Impact of slag on carbonation rate of concrete based on calcium aluminate cement

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Abstract. Throughout their service life, concrete structures are exposed to various environmental conditions that affect their durability. The cementitious matrix inevitably comes into contact with air, which leads to a progressive carbonation reaction. As a result of carbonation, changes occur in the microstructure and porosity of the cementitious matrix. Calcium aluminate cement is produced to increase the resistance of composites to aggressive environments, but its application is limited by the occurrence of conversion process. The addition of slag inhibits the conversion process of calcium aluminate cement and prevents a reduction in compressive strength due to the formation of C_2ASH_8 hydrate, while contributing to the net zero commitment of the cement industry. It remains an open question how these changes in microstructure caused by the addition of slag affect the carbonation rate of calcium aluminate cement-based concrete. Therefore, the objective of this study was to determine the effects of slag on the microstructure and porosity of calcium aluminate-based concrete before and after accelerated carbonation. For this purpose, the mechanical properties, porosity, and reaction product of a concrete mix containing 30% calcium aluminate cement replacement by slag were compared to calcium aluminate cement-based concrete before and after exposure to 3% CO_2 for 7 and 28 days. Thermogravimetric analysis (TGA) and mercury intrusion porosimetry (MIP) were tested to understand the changes in reaction products and pore size distribution, respectively.

1 Introduction

Following the commitments of the cement industry for net zero emissions by 2050, the emphasis is on reducing the clinker-to-cement ratio and development of innovative cement production technologies [1]. In order to reduce the clinker-to-cement ratio, supplementary cementitious materials are often used in practice. Also, the production of alternative cementitious materials, such as calcium aluminate cement (CAC), contributes to the reduction of CO_2 emissions [2]. Calcium aluminate cement is mostly used as alternative to ordinary Portland cement (OPC) where resistance to aggressive environments is needed [3]. With superior durability properties compared to OPC, CAC is resistant to high temperatures and develops high early compressive strength [4]. However, hydration of CAC cement is highly dependent on environmental conditions, such as temperature and relative humidity, which affects hydrate formation. Main phase of CAC cement is monocalcium aluminate (CA) which reacts with water at the beginning of hydration and produces CAH_{10} and C_2AH_8 hydrates. These hydrates are metastable hydrates, and they are transformed into stable hydrates (C_3AH_6 and AH_3 gel) under the influence of temperature and humidity. This process of transforming metastable to stable hydrates is called the conversion process [5]. Conversion process increases the porosity of the cement matrix and consequently decreases compressive strength [6].

The most used supplementary cementitious material for CAC replacement is blast furnace slag (BFS). The high content of silicon dioxide (SiO_2) allows slag to alter the hydration products of CAC cement. By the reaction of CAC cement hydrates with silica straetlingite (C_2ASH_8) is formed [7]. Straetlingite inhibits conversion process, therefore no significant reduction in compressive strength is expected [8].

Carbonation of concrete occurs when carbon dioxide (CO_2) from the air reacts with hydration products inside the concrete and produces calcium carbonate ($CaCO_3$). Large amounts of portlandite in OPC ensure high resistance of Portland cement concrete [4]. The reaction of CO_2 and CAC cement leads to the formation of $CaCO_3$ and AH_3 gel, regardless of the nature of hydrates present [5]. Recently, Alapati and Kurtis [9] showed that CAC concrete has faster carbonation rate compared to OPC concrete. Also, they showed that decomposition of main hydration products can result in a significant decrease in mechanical properties and reduction in capillary porosity. Furthermore, Fernandez-Carrasco et al [10] investigated the possibility of suppressing the conversion process by exposing samples to 100% CO_2 (critical carbonation). They concluded that it is possible, for the samples cured at 25 ° C, to overcome the conversion process, i.e., that after critical carbonation all hydrates carbonate and no metastable hydrates are present that can further transform into stable hydrates. Park at al. [11] came to a similar conclusion. Namely, they cured the samples by carbonation and concluded that metastable hydrates are rapidly transformed into stable hydrates without increasing porosity.

The objective of the present study is to understand the impact of slag addition on microstructural and porosity

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changes of calcium aluminate cement-based concrete before and after accelerated carbonation. Microstructure studies were performed by thermogravimetric analysis (TGA) and mercury intrusion porosimetry (MIP), and mechanical properties by measuring compressive strength. Mixtures without and with replacement 30% of CAC cement by slag were analysed before and after exposure to 3% CO_2.

