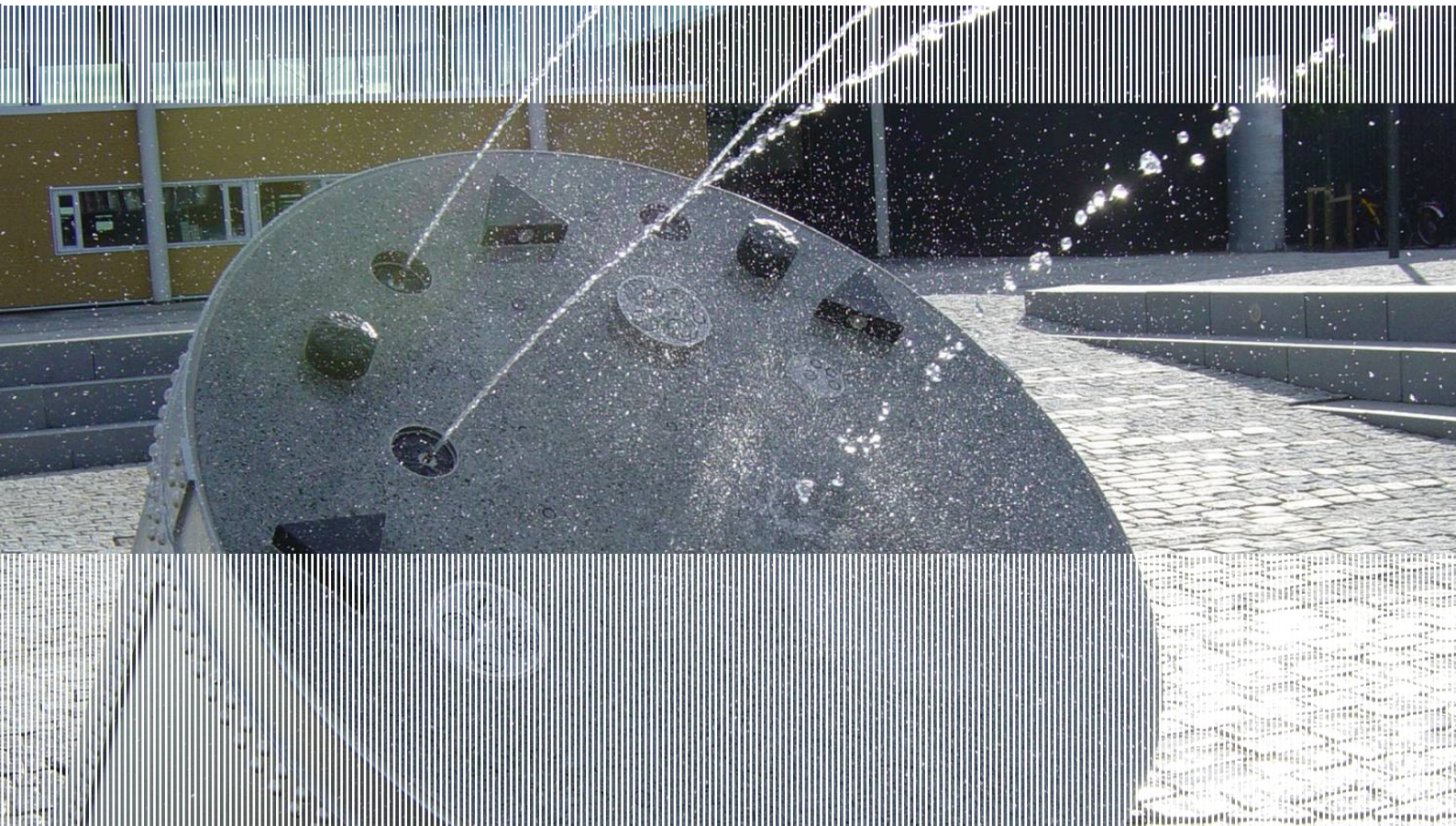# COIN

SINTEF Building and Infrastructure   Tone Østnor and Harald Justnes

Durability of mortar with calcined marl as pozzolan

COIN Project report 49 – 2013

SINTEF Building and Infrastructure

Tone Østnor and Harald Justnes

Durability of mortar with calcined marl as pozzolan

FA 1 Environmentally friendly concrete

SP 1.1 Low carbon-footprint binder system

Cooperation partners / Consortium Concrete Innovation Centre (COIN)

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

Calcined marl – ordinary "blue" clay containing calcium carbonate – has been shown earlier to be an effective pozzolan in cementitious materials in terms of strength if calcined at the correct temperature. Marl is unsuitable for the clay product industry, and might thus be the high-volume available alternative pozzolan globally that the cement and concrete industry is looking for in order to reduce their carbon footprint.

The objective of the present study was to investigate how durability of mortars is affected when calcined marl is replacing cement by volume at levels of 0, 20, 35, 50 and 65vol%.

Excellent strength at both 1 and 28 days relative to reference is obtained when up to 50 vol% is replaced by calcined marl, and the strength continues to increase up to 1 year (last measuring point). The capillary porosity volume is increasing, but the electrical resistivity is also increasing, indicating a pore refinement or segmentation, as well as perhaps reduced ionic strength in the pore water. These are properties that might reduce the propagation rate of rebar corrosion once initiated by carbonation. Furthermore, the chloride ingress is significantly reduced when cement is replaced by calcined marl.

The carbonation rate is increasing with increased cement replacement by calcined marl, but this effect may be counteracted by reducing the water-to-cement ratio (w/c) further. Just note that if w/c is reduced the conventional way by increasing the cementitious binder to aggregate ratio, the effect on reduced CO_2 emission may be considerably reduced due to the higher volume of binder per cubic meter of concrete. Hence, lean concrete mixes should be made with the aid of appropriate plasticizing admixtures.

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Introduction

1.1 Objective

Calcined marl has previously been shown to be an excellent pozzolan giving high strength when replacing cement in mortars.

The objective was now to investigate how durability of mortars is affected when calcined marl is replacing cement.

1.2 Background

Marl, or calcareous clay, is considered "bad" clay for production of burnt clay products (e.g. bricks and light weight aggregate) since it is clay containing substantial amounts of calcium carbonate that will form CaO after burning. This can lead to "pop outs" when calcium oxide reacts with water to calcium hydroxide during service.

Calcined marl is proven in earlier study by Justnes et al [1] to be an effective pozzolan in cementitious products and for this reason marl can be a large resource that is not yet exploited to make blended cements or as a mortar/concrete additive. Marl with 10–20 % $CaCO_3$ was calcined over a range of temperatures from 600 to 1000°C, and the optimum calcination temperature with respect to reactivity as pozzolan seemed to be around 800°C as seen from the plots of compressive and flexural strengths in Figures 1 and 2, respectively.

The next step was to cast mortar where cement was replaced with higher amounts of marl calcined at the optimum temperature of 800°C. The compressive and flexural strengths at 28 days for mortars where cement is replaced with 20, 35 and 50 % calcined marl are plotted in Figures 3 and 4, respectively. Evidently, mortar with 50 % replacement of cement by calcined marl attains the same 28 days strength as mortar with 100 % cement.

