An attempt to apply a slag binder with zeolite in mining construction. Durability and hardness.

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Abstract. The paper presents comparative results of strength tests on mortars, hardness of pastes and their microscopic observations. The focus was on alkali activated ground granulated blast furnace slag (GGBFS) to which the zeolite was introduced. Zeolite positively affects the rheological properties, densifies the microstructure by reducing its permeability and binds Ca(OH)₂. It causes lower susceptibility of the binder to corrosion, which can be affected by mine mineralized waters or brines flowing from the salt beds. To increase the mechanical properties, polymer scattered reinforcement was used, which does not corrode in contact with saline waters, contrary to steel reinforcement. The paper presents the results of: bending strength and compression strength of mortar bars made of slag (S2), slag with zeolite (S3), slag with zeolite and polymer fibers (S5); the Vickers indenter tests results of slag pastes of S2 and S3 as well, up to 90 days of hydration. The 90 day compressive strength was 64.0 MPa; 27.7 MPa and 64.7 MPa, and bending strength: 6.4 MPa; 2.9 MPa and 6.0 MPa, respectively for S2, S3, S5. The Vickers indenter test at HV 1 was as follows: on average 27.04 MPa and 36.69 MPa, respectively for S2 and S3. Microstructure observations were carried out in SEM. The obtained results require further research work.

1. Introduction

Mineral binders in underground mining conditions can be used for making protective and insulating filling belts, shotcrete, insulating and fireproofing there, linking the casing with the rock mass, stoppers in the decommissioned shafts, for repairs and modernization. Mineral binders are also used in concrete for the construction of shafts and tunnels. The three main requirements to concrete used in the mines are: regarding strength, chemical resistance and workability of the mix. Concrete mixes should be transportable, fluid and self-compacting to facilitate the formation of hard-to-reach, densely-reinforced tunnel casings and shafts. Hardened concrete should have strength adequate to the place where it will be working, tightness and chemical resistance due to the presence of strongly saline waterlogged layers of rock mass causing its corrosion. In the mines different kinds of binders are used: from immediate-support binders (Rc = 30 MPa after 24 h) to late-support binders (Rc = 20 MPa after 28 d) and other without special durability requirement – filling binders [1, 2, 3].

In order for the concrete to be durable, it should have a low gas phase content, i.e. a low proportion of pores, because sulfate, magnesium and ammonium ions entering it, can cause corrosion. Chloride ions, in particular corrode steel reinforcement. In exemplary underground mines in Poland, waters have
different degrees of mineralization, depending on the specificity of a given coal basin. For example, waters from the coal mine in the Lublin Coal Basin are characterized by mineralization of $\text{HCO}_3^-\text{Cl}^-\text{Na}$ up to $4.3 \text{ g/dm}^3$, and at the depth of 1000 m, general mineralization is increasing, and the chemical type is changing on $\text{Cl}^-\text{Na}$. The total water mineralization from carboniferous deposits flowing into mining excavations is within limits $5.1-7.4 \text{ g/dm}^3$, and water from Jurassic works: $0.6-2.8 \text{ g/dm}^3$. Whereas mine waters of the Lower Silesian Coal Basin are in the total mass of saline water type: $\text{SO}_4^-\text{HCO}_3^-\text{Mg}^-\text{Ca}^-\text{Na}$, in which the content of chloride ions is $37-137 \text{ mg/dm}^3$. The LGOM copper ore deposit area is spread around 1030 km$^2$. The mineralization of water from the excavations of individual mines stabilizes at the level of: Lubin: $2.2 \text{ g/dm}^3$, Polkowice: $6.3 \text{ g/dm}^3$, Rudna: $112 \text{ g/dm}^3$, and Sierszowice: $93 \text{ g/dm}^3$. This wide range of corrosive ions acting on the concrete binder and reinforcing steel together with a reduced reaction (pH) of mine waters results in damage to the shaft casings, which in turn affects the attachment of girders, piping brackets, cable hangers, and other, but also other construction structures in mining plants [4, 5, 6].

