

GOSPODARKA SUROWCAMI MINERALNYMI - MINERAL RESOURCES MANAGEMENT

2023 Volume 39 Issue 4 Pages 181–196

DOI: 10.24425/gsm.2023.148163



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An assessment of the influence of selected factors on the activity of cement-slag binders

Introduction

One of the main ingredients of cement, in addition to Portland clinker, is granulated blast furnace slag (BFS), which is a by-product of the production of pig iron in blast furnaces at a temperature of 1300–1500°C. It is formed by melting waste rock from the composition of iron ore, flux (mainly limestone and dolomite) and inorganic parts from the combustion of fuel (coke) (Winnie Matthes et al. 2018). As a lower density component, blast furnace slag flows to the surface of the molten iron in the blast furnace and is removed from the blast furnace at regular intervals. The temperature of the BFS after exiting the blast furnace is around 1400°C, and it is rapidly cooled with a stream of water (Pronina et al. 2018; Qin et al. 2019). This latter process is called granulation and it results in a product called granulated blast furnace slag (GBFS); this form of slag is commonly used in cement formulation

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(EN 197-1:2011) and after grinding, it can also be used in concrete composition as a Type II additive (GGBFS) (EN 206:2013+A1:2016).

Despite the numerous scientific and practical experiences of linking the chemical and physical characteristics of GGBFS to its hydraulic activity (Figure 1) (Polder et al. 2014a; Polder et al. 2014b), it remains the subject of numerous studies and discussions (Zhai and Kurumisawa 2021; Li et al. 2021; Wang, Xu and Huang 2022). Due to the complexity of the chemical composition of slag, especially the chemical composition of the glassy phase and its structure, the influence of, most often, ground (GGBSF) on the properties of mortars and concrete (EN 15167-1:2007; ASTM C989M). A series of equations are also used (Table 1) that relate the hydraulic activity of slag to its chemical (EN 197-1:2011; Polder et al. 2014b). Of primary importance in the hydration of cements containing GGBFS, especially in the early stages, is the glass dissolution process. The rate of the reaction of GGBFS with water is limited. Very quickly, a hardly permeable layer of hydrated calcium-deficient aluminosilicates forms on the surface of the slag grains, which slows down further reaction (Winnie Matthes et al. 2018). Most often, only the presence of activators leads to an increase in the concentration of OH- ions in the pore liquid and the breakdown of this envelope. In conditions of industrial concrete production, the role of the activator is played by Ca (OH)₂ hydroxide from the hydration of silicate phases of Portland clinker. The problem limiting the wider use of blast furnace cement CEM III in construction is the relatively low early strengths of this type of cement (Giergiczny et al. 2002; Polder et al. 2014b; Winnie Matthes et al. 2018; Giergiczny 2019).

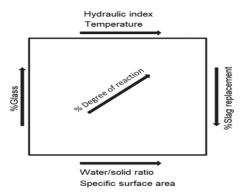


Fig. 1. Factors shaping GGBFS activity (Li et al. 2021)

Rys. 1. Czynniki kształtujące aktywność GGBFS

The aim of this study was to analyze the influence of selected technological factors (the mineral composition of cement, GGBFS grinding grade, cement grinding grade, w/c ratio) on the activity of the cement-slag binder. The activity index was determined according to the methodology contained in (EN 15167-1:2007). The results of the study will be summarized in guidelines for producers and users (mortar and concrete producers) of slag cement.



Table 1 Equations describing the hydraulic activity of the GGBFS (Winnie Matthes et al. 2018)

Tabela 1. Równania opisujące aktywność hydrauliczną GGBFS

| Activity module (M _a) | $M_a = \frac{CaO + MgO}{SiO_2 + Al_2O_3}$ |
|---|---|
| Alkalinity modulus (M _z) | $M_Z = \frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2 + \text{MnO}}$ |
| Activity module (Z) | $Z = \frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2}$ |
| Hydraulic activity module (K) | $K = \frac{Al_2O_3 \cdot CaO}{(Al_2O_3 \cdot SiO_2)^2}$ |
| Hydraulic coefficient (I _h) | $I_{h} = \frac{\text{CaO} + 0.56\text{Al}_{2}\text{O}_{3} + \text{MgO}}{\text{SiO}_{2}}$ |
| Alkalinity modulus | $\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2}$ |
| Nkinamubanzi alkalinity modulus | CaO SiO ₂ |
| Keil F value | $F = \frac{\text{CaO} + 0.5\text{MgO} + \text{Al}_2\text{O}_3 + 0.5\text{SO}_3}{\text{SiO}_2 + \text{MnO}}$ |

1. Characterization of the components used in the tests

The chemical, physical properties and compressive strength of the cements tested were determined according to the methodology contained in EN 196 parts 1, 2, 3 and 6 (EN 196-1:2016; EN 196-2:2016; EN 196-3:2016; EN 196-6:2018). The cements used in the study were four Portland cements CEM I strength class 42.5 and Portland cement CEM I 52.5R obtained from the additional grinding of Portland cement CEM I 42.5R "G". The cements used were differed in both their chemical composition (Table 2) and their mineral composition (Table 3). The mineral composition was calculated according to Bogue's formulas (Locher 2013). The physical properties and compressive strength test results of CEM I Portland cements are shown in Tables 4 and 5.

