Fly ash–limestone ternary composite cements: synergetic effect at 28 days.

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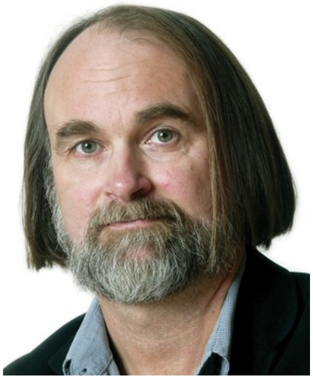

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ABSTRACT

Composite cements containing OPC, fly ash and limestone powder were tested in paste and mortar after 28 days of curing at 20ºC to verify a postulate claiming that calcium aluminate hydrates produced by the pozzolanic reaction of fly ash would react further with limestone to form calcium carboaluminate hydrates and thereby increase the total amount of hydrates and consequently strength. Thermogravimetric tests indicated indeed a change in hydration products when limestone powder was included in the system. This was also confirmed by X-ray diffraction showing the formation of calcium carboaluminate hydrates. It was demonstrated that this synergetic interaction between fly ash and limestone increases the compressive strength more than cement replacement by limestone alone.

Key words: ternary cement, fly ash, limestone, carboaluminate hydrate

1 INTRODUCTION

During cement production large amounts of CO_2 are emitted. In 2000, about 0.87 ton CO_2 per ton clinker was emitted on average, about 40% coming from fuel combustion, grinding and other operations, and 60% from the de-carbonation of limestone to form the clinker phases [1]. In order to reduce these emissions, cement factories have switched over to larger fractions of alternative fuels, optimized energy consumption (e.g. regeneration of heat, optimized the clinker with mineralisers, etc) [2].

The fact that, in the future, emitting CO_2 will come at a price, gives the cement producers a new incentive to reduce the emissions even more. One way of doing that on a short term is by replacing part of the clinker with other materials such as slag, limestone powder, fly ash, silica fume, natural pozzolans etc [3]. The type of replacement materials used depends on their availability (amount available, price, transportation …) and is therefore dependent on the geographical location of the cement plant.

The aim of this study is to contribute to the development of a novel all-round Portland composite cement for the Norwegian market. Currently the cements produced at the Norwegian cement plants are: CEM I [4] Portland cements containing up to 5% limestone powder and CEM II/A-V [4] Portland fly ash cements containing up to 20% fly ash but no limestone powder. In this study, the effect of increasing the replacement levels of the ordinary Portland cement (OPC) (up to 35%), and combining fly ash and limestone powder to replace OPC are investigated.

Limestone powder is known to accelerate the hydration of cement, especially the C_3S phase, by acting as nucleation surface for portlandite and CSH precipitation [5-7]. The accelerating effect can give rise to a slightly higher compressive strength at early age at moderate OPC replacements (<10%). At later age, replacing part of the OPC with limestone powder may result in a strength reduction, due to the replacement of the more reactive component, OPC, with less or non reactive one [8]. This effect is referred to as the dilution effect. Besides this physical effect, the calcium carbonate of the limestone powder is also known to interact with the aluminate phases of OPC [7, 9-13]. In the presence of small amounts of limestone powder, monosulphoaluminate hydrate is replaced by mono- or hemicarboaluminate hydrate and more ettringite. Due to this change in hydration products the volume of the hydration products formed can increase slightly [12-14]. This can in its turn lead to a slight increase in strength and a decrease in permeability. The effect is however limited due to the small amount of aluminate present in the OPC.

ASTM Class F fly ash [15] is a slow reacting pozzolan. It can take up to several weeks before it starts to react significantly at 20°C. The fly ash will not react noticeably during the so-called "incubation period" the length of which is believed to depend mainly on the alkalinity of the pore water [16, 17] and therefore also on the type of cement used [18]. Fly ash reduces early strength due to the dilution effect. However, it can contribute to a higher long-term strength, due to its pozzolanic reaction.

When combining limestone powder and fly ash, a synergetic effect between the two is expected to take place. Fly ash is an aluminate rich pozzolan, as it reacts it will introduce additional aluminates to the system, thereby decreasing the SO_3/Al_2O_3 ratio and amplifying the impact of the limestone powder on the hydration products. The increase of bound water and compressive strength gain resulting from a minor limestone powder addition is therefore is expected to be greater for fly ash containing cements than for OPC. This was first postulated in the COIN application in 2005 (www.coinweb.no). The goal of the study is to validate this postulate concerning the synergetic effect between limestone powder and fly ash.

A preliminary study on fly ash-limestone-calcium hydroxide-alkaline solution [19]: showed a clear interaction between fly ash and limestone powder. More water was bound relative to the fly ash content and the hydration products formed were proven to contain calcium carboaluminate hydrate.

In literature many studies can be found on composite cements containing limestone powder and slag [20, 21], limestone powder and natural pozzolans [22] and even limestone powder and fly ash [23-26] have been investigated. However, these studies focused on heat of hydration, strength and durability, whereas the chemical interaction between the different components was not studied [24]. An exception is Hoshino at al. [27] who studied the addition of limestone powder to slag cements and linked the changes in the hydration phases observed by XRD with the increase in compressive strength. To the author's knowledge, the hydration mechanisms of composite cements containing both limestone powder and fly ash have not been fully investigated yet.

2 EXPERIMENTAL

2.1 Materials

The materials used in this project were: CEM I clinker, siliceous fly ash, limestone powder and natural gypsum. The composition of clinker, fly ash and limestone used as well as their density and specific surface are listed in Table 1. Table 2 gives the mineral composition of the clinker determined by Rietveld analysis. The clinker was interground with 3.7% of gypsum to form OPC, so that the total SO_3 content would be about 3% including the sulphates of the clinker. The gypsum contained 0.18% free water, and had a $CaSO_4 \cdot 2H_2O$ content of 91.39%. The particle size distribution of the different materials was determined with a Mastersizer from Malvern. The results are shown in Figure 1.

