Pergamon

Cement and Concrete Research, Vol. 28, No. 9, pp. 1245–1257, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(98)00115-X

EFFECT OF TEMPERATURE ON THE HYDRATION OF THE MAIN CLINKER PHASES IN PORTLAND CEMENTS: PART I, NEAT CEMENTS

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(Received October 21, 1997; in final form July 3, 1998)

ABSTRACT

The hydration of two Mexican Portland cements has been investigated at five temperatures in the range from 10 to 60°C. Samples were tested after eight periods of hydration during which they were immersed in water for between 1 day and 360 days, using quantitative X-ray diffraction, thermogravimetry, compressive strength determination, and scanning electron microscopy. Increased temperature initially accelerated the hydration of the four major anhydrous phases present in both cements. In the longer term, however, a reduced degree of hydration was observed for the alite and ferrite phases, accompanied by decreased compressive strength and increased apparent porosity. © *1998 Elsevier Science Ltd*

Introduction

Although extensive research into the complex processes involved in the hydration of Portland cement has been carried out, there remain many aspects not yet understood and questions that remain to be answered. Many variables affect the hydration of Portland cement, including the fineness, chemical composition, physical state, and availability of water. Another such factor is the temperature of the hydration process, which is important not only because of climatic variations prevailing throughout the world, but also because of the exothermic nature of the hydration reactions involved. A systematic study of the effect of temperature on the hydration of two Portland cements from Mexico using several experimental techniques is presented here.

An early study of the effect of temperature on the hydration of the calcium silicates in Portland cement was carried out by Copeland and Kantro (1,2), who reported an increased initial rate of hydration of both alite and belite at higher temperatures. For C_3S, however, the degree of hydration at 25°C surpassed that at 50°C beyond approximately 35% hydration or after only about 10 days. The hydration of β-C_2S had a crossover of hydration levels at about 70% hydration for 50°C and 25°C, when the hydration level at 25°C became greater than that

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at 50°C. Eventually the degree of hydration at 5°C also overtook those at the higher temperatures. Kjellsen and Detwiler (3) reported a similar temperature inversion so that the ultimate degree of hydration, evaluated by means of the non evaporable water content, tended to be least at the highest temperature. Increased porosity was noted in pastes hydrated at higher temperatures (4), as well as brighter inner products with grey levels similar to that of CH (5).

The mechanical properties of mortars cured at various temperatures have also been reported (6) to follow a similar pattern as the above, although the strength depends on other factors as well as the hydration of the cement. Verbeck and Helmuth (6) suggested that curing at higher temperatures resulted in a non-uniform distribution of the hydration product within the microstructure, with a high concentration of hydration product building up around hydrating grains and retarding subsequent hydration, while at low temperatures hydration products have sufficient time to diffuse and precipitate relatively more uniformly throughout the cement matrix.

In contrast to these studies, Odler et al. (7) reported the effect of temperature on the hydration of laboratory-synthesised Portland cements up to 28 days but no temperature inversion in the degree of hydration was observed. Later Asaga et al. (8) also concluded that the ultimate degree of hydration was not affected by the curing temperature.

In view of these conflicting reports in the literature, it seemed to be opportune to carry out a thorough investigation, using modern experimental technique, and to study the hydration of two rather different Portland cements over the period of one year and at five temperatures in the range from 10 to 60°C. The hydration of the four major clinker phases was followed by means of quantitative X-ray diffraction analysis (QXDA), the formation of calcium hydroxide by thermogravimetric analysis (TGA), the development of compressive strength by crushing microcubes, and the development of microstructure by backscattered electron imaging (BEI) of selected samples. The intention from the outset was to look out for interrelationships between the results obtained from the various experimental methods.

Experimental

Cements

Two Portland cements were supplied by the Mexican company, Cementos Apasco. Their oxide composition determined by chemical analysis and phase composition as determined by QXDA and Bogue methods are reported in Table 1. Surface area and particle size distribution data are presented in Figure 1. Although the cements, labelled OPCN and OPCS, were supplied as ordinary Portland cement, there are differences between them in their respective alite and belite contents and especially in their C_3A and ferrite contents. The low C_3A content of OPCN suggests that it is similar in composition to sulphate resisting Portland cement.

Curing

The cement was mixed with distilled water, freshly boiled to remove carbon dioxide, at a water:cement ratio of 0.5 and cast into bars of 10 × 10 × 100 mm using Teflon moulds. The cement bars were first cured for 24 h in a controlled environment at 20 ± 1°C and 98% relative humidity. Care was taken to ensure that all the cements were cured under the same

TABLE 1
Oxide and phase composition of the starting materials.

