Published Conference paper

Dubina, Elina, Sieber, Roland, Plank, Johann and Black, Leon (2008) *Effects of pre-hydration on hydraulic properties on Portland cement and synthetic clinker phases.* In: Fentiman, C.H. and Mangabhai, R.J., (eds.) 28th Cement and Concrete Science : Proceedings, 15-16 September 2008, Manchester, England. Cement and Concrete Science. ISBN 13 978-0-9553296-3-0

Effects of pre-hydration on hydraulic properties on Portland cement and synthetic clinker phases

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Extended Abstract: Cement and Concrete Science, University of Manchester, Manchester, 15-16th September 2008.

Abstract The ageing of cements (CEM I 52,5 R and API Oilwell Class G) and also the pure cement clinker minerals (C_3S, pure C_3A, Na_2O-doped C_3A, C_4AF and calcium sulphate hemihydrate) has been studied at 60% and 85% RH using in-situ XRD, calorimetry, ESEM, XPS and FTIR-ATR. This combination of techniques has identified the key components involved in the surface pre-hydration process. Pre-hydration of cement leads to retardation of hydration. In-situ XRD shows the retardation of Portlandite formation after prehydration, which explains the heat development seen via calorimetry. XPS and ESEM investigations show surface modification after prehydration for C_3S, C_3A and doped C_3A (4% Na_2O). Pre-hydration of cement leads to modification of the surface area and surface charge, which can strongly influence the reactivity of bulk cements and their interaction with admixtures. This is relevant to the quality of cement during storage.

Experimental

In order to establish the cause of the ageing phenomena, powdered samples were spread lightly over a tray, and exposed to controlled humidity, in a nitrogen filled glove box, at controlled temperature. Relative humidity was controlled via the use of saturated salt solutions (60% NaBr, 85% KCl). The samples were exposed for predetermined lengths of time (from 1h to 28 days) prior to analysis by each of the techniques listed above.

Results and discussion

This project aimed to investigate the physicochemical effects of water adsorption onto anhydrous cement surfaces and the subsequent influence upon their hydraulic properties. The level of understanding of the effects of storage at high relative humidity on the reactivity of clinker phases (C_3S, C_3A, C_4AF) and cement has been substantially increased by systematic investigations, and the following conclusions can be drawn from the results:

C_3S proved to be particularly sensitive to humidity. The longer the C_3S-samples remained in humid air, the longer the retardation of the hydration became. This retardation also became more pronounced with increasing relative humidity (compare Fig. 1). At high RH (85%), water molecules adsorb onto the mineral surface. The water molecules react with alite on the surface to form of the hydration products: C-S-H-phases and Portlandite, thus making the prehydration process irreversible. These hydration products form a thin layer on the surface of C_3S grains which acts as a barrier upon mixing with water. Thus, for the prehydrated phases, it takes longer for the water to reach the bulk C_3S than for fresh C_3S samples. This assumption was confirmed with analytical methods like isothermal heat flow calorimetry, FT-IR Spectroscopy, ESEM and XPS.

