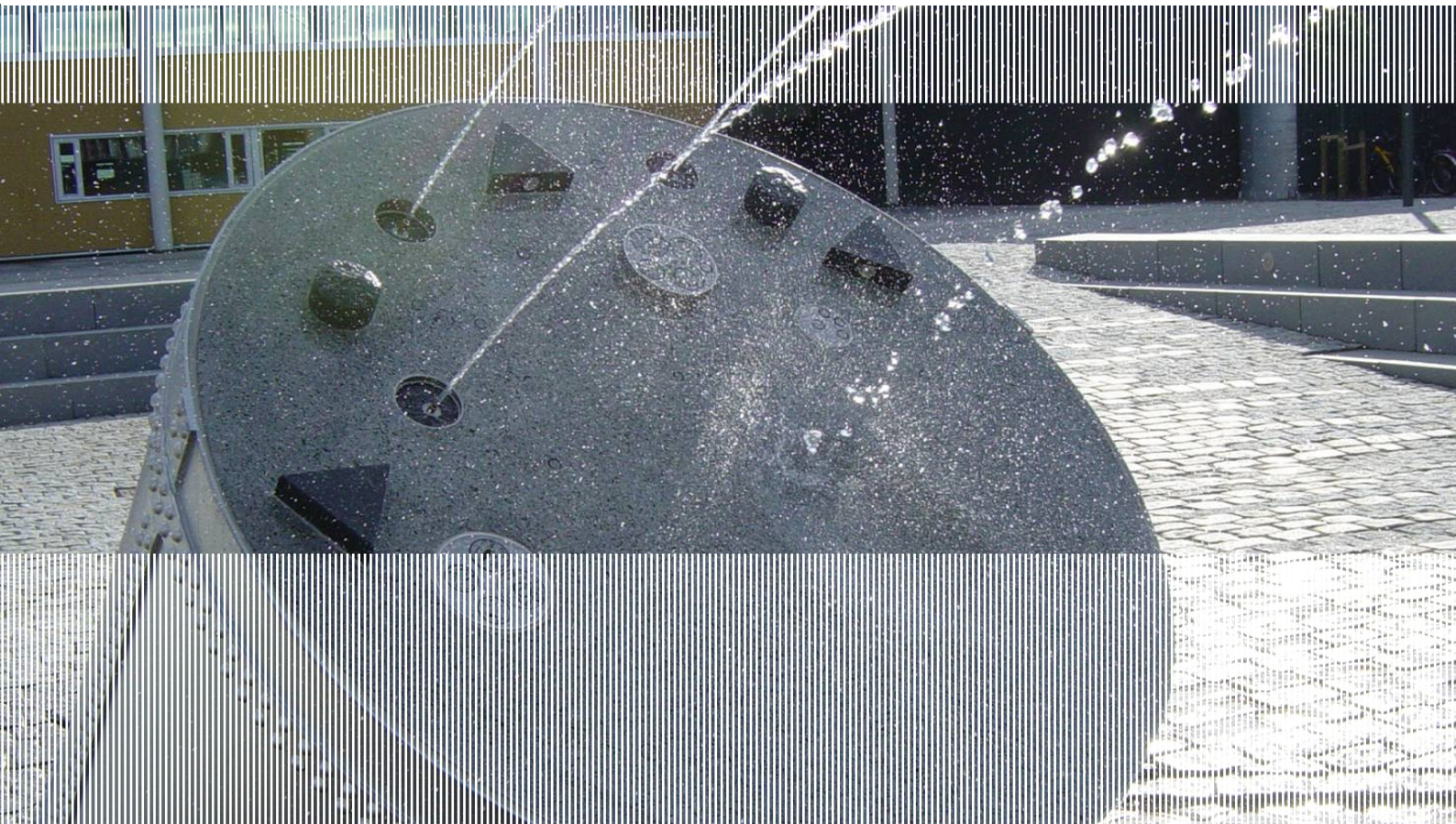


**SINTEF Building and Infrastructure** Klaartje De Weerd, Tone Østnor and Harald Justnes

# Fly ash – Limestone Synergy in Ternary Cements

COIN Project report 46 – 2013



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FA 1 Environmentally friendly concrete

SP 1.1 Low carbon-footprint binder systems

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## Preface

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This study has been carried out within COIN – Concrete Innovation Centre – one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfil this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 – 20 PhD-students, 5 – 10 MSc-students every year and a number of international guest researchers, work on presently eight projects in three focus areas:

- Environmentally friendly concrete
- Economically competitive construction
- Aesthetic and technical performance

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %).

For more information, see [www.coinweb.no](http://www.coinweb.no)

Tor Arne Hammer  
Centre Manager

## Summary

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The objective is to study the parameters of cements and fly ashes in combination with limestone that would optimize the synergistic chemical reaction between fly ash and limestone that leads to more bound water and thereby less porosity and higher compressive strength.

Most notably this will be the reactive aluminate content of cements and fly ashes and how these will be able to combine with limestone to calcium carboaluminate hydrate at a given point in time.

Four cement clinkers with two gypsum levels were combined with four different fly ashes and one limestone powder (the type used for raw meal in cement production).

The study was carried out in two steps: 1) Combination of clinkers with two levels of gypsum (1.5% and 3.0% replacing clinker) and 0 and 5% limestone powder replacing clinker + gypsum. 2) Clinkers, each with 3 % gypsum, replaced with 35% fly ash and where 0 or 5% fly ash was replaced with limestone.

The cement clinkers are usually believed to contain so little aluminate in the form of the mineral  $C_3A$  that the limestone has so little to react with in order to form calcium carboaluminate hydrate and stabilize ettringite (i.e. the synergic reaction) that the influence of limestone on the 28 days strength would be negligible. The 28 d strength was *mostly* unchanged when 5% limestone replaced cement (i.e. clinker + gypsum) which means that limestone actually has the same efficiency factor as cement with respect to 28 d strength, so it is likely that some reaction has happened.

However, there was a huge difference in 28 days strength between the clinkers, ranging from 44.6 MPa to 67.1 MPa when combined with for instance 3% gypsum. The reason for this is discussed, but it was not obvious from the clinker characteristics. Nevertheless, the clinker achieving the highest strength had the highest alite ( $C_3S$ ) content and either an aluminium-rich alite or an x-ray amorphous aluminium containing phase. This clinker was also the only clinker showing a significant strength increase when replaced with 5% limestone, indicating an aluminate interaction in spite of having lower  $C_3A$  content than other clinkers. Limestone replacing cement gave also the same 1 day strength as pure cement, indicating the same efficiency factor as cement.

Among the fly ashes in step 2, there were 3 ordinary fly ashes and 1 rich in anhydrite (12% calcium sulphate). The latter fly ash gave always the highest 28 days strength when 35% was replacing the four different clinkers with 3% gypsum. It raises the question whether or not one just as well could add more gypsum rather than limestone in combination with the fly ashes. Replacing 5% of the other 3 fly ashes with limestone gave always a strength increase, meaning the efficiency factor of limestone is higher than the fly ash, presumably due to the synergic reaction. The strength gain by limestone replacing fly ash combined with the different clinkers gave a good linear correlation with the amount of glass in the fly ash multiplied by the alumina content in that glass. This "multiplication factor" probably corresponds to the amount of alumina "easily" available by the fly ash to the system in the pozzolanic reaction and that the degree of reaction for the 3 fly ashes in the regression was about equal at 28 days.

Finally, mortars where 35% calcined marl replacing the clinkers with 3% gypsum were made in order to compare with the fly ash performance. Calcined marl gave higher strength than any of the fly ashes and even led to higher strength than mortars based on 100% clinker + gypsum for 3 out of 4 clinkers (even for the one with highest strength; 67.1 vs. 75.5 MPa).

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# 1 Introduction

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## 1.1 Principal objectives and scope

The objective is to study the parameters of cements and fly ashes in combination with limestone that would optimize the synergistic chemical reaction between fly ash and limestone that leads to more bound water and thereby less porosity and higher compressive strength.

Most notably this will be the reactive aluminate content of cements and fly ashes and how these will be able to combine with limestone to calcium carboaluminate hydrate at a given point in time.

## 1.2 Background

In the original COIN application under the sub-section **2.1.2 Reduced CO<sub>2</sub> emissions**, it was stated that COIN will concentrate on the “less Portland clinker in cement” approach with focus on *synergistic ternary blends*.

And this COIN application section continued: Supplementary cementing materials as pozzolana are well known in Norway through extensive research and application of Microsilica and in the later years also with fly ash interground with the clinker to modified cement. Cement with interground blast furnace slag is also a well-known combination internationally, but has only been used in the Norwegian market for a few years. There is also a trend for the cement industry to increase the amount of limestone filler in their bagged cements, since it is easy available as raw meal for clinker production. There is now for instance “Swedish Building cement” with 15% limestone filler interground. Limestone (i.e. calcium carbonate) has only a limited reactivity since there is little to react with (e.g. only a fraction of hydrated C<sub>3</sub>A that is not bound by sulphates). An interesting combination could be fly ash or blast furnace slag that produces large amounts of calcium aluminate hydrates together with limestone filler in a ternary blend. This would render a larger fraction of the limestone reacting to form calcium carboaluminate hydrate, Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>·CaCO<sub>3</sub>·11H<sub>2</sub>O. International studies have shown that the carboaluminate reaction is quite fast once calcium aluminate hydrate is available. Thus, such a ternary blend will probably lead to increasing strength and more importantly reduced permeability and thereby increased durability; a concept that will be pursued in COIN. However, replacing cement clinker with other powders will lead to lower early strength, limiting its use to special applications unless counteracted by energy consuming finer grinding. *The overall goal is to identify and document general purpose cementing materials that will decrease CO<sub>2</sub>-emissions by at least 30% from the average outlet of about 900 kg CO<sub>2</sub> per ton Portland cement clinker produced. (The combination of a rather cold climate and high productivity demand in Norway is the reason for a moderate minimum target. But on the other hand it is targeted for general purpose cement, not cement with limited use and thus, low impact on emissions.)*

The postulated principle of synergistic was actually based on the strength increase in limestone blended cement when TIPA (tri-isopropanol amine) was included [1] since this is an admixture well known to accelerate the reaction of C<sub>4</sub>AF that would supply more calcium aluminate hydrates to the system, combined with a more recent theoretical paper [2] proving that the reaction between C<sub>3</sub>A and CaCO<sub>3</sub> is much faster than originally expected and be complete in a matter of days.

The postulated synergy between aluminates (from cement and mineral additives) and limestone was then thoroughly studied and well proven in the PhD of Klaartje De Weerd resulting in a number of papers [3–10]. As an example of the synergistic effect, Fig.1 shows

compressive strength results on mortar prisms after 28 days of curing at 20°C for composite cements containing 65% OPC (Ordinary Portland Clinker) and different combinations of fly ash and limestone powder. A strength gain can be observed when replacing the fly ash partly with limestone powder. The highest strength gain is observed when 5% of fly ash is replaced with 5% of limestone powder while keeping a constant clinker replacement of 35%.

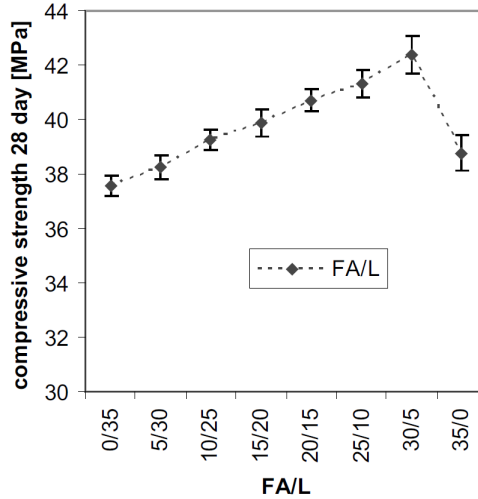


Fig.1 Compressive strength on mortar after 28 days of curing for composite cements containing different amounts of fly ash (FA) and limestone powder (L) after [5].

