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THE EFFECTS OF SOLVENTS ON C–S–H AS DETERMINED BY THERMAL ANALYSIS

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Un-hydrated Portland cement consists of several anhydrous and reactive phases, that when mixed with water react to form hydrates. The main hydration product of Portland cement is calcium silicate hydrate (C–S–H). It is the main binding phase in a concrete system, hence is important to construction chemists. The concrete engineer measures the compressive strength of concrete after prescribed hydration periods, typically 1, 3, 7, 28 days. It is often convenient to mimic these intervals by stopping the hydration reaction at the same times. Several techniques can be employed to stop this hydration reaction. One of which is solvent-based and involves mixing a polar solvent such as acetone or isopropyl alcohol, with the hydrated cement. This mixing should be vigorous enough to blend the free water, in the partially hydrated cement system, with the polar solvent without altering the cement system's matrix. The solvent-water mixture has a much lower boiling point and the mixture quickly evaporates out of the system. This achieves two goals. It stops the hydration reaction at the moment of solvent mixing, and it removes free water to prevent further hydration from occurring. This procedure theoretically leaves behind a dry, chemically unaltered, partially hydrated cement paste. In this way, pastes can be analyzed after the prescribed 1, 3, 7 or 28 days of hydration. This paper uses thermogravimetric analysis (TG) results to investigate the assumption that solvents have no thermodynamic or chemical effect on the hydrated cement paste phases.

Keywords: *C_2S hydrate, C_3S hydrate, DTG, Portland cement, synthetic C–S–H, thermal analysis*

Introduction

The authors of this work are conducting a broad research program into quantifying levels of calcium silicate hydrate in a Portland cement. To do this with confidence two techniques were chosen, X-ray diffraction (XRD) and thermal analysis. Some results from our studies with thermal analysis are presented here.

The hydration reaction of Portland cement is continuous, and one of the products of the reaction is portlandite. Researchers have devised ways of removing the water from the test specimens, to stop hydration, permitting time dependent analysis [1].

Perhaps the most obvious means of removing water from hydrating cement is to heat the samples in an oven at 105°C. Heating was, in this case, avoided due to fear of changing the phase of most interest i.e. C–S–H. The original objective was to quantify the amorphous material generated by cement hydration. These materials reportedly contain loosely bound water that can be removed even by mild heating. Solvent replacement methods to remove water from the samples were initially the preferred technique to stop the hydration reaction, as they are inexpensive, relatively quick and convenient. Other methods considered included evacuation and freeze drying, which require specific equipment. Drying over an anhydrous desiccant such as calcium chloride was also considered but was believed to be too slow.

Very little literature has been published on solvent replacement; however some authors suggest that the use of solvents to stop the hydration reaction is unadvisable. It is unadvisable because the nature of the hydrates can be altered hence unexpectedly raising the errors of the obtained result. They continue by reporting that solvent replacement is experimentally acceptable for X-ray diffraction purposes, but not for thermal analysis [2–4]. This paper further investigates, using thermogravimetric techniques, the reasons behind the altering nature of solvents on the cement hydrates.

Experimental

Initially sealed polyethylene tubes containing cast cement, tricalcium silicate and dicalcium silicate pastes were prepared at various water to cement ratios. They were, at the appropriate hydration times, sliced with a diamond saw and soaked several times in solvent, (acetone or isopropyl alcohol) and then dried in an air-circulating oven at 65°C for 2 min. This paper addresses the results of the 20-day samples at a water to cement ratio of 0.45.

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A second method of grinding the 20-day samples, in a mortar and pestle along with the same and a different solvent, (acetone or isopropyl alcohol) was also used. The samples were then left for several minutes to dry. Once dry it was twice rewetted and ground to ensure complete water removal. Parallel to this work vacuum and freeze-drying techniques were initiated on the 20-day samples.

Various synthetic calcium silicate hydrates (C–S–H) with several different calcia to silica ratios were also made. They were prepared by reacting freshly calcined, reagent grade, $CaCO_3$ and high surface area amorphous SiO_2 (Cabosil®). The powders were weighed to the correct stoichiometric proportions and dry mixed prior to the addition of excess de-ionized and de-aerated water. The high density polyethylene (HDPE) bottles for each system were N_2 purged to remove CO_2 and then placed on a rotating wheel that turned the bottles end over end at a rate of 9 rpm. The system was allowed to react for 10 weeks, (70 days). Prevention of carbonation of both CaO and CSH was difficult. Exposure during reaction and of the final product to CO_2 was avoided by keeping both the reaction materials and the final product in airtight containers that were purged with N_2 gas. These synthetic C–S–H materials were treated with solvents, as described above, and analysed. The results were compared to those of the work initiated in the sealed polyethylene tubes and were reported.