Then it was interesting to see how the compressive strength developed as a function of time since the early strength generally will be lower when cement is replaced by as much as 50% in either mortar/concrete recipes or in blended cements. The compressive strength development for mortar where 50% cement is replaced by marl calcined at 800°C is depicted in Figure 5. The 1 day strength of ≈ 10 MPa seems sufficient for removing formwork in practice.
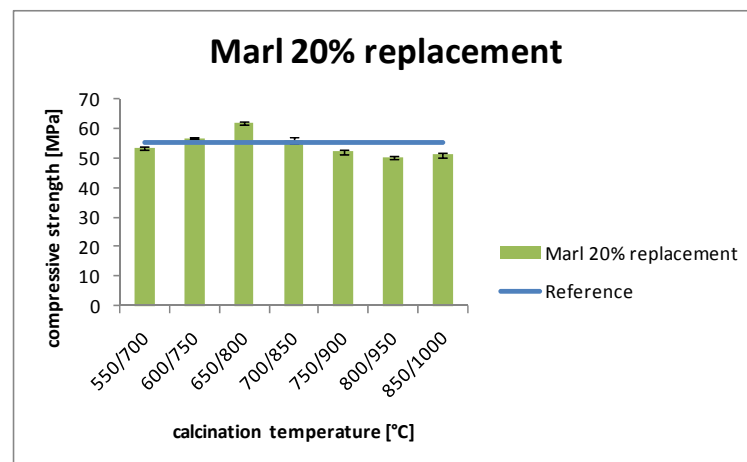
Figure 1 Compressive strengths at 28 days for mortars with 20 % replacement of cement by calcined marl as a function of calcination temperature for the marl. The upper of the two temperatures is what the marl actually experience in the kiln.
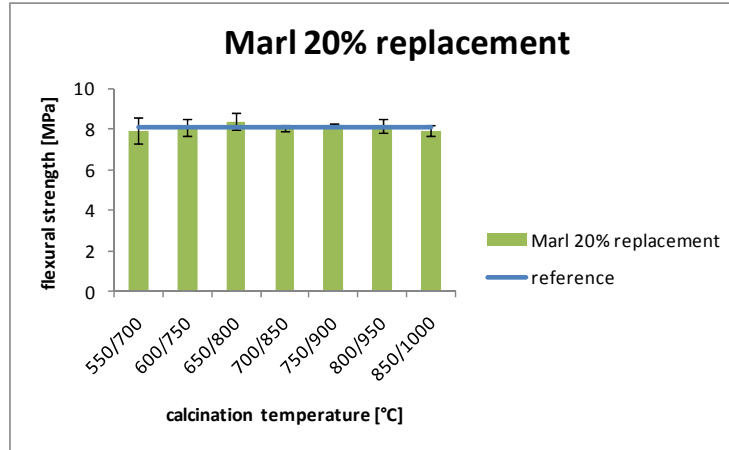
Figure 2 Flexural strengths at 28 days for mortars with 20 % replacement of cement by calcined marl as a function of calcination temperature for the marl. The upper of the two temperatures is what the marl actually experience in the kiln.
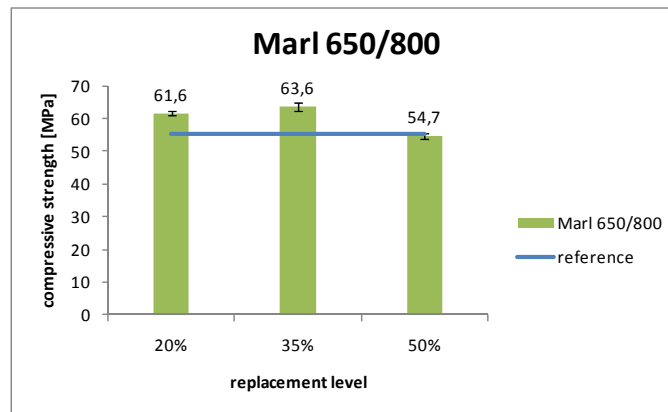
Figure 2 Compressive strength at 28 days for mortars with 20, 35 and 50 % replacement of cement by marl calcined at 800°C. Reference is mortar based on 100 % Portland cement with strength level according to the blue line.
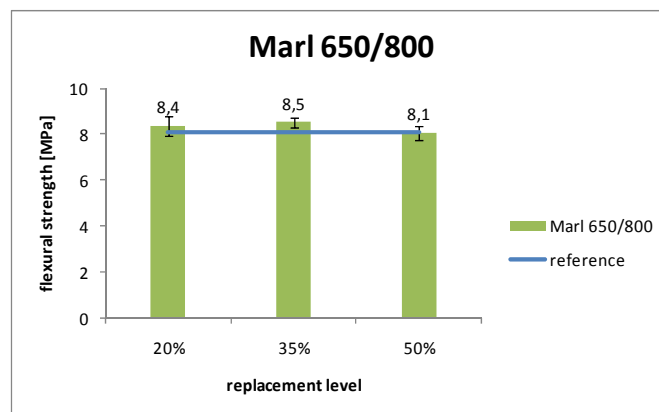
Figure 3 Flexural strengths at 28 days for mortars with 20, 35 and 50 % replacement of cement by marl calcined at 800°C. The reference is mortar based on 100 % Portland cement with strength level according to the blue line.
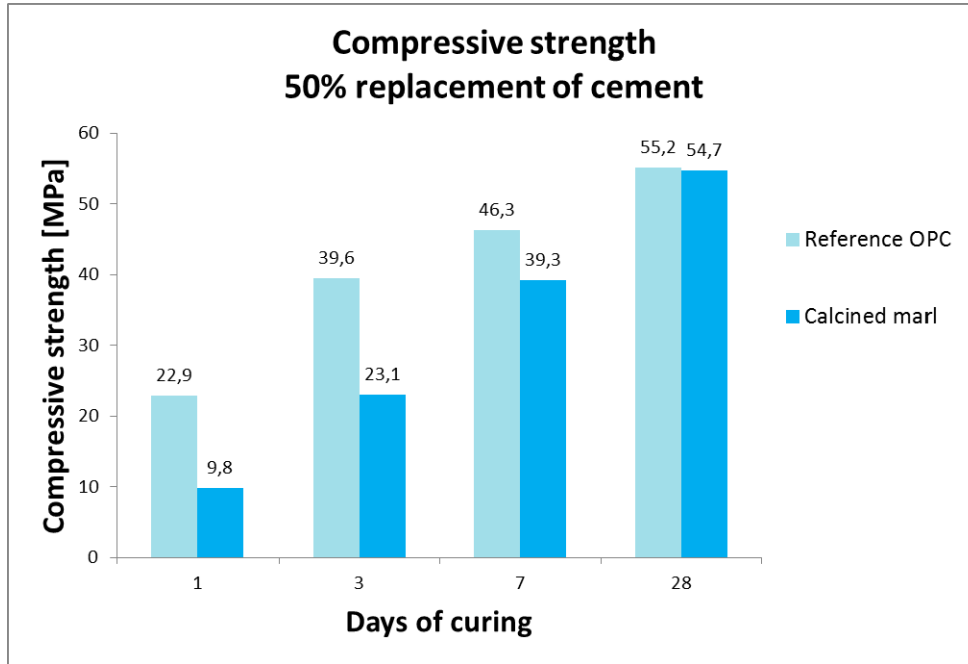
Figure 5 Compressive strength development as function of time for mortar where cement has been replaced with 50 % calcined marl as compared to the strength of mortar with 100 % cement.

