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Sulfate resistance of calcined clay – limestone – Portland cements

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Abstract:

Calcined clays emerge as a promising source of supplementary cementitious material, which can provide a significant lowering of the Portland clinker content in blended cements. This study focusses on sulfate resistance of calcined clay (CC) – limestone (L) – Portland cements for mortars exposed to a 0.11 M Na₂SO₄ solution at 5 and 20 °C after a hydration period of 91 days. The pozzolanicity, compressive strength, pore structure, and sulfate resistance of mortars containing laboratory-made metakaolin or calcined montmorillonite and limestone have been investigated in cements with 35 wt.% replacement of a white Portland or an ordinary Portland cement. The results show that all mortars with $CC/(CC + L) \geq 0.5$ exhibit excellent sulfate resistance. The consumption of portlandite by the pozzolanic reactions of the calcined clays and the dilution of the Portland clinker lead to a lower amount of calcium available for the secondary formation of gypsum and ettringite, which is identified as the main reason for the excellent sulfate resistance of the ternary blends. The results suggest that calcined clay – limestone – Portland cements are included in standards as a new type of sulfate-resisting Portland pozzolana cement and Portland composite cement.

Keywords: Sulfate attack; Calcined clays; Metakaolin; Montmorillonite; Limestone.

1. Introduction

Partial replacement of Portland cement by supplementary cementitious materials (SCMs) represents a common route to reduce CO₂ emissions associated with Portland cement clinker production. Moreover, the average percent of clinker in cement is decreasing which in combination with the world-wide increase in consumption of cement leads to increasing demands for SCMs [1,2]. However, the high demand of SCMs cannot be met only by conventional SCMs, such as silica fume, fly ashes and granulated blast furnace slags, which is further accentuated as the global production of some of these industrial byproducts may significantly decrease in the near future. Recently, significant research efforts have focused on calcined clays as an alternative source of SCMs, as they are produced by thermal treatment of clay minerals which have the immediate advantage that they are naturally abundant in very large quantities in the Earth's crust almost all over the world [3]. The thermal activation of clays takes place at 500 – 900 °C and normally it does not involve direct release of CO₂ from the raw clay material, in contrast to the decarbonation of limestone in the production of Portland clinkers. Thus, the production of calcined clays is less energy demanding and considerably less CO₂ intensive than production of Portland clinkers. More importantly, the replacement level of the Portland cement with calcined clays in combination with limestone can be as high as 50% without causing a significant loss in compressive strength compared to pure Portland cement [4]. This has been attributed to the formation of a larger amount of the calcium alumino-silicate hydrate phase (C-A-S-H) and a synergetic effect between calcined clay and limestone [4,5], mainly resulting from the formation of calcium monocarboaluminate hydrate (Ca₄[Al(OH)₆]₂(CO₃)·5H₂O), as observed earlier for ternary Portland cement – limestone – fly ash blends [6].

A major part of recent studies of calcined clays as SCMs in Portland cement blends have focused on reactivity and the impact on the physical performance (e.g., compressive strength) [3]. However, attention should also be paid to the durability of these new materials, which is the focus of the present work, where sulfate resistance is investigated for Portland cement –

calcined clay – limestone blends. These studies supplement recent work from our group on carbonation and chloride ingress for similar ternary cement blends [7–9].

Sulfate attack may take place when concrete structures are exposed to sulfate-bearing environments such as seawater, groundwater or soils, and it may cause a serious threat to the long-term durability of concrete. Numerous studies have focused on this issue and tried to explain the mechanisms of sulfate attack [10–16]. The interaction of hydrated Portland cement with sulfate ions is usually followed by a secondary formation of ettringite ($\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$) and potentially also gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) [10]. Thaumasite ($\text{Ca}_6[\text{Si}(\text{OH})_6]_2(\text{SO}_4)_2(\text{CO}_3)_2 \cdot 24\text{H}_2\text{O}$) can also form by sulfate attack at low temperature and in the presence of carbonate ions [17,18]. The changes in phase assemblages caused by sulfate attack may lead to expansion, cracking, softening and strength loss.

An efficient approach to improve the sulfate resistance is to partially replace Portland cement with SCMs such as well-known industrial byproducts, *e.g.*, silica fume, fly ashes and slags [16,19–25]. Generally, this improvement has been attributed to a refinement of the pore structure, a lowering of the tricalcium aluminate (C_3A : $\text{Ca}_3\text{Al}_2\text{O}_6$) content and the increased consumption of portlandite ($\text{Ca}(\text{OH})_2$) by the pozzolanic reaction of the SCM [13,15,16,26]. However, the mechanism for a specific system can be more complicated. Refinement of the pore structure for slag-containing mortars may not prevent sulfate attack when the deterioration is governed by the loss of surface rather than expansion in contrast to Portland cement mortars [14]. Instead, an earlier study has shown that compositional effects dominate over physical effects for blends with fly ash on the sulfate resistance of the concrete [27]. Ettringite may still form in blended mortars and/or concretes during sulfate attack as a result of their high Al content, even though the C_3A content is reduced and formation of gypsum is prevented by consumption of portlandite. However, Whittaker *et al.* suggest that the Al availability and Ca demand for formation of ettringite is lower in Portland cement blends with slags [28]. More interestingly, sulfate profiles have shown that sulfate binding before cracking is similar for mortars containing different amounts of silica fume and thereby different Ca/Si ratios, whereas the highest expansion rates are observed for the mortars with the highest Ca/Si ratios [15]. Thus,

a clear relationship between sulfate expansion and formation of ettringite cannot be established. In fact, a crystallization pressure generated in small pores during ettringite formation has been reported to be the reason of expansion caused by ettringite formation [11,14]. Moreover, it has been further confirmed that the crystallization pressure related to ettringite growth is reduced when the Ca/Si of the C-S-H phase is lowered [15].

Similar to fly ashes and slags, a few previous studies have also demonstrated high sulfate resistance of concrete containing calcined clays, *e.g.* metakaolin [29,30], however, without considering the effect of limestone. The results show that the sulfate expansion generally decreases with increasing amount of metakaolin and that it is nearly suppressed when the amount of metakaolin constitutes about 25 wt% of the Portland cement blend. In the current European Standard (EN-197-1:2012) [31], which includes 27 common cements, seven of these cements (*c.f.*, Appendix A, Table 1A) are classified as sulfate-resisting (SR) cements. However, none of these sulfate-resisting cements allow natural calcined pozzolans (Q, calcined clays) as one of the main constituents, despite that natural calcined pozzolans (calcined clays) have also been adopted in the European Standard since 2000 [32] for the production of CEM II Portland-pozzolana cements.

The aim of the present work is to investigate the sulfate resistance of Portland pozzolana and composite cements incorporating calcined clays or combinations of calcined clay and limestone. The pozzolanicity, compressive strength, pore structure and sulfate resistance of mortars are investigated for two series of binary and ternary blends, using a white Portland cement (intermediate C₃A content) and an ordinary Portland cement (high C₃A content) which contain limestone, and either calcined kaolinite (1:1 clay) or calcined montmorillonite (2:1 clay) with a total cement clinker replacement level of 35 wt.%. The mortars of ternary blends with $CC/(CC + L) \geq 0.5$ exhibit excellent sulfate resistance which suggest that these binders are included in standards as a new type of sulfate-resisting Portland pozzolana cement and Portland composite cement. The current standards for sulfate-resisting cements are discussed in Appendix A, where it is proposed that Portland pozzolana cement CEM II/B-Q and Portland composite cement CEM II/B-M (Q-LL), incorporating calcined clays and limestone, can be

included as a new type of sulfate-resisting cement in the European Standard, following further experimental demonstrations on general purpose cements using calcined clay materials prepared on an industrial scale.

2. Experimental

2.1 Materials

The blended cements used in this study were made from two Portland cements (wPc: white Portland cement; oPc: ordinary Portland cement; both cements are CEM I 52.5) and three SCMs: metakaolin (MK), calcined montmorillonite (CMT) and limestone (LS). The wPc was obtained from Cementir Holding SpA and included 3.1 wt.% LS, 4.1 wt.% gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and 1.9 wt.% free lime. The oPc was prepared in the laboratory (Aalborg Portland A/S) by mixing 96.5 wt.% grey clinker with 3.5 wt.% hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$). The MK was produced in the laboratory from kaolinite (Kaolinite SupremeTM from Imerys Performance Minerals, UK) by thermal treatment at 550 °C for 20 h; its actual Si/Al ratio of 1.13 accounts for a minor quartz impurity (~ 2.3 wt.%) in the material. The CMT was produced in the laboratory from montmorillonite (Nanoclay, hydrophilic bentonite, Sigma-Aldrich[®], USA) by thermal treatment at 650 °C for 20 h. The LS was a Maastrichtian chalk from Rørdal, Northern Denmark. The chemical compositions of the constituent materials, determined by X-ray fluorescence (XRF), and their densities are given in [Table 1](#).

The wPc contained 64.9 wt.% alite ($3\text{CaO} \cdot \text{SiO}_2$: C_3S), 16.9 wt.% belite ($2\text{CaO} \cdot \text{SiO}_2$: C_2S) and 7.8 wt.% tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$: C_3A); the content of the silicate phases was determined by ²⁹Si MAS NMR and the quantity of C_3A by mass balance calculations [33]. The small amount of iron in the wPc, determined by XRF analysis, is expected to be incorporated as guest ions in the C_3S , C_2S and C_3A phases. The determined mineral composition has taken into account the quantities of aluminum guest ions in C_3S and C_2S , employing the approach and typical atomic ratios between Al and Si in C_3S and C_2S reported earlier [34]. A standard Bogue calculation [35] for the wPc gives 79.2 wt.% alite, 2.8 wt.% belite, 9.0 wt.% tricalcium aluminate and 0.7 wt.% tetracalcium aluminoferrite ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$: C_4AF). The oPc

contained 64.8 wt.% alite, 7.2 wt.% belite, 10.1 wt.% tricalcium aluminate and 9.7 wt.% tetracalcium aluminoferrite according to a standard Bogue calculation [35] based on the bulk oxide composition in Table 1.