Table 1: Chemical composition, density and Blaine specific surface of the clinker, fly ash and limestone powder

	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	-	3.1	-
Chloride	0.05	-	-
Free CaO	1.9	-	-
Density [kg/m^3]	3150*	2490	2740
Blaine specific surface [m^2/kg]	500*	470	810

* for OPC = clinker + gypsum

Table 2: Mineral composition of the clinker determined by Rietveld analysis

Minerals	%
C_2S	19
C_3S	54
C_3A	11
C_4AF	8

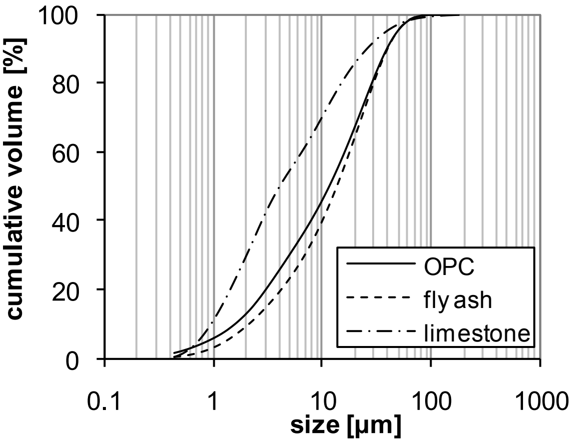

Figure 1: The particle size distribution of the materials used in this study determined by laser diffraction.

2.2 Testing

Table 3 shows the different composite cements which were tested. The experimental matrix can be divided into three main groups, together with the reference (mix 1). In the first group, OPC is gradually replaced by limestone powder, starting at 5% up to 35% in steps of 5% (mix 2 to mix 8). In the second group OPC is similarly replaced with fly ash (mix 9 to mix 15). In the third group different limestone powder and fly ash combinations were tested (mix 16 – mix 21) at a constant OPC replacement level of 35%, which is the potential replacement level for future commercial cements produced in Norway.

Table 3: Composite cement combinations tested (replacement by mass)

mix	OPC	fly ash	limestone
1	100	/	0
2	95	/	5
3	90	/	10
4	85	/	15
5	80	/	20
6	75	/	25
7	70	/	30
8	65	/	35
9	95	5	/
10	90	10	/
11	85	15	/
12	80	20	/
13	75	25	/
14	70	30	/
15	65	35	/
16	65	30	5
17	65	25	10
18	65	20	15
19	65	15	20
20	65	10	25
21	65	5	30

The replacements are done by mass as this is most relevant for cement production. The aim of the study is to develop an all-round Portland composite cement which will be used at fixed w/c ratio's. Furthermore, additional tests showed little difference in compressive and flexural strength when OPC was replaced with crystalline quartz (considered inert material) either by mass or by volume (see Figure 2).

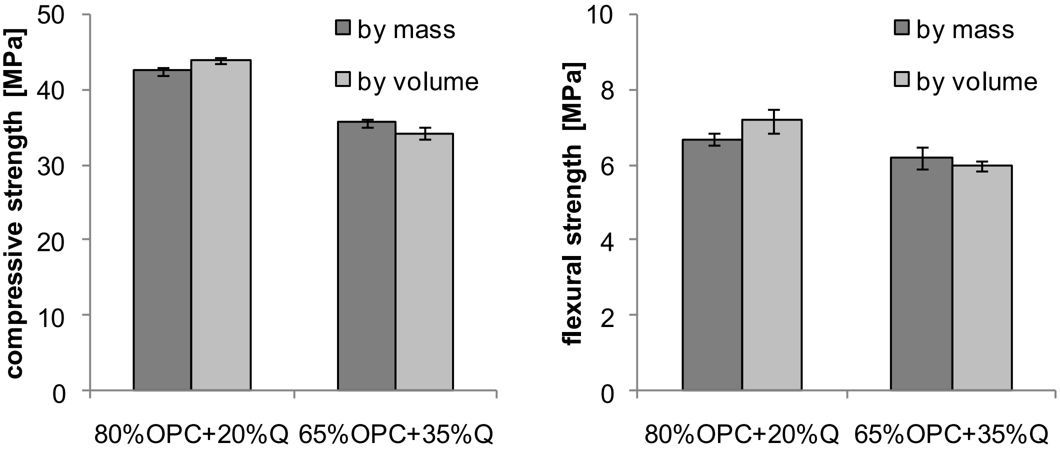

Figure 2: Comparison of the effect of replacement by mass and by volume on 28 day compressive and flexural strength results for two different combinations of OPC and crystalline quartz, Q (density 2700kg/m^3).

Three mortar prisms of 40×40×160 mm were prepared for all the tested combinations according to NS-EN 196-1 (water-to-powder ratio 0.50, powder : sand = 1:3). The flexural and compressive strength was determined after 28 days of curing submerged in saturated lime water.

The volume of air voids in the mortars was determined according to [28]. The mortar samples are first dried in an oven at 105ºC for 1 week. Then their dry mass is determined. After this the samples are submerged in water for a week. When weighing the samples after this, the amount of water taken up due to capillary suction can be determined. During the last step of the procedure the samples are put into a pressure tank at 50 MPa for 2 days. From the mass of the samples weighed immediately after removing them from the pressure tank, one can calculate the volume of air voids in the samples assuming that the air voids fill under pressure, but can not fill by capillary suction due to their large radius.

The volume of air voids of the mortar samples was determined in order to take into account their effect on the compressive strength. The rule of thumb applied, is that a 1% increase in air void volume will lead to a 5% decrease in compressive strength [29]. The results were corrected relative to the average air porosity.

For all tested combinations, 300 ml of paste was made with a water-powder ratio of 0.50. The mixing water was distilled water. No admixtures were used, as all pastes were stable and mixable at this water-to- powder ratio. The pastes were mixed with a Braun MR5550CA high shear mixer. The mixing procedure consisted of mixing for half a minute, resting for five minutes and mixing again for one minute. The paste was poured into 15 ml glass vials and was stored under sealed conditions at 20°C.
To stop the hydration after 28 days, a sample of paste was crushed and washed twice with 150 ml ethanol. The suspension was filtrated. The remaining wet slurry was then poured into a glass vial which was sealed with a plastic lid to avoid evaporation of the ethanol.

Simultaneous TGA/SDTA analyses were performed on these wet slurries with a Mettler Toledo TGA/SDTA851. Samples of about 200mg were weighed into aluminium oxide crucibles. The samples were first dried inside the TGA/SDTA by purging them with N_2 for about 2 hours at 40ºC. The weight of the sample was monitored during drying and the analysis was started when approximately constant weight was reached. This is however not a defined equilibrium condition. One might prefer to dry the samples at a certain RH until equilibrium is reached, but this might lead to carbonation during the handling the samples. By drying the samples in the TGA apparatus, carbonation could be limited to a minimum.

After this the samples were heated from 40ºC to 1,100ºC at a heating rate of 10ºC/min. During the analysis the oven was purged with N_2 at 50ml/min.