All the thermal analysis was performed using a TA Instruments SDT Q600. This combined thermogravimetric/differential thermal analyzer was set up to run samples in nitrogen with a flow rate of 100 mL min^{-1} and a heating rate of 10°C min^{-1}. Results were processed with TA instrument's Universal Analysis 2000 software version 3.9a. In later experiments the instrument parameters were changed slightly to include an isothermal hold at 80°C. This allowed a more accurate quantitative determination of the portlandite and calcite phases, as well as the gel water.

Results and discussion

Hydrated Portland cement, C_3S and C_2S

Figure 1 shows the mass loss curve and its derivative for OPC hydrated for 20 days, dried by two different methods, acetone and freeze-drying. An interpretation of this graph can be described as follows: the evolution of water can be measured at temperatures less than 200°C, with the decomposition of portlandite ($Ca(OH)_2$) at 400–450°C and calcite ($CaCO_3$) at 600–750°C [5].

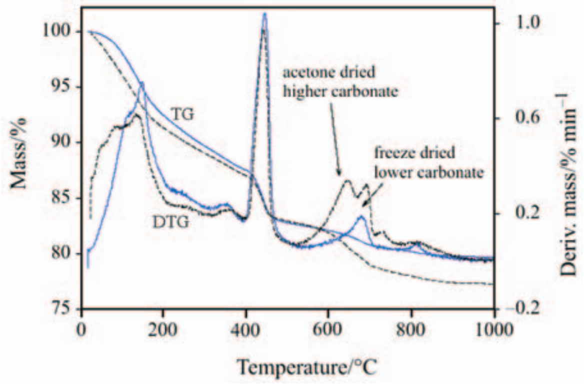

Fig. 1 TG and DTG curves of OPC hydrated for 20 days and dried by acetone and freeze-drying

It can be seen from Fig. 1 that the carbonation peaks of the supposedly identical materials are completely different. This difference could be due to either the drying techniques used, or the experimental measures to prevent carbonation of the sample.

TG results for tricalcium silicate (C_3S) hydrated for 20 days and dried by two different methods, use of isopropyl alcohol and freeze drying are shown in Fig. 2. Again the interpretation of this graph can be described as the evolution of water at temperatures less than 200°C, with the decomposition of portlandite ($Ca(OH)_2$) at 400–450°C and calcite ($CaCO_3$) at 600–750°C. The carbonation peaks of the supposedly identical materials are again different. Whilst this difference is not as clear as in Fig. 1, suspicion is once more cast upon on the drying techniques used, or the experimental measures to prevent carbonation.

TG results for dicalcium silicate (C_2S) hydrated for 20 days and dried first with isopropyl alcohol and second by freeze drying are shown in Fig. 3. This graph shows the evolution of water at temperatures less than 200°C and the decomposition of calcite ($CaCO_3$) at 600–750°C. There is an obvious absence of portlandite which can be explained by the lower reactivity of this phase with water, along with the reduced

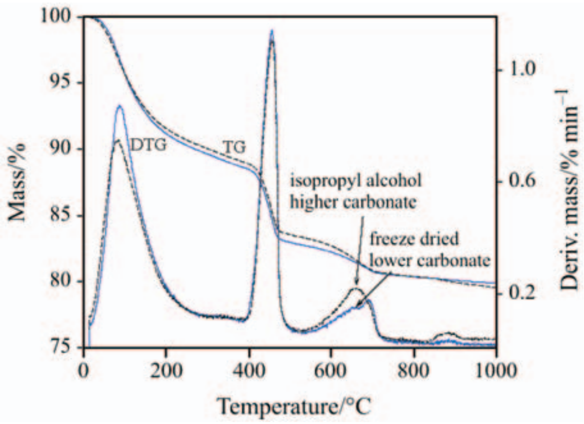

Fig. 2 TG and DTG crves of tricalcium silicate (C_3S) hydrated for 20 days dried first with isopropyl alcohol and second by freeze drying

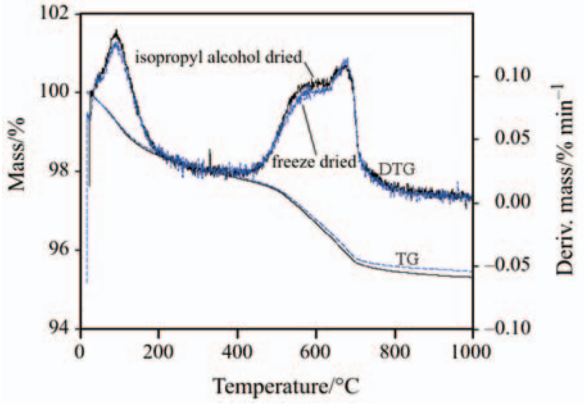

Fig. 3 TG and DTG curves of dicalcium silicate (C_2S) hydrated for 20 days dried first with isopropyl alcohol and second by freeze drying

levels of calcia in the starting component. The lack of portlandite was also observed in the unreported XRD.

