
Published article:

Whittaker, M, Dubina, E, Al-Mutawa, F, Arkless, L, Plank, J and Black, L (2013) *The effect of prehydration on the engineering properties of CEM I Portland cement.* Advances in Cement Research, 25 (1). 12 - 20. ISSN 0951-7197

http://dx.doi.org/10.1680/adcr.12.00030

Advances in Cement Research
Volume 25 Issue 1

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Advances in Cement Research, 2013, **25**(1), 12–20
http://dx.doi.org/10.1680/adcr.12.00030
Paper 1200030
Received 02/05/2012; revised 19/07/2012; accepted 01/08/2012

The effect of prehydration on the engineering properties of CEM I Portland cement

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Prehydration – the reaction between anhydrous cement and water vapour – has deleterious effects on engineering properties such as compressive strength, workability and setting time. This study assessed changes in the engineering properties of CEM I Portland cement exposed to relative humidities (RHs) of 60% or 85% for 7 and 28 days. Thin layers (no more than 2 mm thick) of CEM I 42.5R cement were exposed to controlled RHs of 60% and 85%, followed by assessment of compressive strength, setting time and workability. These measurements were complemented by characterising the prehydrated anhydrous cement using isothermal calorimetry, scanning electron microscopy, X-ray diffraction and thermal gravimetric analysis. Following prehydration at 60% RH, conventional hydration resulted in a negligible reduction in strength development plus a decrease in workability and increase in setting time. At 85% RH, compressive strength was greatly reduced, particularly at early ages. There was also a greater loss of workability and increase in setting time.

Introduction

Prehydration is the reaction of anhydrous cement with water vapour, leading to partial hydration of the surface of the cement grains. Such a situation may arise following prolonged storage. However, this phenomenon may be observed early on when, during grinding of the cement clinker, temperatures are high enough to dehydrate gypsum to the more soluble calcium sulfates (Havard Mork and Gjoerv, 1997; Hewlett, 2004), bassanite or anhydrite, with the release of water. This may lead to the formation of lumps during storage that, along with hydration of the cement, lead to a phenomenon known as silo set (Theisen and Johansen, 1975). Prehydration may therefore be reduced by limiting the gypsum content or by replacing gypsum with other forms of calcium sulfate with lower water contents (Sprung, 1978) and by ensuring adequate storage of the cement.

In addition to the influence mentioned above, factors affecting the degree of prehydration include temperature, relative humidity (RH), time of exposure and particle fineness (Richartz, 1973); smaller particles lead to smaller pore spaces thus resisting water vapour ingress through the cement bed. Previous work (Mejlhede Jensen *et al.*, 1999) has already assessed the reactivity of the clinker phases – tricalcium silicate (C_3S), dicalcium silicate (C_2S) and tricalcium aluminate (C_3A) – by exposing them to different RHs for up to 1 year. Mejlhede Jensen *et al.* observed thresholds below which the phases would not react with water vapour. C_3A prehydrated above 60% RH, producing mostly C_3AH_6, while the thresholds for C_3S and C_2S were much higher, at 85% and 90% RH respectively. Furthermore, the RH appeared to affect the nature of the C-S-H. At a very high RH, silicate prehydration produced C-S-H with $C/S = 1{\cdot}7$, a typical value for conventionally hydrated C_3S. At 83% RH, the molar C/S ratio increased to 3, with little or no CH formation.

More recently, Dubina *et al.* (2011a) used dynamic vapour sorption to ascertain the thresholds with more accuracy, as shown in Figure 1. Calcium oxide (CaO) was the most reactive of all the phases, starting to react at 14% RH, followed by hemihydrate (bassanite) at 34%. Anhydrite, meanwhile, did not prehydrate until 58% RH (gypsum also showed a threshold, of 24%, but this corresponded to a mass change of only about 0·1%, possibly as a result of impurities). Moving on to the principal clinker phases, the threshold for C_3A was dependent upon its crystal structure, with pure, non-doped (cubic) C_3A prehydrating at 80% whereas the onset of prehydration for Na_2O (sodium oxide)-doped C_3A (orthorhombic) was lower, at 55%. The thresholds for the silicate phases were considerably lower than those observed by Mejlhede Jensen *et al.* (1999), being 63% and 64% RH for C_3S and C_2S respectively.

