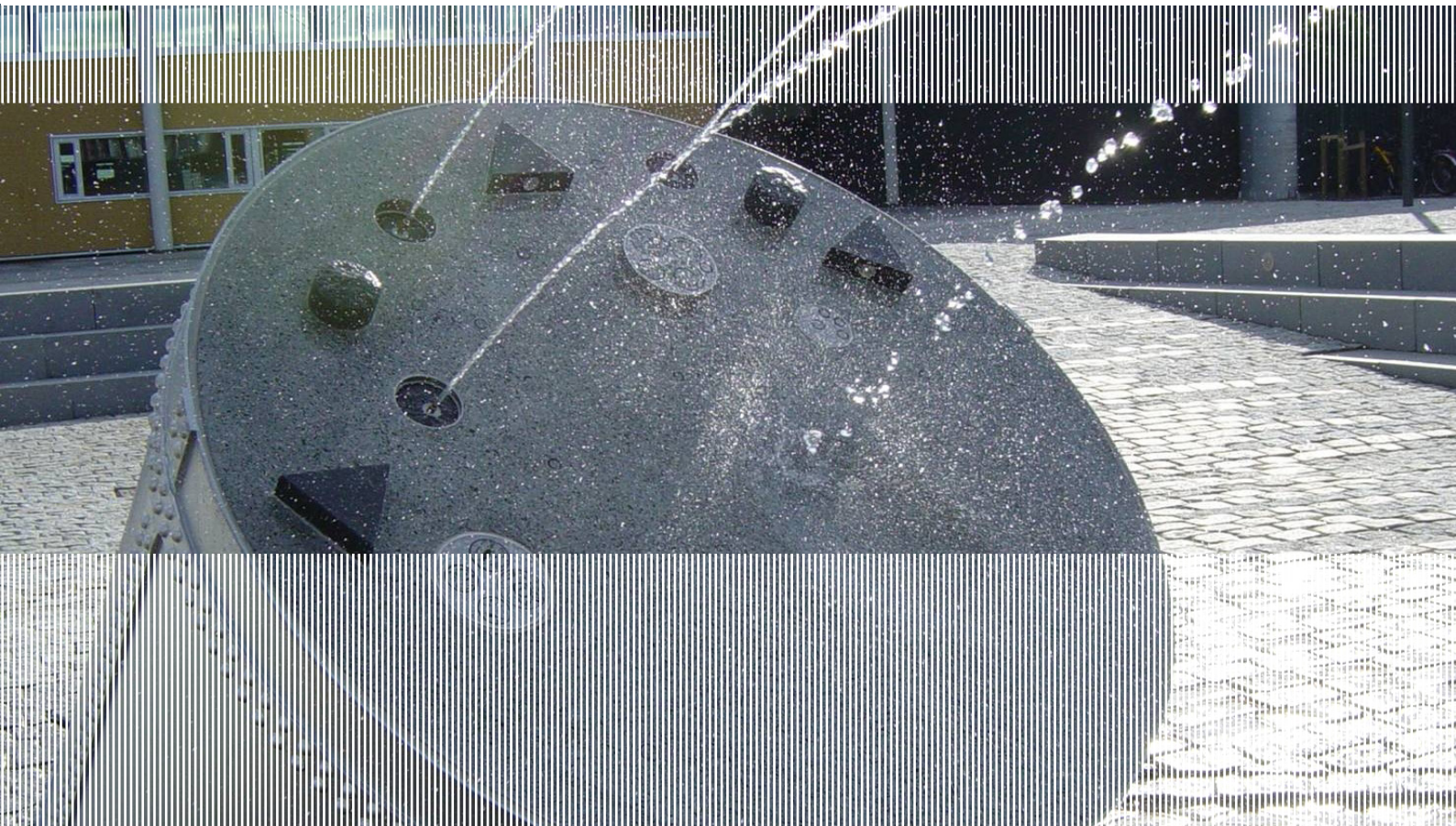# COIN

SINTEF Building and Infrastructure   Tone Østnor and Harald Justnes

Alternative binders based on lime and calcined clay

COIN Project report 68 – 2015

SINTEF

SINTEF Building and Infrastructure

Tone Østnor and Harald Justnes

Alternative binders based on lime and calcined clay

FA 1 Environmentally friendly concrete

SP 1.1 Low carbon-footprint binder systems

COIN Project report 68 – 2015

Alternative binders based on lime and calcined clay

Preface

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

Tor Arne Hammer
Centre Manager

Summary

Alternative binders are in this report defined as binders without Portland cement. In this particular project it will be based on calcined clay or fly ash as a source of reactive silica and alumina in combination with lime and calcium sulphate (e.g. gypsum) and/or calcium carbonate to stabilize special calcium aluminate phases like ettringite and/or calcium monocarboaluminate hydrate, respectively. Gaining strength is all about maximizing the transformation of liquid water to hydrates with hydraulic properties as fast as possible. Hence, admixtures speeding up the reaction kinetics can be part of the formulations as well.

Two synergy principles have been described for making improved binders based on slaked lime and pozzolanic SCMs. One showing how neutral salts may accelerate by forming strong alkaline solutions *in situ*. Another one how calcium carbonate can play a role when alumina containing SCMs are used by leading to an even higher conversion of liquid water into solid hydrates leading to lower porosity and higher strength.

An example have been showed for a binder consisting of calcined clay, slaked lime and calcium carbonate on how mortars can achieve a 28 days compressive strength of about 25 MPa and 3 day strength exceeding 10 MPa when cured at 20°C when accelerated by sodium carbonate. The strength may have been improved further by having a slightly higher ratio of calcium hydroxide.

Calcined marl may substitute for calcined clay, but then the calcium carbonate content should be reduced in accordance with the remaining calcium carbonate content after calcination.

The formulations are not entirely correct according to the outlined 2nd principle since they rely on bulk chemical compositions and the fact that the commercial clay/marl was containing inert quarts or feldspars. Ideally the formulations should be made according to the content of clay minerals and their compositions only after subtracting the inert components. However, such a composition of reactive material may be difficult to arrive at.

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1   Introduction

1.1   Objective

Alternative binders are in this report defined as binders without Portland cement. In this particular project it will be based on calcined clay or fly ash as a source of reactive silica and alumina in combination with lime and calcium sulphate (e.g. gypsum) and/or calcium carbonate to stabilize special calcium aluminate phases like ettringite and/or calcium monocarboaluminate hydrate, respectively. Gaining strength is all about maximizing the transformation of liquid water to hydrates with hydraulic properties as fast as possible. Hence, admixtures speeding up the reaction kinetics can be part of the formulations as well.
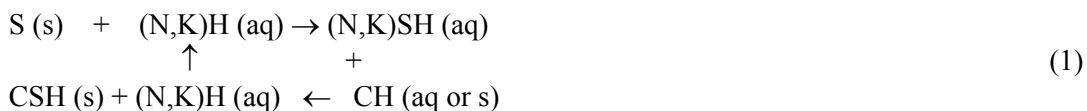
1.2   Background

Lime mortars were used already by the Romans who also discovered that these mortars became stronger when blended with supplementary cementing materials (SCMs) like volcanic ash, diatomaceous earth or even crushed, ground ceramics. In terms of today's demand of sustainability with minimized CO_2 emissions these binders are even worse than Portland cement (unless totally re-carbonated), and the present alternative binder concept is therefore trying to minimize the required lime content relative to SCMs. However, with the requirement of fast construction of the modern world, accelerators are crucial for fast hardening. The alternative is curing at elevated temperatures for prefabricated elements.