Chemical factors cannot be ignored during research on mineral binders for underground mining. Therefore, the authors of this work propose a solution based on the principles of sustainable development and the resource economy of the state in a closed cycle. Previously, several scientists have already dealt with this subject using mixtures of fly ash and cement reinforced with scattered reinforcement for hard coal mines. Other pozzolanic materials are also successfully used to increase the resistivity of concrete. However, additions often lead to a reduction in strength. Therefore, it is proposed to use dispersed reinforcement, and instead of steel reinforcement: highly durable, resilient, non-combustible, corrosion-resistant fiberglass mesh with cementless binders [7, 8, 9, 10, 11, 12, 13].

The authors of this work propose to consider the use of cementless binder in mine conditions, which is alkali activated ground blast furnace slag (AAS). As it has been shown to have good resistance to acidic waters, in particular carbonic acid. Activation, i.e. stimulation for hydration and subsequent binding and hardening, occurs by introducing alkalis: sodium hydroxide or, as in the presented studies, sodium metasilicate, thus calcium and sodium aluminosilicate hydrates (C-A-S-H and C-(N)-A-S-H) are the predominate reaction products. Most of the works focused on metakaolin and fly ash based geopolymers, which properties of the gel phase produced from the alkali-activation of slag are almost the same. An increasing Si/Al ratio in the paste leads to greater mechanical strengths, but also increased stability of the structure which reduces the tendency of the system to form zeolite crystalline structures, which in turn is observed at low Si/Al ratios. Important is also a water capacity values for examined zeolite. Zeolite stabilizes the quality and quantity of air in concrete (divides capillaries and air bubbles into smaller ones), increases the adhesion of the binder to aggregates and fibers, and gives many other beneficial properties. Therefore, in order to improve the rheological properties, but mainly microstructural and sorption of the slag binder, and in order to test the strength of the mixtures, additional zeolite was introduced. In the third slag compound, disintegrated polymer reinforcement was considered not to allow generation of microcracks due to the shrinkage of the silicon gel. It was examined that the effect of GGBFS content and PP fiber dosage in concrete improve mechanical properties of concrete also after exposure to high temperature, what also is important underground in a mine [14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24].

The hardened AAS paste consists of a fairly homogeneous ground mass gel and unreacted slag grains. The research conducted so far on the microhardness of slag paste may not coincide with compressive strength. The reason is in inhomogeneity. An exemplary microhardness of the alkali activated steel slag ground mass gel in sodium silicate-activated slag cement were approximately higher than sodium hydroxide-activated slag cement. That was the reason to use Na$_2$SiO$_3$:5H$_2$O in this work [15].
2. Materials and test methods

2.1. Materials
Granular blast-furnace slag, sodium metasilicate pentahydrate, distilled water, standard sand CEN (by DIN EN 196-1 and PN EN 196-1), zeolite and polymer fibers were used to prepare the mixtures for testing. Activating water was made out of distilled water and Na$_2$SiO$_3$·5H$_2$O in such a way that the ratio of aw/s (activating water/slag) was 0.45, while Na$_2$SiO$_3$/slag = 5% mas. Total content of CaO+MgO+SiO$_2$ in a slag was 88%, a ratio of (CaO+MgO)/SiO$_2$ = 1.29, and the surface area according to Blaine: 3850 cm$^2$/g. The activity indicator after 7 days was 53.4%, and after 28 d = 85.1%.

The properties of ZEOBAU 50 zeolite were as follows: surface area: 13 640 cm$^2$/g, activity indicator D 28: 102 %, standard consistency to determine binding times – 36.5%, the beginning of binding time – 220 min, end of binding time – 265 min, fineness – 17%, density 250 kg/m$^3$, consistency of fresh mortar: H$\_2$O – 275 ml, slump – 175 mm, water demand: 122%.

