The use of thermal analysis to investigate the effects of cellulose ethers on the Portland cement hydration

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Abstract Thermal analysis (DTA) was used for monitoring the proportions of $Ca(OH)_2$ formed at the hydration of simple Portland cement (CEM I 42.5 R) samples, and cement samples with 0.5% addition of unmodified hydroxypropyl methyl cellulose (HPMC), respectively, with the addition of starch ether and polyacrylamide modified HPMC. The proportions of $Ca(OH)_2$ formed after 1, 3, 7, and 28 days of hydration were assessed by the peak areas of the endothermic effect at the temperature range of 493–503 °C, caused by the $Ca(OH)_2$ decomposition. The results obtained based on thermal analysis reflect very well the correlation between the $Ca(OH)_2$ proportions in the samples after different hydration periods and the retarding effect of the hydration processes caused by the cellulose ether's addition. This retarding effect is also evidenced by the setting times of the studied samples and the evolution of their mechanical strengths.

Keywords Cement · Hydration · Cellulose ethers · Thermal analysis

Introduction

Dry mortars are an important group of building materials with a wide range of applications [1]. They represent dry mixtures of cement, aggregates, fillers and chemical additives [1]. The most common dry mortars applications are plasters, tile adhesives and self-leveling underlayers [1].

Application of mortars in thin layer on substrate, or on porous, dry and absorbent substrates determines a certain water loss from the prepared mixture [2]. As a result, the cement has no longer enough water to hydrate and the final properties of the mortar are altered [3]. Thus, cellulose ethers are additives commonly used in mortars as water retention agents, as thickeners and film formers [4] to prevent water loss during mortar application, to improve the workability of the fresh mortar, as well as to increase the hardened mortar adherence to the substrate [3].

Still, one of the side effects of cellulose ether's addition is the cement hydration delay [2, 5–10].

Hardening of Portland cement paste is based on the hydration of mineralogical constituents of cement (C_3S, C_2S, C_3A and C_4AF, where $C = CaO$, $S = SiO_2$, $A = Al_2O_3$ and $F = Fe_2O_3$). The main contribution to the development of mechanical strength over time is due to calcium silicates (C_3S and C_2S) with the formation of calcium silicate hydrates ($mCaO·nSiO_2·pH_2O$) less basic than the silicates from which they are formed ($m/n \leq 2$). As a result, beside the calcium silicate hydrates formed at C_3S and C_2S hydrations, a corresponding excess of $Ca(OH)_2$ (portlandite) results [11].

Monitoring the evolution in time of the hydration process by the proportion of calcium silicate hydrates is rather difficult because of their pronounced early stage gel character, complexity and gradual evolution of the crystallization. In these conditions, measuring the proportion of $Ca(OH)_2$ in time represents an indirect assessment of the cement hydration degree. The effect of m/n ratio of hydrosilicates, which also suffer a variation in time, should also be considered.

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Usually, the assessment of the $Ca(OH)_2$ proportion during cement hydration is made by XRD. This method has the drawback that the intensities of $Ca(OH)_2$ diffraction peaks are influenced not only by the portlandite proportion, but also by its structural characteristics (which may vary over time) and especially by the structural characteristics (X-rays absorption) of other phases in the sample, which represent the majority and suffer significant changes in time.

According to the literature data [12], thermal analysis is a useful method for monitoring the cement hydration. In the present article, differential thermal analysis is used for the assessment of the $Ca(OH)_2$ proportion in the samples. Using a software appliance, the peak surface of the endothermic effect at 493–503 °C, corresponding to the $Ca(OH)_2$ decomposition was measured, as a direct indicator of $Ca(OH)_2$ (portlandite) proportion.

Experimental

In order to perform the thermal analysis and phase analysis by X-ray diffraction a paste made from Portland cement CEM I 42.5 R, water and three commercial cellulose ethers was used.

The composition, physical and chemical characteristics of the Portland cement, taken from the product technical sheet, are shown in Table 1.