During a thermogravimetric analysis (TGA), the weight of the sample is monitored as a function of the temperature. The weight loss observed when the sample is heated from room temperature up to about 600ºC is due to the release of water bound in hydrates (H). Between 450ºC and 550ºC, a sharp weight loss step occurs. This is due to the decomposition of calcium hydroxide (CH). At temperatures above 600ºC carbonates decompose and weight losses are registered as the sample releases CO_2. The carbonates can originate from limestone powder if the sample contained limestone, any dehydrated calcium carboaluminate hydrate formed and/or carbonates which could have formed due to carbonation of the sample.

The weight losses were determined in two different temperature intervals. The weight loss due to the decomposition of CH, ranging from about 450ºC to 550ºC, and the weight loss corresponding to the release of bound water (H), measured between 50°C and about 550-600°C. The start and ending of each temperature interval is determined for each sample based on the DTG-curve.

The standard deviation for the thermogravimetric measurements are 0.3% for the H measurements and 0.05% for the CH measurements. This data is based on the results of three independent experiments.

The weight losses are expressed as a % of the “dry sample mass” or OPC content. The “dry sample mass” is the weight at 600°C.

For some mixes of particular interest small amounts were dried gently over $CaCl_2$ in order to analyse them with an AXS D8 focus X-ray diffractometer. The diffractometer had a CuKα source and a 0.2 mm slit was used. An angular scan was performed for diffraction angles between 5 and 75° 2θ with an increment of 0.04° 2θ and a scanning speed of 0.3 s/step. The XRD-spectra give a qualitative idea of the crystalline hydration products formed, not a quantitative. The spectra are given as a function of the characteristic lattice distance, d.

3 RESULTS AND DISCUSSION

In

Table *4* the compressive and flexural strength, the air porosity and the corrected compressive strength for all tested combinations are given. One can see that fly ash containing cements have a tendency to lower the air content in the mortars. For limestone powder the opposite seems to be the case. This might be due to the effect of these materials on the compactibility of the mortars. Round fly ash particles are known to improve workability and fine limestone powder is known to stabilize and thicken mortars and concretes. By correcting the compressive strength for the air voids, the strength of the fly ash containing mixes is slightly reduced and the limestone containing blends is slightly increased. The trends observed in the results however do not change whether or not the compressive strength is correct for the air content. For the following discussion the not-corrected results will be used.

Table 4: The mean value and standard deviation of the compressive and flexural strength, the air porosity and the corrected compressive strength for all tested combinations after 28 days of curing at 20°C.

mix	C	F	L	flexural	compressive	air porosity	compressive	
							difference	corrected
	[%]			[MPa]	[MPa]	[%]	[%]	[MPa]
1	100	0	0	7.1 ± 0.3	48.3 ± 0.7	2.6 ± 0.2	3.4	49.9
2	95	0	5	7.7 ± 0.1	49.7 ± 0.3	2.7 ± 0.0	4.1	51.8
3	90	0	10	7.7 ± 0.3	48.8 ± 0.4	2.4 ± 0.1	2.5	50.0
4	85	0	15	7.8 ± 0.2	48.1 ± 0.4	2.2 ± 0.2	1.7	48.9
5	80	0	20	7.3 ± 0.1	46.1 ± 0.3	2.1 ± 0.1	0.8	46.5
6	75	0	25	6.8 ± 0.2	42.9 ± 0.3	2.6 ± 0.1	3.4	44.3
7	70	0	30	7.1 ± 0.2	40.7 ± 0.4	2.4 ± 0.1	2.6	41.7
8	65	0	35	6.6 ± 0.2	37.6 ± 0.4	2.5 ± 0.1	2.8	38.6
9	95	5	0	8.0 ± 0.1	49.7 ± 0.8	1.8 ± 0.2	-0.3	49.6
10	90	10	0	7.9 ± 0.2	49.2 ± 1.0	1.5 ± 0.1	-2.3	48.1
11	85	15	0	7.8 ± 0.3	46.5 ± 0.6	1.4 ± 0.1	-2.4	45.3
12	80	20	0	7.6 ± 0.2	45.2 ± 0.4	1.4 ± 0.1	-2.4	44.1
13	75	25	0	7.1 ± 0.5	42.9 ± 1.0	1.4 ± 0.1	-2.4	41.8
14	70	30	0	7.0 ± 0.3	41.2 ± 1.0	1.5 ± 0.2	-1.9	40.4
15	65	35	0	6.2 ± 0.4	38.8 ± 0.7	1.4 ± 0.1	-2.7	37.8
16	65	30	5	7.3 ± 0.1	42.4 ± 0.7	1.6 ± 0.1	-1.3	41.8
17	65	25	10	7.3 ± 0.2	41.3 ± 0.5	1.6 ± 0.0	-1.4	40.7
18	65	20	15	7.3 ± 0.2	40.7 ± 0.4	1.7 ± 0.0	-1.1	40.3
19	65	15	20	6.6 ± 0.2	39.9 ± 0.5	1.6 ± 0.1	-1.6	39.2
20	65	10	25	6.8 ± 0.2	39.2 ± 0.4	1.8 ± 0.0	-0.7	39.0
21	65	5	30	6.3 ± 0.1	38.2 ± 0.4	1.8 ± 0.1	-0.6	38.0

In Figure 3 the compressive strength of cements containing different amounts of either fly ash or limestone powder are given. It can be seen that part of the OPC can be replaced with limestone powder without impairing the compressive strength after 28 days of hydration (up to 15%). Replacing 5% of the OPC by limestone even increases the compressive strength. A similar effect is observed for the fly ash. This might partly be due to better compaction properties of the mortars contain fly ash as the strength increase disappears when the strength is corrected for the air content. It seems as if fly ash has not reacted that much since the compressive strength of the mortars containing fly ash is similar to the ones containing limestone powder.

The flexural strengths of cements containing different amounts of either fly ash or limestone powder are given in Figure 4. The relative standard deviations of the results are large, up to 7%. Even so it can be seen that replacing part of the OPC with limestone powder or fly ash improves the flexural strength up to replacement levels of about 20%.