Unlike conventional hydration, the absence of water in which

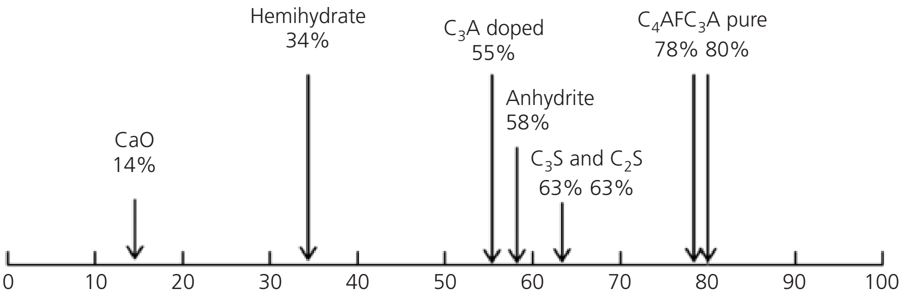


Figure 1. Prehydration threshold of the main phases found in Portland cement (Dubina *et al.*, 2011a, 2011b)

phases can dissolve limits ionic mobility, resulting in localised reactions. Theisen and Johansen (1975) prehydrated C_3A crystals in the absence and presence of gypsum. In the former case, C_3A grains became coated with calcium aluminate hydrates, while in the presence of sulfates ettringite was formed but did not form a continuous layer. Theisen and Johansen suggested that water was adsorbed onto surfaces with hydration occurring in this thin layer alone, creating a physical barrier of hydrates covering the individual C_3A crystals. The formation of ettringite and syngenite has also been found previously (Schmidt *et al.*, 2007; Sprung, 1978).

The interaction of cement with water vapour has detrimental effects on engineering properties, including decreased compressive strength and workability (Theisen and Johansen, 1975; Winnefeld, 2008) and increased setting time and water demand (Schmidt *et al.*, 2007). The aim of this study was to correlate changes in engineering performance with changes in anhydrous cement speciation induced by prehydration under controlled conditions. Prehydration was performed at RHs chosen in response to the thresholds determined by Dubina *et al.* (2011a, 2011b).

Experimental procedure

CEM I 42.5R cement was used, with the finer particle size offering the potential for more extensive prehydration under any given conditions. To properly assess the effects of prehydration, it was necessary to ensure that all of the cement was exposed to water vapour. To achieve this, cement was spread evenly, about 2 mm thick, in plastic trays and then placed in a glove box over saturated sodium bromide or potassium chloride solutions, ensuring a RH of 60% and 85% respectively (Winston and Bates, 1960). No attempt was made to exclude carbon dioxide, meaning that simultaneous carbonation could occur during prehydration. Samples were so exposed for periods of 7 and 28 days; the prehydrated samples are referred to as M*xx*-*yy* where *xx* and *yy* indicate the duration and RH respectively. Fresh, non-prehydrated cement was labelled as M0. The extent of water uptake was initially determined by weighing each tray both with and without its contents before and after exposure. The plastic trays were found to show minimal weight increase upon exposure, while the cement did gain weight.

The produced cements were subjected to characterisation prior to be used to prepare mortar samples that were in turn characterised with respect to their water demand, workability, setting time and unconfined compressive strength.

Anhydrous sample characterisation

The anhydrous cement powder was characterised using a suite of characterisation methods. Loss on ignition (LOI) was determined by heating to 1000°C for 1 h. Phase composition was determined by X-ray diffraction (XRD), using a Bruker AXS D8 Advance, fitted with a Cu Kα X-ray source. Powder samples were analysed over a range of 5 to 70° 2θ and hydrating cement pastes analysed in situ over the range 5 to 40° 2θ. Thermal analysis was performed on a Stanton Redcroft 780 series (STA 1000) under a nitrogen atmosphere, with a 20°C/min heating rate from 20 to 1000°C. Isothermal calorimetry was performed over a 72 h period using a GR150 Wexham JAF isothermal conduction calorimeter, with 30 g of anhydrous cement mixed with water with a water to cement (w/c) ratio of 0·5. Finally, the anhydrous cement powders were examined by scanning electron microscopy (SEM) using a Philips XL30 FEG-ESEM operating at 5 kV.

Mortar preparation, testing and characterisation

Mortar samples were prepared from the as-received and prehydrated cements according to BS 4550-3.4: 1978 (BSI, 1978a) but with some deviation. While the standard stipulates a 1:3:0·4 cement:sand:water mix, this was found in trial runs to lack sufficient workability, especially given findings in the literature that prehydration reduces workability (Winnefeld, 2008). Consequently, a 1:3:0·5 mix was used. Samples were mixed by hand and then vibrated using a standard vibrating table.

