STRUCTURAL CHANGES IN SODIUM CARBONATE ACTIVATED SLAG BINDERS INDUCED BY CO_2 EXPOSURE

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ABSTRACT

The physical and chemical interaction between CO_2 and cementitious materials is referred to as carbonation, and is considered one of the main threats to our built environment. In alkali-activated materials, carbonation reactions can lead to significant changes in phase assemblages, an increase in porosity, and a loss in mechanical strength; however, the kinetics of carbonation are strongly dependent on factors controlling phase assemblage evolution in these systems, such as the type of precursor used in their production, the nature and amount of the activator utilised, and the curing conditions adopted. In this study the structural changes of sodium carbonate activated slag cements induced by accelerated carbonation under controlled exposure conditions (1% CO_2, 65% relative humidity and 23°C) are evaluated. The results are compared with those obtained for specimens exposed to natural carbonation conditions, to identify any changes in the type of carbonation products forming, as a function of CO_2 concentration. Conversely to what has been reported for silicate activated slag systems, when using sodium carbonate as activator, negligible carbonation of the specimens is identified upon natural or accelerated carbonation. The outcomes of this study demonstrate that the development of highly durable and carbonation resistant alkali-activated cements is feasible when using sodium carbonate as the alkali source.

1. INTRODUCTION

Carbon dioxide concentrations are the highest recorded in human history at present. This poses a significant threat to our cement-based built environment, as CO_2 once enters a concrete, it dissolves in pore water leading to an acid-base reaction known as carbonation (Fernandez-Bertos et al. 2004). In Portland cement systems, the formation of $Ca(OH)_2$ buffers the carbonation reaction. As the Portland cement fraction in concretes is reduced by addition of supplementary cementitious materials (SCMs), the content of $Ca(OH)_2$ is depleted by the pozzolanic reaction. This increases the carbonation susceptibility of SCMs containing concretes (Papadakis 2000).

Alkali activated cements are Portland clinker-free systems, produced by the chemical reaction of an alkali-activator and an aluminosilicate source (Provis 2014). For these alternative cements, carbonation has been reported as one of the main durability concerns for their use in structural application. However, the carbonation rates reported for these systems vary significantly under small modifications of the precursors used for their production, the type of activator added, and the carbonation exposure conditions adopted (Bernal et al. 2014). The large number of variables that influence performance poses a great challenge to elucidate the role of different factors in carbonation performance of alkali-activated cements.

Recent studies demonstrated that it is possible to produce carbonation resistance alkali-activated cements using sodium carbonate as activators (Ke X., et al. 2018). This was the consequence of the phase assemblage of these cements, which favours CO_2 uptake without modifying the mechanical performance of the specimens.

In this study, the phase assemblages of solid paste cylinders upon exposure to natural carbonation for 6 months, in a laboratory environment, are reported. Results are compared to those of accelerated carbonation specimens exposed to 1 %$CO_{2(eq)}$, at a relative humidity of 65% and room temperature (21°C).

2. EXPERIMENTAL PROGRAMME

2.1. Materials and sample preparation

A commercial ground granulated blast furnace slag was used, containing CaO (41.3 wt.%), SiO_2 (36.0 wt.%), Al_2O_3 (11.3 wt.%), and MgO (6.5 wt.%). This slag had a Blaine fineness of 5056 ± 22 cm^2/g (average value of four measurements), and an average particle size d_{50} of 11.2 ± 0.1 µm determined using laser diffraction. The activating solution was prepared by pre-dissolving commercial sodium carbonate powder (Sigma Aldrich, Na_2CO_3 ≥ 99.5%) into distilled water.

Sodium carbonate-activated slag pastes were produced with an activator dose of 8 g Na_2CO_3 per 100 g slag, and a water/(slag+Na_2CO_3) mass ratio of 0.40. Pastes were mixed using an overhead mixer with a high-shear blade, cast in centrifuge tubes, then sealed and stored at room temperature (20 ± 3 °C) until testing.

2.2. Response to CO_2 exposure

Cylinder samples cured for 28 and 180 days were exposed to ∼0.04% CO_2, described as *naturally carbonated*, and elevated carbonation conditions (1.0 ± 0.2% CO_2), described as *accelerated carbonated*. Under both carbonation conditions, temperature and relative humidity were controlled at 20 ± 2 ºC and 65 ± 5%. The carbonation depth was determined by spraying a 1 wt.% phenolphthalein solution onto a freshly split surface. Fuchsia colour indicates a pH > 10, while no colour is associated with a reduced pH (< 8).

