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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.

Keywords: Temperature (A); Microstructure (B); Pore solution (B); Hydration products (B)

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 m^2/kg; SRPC: 354 m^2/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 m^3 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/mm^2. 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)

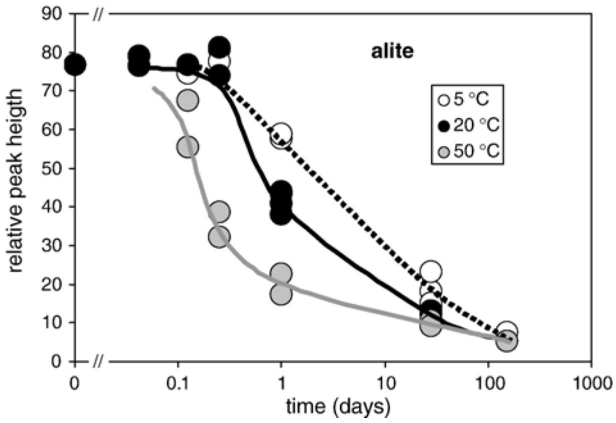

Fig. 1. Relative XRD peak heights of alite in SRPC cement paste (w/c = 0.4) as a function of time and hydration temperature. Lines serve as eye-guide only.

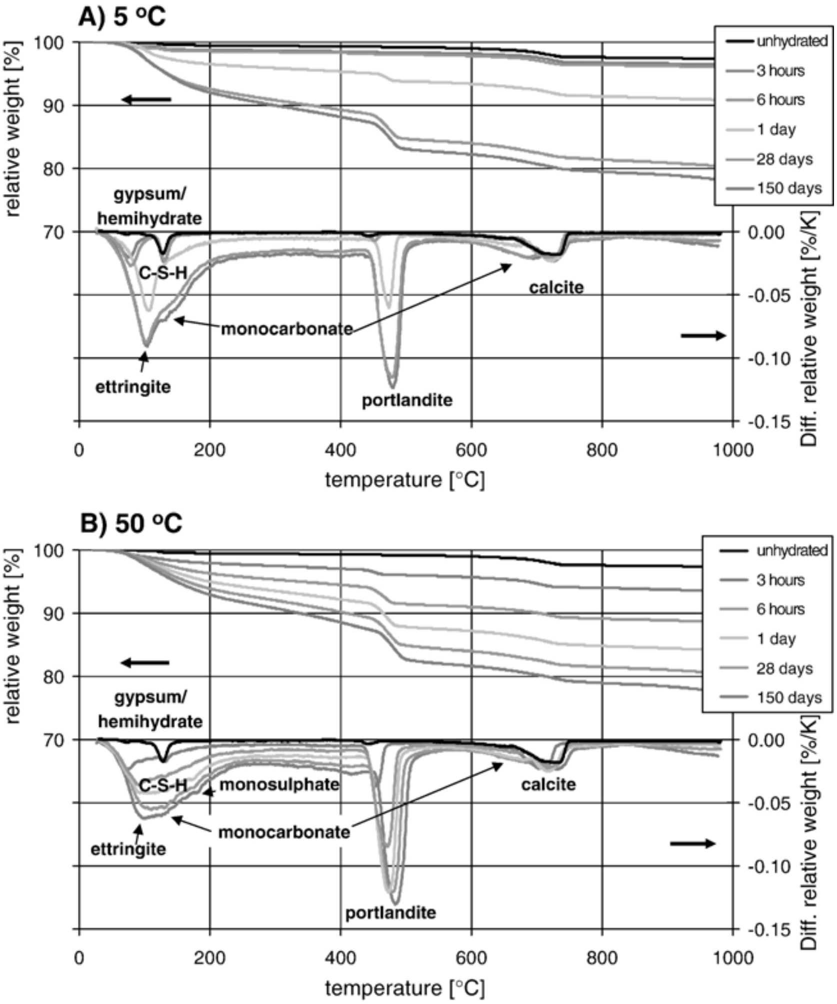

Fig. 2. TGA/DTG data of SRPC cement paste (w/c = 0.4) at A) 5 °C and B) 50 °C as a function of time.

which results in a faster formation of the hydration products. The faster dissolution and precipitation processes at increased temperature are also illustrated by calorimetric measurements, e.g. [1,11] or TGA data (Fig. 2). After 3 h of hydration at 50 °C, portlandite, C–S–H and ettringite have precipitated (Fig. 2).

At 5 °C the dissolution of the clinkers is relatively slow as shown for alite in Fig. 1. Also the consumption of anhydrite and gypsum is slow (Fig. 2), while the hemihydrate present in the cement is dissolved after 1 h of hydration. The slow dissolution of aluminate and ferrite determines the rate of ettringite precipitation and thus the consumption of gypsum and anhydrite. At 5 °C, after 6 h mainly ettringite has formed as hydration product, only after one day significant amounts of portlandite and some C–S–H were detected by TGA.

