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Strength development of calcium aluminate cement with slag

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Abstract

Calcium aluminate cement is used for various applications, in building chemistry, refractory and sewer rehabilitation industry, but its use for structural applications is limited because of the conversion process and limited amount of raw material for production. The addition of Ground Granulated Blast Furnace Slag (GGBFS) can inhibit the conversion process and prevent significant decrease in compressive strength. Moreover, the use of slag as a cement substitute has positive impact on the CO_2 footprint for cement industry. The aim of this paper is to present the influence of different types of GGBFS on mechanical properties of calcium aluminate cement mortar.

Key words: calcium aluminate cement, conversion, slag, stratlingite, compressive strength

Razvoj čvrstoće kalcij-aluminatnog cementa sa zgurom

Sažetak

Kalcij aluminatni cement koristi se za različite primjene, ali upotreba je ograničena zbog procesa konverzije i ograničene količine osnovne sirovine. Dodatak zgure može ublažiti proces konverzije i spriječiti nagli pad tlačne čvrstoće. Također, upotreba zgure kao zamjene za cement smanjuje negativan utjecaj proizvodnje cementa na okoliš. Cilj ovog rada je prikazati utjecaj nekoliko vrsta zgure različitog kemijskog sastava na razvoj tlačne čvrstoće morta s kalcij aluminatnim cementom.

Ključne riječi: kalcij aluminatni cement, proces konverzije, zgura, stratlingit, tlačna čvrstoća

1 Introduction

Calcium aluminate cement (CAC) has been used in the construction industry for more than 100 years and was patented in 1908 by Jules Bied. It was originally used to increase cement resistance to aggressive sulfates and chloride attacks [1]. In relation to Portland cement, other advantages also occur, such as rapid early strength gain, high wear resistance, and resistance to various chemical activities. Due to its unique properties, it is used for various purposes, some of them being emergency and rapid repairs, dam overflows, sewers, industrial floors, as a refractory material, for concreting in cold conditions and in grout mixes for tunnel linings [2,3]. Although it is used for various applications and is one of the most important non-Portland cements, its application is limited due to occurrence of conversion phenomena and limited quantity of the raw material (high quality bauxite) [2]. The production of calcium aluminate cement is 2 million t / year [4] and it is more expensive than Ordinary Portland Cement (OPC) [5]. Basic raw materials for the production of calcium aluminate cement are bauxite and limestone. The raw materials are blended, homogenized, and then melted or sintered at temperatures above 1450 °C (depending on the Al_2O_3 content) [4]. Accordingly, chemical composition of calcium aluminate cement differs from that of Ordinary Portland Cement (OPC). CAC contains higher proportion of alumina and lower proportion of silica compared to OPC [6].

Cement hydration is a chemical process in which minerals react with water to form hydration products. CAC has different hydration products compared to Portland cement. Monocalcium aluminate (CA) is the main phase of the calcium aluminate cement [7]. In contact with water, calcium (Ca^{2+}) and aluminate ($Al\,(OH)_4^-$) ions form four main phases during cement hydration. The first phases, CAH_{10} and C_2AH_8, are referred to as metastable hydrates. Over time, a stable C_3AH_6 hydrate forms from the metastable hydrates [4,5]. With the appearance of C_3AH_6, an AH_3 gel is formed, and water is subsequently released. The conversion process is highly dependent on the temperature and relative humidity of the environment. The conversion is a thermodynamically unavoidable process [7]. The metastable hydrate CAH_{10} forms at temperatures < 15 °C. At temperatures > 30 °C, the initial form of metastable hydrate is C_2AH_8, while at temperatures between 15 °C and 30 °C, both metastable hydrate and AH_3 gel are formed [1,5]. When the temperature rises above 30 °C, the reaction kinetics increases and C_3AH_6 and AH_3 are formed in a short time. The temperature to which the material is exposed determines relative amounts of hydrates formed during hydration of the calcium aluminate cement. Stable hydrates are formed after a certain period of time when the material is exposed to sufficient relative humidity and if temperature of the material is above 20 ° C for at least a certain part of the material's lifetime [5]. The CA hydration process is shown in the following equations [1, 5, 7, 8, 9]:

