COMPARISON OF SOLVENT EXCHANGE AND VACUUM DRYING TECHNIQUES TO REMOVE FREE WATER FROM EARLY AGE CEMENT-BASED MATERIALS

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Abstract

In order to study the progress of hydration at early ages in cement-based materials by thermal analysis, FT-IR and XRD, the ongoing hydration reactions should be stopped after different periods of time by complete removal of the free water from the material, i.e. the water which has not yet participated in the hydration reactions. The replacement of the cement paste pore water by a low surface-tension organic fluid is a common technique to stop the hydration prior to thermal analysis. However, it seems that an interaction is taking place between the organic liquid and the cement hydrates which results in the formation of carbonate-like compounds and an underestimation of the real calcium hydroxide content by thermal analysis. The solvent exchange drying technique is studied for different times of storage in the organic solvent and for cement pastes of different ages. TGA and DSC graphs of these pastes are compared with pastes vacuum dried at 2.5×10^{-2} mbar.

Keywords: Cement, hydration, solvent exchange, vacuum drying, thermal analysis

1. INTRODUCTION

In order to study the progress of hydration in cement-based materials by several techniques such as thermal analysis, Fourier Transform Infrared Spectroscopy (FT-IR) and X-Ray Diffraction (XRD), it is necessary to stop the ongoing hydration reactions by complete removal of the water which has not yet participated in the hydration. Without drying, hydration reactions continue and are even accelerated upon heating. When the free water is removed, the sample can be stored in an inert atmosphere until the moment of testing. Several techniques can be applied to remove the water [1,2]. In this paper, solvent exchange technique, oven drying and vacuum drying are studied by means of Differential Scanning Calorimetry and Thermogravimetry.

Solvents are characterized by a surface tension which is usually much lower than that of other liquids, such as water. Solvent exchange is still a common technique to stop the hydration prior to thermal analysis, although the use of organic liquids is criticized by several authors since some time [3]. Solvents are reported to strongly adsorb on [4] or interact with cement hydrates [5,6,7]. Other authors have reported that no special features were detected by differential thermal analysis, thermogravimetric data and ^{13}C -NMR spectroscopy of cement pastes with organic liquids [8,9,10,11].

Vacuum drying is a fast technique to remove the water from early cement pastes. In the absence of solvents, no interaction products can be formed. In this paper, early cement pastes (6h, 24h and 7 days) are dried using several techniques to study whether peaks at temperatures below 200°C, such as ettringite, AFm and C-S-H peaks, can still be detected in the TGA and DSC graphs.

2. EXPERIMENTS

Cement pastes with a water-cement ratio of 0.45 are prepared, using an ordinary Portland cement (CEM I 52.5 N) and tap water. The pastes are stored in closed recipients until the moment of testing (after 6h, 24h and 7 days of hydration). Before the TGA-DSC-analyses are carried out, the hydration reactions are stopped by different methods to remove the water. After such drying, the samples are stored in closed plastic bags in a desiccator containing silica gel and soda lime to create a dry and CO_2 -free environment.

2.1 Oven drying

At oven drying, the samples are dried at an elevated temperature of 105°C in an atmosphere of uncontrolled humidity for 24 hours.

2.2 Vacuum drying

For the vacuum drying, the samples are introduced without prefreezing in an Alpha 1-2 LD Martin Christ type freeze-dryer. Round bottom flasks containing the samples are connected to a vacuum device consisting of a vacuum chamber with ice condenser and a vacuum pump that allows applying a vacuum of 2.5×10^{-2} mbar. Extracted water is continuously collected in an ice condenser at a temperature of -62°C. The samples are vacuum dried for 2 hours.

2.3 Solvent exchange

For the solvent exchange, the cement pastes are crushed and ground to fine powder. The prepared powders are centrifuged three times for 20 minutes with a solvent to remove the

excess water and to stop the hydration. At the end of every cycle, the solvent is removed and replaced by fresh one. Immediately after the last cycle, the samples are dried at 40°C for 24 hours under vacuum with a pump with an ultimate vacuum of 10mbar. 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.

2.4 Thermal analysis

Different drying methods are compared by thermal analyses with 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 N₂-atmosphere (60ml/min).