The sand used for the mortars was a CEN reference sand (Normensand GmbH, Germany), which has a silica content of at least 98 wt.% and a density of 2650 kg/m³. A superplasticizer (SP, Glenium 27, BASF) was used to achieve similar flow for all mortars. The siliceous fly ash sample (FA) used as a reference in the pozzolanicity tests was obtained by combustion of pulverized coal. It is classified as Category S regarding fineness ($7.4 \pm 0.1\%$) measured by wet sieving, Category A regarding LOI ($1.9 \pm 0.1\%$), and comply with all chemical and physical requirements established by EN 450-1 to consider this material as V according EN 197-1. These requirements relate to the Cl, SO₃, free lime, reactive CaO, reactive SiO₂, SiO₂ + Al₂O₃ + Fe₂O₃, Na₂O_{eq}, MgO and P₂O₅ contents, activity index at 28 and 90 days, soundness, initial setting time and water demand.

2.2 Mortar preparations

Two series of mortars, with the blended cement compositions given in Table 2, were prepared: (i) wPc – MK – LS mortars containing MK (representing 1:1 clays) and using a constant water-to-cement ratio ($w/c = 0.5$) and sand-to-cement ratio ($s/c = 3.0$) by weight. The blended cement compositions of the wPc – MK – LS mortars targeted a replacement of 35 wt.% clinker by SCMs, considering the small amount of LS (3.1 wt.%) in the wPc (*i.e.*, a 31.9 wt.% replacement of the wPc, Table 2). (ii) oPc – CMT – LS mortars containing CMT (representing a 2:1 clay) and targeting comparable compressive strengths by varying the w/c and s/c ratios. The w/c ratios were adjusted according to the empirical equation: $E_{fc} = K \cdot (1/(w/c) - 0.5)$ [36], where E_{fc} is the mean value of compressive strength, K is a constant, which was obtained from preliminary experiments of 28-day compressive strengths for mortars with known w/c ratios ($0.45 \leq w/c \leq 1.25$). The paste volume was controlled to be the same by adjusting the s/c ratio by weight. It was chosen to mix wPc with MK and oPc with CMT, and not the other way

around, for testing sulfate resistance based on the aim of maintaining the whiteness of blended cements containing wPc.

The dosage of superplasticizer was adjusted to achieve a flow within $\pm 5\%$ of the flow of the reference P1 and P2 mortars. The fresh mortars were cast into the molds and cured in a moist cabinet at a temperature of 20.0 ± 1.0 °C and a relative humidity above 90% for 24 h. After demolding, the mortar bars were cured for 91 days in demineralized water in sealed buckets with a water-to-solid ratio of 3:1 by volume at 20.0 ± 1.0 °C. The long curing time prior to the sulfate exposure was chosen to approach a state where further hydration would be minimal and to resample well hydrated concrete in in-situ structures.

2.3 Compressive strength

The compressive strengths were determined for all mortars after hydration for 91 days, using a Toni Technik testing machine with a 300 kN capacity. For the wPc – MK – LS mortars, the strengths were measured on Mini-RILEM mortar bars ($19 \times 19 \times 144$ mm³) [33]. The specimens were sawed into three pieces with an approximate length of 4.6 cm and the reported strengths are the mean value of three measurements. For the oPc – CMT – LS mortar bars ($40 \times 40 \times 160$ mm³), each mortar was cut into two halves and the reported compressive strengths are the average of two measurements. The reported compressive strengths were normalized to the same air content of 2%.

2.4 Pozzolanicity test

The pozzolanicity of the calcined clay blended cements was determined by the Frattini test as described in the European standard EN 196-5: 2011 [37]. For all blended cements, a replacement level of 21 wt.% is selected instead of 35 wt.%, as described in Table 2, to test the minimum clinker replacement allowed for cements CEM IV-A, *i.e.*, the lowest replacement level to get a positive result in a pozzolanicity test for a SR blended cement. Therefore, a cement blend containing siliceous fly ash at a replacement of 21 wt.% was also tested for comparison. After a premixing and homogenization of the Portland cement with SCMs, 20 g

of each cement blend was mixed with 100 mL Milli-Q water in a 500 mL air-tight cylindrical polyethylene bottle. The samples were then stored in an incubator at 40 °C for 8 days. The weight of the entire bottle was measured at 0 and 8 days to exclude that evaporation and/or carbonation had occurred during the storage. After 8 days of hydration, the samples were vacuum filtered. The filtrate was analyzed for hydroxyl ion concentration by titration against 0.1 mol/L hydrochloric acid (HCl) using a methyl orange indicator. Afterwards, the pH of the same solution was adjusted with a NaOH solution (100 g/L) to 12.5 ± 0.2 , followed by determination of the calcium ion concentration by titration against a 0.03 mol/L dehydrated disodium salt of ethylenediaminetetra-acetic acid (EDTA) solution with a calcon indicator.

2.5 Sulfate resistance

The mortar bars for the sulfate attack experiments were prepared by casting mortars into molds ($20 \times 20 \times 160 \text{ mm}^3$) with gauge studs embedded at both ends of the molds along the longitudinal direction. After hydration for 91 days, the initial lengths and masses of the mortars were measured, and for each mix four mortar prisms were submerged in a Na_2SO_4 solution with a concentration of 0.11 M (16.0 g/L) in a sealed plastic container. The high sulfate concentration was chosen in order to represent very severe sulfate exposure conditions defined in the ACI 318-99 standard [38] such as for the saline soils that are widely prevalent in many parts of the world [39]. For the wPc – MK – LS mortars, the samples exposed to the sulfate solution were stored in climate chambers at 5.0 °C and 20.0 °C in order to study thaumasite sulfate attack and conventional sulfate attack, respectively. For the oPc – CMT – LS mortars, samples were stored only at 20.0 °C. The sulfate solution for each mixture was changed each time the length measurement was performed, *i.e.*, weekly at the beginning of the exposure and biweekly, monthly and at longer time intervals with increasing exposure time. The mass of the mortars was determined immediately after the length measurements. The reported masses (m) are normalized to 100.0 g mortar according to equation: $m = (m_t/m_0) \cdot 100.0 \text{ g}$, where m_t is the mass of the mortar after t days of exposure and m_0 is the initial mass of the mortar. A small gain in mass was observed for all mortars after the first 7 days of exposure, which was simply

caused by the ingress of sulfate ions in the reaction products. Thus, the m_0 value is set to the mass of the mortars after 7 days of exposure rather than before exposure, in order to eliminate effects from the initial uptake of sulfate ions on the mass change of the mortars.

2.6 Thermogravimetric analysis

Thermogravimetric analyses (TGA) were performed with a Mettler Toledo TGA/SDTA 851 instrument with a simultaneous thermal analyzer on powdered mortar samples after hydration for 91 days and before exposure to the sulfate solutions. Approximately 50 mg of the powder was heated from 30 to 980 °C at 20 °C/min and with purging N₂.

2.7 Mercury intrusion porosimetry

The pore structure of the mortars after hydration for 91 days was characterized by mercury intrusion porosimetry (MIP) using a combined Pascal 140/440 equipment on samples with grain sizes of 2 – 3 mm. Cut slices with a thickness of about 2 mm of the mortars were sampled and dried by solvent exchange with isopropanol for 2 days, followed by drying in an oven at 50 °C for 24 h. The maximum applied pressure was 200 MPa, corresponding to a minimum pore radius of 3.6 nm. It is known that ink-bottle pores are present in cement-based materials, which are connected to the external surface through smaller neck entrances [40,41]. It is assumed that during extrusion such ink-bottle pores remain mercury filled and that during a second intrusion cycle only the remaining pores will be filled according to their pore size. For this reason two cycles of mercury intrusion/extrusion are carried out [40,41]. The volume of the ink-bottle pores can be obtained by subtraction of the second intrusion (percolated pores) from the first intrusion (total pores).

2.8 Energy dispersive X-ray spectroscopy

The sulfate ingress within the mortar bars were measured by energy dispersive X-ray spectroscopy (EDS) on a Philips XL 30 ESEM FEG electron microscope with an acceleration voltage of 15 keV. The EDS measurements consisted of rectangular grids of 300 points with vertical and horizontal distances between the measurement locations of 14 μm . The measurements were chosen to represent characteristic areas at the investigated depths. For each individual EDS measurement, coordinates were assigned based on the stage control coordinates, which allowed the combination of the different grids in profiles that express the depth as distance from the surface. The actual spots measured were regularly distributed within the grid but were not chosen individually in relation to the sample and are thus randomly distributed. Data fluctuation was high as a result of the heterogeneous microstructure of the cement paste and time constrains for the measurements. Analyses corresponding to epoxy resin in air voids or cracks, aggregates, unreacted clay and clinker particles were removed from the initial data set based on a count rate threshold. Oxide contents (SO_3 and CaO) were calculated from the measured elements, after the EDS measurements were corrected for atomic number (Z), X-ray absorption (A) and X-ray fluorescence (F) effects, the so-called ZAF correction, by the EDAX software used.

3. Results

3.1 Portlandite consumption and pozzolanicity of the calcined clays

The consumption of portlandite due to pozzolanic reaction with the calcined clays (MK and CMT) within the blended mortars was evaluated by thermogravimetric analysis (TGA) after hydration for 91 days. The DTG curves for these mortars are shown in [Figure 1](#), and the amounts of portlandite are given in [Table 3](#). The results show that almost all portlandite has reacted for the ML and M mortars, whereas significant fractions of portlandite remain unreacted in MT mortars containing CMT after hydration for 91 days. The results suggest that only a fraction of CMT has reacted with portlandite due to its relatively lower pozzolanic reactivity compared to the MK.

