Cement and Concrete Research 88 (2016) 60–72

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: www.elsevier.com/locate/cemconres

Experimental studies and thermodynamic modeling of the carbonation of Portland cement, metakaolin and limestone mortars

Zhenguo Shi [a], Barbara Lothenbach [b], Mette Rica Geiker [c], Josef Kaufmann [b], Andreas Leemann [b], Sergio Ferreiro [d], Jørgen Skibsted [a,*]

[a] Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, 8000 C Aarhus, Denmark
[b] Laboratory for Concrete & Construction Chemistry, Swiss Federal Laboratories for Materials Science and Technology (Empa), 8600 Dübendorf, Switzerland
[c] Department of Structural Engineering, Norwegian University of Science and Technology (NTNU), Trondheim 7491, Norway
[d] Aalborg Portland A/S, Cementir Holding S.p.A., 9100 Aalborg, Denmark

ARTICLE INFO

Article history:
Received 5 October 2015
Received in revised form 4 May 2016
Accepted 8 June 2016
Available online 18 June 2016

Keywords:
Carbonation (C)
Portland cement (D)
Metakaolin (D)
$CaCO_3$ (D)
Thermodynamic calculations (B)

ABSTRACT

The carbonation of Portland cement, metakaolin and limestone mortars has been investigated after hydration for 91 days and exposure to 1% (v/v) CO_2 at 20 °C/57% RH for 280 days. The carbonation depths have been measured by phenolphthalein whereas mercury intrusion porosimetry (MIP), TGA and thermodynamic modeling have been used to study pore structure, CO_2 binding capacity and phase assemblages. The Portland cement has the highest resistance to carbonation due to its highest CO_2 binding capacity. The limestone blend has higher CO_2 binding capacity than the metakaolin blends, whereas the better carbonation resistance of the metakaolin blends is related to their finer pore structure and lower total porosity, since the finer pores favor capillary condensation. MIP shows a coarsening of the pore threshold upon carbonation for all mortars. Overall, the CO_2 binding capacity, porosity and capillary condensation are found to be the decisive parameters governing the carbonation rate.

1. Introduction

Significant research efforts focus on the development and characterization of new Portland cement blends including calcined clays [1] as supplementary cementitious materials (SCMs) with the principal aim of reducing CO_2 emissions associated with Portland cement clinker production. Partial replacement of Portland cement by SCMs such as fly ashes and slags represent a common route to reduce CO_2 emissions. The interest in calcined clays reflects both that slags and fly ashes may not be available in sufficient quantities in the future and more importantly, that clays are widely abundant in the Earth's crust. Limestone represents another interesting material, which is commonly added in small amounts to Portland cements, where it increases the early strength, reduces the water demand and improves the rheology of the resulting concrete [2–5]. Limestone provides nucleation sites for the formation and growth of the calcium-silicate-hydrate (C-S-H) phase and it is also partially consumed during hydration, resulting in the formation of calcium monocarboaluminate hydrate ($Ca_4Al_2(OH)_{12}CO_3 \cdot 5H_2O$) [3,5,6]. The combination of limestone with other SCMs has been used to develop ternary cement blends [7]. For example, a synergetic effect between metakaolin and limestone has been observed in ternary Portland cement blends, as seen by an increase in compressive strength [8,9].

Carbonation of concrete is one of the important age-limiting factors for reinforced concrete structures. Given the intrinsically high pH in the pore solution of uncarbonated concrete, a thin passive layer around the steel bars is formed which protects the steel reinforcement against corrosion. However, carbonation of the cement hydrates, e.g., portlandite (CH) and the C-S-H phase, can result in a significant reduction of pH and to a certain level, where the protective layer on the steel bars is destroyed. This problem may become particularly important when SCMs are incorporated in cement blends, since several studies have reported that cement-based materials including SCMs exhibit poor carbonation resistance, e.g. [10–12]. This underlines the research needs for carbonation studies of Portland cement – calcined clay – limestone blends before an industrial realization of these materials can take place.

