

ORIGINAL ARTICLE

1:1 or 2:1 - Does it matter for calcined clay as supplementary cementitious material?

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Abstract

Calcined clays are the most promising future supplementary cementitious material which are capable of replacing fly ashes and blast furnace slag on the long run due to their potential to achieve high cement replacement levels and their global availability. In the last decade most research has focused on calcined clays rich in the 1:1 kaolinite. Clay with less than 20 to 25 % kaolinite were seen as worthless. Even the content of 2:1 phyllosilicates in the kaolinitic clays was neglected and not even mentioned although especially these clays are dominant in areas like central and northern Europe. Here, highly kaolinitic clays are rare or used by other industries leading to high prices. This paper is based on published works and highlights whether information obtained for calcined 1:1 dominated clays can be applied for calcined 2:1 dominated clays or not and where further research is needed.

Keywords

Calcined clay, kaolinite; smectite, illite, availability, production, properties, workability, strength potential, durability

1 Introduction

The intensive use of calcined clays as supplementary cementitious materials (SCM) is engaging research groups around the globe. In Germany, the introduction of CEM II/C-M [1] permits using calcined clays as main constituent of cement with up to 50 wt.% in combination with limestone powder. This combination leads to a significant increase in the performance of the calcined clays used [2]. However, the heterogeneity of clay deposits worldwide somewhat inhibits the wide-spread implementation of clinker-reduced cements with calcined clays. One of the reasons for this is the almost exclusive focus to date on the 1:1 phyllosilicate kaolinite and calcined clays with a kaolinite content higher than 40 wt.%. However, these clays are not equally available worldwide or their use as SCM is often in competition with other industries. For clays with a kaolinite content below 30 wt.%, often referred to as common clays, the 2:1 phyllosilicates gain a significant role for the performance as supplementary cementitious material (SCM) [3]. Thus, quantification of the 2:1 phyllosilicates is essential for the classification of common clays. Compared to kaolinite-rich clays, these common clays have been less addressed by research on calcined clays. Investigations on the 2:1 phyllosilicate muscovite show exemplary that, in addition to reactivity, differences in

physical-hygroscopic properties must be considered as a function of the calcination temperature [4]. The paper at hand summarizes and compares recent essential findings on the differences between 1:1 or 2:1 phyllosilicate dominated calcined clays.

2 Classification and availability

2.1 Classification

Common clays consist usually of a mixture of different phyllosilicates accompanied with various other minerals such as quartz, iron oxides and carbonates. The different phyllosilicates can be classified based on their layer type (1:1, 2:1 and 2:1:1). Their layer charge allows grouping these basic types further and dividing them into sub-groups. The basic classification refers to the tetrahedral and octahedral sheets which form the stack-like structure of the phyllosilicates. The dominant cation in the tetrahedral sheet is silicon, while it is aluminum in the octahedral sheet. More details are provided in [5, 6]. The different stacking order has an impact on the reactivity after calcination when the clays are used as SCMs (see section 4.2).



Figure 1 Exemplary production steps of clay-based SCM: Mining, pre-conditioning, calcination and processing (Source: Liapor GmbH & Co. KG, Pautzfeld).

2.2 Availability

Clay minerals are the product of weathering processes. They originate from rock-forming silicates and result from their interaction with water. In hydrothermal environments alteration of the aluminosilicate source rock can form clay minerals. The results of the degradation are loose, fine grained particles, which can stay as sediments and may undergo further mineralogical and/or chemical alterations [7]. Eventually, the global availability of the different clay types depends on the prevailing climatic conditions over long enduring periods of time. Warm and wet climatic conditions like the ones in equatorial regions favor the formation of 1:1 clay minerals of the kaolinite group. 2:1 clay minerals like illite, smectite and montmorillonite as well as 2:1:1 chlorite are rather formed in cold regions as in the northern or southern hemisphere [8, 9]. Alujas Diaz et al. [10] provide a comprehensive overview on the global occurrence of clay minerals. Maier et al. [11] highlight the domination of 2:1 clay minerals in Germany in their view on local availability of the different clay types.

3 Production

The production of clay-based SCM includes mining, excavation and processing. The latter is mainly a heating process better known as calcination which thus far uses either a flash-calciner or a rotary kiln [12–14]. **Figure 1** gives impressions of the production of a calcined clay with 25 wt.% kaolinite. In the following, CC is used as an abbreviation for "calcined clay" and the subsequent number indicates the kaolinite content of the raw clay (e.g. CC25). In addition to kaolinite, CC25 contains at least 40 wt.% 2:1 phyllosilicates and is thus a mixture of 1:1 and 2:1 phyllosilicates.

