



# An approach to estimate the strength contribution of calcined clays in blended cements

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## ABSTRACT

Current literature about calcined clays as future Supplementary Cementitious Material (SCM) is often limited to the role of 1:1 dominated clays as raw material. However, such clays are the exception in Europe: mixtures of various clay minerals represent the predominant material resources – so-called common clays. Through a comparison with 1:1 dominated clays, this article looks specifically at the suitability of illitic, smectitic and common clays as SCM. The reactivity of eleven different clays was assessed via the  $R^3$  tests and compressive strength tests on mortar with six different cements. The strength contribution of 2:1 dominated clays proved relevant. This holds especially for calcined illite at 2 days and for calcined smectite at 28 days. A significant increase in strength was observed with the 1:1 dominated clays only at 28 days. The strength contribution of the calcined clays varied depending on the cement used. A mathematical model correlates the mineralogy and fineness of the clays with the Activity Index of the blended cements, making it possible to predict strength at 2 and 28 days. This is also possible with the  $R^3$  test, since the heat release of a calcined clay correlates with the Activity Index of the corresponding blended cement.

## 1. Introduction

Global cement demand is forecast to increase by over 1 billion tons by 2050 [1], while the clinker factor will decrease [2]. In order to cope with these developments, clinker in cement must be replaced by alternative materials, so-called Supplementary Cementitious Materials (SCMs). Calcined clays have been worldwide examined for their suitability as SCMs [3–8] due to the global availability of various types of clay as raw material. They fulfil environmental requirements and thus help to alleviate environmental problems [9]. Their use in practice is already taking place, but so far only in small quantities [10].

Calcined clays are by no means the “one” material by default. The naturally occurring clays are very diverse in their composition and there can also be considerable fluctuations within a deposit. Clay minerals are categorised into 1:1, 2:1 and 2:1:1 phyllosilicates based on their layered structure of tetrahedral and octahedral sheets. [11]

The most prominent representative of the 1:1 phyllosilicate is kaolinite. The outer position of its OH<sup>-</sup> groups, which are located on the octahedral sheets, ensures a lower optimal calcination temperature than necessary for 2:1 phyllosilicates, in which the OH<sup>-</sup> groups are enclosed

by the two tetrahedral sheets [12]. Sufficient calcination of kaolin may already be accomplished at 500 °C [13].

Illitic and smectitic clays were investigated mainly as representatives of the 2:1 phyllosilicate [14–18]. Illite is already completely dehydroxylated at 600 °C, but temperatures of up to 900 °C are required to achieve high degree of structural disorder of metaillite. The dehydroxylation of smectite is only completed at 700 °C, but at 800 °C meta-smectite has a sufficient degree of structural disorder [16]. A temperature difference between the dehydroxylation end and the highest reactivity of illite and smectite is also observed in [15,17]. In comparison to [16], a complete dehydroxylation of illite and smectite is achieved in [15] at a lower temperature and in [18] at a higher temperature.

Metakaolinite is highly reactive - determined on the basis of aluminium and silicon ion solubilities and  $R^3$  tests. The reactivity in terms of the same tests is significantly lower for both calcined 2:1 phyllosilicates. The aluminium and silicon ion solubilities of metakaolinite can each be over 10 mmol/l, whereas they are many times lower for the 2:1 phyllosilicates. Due to the different layer structures, the ratio of silicon to aluminium ion is approx. 1:1 in metakaolinite and 2:1

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in 2:1 phyllosilicates. The release of ions is significantly faster in metakaolinite than in 2:1 phyllosilicates. [15,16,19]

Scherb et al. [20] mention a "clear chemical reactivity already during the first day of hydration" for their investigated metakaolinite and metakalinite. At 50 hours, half of the metakaolinite has reacted. But at the same time the degree of hydration of alite (C<sub>3</sub>S phase) is considerably reduced compared to the reference cement. Metakalinite itself reacts significantly less, but the hydration of alite decreases hardly in this blend. Sowidnich et al. [21] identified the accumulation of C-A-S-H phases, which are formed by the aluminium ions of a metakaolinite, on the alite surface as the reason. An influence of the aluminium ions from the calcined clays on the degree of hydration of alite is also confirmed by the findings in [20]. An unreactive 2:1 phyllosilicate (low aluminium ion release rate) hinders the hydration of alite significantly less than a highly reactive 1:1 phyllosilicate (high aluminium ion release rate).

Limestone powder has a positive influence on the early hydration of calcined clays blended cements. In addition to promoting the alite hydration, it pushes the formation of hemi- and monocarboaluminates, which refine the pore structure. Both effects are emphasised when metakaolinite is used [20,22]. This is the reason that studies investigating calcined clay blended limestone cement most often use 1:1 dominated clays [23–26].

Antoni et al. [23] found an early pozzolanicity of metakaolinite because it contributes significantly to compressive strength of blended cement already at seven days. Thus, the strength of the blended cement exceeded the reference depending on the replacement level. In addition, the combination of metakaolinite with limestone powder proves very effective. The established considerable loss of mortar strength at an early hydration age can be explained by the reduction of alite hydration by metakaolinite in [20].

According to the literature [23], the low early strength when using metakaolinite can be improved by adjusting the sulphate content. The addition of sulphate carrier to metakaolinite blended limestone cements resulted in a considerable increase in early mortar strength (at one day). Measurements of the heat flow in the cementitious system revealed that the early onset and intense aluminate peak occurs later and loses intensity as a result of the addition of sulphate carrier.

Scherb et al. [20] observed a 10% increase of the alite hydration by adding sulphate carrier to the blended cement, limestone and metakaolinite system. Without limestone as a binder component, even 15% more alite was hydrated due to the addition of sulphate carrier. Therefore, it can be assumed that the addition of sulphate carrier increases the early mortar strength of metakaolinite blended Portland cement at least to the same extent as the early strength of metakaolinite blended Portland limestone cement.

At a later age the pozzolanicity of illite and smectite is present. In [12], smectite is only assessed as a little pozzolanic at later age and illite even permanently as inert while the calcination temperature was 600 °C in each case. At a higher temperature the pozzolanicity of illite and smectite at 28 days occurs more clearly but at 2 days they are still inert products [27,28].

The early and strong aluminate peak of 2:1 dominated clays in heat flow measurements can be delayed and reduced by the addition of sulphate carrier, analogous to metakaolinite [20]. Increasing the early strength by adding a sulphate carrier is also conceivable when using 2:1 dominated clays but has not been proven.

The addition of sulphate carrier for calcined clay blended cements corresponds to the procedure of a cement plant during the production of the cement. In the tests, no sulphate carriers were added to the blended cements in order to consider only the performance of replacing calcined clays. Not adjusting the sulphate content in the cement corresponds to the production process of a concrete plant in which the calcined clays are used as a type II concrete additive.

Different statements on the early compressive strength contribution in cementitious system are made in the literature when comparing calcined illite, smectite and kaolinite. In [27–29], the early strength

(two days) of mortar prisms with a kaolinitic clay is significantly higher than that of an illitic or smectitic clay. Both of the latter behave similarly in terms of strength. In contrast, in [30] an illitic clay achieves the same early strength contribution (1 day) as a kaolinitic clay. In [31], the smectitic clay provides at 1 day a higher or equal strength contribution - depending on the replacement level - as the kaolinitic clay and at 3 days it is only equal or less. In the comparison of the early strength contribution (1 day) between smectitic and illitic clay in [12], the latter has a slightly higher one, but is still inferior to a kaolinitic clay. The literature cited so far used a Portland cement as initial cement and a replacement took place exclusively with calcined clay. In [14], three different smectitic and one illitic clays were investigated as a component of a blended limestone cement. At 1 day two smectitic clays provided a lower mortar compressive strength and one smectitic clay provided a higher strength than the illitic clay.

It is difficult to understand and interpret the respective findings in the literature because often important details are missing such as the production process, grinding fineness or mineralogy of the calcined clays. In addition, comparisons were made between calcined clays which differ significantly with respect to their calcination temperature, grinding fineness and mineralogy.

In contrast to the impact on early age strength there is common understanding about the strength contribution of the three clay minerals in the cementitious system at 28 days. It increases in the following order: illite - smectite - kaolinite [12,14,16,17,30–32].

Based on the aforementioned information, it can be said that in terms of compressive strength, kaolinites are considered to have significantly more potential than illites and smectites. Much research work has specialized in 1:1 dominated clays, while illitic and smectitic clays have been relegated to the background. From a European point of view, this is not satisfactory, since 1:1 dominated clays occur frequently in Africa, Asia and South America, but only rarely and in small quantities in Europe [33]. Instead, 2:1 dominated or common clays are often dominant there, which also contain impurities in the form of other clay minerals or inert substances such as quartz. For this reason, 1:1 dominated clays are deliberately examined in this study and contrasted with common clays and 2:1 dominated clays. They are to be analysed for their suitability in terms of their strength contribution so that they can be used permanently in the cement and concrete industry and not wrongly excluded from it.