	OPCN	OPCS
CaO	63.6	64.4
SiO_2	20.6	20.9
Al_2O_3	4.6	5.7
Fe_2O_3	3.1	2.9
Na_2O	0.5	0.6
K_2O	0.9	0.6
MgO	1.6	1.9
SO_3	3.5	2.4
C	0.16	0.18
Ins. res.	0.35	0.6
LOI	0.9	0.6
TOTAL	99.5	100.4
Free CaO	1.0	1.0

OPCN	QXDA	BOGUE
C_3S	71.6	52.6
C_2S	10.9	19.4
C_3A	3.7	6.9
C_4AF	10.7	9.4

OPCS	QXDA	BOGUE
C_3S	65.6	50.0
C_2S	16.4	22.2
C_3AF	8.0	10.2
C_4AF	7.4	8.8

conditions, including the mixing time and procedure, the weight of cement powder, and the moulds used. The cement bars were demoulded, grouped according to the set of moulds and selected randomly to form sub-groups for further hydration.

Hydration

Every randomly selected group of cement bars was submerged in a plastic container filled with distilled water, sealed and placed in a water bath at a constant temperature. Five water baths were maintained at temperatures of 10, 20, 30, 40, and 60°C with variation in

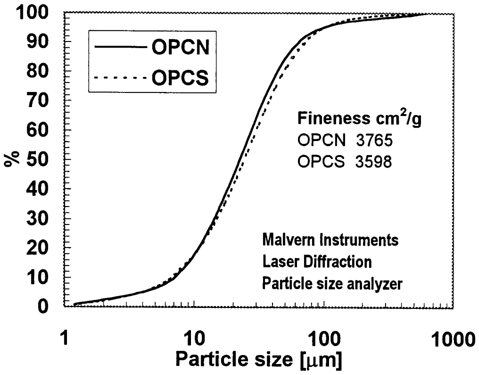

FIG. 1.
Particle size distribution of the starting materials.

temperature of less than ± 0.5°C. From the outset, four samples were randomly extracted from the water baths after periods of 1 day (24 h), 3, 7, 14, 28, 90, 180, and 360 days.

Characterisation

After each curing period, four bars were randomly extracted from the water and cut into halves. Micro-cubes approx. $10 \times 10 \times 10$ mm were carefully cut from a set of halves to be used for mechanical testing and additional cross-sections were cut for examination by SEM. The other set of halves was ground by hand and the relatively coarse powder samples were dried for 24 h in a vacuum desiccator using a rotary pump. Next the powders were further ground by hand to pass a mesh of 125 μm by cycles involving grinding, sieving and re-grinding the unpassed material until all the powder had passed through the sieve. Mechanical mixing of the sieved powder was performed to homogenise it and powders were sealed in glass containers prior to examination by XDA and TGA.

All the samples were examined by quantitative X-ray diffraction and thermogravimetric analysis. The procedure for the former was exactly that described by Gutteridge (9), including the use of the same Siemens D500 diffractometer with copper target and monochromatic K_α radiation and the use of rutile as an internal standard in the ratio of 1 part of rutile to 5 parts of cement by weight. Samples were examined in the range from 24 to 39 °2θ in steps of 0.05 °2θ with a measuring time of 20 s. The method of least squares was used employing software and standards developed by Gutteridge (9). This method uses the whole X-ray pattern to build up a calculated curve that is matched with that of the sample by proportioning the possible phases present by solving a matrix of simultaneous equations. As sample preparation is of prime importance in QXDA, an effort was made to process the powdered samples carefully, following a systematic procedure. The QXDA data are reported referred to the ignited weight, which was obtained from TGA experiments as the loss in mass at 900°C.

TGA curves were obtained using a Stanton-Redcroft TG760. Samples (ca 30 mg) were heated at 20°C/min. in flowing nitrogen (30 mL/min.). The calcium hydroxide content was determined quantitatively from the step observed in the curve between 425 and 450°C, using the procedure described by Taylor (10) and Bland and Sharp (11).

The compressive strength of the microcubes was determined using a Mayes machine. Four cubes were crushed for each sample and the standard deviation, as a percentage of the mean strength, was always $< 15\%$. Samples hydrated at 10° and 60°C were examined by back scattered electron imaging (BEI) on a Cambridge CamScan scanning electron microscope using an acceleration voltage of 20 kV. The specimens were mounted in resin under vacuum, carefully polished by hand down to 0.25 μm, and carbon coated.

