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Effect of temperature on the pore solution, microstructure and hydration products of Portland cement pastes

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Abstract

The effect of temperature on the hydration products and the composition of the pore solution are investigated for two Portland cements from 5 to 50 °C. Increased temperature leads to an initially fast hydration and a high early compressive strength. At 40 and 50 °C, the formation of denser C–S–H, a more heterogeneous distribution of the hydration products, a coarser porosity, a decrease of the amount of ettringite as well as the formation of very short ettringite needles has been observed. At 50 °C, calcium monosulphoaluminate has formed at the expenses of ettringite. In addition, the amount of calcium monocarboaluminate present seems to decrease. The composition of the pore solution mirrors the faster progress of hydration at higher temperatures. After 150 days, however, the composition of the pore solution is similar for most elements at 5, 20 and 50 °C. Exceptions are the increased sulphate concentrations and the slightly lower Al and Fe concentrations at 50 °C.
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1. Introduction

The hydration of cement is sensitive to temperature. Increased temperature promotes the hydration leading to high early strength. At later stages, however, the strength of cements hydrated at increased temperature is reduced compared to those hydrated at room temperature [1–3]. In the case of increased temperature, the initially fast hydration causes the more rapid precipitation of hydration products during the first hours and days, which is responsible for the observed early strength development. This fast hydration in the initial stage leads to a more heterogeneous distribution of the hydration products as the hydrates precipitate around the clinker particles and build up a dense inner shell around the clinkers [4]. At low temperature hydration starts very slowly, which allows the dissolved ions more time for diffusion before the hydrates precipitate and leads to a less dense C–S–H, a more even distribution of hydration products and a lower coarse porosity [4–6].

Different curing temperatures do not only induce changes in the morphology of the solid phases but also influence the composition of the liquid phase. A few studies have investigated the influence of temperature on the composition of the pore solution [7–9]. In this paper, a consistent set of data on the temperature dependence of the morphology, quantity and stability of the hydration products and the composition of the pore solution is presented. The influence of temperature has been investigated using a Portland-limestone cement (PLC) and a sulphate-resisting Portland cement (SRPC). In subsequent paper [10] the influence of temperature on the hydrate assemblage and the composition of the pore solution is calculated with the help of thermodynamic modelling and compared to the experimental data.

2. Materials and methods

Experiments were carried out using a Portland-limestone cement (PLC): CEM II/A-LL 42.5 R and sulphate-resisting Portland cement (SRPC): CEM I 52.5 N. The chemical composition of the materials was determined by X-ray

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Table 1
Composition of the cements used

Chemical analysis [g/100 g]			Normative phase composition [a] [g/100 g]		
	PLC	SRPC		PLC	SRPC
SiO_2	16.6	22.3	Alite	35	61
Al_2O_3	4.4	2.7	Belite	21	18
Fe_2O_3	2.4	1.9	Aluminate	7.6	3.9
CaO	59.5	65.7	Ferrite	7.3	5.8
MgO	1.8	0.85	CaO	1.7	0.45
K_2O	0.83	0.22	$CaCO_3$	16	3.7
Na_2O	0.28	0.13	$CaSO_4$ [b]	3.0	3.6
CaO (free)	1.7	0.45	K_2SO_4 [c]	1.4	0.14
CO_2	7.1	1.6	Na_2SO_4 [c]	0.29	0.09
SO_3	2.5	2.2	K_2O [d]	0.08	0.14
Readily soluble alkalis[c]			Na_2O [d]	0.15	0.09
K_2O	0.75	0.08	MgO [d]	1.8	0.85
Na_2O	0.13	0.04	SO_3 [d]	0.08	0.01

Blaine surface area: PLC: 438 m²/kg; SRPC: 354 m²/kg.

[a] Calculated from the chemical analysis.

[b] SRPC: anhydrite (1.5 g/100 g), hemihydrate (1.1 g/100 g), gypsum (1.3 g/100 g); PLC: anhydrite (0.7 g/100 g), gypsum (2.9 g/100 g).

[c] SRPC: readily soluble alkalis were calculated from the concentrations of alkalis measured in the solution after 5 min agitation at a w/c of 10; present as alkali sulphates. PLC: estimated based on the alkali content and on the alkali distribution given in Taylor (1987).

[d] Present as solid solution in the major clinker phases.

fluorescence (XRF) (Table 1). The SRPC used has relatively low alkali content.