Most important for the transformation into a pozzolanic material is the temperature range of dehydroxylation which depends on the bonding of the hydroxyl groups in the octahedral sheet. Within the line of production, differences between 1:1 and 2:1 dominated clays only exist during the calcination. While kaolinite completely loses its crystallinity and transforms into an X-ray amorphous phase, 2:1 phyllosilicates retain part of the initial crystal structure upon dehydroxylation and usually require higher

calcination temperatures for activation than kaolinite. At the same time they transform into inert high temperature phases at lower temperatures than kaolinite [15]. As a result, their temperature window for thermal activation is narrower and pozzolanic reactivity is lower [10]. **Figure 2** summarizes some practical production temperatures (upper x-axis) and the corresponding CO₂ emission originating from the raw material and the fuel used for production [16] with data from [14]. This illustration clearly shows the great potential of calcined clays as SCM to drastically reduce the CO₂ emissions of modern binders by replacing Portland cement (PC) clinker.

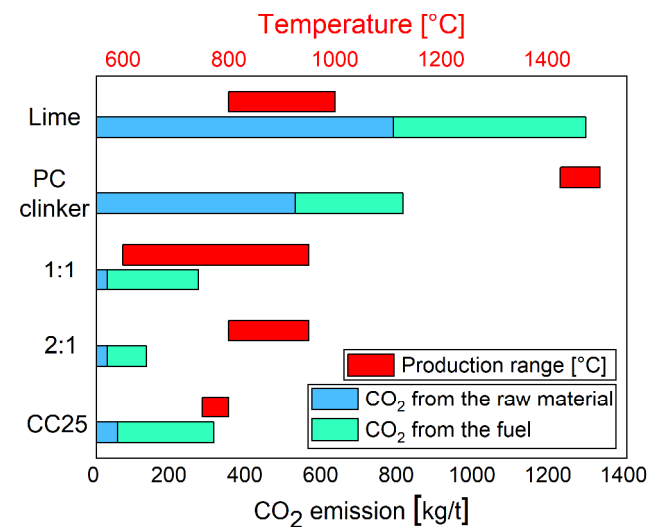


Figure 2 Comparison of CO₂ emission from raw material and fuel for the production of different materials (lower x-axis) after [16] with data from [14] and production range (upper x-axis) with data from [14]. 1:1 represents metakaolinite and 2:1 metapyrophyllite as an example for 2:1 meta-phyllosilicates. Data for CC25 from [17] and Liapor GmbH & Co. KG, Pautzfeld.

It should be pointed out here, that the choice of optimum calcination temperature for different phyllosilicates must not only consider the impact on reactivity as SCM (see section 4.2), but take into account as well the effect of calcination temperature on physical-hygroscopic properties, as they influence durability and workability [4].

4 Material properties

4.1 Physical properties

In addition to the very diverse composition of common clays, their physical properties also vary a lot and are not that easy to categorize [18]. In general, calcined clays tend to have a higher water demand (**Figure 3b**) compared to e.g. glassy fly ash particles. Particle size distribution (PSD) can be adjusted by grinding within a certain range as required. In this way, differences in the physical filler effect can be achieved. However, PSD only describes the outer surfaces, which in the case of calcined clays does not allow a complete statement on the water demand. Also, the BET surface area [19] varies for clay and mica minerals in a very wide range. While mica tends to have a moderate BET surface area, illitic and smectitic clays can exhibit BET surface areas of up to 100 m²/g [20]. For kaolinitic clays, the BET surface area depends on the degree of order of the kaolinite: more disordered kaolinites have a higher surface area. **Figure 3a** summarizes the BET surface area over a wide range of calcined clay compositions. No correlation of the BET surface area with the total phyllosilicate content can be established. The decisive factor is rather the type and order of the clay minerals and whether it is a 1:1 or 2:1 phyllosilicate. On the other hand, the water demand increases in a wide band depending on the total phyllosilicate content (**Figure 3b**). Thus, particle characterization via the BET surface area as a criterion for the water demand and workability is neither trivial nor applicable. Overall, when calcined clays are used as SCM, the mineralogical characterization of the clay and the main physical parameters must not be ignored, and the total phyllosilicate content and the type of predominant phyllosilicate must be considered [18].