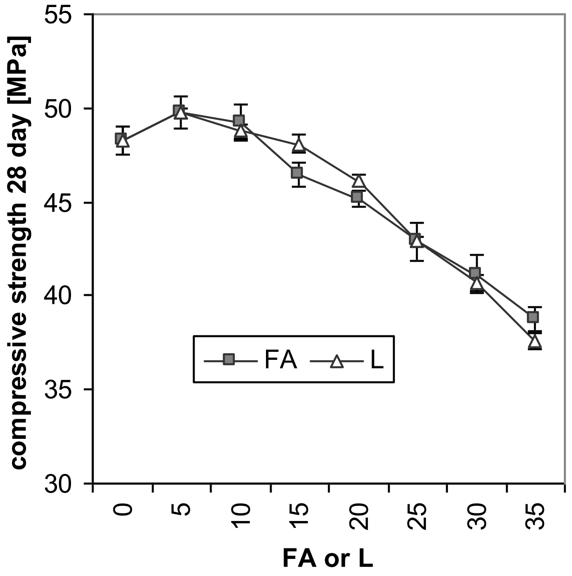

Figure 3: The 28 day compressive strength not-corrected for the air content for cements in which OPC is replaced by fly ash and limestone powder up to 35%.

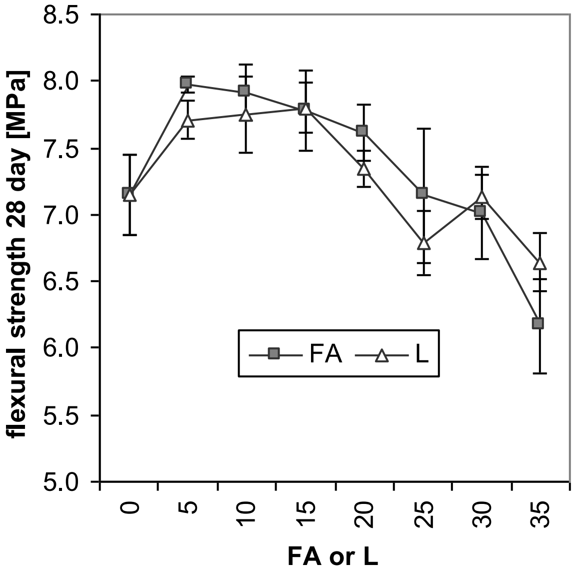

Figure 4: The 28 day flexural strength for cements in which OPC is replaced by fly ash and limestone powder up to 35%.

Figure 5 shows the compressive strength of composite cements in which 35% of the OPC is replaced by different combinations of fly ash and limestone powder. A significant compressive strength increase can be observed when instead of 35% fly ash, a combination of 5% limestone and 30% fly ash is used. This strength increase is about 4 MPa, which is approximately a 10% increase in compressive strength. This indicates that the postulated chemical synergic effect between fly ash and limestone plays a significant role. This beneficial effect on the compressive strength decreases with further increasing limestone powder content. In the corresponding flexural strength results a similar trend can be observed (see Figure 6).

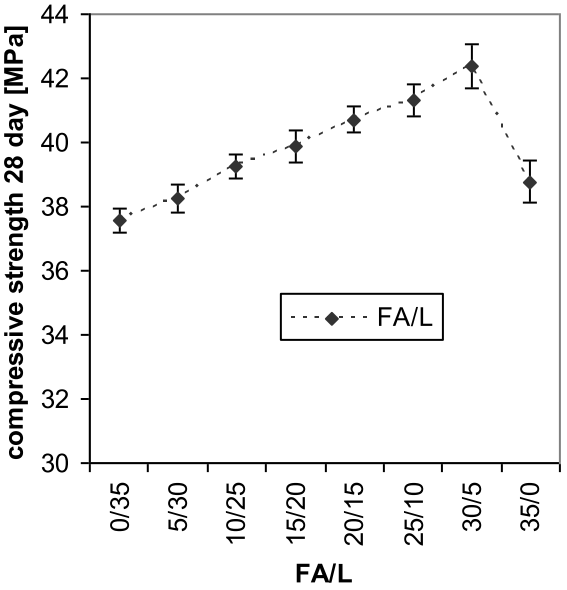

Figure 5: The 28 day compressive strength for composite cements containing 65% OPC and different combination of fly ash and limestone powder.

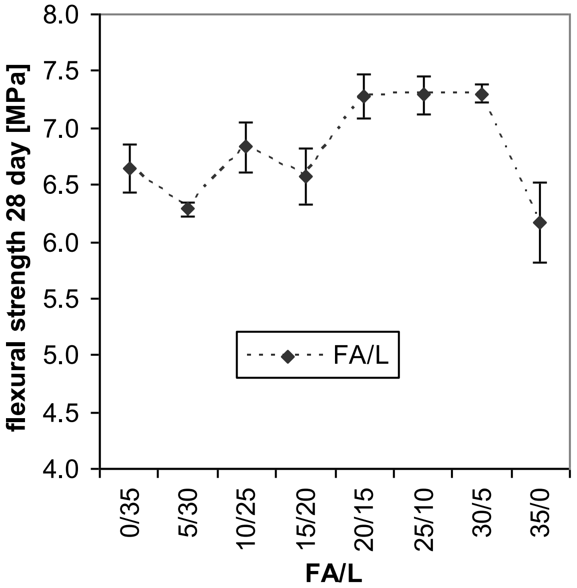

Figure 6: The 28 day flexural strength for composite cements containing 65% OPC and different combination of fly ash and limestone powder.

The compressive strength results of the cements with only fly ash are compared with those of the composite cements containing different combinations of fly ash and limestone powder in Figure 7.

The fly ash curve with filled squares (FA) represents the compressive strength results for cements in which the OPC is replaced only by fly ash. The replacement levels go from 0% in the left of the graph to 35% in the right side in steps of 5%. The dotted with black diamonds (FA+L) represents cements containing 65%OPC and 35% of different combination of fly ash and limestone.

An interesting result is the fact that cement containing 30% fly ash and 70% OPC has a slightly lower compressive strength after 28 days than a cement containing 30% fly ash, 5% limestone and 65% OPC. This means that in this case replacing 5% of the OPC with 5% limestone powder results in a slightly higher compressive strength after 28 days. This result shows that the cement producers could burn 5% less clinker and instead add limestone powder. This is both economically and environmentally beneficial, as less energy is needed and less CO_2 will be emitted.

