work of the team included efforts to use a solid activator in the form of sodium metasilicate. This material has a silicate modulus value of 1, so in terms of workability [31, 32] it is an ideal activator, because previous research has shown that the optimal value of silicate modulus is in the range of 1-2, with increasing value significantly decreases workability time. [29, 30]

One of the essential steps in alkali activation is to determine the optimal amount of activator required for alkali activation of slag, i.e. to introduce an adequate amount of Na_2O into the system. The amount of Na_2O in the case of slag is generally chosen in the range of 2-8% by weight, depending on the chemism of the slag. The properties of the composite together with the amount of Na_2O are also affected by the silicate modulus. According to [32] in the case of low values of the introduced Na_2O, it results in lower strength; In the case of the performed experiments, a basic value of 4.2 wt.% Na_2O, per 100 g of slag was chosen. This value was determined on the basis of the composition of the blast furnace granulated slag as an optimum. This value was subsequently reduced by 15, resp. 30%.

The most interesting results achieved are the following. When the value of the amount of activator decreases by 30%, strengths increase, although the opposite trend was expected. The X-ray diffraction results indicate, that the alkali-activation products of the composite with the original and reduced amounts of activator are very similar, although it was expected that the resulting hydration products would be different due to the reduced amount of activator. It is also interesting that gehlenite (Ca_2Al $[(Si_2O_7])$ was detected by the diffraction in the mixture with the amount of activator reduced by 15%, while akermanite ($Ca_2Mg[(SiAl)O_7]$) was detected in two other mixtures (Rec 1 and Rec3). These minerals belong to the group of melilite, they are similar and are commonly found in alkali-activated materials, as they are the basic minerals of blast furnace slags. It is interesting that in the case of akermanite, it is clear that the mixtures Rec1 and Rec3 contained in a certain amount of magnesium compound, whereas in the mixture Rec2 with gehlenite, magnesium was not present in the system.

The occurrence of quartz is also interesting, it can be assumed that it was contained in the fly ash. Rec1 and Rec3 also contained Hydrocalumite $Ca_2Al(OH)_{6.5}Cl_{0.5}\bullet 3(H_2O)$, which contains chlorine in its structure, can be assumed to have occurred in cement by pass dust. Other differences between samples include that the Rec 1 samples showed Meixnerite and Sylvite minerals, which were included in CPBD.

5. Conclusion

In the next phase of the experiment, X-ray diffraction of individual parts of the alkali-activated system will be performed separately and the individual components of the composite will be monitored. This is necessary in order to determine how and how significantly the fly ash and cement by-pass dust are involved in the formation of hydration processes, or whether they are less reactive and only replace the fine fractions of the aggregate in the composite. The properties of the precipitated efflorescences which form on the surface of the prepared bodies will also be determined and it will be verified whether they are sodium salts, which would indicate possible excess of alkalis in the system. However, these may also be precipitated efflorescences of potassium salts, which are abundant in cement by-pass dust. If the type of alkaline element affects the kinetics of the alkaline activation process differently and different hydration products are formed depending on it **[33]**, it will be necessary to deal in detail with the composition of the individual components of the binder. This can be problematic due to the slightly changing composition of cement by-pass dusts.

Acknowledgments: This research was supported by the project GeoDust (Utilization of secondary raw materials in geopolymers production) which has received funding from the MSCA-RISE -

Marie Skłodowska-Curie Research and Innovation Staff Exchange (RISE) H2020-MSCA-RISE-2016 grant agreement no. 7348336. The authors would like to thank the Department of Thermal Engineering from VŠB - Technical University of Ostrava for performing XRD and XRF analyzes.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Chen, C. et al. Environmental impact of cement production: detail of the different processes and cement plant variability evaluation. *Journal of Cleaner Production* **2010**, 18(5), pp. 478–485. http://dx.doi.org/10.1016/j.jclepro.2009.12.014.
2. Altwair N., Kabir S. Reducing Environmental Impacts through Green Concrete Technology. *Conference: The 3rd Technology and Innovation for Sustainable Development International Conference (TISD2010)* **2010**, Faculty of Engineering.At: Khon Kaen University
3. Bílek V, Khestl F, Mec P. Hybrid Cements with Non Silicate Activators. SSP **2017**;259:30–4. https://doi.org/10.4028/www.scientific.net/ssp.259.30.
4. Van Deventer, J.S.J., Provis, J.L., Duxson, P., **2012**. Technical and commercial progress in the adoption of geopolymer cement. *Minerals Engineering*, 29, pp. 89–104. http://dx.doi.org/10.1016/j.mineng.2011.09.009
5. Provis J.L. Alkali-activated materials, Cement and Concrete Research;114;**2018**;40-48; https://doi.org/10.1016/j.cemconres.2017.02.009.
6. Bílek V, Pytlík D, Bambuchova M. High Performance Concrete with Ternary Binders. KEM **2018**;761:120–3. https://doi.org/10.4028/www.scientific.net/kem.761.120
7. Dyer, T.D., Halliday, J.E., Dhir, R.K. An investigation of the hydration chemistry of ternary blends containing cement kiln dust. *Journal of Materials Science 34* **1999**, pp. 4975–4983. https://doi.org/10.1023/A:1004715806829.
8. Provis J.L., Deventer J.S.J. *Geololymers, Structure, Processing, Properties and Industrial Applications*, Woodhead Publishing Limited **2009** , ISBN 978-1-84569-449-4.
9. Boháčová, J. Study of influence of different types of fillers on properties of geopolymer systems based on alkali activated slags, VŠB – TUO, **2008**.
10. Kumar, S., Kumar, R. ,Mehrotra, S.P. Influence of granulated blast furnace slag on the reaction, structure and properties of fly ash based geopolymer. *Journal of Materials Science* **2010**, 45(3), pp. 607–615. http://dx.doi.org/10.1007/s10853-009-3934-5.
11. Li ZX, Tang JW. The Appropriate Chemical Admixture for Alkali-Activated Cementitious Material. AMR **2012**;534:34–41. https://doi.org/10.4028/www.scientific.net/amr.534.34.
12. Chen K, Yang CH, Wu F, Ye JX, Pan Q, Yu ZD. Development of Alkali Activated Slag Cement Based Ecomaterial and its Environmental Coordination Evaluation. MSF **2009**;610–613:179–84. https://doi.org/10.4028/www.scientific.net/msf.610-613.179.
13. Chi MC, Chen H, Weng TL, Huang R, Wang YC. Durability of Alkali-Activated Fly Ash/Slag Concrete. MSF **2017**;904:157–61. https://doi.org/10.4028/www.scientific.net/msf.904.157.
14. Li Z, Liu XM, Yang DH, Qin WJ, Yang GS, Zhang DL. Research of the SNCR Process and its Application. AMR **2014**;953–954:1307–14. https://doi.org/10.4028/www.scientific.net/amr.953-954.1307.
15. Procházka L, Boháčová J. Verification of Durability Properties of Alkali-Activated Materials Based on Blast Furnace Slag with Fly Ash. SSP **2020**;309:93–7. https://doi.org/10.4028/www.scientific.net/ssp.309.93.
16. Procházka L, Mec P. Possibility of using fly ash after denitrification by SNCR as admixture in alkali-activated materials, Materials Today: Proceedings; 37;1;**2021**;42-47;https://doi.org/10.1016/j.matpr.2020.04.594.