1.3   Utilizing synergic reactions in designing alternative binders

The reaction rate is increased by high pH, but since solutions with high pH is hazardous to handle, the first synergy principle is to find accelerators that by themselves are neutral but that will generate high pH *in situe* in reaction with lime. The second synergy principle is to combine the lime/calcined clay blend with calcium carbonate (limestone) so that the calcium aluminate hydrates formed by the pozzolanic reaction between lime and clay will react further with calcium carbonate and form calcium carboaluminate hydrates. This last step will lead to increased transfer of liquid water to solid hydrates and therefore contribute to higher strength. An alternative to calcium carbonate in the second principle is to use calcium sulphate that depending on the ratio to the reacted aluminate from the clay will form ettringite (AFt) or calcium monosulphoaluminate hydrate (AFm).

1.3.1   Principle of accelerator synergy

To speed up pozzolanic reactions between lime and SCMs, highly alkaline solutions are usually effective and work merely as catalysts as sketched for the reaction loop of lime-silica fume by Justnes [1] (using cement chemist's short hand notation; $C = CaO$, $S = SiO_2$, $H = H_2O$, $N = Na_2O$ and $K = K_2O$):

$$S\,(s)\quad+\quad(N,K)H\,(aq) \rightarrow (N,K)SH\,(aq)$$
$$\uparrow \qquad\qquad +$$
$$CSH\,(s) + (N,K)H\,(aq)\quad \leftarrow\quad CH\,(aq\ or\ s) \tag{1}$$

Reaction (1)) is leading to the well-known overall pozzolanic reaction;

$$S + CH = CSH \tag{2}$$

Alkalis are very important, as blending pure lime (CH) and pure silica fume (S) will take several days to harden, while using simulated pore water of pH 13.5 gives decent 3 day strength [1] at ambient temperature as shown in Fig. 1.
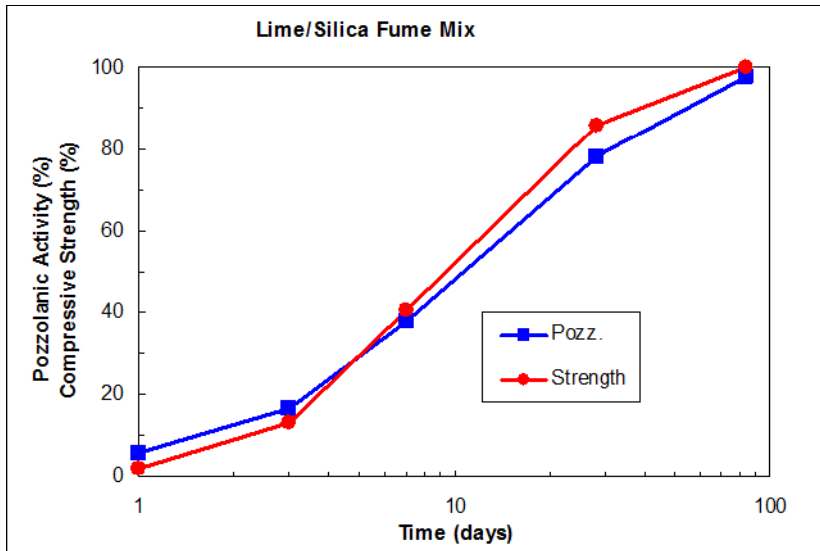
Figure 1: Comparison of compressive strength (relative to 63.9 MPa at 84 days = 100%) development of mortar with reactivity of silica fume in the cementitious material lime /SF with C/S = 1.11 and water-to-solid ratio 0.70 [1].

However, for the sake of the work-environment, strong alkalis present a hazard to handle. It is much safer to handle neutral, soluble salts that will form alkali hydroxides *in situe* when reacting with calcium hydroxide. This is the first synergy principle, and the only requirement of the neutral alkali salt is that its anion will form insoluble calcium salts;

$$xCa(OH)_2 + 2(Na,K)_xA = Ca_xA_2\,(s) + 2x\,(Na,K)OH \qquad (3)$$
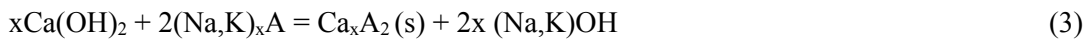
Such possible salts are listed in Table 1 together with the solubility product (K_{sp}) of their corresponding calcium compounds and the equilibrium concentration of calcium.

Table 1: The solubility product (K_{sp}) and equilibrium concentration of calcium for salts of general composition Ca_xA_2 (A = anion). x is the factor in Eq. 3

x	A	K_{sp}	$[Ca^{2+}]$ (mM)
1	OH^-	$5.5\cdot10^{-6}$	11.1
1	F^-	$5.3\cdot10^{-9}$	1.1
2	CO_3^{2-}	$2.8\cdot10^{-9}$	0.053
2	SO_4^{2-}	$9.1\cdot10^{-6}$	3.0
3	PO_4^{3-}	$2.0\cdot10^{-29}$	0.019

The lower the $[Ca^{2+}]$ for salts relative to $Ca(OH)_2$, the more reaction (3) is expected to be shifted to the right, and the more effective the accelerator is expected to be. Fig. 2 shows strength development for lime/silica fume mortars with different accelerators capable of giving pH 14.2 in pore water if Eq. 3 was shifted all the way to the right. In terms of 1 and 3 days compressive strength, the order of efficiency is $Na_3PO_4 > NaF > Na_2CO_3 > K_2CO_3 > 2K_2CO_3 + Na_2CO_3 > KF > Na_2SO_4$. It is not known why potassium salts does not perform as well as corresponding sodium salts, but potassium is thought to have higher affinity to be bound by the CSH gel than sodium, which can be the reason. It is important to note that the common sodium sulphate does not perform very well, while sodium carbonate does due to much less soluble calcium carbonate than gypsum.
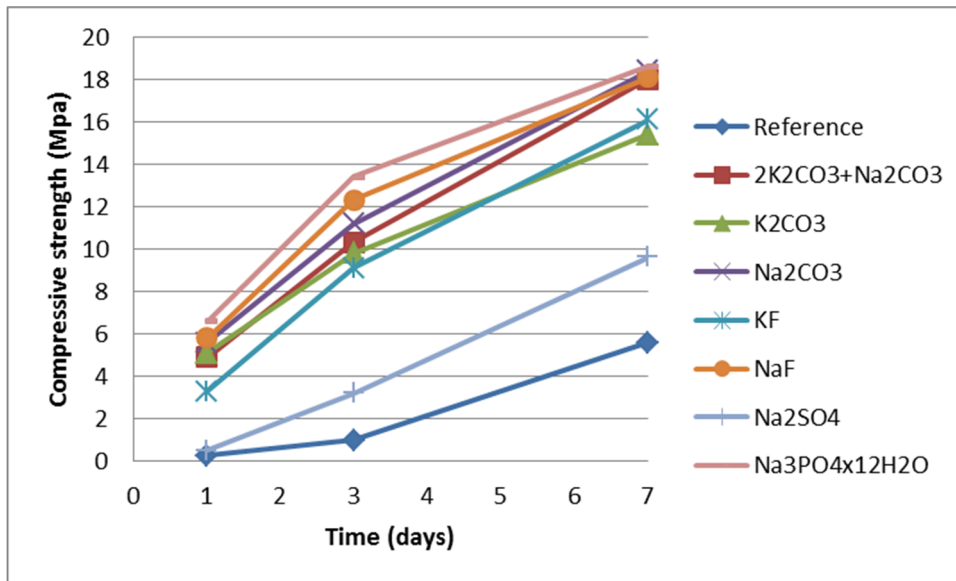
Figure 2: The compressive strength evolution of silica fume/lime mortars [2] with equimolar dosage of different accelerators (i.e. capable of forming same amount of OH⁻).

1.3.2 Principle of maximizing volume of hydrates

Silica fume is the simplest SCM chemically, while aluminosilicates like fly ash and calcined clays are much more complex. In addition to producing amorphous CSH in their reaction with lime, they can also form a wide range of crystalline calcium aluminate hydrates (CAH), including mixed products (CASH) like strätlingite, C_2ASH_8.

