Impact of metakaolin content and fineness on the behavior of calcined clay blended cements admixed with HPEG PCE superplasticizer

Ran Li, Lei Lei[**], Johann Plank[*]

Technische Universität München, Chair for Construction Chemistry, 85747 Garching, Lichtenbergstraße 4, Germany

A B S T R A C T

In this study, three calcined clays (CCs) possessing different metakaolin contents (23; 51 and 86 wt%) were investigated with respect to their pozzolanic reactivity, water demand and workability in the presence of an HPEG PCE superplasticizer. Furthermore, mixed CC samples were prepared by blending a specific CC of low metakaolin content (23 wt%) with pure metakaolin to achieve metakaolin contents of 30, 40 and 51 wt% in the final CC. Results on pozzolanic reactivity from the R^3 test evidenced that increased metakaolin contents result in higher pozzolanic reactivity and improve 1d compressive strength. Whereas, higher metakaolin contents increased water demand significantly. Moreover, PCE dosages of up to 12 times were recorded. Furthermore, it was found that also fineness of the CC influences workability. Fineness mainly affects the water demand, while the metakaolin content plays a dominant role regarding PCE dosage. A mechanistic investigation revealed that in cement pore solution calcined clays initially exhibit a negative surface charge, but then sorb huge quantities of Ca^{2+} which enables PCE to adsorb onto the surfaces of CCs, as was evidenced by zeta potential measurements and from adsorption isotherms.

1. Introduction

Calcined clay blended cements are drawing more and more attention as a new concept for low-carbon cements [1–5]. In the production of calcined clay, a temperature range of 600–800 °C is required [6,7] which is much lower than that of ordinary Portland cement (OPC) at ~ 1450 °C. As a result, the carbon dioxide released from fuel combustion is reduced. More important, an even much higher CO_2 emission resulting from the main source in OPC production, the decarbonization of $CaCO_3$, is prevented [8]. It has been reported that by applying Limestone Calcined Clay blended Cement (LC³), CO_2 emission can be reduced by around 30% [1]. Interestingly, at a cement substitution rate as high as 50%, no major influence on the final compressive strength of concrete has been observed [6,9,10]. Dhandapani et al. discussed the mechanical properties of concretes prepared using LC³ [11]. They found that the 3 day strength of LC³ concrete is slightly lower than that of OPC. Moreover, the 7 and 28 day strengths of LC³ have been reported to be similar to or higher than that of on OPC [10]. This favorable strength development can be attributed to the high pozzolanic reactivity of a calcined clay which carries a significant amount of amorphous alumina that

reacts with limestone to produce carbo-aluminate hydrates. In fact, the pozzolanic reactivity of calcined clays greatly depends on their specific mineral phase composition. Fernandez et al. [9] studied the pozzolanic reactivity of individual calcined pure clay phases. They found that metakaolin possesses by far the highest pozzolanic reactivity, followed by meta montmorillonite and meta muscovite. Consequently, the metakaolin content presents an important parameter with respect to the compressive strength development of a calcined clay blended cement.

On the other hand, it is known that the higher surface area of calcined clays as compared to OPC commonly induces poor workability into such calcined clay blended cements [2,12–16]. Moreover, in addition to the high specific surface area, also the specific mineral composition of the common natural clay can also much impact the rheology of the composite cement. Recent work suggests that compared to OPC, approximately twice the amount of a polycarboxylate (PCE) superplasticizer can be required in calcined clay blended cement (40% cement substitution with calcined clay) [17]. In another case, even 500% more PCE had to be dosed to a calcined clay blended cement of the same cement substitution ratio where the calcined clay contained ~51 wt% metakaolin [12]. These preliminary studies suggest that the metakaolin

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Table 1

Phase composition of the cement sample CEM I 42.5 R used in the study.

Phase	[wt.%]
C_3S, monoclinic	59.72
C_2S, monoclinic	11.53
C_4AF, orthorhombic	10.25
C_3A, cubic	4.42
C_3A, orthorhombic	2.54
Anhydrite ($CaSO_4$)	2.08
Dihydrate ($CaSO_4 \bullet 2H_2O$)	2.13
Hemihydrate ($CaSO_4 \bullet 0.5H_2O$)	0.79
Calcite ($CaCO_3$)	2.54
Dolomite ($CaMg(CO_3)_2$)	1.27
Quartz (SiO_2)	0.48
Portlandite (CH)	0.27
Arcanite (K_2SO_4)	0.41
Periclase (MgO)	0.76
Free lime (*Rietveld*)	0.44
Free lime (*Franke*)	0.35
Total	100.00

Table 2

Metakaolin contents of the calcined clay samples used in this study.

Sample	Metakaolin content [wt.%]
CT-07	23
CCC	51
MK	86
CT-MK 30	30
CT-MK 40	40
CT-MK 51	51
MK-40	55
M1000	65
M1200s	78
Meta Star®	95

Fig. 1. Particle size distribution of the pristine calcined clay samples, as determined via laser granulometry.

content of a calcined clay sample might play a significant role with respect to workability and PCE dosage requirements of such composite cements.

The specific interaction of calcined clays with anionic superplasticizers is vastly unknown. In a first study, Schmidt et al. investigated the interaction of PCE superplasticizers with individual pure meta clays [18]. They found that in synthetic cement pore solution, metakaolin exhibits the most negative surface charge, followed by meta montmorillonite, meta illite and meta muscovite. Obviously, such different surface charges of the meta clays can greatly impact the interaction with PCE and hence workability of the calcined clay blended cement.