$$CA + 10H \rightarrow CAH_{10} \tag{1}$$

$$2CA + 11H \rightarrow C_2AH_8+AH_3 \tag{2}$$

$$3CA + 12H \rightarrow C_3AH_6+2AH_3 \tag{3}$$

$$3C_2AH_8 \rightarrow 2C_3AH_6+AH_3+9H \tag{4}$$

$$3CAH_{10} \rightarrow C_3AH_6+2AH_3+18H \tag{5}$$

These reactions take place in the presence of a solution. The reaction phases are dissolved and the products precipitate from the solution. When stable hydrates begin to form, they will be formed even if the temperature drops during the curing time. The low-density hexagonal phases of metastable hydrates (CAH_{10} and C_2AH_8) fill the space at the beginning of the CAC cement hydration, conferring higher early strength. However, cubic phases of stable hydrates (C_3AH_6 and AH_3) form during the conversion process, decreasing the compressive strength [1,7]. The porosity of the cement matrix increases, which also leads to a decrease in strength, and the bonds between C_3AH_6 and AH_3 become weaker than the bonds between CAH_{10} and C_2AH_8 even at similar porosity [10]. Furthermore, when the minimum strength is reached, the water released by the conversion process can still participate in the hydration of the remaining (non-hydrated) cement particles and thus increase the long term strength [7, 8].

The aim of this study was to investigate in which way the replacement of 30 % of calcium aluminate cement with slag influences development of compressive strength of CAC mortar. Five mixtures with laboratory milled slag, one mixture with industrially milled slag, one mixture with quartz, and one reference mix, were prepared. The specimens were cured in water bath at 20 °C. The compressive strength of all mortar mixtures was monitored for 28 days.

2 Effect of CAC replacement by slag on compressive strength

The influence of the conversion process on compressive strength can be reduced by the use of chemical and / or mineral additives. Most studies have been carried out with the addition of pozzolanic materials such as slag, fly ash, and silica fume [11,12]. Unground BFS (blast furnace slag) has a maximum particle size of 5 mm and is predominantly glassy. The high glass content allows latent hydraulic reactivity, which in turn enables the use of slag in the production of composite cements and for concrete production as a cement substitute. In order to achieve slag compatibility with cement and higher reactivity, the slag in grains must be milled into smaller particle sizes [13]. The addition of slag alters hydration products of CAC cement. Slag contains 32-42 % of silicon dioxide (SiO_2) in its chemical composition [13]. A large amount of SiO_2 in the composition of slag forms compounds that inhibit the conversion process in the conversion of hydrates [3]. Silica reacts with calcium aluminate cement hydrates to form C_2ASH_8 hydrate (Stratlingite or Gehlenite hydrate) [1,3,10,14]. The amount of C_2ASH_8 formed depends on the activation ability of slag to release silica. The activation is assisted by a small amount of alkali metal hydroxide phases in the CA cement [15]. The C_2ASH_8 hydrate formation process is shown in the following equations [1]:

$$2CAH_{10} \xrightarrow{S} C_2ASH_8 + AH_3 + 9H \quad (6)$$

$$C_2AH_8 \xrightarrow{S} C_2ASH_8 \quad (7)$$

The reaction of silica with CAC hydrates reduces the formation of C_2AH_8, and C_2ASH_8 is formed at the same time, depending on the amount of slag with which the cement is replaced. This reaction is beneficial because it reduces the effects of the conversion process, and so no significant decrease in compressive strength can be expected [1,16]. Moreover, the strength increases continuously until the hydration process is completed. The slag has a favourable effect on mechanical properties up to a certain percentage of replacement. If the replacement percentage is too high, the hydraulic phases in the composition are reduced and a large amount of unreacted slag particles ultimately remain. The hydration of unhydrated CAC particles is hindered, resulting in the decrease of compressive strength.

Previous studies by Kirca [16] have shown that a 20 % replacement of cement by slag has no significant effect on the hydration products formed during the hydration of CAC. The conversion of metastable hydrates to stable hydrates was not hindered, suggesting that the addition of 20 % slag is not sufficient to avoid a reduction in strength during the conversion process. On the other hand, if the replacement percentage is increased to 40 %, 60 % and 80 %, the strength reduction after 28 days is avoided due to formation of sufficient amount of Stratlingite [16].

In addition, the formation of C_2ASH_8 (Stratlingite) depends on the temperature to which the sample is exposed. As the curing temperature increases, Stratlingite is formed more slowly than C_3AH_6 and cannot completely replace it. Thus, Kirca et al. [10] conducted a study on the effect of curing temperature and percentage of cement replacement by slag on the development of compressive strength of mortar. The authors concluded that mixes with 20 % replacement by slag cured at a temperature of 20 °C reached the maximum strength after 28 days. When cured at 30 °C, 40 °C and 50 °C, the maximum compressive strength is reached after 210 days, regardless of the curing temperature. Even when 40 % is replaced by slag, the compressive strength increases continuously irrespective of the curing temperature. There is no visible decrease in strength over time due to the formation of Stratlingite instead of the conversion of CAH_{10} hydrate to C_3AH_6 hydrate. The ability to form Stratlingite is reduced at higher temperatures (50 °C) due to faster formation of C_3AH_6 hydrates. Therefore, the lowest strengths are obtained by curing samples at 50 °C. The favourable influence of slag on the development of compressive strength was also confirmed by Majumdar et al. [15]. They investigated the development of compressive strength of concrete with the addition of slag depending on the w/c ratio and curing temperature. Specimens were cured at temperatures of 20 °C and 40 °C. It was concluded that by replacing cement with a 50 % of slag prevents reduction in strength caused by conversion process.