The synergetic effect between fly ash and limestone powder is attributed to impact of the  $\text{CaCO}_3$  from the limestone powder on the AFm phases (i.e. phases of the type calcium monosulphoaluminate hydrate where sulphate can be replaced with a number of anions and aluminate (A) can be partly replaced by iron (F)), which has been documented thoroughly for OPC [2, 11]. However the impact of the limestone powder is amplified as fly ash provides additional aluminates to the system by its pozzolanic reaction with calcium hydroxide from the cement hydration. The effect is demonstrated by Fig. 2 showing the volume of the hydration phases predicted by a thermodynamic Gibbs free energy minimization model, GEMS [12, 13], as function of the combination of fly ash and limestone powder (65% OPC + (35-x)% fly ash + x% limestone). Small additions of limestone powder result in the formation of calcium hemicarboaluminate hydrate (in short called hemicarbonate) instead of calcium monosulphoaluminate hydrate (in short called monosulphate) and thereby stabilizing ettringite. Larger limestone additions leads to the formation of calcium monocarboaluminate hydrate (in short called monocarbonate). Due to the difference in specific volume of these phases, and higher amount of hydrate water in ettringite or  $\text{AF}_t$  (32 mole) vs.  $\text{AF}_m$  (12 mole), an increase in the total volume of hydration phases can be observed. This will in turn lead to a reduction in porosity and consequently to an increase in strength.

It should be mentioned that even though the enhancement of monocarbonate formation by fly ash and limestone was postulated in the original COIN application, the phase of hemicarbonate was not foreseen, and maybe more importantly the stabilization of ettringite on the expenses of monosulphate leading to even more bound water in the system and thereby higher strength.

The synergistic effect was demonstrated for one type of clinker and fly ash in the PhD of Klaartje De Weerd. Hence there was a need to verify whether this synergetic effect between fly ash and limestone is valid for different fly ashes and clinkers, and in particularly the effect of varying alumina content both in clinker and in fly ash. Therefore, the PhD work was extended accordingly as an activity in COIN and this report is a part of the result reporting from that activity.



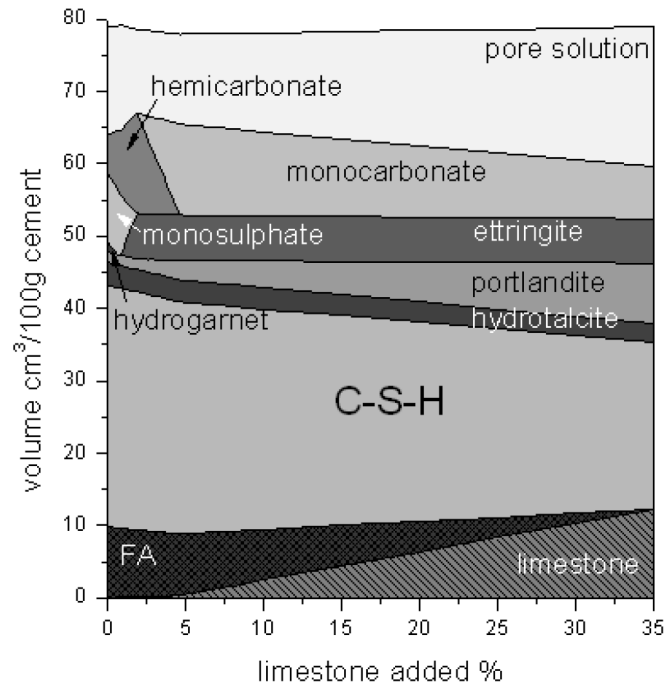


Fig.2 Phase assemblage predicted by GEMS for different combinations of fly ash and limestone powder replacing 35% of the OPC (65% OPC + (35-x)% fly ash + x% limestone) after [10].

## 2 Experimental

### 2.1 Materials

The materials used in this study were 4 different Portland clinkers, 4 different fly ashes, one type of limestone powder and laboratory grade gypsum.

The chemical composition of the clinkers as determined by XRF and their physical properties; loss on ignition to 950°C (%), specific surface according to the Blaine method (m<sup>2</sup>/kg) and density by Helium pycnometry (kg/dm<sup>3</sup>) are given in Table 1. Table 2 shows the content of the main phases for the different clinkers as obtained by Rietveld analyses of the X-ray diffraction profiles, which is significantly more correct than by the Bogue-analyses in Table 3 based on mass balances and the assumptions that only the pure phases C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF exist, and that A/F = 1 in the latter phase.

The chemical composition of the fly ashes as determined by XRF and their physical properties; specific surface according to the Blaine method (m<sup>2</sup>/kg) and density by Helium pycnometry (kg/dm<sup>3</sup>), are given in Table 4. The main oxides composing the reactive glassy phase of the fly ashes shown in Table 5 were obtained by subtracting the oxides present in the inert crystalline phases determined by Rietveld analyses of X-ray diffraction profiles from the total amount of oxides determined by XRF.

The limestone powder had a CaCO<sub>3</sub> content of 81% as determined by both Rietveld analysis of the X-ray diffraction profile, as well as thermogravimetric analysis (TGA). The limestone was of the quality used for composition of the raw meal for clinker production at Norcem.

Table 1 Chemical composition (%) and physical properties of the clinkers

Cements	$\alpha$	$\beta$	$\gamma$	$\delta$
SiO <sub>2</sub>	20.3	21.3	21.8	23.4
Al <sub>2</sub> O <sub>3</sub>	5.7	5.4	4.3	4.0
Fe <sub>2</sub> O <sub>3</sub>	3.3	3.9	5.6	0.2
CaO	61.3	63.5	61.4	67.0
MgO	2.9	1.9	2.1	1.1
K <sub>2</sub> O	1.2	0.4	0.4	0.5
Na <sub>2</sub> O	0.5	0.3	0.3	0.0
SO <sub>3</sub>	1.5	0.4	1.2	1.6
LOI 950°C	1.9	0.5	0.5	0.7
Sum above	98.6	97.6	97.6	98.5
Blaine (m <sup>2</sup> /kg)	449	432	426	457
Density (g/cm <sup>3</sup> )	3.1	3.1	3.2	3.1

Table 2 XRD-Rietveld analysis of the clinker phases (%)

cements	$\alpha$	$\beta$	$\gamma$	$\delta$
C <sub>3</sub> S	49.1	59.9	45.6	63.6
C <sub>2</sub> S	25.6	18.8	33.3	30.3
C <sub>3</sub> A	10.0	4.6	0.3	3.2
C <sub>4</sub> AF	10.2	14.1	18.5	0.0
Sum	94.9	97.4	97.7	97.1

From the low  $C_3A$  content of clinker  $\gamma$  in Table 2, it can be seen that it is a sulphate resistant cement clinker. The absence of the  $C_4AF$  in clinker  $\delta$  reveals that it is a white clinker.

Table 3 Mineral composition of the clinkers from Bogue-calculations based on the oxide compositions in Table 1.

<b>cements</b>	<b><math>\alpha</math></b>	<b><math>\beta</math></b>	<b><math>\gamma</math></b>	<b><math>\delta</math></b>
$C_3S$	52.3	54.8	47.4	67.8
$C_2S$	18.8	19.8	26.8	16.0
$C_3A$	9.5	7.7	1.9	10.3
$C_4AF$	10.0	11.8	17.0	0.6
<b>Sum</b>	<b>94.9</b>	<b>97.4</b>	<b>97.7</b>	<b>97.1</b>

Table 4 Chemical composition (%) and physical properties of the fly ashes

<b>Fly ash</b>	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
$SiO_2$	52.9	47.6	53.7	38.7
$Al_2O_3$	26.4	27.8	22.7	19.6
$Fe_2O_3$	6.3	5.5	5.7	6.0
CaO	3.3	7.2	5.1	17.9
MgO	2.8	2.3	2.3	2.0
$K_2O$	3.0	1.4	2.1	2.5
$Na_2O$	1.0	0.6	1.0	0.7
$SO_3$	0.2	0.5	0.2	6.6
LOI	1.8	3.3	4.5	3.4
Sum above	97.7	96.2	97.3	97.4
Blaine ( $m^2/kg$ )	250	400	395	734
Density ( $g/cm^3$ )	2.2	2.4	2.3	2.6

Table 5 Glass composition (%) of the fly ashes

<b>Fly ash</b>	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
$SiO_2$	38.0	30.1	39.4	26.3
$Al_2O_3$	15.6	10.3	13.9	19.6
$Fe_2O_3$	4.3	5.5	6.6	6.6
CaO	2.4	5.6	4.7	11.5
MgO	2.8	2.3	2.3	2.3
$K_2O$	3.0	1.4	3.0	3.0
$Na_2O$	1.0	0.6	0.5	0.5
Sum above	67.1	55.9	70.4	69.8
<i>total amorphous</i>	<i>69.6</i>	<i>59.1</i>	<i>73.2</i>	<i>64.5</i>

Fly ashes A, B and C are siliceous fly ashes according to EN 197-1 as their CaO content is lower than 10% as shown in Table 4. Fly ash D, on the other hand, is denoted as calcareous fly ash due to its high content of CaO.

## 2.2 Strength test

Mortar mixes were made consisting of 450 g reactive powder (i.e. clinker, gypsum, fly ash and limestone), 1350 g norm sand (sand : reactive powder = 3:1) and water to make a water-to-reactive powder ratio of 0.50. This makes about one liter of fresh mortar sufficient to fill 3 pieces of 40x40x160 mm RILEM steel moulds. The mortar prisms were demoulded after 1 day and allowed to cure until 28 days in saturated lime water at 20°C. Then the flexural strength was tested in a 3 point bending mode on the three parallel prisms and the compressive strength on the 6 resulting end-pieces.

## 2.3 Test programs

The test program was divided in 2 steps.

In step 1, all clinkers were blended with 2 levels of gypsum (1.5% and 3% *replacing* clinker) and blended with 0, 3 and 5% limestone powder as a *clinker only replacement*. This means that the mix with lowest content of gypsum and no limestone had the highest clinker content of  $450\text{g} \times (1-0.015) = 443\text{ g}$ , and the mix with the highest gypsum and limestone content had the lowest clinker content of  $450\text{g} \times (1-0.03-0.05) = 414\text{ g}$ , or 6.5% less than the one with the highest clinker content. The strength was measured for all clinkers at 28 days, and as an addition for 2 clinkers at 1 day just after demoulding to check the filler effect of the limestone powder.

In step 2, clinker was replaced with 3% gypsum, and clinker with gypsum was replaced either with 35% fly ash and no limestone or 30% fly ash and 5% limestone as outlined in Table 6 for clarity. The mixes were performed for all combinations of the 4 clinkers and the 4 fly ashes.

Table 6 Mix compositions tested

Mixes	35-0	30-5
97% clinker + 3% gypsum	65%	65%
fly ash	35%	30%
limestone	0%	5%

In addition, as comparison, mixes were made where all clinkers were replaced with 35% calcined "marl" (or more correctly "calcareous mud" since it contained only 20%  $\text{CaCO}_3$  prior to calcination and the remainder largely being clay minerals).

This means that the reactive powder mix consisting of clinker, gypsum, fly ash and limestone had a constant clinker content of  $450\text{ g} \times (1-0.03-0.35) = 279\text{ g}$  for all the batches.

In the second step only 5 end pieces instead of 6 from the mortars as usual were used for parallel testing of compressive strength, the 6<sup>th</sup> end-piece was stored in lime water until further testing of the microstructure at a later point (COIN activity in 2013).

### 3 Results and discussion

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#### 3.1 Step 1 – strength of mortar based on clinker, gypsum and limestone

##### 3.1.1 28 days strengths

The compressive and flexural strength together with their standard deviations after 28 days curing are given for all the mixes of clinkers  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  in Tables 7-10, respectively. Comparative plots for the compressive and flexural strength at 28 days for all mixes are shown in Figures 3 and 4, respectively.

Clinker  $\alpha$  with gypsum level of 3.0% gives higher compressive strength (about +13% or 5 MPa extra) both without and with limestone compared to the series with 1.5% gypsum. There is no effect on the compressive strength by limestone filler replacing clinker at any of the 3 limestone levels (0, 3 and 5%), which means that limestone has the same efficiency factor as clinker probably due to the relatively high  $C_3A$  (10.0%) or total  $Al_2O_3$  (5.7%) content for calcium carbonate to react with.