The CAH formation opens up for another principle of synergy to convert even more liquid water into solid hydrates, and hence reduce porosity and increase strength. Let us for simplicity assume the CAH to be calcium aluminate hexahydrate (C_3AH_6) that will react with limestone to form calcium carboaluminate hydrate ($\underline{C}$ is short hand for CO_2);

$$C\underline{C} \quad + \quad C_3AH_6 + 5\,H = \quad C_4A\underline{C}H_{11} \quad\quad\quad\quad (4)$$

m = 1.00 g	3.78	0.90	5.68
M = 100.09 g/mol	378.29	18.02	568.50
n = 9.99 mmol	9.99	49.95	9.99
ρ = 2.67 g/ml	2.52	0.998	2.17
V = 0.375 ml	1.500	0.902	2.618
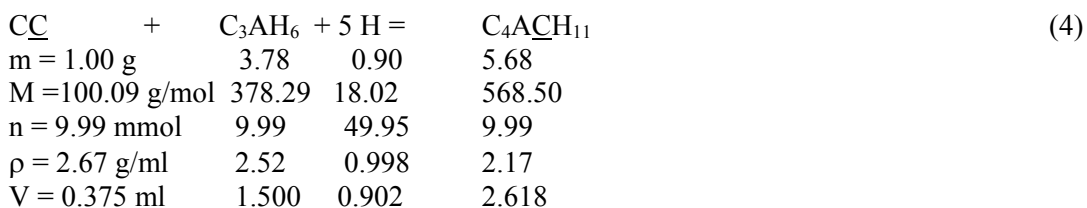
According to Eq. 4, 100 g calcium carbonate (1 mol) would then bind 90 g (5 mol) extra water. The total increase in volume of solids according to Eq. 4 is then (2.618-(0.375+1.500))·100vol%/(0.375+1.500) = 40 vol%. So with a lot of C_3AH_6 produced, this will matter.

The above synergy principle has been studied for fly ash blended cement with limestone, and it has been shown that the fly ash blended cement containing limestone resulted in higher compressive strength than without [3-6].

2   Materials and experiments

2.1   Materials

Since the source of aluminosilicate for the alternative binder can be both fly ash (FA) from coal fired energy plants and from calcined clay (after all fly ash comes from clay contaminations in the coal) and marl (mixture of clay and calcium carbonate), both sources were tried initially with compositions as given in Table 2.

Table 2 Chemical composition (%) and physical properties of fly ashes, marl and clay

Oxide	NORCEM FA	STEAG FA	Marl	Clay
SiO_2	52.9	38.7	49.6	61.7
Al_2O_3	26.4	19.6	18.1	30.5
Fe_2O_3	6.3	6.0	10.6	3.5
CaO	3.3	17.9	14.1	0.1
MgO	2.8	2.0	2.9	0.4
K_2O	3.0	2.5	2.4	3.3
Na_2O	1.0	0.7	0.7	-
SO_3	0.2	6.6	0.5	-
Sum above	95.9	94.0	98.9	99.5
Blaine (m^2/kg)	250	734	-	-
Density (g/cm^3)	2.2	2.6	-	-

The clay mineral in the marl was mostly a smectite ($\approx$ 54%) with major secondary material being calcite ($\approx$25%), while the clay consisted mostly of kaolin ($\approx$ 47%) with major secondary mineral being potassium feldspar ($\approx$ 34%) and quartz ($\approx$ 18%). The marl and clay were provided by Saint-Gobain Weber who calcined it in a rotary kiln close to industrial conditions. The calcined clay was ground to d_{50} = 7 µm while the fly ashes were used as received. The superplasticizer used was SIKA FB2 for mixes 1-9 in Table 3, and for further mixes Dynamon SP 130 supplied by Mapei AS Norway was used.

2.2   Design of alternative binders

Both calcined clays and fly ashes are largely aluminosilicates and the binder mix design was based on the proceeding reasoning. As a first approximation we can say that the maximum consumption of lime (CH) for all silica (S) is molar 1:1 according to the following reaction (using cement chemist short hand notation where C = CaO, S = SiO_2, A = Al_2O_3, $\underline{C}$ = CO_2 and H = H_2O):

$$CH + S = CSH \tag{5}$$

The maximum consumption of lime (CH) for all alumina (A) is molar 3:1 according to the following reaction:

$$3\,CH + A + 3\,H = C_3AH_6 \tag{6}$$

If gypsum is added to the system in excess, ettringite may form;

$$C_3AH_6 + 3\,CSH_2 + 26\,H = C_3AH_6 \cdot 3C\underline{S} \cdot 32H \tag{7}$$

If too little gypsum is added, ettringite may convert to calcium monosulphate hydrate when sufficiently aluminate has reacted to C_3AH_6 or equivalent:

$$C_3AH_6 \cdot 3CS \cdot 32H + 2\ C_3AH_6 = 3\ C_3AH_6 \cdot CS \cdot 12H + 8\ H \qquad (8)$$
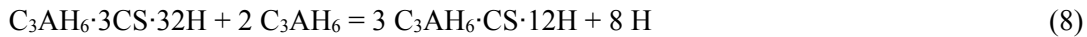
But if excess limestone (C$\underline{C}$) is added with it, the initially formed ettringite being good for early strength will be stabilized since calcium monocarboaluminate hydrate will form instead:

$$C_3AH_6 + C\underline{C} + 6\ H = C_3AH_6 \cdot C\underline{C} \cdot 12H \qquad (9)$$

So there should be a content of gypsum (3:x) to improve early strength and the rest of the A balanced with limestone (1:1-x) for later strength in order to avoid detrimental DEF in a dense system. The gypsum should be kept so low that the initial ettringite formation does not lead to unacceptable expansion in the early age.

The mortars were made according to Table 3. The w/b ratio was 0.63 in all the mortars while maintaining the flow by varying the amount of superplasticizer in the range 0.4 – 2.0 % (of binder weight). The mortar mixes were cast in 40•40•160 mm moulds and 100•200 mm cylinders. After 24 hours the prisms and cylinders were removed from the moulds and stored in a cabinet at 90 % RH and 23 ± 2 ºC.

Table 3 Mortar mix design

Mix no.	1	2	3	4	5	6	7	8	9
Marl [g]	200	200	200	-	-	200	200	200	200
STEAG FA [g]	-	-	-	-	200	-	-	-	-
Norcem FA [g]	-	-	-	200	-	-	-	-	-
Lime [g]	120	120	120	100	90	120	120	120	140
Limestone [g]	20	20	20	15	20	20	20	20	40
Gypsum [g]	40	40	40	25	15	40	40	40	-
DIN sand [g]	1350	1350	1350	1350	1350	1350	1350	1350	1350
Water[g]	240	240	240	240	240	240	240	240	240
Na_2SO_4* [g]	-	10	-	-	-	10	10	-	-
Na_2CO_3* [g]	8	-	-	8	8	10	-	-	11
TerAcc*# [g]	-	-	1	-	-	-	-	0.9	-

*Dissolved in the mixing water. #TerAcc is a ternary accelerator blend

In addition, pastes were made by manual stirring in a cup. The compositions are given in Table 4. The first mix without plasticizer was very dry as can be seen from the right photo in Fig. 3, and become considerably more fluid when the plasticizer was include as seen from the left photo of Fig. 3, even when the accelerator dosage was increased by 11%.