2 Materials and methods

The calcium aluminate cement and granulated blast furnace slag (GBFS) obtained by Calucem d.o.o. were used. Two concrete mixes were prepared to estimate influence of GBFS on durability properties of calcium aluminate cement-based concrete. To assess the impact of GBFS on durability properties of CAC concrete, a comparison of the system without slag (labelled CAC100) and with 30% replacement of CAC cement by slag (labelled CAC70SL30) was made. The samples were prepared with 420 kg/m^3 of calcium aluminate cement, river aggregates and water to binder ratio of 0.45. Before casting laboratory and all components were conditioned at 20 °C. The samples were covered and stored in cube moulds 15x15x15 cm for 24h in humidity chamber at 20 °C with relative humidity of 95 %. After 24h samples were demoulded and placed in water at 20 °C in humidity chamber for 28 days. After 28 days of curing in water cubes were removed from water and transferred to a laboratory air drying environment (18 °C to 25 °C and 50 % to 65 % relative humidity) for 14 days. After 42 days of curing samples were placed in carbonation chamber with carbon dioxide concentration of 3.0 ± 0.5 %, temperature of 20 ± 2 °C and relative humidity of 57 ± 3 % for 7 and 28 days.

The compressive strength measurements were conducted on non-carbonated samples cured in water for 28 and 56 days and carbonated samples after 28 days of carbonation. TG was conducted using TA Instrument Discovery TGA 55. The samples were heated from 30 to 1000 °C at a heating rate of 10°/min in an N_2 environment with a flow rate of 40 Cc/min. MIP measurements were conducted using AutoPore IV 9500 in a pressure range of 0.0033 MPa to 206.69 MPa and contact angle of 130°.

3 Results and discussion

3.1. Thermogravimetric analysis (TGA)

The Thermogravimetric analysis was tested on non-carbonated and carbonated samples. For this purpose, after carbonation, the powder was extracted from the samples. The effects of carbonation on the formation of phases in the cement matrix are shown in Fig. 1 for pure CAC mixture. The carbonation of pure CAC mixture results in decomposition of CAH_{10} phase to calcium carbonate ($CaCO_3$) and AH_3 gel. By prolonged carbonation up to 28 days a larger amount of CAH_{10} phase is decomposing. Additionally, with significant decomposition of CAH_{10} phase, decomposition of C_3AH_6 phase occurs, but carbonation of that phase is not so significant compared to the carbonation CAH_{10} phase. Also, from Fig. 1 it can be seen that CAH_{10} phase decomposes at temperatures below 100 °C, AH_3 gel and C_3AH_6 phase at 230 °C – 280 °C and $CaCO_3$ at temperatures higher than 600 °C.

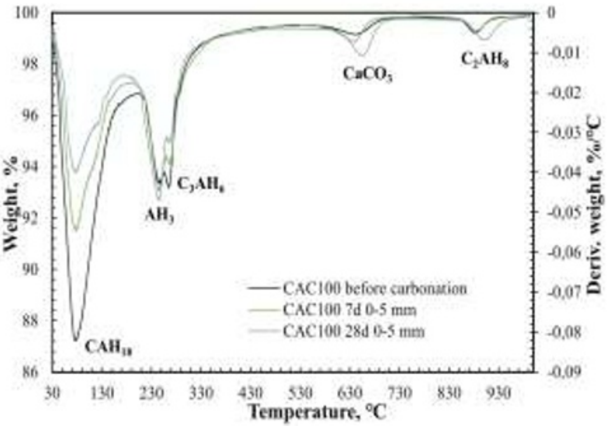

Fig. 1 TG curves of non-carbonated and carbonated CAC100 sample

Fig. 2 shows samples sprayed with phenolphthalein after 7 days and 28 days of exposure to CO_2. It is noticeable that the CAC70SL30 sample has higher depth of carbonation after 7 days and 28 days of exposure.