4.2 Reactivity

For characterizing reactivity, the isothermal calorimetry and bound water test regulated in ASTM C1897 - 20 [21] has proven to be effective [22]. In order to obtain a more

precise view on the differences of reactivity between 1:1 and 2:1 phyllosilicates, the solubility of silicon and aluminum ions in alkaline solution can be used additionally. It yields a very good correlation to the heat of hydration obtained in isothermal calorimetry test [3] as illustrated in **Figure 4a and b** for four calcined clays. The comparison with the materials used in the round robin test - RILEM TC 267-TRM [22] shows that all CC investigated have a higher reactivity than the fly ash used. CC with a kaolinite content of about 40 wt.% yield values in the range of slag. Approximately the same reactivity can be achieved with a CC without any kaolinite, but with a high 2:1 phyllosilicate content (CC0). CC with high kaolinite content (e.g. CC82) clearly exceeds the reactivity of slag. Nevertheless, a closer look at the ion solubility shows that CC with exclusively kaolinite possess a ratio of soluble silicon to aluminum ions close to one (**Figure 4a**, CC82). CC with a high content of 2:1 phyllosilicates can have a significantly higher silicon to aluminum ratio of 1.5 to 2.5 at its optimum calcination temperature (**Figure 4a**). Higher dissolution rates of aluminates and silicates are observed for 1:1 compared to 2:1 meta-phyllosilicates [23]. Based on the higher number of hydroxyl groups for 1:1 meta-phyllosilicates, the higher reactivity is due to the complete transformation to an X-ray amorphous phase and thus higher loss of crystallinity upon calcination compared to 2:1 meta-phyllosilicates [24, 25].

Since calcined clays do not have a glassy surface, they can provide pozzolanic reactivity at very early times (already during the first day and thus during the main reaction of the clinker phases) [26]. The chemical reactivity during the first 48 h was demonstrated for a calcined illitic clay without kaolinite [27]. The reaction of the calcined clays is a largely congruent dissolution process for meta-phyllosilicates treated at their optimum calcination temperature [23, 28]. Overall, calcined clays provide a great potential for replacing large amounts of clinker as reactive component in composite cements.

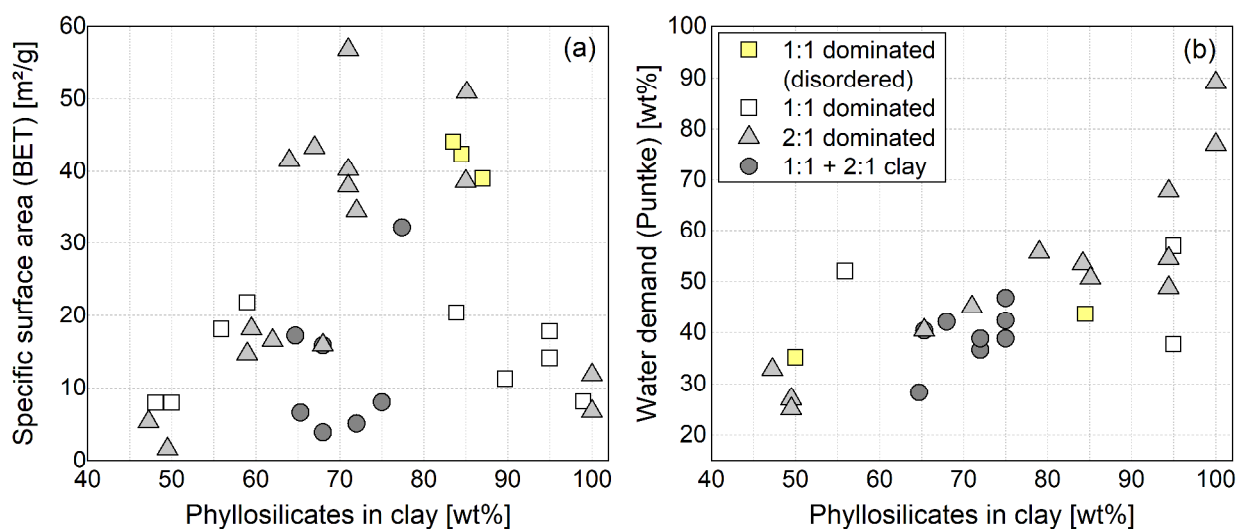


Figure 3 Correlation of the total phyllosilicate content in the clay with the specific surface area (BET) (a) and the water demand (Puntke) (b) after [18].