Errors in QXDA and TGA Determinations

Based on measurements on samples of known composition, Gutteridge (9) concluded that the precision of his QXDA procedure was high and that the accuracy was acceptable. The relative error associated with the analyses of the independent clinker phases varied inversely with the amount of the anhydrous phase present. In this study when the measured content was 15% or greater, the relative error was estimated to be less than 5%. Even at low measured contents in the range 2–8%, the absolute errors were less than 1%.

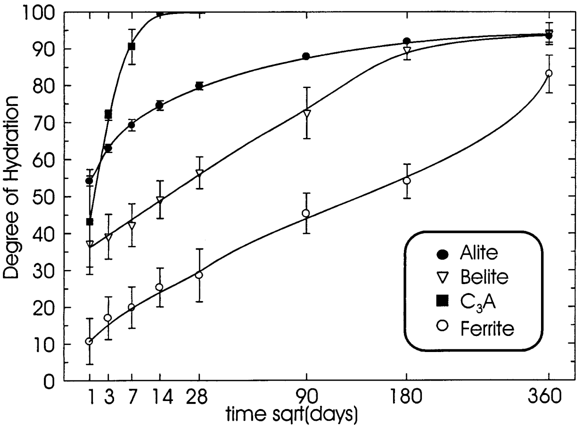

FIG. 2.

Data for the hydration of OPCN at 20°C, including error bars considering ranges of absolute errors according to ref (9).

Data for the degree of hydration (DOH) at 20°C of the four principal clinker phases present in OPCN are presented in Figure 2, where error bars are included for the DOH to show the precision of the method. The QXDA data obtained at each temperature give a clear indication of the relative rates of hydration of each phase, especially alite. Error bars are not included in subsequent plots because they are already "busy." The data shown in Figure 2 confirm the well established sequence of reactivity of the anhydrous phases with decreasing rate of hydration observed in the sequence: C_3A, alite, belite, ferrite.

The error in the determination of the CH content by TGA also increased at lower concentrations, but, as CH is a hydration product, the CH determinations became more reliable as the hydration process progressed. Repetition of CH determination for five cements at various DOH gave estimated errors of less than 3%.

Results

Quantitative X-ray Diffraction

The rate of hydration of alite for both cements is shown in Figure 3. Alite is the major clinker phase present and its degree of hydration is similar to the total degree of hydration of the cement. In the early stages of hydration, the rate of hydration of alite increased markedly with increasing temperature for both cements, but this did not hold at later ages. A temperature inversion effect was observed in that the highest ultimate degree of hydration was observed at 10°C and the lowest at 60°C for both cements. The cross-over took place after approximately 90 days for OPCN, but after only 28 days for OPCS. The alite in OPCN reacted faster initially than that in OPCS. After 24 h hydration, the difference between the extent of hydration of alite at the extreme temperatures was about 15% for OPCN but over 25% for OPCS. The alite in OPCS, however, showed a rapid increase in reactivity from 1–3 days at

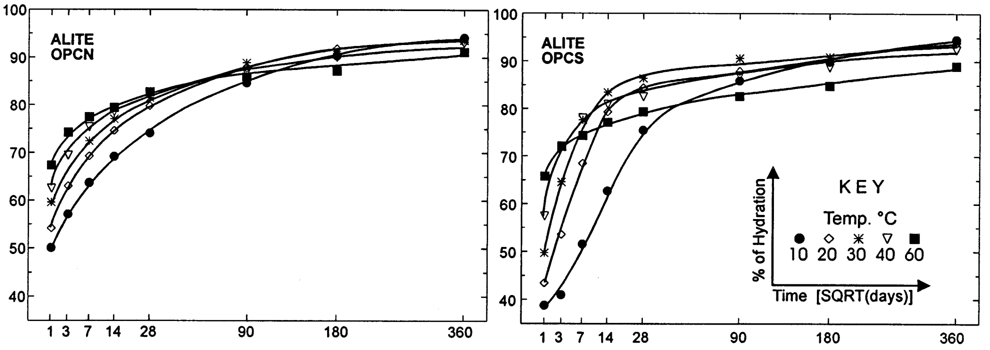

FIG. 3.
Degree of hydration of alite vs. time in OPCN and OPCS.

20 and 30°C, and from 3–28 days at 10°C. The consequence was that for OPCS, the degree of hydration of alite at 60°C was less than at 20°C after 14 days and less than at 10°C after 90 days. There are clearly differences in the behaviour of the alite in the two cements, even though they were both supplied as "ordinary Portland cement."