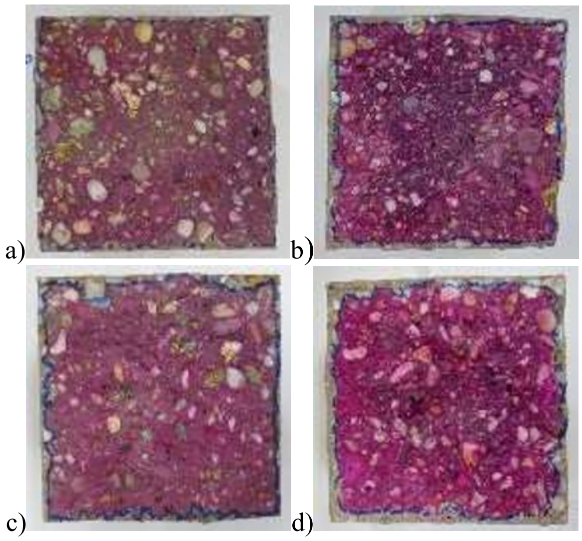

Fig. 2 Samples sprayed with phenolphthalein after 7 days of carbonation: a) CAC100, b) CAC70SL30, and 28 days of carbonation: c) CAC100, d) CAC70SL30

The effects of carbonation on the formation of phases for mixture with replacement 30% of CAC by slag after 7 and 28 days of carbonation are shown in Fig. 3. Metastable phases CAH_{10} and C_2AH_8 carbonate initially followed by straetlingite (C_2ASH_8) carbonation. The decomposition of these three phases produces AH_3 gel and $CaCO_3$. The formation and decomposition of C_3AH_6 phase is similar after 7 and 28 days of carbonation, and the temperatures at which phases are decomposed are similar to those of pure CAC cement mixture. The intensity of peak corresponding to the decomposition of calcium carbonate is more intense for CAC70SL30 compared to pure CAC mix which implies that mix with replacement has faster carbonation rate.

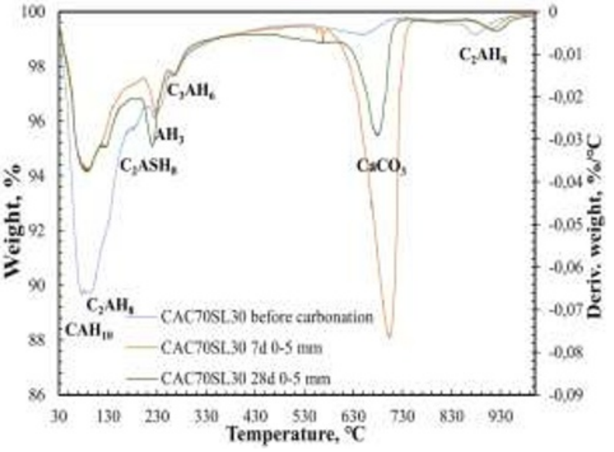

Fig. 3 TG curves of non-carbonated and carbonated CAC70SL30 sample after 7 days and 28 days of carbonation at different depths

3.2. Mercury intrusion porosimetry (MIP)

The Mercury intrusion porosimetry was tested on non-carbonated samples and on the samples after 7 and 28 days of carbonation. The pore volume distribution measured by MIP, for both samples, are shown in Fig. 4, Fig. 5 and Table 1. The total porosity of both samples is reducing after 28 days of carbonation. From Fig. 4 it can be seen that, for sample before carbonation, significant volume of pores is from 0.07 to 0.4 µm, and after 7 days and 28 days of carbonation this volume decreases and divides in two different peaks.

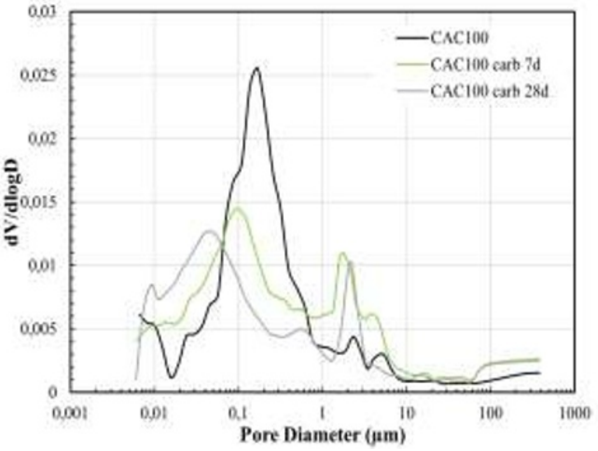

Fig. 4 MIP of non-carbonated and carbonated CAC100 sample

In the case of a mix with replacement 30% of CAC cement by slag, carbonation also reduces capillary porosity, but significantly increases porosity in gel pore size range (Fig. 5). The sample CAC70SL30 has a higher total porosity compared to pure CAC sample for both non-carbonated and carbonated samples, but CAC70SL30 sample has a higher decrease in total porosity after carbonation.