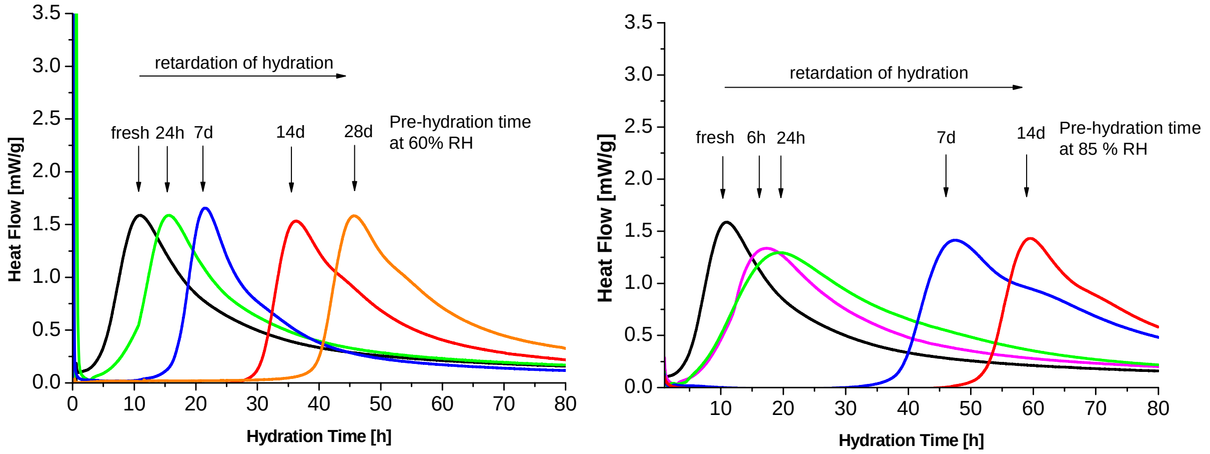

Fig.1 Heat of hydration of C_3S samples (w/ C_3S = 0,5); **a)** after storage at 60 % RH; **b)** after storage at 85 % RH

XPS can be used to reveal changes in the extent of silicate polymerisation upon hydration within the topmost 10 nm[1]. Figure 2 shows the Si 2p spectra of the C_3S sample exposed to 80% RH for up to 3 days. The fresh sample gave a peak at ~101 eV, typical of C_3S, with a slight shoulder due to the presence of some C-S-H. Exposure to moist air led to the growth of a peak to higher binding energy, at ~102.1 eV, typical of C-S-H[2]. The precise thickness of this surface hydrate layer is unknown, but given an analysis depth of 10 nm, the presence of residual intensity at 101 eV indicates that the C-S-H layer must be thinner than this.

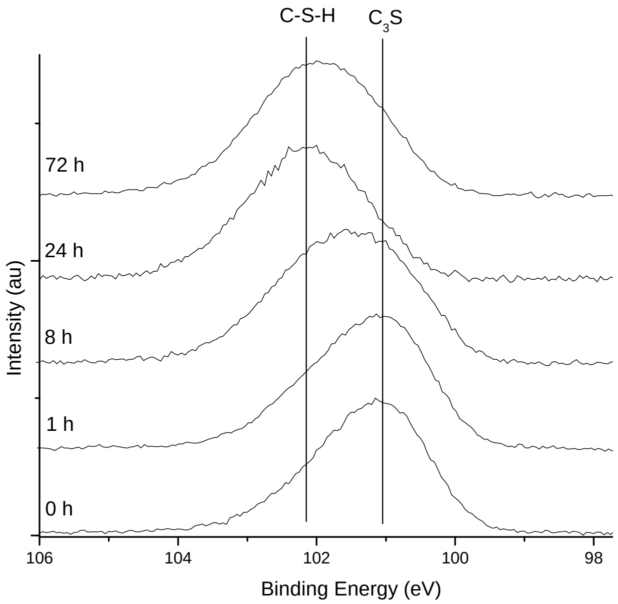

Fig.2 Si 2p spectra from C_3S exposed to 85% RH for up to 3 days, showing the formation of C-S-H on the sample surface.

A similar effect was observed for C_3A, where prehydration formed a protective layer of a C-A-H-phase. The next step was to investigate the sensitivity of pure and Na_2O-doped C_3A towards humidity with time. It was concluded that the extent of surface hydration depended on the exposure time and on the modification of the C_3A. The experiments showed that the surface of the doped C_3A upon exposure at 85 % RH explicitly became more prehydrated than the pure C_3A-phases. Therefore the doped C_3A phase is much more reactive than pure C_3A (compare Fig. 3). This behaviour can be ascribed to the structural difference of the two modifications, as was also observed by ESEM. The impact of atmospheric humidity causes condensation on the edges and cracking of the C_3A grains, favouring the formation of C-A-H-phases.