The chemical composition of the applied granulated blast furnace slag and zeolite is shown in the table 1.

| oxide         | Content (% by mass) | slag   | zeolite |
|--------------|---------------------|--------|---------|
| CaO          | 43.27               | 3.08   |
| SiO$_2$      | 40.43               | 70.77  |
| Fe$_2$O$_3$  | 0.81                | 1.50   |
| Al$_2$O$_3$  | 7.88                | 12.56  |
| MgO          | 6.97                | 0.65   |
| SO$_3$       | 0.25                |        |
| sulfide(2-)  | 0.50                |        |
| Na$_2$O      | 0.46                | 0.59   |
| K$_2$O       | 0.29                | 3.40   |
| TiO$_2$      | 0.28                | 0.15   |
| MnO          | 0.16                | 0.04   |
| P$_2$O$_5$   | 0.02                | 0.03   |
| loss on ignition | 0.46       | 7.27   |

Preparation of mortar samples for compression and bending strength tests was carried out based on the appropriate standard for 3 mixtures. 21 beams with mass compositions given in table 2 and a ratio aw/s (activating water/slag) equal to 0.45 (mas.) were prepared from each mixture, for one mixture at one time. During the first 30 seconds water with standard sand were mechanically mixed and then slag was added (mixed with zeolite and fibers). The mixtures were placed in forms 40×40×160 mm (figures 1, 2, 3), which were tightly covered with foil. They bound and hardened at temperature 20 ± 2°C, and after the demoulding, which took place after 2 or 4 days, the samples were stored in a cardboard box so that the moisture did not escape too quickly [25].

For the hardness tests, slag and slag pastes combined with zeolite activated with aqueous sodium metasilicate solution were prepared. Mixtures of pastes, whose mass composition is shown in table 3, hydrated in a specially prepared form of silicone rubber giving smooth surfaces. The cubes with dimensions 10×10×10 mm were obtained. They were demoulded after 2 days of binding and transferred to a tight closed plastic string bag where they stayed throughout the study period. Before the Vickers
test, the upper plane of each sample was grinded to be relatively parallel to the bottom plane that was tested.

Table 2. The composition of mortar mixtures S2, S3 and S5 series.

| Series | Slag (g) | Sand (g) | Activating water<sup>a</sup>, g | Zeolite (g) | Fibres<sup>b</sup> (g) |
|--------|---------|---------|-------------------------------|-------------|---------------------|
|        |         |         | Distilled water               | Na<sub>2</sub>SiO<sub>3</sub> |         |
| S2     | 3000    | 9000    | 1089,3                        | 150         | -                   |
| S3     | 3000    | 9000    | 1089,3                        | 150         | 300                 |
| S5     | 3000    | 9000    | 1089,3                        | 150         | 300                 |
|        |         |         |                               |             | 16,38               |

<sup>a</sup> 1350,30 g (sodium pentahydrate metasilicate + distilled water)

<sup>b</sup> length: 38 mm

Table 3. Composition of mortar mixes of S2 and S3 series.

| Series | Slag (g) | Activating water (g) | Zeolite (g) |
|--------|---------|----------------------|-------------|
| S2     | 300     | 135                  | -           |
| S3     | 300     | 135                  | 30          |

Figure 1. Series S2 before and after manual compacting.

Figure 2. Series S2 just after compaction.

Figure 3. Series S3 after 2 days of hardening.

2.2. Methods

The bending of the mortar beams was examined by a three-point load method (figure 4), and compressive strength was tested on broken bar beams in an automatic apparatus with strength registration, giving values in [MPa] and [N]. The strength was tested after (2), (4), 7, 28, 90 days of hydration, the samples were also weighed. The results are given as the arithmetic average out of three and six results for bending and compression, respectively.