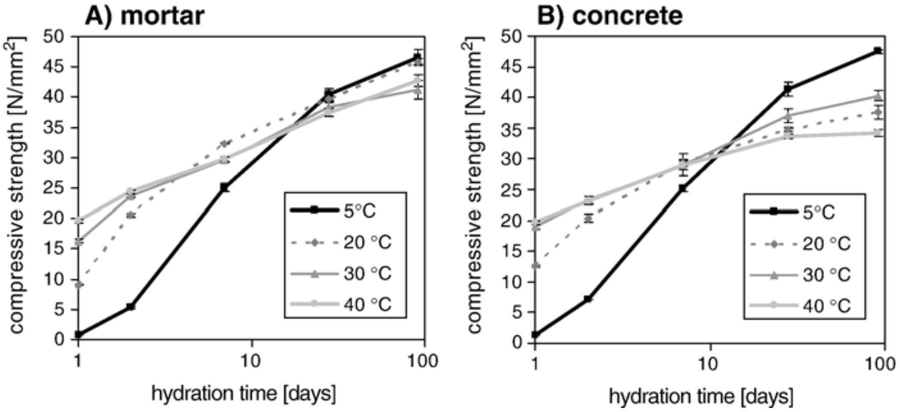

Fig. 3. Compressive strength (in N/mm^2; standard deviation indicated by bars) of A) PLC mortar (mean of 6 samples) and B) concrete (mean of 3 samples) as a function of time.

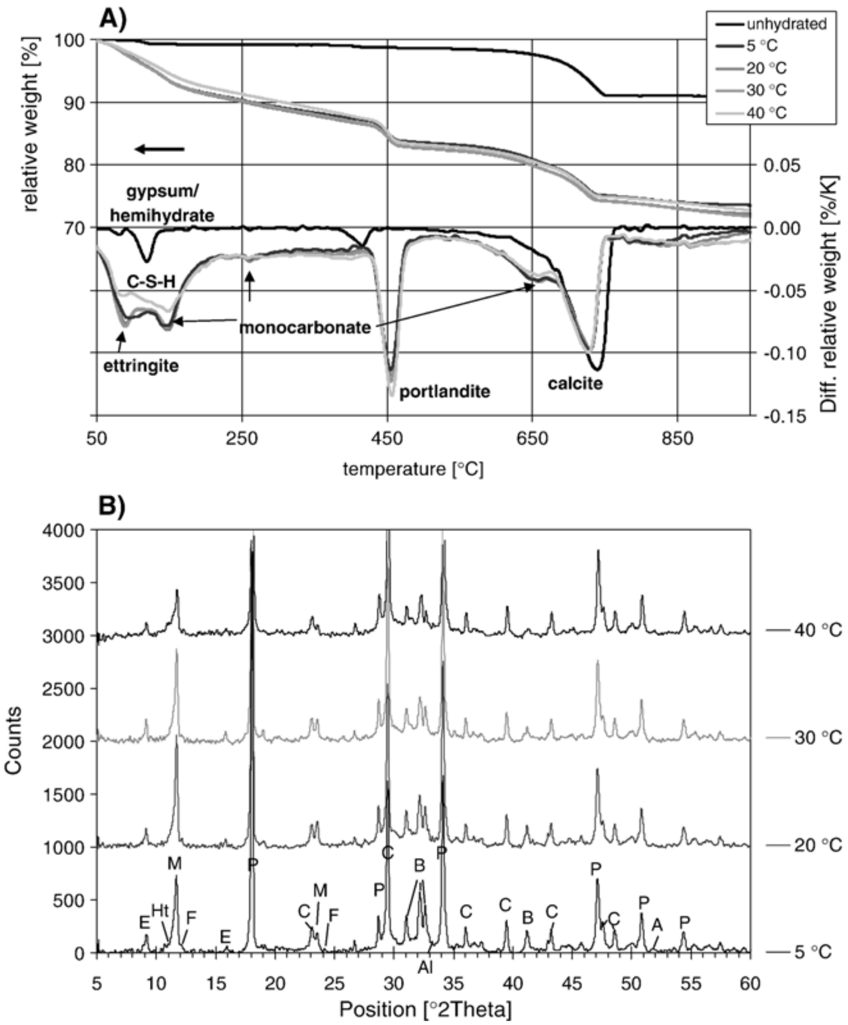

Fig. 4. A) TGA/DTG and B) XRD data of PLC cement paste (w/c = 0.5) hydrated at 5, 20, 30 and 40 °C for 28 days. A: alite, Al: aluminate, B: belite, C: calcite, E: ettringite, F: ferrite, Ht: hydrotalcite; M: calcium monocarboaluminate, P: portlandite.

Strength development at 5 °C is initially very slow, while at temperatures above room temperature a faster strength development is observed (cf. strength data for PLC given in Fig. 3). The strength of the samples cured at 40 °C increases only little after the first two days. In contrast, the strengths of the samples cured at 5 °C increases continuously such that after 28 and 91 days the mortar and the concrete samples cured at this temperature exhibit the highest compressive strength (Fig. 3). These observations are in agreement with many literature data (e.g. [3,12]). The strength development as a function of time and temperature is very similar for the mortar and concrete samples with the exception of the samples cured for 91 days at 40 °C for which a lower compressive strength of the concrete sample was determined.