Table 4 Composition of pastes

Component	Clay 1 paste	Clay 2 paste	Marl paste
Calcined clay	20 g	20 g	-
Calcined marl	-	-	20 g
Calcium hydroxide	14 g	14 g	14 g
Calcium carbonate	4 g	4 g	4 g
Water	26.6 g	26.6 g	26.6 g
Sodium carbonate*	1.10 g	1.22 g	1.22 g
SP-130 plasticizer	-	2.09 g	2.09 g

*Dissolved in the water before mixing

Figure 3: Calcined clay 1 paste mix without plasticizer (right) and calcined clay 2 mix with plasticizer and 10.8 % increased amount of accelerator (left). Both pastes had w/b = 0.70.

2.3 Strength measurements

The compressive and flexural strength were measured on the 160·40·40 mm prisms at 1, 3, 7, 28 and 90 days of curing at 90 % RH and 23 °C according to NS-EN 196-1. There were 3 parallel prisms for the flexural strength and six parallels for the compressive strength since it was measured on the end-pieces of the three prisms.

2.4 Capillary suction measurement

The capillary suction technique was performed on four parallel 20 mm slices sawn from cast cylinders from each mortar mixture. The specimens were dried at 105°C drying before capillary suction measurements.

The procedure consists of 6 important steps for the specimen:

1. Drying the specimen to constant weight at 105°C
2. Water saturation by submersion 3 days in water at 1 atm
3. Pressure saturation by submersion 3 days in water at 80 atm
4. The outer volume (V) is recorded by differential weighing the specimen under water and saturated surface dry in air according to the principle of Archimedes.
5. Drying the specimen to constant weight at 105°C

From these 5 steps, was the initial moisture content, total porosity (ε_{tot}), capillary porosity (ε_{cap}), entrained air volume (ε_{air}), average density of mortar solids (ρ_s) and dry density of mortar (ρ_d) calculated as closer described by Justnes et al [7].

2.5 Scanning electron microscope (SEM) investigations

Samples from paste mixes were cast in epoxy resin, plane polished to achieve a cross-section of the material and sputtered with carbon. The instrument used in this study was JEOL JXA – 8500F Electron Probe Micro analyser. The samples were analysed in the BSE (back scattered electron) mode where dense compounds and/or compounds composed of heavy elements appear bright (e.g. unreacted C_4AF mineral in cement) and compounds of low density and/or composed of elements with low atomic number appears dark (e.g. CSH). Details of interest were first checked for elements by EDS (energy dispersive spectra) semi-

quantitatively, and further quantitatively by WDS (wave length dispersive spectra) for compositional determination.

2.6 Thermo gravimetric analysis (TGA)

Samples of paste were analysed by thermogravimetric analysis and simultaneous differential thermal analyses (TGA/SDTA) with a Mettler Toledo TGA/SDTA 851. About 150 mg of the sample was weighed into aluminium oxide crucibles. The sample was heated from 40°C to 900°C with a heating rate of 10°C/min. The purge gas was nitrogen (N_2) with a flow of 50 ml/min.

The mass loss up to 400 is considered to be the dehydration of various hydration products. The mass loss from 450-550°C is caused by the thermal decomposition of calcium hydroxide (CH).The total mass loss from 105-550°C is taken as total chemical bound water. The mass loss in the higher temperature range from about 600°C to 950°C is attributed to the decomposition of carbonates.

The lower and upper limits of these temperature intervals were determined from the DTG (the first derivative) curve. The first interval starts at 40°C and ends and the beginning of the decomposition peak of calcium hydroxide in the DTG curve. The third interval starts where the decomposition peak of calcium hydroxide flattens out (about 600°C) and reaches up to 900°C.

2.7 X-ray diffraction analysis (XRD)

Samples from paste mixes cured at 90 % RH and 20°C were analysed by AXS D8 focus X-ray diffractometer. Prior to these analyses the samples were dried in a desiccator at 30 % RH using calcium chloride as a drying agent. The dry powders were submitted to an angular scan between 5 and 75° 2θ with a step size of 0.06° and a step time of 1.0 s.

3   Results and discussion

3.1   Compressive strength of mortars

As a first screening series only small mixes were made of series 1-6 were one set of 3 RILEM prisms were cast and compressive strength after 1 day was reported as an average of the 6 prism end-pieces with standard deviations as given in Table 5, while several sets were made for mixes 7-9 to see how they would develop further. In particular mix 9 seemed promising with higher 1 day strength, so a larger batch was made and it is the results of the second, larger batch that are presented in Table 5. A large mix 9 was repeated with calcined clay (composition in Table 1) rather than calcined marl and without changing the other components of the mixture. This is called mix 9* in Table 5.

Table 5 Compressive strength (MPa) for mixes 1-9

Mix number	Average compressive strength ± standard deviation [MPa] at ages [days]			
	1 day	3 day	28 day	90 day
1	1.6±0.0	-	-	-
2	1.9±0.0	-	-	-
3	1.4±0.0	-	-	-
4	1.3±0.0	-	-	-
5	No strength gain	-	-	-
6	1.3±0.0	-	-	-
7	1.4±0.1	7.3±0.3	20.4±0.2	-
8	1.1±0.0	6.8±0.2	18.6±0.1	-
9	3.0±0.1	7.1±0.2	18.4±0.2	20.9±0.2
9*	3.0±0.1	14.2±0.7	24.2±0.4	26.5±1.1

*The calcined marl was replaced with calcined clay (composition in Table 2) without changing content of the other components in mix 9.

3.2   Capillary suction by mortars

The average capillary suction profiles for the 3 individual discs from two batches of mix 9 are plotted in Figs. 4 and 5, while the data extracted from these profiles are listed in Table 6 including their standard deviation. Fig. 6 shows a photo of the discs on the grid over water.

Table 6 Mortar properties extracted from the capillary suction experiments

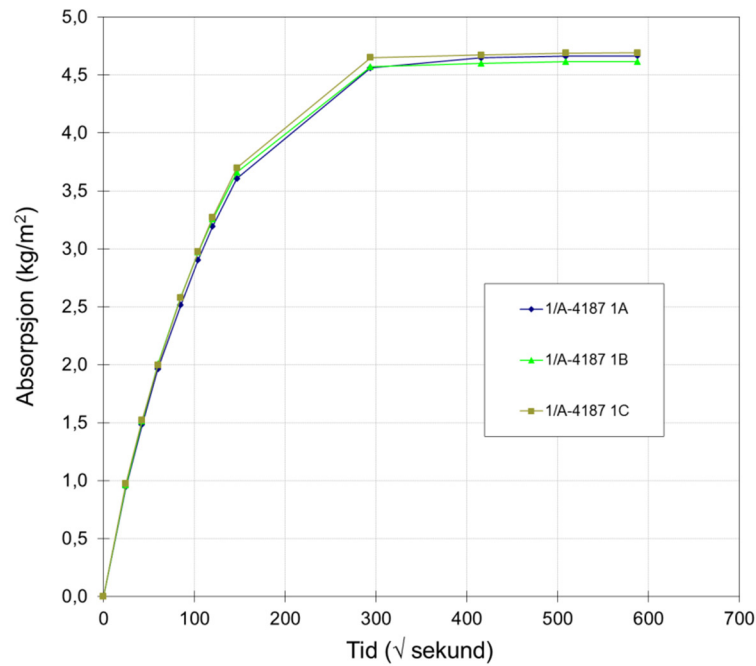| Sample from mix 9*	Capillary porosity ε_{cap} [vol%]	Air content ε_{air} [vol%]	Average density of solids, ρ_s [kg/m^3]	Dry density ρ_d [kg/m^3]
1	25.4 ± 0.2	3.5 ± 3.5	2619 ± 0	1865 ± 2
2	25.2 ± 0.5	3.8 ± 5.0	2613 ± 6	1857 ± 5