To summarize, the metakaolin content present in a calcined clay appears to generally exercise a positive effect on the early strength development of such composite cements while it negatively affects workability. However, the impact of different kinds and concentrations of metakaolin in calcined clay samples is yet unknown. Thus, it is necessary to better understand the role of metakaolin in calcined clay composite cements in terms of water demand, PCE dosage requirement, early strength development and its surface chemistry in the cement pore solution. For this reason, in this study the impact of the metakaolin contents present in different calcined clay samples was investigated with respect to workability and strength development. Three calcined clay samples possessing increasing metakaolin contents were selected: CT-07 (23 wt%), CCC (51 wt%) and a relatively pure metakaolin, MK (86 wt%). In the first step, the pozzolanic reactivity of the three calcined clay samples was assessed via the R^3 method. Second, calcined clay samples holding stepwise increased metakaolin contents of 30, 40 and 51 wt% were prepared by mixing the respective amounts of MK into CT-07 to achieve such stepwise increases in the metakaolin content. From these experiments it was hoped to elucidate the effects of an increasing metakaolin content present in the cement. As superplasticizer, a benchmark commercial HPEG PCE was selected to investigate the impact of metakaolin on the workability of such cements. Also, the 1 day compressive strengths of mortars prepared from composite cements holding calcined clays of increasing metakaolin content (Portland cement substitution ratio 30 wt%) were compared under two different conditions: (1) applying the same PCE dosage; and (2) adjusting comparable mortar fluidity by using different PCE additions. Furthermore, water demand and PCE dosage requirement of all composite cements were determined via mini slump tests in order to get a comprehensive understanding of the influence of the fineness and the content of metakaolin present in calcined clay on the properties of a composite cement. Moreover, zeta potential and Total Organic Carbon (TOC) measurements were utilized to uncover the mechanism underlying the negative effect of metakaolin

on the workability of those composite cements. The overall aim of this study was to gain more knowledge about the relevance of the metakaolin content regarding workability and compressive strength development of low carbon calcined clay composite cements.

2. Materials and methods

2.1. Cement

The cement used in this study was an ordinary Portland cement (CEM I 42.5 R) provided by Schwenk cement company (Ulm, Germany). Its phase composition was determined by quantitative XRD analysis involving *Rietveld* refinement (Table 1). Its average particle size (d_{50} value) was found at 18.52 μm (laser granulometer, Cilas 1064, Cilas, Marseille) and a density of 3.15 g/cm^3 (Helium pycnometry) was recorded.

2.2. Calcined clay samples

Several calcined clay samples exhibiting different metakaolin contents were utilized in this study (Table 2). Sample CT-07 was produced in an industrial rotary kiln by exposure to a calcination temperature of 750 °C for about 30 min. It was provided by Universität der Bundeswehr, Munich, Germany. It contains ~23 wt% metakaolin. Sample CCC presents a calcined clay sample from Sinoma International Engineering Co., Ltd., Beijing. Its metakaolin content was determined at ~51 wt%.

Table 3

Particle size and specific surface area of the OPC and calcined clay samples investigated.

Samples	d_{10}	d_{50}	d_{90}	BET value [m^2/g]
OPC	1.36	18.52	51.78	1.77
CT-07	1.79	14.68	38.57	3.89
CCC	2.18	10.42	26.16	12.43
MK	1.11	10.32	42.44	20.82
CT-MK30	1.57	14.76	40.23	5.86
CT-MK40	1.21	13.48	40.07	8.51
CT-MK51	1.33	12.88	38.46	11.44
MK-40	0.91	9.35	45.73	16.75
M-1000	2.01	11.7	49.53	20.05
M1200s	0.34	5.79	26.89	23.52
Meta Star® 501	0.81	4.70	24.38	37.92

Table 4

Packing density and water film thickness of OPC and composite cement samples.

Samples	Packing density	Water film thickness [µm] at W/CM ratio by volume = 1
OPC	0.593	0.177
OPC: CT-07	0.553	0.077
OPC: CCC	0.540	0.028
OPC: MK	0.514	0.012
OPC: CT-MK30	0.551	0.057
OPC: CT-MK40	0.556	0.050
OPC: CT-MK51	0.508	0.006
OPC: M1000	0.490	0.005
OPC:M1200s	0.418	0.004
OPC:MK-40	0.548	0.002
OPC:Meta Star® 501	0.483	0.004
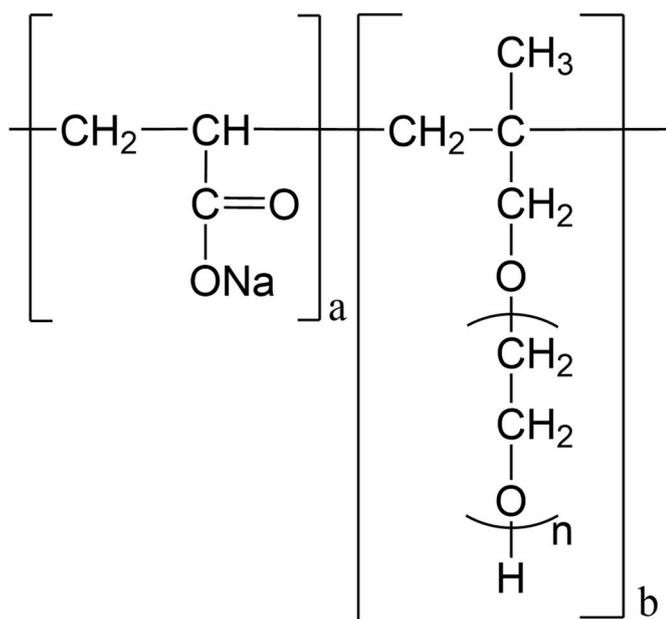
Fig. 2. Chemical structure of the HPEG PCE sample used in the study.

Sample MK presents a relatively pure metakaolin which was prepared industrially via flash calcination between 550° and 650 °C from a natural clay mineral containing 86.3 wt% kaolin (sample provided by Universität der Bundeswehr, Munich).

Moreover, mixtures exhibiting stepwise ascending metakaolin contents were prepared by blending CT-07 with MK at different weight proportions to achieve increasing total metakaolin contents of 30; 40 and 51 wt%. These calcined clay samples were named CT-MK 30, CT-MK

40 and CT-MK 51, respectively.

Additionally, four more industrial metakaolin samples provided by Imerys S.A. (Paris, France) were investigated in the second part of this study. Their metakaolin contents were specified by the suppliers as ~55 wt% (MK 40), ~65 wt% (M1000), ~78 wt% (M1200s) and ~95 wt% (MetaStar®).