The focus of the paper is on two questions: To what extent do different calcined clay minerals contribute to the compressive strength in blended cements at different times? Does this strength contribution correlate with specific clay properties?

For this reason, eleven different clays were selected and tested in calcined form for their reactivity by means of heat release in the calorimeter. The strength contribution of each calcined clay is evaluated via compressive strength tests of mortar prisms with six different cements at 2 and 28 days. In the course of this, the performance of 2:1 dominated clays is compared with that of 1:1 dominated clays. The clay mineralogy of the 2:1 dominated clays plays a decisive role. The compressive strength results are set in relation to the measured heat release of the calcined clays (R<sup>3</sup> test) and hydration heat of calcined clays blended cements in order to make predictions for the strengths on the basis of these. Statistical software JMP is used to find correlations between the compressive strength and clay mineralogy and thus another way to predict the strength.

It is a novel approach, as for the first time many calcined clays with different mineralogy are combined with several different cements in order to handle the mentioned study's objectives.

## 2. Materials and methods

### 2.1. Cements

Five Portland cements and one Portland limestone cement from

**Table 1**  
Mineralogical composition of cements (provided by the producer).

Mineralogical composition	CEM I 52.5 R (bs)	CEM I 52.5 R (ft)	CEM I 42.5 N	CEM I 42.5 R	CEM II/A-LL 32.5 R <sup>a</sup>	CEM I 42.5 R SR0
C <sub>3</sub> S [%]	55.1	59.6	60.4	61.6	50.7	53.5
C <sub>2</sub> S [%]	20.4	18.1	18.2	18.2	14.1	19.8
C <sub>3</sub> A [%]	8.9	6.7	6.5	5.8	5.5	0.0
C <sub>4</sub> AF [%]	7.6	8.4	8.3	9.0	6.8	18.6
Sulphate carrier [%]	3.6	2.3	2.4	2.4	2.9	2.8

<sup>a</sup> Calcite content is 16.3 %

Germany were used. Table 1 shows the mineralogical composition provided by the producer. The sulphate carriers are mainly anhydrite and small amounts of hemihydrate. Dihydrate is hardly present.

The physical parameters of the cements are given in Table 2. Particle density was determined with a Helium pycnomatic ATC (Thermo Fisher Scientific) according to DIN EN ISO 17892-3 [34]. BET specific surface area (BET SSA) was measured with SA-9601 MP (Horiba Instruments Inc.) according to DIN ISO 9277 [35] and particle size distribution was obtained via static laser light diffraction using a Bettersizer S3 Plus (3 P Instruments) (App. 1a). The parameter  $d'$  given in Table 2 indicates the grain diameter at a passage of 63.2 Vol.-% according to DIN 66 145 [36]. Water demand of cements was measured according to DIN EN 196-3 [37] to achieve standard stiffness and Blaine specific surface area (Blaine SSA) according to DIN EN 196-6 [38]. Compressive strength at 2 days ( $f_{2d}$ ) and 28 days ( $f_{28d}$ ) was determined on mortar prisms according to DIN EN 196-1 [39].

## 2.2. Clays

The tested clays are from Germany with the exception of PP. They vary greatly in their composition (Table 4). PP, FUP, RKUP, CT7 and OC were used and published in previous studies [19,22,40]. Clays were calcined and ground in various ways. PP and CT7 were produced industrially, FUP, RKUP and OC internally in the laboratory and GFU, GUS, Sml, Ill-E, Ill-A and Smk externally under comparable laboratory conditions. A quartz powder permanently supplements the test series which was ground with a vibration disc mill. The procedure of calcination and grinding of the clays is summarized in Table 3. GFU and GUS were thermomechanically activated in a pilot plant, i.e. calcined via hot gas generator and ground via vertical roller mills at the same time.

For separate calcination the individual temperatures were selected taking into account the thermogravimetric analyses to ensure complete dehydroxylation of the clays. They were verified by means of infrared spectroscopy. The disappearance of the OH bands confirmed complete dehydroxylation. For the thermomechanical activated clays GFU and GUS, only maximum temperatures were reached of 500 and 520 °C resp. These temperatures were sufficient to obtain a metakaolinite, but they were not sufficient for a satisfactory activation of the existing illite despite proven dehydroxylation [13].

X-ray diffraction (XRD) was used to determine mineralogical composition of the raw clay on powder samples after side-loading preparation (see App. 2 A and B). The identification of the clay minerals was performed on oriented mounts of the < 2 µm fraction prepared by the glass slide method [41] in air dried (AD) and glycolated (EG) condition (see App. 2 C and D). The exact procedure is given in [19]. XRD was performed in a PANalytical Empyrean diffractometer equipped with a Bragg-Brentano<sup>HD</sup> monochromator and a PIXcel<sup>1D</sup> detector at 40 kV and 40 mA using CuK $\alpha$  radiation (1.5406 Å). The evaluation of the data was performed with Profex-BGMN [42,43] by Rietveld refinement [44,45]. Table 4 shows the mineralogy of the raw clays. For the assessment of the reactivity of the individual clay minerals the 2:1 phyllosilicates smectite, smectite-illite, illite and muscovite were considered separately. Quartz, carbonates and other accompanying minerals were summarized as inert.

The physical properties of the ready to use calcined clays are shown

in Table 5. The particle density [34] and BET SSA [35] were determined in the same way as for the cements. The Puntke method [46] was used for the water demand of the calcined clays. The particle size distribution (App. 1b) was measured with the Bettersizer S3 Plus and the diameters at 10, 50 and 90 Vol.-% passing were given as  $d_{10}$ ,  $d_{50}$  and  $d_{90}$ . Despite the same grinding time in the laboratory's vibrating disc mill, there were major differences in the grinding fineness. This was due to the quartz present in the clays.

The clays were only used in calcined and ground form for calorimeter measurements and for producing the mortars as a 20 wt% cement replacing material. Sulphate carrier was not used for the tests.

## 2.3. Experimental investigations

Reactivity of the calcined clays was measured as heat release in the R<sup>3</sup> test according to DIN EN 17979 (test method A) [47] using a TAM Air isothermal calorimeter (TA instruments). After weighing the individual components (2 g calcined clay, 6 g portlandite, 1 g limestone, 10.8 g test solution), the samples were placed in a drying oven at 40 °C overnight. The solids of the sample were mixed by hand for 30 seconds and with water for one minute. The paste was completely filled into sample crucibles and placed in the 40 °C warm calorimeter. The recording of the cumulative heat flow started at 75 min and was finished at 168 hours. This procedure was carried out two times, the results normalized to 1 g of SCM and averaged.

The influence of the calcined clays on the hydration kinetic of CEM I 42.5 R and CEM II/A-LL 32.5 R was investigated using isothermal calorimetry on blended cement pastes. The cement pastes, consisting of 4 g cement, 1 g calcined clay and 2.5 g water, were stirred manually and externally for one minute after the binder was mixed by hand for 30 seconds. The composition of the paste is the one used later for the mortar tests. Approx. 3 g of paste were filled into sample crucibles and put into the 25 °C warm calorimeter. The reference samples in the calorimeter consist of 2 g quartz sand and 1 g water. The heat flow was recorded for 48 hours and normalized to 1 g of binder (cement and SCM). The measurements were repeated twice. By integrating the heat flow over time from 0.5 to 48 hours the hydration heat was calculated. The starting value of 0.5 hours was chosen owing to the lack of reproducibility of the initial heat flow due to external mixing. At that time all samples had completed the initial period and were at the beginning of the rest period.

Mortar prisms were produced according to DIN EN 196-1 [39] and tested at 2 and 28 days in order to determine the strength contribution of the calcined clays. The mortar consists of 1350 g standard sand, 225 g water and 450 g blended cement. As the reference cement was replaced by calcined clay, the water/binder ratio remains constant at 0.5. With a replacement level of 20 wt%, the binder consisted of 360 g reference cement and 90 g calcined clay. Before the binder is automatically mixed with sand and water at specified time and speed, the blended cements were homogenized by mixing them by hand for one minute each. No superplasticizer was used in the production of the mortar. After the mortar was filled into the formwork with constant compaction, it was stored in the formwork for 24 hours (20 °C, 95 % relative air humidity) and in water (20 °C) until it was tested. The Activity Index (AI) were calculated on basis of the measured compressive strengths.