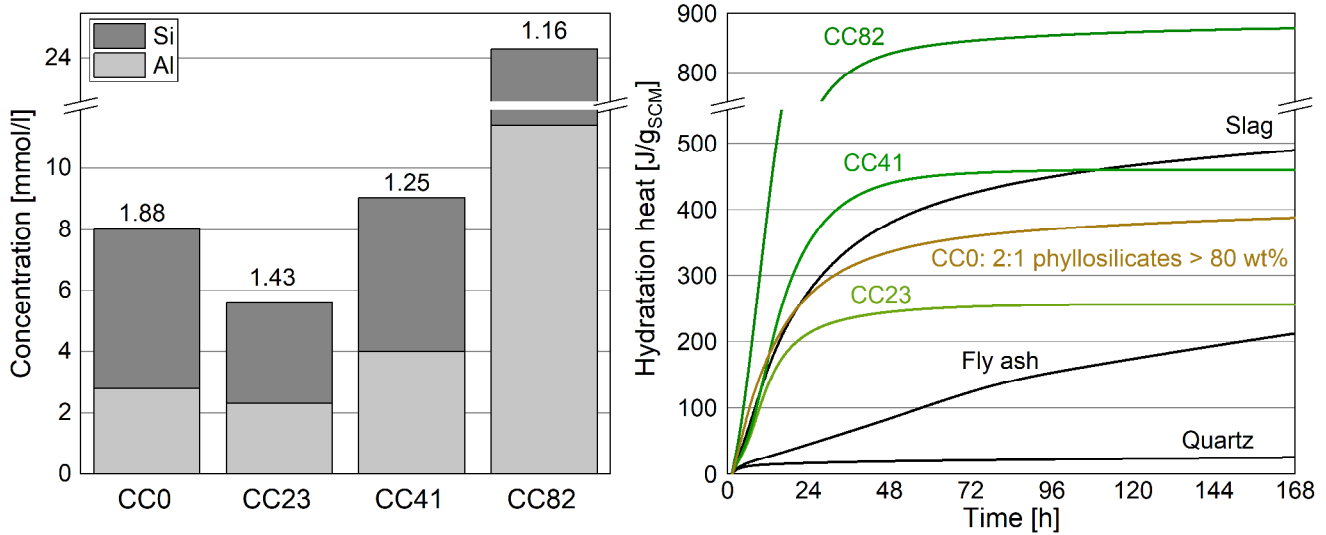


Figure 4 Solubility of silicon and aluminium ions in alkaline solution (a) and evolved heat based on R³ reactivity test (b) after [29], own results from round robin test - RILEM TC 267-TRM (quartz, fly ash and slag) [22] The number above the bar represents the silicon to aluminium ratio.

5 Reaction kinetics and phase formation

The reaction kinetics of cement during early hydration is strongly influenced by the use of calcined clays. As already known from other SCMs (limestone powder or fly ash), the use of calcined clays yields a filler effect if its fineness is sufficient [30, 31]. The dilution of the cement system and additional surface areas accelerate the silicate clinker reaction and thus shorten the dormant period [32]. Calcined clays massively accelerate the aluminate clinker reaction [33]. Zunino and Scrivener [34] ascribe the acceleration of the silicate clinker reaction as reason for the acceleration of the aluminate clinker reaction regardless of the SCM used. The earlier C-S-H formation and adsorption of sulfates on the C-S-H surfaces leads to accelerated sulfate carrier dissolution and thus accelerated aluminate clinker reaction. By comparing a fine limestone powder and calcined clays with different kaolinite contents, Maier et al. [29] demonstrated that, in addition to the surfaces of the C-S-H, the negatively charged surfaces of phyllosilicate particles (see Section 6) also influence the dissolution of the sulfate carrier. Even though this effect seems to be stronger for 1:1 dominated clays, it was also confirmed in pure C₃A - sulfate carrier systems diluted with quartz for a 2:1 phyllosilicate dominated illitic clay [33]. **Figure 5** shows the effect of sulfation on a kaolinite-rich (CC82) and kaolinite-poor (CC23) calcined clay. CC82 underlines the high sulfate demand of 1:1 dominated clays with high kaolinite content. A significantly lower sulfation is required (2.66 wt.% calcium sulfate (C\$)) to match the hydration curve of the PLC-30CC23 system to the original heat flow curve of PLC. In comparison, 2:1 dominated clays even with high meta-phyllosilicate content can be adjusted by significantly lower sulfate contents [33, 35].

The general phase assemblage of a binder hardly differs by the use of calcined clays after 180 d [36]. In pure Portland cement systems, accelerated ettringite formation is followed by a further reaction to monosulfate (AFm-MS) after reaching the maximum ettringite content during the main reaction of the cement clinker [37]. This is also known for carbonate-free systems with calcined clays [26, 38]. The addition of calcite stabilizes ettringite and leads to the formation of hemi- or monocarboaluminates (AFm-

Hc or AFm-Mc) [38, 39]. The addition of calcined clays and thus more aluminum to the system favors the formation of AFm-Hc during early hydration [40]. This was demonstrated for both 1:1 and 2:1 phyllosilicate dominated clays [41, 42]. In addition, there is an increased incorporation of aluminum in the C-S-H phase [43]. When comparing 1:1 to 2:1 phyllosilicate dominated clays, the main difference lies in the availability of aluminum. At later hydration ages aluminum-rich clays can lead to higher amounts of AFm phases and the formation of strätlingite [44-46] as well as during the first day in systems without silicate clinker reaction [33].