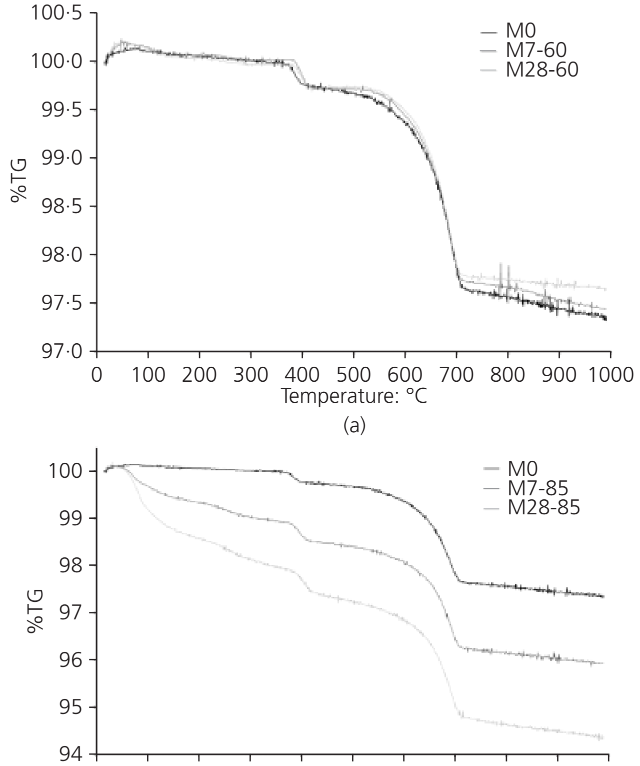
Standard consistency and setting times were measured using the Vicat penetration method according to BS 4550-3.5: 1978 (BSI, 1978b) and BS 4550-3.6: 1978 (BSI, 1978c) respectively. These tests used cement pastes rather than mortars, assuming the aggregate to be inert. Finally, workability was determined by using a flow table test in accordance with BS 4551-1: 1998 (BSI, 1998). This test was used in place of the standard slump test because the quantity of the mixes was insufficient to fill the slump mould. The flow table test was performed on the mixes used to cast the cubes for the strength test.

The compressive strength of mortar cubes was also tested in accordance with BS 4550-3.4: 1978 (BSI, 1978a), but with cube size reduced from 70·7 mm to 50·0 mm due to sample availability. Samples were tested after curing for 1, 7 and 28 days. All mixes were kept in a curing chamber at 99% RH at 20°C until tested.

Results and discussion

The anhydrous cement gained weight upon prehydration, with weight gain increasing with both RH and duration. For the samples exposed to 85% RH, the weight gains were 1·42% and 3·01% for M7-85 and M28-85 respectively, while M28-60 gained only 0·44%. The difference between the results obtained at 60% and 85% reflects prehydration below and above the thresholds of the silicate phases, which comprise the bulk of the cement.

The thermal gravimetric analysis (TGA) trace of the as-received clinker (M0) shows two mass losses (Figure 2) – at around 400°C due to the dehydroxylation of portlandite and between 500 and 700°C due to decarbonation of calcium carbonate (Alarcon-Ruiz *et al.*, 2005). The calcium carbonate is present in the anhydrous material, being added in small quantities to all cements within EN 197-1 (BSI, 2011). The presence of portlandite can be understood if one considers the prehydration threshold of free lime. It is known that free lime prehydrates very readily (Dubina *et al.*, 2011b) and, given the lack of evidence for any other hydration products in the anhydrous samples, it is reasonable to assume that the portlandite arises from prehydration of the small quantities of free lime in the cement clinker. The levels of portlandite correspond to about 0·7% free lime in the anhydrous clinker, which is not unusual.



(a)

(b)

Figure 2. TGA curves of the as-received cement and of the prehydrated cement at (a) 60% RH and (b) 85% RH

Following prehydration, all samples still contained both portlandite and calcium carbonate. Prehydration at 60% RH showed no increase in portlandite content, indeed a slight decrease was observed with a corresponding increase in calcium carbonate content. Portlandite is a hydration product of alite and belite and, because the RH was below the prehydration threshold of these phases, no portlandite was expected to form. A RH of 60%, however, was sufficient to induce slight carbonation of the portlandite formed by prehydration of the free lime.

Increasing the RH to 85% triggered silicate prehydration, with the production of portlandite. After 7 days the portlandite content had increased from 0·76% to 1·42%, with a further increase to 1·78% after 28 days, expressed as ignited base weight. With the silicate prehydration came the formation of C-S-H, the presence of which was reflected by an increased continual mass loss to 700–800°C, but particularly below 100°C, due to the loss of bound water (Dweck *et al.*, 2000; Ramachandran and Haber, 2001). The increased availability of portlandite from silicate prehydration, plus the availability of water, also enabled carbonation. Consequently, there was a slight increase in the calcium carbonate content following prehydration at 85% RH for 28 days. The extent of portlandite carbonation is summarised in Table 1. Carbonation was slight, but was more extensive following prehydration at 85% RH.

In addition, prehydration led to the appearance of other features noticeable in the differential thermal analysis (DTA) tracings. Prehydration led to the appearance of slight mass losses and endotherms at approximately 250°C, which have previously been ascribed to the presence of hexagonal hydrates from the reaction of C_3A in the absence of gypsum (Alarcon-Ruiz *et al.*, 2005; Ramachandran and Haber, 2001). These features were observed after prehydration at 60% and 85% RH, but were more visible at higher RH values.

