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Synergy between fly ash and limestone powder in ternary cements

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ABSTRACT

The interaction between limestone powder and fly ash in ternary composite cement is investigated. Limestone powder interacts with the AFm and AFt hydration phases, leading to the formation of carboaluminates at the expense of monosulphate and thereby stabilizing the ettringite. The effect of limestone powder on OPC may be restricted due to the limited amount of aluminate hydrates formed by the hydration of OPC. The additional aluminates brought into the system by fly ash during its pozzolanic reaction amplify the mentioned effect of limestone powder. This synergistic effect between limestone powder and fly ash in ternary cements is confirmed in this study and it translates to improved mechanical properties that persist over time.

1. Introduction

It is estimated that cement production is responsible for about 5% of the global man-made CO_2 emissions [1]. This fact, together with the still increasing volume of cement produced worldwide renders the cement industry an important contributor to the global CO_2 emission. For each ton of cement produced on average 0.87 tons of CO_2 is emitted [1]. The cement industry is putting huge efforts into reducing the emission during cement manufacturing, for example by using alternative fuels and by optimising the heat transfer in the production of clinker. An additional option widely adopted is the use of blended cements in which part of the clinker is replaced by "supplementary cementing materials" (SCM) or fillers. Supplementary cementing materials such as silica fume, fly ash, ground granulated blast furnace slag and natural pozzolans have been used for many years. As the pressure to reduce emissions is rising, research is being directed towards increasing the replacement levels of clinker and optimising different combinations of supplementary materials.

In this study ternary cements containing ordinary Portland cement (OPC) and different replacement levels of limestone powder and siliceous class F fly ash are investigated. The effect of limestone powder on OPC is twofold. Fine limestone powder exerts a physical filler effect on the OPC hydration. Replacing part of the OPC with limestone will increase the effective water to OPC ratio, and provide additional surface for precipitation of hydration products, thereby promoting the early age hydration of the OPC [2–5]. Besides the filler effect, there is also a chemical effect: the calcium carbonate of the limestone powder can interact with the aluminate hydrates formed by OPC hydration [6–9]. Calcium monosulphoaluminate hydrate is unstable in the presence of calcium carbonate, and instead calcium mono- and hemicarboaluminate hydrate will form. This leads to the stabilisation of the ettringite and will result in an increase in the total volume of the hydration products [9–12], which potentially might result in a decrease in porosity and thus an increase in strength. The effect of this chemical interaction in an OPC–limestone system is, however, not so pronounced due to the limited aluminate content in the anhydrous clinker. In an ordinary Portland cement the limestone filler is therefore often considered inert. Additional calcium aluminate hydrates may be produced by supplementary cementitious materials (SCM's) containing aluminates (e.g. slag, fly ash, metakaolin). The chemical interaction between calcium aluminate hydrates and calcium carbonate might therefore be of greater importance in cements containing fly ash or other aluminates containing SCMs [13].

A clear demonstration of interaction between fly ash and limestone powder was observed when studying fly ash–limestone–calcium hydroxide mixes prepared with a high alkaline solution ($pH = 13.2$) [14]. More water was bound relative to the fly ash content, and the hydration products formed were altered when limestone was included in the system. The calcium aluminate hydrates formed during the pozzolanic reaction reacted with the calcium

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carbonate of the limestone powder, and formed calcium carboaluminate hydrates.

In a study evaluating the effect of fineness of the different materials in a ternary composite cement, a substantial strength increase was observed after 28 days of curing when combining fly ash and limestone powder compared to only using fly ash [15]. However the tests were only performed on very fine ground materials. Subsequently, a series of mortar and paste mixes were prepared with ternary cements containing OPC, limestone powder and fly ash, but from an industrial point of view, more realistic finenesses [16,17]. The samples were tested after 28 days of curing at 20 °C. A similar strength increase was observed when a small part of the fly ash was replaced by limestone powder as in [15].

The aim of this study is to investigate the interaction between limestone powder and fly ash in ternary composite cements after longer times, up to 140 days of hydration. Both compressive and flexural strength of mortars have been measured. In addition, thermogravimetric analysis (TGA) was used to determine the content of bound water and calcium hydroxide and X-ray diffraction (XRD) was applied to identify the AFm and AFt phases.

2. Materials and experimental

The materials used in this study were: ordinary Portland clinker, a class F ASTM siliceous fly ash (FA), limestone powder and natural gypsum. The chemical composition of the ordinary Portland clinker, fly ash and limestone powder are given in Table 1. The natural gypsum contained 0.2% free water, and had a $CaSO_4{\cdot}2H_2O$ content of 91.4%. Additional properties of the fly ash are found in [18]. The $CaCO_3$ content of the limestone as determined by TGA was about 81%.

The materials were ground in a laboratory ball mill with a capacity of about 9 kg. Fly ash and limestone powder were ground separately. The clinker interground with 3.7% of gypsum by mass is referred to as OPC. The Blaine specific surface and density are given in Table 1. The finenesses of the different materials were selected based on the results found in a previous study [15]. The fly ash was ground for 15 min in order to crush the largest particles. This corresponds to common practice in Portland fly ash cement manufacturing, where the fly ash is added in the air separator at the end of the cement mill. In that case, the largest particles will be returned to the ball mill and be crushed.

Table 2 shows the different composite cements which were tested. The experimental matrix can be divided into three main groups and the reference, 100% OPC (mix 1). In the first group, OPC is gradually replaced by limestone powder, in steps of 5% up to 35% (mix 2–8). In the second group OPC is similarly replaced with fly ash (mix 9–15). In the third group different limestone powder and fly ash combinations were tested (mix 16–21), all at a total OPC replacement level of 35% by mass.

Table 1
Chemical composition and physical characteristics of the clinker, fly ash and limestone.