3.2. Solid phases in mature pastes

3.2.1. Portland-limestone cement

The TGA/DTG data of the unhydrated PLC indicate the presence of gypsum, hemihydrate, portlandite and calcite. At 5, 20, 30 and 40 °C ettringite (14±3 wt.%), C–S–H, calcium monocarboaluminate and portlandite (15±1 wt.%) have precipitated in PLC pastes hydrated for 28 days (from TGA data, Fig. 4A). In addition, 13±1 wt.% calcite is present in the hydrated samples. The TGA/DTG analysis indicates that, after 28 days of hydration, the content of chemically bound water (16–17 wt.%) is similar at all temperatures (cf. Fig. 4A), even though higher strength was determined for the samples hydrated at 5 °C (Fig. 3). The XRD data confirm the presence of ettringite, portlandite, calcium monocarboaluminate, and calcite in all hydrated samples (Fig. 4B). In addition, belite and traces of hydrotalcite are present. The clinker phases alite and aluminate have been consumed to a large extent after 28 days.

While the same phases were identified at 5 and at 40 °C, small differences in the quantities were found. At 40 °C, less belite, calcium monocarboaluminate and 1–3 wt.% less ettringite, but slightly more calcite and portlandite are present after 28 days. Both the TGA/DTG and XRD data give consistent trends between higher and lower temperatures. TGA/DTG indicates that the amount of C–S–H remains approximately constant (Fig. 4A) even though this is difficult to estimate as ettringite (main weight loss at 100 °C) and calcium monocarboaluminate (main weight loss at 150 °C) overlap the weight loss of C–S–H.

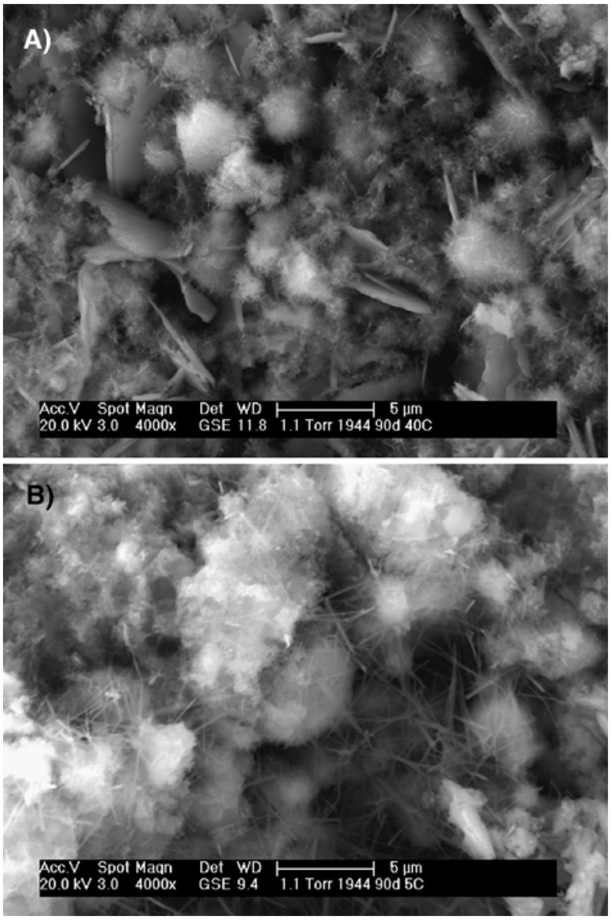

Fig. 5. Microstructure (ESEM, fractured surfaces) of PLC mortar samples hydrated for 91 days at A) 40 °C and B) 5 °C.

ESEM images of the fresh fractured surface of the mortar samples hydrated for 91 days show the presence of hexagonal platelets, calcite, C–S–H and ettringite (Fig. 5). Qualitative EDX of these hexagonal platelets shows besides Ca and Al also the presence of C, and minor quantities of Mg and Si, suggesting calcium monocarboaluminate intermixed with other solids. The hexagonal platelets were much more prominent in samples hydrated at 20 and 40 °C than at 5 °C. Similar platelets were also observed in SEM pictures of the polished mortar and cement paste samples. In general, the different hydration products are more easily detectable in the samples hydrated at higher temperatures due to their more heterogeneous distribution. At lower temperature the precipitating hydrates are more closely intermixed. This agrees well with the findings of Kjellsen et al. [13], who observed a more uniform distribution of the hydrates at 5 °C accompanied by a decrease of (larger) pores. A lower fraction of coarser pores at 5 °C is also observed in the samples investigated (Table 2). The analysis of the BSE-image of the PLC shows an increase of the coarser porosity with increasing temperature.

In the samples hydrated at 5 °C, prismatic ettringite needles with a length of 2–4 µm are conspicuous in the ESEM images (Fig. 5). At higher temperature the ettringite needles are significantly smaller: 1–2 µm at 20 °C and ≤ 1 µm at 40 °C. The slower formation of ettringite at lower temperatures promotes the formation of larger crystals. The presence of long ettringite needles at 5 °C has been previously reported by Stark et al. [14].