In addition to the metakaolin content, these calcined clay samples also differ with respect to their particle size distribution. Fig. 1 displays the particle size distribution of CT-07, CCC and MK samples as captured via laser granulometry (Cilas, Marseille/France). Apparently, sample CCC exhibits a relatively narrow particle size distribution while CT-07 and MK possess a comparably broad distribution.

More specifically, Table 3 lists the d_{10}, d_{50} and d_{90} values and the specific surface areas (BET values) of these three calcined clays as well as of the blended calcined clay samples CT-MK 30, CT-MK 40 and CT-MK 51. Of all samples, the pure metakaolin (MK) exhibits the highest specific surface area, followed by CCC and CT-07 which is in line with their metakaolin contents. As for the blends of calcined clays, their specific surface area increases as more MK was incorporated.

2.3. PCE superplasticizer

The HPEG precast PCE superplasticizer sample was obtained from JILIN Chemical Industrial Co. (Jilin, China). This polymer presents a commercial benchmark PCE which exhibits a M_w of 35, 000 Da and an excellent macromonomer conversion rate of ~92%. Fig. 2 shows its chemical structure. It is characterized by medium molar ratio of acrylic acid to ω-hydroxy polyethylene glycol methallylether macromonomer and a long side chain which is commonly used in precast concrete.

2.4. Packing density and water film thickness of cementitious materials

The packing density of the OPC and calcined clay blended composite cements at OPC: CC by mass ratio of 70:30 was measured using the wet packing method [19,20]. And the water film thickness (WFT) was calculated at a fixed w/cm ratio of 1 (by volume) according to the equations published in Ref. [21].

2.5. Pozzolanic reactivity of calcined clay samples

In order to assess the pozzolanic reactivity of the calcined clay samples, the rapid, relevant and reliable (R^3) method was applied [22]. The cumulative heat of reaction was measured in an isothermal calorimeter (TAMAir Instrument, Thermometric AB, Sweden) at 40 °C for over 72 h. In sample preparation, the calcined clays were mixed with portlandite at a wt. ratio of 1:3 and a water-to-solid ratio of 1.2 was applied. In addition, soluble alkalis and sulfate were added to reproduce the conditions (pH etc.) present in cement pore solution and to accelerate the pozzolanic reaction. An SO$_3$/calcined clay ratio of 0.06 and a K$_2$O/calcined clay ratio of 0.08 were used. These ratios were identified in early works by Avet et al. to ensure high pozzolanic reactivity [22]. Potassium hydroxide (88.2% purity) from VWR (Radnor, USA) and potassium sulfate (99% purity) from Merck (Darmstadt, Germany) were dissolved in DI water to adjust those parameters.

2.6. Dispersing performance

A Vicat cone was applied for spread flow measurement to determine fluidity of OPC and the composite cements prepared from different calcined clays at an OPC:CC ratio of 70:30 wt/wt. %. The water-to-binder ratio was fixed at 0.5.

In the experiment, 300 g of OPC or composite cement were added to 150 mL of water placed in a porcelain cup and stirred manually for 10 s with a spoon. Then the PCE solution which was pre-weighted was added to the mixture and stirring was continued for another 50 s. After resting for 1 min, the suspension was mixed for an additional 1 min. The water

Table 5
SCPS-to-solid ratios of calcined clay samples to achieve a paste spread flow of 18 ± 0.5 cm as determined via mini slump test.

Calcined clay sample	CT-07	CCC	MK
SCPS-to-solid ratio	0.77	1.2	1.14

present in the PCE solution was subtracted from the total amount of mixing water to perform all experiments at exactly the same w/b ratio. Then the paste was immediately poured into a Vicat cone (height 40 mm, top diameter 70 mm, bottom diameter 80 mm) which was placed on a glass plate. After the cone was lifted vertically, the resulting spread of the cement paste was measured twice, in two perpendicular direction. The dosages of PCE required for each composite cements to reach a final spread flow of 26 ± 0.5 cm were recorded.

When the water demand was determined, no superplasticizer was added and the water-to-binder ratio to achieve a spread flow of 18 ± 0.5 cm (= base consistency) was measured. As mixing water, a synthetic cement pore solution (SCPS) [23] was used to mimic the ionic environment present in cement. Table 5 shows the water requirement of each neat calcined clay sample at a spread flow of 18 ± 0.5 cm.

2.7. Zeta potential

The surface charge of selected calcined clays was determined via zeta potential measurement on a Model DT-1200 Electroacoustic Spectrometer (Dispersion Technology, Inc., NY, USA). The calcined clay samples were suspended in synthetic cement pore solution (SCPS; for its ionic composition refer to Ref. [23]) at various SCPS/solid ratios.

In measurement, 30 mL of a 0.6 M $Ca(NO_3)_2$ solution were titrated in 60 steps to the calcined clay slurry until saturated adsorption of Ca^{2+} was achieved. During the $Ca(NO_3)_2$ titration, the pH value was kept constant at the initial pH value by minor additions of 30 wt% aqueous NaOH.

2.8. PCE adsorption

Polymer adsorption on calcined clays was investigated based on the depletion method using TOC analysis. In the experiments, all calcined clay samples were dispersed in SCPS at the different w/s ratios as shown in Table 5.

In measurement, at first different concentrations of HPEG PCE solutions (0.1; 0.2; 0.4; 0.6; 0.8; 1.0; 1.2; and 1.5% by weight of calcined clay) were prepared in SCPS. After mixing the calcined clay sample and the PCE solutions, the slurries were homogenized on a wobbler for 2 min and then separated via centrifugation at 8500 rpm for 10 min. Next, the supernatant was extracted with a syringe and filtered through a 0.2 μm polyethersulfone syringe filter. Then the filtrate was diluted with DI water and 10 drops of 1 M HCl. The TOC measurement was conducted on a LiquiTOC analyzer (Elementar, Hanau, Germany). Each sample was measured twice and the average value was taken as the final result.