The development of compressive strength mainly depends on the percentage of cement replacement by mineral additive, curing temperature and relative humidity. From the above examples, it can be concluded that the addition of slag has a positive effect on the development of CAC strength at later ages, but the main disadvantage of replacing cement with slag is that an increase in the percentage of replacement reduces the early strength of the concrete. By replacing the cement with a sufficient amount of slag (up to 50 %), the conversion process can be mitigated or even prevented.

3 Mechanical properties of calcium aluminate cement with slags

The research presented in this paper is carried out as part of the EU project “Development of a new innovative ECO_2Flex product“under the coordination of Calucem. The aim of the project is to develop an innovative technological solution in the construction industry to reduce CO_2 emissions and energy in the production of cement. In order to minimize the impact of CO_2 emissions, a part of the CAC will be replaced by supplementary cementitious materials (SCM). To evaluate the impact of replacing the CAC with slag, 30 % of cement was replaced with slag. Five laboratory milled BFS samples (S1, S2, S3, S4, S5) and one industrially milled slag sample (S6) were investigated. In addition, a mixture with 30 % replacement by quartz (Q) and a reference mix (CAC) were prepared. A special calcium aluminate cement produced by Calucem was used. CEN standard sand and tap water were used to prepare the mortar mixes. The slags were first dried in an oven at 105 °C for 24 hours and then milled in a laboratory disk mill for 5 minutes. The compressive strength of mixes was determined according to EN 14647. The composition of the mortar was 1350 g CEN standard sand, 500 g binder (CAC and/or slag and/or Quartz), and 200 g water. The water to binder ratio was 0.4 for all mortar mixes. Before mortar casting, all components were conditioned at 20 °C. The specimens were covered and stored for 6h in metal moulds measuring 40x40x160 mm in a humidity chamber at 20 °C, with a relative humidity of 95 %. After 6h, the specimens were demoulded and tested for the six-hour compressive strength. The remaining specimens for testing compressive strength after 24h, 7d and 28d were stored in water at 20 °C in the humidity chamber until the day of testing.

3.1. Characterization of slag

Main chemical constituents of all slags used are SiO_2, CaO and Al_2O_3. Compared to CAC cement, all slags have a significantly higher amount of SiO_2 and lower amount of Al_2O_3. The glass content of all slags was higher than 99 % determined by quantitative X ray diffraction using the Rietveld method. Five of the slags (S1, S2, S3, S4, S5) were obtained in grains (d_{50}=0,66 to 1,2 mm) and one was obtained industrially milled (S6). In order to achieve slag compatibility with cement, and to ensure higher reactivity, the slag in grains was milled for 5 minutes in a laboratory disk mill. Prior to milling, the slags were dried in oven for 24h at 105 °C due to their varying moisture content. The particle size distribution by laser diffraction for all slags, quartz powder, and CAC, is shown in Figure 1.

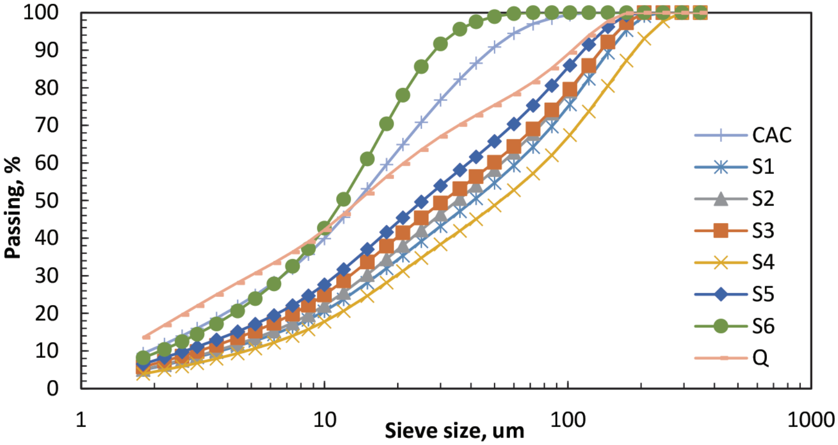

Figure 1. Particle size distribution of slags and CAC

The results show a similar particle size distribution for all laboratory-milled slags. The values of Blaine, d_{10}, d_{50} and d_{90} of slag, quartz and calcium aluminate cement used, are shown in Table 1. It can be observed that slag that was industrially milled (S6) had the finest particle size distribution compared to other slags, but also compared to cement and quartz used in this study.