3.2.2. Sulphate-resisting Portland cement

The TGA/DTG data of the unhydrated SRPC indicate the presence of gypsum, hemihydrate, portlandite and calcite. In the SRPC pastes hydrated for 150 days ettringite, C–S–H, portlandite, calcite and traces of calcium monocarboaluminate are detected by XRD and TGA/DTG (Fig. 6). From TGA data the content of portlandite and calcite was calculated to be 17–19 wt.% and 2–3 wt.%, respectively. In addition, belite and traces of alite are present in the samples hydrated for 150 days (Fig. 6B).

After 150 days more belite is still present at 5 °C than at higher temperatures. At 50 °C less ettringite and calcium monocarboaluminate has formed than at 5 and 20 °C. The content of chemically bound water (14–17 wt.%) is comparable at 5, 20 and 50 °C (cf. Fig. 6A). No clear dependence of the portlandite content on temperature is observed. At 50 °C, calcium monosulphoaluminate forms at the expenses of ettringite and calcium monocarboaluminate (Fig. 6). The formation of calcium monosulphoaluminate at increased temperature agrees with the findings of former studies [15–17] that showed that increased temperatures promote the formation of calcium monosulphoaluminate, while the stability of ettringite decreases.

The results from the ESEM investigation of the coated and polished surfaces of the SRPC are similar to those found for PLC. In the SRPC samples an increase of the coarser porosity is observed at 50 °C (Table 2). At 50 °C relatively thick (approx. 1 µm) AFm-type platelets are present (Fig. 7A), EDX-analysis suggest that these are calcium monosulphoaluminate platelets.

The inner product (IP) of the samples hydrated at 50 °C shows a lighter grey value in the SEM/BSE than the IP hydrated at 5 °C (Fig. 7), which indicates the formation of denser hydration shells at higher temperature. Comparison of the mean atomic ratios of the IP (Table 2) showed no significant difference in the Ca/Si ratios which agrees with the findings of Kjellsen [18] and Famy et al. [19]. These authors showed that the difference in grey scale observed at different temperatures is not caused by difference in the chemical composition but by the formation of a denser IP at higher temperature.

Table 2
Mean atom ratios for inner C–S–H gel at different temperatures from EDX analysis and coarse porosity as estimated from image analysis (standard deviation in parentheses)

Temp [°C]	PLC (91 days)			SRPC (150 days)		
	5	20	40	5	20	50
Ca/Si	1.62 (0.08)	1.66 (0.17)	1.72 (0.16)	1.56 (0.14)	1.52 (0.10)	1.59 (0.16)
Al/Ca	0.17 (0.04)	0.10 (0.05)	0.09 (0.04)	0.08 (0.02)	0.07 (0.02)	0.07 (0.02)
S/Ca	0.048 (0.018)	0.037 (0.009)	0.043 (0.015)	0.037 (0.013)	0.033 (0.011)	0.032 (0.009)
Porosity (vol.%)	9 (3)	12 (3)	17 (2)	11 (1)	12 (1)	14 (2)

