Study on mechanical properties of alkali-activated material before and after mechanical activation

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Slag is one of the by-products of energy industry which is suitable for secondary industrial processing. Although slag has been successfully used in industrial production for several decades, its use does not achieve the level of its potential. Slag can be used as alkali-activated materials and utilised in the synthesis of geopolymers. Geopolymers are inorganic polymeric materials with three-dimensional SiOAl frameworks synthesised from aluminosilicates which dissolved in the alkaline medium. This work describes the improvement of mechanical properties of alkali-activated binders – geopolymers made of slag. The effect of mechanical activation on mechanical properties of geopolymers was examined. Mechanical activation was made with a ball mill and different time of milling. Synthesis of geopolymers was carried out in drier at 80°C. Samples were made before and after mechanical activation. The differences in strengths of samples were examined. Mechanical properties such as compressive and flexural strength that was measured were the most significant attributes. Samples were tested after 7, 28 and 90 days. Results show that the mechanical activation is an important factor in the synthesis of slag based geopolymers, which has better properties after mechanical activation.

Key words: *slag, mechanical properties, geopolymers, strength, water absorption, mechanical activation*

Introduction

Ground granulated blast-furnace slag (GGBFS) is a coproduct of the steel industry by adding limestone to ore to remove non-ferrous contaminants, and it consists of four major chemical components: CaO, SiO_2, Al_2O_3 and MgO (Snellings et al., 2012; Zawrah et al., 2016). As one of the main by-products during the process of iron and steel making, blast furnace slag is discharged in a super-high temperature of 1450–1650 °C. (Wang et al., 2015).These components are highly reactive with alkaline solutions to form alkali-activated GGBS (Arai et al., 2017). Blast furnace slag is a residual product obtaining pig iron. If cooled rapidly, it will have an amorphous structure, and when grinded, it will show excellent binding properties with the portland cement (Ustabaş, 2018).

Slag can be used as alkali-activated materials and utilised in the synthesis of geopolymers. The term geopolymer was first used by Joseph Davidovits. He defined the material that is formed in inorganic polycondensation called geopolymerization. In geopolymerization reaction, three-dimensional structures of AlO_4 and SiO_4 tetrahedra are created. Later the term geopolymer was used for all alkali activated aluminosilicate (Davidovits, 1991; Škvára, 2007).

Geopolymers now represent a new group of organic substances, because they have significant environmental and energy potential. They belong to a group of the inorganic polymer covalently bound macromolecules with the chain consisting of -Si-O-Al-O-. Geopolymers are obtained from the chemical reaction of alumino-silicate oxides with sodium silicate solutions in a highly alkaline environment. As an alkali activating solution, a strongly alkaline aqueous solution of sodium or potassium hydroxide is most commonly used (Škvára, 2007; Xu et al., 2000).

The reaction mechanism and strength development of the geopolymer are influenced by the type and concentration of the alkaline solution, curing temperature, curing conditions and specific surface area. The alkali activator is designed to activate multiple calcium aluminium silicate minerals and is the most important factor in the hydration of these aluminium silicate minerals. Currently, the commonly used alkali activators include sodium silicate, sodium carbonate and NaOH (Kürklü 2016, Wang et al. 2016).

Geopolymers find a broad range of applications in the field of transportation, emergency repairs, metallurgy, coating, membrane materials, and nuclear waste disposal. Geopolymers have become a potential alternative binder to ordinary Portland cement (OPC) in some applications due to its sustainability criteria of lower emission of greenhouse gases and low energy consumption (Liew et al., 2017). Although significant commercial and technological potential, geopolymers' easy-brittle character limits their extensive applications, where great efforts are made to overcome such shortcomings. Numerous studies are dedicated to optimise the strength of geopolymer products and to understand the mechanism of geopolymerization (van Deventer, 2007; Zhang, 2015; He, 2013; Zhang, 2014).