	Clinker	Fly ash	Limestone
SiO_2	20.8	50.0	12.9
Al_2O_3	5.6	23.9	2.7
Fe_2O_3	3.2	6.0	2.0
CaO	63.0	6.3	42.3
MgO	3.0	2.1	1.8
SO_3	1.5	0.4	–
P_2O_5	0.1	1.1	–
K_2O	1.3	1.4	0.6
Na_2O	0.5	0.6	0.5
Na_2O Eq.	1.4	1.6	
LOI	0.3	3.6	37.7
Carbon	0.1	3.1	–
Chloride	0.05	0.0	–
Free CaO	1.9	–	–
Blaine surface (m^2/kg)	500*	470	810
Density (kg/m^3)	3150*	2490	2740

* For OPC = clinker + gyspum.

Table 2
Experimental matrix.

Mix	Composition		
	OPC (%)	FA	L
1	100	0	0
2	95	0	5
3	90	0	10
4	85	0	15
5	80	0	20
6	75	0	25
7	70	0	30
8	65	0	35
9	95	5	0
10	90	10	0
11	85	15	0
12	80	20	0
13	75	25	0
14	70	30	0
15	65	35	0
16	65	30	5
17	65	25	10
18	65	20	15
19	65	15	20
20	65	10	25
21	65	5	30

Three mortar prisms (40 × 40 × 160 mm) were prepared for each testing age and material combination, according to EN 196-1 (water-to-binder ratio 0.50, binder:sand = 1:3). The samples were cured at 20 °C, submerged in a saturated $Ca(OH)_2$ solution.

For all the mortar mixes, corresponding cement pastes with water-to-binder ratio of 0.5 were prepared using a vacuum mixer from Renfert. The pastes were poured into 20 ml cylindrical plastic bottles and stored under sealed conditions at 20 °C. The hydration of the samples was stopped after 1, 28, 90 and 140 days of curing via solvent exchange using isopropanol and ether. The samples were stored for about 2–3 h in a desiccator over silica gel, prior to analysis, to let the remaining ether evaporate. Simultaneous TGA/SDTA analyses were performed on the dried powders using a Mettler Toledo TGA/SDTA851. Samples of about 50 mg were weighed into aluminium oxide crucibles. The samples were heated from 30 °C to 980 °C at a heating rate of 20 °C/min. During the analysis the oven was purged with N_2 at 50 ml/min. During a thermogravimetric analysis (TGA), the weight of the sample is monitored as a function of the temperature. The amount of bound water (H) and calcium hydroxide (CH) are determined as described in [15]. Both are expressed as a % of the dry sample weight and as a % of OPC content in the sample. The standard deviation on three independent measurements at all tested ages is not larger than 0.1% for H and 0.2% for CH.

In order to focus on the effects of small limestone replacements in both ordinary Portland cement and fly ash cement, thermogravimetric curves and X-ray diffraction patterns of the four following mixes of particular interest were studied:

- 100% OPC (reference)
- 95% OPC + 5% limestone powder
- 65% OPC + 35% fly ash
- 65% OPC + 30% fly ash + 5% limestone powder

For the X-ray diffraction (XRD), larger paste samples of about 60 ml were prepared for each combination. After 1, 28, 90 and