Figure 4: Capillary suction profiles of 1st batch of mortars with recipe mix 9
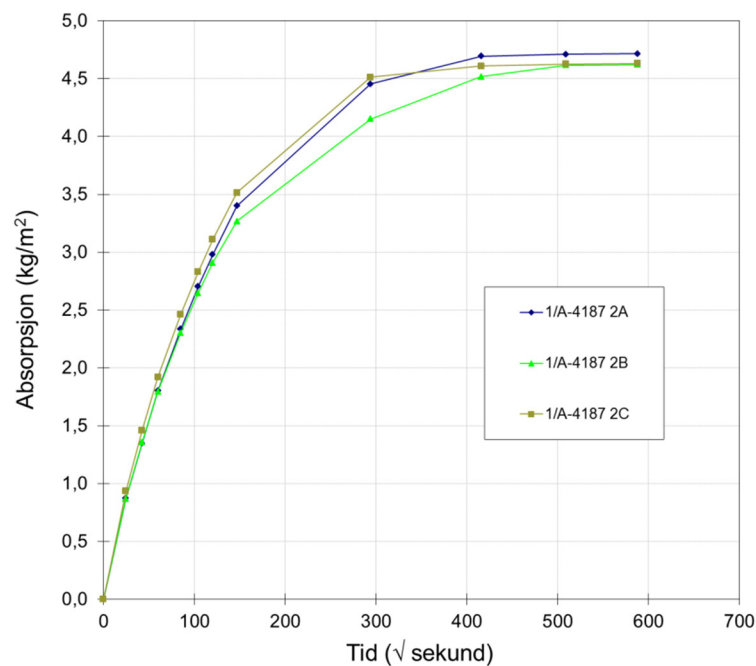

Figure 5: Capillary suction profiles of 2nd batch of mortars with recipe mix 9

An attempt was also made to measure capillary suction of mix 8 with gypsum, but these discs were swelling and cracking as seen from Fig. 7. This is probably because mix 8 contained gypsum forming ettringite that was decomposed during drying and reformed upon wetting. However, the prism was also expanding too much (+0.2%), so the concept of including gypsum in the mixes was dropped (or should be reduced) for further research.

Figure 6: Mortar discs of Mix 9 in the capillary suction set-up.

Figure 7: Mortar discs of Mix 8 in the capillary suction set-up. Note that the discs are swollen to an extent that cracks are induced.

3.3 Paste mixes with calcined clay

A segment (7-15° 2θ) of the X-ray diffractogram of lime-calcined clay binder hardened for 28 days are shown in Fig. 8. Next to the peak of an illite contamination is the major peak of calcium monocarboaluminate hydrate (marked CAH) confirming the predicted reaction pattern in Eq. 9. The CAH peak is also present in the calcined marl paste as expected.
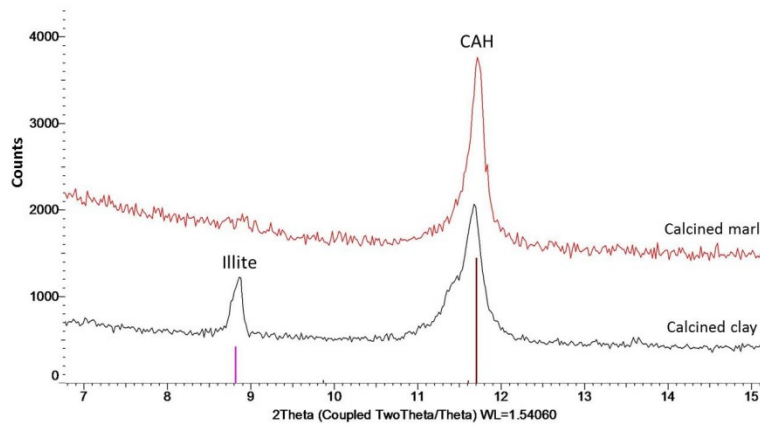
Figure 8: XRD segment showing illite peak to the left and calcium monocarboaluminate hydrate to the right.

The thermogravimetry (TG) curves and the derivative (DTG) of the lime-calcined clay 1 paste just after mixing (0 days) and after 31 days curing are showed in Fig. 9, while the curves for lime-calcined marl paste after 0 and 28 days curing are depicted in Figure 10.
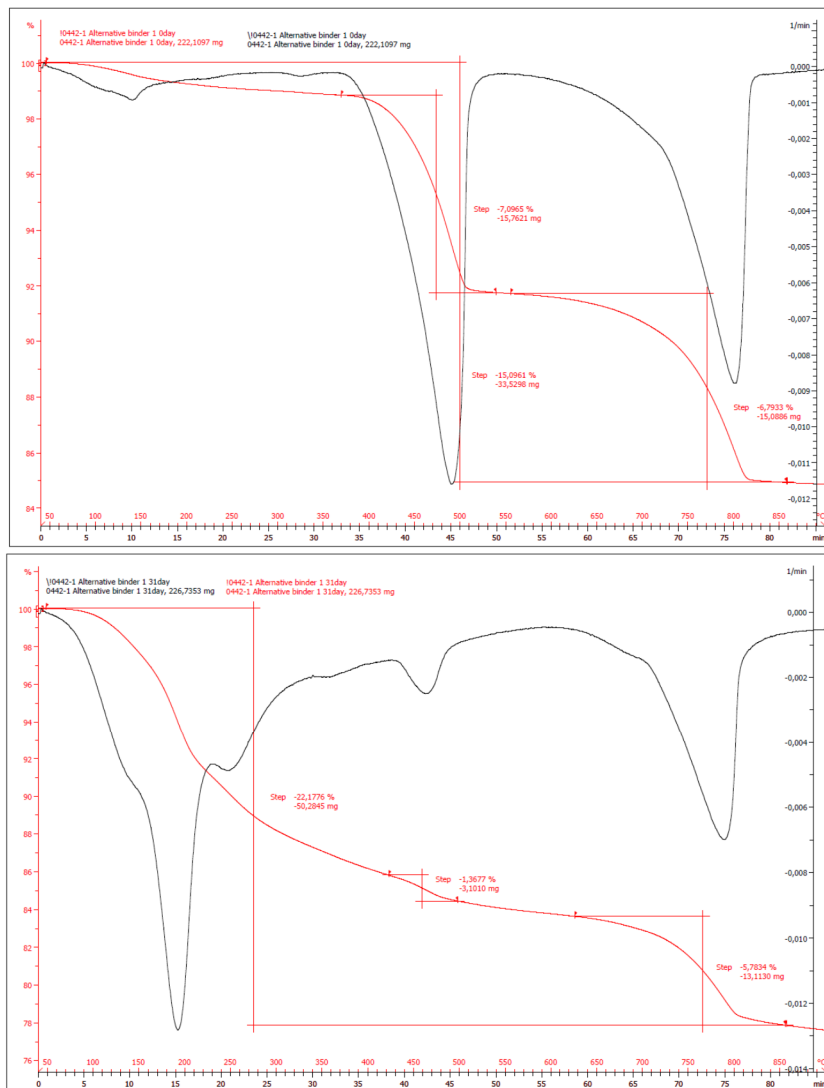