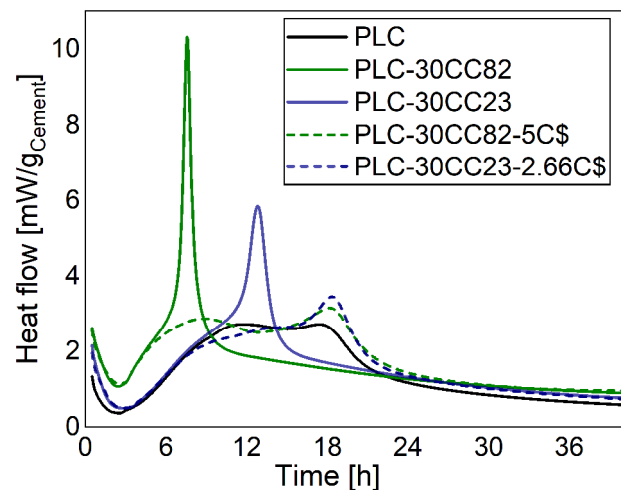


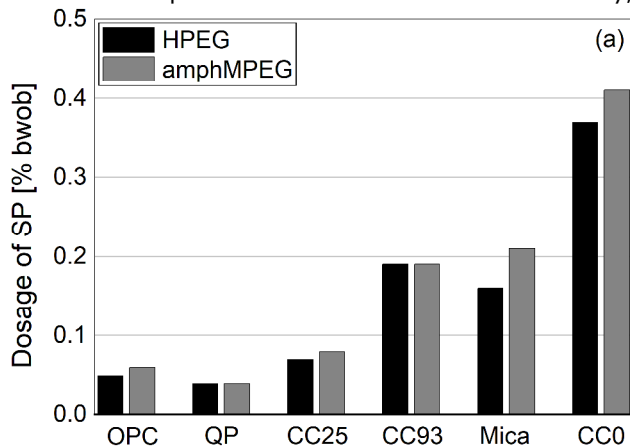
Figure 5 Sulfate adjustment of PLC systems blended with 30 wt.% calcined clays after [29].

6 Workability

Both, calcined 1:1 and 2:1 phyllosilicates exhibit in parts strongly negative zeta potential in deionized water, in sodium hydroxide solution and in a synthetic cement pore solution [47, 48]. Titration of calcium to various meta-phyllosilicates (metamuscovite, metallite, metasmectite and metakaolinite) proves that for high concentrations of calcium in the pore solution, the zeta potential can become positive which is crucial for the adsorption of anionic superplasticizers [29, 47]. Overall, the absolute values of the

zeta potential of the various meta-phyllsilicates for different environmental conditions vary over a wide range. Thus, the adaptation of the appropriate superplasticizer for different calcined clays is a challenge.

Workability is strongly affected by the calcined clay content in a binder and the content of meta-phyllsilicates in the calcined clay. The use of calcined clays with a high amount of metakaolinite worsens rheology [2, 49]. PCE based superplasticizers are the most powerful in calcined clay blended cementitious systems [50, 51]. Schmid and Plank [52] demonstrated the influence of different PCE types (HPEG-, MPEG- and IPEG-based) on their dispersing performance in calcined clay blended cementitious systems, where the HPEG-based PCE was found to be the most effective. Sposito et al. [20] confirmed this finding in an investigation (**Figure 6a**) with lower dosages of the HPEG-based compared to the MPEG-based PCE. Thereby,



for calcined clays with high meta-phyllsilicate content, both 1:1 (CC93) and 2:1 (mica and CC0) exhibit a significantly increased superplasticizer demand. This is also confirmed when looking at the efficiency of the PCEs (**Figure 6b**). Although a decrease of the yield stress can be observed for the three previously mentioned almost pure meta-phyllsilicates (CC93, mica and CC0), this does not lead to a decrease in viscosity. The calcined common clay CC25, on the other hand, has a significantly lower superplasticizer demand and better workability. Quartz and other accompanying minerals lead to a reduction of the total surface area, the water demand and consequently improve the interaction with PCEs as well as the workability. Thus, no systematic difference can be identified in the comparison of the 1:1 and 2:1 meta-phyllsilicates. Rather, the total phyllsilicate content of the calcined clays and an adjustment of the superplasticizer is crucial.

