Influence of slag on durability of calcium aluminate cement concrete

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Abstract. The durability of calcium aluminate cement (CAC) in aggressive environments is often correctly cited as one of the greatest advantages of this material. An inevitable phenomenon in the hydration of calcium aluminate cement is the conversion process that increases the porosity of the cement matrix and impairs the durability of the calcium aluminate cement-based concrete. The addition of slag reduces the negative impact of the conversion process, and thus no significant change in the porosity of the cement matrix should be expected. The aim of this preliminary study is to provide an insight into the basic durability properties of calcium aluminate cement with and without slag addition. For this purpose, a set of durability properties of calcium aluminate cement concrete with 30% cement replacement by granulated blast furnace slag were tested and compared with those of a pure calcium aluminate cement concrete. The studied properties were water permeability, chloride diffusion, carbonation, gas permeability and freeze-thaw The results presented in the study serve to further focus on specific applications of such a material.

Keywords: calcium aluminate cement, slag, durability, porosity, conversion process.

1 Introduction

Calcium aluminate cement (CAC) was produced to increase the resistance of ordinary Portland cement to aggressive sulfates and chlorides [1]. Therefore, the durability of CAC is considered to be one of the greatest advantages of this material. Metastable hydrates (CAH_{10} and C_2AH_8) of with hexagonal phase structures and low density are formed at the beginning of hydration of CAC cement conferring high early strength. However, over time or with increasing temperature, metastable hydrates are transformed into stable hydrates (C_3AH_6 and AH_3) with cubic phase structures and high density, *i.e.* conversion occurs [2]. During the conversion process, the porosity of the cement matrix increases which leads to a decrease in compressive strength [3]. By use of mineral additives rich in silica (SiO_2) strength loss caused by conversion process can be mitigated by the formation of straetlingite (C_2ASH_8) [4]. Changes in mechanical properties caused by the conversion process have already been extensively investigated, while the durability of concrete based on calcium aluminate cement with the addition of SCMs has not been studied so extensively. Hence, the aim of this study is to investigate the influence of slag addition on the basic durability properties of calcium aluminate cement.

2 Materials and methods

The calcium aluminate cement (CAC) and granulated blast furnace slag (GBFS) used in this study were supplied by Calucem d.o.o. from Pula, Croatia. To evaluate the influence of slag on durability properties of calcium aluminate cement concrete, 30% of cement was replaced by GBFS. All durability tests were conducted on concrete level. The concrete samples were prepared with water to binder ratio of 0.45, with 420 kg/m^3 of CAC and river aggregates. The samples were covered and stored in cube molds 15x15x15 cm for water permeability (HRN EN 12390-8), carbonation (HRN EN 12390-12) and freezing and thawing (HRN CEN/TS 12390-9) tests and in cylinder molds ø10x20 cm for chloride migration (NT BUILD 492) and gas permeability tests (EN 993-4). After 24h samples were demolded and placed in water at 20°C in the humidity chamber (RH=95%) until testing.

3 Results

The permeability of concrete defines its resistance to penetration of aggressive substances from the environment. In order to determine the permeability of concrete, both gas and water permeability investigations were used. The gas permeability measurement was conducted after 42 days of curing (28 days in water and 14 days in laboratory conditions). Fig. *1* a) shows the gas permeability coefficient for reference mixture and mixture with 30% replacement of CAC cement by slag. The mixture with addition of slag has higher gas permeability coefficient than the reference mixture.

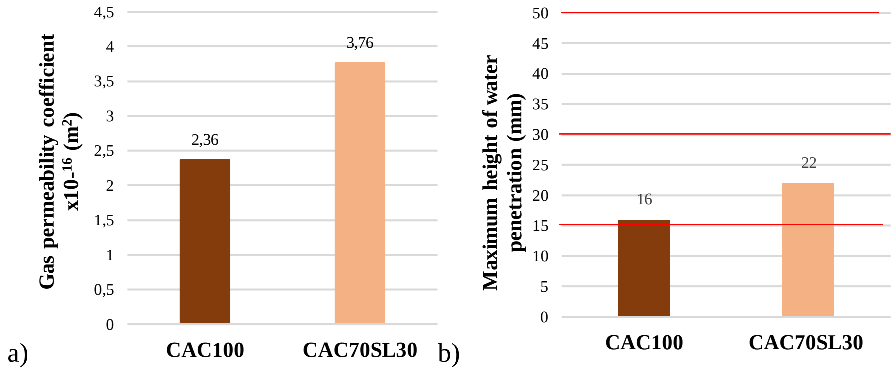

Fig. 1 a) Gas permeability coefficient for reference mix and mix with replacement, b) Maximum height of water penetration for reference mix and mix with replacement

Water permeability measurements were carried out on cube samples. Three samples were tested for each mixture after 28 days of curing. The results of water penetration measurement are shown in Fig. ***1*** b). The standard for water permeability test for OPC defines three classes: maximum height of water penetration of 50 mm for class 1, 30 mm for class 2, and 15 mm for class 3. Both mixtures belong to class 2, but the reference mixture has lower water penetration depth than the mixture with 30% replacement of cement by slag.