Figure 9: The TG and DTG curves of the lime-calcined clay paste just after mixing (upper graph) and after 31 days curing (lower graph).
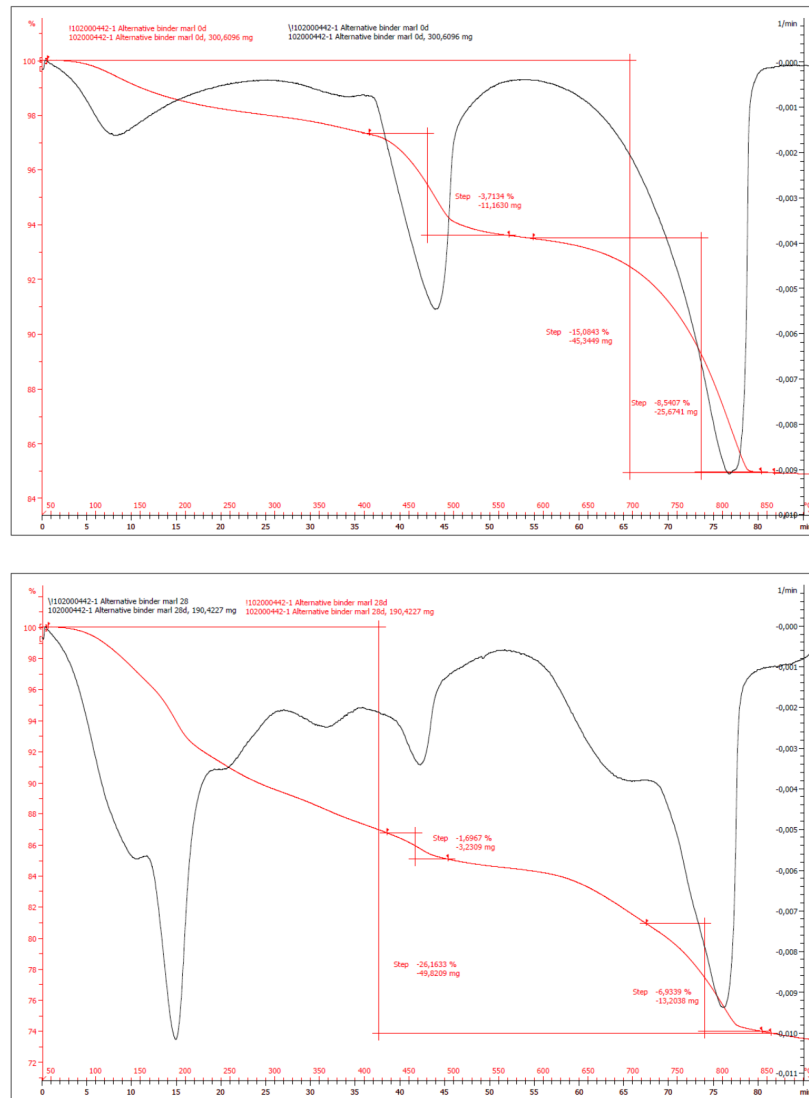
Figure 10: The TG and DTG curves of the lime-calcined marl paste just after mixing (upper graph) and after 28 days curing (lower graph).

The amount of calcium hydroxide in the samples was calculated from the weight loss due to dehydration of calcium hydroxide. This weight loss results in a marked step in the TG curve between about 400°C and 550°C. The dehydration reaction of calcium hydroxide is shown in equation 10.

$$Ca(OH)_2 \text{ (74 g/mol)} \rightarrow CaO + H_2O \text{ (18 g/mol)} \tag{10}$$
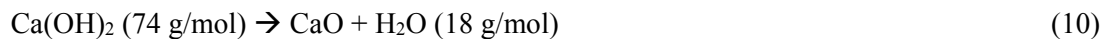
Therefore the amount of calcium hydroxide can be calculated by multiplying the measured weight loss due to the dehydration of calcium hydroxide with 74/18.

The pozzolanic activity is the ratio between the amount of calcium hydroxide consumed between 0 and 28 or 31 days, and the amount of calcium hydroxide at day 0. Table 7 shows the results as a percentage of the sample mass along with relative mass loss for other temperature ranges. As comparison from our experience pozzolanic materials like silica fume and metakaoline has a calcium hydroxide consumption of about 82 % and 89 % respectively, after 28 days of curing.

Table 7: The mass losses for different temperature ranges as % of the total sample mass after mixing (0 day) and after 28 or 31 days of curing, and the pozzolanic reactivity (pozz).

Paste sample	Age	Mass loss Ca(OH)$_2$	Δ = pozz	Mass loss ca 850 °C	Δ	Mass loss 40-900 °C	Δ
Calcined clay 1	0 day	7.1	80.3	6.8	14.7	15.1	47.0
	31 days	1.4		5.8		22.2	
Calcined clay 2	0 day	5.9	78.0	8.7	14.9	15.7	50.3
	31 days	1.3		7.4		23.6	
Calcined Marl	0 day	3.7	54.1	8.5	18.8	15.1	73.5
	28 day	1.7		6.9		26.2	

The total mass losses after 0 and 31 days are 15.1 and 22.2%, respectively, for calcined clay 1 paste. If the carbonate peak is omitted, the change is from 8.3 to 16.4%, or 8.1% extra water is bound in the period. The mass loss due to calcium hydroxide seems considerably reduced in the period, indicating that too little was added, and may be the direct reason for the modest strength increase from 28 to 90 days for the mortar (see mix 9* in Table 5). The reason might be that the formed CSH had a higher C/S than 1 as assumed in the formulation. However, the lime content was kept low in an attempt to make the overall composition environmental friendly (to reduce the carbon footprint) and the strength may increase if a bit more lime is added.

The calcined marl paste has nearly the same total mass losses as for calcined clay paste after 0 and 28 days curing of 15.1 and 26.2%, respectively, corresponding to a mass loss of water when carbonate peak is excluded to 6.6 and 19.3%, respectively, leading to 12.7% extra bound water in the period. In spite of more bound water, the corresponding mortar mix 9 in Table 5 exhibit less strength than 9*. From the lower DTG curve of the calcined clay paste in Fig. 9 and from the calcined marl paste in Fig. 10, it is obvious from in particular the first peaks 50-300°C that the hydration products are different, or at least the relative distribution between the 3 peaks in the range. The calcined marl paste also has a more dominating peak/shoulder at about 700°C that are not subtracted, so if this is CO_2 loss from a carbonate product rather than water, the situation may be different.

Fig. 11 show two back scattered electron (BSE) images of calcined clay paste indicating the importance of dispersing the samples properly as lumps of calcium hydroxide might persist since the high initial pH of the pore solution will depress CH solubility and rather dissolve silicate and aluminate species that will diffuse into this lumps and react there. If one consider the solubility product of calcium hydroxide;

$Ca(OH)_2 = Ca^{2+} + 2OH^-, K_{sp} = [Ca^{2+}] \cdot [OH^-]^2 = 5.5 \cdot 10^{-6}$

Alone $[Ca^{2+}] = \frac{1}{2}[OH^-] \rightarrow [OH^-] = 2.22 \cdot 10^{-2} \rightarrow pH = 12.35$ and $[Ca^{2+}] = 1.11 \cdot 10^{-2}$

If $pH = 14 \rightarrow [OH^-] = 1 \rightarrow [Ca^{2+}] = K_{sp} = 5.5 \cdot 10^{-6}$

That means that when pH is raised to 14, the solubility of calcium cations, $[Ca^{2+}]$, is suppressed by a factor of about 2,000! This is called the "common ion" effect. So alumina and silica will be more soluble than calcium.