**Table 2**  
Physical parameters of cements.

Parameter	Standard	CEM I 52.5 R (bs)	CEM I 52.5 R (ft)	CEM I 42.5 N	CEM I 42.5 R	CEM II/A-LL 32.5 R	CEM I 42.5 R SR0
Particle density [g/cm <sup>3</sup> ]	[34]	3.17	3.14	3.15	3.14	3.09	3.20
BET SSA [m <sup>2</sup> /g]	[35]	1.5	1.8	0.8	1.0	1.3	1.4
d' [μm]	[36]	11.9	12.4	31.9	26.9	27.9	16.6
Water demand [%]	[37]	33	36	27	28	26	30
Blaine SSA [cm <sup>2</sup> /g]	[38]	5630	6225	2742	3340	3507	4820
f <sub>2d</sub> [N/mm <sup>2</sup> ]	[39]	41.0	44.1	19.0	24.3	20.5	27.5
f <sub>28d</sub> [N/mm <sup>2</sup> ]	[39]	71.0	68.3	55.3	54.8	50.0	56.5

**Table 3**  
Procedure of calcination and grinding.

Clay	Calcination temperature [°C]	Type of calcination	Type of grinding after calcination
PP	600	Industrial flash calciner	-
FUP	800	Muffle furnace	Vibrating disk mill
GFU	500		Thermomechanical activation
RKUP	800	Muffle furnace	Vibrating disk mill
GUS	520		Thermomechanical activation
CT7	750	Industrial rotary kiln	Industrial roller mill
OC	680	Muffle furnace	Vibrating disk mill
Sml	840	Bogie hearth furnace	Drum mill
Ill-E	840	Bogie hearth furnace	Drum mill
Ill-A	840	Bogie hearth furnace	Drum mill
Smk	840	Bogie hearth furnace	Drum mill

2.4. Statistical calculations

The statistical software JMP (SAS Institute) was used in chapter 4.3 to find a correlation between mineralogy and fineness of the calcined clays and their strength contribution in form of Activity Index. The method of standard least squares was selected for calculating the individual parameters α<sub>i</sub> of the variables i. This searches for the highest coefficient of determination R<sup>2</sup>. The interpretation of the resulting R<sup>2</sup> coefficient is based on [48]. A R<sup>2</sup> coefficient above 0.7 is considered as a high correlation and above 0.9 as a very high correlation.

A linear equation with the clay mineral content and the grinding fineness of the calcined clays in the form of d<sub>50</sub> serves as a mathematical model:

$$AI_{JMP} = \alpha_0 + \alpha_K \cdot K + \alpha_S \cdot S + \alpha_{IS} \cdot IS + \alpha_I \cdot I + \alpha_{d_{50}} \cdot d_{50} \tag{1}$$

$$= \alpha_0 + \alpha_I \cdot (A_K \cdot K + A_S \cdot S + A_{IS} \cdot IS + A_I \cdot I + A_{d_{50}} \cdot d_{50}) \tag{2}$$

with α<sub>K</sub> = α<sub>I</sub> · A<sub>K</sub>; α<sub>S</sub> = α<sub>I</sub> · A<sub>S</sub>; α<sub>IS</sub> = α<sub>I</sub> · A<sub>IS</sub>; α<sub>I</sub> = α<sub>I</sub> · A<sub>I</sub>; α<sub>d<sub>50</sub></sub> = α<sub>I</sub> · A<sub>d<sub>50</sub></sub>

α<sub>i</sub> are the parameters calculated by the software that weight the variables. The content of the clay minerals (K: kaolinite, S: smectite, IS: illite-smectite mixed-layer, I: illite) in the raw clay is used in the unit wt% and the particle diameter d<sub>50</sub> in the unit μm. GUS and GFU contain illite, but as this clay mineral was not sufficiently activated at the low calcination temperatures, it is considered to have inert behaviour. Muscovite is also

**Table 4**  
Mineralogical composition of raw clays (partly from [19,22,40]).

Clay	Clay group	Mineralogy [wt%]					
		Kaolinite	Smectite	Smectite-Illite	Illite	Muscovite	Inert
PP	1:1 dominated clay	93					7
FUP	1:1 dominated clay	71			13		15
GFU	1:1 dominated clay	55			9		35
RKUP	1:1 dominated clay	45			3		52
GUS	Common clay	31	5		15	23	26
CT7	Common clay	23		32	5		35
OC	Common clay	20		38		6	34
Sml	2:1 dominated clay	11	33		33		23
Ill-E	2:1 dominated clay	10			67	7	16
Ill-A	2:1 dominated clay	7			67	5	21
Smk	2:1 dominated clay	7	54		4		35

regarded as an inert material due to its lack of reactivity [20,49].

The measured Activity Indexes of mortar prism with quartz and all clays averaged over all cements were used for the calculations as data basis. This approach puts the focus on impact of the calcined clays and not on that of the different cements. By mathematically excluding the parameter of illite α<sub>I</sub>, the parameters of the other clay minerals are set in relation to illite. A<sub>I</sub> can be seen as a weighting factor. Since illite was selected as reference point, its weighting factor A<sub>I</sub> has a value of 1.0.

**Table 5**  
Physical properties of ground calcined clays and quartz.

Material	Grain size [μm]			BET SSA [m <sup>2</sup> /g]	Water demand [%]	Particle density [g/cm <sup>3</sup> ]
	d <sub>10</sub>	d <sub>50</sub>	d <sub>90</sub>			
PP	1.0	4.8	39.2	18	57	2.61
FUP	3.5	60.9	253.7	8	44	2.61
GFU	1.7	12.6	29.5	26	43	2.62
RKUP	0.9	4.2	40.9	8	47	2.68
GUS	1.9	12.3	31.8	27	50	2.64
CT7	1.9	12.5	33.8	6	39	2.60
OC	1.7	12.8	67.6	36	33	2.67
Sml	1.6	14.8	68.2	51	51	2.74
Ill-E	1.9	15.8	54.6	71	53	2.71
Ill-A	1.7	15.6	64.2	67	56	2.70
Smk	1.4	14.4	60.6	38	45	2.71
Quartz	3.1	40.6	123.7	1	17	2.65

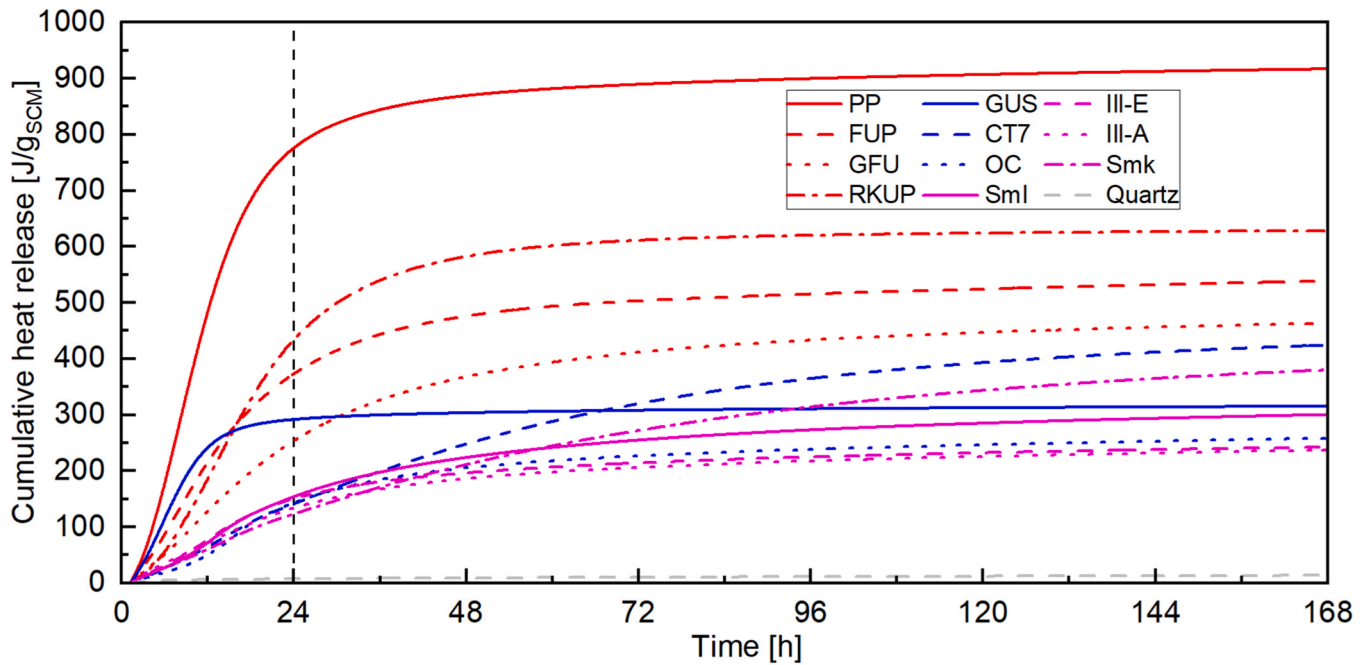


Fig. 1. Cumulative heat release of calcined clays in R<sup>3</sup> test according to DIN EN 17979 [47].