Calcined marl may be considered "industrial pozzolan" within the European cement standard (EN 197-1), and it may be feasible to make a pozzolanic cement with up to 55 % clinker replacement (CEM IV/B) considering the 28 day strength and sufficient early strength shown in Figure 1-5.

Note that all cement replacements by calcined marl was made by mass. Since calcined marl has a lower density than cement, that will result in higher total binder volume. Thus, the cement replacements in the present study reported in the following was done by volume% to keep the binder volume constant. Solid densities for cement and calcined marl were assumed to be 3.15 and 2.67 g/ml, respectively.

2 Experimental

2.1 Materials

The marl was provided by Saint-Gobain Weber who calcined it in a rotary kiln close to industrial conditions The calcined marl were ground to $d_{50} = 7$ µm. Normal Portland cement (CEM I 42.5R according to NS-EN 197-1) produced by Norcem, Brevik, Norway, was used for all the mortar mixes. The aggregate used was 0–8 mm crushed granite rock from Årdal, Norway. The superplasticizer used was Dynamon SP 130 supplied by Mapei AS Norway.

2.2 Mortar mix design

The mortars were made with 0, 20, 35, 50 and 65 % replacement of cement with marl by volume to secure a constant volume of binder. The consistency of fresh mortar was determined using a flow table. The aim was to obtain a w/b ratio of 0.5 in all the mortars while maintain the flow by varying the amount of superplasticizer in the range 0.1–0.8 % (of binder weight). The flow of all mortars was within ± 5 % of the reference. 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 °C.

2.3 Strength measurements

The compressive and flexural strength were measured on the 160·40·40 mm prisms at 1, 3, 7, 28, 90 and 365 days of curing 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. After drying the discs are placed on a grating 1 mm below the water surface in a covered box. The increase in weight as specimen suck water is monitored for 4 days and plotted versus square root of time.

The procedure consists of 6 important steps for the specimen:

1. Drying to constant weight (W_1)
2. Capillary suction for 4 days with weight monitoring
3. Water saturation by submersion 3 days in water at 1 atm (W_2)
4. Pressure saturation by submersion 3 days in water at 80 atm (W_3)
5. 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.
6. Drying the specimen to constant weight at 105°C (W_4)

From these 6 steps, one can calculate 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) as closer described by Justnes et al [2].

2.5   Electrical resistivity measurement

The resistivity measurements were performed at 20 ºC on the 20 mm discs from the capillary suction experiment after they were water saturated. Conducting gel was applied on the end surfaces ensuring electrical contact before placing two steel plates towards them and the resistivity was measured using a multimeter in the AC mode and a frequency of 1 MHz.

2.6   Chloride ingress measurements

The determination of chloride penetration resistance was performed according to NT Build 443. The specimens were immersed in chloride solution (165 g NaCl per liter) for 35 days. At the end of the exposure period thin layers (1 mm layers first 4 mm and then 2 mm) were ground inwards from the exposed surface. The chloride content for these layers was determined by spectrophotometric method. The obtained chloride content versus time profiles was then fitted to the solution of Fick's 2nd law of diffusion and an apparent chloride diffusion coefficient calculated.

2.7   Carbonation resistance measurement

Determination of resistance to carbonation was performed according to NS-EN 13295 on all the mixes after 90 days of curing. The prisms were stored in a cabinet with an atmosphere of 1 % CO_2 and 60 ±10 % RH secured by flowing gas of that composition and by replacing the desiccating agent "blue gel" (silica gel with indicator) whenever needed. After 8 weeks the prisms were split in two and the carbonation depth were measured on the surface sprayed with phenolphthalein becoming pink if pH > 10 and colourless if pH < 10. The splitting and testing of carbonation depth were repeated periodically.

2.8   Expansion measurements due to sulphate attack

Two sets of 3 prisms with embedded studs from each mortar mix were submersed in 5 % sodium sulphate (Na_2SO_4) solution at 20 and 5ºC, respectively, and the prisms were weighted above and below water for calculation of the volume, followed by uniaxial length measurements each month. The prisms were submerged 3 days in water before measuring their length as a starting point before sulphate exposure. The 5ºC test was carried out in case thaumasite was formed by the carbonate in the calcined marl.

2.9   Scanning electron microscope (SEM) investigations

One sample from all the mortar mixes cured for 90 days 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.

3   Results

3.1   Compressive and flexural strengths

The values of the compressive strengths with their standard deviations at different ages are listed in Table 1, while the compressive strength evolution for all mortars as a function of time on a logarithmic scale is plotted in Figure 6. Corresponding values for flexural strength are listed in Table 2 and plotted in Figure 7, respectively.

Table 1 Compressive strength development for mortar mixes where cement is replaced with marl

Cement replacement by marl [%]	Average compressive strength ± standard deviation [MPa] at ages [days]					
	1	3	7	28	90	365
0 (Reference)	22.0±0.3	40.4±1.0	46.2±1.0	53.5±0.6	61.1±1.6	67.9±0.9
20	17.9±0.4	35.5±0.5	44.0±1.0	57.3±1.3	65.6±0.9	70.8±1.3
35	14.0±0.1	31.2±0.4	42.5±0.6	57.0±0.8	62.8±1.6	68.4±1.0
50	9.5±0.2	23.6±0.3	38.8±0.4	51.0±1.2	54.2±1.1	63.6±1.3
65	5.7±0.1	15.8±0.3	27.6±0.1	38.1±1.2	43.5±1.0	55.9±1.3

Figure 6   Compressive strength development of mortar where cement has been replaced by 0 (M0), 20 (M20), 35 (M35), 50 (M50) and 65 (M65) vol% calcined marl.