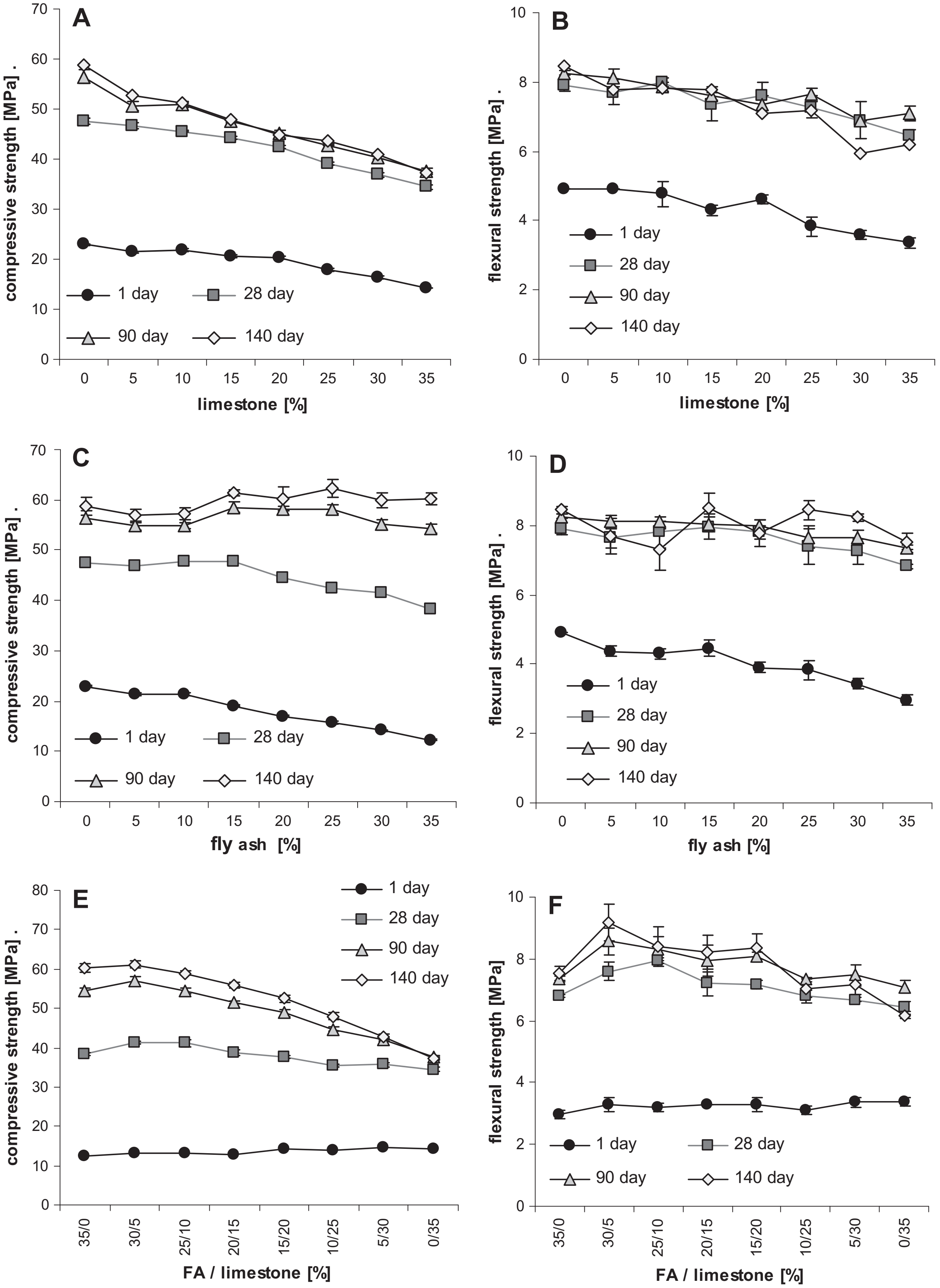

Fig. 1. The compressive and flexural strength with standard deviation (bars) after 1, 28, 90 and 140 days of curing for: (A) and (B) limestone blended cements, (C) and (D) fly ash blended cements, and (E) and (F) composite cements containing both fly ash and limestone.

140 days of sealed curing at 20 °C, discs with a diameter of about 30 mm and a thickness of 3–5 mm were cut from the paste samples using a water lubricated saw and the top layer was removed using fine sand paper. The discs were analysed using a PANalytical X'Pert Pro MPD diffractometer in a $\theta - 2\theta$ configuration with an incident beam monochromator and Cu Kα radiation ($\lambda = 1.54$ Å).

Table 3
Compressive (σ_{comp}) and flexural strength (σ_{flex}) after 1, 28, 90 and 140 days of curing, of all tested combinations.

Mix	Composition			1 day		28 days		90 days		140 days	
	OPC (%)	FA	L	σ_{comp} (MPa)	σ_{flex}	σ_{comp} (MPa)	σ_{flex}	σ_{comp} (MPa)	σ_{flex}	σ_{comp} (MPa)	σ_{flex}
1	100	0	0	22.9	4.9	47.5	7.9	56.5	8.3	58.7	8.4
2	95	0	5	21.4	4.9	46.6	7.7	50.6	8.1	52.7	7.8
3	90	0	10	21.7	4.8	45.5	8.0	50.9	7.9	51.1	7.8
4	85	0	15	20.6	4.3	44.3	7.4	47.7	7.6	47.8	7.8
5	80	0	20	20.3	4.6	42.5	7.6	45.1	7.4	44.9	7.1
6	75	0	25	18.0	3.8	39.1	7.3	42.8	7.6	43.6	7.2
7	70	0	30	16.3	3.6	36.9	6.9	40.4	6.9	40.9	5.9
8	65	0	35	14.2	3.4	34.4	6.4	37.5	7.1	37.2	6.2
9	95	5	0	21.2	4.4	46.9	7.6	54.9	8.1	56.8	7.7
10	90	10	0	21.4	4.3	47.6	7.8	54.9	8.1	57.2	7.3
11	85	15	0	19.1	4.5	47.8	8.0	58.4	8.0	61.4	8.5
12	80	20	0	17.0	3.9	44.6	7.8	58.2	8.0	60.2	7.8
13	75	25	0	15.8	3.8	42.6	7.4	58.2	7.7	62.3	8.5
14	70	30	0	14.1	3.4	41.4	7.3	55.1	7.7	59.9	8.2
15	65	35	0	12.3	3.0	38.3	6.8	54.4	7.4	60.2	7.5
16	65	30	5	13.2	3.3	41.2	7.6	56.9	8.6	61.1	9.2
17	65	25	10	13.3	3.2	41.2	7.9	54.5	8.3	59.0	8.4
18	65	20	15	12.9	3.3	38.6	7.2	51.4	7.9	55.8	8.2
19	65	15	20	14.2	3.3	37.5	7.2	48.9	8.1	52.5	8.4
20	65	10	25	13.9	3.1	35.4	6.8	44.7	7.3	48.0	7.1
21	65	5	30	14.6	3.4	35.7	6.7	42.1	7.5	42.7	7.2

3. Results

3.1. Flexural and compressive strength

The compressive and flexural strength of the *limestone blended cements* decrease with increasing limestone powder replacement at all ages from 1 to 140 days (Fig. 1A and B). The main compressive and flexural strength gain takes place during the first 28 days of curing as might be expected. The flexural strength and the compressive strength do not seem to change after 28 and 90 days of curing, respectively.

The compressive and flexural strength after 1 day of curing decreases with increasing fly ash replacement for the *fly ash blended cements* (Fig. 1C and D). The fly ash blended cements containing up to 15% fly ash obtain a similar compressive strength as the OPC reference after 28 days, while higher replacement levels lead to a reduction in compressive strength. After 90 and 140 days of curing, all tested fly ash blended cements reach compressive and flexural strength levels equal to the OPC reference regardless of the fly ash content. The main strength development occurs during the first 28 days. However, there is still a considerable strength increase between 28 and 90, and 90 and 140 days especially for the mixes containing large volumes of fly ash (>15%). The flexural strength, on the other hand, does not change greatly after 28 days of curing.

Table 3 shows the compressive and flexural strength results of the different tested combinations. It can be seen that at the same replacement level the limestone blended cements (mix 2–8) develop a slightly higher strength than the fly ash blended cements (mix 9–15) after 1 day. After 28 days, however, the fly ash blended cements surpass the limestone blended cements and at 90 and 140 days the gap between the two increases with increasing replacement level.