It is known from previous studies that C_3A is extremely susceptible to prehydration (Mejlhede Jensen *et al.*, 1999), as supported by the similarity between the DTA traces obtained after prehydration for 7 and 28 days. C_3A, depending in the sodium content (Bye, 2011), can adopt either a cubic and orthorhombic crystal structure, the latter being the more reactive (Figure 1). While calcium aluminate hydrates carbonate readily to form calcium hemi- and monocarboaluminate, Black *et al.* (2006) and Ramachandran and Chun-Mai (1986) reported two peaks for such

Sample	LOI: %	$Ca(OH)_2$: %	$CaCO_3$: %	$Ca(OH)_2$ from carbonation
60% RH				
Fresh	2·8	0·76	4·22	—
7 day	3·2	1·14	4·45	0·17
28 day	3·5	1·08	4·54	0·24
85% RH				
Fresh	2·5	0·76	4·22	—
7 day	4	1·42	4·28	0·44
28 day	5·3	1·78	4·65	0·32

Table 1. Weight gain and LOI of the anhydrous cement associated with prehydration

phases, at 150–60°C and 235–245°C, of which only the second was present in the current study. Thus, the presence of such phases can be discounted. Similarly, DTA of ettringite shows an endothermic mass loss at between 170 and 200°C (Ramachandran and Haber, 2001), a feature similarly not observed in this study. Thus, while conventional hydration of C_3A in the presence of sulfate leads to the formation of ettringite, the limited ionic mobility under prehydrating conditions appears to preclude ettringite formation, and the hexagonal calcium aluminate hydrates are formed instead.

All of the prehydrated samples also showed endothermic mass losses over the range 120–130°C attributed to the presence of either ettringite, formed by way of the reaction of C_3A in the presence of sulfates, or gypsum, formed by way of the reaction of the bassanite or anhydrite with the water vapour (Figure 3). The presence of gypsum subsequently proved key to explaining some of the observations regarding engineering properties.

To investigate the physical appearance of samples following prehydration, samples were examined by low-vacuum SEM (Figure 4). Micrographs from the as-received sample (M0) showed surfaces free of surface hydration products; the small particles seen in the micrographs were fine deposits rather than hydration products.

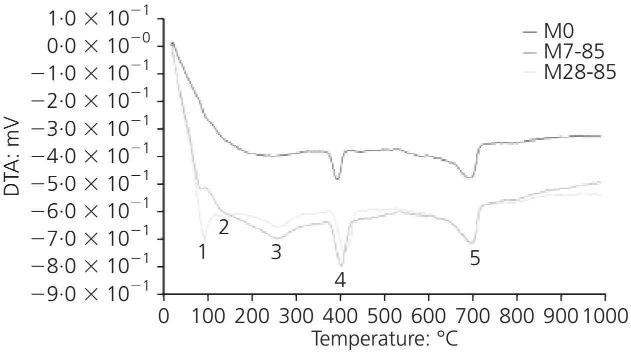
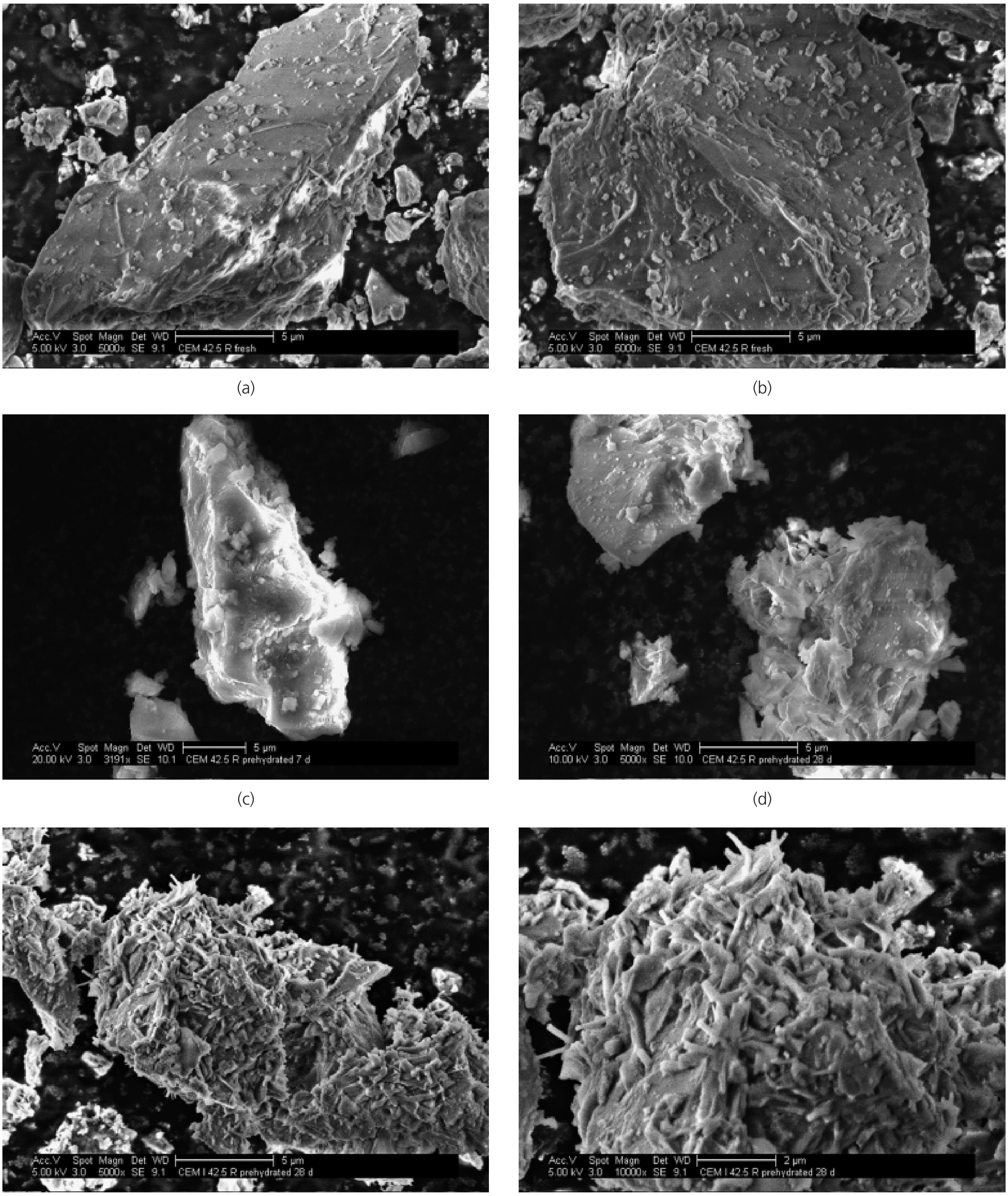