Table 2 Flexural strength development of mortar mixes where cement is replaced with marl

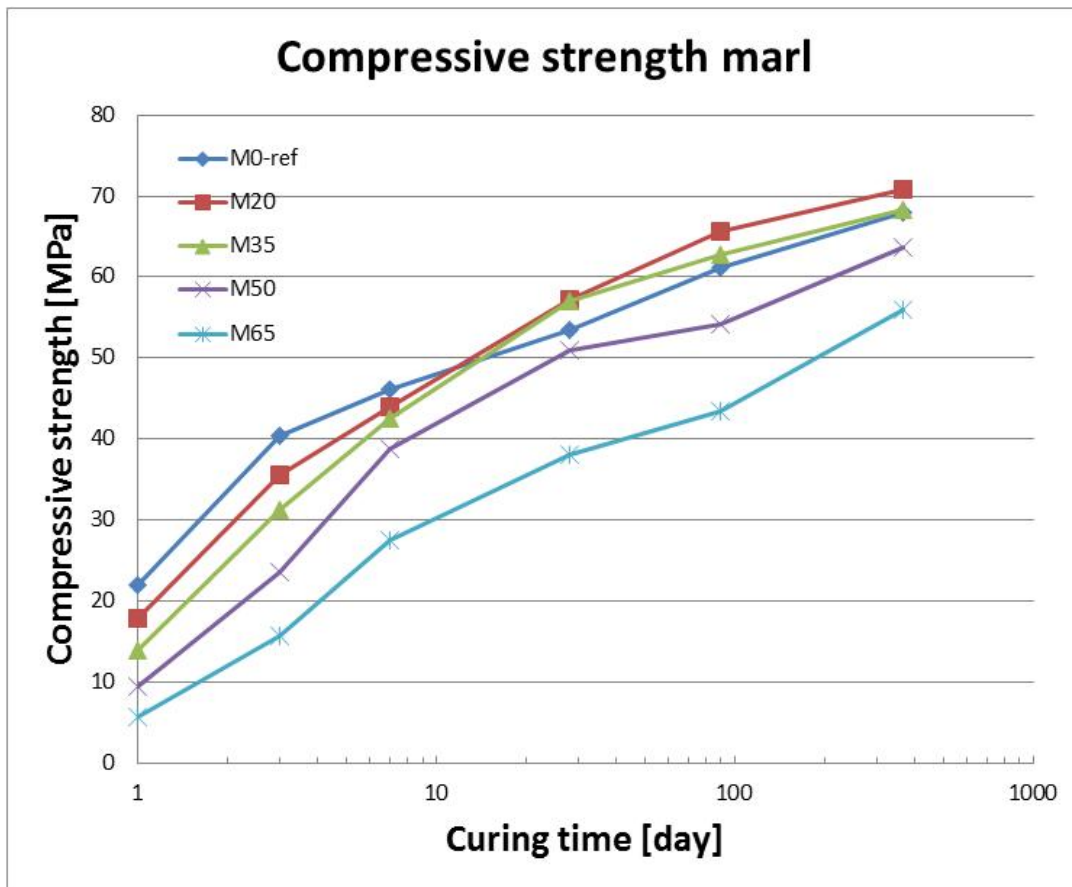| Cement replacement by marl [%]	Average flexural strength ± Standard deviation [MPa] at ages [days]					
	1	3	7	28	90	365
0 (Reference)	4.8±0.1	6.7±0.4	7.4±1.0	7.8±0.3	8.4±0.4	8.8±0.4
20	3.8±0.3	5.9±0.2	7.2±0.2	7.4±0.2	7.7±0.6	9.0±0.5
35	3.1±0.1	5.4±0.2	6.5±0.2	7.6±0.5	8.3±0.2	7.9±0.2
50	2.2±0.1	4.5±0.2	5.9±0.3	6.5±0.3	6.8±0.4	8.3±0.9
65	1.3±0.1	3.2±0.1	4.9±0.2	5.2±0.4	6.1±0.3	6.8±0.4
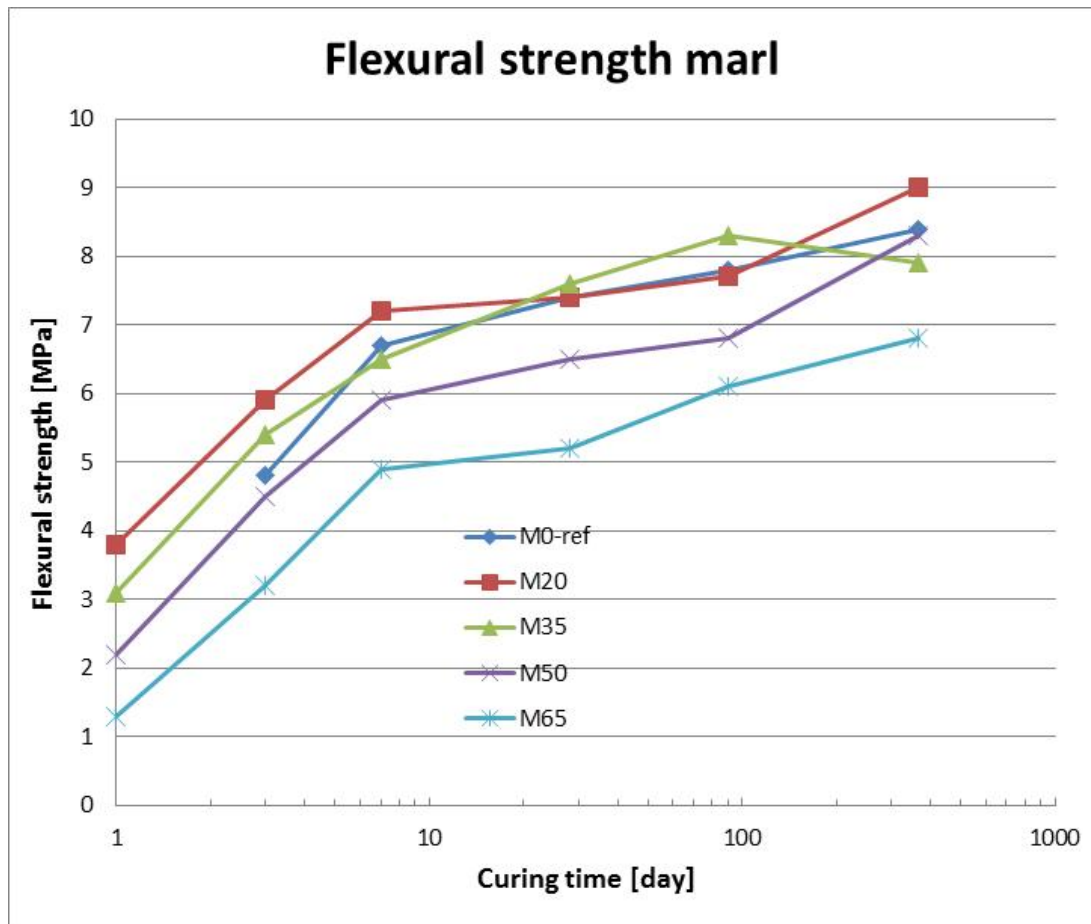
Figure 7 Flexural strength development of mortar where cement has been replaced by 0 (M0), 20 (M20), 35 (M35), 50 (M50) and 65 (M65) vol% calcined marl.

