Technological characterisation of selected mineral additives

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Abstract. The paper was aimed on testing the technological properties of product "Zeoslag" which consists of 10% of zeolite and 90% of ground granulated blast furnace slag. Both the Perlite and Zeolite were tested for comparison, and also cement as reference material. Mineral additives were tested according to standard for testing the slag - the binder here consists of 50% of additive to be tested and 50% of cement. Normalized sand and water according to standard recipe were used to make a testing mixtures. Following technological parameters of additives were tested: water demand for standard consistency, flexural and compressive strength development (2, 7 and 28 days) and activity index. Parameters are discussed in the terms of chemical character of additives. At the given range of modulus of hydraulicity (0.02 – 2.44), the experiment showed tight nonlinear relationship between it and strength characteristics of additive-based mortars.

1. Introduction
Concrete additions are defined as finely divided materials used in cement-based mixtures in order to improve or to obtain desired fresh and hardened concrete properties. The EN 206 [1] lists two types of inorganic additions:

- Nearly inert additions (type I): Virtually inactive materials such as rock powders (lime fillers or quartz dust) and color pigments. Pigmented metal oxides (mainly iron oxides) are used to color concrete. They must remain color-fast and stable in the alkaline cement environment. With some types of pigment, the water requirement of the mix can increase.
- Pozzolanic or latent hydraulic additions (type II): [1] considers only fly ash and silica fume as well as ground granulated blast furnace slag as suitable additives for concrete production with the recommendations how to involve them to the water/binder ratio (k-value).

In the research and development phase of cement composites, a lot of other additives are considered for application in the mixture, while their influences on a wide range of parameters are evaluated. First of all, their pozzolanic or latent hydraulic ability is valuable. Solid industrial by-products (siliceous and aluminous), as well as some natural pozzolanic materials are being increasingly used in the cement and concrete industry, mainly due to environmental and economic effect. Moreover, the incorporation of these materials in concrete gives encouraging results with regards to the mechanical and durability properties of concrete [2].

Construction and demolition waste like glass, brick and concrete dust, seems to be valuable source of mineral fines [3-7]. Lot of studies present generally positive influence of powder additives on the properties of cement-based mixtures [8-10].

The stability or resistance to segregation of the plastic mixture is attained by increasing the total quantity of fines in the mixture and/or by using admixtures that modify the viscosity. Increased fines content can be achieved by increasing the content of cementitious materials or by incorporating
mineral fines; they are used to improve the grading curve. Special requirements for aggregate grading are to be taken into account and especially fine particles (so called “micro filler”) content should be controlled [11]. Micro fillers improve mix workability and provide particle dense packing in hydrated cement paste. High fluidity with relatively low water content is achieved by the use of a superplasticizing and air entraining admixtures.

Chemically active mineral additives (highly reactive pozzolan) increase the cohesiveness of concrete and require more water to maintain workability; however, the requirement of water may be offset by adding plasticizer. The workability of concrete with micro-filler mineral additives greatly depends on the particle size, specific surface area, particle shape, and replacement level. Higher fines content is recommended for easy workable concretes; however, there is also a risk of negative influence here, mainly due to shrinkage [12].

This paper presents following technological parameters of selected additives (Zeolite, Perlite and Zeoslag) – water demand for achievement of standard consistency, flexural and compressive strength development (2, 7 and 28 days) and activity index. Parameters are discussed in the terms of chemical character of additives. The paper is focused on the “Zeoslag” product, which consists of 10% of zeolite and 90% of ground granulated blast furnace slag, and its comparison with other fine-grain materials.

2. Experiment
The paper is aimed on the testing of technological properties of product “Zeoslag” and its comparison with other selected fine-grain materials. The Zeoslag is product being supposed to be a supplementary cementitious material (additive), while it consists of 10% of zeolite and 90% of ground granulated blast furnace slag (GGBFS).

For comparison, the cement, zeolite and perlite were involved to the experiment, too. Following testing was performed:
• chemical composition: using XRF analysis. The main oxides (MgO, Al₂O₃, SiO₂, CaO a Fe₂O₃) were determined by this testing, following by calculation of basic modulus to compare hydraulic activity of materials. The materials have been verified if they meet the typical character of the hydraulicity (Table 3), using the Rankin classification, given in Table 1,

| Kind of material     | CaO/SiO₂ ratio |
|----------------------|----------------|
| Hydraulic            | > 2            |
| Latent hydraulic     | 1 - 1.5        |
| Pozzolanic           | < 0.5          |

Table 1. Rankin classification of hydraulicity.