Clinker  $\beta$  with gypsum level of 3.0% gives higher compressive strength (about +10% or 5 MPa extra) without limestone compared to the mix with 1.5% gypsum. There is no effect on the compressive strength by limestone filler replacing clinker at the highest gypsum level, but there is a steady decline of compressive strength with increasing limestone replacement for the lowest gypsum level. The  $C_3A$  content is lower (4.6%) than for clinker  $\alpha$ , but total  $Al_2O_3$  (5.4%) is roughly the same. Total  $Al_2O_3$  is indicative of the potential calcium aluminate hydrate that can be formed and react with calcium carbonate, and it is distributed between  $C_3A$ ,  $C_4AF$  and as a contaminant in  $C_3S$ .  $C_3A$  and  $C_3S$  react much faster than  $C_4AF$  and are expected to release their aluminate faster to the synergic reactions with limestone. In spite of the same total  $Al_2O_3$ , the  $\beta$  clinker has lower  $SO_3$  content than in  $\alpha$  clinker (0.4% versus 1.5%  $SO_3$ , which would correspond to 0.9% versus 3.2% in terms of gypsum). It seems therefore that clinker  $\beta$  with 1.5% gypsum added is under-sulphated in order to take full advantage of the extra ettringite formation associated with the formation of carboaluminates in the synergic reaction with limestone as an explanation of the decline in strength with increasing limestone replacing clinker, while this is not the case for the 3% gypsum level.

For the  $\gamma$  clinker without limestone, the 3% gypsum gives higher strength than for 1.5% gypsum (64.1 vs. 62.9 MPa), but not significantly considering the unusual high standard deviation (2.7 MPa) for the highest strength. With limestone the strength level is independent of gypsum level and with a slight tendency (may not be significant) of decreasing strength with increasing clinker replacement with limestone. Clinker  $\gamma$  is the one with lowest content of  $C_3A$  (0.3%) amongst the clinkers tested, but with a total  $Al_2O_3$  content of 4.3% mostly bound as  $C_4AF$  (18.5%).

For the  $\delta$  clinker without limestone the strength is the same irrespectively of the gypsum content, but when clinker is replaced with limestone the strength increases significantly more for the lowest gypsum content than for the higher gypsum dosage. This clinker contains only 3.2%  $C_3A$  and no  $C_4AF$ , but with a total  $Al_2O_3$  content of 4.2% presumably mostly bound as contaminations in the high content of  $C_3S$  (63.6%) since  $C_3A$  only can account for 1.2% of total  $Al_2O_3$ . Due to the lack of iron in clinker  $\delta$ , it is likely that some fluoride is used as a fluxing agent in the clinkerization process, which in turn will enhance inclusion of alumina into the  $C_3S$  phase. Comparing the mineral composition by Bogue calculation in Table 3 vs. the Rietveld analysis of XRD in Table 2, it is clear that the calculated  $C_3A$  content is much higher than observed (10.3% vs. 3.2%) indicated a high content of alumina in  $C_3S$  or the existence of another alumina bearing phase not detectable by XRD (e.g. gehlenite glass). All alumina is assumed to be readily available for this clinker since  $C_3S$  and  $C_3A$  are the fastest reacting phases. Thus, 1.5% gypsum seems to under-sulphate this clinker and can explain the

Table 7 Compressive ( $\sigma_c$ ) and flexural ( $\sigma_f$ ) strength (in MPa) with standard deviations (St. dev.) for all mixes with clinker  $\alpha$  at 28 days age.

Sample	Individual $\sigma_c$	Average $\sigma_c$	St. dev. $\sigma_c$	Individual $\sigma_f$	Average $\sigma_f$	St. dev. $\sigma_f$
$\alpha$ -0%L/1.5%G	39.3	<b>39.5</b>	<b>0.8</b>	6.5	<b>6.6</b>	<b>0.1</b>
	39.7			6.7		
	38.6			6.7		
	40.5					
	38.6					
	40.1					
$\alpha$ -0%L/3%G	43.9	<b>44.6</b>	<b>0.6</b>	7.6	<b>7.2</b>	<b>0.3</b>
	44.7			7.1		
	43.9			7.0		
	45.1					
	44.9					
	45.1					
$\alpha$ -3%L/1.5%G	40.5	<b>40.9</b>	<b>0.4</b>	6.4	<b>6.8</b>	<b>0.3</b>
	41.1			6.9		
	40.5			7.0		
	41.1					
	40.5					
	41.4					
$\alpha$ -3%L/3%G	45.1	<b>44.9</b>	<b>0.5</b>	7.5	<b>7.7</b>	<b>0.3</b>
	44.7			7.6		
	44.5			8.0		
	44.9					
	44.5					
	45.7					
$\alpha$ -5%L/1.5%G	40.7	<b>40.5</b>	<b>0.6</b>	6.7	<b>6.8</b>	<b>0.3</b>
	40.3			7.2		
	39.7			6.6		
	40.3					
	40.3					
	41.4					
$\alpha$ -5%L/3%G	43.6	<b>44.5</b>	<b>0.9</b>	7.2	<b>7.4</b>	<b>0.2</b>
	45.5			7.5		
	43.6			7.6		
	44.3					
	44.5					
	45.5					

Table 8 Compressive ( $\sigma_c$ ) and flexural ( $\sigma_f$ ) strength (in MPa) with standard deviations (St. dev.) for all mixes with clinker  $\beta$  at 28 days age.

Sample	Individual $\sigma_c$	Average $\sigma_c$	St. dev. $\sigma_c$	Individual $\sigma_f$	Average $\sigma_f$	St. dev. $\sigma_f$
$\beta$ -0%L/1.5%G	54.7	<b>54.9</b>	<b>0.6</b>	7.1	<b>7.2</b>	<b>0.2</b>
	55.3			7.0		
	53.9			7.4		
	54.5					
	55.7					
	55.0					
$\beta$ -0%L/3%G	59.3	<b>60.1</b>	<b>0.5</b>	7.8	<b>7.6</b>	<b>0.3</b>
	60.1			7.7		
	59.5			7.2		
	60.5					
	60.5					
	60.5					
$\beta$ -3%L/1.5%G	52.2	<b>52.5</b>	<b>0.5</b>	7.6	<b>7.5</b>	<b>0.2</b>
	53.2			7.7		
	52.0			7.3		
	52.8					
	52.2					
	52.6					
$\beta$ -3%L/3%G	60.1	<b>60.2</b>	<b>0.6</b>	7.4	<b>7.8</b>	<b>0.3</b>
	60.1			8.0		
	60.3			7.9		
	60.1					
	61.1					
	59.3					
$\beta$ -5%L/1.5%G	49.9	<b>50.1</b>	<b>0.8</b>	7.5	<b>7.5</b>	<b>0.1</b>
	48.6			7.6		
	50.3			7.5		
	50.5					
	50.5					
	50.9					
$\beta$ -5%L/3%G	58.6	<b>59.6</b>	<b>0.6</b>	7.4	<b>7.7</b>	<b>0.4</b>
	60.1			7.7		
	59.5			8.1		
	59.5					
	60.1					
	59.9					

Table 9 Compressive ( $\sigma_c$ ) and flexural ( $\sigma_f$ ) strength (in MPa) with standard deviations (St. dev.) for all mixes with clinker  $\gamma$  at 28 days age.

Sample	Individual $\sigma_c$	Average $\sigma_c$	St. dev. $\sigma_c$	Individual $\sigma_f$	Average $\sigma_f$	St. dev. $\sigma_f$
$\gamma$ -0%L/1.5%G	63.8	<b>62.9</b>	<b>1.1</b>	7.8	<b>7.6</b>	<b>0.3</b>
	52.7			7.6		
	62.9			7.3		
	63.4					
	63.4					
	61.1					
$\gamma$ -0%L/3%G	62.2	<b>64.1</b>	<b>2.7</b>	7.6	<b>7.8</b>	<b>0.3</b>
	58.9			7.7		
	63.5			8.1		
	68.8					
	62.9					
	62.9					
$\gamma$ -3%L/1.5%G	61.8	<b>61.8</b>	<b>0.5</b>	8.1	<b>7.9</b>	<b>0.2</b>
	62.4			7.9		
	61.1			7.7		
	61.7					
	61.5					
	62.5					
$\gamma$ -3%L/3%G	61.5	<b>62.3</b>	<b>1.1</b>	?	<b>?</b>	<b>?</b>
	61.9			?		
	62.6			?		
	64.0					
	60.8					
	63.0					
$\gamma$ -5%L/1.5%G	61.1	<b>61.7</b>	<b>1.1</b>	8.0	<b>8.1</b>	<b>0.2</b>
	60.6			8.3		
	62.8			7.9		
	61.1					
	63.1					
	53.9					
$\gamma$ -5%L/3%G	60.5	<b>61.1</b>	<b>0.7</b>	8.9	<b>8.4</b>	<b>0.4</b>
	61.4			8.2		
	61.0			8.2		
	60.3					
	62.3					
	60.9					

? = not measured



Table 10 Compressive ( $\sigma_c$ ) and flexural ( $\sigma_f$ ) strength (in MPa) with standard deviations (St. dev.) for all mixes with clinker  $\delta$  at 28 days age.

Sample	Individual $\sigma_c$	Average $\sigma_c$	St. dev. $\sigma_c$	Individual $\sigma_f$	Average $\sigma_f$	St. dev. $\sigma_f$
$\delta$ -0%L/1.5%G	57.1	<b>67.1</b>	<b>1.7</b>	7.7	<b>7.8</b>	<b>0.1</b>
	66.9			7.7		
	67.6			7.9		
	65.0					
	58.1					
	69.0					
$\delta$ l-0%L/3%G	67.9	<b>67.1</b>	<b>2.1</b>	8.7	<b>8.4</b>	<b>0.3</b>
	66.6			8.4		
	64.3			8.2		
	67.9					
	70.3					
	65.8					
$\delta$ -3%L/1.5%G	67.2	<b>73.4</b>	<b>1.4</b>	8.6	<b>8.6</b>	<b>0.0</b>
	73.1			8.6		
	71.9			8.6		
	73.4					
	75.3					
	66.8					
$\delta$ -3%L/3%G	70.1	<b>68.5</b>	<b>1.5</b>	8.8	<b>8.5</b>	<b>0.3</b>
	66.9			8.5		
	68.1			8.3		
	69.9					
	69.4					
	66.6					
$\delta$ -5%L/1.5%G	75.5	<b>72.7</b>	<b>1.7</b>	8.7	<b>8.4</b>	<b>0.3</b>
	71.1			8.2		
	72.9			8.2		
	72.5					
	70.7					
	73.5					
$\delta$ -5%L/3%G	63.6	<b>69.8</b>	<b>1.6</b>	8.8	<b>8.6</b>	<b>0.2</b>
	69.8			8.6		
	69.0			8.4		
	68.1					
	72.5					
	69.6					

more beneficial effect of limestone at this gypsum level since may be some ettringite relative to none is formed together with carboaluminate, while for the higher gypsum level there is less AFm for carbonate to react with since some has already reacted to ettringite that is stable towards calcium carbonate.

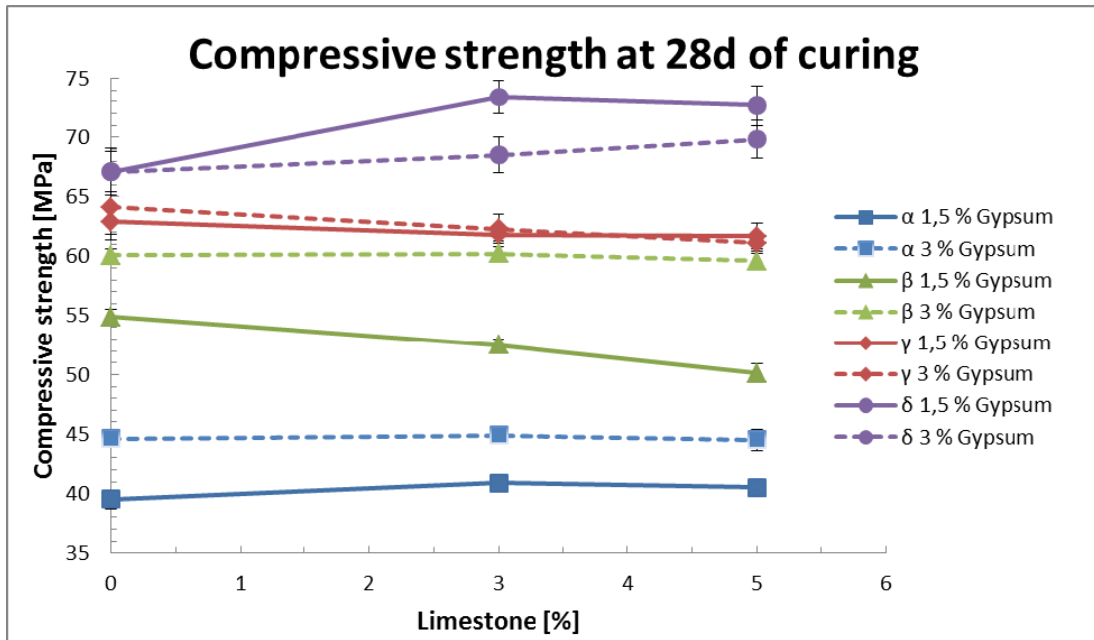


Fig. 3 Comparative plots of compressive strength at 28 days for mortars of all clinkers with 2 levels of gypsum as a function of limestone powder content when cured at 20°C.