3.2   Results from capillary suction experiments

The average capillary suction profiles for the 4 individual discs for each mortar mix is plotted in Figure 8, while the data extracted from these profiles are listed in Table 3 including their standard deviations.
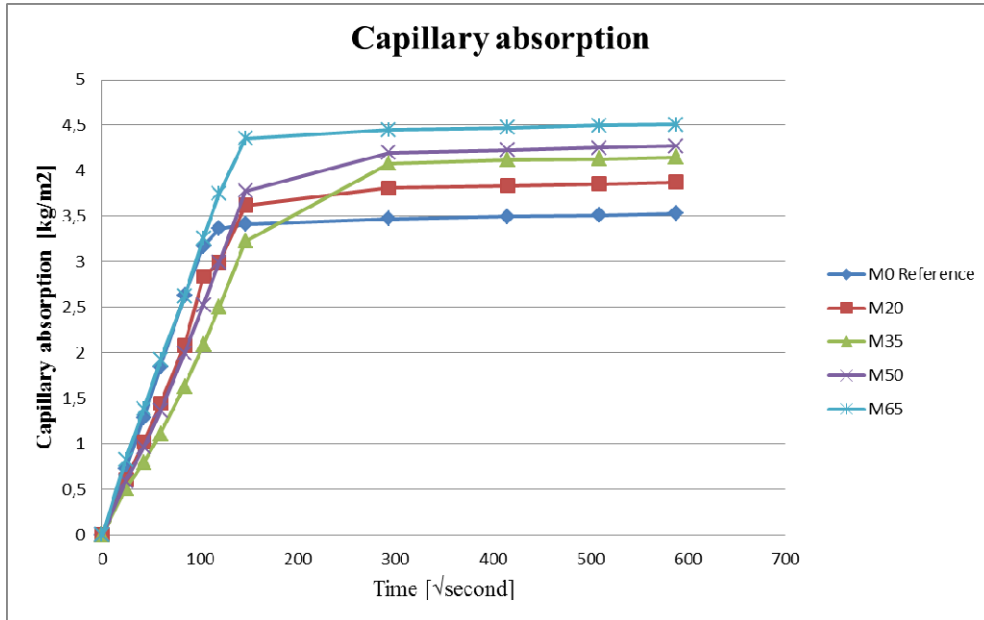
Figure 8 Capillary suction profiles of mortars where cement is replaced with 0 (M0), 20 (M20), 35 (M35), 50 (M50) and 65 (M65) vol% calcined marl.

Table 3 Mortar properties extracted from the capillary suction experiments

Cement replacement by marl [%]	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]
0 (Reference)	17.3±2.3	3.4±6.7	2682±2	2123±14
20	19.4±0.9	2.4±9.2	2705±2	2110±4
35	20.6±0.7	2.1±6.2	2717±2	2094±9
50	21.1±0.6	2.1±8.9	2713±1	2080±7
65	22.6±0.4	2.3±3.9	2702±3	2027±4

3.3 Electrical resistivity

The electrical resistivity of the different mortars as a function of cement replacement by calcined marl is given in Table 4 for different storage times in lime water.

Table 4 Electrical resistivity for mortars where cement is replaced by calcined marl

Cement replacement by marl [%]	Resistivity [ohm-m]			
	8 weeks	16 weeks	20 weeks	24 weeks
0 (Reference)	93±6	132±35	151±25	141±26
20	182±20	233±27	309±32	294±27
35	208±12	355±15	506±12	498±10
50	492±34	791±37	1150±44	1064±35
65	229±9	315±13	522±19	430±19

3.4 Chloride ingress

The chloride ingress profiles for mortars with different cement replacements by calcined marl are plotted in Figure 9, while the parameters obtained from the curve fitting are listed in Table 5.
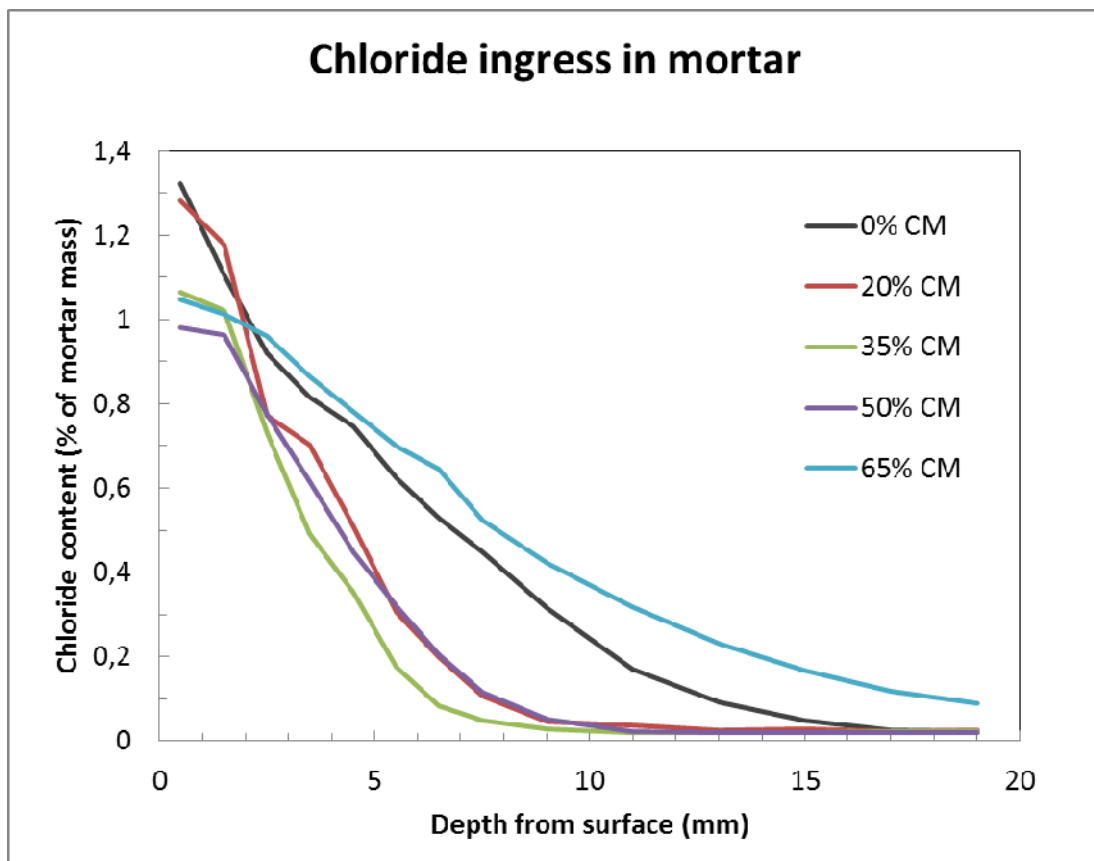

Figure 9 Chloride ingress in mortars where cement is replaced with 0 (M0), 20 (M20), 35 (M35), 50 (M50) and 65 (M65) vol% calcined marl after 35 days of exposure to a solution of 165 g NaCl per liter (average of 3 parallels).

Table 5   Parameters obtained from curve fitting of the chloride ingress profiles according to mathematical solution of Fick's 2nd law of diffusion; the chloride surface concentration, C_0 (% of mortar mass), the apparent diffusion coefficient, D_{app} (10^{-12} m^2/s) and the amount of chloride intrusion, ingress (g Cl^-/m^2 surface).

