

Note

ESTIMATION OF THE DEGREE OF HYDRATION IN MODIFIED ORDINARY PORTLAND CEMENT PASTES BY DIFFERENTIAL SCANNING CALORIMETRY. PART II

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INTRODUCTION

In a recent publication [1], it has been shown that the addition of equal molar amounts of calcium chloride, calcium nitrate or sodium thiocyanate to ordinary Portland cement (OPC) paste resulted in varying degrees of hydration. To compare the role of the anions on an equal molar basis, studies on OPC hydration in the presence of the same cation using calcium thiocyanate have now been carried out. The materials and techniques employed were identical to those reported previously [1]. Calcium thiocyanate was added at the same rate of 0.0901 mol per kilogram of cement and a water:cement ratio of 0.5 was used. The data previously reported on OPC–admixture–water systems are followed here.

OPC–Ca(SCN)₂–H₂O SYSTEM

The phases identified by X-ray diffraction (XRD) in the present system were identical to those in the OPC–NaSCN–H₂O system [1], but their relative intensities were clearly different. DSC curves of the hydrated pastes in this mix can be interpreted in line with the XRD results. Typical DSC curves are shown in Fig. 1, which are of the samples hydrated for 1 h, 6 h and 3 days. Ettringite (C₃A3C \bar{S} ·32H) and C–S–H gel are responsible for the well-developed endotherms in the temperature range 110–130°C. The small endotherm at 145°C in the curve A is due to gypsum (C \bar{S} ·2H) and the shoulder around 180°C, in curve C, confirmed the presence of mono-sulphate (C₃A·C \bar{S} ·12H) after hydration for 3 days. Calcium hydroxide (CH) increased throughout as shown by the endothermic peaks around

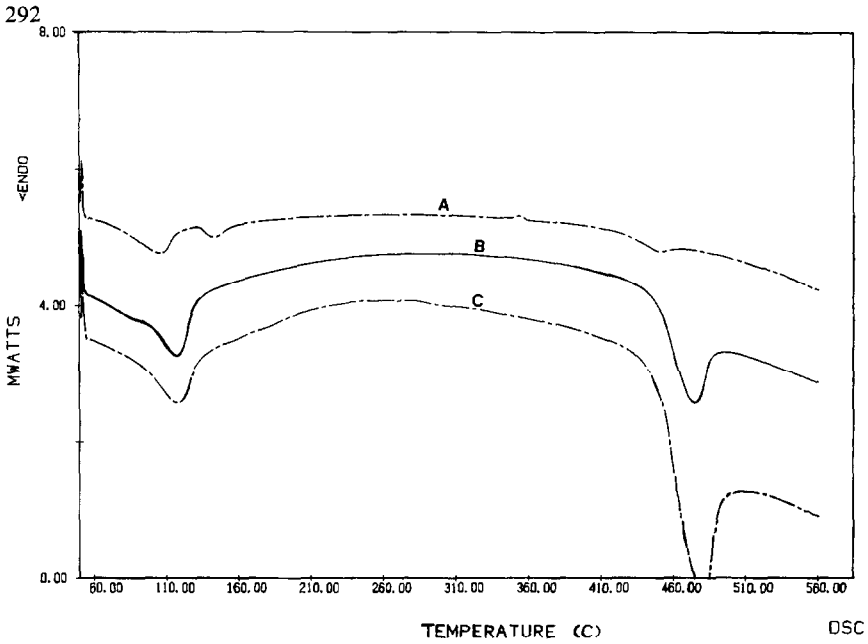


Fig. 1. DSC curves of the samples hydrated for 1 h (curve A), 6 h (curve B) and 3 days (curve C) in OPC-Ca(SCN)₂-H₂O system.

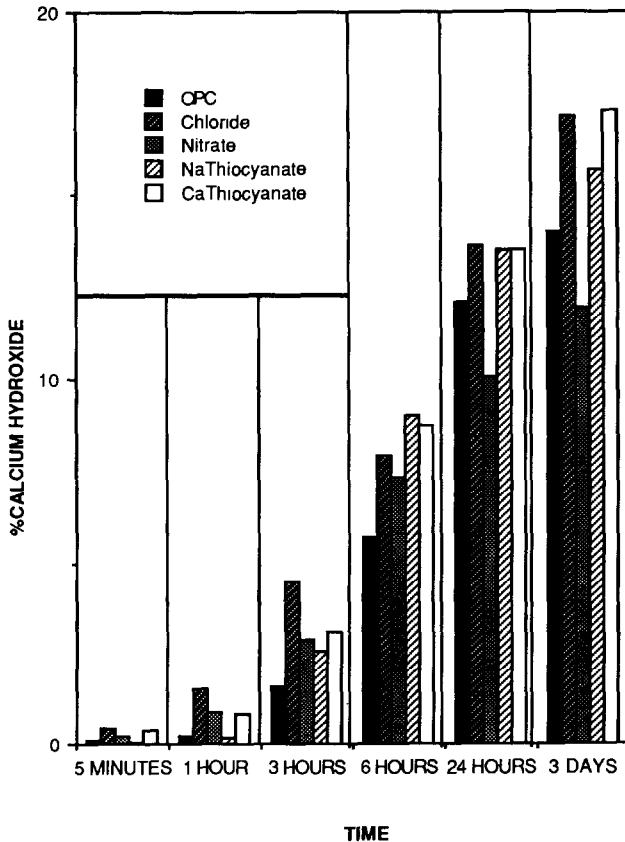


Fig. 2. Percentage calcium hydroxide formed with time.