2.9. Compressive strength

Compressive strength of cement mortar specimens prepared from OPC or OPC:CC 70:30 composite cements was tested after 24 h of hydration following DIN EN 196-1 standard [24]. From each mix, three sets of mortar prisms (40 × 40 × 160 mm dimension) were prepared. After 24 h, the specimens were demolded and stored in a climate chamber at 20 ± 1 °C and a relative humidity of ~90%. For 28 d sample, the specimens were cured under water in the climate chamber. Then compressive strengths were measured on a test apparatus provided by ToniTechnik (Berlin, Germany).

Since the water demand of each calcined clay sample was significantly different, the amount of PCE required for each mortar sample was also different. Therefore, in order to exclude the influence of different
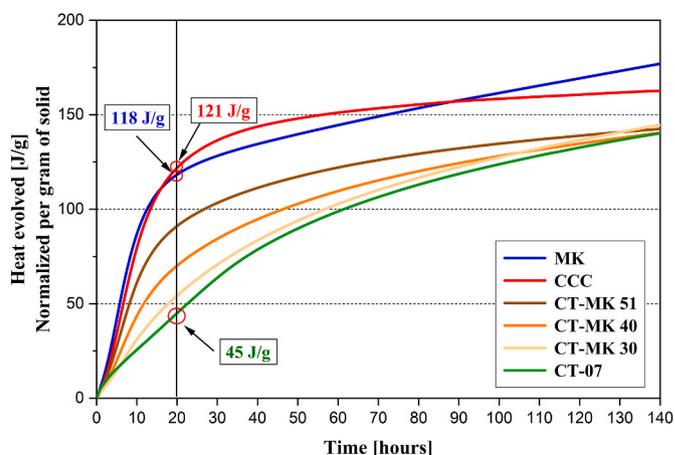
Fig. 3. Heat release from different calcined clay-portlandite samples at 40 °C, according to the R^3 method [22].

PCE dosages on strength development, the compressive strengths of the different composite cements were compared under two scenarios: 1) at the same PCE dosage, but at different fluidity; 2) at the same fluidity (spread flow of 22 cm), but with different PCE additions to achieve the same fluidity.

To all the mortar samples, few drops of defoamer (SURFYNOL MD 40 from Air Products, Utrecht/Netherlands) were applied to achieve exactly comparative mortar density.

3. Results

3.1. Pozzolanic reactivity of the calcined clay samples

It is well established that metakaolin possesses higher pozzolanic reactivity than other meta clays such as meta montmorillonite and meta illite [9]. Consequently, the content of metakaolin in a calcined clay presents one of the most important parameters influencing the property of the composite cement. Its high pozzolanic reactivity promotes the early strength of a calcined clay composite cement.

Therefore, firstly the pozzolanic reactivity of all calcined clay samples was determined via the R^3 method, and the results are displayed in Fig. 3. It was found that, generally, calcined clay samples possessing high metakaolin content exhibit higher pozzolanic reactivity. After 140 h, CT-07 produced the lowest total heat release of 140 J/g while the heat release from CCC and MK samples were much higher (162 and 177 J/g, respectively). Interestingly, a high metakaolin content actually accelerates the speed of heat release at the beginning of the reaction. For example, at 20 h only 45 J/g heat were released from CT-07 while a much higher heat release was recorded for MK (118 J/g) and CCC (121 J/g) samples resulting from their higher metakaolin contents. As for the blended calcined clay samples CT-MK 30; 40 and 51, their heat release at 20 h increased gradually from 54 J/g to 90 J/g as the metakaolin content ascended from 30 to 51 wt%.

This trend can be explained by the different pozzolanic reactivity of the meta minerals. Apart from 23 wt% metakaolin, CT-07 sample contains ~27 wt% meta illite-smectite phase which has a lower pozzolanic reactivity than metakaolin. This explains the slow heat release from CT-07 and its mixtures.

According to the data from the R^3 method, samples MK and CCC possess highest and almost comparable pozzolanic reactivity, while CT-07 sample attains a much lower value. In CT-MK 30, CT-MK 40 and CT-MK 51, the pozzolanic reactivity increases with ascending metakaolin content and lies between that of CT-07 and MK.
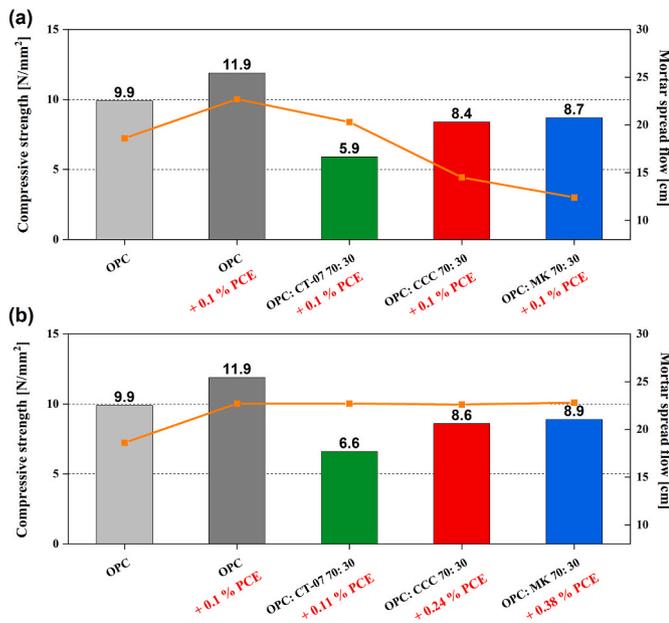
Fig. 4. 1 d compressive strength of mortar specimens prepared from OPC and OPC:CC 70:30 composite cements: (a) at the same dosage of HPEG PCE; (b) at the same mortar fluidity adjusted by different HPEG PCE additions.

Table 6
Raw mortar densities (fresh mortar densities) of the composite cement mortar samples.