Results for the rate of hydration of belite are shown in Figure 4. The hydration kinetics are strongly temperature-dependent for both cements. Increasing temperature increased the rate of reaction of belite. As for the alite, there are differences in the pattern of hydration observed in the two cements. No crossovers were observed except perhaps with OPCS at about 90% fraction reacted, but this is uncertain because the accuracy of the QXDA was reduced at this level of hydration. The rate of hydration of belite in OPCS was observed to be slower than that in OPCN, but it accelerated after 3 days at 30 and 40°C, 7 days at 20°C, and 28 days at 10°C. All the belite in OPCN was observed to react at 60°C (after 28 days), at 40°C (after 90 days) and at 30°C (after 360 days), whereas about 10% of the belite in OPCS remained unreacted after 1 year at all temperatures in the range 20–60°C.

The rate of hydration of C_3A was more difficult to follow because of the small amounts

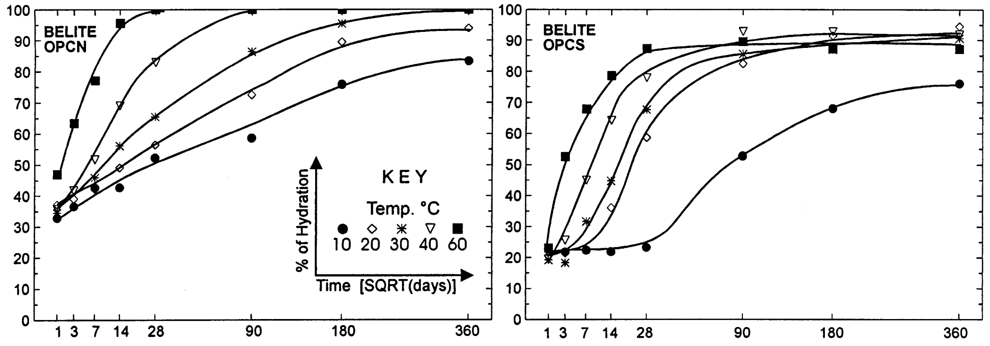

FIG. 4.
Degree of hydration of belite vs. time in OPCN and OPCS.

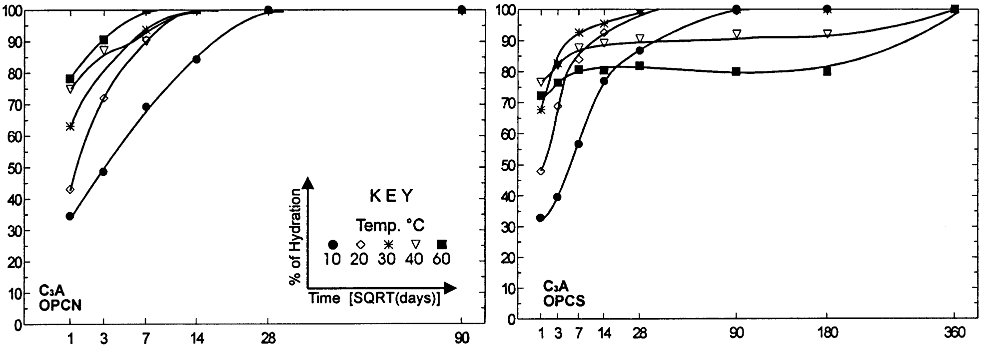

FIG. 5.

Degree of hydration vs. time for C_3A in OPCN and OPCS.

present and its high reactivity. Data for both cements are shown in Figure 5, but the scale for time has been changed in Figure 5A. Tricalcium aluminate was very reactive at all the temperatures investigated, but the rate of hydration was still dependent upon temperature as can be seen from Figure 5. The difference in the extent of hydration at 10° and 60°C after 24 h was greater than 40% for both cements. For OPCN the C_3A was fully reacted within 28 days at all temperatures, whereas for OPCS a temperature inversion was observed and after 180 days some of the C_3A was still unreacted for 40°C and 60°C. The crossover for the 10°C and 60°C was after about 14 days. When hydrated at 20°C and 30°C all of this phase appeared to have reacted after 28 days in OPCS, as in OPCN.