Portland cements CEM of the 42.5-strength class used in the study had a specific surface area of 3,350 cm²/g (CEM I 42.5N SR/NA) to 4,250 cm²/g (CEM I 42.5R NA), while the CEM I 52.5R Portland cement had a much higher specific surface area of 4,920 cm²/g.

Table 2. Chemical compositions of Portland cements used CEM I

Tabela 2. Składy chemiczne zastosowanych cementów portlandzkich CEM I

| | | Content of the co | omponent (% by weight) in cement | | | | |
|---------------------------------|---|-------------------|----------------------------------|-------------------|-----------------------|-----|-----|
| Ingredient | CEM I 42.5R CEM "G" (producer 1) I 52.5R | | CEM I 42.5R "O" (producer 2) | CEM I 42.5R NA | CEM I 42,5N SR5/NA | | |
| SiO ₂ | 19.8 | | 19.9 | 20.6 | 21.2 | | |
| Al_2O_3 | 5.1 | | 6.2 | 4.7 | 3.6 | | |
| Fe ₂ O ₃ | 2.6 | | 2.7 | 2.8 | 3.2 | | |
| CaO | 64.0 | | 62.6 | 64.4 | 66.0 | | |
| MgO | 1.6 | | 1.5 | 1.2 | 0.7 | | |
| Na ₂ 0 | 0.1 | | 0.1 | | 0.3 | 0.2 | 0.2 |
| K ₂ O | 0.7 | | 0.7 | 0.4 | 0.3 | | |
| Na ₂ O _{eq} | 0.6 | | 0.8 | 0.5 | 0.4 | | |
| SO ₃ | 3.0 | | 2.6 | 2.8 | 2.6 | | |
| Cl | 0.07 | | 0.05 | 0.02 | 0.06 | | |
| Insoluble residue | 0.4 | | 0.8 | 0.6 | 0.5 | | |
| Loss of ignition | 2.8 | | 3.1 | 2.9 | 2.2 | | |

Table 3. Composition of Portland cement phases CEM I

Tabela 3. Skład fazowy cementów portlandzkich CEM I

| | | Content of the co | omponent (% by weight) in cement | | | | |
|-------------------|--|-------------------|----------------------------------|-------------------|-----------------------|--|--|
| Phase component | CEM I 42.5R CEM ,,G" (producer 1) I 52.5R | | CEM I 42.5R "O" (producer 2) | CEM I 42.5R NA | CEM I 42,5N SR5/NA | | |
| C ₃ S | 63 | 9 | 60.7 | 62.4 | 57.7 | | |
| C ₂ S | 8.9 | | 11.6 | 12.2 | 17.5 | | |
| $C_3S + C_2S$ | 72.8 | | 72.3 | 74.6 | 75.2 | | |
| C ₃ A | 9 | .1 | 11.9 | 7.6 | 4.0 | | |
| C ₄ AF | 7.8 | | 8.2 | 8.5 | 9.8 | | |
| CS | 5.1 | | 4.4 | 4.7 | 4.3 | | |

CaO - C, $SiO_2 - S$, $Al_2O_3 - A$, $Fe_2O_3 - F$, $SO_3 - \bar{S}$.



Table 4. Physical properties of Portland cements CEM I

Tabela 4. Właściwości fizyczne cementów portlandzkich CEM I

| | Assay of the cement to be tested | | | | | | | |
|--|------------------------------------|----------------|------------------------------------|-------------------|--------------------------|--|--|--|
| Properties | CEM I 42.5R "G" (producer 1) | CEM I 52.5R | CEM I 42.5R "O" (producer 2) | CEM I 42.5R NA | CEM I 42.5N SR5/NA | | | |
| Specific density (g/cm ³) | 3.10 | 3.11 | 3.07 | 3.09 | 3.11 | | | |
| Volume stability (mm) | 0.4 | 0.4 | 0.2 | 0.4 | 1.0 | | | |
| Start of setting time (mm) | 209 | 167 | 183 | 191 | 165 | | | |
| Specific surface area according to Blaine (cm ² /g) | 3,850 | 4,920 | 4,250 | 3,950 | 3,350 | | | |

Table 5. Compressive strength of tested Portland cements CEM I

Tabela 5. Wytrzymałość na ściskanie badanych cementów portlandzkich CEM I

| Term | Compressive strength (MPa), cement | | | | | | | | | |
|-----------------------|------------------------------------|----------------|---------------------------------|-------------------|-----------------------|--|--|--|--|--|
| of the examination | CEM I 42.5R "G" (producer 1) | CEM I 52.5R | CEM I 42.5R "O" (producer 2) | CEM I 42.5R NA | CEM I 42.5N SR5/NA | | | | | |
| 2 days | 32.2 | 39.6 | 29.4 | 28.4 | 25.7 | | | | | |
| 7 days | 49.8 | 57.5 | 46.4 | 52.2 | 41.4 | | | | | |
| 28 days | 58.6 | 67.9 | 58.6 | 61.4 | 54.8 | | | | | |
| 56 days | 60.2 | 70.1 | 63.4 | 66.4 | 63.8 | | | | | |
| 90 days | 63.7 | 70.6 | 64.9 | 66.6 | 66.4 | | | | | |