The results from the Frattini test for the blended cement pastes containing 21 wt.% SCMs at 40 °C are presented in [Figure 2](#) by the CaO equivalent (mmol/L) as a function of the OH⁻ concentration (mmol/L) and compared to the lime saturation curve. In comparison to the reference blends, *i.e.*, the Portland cement blends (P1 and P2) and the Portland cement-limestone blends (L1 and L2), the calcium concentration of the cement blends containing calcined clays and fly ash are below the saturation curve after 8 days of reaction at 40 °C. The results indicate that portlandite released during Portland cement hydration has been consumed by the calcined clays and fly ash, and thus that these materials are pozzolanic. Moreover, increasing the amounts of calcined clays in the blended cements (*i.e.*, the MK/(MK + L) and CMT/(CMT + L) ratios) leads to a further consumption of portlandite and consequently of the Ca²⁺ ions released. At the same replacement level of Portland cement, the result for the sample containing fly ash is found to be much closer to the saturation curve compared to the samples containing the same amount of calcined clays. This observation suggests that the calcined clays used in this study exhibit higher pozzolanic reactivity than the fly ash.

3.2 Compressive strengths

The compressive strengths of the mortars hydrated for 91 days are shown in [Figure 3](#) for the wPc – MK – LS mortars with the same w/c ratio and s/c ratio and for the oPc – CMT – LS mortars with comparable target compressive strengths, obtained by varying the w/c ratio and s/c ratio. The wPc mortar with 35 wt.% limestone (L1) exhibits a considerable lower compressive strength as compared to P1 mortar as a result of the dilution effect. With the same replacement level, the M mortar is observed to have higher compressive strength than the L1 mortar whereas the combination of MK and LS (ML mortar) results in higher compressive strength than both the L1 and M mortars. This has been ascribed to the synergetic effect between MK and LS [4,5]. In contrast, the oPc – CMT – LS mortars were designed to have similar 28-day compressive strengths, obtained by varying the w/c and s/c ratios (see Experimental section), and the measured compressive strengths after 91 days of hydration show that this physical performance of the mortars is largely achieved.

3.3 Mercury intrusion porosimetry (MIP)

The MIP intrusion curves for the first and second intrusion cycles for the studied mortars after hydration for 91 days are shown in [Figure 4](#). For the wPc – MK – LS mortars, it can be seen that the incorporation of metakaolin in the M and ML mortars results in a refined microstructure with lower threshold pore size (breakthrough pore size) than for the reference mortar (P1). Their total intruded porosities from the first intrusion are almost identical, whereas the percolated porosity from the second intrusion is relatively higher for the P1 mortar. The largest total intruded porosity is observed for the L1 mortar which also exhibits the highest threshold pore size. The differences in threshold pore size reflect the pore connectivity, which is lower for the M and ML mortars and higher for the L1 mortar as compared to the P1 mortar. The results after the second intrusion also reveal that the incorporation of MK in the mortars results in a larger fraction of ink-bottle pores which are not captured in the second intrusion. For the oPc – CMT – LS mortars ([Figure 4c,d](#)) with comparable target compressive strengths, the results generally show similar porosity and threshold pore size for all mortars, although the MT mortar shows slightly lower values. This lower porosity is in accordance with the slightly higher compressive strength observed for the MT mortar ([Figure 3b](#)).

3.4 Sulfate expansions

The length changes for the wPc – MK – LS and oPc – CMT – LS mortar bars exposed to the Na₂SO₄ solution for up to 396 and 719 days, respectively, and at 20 °C and 5 °C for the wPc – MK – LS mortars are shown in [Figure 5](#). The ambient and low temperature represent the conditions that are generally used for investigation of conventional sulfate attack and sulfate attack caused by thaumasite formation, respectively. The results show that expansions caused by sulfate attack are observed for the reference mortars (P1, L1, P2, and L2) exposed to the Na₂SO₄ solution. The difference in deterioration for the individual mortars is reflected by the error bars shown in [Figure 5](#), which increases with the exposure time. Comparison of the expansion for the P1 and L1 mortars at 20 °C and 5 °C for the wPc – MK – LS mortars indicates

that the expansion of the P1 and L1 mortars develops much faster at lower temperature than at room temperature, in particular for the L1 mortar. Furthermore, the limestone containing mortars (L1) degrade much more severely at 5 °C than the mortars at 20 °C at the same level of expansion, as witnessed by the larger error limits of the expansion (Figure 5) of the mortar bars at low temperature. The results indicate that the degradation is much more severe for the mortar samples exposed to the same Na₂SO₄ solution when thaumasite is formed at 5 °C as previously reported, e.g. by Schmidt *et al.* [18]. The porosity of P2 is higher than that of P1 after the initial 91 days of hydration (Figure 4) and hence it is more susceptible to sulfate attack. On the other hand, L2 with a much lower porosity than L1 develops a much faster sulfate expansion. Therefore, the main driving force for sulfate expansion in these CEM I and CEM II/B-L cements seems to be the C₃A content of the clinker.

No expansion has been observed for the mortars containing MK and CMT. Not even a visible deterioration on the surface (e.g. surface spalling) has been observed up to 617 and 719 days for these mortars, in contrast to the reference mortars as shown in Figure 6. An earlier study of Portland cement – MK blends [30] showed that the expansion of the concrete prisms exposed to sulfate solution decreased with increasing dosages of MK. However, the maximum replacement of Portland cement was 15 wt.% [30] and thus the expansion was not completely suppressed in contrast to the observations in the present study. It is remarkable that both the CMT containing blends, which are designed to have a comparable 28-days strength and porosity as the reference mortars (P2 and L2), as well as the MK containing blends with finer pore structures than the reference mortars (P1 and L1) do not show any significant expansion. Although the ML mortar contains significant amounts of limestone, no expansion is observed even at low temperature. This agrees with the observation of Bellmann *et al.* [42] who observed no or much less thaumasite formation in the absence of portlandite.

3.5 Mass changes

In addition to the expansion caused by sulfate attack, weight changes of the samples after exposure to the Na₂SO₄ solution have also been measured, since a mass increase may reflect the formation of secondary ettringite and potentially also gypsum and/or thaumasite as a result

of interactions of the hydrated cements with sulfate ions. The mass changes as function of the square root of time and normalized to 100 g of mortar are shown in [Figure 7](#) for the wPc – MK – LS and the oPc – CMT – LS mortar bars exposed to the 0.11 M Na₂SO₄ solution at 20 °C and 5 °C. The results show that the mass increases for all reference mortars (P1, L1, P2 and L2) after prolonged exposure times. It is also noted that there is minor loss in mass for the P1 mortar at the beginning of the exposure to sulfate ions. This minor decrease in mass is expected to be associated with leaching of calcium, which has also been observed in earlier studies of mortars exposed to sulfate solution [[12,43](#)]. Before exposure to the Na₂SO₄ solution, all of the mortars have been cured in demineralized water for 91 days and thereby, only a minor degree of continued hydration is expected during the subsequent exposure to the Na₂SO₄ solutions. Thus, neither water absorption nor further hydration is expected to significantly affect the mass variations determined for the mortars in this period, and the mass changes of the mortars can mainly be attributed to sulfate ingress and leaching. The mass changes of the mortars exposed to the sulfate solution result from the balance between sulfate attack and leaching of calcium ions. Sulfate attack dominates over leaching for the P1 and L1 mortars for the whole exposure period, for which the mass increases at both 20 °C and 5 °C. On the other hand, the mass decreases initially for all mortars containing MK and CMT indicating that leaching dominates. However, the mass starts to increase after 133 days of exposure ($d^{1/2} = 11.5$) for the CMT containing mortars. The weight increase of the CMT mortars after 133 days of exposure is most likely attributed to the continued hydration of the remaining raw materials, *i.e.*, calcined montmorillonite as CMT reacts more slowly and to a lesser extent than MK [[44](#)]. The well-preserved mortar surface, the negligible sulfate expansion and the moderate mass loss of the mortars containing MK and CMT strongly suggest that sulfate attack do not take place in these mortars, and if any, at a very limited extent and/or slow rate as discussed in the following section.

In general, the measured mass changes ([Figure 7](#)) support the expansion data ([Figure 5](#)) very well, and the negligible expansions for the MK and CMT mortars are clearly due to the lack of formation of secondary sulfate-containing products such as ettringite and gypsum. The

relationship between the sulfate expansion and mass variation for the reference mortars (P1, L1, P2 and L2) at 20 °C and 5 °C are shown in [Figure 8](#). The results show an increase in expansion with increasing mass for all reference mortars. It is interesting that the data show initially a shift towards a higher mass gain for the L1 mortars as compared to the P1 mortars at the same level of expansion. This shift can be explained by the fact that the formed sulfate products initially tend to fill part of the larger pores before generating expansion [\[14\]](#), since a larger porosity is observed for the L1 mortar as compared to the P1 mortar ([Figure 4](#)). No such obvious shift is observed for the P2 and L2 mortars, which reflect that these mortars have similar pore structures.

3.6 Energy dispersive X-ray spectroscopy

In order to confirm the occurrence of sulfate attack and calcium leaching within the studied mortar bars, as indicated by the sulfate expansions and mass losses in [Figures 5](#) and [7](#), energy dispersive X-ray spectroscopy (EDS) has been performed on selected mortar samples to study their sulfate and CaO profiles and changes in phase assemblages. The results are obtained for the P1 and ML mortars after 42 days of exposure to the 0.11 M sulfate solution (16 g/L Na₂SO₄) at 20 °C, *i.e.*, prior to the formation of significant cracks. The sulfate and CaO profiles in [Figure 9](#) reveal that a high sulfate binding is observed close to the surface of the P1 mortar. The bound sulfate content decreases to the original SO₃ content of the wPc of 3.4 wt.% at a 2 – 3 mm depth. For the ML mortar, sulfate binding is only observed close to the sample surface at a depth of 0.3 mm, under the same exposure condition and period as for the P1 mortar. For deeper depths, the SO₃ concentration is nearly constant and originates mainly from the SO₃ content of the wPc component in the mortar. The CaO profiles show the occurrence of leaching during exposure, in particular for the P1 mortar, whereas the changes are very small for the ML mortar.