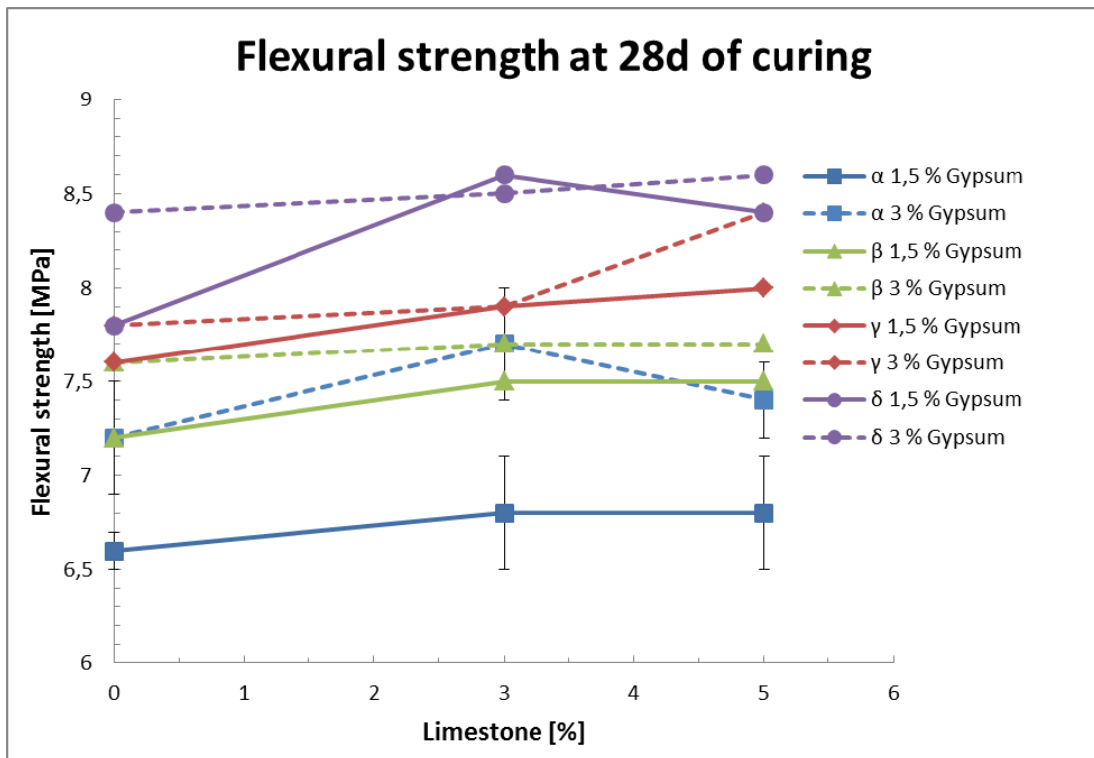


Fig. 4 Comparative plots of flexural strength at 28 days for mortars of all clinkers with 2 levels of gypsum as a function of limestone powder content when cured at 20°C.

When looking at the compressive strength plots of Fig. 3, the most striking effect is the huge difference ranging from 44.6 MPa for clinker  $\alpha$  to 67.1 MPa for clinker  $\delta$  in the case of 3% gypsum and no limestone powder. There is no apparent correlation between the chemical and physical parameters of clinker and the resulting compressive strength. In this respect, clinker  $\beta$  seems to achieve lower strength than expected, while clinker  $\gamma$  achieves higher strength than expected.

However, it is possible to get a linear correlation ( $r^2 = 0.9983$ ) between a calculated factor

$$\text{Blaine} \cdot (a \cdot \%C_3S + b \cdot \%C_2S + c \cdot \%C_3A + d \cdot \%C_4AF)$$

and observed compressive strength when  $a = 0.8$ ,  $b = 0.7$ ,  $c = 0.0$  and  $d = 0.9$  as shown in Fig. 5. The factors a-d will then be a multiplication of degree of reaction of the mineral and its relative contribution to strength. This would make sense for b versus a since even though alite probably has higher degree of hydration than belite at 28 days, the hydration product of belite is believed to contribute more to strength than for alite. However, it does not make sense to set  $c = 0$  since that would mean in spite of high degree of  $C_3A$  hydration that its hydration products would contribute insignificantly to 28 days compressive strength.

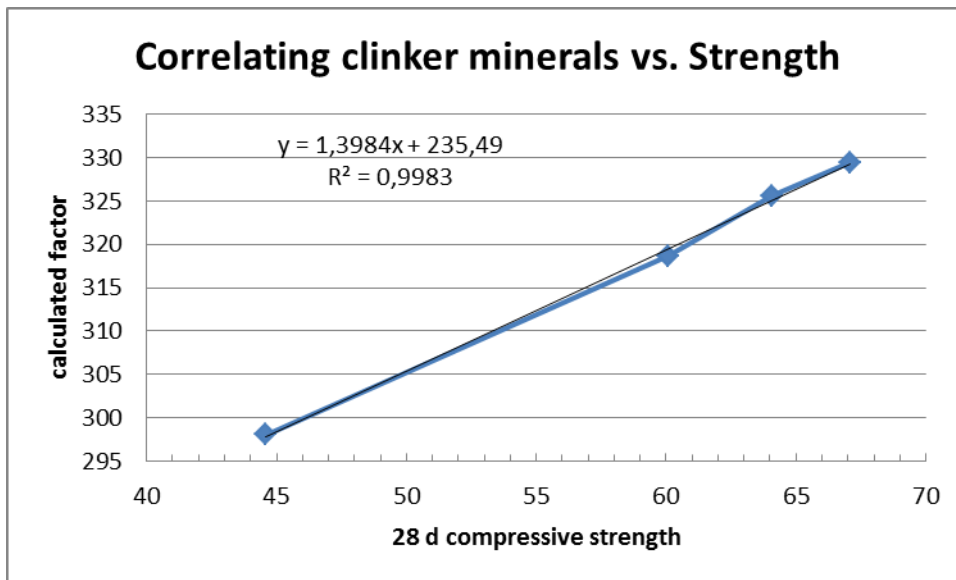


Fig. 5 An attempt to correlate characteristics of clinkers to their strength when they all are replaced with 3% gypsum.

A more complex approach is needed to explain the difference in strength levels, and TAC 1 in COIN decided to investigate the microstructure of hydrated clinkers in 2013 as well as differences in reactivity of interstitial phases ( $C_3A + C_4AF$ ) after extraction from the clinkers.

### 3.1.2 1 day strengths

The two clinkers  $\alpha$  and  $\delta$  was selected for extra mixes with all levels of limestone and the highest gypsum level (3%) in order to measure the strengths after demoulding at 1 day to check the magnitude of the filler effect of limestone powder. The compressive and flexural strength together with their standard deviations after 1 day (exactly 24 h) curing are given for these additional mixes of clinkers  $\alpha$  and  $\delta$  in Tables 11 and 12, respectively. Comparative plots for the compressive and flexural strength at 1 day for the additional mixes of both clinkers are shown in Figures 6 and 7, respectively.

Table 11 Compressive ( $\sigma_c$ ) and flexural ( $\sigma_f$ ) strength (in MPa) with standard deviations (St. dev.) for all mixes with clinker  $\alpha$  and 3% gypsum at 1 days age.

Sample	Individual $\sigma_c$	Average $\sigma_c$	St. dev. $\sigma_c$	Individual $\sigma_f$	Average $\sigma_f$	St. dev. $\sigma_f$
$\alpha$ -0%L/3%G	14.9	<b>14.9</b>	<b>0.2</b>	3.3	<b>3.3</b>	<b>0.1</b>
	14.6			3.2		
	14.7			3.4		
	15.1					
	14.9					
	15.2					
$\alpha$ -3%L/3%G	15.3	<b>15.2</b>	<b>0.1</b>	3.4	<b>3.4</b>	<b>0.2</b>
	15.1			3.2		
	15.1			3.6		
	15.2					
	15.5					
	15.2					
$\alpha$ -5%L/3%G	15.5	<b>15.1</b>	<b>0.3</b>	3.6	<b>3.5</b>	<b>0.1</b>
	15.1			3.5		
	15.2			3.5		
	15.3					
	14.7					
	14.8					

As seen from the results in Table 11, replacing clinker  $\alpha$  with limestone up to 5% did not change the compressive strength significantly, meaning that the efficiency factor of limestone is equal to clinker in terms of strength. The synergistic reactions have probably not taken place this early, so the equal efficiency factor of limestone powder and clinker is attributed to 1) the acceleration of setting due to calcium carbonate acting as nucleation sites for early hydration products and 2) acceleration of the hydration rate due to the dispersion effect of limestone powder bringing cement grains further apart and exposing more reacting surface towards water at the early stage.

Table 12 Compressive ( $\sigma_c$ ) and flexural ( $\sigma_f$ ) strength (in MPa) with standard deviations (St. dev.) for all mixes with clinker  $\delta$  and 3% gypsum at 1 days age.

Sample	Individual $\sigma_c$	Average $\sigma_c$	St. dev. $\sigma_c$	Individual $\sigma_f$	Average $\sigma_f$	St. dev. $\sigma_f$
$\delta$ -0%L/3%G	26.7	<b>26.6</b>	<b>0.4</b>	5.2	<b>5.1</b>	<b>0.3</b>
	26.2			5.3		
	26.6			4.7		
	27.3					
	26.6					
	26.1					
$\delta$ -3%L/3%G	26.0	<b>26.4</b>	<b>0.5</b>	5.0	<b>5.0</b>	<b>0.2</b>
	25.9			5.2		
	26.1			4.9		
	26.9					
	26.8					
	27.1					
$\delta$ -5%L/3%G	26.2	<b>26.5</b>	<b>0.4</b>	5.2	<b>5.1</b>	<b>0.2</b>
	26.1			4.9		
	26.1			5.3		
	26.9					
	26.6					
	26.8					

As seen from the results in Table 12, replacing clinker  $\delta$  with limestone up to 5% did not change the compressive strength significantly, meaning that the efficiency factor of limestone is equal to clinker in terms of strength. The synergistic reactions have probably not taken place this early, so the equal efficiency factor of limestone powder and clinker is attributed to 1) the acceleration of setting due to calcium carbonate acting as nucleation sites for early hydration products and 2) acceleration of the hydration rate due to the dispersion effect of limestone powder bringing cement grains further apart and exposing more reacting surface towards water at the early stage.

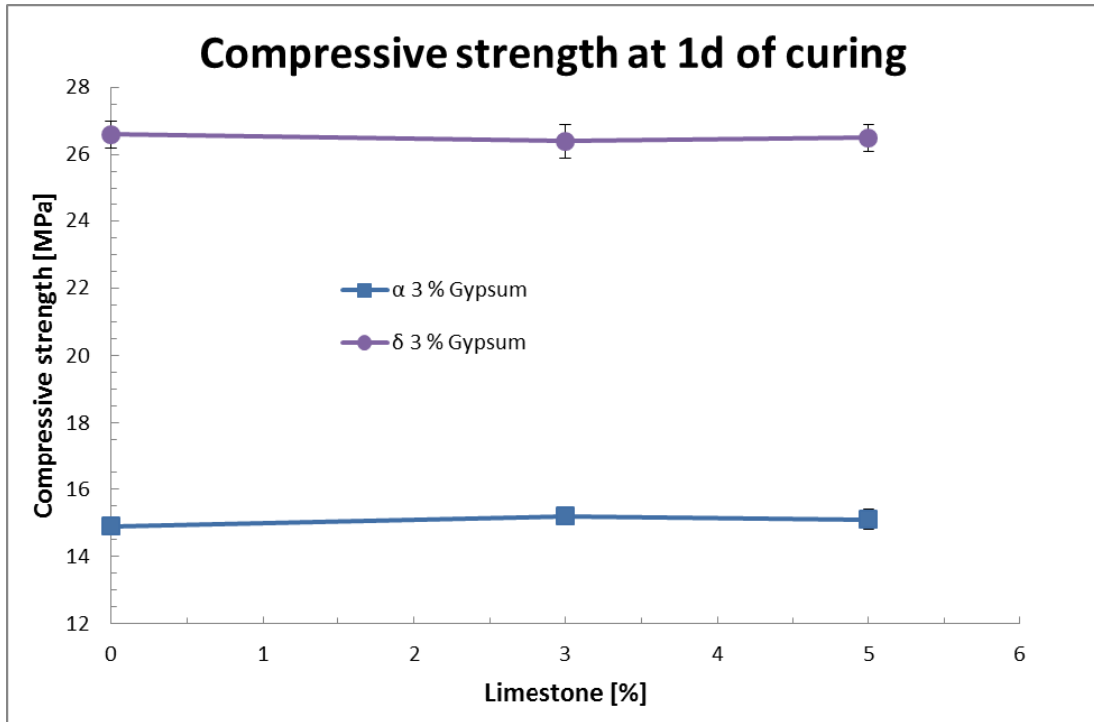


Fig. 6 Comparative plots of compressive strength at 1 day for clinkers  $\alpha$  and  $\delta$  with 3% gypsum as a function of limestone powder content.