Table 6

Cumulative heat release of calcined clays and quartz in R<sup>3</sup> test at 24 hours, 168 hours and their difference Δ.

Material	PP	FUP	GFU	RKUP	GUS	CT7	OC	Sml	III-E	III-A	Smk	Quartz	
Clay group*	1:1	1:1	1:1	1:1	Com.	Com.	Com.	2:1	2:1	2:1	2:1		
Cumulative heat release [J/g SCM]	24 h	776	373	254	434	281	141	143	154	150	134	123	7
	168 h	917	538	463	628	315	424	258	300	242	237	380	14
	Δ	141	165	209	194	34	283	115	146	92	103	257	7

\* 1:1 = 1:1 dominated clay, Com. = Common clay, 2:1 = 2:1 dominated clay

Quartz itself as a completely inert sample only has an influence via  $\alpha_{d50}$ , i.e. the parameter and weighting factor of the quartz is 0 ( $\alpha_Q = A_Q = 0$ ).

### 3. Results

#### 3.1. Reactivity of calcined clays in R<sup>3</sup> tests

The cumulative heat release over time of the calcined clays in R<sup>3</sup> tests is shown in Fig. 1. The values at 24 hours, 168 hours and their difference are summarized in Table 6.

The 1:1 dominated clays (Table 4) consistently have the highest cumulative heat release. At just twelve hours, they have already developed a considerable cumulative heat release. Despite a lower kaolinite content of 31 wt%, GUS behaves similar until twelfth hour compared with the 1:1 dominated clays. At 24 hours, the 1:1 dominated clays reach a cumulative heat release between 254 and 776 J/g SCM and at 168 hours between 463 and 917 J/g SCM. The cumulative heat release of the 2:1 dominated clays is many times lower. They range from 123 to 154 J/g SCM at 24 hours and from 237 to 380 J/g SCM. Within the 2:1 dominated clays there is a different behaviour of the clays. Up to 36 hours, the smectitic clay Smk has a lower cumulative heat release than the illitic clays III-A and III-E. While Smk releases a noticeable amount of heat up to the seventh day, this is not the case with the illitic clays. Smk triples its cumulative heat release from 24 hours to 168 hours, so it even exceeds the increase of 1:1 dominated clays in the same time span.

The faster and higher reactivities of 1:1 dominated clays than 2:1 dominated clays in the R<sup>3</sup> test are in line with the time-dependent aluminium and silicon ion solubilities of metakaolinite, metallite and

metasmectite in [16]. The heat release of the various clay minerals per unit is not the same. Therefore, it is not possible to draw conclusions about the degree of clay reaction from their cumulative heat release.

The higher grinding fineness of RKUP ensures that it has a higher cumulative heat release (from the 16th hour onwards) than FUP despite its lower kaolinite content. In [19] the kaolinite content is the decisive criterion for the heat release in the R<sup>3</sup> test. Both variables behave directly proportional to each other which is also confirmed by [50].

#### 3.2. Heat flow of calcined clays on cement pastes

The heat flow of the calcined clay blended cements was determined on CEM I 42.5 R (a) and CEM II/A-LL 32.5 R (b). Fig. 2a and b show the results.

The heat flow of the two cements corresponds to that described in the common literature, for example in [51]. Replacement with calcined clay results in a more pronounced aluminate peak, which can also lead to an overlap with the silicate peak depending on the type of clay [22]. This can be caused by the filler effect of the clays [23] and the sulphate absorption of the clays [52], which leads to undersulphation of the blended cements [20].

It is noticeable in Fig. 2a that blends with CEM I 42.5 R and CT7 have the most similar behaviour to the pure cement of all clays. The other extreme of the clays is PP blend, which exhibits a very pronounced peak due to the overlapping of the silicate and aluminate peaks. The peaks of all other clay blends lie on a hyperbola-like curve between the aforementioned. The peaks of the two illitic clays immediately follow that of the PP and occur earlier and more strongly than those of the other 1:1 dominated clays.

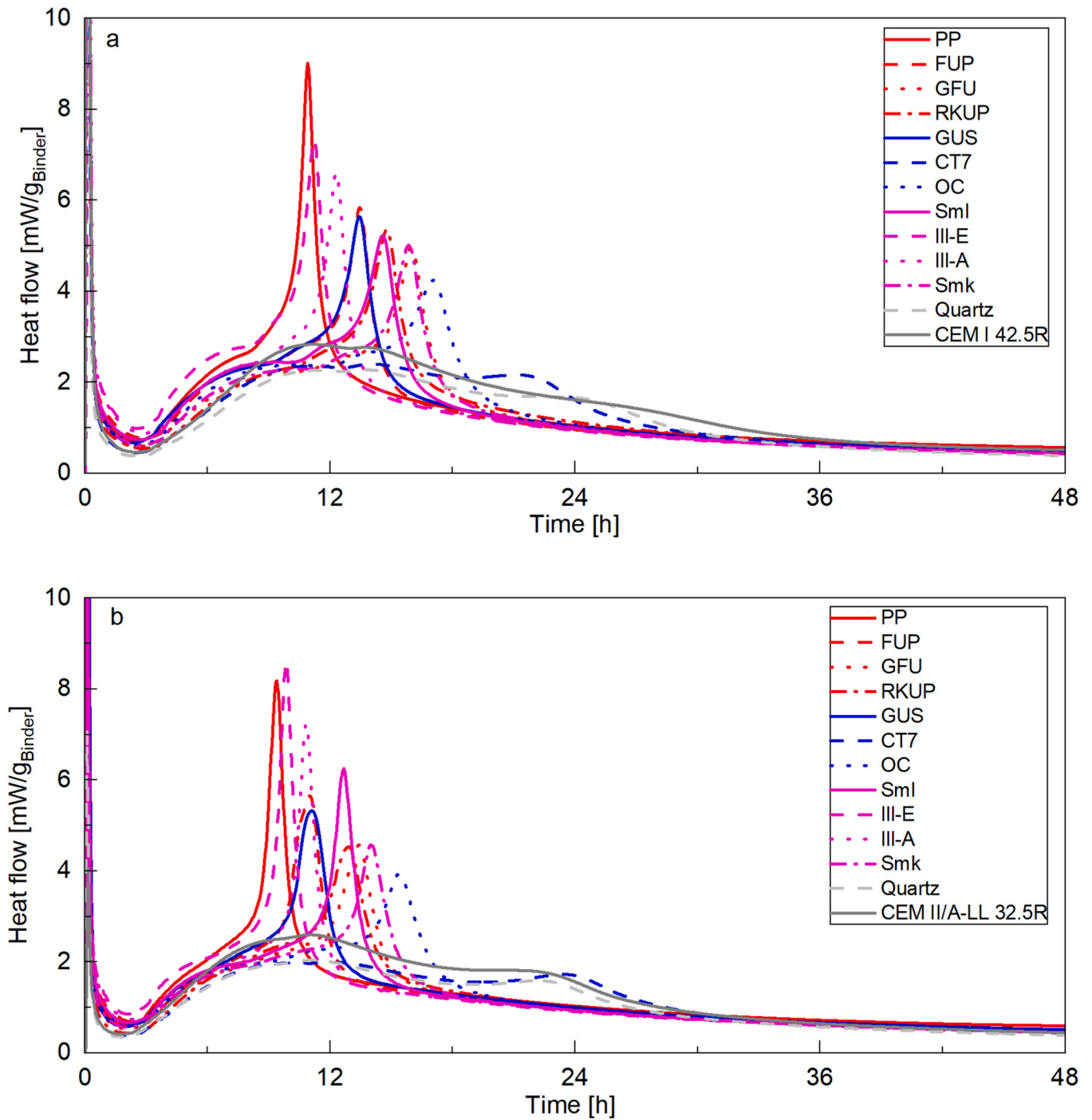


Fig. 2. Heat flow of calcined clays with a replacement level of 20 wt% in CEM I 42.5 R (a) and CEM II/A-LL 32.5 R (b) at a water to binder ratio of 0.5.

Table 7

Hydration heat of calcined clays and quartz at 48 hours in blended cements.