In the studied mortars, the unhydrated cement, metakaolin and limestone are finely intermixed with the hydration products. EDS analyses can be used to study the changes in phase assemblages, as illustrated in [Figure 10](#), in which S/Ca ratio is plotted as a function of Al/Ca ratio at different depths from the surface of the P1 and ML mortars after 42 days of

exposure to the sulfate solution. The results show clearly the formation of a significant fraction of both gypsum and ettringite in the surface proximity (ca. 0.4 mm) for the P1 mortar. However, gypsum is not formed at a much deeper depth, and at the same time the amount of ettringite is also reduced, which is consistent with the reduced sulfate binding as a function of ingress depth as seen in Figure 9. Only a low amount of gypsum is observed on the surface of the P1 mortar as a result of the calcium leaching as seen in Figure 9. For the ML mortar, the formation of a lower amount of ettringite and only a trace of gypsum is observed on the surface and/or its proximity, which is also consistent with the minor amount of sulfate binding observed from its sulfate profile as shown in Figure 9. The core of the mortars, which is not affected by sulfate ions, in a depth over 4 mm from the surface (according to Figure 9) is further analyzed to show the difference in C-S-H composition of the hydrated cements. A shift in the concentration of points for the C-S-H phases towards lower Ca/Si ratio and higher Al/Si is observed for the ML mortar in comparison with the P1 mortar (Figure 11). This observation reflects that partial replacement of Portland cement by metakaolin leads to a reduction in the Ca/Si ratio of C-S-H as a result of the reduced availability of calcium, in accordance with experimental observations by ^{29}Si NMR [45] and thermodynamic modelling [7]. The increase in the Al/Si ratio for the C-S-H phase with increasing MK content is also supported by ^{27}Al MAS NMR [45]. It is remarkable that although the ML mortar is rich in Al, no expansion is observed for this mortar as a result of the lack of calcium.

4. Discussion

4.1 Physical restrictions

An efficient approach to enhance the sulfate resistance of Portland cement binders is to partially replace the Portland cement with a silica-rich SCM such as silica fume, fly ash, granulated blast furnace slag and metakaolin [16,19,30]. A generally accepted explanation for the improved sulfate resistance of these systems is the refinement of the pore structure caused by the silica-

rich SCMs [21,22,29]. The lack of pore-structure refinement can also explain the increased sulfate expansion observed for the L1 mortar, as compared to the P1 mortar, despite its lower C_3A content, which is a result of the dilution, reflecting that the L1 mortars exhibit larger porosity and higher pore connectivity. However, the refinement of the pore structures for the MK mortars appears not to be sufficient to explain their very high sulfate resistance, since a denser pore structure does not necessarily lead to an intact surface, as observed for these mortars. In contrast to the intact surface observed for MK and CMT mortars, significant surface deterioration has been observed for slag mortars [16,46] where a similar pore refinement has been observed. Studies has demonstrated that the deterioration of slag cement blends occurs to a larger extent through the loss of mortar surface as compared to expansion [16,46]. However, the loss of surface neither is observed for the MK containing mortars with refinement of pore structure nor for the CMT mortars with coarser pore structures than MK mortars. The observation of intact surfaces for both the MK and CMT mortars suggests that the refinement of the pore structure for the MK mortars is not the principal factor for their high sulfate resistance.

4.2 Chemical effects

In addition to the possible physical restrictions discussed above, the impact of the chemical composition of the cement (CaO and C_3A contents) on sulfate expansion also needs consideration, as it affects the formation of ettringite and gypsum. The results in this study show that a lower sulfate expansion is observed for the L2 mortar as compared to the P2 mortar (Figure 5c), which is mainly ascribed to the dilution effect of the C_3A content, since these mortars were designed to have similar compressive strengths and thereby comparable pore structures (see Figure 3b and Figure 4c,d). However, the higher Al_2O_3 content alone of the blended cements cannot explain the very high sulfate resistance of the mortars containing MK and CMT, since the amount of ettringite formed is not just limited by the availability of Al_2O_3 (as in the case of SR cements) but also by the availability of CaO [25,47]. In this case it is preferentially the availability of calcium, *i.e.*, the absence of portlandite, which lowers the formation of ettringite. The consumption of portlandite by the calcined clays in the MK

containing mortars (as seen in Figure 1a and Table 3) lowers the amount of calcium ions available for the secondary formation of sufficient gypsum and ettringite (Figure 10), such that no expansions of these mortars are observed (see Figure 5a,b). However, it should be noted that the improvement of sulfate resistance would be less efficient if the replacement level of Portland cement by calcined clays were lower, as reported by Al-Akhras [30], since a lower fraction of calcined clays will result in a smaller extent of reduction in portlandite [48]. It has been reported that a limited CaO content and a low Ca/Si ratio of the C-S-H gel lower the oversaturation with respect to ettringite [15] or even prevent its formation [47]. Also the formation of thaumasite is suppressed in the absence of portlandite [42]. For the CMT containing mortars, although a significant fraction of portlandite is still present as a result of the lower reactivity of CMT compared to MK, no significant expansion (Figure 5) and obvious surface deterioration (Figure 6) is observed after 719 days of exposure. Despite the CMT blends exhibit a higher portlandite content, which may lead to the formation of additional ettringite, an earlier study of sulfate attack for slag cements have shown that ettringite formation cannot solely be the reason for the cracking [28]. Moreover, it is expected that the amount of portlandite in the CMT mortars would continuously decrease as a result of the ongoing hydration of the unreacted CMT. This hypothesis is supported by the increased mass of the mortars after 133 days of exposure as seen in Figure 7. As a result of the continuous consumption of portlandite by the pozzolanic reaction, the availability of Ca for formation of ettringite continuously decreases, thereby reducing the risk of expansion. In this context it should be noted that a full consumption of portlandite has not been observed for calcined clay – limestone – Portland cement blends incorporating industrial sources of metakaolin (*i.e.*, LC³-50 blends) [48]. Thus, these blends may resemble the CMT-containing blends studied in the present work.

Earlier studies have reported that no clear correlation exists between the density of the pore structure and susceptibility to sulfate attack [11,14]. In addition, a sufficient crystallization pressure has to develop in order to result in cracking and expansion [11,14,15]. It has been found that the presence of less portlandite and/or a low-Ca C-S-H phase lowers the

supersaturation of the pore solution with respect to ettringite, and thus prevents the development of high ettringite crystallization pressures [15,47]. In fact, in the present study the surface of the calcined clay – limestone mortars is intact (Figure 6) and lack of gypsum (Figure 10), indicating that the crystallization pressure is insufficient to cause cracking in the mortars with MK or CMT. This is also supported by the fact that only minor additional sulfate binding is observed, which again is related to the lack of calcium in the calcined clay – limestone mortars as seen in Figure 11.

5. Conclusions

In the present work the pozzolanicity, sulfate resistance, compressive strength and pore structure have been determined for Portland cement mortars containing a 35 wt.% replacement of the cement clinkers by calcined clays and limestone. Based on these results, the following conclusions can be made:

- (1) 35 wt.% of the Portland clinkers can be replaced by calcined clays and limestone without significantly affecting the compressive strength.
- (2) Calcined clays are found to exhibit much higher pozzolanic reactivity than fly ash after 8 days of hydration at 40 °C when they are used to replace 21 wt.% Portland clinker.
- (3) All the studied mortars containing calcined clays (either metakaolin or calcined montmorillonite) exhibit excellent sulfate resistance, independent of the compressive strength and pore structures, compared to the reference mortars. The consumption of portlandite by calcined clay reaction leads to a lower amount of calcium ions available for the secondary formation of gypsum and ettringite, which is identified as the main reason for their excellent sulfate resistance. The experiments conducted for the metakaolin containing mortars at 5 °C suggest that also the expansion due to thaumasite formation is suppressed even if the sample contains limestone.
- (4) Based on these findings, it is proposed that some calcined clay – limestone Portland cement compositions may be considered as sulfate-resisting cements in the standards (Table A1).

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Appendix A: Perspectives of sulfate-resisting cements incorporating calcined clays

Natural calcined pozzolans (calcined clays) have been adopted in the European Standard since 2000 [32] for the production of CEM II Portland-pozzolana cements. In the current European Standard (EN-197-1:2012) [31], which includes 27 common cements, seven of these cements (Table A1) are classified as sulfate-resisting (SR) cements. However, depending on the type of cement, minimum replacement levels of fly ash or slag are required as for some SR cements (Table A1). In addition, they shall meet other different requirements (Table A2). Some SR cements must fulfill requirements to the tricalcium aluminate (C_3A) content of the clinker and the SO_3 content of the final cement, depending on cement type and strength class (CEM I and CEM IV, Table A2), whilst SR pozzolanic cements (CEM IV) must also pass the pozzolanicity test according to the standard procedure EN 196-5 at eight days [37]. The CEM III/B and CEM III/C classifications have no requirements to the C_3A content of the clinker but the final cements should have a total SO_3 content below 4 wt.% for CEM III/B and 4.5 wt.% for CEM III/C. The CEM I and CEM IV (A and B) classified as SR cements are required to have a C_3A content of ≤ 5.0 wt.% and 9.0 wt.%, respectively. In addition, the SO_3 content in the cement should be ≤ 3.0 wt.% for the low strength classes (32.5 N, 32.5 R and 42.5 N), while the SO_3 content in the high strength classes (42.5 R, 52.5 N and 52.5 R) can be up to ≤ 3.5 wt.%. However, none of these sulfate-resisting cements allow natural calcined pozzolans (Q, calcined clays) as one of the main constituents in the manufacture of neither SR pozzolanic CEM IV (A and B) nor SR Portland – pozzolana cements CEM II/B-Q, or Portland – composite cements CEM II/B-M (Q-LL), as proposed in the present study.

The annex A of EN 197-1: 2012 [31] provides also a list of other common cements considered as sulfate resisting by national standards in different CEN (European Committee for Standardization) Member Countries, but they do not fulfill all the requirements in Table A2 for the seven SR cements listed in Table A1. The list shows a wide variety of cements that have been classified in the EU member countries as sulfate resisting. However, only few national standards and countries (Austria, Italy and Portugal) consider calcined natural pozzolans (Q,

e.g., calcined clays) as suitable SCMs for the production of CEM II/A-M and/or CEM II/B-M sulfate-resisting cements. Several countries apply further restrictions to the production of concrete to be used in a sulfate environment, such as a minimum cement content and/or a maximum water-to-cement ratio that vary depending on the cement type and the type and concentration of sulfate ions in the sulfate-rich environment. These specific restrictions reflect different geographical and climatic conditions under which sulfate attack may take place.