The pH change induced by carbonation of concrete is ascribed to carbonation reactions of portlandite (CH) and the C-S-H phase, which result in the formation of $CaCO_3$ and $CaCO_3$ and/or amorphous silica, respectively. ^{29}Si NMR studies [13–15] have shown that the carbonation of the C-S-H phase takes place in two steps. Firstly, calcium is gradually removed from the interlayer and the defect sites in the silicate chains until Ca/Si = 0.67 is reached. After that the C-S-H decomposes by consumption of the Ca^{2+} ions in the principal layers, forming an amorphous silica phase. Hydrated Portland cement – SCM blends contain generally a smaller amount of portlandite compared to hydrated pure

---

[*] Corresponding author. Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, DK-8000 Aarhus C, Denmark.
E-mail address: jskib@chem.au.dk (J. Skibsted).

http://dx.doi.org/10.1016/j.cemconres.2016.06.006
0008-8846/© 2016 Elsevier Ltd. All rights reserved.

Portland cements, since a part of the portlandite has been consumed by reaction with the SCMs forming additional C-S-H phase. This lower amount of portlandite may account for the faster carbonation process for Portland cement – SCM blends, compared to pure Portland cement, as mentioned in earlier studies [10,11]. However, it seems of minor importance for the carbonation resistance, if the CaO buffering the ingression of CO_2 is present in portlandite or in C-S-H [12]. A decisive material parameter for the carbonation resistance is the buffer capacity per volume of cement paste that can be expressed as the ratio between mixing water and CaO reacting with CO_2 [12]. Moreover, the lack of portlandite cannot solely explain the variations in carbonation depths, when the depths are measured by the phenolphthalein indicator method, since several of the hydrate phases are not completely carbonated within the carbonation depths as revealed by thermogravimetric analysis [16,17]. Thus, it is necessary to compare the actual and potential CO_2 binding of the different binders in order to better understand their carbonation performance.

The carbonation profiles have been thoroughly studied by various techniques on pure Portland cement and Portland cement – fly ash blends, revealing that the carbonation depths do not necessarily exhibit a sharp reaction front [11,17]. However, the corresponding pH profiles are not known, since they are difficult to measure experimentally as a result of drying of the samples during carbonation. McPolin et al. [18] have measured the pH profiles after carbonation by pore solution expression and leaching methods. However, these methods can only provide an estimate of the real pH values because partially carbonated large crystals of portlandite are cracked during the measurements which may change the pH of the pore solution. In addition, the phenolphthalein method indicates a gradual change in color from colorless to fuchsia, reflecting pH changes from 8.2 to 10.0 in solution. This gradual color change has not been documented for the carbonation front in Portland cement-based concrete or mortars measured by the phenolphthalein method. It is not clearly documented at which pH levels the phenolphthalein method reflects the carbonation depths in concrete.

Another impact of carbonation on concrete is the changes in microstructure, originating from differences in molar volumes of the hydrated and carbonated phases. Predictions become complex when the molar volume of the C-S-H phase changes with carbonation as a result of changes of the Ca/Si ratio [11,15,19]. Moreover, the different polymorphs of $CaCO_3$ exhibit different unit cell volumes [20]. Several studies have reported a reduction of the porosity for pure Portland cement [12,19,21–24], whereas an increase of the total porosity has been measured by different techniques for Portland cement – SCM blends [12,25]. In contradiction Morandeau et al. [11] reported that the total porosity decreased for a Portland cement paste with 60 vol% of fly ash, however, its microstructure was rearranged and large capillary pores were created. The same work [11] also reviewed some earlier studies and stated that there is a shift in the porosity towards larger pore radii during carbonation as measured by mercury intrusion porosimetry. Johannesson et al. [26] reported that the difference in pore size distribution is more pronounced than the difference in specific surface area for carbonated and non-carbonated Portland cement mortars. In addition, the presence of some microcracks has been noticed as a result of the volume increase of the solid during carbonation [27]. The earlier studies show some discrepancies and lack of explanations in the interpretation of the microstructural changes caused by carbonation.

