DEVELOPMENT OF SAMPLE PREPARATION AND ITS INTERACTION WITH STRONGLY CARBONATING ENVIRONMENT

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Abstract

The main issue described in this paper, is the partial replacement of the classical hydration process by a controlled carbonation process, which leads to significant strength increases in the early stages of hydration. The main advantage of this method is that curing occurs even for normally non-hydraulic minerals. These are confirmed by a cement and steel slag carbonation results achieved in this experiment. Initial strengths of both materials were increased, and the mineral calcite was formed as the main carbonation product.

Keywords

Cement, emissions, carbonation hardening, hydration

1 INTRODUCTION

Ordinary Portland cement (OPC) is composed of four main phases, the minerals alite (C_3S), belite (C_2S), tricalcium aluminate (C_3A), brownmillerite (C_4AF) and a regulator, gypsum [1]. When OPC is mixed with water, it forms a slurry that solidifies and hardens [2]. When mixed with water, C_3A and C_4AF first react with water. The long-term product is then the mineral C_3AH_6. This reaction is gradually accompanied by the dissolution of present calcium silicates. This results in the formation of portlandite and subsequently CSH gels. Gypsum dissolves after mixing with water and forms needle-like grains of ettringite on the surface of C_3A grains [3]. This retards the formation of rapidly solidifying hydroaluminates. For a complete hydration of the clinker minerals, 21-24% water is required. In practice, higher values of the water coefficient are commonly used. The reason is to create better viscous properties of the mixture. Excess water remains in the pore system and is often referred to as gel water [4].

An important aspect for hydration, besides the number of phases, is also their polymorphism. This can best be illustrated with the mineral belite. In OPC, belite is found in the metastable form β-C_2S, which reacts with water as C_3S to form the same hydrating products. The reaction is slower than that of alite because less $Ca(OH)_2$ is formed, which is the driving force for maintaining a strongly basic pH [3], [5]. For example, the author of the experiment reports that the hydration rate of β-C_2S was only 14% after one year [6]. In contrast, the γ-C_2S modification does not form any hydration products [3].

However, the situation is different and more complicated in the case of curing by controlled carbonation in early stages. This process is now being addressed by many authors around the world. The method allows CO_2 gas to be permanently incorporated into the structure of the material. The main product of this process is the mineral calcite, $CaCO_3$, and minerals such as portlandite, belite, alite have been proved for this purpose. It is thanks to the controlled carbonation process that the otherwise hydraulically unreactive minerals, such as γ-belite, can be hardened [7]. Therefore, other materials that are themselves hydraulically unreactive can also be cured by this process. A typical example is slag, which is rich in γ-C_2S and often also contains CaO and MgO [8].

This method is therefore currently important for reducing the environmental impact of the cement industry.

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2 METHODOLOGY

Materials and preparation

The aim of the experiment was to investigate the hydration process of Portland cement (CEM I 42.5 N) combined with controlled carbonation in the early stages. Furthermore, the interaction of hydraulically non-reactive steel slag with a high CO_2 concentration environment was assessed. These raw materials were subjected to basic physical tests to determine their description. These included the determination of chemical and mineralogical composition, as well as the determination of specific gravity and specific surface area. These input data were important to plan the experimental tests and subsequently a better understanding of the obtained results.

For these purposes, the slag delivered from the steelworks in Trinec,CZ was crushed in a Retsch laboratory jaw crusher and subsequently ground in a laboratory ball mill. Grinding was carried out in the range of 15-45 minutes to achieve different specific surfaces and particle sizes. The cement used was not treated in any way prior to measurement and use.

Preparation of test samples

To monitor the carbonation of the samples in the early stages, it was necessary to prepare the samples by pressing. For this purpose, it was necessary to conduct a pilot study to determine suitable pressing conditions. The mixtures for pressing were prepared in a HOBART laboratory mixer by mixing the test material with an appropriate amount of water. The actual pressing was carried out on a hand-held REDATS II-380 hydraulic press. The samples produced were in the form of 30 mm diameter cylinders and 40×40×160 mm standard prisms. To make the mechanical properties of the cylinders and prisms comparable, the aim was to achieve the same bulk weights for both samples of each material. Therefore, the same pressure was subsequently applied to the prismatic samples. After the pressure was released and the samples were unmoulded, they were weighed, and their dimensions were measured to calculate the bulk weight.