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In last years, different studies have investigated the possibility of using different types of wastes mixed with fly ash or slag as raw materials (Mádai, 2015; Musci, 2014). The selection of the materials to create geopolymers depends on influences such as availability, disposal urgency, the difficulty for recycling and final applications (Toniolo, 2017). Research has shown that it is possible to develop geopolymer concretes based solely on waste materials activated directly, without the presence of Portland cement, utilising an alkaline activator. A major benefit of geopolymer concrete is that the reduction of CO_2 emission by 26–45 % with the replacement of PC with no adverse economic effects (Wardnoho et al., 2017; Karthnik et al., 2017).

The primary aim of this paper is to demonstrate that mechanical activation of GGBFS improves mechanical properties of all geopolymers made in our research.

Materials and Methods

The material used for alkali activation was blast furnace slag (BFS) and same material after mechanical activation in a ball mill (GGBFS). Milling was performed in laboratory ball mill with steel balls with different diameters. The laboratory mill used for mechanical activation had volume 30 dm^3 and was filled with steel ball with diameters ranging from 2 to 10 cm. Material for mechanical activation with steel balls formed 40 % of mill volume. Revolution was adjusted to 90 per minute. Mechanical activation was performed in two stages. The first stage was after 20 minutes and the second stage after 60 minutes. After grinding stage, d80 was 90 μm. Particle size distribution is shown in figure 1. The material was homogenised before alkali activation. No other treatment was applied to the material.

The chemical composition of BFS is shown in Table 1. The activation solution was prepared by mixing solid NaOH pellets with Na-water glass and water. Sodium water glass from the Kittfort Praha Co. with the density of 1.328- 1.378 g/cm^3 was used. It contains 36 - 38 % Na_2SiO_3 and the molar ratio of SiO_2/Na_2O is 3.2 - 3.5. Solid NaOH with the density of 2.13 g/cm^3 was obtained from Kittfort Praha Co. containing at least 97 % - 99, 5 % of NaOH.

The effect of three main parameters was examined: the amount of Na_2O from slag weight, SiO_2/Na_2O ratio in the activation solution on strengths of geopolymers and the amount of water content. Five different mixtures were designed in which amount of Na_2O was varying from 5 to 9, where SiO_2/Na_2O ratio and water content was constant. Another five mixtures where the SiO_2/Na_2O ratio was adjusted from 1.1 to 1.3 and other two parameters where constant. Last experiments setting was following: water to slag ratio was varying from 23 to 31 % and other two parameters where constant. The water to fly ash ratio was adjusted to 0.25.

BFS and GGBFS mixtures were stirred with activation solution for 10 minutes until the creation of homogenous mixture. The mixture was then filled into prismatic moulds with the dimensions 40x40x160 mm and compacted on the vibration table VSB-40 for 10 minutes at the frequency 50 Hz. The pastes were cured in a hot air drying chamber at 80 °C for 6 hours. After that, the samples were removed from the forms, marked, and stored in laboratory conditions until the moment of the strength test. The values of compressive strength were determined after 7, 28, and 90 days according to the Slovak Standard STN EN 12390-3. The compressive strength of the hardened samples was determined after 7, 28, and 90 days using the hydraulic machine Form+Test MEGA 100-200-10D.

Results

Chemical analysis of BFS is given in Table 1. Grain size distribution of BFS and after mechanical activation of slag material, before alkali-activation is given in Figure 1. Note the shift of distribution towards lower sizes, within the same range. The 80 % particle size of raw slag was 1,8 mm. During the mechanical activation, the particle size was significantly decreased, after 60 minutes of the milling process 80 % of the slag was finer than 90 μm.

Tab. 1. Chemical composition

Material	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	Other
BFS [%]	40.3	37.01	12.1	8.51	0.3	1.78