Cement replacement	Parameters from Cl^- profile		
by marl [%]	C_0 (%)	D_{app} (10^{-12} m^2/s)	Ingress (g Cl^-/m^2)
0 (Reference)	1.29±0.11	8.2±1.9	188±37
20	1.68±0.10	1.9±0.2	119±0
35	1.54±0.10	2.0±0.2	105±2
50	1.32±0.04	3.3±0.2	117±3
65	1.18±0.03	16.1±1.4	227±11

3.5   Carbonation resistance

A photo of the different mortar mixes tested with phenolphthalein indicator after 25 weeks exposure to 1% CO_2 is reproduced in Figure 10, while the actual read carbonation depths are listed in Table 6. The carbonation depths plotted versus square root of hours are shown in Figure 11. All samples were cured for 90 days at 23°C and 90 % RH prior to CO_2 exposure.

Figure 10 Measured carbonation depth of all mortars where cement is replaced with 0, 20, 35, 50 and 65 vol% calcined marl (from the left to the right) after exposure for 1 % CO_2 in 25 weeks.

Table 6 Measured carbonation depth of all mortar mixes exposed in 1 % CO_2 for 33 weeks

Cement replacement by marl (%)	Carbonation (mm) depth after					
	8 weeks	16 weeks	20 weeks	25 weeks	29 weeks	33 weeks
0 (Reference)	0	0	2.0	3.5	3.2	4.8
20	0.5	2.5	2.5	4.5	6.3	6.5
35	1.5	3.5	5.5	6.5	9.9	14.8
50	2.5	5.0	9.0	11.0	15.3	>20
65	4.0	7.5	14.0	18.0	>20	>20
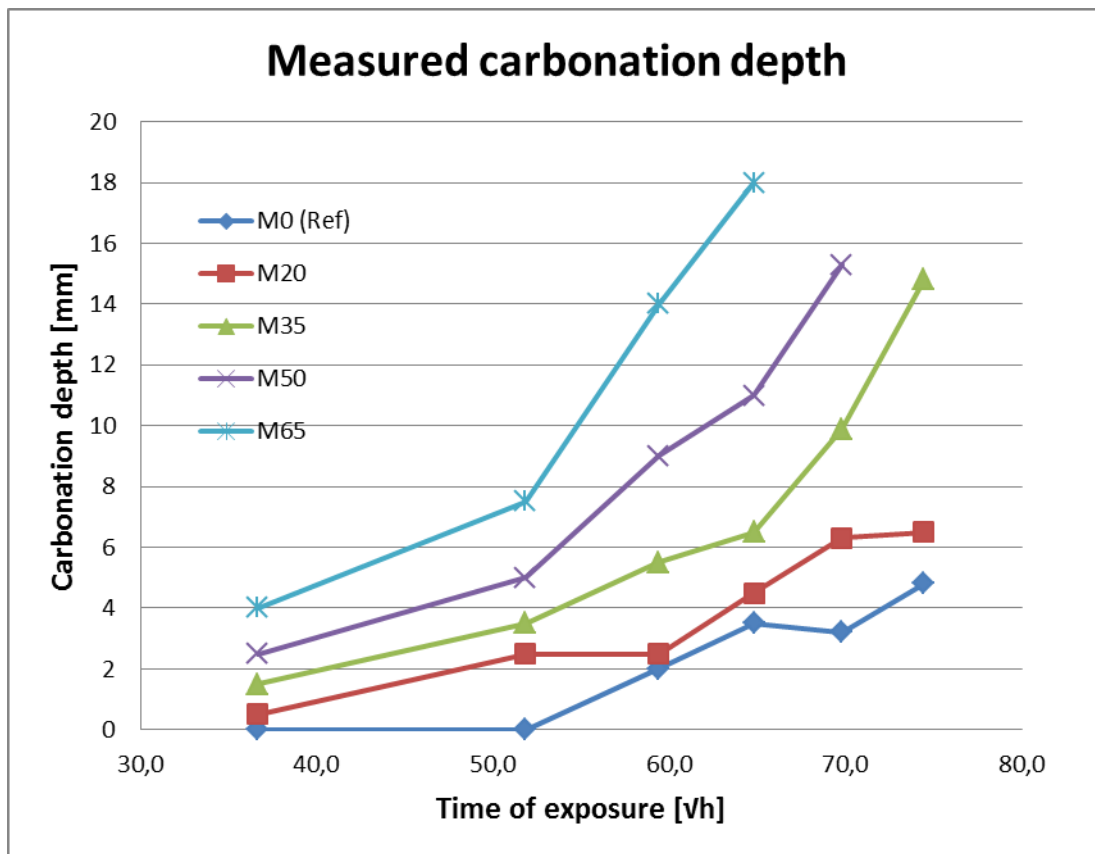
Figure 11 Carbonation depth versus square root of time of mortar where cement is replaced with 0 (M0), 20 (M20), 35 (M35), 50 (M50) and 65 (M65) vol% calcined marl.

3.6 Expansion due to sulphate attack

The linear expansions of the mortar prisms at 5 and 20°C after 10 months exposure are listed in Table 7, while the mass increases of the mortars exposed to 5% sodium sulphate (Na_2SO_4) solution for 10 months at 5 and 20°C are plotted in Figures 12 and 13, respectively.

Table 7 Linear expansion (%) of mortar prisms (160 mm length) where cement is replaced with various amounts of calcined marl after 10 months exposure to 5% Na_2SO_4 at 5 and 20°C.

Cement replacement by marl (%)	Linear expansion (%) with standard deviations (3 parallels)	
	At 5°C	At 20°C
0 (Reference)	0.0140±0.0018	0.0087±0.0011
20	0.0018±0.0014	0.0097±0.0008
35	0.0054±0.0007	0.0060±0.0013
50	0.0026±0.0034	0.0029±0.0020
65	-0.0028±0.0147	0.0051±0.0015