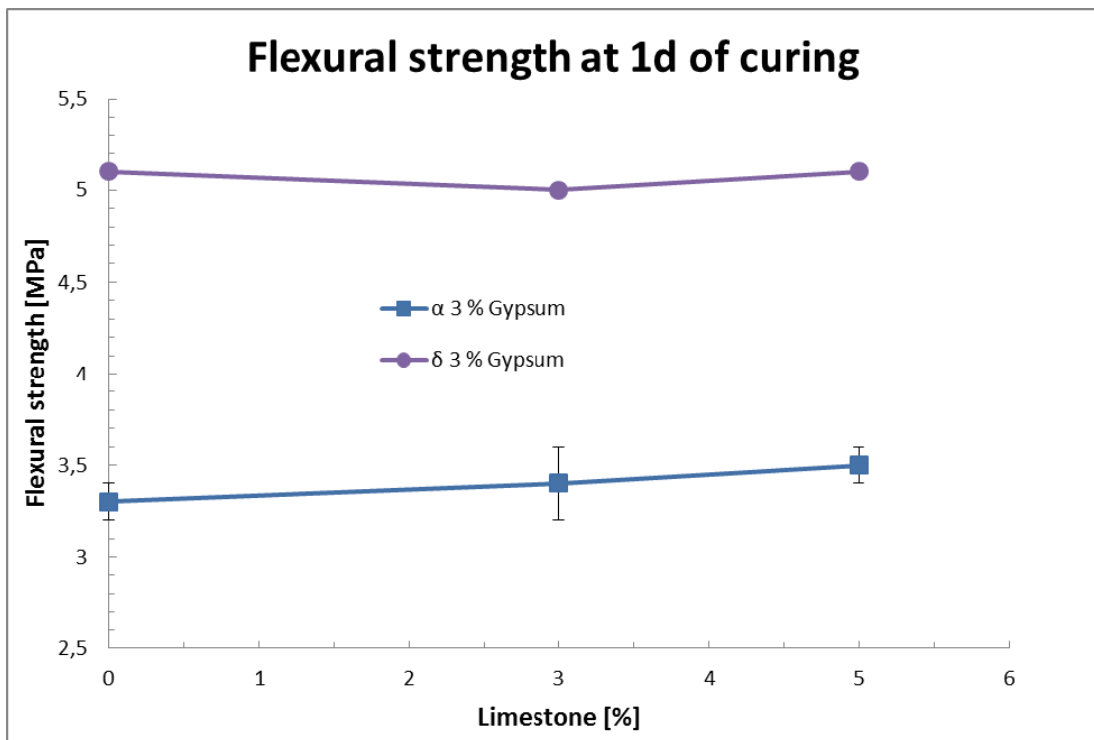


Fig. 7 Comparative plots of flexural strength at 1 day for clinkers  $\alpha$  and  $\delta$  with 3% gypsum as a function of limestone powder content.

### 3.2 Step 2 – strength of mortar based on clinker, gypsum, fly ash and limestone

The compressive ( $\sigma_c$ ) and flexural ( $\sigma_f$ ) strength with standard deviations for all 4 clinkers with 3% gypsum replaced with 35% fly ash and 30% fly ash + 5% limestone, respectively, were measured for all 4 fly ashes. The results are presented in Tables 13–16 for clinkers  $\alpha$ – $\delta$ , respectively, together with the results of a mix where 35% calcined "marl" was used to compare it to the performance of 30% fly ash + 5% limestone.

The difference in performance of the fly ashes and their response to the synergic reaction with limestone are illustrated with respect to *compressive strength* in Figures 8, 10, 12 and 14 for clinkers  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ , respectively.

The difference in performance of the fly ashes and their response to the synergic reaction with limestone are illustrated with respect to *flexural strength* in Figures 9, 11, 13 and 15 for clinkers  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ , respectively.

One remarkable observation from the tables and figures is that fly ash D always leads to much higher compressive strength compared to the other fly ashes. One of the major differences to the others is the high sulphate content (6.6% vs.  $\leq 0.5\%$  SO<sub>3</sub>) of fly ash D and high calcium content (17.9% vs.  $\leq 7\%$  CaO). Subtracting the CaO in the glass phase of fly ash D it would fit largely to a calcium sulphate content of 12.5% and anhydrite was indeed detected by XRD. This combined with much higher Blaine value (i.e. specific surface) of fly ash D (734 vs.  $\leq 400$  m<sup>2</sup>/g) would speed up the reactivity of the fly ash and much more ettringite will form with a high amount of chemically bound water. *The question then arises; could one just as well add gypsum rather than limestone to obtain a higher compressive strength?* There is a lot of cheap gypsum around and it is already imported to the cement plant in large amounts. This would also preserve limestone as a valuable resource for the raw meal of clinker. However, in such a case length change should be measured carefully to monitor if an effect like detrimental DEF (delayed ettringite formation) will occur.

Another striking observation from the tables and figures is that 35% marl calcined at 800°C leads to an even higher strength than 35% fly ash D replacement or 30% fly ash D + 5% limestone for all clinkers. This could be due to its high specific surface as it upon grinding readily falls apart to a powder with average particle size of 7  $\mu$ m. Otherwise it consist of 49% SiO<sub>2</sub>, 18% Al<sub>2</sub>O<sub>3</sub>, 10% Fe<sub>2</sub>O<sub>3</sub> and 14% CaO (basically calcium carbonate) prior to calcination. This composition is not all that different from the total composition of fly ashes A, B and C (with the exception of higher CaO), but in particular the SiO<sub>2</sub> content is significantly higher than for fly ash D.

The replacement of clinker with 3% gypsum by 35% calcined marl actually gave higher or equal 28 strength than clinker with 3% gypsum alone for all but one clinker. The relative change in 28 days strength was +27.8%, +1.2%, -17.6% and +12.5% for clinkers  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ , respectively. In particular the improvement of strength for the  $\alpha$  clinker by calcined marl was remarkable, while also simultaneously the decline in strength for clinker  $\gamma$  is hard to explain.

An overview of how 5% limestone replacing clinker with 3% gypsum compared to replacing fly ash in the case of 35% fly ash replacing clinker with 3% gypsum is gathered in Table 17.

Table 13 Compressive ( $\sigma_c$ ) and flexural ( $\sigma_f$ ) strength (in MPa) with standard deviations (St. dev.) for clinker  $\alpha$  and 3% gypsum replaced with 35% fly ash and 30% fly ash + 5% limestone, respectively, for the fly ashes A, B, C and D.

Sample	Individual $\sigma_c$	Average $\sigma_c$	St. dev. $\sigma_c$	Individual $\sigma_f$	Average $\sigma_f$	St. dev. $\sigma_f$
$\alpha$ -35%FA-A/0%L	34.3 & 34.3	<b>34.6</b>	<b>0.4</b>	6.4	<b>6.5</b>	<b>0.1</b>
	35.3 & 34.5			6.6		
	34.5			6.6		
$\alpha$ -30%FA-A/5%L	37.2 & 37.6	<b>37.8</b>	<b>0.6</b>	7.4	<b>7.1</b>	<b>0.2</b>
	38.2 & 38.6			7.0		
	37.2			7.0		
$\alpha$ -35%FA-B/0%L	33.9 & 34.5	<b>34.1</b>	<b>0.6</b>	6.6	<b>6.2</b>	<b>0.5</b>
	34.7 & 33.2			5.6		
	34.1			6.4		
$\alpha$ -30%FA-B/5%L	33.6 & 35.1	<b>34.4</b>	<b>0.6</b>	7.1	<b>7.1</b>	<b>0.2</b>
	34.3 & 34.7			7.3		
	34.5			6.9		
$\alpha$ -35%FA-C/0%L	33.2 & 32.2	<b>32.6</b>	<b>0.8</b>	6.7	<b>6.6</b>	<b>0.1</b>
	32.8 & 31.4			6.6		
	33.4			6.5		
$\alpha$ -30%FA-C/5%L	35.7 & 34.5	<b>34.6</b>	<b>1.1</b>	7.2	<b>6.9</b>	<b>0.3</b>
	35.7 & 34.1			6.7		
	33.0			6.9		
$\alpha$ -35%FA-D/0%L	49.5 & 48.2	<b>47.4</b>	<b>1.6</b>	7.6	<b>7.7</b>	<b>0.1</b>
	47.4 & 45.3			7.8		
	46.4			7.8		
$\alpha$ -30%FA-D/5%L	49.1 & 48.2	<b>48.1</b>	<b>0.6</b>	8.1	<b>7.8</b>	<b>0.4</b>
	47.6 & 47.6			7.4		
	48.2			7.8		
$\alpha$ -35%Marl/0%L	57.6 & 56.8	<b>57.0</b>	<b>0.4</b>	8.3	<b>8.4</b>	<b>0.2</b>
	57.0 & 57.0			8.6		
	56.4			8.3		



Table 14 Compressive ( $\sigma_c$ ) and flexural ( $\sigma_f$ ) strength (in MPa) with standard deviations (St. dev.) for clinker  $\beta$  and 3% gypsum replaced with 35% fly ash and 30% fly ash + 5% limestone, respectively, for the fly ashes A, B, C and D.

Sample	Individual $\sigma_c$	Average $\sigma_c$	St. dev. $\sigma_c$	Individual $\sigma_f$	Average $\sigma_f$	St. dev. $\sigma_f$
$\beta$ -35%FA-A/0%L	38.4 & 39.3	<b>38.4</b>	<b>0.5</b>	6.6	<b>6.1</b>	<b>0.7</b>
	38.2 & 38.0			5.3		
	38.2			6.3		
$\beta$ -30%FA-A/5%L	42.6 & 43.4	<b>43.4</b>	<b>0.6</b>	6.6	<b>6.4</b>	<b>0.4</b>
	43.2 & 43.9			6.7		
	44.1			6.0		
$\beta$ -35%FA-B/0%L	38.4 & 38.9	<b>38.5</b>	<b>0.3</b>	6.3	<b>6.1</b>	<b>0.3</b>
	38.4 & 38.2			6.2		
	38.4			5.7		
$\beta$ -30%FA-B/5%L	41.4 & 41.1	<b>41.5</b>	<b>0.3</b>	6.7	<b>6.6</b>	<b>0.1</b>
	41.8 & 41.8			6.6		
	41.4			6.6		
$\beta$ -35%FA-C/0%L	36.4 & 37.8	<b>37.0</b>	<b>0.6</b>	5.8	<b>6.0</b>	<b>0.2</b>
	36.6 & 37.2			6.1		
	37.2			6.2		
$\beta$ -30%FA-C/5%L	40.3 & 42.4	<b>41.8</b>	<b>0.8</b>	6.7	<b>6.6</b>	<b>0.1</b>
	42.0 & 42.2			6.5		
	42.0			6.6		
$\beta$ -35%FA-D/0%L	50.5 & 47.6	<b>48.1</b>	<b>3.2</b>	7.7	<b>7.2</b>	<b>0.5</b>
	49.9 & 42.6			6.7		
	49.7			7.2		
$\beta$ -30%FA-D/5%L	52.6 & 50.5	<b>51.9</b>	<b>0.9</b>	7.7	<b>8.0</b>	<b>0.3</b>
	52.6 & 51.8			8.3		
	52.2			7.9		
$\beta$ -35%Marl/0%L	61.1 & 61.1	<b>60.8</b>	<b>0.8</b>	7.2	<b>7.5</b>	<b>0.3</b>
	61.1 & 59.5			7.4		
	61.4			7.8		

Table 15 Compressive ( $\sigma_c$ ) and flexural ( $\sigma_f$ ) strength (in MPa) with standard deviations (St. dev.) for clinker  $\gamma$  and 3% gypsum replaced with 35% fly ash and 30% fly ash + 5% limestone, respectively, for the fly ashes A, B, C and D.