Figure 3. DTA tracings of cement prehydrated at 85% RH. Identified endothermic peaks include: 1, C-S-H; 2, gypsum and/or ettringite; 3, C-A-H; 4, portlandite; 5, calcite

Figures 4(c) and 4(d) show micrographs of samples M7-60 and M28-60 respectively. The cement grains were seemingly unaffected after prehydration for 7 days. Prehydration for longer periods resulted in very limited formation of plate-like crystals on the grain surfaces. At this humidity, only hemihydrate and doped C_3A are affected by prehydration. Prehydration at 85% RH showed a much greater localised reaction after just 7 days (Figure 4(e)) where the surfaces of the particles are covered with a fine layer of platy crystals. These could be hexagonal hydrates (e.g. C_4AH_x), cubic hydrates (C_3AH_6) or portlandite, but given the thermal analysis data presented earlier, the presence of hexagonal hydrates appears most likely.

Sample M28-85 (Figure 4(f)) showed the most extensive surface alteration, with the entire surface being covered with platy crystals interspersed with isolated needle-like crystals. This 'protective' layer of hydrates forms on the surfaces of the clinker grains, impeding the ingress of water, and thus disrupting any subsequent hydration. The aforementioned needles were very fine, typically less than 1 μm long, and on first appearance appeared to be ettringite. These results agree with those of Theisen and Johansen (1975) who observed hexagonal platy crystals on C_3A prehydrated in the absence of gypsum and needle-like crystals in the presence of gypsum. However, gypsum can also assume a needle-like morphology when formed by the hydration of anhydrite or bassanite (Taylor, 1997). XRD analysis of M28-85 (not shown) showed very small reflections of ettringite at 9·0865° (100) and 15·7715° (110) respectively, promoting the idea that the needle crystals are ettringite rather than gypsum, agreeing with the results obtained by Dubina *et al.* (2010) when working on C_3A–calcium sulfate mixtures. However, in CEM I cements, as opposed to stoichiometric C_3A–sulfate mixtures, the C_3A and sulfate levels are low



(a) (b)

(c) (d)

(e) (f)

Figure 4. LV-SEM micrographs of (a, b) anhydrous cement (M0), (c) M7-60, (d) M28-60, (e) M7-85 and (f) M28-85

enough such that the two phases may not often come into intimate contact, thus reducing the likelihood of ettringite formation.

Isothermal conduction calorimetry (Figure 5) provides further information on how normal cement hydration is affected by prehydration. Prehydration at 60% RH showed little difference in the total heat evolved (Figure 5(a)), but there was a reduction in the maximum heat rate plus slight retardation with prolonged exposure. However, the most obvious change was in the shape of the heat evolution trace, with heat evolution approaching a maximum before a sudden second heat evolution about an hour after the first. Similar results were observed by Winnefeld (2008). The precise reason for this is uncertain. Possible explanations include the hydration products acting as nucleation sites or the formation of secondary ettringite from the reaction of hexagonal aluminate hydrates with sulfates (Fu *et al.*, 1996; Janotka, 2001). Aluminate hydrates were identified in samples M7-85 and M28-85 by TGA as slight mass losses at ~250°C. However, in situ XRD of hydrating pastes, as discussed later, appears to disprove this explanation.