17. Štěpánková E, Kalina L, Bílek Jr. V, Bartoníčková E. Utilization of By-Pass Cement Kiln Dust in Alkali-Activated Materials. KEM **2018**;761:23–6. https://doi.org/10.4028/www.scientific.net/kem.761.23.

18. Tkaczevska, E. The influence of cement bypass dust on the properties of cement curing under normal and autoclave conditions. *Structure and Environment* **2019**, 11(1), pp.5–22. : http://dx.doi.org/10.30540/sae-2019-001.

19. Ahmari, S., Zhang, L. Utilization of cement kiln dust (CKD) to enhance mine tailings-based geopolymer bricks. *Construction and Building Materials* **2013**, 40, pp. 1002–1011. http://dx.doi.org/10.1016/j.conbuildmat.2012.11.069.

20. Štěpánková E, Kalina L, Bílek Jr. V, Bartoníčková E. Utilization of By-Pass Cement Kiln Dust in Alkali-Activated Materials. KEM **2018**;761:23–6. https://doi.org/10.4028/www.scientific.net/kem.761.23.

21. Kubátová D, Rybová A, Zezulová A. The Hydrothermal Stability of Alkali-Activated Fly Ash/Slag Pastes by the Incorporation of Cement Kiln Dust. SSP **2019**;296:15–20. https://doi.org/10.4028/www.scientific.net/ssp.296.15.

22. Sikorová, V. Methods of using cement kiln by-pass dust in building materials technology. Brno **2019**, Thesis.

23. Adaska, P.E., W.S., Taubert, D.H. Beneficial Uses of Cement Kiln Dust. *2008 IEEE Cement Industry Technical Conference Record* **2008**. http://dx.doi.org/10.1109/citcon.2008.24.

24. Kotouč Štramberk, **2020** https://www.cemix.cz/kotouc/cz

25. Ismail, I. et al. Microstructural changes in alkali activated fly ash/slag geopolymers with sulfate exposure. Materials and Structures **2012**, 46(3), pp.361–373. http://dx.doi.org/10.1617/s11527-012-9906-2

26. Procházka, L.; Boháčová, J. Effect of Admixtures on Durability Characteristics of Fly Ash Alkali-activated Material. *Emerging Science Journal* **2020**, 4(6), 493–502. doi:10.28991/esj-2020-01247

27. Penta chemical unlinited – chemikalie **2020** https://www.pentachemicals.eu/chemikalie

28. ČSN EN 196-1 Methods of testing cement – Part 1: Determination of strength.

29. Koňařík J. Influence of activator on basic properties of alkali activated systems, VŠB – TUO, **2014**.

30. Mec, P., Boháčová, J., Závrský, P. Testing of Possible Use of Fine-Grained Alkali Activated Composites in the Construction Industry. *Materials Science Forum* **2016**, 865, pp.47–52. : http://dx.doi.org/10.4028/www.scientific.net/msf.865.47

31. Serdar A, Bülent B. Effect of activator type and content on properties of alkali-activated slag mortars,Composites Part B: Engineering;57;2014;166-172;https://doi.org/10.1016/j.compositesb.2013.10.001

32. Amer I, Kohail M, El-Feky M.S., Rashad A, Khalaf M.A. A review on alkali-activated slag concrete, Ain Shams Engineering Journal;2021;https://doi.org/10.1016/j.asej.2020.12.003

33. Fernández-Jiménez, A., Palomo, A., & Criado, M. (2006). Alkali activated fly ash binders. A comparative study between sodium and potassium activators. Materiales De Construcción, 56(281), 51–65. https://doi.org/10.3989/mc.2006.v56.i281.92