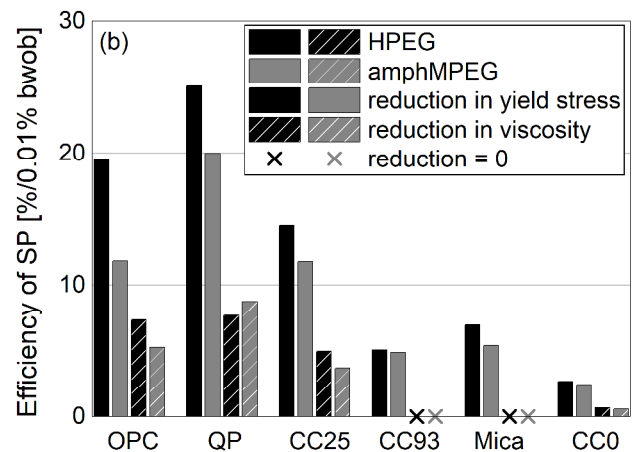


Figure 6 Superplasticizer (SP) dosage (a) and SP efficiency (b) of cement pastes with a replacement level of 20 wt.% after [20].

7 Strength potential

The strength potential of calcined clay blended cements is significantly influenced by the chemical-pozzolanic reactivity of calcined clay, physical effects and finally also by the interaction calcined clay - cement clinker. In contrast to established SCMs, the pozzolanic reaction already starts in the first two days. The formation of early chemical pozzolanic reaction products is dominated by C-S-H and Aft phases, with a prevailing Aft formation even with 2:1 phyllsilicates in the presence of sulfates [46, 53]. Nevertheless, for blended cements with calcined clay the early strength remains significantly lower than in Portland cement systems and requires future research.

The strength development (2 to 90 days) follows the classical pozzolanic reaction and is additionally enhanced for aluminum-rich clays (1:1), especially by the highly reactive metakaolinite, by an AFm phase formation [45]. At the aimed-for high replacement levels, the impact of metakaolinite in blended systems is too intense and can even impede the clinker reaction [29, 35]. A high sodium equivalent of the cement promotes the pozzolanic reaction (**Figure 7**).

A considerable influence on the compressive strength in ternary blends systems results from the combination of calcined clays and limestone. Positive synergy effects were demonstrated with increasing metakaolinite content and lead to higher compressive strength values [44, 54].

Calcined clays with a high 2:1 content react more moderately than 1:1 clays. Calcined montmorillonite reacts slower than metakaolin, but blends can in some cases catch up the strength of blends with calcined 1:1 dominated clays at late ages [55]. **Figure 8** shows exemplary that a calcined common clay (CC25) can yield activity indices of more than 100 % not only with Portland cement but even with various CEM II. In the end only a slag cement (CEM III/A) outperforms the blend in its post-hardening potential [56]. Thus, even 2:1 clays with weaker performance in the reactivity tests can yield sufficient strength as blended cement.

Such results indicate the potential of calcined common clays even for higher substitution rates and are consequently predestined for blended cements in the future.

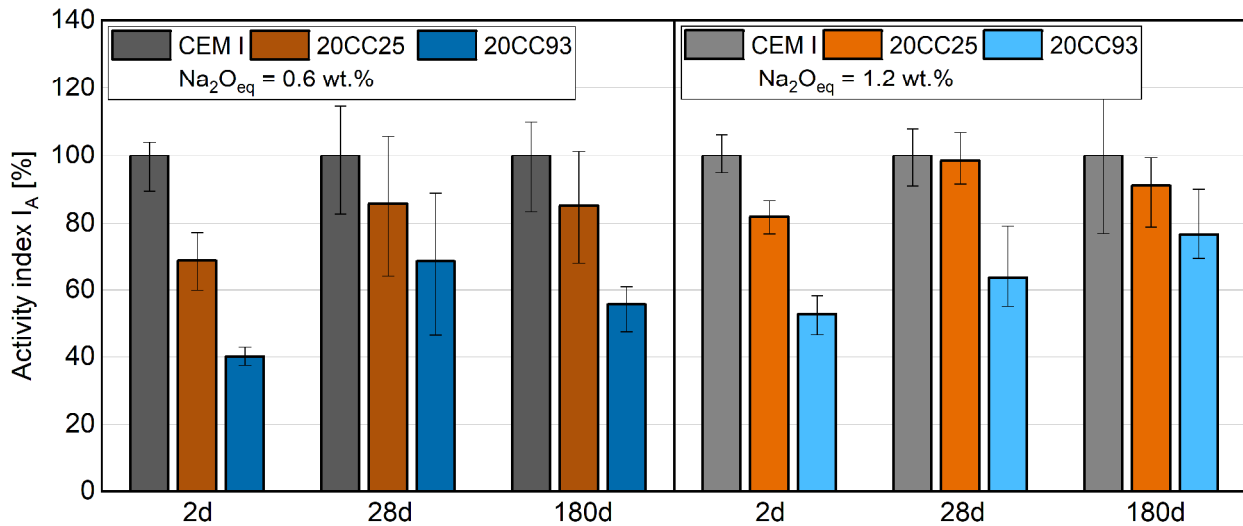


Figure 7 Impact of $\text{Na}_2\text{O}_{\text{eq}}$ on the strength activity index I_A of cement blended with a calcined common clay (CC25) and metakaolinite (CC93). The water binder ratio was adjusted determined in accordance with DIN EN 196-3 [57] to achieve the standard stiffness [45]