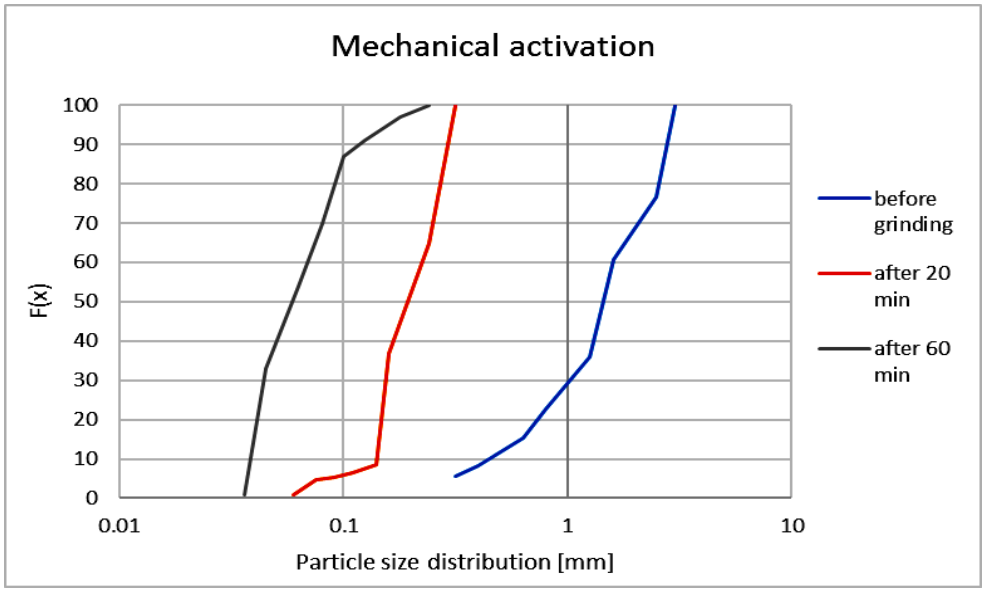

Fig. 1. Particle size distribution before grinding and after 60 minutes of grinding.

Surface morphology of GGBFS was measured by scanning electron microscopy MIRA 3 FE-SEM microscope (TESCAN, Czech Republic) equipped with a high-resolution cathode (Schottky field emitter) and with three-lens Wide Field Optics^{TM} design. Typical SEM micrographs of GGBFS after grinding are given in Figure 2. As shown, slag after mechanical activation in ball mill has plate-like and needle-like structures. SEM images have been taken at different magnification. The SEM images of GGBFS display rough and angular shape.