Similarly, XPS clearly revealed the effects of prehydration within one hour on the surfaces of the pure and doped C_3A samples. Figures 4 a and b show, as examples, the Al 2p and C 1s spectra respectively recorded from the doped C_3A sample. Fresh pure and doped C_3A both gave Al 2p peaks at 73.0 eV, with the growth of peaks at 73.8 and then 74.3 eV. The shift to higher binding energy in the Al 2p spectra indicates the formation of a C-A-H phase, and, based upon the marked growth in the peak attributed to carbonate in the C 1s spectra, the formation of a calcium carboaluminate phase. A C_4AH_{13} standard gave an Al 2p peak at 73.8

eV, indicating that this phase may form upon the initial exposure of C_3A to moist air. Or, more accurately, that a C-A-H phase forms initially, the precise water content cannot be determined by XPS, which is a high vacuum technique. Furthermore, quantification of the photoelectron spectra indicated a Ca:C ratio for three day old C_3A of 4:1, indicating the formation of calcium monocarboaluminate ($3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$). This agrees with the bulk carbonation behaviour of C_3A pastes, as studied previously by Raman spectroscopy[3].

The XPS results agreed with the other techniques, in that prehydration of the doped C_3A was most extensive. As seen in Figure 4a, after exposure for one day there was no evidence of an Al 2p signal due to C_3A, whilst the unhydrated phase could still be detected in the Al 2p spectrum of pure C_3A after this time. Furthermore, the level of carbonate was much greater in the doped C_3A, which indicates that carbonation did not just yield calcium monocarboaluminate, but possibly also sodium carbonate. Further work is required to elucidate the carbonation behaviour of this sample.

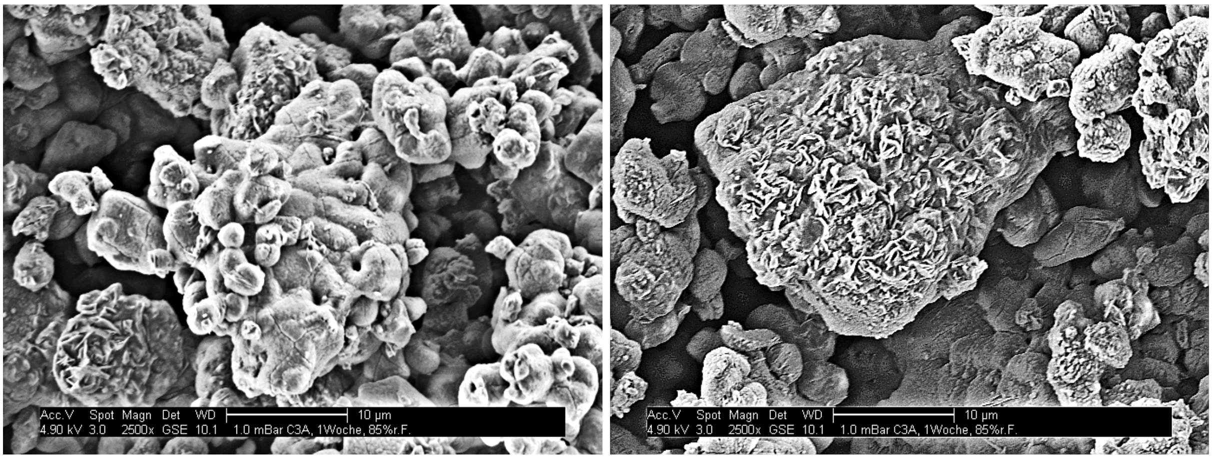

Fig. 3 ESEM photographs; **on the left**: pure C_3A after 7 d at 85 % RH; **on the right**: doped C_3A after 7 d at 85 % RH