Analyzing the phase composition of the tested cements (Table 3), the highest content of tricalcium silicate C_3S (63.9%) was contained in Portland cement CEM I 42.5R "G", while the lowest was in CEM I 42.5N SR5/NA (57.7%), with the latter type having the highest total amount of silicate phases (C_3S and C_2S) – 75.2%; Table 3). Portland cement CEM I 42.5R "O" had the highest content of tricalcium aluminate C_3A (11.6%), and Portland cement CEM I 42.5N SR5/NA had the lowest (4.0%).

Portland cement CEM I 42.5 R and 52.5 R G had the highest early compressive strength (after two days of setting) and Portland cement CEM I 42.5 N SR5/NA had the lowest early compressive strength (Table 5). After twenty-eight days of hardening (the standard term), the tested cements have compressive strengths well above the level required for the declared compressive strength class of the cement.

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In this study, ground granulated blast furnace slag (GGBFS) with the chemical composition listed in Table 6 and a specific surface area was used: 3,600 cm²/g (GGBFS IA), 4,040 cm²/g (GGBFS IB) and 5,020 cm²/g (GGBFS IC). The slag was milled in a laboratory ball mill. The weight ratio of (CaO + MgO)/(SiO₂) in the slag was 1,23 and met the requirements of EN 197-1 (EN 197-1:2011) (minimum 1.0).

Chemical composition of ground granulated blast furnace slag (GGBFS)

Tabela 6. Skład chemiczny zmielonego granulowanego żużla wielkopiecowego (GGBFS)

| Ingredient | CaO | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | MgO | K ₂ O | Na ₂ O | SO ₃ | MnO | Insoluble residue |
|----------------------------------|------|------------------|--------------------------------|--------------------------------|-----|------------------|-------------------|-----------------|-----|-------------------|
| Ingredient content [% by weight] | 42.1 | 39.4 | 7.7 | 1.3 | 6.2 | 0.4 | 0.4 | 1.4 | 0.2 | 0.3 |

Figure 2 presents a diffractogram of ground granulated blast furnace slag made with a Philips PW 1140 diffractometer. The diffractogram shows a characteristic elevation of the background for the glassy phase, while reflections from the crystalline phases are of very low intensity and come from quartz, merwinite calcite and acermanite. The content of the glassy phase in GGBFS, as determined by the optical microscopy method given in Appendix C of PN-B-19707 (PN-B-19707:2012), was 95.9%.

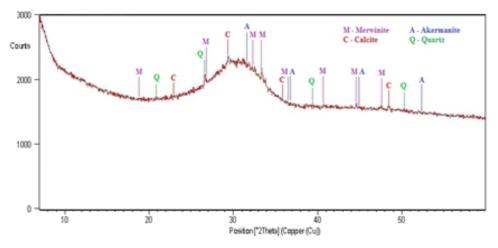


Fig. 2. Diffractogram of granulated blast furnace slag

Rys. 2. Dyfraktogram granulowanego żużla wielkopiecowego



2. Results of activity index studies and their discussion

According to the provisions of EN 15167-1:2007 (EN 15167-1:2007), the activity index of ground granulated blast furnace slag is defined as the ratio of the compressive strength of standard mortar made from a binder consisting of 50% (by weight) of ground granulated blast furnace slag and 50% (by weight) of Portland cement CEM I comparative to the compressive strength of mortar made from Portland cement CEM I (100%) comparative. As required by the standard (EN 15167-1:2007), the size of the activity index after seven days of setting should be \geq 45% of the strength of CEM I comparative cement, and after twenty-eight days of setting, it should be \geq 70%.

Strength tests were conducted on standard mortars prepared in accordance with EN 196-6 standard (EN 196-6:2018). The specimens, measuring 40 mm x 40 mm x 160 mm, were stored for the first twenty-four hours in a climatic chamber where the temperature was maintained at $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and humidity at $95\% \pm 5\%$. After unmolding, the samples were then stored in water at $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for periods of 1 day, 6 days, 27 days, 55 days, 89 days, 179 days and 359 days. Based on the strength test results obtained, activity indices were determined for granulated blast furnace slag over a much wider range than required by the standard (Zhai and Kurumisawa 2021), specifically after 2, 7, 28, 56, 90, 180 and 360 days of setting.