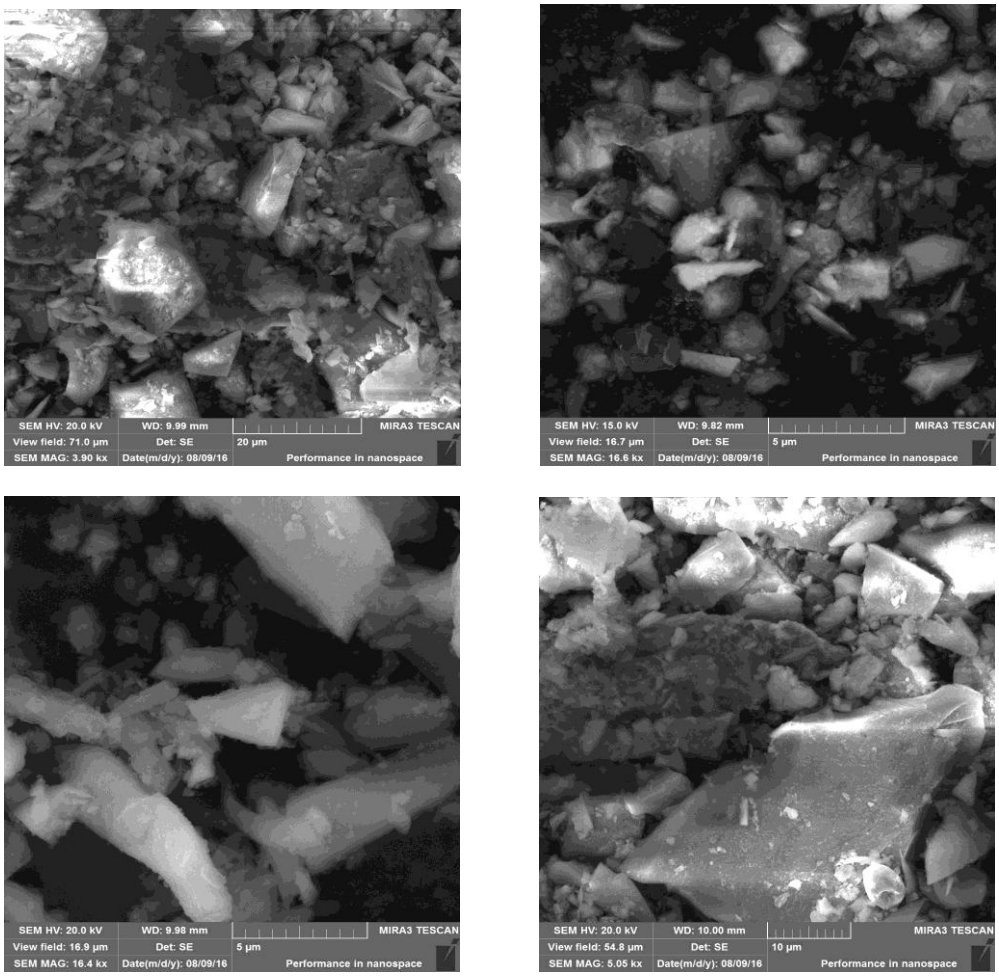

Fig. 2. SEM pictures of GGBFS.

In this study, mechanical activation and 3 parameters of alkali-activated materials were tested how they affect the strengths of hardened geopolymers. From the design of experiments, 28 samples were tested after 7, 28 and 90 days. Compressive and flexural strengths tests were made. These results are presented in this section.

Amount of Na_2O:

For the first series of alkali activation, samples were made by changing amount of Na2O in the mixture from 5-9, and the SiO_2/Na_2O ratio (1.2) with water to slag ration were constant (25). The focus was not only on mechanical activation but also on this parameter. Results are shown in Figures 3 and 4.

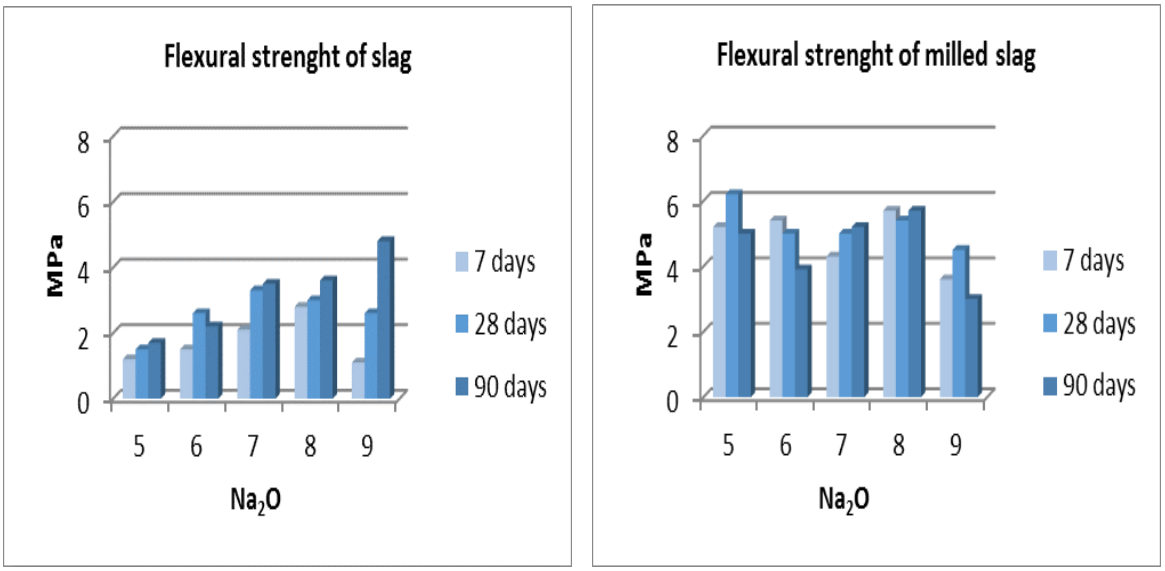

Fig. 3. Flexural strengths of BFS and GGBFS.

From the diagrams, we can see that mechanical activation helped geopolymers achieve bigger strengths, but the amount of Na_2O was lower. In BFS geopolymers it was opposite, the biggest strengths were when the amount of Na_2O was increased. The highest flexural strength with BFS was 4,8 MPa after 90 days of ageing the material made with 9 % amount of Na_2O. GGBFS achieved the highest flexural strength on 28th day 6,2 MPa.