Data for the rate of hydration of the ferrite phase are shown in Figure 6. The temperature inversion, is shown dramatically in the hydration of the ferrite phase in both cements. Because the ferrite phase shows the lowest reactivity of the four clinker phases, the results demonstrate that even after hydration for a year there remains a fraction of unreacted ferrite in the cement at all the temperatures investigated. Interestingly, however, the highest degree of hydration after one year were those at 10°C, with the lowest at 40°C and especially at

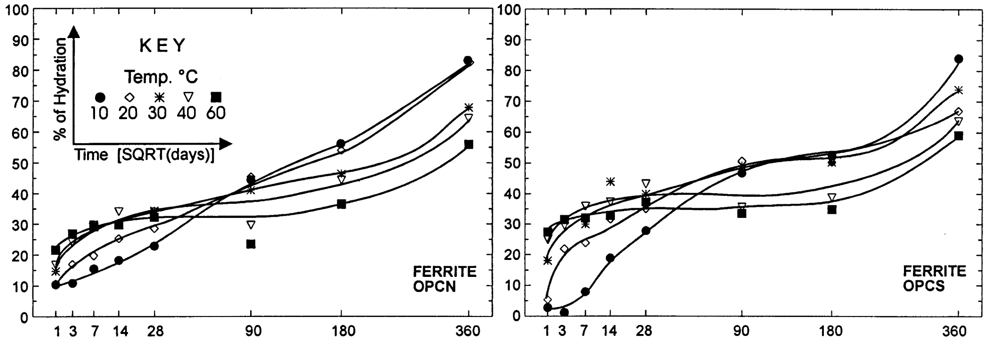

FIG. 6.

Degree of hydration vs. time for the ferrite phase in OPCN and OPCS.

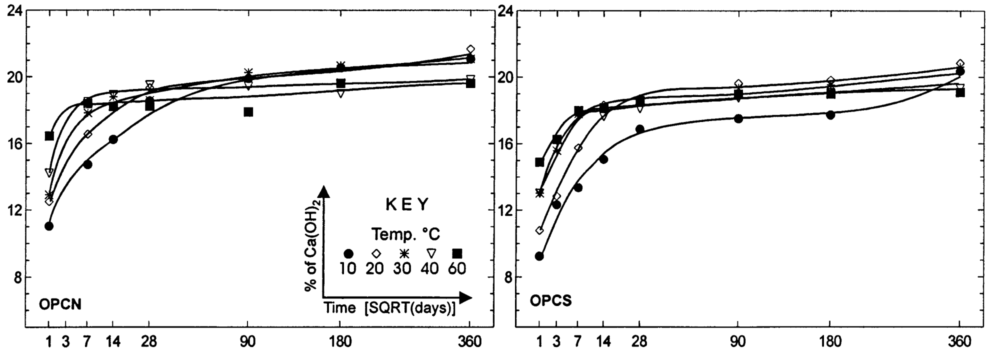

FIG. 7.
Amount of calcium hydroxide formed vs. time for OPCN and OPCS.

60°C. The crossover points were similar for both cements, and took place between 28 and 90 days at a fraction reacted between 30% and 40%.

Thermogravimetry

The amount of calcium hydroxide, CH, formed was estimated from the step in the TGA curve between 425 and 450°C and is shown in Figure 7. There was a marked variation in the initial rate of CH formation at different temperatures, but these differences became smaller at longer periods of hydration. The difference in rates of reaction between the two cements is evident and the overall effect is that the curves shown in Figure 7 resemble those shown in Figure 3 for the hydration of alite. This is not unexpected, because the major part of the CH formed is from the hydration of alite.

The temperature inversion observed during the hydration of alite was also observed in Figure 7 for CH production. The CH formation curve for OPCN hydrated at 10°C cuts that at 60°C between 28 and 90 days' hydration, but at a much later time for OPCS. The slower rate of formation of CH in OPCS is due to the slower rate of hydration of alite in this cement (Fig. 3) and the higher belite (and lower alite) content of OPCS which hydrated only slowly (Fig. 4).

Compressive Strength

The development of compressive strength for the two Portland cements hydrated at a range of temperatures is shown in Figure 8. Although each point in Figure 8 represents the mean of four cubes tested, error bars are not included to avoid presenting a very busy plot.

Once more the difference in the reactivity between the cements was apparent. OPCS was more sensitive to changes in temperature, especially in the early stages when it developed strength more slowly than OPCN at 10°C and 20°C. There is again some similarity between the curves shown in Figure 8 and those for the hydration of alite shown in Figure 3, which is reasonable as the hydration of alite makes the major contribution to strength development,

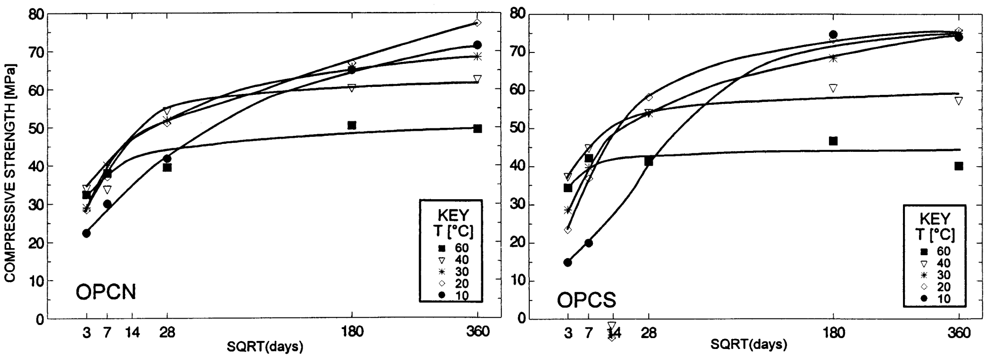

FIG. 8.
Compressive strength development vs. time for OPCN and OPCS.