Figure 12 Relative mass increase of mortars where cement is replaced with 0 (M0), 20 (M20), 35 (M35), 50 (M50) and 65 (M65) vol% calcined marl as a function of time when exposed to 5 % Na_2SO_4 solution at 5°C.
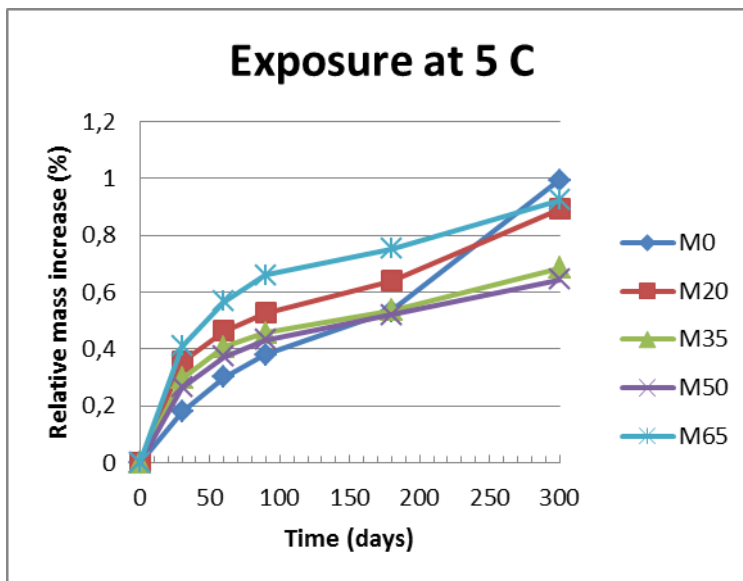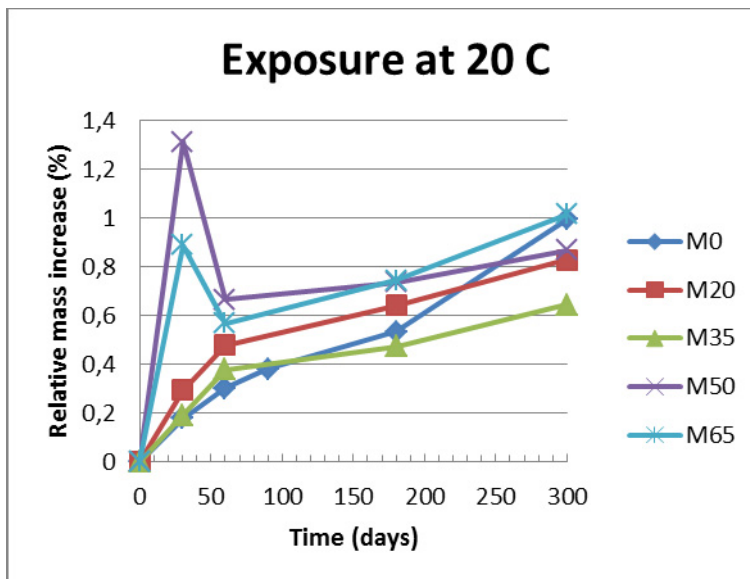

Figure 13 Relative mass increase of mortars where cement is replaced with 0 (M0), 20 (M20), 35 (M35), 50 (M50) and 65 (M65) vol% calcined marl as a function of time when exposed to 5 % Na_2SO_4 solution at 20°C.

3.7   Microstructure by SEM

Selected images are shown from the microstructure study. Figure 14 compare directly the microstructure of the reference with the microstructure of mortar where 65 vol% cement has been replaced with calcined marl. Figure 15 shows an unreacted, or partly reacted, calcined marl particle and some reaction products consisting of calcium aluminate hydrates as revealed by EDS.

Figure 14 Image of reference mix (top image) and mix with 65 % replacement of cement with calcined marl (lower image) after 90 days hydration.

Figure 15 Image of reacting clay particle (middle) with some dark grey CAH products above

4 Discussion

The compressive strength at 28 days is about equal to or higher than reference for cement substitution of calcined marl up to 50 %. For the higher substitution, the compressive strength is substantially lower proba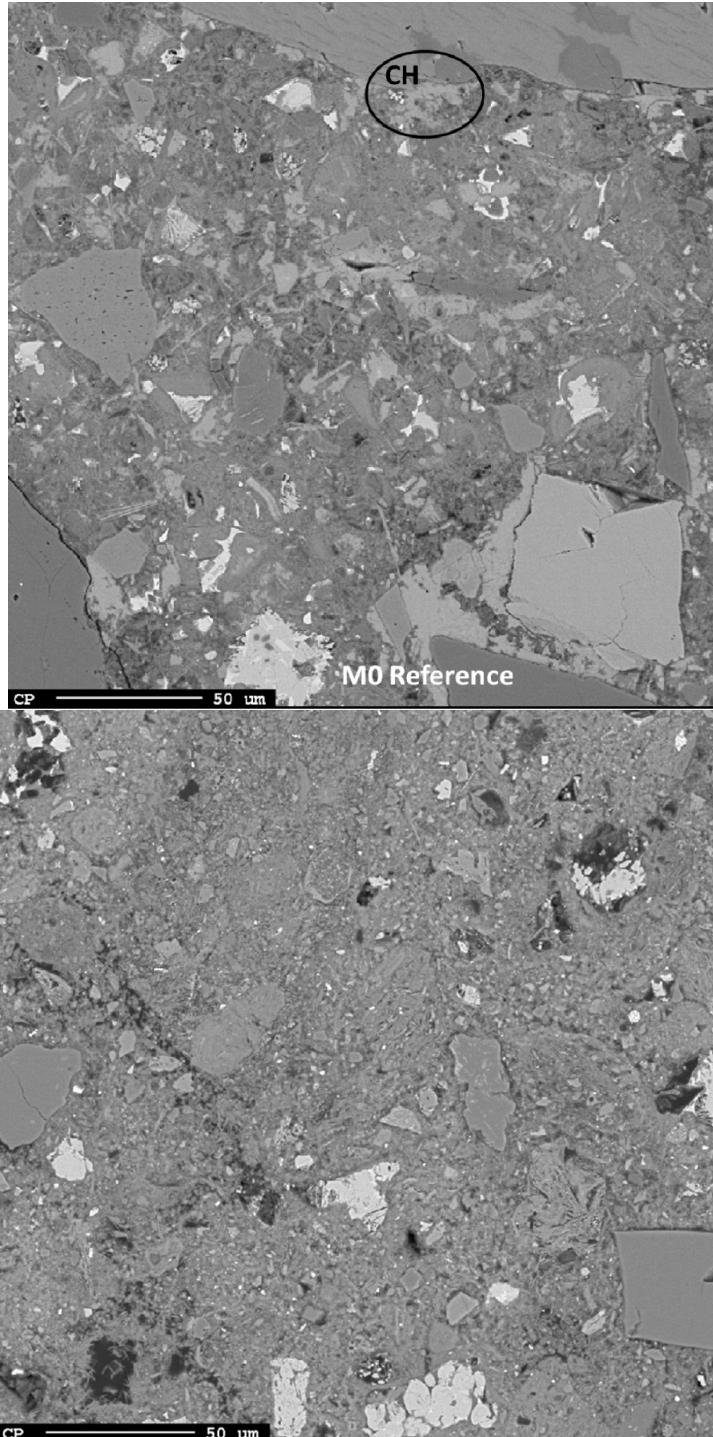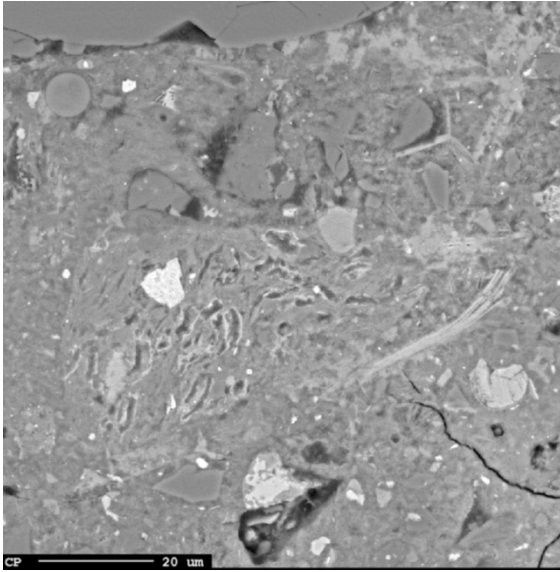bly because all calcium hydroxide has been used up (see images in Figure 14 for evidence) in the pozzolanic reaction already at 50 % substitution. The faster strength gain of the reference from 28 to 90 days compared to mortar with $\geq 50 \%$ replacement is an indication of this, but it is peculiar that the strength gain from 90 to 365 days is greater for mortar with the higher cement replacements with no calcium hydroxide present than for the reference again.