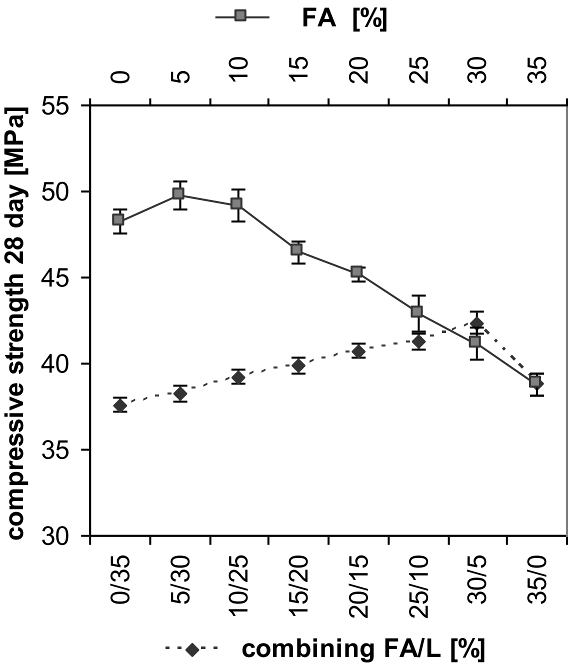

Figure 7: Comparing the 28 day compressive strength of the composite cements with different combination of fly ash and limestone powder and 65% OPC (lower abscissa), and the cements in which OPC is gradually replaced by fly ash (upper abscissa). Different abscissae were used to be able to compare cements with different OPC content and evaluate whether part of the OPC can be replaced by limestone powder without impairing the strength.

In Figure 8 the compressive strength results are compared with the thermogravimetric (TG) results for different replacement levels of OPC with limestone powder.

The decrease in calcium hydroxide per *dry content*, when the OPC is increasingly replaced by limestone powder, is due to the dilution effect. OPC is the major reactive component, and as the amount of OPC decreases in the sample the amount of reaction products, such as CSH and CH, will also decrease.

More interesting is the observation that the amount of CH per *OPC content* decreases slightly when 5% and even 10% of OPC is replaced by limestone powder. Due to the filler effect of the limestone powder one would expect that the amount of CH would increase, but the amount of produced CH only starts to increase when 15% or more of the OPC is replaced by limestone powder.

When 5 % of OPC is replaced by limestone powder, the amount of bound water (H) per OPC and the compressive strength increases, but the CH content decreases. A strength increase should correspond to an increase in hydration products formed (H). Assuming the following reaction for the hydration of the main OPC mineral alite (C_3S):

$$C_3S + 2.3\ H \rightarrow C_{1.7}SH + 1.3\ CH \qquad (1)$$

According to equation 1, a strength increase caused by an increase of hydration products like CSH would also implicate an increase in CH if the C/S of CSH remains constant. A decrease in the amount of CH and a corresponding increase in strength can only be explained by either the formation of CSH with a higher C/S ratio or the formation of other hydration products (e.g. alumina or iron rich hydration products) consuming CH.

The decrease in calcium hydroxide can be explained by the formation of calcium hemicarboaluminate hydrate ($C_3A \cdot 0.5CaCO_3 \cdot 0.5Ca(OH)_2 \cdot 11.5H_2O$) that in accordance with the formula will consume half a mole $Ca(OH)_2$ per mole $CaCO_3$ [7, 11, 27].

The amount of chemically bound water gives an indication about the degree of hydration, and therefore also for the strength development for a given cement. The compressive strength and amount of chemically bound water follow the same trend as they both increase when 5% of the OPC is replaced by limestone powder. For higher replacement levels (>5%) both properties decrease steadily (see Figure 8).

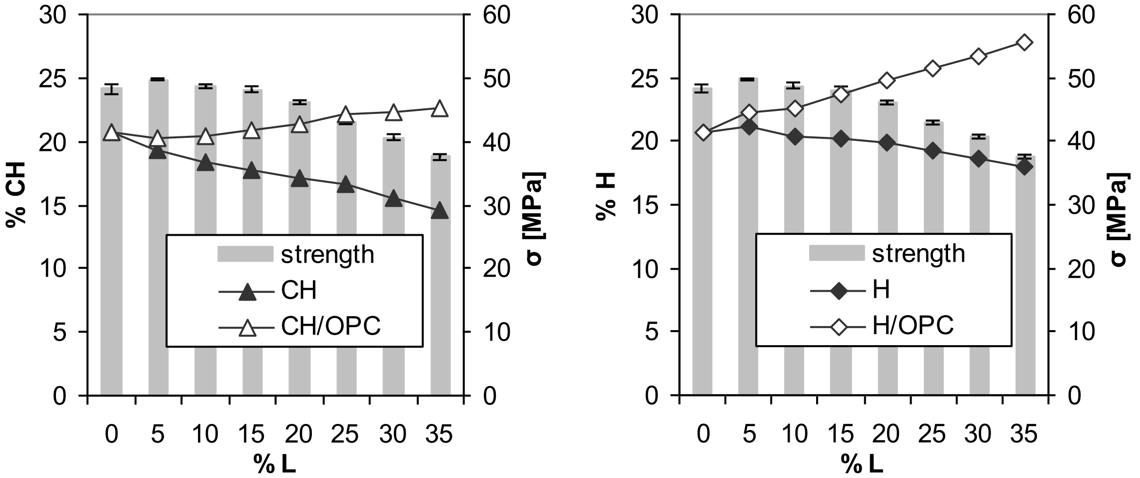

Figure 8: Comparison between the compressive strength and the amount of calcium hydroxide (CH) and bound water (H) both relative to the dry samples mass and the OPC content for limestone cements after 28 days of curing at 20°C.

In Figure 9 the compressive strength results are compared with the thermogravimetric (TG) results for different replacement levels of OPC with fly ash.

The amount of calcium hydroxide (CH) is given both relative to the dry sample mass and to the OPC content. The amount of CH relative to the dry sample mass, decreases due to the dilution effect. The amount of CH relative to the OPC content on the other hand increases due to the filler effect. Fly ash can react with the CH in a pozzolanic reaction and form hydration products similar to the ones of OPC. From the compressive strength results, it appeared that fly ash had not reacted that much after 28 days of curing at 20°C. The strength of the fly ash cements was similar to the corresponding limestone cements. The amount of CH relative to the OPC content flattens out at replacement levels above 15% and even decreases a bit at 35%. This might indicate that the fly ash has reacted somewhat. As more fly ash is present some more CH has been consumed.

The compressive strength is compared with the amount of bound water in Figure 9. The results correlate quite well as both the compressive strength and amount of chemically bound water are quite similar for the reference up to the one containing 10% fly ash but then decrease with increasing replacement level. The decreasing trend is due to the dilution effect. The filler effect on the other hand is visible when the amount of chemically bound water is expressed relative to the amount of OPC. The amount of chemically bound water relative to the OPC content increases with increasing OPC replacement.