The commercial cellulose ethers used are based on hydroxypropyl methyl cellulose (HPMC). One of these is an unmodified HPMC with 30,000 mPa s viscosity (HPMC 30) and the other two are a blend of unmodified (HPMC), with starch ether and polyacrylamide. The viscosities of the modified HPMC are 30,000 mPa s (HPMC 75), and 50,000 mPa s (HPMC 100), respectively. Table 2 presents typical properties of unmodified HPMC as shown in product data sheet.

The compositions of the studied cement pastes are shown in Table 3.

The proportion of portlandite from samples without cellulose ethers, respectively with 0.5% ether, after 1, 3, 7 or 28 days of hydration, was determined by thermal analysis. To stop the cement hydration, after each of these periods, samples were grounded, washed with absolute methanol and then with ethyl ether, and dried in oven at 50 °C. Thermal analyses were performed with a NETZSCH-STA 449 instrument. The TG/DTA curves were recorded in the range of 25–1,200 °C, with a heating rate of 10 K min^{-1}, using Pt crucibles, in artificial air, at 20 mL min^{-1} flow rate.

The phase analyses of the samples, after 1 and 28 days of hydration were determined by XRD using a DRON 3 diffractometer, $Cu_{K\alpha}$ radiation.

Table 1 Properties of Portland cement

Chemical characteristics/%	
CaO	64.5
SiO$_2$	19.8
SO$_3$	2.84
Al$_2$O$_3$	4.3
Fe$_2$O$_3$	2.9
MgO	1.24
Na$_2$O	0.19
K$_2$O	0.73
Na$_2$O eq	0.67
Cl$^-$	0.01111
LOI (PC)	3.02
IR	0.33
Cement composition/%	
Clinker Portland	96
Limestone	4
Gypsum	4
Physical characteristics	
Specific surface (Blaine)/cm^2/g	3,700
Cement density/g/cm^3	3.0
Standard consistency/%	26.2
Initial setting time/min	145
Stability/mm	0
Heat of hydration/J/g	330

Table 2 Typical properties of unmodified HPMC

Degree of substitution (OCH$_3$)	1.1–1.55
Methoxy content/%OCH$_3$	19–24
Average molecular substitution (POOH)	0.12–0.33
Hydroxypropoxyl content/%POOH	4–12
Moisture/wt%	Max. 5
Ash/wt% (as sulphate)	Max. 1
pH-value	5.5–8.0
Particle size/100% through	0.150 mm

Table 3 The composition of the cement pastes

Sample no.	Component		(HPMC/CEM)·100	(Water/CEM)·100
1	CEM I42.5R	–	–	32
2	CEM I42.5R	HPMC 30	0.5	32
3	CEM I42.5R	HPMC 75	0.5	32
4	CEM I42.5R	HPMC 100	0.5	32

In order to establish the effect of the cellulose ethers in dry mortars, the setting times and mechanical strengths after 28 days were carried out on mixtures prepared

Table 4 The compositions of the studied mortars

Component	Sample no./wt% of dry mix			
	M1	M2	M3	M4
CEM I 42.5 R	30	30	30	30
Limestone filler/<90 μm	10	10	10	10
Quartz sand 0.1–0.4 mm	60	60	60	60
HPMC 30*	–	0.5	–	–
HPMC 75*	–	–	0.5	–
HPMC 100*	–	–	–	0.5
Water	20	28	37	40

* Addition of HPMC is given in % over 100

Fig. 1 DTA and TG curves of sample 1 (without HPMC) after 1 day of hydration

according to a classical dry mortar recipe: Portland cement, limestone filler and quartz sand of 0.1–0.4 mm grain size.

Table 4 presents the recipes of the obtained mortars, based on which the setting time and mechanical strength were determined.

The setting time was determined according to SR EN 13454-2 [13], with a MATEST Vicat needle instrument. The mould with fresh mortar was maintained in a medium with 95 ± 5% humidity, at 23 ± 2 °C. For fresh mortar preparation, the raw materials were dry homogenized and then mixed with distilled water for 90 s.

Mechanical strengths were performed on prismatic specimens (40 × 40 × 160 mm), according to SR EN 1015-11 [14] and compacted with the MATEST jolting apparatus. As regards the curing of prisms, the moulds were kept in a polyethylene bag for 2 days, and then the samples were de-moulded and stored for 26 days in a polyethylene bag. Mechanical strengths after 28 days of hydration were determined using a MATEST E160 hydraulic press. Working speeds were 50 N/mm² for flexure strength and 2,400 N/mm² for compressive strength.