The present study demonstrates that the studied calcined clays have higher pozzolanic reactivity than the studied fly ash as revealed by the Frattiniti tests on samples with a 21 wt% replacement level (Figure 2). The mortars made from calcined clay – limestone cements show excellent sulfate resistance and at the same time a high compressive strength. Although the C₃A content of ordinary Portland cements is relatively high (>9 wt.%), as compared to that specified in the standard for sulfate-resisting cements [31], no expansion or any other sign of sulfate attack on the surface, edges or vertices are observed for the calcined clay – limestone cement mortars over one year of exposure to sulfate solution. Based on these results and discussion, it can be expected that no damage will occur for these mortars in the long term under the studied exposure conditions. The studied calcined clay – limestone Portland cement blends exhibit a comparable or superior pozzolanicity and sulfate resistance to those of sulfate-resisting cements, which strongly suggests that calcined clay and limestone should be included as feasible main constituents to manufacture sulfate-resisting cements (Table A1).

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Tables

Table 1. Chemical and mineralogical composition (wt.%) and physical properties for the starting materials.

	Cement type: CEM I -52.5		SCMs ^a			
	wPc	oPc	LS	MK	CMT	FA
<i>Chemical composition</i>						
SiO ₂	21.81	18.86	3.92	52.84	63.63	56.81
Al ₂ O ₃	3.56	5.84	0.33	39.49	19.94	21.63
Fe ₂ O ₃	0.24	3.2	0.14	1.42	3.90	6.72
CaO	66.13	65.05	53.73	0.22	1.20	4.76
MgO	1.1	0.89	0.35	0.48	4.62	2.05
K ₂ O	0.43	0.51	0.05	1.00	0.15	2.52
Na ₂ O	0.04	0.24	0.08	0.05	3.82	1.13
SO ₃	3.37	3.49	0.05	0.06	0.73	0.75
TiO ₂	0.21	0.304	0.02	0.88	0.35	0.89
Cl	0.003	0.004	0.01	0.003	0.06	0
P ₂ O ₅	0.04	0.32	0.1	0.11	0.04	0.63
Cr ₂ O ₃	0.02	0.012	0	0.008	0.005	0.013
LOI	2.57	0.6	41.8	3.55	1.34	2.06
<i>Mineralogical composition</i>						
C ₃ S	64.9	65.0	-	-	-	-
C ₂ S	16.9	5.0	-	-	-	-
C ₃ A	7.8	10.1	-	-	-	-
C ₄ AF	-	9.7	-	-	-	-
Gypsum	4.11	-	-	-	-	-
Hemihydrate	-	3.5	-	-	-	-
Carbon content	0.37	-	-	-	-	-
CaCO ₃	3.1	-	93.8	-	-	-
C ₃ A content of clinker	8.4	10.4				
<i>Physical properties</i>						
Blaine fineness (m ² /kg)	387	-	1211	1891	-	
Density (kg/m ³)	3080	3155	2700	2530	2595	

^a MK: metakaolin; CMT: calcined montmorillonite; FA: fly ash; LS: limestone.

Table 2. Mortar constituents (wt.%), sand to binder ratio (s/b) and water to binder ratio (w/b), both ratios by weight^a

	CC/(CC+LS), (g/g)	wPc	oPc	MK	CMT	LS	SP	w/b	s/c	Paste volume (%)
wPc – MK – LS mortars										
P1	-	100						0.5	3	42.1
L1	MK/(MK+LS) = 0	68.1				31.9		0.5	3	42.6
ML	MK/(MK+LS) = 0.75	68.1		25.5		6.4	1.78	0.5	3	43.3
M	MK/(MK+LS) = 0.94	68.1		31.9			2.23	0.5	3	43.4
oPc – CMT – LS mortars										
P2	-		100					0.5	3	41.9
L2	CMT/(CMT+LS) = 0		66.0			34.0	0.95	0.41	2.7	42.0
MT-0.5	CMT/(CMT+LS) = 0.5		66.0		17.0	17.0	0.43	0.48	3.0	42.0
MT-0.75	CMT/(CMT+LS) = 0.75		66.0		25.5	8.5	0.31	0.5	3.1	42.0
MT	CMT/(CMT+LS) = 1		66.0		34.0		1.06	0.44	2.9	42.0

^aCC: calcined clay; LS: limestone; MK: metakaolin; CMT: calcined montmorillonite; SP: superplasticizer; w/c: water-to-cement ratio (g/g); s/c: sand-to-cement ratio (g/g).

Table 3. Quantification of portlandite (CH) for the cement mortars after 91 days of hydration as determined by TGA (g CH per 100 g of dry mortar at 500 °C)

mortar	CH (g/100g)	mortar	CH (g/100g)
P	3.97	P'	3.15
L	2.13	L'	2.22
ML	0.39	MT-0.5	1.35
M	0.14	MT-0.75	1.49
		MT-1	1.65

Table A1. Existing (CEM I, CEM III, and CEMIV) and proposed (*CEM II*) sulfate-resisting cements, following the European Standard: EN 197-1:2012 [31].

Main cement type	Types of sulfate-resisting common cement ^a		Main constituents (wt.%) ^b					
			Clinker	Blast-furnace slag	Siliceous fly ash	Pozzolana		Limestone
						Natural	Calcined	
K	S	V	P	Q	LL			
CEM I	Portland cement	CEM I-SR 0 ^c	95 - 100					
		CEM I-SR 3 ^c						
		CEM I-SR 5 ^c						
CEM II	Portland-pozzolana cement	CEM-II/B-Q-SR ^d	65-79			21-35		
	Portland composite cement	CEM II/B-M (Q-LL)-SR ^d	65 - 79			21 – 35 ^e		
CEM III	Blast furnace slag cement	CEM III/B-SR	20 - 34	66 -80				
		CEM III/C-SR	5 - 19	81 - 95				
CEM IV	Pozzolanic cement	CEM IV/A-SR	65 - 79			21 - 35		
		CEM IV/B-SR	45 - 64			36 - 55		

^a Abbreviations: SR - sulfate resisting; A, B, C - different replacement levels; M – mixture of constituents. These main constituents other than the clinkers must be declared by designation of the cement.

^b Minor additional constituents are 0 - 5 wt.% for all cement types.

^c The C₃A content of the Portland clinkers are 0 %, ≤ 3 %, ≤ 5 % for these three CEM-I cements, respectively.

^d Proposed sulfate-resisting Portland – pozzolana and Portland composite cements, including calcined clays (Q) and limestone (LL) based on the experiments in the present work.

^e The calcined clay content (Q) shall be equal or higher than the limestone content (LL) following the experiments in the present work.

Table A2. Additional requirements for sulfate-resisting common cements given as characteristic values [31].

Property	Test reference	Cement type	Strength class	Requirements	
Sulfate content (as SO ₃)	EN 196-2	CEM I-SR 0	32.5 N	≤ 3.0 %	
		CEM I-SR 3	32.5 R		
		CEM I-SR 5	42.5 N		
		<i>CEM II/B-Q-SR</i>	42.5 R	≤ 3.5 %	
		<i>CEM II/B-M (Q-LL)-SR</i>			
		CEM IV/A-SR			
CEM IV/B-SR					
C ₃ A in clinker	EN 196-2	CEM I-SR 0	All	= 0 %	
		CEM I-SR 3		≤ 3 %	
		CEM I-SR 5		≤ 5 %	
	- ^a	<i>CEM II/B-Q-SR</i>		≤ 9 %	
		<i>CEM II/B-M (Q-LL)-SR</i>			
		CEM IV/A-SR			
Pozzolanicity	EN 196-5	<i>CEM II/B-Q-SR</i>	All		Satisfies the test at 8 days
		<i>CEM II/B-M (Q-LL)-SR</i>			
		CEM IV/A-SR			
		CEM IV/B-SR			

^a A test method to determine the C₃A content in clinkers from the analysis of a spot sample of cement is currently under development. Until this method is available, it shall be determined on the basis of the analysis of clinker as part of the manufacturer's factory production control.

Figures

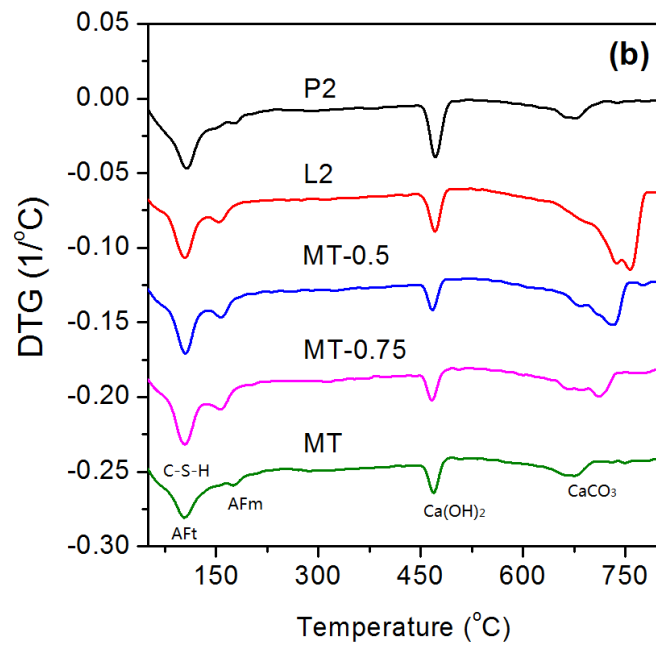


Figure 1. DTG curves for (a) wPc – MK – LS and (b) oPc – CMT – LS mortars after 91 days of hydration.