Sample	Individual $\sigma_c$	Average $\sigma_c$	St. dev. $\sigma_c$	Individual $\sigma_f$	Average $\sigma_f$	St. dev. $\sigma_f$
$\gamma$ -35%FA-A/0%L	34.7 & 36.4	<b>35.9</b>	<b>0.9</b>	6.2	<b>6.2</b>	<b>0.1</b>
	35.3 & 35.9			6.3		
	37.4			6.1		
$\gamma$ -30%FA-A/5%L	39.5 & 40.3	<b>40.1</b>	<b>0.6</b>	6.6	<b>6.8</b>	<b>0.2</b>
	39.5 & 40.9			6.9		
	40.5			6.9		
$\gamma$ -35%FA-B/0%L	32.6 & 35.5	<b>34.5</b>	<b>1.5</b>	6.1	<b>5.8</b>	<b>0.4</b>
	33.2 & 35.1			5.4		
	35.9			6.0		
$\gamma$ -30%FA-B/5%L	35.5 & 37.4	<b>36.7</b>	<b>0.8</b>	6.3	<b>6.0</b>	<b>0.3</b>
	36.4 & 36.6			6.0		
	37.4			5.7		
$\gamma$ -35%FA-C/0%L	33.9 & 35.1	<b>34.4</b>	<b>0.5</b>	5.9	<b>5.8</b>	<b>0.2</b>
	33.9 & 34.5			6.0		
	34.7			5.6		
$\gamma$ -30%FA-C/5%L	37.8 & 37.8	<b>38.0</b>	<b>0.4</b>	6.2	<b>6.4</b>	<b>0.2</b>
	37.6 & 38.4			6.5		
	38.6			6.4		
$\gamma$ -35%FA-D/0%L	46.6 & 45.7	<b>45.4</b>	<b>0.9</b>	7.4	<b>7.0</b>	<b>0.4</b>
	44.7 & 45.7			6.8		
	44.5			6.7		
$\gamma$ -30%FA-D/5%L	45.7 & 45.5	<b>45.6</b>	<b>0.5</b>	7.4	<b>7.7</b>	<b>0.2</b>
	46.4 & 45.5			7.8		
	45.1			7.8		
$\gamma$ -35%Marl/0%L	53.6 & 52.6	<b>52.8</b>	<b>0.6</b>	8.4	<b>8.0</b>	<b>0.5</b>
	53.2 & 52.2			7.4		
	52.4			8.1		

Table 16 Compressive ( $\sigma_c$ ) and flexural ( $\sigma_f$ ) strength (in MPa) with standard deviations (St. dev.) for clinker  $\delta$  and 3% gypsum replaced with 35% fly ash and 30% fly ash + 5% limestone, respectively, for the fly ashes A, B, C and D.

Sample	Individual $\sigma_c$	Average $\sigma_c$	St. dev. $\sigma_c$	Individual $\sigma_f$	Average $\sigma_f$	St. dev. $\sigma_f$
$\delta$ -35%FA-A/0%L	55.7 & 55.7	<b>55.7</b>	<b>0.2</b>	8.2	<b>8.0</b>	<b>0.2</b>
	55.5 & 55.9			8.0		
	55.5			7.9		
$\delta$ -30%FA-A/5%L	57.0 & 58.0	<b>58.2</b>	<b>0.9</b>	8.3	<b>7.9</b>	<b>0.7</b>
	57.8 & 59.1			7.1		
	59.1			8.4		
$\delta$ -35%FA-B/0%L	52.8 & 52.0	<b>51.4</b>	<b>1.4</b>	7.8	<b>7.8</b>	<b>0.4</b>
	52.4 & 50.3			7.4		
	49.7			8.1		
$\delta$ -30%FA-B/5%L	54.5 & 53.9	<b>54.2</b>	<b>0.6</b>	7.5	<b>7.9</b>	<b>0.3</b>
	55.1 & 53.6			8.1		
	54.1			8.0		
$\delta$ -35%FA-C/0%L	54.9 & 54.5	<b>54.7</b>	<b>0.5</b>	8.1	<b>7.7</b>	<b>0.4</b>
	54.5 & 54.1			7.6		
	55.5			7.4		
$\delta$ -30%FA-C/5%L	58.2 & 56.1	<b>57.1</b>	<b>0.9</b>	8.1	<b>7.9</b>	<b>0.2</b>
	57.0 & 56.4			7.8		
	57.6			7.9		
$\delta$ -35%FA-D/0%L	63.9 & 64.6	<b>64.5</b>	<b>0.4</b>	7.8	<b>8.4</b>	<b>0.5</b>
	64.8 & 64.3			8.6		
	64.8			8.7		
$\delta$ -30%FA-D/5%L	66.1 & 66.8	<b>67.0</b>	<b>0.6</b>	8.8	<b>8.8</b>	<b>0.1</b>
	67.3 & 67.7			8.9		
	66.9			8.7		
$\delta$ -35%Marl/0%L	76.4 & 75.9	<b>75.5</b>	<b>1.2</b>	9.4	<b>9.0</b>	<b>0.4</b>
	76.6 & 74.4			8.7		
	74.0			8.9		

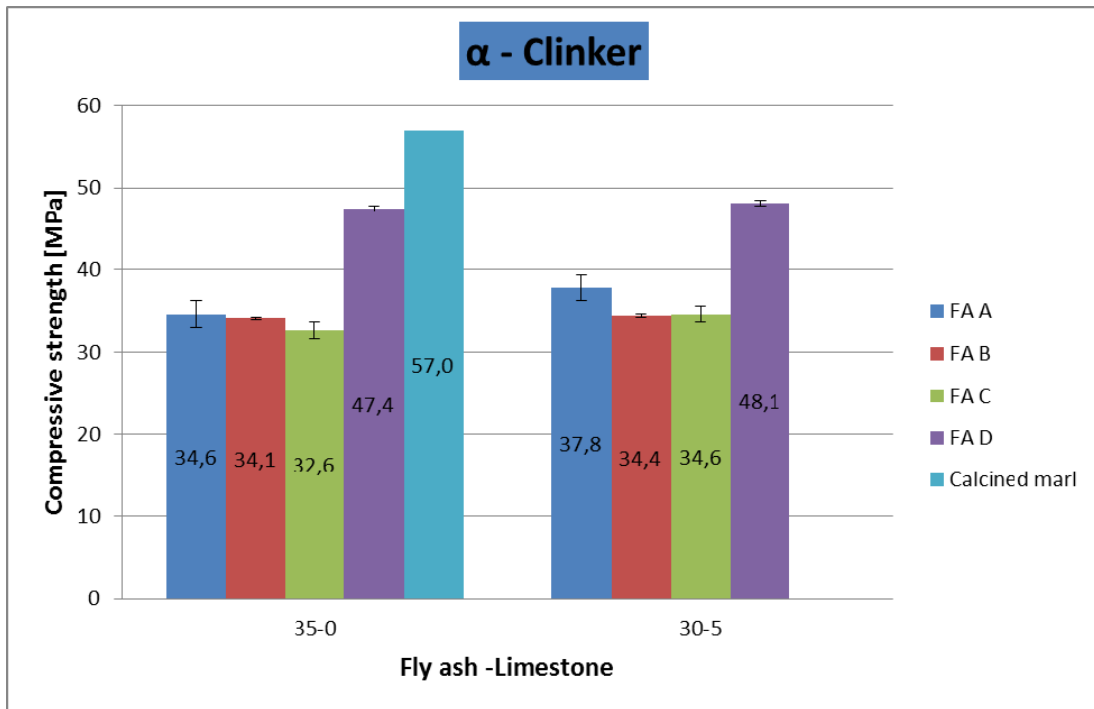


Fig. 8 The effect of different fly ashes on the compressive strength of clinker  $\alpha$  and their response to combination with lime stone powder. The result is also compared to 35% calcined "marl" replacing the clinker with 3% gypsum.

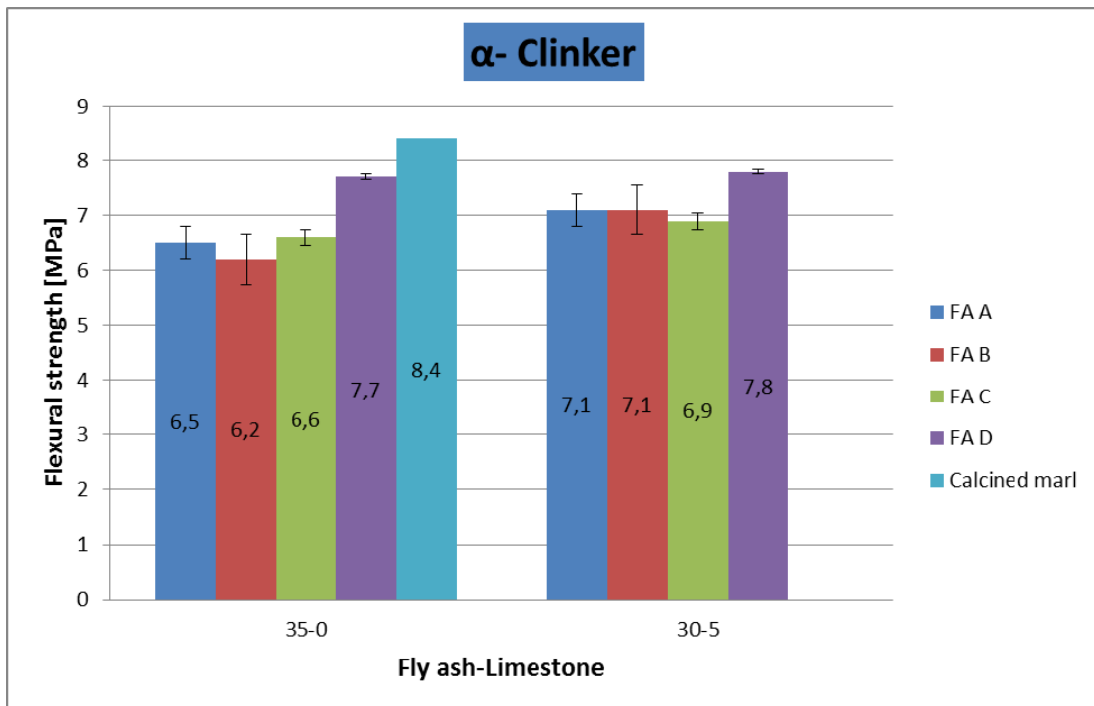


Fig. 9 The effect of different fly ashes on the flexural strength of clinker  $\alpha$  and their response to combination with lime stone powder. The result is also compared to 35% calcined "marl" replacing the clinker with 3% gypsum.

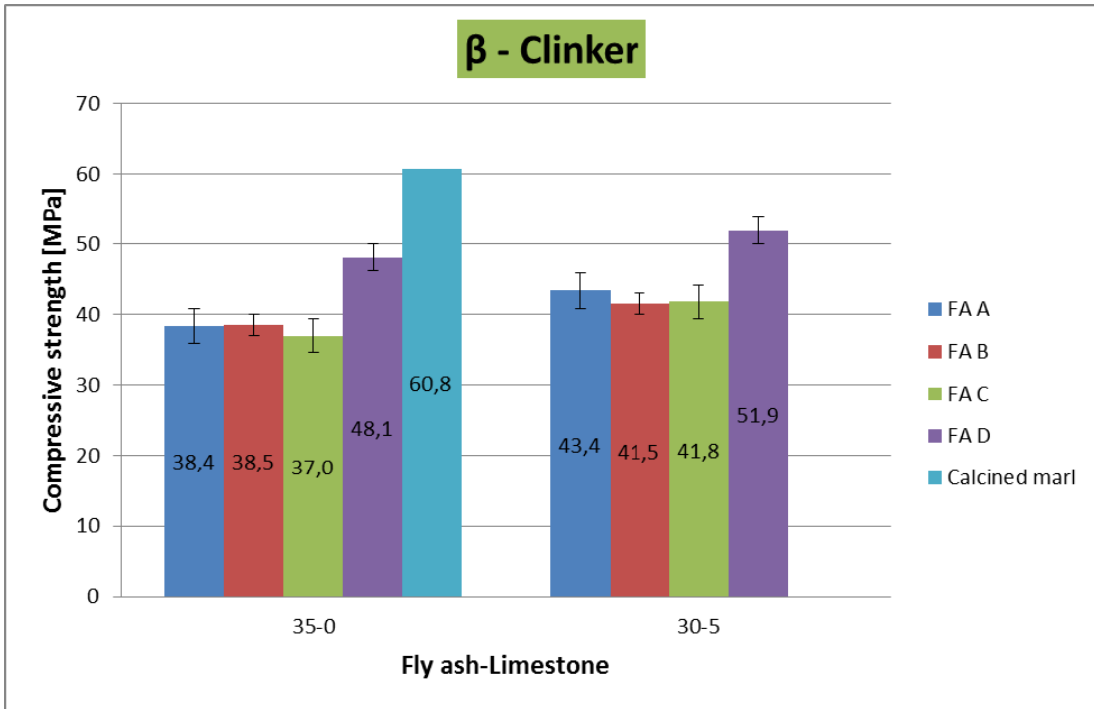


Fig. 10 The effect of different fly ashes on the compressive strength of clinker  $\beta$  and their response to combination with lime stone powder. The result is also compared to 35% calcined "marl" replacing the clinker with 3% gypsum.