Paste specimens from the non-carbonated core and the carbonated edge of the sample were analysed, with the aim to account for the structural evolution taking place in these cements as they continued to mature during the period of CO_2 exposure. Specimens were analysed through: (i) X-ray diffraction (XRD), using a Bruker D2 Phaser instrument with Cu-Kα radiation and a nickel filter, a step size of 0.02° and a counting time of 1 s/step, from 5° to 55° 2θ; and (ii) thermogravimetry-mass spectroscopy (TG-MS), in a Perkin Elmer TGA 4000 instrument coupled with a Hiden mass spectrometer: 30 mg of sample was tested from 30°C to 1000°C at a heating rate of 10°C/min, under nitrogen flowing at 40 mL/min.
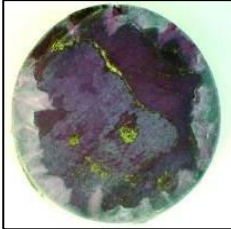
3. RESULTS AND DISCUSSION

3.1. Carbonation profile

A sharp carbonation front was not identified, either in naturally or accelerated carbonated specimens. Instead, changes in colour along with severe cracking were observed (see Table 1). These results are consistent with other studies

(Nedeljković et al. 2018) identifying a correlation between light grey regions, and the colourless regions observed after spraying of the phenolphthalein indicator. Changes in colour from dark green to light grey of slag-based specimens are associated with the oxidation of sulfides present in the slag as oxygen enters the material (Chaouche et al. 2017).

Table 1. Photographs of specimens exposed to 1% $CO_{2(eq)}$ for 14 days. All samples have a 15.5 mm diameter

Curing age	No indicator	With indicator
28 days		
180 days		

After 6 months of natural carbonation all samples, independent of the curing time, presented a few millimeters of light grey areas. Conversely, when exposing cylinder specimens to accelerated carbonation, significant differences were observed, when samples were cured for 28 or 180 days prior to CO_2 exposure. 28-day cured samples were completely carbonated after 14 days of 1% CO_2 exposure, exhibiting significant cracking, while those cured for 180 days presented just a few millimeters of colouration/alkalinity change (Table 1). These results highlight that extended curing times improves the resistance to carbonation of sodium carbonate activated slag cements. This is likely due to densification of the material as reaction progresses, as well as formation of an increased fraction of reaction products with the ability to chemically bind CO_2 at extended curing times (Ke et al. 2018).

3.2. X-ray diffraction

X-ray diffraction patterns of 28-day cured specimens after 7 days of natural and accelerated carbonation are shown in Fig. 2. Similar phase assemblages are observed at the edge and centre of the tested cylinders according to the carbonation exposure conditions. In the case of accelerated carbonated specimens, this is consistent with the total carbonation of the samples (Fig 1); however,

as naturally carbonated specimens presented clear 'carbonated' and 'non-carbonated' regions it was expected that there would be more significant differences in the phase assemblage evolution between the edge and centre of the specimens. This indicates that even under natural carbonation conditions, some degree of carbonation will occur in the core of highly dense samples.

Prior to carbonation, the main crystalline phases identified are an aluminum substituted calcium silicate hydrate (powder diffraction file (PDF) # 00-019-0052), along with a layered double hydroxide with a hydrotalcite type structure (PDF# 00-014-0525). Traces of the calcium carbonate polymorphs vaterite (PDF# 00-033-0268) and calcite (PDF# 00-005-0586) were identified in non-carbonated samples, most likely as a consequence of weathering of the samples during testing, as these phases were not observed in the anhydrous slag (Ke et al. 2018) prior to mixing.
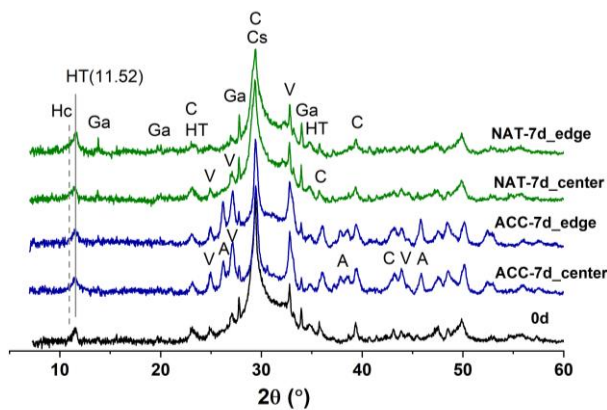

Fig 2. X-ray diffractograms of 28 d cured sodium carbonate activated slag cements carbonated under natural and accelerated conditions.

Upon carbonation all samples exhibit formation of hemicarboaluminate (PDF # 00-036-0129), along with increasing intensity of reflections corresponding to vaterite and calcite, consistent with the decalcification of C-A-S-H type gels, observed in previous studies in carbonated alkali-activated slag cements (Ke et al. 2018). In the case of accelerated carbonated pastes, it is clear that there is a sharpening of the C-A-S-H reflection, along with a reduction in intensity of the diffusive scattering. Formation of the calcium carbonate polymorphs aragonite (PDF # 00-041-1475) was solely observed under accelerated carbonation conditions. Aragonite was not identified as a carbonation product in cements with comparable chemistry tested using powdered samples (Ke et al. 2018). This indicates that the carbonation reaction products change depending on testing solid or powdered samples, due to differences in internal relative humidity and CO_2 concentrations in the tested specimens.