Samples	Raw mortar density [g/cm³]
OPC	2.282
OPC + 0.10% HPEG PCE	2.308
OPC: CT-07 + 0.10% HPEG PCE	2.263
OPC: CCC + 0.10% HPEG PCE	2.259
OPC: MK + 0.10% HPEG PCE	2.248
OPC: CT-07 + 0.11% HPEG PCE	2.302
OPC: CCC + 0.24% HPEG PCE	2.268
OPC: MK + 0.38% HPEG PCE	2.254

3.2. Strength development

In the next step, the 1 d and 28 d compressive strengths of composite cements containing 30 wt% of the calcined clays were tested and compared to that of OPC. To exclude the effect of different PCE dosages on the strength development, the mortars were compared for two cases: 1) at the same PCE dosage of 0.10% bwob which results in different fluidity; 2) at the same fluidity of 22 cm spread flow, but using different PCE additions, as shown in Fig. 4. All mortar samples were adjusted to comparable raw mortar densities by using a defoamer (see Table 6).

As is shown in Fig. 4 (a), all samples prepared from the composite cements exhibit significantly lower 1d strengths as compared to OPC. For example, the specimen holding CT-07 possessing the lowest metakaolin content develops only ~50% of the compressive strength of OPC. While at increasing metakaolin contents, a gain in early strength is observed. Albeit, as is also evidenced from Fig. 4 (a), the presence of metakaolin generally reduces workability, and the higher the metakaolin content the stronger is the decrease in fluidity. The results signify that while a higher metakaolin content in the calcined clay boosts early strength development, it is highly disadvantageous with respect to workability.

Interestingly, when mortars adjusted to the same fluidity by admixing different PCE dosages were compared, then almost similar strength values as recorded in Fig. 4 (a) at constant PCE addition of 0.1% bwob were found (Fig. 4 (b)). This signifies that the impact of PCE on the early strength development of OPC:CC composite cements essentially is
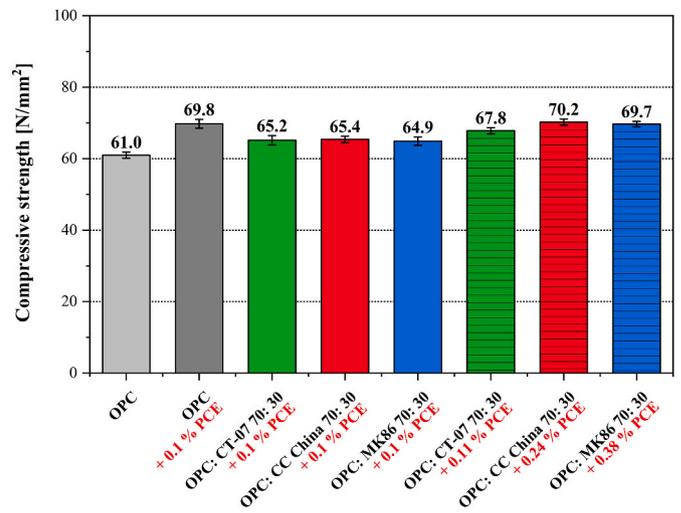
Fig. 5. 28 d compressive strength of mortar samples prepared from OPC and OPC:CC 70:30 composite cements.
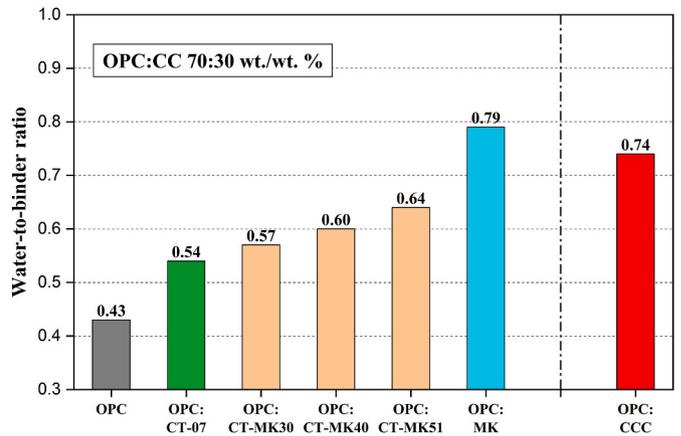
Fig. 6. Water demand of different calcined clay blended cements formulated at an OPC:CC ratio of 70:30; no PCE added.

negligible as compared to that of the metakaolin content. It also suggests that achieving high workability in calcined clay blended cements does not necessarily come at the price of decreased early strength.

Fig. 5 displays the 28 d compressive strength results of OPC and OPC: CC 70:30 composite cements containing different amount of PCEs. It can be seen from the results that all mortar samples show similar compressive strengths after 28 days of curing. In particular, there is no significant difference in compressive strength for composite cements possessing different calcined clays. This implies that the high metakaolin content in calcined clay is more favorable for early strength, e.g. 1 day, rather than 28 days.

In addition, a slightly increase in strength can be observed due to the higher PCE addition. This result is in line with the early strength development of OPC at 1 day. It should be noted that the results shown here relate to this specific precast type HPEG polymer which possesses a relatively long side chain and might differ for other PCE products.

3.3. Water demand of calcined clay blended cements

In order to uncover the effects of fineness and metakaolin content of calcined clay samples on the workability of blended cement, the water demand of composite cements containing 30 wt% of different calcined clay samples with varying metakaolin contents were compared to that of neat OPC. For this purpose, the water-to-binder ratios required to
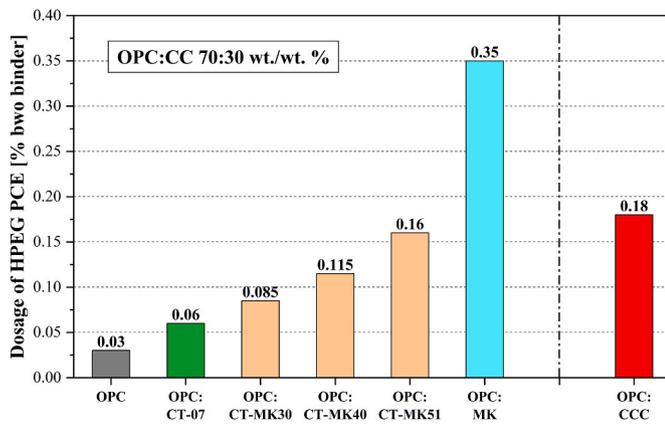
Fig. 7. HPEG PCE dosages required for different calcined clay blended cements containing OPC:CC at a wt. ratio of 70:30 to achieve the same paste spread flow of 26 cm; w/c ratio = 0.5.