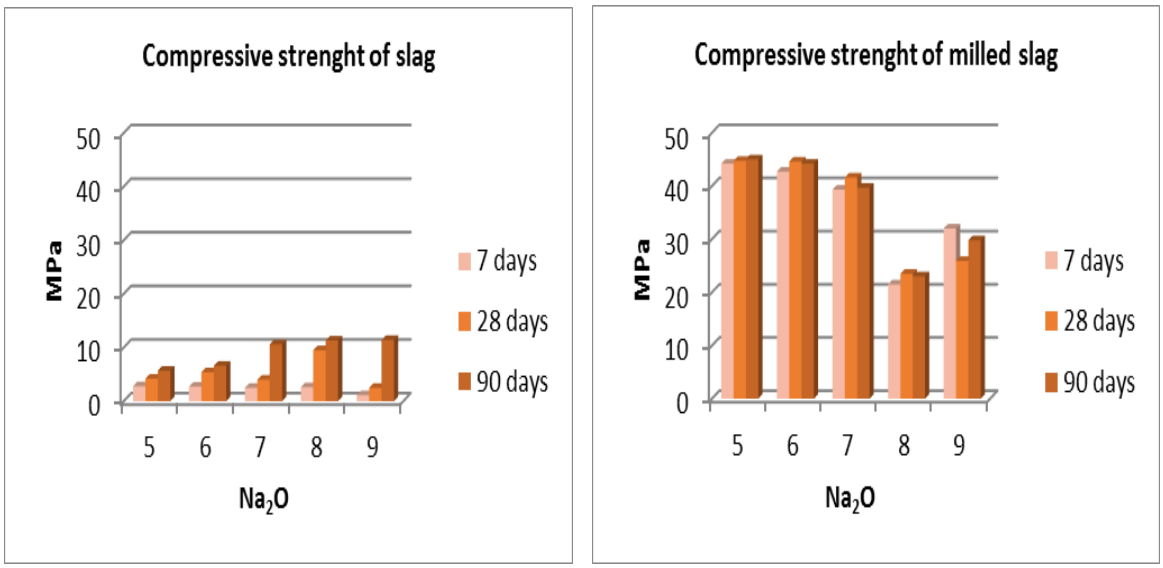

Fig. 4. Compressive strengths of BFS and GGBFS.

Compressive strengths results show that mechanical activation is essential to achieve higher strengths. In BFS samples strength grows over the time to achieve their maximum on 90th day and growth was obvious. After grinding strengths were much higher, but it not always grows in time. The biggest strength was in the sample

made by 5 % of Na_2O in mixture 45 MPa. The samples made before mechanical activation with 9 % Na_2O has the highest strength 11,2 MPa.

Sio_2/Na_2O Ratio:

For the second series of alkali activation, samples were made by changing amount of SiO_2/Na_2O ratio in the mixture from 1.1 to 1.3, and Na_2O content (8) with water to slag ratio were constant (25). The focus was not only on mechanical activation but also on this parameter. Results are shown in Figures 5 and 6.