Table 7. Compressive strengths of the cement-slag binder (GGBFS IA – specific surface area 3,600 cm²/g)

| Tabela 7. Wytrzymałości na ściskanie spoiwa cementowo-żużlowego (GGBFS IA – pow. wł. 3600 cm ² / | Tabela 7. | Wytrzymałości na ściskanie s | spojwa cementowo-żużlowego | (GGBFS IA - pow. wł | $3600 \text{ cm}^2/\text{g}$ |
|---|-----------|------------------------------|----------------------------|---------------------|------------------------------|
|---|-----------|------------------------------|----------------------------|---------------------|------------------------------|

| | Specific | Compressive strength (MPa) after | | | | | | |
|---|---|----------------------------------|-----------|------------|------------|------------|-------------|-------------|
| Type of binder | surface area of binder (cm ² /g) | 2 days | 7 days | 28 days | 56 days | 90 days | 180 days | 360 days |
| CEM I 42.5R "G" (100%) | 3,580 | 32.3 | 49.8 | 58.6 | 60.2 | 63.7 | 68.5 | 73.1 |
| CEM I 42.5R "G" (50%) + + GGBFS (50%) | 3,590 | 11.2 | 27.8 | 47.9 | 56.0 | 58.7 | 62.7 | 66.1 |
| CEM I 42.5R "O" (100%) | 4,390 | 29.4 | 46.4 | 58.6 | 63.4 | 64.9 | 65.2 | 69.4 |
| CEM I 42.5R "O" (50%) + + GGBFS (50%) | 3,990 | 9.4 | 20.6 | 48.3 | 60.1 | 64.7 | 67.8 | 71.4 |
| CEM I 42.5R NA (100%) | 3,807 | 28.4 | 52.2 | 61.4 | 66.4 | 66.6 | 69.4 | 74.2 |
| CEM I 42.5R NA (50%) + + GGBFS (50%) | 3,700 | 11.1 | 29.7 | 54.1 | 60.6 | 64.2 | 66.4 | 76.7 |
| CEM I 42.5N SR5/NA (100%) | 3,286 | 25.7 | 41.4 | 54.8 | 63.8 | 66.4 | 68.6 | 71.5 |
| CEM I 42.5N SR5/NA (50%) + GGBFS (50%) | 3440 | 11.0 | 23.3 | 45.8 | 53.6 | 58.3 | 63.6 | 71.1 |

Table 8. Compressive strengths of the cement-slag binder (GGBFS IB – specific surface area 4,040 cm²/g)

Tabela 8. Wytrzymałości na ściskanie spoiwa cementowo-żużlowego (GGBFS IB – pow. wł. 4040 cm²/g)

| | Specific | Compressive strength (MPa) after | | | | | | |
|---|--|----------------------------------|-----------|------------|------------|------------|-------------|-------------|
| Type of binder | surface area of binder (cm ² /g) | 2 days | 7 days | 28 days | 56 days | 90 days | 180 days | 360 days |
| CEM I 42.5R "G" (100%) | 3578 | 32.3 | 49.8 | 58.6 | 60.2 | 63.7 | 68.5 | 73.1 |
| CEM I 42.5R "G" (50%) + + GGBFS (50%) | 3810 | 11.8 | 29.7 | 52.2 | 59.8 | 63.0 | 62.7 | 66.1 |
| CEM I 42.5R "O" (100%) | 4390 | 29.4 | 46.4 | 58.6 | 63.4 | 64.9 | 65.2 | 69.4 |
| CEM I 42.5R "O" (50%) + + GGBFS (50%) | 4216 | 9.5 | 21.2 | 51.2 | 61.1 | 64.2 | 68.6 | 73.3 |
| CEM I 42.5R NA (100%) | 3807 | 28.4 | 52.2 | 61.4 | 66.4 | 66.6 | 69.4 | 74.2 |
| CEM I 42.5R NA (50%) + + GGBFS (50%) | 3924 | 11.8 | 29.8 | 57.4 | 63.0 | 63.5 | 70.1 | 74.0 |
| CEM I 42.5N SR5/NA (100%) | 3286 | 25.7 | 41.4 | 54.8 | 63.8 | 66.4 | 68.6 | 71.5 |
| CEM I 42.5N SR5/NA (50%) + GGBFS (50%) | 3664 | 11.1 | 25.8 | 48.2 | 57.4 | 60.5 | 64.8 | 69.3 |

Table 9. Compressive strengths of the cement-slag binder (GGBFS IC – specific surface area 5,020 cm²/g)

Tabela 9. Wytrzymałości na ściskanie spoiwa cementowo-żużlowego (GGBFS IC – pow. wł. 5020 cm²/g)