Prehydration at 85% RH had a more profound effect on hydration. Total heat evolution was significantly reduced, with a 17·9% reduction compared to M0 (Figure 5(c)) after prehydration for 28 days. Similarly, the maximum heat rate was both significantly reduced and retarded, as had been seen previously when studying pure C_3S samples (Dubina *et al.*, 2010). However, cement prehydrated for 28 days was retarded less than cement prehydrated for 7 days. This contradicts previous research (Schmidt *et al.*, 2007; Sprung, 1978; Winnefeld, 2008) which has generally shown an increased delay in hydration with prehydration. The precise reason for this is uncertain, although it might be due to the greater gypsum content found in M7-85, as evidenced by XRD. Furthermore, the prehydrated cement showed a broader alite hydration peak, perhaps due to the formation of the physical barrier to hydrations controlling the ingress of water.

In addition to characterisation of the samples, the engineering performance of the cement prehydrated under different conditions was also studied. Figure 6 shows the evolution of strength of the prehydrated cements normalised to that of the non-prehydrated cement. Prehydration at 60% RH had little effect on compressive strength, but increasing the RH to 85% had severe consequences, with a marked loss in strength, particularly at early ages. This

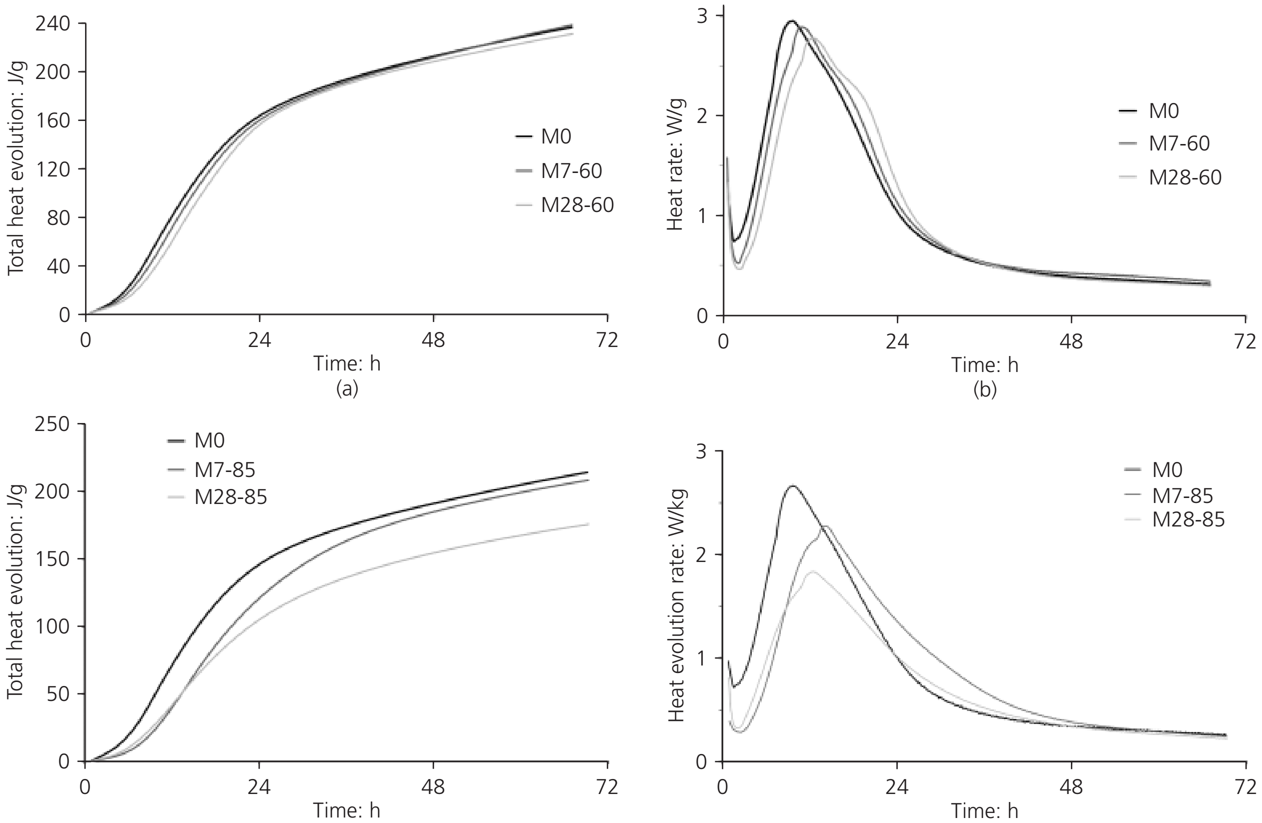


Figure 5. (a) Heat evolution rate and (b) total heat evolved of cement prehydrated at 60% RH. (c) Heat evolution rate and (d) total heat evolved at 85% RH