The hypotheses for the strength gain without calcium hydroxide can be several;
1) The mortar with high replacements of cement has more unreacted cement than the reference at 90 days that can further hydrate and give more calcium hydroxide for further pozzolanic reaction.
2) There are two types of CSH in the system. One with high C/S form hydration of cement and one with low C/S from the direct pozzolanic reaction between calcined marl and calcium hydroxide. The one with higher C/S has higher solubility of Ca^{2+} and is considered weaker mechanically than the one with lower C/S. Slowly the two different CSHs will equilibrate and one ends up with an overall stronger CSH with intermediate C/S.
3) The solubility of Ca^{2+} from CSH with high C/S and pH is so high that one can have a direct further pozzolanic reaction with unreacted calcined marl.
4) The silicate anions of in particular CSH with low C/S will polymerize over time creating longer chain lengths of the CSH which may lead to even higher strength.

In addition to the CSH, calcined marl will also form calcium aluminate hydrates (CAH). Since some of the calcium carbonate in marl is maintained in the calcination, there may also be formation of calcium carboaluminate hydrates in a secondary reaction between calcium carbonate and calcium aluminate hydrates from the pozzolanic reaction. This would be in analogy to the synergy between limestone and fly ash found by De Weerdt and Justnes [3] and De Weerdt et al. [4] and could be an explanation of the unusual high strength achieved by calcined marl as an pozzolan.

Calcined marl seems to be faster reactive than fly ash, probably because it is calcined below its sintering temperature so not much glass is formed, but rather dehydroxylated clay sheet remains. The lumps from the rotary kiln is also very easily ground to particles of about 7 μm as they actually collapse into dust upon impact. The higher reactivity is also seen by the higher early strength (1 and 3 days) than for mortars with similar substitution of cement by fly ash.

Data from the capillary suction experiments also show that the volume of capillary pores increases with cement substitution by calcined marl. This is natural since the pozzolanic reaction consumes crystalline calcium hydroxide and partly converts it into porous calcium silicate hydrate gel (CSH), along with some crystalline calcium aluminate hydrates and Strätlingite (C_2ASH_8). Similar features are seen when cement is substituted by for instance silica fume.

At the same time there seems to be a pore refinement induced by the calcined marl replacement as the electrical resistivity increases with increasing cement replacement until 50%. It is reduced again somewhat for 65 % replacement probably due to a lot of unreacted calcined marl since calcium hydroxide is depleted. The electrical resistance increase from 8 to 20 weeks and seems to flatten out (a small decrease) from 20 to 24 weeks. The electrical resistance increase much more (+133 %) from 8 to 24 weeks for mortar where cement is replaced with 50% calcined marl than for the reference mortar (+62 %) even when it starts

from a 5-fold value at 8 weeks. In addition to pore refinement, the increased electrical resistivity might be that the ionic strength of the pore water is reduced. Nevertheless, increased electrical resistivity might mean reduced rate of rebar corrosion once initiated by for instance carbonation.

Calcined marl replacing cement in mortars reduced chloride ingress until 50 % replacement as can be seen directly from the chloride profiles in Figure 9. The ingress increases again for 65 % replacements due to the same reasons as discussed under electrical resistance. Mortar where 50 % calcined marl replaces cement has an apparent diffusion coefficient for chlorides of 40 % of reference with 100 % cement, while the values for mortars with 20 and 35 % replacement is an apparent diffusion coefficient for chlorides of about 24 % of reference. The reasons for the reduced chloride ingress can both be the pore refinement by calcined marl replacing cement as well as increased chloride binding by the higher content of CAH produced by the pozzolanic reaction that can lead to formation of Friedel's salt in reaction with chlorides.

The carbonation rate steadily increases with increasing cement replacement by calcined marl, and there seems to be an extra increase in rate somewhere between 20 and 35 % replacement of cement. When the carbonation depth is plotted versus square root of time, the curve is usually is expected to be linear as a sign of diffusion controlled reaction. However, in this case it seems to be exponential. The decreased carbonation resistance seems to be the only drawback for cement replacements in general. However, one should be careful of drawing conclusions from accelerated carbonation experiments with increased CO_2 concentrations (1 % CO_2 in this case), as carbonation rates of concrete where cement is replaced by supplementary cementing materials (SCMs) under natural conditions (about 380 ppm or 0.038 % CO_2) is reported to behave in a linear manner when monitored over several years.

The expansion of mortar due to sulphate attack is yet too small relative to the standard deviations in order to draw any absolute conclusions. However, there is a weak tendency of the reference of having higher expansion than mortars where cement is replaced by calcined marl, in particular when exposed to 5 % Na_2SO_4 at 5°C rather than 20°C. The expansions are still small and ten months seems too early, but the measurements continue and the sulphate solution should perhaps be replenished more often. However, all specimens are stored under same conditions for a relative comparison.

The microstructure comparison in Figure 14 evidently shows a lot of calcium hydroxide appearing as light grey material, which is totally absent in the image of 65 % replacement. Figure 15 shows an unreacted calcined marl particle (kind of porous in the centre of the image) with some evenly darker grey compounds above it determined to be calcium aluminate hydrates by EDS. The pozzolanic product of calcined marl is believed to be CSH-gel, calcium aluminate hydrates (including calcium carboaluminate hydrates) and mixed compounds like strätlingite (C_2ASH_8). The products are interweaved and hard to single out for analyses. One has to rely on growth of larger, uniform compounds in voids for proper analysis.

5   Conclusions

Calcined marl – ordinary "blue" clay contaminated with calcium carbonate – has been shown to be an effective pozzolan in cementitious materials if calcined at the correct temperature. Marl is unsuitable for the clay product industry, and might thus be the high-volume available alternative pozzolan globally that the cement and concrete industry is looking for in order to reduce their carbon footprint.

Excellent strength at both 1 and 28 days relative to reference is obtained when up to 50 vol% is replaced by calcined marl, and the strength continues to increase up to the last measuring point of 1 year. The capillary porosity volume is increasing, but the electrical resistivity is also increasing, indicating a pore refinement or segmentation, as well as perhaps reduced ionic strength in the pore water. This is properties that might reduce the propagation rate of rebar corrosion once initiated by carbonation. Furthermore, the chloride ingress is significantly reduced when cement is replaced by calcined marl.

The carbonation rate is increasing with increased cement replacement by calcined marl, but this effect may be counteracted by reducing the water-to-cement ratio (w/c) further. Just note that if w/c is reduced the conventional way by increasing the cementitious binder to aggregate ratio, the effect on reduced CO_2 emission may be considerably reduced due to the higher volume of binder per cubic meter of concrete. Hence, lean concrete mixes should be made by the aid of appropriate plasticizing admixtures.

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