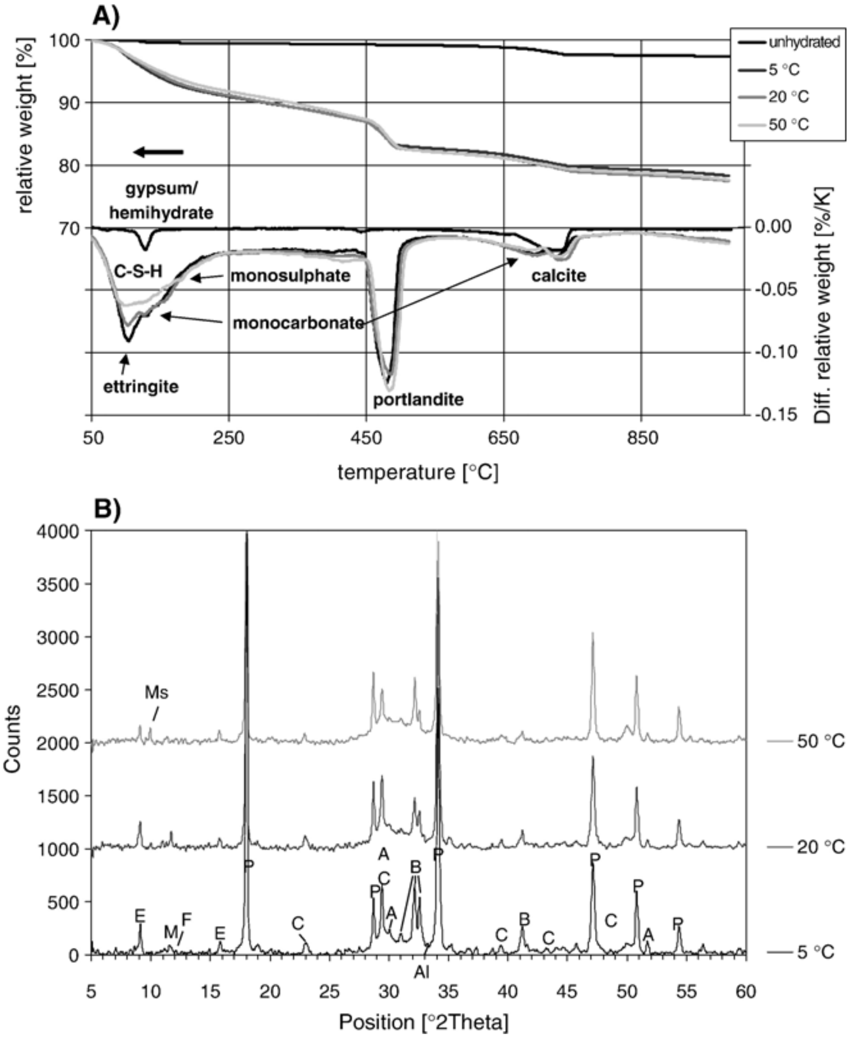

Fig. 6. A) TGA/DTG and B) XRD data of SRPC cement paste (w/c = 0.4) hydrated at 5, 20 and 50 °C for 150 days. A: alite, Al: aluminate, B: belite, C: calcite, E: ettringite, F: ferrite, Ht: hydrotalcite; M: calcium monocarboaluminate; Ms: calcium monosulphoaluminate; P: portlandite.

3.3. Composition of the pore solution

During the first hours of the hydration process the composition of the pore solution of SRPC is dominated by the presence OH^-, K, Na, Ca and sulphate (Fig. 8). At 20 °C, the composition of the pore solution is more or less constant during the first 6 h. After that sulphate and Ca concentrations decrease. Initially, the concentrations of sulphate and Ca are limited by the presence of portlandite and gypsum. Due to the precipitation of ettringite, hemihydrate, gypsum and anhydrite are consumed with time and the sulphate concentration decreases drastically after about 1 day. At the same time, OH^- concentrations increase, as the electroneutrality of the solution is maintained. The increase of pH leads to a lower Ca and higher Al concentration. A more detailed discussion of the hydration of SRPC at 20 °C is given in Lothenbach and Wieland [20].

At 5 and 50 °C the trends of concentration curves are similar to those at 20 °C (Fig. 8). At 50 °C, however, the steep decrease of the sulphate and Ca concentrations takes place between 3 to 6 h, indicating that the hydration is faster than at 20 °C. At 5 °C, the steep decrease of the sulphate and Ca concentrations is observed after more than 1 day. Similarly, the alkali concentrations increase faster at 50 °C and slower at 5 °C, indicating again the faster progress of hydration at 50 °C.

After 150 days, most elements in the pore solution show similar concentrations at 5, 20 and 50 °C with the exception of sulphate, aluminium and iron. Sulphate concentrations are significantly increased at 50 °C, while the Al and Fe concentrations are slightly decreased. The solubility of ettringite increases strongly with increasing temperature [15]. This leads to the observed increase of sulphate concentration in the pore solution and also to the precipitation of calcium monosulphoaluminate instead of ettringite at higher temperatures [17]. Note, however, that not only the temperature determines whether calcium monosulphoaluminate or ettringite or both are present, but also the chemical environment such as the sulphate concentration and pH value of the pore solution [9,16,21].

Investigations concerning the composition of the pore solution at different temperatures are scarce. Wieker et al. [7] observed an increase in the S concentration with increasing temperature which agrees well with our results. Recently, Thomas et al. [8] reported for an OPC hydrated for 28 days, that

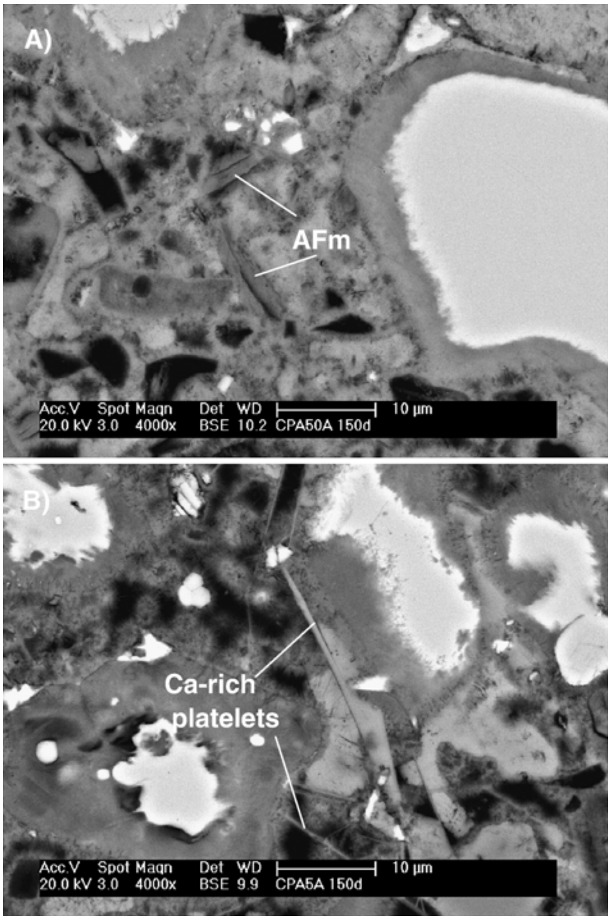

Fig. 7. Microstructure (ESEM/BSE) of polished SRPC samples hydrated for 150 days at A) 50 °C and B) 5 °C.

hydration temperatures between 20–50 °C have no significant influence on the measured alkali, OH-, Ca and Si concentrations. Furthermore, they observed lower Al-concentrations and (slightly) higher S concentrations at higher temperatures. Both findings are in good agreement with the present study.