The hardness test of the cubes of hardened slag paste was carried out using the apparatus „SHVS-500” (figure 5). Using the Vickers' indenter, a "hardness tests with low loading force" were made. The loading force was 9.807 N (hardness symbol: HV1). A pressing time of 10 seconds was used, the length of the diagonals was determined manually and the hardness was calculated automatically. Results from hardness of slag paste were prepared as the arithmetic average out of the averages for 3 cubes. There were 12 to 16 measurements per 1 cube. The standards in force in Poland are dedicated mainly to metals,
however, Glinicki et al. noticed that ASTM E384 does not refer to a specific material in conjunction with the Vickers indenter hardness test method [26, 27, 28, 29].

Several photos were taken under the Tescan Mira 3 electron microscope at a given time of hydration and hardening.

Figure 4. Three-point test of the bending strength of the mortar beam.

Figure 5. Examination of slag paste cube by Vickers indenter.

3. Test results and Discussion
The zeolite was introduced into the S3 blend due to improved workability. The fresh mixture of mortar S3 (slag series with zeolite) was characterized by increased fluidity compared to S2. The mixture of S3 mortar was also more viscous, it could be poured into the mold and not put with a spatula, as in the case of S2 (figure 1). Up to 1 hour the fresh mortar of S3 was packing up by itself in the form, it gives up a smaller volume despite the addition (zeolite).

3.1. Strength tests
The results of bending strength test of mortars of S2, S3 and S5 series after (2), (4), 7, 28 and 90 days of hydration and hardening was placed in figure 6, while the results of compressive strength tests of previously broken mortar beams were placed in figure 7. S3 mortar was tested only on the 4th day of hydration, because after 2 days the bars were too moist and cracked during demolding (figures 6 and 7).

The results of strength tests show that the mechanical properties of mixtures change over time. In particular, the strength of slag mortars (S2) increases up to 90 days. The addition of zeolite in the amount of 10% to the mass of the slag resulted in the reduction of mechanical properties by as much as half, and this decrease increased with time of hydration in relation to the pure slag mortar (S2). However, you do not have to be surprised. The mixture has been designed without taking into account the water capacity value of this zeolite. Therefore, in the subsequent stages of research work, the water demand of zeolite must be taken into account. As can be assumed, the strength properties of the next series of mortar, S5, to which fibers were added, in the amount of 0.12% by mass, also decreased due to the additional absorption of water by fibers. In particular, bending strength was lower. However, the compressive strength of S5 mortar with fibers in the initial hydration phase was higher than that of S2 series, but in the 90th day it has already leveled out.

A typical turquoise shade for blast furnace slag in the middle of the fracture of mortar beam and a number of air pores, scattered reinforcement are visible in figure 8. An image of the S5 microstructure made under the electron microscope (figure 9) looks as follows: due to the insufficient water content in paste matrix, the C-S-H phase is not compacted enough (not packed enough). Therefore, the grain (slag or zeolite) is well surrounded by the C-S-H phase, but unfortunately this can not be said about the fiber.
Figure 6. The flexural (bending) strength of activated mortars: S2 – slag, S3 – slag with zeolite, S5 – slag with zeolite and 38 mm length fibres.

Figure 7. Compressive strength of mortars: S2 – slag, S3 – slag with zeolite, S5 – slag with zeolite and 38 mm length fibres.

The average mass calculated for the three mechanically examined bars within 90 days of hydration was decreasing. Starting from the 2nd day: in the case of S2, the weight decreased from 570 to 560 grams (weight loss: 1.75%). In the case of S3, the weight decreased from 568 to 539 grams (5%). In the case of S5, the weight decreased from 628 to 604 grams (4%), while on the 28th day it was the smallest = 591 grams. This trend coincides with the change of bending strength (figure 6).
Figure 8. Series S5, fracture of the hard beam after bending strength test, plane 4×4 cm.

Figure 9. Series S5, fracture made after 4 months of hardening, SEM-BSE image.