Material		PP	FUP	GFU	RKUP	GUS	CT7	OC	Sml	III-E	III-A	Smk	Quartz
Clay group*		1:1	1:1	1:1	1:1	Com.	Com.	Com.	2:1	2:1	2:1	2:1	
Hydration heat at 48 h [J/g Binder]	CEM I 42.5 R	234	216	214	221	222	218	225	220	227	221	215	201
	CEM II/A-LL 32.5 R	215	203	197	202	205	194	203	201	205	195	197	182

\* 1:1 = 1:1 dominated clay, Com. = Common clay, 2:1 = 2:1 dominated clay

The same observations hold for the blends with CEM II/A-LL 32.5 R, but the amplitude of the peaks of blends with the illitic clays III-E, III-A and the smectitic-illitic Sml increase by approx. 1 mW/g binder, while

those of the other clay blends decrease slightly. This indicates a possible increased sulphate demand when limestone powder is used in combination with metakillite as opposed to combinations with metakaolinite or

metasmeectite. This statement was not further investigated because it is beyond the topic of the paper.

The hydration heat of the blended cements at 48 hours is summarised in Table 7. Without replacement, the hydration heat was 239 J/g binder for CEM I 42.5 R and 216 J/g binder for CEM II/A-LL 32.5 R. The small difference of the individual hydration heats within a cement is striking. For both cements, the difference is only 20 W/g binder each for the calcined clays with the lowest and highest hydration heat at 48 hours, whereas in the  $R^3$  test the difference of the individual cumulative heat release is 653 W/g SCM at 24 hours and 680 W/g SCM at 168 hours. Metakaolinite reduces alite hydration more than metasilite [20], so that the high reactivity of the 1:1 dominated clays in the  $R^3$  test does not occur in blended cements. The 1:1 dominated clays do not always have the highest hydration heat. In both cements, Ill-E has the second highest hydration heat and puts it ahead of FUP, GFU and RKUP. The blended cements did not achieve the hydration heat of the reference cements in both test series.

### 3.3. Compressive strength

The compressive strengths of mortar prisms with a replacement level of 20 wt% calcined clays in different cements at 2 (empty symbols) and 28 days (filled symbols) are shown in Fig. 3. The order was chosen so that the kaolinite content of the raw clays decreases from left to right. The values of the compressive strength are summarized in App. 3.

With the exception of PP, the strength of the calcined clays at 2 days appears to increase minimally to the right until Ill-A. The mortars with Smk and quartz on the right side of the graphic have a lower strength. Despite great differences in the mineralogy of the calcined clays the curves of the six different cements run almost parallel. This means that the impact of calcined clay mineralogy on early strength of blended cements is similar irrespective of the cement.

The blended systems with the highest strength class of the cement (CEM I 52.5 R (ft) & CEM I 52,5 R (bs)) maintain their higher compressive strengths. Therefore, the calculated Activity Indexes of the blended cements are used to compare their performances. The values are shown graphically in Fig. 4 and tabular in App. 4. The course of the curves of each individual blended cement remains the same as in Fig. 3,

so that with the exception of PP the illitic clays have the highest Activity Index at 2 days. For most clays, the highest Activity Indexes are achieved with CEM I 52.5 R (ft) and CEM I 52.5 (bs) and the lowest Activity Indexes with CEM I 42.5 R SR0. The closely spaced curves indicate small differences in the Activity Indexes between the cements.

At 28 days, most mortars with 1:1 dominated clays have the highest strength for each cement. Mortars with CT7 and Smk stand out from the common and 2:1 dominated clays with their high values. The six cements are similarly influenced by the different clays and thus the curves run largely parallel.

The increase in strength at 28 days with CEM II/A-LL 32.5 R due to the replacement of calcined clay is especially noticeable when analysing the Activity Indexes. For all clays, the highest Activity Indexes are achieved with a blended limestone cement. This emphasizes the strong synergistic effects between limestone powder and calcined clays as known from e.g. [23,26]. In most cases, the lowest Activity Index were obtained when using CEM I 52.5 R (bs). There are greater differences for Activity Index at 28 days within a blended cement and between the different blended cements than for the Activity Index at 2 days.

In further course, Activity Indexes are used to illustrate the strength contribution of calcined clays.

According to the characteristic compressive strengths of DIN EN 197-1 [53], the blended cements are classified into strength classes based on their measured strengths at 2 and 28 days. The deviations from the original designation of the reference cements are only minor. Blended cements with CEM I 52.5 R (bs) and (ft) and CEM I 42.5 N still complied with the limit values of their strength class. In case of CEM I 42.5 R this applies only for the replacement with PP and Ill-A. All other clay blends must be classified as 42.5 N. An upgrade of the strength class to 42.5 N is possible with all clays when used in combination with CEM II/A-LL 32.5 R although it must be pointed out, that this pure cement already meets the class requirements. Similarly, strength class upgrade to 52.5 N is possible for calcined clays – except OC, GUS and RKUP - in CEM I 42.5 R SR0, which already meets the strength requirements for the same class.

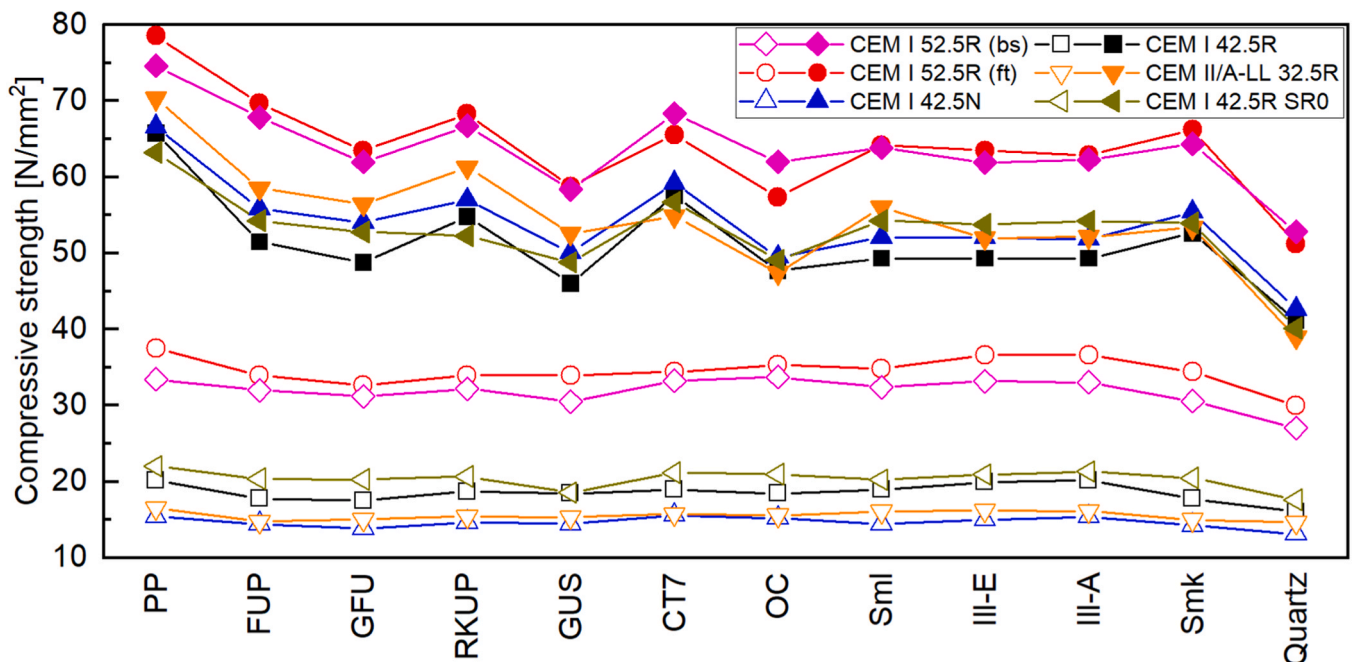


Fig. 3. Compressive strengths of mortar prisms with a replacement level of 20 wt% calcined clays in different cements at 2 (empty symbols) and 28 days (filled symbols) according to DIN EN 196-1 [39]. Connection lines don't have physical meaning.