In Figure 10 and Figure 11 the compressive strength results are compared with the thermogravimetric (TG) results for different combinations of fly ash and limestone powder replacing 35% of the OPC.

When 5% to 15% of the fly ash is replaced by limestone, the amount of CH decreases compared to the cement with 35% fly ash. Initially one would expect the opposite as the fly ash should consume CH during its pozzolanic reaction. Therefore a higher amount of fly ash should lead to less CH. The amount of produced CH starts to increase only when 20% of the limestone powder or more is included in the system. The decrease in CH is accompanied by an increase in compressive strength. The reason is probably, as described for OPC/limestone, that calcium hemicarboaluminate hydrate is formed.

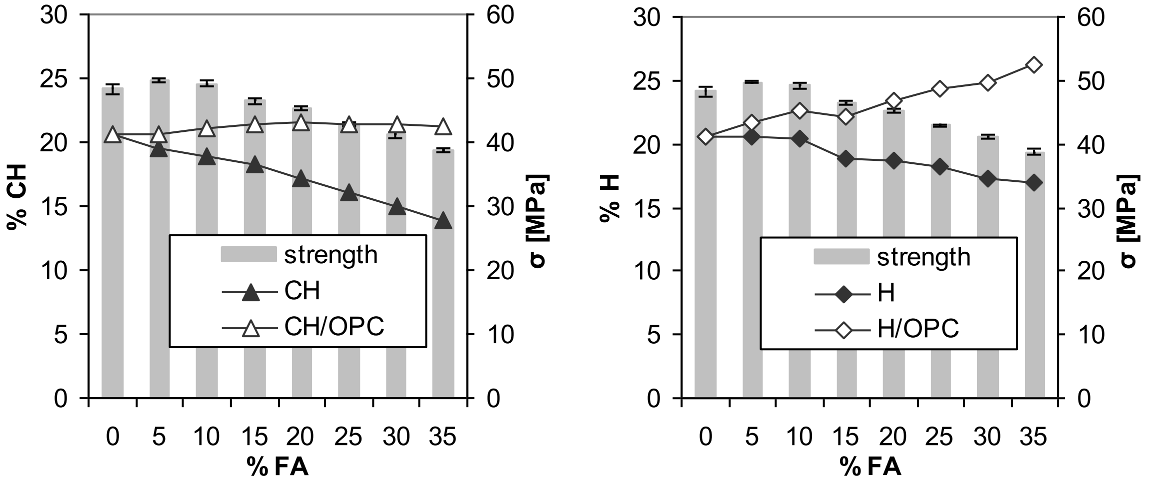

Figure 9: Comparison between the compressive strength and the amount of calcium hydroxide (CH) and bound water (H) both relative to the dry samples mass and the OPC content for fly ash cements after 28 days of curing at 20°C.

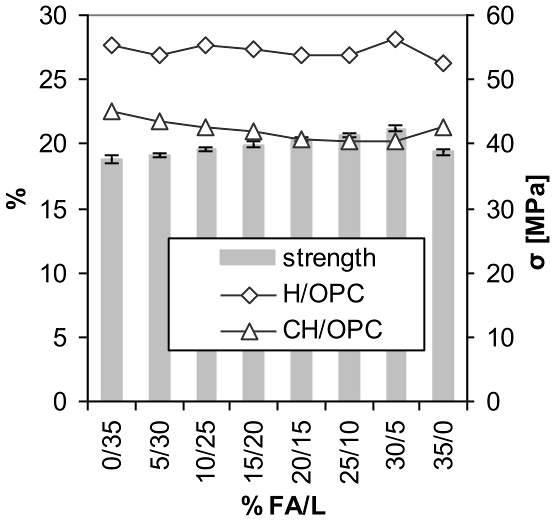

Figure 10: Comparison between the compressive strength and the amount of calcium hydroxide (CH) and bound water (H) relative to the OPC content for composite cements containing 65% OPC and a combination of fly ash and limestone powder after 28 days of curing at 20°C.

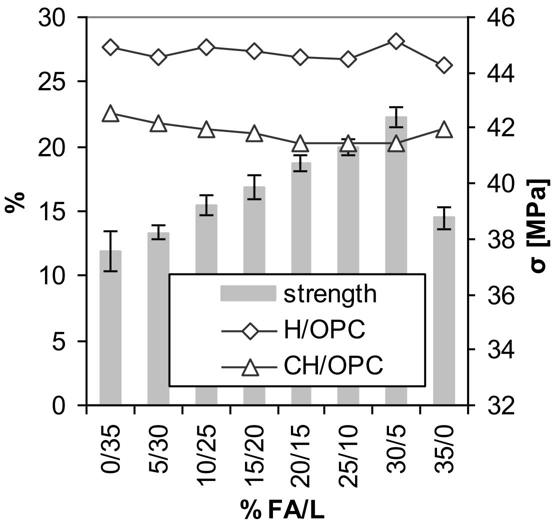

Figure 11: Magnification of the ordinate in Figure 10 in order to visualize the synergetic effect better.

From the previous results it can be concluded that an interesting phenomenon occurs when small amounts of limestone are used to replace both ordinary Portland cement and fly ash cement. The amount of CH decreases and the compressive strength increases. The effect on the fly ash cement seemed to be stronger than on the OPC, although the fly ash had not react that much. The thermogravimetric curves (TG-curves) and the differential thermogravimetric curves (DTG-curves) of some interesting combinations were compared in order to understand this phenomenon better. In Figure 12 the TG and DTG are depicted for 100%OPC cement and 100%OPC+5%L. Figure 13 shows the corresponding curves for 65%OPC+35%FA and 65%OPC+30%FA+5%L.

From Figure 12 it can be seen that the limestone containing cement binds about the same amount of water than the reference, as they reach about the same total weight loss at about

600°C. Some differences can be seen between the DTG-curves of the two cements. First there is the peak just above 100°C. This peak is partly due to the decomposition of ettringite. Limestone powder seems to stabilize the ettringite as expected. This peak should however always be interpreted with care as it is very sensitive to the preparation of the samples and the pre-drying. Secondly there is dissimilarity between 600°C and 800°C. This is due to the decomposition of the $CaCO_3$ present in the limestone powder. A remarkable difference between the two curves is the double peak for the reference around 180°C, which turns into a single peak when limestone is included in the system. The curves are also different between 200 and 400°C. The differences indicate that there is a change in hydration products when limestone powder is included in the system.