Hydration process

One set of the samples intended for hydraulic curing was immediately placed in water after moulding and determination of the bulk density. The samples were tested after 1 and 8 days. The temperature of the water corresponded to the ambient air temperature and varied between 18 and 20 °C.

Carbonation hardening process

On the other hand, the samples intended for curing by controlled carbonation were placed in a pressure carbonation chamber after pressing and determination of the bulk density. Carbonation was carried out at increased pressure of 1 bar, temperature of 18-20 °C, relative humidity of 92±3 % and high CO_2 concentration for 24 h. The concentration levels exceeded the maximum values of commercial measuring devices and were not determined during the measurement.

After depressurization of the chamber, the bulk weights of the samples were redetermined. Next, one set of samples were tested for compressive flexural strength and compressive strength. After these destructive tests, the samples were subjected to mineralogical composition, specific gravity and texture assessment. Another set was placed in water storage for the next 7 days, after which the samples were tested in the same way as the previous set.

Analysis and testing methods

The particle size of cement and steel slag was measured by dry-way process on a Malvern Mastersizer 2000.

The raw materials were also analysed using a PC-Blaine Star to determine their specific surface area and the specific gravity of all tested materials was analysed using a Micromeritics AccuPye II 1340 gas pycnometer.

Compressive flexural strength and compressive strength were tested on prismatic samples after 24 h of curing in accordance with standard CSN EN 196-1 [9]. Compressive strength was also tested on cylinder samples after 24 h of curing process for comparison.

The determination of the mineralogical composition was carried out by powder X-ray diffraction on a Panalytical Empyrean instrument, λ=1.540598 for Kλ1 radiation, Cu – anode, voltage 45 kV, and current 40 mA. The evaluation of the results was carried out using HighScore Plus software. In addition to samples cured for 24 h, samples with longer water storage were also analysed. Records comparing individual measurements were made using Data Viewer software.

All these XRD analyses were complemented by microstructure images from the VHX digital microscope and the TESCAN MIRA3 electron microscope. In all cases, fractions of the specimens after strength tests were used as samples.

3 RESULTS

Determination of pressing conditions

The pressing was first tested on cylinders, where it was found that approximately 50-55 g of wet cement (10 % moisture) and a pressure of 15 MPa is suitable for creating samples with sufficient handling strength and aspect ratio close to 1:1. In all cases, the pressing process was carried out for 30 s.

In the second step, a suitable slag fineness was assessed (Fig. 1). In terms of pressing, no difference was observed between the tested samples. In the controlled carbonation test, the samples with the higher specific surface area were found to be so compact that no carbonation of the centres occurred. The best carbonation of the centre was observed for the least processed slag under these pressing conditions. Therefore, the slag that underwent only crushing was chosen for the final test.

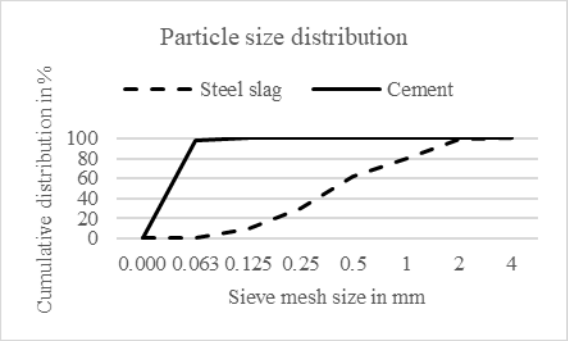

Fig. 1 Particle size distribution of cement and slag used for final test.

Bulk density

The bulk densities of the cement samples were 2.070 kg/m^3 (cylinders) and 1.910 kg/m^3 (prisms) respectively after pressing. The samples made of steel slag had higher bulk density values, namely 2.090 kg/m^3 (prisms) and 2.230 kg/m^3 (cylinders). The reason why the volume weights of the test prisms are lower is due to the slight deformation of the mould walls. This led to some of the force being distributed laterally. The resulting prisms then had a slightly convex shape in one axis.

For all tested samples, the bulk densities were higher after carbonation hardening. This is due to the increase in weight. The weight of slag increased on average by 1,8 % and the weight of cement by 4,2 % for the test set of samples.

Strength

At the outset it must be said that the strengths established are rather informative and cannot be interpreted as entirely accurate. The main reason for this is the overall small number of test samples. This is because the determination of the strengths was not the main objective of the experiment. Informative strength results can be seen in Tab. 1. The table shows the strengths after 1 day of curing. In addition, the compressive strengths of the cement prisms after 8 days of curing are given.