Unlike Figs 1 and 2 the carbonation peaks in Fig. 3 are virtually identical. This rather confusing result casts doubt on the suspicion that the experimental measures to prevent carbonation are at fault, leaving the hypothesis that the solvent drying method was affecting the results. Further investigation was required, and work was initiated using the pure synthetic materials.

Synthetic calcium silicate hydrates (C–S–H)

C–S–H prepared at Ca/Si ratio=1.5 and above contains excess portlandite that cannot dissolve in the mixture because of its solubility limits. As the starting materials were preparations of C–S–H with two different Ca/Si ratios, 1.2 and 1.7, the first C–S–H with a Ca/Si ratio of 1.2 does not contain portlandite and the second at Ca/Si=1.7 contains a small amount.

The derivative mass loss curves for the C–S–H preparation containing no portlandite (Ca/Si=1.2) is shown in Fig. 4. Similar to the dicalcium silicate results shown in Fig. 3, there is no sign of significant carbonation activity.

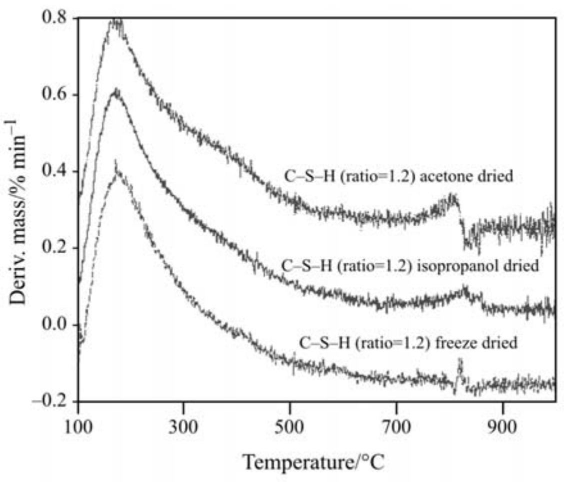

Fig. 4 DTG curves for C–S–H (Ca/Si=1.2) subjected to three different drying methods

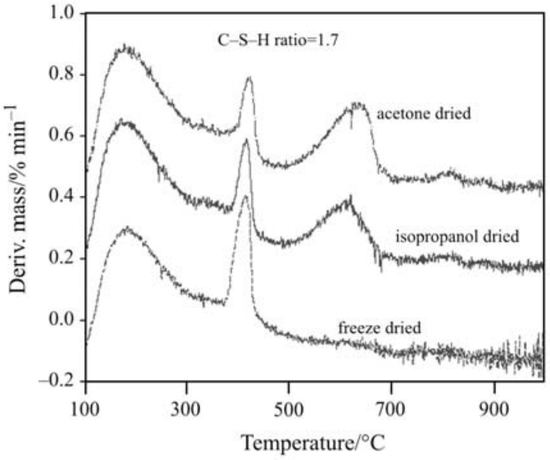

Fig. 5 DTG curves for C–S–H (Ca/Si=1.7) subjected to three different drying methods

The DTG for C–S–H (Ca/Si=1.7) containing residual portlandite are shown in Fig. 5. Markedly different phase behaviour to that shown in Fig. 4 is observed. A significant thermal event takes place at ~630°C, and is assigned to calcium carbonate. This event is more clearly understood when the solvent dried curve is subtracted from the freeze-dried curve (Fig. 6). This clearly shows that the water of the C–S–H gel (100–200°C) is not particularly susceptible to the solvent treatment, but that the $Ca(OH)_2$ (portlandite) determination is highly susceptible.

It is useful to re-examine the original work presented in Figs 1–3. In the presence of portlandite (the OPC and the C_3S paste samples) significant differences in the carbonation behaviour are observed, in contrast to the C_2S which has no $Ca(OH)_2$. Further when the data from Figs 1 and 2 are examined more closely there is a corresponding reduction in the portlandite.