Results and discussion

Thermal analysis

Sample 1 (without HPMC) and samples 2, 3 and 4 (with 0.5% simple or modified HPMC) show a similar thermal behaviour after different periods of hydration (1, 3, 7 and 28 days).

Figure 1 shows the thermal analysis (DTA and TG) results of sample 1 (standard), after 1 day of hydration. The endothermic effects accompanied by mass loss below 350 °C are assigned to the water removal from the gel pores of the calcium silicate hydrates [12, 15–20], calcium aluminates hydrates [11, 21] and hydrated calcium sulphoaluminates [11, 21] formed on cement hydration.

The endothermic effect at 493.4 °C is assigned to $Ca(OH)_2$ decomposition. This effect is very clear and can
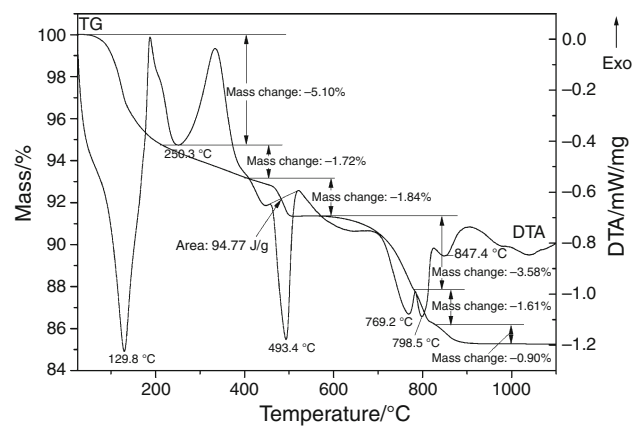
be used with a good accuracy to assess the proportion of $Ca(OH)_2$ from the samples through the peak area of this effect, from which the enthalpy is calculated, by relating to the weight of the sample (J/g). If we admit that by the hydration of C_3S and C_2S from the cement, the same hydration products (calcium silicate hydrates) are resulted, with the release of a $Ca(OH)_2$ excess, then the proportion of $Ca(OH)_2$ in the sample is in direct correlation with the degree of cement hydration, especially in respect of C_3S and C_2S.

The effect assigned to the portlandite dehydration is preceded by a weak endothermic effect, in some samples as a shoulder, assigned to the water removal from the calcium hydrosilicates resulting at the cement hydration (probably afwillite).

Endothermic effects with the maximum at 769.2 and 798.5 °C can be assigned to the successive constitution water removal from the tobermorite-type hydrosilicates.

According to the literature data, the portlandite formed at calcium silicates hydration, and the CaO formed when heated above 500–600 °C may react with CO_2 from the air to form carbonates that decompose at temperatures above 700 °C [18].

Carbonates are available in three forms: vaterite, aragonite and calcite [22, 23].

Portlandite carbonation occurs in sequential steps [17] as follows: hexagonal portlandite → calcium carbonate hydroxy hydrate → calcium carbonate hydrate → hexagonal vaterite and/or orthorhombic aragonite → rhombohedral calcite [22].

According to Stepkowska [11], carbonate particles are very fine nanocrystals in cement pastes, and therefore their decomposition temperature is lower than 898.6 °C.

Thus, in the literature, various temperature ranges of calcium carbonate decomposition are given: 600–800 °C [15, 19], 740–780 °C [16], 600–700 °C [11], 697–724 °C [24] and 550–1050 °C [12]. Stepkowska [22] shows that

calcite decomposes over 800 °C, and calcium carbonate hydroxy hydrate and calcium carbonate hydrate decompose at lower temperatures. In [20], the temperature for decomposition of $CaCO_3$ formed by portlandite carbonation is given as ranging between 600 and 700 °C.

Following the literature data, we can assume that the endothermic effects with maximum at 769.2 and 798.5 °C can be assigned to the decomposition of calcium carbonates formed after portlandite carbonation.