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Tab. 1 Mechanical properties of tested samples.

Material	**Hardening conditions**	**Compressive flexural strength [MPa]**	**Compressive strength [MPa]**	
		Prisms	Cylinders	Prisms
CEM I 42.5 N	24 h, carbonation	7.7	48.1	47.2
	24 h, carbonation + 7 d, water	-	-	39.3
	24 h, water	2.0	-	33.9
	8 d, water	-	-	53.2
Steel slag	24 h, carbonation	7.8	37.9	36.4
	24 h, water	0.1	-	0.4

Depth of carbonation

A phenolphthalein solution was applied to the cross-section of the samples immediately after compressive flexural strength. In both samples, carbonation occurred throughout the sample cross-section during carbonation hardening. However, the cement sample showed discolouration at several points in the cross section, see Fig. 2. Visual comparison with the samples from the water storage shows a significant change in pH during carbonation.

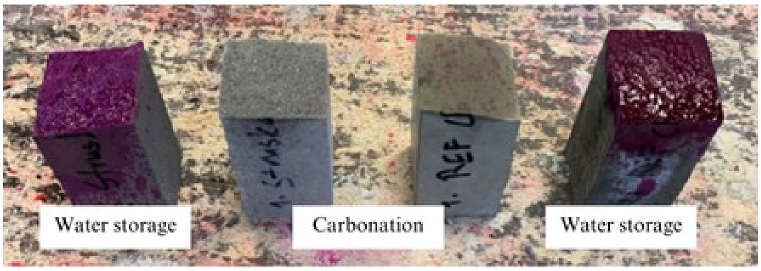

Fig. 2 Carbonation depth of slag samples (left) and cement samples (right) after 24 h.

XRD analysis

The Portland cement used consisted mainly of the minerals alite, belite, tricalcium aluminate, brownmillerite and, to a lesser extent, gypsum. The same main clinker minerals were also identified in the samples after 1 day of conventional hydration. In addition, the minerals portlandite and ettringite were present in the sample. The diffractions of these two minerals were more intense after 8 days of hydration and, conversely, the intensities of the clinker minerals decreased. Tricalcium aluminate was not detected after 8 days of hydration. The samples of cement cured by controlled carbonation showed the presence mainly of alite, calcite, brownmillerite and belite after 24 h. The subsequent 7 days in water also resulted in the formation of ettringite, but the mineral portlandite was not detected. These results can be seen in Fig. 3. The individual letters above the diffraction lines indicate the first letter of the mineral corresponding to that line, i.e. A for alite, B for belite, C for calcite, etc.

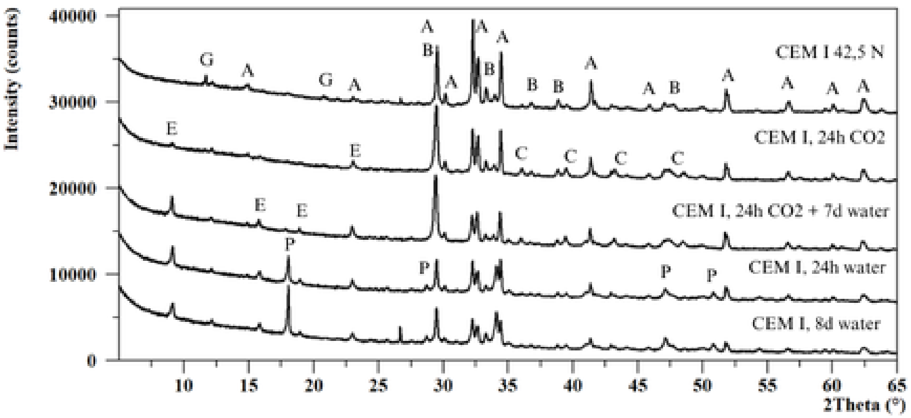

Fig. 3 Mineralogy composition of cement samples before and after different curing process.

The mineralogy of steel slag (Fig. 4) is more complex than that of cement, but the main phases of the slag used are belite in gamma modification, periclase, mayenite, and hydrogrossular. After 24 hours in water, the main diffraction line ($2\Theta=29,4640$) of calcite were detected. More intense diffraction lines were detected in samples carbonated for 24 h.