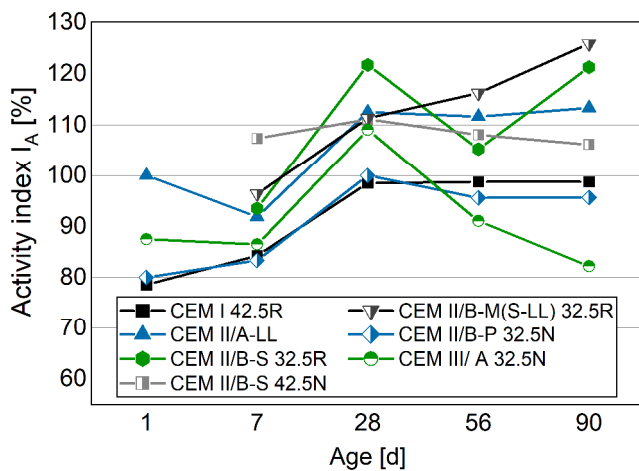


Figure 8 Activity indices for different cements blended with 20 wt.% CC25 [56].

8 Durability

8.1 Microstructure

Studies on the impact of metakaolinite on pore size distribution are mostly limited to low Portland cement replacements, in the range of 10–15 wt.%. A metakaolinite content up to 15 wt.% was studied in [58]. A further analysis of the pore size distribution in those samples showed an increased pore fraction $<20 \text{ nm}$ with higher metakaolinite content and a decreased pore fraction $\geq 20 \text{ nm}$ when the metakaolinite content was lower. This confirmed the pore size refining effect due to the pozzolanic reaction of metakaolinite (Figure 9) [24, 45].

The addition of limestone to 1:1 dominated clays positively influences the pore structure of the binder. Antoni et al. demonstrated that a cement blend with 30 wt.% 1:1 dominated clay and 15 wt.% limestone powder produced a more refined pore structure compared to cements produced with 45 wt.% 1:1 dominated clay replacement alone [59]. Studies have shown that the calcined clay-limestone system manufactured with clays containing 20–60 wt.% kaolinite formed a higher amount of AFm-Mc and AFm-Hc phases than OPC alone [44]. Thus, the calcined

clay-limestone interaction favors the formation of carboaluminate phases and refines the porosity. Another study [60] revealed that deposition of these carboaluminate phases occurs along with large pore spaces. There is a lower tendency to form such hydrate phase at later ages or at lower water to binder ratios. This is due to the significant pore size refinement which has already occurred during early hydration and limits the formation of such crystalline hydrate phase. This is confirmed by the higher amount of carboaluminate phases formed at higher water to binder ratios [24].

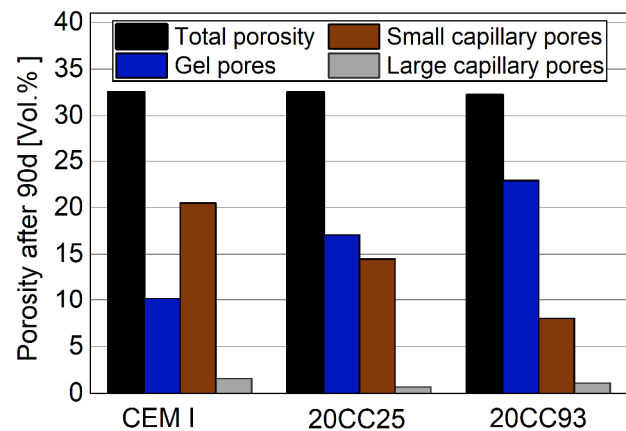


Figure 9 Impact of calcined clays with different content of metakaolinite on the formation of pores after [45].

The critical pore entry declined with increasing metakaolinite content [61]. No clear difference [62] or even an increase of the critical pore entry [63] was reported for blended binders with calcined 2:1 illite dominated clays compared to the reference OPC system.