Even if the thermal analyses were performed in synthetic air, the presence of CO_2 in samples can be explained as a result of the thermal degradation of CE for samples 2–4.

In sample 1, CE is missing and, as a consequence, the $CaCO_3$ proportion formed according to the proposed mechanism is insignificant. On the other hand, the intensity and temperature of the two endothermic effects which occur between 760 and 800 °C are practically identical in samples 1–4. In these conditions, we accept that these effects are due to the overlapping of the dehydration effects of some calcium silicates over the $CaCO_3$ decarbonation.

The weak endothermic effect at 847.4 °C, accompanied by 0.90% mass loss is assigned to the $CaCO_3$ decomposition. The calcium carbonate may come mainly from the used cement, to which a small proportion of carbonate resulted by partial carbonation of $Ca(OH)_2$ may be added.

This succession of endothermic effects is found, with very small differences, for all hydrated samples subjected to thermal analysis. A clear difference is noted for the intensity of the endothermic effect assigned to $Ca(OH)_2$ decomposition. Using this effect to assess the proportion of portlandite from the hydrated samples, thermal analyses were performed under the same conditions, for a $Ca(OH)_2$ sample obtained by the hydration of CaO freshly prepared by decomposition of $Ca(NO_3)_2$, which was annealed at 900 °C for 1 h (Fig. 2).

Regarding the endothermic effect at 528.4 °C, which is due to the pure $Ca(OH)_2$ decomposition, it should be noted that this temperature is higher than the temperature corresponding to the same process in hydrated cement samples. This is normal, since the amount of $Ca(OH)_2$ is higher and the pure $Ca(OH)_2$ sample develops better crystallization than the calcium hydroxide from hydrated cement sample.

It is necessary to underline that the thermal analysis of pure $Ca(OH)_2$ performed in identical conditions as the thermal analysis of the hydrated cement samples does not highlight similar endothermic effects on the DTA curve, in the range of 760–800 °C.

Only a slight mass loss on the TG curve can be noted because of a very small proportion of $CaCO_3$.

The DTA curves for samples 1, 2, 3 and 4 are presented after 1 day of hydration (Fig. 3), after 3 days (Fig. 4), after 7 days (Fig. 5) and after 28 days of hydration (Fig. 6).
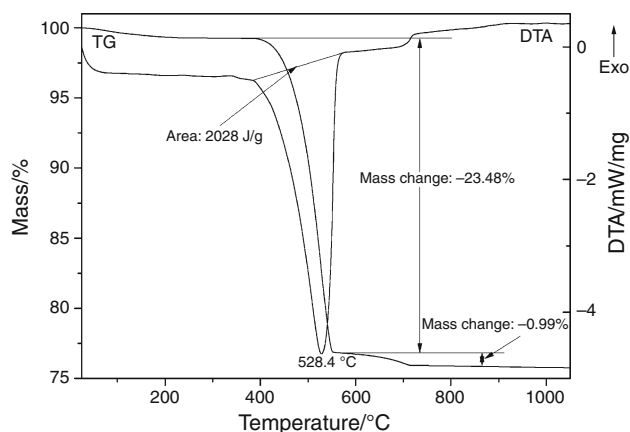

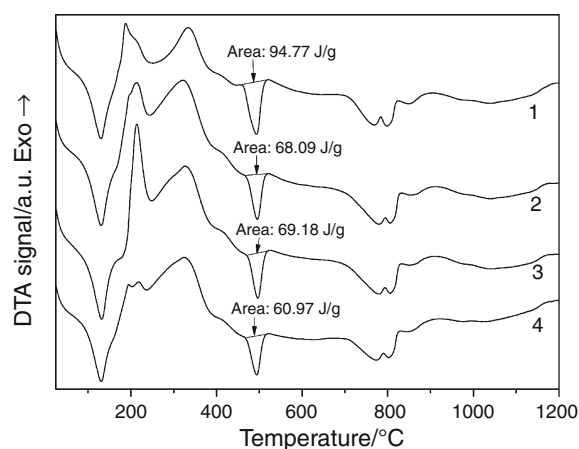**Fig. 2** DTA and TG curves of $Ca(OH)_2$ obtained from $Ca(NO_3)_2$