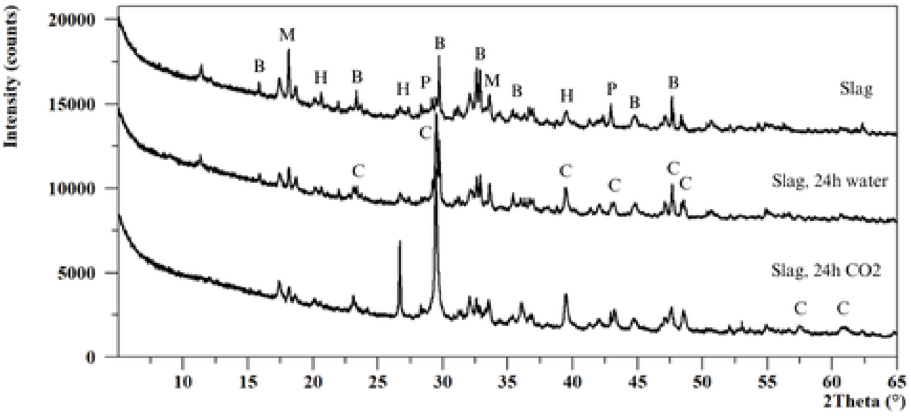

Fig. 4 Mineralogy composition changes of slag depending on the type of treatment.

By comparing the results of slag and cement, it can be said that the same main product, calcite, is produced in the process of controlled carbonation.

Optical microscopy

The following optical microscope images (Fig. 5) show the different microstructures of the individual samples. Calcite crystals are more developed in the samples that were cured by controlled carbonation. In contrast, the calcite contained in the slag from the water storage shows a rather undeveloped gel-like character formation.

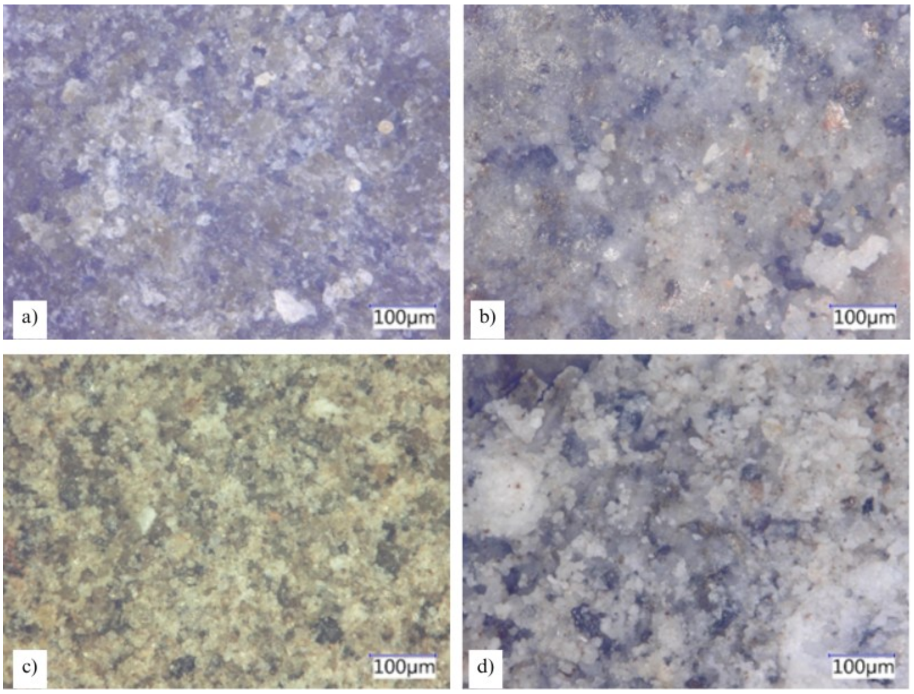

Fig. 5 Development of calcite crystals in cement and slag in different periods; a) Cement sample after 8 days in water, b) Slag after 24 h in water, c) Cement after 24 h of carbonation, d) Slag after 24 h of carbonation.

Electron microscopy

Under conditions of controlled carbonation, SEM images (Fig. 6 and Fig. 7) show crystallization of calcite on the surface of clinker grains. Under this layer of calcite, the grains retain their original shape. The subsequent rehydration process shows signs of slower progress. The amount and size of the CSH gel and ettringite crystals is lower than in normal hydration in water storage.