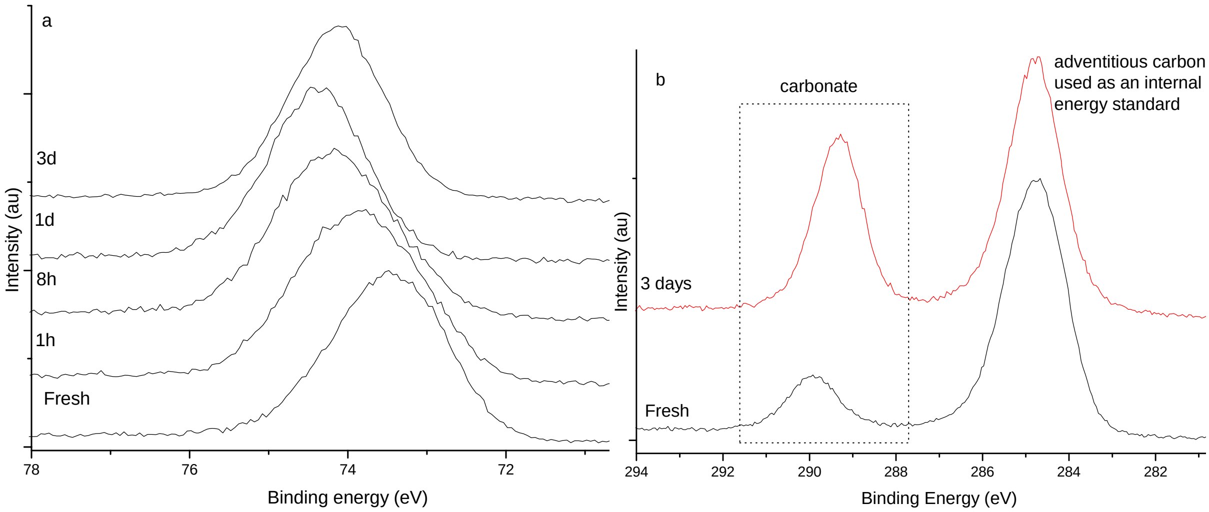

Fig. 4 XPS spectra recorded from the doped C_3A sample. The Al 2p spectra (a) show the formation of a C-A-H phase, followed by calcium monocarboaluminate. The C 1s spectra (b) indicate that carbonation of the prehydrated surface layer was quite extensive.

As an example for sulphates, the hemihydrate was examined. Upon storage, a gypsum layer was formed on its surface. During the hydration of the stored hemihydrate, gypsum accelerated the reaction. This gypsum layer on the surface of the hemihydrate was detected by X-ray diffraction analysis.

Furthermore, a binary mixture of C_3A and hemihydrate in molar ratio 1:1 was stored in a humid atmosphere and then the hydration reaction was investigated. Upon storage of the mixture at 85 % RH, crystals of ettringite started forming just one week later. The reaction behaviour of the system was strongly affected. At the onset of hydration, acceleration of the reaction due to the gypsum particles took place. However, a delay in the induction period was then observed, which can be attributed to the ettringite layer on the C_3A grains. With Na_2O doping of the aluminate phase, this effect became stronger.

Experiments on the clinker showed that C_4AF was the least affected by storage at high humidity. In comparison with other clinker phases, the ferrite phase develops the lowest reaction enthalpy and therefore is less reactive than alite or aluminate.

Investigations on calcined lime (CaO) showed, as expected, that lime favours water absorption from the atmosphere even in very short exposure times. Apart from portlandite reflections, strong calcite reflections were also observed by XRD, which indicates that the atmosphere was not completely free of CO_2.

In the last part of this study, the effect of storage at 60 % and 85 % RH was investigated for two commercial cements. The experimental results have significant practical relevance. After the storage, both cements showed a noticeable change in reactivity. Storage at 85 % RH showed a stronger effect on the hydration behaviour. The sensitivity towards storage for the cements depends on their chemical composition as well as the C_3S and C_3A content. The main reaction, as determined by heat flow calorimetry, experienced a delay after prehydration. For a C_3A rich cement there was also a decrease in the maximum heat flow. The reactivity of both cements was further studied by in-situ XRD. The results for both cements are in agreement with the heat flow calorimetry, regarding the delay of the portlandite formation. The C_3A rich cement showed, after exposure to humidity, increased ettringite formation upon hydration. This means that ettringite is formed in aged cement during storage. This effect is explained by the higher solubility of anhydrite initially present in the cement. Upon storage of the anhydrite at high RH, gypsum grains are formed on the surface. This increases the sulphate solubility and accelerates ettringite formation. The electron microscopy studies on cement showed that at 85 % RH, many different phases begin to form on the surface of the cement. Ettringite crystals as well as C-S-H-phases could be recognised based on their morphology.

Acknowledgement

The authors are grateful to Nanocem for financial support of this work.

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