Modulus of basicity (Mz) and modulus of hydraulicity (HM) were calculated using following formulas:

\[
M_z = \frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}
\]

\[
HM = \frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}
\]

• determining the amount of water for standard consistency of binder paste (STN EN 196-3: Methods of testing cement. Part 3: Determination of setting times and soundness),
• initial setting time (STN EN 196-3: Methods of testing cement. Part 3: Determination of setting times and soundness)
• flexural strength after 2, 7 and 28 days of setting and hardening (STN EN 196-1: Methods of testing cement. Part 1: Determination of strength)
• compressive strength 2, 7 and 28 days of setting and hardening (STN EN 196-1: Methods of testing cement. Part 1: Determination of strength)
• activity index after 2, 7 and 28 days of setting and hardening (STN EN 15167-1 Ground granulated blast furnace slag for use in concrete, mortar and grout. Part 1: Definitions, specifications and conformity criteria)

As given above, samples of mixtures for testing the strength characteristics and calculating the activity index were prepared according to standard for testing the GGBFS. The binder here consists of 50% of additive to be tested and 50% of cement. Whole mixture is as follows: 225 g of cement, 225 g of additive, 225 g of water and 1350 g +/- 5 g of normalized sand. Next, the activity index is calculated as a ratio of compressive strength of this mixture and compressive strength of sample consisting of 100% of cement.

Following criteria for the activity index are given in the standard: it should be higher than 45% after 7 days and higher than 70% after 28 days of setting and hardening.

3. Results

3.1. Chemical analysis

Chemical composition of tested materials is given in Table 2. Parameters defining the character of materials (Modulus of basicity, Modulus of hydraulicity and CaO/\(\text{SiO}_2\) ratio) are evaluated in Table 3.

| Material | MgO (%) | Al\(_2\)O\(_3\) (%) | SiO\(_2\) (%) | CaO (%) | Fe\(_2\)O\(_3\) (%) |
|----------|---------|-----------------|--------------|---------|------------------|
| CEM I 42.5 N | 9.03    | 2.97            | 20.34        | 64.1    | 2.99             |
| Zeolite   | 1.16    | 11.61           | 78.75        | 3.50    | 1.73             |
| Zeoslag   | 8.12    | 6.74            | 43.29        | 26.8    | 0.37             |
| Perlite   | 0.93    | 12.06           | 73.11        | 1.59    | 2.39             |

| Material | Modulus of basicity | Modulus of hydraulicity | CaO/\(\text{SiO}_2\) | Character of materials |
|----------|---------------------|-------------------------|---------------------|-----------------------|
| CEM I 42.5 N | 3.14               | 2.44                    | 3.15                | hydraulic             |
| Zeolite   | 0.05               | 0.04                    | 0.04                | pozzolanic            |
| Zeoslag   | 0.69               | 0.53                    | 0.62                | pozzolanic/latent     |
| Perlite   | 0.03               | 0.02                    | 0.02                | pozzolanic            |

The results confirm the chemical character of individual materials; the Zeolite and Perlite are of pozzolanic one, while Zeoslag gains latent hydraulic character thanks to GGBFS.

3.2. Amount of water for standard consistency of binder paste and initial setting time

Results are given in Table 4.

| Mixture       | Amount of water (g) | Amount of water (%) | Initial setting time (min) |
|---------------|---------------------|---------------------|---------------------------|
| CEM I 42.5 N  | 140.1               | 100.0               | 190                       |
| Zeolite       | 177.4               | 126.6               | 320                       |
| Zeoslag       | 145.1               | 103.6               | 270                       |
| Perlite       | 171.9               | 122.7               | 250                       |
Comparing the cement-based binder, the highest water demand was found for the Zeolite, following by Perlite. The Zeoslag product needs only a bit more water than the reference sample (by 3.6%). However, its initial setting time does not correspond exactly with this, being longer than that of the Perlite. Although the Zeolite and Perlite are of similar chemical composition, as well as the water demand, the initial setting time of Zeolite is much more longer than that of Perlite (by 70 minutes).