Fig. 3 DTA curves of sample *1* (without HPMC), *2* (0.5% HPMC 30), *3* (0.5% HPMC 75), *4* (0.5% HPMC 100) after 1 day of hydration
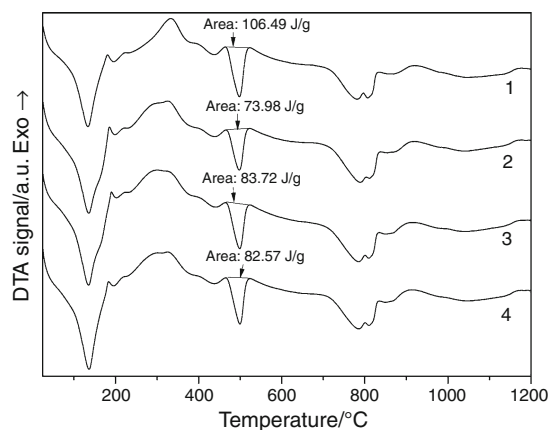

Fig. 4 DTA curves of sample *1* (without HPMC), *2* (0.5% HPMC 30), *3* (0.5% HPMC 75), *4* (0.5% HPMC 100) after 3 days of hydration

There is a great similarity of the DTA curves for all these samples, which means that the nature of the phases resulting from the cement hydration, in all samples, is
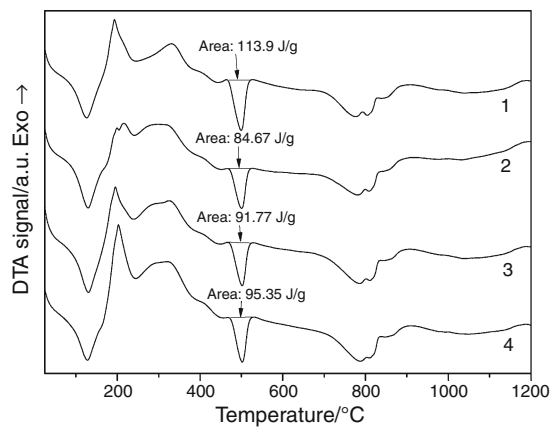
Fig. 5 DTA curves of sample *1* (without HPMC), *2* (0.5% HPMC 30), *3* (0.5% HPMC 75), *4* (0.5% HPMC 100) after 7 days of hydration
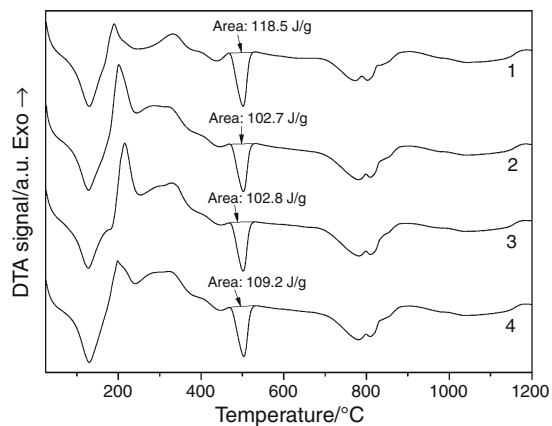

Fig. 6 DTA curves of sample *1* (without HPMC), *2* (0.5% HPMC 30), *3* (0.5% HPMC 75), *4* (0.5% HPMC 100) after 28 days of hydration

Table 5 Temperature and decomposition enthalpy of $Ca(OH)_2$ from hydrated samples

Sample no.	1	2	3	4
1 day				
Decomposition temp. of $Ca(OH)_2$/°C	493.4	495.3	496.7	493.9
Enthalpy/J/g	94.77	68.09	69.18	60.97
3 days				
Decomposition temp. of $Ca(OH)_2$/°C	498.2	497.9	498.9	499.7
Enthalpy/J/g	106.49	73.98	83.72	82.57
7 days				
Decomposition temp. of $Ca(OH)_2$/°C	499.7	500.7	501.9	502.1
Enthalpy/J/g	113.9	84.67	91.77	95.35
28 days				
Decomposition temp. of $Ca(OH)_2$/°C	501.4	502.4	501.9	503.4
Enthalpy/J/g	118.5	102.7	102.8	109.2

Table 6 Proportion of $Ca(OH)_2$ from studied samples

Sample no.	% of $Ca(OH)_2$ from studied samples			
	1 day	3 days	7 days	28 days
1	4.67	5.25	5.62	5.84
2	3.36	3.65	4.18	5.06
3	3.41	4.13	4.53	5.07
4	3.01	4.07	4.7	5.38

practically the same. This finding is consistent with the literature data regarding the effect of CE on Portland cement hydration [2, 8, 25].