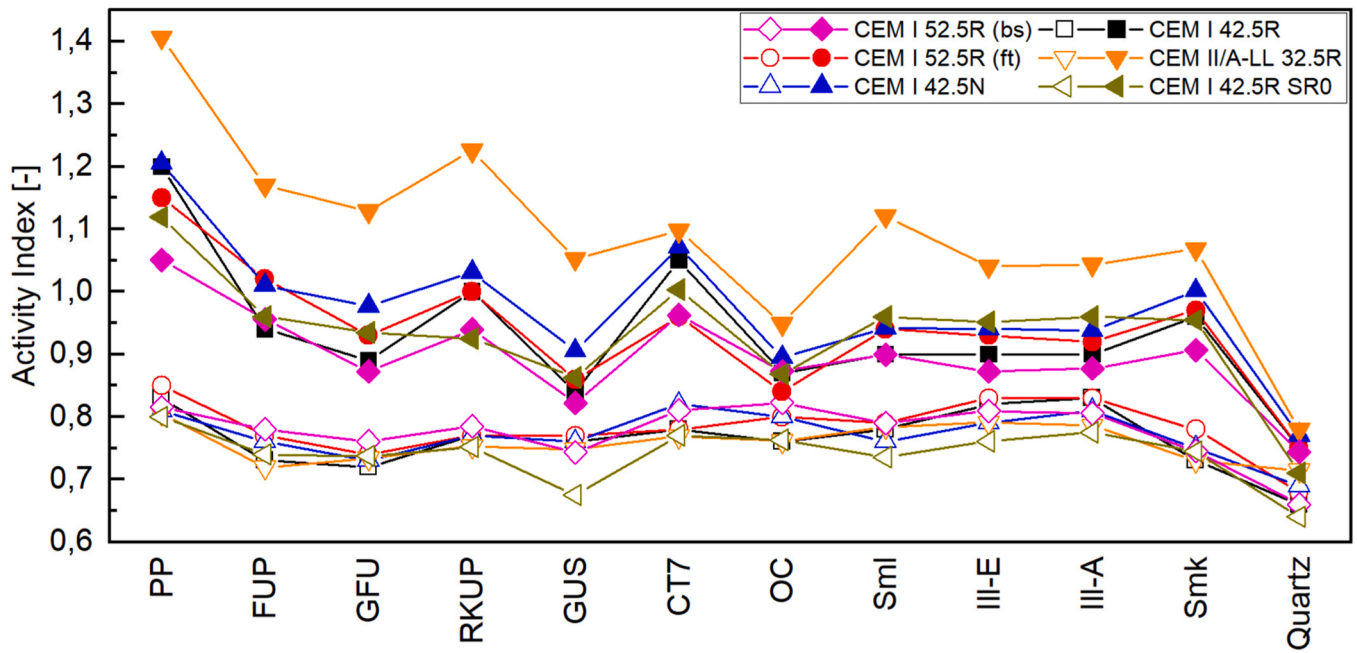


Fig. 4. Activity Index of mortar prisms with a replacement level of 20 wt% calcined clays in different cements at 2 (empty symbols) and 28 days (filled symbols) according to DIN EN 196-1 [39]. Connection lines don't have physical meaning.

Table 8

Mineralogical boundaries of the created clay groups.

Clay group	Kaolinite		Illite and/or Smectite		Investigated clays
	Minimum [wt%]	Maximum [wt%]	Minimum [wt%]	Maximum [wt%]	
1:1 dominated clays	45	93	0	13	PP, FUP, GFU, RKUP
Common clays	20	31	20	38	GUS, CT7, OC
2:1 dominated clays	7	11	58	67	Sml, III-E, III-A, Smk

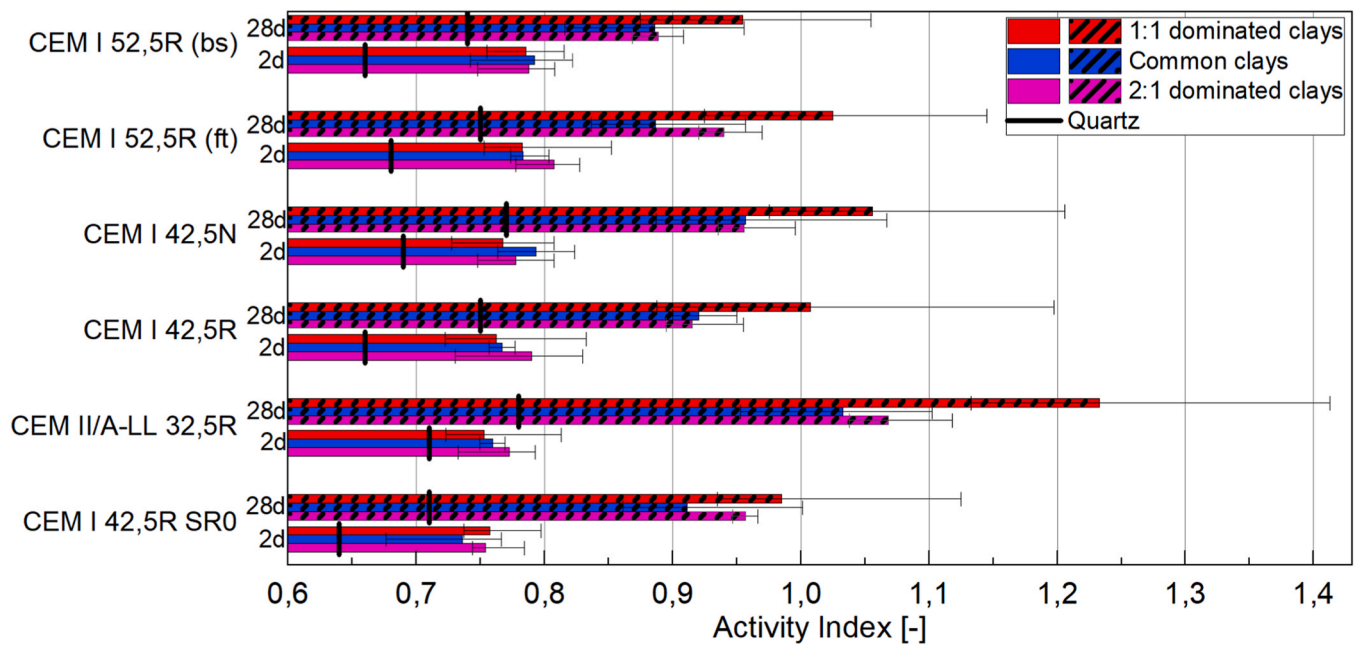


Fig. 5. Activity Index of mortar prisms with a replacement level of 20 wt% calcined clays in different cements at 2 (without pattern) and 28 days (with pattern) averaged for clay groups.



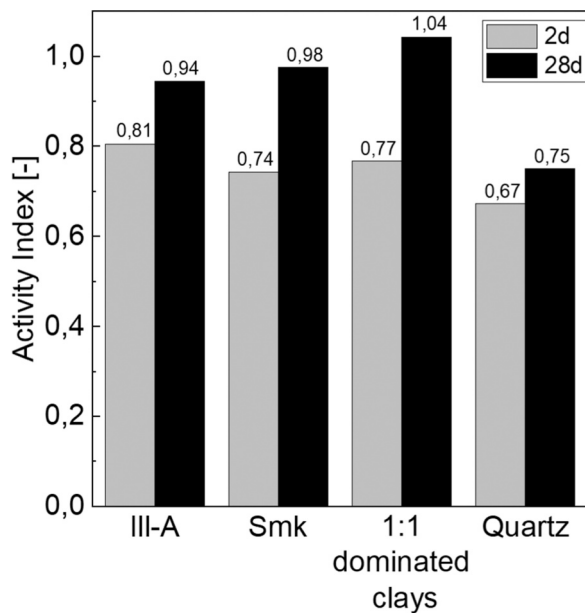


Fig. 6. Activity Index of mortar prisms with Ill-A, Smk, 1:1 dominated clays and quartz (20 wt% replacement level) at 2 and 28 days averaged over all cements. The values of Activity Index are illustrated above the columns and also averaged over all cements.

#### 4. Discussion

Due to the diversity of the clays analysed, it is necessary and useful to categorise them into groups based on their mineralogical composition and in particular owing to the proportion of different phyllosilicates. Even after thermal activation the 2:1 phyllosilicate muscovite “acts solely as filler without chemical reaction during early hydration” [20] and there is no prospect of any significant change with ongoing hydration process because its aluminium and silicon ion solubilities are negligible low compared to kaolinite and illite [49]. For this reason, it is regarded as an inert material and not included in the grouping. The clay mineralogy considered consists of the reactive clay minerals kaolinite, smectite and illite and of inert components, with quartz occurring most often. Following the existing categorisation of clay deposits [54] and classification of clay minerals [11], the clays are divided into the groups 1:1 dominated, common and 2:1 dominated clays. Table 8 shows the mineralogical boundaries of the groups and the affiliation of the investigated clays. The boundaries are values of the clay mineralogy of Table 4, so that gaps occur between the individual clay groups.

Clays with at least 40 wt% kaolinite are considered to be 1:1 dominated and a maximum limit of 30 wt% kaolinite is specified for common clays in [11].

The group of 2:1 dominated clays includes two illitic clays Ill-E and Ill-A, a smectitic clay Smk and an illitic-smectitic clay Sml.