From Figure 13 it can be seen that when 5% of the fly ash is replaced by limestone powder more water is bound, as the total weight loss at about 600°C is larger. The DTG curves are fairly similar to the once shown in Figure 12, except for the weight changes at 750°C and higher, caused by the fly ash present in the system and the lower content of calcium hydroxide (between 400 and 500°C) due to the both dilution effect and slight pozzolanic reaction of the fly ash. Once more, the double peak around 180°C shown for the fly ash cement without limestone powder, turns into a single peak when limestone is included in the system and the ettringite appears to be stabilized.

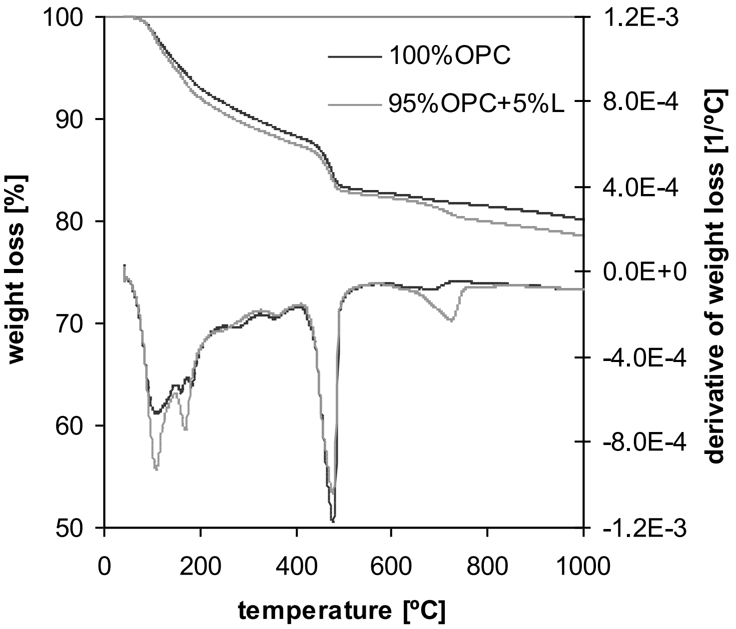

Figure 12: Thermogravimetric curves (TG) and differential thermogravimetric curves (DTG) for the reference (100% OPC) and a limestone cement (5% limestone powder + 95% OPC hydrated for 28 days).

In order to try to understand this change in hydration products X-ray diffraction analysis were performed. The cements tested were:

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

The pastes had hydrated for 28 days at 20°C when they were analysed.

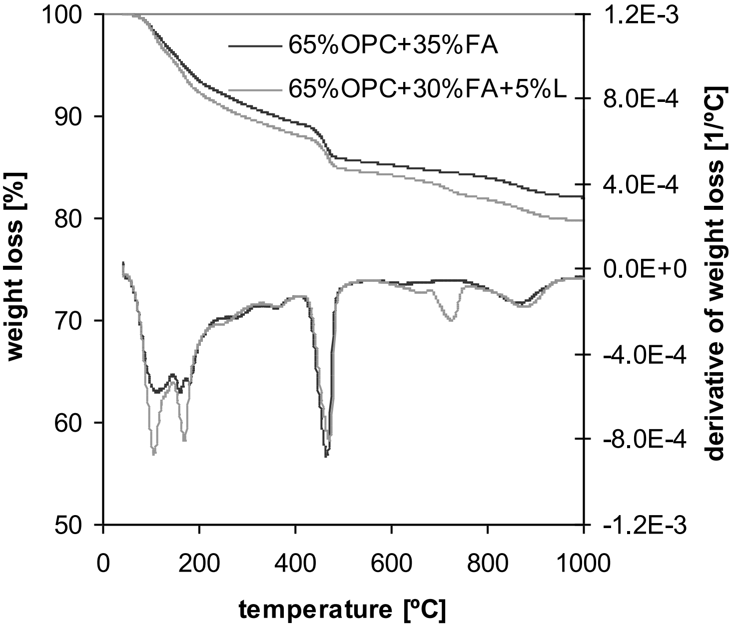

Figure 13: Thermogravimetric curves (TG) and differential thermogravimetric curves (DTG) for a fly ash cement containing 65% OPC and 35% fly ash and a composite cement containing 65% OPC, 5% limestone powder and 30% fly ash hydrated for 28 days.

In Figure 14 the XRD spectra of the tested cements are shown. The d-range of particular interest was enlarged and is shown in Figure 15. The main crystalline phases were:

• CH	portlandite	$Ca(OH)_2$
• Q	quartz	SiO_2
• $C\underline{C}$	calcium carbonate	$CaCO_3$
• E	ettringite	$C_3A \cdot 3CaSO_4 \cdot 32H_2O$
• MS	calcium monosulphoaluminate hydrate	$C_3A \cdot CaSO_4 \cdot 12H_2O$
• $M\underline{C}$	calcium monocarboaluminate hydrate	$C_3A \cdot CaCO_3 \cdot 11H_2O$
• $H\underline{C}$	calcium hemicarboaluminate hydrate	$C_3A \cdot 0.5CaCO_3 \cdot 0.5Ca(OH)_2 \cdot 11.5H_2O$

It can be seen that when limestone powder is present the calcium monosulphate hydrate disappears and instead ettringite, calcium monocarbonate hydrate and calcium hemicarbonate hydrate are formed.

The effect of small additions of limestone powder seemed to be more pronounced for the fly ash cements than for the ordinary Portland cement. This might be due to the liberation of additional aluminates by the fly ash. They cause a decrease of the sulphate/aluminate ratio of the system. Therefore relatively more calcium monosulphate hydrate than ettringite will form in the fly ash blended cement. The presence of limestone will then have a larger impact as more calcium monosulphate hydrate will shift to ettringite in a fly ash containing cement as calcium monocarboaluminate hydrate and calcium hemicarboaluminate hydrate are formed. This process will lead to relatively more bound water and higher total volume of hydrates, which in turn will decrease porosity and increase strength even more in the case of fly ash blended cements compared to OPC. The chemistry of this synergy was recently elaborated by De Weerdt and Justnes [30] .

The applicability of this study is proven by a pilot project recently launched by the Norwegian cement manufacturer Norcem using a “low carbon”, environmentally friendly cement containing 65%OPC, 30% fly ash and 5% limestone [31] .