In naturally carbonated specimens gaylussite (PDF # 00-021-0343) is observed. Higher intensity reflections of hydrotalcite and gaylussite were identified at the edge of the sample. Gaylussite has been identified as a reaction product forming at early age (<7 d) in sodium carbonate activated slag cements (Bernal et al. 2015). The fact that this phase is present in aged samples, after natural carbonation, might indicate that this phase is not fully dissolved at longer curing times. Instead, what might be changing over the time of curing is its crystallinity.

3.3. Thermogravimetry analysis

The derivative of the mass loss, along with mass spectrometry results, for samples after 7 days of natural and accelerated carbonation are shown in Fig 3. The mass loss below 200°C is mainly attributed to removal of water loosely bound to the hydrated products forming in these cements, including a C-A-S-H type gel. The distinct shoulder observed at 133 °C is attributed to dehydration of LDH type phases, mainly hemi- and monocarboaluminates (Lothenbach et al. 2008), as observed by XRD (Fig. 2). In accelerated carbonated specimens, significant mass losses between 200 and 650 °C are identified, consistent with the decarbonisation of the different calcium carbonate polymorphs present in these specimens.
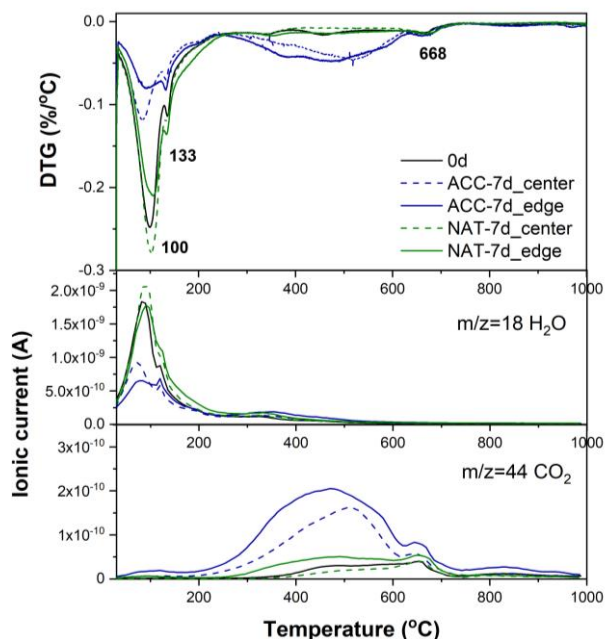

Fig 2. Derivative of the mass loss and mass spectrometry results for sodium carbonate activated slag pastes exposed to natural and accelerated carbonation

Slight differences in mass loss were identified between 200 and 400 °C in accelerated carbonated samples collected from the edge and from the centre of the solid tested specimens. This is consistent with the observed differences in the

XRD reflections corresponding to aragonite andvaterite (Fig 2). This indicates that at the surface of the samples formation of aragonite prevails over other calcium carbonate polymorphs, despite the fact that it is expected that the CO_2 concentration at the edge of the sample is higher than in the centre of the specimens.

Although some carbonation products were identified by XRD (Fig 2) in naturally carbonated pastes, in both the edge and centre of the specimens, the thermogravimetry results indicate that these phases are presented in negligible amounts. This indicates that the evaluated specimens did not experience significant carbonation after 7 days of CO_2 exposure under natural conditions, consistent with the observed by Ke et al. (2018). In that study it was concluded that sodium carbonate activated cements have the ability to withstand exposure to CO_2.

4. CONCLUSIONS

Significant differences in carbonation progress are identified in alkali-activated slag specimens with different curing durations prior accelerated carbonation testing. This is likely consistent with the densification of the specimens as reaction progresses, and formation of larger fraction of CO_2-binding phases (e.g layered double hydroxides) takes place. These results highlight that resistance to carbonation of sodium carbonate activated slag cements significantly improves as the material ages.

Different carbonation reaction products were identified in specimens exposed to natural or accelerated carbonation conditions. Vaterite and calcite are the main carbonation reaction products observed under natural carbonation conditions, along with gaylussite, which seems to be a carbonation product of the pore solution. At high CO_2 concentrations, the three calcium carbonate polymorphs were observed, where aragonite seem to be the main carbonate forming at the surface of the specimens.

These results elucidate for sodium carbonate activated slag cement that the type and amount of carbonation products forming under natural and accelerated carbonation conditions are different. The evaluation of paste monoliths instead of powdered samples also reveals the strong effect of CO_2 gradients within the sample, and/or changes in internal humidity from the surface of the centre of the specimens, leading to formation of different types and amounts of carbonation products. It is thus recommended for microstructural studies to involve the evaluation of solid samples so that phase assemblage changes likely to occur during service can be more accurately identified.

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