In the left BSE of Fig. 11; Composition in point 1 as analysed by energy dispersive spectroscopy is in atom% 22.0 Ca, 11.0 Al, 5.6 Si, leading to a molar ratio Ca/Al = 2.0 corresponding to a C$_4$A.. phase that most probably is the calcium monocarboaluminate hydrate C$_4$A$\underline{C}$H$_{12}$ that also is proven to exist by XRD. The composition in point 2 is in atom% 29.1 Ca, 6.3 Si, 1.1 Al, meaning it is a CH lump that mostly Si has diffused into.
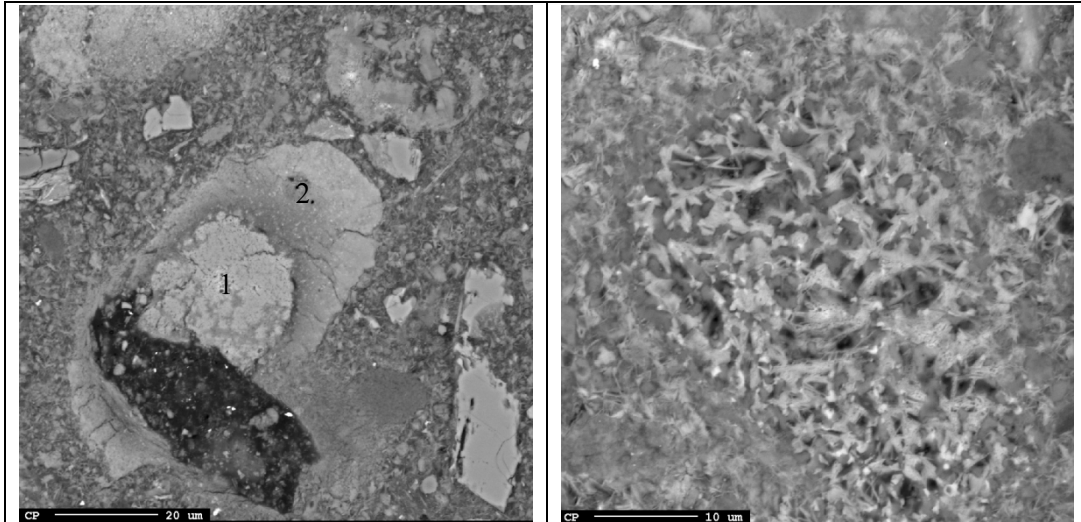
Figure 11: BSE images of hardened calcined clay 1 (left) and 2 (right) pastes showing regions of two phases originating from ill-dispersed calcium hydroxide particles with depressed solubility due to high pH.

The right BSE in Fig. 11 shows a 2-phase area where the bright details consist of 20.4 Ca, 16.2 Al, 3.2 Si in atom% and the grey details consist of 27.7 Ca, 10.5 Al, 8.2 Si in atom%. Again, the whole area of about 20x15 µm probably have been an undispersed CH powder grain that Al and Si species has diffused into and reacted since CH has low solubility due to high pH.

Fig. 12 shows BSEs of two details from the calcined clay 2 pastes, a CSH in the centre of the left BSE and some pure compound growing out of the left side of an air void (circular pore of diameter 30 µm). The composition in the black spot in left BSE (analysis point marked by electron beam) is in atom% 22.1 Ca, 18.5 Si and 3.2 Al giving atomic ratio Ca/Si = 1.2 and showing that is a CSH with some bridging AlO_4 between silicate dimer anions common for Al-containing SCMs. The composition of thin needle-like "nest" in the right BSE was analysed as a 5µm circular area to 19.5 Ca, 9.7 Al, 3.2 Si as atom% corresponding to a molar ratio Ca/Al = 2.01which again will be a C_4A.. phase, most probably $C_4A\underline{C}H_{12}$ or calcium monocarboaluminate hydrate, which also was proven by XRD to exist in the sample.
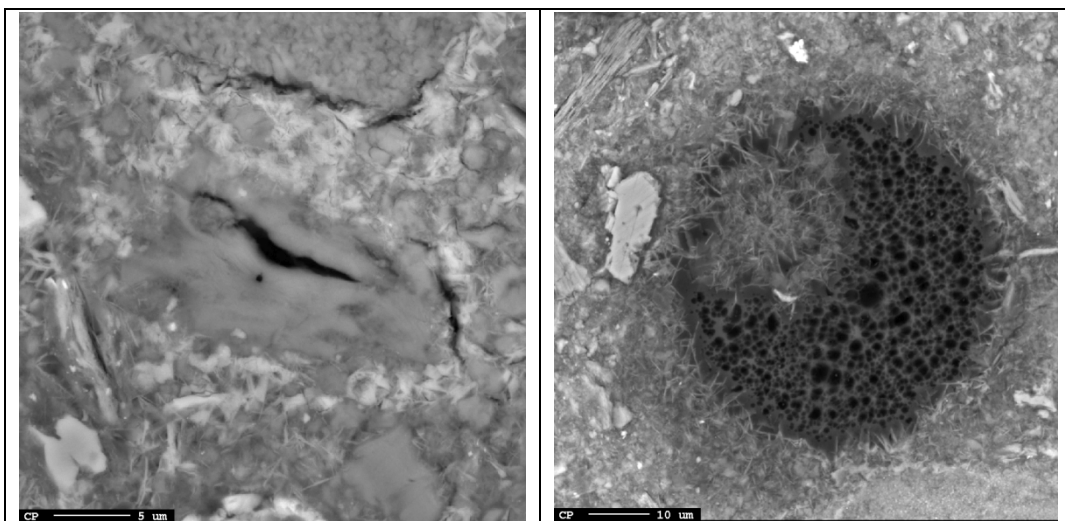

Figure 12: BSEs of calcined clay 2 pastes showing light grey hydration product to the left and a "nest" of a pure compound growing into a circular air void to the right.

Among the many different features of the calcined clay paste, there was also another 2-phase area shown as an overview to the left and as a close up to the right of Fig. 13. The composition of the bright phase was in atom% 22.6 Ca and 16.2 Al giving atomic ratio Ca/Al = 1.4 that could indicate the phase C_3AH_6 which should have Ca/Al = 1.5 theoretically. The grey phase consisted of 27.2 Ca, 15.3 Si and 1.6 Al in atom% giving Ca/Si = 1.78 or Ca/(Si+Al) = 1.61, so it is a CSH with some Al but with much higher C/S than predicted ($\approx$ 1) explaining perhaps the early depletion of calcium hydroxide.
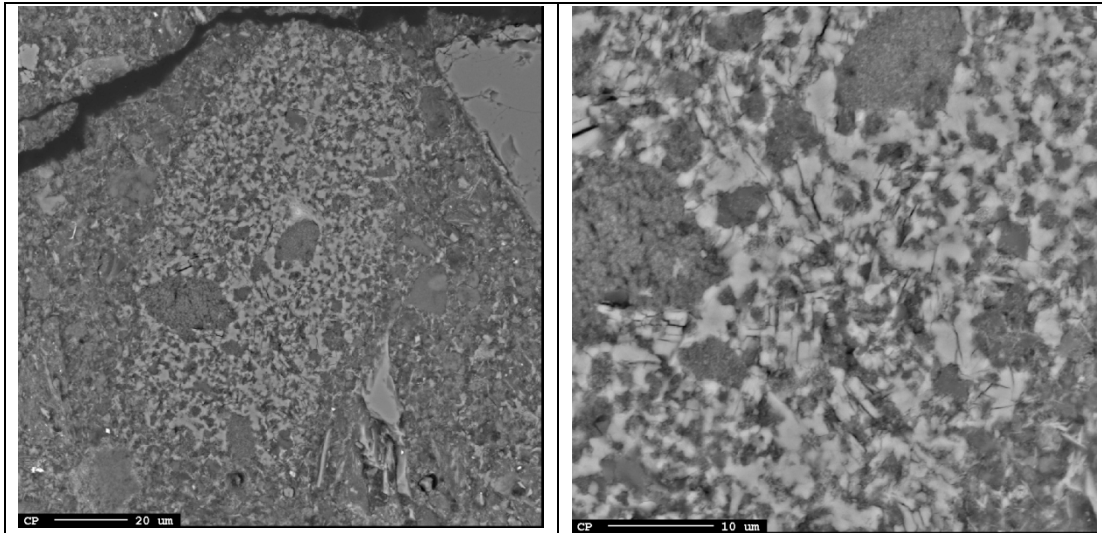

Figure 13: An overview of a 2-phase area (left) and a close-up of it (right) for the calcined clay 1 paste.