In all cases, water, cements, and aggregates were stored for 2 days at the respective temperatures before mixing. From PLC mortar prisms (4 cm × 4 cm × 16 cm) were prepared according to EN 196-1 using 3 kg quartz aggregate (0–2 mm) per kg cement but using a w/c=0.58 instead of 0.5. Concrete cubes were prepared using a w/c of 0.58, 300 kg cement and 1931 kg aggregate (0–32 mm) per m³ concrete. The specimens were cured at 5, 20, 30 and 40 °C, respectively, demoulded after 24 h and immediately covered with plastic. The compressive strength of the concrete samples was measured according to EN 12390-3 and compressive strength of the mortar samples according to EN 196-1.

Cement paste samples were prepared from SRPC and PLC. For short-term hydration experiments, i.e. up to 6 h, small samples of ~100 g were prepared in the glove box and aged at the appropriate temperature under a N_2-atmosphere. The pore solutions of SRPC samples were collected by vacuum filtration using 0.45 μm nylon filters. The separation of liquid and solid phase by vacuum filtration was done within one to two min in order to minimise temperature change within the samples. The solutions were immediately acidified and diluted to prevent the precipitation of solids. For longer hydration times, larger cement paste samples consisting of 1 kg cement and the appropriate amount of water were mixed twice for 90 s according to EN 196-3. The pastes were cast in 0.5 l PE-bottles, sealed tightly to exclude the ingression of CO_2 and the evaporation of water and stored at the appropriate temperature. A portion of the solid was removed before the sampling of the pore solution for the analyses of the solid phases. Pore fluids of the hardened SRPC samples were extracted using the steel die method and pressures up to 530 N/

mm². Again care was taken to minimise temperature change during extraction. The whole extraction procedure of the pore solution used approx. 10 min, the temperature within the sample, however, was buffered by the relatively large volume of the samples. The solutions were immediately filtered using 0.45 μm nylon filters. After filtration an aliquot was diluted with HNO_3 (6.5%) to prevent the precipitation of solid phases. The remaining solution was used for pH measurements. The pH electrode was calibrated using KOH solutions of known concentrations. The total concentrations of the Na, K, Ca, Al, S, and Si were determined using inductively plasma optical emission spectroscopy (ICP-OES). Sulphate concentrations were also determined by ion chromatography (IC); concentrations agreed within ±20% with the ICP-OES data for S.

The solid fractions of the PLC and SRPC pastes were crushed and ground in acetone, dried at 40 °C and then used for XRD and thermogravimetric analysis (TGA). TGA was carried out in N_2 on about 10 mg of powdered cement pastes at 20 °C/min up to 980 °C. The TGA data were used to calculate the content of portlandite, calcite and ettringite in the hydrated samples. The content of "chemically bound" water was determined from the weight loss between 40 to 500 °C. Cement paste and mortar samples for ESEM studies were dried in the vacuum oven at 40 °C. Fresh fractured surfaces were examined by environmental scanning electron microscopy (Philips ESEM FEG XL 30) using the low vacuum mode (at 1 Torr H_2O), polished samples using back-scattered, secondary electron (BSE) images and EDX-analysis. The polished samples were pressure impregnated with epoxy resin, polished and carbon coated. BSE images of the polished samples were used to estimate the porosity based on image analysis using the different grey levels. The porosity estimated from BSE images is a relative estimate only and underestimates the total porosity as only the coarser pores (>0.5 μm) are considered.

3. Results

3.1. Progress of hydration and strength development

Increased temperature initially accelerates the dissolution of the anhydrous clinker phases (cf. XRD data given in Fig. 1)
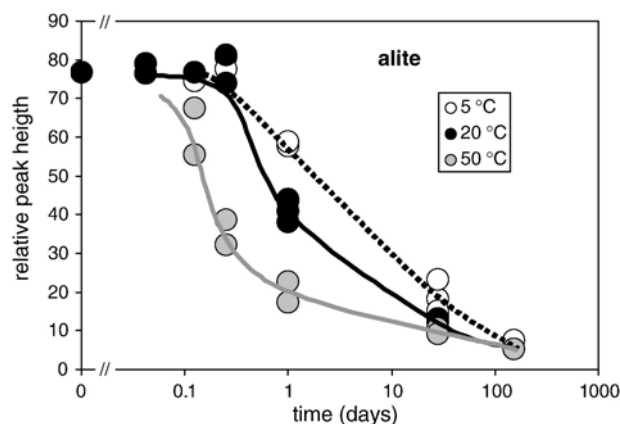

Fig. 1. Relative XRD peak heights of alite in SRPC cement paste (w/c=0.4) as a function of time and hydration temperature. Lines serve as eye-guide only.