Samples 28 days and 56 days old were used for testing chloride migration coefficient. The chloride penetration depth is measured from the visible white silver chloride precipitation, after which the chloride migration coefficient is calculated. The results of chloride migration coefficient for each mixture are shown in Fig. ***2*** a). The usual values defining OPC concrete quality based on the chloride migration coefficient are: very good (<$2x10^{-12}$ m^2/s), good ($2x10^{-12}$ - $8x10^{-12}$ m^2/s), satisfactory ($8x10^{-12}$ - $16x10^{-12}$ m^2/s) and unsatisfactory (>$16x10^{-12}$ m^2/s). The reference mixture has a lower migration coefficient for both ages of testing compared to mixture with replacement, which means highest resistance to chloride penetration. The replacement of CAC cement by slag reduces the resistance of concrete to chloride penetration. After 56 days of curing coefficient in the case of concrete with slag is decreasing because of the slow reactivity of slag.

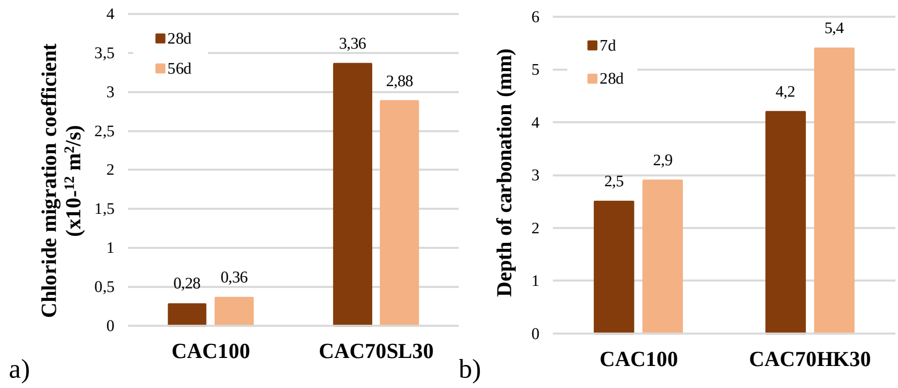

Fig. 2 a) Chloride migration coefficient for reference mix and mix with replacement, b) Carbonation depth for reference mix and mix with replacement

For carbonation depth measurement cube samples were used. After a period 42 days of preconditioning the samples (28 days in water and 14 days in laboratory conditions), the test was carried out under controlled exposure conditions (at 20°C with 57±3 % relative humidity) using an increase level of carbon dioxide (3% of concentration). Carbonation depth was measured after 7 and 28 days of exposure to CO_2. The results of resistance to CO_2 penetration are shown in Fig. ***2*** b). The mixture with replacement by slag show slightly faster carbonation rate than reference mixture at both days of testing. These results are attributed to the higher gas permeability of mixture with 30% replacement of CAC cement by slag.

Freezing and thawing with de-icing salts was tested over 56 cycles. According to the standard for exposure class XF4, mean weight loss per cycle should be less than 0.5 kg/m^2 and individual weight loss less than 1 kg/m^2. Both mixtures did not meet the requirements of the standard. The reference mixture has similar behavior to the classical OPC system without chemical additives. Additionally, mix with replacement has significantly worse behavior after 7 days compared to reference mixture.

Table 1 Mean value of scaling per cycle of freezing and thawing

	Cycle	CAC100	CAC70SL30
Δm_{mean} (kg/m^2)	7±1	0.09	1.48
	14±1	0.39	3.07
	28±1	1.12	4.18
	42±1	1,47	5.19
	56±1	1.71	5.93

4 Conclusion

The main objective of this preliminary study was to assess the basic durability properties of concrete based on calcium aluminate cement with and without addition of slag. The analysis of the results shown that concrete based on calcium aluminate cement has very good resistance to the penetration of aggressive substances from the environment, especially in the case of chloride penetration. On the other hand, replacing 30% of CAC cement with GBFS results in a slight decline in the resistance of concrete, compared to the resistance of concrete without GBFS. It should be emphasized that based on these results and conclusions there is a need for further research on calcium aluminate cement with and without mineral additives.

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