in addition to microstructural factors. The temperature inversion is clearly evident with the 10°C and 60°C curves in Figure 8 intersecting after about 28 days for both cements. The highest compressive strengths after hydration for one year were obtained at the lowest temperatures (10° and 20°C), whereas the strength obtained at 40°C and at 60°C were lower. The compressive strength at 60°C increased very little beyond 14 days' hydration.

Scanning Electron Microscopy

The observations are presented in the backscattered electron imaging mode of polished samples, because it allows advantages over secondary electron images in terms of the compositional contrast that can be perceived. Higher atomic elements appear brighter in BEI, so that differences in the grey level observed in hardened cement paste allow the distinction in descending order of brightness between anhydrous phases, calcium hydroxide, C-S-H gel, and porosity (12,13).

BEI for OPCN and OPCS hydrated at 10° and 60°C for 360 days are shown in Figure 9 at two magnifications. In Figures 9A and 9C, some fully hydrated cement grains can be easily distinguished after hydration at 10°C and only a few partially hydrated grains could be observed in both cements. In contrast, in Figures 9B and 9D, at 60°C, some partially hydrated cement grains can be observed as a grey rim of hydration products formed around a white core of anhydrous cement (e.g., in the upper left hand corner of Fig. 9B). These observations are compatible with those reported above for the degree of hydration, which was lower at 60°C than at 10°C after 1 year.

Some high sulphur-containing platy clusters were observed in Figures 9A and 9C and are attributed to AFm, which was detected by EDS. These clusters were observed only in the microstructures of the plates cured at 10°C and not at 60°C. X-ray diffraction patterns of both cements at 10°C and 60°C showed ettringite peaks, while monosulphate peaks appeared only at 10°C for both cements.

An important difference between the micrographs obtained after hydration at 10°C and those at 60°C is the amount of apparent porosity, which given the resolution of BEI is the coarse capillary porosity. The pores appear black in Figure 9 and it can be seen that more