Table 1 Comparison of Blaine, d_{10}, d_{50} and d_{90}

	Blaine [cm²/g]	d_{10} [µm]	d_{50} [µm]	d_{90} [µm]
CAC	4000	1,9	14	49
S1	2076	3,6	41	160
S2	2178	3,6	36	145
S3	2407	3	31	145
S4	1768	4,9	52	190
S5	2668	2,6	26	125
S6	3715	2,1	12	29
Q	2800	0	15	110

3.2. Development of strength

The compressive strength test results are shown in Figure 2 and the results of the compressive strength relative to the pure CAC mix are shown in Figure 3.The measurements were carried out on mortar samples after 6 hours, 24 hours, 7 days, and 28 days. It can be observed that mixes with the 30 % slag replacement have lower initial strength than the pure CAC mix. Moreover, the replacement of CA cement with slag reduced the compressive strength by 30-60 % in the first 6 hours.

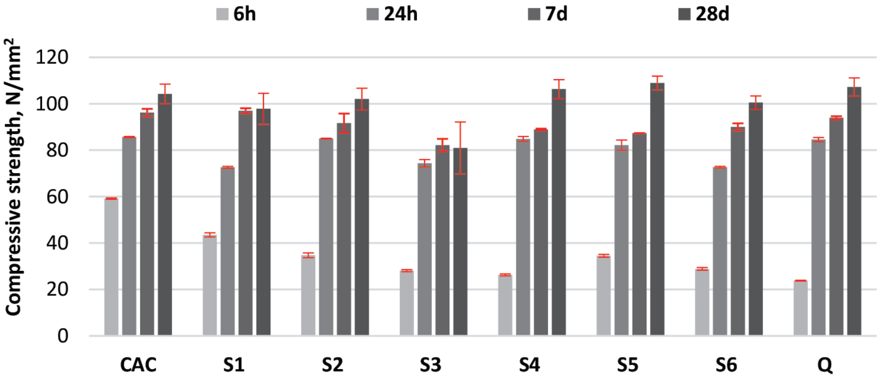

Figure 2. Compressive strength results of mortars

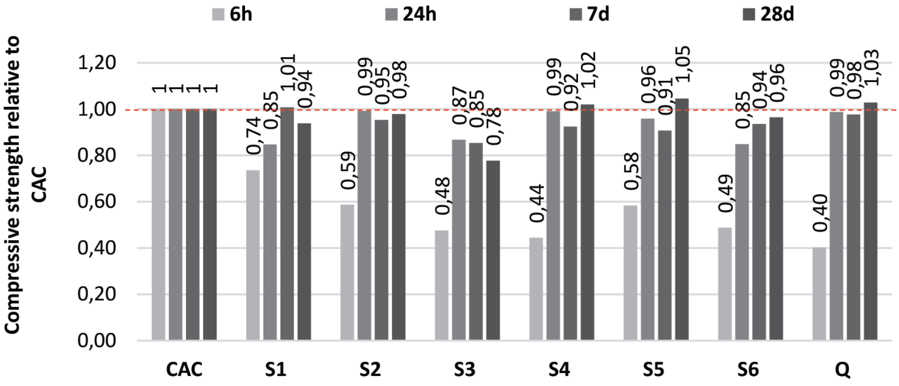

Figure 3. Relative compressive strength of mortars

After 24h, the slag starts to contribute to the development of compressive strength in all mixes. In fact, after 24 hours, all the mixes have compressive strength similar to that of the reference CAC mix. The highest initial compressive strength was developed by the mixture with slag S1. Moreover, at later ages (7 and 28 days), the mixes replaced with S1, S4 and S5 slags even have higher compressive strength compared to the pure CAC mix. Mixes S4 and S5 have higher compressive strength after 28 days compared to the pure CAC mixture. After 28 days of curing, more than 90 % of the CAC compressive strength is achieved in all mixes, except for the slag S3. It should be noted that quartz, which has a filler effect in the OPC systems, actively participates in hydration in the CAC systems and contributes to the development of compressive strength. The analysis of results shows that a 30 % replacement of the CAC cement by slag can cause a uniform development of compressive strength.

4 Conclusion and further research

The main goal of this study was to determine the effect of replacing 30 % of the calcium aluminate cement with slag on the development of compressive strength of mortar. From the analysis of the results, it can be concluded that the slags used in this study have the potential to replace some of the CAC cement in mortar. The initial compressive strengths are lower than the compressive strength of the reference mix. By replacing 30 % of the cement with slag, almost the same compressive strength can be achieved after 28 days as in the reference mix. Conversion process in CAC cement can be predicted by curing specimens at elevated temperatures (38 °C and 50 °C), and so further research will focus on the methods aimed at accelerating conversion process at elevated temperatures.

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