Back-scattered electron (BSE) images of the paste based on calcined marl are reproduced in Fig. 14 showing remains of partly reacted calcined marl particles of 15-20 μm size partly delaminating from the matrix due to drying shrinkage caused by the vacuum in the electron microscope to the left. The brighter details within these particles are rich in calcium (original calcium carbonate inherent in the marl). The nearly white particles between the calcined marl particles in the matrix are calcium carbonate deliberately added to the paste.
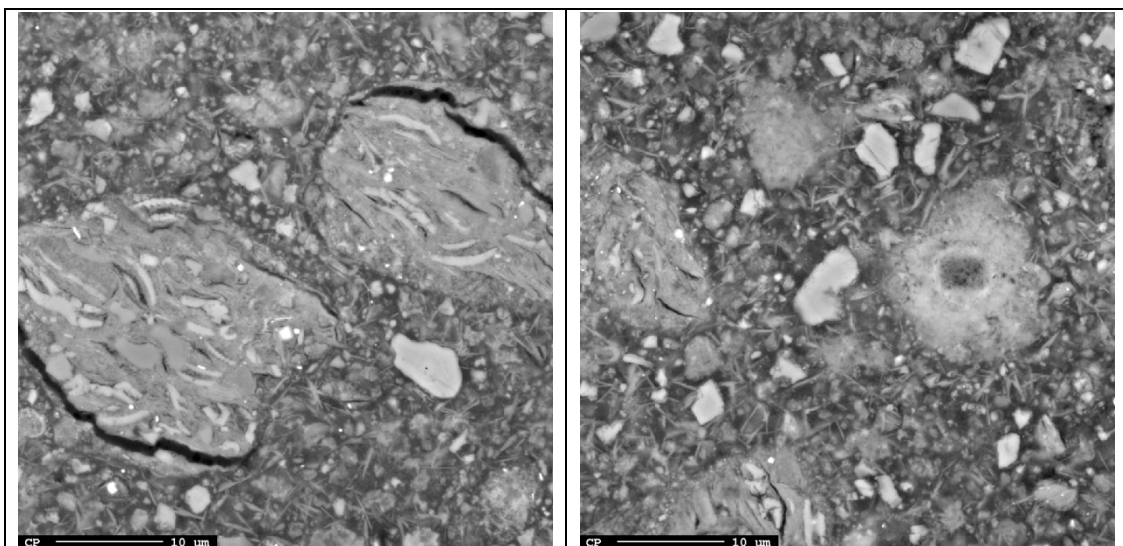

Figure 14: An overview of the microstructure of hardened paste based on calcined marl

The diffuse, light grey particle to the far right of the right image in Fig. 14 is an about 10 μm diameter undispersed lump of calcium hydroxide that dissolved aluminate and silicate species has diffused into and reacted since the solubility of calcium hydroxide is depressed by the high pH as explained earlier. The rectangular mark in the particle is the result of a de-focused electron beam analysing its content by energy dispersive spectrum (EDS) to 20.6 Ca, 11.4 Si, 1.3 Al and 4.1 Na as atom%. The sodium comes from the added sodium carbonate to accelerate the reactions.

The grey mass in the matrix is essential epoxy to hold the material together during polishing. The more obvious presence of it compared to the clay 1 paste indicates that this sample is more porous. Throughout the matrix there are also a lot of thin needle-like hydration products (possibly flakes that are cut through looking like needles in a cross-section) that are not so prominent in the paste based on calcined clay (comparing Fig. 14 with Fig. 11). The clay mineral dominating calcined marl is a smectite, while in the calcined clay it is kaolin. Albeit both are aluminosilicate, the reaction products do not need to be the same as the kinetics of dissolution and species in solution may be different. The atomic Al/Si ratio in kaolinite is 1 (composition $Al_2Si_2O_5OH_4$), while smectites generally are richer in silicon than aluminium depending on their iron content.

Fig. 15 shows some close-up images of the microstructure of hardened paste based on calcined marl. Knowing that that a single point element analysis encompasses 1 μm^3, it is impossible to measure the composition of the very thin needles without getting "contaminations" from surrounding material. Nevertheless, and attempt was made for a fibre cluster in the centre of the left image of Fig. 15. Note that the decomposition by the heat of the electron beam under vacuum indicates that these are indeed hydrates. The composition in atom% was 8.6 Ca, 10.2 Al and 15.0 Si, while a similar cluster in another region gave a similar composition of 9.6 Ca, 9.7 Al and 13.5 Si considering the inhomogeneity. However, the composition did not fit to any known compound as the silicon content was too high to be Strätlingite, C_2ASH_8. The left image of Fig. 15 shows a lump large enough to be analysed by EDS with a defocused beam leaving a rectangular mark also indicating that it is a hydrate. The composition in atom% turned out to be 21.2 Ca, 11.3 Si, 1.4 Al and 2.5 Na. It can originate in a small calcium hydroxide particle that has been reacted through by dissolved silicate to a kind of CSH with C/S = 1.9.
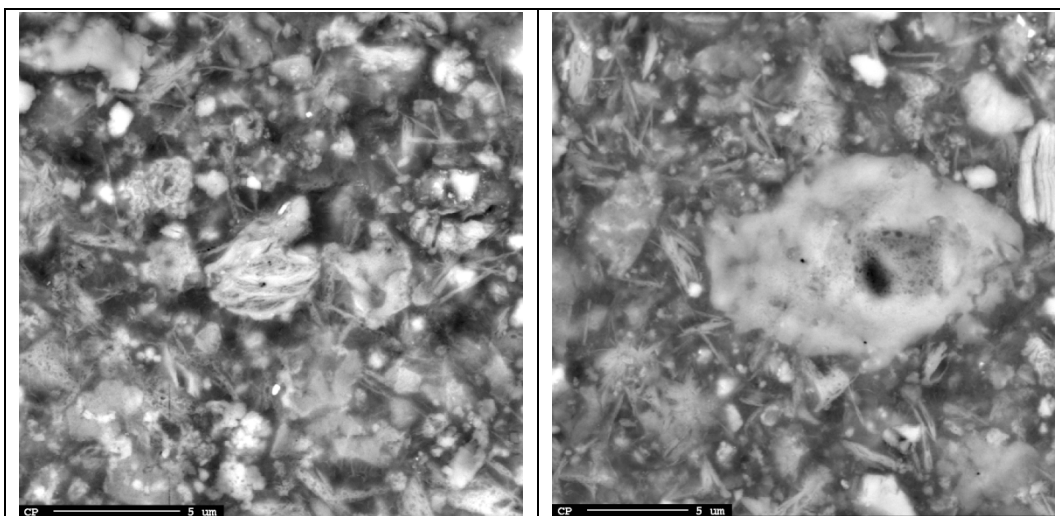

Figure 15 Close-ups of the microstructure of hardened paste based on calcined marl.

4   CONCLUSIONS

Two synergy principles have been described for making improved binders based on slaked lime and pozzolanic SCMs. One showing how neutral salts may accelerate by forming strong alkaline solutions *in situ*. Another one how calcium carbonate can play a role when alumina containing SCMs are used by leading to an even higher conversion of liquid water into solid hydrates leading to lower porosity and higher strength.

An example have been showed for a binder consisting of calcined clay, slaked lime and calcium carbonate on how mortars can achieve a 28 days compressive strength of about 25 MPa and 3 day strength exceeding 10 MPa when cured at 20°C when accelerated by sodium carbonate. The strength may have been improved further by having a slightly higher ratio of calcium hydroxide.

Calcined marl may substitute for calcined clay, but then the calcium carbonate content should be reduced in accordance with the remaining calcium carbonate content after calcination.

The formulations are not entirely correct according to the outlined 2nd principle since they rely on bulk chemical compositions and the fact that the commercial clay/marl was containing inert quarts or feldspars. Ideally the formulations should be made according to the content of clay minerals and their compositions only after subtracting the inert components. However, such a composition of reactive material may be difficult to arrive at.

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