##### 4.1. Strength contribution of the different clay groups

The Activity Indexes in Fig. 5 show the average value of all members of the respective clay group. In addition, the Activity Index of the blends with quartz is indicated by a vertical line. The individual values are given in App. 4. At 2 days the Activity Index of the mortar prisms based on the three different clay groups is between 0.74 and 0.81 and is between 0.89 and 1.23 at 28 days. This increase in Activity Index between 2 and 28 days is due to the pozzolanic reactivity of the calcined clay. The

entire pozzolanic potential can also be seen in relation to the quartz blends. At 2 days their Activity Index is between 0.64 and 0.71 and between 0.71 and 0.78 at 28 days. The clear positive effect of the calcined clays on the Activity Index proves their chemical reaction already at 2 days. It cannot be attributed to physical factors alone, although the quartz powder is coarser than most calcined clays. According to Lawrence et al. [55], an Activity Index approx. 5 % higher can be expected for a similar grinding fineness of the quartz at 2 and 28 days. Nevertheless, the Activity Index of quartz blends would still be lower than those achieved with the calcined clays.

At 2 days, the Activity Indexes differences are rather small (3 %) between the three clay groups for a given cement so that the clay mineralogy does not play a significant role at this age. The strength advantage of kaolinite over illite and smectite cannot be confirmed [12, 27–29]. 1:1 dominated, 2:1 dominated and common clays can provide for the highest as well as the lowest AI. Most often the 1:1 dominated clays perform the worst and the 2:1 dominated clays the best, so that they have the highest Activity Index averaged over all cements. The different cements yield no major differences in Activity Index at 2 days. Relevant for the poor performance of the 1:1 dominated clays at an early age is the inhibition of alite hydration by metakaolinite [20]. A proper sulphate adjustment can counteract this and significantly improve the early strength of 1:1 dominated clays blended cements [23].

The influence of the cement on the reaction of the calcined clays is to be investigated in a further study in order to be able to make a statement based on the cement mineralogy.

The picture changes at 28 days. The results differ for the three clay groups and a given cement. The 1:1 dominated clays yield by far the highest Activity Index irrespective of the cement used. The 2:1 dominated clays are at or above the level of the common clays. With CEM I 52.5 R (ft), CEM I 42.5 N, CEM I 42.5 R and CEM II A-LL 32.5 R, the 1:1 dominated clays ensure an Activity Index greater than 1.0.

At 28 days, the choice of cement becomes decisive as it clearly influences the Activity Index of each clay group. CEM II/A-LL 32.5 R has the most pronounced impact. Its Activity Indexes exceed the value of 1.0 for all three clay groups and are significantly higher than with the other cements. This is due to following reasons.

First, inert constituents were replaced by calcined clay. If the used Portland limestone cement is considered to be a product of 84 wt% Portland cement and 16 wt% limestone powder, 16.8 wt% Portland cement and 3.2 wt% limestone powder are replaced by 20 wt% reactive calcined clay. The - albeit only slight - exchange of an inert substance with a pozzolanic substance automatically ensures increasing strength with increasing age.

Second is the use of limestone and the combination of limestone and calcined clay in cement. Only limestone powder in cement stabilises ettringite and reduces porosity. Instead of reacting to form monosulphate, the primary ettringite is retained, which together with the newly formed hemi- and monocarboaluminates (AFm phases) ensures minimal porosity in the mortar [56,57]. In [23] the synergy of limestone and metakaolinite is described. Calcium carbonate with the aluminium ion of the metakaolinite leads to the forming of hemi- and monocarboaluminates. These AFm phases refine the pore structure [22], which increases the compressive strength [58]. Hemi- and monocarboaluminates are also formed when common or 2:1 dominated clays are used in Portland cement [20,22,59]. Consequently, a synergy of limestone and common or 2:1 dominated clays also occurs, resulting in a refinement of the pore structure and an increase in compressive strength. Furthermore, Scherb et al. [20] report an increase of the alite hydration through the addition of limestone in a calcined clay blended cement. With metakaolinite this effect is more pronounced than with 2:1

dominated clays. In addition to the higher ion amount of the 1:1 than 2:1 dominated clays [16], this provides an explanation for the greater difference in Activity Index between clay groups in limestone cements than in Portland cements at 28 days. Since [20] refers to 50 hours on pastes, these findings can be found on mortars at 28 days, but not at 2 days. The Activity Index of 1:1 dominated clays at 28 days is approx. 20 % higher than that of 2:1 dominated clays and common clays. For the Portland cements, this difference is a maximum of 10 %.

#### 4.2. Differentiation of the strength contribution according to clay minerals

In the previous chapter, illitic and smectitic clays were considered together as 2:1 dominated clays based on structural properties. However, their strength contribution differs considerably, so that the Activity Indexes of both clays blended cements are unsatisfactory averaged with such a grouping. In this chapter, the necessary separation of the 2:1 dominated clays into illitic and smectitic clays at 2 and 28 days becomes clear.

Ill-A (67 wt% illite) and Smk (54 wt% smectite) are discussed in detail in the following. Both have the same low kaolinite content of 7 wt%. Ill-E is not considered here, since it yields almost the same information as Ill-A. The group 1:1 dominated clays was selected as representative of kaolinite for a comparison with illite and smectite. The average kaolinite content of the four clays of the 1:1 dominated group is 66 wt% and thus has a similar content of primary phases as Ill-A. A single 1:1 dominated clay was not selected as a comparative clay because the content of the primary phase and grinding fineness both differ too much from Ill-A and Smk. In addition, the performance of 1:1 dominated clays is strongly influenced by the degree of disorder of its kaolinite [60]. By using the clay group averaged over all 1:1 dominated clays, the influence of these effects is masked.

Fig. 6 presents the corresponding clays and clay group with Activity Index at 2 and 28 days. They are complemented by quartz for comparison. In this case, the Activity Indexes are averaged over all six cements (see App. 4). A separate analysis for the individual cements yields comparable results and thus is not displayed here.

Ill-A provides the highest Activity Index at 2 days and Smk the lowest of the clay minerals analysed here. 1:1 dominated clays rank in between. The strength contribution of the clay minerals at 2 days increases in the following order: smectite - kaolinite - illite. Different studies came to different results for the early strength contribution of the various clay minerals. Metakaolinite was predominantly found to yield the highest strength contribution followed by metacillite and then metasmectite [12, 27–29]. The well-known order of early reactivity (metakaolinite > metacillite > metasmectite) established in various reactivity tests [16, 19, 50] - and also confirmed here in the  $R^3$  tests - is not reflected here in the strengths of the mortars. The high initial reactivity of metakaolinite also occurs in the cementitious system but at the same time the alite hydration is hampered [20]. Metacillite reacts less itself and has less influence on alite hydration. There are no published data for metasmectite so far, but in our  $R^3$  tests metasmectite has a lower reactivity than metacillite up to 36 hours. Based on these results, the Activity Indexes at 2 days are plausible.

It was demonstrated in [23] that the early strength of a 1:1 dominated clay blended limestone cement is improved by adding sulphate carriers. As explained in the introduction, this increase in strength generally occurs with calcined clay blended cements. The strength gain with 2:1 dominated clays will not be as high as with 1:1 dominated clays, as the hydration of alite is significantly less slowed down in their presence [20]. However, adjusting the sulphate content is carried out in practice in a cement plant, but this does not hold to the use of calcined clay as a type II concrete additive in concrete production, which is the focus of this study.

At 28 days, the strength contribution of the calcined clays increases in the following order: illite - smectite - kaolinite which is in line with other studies [12, 16, 17, 32]. The faster and greater release of ions is one reason for the good performance of metakaolinite [12, 13, 15]. Added to this is its rapid reactivity: [16] reports an almost complete reaction of metakaolinite at 28 days in the hydrated calcium hydroxide paste. In contrast, metacillite only achieved a degree of reaction of less than 30 wt% and metasmectite of less than 60 wt%. This is in line with the present study which found a higher reactivity for smectite than for illite in terms