The TGA-signal is used to calculate the weight loss during heating and to estimate the Ca(OH)₂ content. The weight loss between 105°C and 1000°C is calculated according to formula (1). This weight loss is a measure of the degree of hydration, although it also incorporates the weight loss due to the decarbonation of the carbonate phases.

$$m_{105^{\circ}\text{C}-1000^{\circ}\text{C}} [\%] = \frac{m_{105^{\circ}\text{C}} - m_{1000^{\circ}\text{C}}}{m_{1000^{\circ}\text{C}}} \quad (1)$$

The Ca(OH)₂ content is calculated according to formula (2).

$$\text{Ca(OH)}_2 [\%] = \text{WL}_{\text{Ca(OH)}_2} [\%] \cdot \frac{\text{MW}_{\text{Ca(OH)}_2}}{\text{MW}_{\text{H}_2\text{O}}} \quad (2)$$

WL_{Ca(OH)₂} is the weight loss during the dehydration of Ca(OH)₂ as percentage of the ignited weight and calculated according to the method described by Taylor [2]. This takes into account the continuous loss due to the gradual decomposition of the C-S-H phase and the hydrated aluminate phase. MW_{Ca(OH)₂} and MW_{H₂O} represent the molecular weight of Ca(OH)₂ and water.

As a measure for the amount of carbonate-like phases that are assumed to be formed during drying and sample preparation, the weight loss WL_{Carbonate} due to the decomposition of these phases is calculated as percentage of the ignited weight.

3. RESULTS

The DSC signal and the derivative of the TGA signal (DTG) are shown for different times of hydration. Figures 1, 2 and 3 are plotted on the same scale, allowing the comparison of the graphs with each other.

3.1 After 6 hours of hydration

After 6 hours of hydration, the DSC and DTG graphs (Figure 1) show for all samples, except for the oven dried sample, a small peak at 105°C corresponding to the C-S-H phase and a small peak at 125°C due to the decomposition of ettringite. During oven drying at 105°C, ettringite dehydrates and disappears in the results of the thermal analysis.

At around 450°C, the dehydration of Ca(OH)_2 generates an endothermal peak. All samples are carbonated, indicated by the decomposition of CaCO_3 at 700°C, especially the sample treated with methanol exchange. The DSC signal shows a small, broad peak at 630°C for the samples dried by solvent exchange.

Figure 1 – DSC (left) and DTG (right) graphs for cement pastes ($w/c=0.45$) after 6 hours of hydration (I: vacuum drying, II: oven drying, III: solvent exchange by ethanol, IV: solvent exchange by ethanol + ether, V: solvent exchange by methanol)

3.2 After 24 hours of hydration

After 24 hours of hydration, the ettringite peak has disappeared and the DSC and DTG graphs (Figure 2) show the presence of the C-S-H phase at a temperature of 105°C. For the oven dried sample only a broad peak at 180°C is present. The DTG graphs still have a peak at 700°C, due to the decomposition of CaCO_3 . For the samples dried by solvent exchange and in the oven, an additional peak at 630°C is detected.

A broad peak between 700°C and 800°C appears in the DSC graph for the sample dried with ethanol and ether, which indicates an interaction between the solvent and the cement hydrates.

Figure 2 – DSC (left) and DTG (right) graphs for cement pastes ($w/c=0.45$) after 24 hours of hydration (I: vacuum drying, II: oven drying, III: solvent exchange by ethanol, IV: solvent exchange by ethanol + ether, V: solvent exchange by methanol)

3.3 After 7 days of hydration

After 7 days of hydration, a small peak at 165°C appears in the DSC and DTG graphs (Figure 3) of the vacuum dried sample and the samples dried by solvent exchange due to the dehydration of the AFm phase. For the oven dried sample the peak at 180°C becomes larger.

Broad peaks at high temperatures are detected in the DSC graphs of the sample dried with ethanol and ether and the sample dried with only ethanol, indicating an interaction between the solvents and the cement hydrates. The carbonation of the vacuum dried sample is limited.

Figure 3 – DSC (left) and DTG (right) graphs for cement pastes ($w/c=0.45$) after 7 days of hydration (I: vacuum drying, II: oven drying, III: solvent exchange by ethanol, IV: solvent exchange by ethanol + ether, V: solvent exchange by methanol)

3.4 Influence of time of storage in solvent

The influence of the time of storage in the solvent is studied. The samples discussed in the previous paragraphs are vacuum dried immediately after the last cycle of rinsing and centrifuging with solvent. In Figure 4, those samples are compared with samples that are stored in the solvent for 24 hours before vacuum drying at 40°C.

Figure 4 shows a large peak at 90°C for the samples stored in the solvent for 24 hours after 6 hours of hydration. Prolonged storage in a solvent causes a strong interaction or adsorption of the solvents which can not be removed by vacuum drying at 40°C. The amount of carbonate phases slightly increases during long storage.

A broad peak at high temperatures is detected in the DSC graphs of the 7 days old cement pastes dried by solvent exchange. For the methanol exchange, this peak is not clearly visible after 2 hours of storage, but becomes very large after 24 hours of storage in the solvent.