3.3. Flexural strength
Results of flexural strength after 2, 7 and 28 days of setting and hardening are given in Table 5.

| Mixture     | f\(_{f 2}\) [MPa] | f\(_{f 7}\) [MPa] | f\(_{f 28}\) [MPa] |
|-------------|------------------|------------------|------------------|
| CEM I 42.5 N| 3.5              | 7.0              | 8.0              |
| Zeolite     | 1.1              | 3.0              | 5.5              |
| Zeoslag     | 2.7              | 5.5              | 7.0              |
| Perlite     | 1.5              | 3.5              | 4.5              |

The flexural strength of samples corresponds with the assumption based on chemical character of tested additives. The highest values were achieved by mixture containing cement only, followed by Zeoslag product.

The lowest values were measured for Zeolite and Perlite, while they are close to each other (1.1 and 1.5 MPa; 3.0 and 3.5 MPa; 5.5 and 4.5 MPa - values after 2, 7 and 28 days respectively). The strength development is quite interesting; while Perlite gives little bit better results than zeolite in early ages (2 and 7 days), after 28 days the zeolite is better (by 1 MPa). The strength development is given in figure 1.

![Figure 1. Flexural strength of standard mortars with additives.](image)

3.4. Compressive strength and activity index
Results of strength and activity index after 2, 7 and 28 days of hardening are given in Table 6.

| Mixture     | f\(_c 2\) [MPa] | f\(_c 7\) [MPa] | f\(_c 28\) [MPa] | AI\(_2\) (%) | AI\(_7\) (%) | AI\(_28\) (%) |
|-------------|----------------|----------------|----------------|-------------|-------------|-------------|
| CEM I 42.5 N| 14.0           | 46.5           | 51.5           | 100         | 100         | 100         |
| Zeolite     | 4.0            | 9.5            | 25.0           | 28.6        | 20.4        | 48.6        |
| Zeoslag     | 6.8            | 19.7           | 45.3           | 48.3        | 42.4        | 88.0        |
| Perlite     | 4.5            | 10.5           | 19.0           | 32.1        | 22.6        | 36.9        |

Similarly, the same order of values was detected for compressive strength. The highest values were achieved by mixture containing cement only, followed by Zeoslag product. While values of zeolite
and perlite are close to each other again (4.0 and 4.5 MPa; 9.5 and 10.5 MPa; 25.0 and 19.0 MPa - values after 2, 7 and 28 days respectively), the difference between values of cement-based sample and Zeoslag are more significant than in the case of flexural strength. However, taking into account the rate of cement replacement (50%), the 28-day compressive strength of sample "Zeoslag" (45.3 MPa) is very promising.

The strength development of both the Perlite and Zeolite samples are the same as in the case of flexural strength: Perlite gives little bit better results than Zeolite in early ages (2 and 7 days), but after 28 days the Zeolite is better by 6 MPa).

The limit for activity index is reached only by Zeoslag sample after 28 days, however the value after 7 days lacks a little to reach the limit.

![Figure 2. Compressive strength of standard mortars with additives.](image)

The dependence between modulus of hydraulicity and strength characteristics is given in figure 3.

![Figure 3. Dependence between modulus of hydraulicity and strength characteristics of standard mortars with additives.](image)

Tight nonlinear dependence was found between modulus of hydraulicity and strength characteristics. R² value of 0.985 was found in case of compressive strength and R² value of 0.981 was found in case of flexural strength.
4. Conclusion

The paper was aimed on testing the technological properties of product "Zeoslag" which consists of 10% of zeolite and 90% of ground granulated blast furnace slag. Both the Perlite and Zeolite were tested for comparison, and also cement as reference material. Mineral additives were tested according to standard for testing the slag - the binder here consists of 50% of additive to be tested and 50% of cement. Normalized sand and water according to standard recipe were used to make a testing mixtures. The chemical analysis confirmed the chemical character of individual additives; the zeolite and perlite are of pozzolanic one, while zeoslag gains latent hydraulic character thanks to GGBFS. To have a standardized consistency, the Zeoslag needs only a bit more water than the reference sample (by 3.6%). Both the Zeolite and Perlite need for more water. Zeolite has the longest initial setting time (320 min). Perlite has higher strength characteristics than zeolite in early ages (2 and 7 days of setting and hardening), but lower after 28 days. After 28 days, the strength characteristics of Zeoslag are close to the reference sample. This is positive finding, taking into account the rate of cement replacement (50%). Regarding dependences between modulus of hydraulicity and strength characteristics, experiment showed tight nonlinear dependence at the given range of modulus of hydraulicity (0.02 – 2.44).

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