Studying the hydration processes of Portland cement [2, 25] and C_3S [8], in the presence of cellulose ethers of the same type as those used by us (namely HPMC), various authors have concluded that the hydration products in cement pastes modified with CE are the same as those in the unmodified cement paste. No new products are found in the modified cement pastes, only their formation time is longer than that in unmodified cement pastes.

Regarding the effect of cellulose ethers on C_3A hydration, systematic studies [9] have shown that CE induce a weak slowing down of C_3A dissolution, ettringite precipitation and a strong reduction of calcium hydroaluminates precipitation [9].

Cement used in this study is characterized by a low Al_2O_3 content (4.3%) and thus, a low content of C_3A. This justifies the interest focused on C_3S and C_2S hydration.

The differences between mechanical strength of samples after 28 days of hydration should be correlated mainly with C_3S and C_2S hydration.

The degree of cement hydration and hence the proportion of $Ca(OH)_2$ from the samples, varies with the duration of the hydration processes and for the same duration it varies as a result of the CE presence.

The temperature at which the dehydration of $Ca(OH)_2$ occurs with maximum speed and the enthalpy corresponding to this process, for all samples, is summarized in Table 5.

By reporting this enthalpy to the enthalpy of pure $Ca(OH)_2$ dehydration process (Fig. 2), the content of $Ca(OH)_2$ was calculated from hydrated samples after different periods of hydration. The values obtained are shown in Table 6.

It is noted that after 1 day of hydration, the content of $Ca(OH)_2$ in the standard sample (1) is the largest. Samples containing cellulose ethers have a significantly smaller content of $Ca(OH)_2$. These results reflect the cellulose ether's effect of slowing down the cement hydration

Table 7 Initial and final setting times and mechanical strengths after 28 days of studied mortars

Sample no.	Initial setting time/min	Final setting time/min	Flexure strength/N/mm^2	Compressive strength/N/mm^2
M1	192	239	4.35	30.06
M2	379	529	2.04	6.35
M3	575	695	1.83	5.25
M4	699	879	1.15	3.67

processes, which is in full agreement with the setting time of the cement pastes (Table 7).

After 3 and 7 days of hydration, the samples with CE addition have also a lower content of Ca(OH)$_2$ than the similar standard sample (1). After 28 days of hydration, the Ca(OH)$_2$ content in samples containing CE is still small, but is close to those from sample 1.

Regarding the nature of CE used, significant differences between samples are noted: CE used in sample 4 (HPMC 100, modified with starch ether and polyacrylamide) has the most pronounced retarding effect at 1 day of hydration, but after 7 and especially 28 days of hydration, allows the closest degree of hydration comparing to sample 1; CE used in sample 2 (HPMC 30 unmodified), has a moderate effect to slow the hydration processes after 1 day, but after 3 and 7 days of hydration, this effect is the most intense.

It is essential that the method used for monitoring the degree of hydration of cement pastes with the addition of CE, based on the enthalpy of dehydration process of Ca(OH)$_2$ offers the possibility of a relatively rigorous quantitative assessments to quantify the effect of cellulose ethers used, so that their nature can be chosen depending on the intended purpose.

Setting time and mechanical strength

Initial and final setting times, flexure strength and compressive strength after 28 days, of mortars M1–M4 (Table 2), are shown in Table 7.

From the presented data a significant difference in the behaviour of mortars containing cellulose ethers (M2–M4) compared with the standard mortar (M1) without cellulose ethers is noted. The setting times of mortars containing HPMC are much longer than those of standard (initial setting time takes place after 699 min for M4 compared with 192 min for M1), and the mechanical strengths are much lower (compressive strength 3.67 N/mm^2 for M4 respectively 30.06 N/mm^2 for M1).