Figure 4 – DTG graphs for cement pastes (w/c=0.45) after 6 hours of hydration (left) and DSC graphs for cement pastes (w/c=0.45) after 7 days of hydration (right) for different times of storage in the solvent (IIIa: in ethanol for 2 hours, IIIb: in ethanol for 24 hours, IVa: in ethanol + ether for 2 hours, IVb in ethanol + ether for 24 hours, Va: in methanol for 2 hours, Vb: in methanol for 24 hours)

4. DISCUSSION

The weight losses and the Ca(OH)_2 content calculated after the different drying methods are summarized in Table 1.

During oven drying, the hydraulic reactions can continue and are even accelerated. The Ca(OH)_2 content of the cement pastes hydrated for 6 and 24 hours and still having a high amount of free water, is the highest for the oven dried samples. On the other hand, some hydration products dehydrate during oven drying. The weight loss between 105°C and 1000°C is the lowest for the oven dried samples. In Figure 1, no ettringite peaks are found for these samples. Furthermore, the DSC and DTG graphs of the oven dried sample completely differ from the other samples at temperatures below 200°C.

The solvent exchange is criticized by several authors since some time [3], but it is still frequently used to stop the hydration reactions prior to thermal analysis or XRD [12,13]. It is reported that methanol reacts with Ca(OH)_2 forming $\text{Ca(OCH}_3)_2$, methylated complexes [6] or carbonate-like products [7], although this is not accepted by all investigators [9]. Furthermore, carbon dioxide is more soluble in methanol-water mixtures than in water [14]. Carbonation by atmospheric CO_2 can be increased in the presence of methanol. Hansen et al. [11] did not find any chemical interaction between ethanol and the cement hydrates by ^{13}C -NMR spectroscopy. However, Figures 2 and 3 show a considerable interaction between the ethanol and/or ether and the cement hydrates, resulting in a broad endothermal peak in the DSC-spectrum. For the

samples dried by methanol exchange, this peak also appears after 24 hours of storage in the solvent (Figure 4). Chemical analysis of the remaining solvents and evolved gas analysis will be carried out to study the type of reaction products. Table 1 shows the large weight losses during the decomposition of the carbonate phases for the samples dried by solvent exchange. Because of the possible interaction of the solvents with Ca(OH)_2 and the possible formation of carbonate-like materials, the estimation of the Ca(OH)_2 and CaCO_3 content and the degree of hydration by TGA- or DSC-analysis should be questioned after solvent exchange drying.

Vacuum drying is a rather easy technique when compared to solvent exchange. Ettringite peaks can be detected in the DSC and DTG graphs (Figure 1) of early pastes. After 24 hours, the water loss of the C-S-H phase at 105°C is visible. Table 1 shows that the weight loss during the decomposition of the carbonate phase is much lower than the weight loss after the other drying techniques. An additional advantage of vacuum drying is that no interaction products can be formed and that the calculated Ca(OH)_2 content is a good approximation of the real content [2].

Table 1: Weight loss and Ca(OH)_2 content of cement pastes after 6h, 24h and 7 days of hydration, dried by several drying techniques

		$m_{105^\circ\text{C}-1000^\circ\text{C}}[\%]$	$\text{Ca(OH)}_2[\%]$	$\text{WL}_{\text{Carbonate}}[\%]$
6h	Vacuum drying	4.2	1.5	0.9
	Oven drying	3.6	1.9	1.3
	Solvent exchange	Ethanol	4.1	1.2
		Ethanol+ether	4.3	1.4
		Methanol	3.8	1.2
24h	Vacuum drying	11.7	9.8	0.7
	Oven drying	11.0	11.0	1.8
	Solvent exchange	Ethanol	13.3	10.4
		Ethanol+ether	12.9	10.4
		Methanol	13.9	10.3
7d	Vacuum drying	19.1	15.8	0.5
	Oven drying	16.9	15.0	1.9
	Solvent exchange	Ethanol	19.8	14.9
		Ethanol+ether	19.7	15.0
		Methanol	19.6	14.2

5. CONCLUSIONS

Several techniques can be used to dry early cement pastes prior to analysis. Oven drying accelerates the hydration reactions, can cause dehydration of some cement hydrates and should therefore be avoided. Solvent exchange results in large endothermal peaks at temperatures between 600°C - 800°C , due to a considerable interaction between the solvents and the cement hydrates. This technique is rather labour-intensive and can result in a wrong estimation of the Ca(OH)_2 content and the degree of hydration. It is found that after vacuum

drying at 2.5×10^{-2} mbar for 2 hours, ettringite peaks are still present in the DSC-TGA graphs of 6-hour old cement pastes. In absence of solvents, this technique is an easy and fast preparation method prior to thermal analysis and XRD.

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