4. Discussion

4.1. Comparison of hydrates formed in PLC and SRPC

In PLC less portlandite, but more calcium monocarboaluminate, calcite and hydrotalcite are present than in SRPC as shown by comparison of the TGA and XRD results of the two cements (Figs. 4 and 6). The alite content of the unhydrated PLC is with 35 wt.% relatively low, thus, hardly any alite is detected in samples hydrated for 28 days (Fig. 4). In contrast, SRPC contains approx. 60 wt.% of alite and even after 150 days, small quantities can be identified by XRD (Fig. 6). Especially as at w/c = 0.4 and prolonged hydration times the availability of water may be the limiting factor which retards hydration.

The relatively large quantities of calcium monocarboaluminate observed in the PLC are caused by the high Al/SO_3 ratio of 2.8 mol/mol of the cement (cf. Table 1) and not by the large reservoir of calcite present in PLC. In both cements, even after hydration times of 91 and 150 days, significant fractions of calcite are still present indicating that not the availability of calcite is the limiting factor for the formation of calcium monocarboaluminate. In PLC with an Al/SO_3 ratio of 2.8 mol/mol even after the formation of ettringite (Al/SO_3 = 0.67) and hydrotalcite – which consume only a small fraction of the Al present in the cement – significant amounts of Al are present in the system which can precipitate during hydration as calcium monocarboaluminate (cf. Fig. 4). In contrast, SRPC has a smaller Al/SO_3 ratio of 1.9 mol/mol which reduces the amount of calcium monocarboaluminate formed (Fig. 6). The lower amount of hydrotalcite found in SRPC is caused by the lower amount of MgO (Table 1). It is found that the differences found between the two hydrated cements can be attributed to differences in their chemical compositions.

4.2. Effect of temperature on hydrates

Elevated temperatures have a similar influence on both, the Portland-limestone cement and the sulphate-resistant Portland cement. The temperature determines which solid phase forms and how much of each solid precipitates. Between 5 and 30 °C the differences in the amount of hydrates formed are small. At 40 °C, less ettringite and calcium monocarboaluminate were observed for PLC. In addition, the appearance of calcium monosulphoaluminate was observed at 50 °C for SRPC, while less ettringite and calcium monocarboaluminate were present. The transformation of ettringite to calcium monosulphoaluminate around 50 °C in Portland cement systems has been reported previously, e.g. [17,22], while little is known about the stability of calcium monocarboaluminate in Portland cement at higher temperatures. The content of other solids in the cement remains basically unchanged between 5 and 50 °C. As more Al (and Fe) per sulphate is bound in calcium monosulphoaluminate than in ettringite (2 instead of 0.67), the presence of calcium monosulphoaluminate reduces the amount of Al that is available to form calcium monocarboaluminate. The lower fraction of ettringite present at 40 and 50 °C decreases due to its low density the volume of the hydrates and increases porosity.

During hydration, rims tend to form around the cement grains. These rims are denser at higher temperature. The darker grey levels of the hydration rims indicate the formation of a denser inner product which leaves free space (porosity) elsewhere in the cement. It has been proposed [4,5] that these denser hydration rims slow down the hydration at increased temperatures. The enhanced hydration rates and the denser hydration rims formed at higher temperature result in a more heterogeneous distribution of hydration products [13,18]. This gives rise to a coarser porosity and an increase of the mean pore radii [5,6,23]. In the case of lower temperature the hydrates are more homogeneously distributed which results not only in smaller pores but also leads to a better interlocking of the different phases. In addition, at 5 °C relatively long ettringite needles have been formed (Fig. 5) which could lead to better interlocking of the solids.