It is also noted a dependence of these properties from HPMC's modification, namely: comparing sample M2, which contains unmodified HPMC, with the sample M3, which contains HPMC modified with starch ether and

polyacrylamide, (both HPMCs having the same viscosity), it is found that setting times increase (initial setting time increases from 379 min for M2 to 575 min for M3), and mechanical strengths decrease (compressive strength decreases from 6.35 N/mm^2 for M2 to 5.25 N/mm^2 for M3).

For M3 and M4 mortars, which contain modified HPMC with different viscosities, it is noted that M4 mortar containing HPMC with 50,000 mPa s viscosity, has longer setting times and lower mechanical strengths than those of the M3 mortar containing HPMC with 30,000 mPa s viscosity.

X-ray diffraction

Portland cement hydration processes with and without CE addition were pursued by X-ray diffraction phase analysis.

Figure 7 presents the XRD patterns of unhydrated CEM I 42.5 R and of the studied samples after 1 day of hydration. Figure 8 shows the diffraction patterns of the samples after 28 days of hydration.

The X-ray diffraction patterns of unhydrated cement (CEM I 42.5 R) (Fig. 7) show that its main mineralogical constituents are C$_3$S, C$_2$S, C$_3$A and C$_4$AF. Along with these, a small amount of calcite is present.
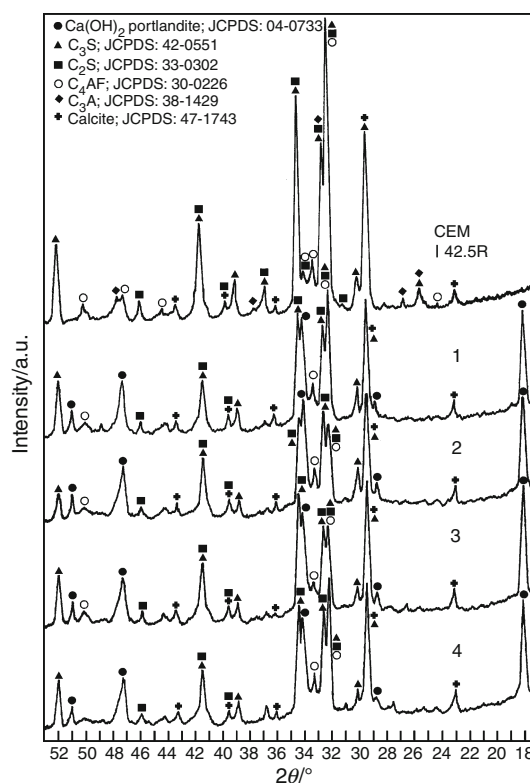

Fig. 7 X-ray diffraction patterns of unhydrated cement and of sample *1* (without HPMC), *2* (with HPMC 30), *3* (with HPMC 75), and *4* (with HPMC 100) after 1 day of hydration
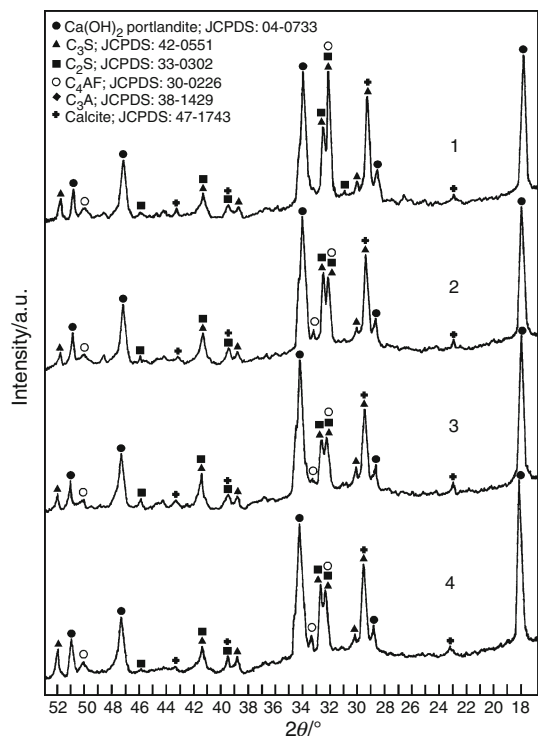
Fig. 8 X-ray diffraction patterns of sample *1* (without HPMC), *2* (with HPMC 30), *3* (with HPMC 75) and *4* (with HPMC 100) after 28 days of hydration