The compressive and flexural strength results for the *composite cements containing 65% OPC and 35% of a combination of limestone powder and fly ash* are shown in Fig. 1E and F. After 1 day of curing, limestone powder seems to promote the early age hydration more than fly ash as the compressive strength tends to increase as limestone replaces fly ash. After 28 days, on the other hand, the blend with 35% limestone powder has an average compressive strength of 34.4 MPa and the one with 35% fly ash 38.3 MPa (Table 3).

The maximum 28 day compressive strength is obtained for the mixes containing 30% fly ash and 5% limestone (41.2 MPa) or 25% fly ash and 10% limestone powder (41.2 MPa). Up to 15% limestone powder (38.6 ± 0.8 MPa) can be used instead of fly ash without impairing the strength at 28 days relative to the 65% OPC and 35% FA blend (38.3 ± 0.4 MPa). A compressive strength increase of about 8% was obtained at 28 days when replacing 5% fly ash by 5% limestone in the 35% fly ash mix. This is comparable to the about 10% compressive strength increase reported after 28 days of curing in our preceding study [15] for a parallel series of the same mixes. After 90 days of curing a similar but slightly smaller strength increase when replacing a small part of the fly ash with limestone powder in the composite cements can be observed (Fig. 3E, Table 3). A strength increase of 5% is obtained (54.4 MPa versus 56.9 MPa). The effect is further reduced at 140 days. At this age similar strength performances are obtained for the 35% fly ash and 30% fly ash and 5% limestone blends (60.2 MPa versus 61.1 MPa). Replacing 5–10% of the fly ash with limestone appears also to be beneficial for the flexural strength after 28, 90 and 140 days. The main compressive and flexural strength development occurs during the first 28 days. After 28 and even 90 days there is considerable compressive and flexural strength increase for the mixes with high fly ash content. When comparing mix 14 (70% OPC and 30% fly ash) and mix 16 (65% OPC, 5% limestone and 30% fly ash), it can be seen that they develop about the same compressive strength at all tested ages, indicating that 5% of OPC can be replaced by limestone powder in a Portland fly ash cement without impairing the strength.

3.2. Amount of bound water (H) and calcium hydroxide (CH)

Fig. 2 shows the amount of bound water (H) relative to the dry content and the OPC content.

Both for the *limestone and fly ash blended cements*, the amount of bound water per dry content decreases (Fig. 2A and C), and the amount of bound water relative to the OPC content increases (Fig. 2B and D), with increasing replacement level, except for the 5% replacement of the OPC with limestone powder that shows no reduction in the amount of bound water relative to the dry content.

The amount of bound water for the *composite cements containing 65% OPC and 35% of a combination of fly ash and limestone powder* (Fig. 2E) is similar for all tested combinations after 1 day of curing. However, the amount of bound water increases as limestone powder and fly ash are combined instead of just using one of them after