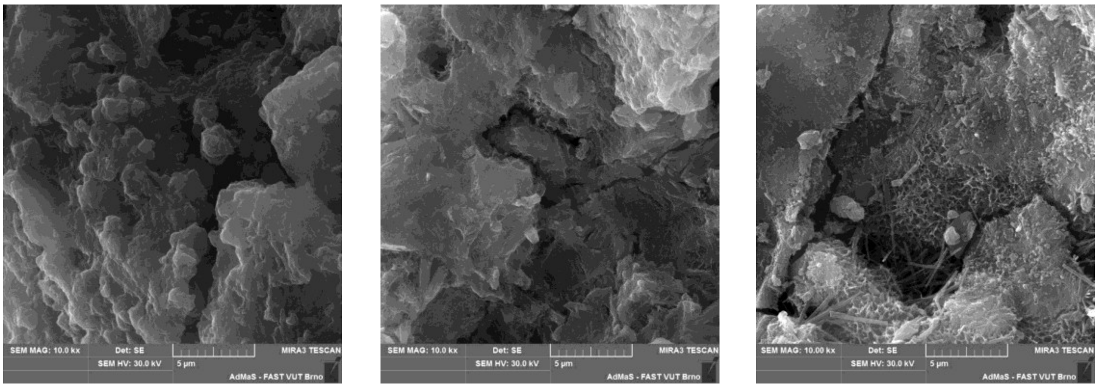

Fig. 6 SEM images of cement structure after different curing process; Cement after 24 h of carbonation (left), Cement after 24 h of carbonation and 7 d in water (middle), Cement after 8 d in water (right).

As indicated by the results described above, the formation of calcite is more intense in the case of slag. Crystallization also takes place on the surface of the grains, but the resulting crystal structures are much more intergrown.

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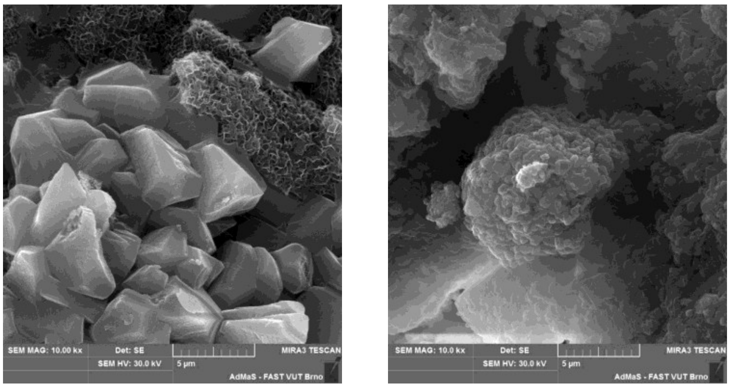

Fig. 7 SEM images of steel slag after water and carbonation curing; Slag after 24 h in water (left), Slag after 24 h of carbonation (right).

4 DISCUSSION

The designed pressing conditions (moisture 10 %, pressure 15 MPa, duration 30 s) were proven to be suitable. For further research it is suggested to reduce the pressure to create samples with higher porosity. This is the main material parameter entering the process, besides the mineralogical composition. Relative humidity 92±3 %, pressure 1 bar, and temperature 19±1 °C proved to be sufficient for carbonation of the whole sample cross-sections.

In both tested materials, OPC and steel slag, calcite was formed, as expected, during controlled carbonation curing. The carbonation of slag is more intense when comparing xrd records and microstructure. Calcite crystals are larger in slag, which confirms the conclusions of foreign authors [5], [7] regarding the behaviour of γ-C_2S in strongly carbonating conditions.

The strength of cylinders and test prisms was comparable, despite the small number of tested samples. The results confirm the general trend that higher bulk density results in higher strength. However, the increases of bulk density during carbonation are strongly dependent on the original bulk weight of the pressed samples. For example, the increases were higher in the pilot samples with lower bulk density after unmoulding. It is important to determine the ideal sample porosity or bulk density for each material, which must be sufficient for CO_2 penetration but still suitable for maximum possible calcite crystal intergrowth.

5 CONCLUSION

The summary of the main results of the research are:

- the ability of steel slag to harden by controlled carbonation has been proven,
- the early phase of cement hydration is slowed down due to carbonation hardening,
- in both cases, the main product of carbonation is calcite,
- crystal growth is more intense in steel slag,
- strength of cylinders and test prisms are comparable.

In summary, it is necessary to test samples of different bulk weights to obtain the best possible results. This should be easily achieved by changing the pressing pressure.

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