Fig. 8. Zeta potential values of the calcined clay samples suspended in SCPS, measured after 4 min.

achieve a spread flow of 18 ± 0.5 cm were determined. The results are displayed in Fig. 6.

The results signify that all composite cements exhibit a higher water demand than for OPC which was found at 0.43. This effect can be attributed to the higher water requirement of calcined clay in general, and in particular to increased metakaolin contents [12]. As such, the OPC:MK 70:30 sample possessing the highest metakaolin content also records the highest water demand of 0.79. This is owed to the fact that MK exhibits the highest specific surface area of 20.82 m^2/g (see Table 3). Moreover, the water demand of the composite cements increases linearly from 0.54 to 0.64 with ascending metakaolin content in the calcined clay sample. This increase may originate from the finer particles when more metakaolin is incorporated.

It is worth noting that the blends OPC:CT-MK 51 and OPC:CCC show quite a different water demand (0.64 versus 0.74), although both CT-MK 51 and CCC exhibit the same metakaolin content of 51 wt%. This difference can be attributed to the different specific surface areas of those two samples. As was displayed in Table 3, CCC exhibits a higher BET value of 12.43 m^2/g as compared to 11.44 m^2/g for CT-MK51. Apparently, the higher particle fineness in CCC explains the higher water demand. It is in line with findings from Mantellato et al. [25] who reported that the yield stress of a cement paste increases exponentially with the increase of the specific surface area.

3.4. Dispersing performance of HPEG PCE in CC blended cements

In the following, the dispersing performance of the HPEG PCE sample in composite cements containing 30 wt% of different calcined clays with varying metakaolin contents was assessed using the "mini slump" test. There, the PCE dosage required to achieve a cement paste spread flow of 26 ± 0.5 cm at a water-to-binder ratio of 0.5 is determined. The results are exhibited in Fig. 7.

As displayed in Fig. 7, the dosage of HPEG PCE required to reach the targeted spread flow of 26 cm increases steadily with ascending metakaolin content present in the composite cements. For example, the PCE demand doubles from 0.03% to 0.06% bwob just when 30% of the OPC are substituted with CT-07. For blends containing CCC and pure MK, the PCE dosages even increase by a factor of 6 to 0.18% (for CCC) and 12 times to 0.35% (for MK). Again, the CT-MK mixtures which require PCE dosage of 0.085%–0.16% bwob are situated in between the dosages of their educts CT-07 and MK blended with OPC.

As was expected from the results shown before for the water demand (see Fig. 6), PCE dosages increase with ascending metakaolin content in the calcined clay sample, however at a much steeper pace as compared to the water demand. It suggests that such low carbon cements are characterized by a generally higher PCE dosage requirement.
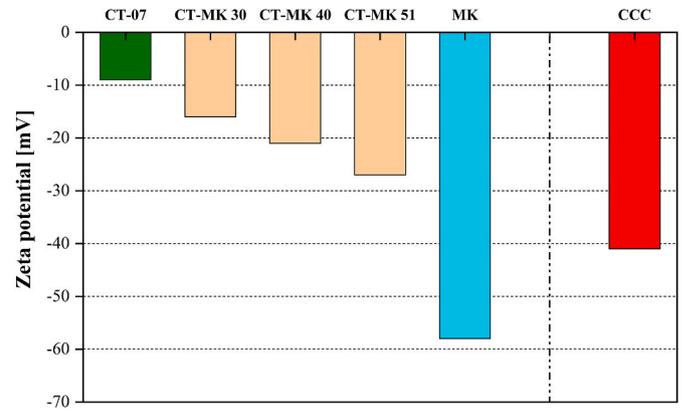
Interestingly, the difference between CT-MK51 and CCC with respect to the PCE dosage is smaller here than in the water demand. For example, the water demand of CT-MK 51 and CCC composite cements which possess the same metakaolin content differed noticeably at 0.64 and 0.74, while the PCE dosages were almost comparable at 0.16% and 0.18% bwob, respectively. This minor difference can be attribute to the higher specific surface area of CCC as compared to CT-MK 51 (see Table 3). It signifies that in a calcined clay the metakaolin content plays a more dominant role for the dispersing effectiveness of PCEs, while the specific surface area exercises a more pronounced effect on the water demand.

In addition, the results for packing density and water film thickness are corelated with the results for HPEG PCE polymers on dispersion properties. As listed in Table 4, OPC sample possessing the highest packing density of 0.593 and highest WFT value of 0.177. When the calcined clay samples were added into the system, the packing density and water film thickness for all samples decreased. Addition of CT-07 decreases the values the least while MK sample decreases the most. And CCC, MK30, MK40 and MK51 samples are in between. In theory, a higher the packing density of the cementitious material particle leads to a better workability [19,21,26]. In this study, these results are consistent with the dispersing performance of HPEG PCE that the composite cement contains MK presents the most difficult one for dispersing, while CT-07 is the easiest with MK30, MK40 and MK51 in between.

It is worth to notice that the addition of metakaolin does not always decrease the packing density of the samples. Marchetti et al. [21] found that the addition of metakaolin increased the packing density of the composite cement. However, the better fluidity can be directly related to water film thickness, with higher values of WFT being associated with a better fluidity of the composite cement.

To summarize, the metakaolin content of composite cements strongly affects the dispersing performance of polycarboxylate superplasticizers. The higher the content of metakaolin in the calcined clay, the higher is the amount of PCE required to achieve sufficient workability. To understand the reason behind this, the mechanism controlling the influence of metakaolin on PCE performance and workability was investigated.