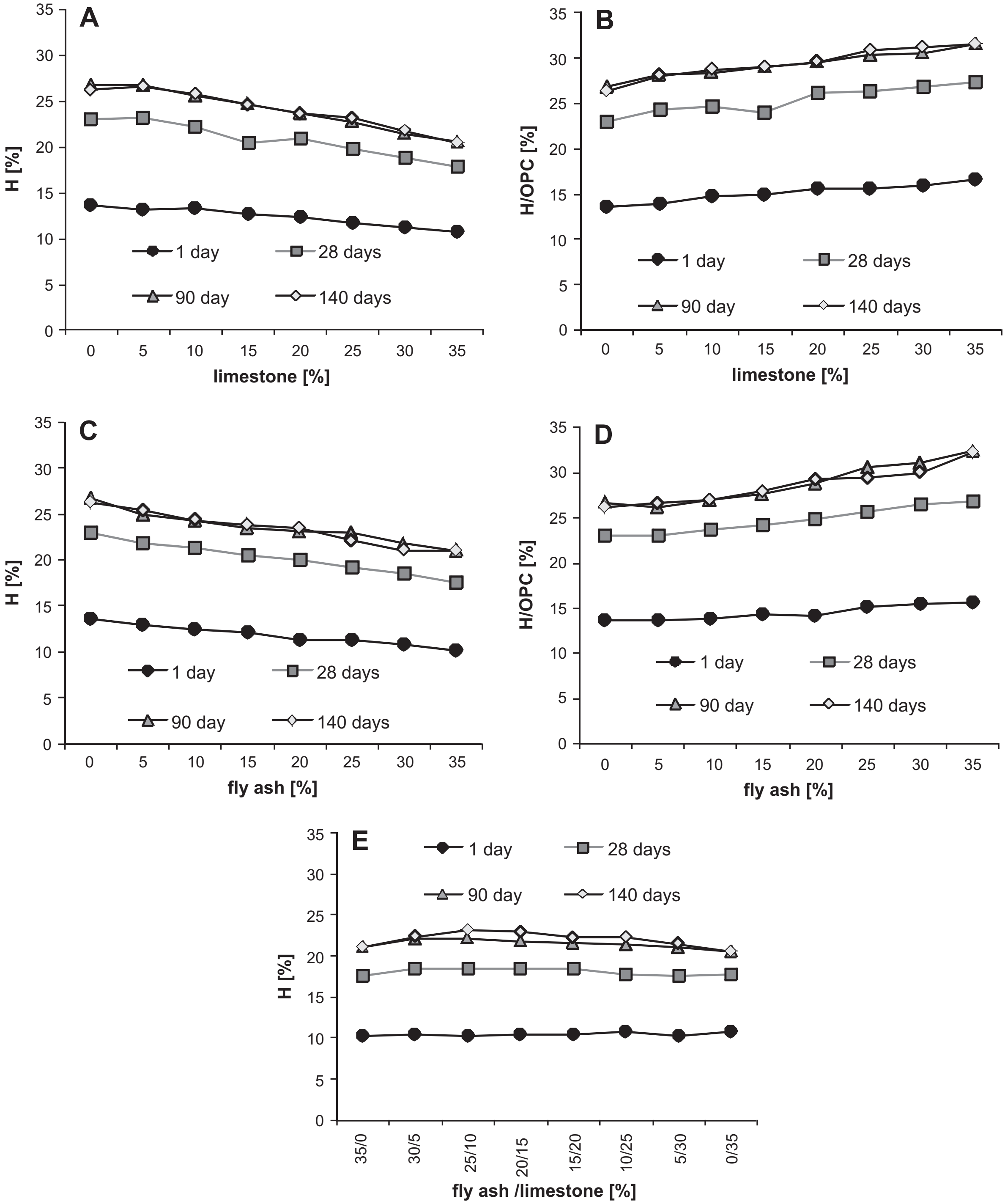

Fig. 2. The amount of bound water (H) per dry content and per OPC after 1, 28, 90 and 140 days of curing for: (A) and (B) limestone blended cements, (C) and (D) fly ash blended cements, and (E) composite cements containing both fly ash and limestone.

28, 90 and 140 days. The maximum amount is obtained for 25% fly ash and 10% limestone powder after 90 and 140 days.

The main part of the bound water is bound during the first day and the following 28 days. The amount of bound water increases slightly up to 90 days, but generally does not change thereafter.

Fig. 3 depicts the calcium hydroxide content (CH) both relative to the dry content and the OPC content.

The CH content per dry content decreases with increasing limestone or fly ash replacement for the *fly ash and limestone blended cements* (Fig. 3A and C). The CH content per OPC increases with increasing limestone or fly ash replacement at 1 day (Fig. 3B and D). However at later ages, different trends are observed for limestone and fly ash blended cements. For the *limestone blended cements* there is a decreasing trend in the CH content per OPC at 5–10% limestone, but the amount tends to increase again at higher replacement levels. For the *fly ash blended cements* with high fly ash content (⩾20%) a decrease in CH content can be observed after 28 days. The higher the fly ash content, the more prominent is the CH reduction.

The CH content for the *composite cements containing 65% OPC and 35% of a combination of fly ash and limestone powder* is similar for all tested combinations after 1 day (Fig. 3E). At later ages, the

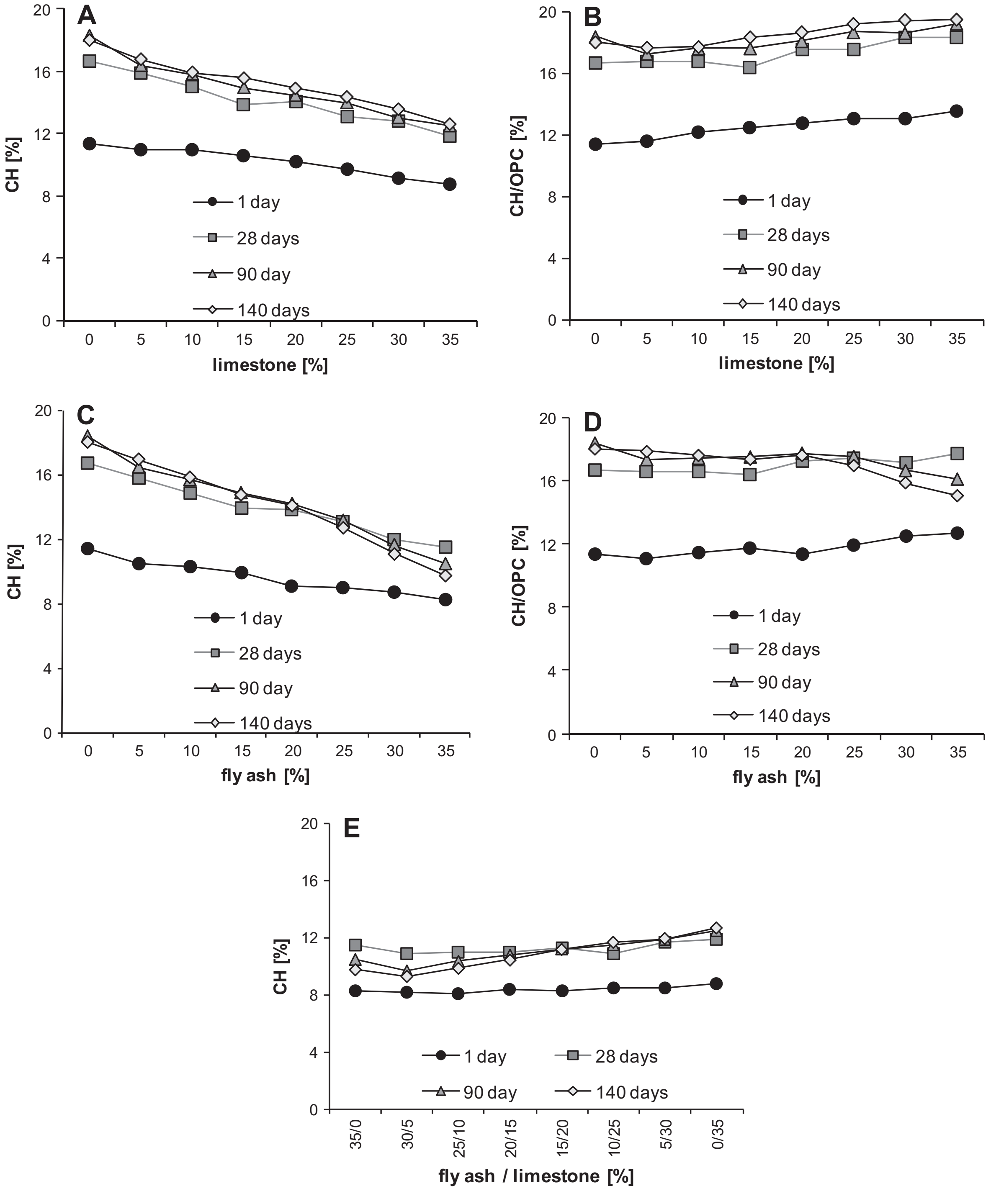

Fig. 3. The calcium hydroxide content (CH) per dry content and per OPC after 1, 28, 90 and 140 days of curing for: (A) and (B) limestone blended cements, (C) and (D) fly ash blended cements, and (E) composite cements containing both fly ash and limestone.