| | Specific | Compressive strength (MPa) after | | | | | | |
|---|---|----------------------------------|-----------|------------|------------|------------|-------------|-------------|
| Type of binder | surface area of binder (cm ² /g) | 2 days | 7 days | 28 days | 56 days | 90 days | 180 days | 360 days |
| CEM I 42.5R "G" (100%) | 3,578 | 32.3 | 49.8 | 58.6 | 60.2 | 63.7 | 68.5 | 73.1 |
| CEM I 42.5R "G" (50%) + + GGBFS (50%) | 4,300 | 12.3 | 31.4 | 53.8 | 61.0 | 63.1 | 67.1 | 71.6 |
| CEM I 42.5R "O" (100%) | 4,390 | 29.4 | 46.4 | 58.6 | 63.4 | 64.9 | 65.2 | 69.4 |
| CEM I 42.5R "O" (50%) + + GGBFS (50%) | 4,705 | 9.8 | 22.6 | 53.6 | 63.0 | 64.4 | 69.0 | 71.1 |
| CEM I 42.5R NA (100%) | 3,807 | 28.4 | 52.2 | 61.4 | 66.4 | 66.6 | 69.4 | 74.2 |
| CEM I 42.5R NA (50%) + + GGBFS (50%) | 4,414 | 13.0 | 32.3 | 60.7 | 67.8 | 68.5 | 72.9 | 76.2 |
| CEM I 42.5N SR5/NA (100%) | 3,286 | 25.7 | 41.4 | 54.8 | 63.8 | 66.4 | 68.6 | 71.5 |
| CEM I 42.5N SR5/NA (50%) + GGBFS (50%) | 4,153 | 11.5 | 26.5 | 54.9 | 62.6 | 65.2 | 68.7 | 70.1 |

■ 360 days

CEM I

42.5N

SR5/NA



The obtained activity index values were analyzed in two periods – from 2 to 28 days of setting and from 28 days to 360 days. Tables 7 to 9 show the results of compressive strength tests of cement-slag binders, and Figures 3 to 5 present the obtained activity indexes.

Analyzing the test results in Tables 7 to 9 and Figures 3 to 5, the introduction of 50% ground GGBFS into the composition of cement causes a significant decrease in compressive strength in the initial period of setting (two and seven days), as can be seen in Figure 6. Increasing the fineness of GGBFS causes a slight increase in early strength (Figure 6). Such a significant decrease in strength limits the wider use of blast furnace cements CEM III/A,B in fine- and large-scale prefabrication and during periods of reduced outdoor temperature (in Polish conditions during autumn and winter).

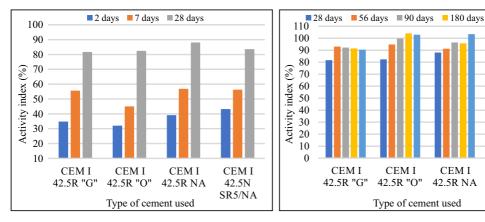


Fig. 3. Activity indicators with GGBFS IA slag

Rys. 3. Wskaźniki aktywności z użyciem żużla GGBFS IA

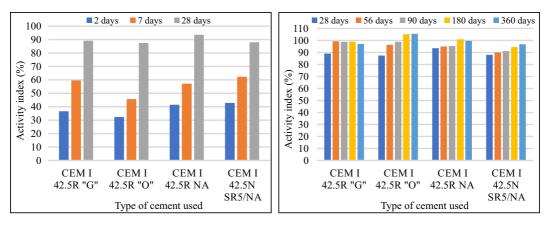


Fig. 4. Activity indicators with GGBFS IB slag

Rys. 4. Wskaźniki aktywności z użyciem żużla GGBFS IB



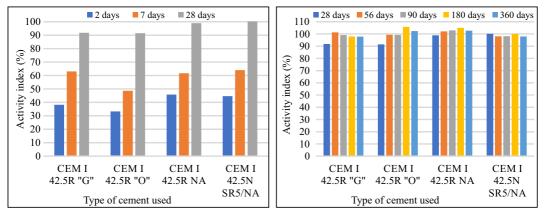


Fig. 5. Activity indicators with GGBFS IC slag

Rys. 5. Wskaźniki aktywności z użyciem żużla GGBFS IC

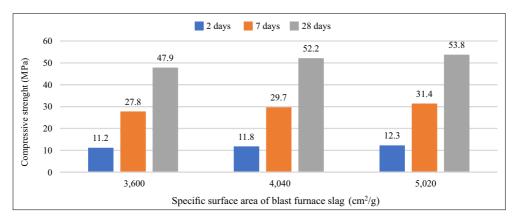


Fig. 6. Specific surface area of blast furnace slag vs. compressive strength of the binder (Portland cement CEM I 42.5R "G")

Rys. 6. Powierzchnia właściwa żużla wielkopiecowego a wytrzymałość na ściskanie spoiwa (cement portlandzki CEM I 42,5R "G")

The effect of the degree of grinding of cement (Portland clinker) on the level of the early strength of a binder containing 50% ground slag was analyzed. The results in Figure 7 indicate that this is a more efficient way of obtaining higher early compressive strengths than the grinding of slag. This is also an important economic factor because slag grinding is much more difficult (the material is much harder than Portland clinker), which is important in terms of electricity consumption for grinding and the efficiency of the grinding plant. The higher degree of grinding of cement accelerates the cement setting and hardening process (degree of over milling) and the amount of Ca (OH)₂ from the hydration of silicate phases

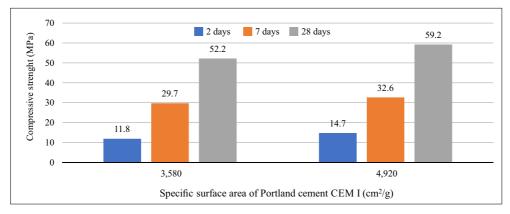


Fig. 7. Specific surface area of Portland cement CEM I and binder compressive strength (blast furnace slag with an area of $4,040~{\rm cm^2/g}$)

Rys. 7. Powierzchnia właściwa cementu portlandzkiego CEM I a wytrzymałość na ściskanie spoiwa (żużel wielkopiecowy o powierzchni 4040 cm²/g)

of Portland clinker (C₃S and C₂S) increases, and thus the activation process of GGBFS becomes more efficient.