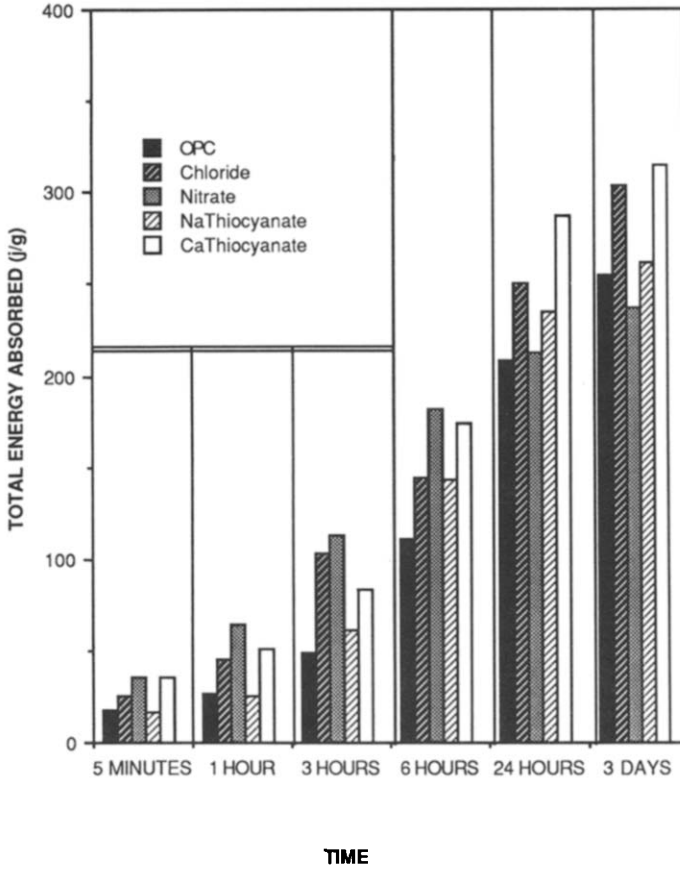


Fig. 3. Total energy absorbed with time.

460°C. The DSC data for this system are presented in Figs. 2 and 3. Whereas Fig. 2 shows the variation in the relative amounts of calcium hydroxide formed, Fig. 3 presents the total amounts of energy absorbed by ettringite, C-S-H and calcium hydroxide vs. time. It is clear that calcium thiocyanate accelerates the formation of calcium hydroxide as well as the total reaction product. In comparison with the chloride, less calcium hydroxide but more ettringite had formed during the first 3 h. After longer hydration, however, slightly more calcium hydroxide was detected on adding the thiocyanate than when the chloride was the additive.

DISCUSSION

The mixes examined using calcium thiocyanate and those reported previously, despite their differing degrees of hydration, do not differ in the nature of their products except after hydration for 3 days. On adding calcium

chloride, a C_4AH_{13} -chloroaluminate solid solution was identified. However, the possibility that C_4AH_{13} was present cannot be totally ruled out since both phases give the same XRD peak and DSC endotherm [1]. The results for the nitrate and thiocyanates showed no evidence for the formation of any nitrate- or thiocyanate-based compounds, even after one year. Whereas a C_4AH_{13} -monosulphate solid solution was detected after hydration for 3 days, when the nitrate was incorporated, monosulphate was the phase identified in the corresponding samples when sodium thiocyanate or calcium thiocyanate was the additive. No such phase, however, was detected in the neat OPC or sucrose mix.

It is now clear that the addition of admixtures influences the total amounts of reaction products formed and the amounts of calcium hydroxide formed and modifies the reaction products after hydration for 3 days. Moreover, the initial reaction products from 5 min to 3 h also contained calcium sulphate dihydrate, which was not present in the anhydrous cement. The amounts of gypsum formed are shown by XRD and DSC to increase considerably on adding calcium-based salts. This is to be expected since the liquid phase became supersaturated with respect to both sulphate and calcium. It is clear therefore that this gypsum forms from solution. Comparison of the results in Fig. 2 with those in Fig. 3 reveals that more ettringite had formed on adding the nitrate than when the chloride or thiocyanate was the additive. This is in line with the XRD results which also indicated that slightly less ettringite had formed on adding the thiocyanate than when chloride was used. Since the total amounts of sulphate present initially in these mixes can be considered to be equal, it would seem reasonable to suggest that some sulphate was incorporated into the hydration products on adding the chloride or thiocyanate. On the basis of the amounts of calcium hydroxide formed, however, the performances of the thiocyanate and nitrate were very similar during the first 3 h. After longer hydration the amounts of calcium hydroxide in the thiocyanate and chloride mixes were almost identical while those in the nitrate were less than those in OPC. This indicates that while the chloride, nitrate and thiocyanate accelerate the set to varying degrees, only the chloride and thiocyanate can be candidates for strength acceleration. Preliminary work carried out on mixes incorporating these admixtures showed good correlation between the stiffening rates and calcium hydroxide formation in support of this argument.

The influence of the admixture cation on the degree of hydration can be seen by comparing the performance of calcium thiocyanate with that of sodium thiocyanate. It is evident that more calcium hydroxide as well as total reaction product was produced on using the former. Nonetheless, sodium thiocyanate appears to be more effective in the long term than for set acceleration since much more calcium hydroxide than was in the OPC paste had formed after hydration for longer than 6 h. It follows therefore that an acceleration mechanism in which the cation-anion combination is

the controlling factor is operative. Evidence gathered from the chemical environment of these systems by extracting and analysing the liquid phase during the first 3 h confirms the findings above and will be the subject of future reports.

ACKNOWLEDGMENTS

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REFERENCE

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