3.5. Mechanistic study

It is well established that – among other parameters - the surface charge of cement particles much determines the adsorption and thus the dispersing performance of PCEs [27]. Therefore, it is desirable to understand the surface charge developed by calcined clays in cementitious systems. For that reason, zeta potential measurements were performed in the following.
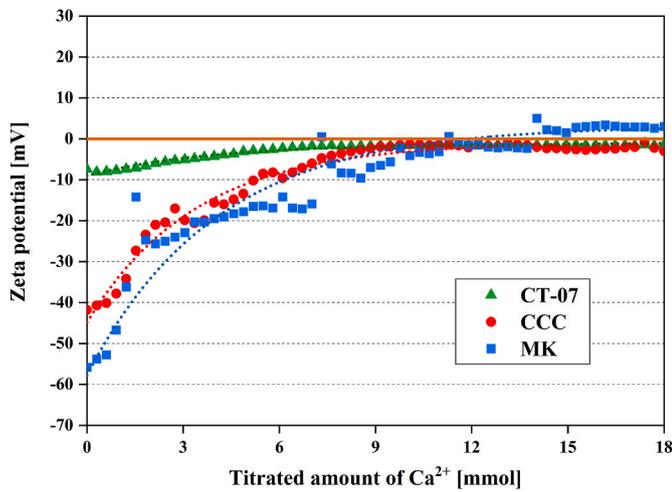
Fig. 9. Zeta potentials of calcined clay samples suspended in SCPS as a function of the volume of $Ca(NO_3)_2$ solution added; SCPS/s ratios: CT-07 = 0.77; CCC = 1.2; MK = 1.14.

3.5.1. Zeta potential measurements

To account for the different water demands of the calcined clay samples, all zeta potential measurements were performed at w/s ratios achieving a suspension spread flow of 18 ± 0.5 cm in SCPS.

As displayed in Fig. 8, all calcined clay samples develop a negative surface charge covering a broad range from – 9 mV (for CT-07) to – 58 mV (for MK). For the blends of CT-07 and MK, the surface charges increase steadily from −16 mV to −27 mV as the metakaolin content increases. This result correlates well with the PCE dosage requirements as shown in Fig. 7. Moreover, the pure MK sample stands out owed to its most pronounced negative surface charge of −48 mV as compared to the other calcined clays. This finding corroborates that the metakaolin content much impacts the negative surface charge of a cement sample, which directly affects the PCE demand of such composite cements.

The result from above is surprising because negatively charged PCE polymers are not supposed to adsorb on negatively charged surfaces of calcined clays, assuming that the clay surfaces are homogeneously charged. Hence, supposedly another effect comes into play here. Generally, it needs to be considered that zeta potential measurement of calcined clay samples in SCPS are not fully representative for the actual situation in cement where Ca^{2+} adsorbed by the calcined clay will be replenished immediately by continuous dissolution from the clinker phases into the pore solution [12]. Whereas in SCPS, the concentration of Ca^{2+} ions is limited and is not replenished in case of an uptake by the calcined clay. Hence, in the next step it was investigated whether the calcined clays would adsorb significant quantities of Ca^{2+} ions from the pore solution.

For that reason, zeta potential measurements on suspension of the calcined clay samples in SCPS were repeated while titrating a Ca^{2+} solution to the system to mimic the replenishment of Ca^{2+} by cement. Here, CT-07, CCC and the pure MK sample were measured to gain an insight into the actual surface charge of the calcined clays in cement.

As displayed in Fig. 9, at step-wise addition of Ca^{2+} the zeta potentials of all three calcined clays shifted gradually to less negative values until a plateau around the isoelectric point was reached. This finding confirms that the surfaces of the calcined clays are densely occupied by Ca^{2+} ions which can easily facilitate the adsorption of negatively charged PCE polymers by docking onto those surface Ca^{2+} ions.

Interestingly, the three calcined clay samples bind different amounts

of Ca^{2+} ions to reach the point of saturated adsorption. As an example, for CT-07 a constant zeta potential signifying saturated adsorption is reached after the addition of approximately 7.5 mmol Ca^{2+} ions, while it requires 10 mmol and 15 mmol Ca^{2+} for CCC and MK, respectively. These observations are in line with the initial zeta potentials of the clays which is as expected since a more negative surface charge will demand a higher number of Ca^{2+} ions to reach charge neutralization.

It can be speculated that surfaces packed more densely with Ca^{2+} ions should adsorb more PCE which could explain the sharp increase in PCE dosages for composite cements containing calcined clays, especially of high metakaolin content. To elucidate, in the next section PCE adsorption on these three calcined clay samples was quantified.

3.5.2. PCE adsorption on calcined clay

Adsorption of the HPEG PCE polymer on three calcined clay samples CT-07, CCC and MK in SCPS was investigated at the different water-to-solid ratios listed in Table 5.

First, as is shown in Fig. 10, *Langmuir*-type adsorption isotherms were detected for all calcined clay samples. They are characterized by a steep increase in the adsorbed amount at low PCE dosages until the uptake levels out at a plateau which represents the point of saturated adsorption. In accordance with the high sorption of Ca^{2+} ions as demonstrated before (see Fig. 9), all three calcined clay samples adsorbed significant amounts of the anionic PCEs.