3.2. Hardness test
The results of testing the hardness of S2 and S3 series of pastes after 2, 5, 7, 9, 28, 61 and 90 days of hydration and hardening are included in figure 10. Whereas the average weight loss for 3 cubes of one series after equal times is shown in figure 11. The hardness examined by the Vickers indenter of the slag with the addition of zeolite (S3) is evidently higher than the hardness of the slag paste (S2), at each hydration time. The greatest difference appeared from 28th day, however, it seems that tests between 9 and 28 days should be densely performed.

Figure 10. Vickers hardness of S2 and S3 paste series in the time of hydration.
The hardness of S2 increased by about 346% and S3 by about 397%, from 2nd to 90th day. The increase in the hardness of the slag matrix was undoubtedly influenced by the addition of zeolite. Zeolite stabilizes the quality and quantity of air in the concrete (divides the capillaries and air bubbles into smaller ones), increases the adhesion of the binder to the aggregate and fibers [23].

There was also a significant loss of paste mass in both series after 90 days by approx 8.5%, while the change in the mass of the S3 series can be attributed to the decreasing exponential function. This loss can be explained by the escape of water vapor. Although, the samples were stored in string bags that did not become moist. In addition, gas, most likely hydrogen sulphide, was evolved from the samples for a long time, it was palpable.

**Figure 11.** Mass loss of S2 and S3 slag pastes during the time of hydration.

### 3.3. Examination of microstructure
First observation of the microstructure of mortar, has already been described in the 3.1. point. The increase in the density of the activated blast furnace slag due to the addition of zeolite, can be more accurately observed in figures 12 and 13, made after 50 days of hydration. The tested sample of activated slag without the addition of zeolite was characterized by low porosity (figure 12), when the sample of activated slag with the addition of zeolite was characterized by a much more compact microstructure and, of course, by much more grains (figure 13).

The microstructure of pore wall surfaces was different of the S2 and S3 hardened paste. In the case of S2, can be noticed numerous forms of wavy and jagged structure. In case of S3, the zeolite affected the larger packing of the microstructure, where probably unreacted grains occurred inside the amorphous phase (darker areas) – figures 14 and 15. The microstructure with a larger specific surface, as in the case of S2 (figure 14), is most likely to be more reactive, i.e. less resistant to corrosive factors.

### 4. Conclusions
The problem of modifying the microstructure of concrete for mine and underground construction undertaken in the work is important for durability and strength reasons. To reduce the corrosivity of concrete, its microstructure should be compacted in the solid phase, i.e. the permeability should be reduced. This is possible by adding a zeolite. Microscopic observations showed that the zeolite reduces the specific surface area of the slag paste. The hardness tests indicated that the addition of zeolite affected the increase in the density of activated blast furnace slag, what also should reduce chemical reactivity with aggressive ions. This is particularly required when in contact with aggressive mine
waters. The main phase of slag hydration, the most simply referred to C-S-H gel, has a significant shrinkage in air atmosphere, so it seems that it prefers a moist to wet environment.

Unfortunately, at this stage of the research, the zeolite series did not reach the desired strength values. Mortars with the addition of zeolite and fibers had better strength parameters, but also unsatisfactory. In the further stage of the research, the strength indexes should be improved, that is, increase the coherence of the matrix by taking into account the zeolite's water demand and again check the strength of the slag mortar beams with the addition of zeolite together with the fibers.

**Figure 12.** Microstructure of activated blast furnace slag without the addition of zeolite, SEM-BSE image after 50 days of hydration.

**Figure 13.** Microstructure of activated blast furnace slag with the addition of zeolite, SEM-BSE image after 50 days of hydration.

**Figure 14.** Wall microstructure of the pore of the AAS without the addition of zeolite, SEM-BSE image after 50 days of hydration.

**Figure 15.** Wall microstructure of the pore of the AAS with the addition of zeolite, SEM-BSE image after 50 days of hydration.
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