The content of calcium silicates ($C_3S + C_2S$) was the lowest in Portland cement CEM I 42,5R "O" and amounted to 72.3%, while in Portland cements CEM I 42,5N SR5/NA and CEM I 42,5R NA the total content of C_3S and C_2S was the highest and amounted to about 75% (Figure 8). The results in Figure 7 show that cements containing a high content of silicate phases, especially C_3S , have the highest activity index. The product of C_3S allite hydration is the C-S-H phase and calcium hydroxide Ca (OH)₂, which affects the pH in the pore liquid.

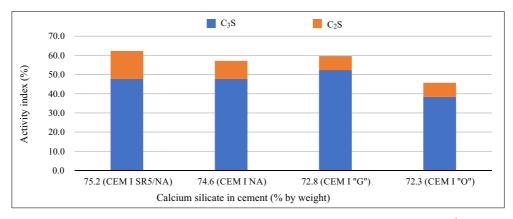


Fig. 8. Calcium silicate content (C₃S + C₂S) in Portland cements (blast furnace slag 4,040 cm²/g)

Rys. 8. Zawartość krzemianów wapnia (C₃S + C₂S) w cementach portlandzkich (żużel wielkopiecowy o powierzchni 4040 cm²/g)

Analyzing the relationship between the magnitude of the activity index and the content of tricalcium aluminate (C₃A), a trend can be observed that as the content of this phase in the cement increases, the activity indices decrease during the initial hardening period (after seven days of maturation), as shown in Figure 9. The highest seven-day activity indices were obtained on Portland cement CEM I 42.5N SR5/NA with a phase content of C₃A – 4.0%.

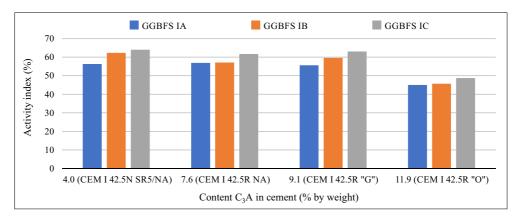


Fig. 9. Correlation between C₃A content in cement and seven-day activity index

Rys. 9. Zależność pomiędzy zawartością C₃A w cemencie a siedmiodniowymi wskaźnikami aktywności

At later setting times (twenty-eight days and longer), the activity index of all tested cement-slag binders reaches a level of 90.0% to 106.0% (Figures 3 to 5), which fully confirms the fact known from the literature that at later setting times, the compressive strength (durability) of cement-slag binders is comparable to that of cement composites on Portland cement CEM I (Ueki 2015; Matthes et al. 2018; Qin et al. 2019). This also confirms the desirability of the provisions in PN-B-06250 (PN-B-06265:2018-10) with regard to determining the durability characteristics of concrete on blast furnace cement CEM III at an equivalent time, i.e. ninety days after setting, and not after twenty-eight days, as is generally accepted in the construction industry.

An important factor affecting the strength levels of cement mortars and concretes is the water/cement ratio (w/c), and in the case of cement-slag binders, the w/s ratio, where s = cement + slag). Figure 10 shows the obtained compressive strength levels of mortars of standard composition made with w/s ratios of 0,3, 0,4 and 0,5.

It is evident that this is the most effective way to increase the compressive strength of the cement-slag binder, both the early strength and the normal strength (twenty-eight days after setting). The obtained compressive strengths two days after setting at w/s 0,3 and 0,4 allow a much wider use of blast furnace cements CEM III/A,B (EN 197-1:2011) containing 50.0% and more GGBFS in prefabrication and concretes with high compressive strength classes.

Fig. 10. Effect of w/s ratio on compressive strength of binder 50% CEM I 42.5R "G" + 50% GGBFS IB)

Rys. 10. Wpływ stosunku w/s na wytrzymałość na ściskanie spoiwa 50% CEM I 42,5R "G" + 50% GGBFS IB)

Increasing the proportion of GBFS in the composition of cement also has a certain environmental effect. Assuming a CO₂ emission level from the production of 1 Mg of clinker of about 800 kg (Ueki 2015), the use of 1 mln GBFS in the cement composition reduces CO₂ emissions by about 800 Mg. It is also reduced by about 1.7 million tons of natural raw materials, mainly limestone and marl, needed to produce 1 million tons of Portland clinker (SPC 2020).

Conclusions

The study confirmed that ground granulated blast furnace slag is a full-value cement component and a Type II additive in the formulation of concrete. It is the closest to the standard non-clinker main component of cement in terms of chemical and phase composition.