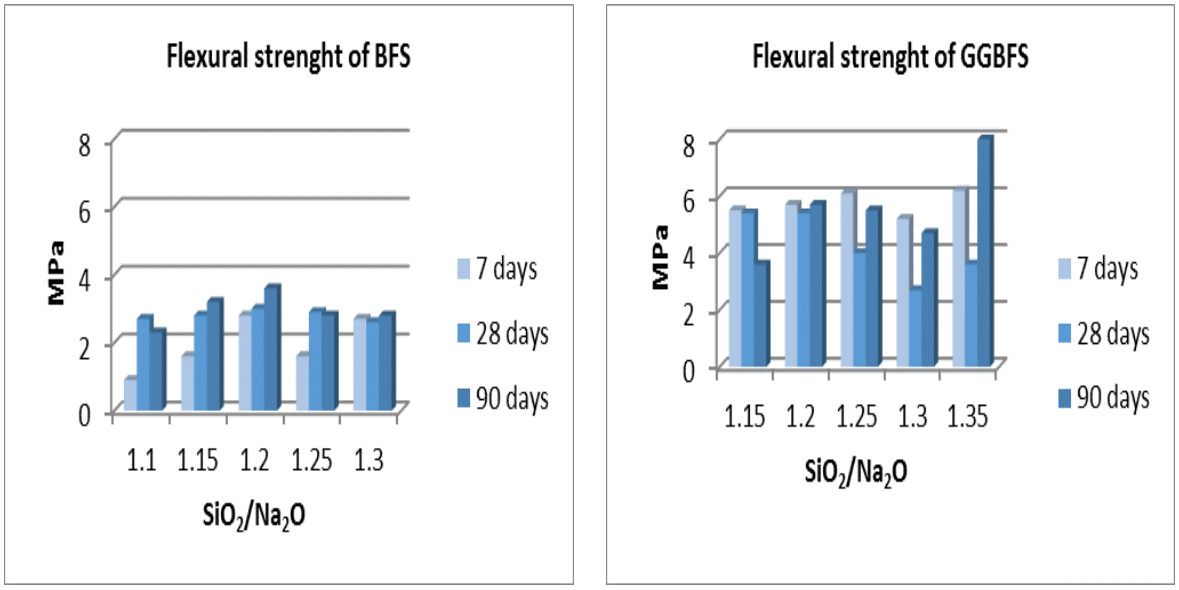

Fig. 5. Flexural strengths of BFS and GGBFS.

In this case, results show that SiO_2/Na_2O ratio has a negligible or minor effect on flexural strengths in BFS, and it is about same, but after grinding, the strengths are higher. The highest flexural strength was with 1.35 SiO_2/Na_2O ratio 8 MPa. Before MA the highest flexural strength was 3,6 MPa where the amount of SiO_2/Na_2O ratio was adjusted to 1,2. After grinding, the phenomenon of decreasing strengths over time occurred, but the strength increased significantly on the 90^{th}-day.