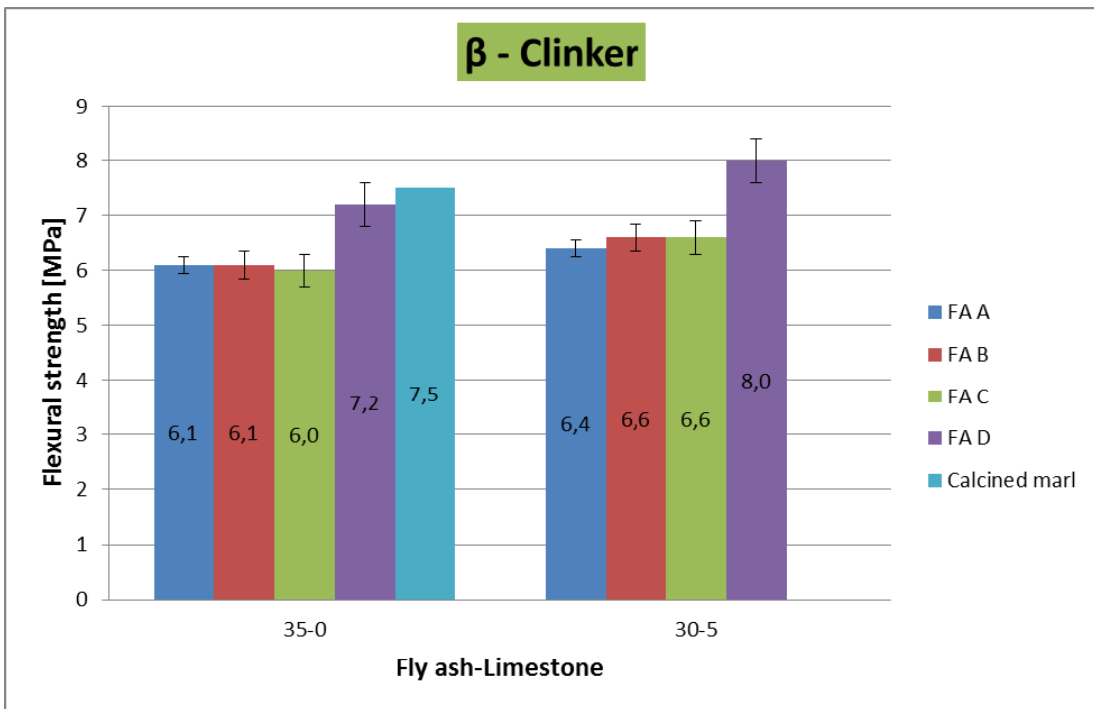


Fig. 11 The effect of different fly ashes on the flexural strength of clinker  $\beta$  and their response to combination with lime stone powder. The result is also compared to 35% calcined "marl" replacing the clinker with 3% gypsum.

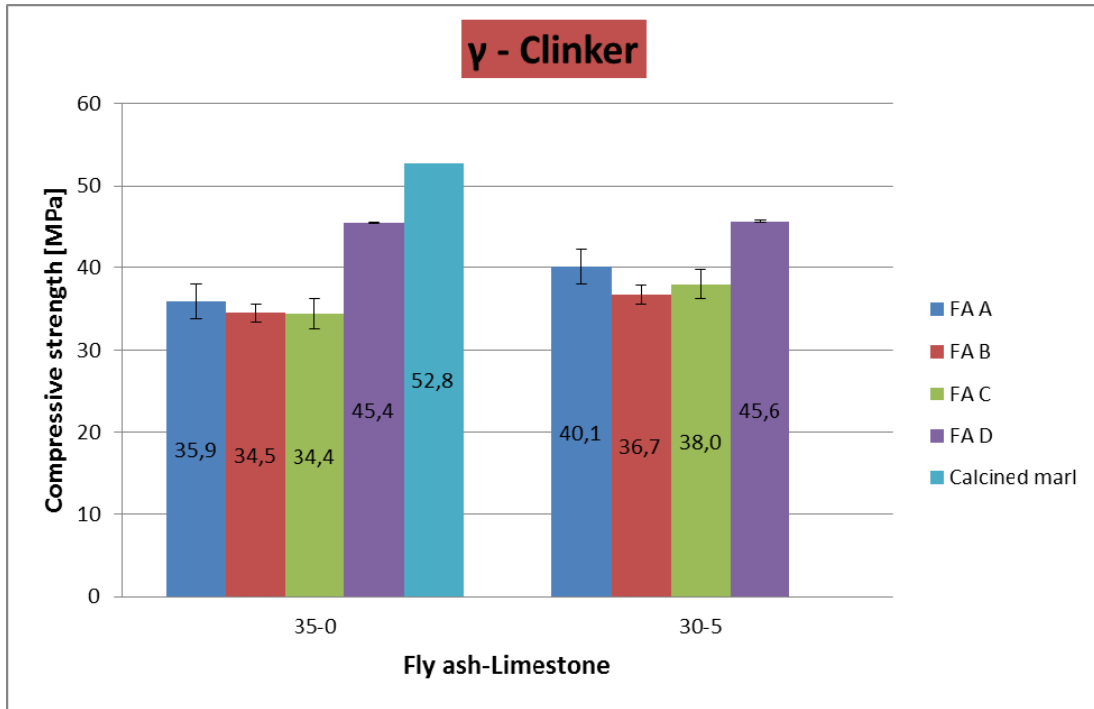


Fig. 12 The effect of different fly ashes on the compressive strength of clinker  $\gamma$  and their response to combination with lime stone powder. The result is also compared to 35% calcined "marl" replacing the clinker with 3% gypsum.

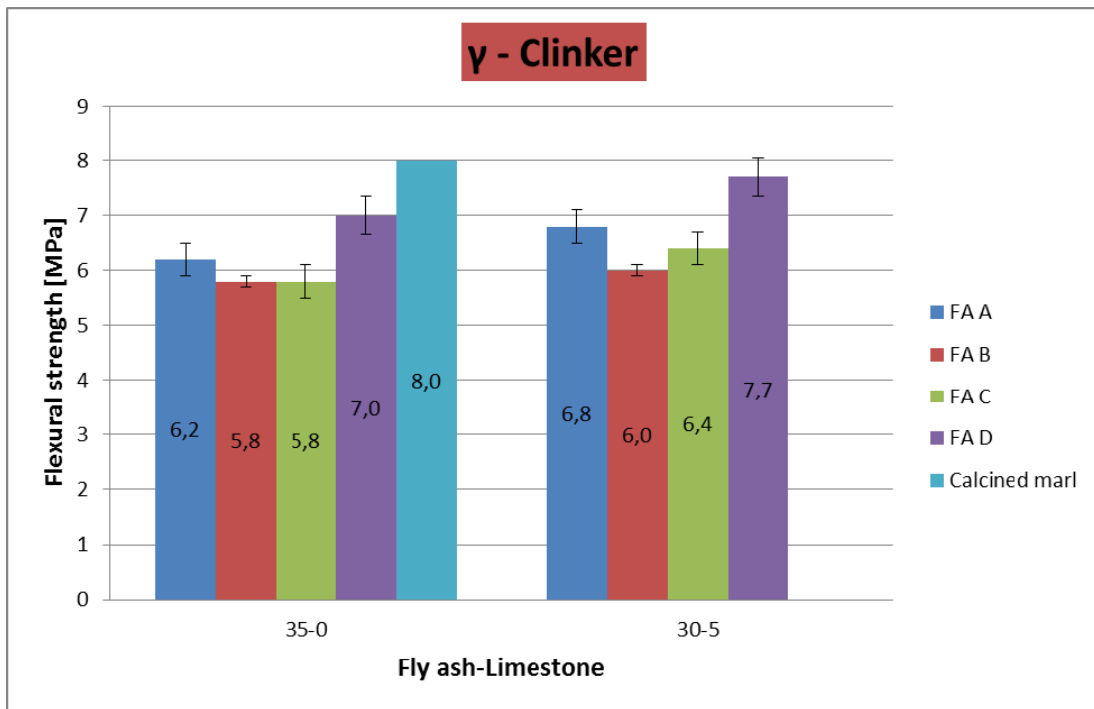


Fig. 13 The effect of different fly ashes on the flexural strength of clinker  $\gamma$  and their response to combination with lime stone powder. The result is also compared to 35% calcined "marl" replacing the clinker with 3% gypsum.

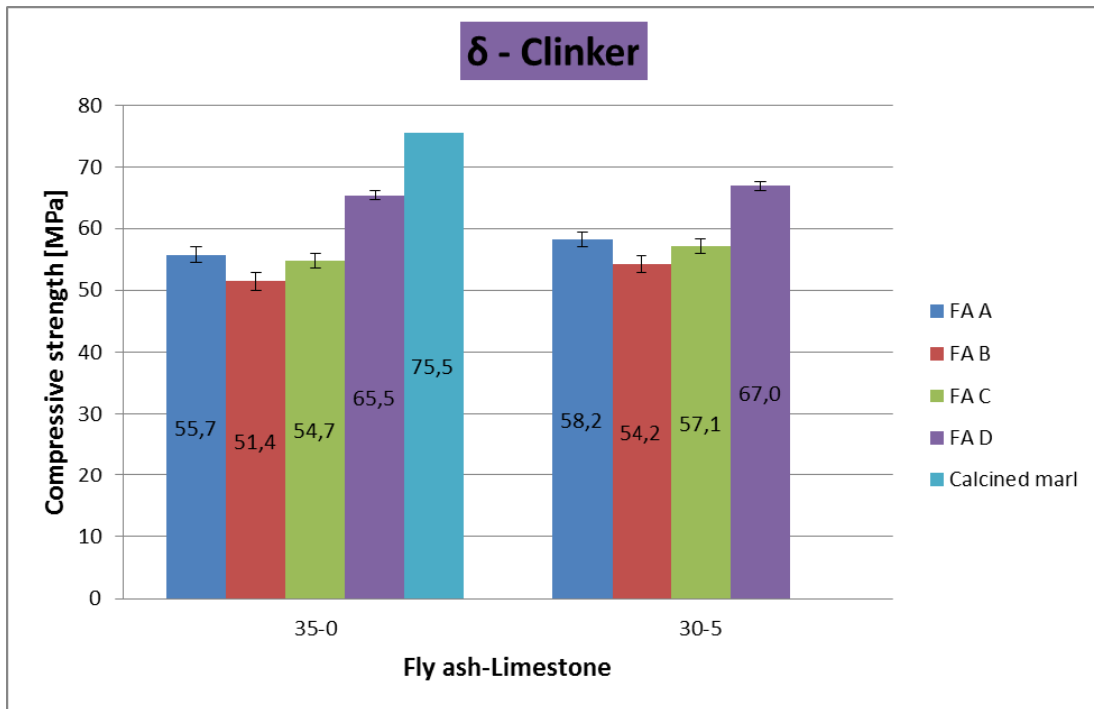


Fig. 14 The effect of different fly ashes on the compressive strength of clinker  $\delta$  and their response to combination with lime stone powder. The result is also compared to 35% calcined "marl" replacing the clinker with 3% gypsum.