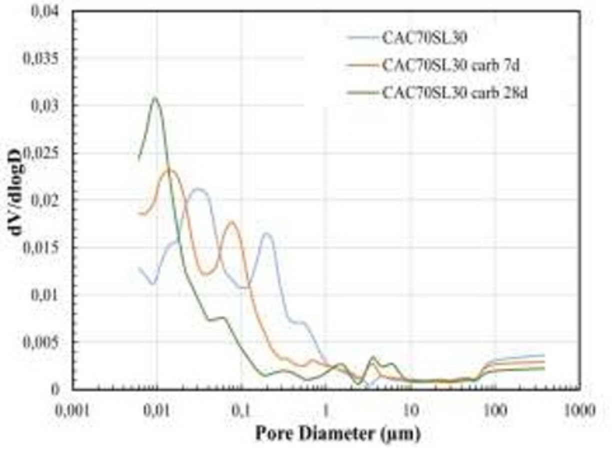

Fig. 5 MIP of non-carbonated and carbonated CAC70SL30 sample

Table 1 Total porosity of samples tested before and after carbonation

Sample	Porosity (%)		
	Before carbonation	7 days	28 days
CAC100	6.15	6.29	5.26
CAC70SL30	7.93	7.16	5.62

3.3 Compressive strength

The compressive strength was measured after 28 days and 56 days of curing in water for samples that were not exposed to carbonation. Additionally, the compressive strength was measured on samples that were exposed to carbonation, after 28 days in carbonation chamber. Fig. 6 shows the results of compressive strength measurements for non-carbonated and carbonated samples.

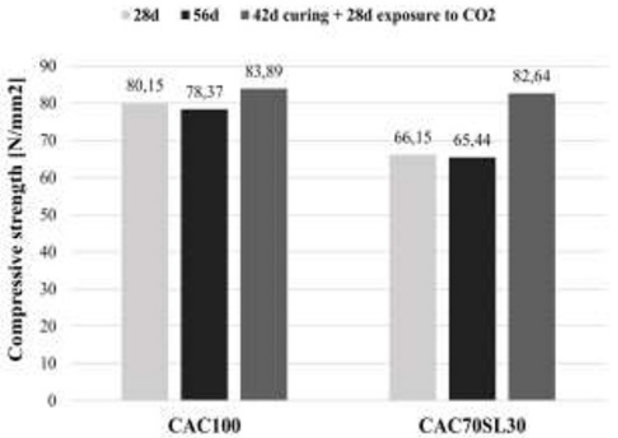

Fig. 6 Compressive strength of non-carbonated and carbonated samples

Non-carbonated samples of pure CAC mixture have 20-25 % higher compressive strength after 28 days and 56 days of curing in water compared to mix with replacement 30% of CAC by slag. The compressive strength of these samples is expected to be higher because there is more cement material that during the hydration process reacts with water and contributes to the development of higher compressive strength. After 28 days of carbonation the compressive strength values are similar for both mixtures.

Increase of 20% in compressive strength between non-carbonated and carbonated CAC70SL30 sample is attributed to faster carbonation rate and higher decrease in total porosity after carbonation.

4 Conclusion

The TG analysis, MIP and compressive strength measurements performed in this research were used for better understanding microstructural and mechanical changes of calcium aluminate cement concrete after exposure to accelerated carbonation. It was found that when exposed to accelerated carbonation, metastable hydrates carbonate to form calcium carbonate and AH_3 gel. Additionally, in a mixture with 30% cement replacement by slag, straetlingite is formed which carbonates after metastable hydrates and contributes to the formation of calcium carbonate and AH_3 gel. The total porosity of both mixtures decreases after carbonation, but for the mixture with replacement CAC cement by slag, the decrease in total porosity is greater and affects a significant increase in strength after carbonation.

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