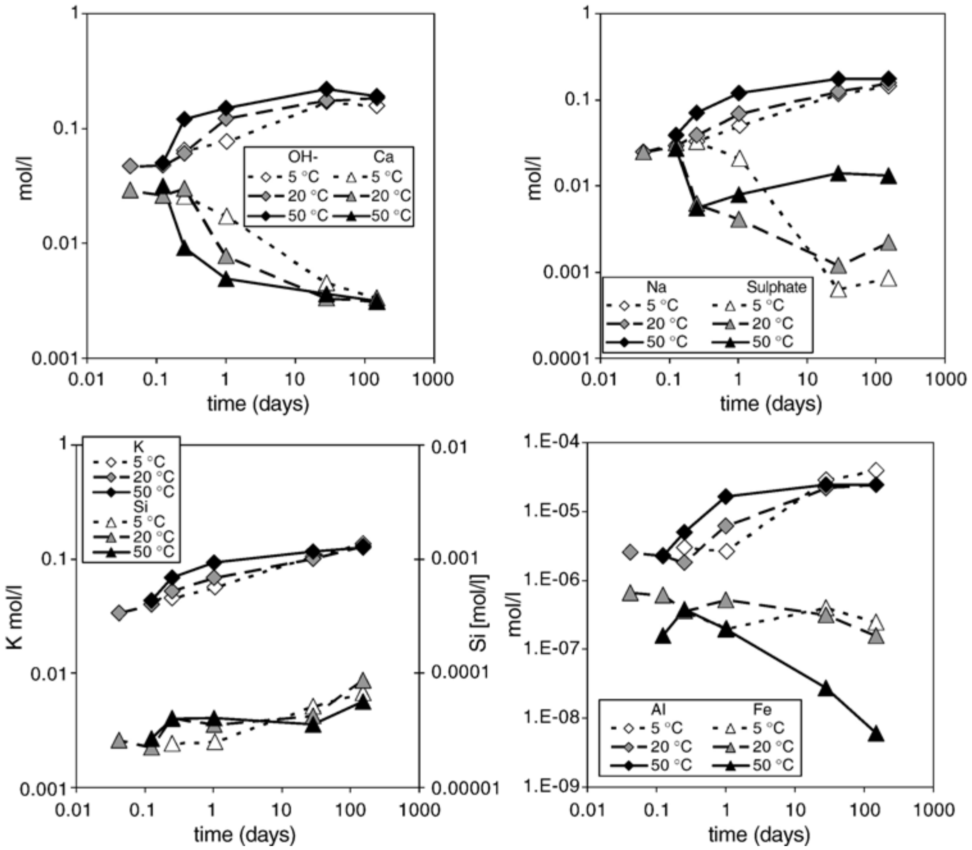

Fig. 8. Measured concentrations in the pore solutions of SRPC hydrated at 5, 20, 50 °C. The concentrations refer to total concentrations with exception of OH^- which refers to the free concentration. The lines are intended as eye guides only.

In the cement samples investigated in this paper, no statistically significant differences were found in Ca/Si, Al/Ca, S/Ca or Mg/Ca ratios of inner product of the samples prepared at the various temperatures (Table 2) due to the error associated with the measurements. A trend to higher Ca/Si and lower Al/Ca ratio at higher temperature was previously indicated by Famy et al. [19] and Kjellsen and Jennings [24]. In contrast, Escalante-Garcia and Sharp [25] observed a lower Ca/Si and Al/Ca and higher S/Ca ratios at higher temperature.

Higher temperature was found to increase the coarse porosity due to the formation of denser C–S–H and by reducing the fraction of ettringite present. Porosity generally correlates negatively with measured compressive strength; i.e. strength increases with decreasing porosity. The lower compressive strength observed at increased temperatures is probably mainly caused by the observed increase in porosity. In additions, strength could also be lowered by a weaker interlocking between the hydrates caused by their more heterogeneous distribution and the presence of very short ettringite needles.

5. Conclusions

At increased temperatures a higher early compressive strength as well as a faster initial progress of hydration was observed than at lower temperatures. In the SRPC hydrated at 50 °C the formation of calcium monosulphoaluminate at the expenses of ettringite was observed, while the amount of the other hydrates remained relatively unchanged. In addition, in both cements the amount of calcium monocarboaluminate present seems to decrease with increasing temperature. Little is known about the stability of calcium monocarboaluminate at higher temperature and further investigations are needed to confirm our findings. The analysis of the pore solution supported the data gained from the solid phase. The faster hydration at increased temperatures was reflected in the changes of Na, K, OH, S and Ca concentrations in the pore solution. The observation of higher sulphate concentrations at higher temperatures agrees with the formation of calcium monosulphoaluminate at 50 °C [10].

The 28 and 91 day compressive strength of the investigated PLC mortar and concrete samples was slightly reduced at 40 °C, while the observed degree of hydration was similar. In addition the following changes have been observed:

i. precipitation of a denser inner C–S–H,
ii. decrease of the ettringite content at 40 °C and above,
iii. heterogeneous distribution of the hydration products and the resulting coarser porosity and
iv. differences in morphology of the precipitating ettringite (very short needles at 40 °C).

The denser inner C–S–H as well as the decrease of the content of ettringite at higher temperature lead to higher (capillary) porosity and thus to a lower compressive strength.

The comparison of the hydrated SRPC and PLC shows that at 20 °C in both systems the same hydrates have precipitated. However, the differences in the chemical composition of these cements result in clear differences in the amount of the hydrates that were formed.

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References

[1] B. Lothenbach, C. Alder, F. Winnefeld, P. Lunk, Einfluss der Temperatur und Lagerungsbedingungen auf die Festigkeitsentwicklung von Mörteln und Betonen, Beton 55 (12) (2005) 604–609.

[2] J.I. Escalante-Garcia, J.H. Sharp, The microstructure and mechanical properties of blended cements hydrated at various temperatures, Cem. Concr. Res. 31 (5) (2001) 695–702.

[3] W.H. Price, Factors influencing concrete strength, J. Am. Concr. Inst. 47 (31) (1951) 417–432.

[4] K.O. Kjellsen, R.J. Detwiler, Reaction-kinetics of Portland-cement mortars hydrated at different temperatures, Cem. Concr. Res. 22 (1) (1992) 112–120.

