Phase assemblage of composite cements

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ARTICLE INFO

ABSTRACT

The phase assemblage of binary Portland cements with 45 wt% replacement by calcareous fly ash and slag has been investigated by experiment, mass balance and thermodynamic simulations. The input for these calculations was based on clinker reaction measured by XRD-Rietveld refinement, on SCM reaction measured by SEM-EDS full element mapping and on C-S-H composition by SEM-EDS point analyses. A sensitivity analysis estimates the uncertainty of determination of phase volume as at best $\pm$ 2 cm^3/100 cm^3, and thus of rather semi-quantitative character. The differences between experiment and calculations regarding AFt/AFm, C-S-H and portlandite were assessed. Gel/space ratios computed using the volumes of all hydrates showed a clear correlation to compressive strength, which was unaffected by the mix composition. This suggests that the type of hydrates formed has little or no influence on the compressive strength and that the key factor is the space filling.

1. Introduction

The quantitative determination of the phase assemblage in hydrated composite cements is a challenging task due to the presence of several amorphous phases. These mainly concern one or more glassy phases from the anhydrous supplementary cementitious material (SCM) and the principal hydration product, C-S-H. Some of the AFm hydrates may also form in a poorly crystalline form, which is important in composite pastes as their content can increase significantly if the incorporated SCMs are rich in reactive alumina.

The currently available techniques for characterization of phase assemblage of hydrated cements often struggle to distinguish and accurately quantify multiple amorphous phases. Thermogravimetric analysis (TGA) enables identification of hydrate phases in cement paste but due to proximity of the temperatures of thermal decomposition of many of the hydrates, quantitative results can only be obtained for portlandite. X-ray powder diffraction (XRD) with Rietveld refinement is a powerful technique to quantify crystalline phases in cement paste but fails to distinguish between multiple amorphous components without prior calibration. Despite advanced approaches such as PONKCS (Partial Or Not Known Crystal Structure) [1,2] an accurate quantification of individual amorphous phases remains very challenging [3]. Electron microscopy with image analysis can be used to analyse the main hydration products [4] and to extract anhydrous SCM particles [5]. However, the quantification of hydrates is rendered impossible by fine intermixing of C-S-H and other hydrates and porosity at a sub-micron scale below the resolution limit of the scanning electron microscope.

To overcome the limitations of experimental techniques, analytical approaches such as thermodynamic simulations [6–8] and mass-balance [9,10] have been proposed to calculate the phase assemblage from the quantities of clinker and SCMs reacted. Thermodynamic simulation models an equilibrium phase assemblage whereas mass-balance distributes the reacted elements among phases assumed to precipitate in the analysed system. Studies of composite cements containing siliceous fly ashes [11,12] showed that XRD-Rietveld and thermodynamic simulations for the evolution of amount of portlandite and ettringite over time, agree within $\pm$ 5–10 wt.-%. Further, in the above studies, De Weerdt et al. [11] showed good correlation of coarse porosity measured by electron microscopy with compressive strength, while Zajac and Ben Haha [12] used the modelled phase volumes to calculate total porosity and relate it to strength. It is generally accepted that compressive strength is a function of the amount of hydrates formed. This dependence has been studied by many researchers and notably Powers, who provided an empirical relationship of compressive strength vs. gel/space ratio of Portland cements [13,14]. More recently, Lam and Poon have calculated these values for fly ash blended cements but observed significant scatter [15]. This was likely because the gel/space ratio was calculated from the degree of reaction of clinker and fly ash, assuming that the volume of hydrates is around 2.06 of the volume of binder reacted. However, the type and amount of hydration products formed in the presence of SCMs may differ significantly from those in Portland cements and may vary according to the type and amount of SCM. It thus seems that the assessment of strength vs. gel/space of

composite cements should be based on more precise a determination of the amount of "gel". A promising result has been presented by Schöler et al. [16], who compared compressive strength of fly ash and slag cements with the total volume of hydrates calculated by thermodynamic modelling.

The aim of this study was to quantify and compare the phase assemblages of binary cements with high replacement (45 wt%) by calcareous fly ash and slag using thermodynamic modelling and mass balance and to look at their correlation to compressive strength. The input for the calculations was the amount of clinker reacted measured by XRD-Rietveld and the amount of slag and fly ash reacted measured by scanning electron microscopy using the technique described in [5]. The calculated phase assemblages were compared with experimental phase assemblages by XRD-Rietveld refinement. A sensitivity analysis was carried out to determine how an uncertainty linked to the modelling input affects the total volume of hydrates predicted. Capillary porosity obtained from the thermodynamic and mass-balance simulations and that measured by mercury intrusion porosimetry were compared to the compressive strength of mortars. Further, Power's gel/space ratio was calculated from the total volume of hydrates modelled and compared to the compressive strength.