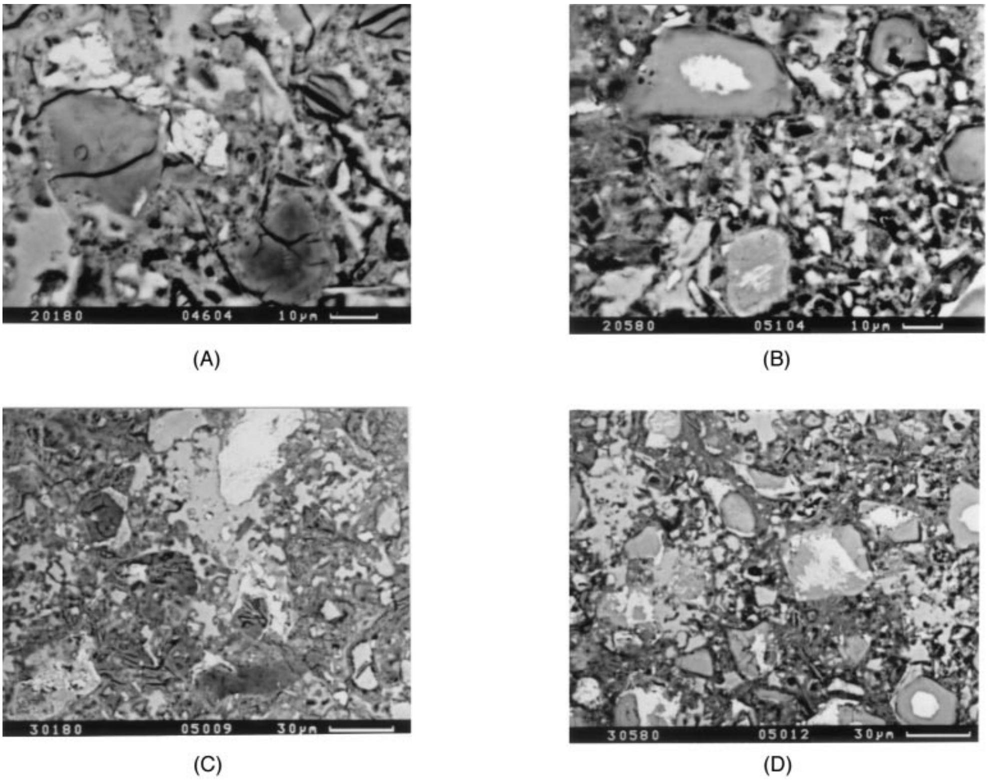

FIG. 9.
Backscattered electron images of polished samples hydrated at 10°C and 60°C for 360 days. (*A*) OPCN, 10°C; (*B*) OPCN, 60°C; (*C*) OPCS, 10°C; (*D*) OPCS, 60°C.

pores are apparent in the microstructures of the cement pastes hydrated at 60°C, whereas those hydrated at 10°C show a more compact and more homogeneously distributed structure with less apparent porosity.

Another interesting observation is that in the micrographs of the cements hydrated at 60°C, there appears to be a gap, or a black thin rim, around some of the hydrated cement grains (Figs. 9B and 9D). This is not the case for the specimens hydrated at 10°C, where there is a smooth transition between the hydrated grains and the matrix (Figs. 9A and 9C).

Discussion

Increase in the temperature of hydration in the range from 10 to 60°C produced noticeable variations in the rate of hydration and the ultimate degree of hydration of the individual clinker phases and in the properties of the two cements studied. The relative differences were more apparent at the extreme hydration temperatures, since comparison between data obtained at the intermediate temperatures is less distinguishable given the reduced accuracy of the method at lower anhydrous phase contents. Increased hydration temperature initially increased the rate of hydration of the four main clinker compounds, in accordance with results published by other workers using X-ray diffraction (1) and non evaporable-water content (3). The hydration characteristics were, however, different for each individual phase, although the phases followed similar patterns for each Portland cement. The temperature inversion associated with the hydration of the alite and the ferrite phase can be seen in Figures 3 and 6, respectively, such that the degree of hydration in the longer term was lower for pastes cured at the highest temperatures and vice-versa. This observation was supported by results obtained using other techniques. Thus the amount of calcium hydroxide formed, as determined from thermogravimetric analysis (Fig. 7), further established the temperature inversion phenomenon of the alite.

This phenomenon is also supported by the BEI observations (Fig. 9) which showed that only limited hydration had been achieved for some of the cement grains hydrated at 60°C. After hydration for a year, a rim of hydration product could be detected surrounding a core of anhydrous material (Figs. 9B and 9D), whereas most of the grains in the pastes hydrated at 10°C were fully hydrated. The partially hydrated grains are the larger grains present (>15 μm). Many of the smaller grains had fully hydrated in the initial curing period of 24 h at 20°C, which was common to all the cements investigated.

The question arises why the observed temperature inversion apparent from our investigation is apparently different from that reported by Asaga et al. (8). In fact, the two investigations carried out somewhat different studies and the results are not necessarily in conflict. Asaga et al. reported the hydration behaviour of one cement at four temperatures (0, 20, 50, 80°C), at low w:c ratios (0.3 and 0.4) and for up to a maximum of 91 days (or only 28 days at 0°C). The closest comparison with the present work is to compare Asaga's data at 0°C and 50°C with our new data at 10° and 60°C. When it is remembered that Asaga et al. followed the hydration behaviour at 0°C for only 28 days, the similarities are striking. Their figures clearly indicate a temperature inversion for the degree of hydration of alite and the amount of CH formed, similar to that reported in the present work and originally by Copeland and Kantro (1,2). Unfortunately Asaga et al. do not report data for the hydration of belite, C_3A and the ferrite phase at 0°C, but the curve for the degree of hydration of ferrite at 20°C crosses that at 50°C after about 14 days. As reported in the present study, the rate of hydration of belite is strongly temperature dependent and the degree of hydration reported by Asaga et al. after 91 days decreases with decreasing temperature, although that at 50°C is close to that at 80°C. There is, therefore, on close examination, little conflict and considerable agreement between the data presented by Asaga et al. (8) and those reported here. To observe the temperature inversion effects reported in this paper for the rate of hydration of the anhydrous phases, it is important to follow the kinetics of hydration for at least 180 days (see Figs. 3, 4, and 6).