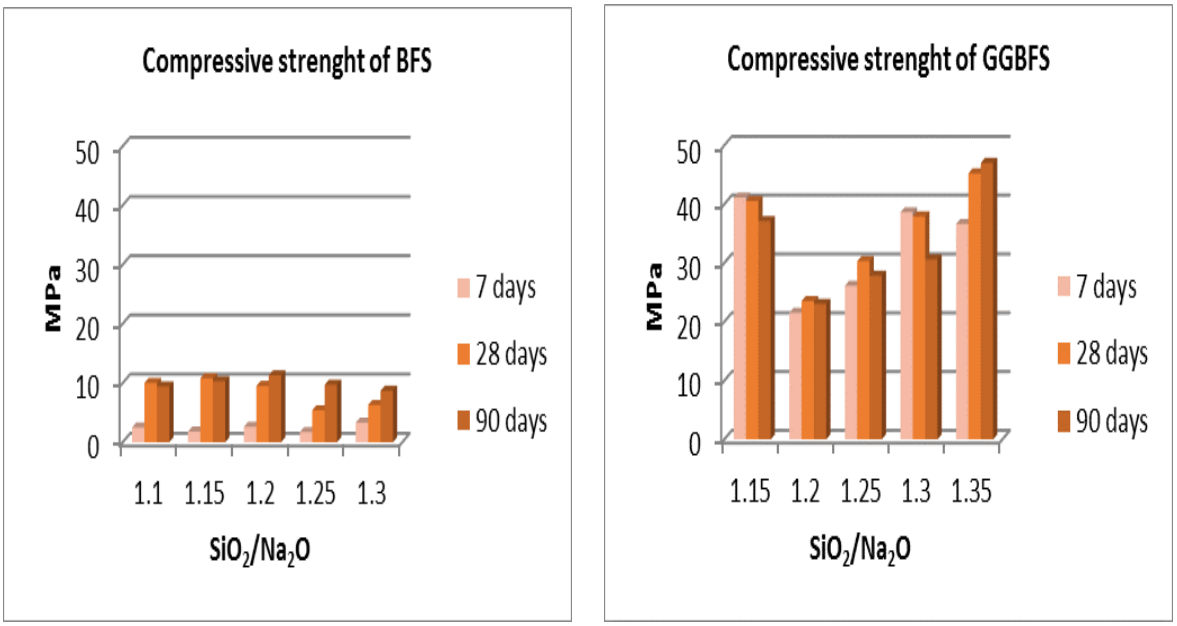

Fig. 6. Compressive strengths of BFS and GGBFS

Similar results were obtained after compressive strengths testing. The SiO_2/Na_2O ratio in BFS did not show any differences in different amounts, but strengths were increased over the time. The highest compressive was

11,3 MPa with 1,2 SiO_2/Na_2O ratio for BFS testing. Results after grinding shows the phenomenon as it was with flexural strengths. The highest strengths were not always on the 90th day but were much higher than before grinding. The samples with 1,35 SiO_2/Na_2O ratio after the 90th day achieved the highest strength from all samples during this set of testing 47 MPa.

Water to slag ratio:

For the last series of alkali activation, samples were made by changing water to slag ratio from 23 % to 31 %. The SiO_2/Na_2O ratio in the mixture (1.2) and Na_2O content (8) were constant. The focus was not only on mechanical activation but also on this parameter. Results are shown in Figures 7 and 8.

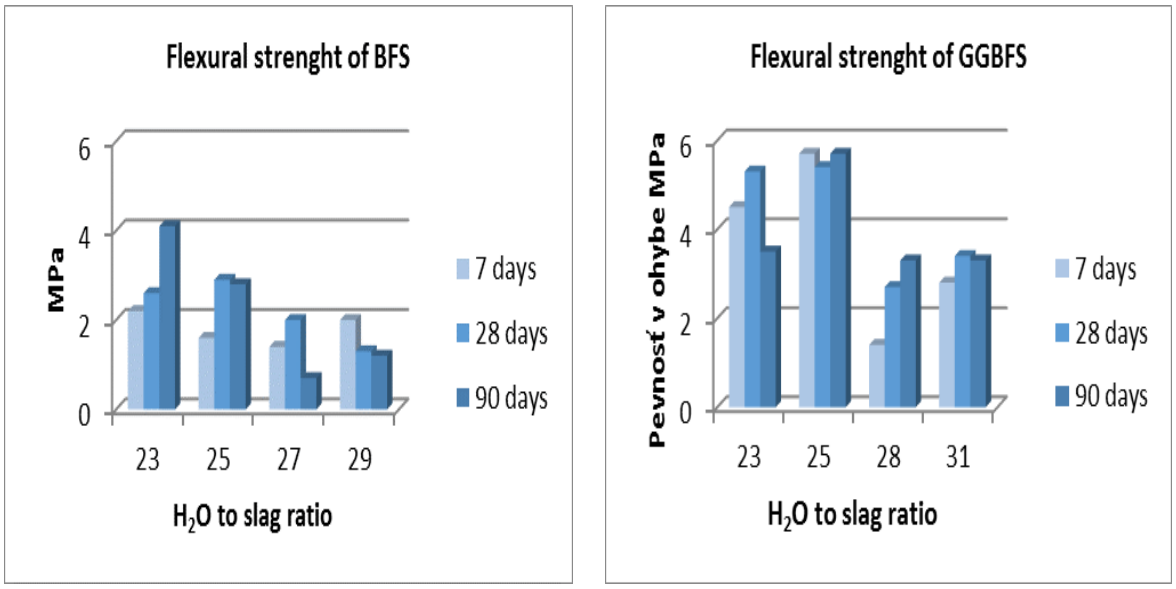

Fig. 7. Flexural strengths of BFS and GGBFS

As expected, the water content in mixture shows that when less water is in alkali activation, the higher strengths are obtained with our material. Also as from previous diagrams, we can see that grinding is an important factor because it improves strength also in this case. The best result for BFS was with 23 % water content 4,1 MPa flexural strength. For GGBFS it was with water content 25 % and on all days of testing flexural strength was similar 5,5 MPa.