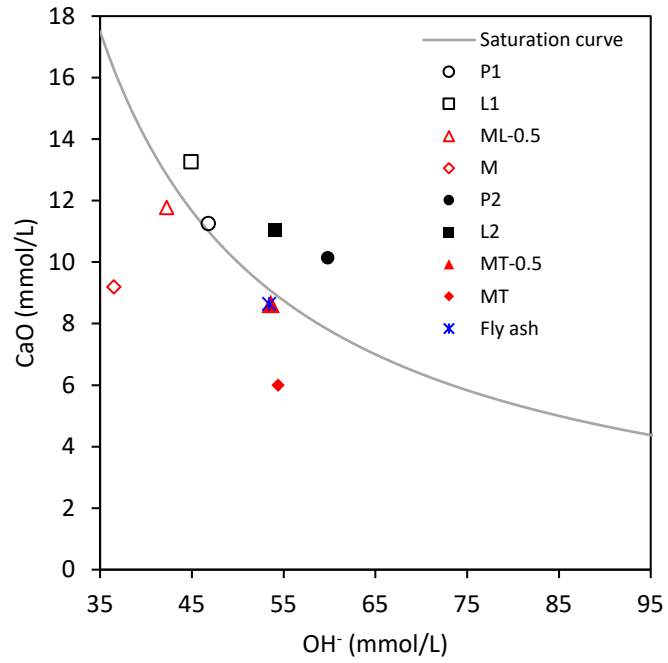


Figure 2. Frattoni diagram for assessing the pozzolanicity after 8 days of hydration at 40 °C for the wPc (P1 to M) and oPc (P2 to MT) blended cements containing 21 wt.% SCMs.

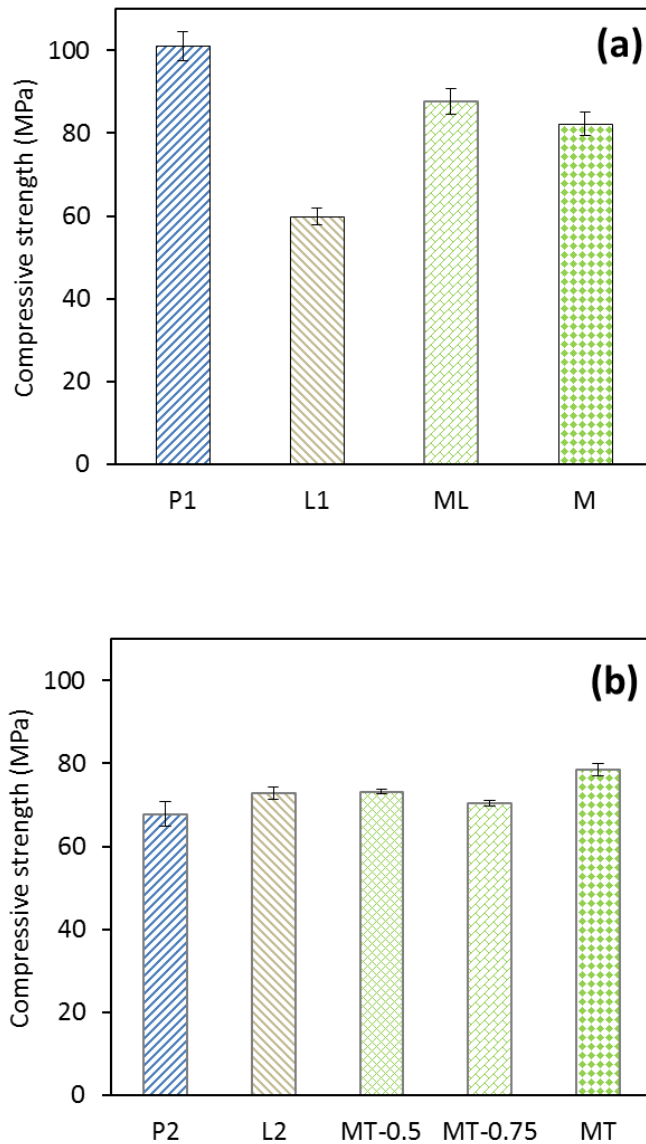


Figure 3. Compressive strengths after 91 days of hydration for (a) wPc – MK – LS mortars with the same w/b ratio and b/s ratio and (b) oPc – CMT – LS mortars with comparable target compressive strengths by varying the w/b ratio and b/s ratio. Note that the data in part (a) is from a previous study [23] using mini-RILEM ($20 \times 20 \times 150 \text{ mm}^3$) mortar prisms whereas the compressive strengths in part (b) are measured on standard EN-sized ($40 \times 40 \times 160 \text{ mm}^3$) mortar bars.

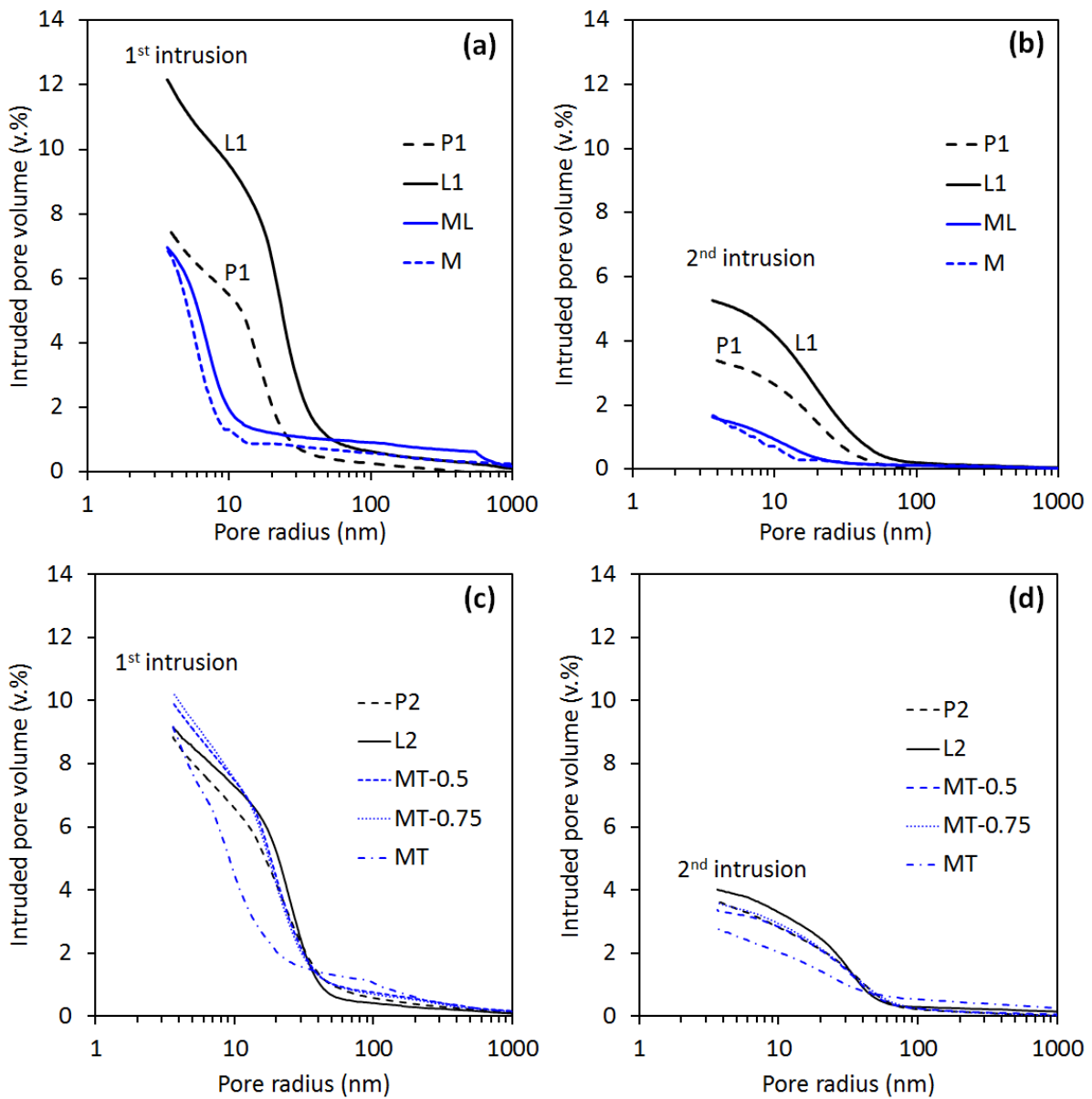


Figure 4. Intrusion curves from the first and second intrusion cycles after 91 days of hydration for (a, b) wPc – MK – LS mortars with the same w/b ratio and b/s ratio, and (c, d) oPc – CMT – LS mortars with comparable target 28-day compressive strengths by varying the w/b ratio and b/s ratio. The data presented in (a) and (b) are identical to those from previous study [34].