The present work is a part of a series of durability investigations of Portland cement – metakaolin – limestone blends, all focusing on a replacement level of 35 wt% of Portland clinker [28]. This paper focusses on the carbonation of Portland cement – metakaolin blends with and without limestone, with the goal of determining the carbonation resistance for these metakaolin blends and key factors associated with the carbonation processes. For comparison, a reference of pure Portland cement and a limestone Portland cement with a 35 wt% of replacement are also investigated. Moreover, the present work utilizes the results from a ^{29}Si NMR and XRD study of paste samples of the same blends by Dai et al. [29], which revealed the degree of reaction for the principal phases. Analysis of the phase assemblages and microstructure in the blends may form the basis for a better understanding of the differences in carbonation resistance for Portland cement – SCM blends. The phenolphthalein spray method is used to measure carbonation depths whereas mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM) are applied to characterize the changes in microstructures due to carbonation. Thermogravimetric analysis (TGA) and thermodynamic modeling are employed to investigate the actual and potential CO_2 binding for the different blends. Thermodynamic modeling is also used to examine changes in total porosity and pH in relation to phase changes. Finally, the carbonation resistance of the studied blends is evaluated in terms of pore-structural changes, capillary condensation, CO_2 binding and calculated pH profiles.

2. Experimental

2.1. Materials

The binders used in this study were made from a white Portland cement (wPc, CEM I 52.5 N) and two SCMs: metakaolin (MK) and limestone (LS). The wPc was obtained from Aalborg Portland A/S, Denmark, and included 3.1 wt% LS, 4.1 wt% gypsum and 1.9 wt.% free lime. The MK was produced in the laboratory from kaolinite (Kaolinite Supreme™ from Imerys Performance Minerals, UK) by thermal treatment at 550 °C for 20 h. The limestone was a Maastrichtian chalk from Rørdal, Northern Denmark. The chemical compositions of the starting materials, determined by X-ray fluorescence (XRF), and their physical properties are given in Table 1. The wPc contained 64.9 wt% alite,16.9 wt% belite and 7.8% C_3A where the content of the silicate phases was determined by ^{29}Si MAS NMR and the quantity of the aluminate phase by mass balance calculations [29]. The C_4AF phase was not taken into account as the small amount of iron is expected to be incorporated as guest-ions in the alite, belite, and calcium aluminate phases. The sand used for the mortars was a CEN reference sand (Normensand GmbH, Germany), which has a silica content of at least 98 wt% and a density of 2650 kg/m^3. A superplasticizer (SP, Glenium 27, BASF) was used to achieve similar flow for all mortars.

2.2. Mortar preparations

The compositions of the binders (Table 2) targeted a replacement of 35 wt% white Portland clinker by the SCMs. Considering the small amounts of LS and gypsum in the wPc this resulted in actual binder compositions with 31.9 wt% replacement of the wPc. The blends were used to produce mortars with a constant water-to-binder ratio (w/b = 0.5) and binder-to-sand ratio (b/s = 1/3), both ratios by weight. The

Table 1
Chemical composition (wt%), density and Blaine fineness for the starting materials.

	wPc	LS	MK
SiO_2	21.81	3.92	52.84
Al_2O_3	3.56	0.33	39.49
Fe_2O_3	0.24	0.14	1.42
CaO	66.13	53.73	0.22
MgO	1.10	0.35	0.48
K_2O	0.43	0.05	1.00
Na_2O	0.04	0.08	0.05
SO_3	3.37	0.05	0.06
TiO_2	0.21	0.02	0.88
P_2O_5	0.04	0.10	0.11
LOI	2.57	41.8	3.55
Density (kg/m^3)	3080	2700	2530
Blaine fineness (m^2/kg)	387	1211	1891
Carbon content	0.37	–	–
$CaCO_3$	3.1	93.8	–