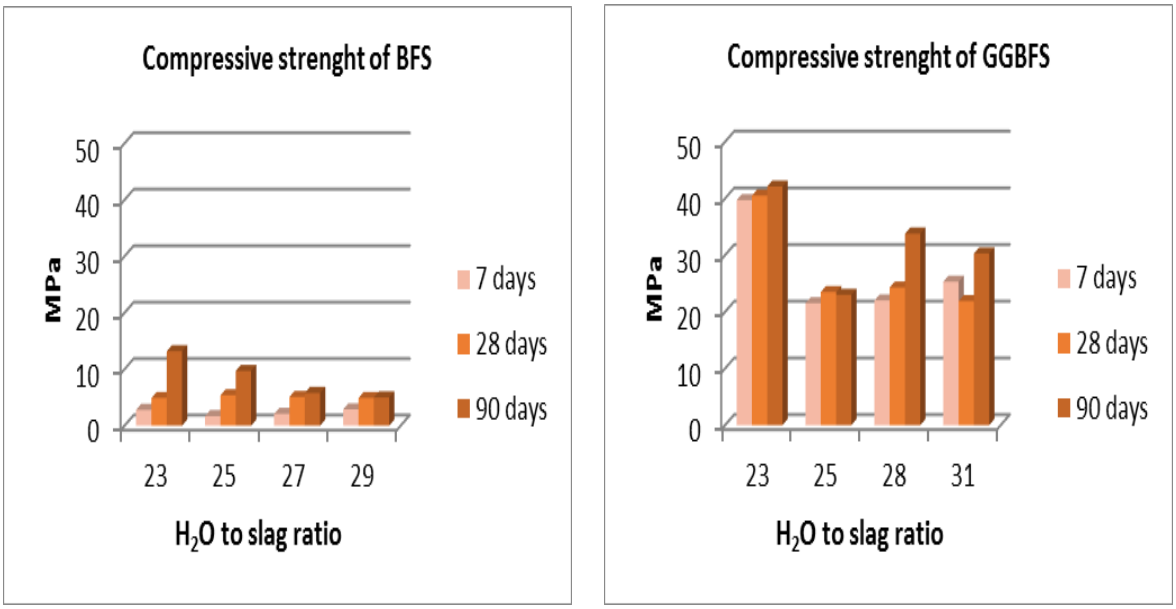

Fig. 8. Compressive strengths of BFS and GGBFS

Compressive strengths results show that when less water is in the mixture, the higher the strength will be. Almost all samples showed the biggest strengths at the 90th day. As in previous results, mechanical activation significantly improved mechanical strengths. The material before mechanical activation with lowest water content 23 % has the highest compressive strength 13,2 MPa. Compressive strength tests after mechanical activation show the highest strength with samples made by 23 water content 41 MPa.

Conclusion

Mechanical activation of the BFS by a laboratory mill leads to a reduction in particle size and an increase in the specific surface area. The mineral compositions of the BFS were not changed, but the crystal structure was effectively destroyed, resulting in a lower degree of crystallinity and less polymerisation of SiO_4. The amount of reactive silica and aluminium in the slag is improved by the combined effect of the decrease in particle size and damage to the microstructure; this promotes the geopolymerization process because the reactivity of the slag is enhanced.

The superior performances of geopolymers based on the properties of activated blast furnace slag, such as a high compressive strength and high flexural strength are attributed to the optimized distribution of particle size and increase in the amount of reactive constituents after mechanical activation, which result in an ordered and a compact intrinsic structure, as well as a deeper reaction. The improvements in the performance of the geopolymers depend on the increase in the reactivity of the blast furnace slag.

Alkali-activated materials – geopolymers, are a new generation of inorganic binders. Any aluminosilicate materials can be used to prepare geopolymers, including slag. Two series of geopolymers derived from a BFS were prepared. The geopolymers in this study have been prepared by the alkali activation solution consisting of NaOH, water glass and water to activate BFS. Mechanical activation is an essential approach to improve mechanical strength. In all tests and all different parameters change, one conclusion is obvious, that grinding significantly improve strengths, compressive and also flexural.

This study suggests that it is feasible to prepare high-quality geopolymers from blast furnace slag after mechanical activation.

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