



## Effect of free water removal from early-age hydrated cement pastes on thermal analysis

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### ARTICLE INFO

#### Article history:

Received 21 June 2007

Received in revised form 13 May 2009

Accepted 18 June 2009

#### Keywords:

Cement hydration  
Drying techniques  
Solvent exchange  
Oven drying  
Vacuum drying  
Thermal analysis  
XRD  
FT-IR

### ABSTRACT

In order to follow the progress of cement hydration by analytical techniques, the ongoing hydration reactions must be stopped by complete removal of free water. A comparison between solvent exchange, oven drying and vacuum drying, using thermal analysis, is presented for early-age hydrated cement pastes. Results show that oven drying at 105 °C accelerates hydration, causes dehydration of some hydrated cement phases and favours carbonation. Solvent exchange with ethanol, ether and methanol results in a strong absorption and an incomplete removal of solvents. FT-IR and XRD gave evidence of the formation of carbonate-like phases due to an interaction upon heating, i.e. during thermal analysis, between the strongly absorbed solvents and the cement compounds or hydrates. Vacuum drying reveals reliable results as no interaction products can be formed and the  $\text{Ca}(\text{OH})_2$  content, determined by thermal analysis, gives a good approximation of the real amount of  $\text{Ca}(\text{OH})_2$ .

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### 1. Introduction

Water is essential for cement to harden by hydration. Amorphous calcium silicate hydrate (C–S–H) is the main hydration product that is responsible for the hardening of cement, together with other hydration products, such as AFm and ferrite phase. At any stage of hydration, the hydrated cement paste mainly consists of those hydration products of various compositions, calcium hydroxide crystals, unhydrated cement compounds and water in the pore structure. This water, held in varying degrees of firmness, is generally classified according to the degree of ease with which it can be removed from the hydrated cement paste. In the model of Feldman and Sereda [1], four types of water are distinguished: capillary water, adsorbed water, interlayer water and chemically combined water [2,3]. *Capillary water*, generally called *free water*, is the water that is present in capillaries larger than about 50 Å and is beyond the influence of attractive forces exerted by the solid surface. *Adsorbed water* is close to the solid surface where water molecules are physically held by the surface forces of the gel particles. *Interlayer water* refers to the water associated with the C–S–H structure.

It is accepted that a monomolecular water layer between the C–S–H layers is strongly held by hydrogen bonding. *Chemically combined water* is an integral part of the structure of the cement hydration products and can only be removed by thermal dehydration.

The progress of cement hydration can be studied by following the formation of hydration products at certain stages, using analytical techniques, such as thermal analysis, Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). Particularly for the early-age hydration reactions, it is crucial to stop the ongoing hydration by removal of free water, which has not participated in the reaction yet, prior to the investigation. Without its removal, hydration reactions will continue, leading to a wrong estimation of the reaction process and the amount of hydration products. The water content, removed from the hydrated cement paste during drying, can only be defined in relation to a specified drying condition [4]. The vapour pressure during drying, the drying history and the rate at which the water is removed influence the water content after drying. For instance, after intensive drying at high temperatures or at low pressures, some cement hydrates may partially or completely dehydrate and information on those phases will be lost. When choosing a drying technique, the aim of drying, i.e. the tests that have to be carried out on the dried samples and the properties that need to be investigated, should always be considered. When the structure of the hardened sample should be preserved prior to microstructural studies, the least aggressive drying technique

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should be used. For chemical and analytical analyses, such as thermal analysis, FT-IR and XRD, powdered samples are required and preservation of the microstructure is not important.

Several techniques can be applied to remove the free water, affecting the degree of water removal in different ways, i.e. at low pressures (P-drying [5], D-Drying (or dry-ice drying) [6], freeze-drying [7,8], vacuum drying [9]) or at high temperatures (oven drying [10]). In addition, solvent exchange is a frequently used technique to stop the hydration reactions. This technique is based on the replacement of free water in the capillary pores of the hydrated cement paste, using a low surface-tension organic liquid, such as ethanol, ether, methanol, acetone, and isopropanol. The use of solvents has been criticized by several authors since some time, due to their possible interactions with the cement hydrates [11–15]. Nevertheless, there has not been agreement in the literature, because some authors have reported opposite results [16–18], and solvent exchange is still used rather often prior to thermal analysis and other analytical measurements.

This paper presents some new data on the influence of drying techniques on the results of thermal analysis of early-age cement pastes. The hydration reactions are stopped in cement pastes, hydrated for 6 and 24 h and 7 days, by vacuum drying, oven drying and solvent exchange with several solvents. The thermoanalytical results are verified by FT-IR spectroscopy and XRD.

## 2. Research programme

### 2.1. Sample preparation

Cement paste with a water–cement ratio of 0.45 is prepared using an ordinary Portland cement (CEM I 52.5 N) and tap water. The specifications of the cement are presented in Table 1. The paste is stored in closed recipients until the moment of testing.