2. Materials and experimental methods

2.1. Materials

One Portland cement (PC), one slag (S) and two calcareous fly ashes (FA1 and FA2) characterised in a previous study [5,17] were the primary materials in this study. Their chemical composition was measured by X-ray fluorescence and their phase composition was analysed by X-ray diffraction with quantitative Rietveld refinement. The results are shown in Table 1. The XRF, as mainly dependent on the calibration, has the uncertainty of around $+/0.1$ wt%. The XRD-Rietveld depends much more on the user and thus our estimate of the uncertainty of reproducibility of the result is $+/- 1$ wt%. The particle size distributions of the raw materials were measured by laser diffraction using a Malvern MasterSizer S, the results are shown in Fig. 1. The densities of the raw materials were determined by helium pycnometry as: 3100 kg/m^3 – PC, 2900 kg/m^3 – S, 2700 kg/m^3 – FA1 and FA2.

2.2. Preparation of pastes

Binary composite cements were prepared by mixing 55 wt% PC and 45 wt% fly ash (PC-FA1, PC-FA2) or slag (PC-S). Comparison samples were a non-substituted PC and a mix of PC with 45 wt% quartz inert filler (PC-Q). Gypsum was added to adjust the SO_3 content of all the cements to 3.25 wt%. The pastes were prepared by mixing the powders with water (water/binder = 0.4) using a laboratory mixer at 1600 rpm for 2 min. The pastes were then cast in plastic cylinders, sealed and
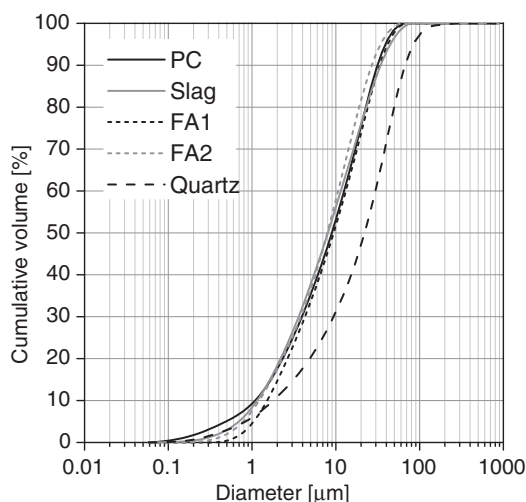

Fig. 1. Particle size distribution of anhydrous materials measured by laser diffraction.

cured at 20 °C until testing. After 1, 7, 28, 56, 90, and 365 days discs were cut from the cylinders and polished delicately using grade 1200 sandpaper. Immediately after, the discs were analysed by X-ray diffraction. Companion discs were prepared for electron microscopy and mercury intrusion porosimetry. To stop hydration, the discs were immersed in isopropanol for 7 days and then stored in a vacuum desiccator for another 7 days to evaporate the isopropanol. For microscopy, these dried discs were impregnated with epoxy resin, gradually polished down to 1/4 μm with diamond powders and covered with a conductive layer of ≈ 10 nm carbon. More details on sample preparation, processing and characterization can be found in [18].

2.3. X-ray powder diffraction (XRD)

X-ray powder diffraction was carried out using a Panalytical PW3701 X'Pert diffractometer with Cu-Kα radiation, fixed divergence slit of 0.5° and an X'Celerator detector. The X-ray generator was operated at 45 kV and 40 mA. The scanning range was 8° to 65° 2θ and the step size was 0.0167°. The results were analysed using X'Pert HighScore Plus 4.1 software with rutile as an external standard, following the procedures described in [18]. The refined parameters were the shift due to specimen height, background composed of a first order Chebyshev polynomial and 1/X parameter, phase scale factors, unit cell parameters up to 1% variation, and the peak width.

2.3.1. Reaction of clinker

The determination of the degree of reaction of clinker by XRD-Rietveld refinement in the presence of SCMs is more challenging than in an unsubstituted cement. As the proportion of clinker is lower in

Table 1
Bulk chemical analysis by XRF and phase composition by XRD-Rietveld [wt%].

	PC	FA1	FA2	S	Q		PC	FA1	FA2	S	Q
Al_2O_3	5.5	19.8	18.2	11.6	1.6	C_3S	66.3	–	–	–	–
SiO_2	20.7	42.3	33.6	36.7	97.0	C_2S	8.3	2.5	0.5	–	–
CaO	65.7	20.7	26.5	38.9	0.1	C_3A	8.7	2.0	4.0	–	–
Na_2O	0.2	0.3	1.9	0.2	–	C_4AF	7.7	1.0	1.5	–	–
K_2O	0.4	1.5	0.4	0.7	1.0	Quartz	0.5	1.3	3.5	–	97.3
MgO	1.5	2.2	6.4	7.8	0.1	Mullite	–	–	–	–	2.7
Fe_2O_3	2.7	8.2	6.4	0.5	–	Dolomite	1.1	–	–	–	–
SO_3	2.6	1.4	2.2	2.8	–	Calcite	1.8	–	–	–	–
TiO_2	0.3	0.7	1.3	0.9	–	Periclase	–	–	2.0	–	–
P_2O_5	0.2	0.3	0.9	–	–	Gypsum	2.6	–	–	–	–
						Anhydrite	3.0	1.8	2.0	–	–
						Free lime	–	1.7	0.6	–	–
Sum	99.8	97.2	97.7	100.0	99.8	Amorphous	–	89.7	85.9	100.0	100.0