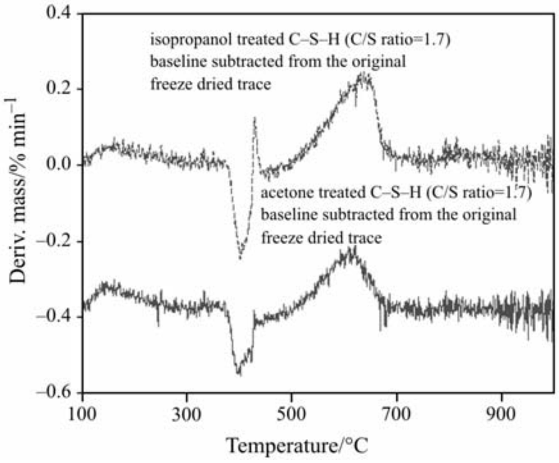

Fig. 6 DTG curves for the isopropanol and acetone treated C–S–H (Ca/Si=1.7) materials obtained after subtraction of the freeze dried derivative curve

The authors carefully considered the assignment of the 630°C event to calcite. Usually calcite in Portland cement (both hydrated and unhydrated) decomposes between the temperatures of 700 and 725°C – much higher than the 630°C observed here. Aldrich technical grade $CaCO_3$ was found to decompose at 785°C, and natural Icelandic Spar at 850°C. Boynton records that the decomposition of calcite is affected by surface area, particle size, partial pressure of CO_2 and impurities such as magnesium [6].

Other possible assignments of the 630°C peak would include some organic chemistry. It is possible for acetone to combine forming diacetone alcohol or 4-hydroxy-4-methyl-2-pentanone. This reaction is reversible and occurs in the presence of a base catalyst. A commonly reported catalyst is barium hydroxide, which has similar properties to that of calcium hydroxide [7]. The reaction is known as an aldol reaction, and exhibits a mechanism involving stepwise nucleophilic enolic donor molecules and electrophilic acceptor molecules. This reaction is not limited to dimers (diacetone alcohol). The polymerisation reaction will continue until an elimination reaction occurs. The reaction product in this case however, is thought to be the dimer (diacetone alcohol) that has a boiling point of 166°C.

It is interesting to speculate that diacetone alcohol, which has a high boiling point, low vapour pressure (<1 mm Hg or <133.3 Pa (20°C)) and exhibits an affinity for base hydroxides, may form an undetectable film around the portlandite upon drying. The film-coated materials are then put into the furnace of the TG and heated. Under these conditions the film will presumably either decompose or evaporate, depending on the bonding properties. During this decomposition or evaporation CO_2 maybe evolved to react with the surface of the portlandite [8], forming a calcium carbonate with low crystallinity. This low crystalline calcite will presumably have a reduced (630°C) dissociation temperature.

Alcohols are not known to undergo the same type of aldol reaction, however they do undergo elimination reactions in the presence of base catalysts. Again an organic film around the portlandite catalyst is conceivable.

Conclusions

This work agrees with other researchers who indicate that solvents alter sample composition of hydrated Portland cement. Careful planning should be employed when designing experiments that involve either TG or XRD to quantify cement phases.

It has been observed that the major phase discrepancies are associated with portlandite and calcite. As portlandite can catalyze organic reactions at room temperature, it is hypothesized that these reactions induce a change in the portlandite to a low dissociation temperature form of calcite. When no portlandite is present these unwanted reactions do not occur.

Unlike other authors, who used the more sensitive BET (Brunauer, Emmet and Teller) adsorption methods, this TG study does not see alterations in the gel phase.

References

1 V. S. Ramachandran R. F. Feldman and J. J. Beaudoin, Concrete Science, Heyden & Son Ltd., London, UK 1981.
2 R. L. Day, Cem. Concr. Res., 11 (1981) 341.
3 H. F. W. Taylor and A. B. Turner, Cem. Concr. Res., 17 (1987) 613.
4 H. F. W. Taylor, Cement Chemistry, Academic Press Ltd., London 1990.
5 V. S. Ramachandran, R. M. Paroli, J. J. Beaudoin and A. H. Delgado, Handbook of Thermal Analysis of Construction Materials, Noyes Publications/Williams Andrew, New York 2003.
6 R. S. Boynton, Chemistry and Technology of Lime and Limestone, John Wiley and Sons, New York 1980.
7 P. Kustrowski, D. Sulkowska, R. Pytlowany and R. Dziembaj, React. Kinet. Catal. Lett., 81 (2004) 3.
8 J. J. Beaudoin, Mater. Struct., 20 (1987) 27.

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