Although the development of mechanical strength depends not only on the degree of hydration of the anhydrous phases, but also on other factors, notably the pore structure, the development of compressive strength with time (Fig. 8) showed similar behaviour to the DOH of alite. Hydration at relatively high temperatures (40° and 60°C) certainly had a deleterious effect on the mechanical properties in the long term, as had been suggested previously (6). This reduction in ultimate compressive strength compared with pastes hydrated at 10° or 20°C is almost certainly associated with the observation, by BEI, of an increase in apparent porosity. Kjellsen et al. (4), using BEI image analysis, also reported similar observations to those reported here, including increased porosity at higher temperatures for cement pastes up to 70% hydrated.

An additional factor may be the observation by BEI of black rims around some of the cement grains after hydration at 60°C. These rims are in effect discontinuities within the paste matrix and contribute negatively to the mechanical properties, and perhaps retard further hydration of the grains. In contrast to the high temperature cured pastes, such discontinuities were not observed in the low temperature cured cement pastes, where a smoother transition was observed between the inner products within the hydrated grains and the outer products, as shown for some of the cement grains in Figures 9A and 9C. The pastes cured at 10°C showed some cracks in the micrographs, but it is believed that these were produced during the drying process and vacuum treatment.

If one takes the grey level of the CH crystals in BEI as a reference, the inner products in the cement pastes cured at 10°C appeared to have a darker grey level than most of those formed at 60°C, suggesting that for the latter, the inner products of the larger grains were more compact, leaving free space elsewhere in the microstructure and hence increasing the porosity. These compact hydration rims could act as barriers to further hydration where diffusion of reactants is retarded. Verbeck and Helmuth (6) have suggested that at low temperatures there is more time for the hydration products to diffuse than at higher temperatures, which is consistent with observations reported here that the matrix formed at 10°C is more homogeneous and less porous than that formed at 60°C. The darker cement grains observed in products hydrated at 10°C are taken to indicate a less compact inner product with some C-S-H deposited in the outer product, whereas at 60°C there was less time for diffusion and the product remained within the original grain. Scrivener (14) observed different grey levels in the inner products (in the same clinker grain) of a cement that was heat treated at 80°C and subsequently cured at 20°C, the latter showed a darker colour. Kjellsen et al. (4) also observed two different densities of C-S-H at 50°C, while only one C-S-H density was noted at 5°C.

Conclusions

An investigation into the hydration of two Mexican Portland cements hydrated at five temperatures in the range from 10°C to 60°C has been carried out using several experimental techniques. The results from QXDA, supported by TGA and compressive strength tests demonstrated conclusively that the anhydrous phases in the cements had different rates of reaction. There was generally good agreement among the results obtained from the various experimental methods.

Some previous observations (1–6) relating to the hydration of Portland cement at different temperatures were confirmed and new observations have been made. An increase in hydration temperature accelerated the early hydration of the anhydrous phases in the cements in different ways. The observed reactivities were in decreasing order: C_3A, C_3S, C_2S and C_4AF. A temperature inversion was established for the hydration of alite and the ferrite phase in both cements, with the lowest ultimate degree of hydration corresponding to the highest hydration temperature and vice-versa. The amounts of calcium hydroxide determined from TGA correlated well with the degree of hydration of the alite in both cements, while BEI images showed much less anhydrous cement remaining at 10°C than at 60°C after 360 days. These observations are in accordance with the temperature inversion phenomenon. The development of compressive strength in the two cements followed similar patterns to those of alite hydration. After hydration for one year at 60°C, there was greater apparent porosity as observed by BEI than at 10°C, the partially hydrated grains were lighter grey in colour, and there were some rims of discontinuity around some of these grains. All these factors, especially the higher porosity, are believed to contribute to the lower ultimate compressive strengths observed at 60°C. The microstructures observed after hydration for one year at 10°C were, on the other hand, more homogeneous and lower in porosity, leading to higher compressive strengths.

The hydration kinetics of belite were shown to be strongly dependent upon temperature for both cements. The rate of hydration of belite in OPCS was slower than that in OPCN and some belite remained unreacted after a year in OPCS at all temperatures, whereas that in OPCN had fully reacted after about 28 days at 60°C and after one year at 30°C. The tricalcium aluminate was very reactive in both cements at all the temperatures investigated and had fully reacted within 28 days. AFm clusters formed from the hydration of C_3A were observed in the microstructure of pastes hydrated at 10°C but not in those hydrated at 60°C.

Acknowledgments

J.I. Escalante acknowledges the financial support provided by CONACYT Mexico for this research at the University of Sheffield. Cementos Apasco kindly supplied the cements and chemical analysis. Quantitative X-ray diffraction analysis was carried out under the guidance of W.A. Gutteridge, but the interpretation of the results obtained is the responsibility of the authors. Helpful discussions were held with D.C. Spooner, W.A. Gutteridge, C.D. Lawrence, and R. Yang.

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