CH content tends to decrease with increasing fly ash content. However, the combination containing 35% fly ash does not show the minimum CH content. Interestingly, the minimum is reached for the combination containing 30% fly ash and 5% limestone.

3.3. Changes in the hydration products

Fig. 4 depicts the thermogravimetric curves (TG-curves) and the differential thermogravimetric curves (DTG-curves) for 100% OPC cement and 100% OPC + 5% L after 28 and 140 days of hydration. Fig. 5 shows the corresponding curves for 65% OPC + 35% fly ash and 65% OPC + 30% fly ash + 5% limestone. The dark curves represent the combinations without limestone powder and the brighter curves those containing 5% limestone powder. From Fig. 4 it can be seen that the limestone containing cement (95% OPC + 5% limestone) binds about the same amount of water as the reference (100% OPC) after both 28 and 140 days of curing, as their total weight loss at about 550 °C is similar. Some differences can be observed between the DTG-curves of the two cements. The peak above 100 °C, partially due to the decomposition of ettringite

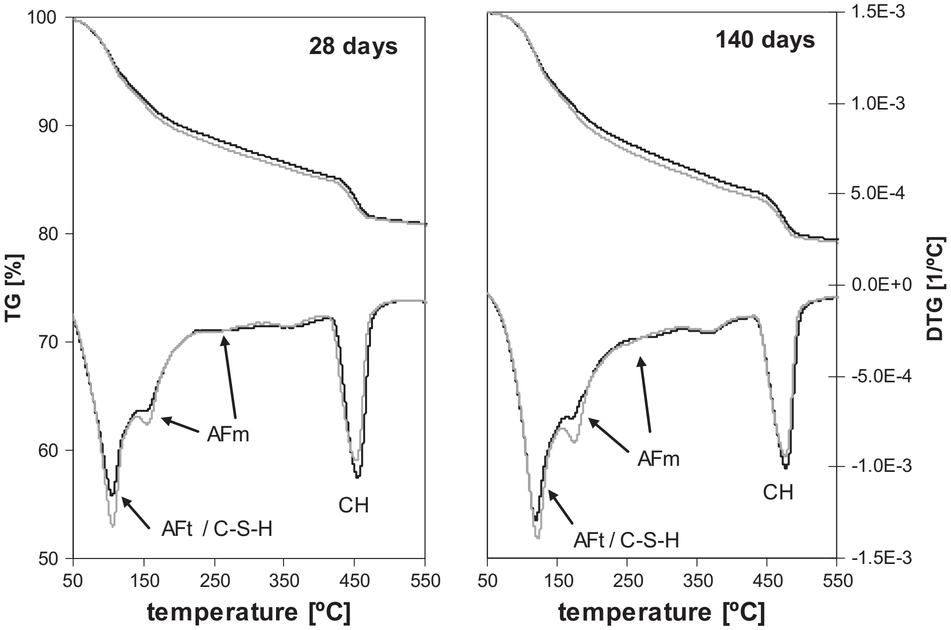

Fig. 4. The thermogravimetric (TG) and differential thermogravimetric (DTG) results for 100% OPC (dark) and 95% OPC + 5% L (bright) after 28 and 140 days of sealed curing.

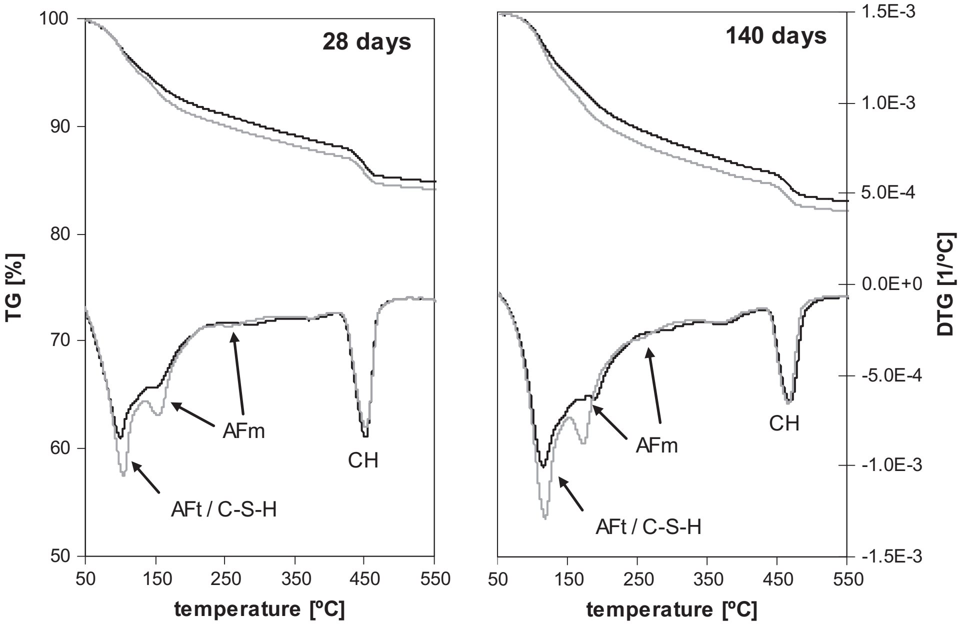

Fig. 5. The thermogravimetric (TG) and differential thermogravimetric (DTG) results for 65% OPC + 35% FA (dark) and 65% OPC + 30% FA + 5% L (bright) after 28 and 140 days of sealed curing.