8.2 CH-consumption and carbonation

1:1 dominated clays are highly reactive as pozzolanic material which is reflected in a high consumption of calcium hydroxide (CH). Increasing the replacement level reduces drastically the CH-content [64] which is accompanied by an increase in the depth of carbonation. On the other hand

the use of 1:1 dominated clays promotes a pore refinement (see section 8.1), which reduces the gas permeability and finally yields a depth of carbonation in blended cements comparable to established binders [65]. Calcined 2:1 dominated clays exhibit a far more moderate decline of CH in blended cement paste (**Figure 10**), but may exhibit higher values for the depth of carbonation as blends made with calcined clays with a higher content of 1:1 phyllosilicates [66].

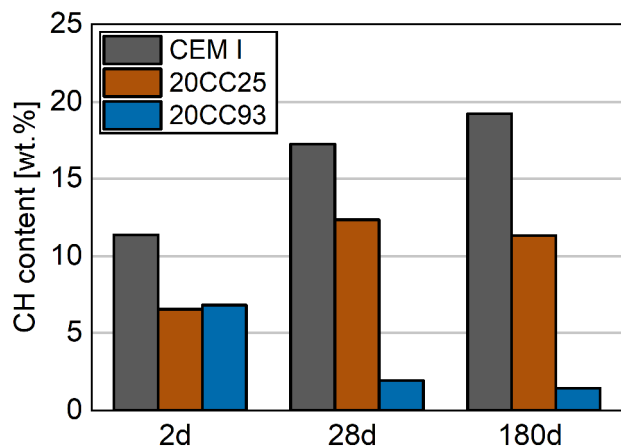


Figure 10 Comparison of the impact of metakaolinite content on CH-content of cement pastes after [45].

8.3 Resistance against chlorides

A slight increase in the chloride penetration resistance was observed by [67] in a binary binder made with calcined illitic clay compared to OPC while [68] found an opposite effect. The resistance increases for binary and ternary blends with increasing metakaolinite content [68–71]. Final differences in the effect of 1:1 and 2:1 are hence still under discussion. Chloride binding capacity of limestone calcined clay cements was investigated by [72]. They used calcined clays with a content of 40 to 80 wt.% metakaolinite for LC³-50 blends. An increasing pH led in their investigation to decreasing incorporation of chloride into Friedel's salt and AFm-Hc. Interestingly, chloride binding capacity reached an optimum for a metakaolinite content of approximately 50 wt.%.

Pillai et al. [70] observed an increased consumption of CH in ternary blends due a high metakaolinite content of approximately 58 wt.% of the calcined clay which lowered the pH and reduced the chloride corrosion threshold below 40 wt.% of the reference OPC. Up to now, there is no such information available for calcined clays with a low content of metakaolinite or other meta-phyllosilicates.

9 Summary and Conclusions

The following conclusions can be drawn:

- 1:1 and 2:1 dominated clays are not evenly available. Thus the latter are more in the focus as SCM in northern and central European countries like e.g. Germany.
- Full-scale productions of calcined clays are not yet installed in numbers sufficient to cover the quantities needed to replace fly ashes and blast-fur-

nace slag as future SCM. Nevertheless, technology and knowledge are available.

- 1:1 and 2:1 dominated clays both exhibit broad spectra of physical properties. Thus, there is neither a typical 1:1 nor a typical 2:1 clay.
- Calcined 1:1 dominated clays exhibit a higher reactivity than calcined 2:1 dominated clays as found in specific tests. Both calcined 1:1 and 2:1 dominated clays have a significant impact on the reaction kinetics when used in blended cementitious binders. Finding the optimum sulfation is significantly more complex for systems blended with calcined 1:1 dominated clays.
- There are only minor differences in the phase formation during early hydration due to the type of calcined clay. This holds as well for the general phase assemblage. Later on, aluminum-rich calcined clays with a high content of 1:1 dominated clays form more carboaluminate and especially strätlingite.
- To date, there is no superplasticizer available that is suitable for all calcined clays. Not only blended cementitious systems with metakaolin are difficult to liquefy, but also systems using calcined 2:1 dominated clays with high phyllosilicate content are critical.
- Calcined common clays with a high content of 2:1 phyllosilicates can lead to sufficient strength in cementitious systems even though they yield low values in reactivity tests. This highlights the need for more research especially with a focus on early age strength. The data for 2:1 dominated clays is significantly less than 1:1 dominated clays.
- Blends with calcined clays yield a refined microstructure. This effect is more pronounced for 1:1 dominated clays. However, calcined 1:1 dominated clays consume more calcium hydroxide and reduce the pH value.
- The use of calcined 1:1 dominated clays decreases the chloride ingress more than calcined 2:1 dominated clays and have a higher chloride binding potential but yield no benefit with respect to chloride induced steel corrosion.

Summarizing the different aspects highlighted in this paper we conclude that it often does matter whether it is a 1:1 or a 2:1 calcined clay that should be used as supplementary cementitious material.

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