An impediment to the widespread use of cement-slag binders (slag cements) containing 50% GGBFS or more is the low early strength (low activity indices) during the initial setting period (after two and seven days). The results showed that milling GBFS to high specific surfaces is an energy-intensive and inefficient process. Higher activity indices are obtained by the finer grinding of Portland cement (Portland clinker) to a higher specific surface area.

Through analyzing the effect of the phase composition of cement on the level of compressive strength, it can be concluded that cements containing higher contents of silicate phases $(C_3S + C_2S)$ have higher activity indexes, while Portland cement with the highest content of tricalcium aluminate (C₃A) had the lowest activity index magnitudes.

The most effective strategy for increasing the early and normal compressive strength of cement composites is to lower the water/binder (w/s) ratio by using the latest genera-



tion of chemical liquefaction admixtures (superplasticizers). The achieved levels of early strength at low w/s enables the wider use of blast furnace cements in all areas of construction, starting with concrete accessories through large-dimensional precast and ending with high-strength concretes.

Compressive strength levels of cement-slag binders (blast furnace cements) twenty-eight days after setting and beyond (tested up to 365 days) are close to or higher than the compressive strength level of Portland cement CEM I.

Increasing the share of GGBFS in the composition of cement leads to a significant reduction in CO₂ emissions from the production of Portland clinker and a significant reduction in the consumption of natural resources in its production process.

REFERENCES

ASTM C989/C989M-18a - Standard Specification for Slag Cement for Use in Concrete and Mortars.

EN 15167-1:2007 – Ground granulated blast furnace slag for use in concrete, mortar and grout – Part 1: Definitions, specifications and conformity criteria.

EN 196-1:2016 – Methods of testing cement – Part 1: Determination of strength.

EN 196-2:2016 - Methods of testing cement - Part 2: Chemical analysis of cement.

EN 196-3:2016 - Methods of testing cement - Part 3: Determination of setting times and soundness.

EN 196-6:2018 – Methods od testing cement – Part 6: Determination of fineness.

EN 197-1:2011 - Cement - Part 1: Composition, specifications and conformity criteria for common cements.

EN 206:2013+A1:2016 - Concrete - Specification, performance, production and conformity.

Giergiczny, Z. 2002. Cements with mineral additives in new generation concrete technology (*Cementy z dodatkami mineralnymi w technologii betonów nowej generacji*). Opole: Górażdże Cement SA (*in Polish*).

Giergiczny, Z. 2019. Fly ash and slag. Cement and Concrete Research 124, DOI: 10.1016/j.cemconres.2019.105826.

Li et al. 2021 – Li, J., Zhang, W., Garbev, K. AND Monteiro, P.J.M. 2021. Coordination environment of Si in calcium silicate hydrates, silicate minerals and blast furnace slags: A XANES database. *Cement and Concrete Research* 143(2), DOI: 10.1016/j.cemconres.2021.106376.

Liu et al. 2019 – Liu J., Yu, Q., Zuo, Z., Yang, F., Han, Z. and Qin, Q. 2019. Reactivity and performance of dry granulation blast furnace slag cement. *Cement and Concrete Composites* 95, pp. 19–24, DOI: 10.1016/j.cemconcomp.2018.10.008.

Locher, F.W. 2013. Cement: principles of production and use.

Matthes et al. 2018 – Matthes, W., Vollpracht, A., Villagrán-Zaccardi, Y., Kamali-Bernard, S., Hooton, D., Gruyaert, E., Soutsos, M. and De Belie, N. 2018. Ground granulated blast-furnace slag. RILEM State-of-the-Art Reports. [In:] Properties of fresh and hardened concrete containing supplementary cementitious materials. DOI: 10.1007/978-3-319-70606-1 1.

PN-B-06265:2018-10: Concrete – Requirements, properties, production and conformity – National additions to EN 206+A1:2016-12 (Beton – Wymagania, właściwości, produkcja i zgodność – Krajowe uzupełnienie PN-EN 206+A1:2016-12) (in Polish).

PN-B-19707:2012: Cement. Special cement. Composition, requirements and conformity criteria (in Polish).

Polder et al. 2014a – Polder, R.B., Nijland, T., de Rooij, M., Larsen, C.K. and Pedersen, B. 2014. *Innovation Based on Tradition: Blast Furnace Slag Cement for Durable Concrete Structures in Norway?*

Polder et al. 2014b – Polder, R.B., Nijland, T.G. and de Rooij, M.R. 2014. Slag cement concrete – the Dutch experience. Statens Vegvesenes Rapoorter.

Pronina et al. 2018 – Natalja Pronina, N., Krüger, S., Bornhöft, H., Deubener, J. and Ehrenberg, A. 2018. Cooling history of a wet-granulated blast furnace slag (GBS). *Journal of Non-Crystalline Solids* 499(3), pp. 344–349, DOI: 10.1016/j.jnoncrysol.2018.07.054.