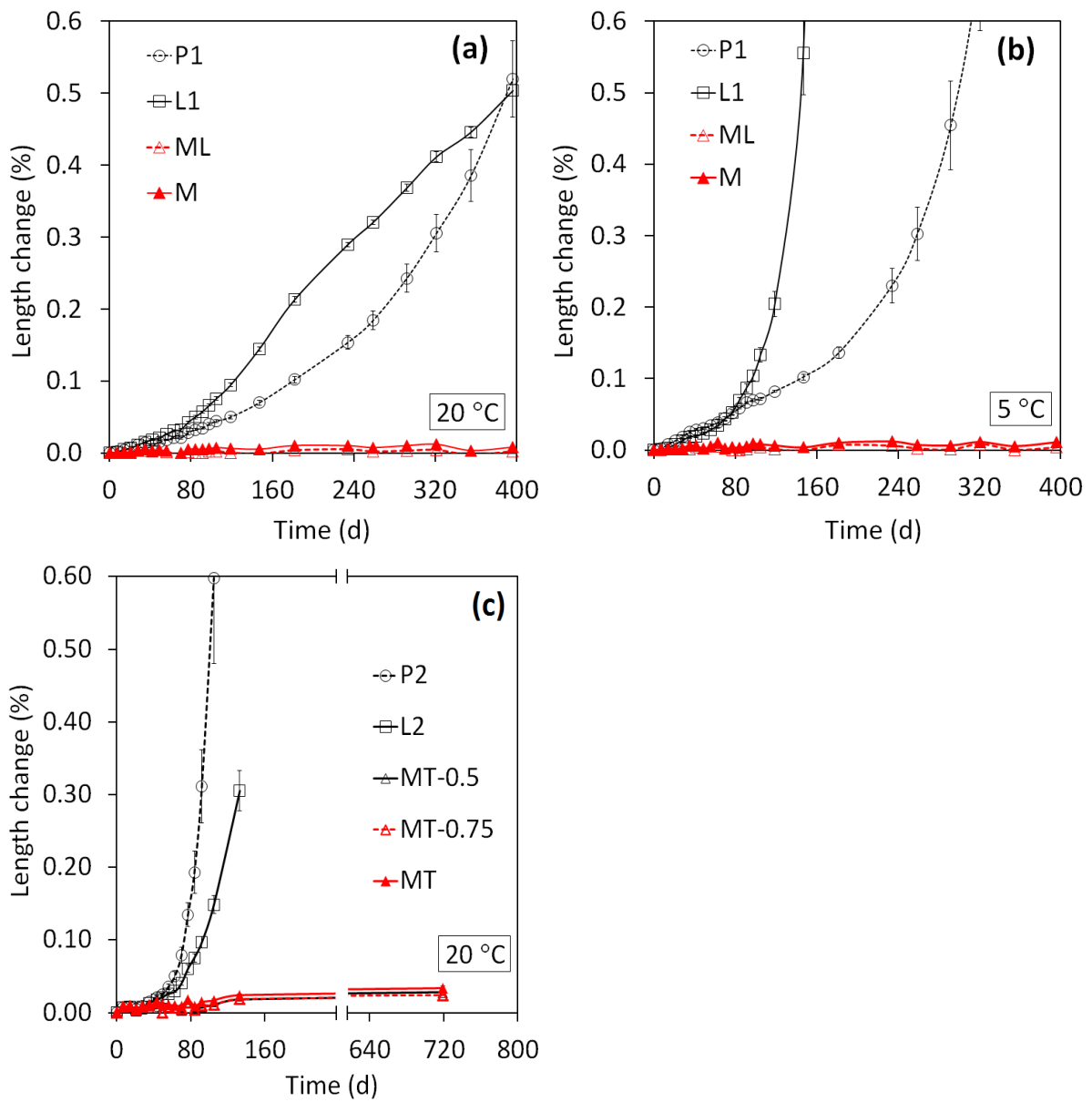


Figure 5. Length changes for (a, b) wPc – MK – LS and (c) oPc – CMT – LS mortar bars exposed to 0.11 M sulfate solution (16 g/L Na₂SO₄) at 20 °C and 5 °C. The last expansion measurements for the CMT mortars were performed after 719 days exposure.

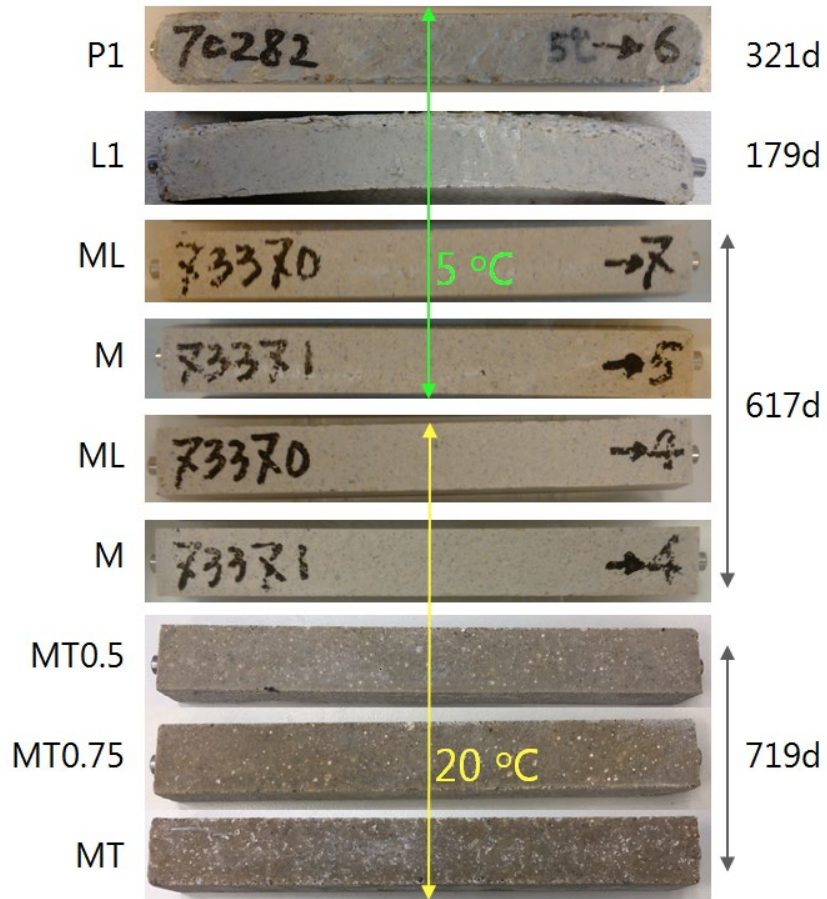


Figure 6. Visual inspection of the surface of wPc (from P1 to M) and oPc (from MT0.5 to MT) blends containing calcined clays after exposure to the 0.11 M sulfate solution (16 g/L Na₂SO₄).

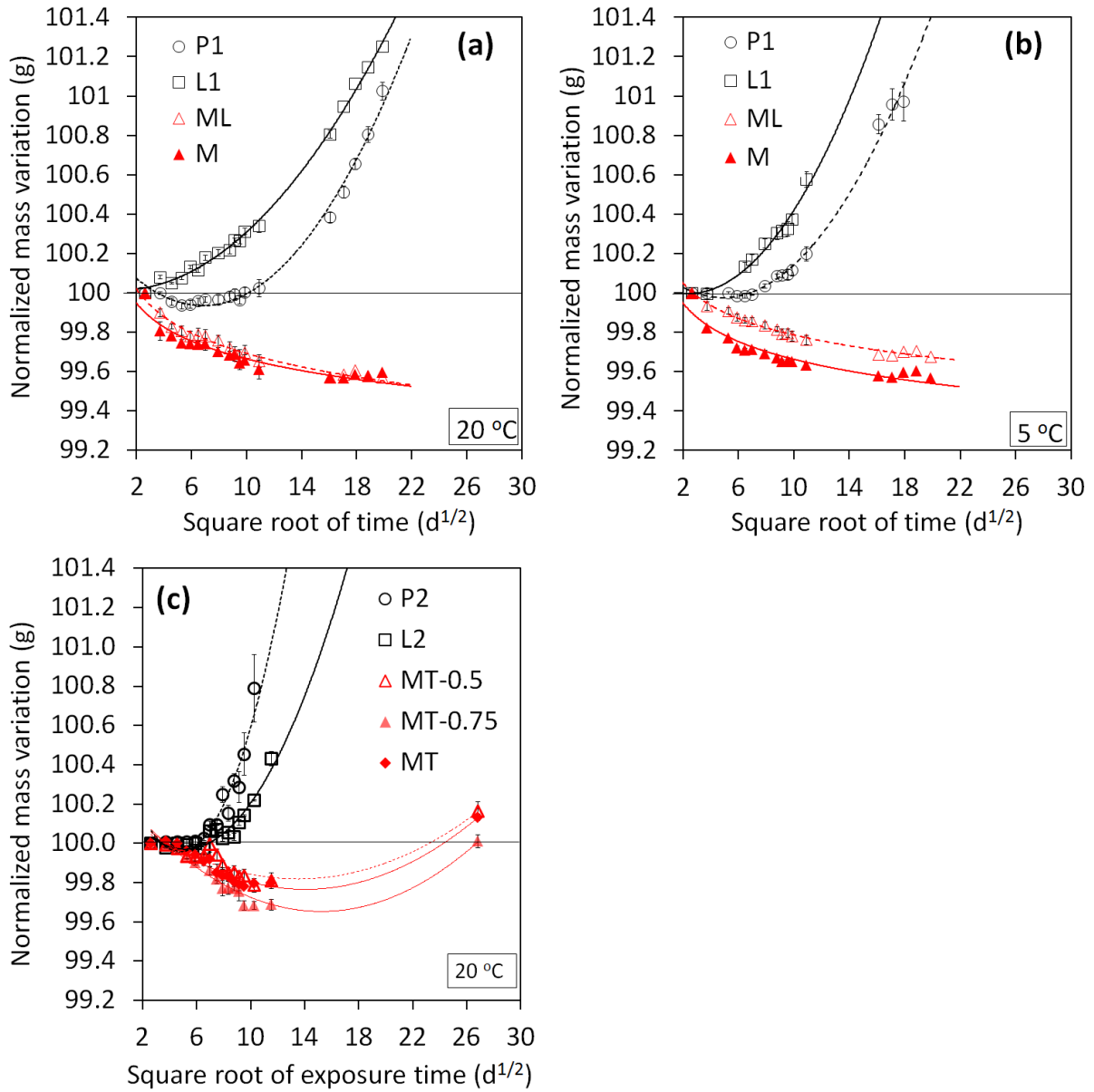


Figure 7. Mass changes for (a, b) the wPc – MK – LS mortars and (c) the oPc – CMT – LS mortars exposed to the 0.11 M Na₂SO₄ solution at (a, c) 20 °C and (b) 5 °C. The initial masses prior to sulfate exposure are normalized to 100 g (*c.f.* Experimental section 2.5).