### 2.2. Drying techniques

Removal of free water from hydrated cement pastes is carried out by solvent exchange, oven drying and vacuum drying at 6 h, 24 h and 7 days of hydration. After drying, the samples are stored in air-tight plastic cups in a desiccator containing silica gel and soda lime to create a dry and CO<sub>2</sub>-free environment.

#### 2.2.1. Solvent exchange

For the solvent exchange method, cement paste is crushed and ground to fine powder. The powdered samples are mixed with a solvent and centrifuged successively three times for 20 min. At the end of every cycle, the solvent is removed and replaced by fresh one. This procedure of mixing and centrifuging takes 2 h. After the last cycle of centrifuging, the samples are dried at 40 °C for 24 h under an ultimate vacuum of 10 mbar. Three types of organic solvents are used: pure ethanol, pure methanol and three cycles of pure ethanol followed by one cycle of pure ether to remove the ethanol.

#### 2.2.2. Oven drying

After grinding the hydrated cement paste, powdered samples are dried at an elevated temperature of 105 °C in an atmosphere of uncontrolled humidity for 24 h. Even though the oven drying is known to have adverse consequences, such as the removal of chemically bound water of some hydrated phases, it has been in-

cluded in the research programme for comparison with other drying techniques. In practise, it is still rather often used [10].

#### 2.2.3. Vacuum drying

Vacuum drying is carried out using an Alpha 1-2 LD Martin Christ type freeze-dryer without prefreezing the samples. Round bottom flasks, containing the powdered or wet pastes, are connected to the device, consisting of a vacuum chamber with an ice condenser and a vacuum pump that allows applying a vacuum of  $2.5 \times 10^{-2}$  mbar. Extracted water is continuously collected in an ice condenser at a temperature of –62 °C, corresponding to a water vapour pressure of  $8 \times 10^{-3}$  mbar. Samples are vacuum dried for 2 h. The vacuum applied by the pump, increases the rate of water removal. Thin layers of paste or small amounts of powder are spread on the walls of the flasks. Immediately after connecting to the vacuum system, the temperature of the sample drops, because of the extraction of latent heat, and the hydration reactions are stopped.

This vacuum drying is very similar to the frequently used P-drying and D-drying techniques. P-drying occurs over a magnesium perchlorate hydrate Mg[ClO<sub>4</sub>]<sub>2</sub>·H<sub>2</sub>O with a partial vapour pressure of  $10.7 \times 10^{-3}$  mbar [5] and D-drying is carried out with a cold trap at –79 °C (dry-ice) and a corresponding water vapour pressure of  $0.67 \times 10^{-3}$  mbar [6].

### 2.3. Experiments

After removal of free water from early-age hydrated cement pastes by solvent exchange, oven drying and vacuum drying, the samples are analyzed by thermal analysis. Thermal analysis is carried out using a Netzsch STA 409 PC, a simultaneous Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC) system. The samples are heated from room temperature to 1000 °C with a heating rate of 10 °C/min in a N<sub>2</sub> atmosphere (60 ml/min). While the TGA signal is used to calculate the weight loss during heating and to estimate the content of Ca(OH)<sub>2</sub> and carbonated phases, the first derivative of this weight loss (DTG) is used to follow the hydration reactions qualitatively. The weight loss between 20 °C and 1000 °C is calculated according to formula (1). This is an empirical measure of the degree of hydration, although it also incorporates the weight loss due to the decarbonation of the carbonate phases. Furthermore, the water content of the hardened paste, and, therefore, the weight loss between 20 °C and 1000 °C, depend on the drying technique.

The calcium hydroxide content, formed during hydration, is determined using formula (2).  $WL_{Ca(OH)_2}$  is the weight loss during the dehydration of Ca(OH)<sub>2</sub> as percentage of the ignited weight and calculated according to the method described by Taylor [4]. This takes into account the continuous loss due to the gradual decomposition of the C–S–H and the hydrated aluminate phase.  $MW_{Ca(OH)_2}$  and  $MW_{H_2O}$  represent the molecular weight of Ca(OH)<sub>2</sub> and water. As a measure of the amount of carbonate and carbonate-like phases, the weight loss  $WL_{Carbonate}$ , due to the decomposition of these phases, is calculated as percentage of the ignited weight.

$$m_{20-1000\text{ }^\circ\text{C}}[\%] = \frac{m_{20\text{ }^\circ\text{C}} - m_{1000\text{ }^\circ\text{C}}}{m_{1000\text{ }^\circ\text{C}}} \quad (1)$$

$$Ca(OH)_2[\%] = WL_{Ca(OH)_2}[\%] \cdot \frac{MW_{Ca(OH)_2}}{MW_{H_2O}} \quad (2)$$

**Table 1**  
Chemical composition of cement CEM I 52.5 N (provided by manufacturer).

	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	Cl <sup>-</sup>	Loss on ignition	Insoluble residue
wt.%	61.7	17.2	5.7	3.9	0.8	0.41	0.77	3.1	0.04	1.6	0.7

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