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- SPC 2020. Cement industry's contribution to the Polish economy. Report. [Online:] https://www.polskicement.pl/ wp-content/uploads/2020/10/EY-Raport-wp%C5%82ywu-podsumowanie-EN.pdf [Accessed: 2023-10-10].
- Ueki, Y. 2015. History and Utilization of Portland Blast Furnace Slag Cement. Nippon steel & sumitomo metal technical report 109, pp. 109-113.
- Wang et al. 2022 Wang, Y., Xu, L., He, X., Su, Y., Miao, W., Strnadel, B. and Huang, X. 2022. Hydration and rheology of activated ultra-fine ground granulated blast furnace slag with carbide slag and anhydrous phosphogypsum. Cement and Concrete Composites 133, DOI: 10.1016/j.cemconcomp.2022.104727.
- Zhai, Q. and Kurumisawa, K. 2021. Effect of accelerators on Ca(OH)₂ activated ground granulated blast-furnace slag at low curing temperature. Cement and Concrete Composites 124, DOI: 10.1016/j.cemconcomp.2021.104272.
- Zhai, Q. and Kurumisawa, K. 2022. Effects of cation in sulfate chloride and nitrite on Ca(OH)2 activated ground granulated blast-furnace slag. Cement and Concrete Composites 133, DOI: 10.1016/j.cemconcomp.2022.104648.

AN ASSESSMENT OF THE INFLUENCE OF SELECTED FACTORS ON THE ACTIVITY OF CEMENT-SLAG BINDERS

Keywords

granulated blast furnace slag, activity index, degree of grinding, w/s ratio, blast furnace cement CEM III

Abstract

The article analyzes the influence of selected factors on the activity rate of cement binder containing 50% of ground granulated blast furnace slag in its composition. These factors are the chemical and mineral composition of Portland cement CEM I, the degree of grinding of granulated blast furnace slag and Portland cement, and the water/binder ratio. This slag content is characteristic for blast furnace cement CEM III/A. In addition to the application effects, this type of cement is a low-carbon binder (there is a reduction of CO₂ emissions by about 45% compared to Portland cement CEM I). The use of this type of cement in the composition of concrete enables the obtaining of concrete with a very small carbon footprint. Based on the results of our own research, it was found that such a high proportion of ground granulated blast furnace slag in the binder composition leads to a significant reduction in the early compressive strength of standard mortars (after two and seven days of setting). This results in a significant reduction in the use of these types of binders (cements) in selected areas of construction, e.g. prefabrication and high-strength concrete. Analyzing the obtained results of their own research, the authors concluded that the early strength of these types of binders can be significantly improved by increasing the specific surface area (degree of grinding) of Portland cement CEM I and lowering the water/slag ratio (w/s, where: s = cement + slag). The proposed material and technological modifications also enable the obtaining of higher compressive strength at all tested dates. The strength of the standard (after twenty-eight days and over longer periods) is comparable to or higher than that of Portland cement CEM I.

OCENA WPŁYWU WYBRANYCH CZYNNIKÓW NA AKTYWNOŚĆ SPOIW CEMENTOWO-ŻUŻLOWYCH

Słowa kluczowe

granulowany żużel wielkopiecowy, wskaźnik aktywności, stopień rozdrobnienia, stosunek w/s, cement hutniczy CEM III

Streszczenie

W artykule przeanalizowano wpływ wybranych czynników: składu chemicznego i mineralnego cementu portlandzkiego CEM I, stopnia przemiału granulowanego żużla wielkopiecowego i cementu portlandzkiego oraz stosunku woda/spoiwo na kształtowanie się wskaźnika aktywności spoiwa cementowo-żużlowego zawierającego w swoim składzie 50% zmielonego granulowanego żużla wielkopiecowego. Taka zawartość żużla jest charakterystyczna dla cementu hutniczego CEM III/A. Oprócz efektów aplikacyjnych, ten rodzaj cementu jest spoiwem niskoemisyjnym (redukcja emisyjności CO₂ o około 45% w stosunku do cementu portlandzkiego CEM I). Stosowanie tego rodzaju cementu w składzie betonu pozwala na uzyskanie betonu o bardzo małym śladzie węglowym. Na podstawie wyników badań własnych stwierdzono, iż tak wysoki udział zmielonego granulowanego żużla wielkopiecowego w składzie spoiwa prowadzi do znaczącego obniżenia wytrzymałości na ściskanie wczesnej (po 2 i 7 dniach dojrzewania) zapraw normowych. Skutkuje to znaczącym ograniczeniem stosowaniem tego rodzaju spoiw (cementów) w wybranych obszarach budownictwa, np. prefabrykacji i betonach wysokich wytrzymałości. Analizując uzyskane wyniki badań własnych autorzy doszli do wniosku, że wytrzymałość wczesną tego rodzaju spoiw można znacząco polepszyć poprzez zwiększenie powierzchni właściwej (stopnia przemiału) cementu portlandzkiego CEM I i obniżenie stosunku woda/spoiwo (w/s, gdzie: s = cement + żużel). Zaproponowane modyfikacje materiałowo-technologiczne pozwalają także na uzyskanie wyższych wytrzymałości na ściskanie we wszystkich badanych terminach. Wytrzymałość normowa (po 28 dniach) i w dłuższych terminach jest porównywalna lub wyższa niż cementu portlandzkiego CEM I.