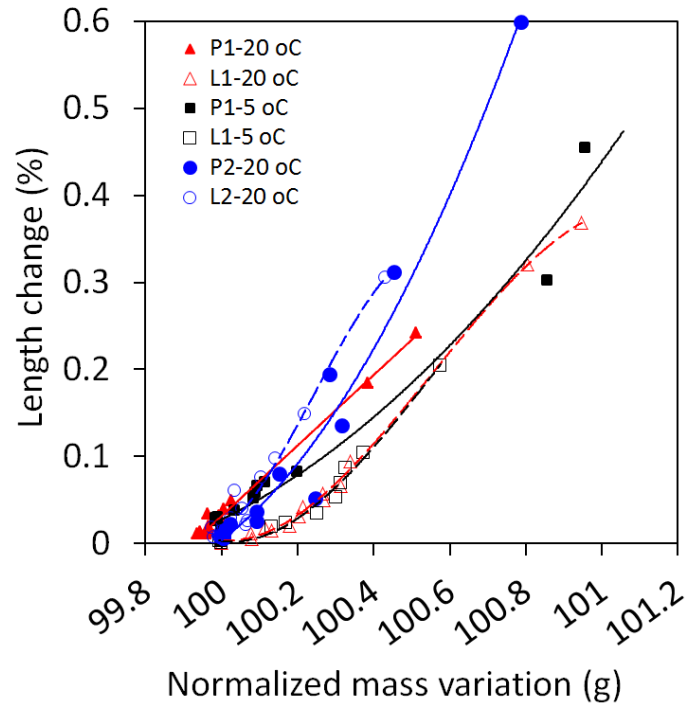


Figure 8. Relationship between length change and mass change for the reference mortars after exposure to 0.11 M sulfate solution (16 g/L Na₂SO₄) at 20 °C and 5 °C. The data for MK and CMT mortars are not plotted as they have negligible mass increase and expansion.

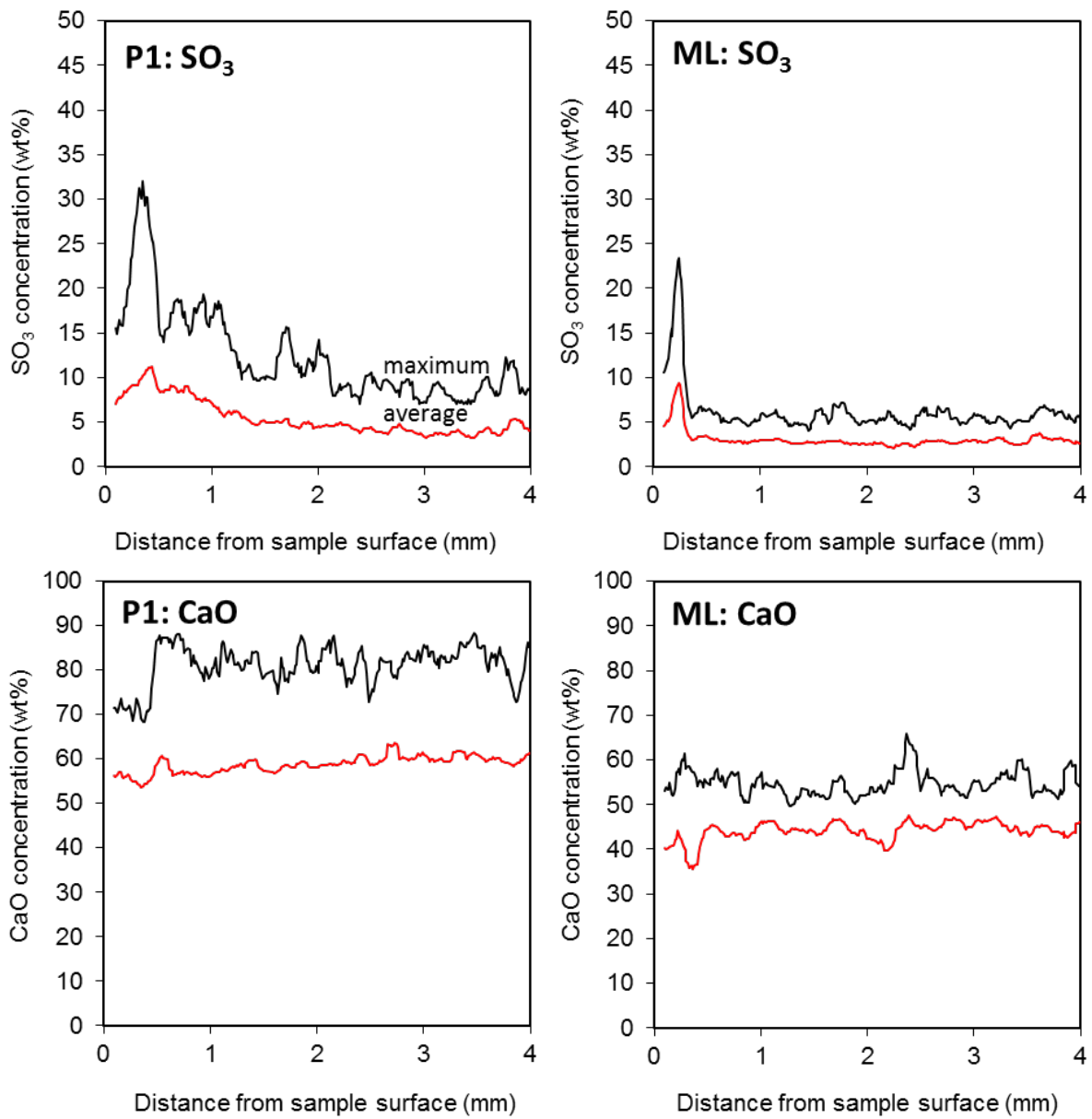


Figure 9. Sulfate and calcium oxide profiles for the P1 and ML mortars after 42 days of exposure to the 0.11 M (16 g/L) Na_2SO_4 solution at 20 °C. The red lines connect moving averages of 8 median values for each depth whereas the black lines correspond to the moving average of the maximum SO_3 and CaO values measured, thus being more sensitive to sulfate uptake and calcium leaching.

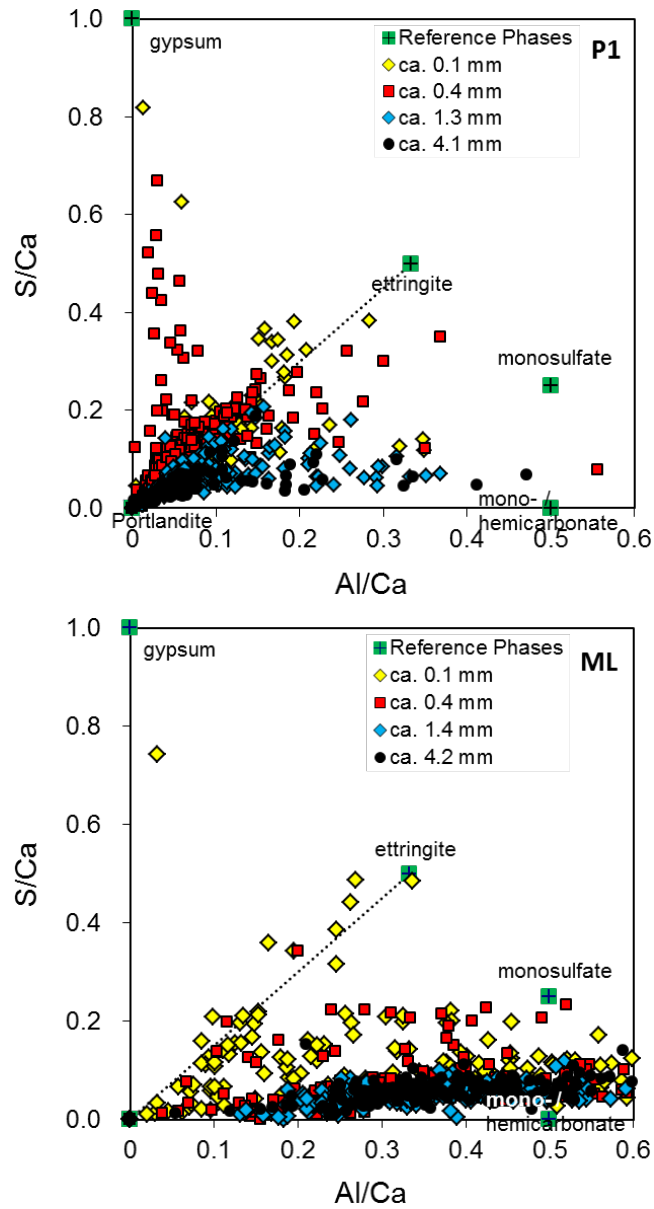


Figure 10. EDS dot plots of S/Ca versus Al/Ca atomic ratios at different depths from the exposing surface of the P1 and ML mortars after 42 days of exposure to the 0.11 M sulfate solution (16 g/L Na₂SO₄) at 20 °C.

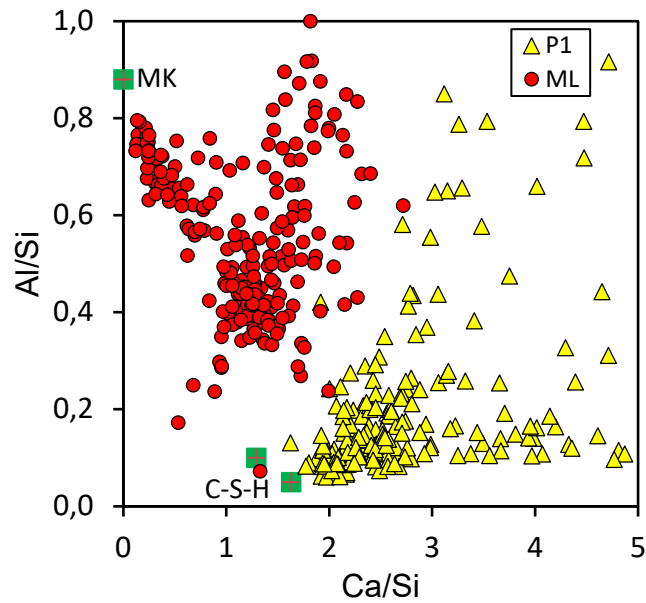


Figure 11. EDS plot showing the Al/Si ratios as function of the Ca/Si ratios for the C-S-H phase in the region of the unaffected matrix for the P1 and ML mortars after 42 days of exposure to the 0.11 M sulfate solution (16 g/L Na₂SO₄) at 20 °C. The Al/Si ratio of MK is calculated from the chemical composition given in Table 1. The Al/Si ratios of the C-S-H phases indicated for P1 and ML mortars are 0.05 and 0.1 respectively, which were determined from NMR data in the previous study on the similar binder materials [45]. The Ca/Si ratios of the C-S-H phases indicated for P1 and ML mortars are 1.63 and 1.29 respectively, which were calculated by thermodynamic modelling for the same binder materials [7].