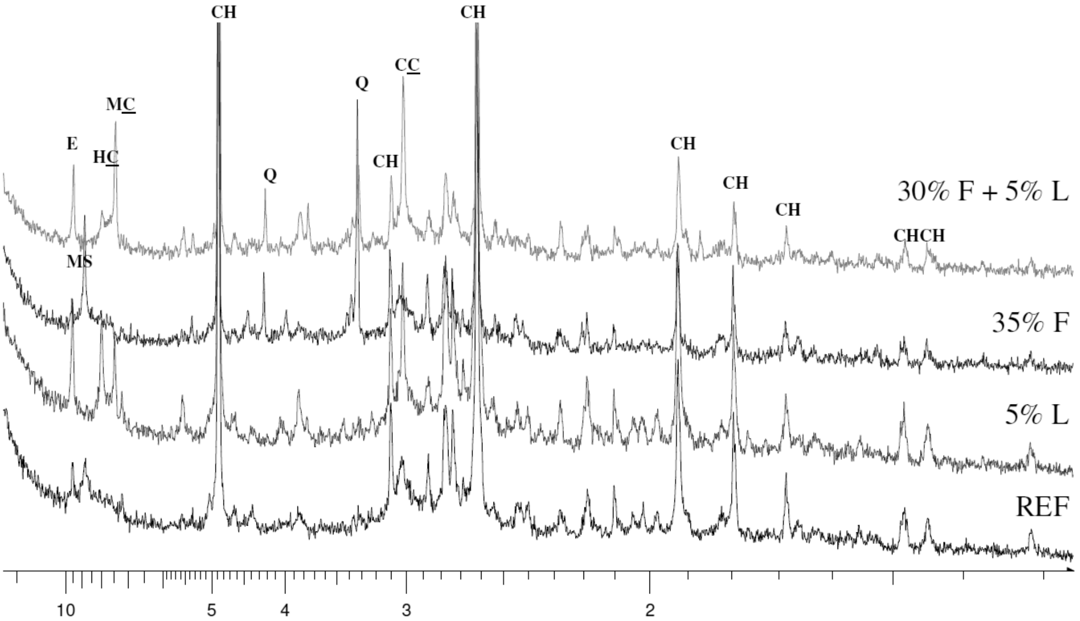

Figure 14: X-ray spectra for 100% OPC (REF), 95% OPC and 5% L (5% L), 65% OPC and 35% FA (35% F), and 65% OPC, 30% FA and 5% L (30% F + 5% L) all hydrated for 28 days at 20°C.

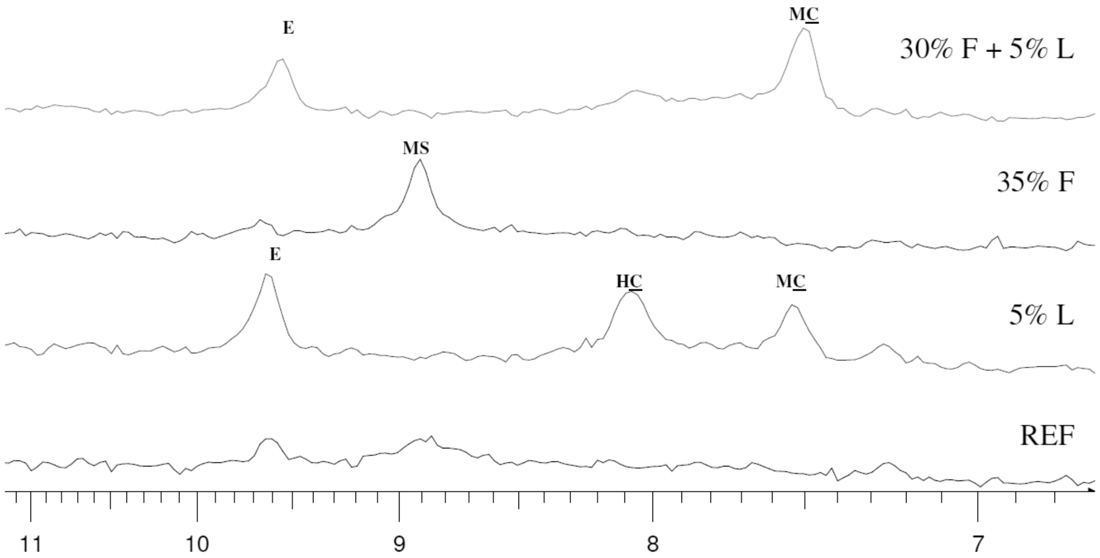

Figure 15: Zoomed in on the X-ray spectra for 100% OPC (REF), 95% OPC and 5% L (5% L), 65% OPC and 35% FA (35% F), and 65% OPC, 30% FA and 5% L (30% F + 5% L) all hydrated for 28 days at 20°C.

4 CONCLUSION

The compressive strength results at 28 days indicated a synergetic interaction between fly ash and limestone powder. Replacing 5% of fly ash with 5% of limestone powder in the 65% OPC + 35% FA cement resulted in a strength increase of about 10% (from 38 MPa to 42 MPa). The replacement of 5% OPC with limestone powder only resulted in a strength increase of about 4% (from 49.9 MPa to 51.8 MPa). Moreover, the combination 65% OPC + 30% FA + 5% L had a higher compressive strength after 28 days than the cement prepared with 70% OPC + 30% FA (41 MPa). This means that in this case it would be more beneficial to use 5% of limestone instead of 5% of OPC.

The thermogravimetric results showed that the hydration products change when limestone powder is included in the system. Moreover small additions of limestone resulted in a slight decrease of calcium hydroxide, indicating a possible formation of calcium hemicarboaluminate hydrate.

The X-ray diffraction results showed a change in crystalline hydration products. Calcium monosulphoaluminate hydrate disappears when limestone powder is present and instead ettringite, calcium monocarboaluminate hydrate and calcium hemicarboaluminate hydrate form.

It can be concluded that minor additions of limestone powder can have a beneficial effect on the strength development of Portland cement after 28 days of hydration most likely related to the interaction with the AFm and AFt phases. For fly ash containing cements this effect seems to be even greater.

Further research should be done to further explain this phenomenon. For example figuring out whether this is a pure chemical interaction or are there as well some physical effects playing a role in this, quantifying the chemical and physical effect etc. It is also important to look at how the interaction between fly ash and limestone powder evolves over time and how it will affect creep, shrinkage, durability, etc.

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