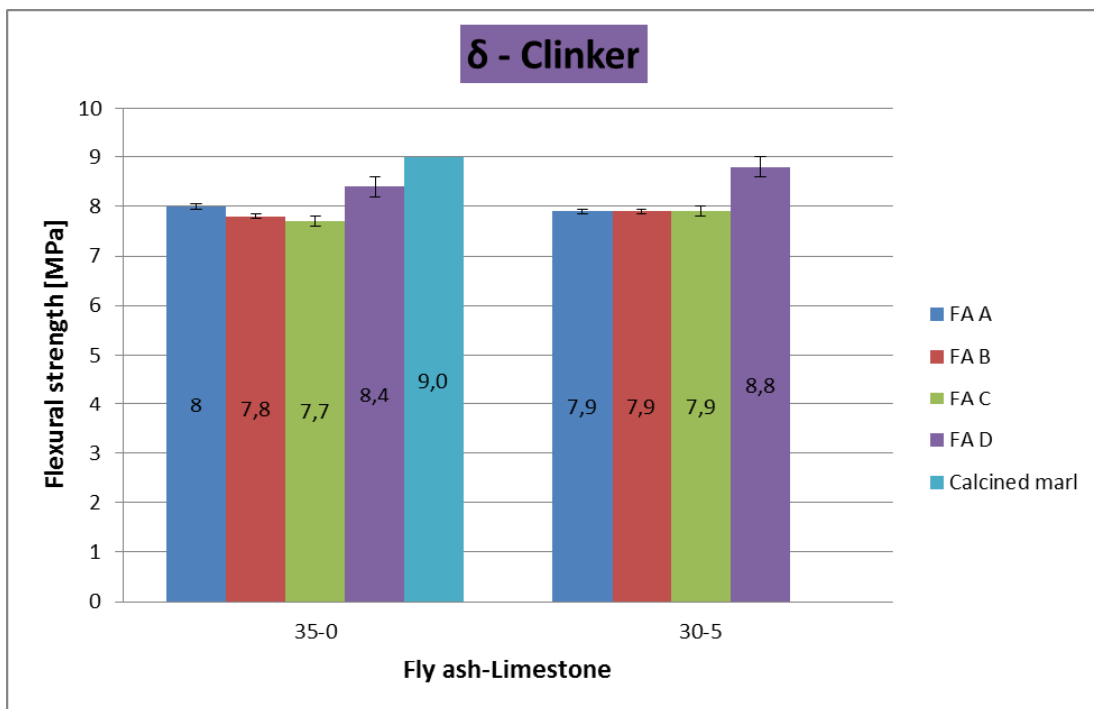


Fig. 15 The effect of different fly ashes on the flexural strength of clinker  $\delta$  and their response to combination with lime stone powder. The result is also compared to 35% calcined "marl" replacing the clinker with 3% gypsum.

Table 17 An overview on how 5% limestone improve 28 days strength when replacing clinker without fly ash and when replacing fly ash when 35% clinker is replaced with fly ash.

Clinker with 3% G	0% L $\sigma_c$ (MPa)	5% L $\sigma_c$ (MPa)	$\Delta$ (%)	35% FA $\sigma_c$ (MPa)	30/5% FA/L $\sigma_c$ (MPa)	$\Delta$ (%)
$\alpha$	44.6±0.6	44.5±0.9	-0.2	A 34.6±0.4	A 37.8±0.6	+9.2
				B 34.1±0.6	B 34.4±0.6	+0.9
				C 32.6±0.8	C 34.6±1.1	+6.1
				D 47.4±1.6	D 48.1±0.6	+1.5
$\beta$	60.1±0.5	59.6±0.6	-0.8	A 38.4±0.5	A 43.4±0.6	+13.0
				B 38.5±0.3	B 41.5±0.3	+7.8
				C 37.0±0.6	C 41.8±0.8	+13.0
				D 48.1±3.2	D 51.9±0.9	+7.9
$\gamma$	64.2±2.7	61.1±0.9	-4.8	A 35.9±0.9	A 40.1±0.6	+11.7
				B 34.5±1.5	B 36.7±0.8	+6.4
				C 34.4±0.5	C 38.0±0.4	+10.5
				D 45.4±0.9	D 45.6±0.5	+0.4
$\delta$	67.1±2.1	69.8±1.6	+4.0	A 55.7±0.2	A 58.2±0.9	+4.5
				B 51.4±1.4	B 54.2±0.6	+5.4
				C 54.7±0.5	C 57.1±0.9	+4.4
				D 64.5±0.4	D 67.0±0.6	+3.9

The relative change of 28 days strength for clinkers  $\alpha$  and  $\beta$  with 3% gypsum when replaced with 5% limestone is negligible ( $\approx 0$ ) which means that the efficiency factor in terms of compressive strength is the same for clinker with gypsum and limestone. For clinker  $\gamma$  there is  $\approx 5$  % decline in strength indicating that there is NO contribution from limestone to strength (i.e. efficiency factor  $\approx 0$ ) in this case. For the  $\delta$  clinker, on the other hand, there is a 4% strength increase when clinker with 3% gypsum is replaced with 5% limestone, indicating an efficiency factor of  $\approx 2$  for the limestone (i.e. nearly the double of the clinker).

The effect of replacing 5% fly ash with limestone seems to be better for fly ashes A and C for clinkers  $\alpha$ ,  $\beta$  and  $\gamma$ , while there is more or less an equal effect between the fly ashes for clinker  $\delta$  according to Table 17. Fly ashes A and C have the highest glass content of the 4 and higher  $Al_2O_3$  content than B. However, in all cases there is a beneficial (i.e. positive) effect on 28 d strength by replacing fly ash with 5% limestone, meaning that the efficiency factor of limestone is higher than fly ash, albeit the effect is below 1% for fly ash B with clinker  $\alpha$  and for fly ash D with clinker  $\gamma$ .

In Fig. 16, efforts are made to correlate the relative strength increase  $\Delta$  (%) after 28 days for the 30/5 FA/L vs. 35 FA in Table 17 with the  $Al_2O_3$  content of the glass phase multiplied with the total amount of glass of the fly ashes as a characteristic “fly ash factor”. Fly ash D is not included since this is not a “normal” fly ash. The results in Figure 16 shows quite a linear relation between the strength gain when 5% fly ash is replaced with limestone and this factor. The results of the linear regression (strength gain) =  $a \cdot$  (fly ash factor) +  $b$  are given in Table 18. The strength gain is increasing with increasing “fly ash factor” for all clinkers, except for clinker  $\delta$  that seems to be independent of the “fly ash factor”. Perhaps this is because clinker  $\delta$  by itself achieved a considerable strength gain when replaced with limestone without fly ash, unlike the other clinkers. In addition, clinker  $\delta$  has extremely low alkali content (0.33%  $Na_2O_{eq}$ ) and no sodium (!) that otherwise would have accelerated fly ash reactivity. Actually, factor  $a$  (i.e. the slope of the correlation) in Table 18 seems more or less to be proportional with the  $Na_2O_{eq}$  of the clinkers (if that of clinker  $\delta \approx 0$ ).



Table 18 Parameters for the linear regression of (strength gain) = a·(fly ash factor) + b for different clinkers as compared to their total alkali content as Na<sub>2</sub>O<sub>eq</sub> (%).

Clinker	a	b	r <sup>2</sup>	Na <sub>2</sub> O <sub>eq</sub>
α	0.0158	-8.8550	0.9408	1.29
β	0.0115	0.8388	0.9825	0.56
γ	0.0107	-0.1701	0.9928	0.56
δ	-0.0021	6.6486	0.9508	0.33

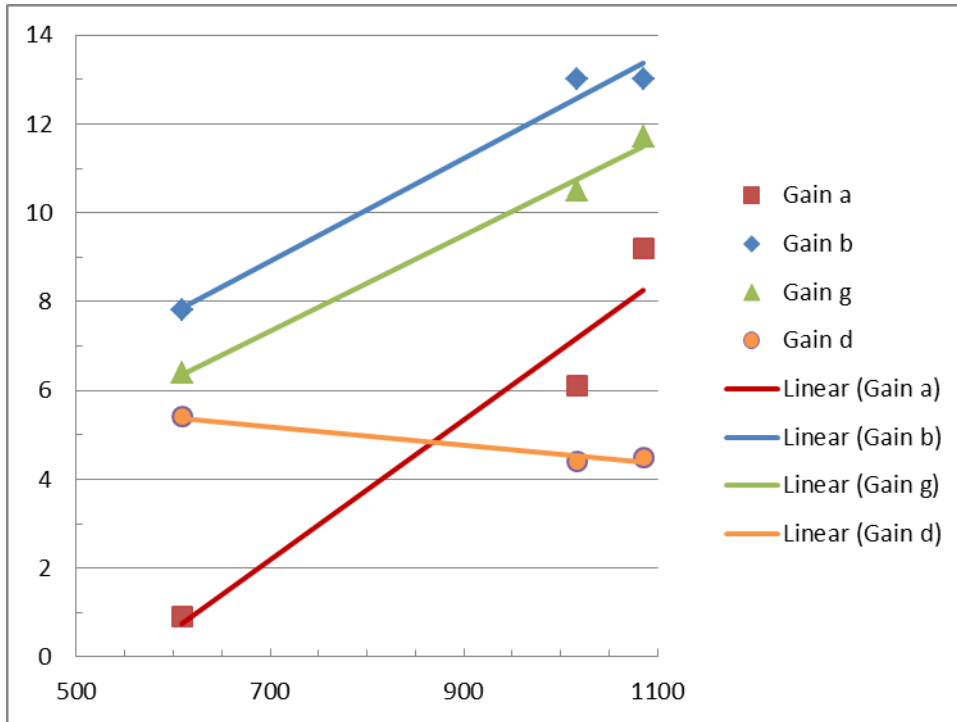


Fig. 16 Linear correlation between the relative strength gain between clinker with 3% gypsum replaced with 35% fly ash and the one replaced with 30% fly ash and 5% limestone (y-axis) and the “fly ash factor” being a multiplication of the Al<sub>2</sub>O<sub>3</sub> content of the glass phase of the fly ash and its total amount of glass.

The relative good linear correlation shown in Fig. 16 could perhaps be further improved by multiplying the “fly ash factor” with the reaction degree of the fly ash glass phase since this really would have been a measure of how much Al<sub>2</sub>O<sub>3</sub> the fly ash would have released to the cementitious system. However, this is difficult to detect and the already good linear fit indicates that the glass reaction degree of fly ashes A, B and C after 28 days are about equal.

## 4 Conclusion

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The following conclusions can be drawn from this study carried out in two steps:

1. Combination of four clinkers with two levels of gypsum (1.5% and 3.0% replacing clinker) and 0 and 5% limestone powder replacing clinker + gypsum.
2. Four clinkers with 3 % gypsum replaced with 35% fly ash and where 0 or 5% fly ash was replaced with limestone.

For step 1, the 28 d strength was *mostly* unchanged when 5% limestone replaced cement (i.e. clinker + gypsum), which means that limestone actually has the same efficiency factor as cement with respect to 28 d strength, so it is likely that some synergic reaction has taken place between calcium carbonate and calcium aluminate hydrates.

There was a huge difference in 28 days strength between the clinkers ranging from 44.6 MPa to 67.1 MPa when combined with for instance 3% gypsum. The reason for this was not obvious from the clinker characteristics.

Among the fly ashes in step 2, there were 3 ordinary fly ashes and 1 rich in anhydrite (12% calcium sulphate). The latter fly ash gave always the highest 28 days strength when 35% was replacing the four different clinkers with 3% gypsum. It raises the question whether or not one just as well could add more gypsum rather than limestone in combination with the fly ashes to achieve higher strength.

Replacing 5% of the other 3 fly ashes with limestone gave always a strength increase, meaning the efficiency factor of limestone is higher than the fly ash, presumably due to the synergic reaction. The strength gain by limestone replacing fly ash combined with the different clinkers gave a good linear correlation with the amount of glass in the fly ash multiplied with the alumina content in that glass. This "multiplication factor" probably corresponds to the amount of alumina "easily" available by the fly ash to the system in the pozzolanic reaction and that the degree of reaction for the 3 fly ashes in the regression was about equal at 28 days.

Mortars where 35% calcined marl replacing the clinkers with 3% gypsum were made in order to compare with the fly ash performance. Calcined marl gave higher strength than any of the fly ashes and even lead to higher strength than mortars based on 100% clinker + gypsum for 3 out of 4 clinkers (even for the one with highest strength; 67.1 vs. 75.5 MPa).

## 5 Acknowledgement

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