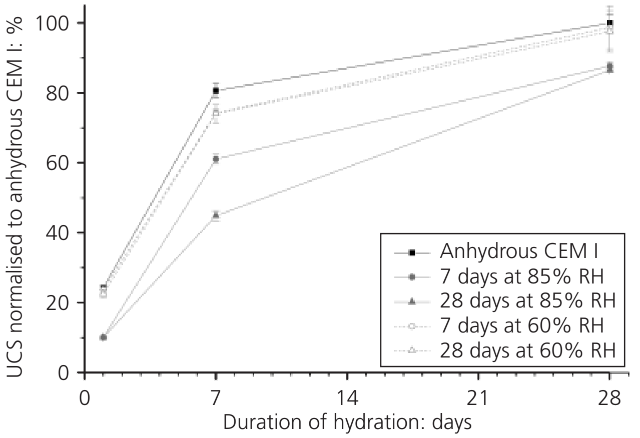


Figure 6. Compressive strength evolution of prehydrated cement

difference can be explained by considering the prehydration threshold of alite (63%), since alite hydration is responsible for early age strength development. Using the presence of portlandite as a measure of alite hydration, TGA data (Table 1) showed that alite was not affected at 60% RH, but increasing the RH to 85% led to alite prehydration. This prehydration led to a loss in reactivity as measured by calorimetry, the consequent reduction in compressive strength and also by thermal analysis of the hydrated pastes (not shown). Loss of strength attainment following prehydration has been reported previously (Theisen and Johansen, 1975) and Winnefeld (2008) found that after only 2 days of ageing at 90% RH, the strength of the mortars no longer satisfied the required strength set out in BS EN 197-1: 2011.

In addition, workability continually decreased with prolonged prehydration (Table 2), the severity of which increased with increasing RH. This is most likely due to the formation of hydrates on the particles' surface, resulting in rougher particles interlocking and increasing the effective particle size. Consequently, it follows that more water was needed to achieve pastes of standard consistency for Vicat testing after prehydration. A fresh paste achieved standard consistency with a w/c ratio of 0·32. When prehydrating at a RH of 60%, the w/c ratio increased to 0·325 and 0·35 after 7 days and 28 days of prehydration respectively to achieve standard consistency. At 85% RH, standard consistency was found at a w/c of 0·34 and 0·495 after 7 and 28 days of prehydration respectively.

Sample	Workability: mm	Initial setting time: min	Final setting time: min
M0	133	100	265
M7-60	127	135	260
M28-60	123	145	310
M7-85	121	240	440
M28-85	118	195	480

Table 2. Workability and setting time data for the various samples

Prehydration also led to marked changes in setting times and behaviour. Ostensibly, prehydration led to increased setting times, as shown in Table 2. Retardation was greater following prehydration at 85% RH and, for prehydration at 60% RH, retardation increased with the duration of prehydration. However, for cement prehydrated at 85% RH, the relationship was not so straightforward. While the overall delay may be explained by the formation of a barrier covering the grains limiting water ingress and hence reaction, initial setting was delayed most after prehydration for only 7 days. This agrees with the calorimetry data where the maximum heat evolution was retarded to the greatest extent for M7-85. But this was not the most striking change in the setting time. Figure 7 shows how prehydration led to an unusual hardening–softening–rehardening behaviour. This phenomenon led to the pastes showing two 'initial setting times' (i.e. where the paste showed a penetration depth of 35 mm). Given the practical implications of the initial setting time (i.e.

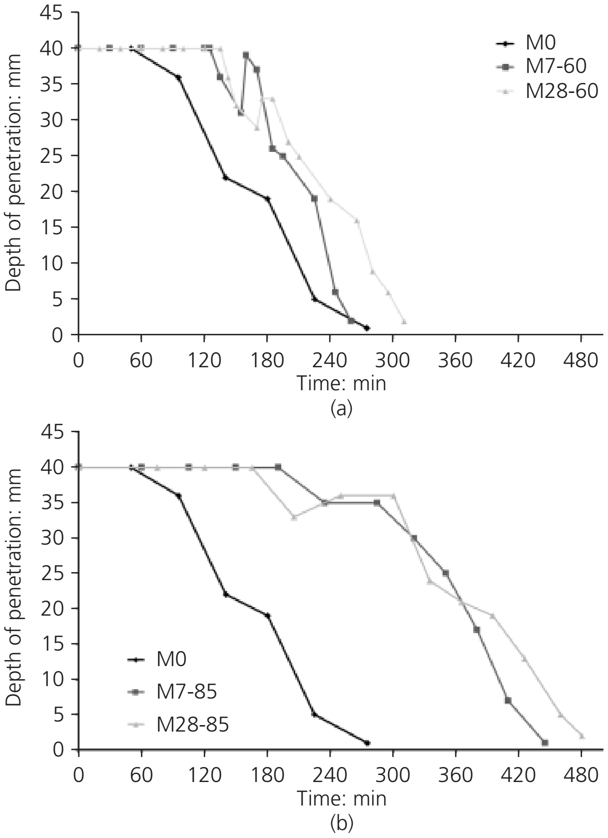


Figure 7. Setting time measured by Vicat penetration of cement prehydrated at (a) 60% RH and (b) 85% RH

the point at which a paste is no longer considered workable), the initial setting time reported in Table 2 is the value obtained when the penetration depth reaches 35 mm for the first time. Soon after the initial hardening, all of the pastes prepared from prehydrated cement softened (i.e. penetration decreased). The precise reason for this behaviour is unknown, and was thus investigated further; it may be due to gypsum formation upon prehydration