[5] J.I. Escalante-Garcia, J.H. Sharp, Effect of temperature on the hydration of the main clinker phases in Portland cements: Part I, neat cements, Cem. Concr. Res. 28 (9) (1998) 1245–1257.

[6] J. Komonen, V. Penttala, Effects of high temperature on the pore structure and strength of plain and polypropylene fiber reinforced cement pastes, Fire Technol. 39 (1) (2003) 23–34.

[7] W. Wieker, T. Bade, A. Winkler, R. Herr, On the composition of pore solutions squeezed from autoclaved cement pastes, in: A. Nonat, J.C. Mutin (Eds.), Proc. Intern RILEM Workshop Hydration Setting, Dijon, E & FN Spon, London, 1992, pp. 125–135.

[8] J.J. Thomas, D. Rothstein, H.M. Jennings, B.J. Christensen, Effect of hydration temperature on the solubility behavior of Ca-, S-, Al-, and Si-bearing solid phases in Portland cement pastes, Cem. Concr. Res. 33 (12) (2003) 2037–2047.

[9] V. Michaud-Poupardin, D. Sorrentino, Application of a thermodynamic analysis of the "$CaO–Al_2O_3–CaSO_4$–alkali–H_2O" system to real OPC mortars at 90 °C, in: G. Grieve, G. Owens (Eds.), Proc. 11th Intern. Cong. Chem. Cem., Durban, South Africa, 2003, pp. 1903–1912.

[10] B. Lothenbach, T. Matschei, G. Möschner, F.P. Glasser, Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement, Cem. Concr. Res. (submitted for publication).

[11] J.I. Escalante-Garcia, J.H. Sharp, The effect of temperature on the early hydration of Portland cement and blended cements, Adv. Cem. Res. 12 (3) (2000) 121–130.

[12] I. Odler, S. Abdul-Maula, L. Zhongya, Effect of hydration temperature on cement paste structure, in: L.J. Sruble, P.W. Brown (Eds.), Proc. Mat. Res. Soc. Symp., 1987, pp. 139–144.

[13] K.O. Kjellsen, R.J. Detwiler, O.E. Gjorv, Development of microstructures in plain cement pastes hydrated at different temperatures, Cem. Concr. Res. 21 (1) (1991) 179–189.

[14] J. Stark, B. Möser, F. Bellmann, New approaches to cement hydration in the early hardening stage, in: G. Grieve, G. Owens (Eds.), Proc 11th Int Congr Chem Cem, Durban, South Africa, 2003, pp. 261–277.

[15] R.B. Perkins, C.D. Palmer, Solubility of ettringite ($Ca_6[Al(OH)_6]_2(SO_4)3\cdot 26H_2O$) at 5–75 °C, Geochim. Cosmochim. Acta 63 (13/14) (1999) 1969–1980.

[16] F.P. Glasser, D. Damidot, M. Atkins, Phase development in cement in relation to the secondary ettringite problem, Adv. Cem. Res. 26 (7) (1995) 57–68.

[17] H.M. Sylla, Reaktionen im Zementstein durch Wärmebehandlung, Beton 38 (11) (1988) 449–454.

[18] K.O. Kjellsen, Heat curing and post-heat curing regimes of high-performance concrete: influence on microstructure and C–S–H composition, Cem. Concr. Res. 26 (2) (1996) 295–307.

[19] C. Famy, K.L. Scrivener, A.K. Crumbie, What causes differences of C–S–H gel grey levels in backscattered electron images? Cem. Concr. Res. 32 (9) (2002) 1465–1471.

[20] B. Lothenbach, E. Wieland, A thermodynamic approach to the hydration of sulphate-resisting Portland cement, Waste Manage. 26 (7) (2006) 706–719.

[21] D. Damidot, F.P. Glasser, Thermodynamic investigation of the $CaO–Al_2O_3–CaSO_4–H_2O$ system at 50 °C and 85 °C, Cem. Concr. Res. 22 (1992) 1179–1192.

[22] A.N. Christensen, T.R. Jensen, J.C. Hanson, Formation of ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$, AFt, and monosulfate, $Ca_4Al_2O_6(SO_4)\cdot 14H_2O$, AFm-14, in hydrothermal hydration of Portland cement and of calcium aluminum oxide — calcium sulfate dihydrate mixtures studied by in situ synchrotron X-ray powder diffraction, J. Solid State Chem. 177 (6) (2004) 1944–1951.

[23] A.A. Almusallam, Effect of environmental conditions on the properties of fresh and hardened concrete, Cem. Concr. Compos. 23 (4–5) (2001) 353–361.

[24] K.O. Kjellsen, H.M. Jennings, Observations of microcracking in cement paste upon drying and rewetting by environmental scanning electron microscopy, Adv. Cem. Based Mater. 3 (1996) 14–19.

[25] J.I. Escalante-Garcia, J.H. Sharp, Variation in the composition of C–S–H gel in Portland cement pastes cured at various temperatures, J. Am. Ceram. Soc. 82 (11) (1999) 3237–3241.