(AFt), is larger in the presence of limestone, showing that limestone powder seems to stabilize the ettringite as expected [8,9,11,13,17]. The limestone containing cement has a clear single peak at about 180 °C whereas the reference develops a smaller peak with a slight shoulder at higher temperatures. These peaks are associated with the decomposition of AFm phases such as monosulphate, mono- and hemicarbonate [19].

From Fig. 5 it can be seen that when 5% fly ash is replaced by 5% limestone powder slightly more water is bound. When the DTG-curves of the two cements are compared, similar observations can be made as for Fig. 4, except that the effect tends to be more pronounced.

In Fig. 6 the X-ray diffraction patterns at low angle (8–13°2θ) for the different tested combinations cured for 1, 28, 90 and 140 days are shown. After 1 day of hydration the diffraction pattern of the different tested mixes are quite similar, as they all contain ettringite (9.1 2θ) and some hemicarbonate (10.8 2θ).

At later ages (28, 90 and 140 days), ettringite, calcium monocarbonate hydrate (11.7 2θ) and calcium hemicarbonate hydrate are formed in the mixes containing limestone powder. In the absence of limestone only calcium monosulphate hydrate and ettringite are observed. Two types of monosulphate were observed: monosulpoaluminate (Ms, 9.9 2θ) and hydroxyl-AFm type solid solution (Ms*, 10.4 2θ) in which part of sulphate is substituted by hydrox-

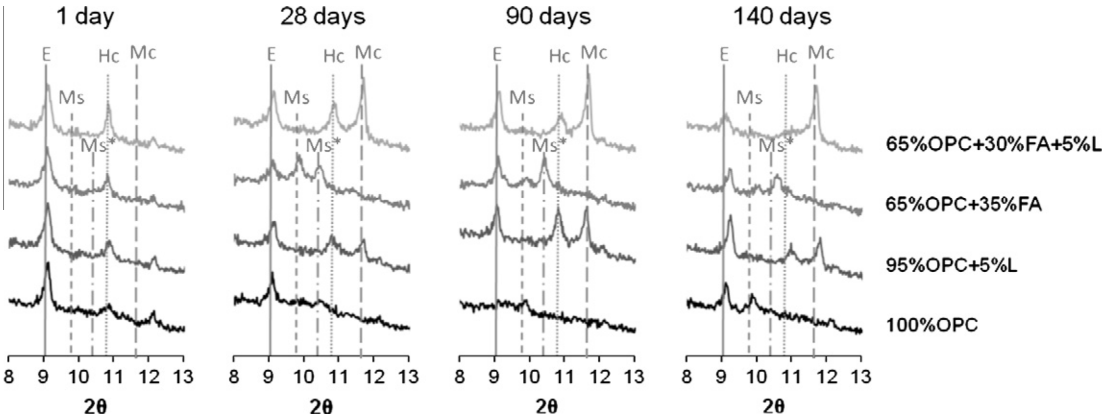

Fig. 6. X-ray diffraction patterns at low diffraction angle (8–13°2θ) for 100% OPC, 95% OPC + 5% L, 65% OPC + 35% FA and 65% OPC + 30% FA + 5% L after 1, 28, 90 and 140 days of sealed curing (E = ettringite, Ms = monosulphate, Ms* = hydroxyl-AFm, Hc = hemicarbonate, Mc = monocarbonate).

ides [9,11]. Note that these results were not interpreted quantitatively. The AFm and AFt phases were found to be very sensitive and tended to decompose upon handling, as can be seen from 100% OPC mix at 90 days in which all of the AFt and AFm phases have disappeared.

4. Discussion

The compressive strength of *limestone blended cement* decreases with increasing OPC replacement at all tested ages. In a previous study [17], up to 15% of the OPC could be replaced by limestone powder without impairing the compressive strength after 28 days of curing under the same curing conditions. Similar results were also obtained by others [2,20]. However, no strength increase was observed at low replacement levels in this study. It should be noted that the effect of limestone powder on the compressive strength is likely to be more pronounced at lower w/b ratios [21].

According to the thermogravimetric results (H and CH), two mechanisms can be distinguished: the *filler effect* related to the increase of the amount of bound water (H) and calcium hydroxide (CH) relative to the OPC content with increasing replacement of OPC with limestone (Figs. 2B and 3B). Indeed, replacing OPC with limestone raises the effective water to OPC ratio, and the limestone powder provides additional surface for the precipitation of hydrates; both effects promote clinker hydration. And the *dilution effect* is caused by the reduction in the amount of the most reactive component, OPC, in the system. At replacement levels larger than 5%, the H and CH per dry content and the compressive strength decrease with increasing replacement of OPC by limestone indicating that the filler effect can not compensate for the dilution effect at all tested ages (Figs. 2A and 3A).

At low limestone replacement (up to 10%) of the OPC, the amount of bound water per OPC increases (Fig. 2B), but at the same time the amount of CH per OPC decreases after 28, 90 and 140 days (Fig. 3B). During the hydration of OPC, an increase in the amount of CH is generally accompanied by an increase in the amount of H, such as during the hydration of the main clinker mineral alite (C_3S): $C_3S + 2.3\ H \rightarrow C_{1.7}SH + 1.3\ CH$. The decrease in CH therefore indicates a change in the nature of the hydration products formed, which is confirmed by the changes in the TG and DTG (see Fig. 4). The presence of limestone leads to the formation of carboaluminate hydrates, as observed with XRD (Fig. 6). This reaction might cause the decrease in CH as reported in previous studies [8,9,11,13,17]. The increase of the amount of CH per OPC for higher replacement (>10%) can be related to a larger filler effect promoting the CH production which compensates for the consumption of CH by the hemicarbonate formation [7], or the formation of monocarboaluminate instead of hemicarboaluminate, which does not consume CH [6,9,11].