In situ XRD analysis (Figure 8) was performed on the prehydrated samples at 85% RH in an attempt to explain the unusual setting time observed. M0 did not show any signs of gypsum at the start of the reaction, with ettringite forming from the onset of hydration and portlandite formation starting after just 3·5 h. Gypsum, present after prehydration for 7 days at 85% RH, was totally consumed after 8 h of hydration, with a delay and reduction in ettringite and portlandite formation, the latter starting to precipitate after 5 h of hydration. M28-85 also showed gypsum formation upon prehydration but in a reduced concentration compared with M7-85. It was fully consumed after 5 h of hydration, coinciding with portlandite formation. The smaller initial gypsum content in M28-85 could explain why the initial setting time was less retarded. It would therefore appear that hardening could be caused by the consumption of gypsum and the possible formation of ettringite, while rehardening coincided with portlandite formation, indicating the onset of alite hydration. There were, however, no discernable compositional changes associated with the observed softening behaviour, perhaps indicating a physical or morphological explanation.

Conclusion

This paper has demonstrated that prehydration is characterised by the formation of a barrier of hydrates covering the surface of cement grains. The extent to which this occurs depends on the RH. Consequently, prehydration has a detrimental effect on the engineering properties of Portland cement, including strength, setting time and workability. Prehydration at 60% or 85% RH decreased workability and increased setting times while compressive strength was only adversely affected after prehydration at 85% RH. These observations may be understood by considering the threshold RH values for the principal clinker phases, with only sulfate and aluminate phases reacting with water vapour at 60% RH while alite and belite also reacted at 85% RH. Characterisation of the anhydrous prehydrated cement samples has been used to explain some of the changes in engineering performance, for example, the formation of gypsum, calcium aluminate hydrates and calcium silicate hydrate plus portlandite. The unusual softening behaviour observed cannot yet be explained, but may be due to morphological changes of individual hydrate phases.

Acknowledgement

The authors wish to thank Nanocem for financial support of Elina Dubina in her studies.

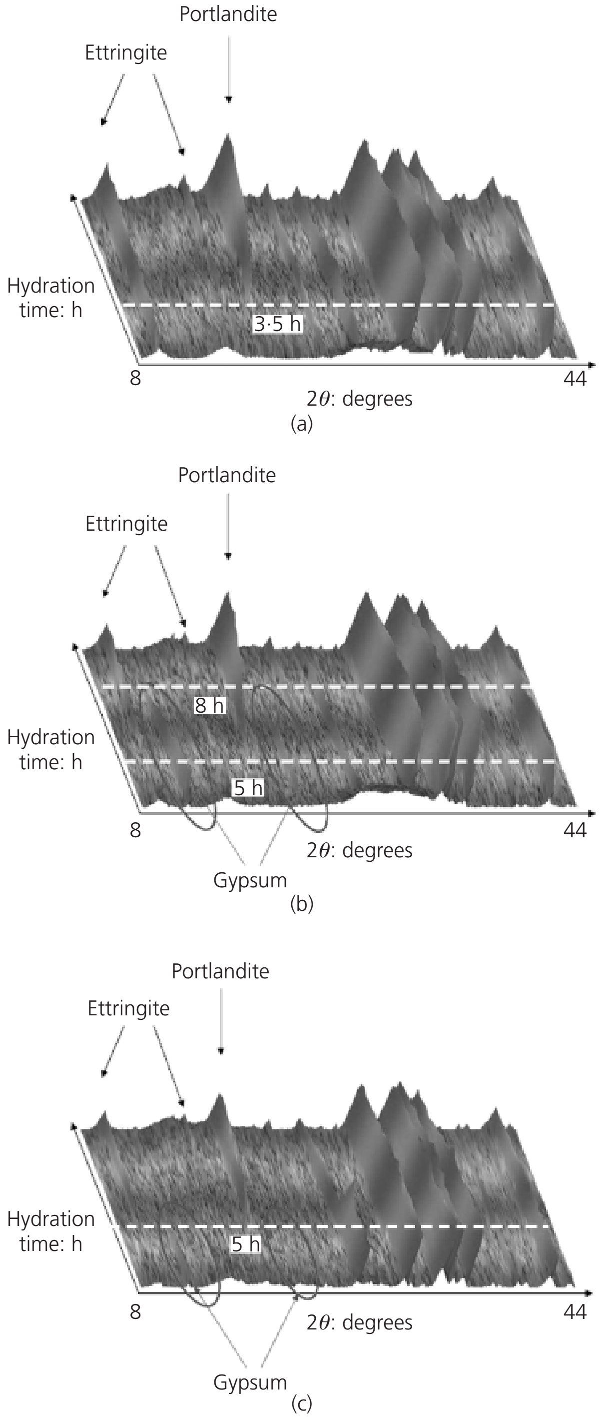


Figure 8. In situ XRD of (a) M0, (b) M7-85 and (c) M28-85

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