Significantly higher adsorbed amounts were observed for the MK sample as compared to CT-07 and CCC. More specifically, MK reached the point of saturated adsorption at ~5.0 mg PCE/g calcined clay, while CT-07 and CCC attained their plateau at ~2.0 and ~3.0 mg PCE/g calcined clay, respectively. These results confirm the conclusion derived from the different uptake of Ca^{2+} as evidenced in the zeta potential measurements (see Fig. 9) and also are in accordance with the results on the PCE dosage requirement (Fig. 7). With rising metakaolin content, the zeta potential in SCPS becomes more negative which attracts more Ca^{2+} ions and prompts higher PCE dosages as is evidenced by higher PCE adsorption on the calcined clay particles. Consequently, in calcined clays which are rich in metakaolin higher PCE dosages can be expected to achieve sufficient workability.
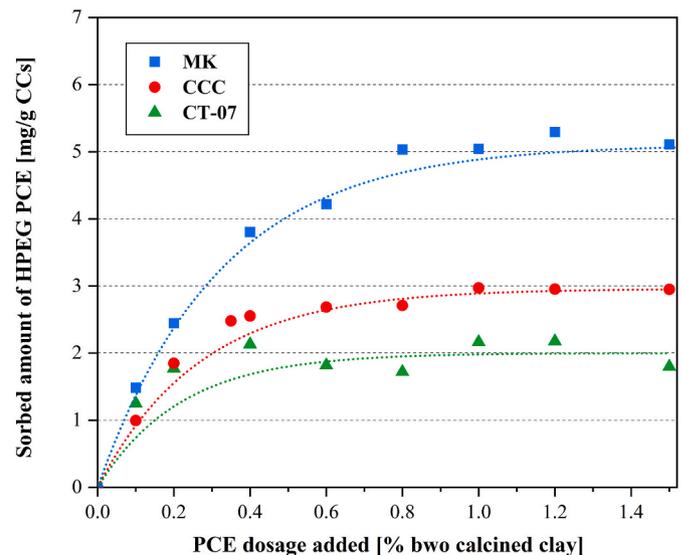
Fig. 10. Adsorbed amounts of the HPEG PCE on the neat calcined clay samples; SCPS/s ratios: CT-07 = 0.77; CCC = 1.2; MK86 = 1.14.
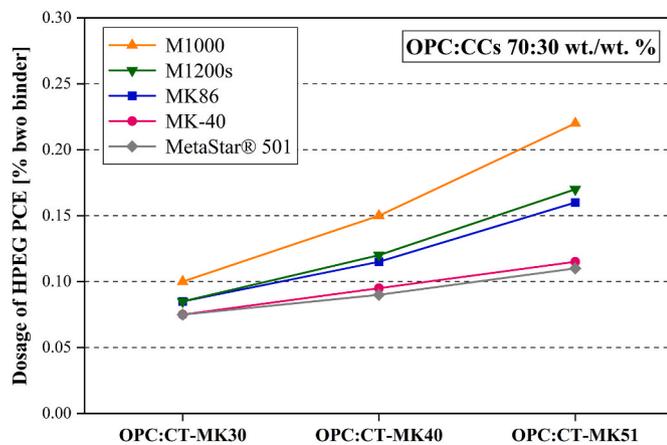
Fig. 11. PCE dosages required for composite cements containing OPC and a blend of CT-07 with different industrial metakaolin products to achieve a paste spread flow of 26 cm (OPC:CCs 70:30, w/c ratio = 0.5).

3.6. Impact of different metakaolin samples on workability

To check on the results obtained so far with one specific metakaolin sample (MK), more products from several sources possessing different mineral composition, particle size distribution, surface charge and degree of calcination were tested. Their metakaolin contents varied between 55 wt% and 95 wt%, as is displayed in Table 2. Their PCE dosage requirement was compared with that of the MK sample. The aim of this analysis was to confirm the concept that high metakaolin content in a calcined clay will always prompt higher PCE dosages.

In the experiments, all metakaolin samples were blended with CT-07 to achieve metakaolin contents of 30, 40 or 51% by weight of the calcined clay. Then the dispersing performance of the HPEG PCE in those composite cements containing 30 wt% of the calcined clay blends was tested using the "mini slump" test, and the PCE dosages required to achieve a paste spread flow of 26 ± 0.5 cm at a water-to-binder ratio of 0.5 was recorded.

As displayed in Fig. 11, all composite cements show a higher PCE demand at increased metakaolin contents. This is in line with the observations made before. Here the highest PCE demand was detected for cements blended with M1000 metakaolin sample characterized by a medium specific surface area (22.05 m^2/g) which is much less than that of the MetaStar® sample (37.92 m^2/g) which however demands less PCE (see Fig. 11). However, this result also signifies that the metakaolin content and particle size of calcined clay are not the only parameters which determines the PCE demand. The calcined clay blended composite cements clearly present complex systems, hence their fluidity can be influenced by multiple factors including, but not limited to, particle fineness, packing densities, water film thickness, mineral phase composition, calcination temperature and conditions (flash vs. rotary kiln) etc.

4. Conclusion

In this study, composite cements containing different calcined clays with varying metakaolin contents were investigated to evaluate the impact of the metakaolin content and fineness of the calcined clays on the fluidity of composite cements. In order to do that, three calcined clay samples holding 23% (CT-07); 51% (CCC) and 86% (MK) metakaolin and mixtures of a base calcined clay sample (CT-07) of relatively low metakaolin content (~23 wt%) with a relatively pure metakaolin sample (86 wt%) to achieve increasing metakaolin contents (30; 40 and 51 wt %) in the blended were studied. Pozzolanic reactivity, water demand, PCE dosage requirement and compressive strength of the blended cements were determined at an OPC substitution ratio of 70:30.

From the results obtained, the following conclusions can be drawn:

1. Increased metakaolin content in a calcined clay sample fosters its pozzolanic reactivity and early strength, however, there is no significant influence on 28 d strength. Also, it increases the water demand and prompts higher superplasticizer dosages.
2. Water demand and PCE dosage of such composite cements are closely related to the metakaolin content and particle fineness. While fineness mainly affects the water demand, the metakaolin content plays a dominant role with respect to PCE dosage.
3. A direct correlation exists between PCE dosage and the metakaolin content present in a calcined clay. This can be explained by the more negative surface charge of metakaolin-rich samples which sorb increased amounts of Ca^{2+} from the pore solution and then allow more PCE superplasticizer to adsorb onto their surfaces.
4. This behavior was confirmed for several commercial metakaolin samples from different sources. PCE dosages generally increase with ascending metakaolin contents in the calcined clay blended cement.

In the future, new technologies for chemical admixtures which can integrate both diverging properties of high fluidity and at the same time sufficient early strength need to be developed.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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