For the *fly ash blended cement* it was observed that fly ash, similar to the limestone powder, exerts a filler effect on the OPC hydration which does not compensate for the dilution effect after 1 day: increasing H and CH per OPC, but decreasing it per dry content, as well as decreasing the compressive and flexural strength with increasing OPC replacement. At later ages, the pozzolanic reaction of the fly ash plays an important role for the fly ash blended cements. Contrary to the limestone blended cements, there is still a considerable strength increase after 28 days with higher replacement levels as expected. The extent of the fly ash reaction is recently documented in [18]. The amount of CH gives an indication for the pozzolanic reactivity of the fly ash, as fly ash consumes CH during its pozzolanic reaction. Care should be taken when interpreting these results as the filler effect of the fly ash initially increases the CH/OPC content with increasing fly ash content. However, after 28 days a consumption of CH can be observed for the fly ash blended cements with high fly ash content (>20%) (Fig. 3D). Furthermore, the dissolved species from the fly ash may also react directly with the C–S–H gel [22–24]. The latter reaction mechanism would lower the Ca/Si ratio and possibly increase the Al/Si ratio in the C–S–H gel.

An OPC or a limestone containing cement shows an almost linear trend between compressive strength and the amount of bound water (H) (Figs. 1C and 2C) [15]. However, this relation is not valid in the case of FA blended cements due to two major facts: curing conditions and the nature of the pozzolanic reaction products. The mortars were stored in saturated CH solution, whereas the paste samples were cured under sealed conditions. The pozzolanic reaction might in the case of the mortar samples have been altered due to the continuous access to water and CH and a possible leaching of alkali (pH solution 12.5, pH mortar 13.5). The pozzolanic reaction products of the fly ash were found to enhance the mechanical properties without necessarily binding more water than what is inherent in the CH.

At all tested ages, 5% of the fly ash in the blended fly ash cement (65% OPC + 35% fly ash) can be replaced with limestone powder (resulting in 65% OPC + 30% fly ash + 5% limestone) without impairing the compressive and flexural strength (Fig. 1E and F). At 28 days a compressive strength increase of 8% is observed, however the effect diminishes over time: 5% increase at 90 and 2% at 140 days. The increasing contribution of the pozzolanic reaction of fly ash to the compressive strength, probably explains the reduction of the effect over time. Also 5% OPC in the 70% OPC + 30% fly ash blend can be replaced by 5% limestone powder resulting in the combination 65% OPC + 30% fly ash + 5% limestone powder without reducing the compressive and flexural strength at all tested ages (Table 3).

Both observations are important for the cement manufacturers producing fly ash blended cements. As limestone powder is the main raw material for OPC, it is always available in abundance at cement plants. Fly ash on the other hand has to be carefully selected and purchased from coal fired power plants and transported to the cement plant. In the future good quality fly ash can also be scarce as the demand increases as blended cements gain popularity. Being able to replace part of the fly ash with limestone powder renders the cement production less dependent on the fly ash supply and is economically beneficial. Being able to replace 5% of the OPC with limestone powder results in a reduction of costs and emissions related to the clinkerization.

Replacing 5% of the fly ash with limestone powder in a 65% OPC + 35% fly ash cement in addition to producing a strength increase, also results in a decrease in CH content at 28, 90 and 140 days (Fig. 3E). The CH content normally decreases with increasing fly ash content. The observed decrease in CH with less fly ash therefore indicates a similar reaction to the one observed for minor additions of limestone powder to OPC: the formation of hemicarbonate (Fig. 6), with calcium being supplied by OPC as opposed to the fly ash, due to its higher CaO content (Table 1).

The effect of the presence of 5% limestone powder seems to be more pronounced for the fly ash cements than for the ordinary Portland cement (Figs. 4 and 5). As the fly ash reacts, aluminates are liberated by dissolution of fly ash, thereby decreasing the sulphate/aluminate ratio. Therefore more ettringite will decompose after sulphate depletion and react with the additional aluminates to form calcium monosulphate hydrate. The presence of limestone will then have a larger impact as this will stabilize the ettringite by reacting with the additional aluminates provided by the fly ash to form calcium carboaluminate hydrates. The net result is more ettringite, more chemically bound water and a larger volume of hydrates leading to less porosity and thereby higher strength, i.e. a true synergistic effect exists and can be used to advantage. The chemistry of this synergy was recently elaborated in [16].

5. Conclusions

The key observation in this study is the confirmation of the synergetic interaction between limestone powder and fly ash and its persistence over time. The presence of limestone leads to the formation of mono- or hemicarboaluminate hydrates instead of monosulphoaluminate hydrate and stabilizes thereby the ettringite. This leads to an increase in the volume of hydrates and a subsequent decrease in porosity and an increase in strength. Fly ash, on the other hand, can provide additional aluminates which will lower the sulphate/aluminate ratio and thereby amplify the impact of the limestone.

Replacing 5% of the OPC with limestone powder at a water-to-binder ratio of 0.5 resulted in a reduction in compressive and flexural strength, whereas replacing 5% of the OPC with limestone powder in a fly ash blended cement with 30% fly ash and 70% OPC produced no strength loss. The composite cements consisting of 65% OPC, 30% fly ash and 5% limestone powder have a slightly higher or similar strength compared to the 65% OPC and 35% fly ash and the 70% OPC and 30% fly ash blends at 28, 90 and 140 days. This means that, 5% of OPC or 5% of fly ash can be replaced with 5% limestone powder in this system, without impairing the compressive and flexural strength. The TGA and XRD results confirmed the change in the hydration products when limestone is included in the system.

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