Table 8 The height of the most intense X-ray diffraction maximum for Ca(OH)$_2$ at $2\theta = 18.089°$ ($\lambda_{CuK\alpha}$) in the hydrated samples

Sample no.	The height of X-ray diffraction maximum of Ca(OH)$_2$ at $2\theta = 18.089°$ ($\lambda_{CuK\alpha}$) in hydrated samples	
	1 day	28 day
1	h	h′
2	0.86 h	1.01 h′
3	h	1.10 h′
4	0.88	1.27 h′

In other words, some of the samples with the addition of CE, which presented longer setting times and lower mechanical strengths than those of the standard sample, have the maximum peak corresponding to portlandite from X-ray diffraction pattern equal or even more intense than the standard sample. This apparent anomaly is explained by the fact that the intensity of these peaks is influenced not only by the proportion at which portlandite is present, but also by its structural characteristics (which may vary over time) and especially by the structural characteristics (X-ray absorption) of other phases from the sample (which are the majority).

In these circumstances, it is clearly evident that the results obtained from thermal analysis regarding the effects of cellulose ethers on the evolution of Portland cement hydration processes give a more accurate image compared with information that can be obtained using X-ray diffraction patterns.

Conclusions

The assessment of the degree of Portland cement hydration through the surface area of the endothermic effect at 493–503 °C on the DTA curves, which is due to the decomposition of the Ca(OH)$_2$ formed at the calcium silicate hydration, proved to be a very accurate method.

It was noted that the surface area of this effect is smaller in samples containing HPMC than in the one without HPMC, indicating a lower degree of cement hydration.

The shape of the DTA curves is similar for all samples, which indicates that no new hydration phases are formed in samples with HPMC compared to the one without HPMC.

Initial setting times, final setting times and mechanical strengths of the studied mortars are strongly dependent on the degree of cellulose ethers modification.

Mortars with HPMC have longer initial setting times and final setting times as well as significantly lower mechanical strengths than those of the mortars without HPMC. These influences are more pronounced for the HPMC modified with starch ether and polyacrylamide and

As a consequence of cement hydration, it is noted the decrease of diffraction peaks intensity of its mineralogical compounds with the formation of some hydration products (mainly gels) in the early stages of hydration and release of Ca(OH)$_2$ excess as portlandite. The diffraction peak of portlandite appears clearly on all X-ray diffraction patterns of hydrated samples.

An assessment of the samples hydration degree was attempted through the proportion of portlandite using the peak from X-ray diffraction pattern with maximum intensity at $2\theta = 18.089°$ ($\lambda_{CuK\alpha}$).

For this purpose, the height of this peak in XRD pattern of sample 1, hydrated 1 day, was noted with h, and the height of the same peak of sample 1, after 28 hydration days, was noted with h′.

Table 8 presents the relative heights of portlandite maximum from the diffraction patterns of the samples hydrated 1 day, compared with h (which correspond to sample no 1, after 1 day of hydration), as well as the relative heights of portlandite maximum from the diffraction patterns of the samples hydrated 28 days, compared with h′ (h′ > h) (which correspond to sample no. 1 after 28 days of hydration).

It is noted that the relative values of the intensities of the diffraction peaks do not reflect the cellulose ethers retarding effect on the hydration processes of Portland cement.

with higher viscosity (50,000 mPa s compared with 30,000 mPa s).

The retarding effect of HPMC on the cement hydration, as revealed by the thermal analysis, setting times and mechanical strength tests, is not visible in the case of the phase analysis by X-ray diffraction. Therefore, the use of diffraction peak characteristic for $Ca(OH)_2$ at $2\theta = 18.089°$ ($\lambda_{CuK\alpha}$) is not an accurate method for assessing the degree of Portland cement hydration.

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