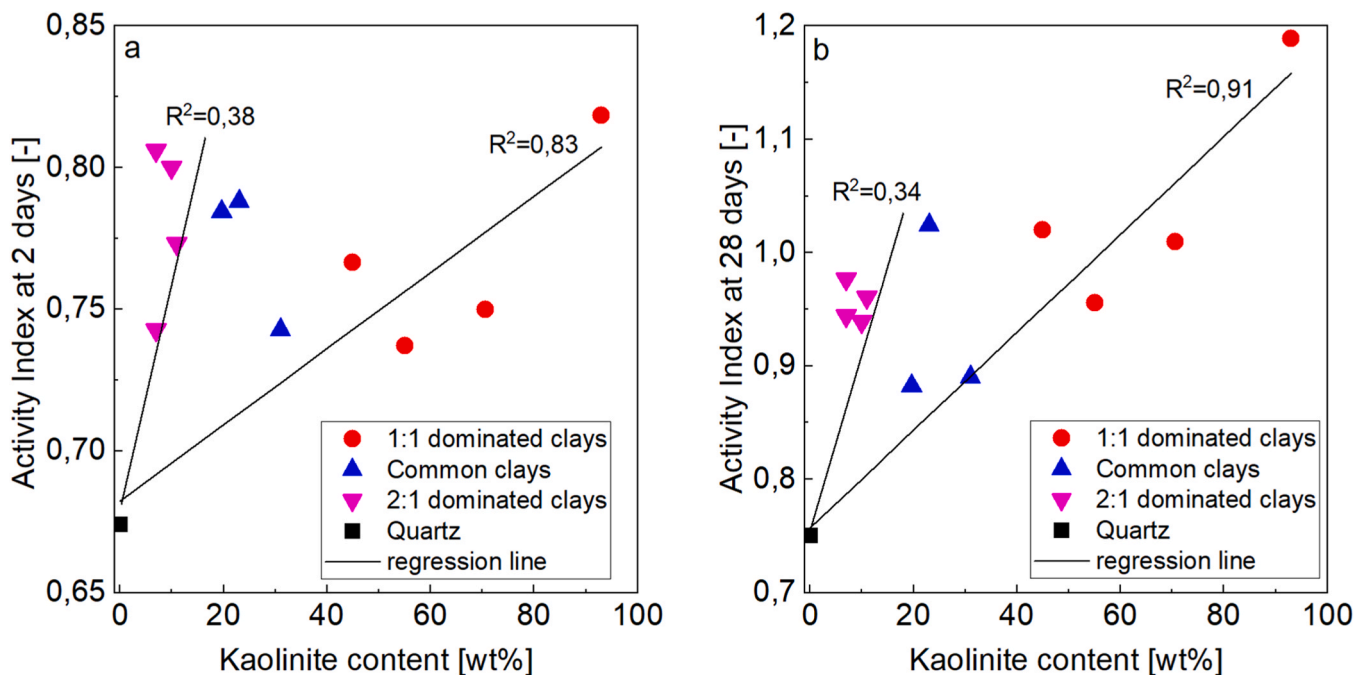


Fig. 7. Activity Index of the mortar prisms with a replacement level of 20 wt% calcined clays at 2 (a) and 28 days (b) averaged over all cements as a function of the kaolinite content of the clays. Two regression lines formed for clays with a kaolinite content of more or less than 30 wt%. Quartz is considered in both cases.

of the own R<sup>3</sup> tests at 168 hours and the mortar strengths at 28 days.

### 4.3. Correlation between clay mineralogy and compressive strength

In this chapter, a correlation is established between the mineralogy and grinding fineness of the clays and the Activity Index of the mortars produced from them. The kaolinite content itself is not sufficient to make a clear statement about the expected Activity Index at 2 and 28 days. Fig. 7a and b highlight again that the sole consideration of the kaolinite content will not explain the Activity Index. Clays with a low kaolinite content can cause higher Activity Index than clays with a high kaolinite content. It is essential to take illite and smectite into account.

In the literature [50], the impression is given that the compressive strength alone depends on their metakaolinite content when using calcined clays. This is correct insofar as only clays were analysed that contained metakaolinite as the primary clay mineral. The current investigations confirm this correlation and found a further correlation for 2:1 dominated clays. This results in a regression line for 1:1 dominated clays and for 2:1 dominated clays, where different common clays can be added in each case. While GUS (31 wt% kaolinite) fits the regression line for 1:1 dominated clays, CT7 (23 wt% kaolinite) and OC (20 wt% kaolinite) fit the one for 2:1 dominated clays. This means that a kaolinite content of 30 wt% can be used as a reasonable criterion for setting up two regression lines in this study. The content of other clay minerals and grinding fineness play a decisive role for the affiliation of the common clays.

The quality of the correlation for 1:1 dominated clays (R<sup>2</sup>=0.83 & 0.91) is at a comparably high level as in [50]. The R<sup>2</sup> coefficients of the regression lines for 2:1 dominated clays have a low quality of the correlation, which may be due to the limited variation of their kaolinite content. Generally, such a small span is not a good basis for calculating the R<sup>2</sup> coefficient. In addition, there are only a small number of samples. Further investigations on 2:1 dominated clays will provide clarity. The Fig. 7a and b are not suitable for giving a strength prediction, but illustrates that 2:1 dominated clays despite low kaolinite content can have a similar strength contribution as 1:1 dominated clays.

Obviously, the 2:1 phyllosilicates must also be taken into account in addition to kaolinite. Using the grinding fineness of the calcined clays, a relationship between clay mineralogy and Activity Index could be established with the statistical software JMP.

Table 9 presents the calculated parameters  $\alpha_i$  and weighting factors  $A_i$  of the variable  $i$  at 2 and 28 days. R<sup>2</sup> coefficients of 0.96 and 0.88 show a very high and high correlation. The signs of the parameters are comprehensible. The positive sign for the clay minerals means that the Activity Index increases with increasing content. The sign of  $\alpha_{d_{50}}$  is negative because the Activity Index decreases with lower grinding fineness (higher  $d_{50}$ ).

To understand the Table 9, it is important to know that it is not possible to compare the parameters of kaolinite, smectite, illite-smectite, illite and  $d_{50}$  ( $\alpha_K, \alpha_S, \alpha_{IS}, \alpha_I, \alpha_{d_{50}}$ ) between 2 and 28 days, because their

**Table 9**

Calculated parameters  $\alpha_i$  and weighting factors  $A_i$  of the variables  $i$  at 2 and 28 days based on the Activity Index measured with the mortar prisms averaged over all cements (K: kaolinite, S: smectite, IS: illite-smectite mixed-layer, I: illite).

Variable $i$	2 days		28 days	
	$\alpha_i$	$A_i$	$\alpha_i$	$A_i$
0	0.7110927		0.8027589	
K	0.0011113	0.76	0.0040447	2.07
S	0.0005771	0.40	0.0027622	1.42
IS	0.0017120	1.18	0.0021542	1.10
I	0.0014528	1.00	0.0019510	1.00
$d_{50}$	-0.000973	-0.67	-0.001708	-0.88
Coefficient of determination R <sup>2</sup>	0.96		0.88	

**Table 10**

Calculated Activity Index with the parameters of JMP for clay groups and pure clay minerals. Variable values of the clay groups are averaged from the corresponding clays.  $d_{50}$  of 25  $\mu\text{m}$  is assumed for all clay minerals.

Clay groups					
	Age	1:1 dominated clays	Common clays	2:1 dominated clays	$\Delta\text{max}$
$AI_{\text{JMP}}$	2d	0.77	0.77	0.78	0.01
$AI_{\text{JMP}}$	28d	1.04	0.94	0.96	0.10
Clay minerals					
	Age	100 % kaolinite	100 % smectite	100 % illite	$\Delta\text{max}$
$AI_{\text{JMP}}$	2d	0.81	0.75	0.84	0.09
$AI_{\text{JMP}}$	28d	1.18	1.05	0.97	0.21

values depend on the intersection of the straight line with the vertical axis (parameter  $\alpha_0$ ) and this is determined arbitrarily by JMP in order to obtain the best correlation. A comparison of the parameters  $\alpha_i$  or weighting factors  $A_i$  of the clay minerals with each other at 2 or 28 days provides information about their importance and thus also about their strength contribution. According to JMP, the contribution increases at 2 days in the order smectite < kaolinite < illite and at 28 days in the order illite < smectite < kaolinite. These are the same orders as found on basis of mortar prisms with the different largely pure clays in Chapter 4.2.

Calculations according to Eq. 1 with the parameters from Table 9 show that the Activity Index differences between the clay groups from Chapter 4.1 are significantly smaller than those between pure clay minerals. The calculated Activity Index ( $AI_{\text{JMP}}$ ) for clay groups and pure clay minerals at 2 and 28 days and their maximum Activity Index differences ( $\Delta\text{max}$ ) are summarised in Table 10. For this purpose, the variable values of the clay groups are averaged from the corresponding clays and a  $d_{50}$  of 15  $\mu\text{m}$  is assumed for the pure clay minerals.

The deviations between the calculated  $AI_{\text{JMP}}$  of the clay groups (Table 10) and the measured Activity Index of the clay groups averaged over all cements (App. 4) are only marginal. The calculations with JMP are successful in terms of quality - not least because the R<sup>2</sup> coefficients are around 0.9.

The largest differences of clay groups in  $AI_{\text{JMP}}$  are 0.01 at 2 days and 0.10 at 28 days. In comparison, a clay of 100 % illite has a 0.09 higher Activity Index at 2 days than a clay of 100 % smectite and the same grinding fineness. At 28 days, the greatest difference is found between a clay of 100 % kaolinite and 100 % illite. Their difference in Activity Index is calculated as 0.21.

It is obvious that pure clay minerals have a more significant impact on the Activity Index than the selected clay groups. In particular, the generalisation of smectite and illite as the clay group "2:1 dominated clays" causes that similar Activity Indexes are achieved as with other clay groups. For this reason, it is important to separate the 2:1 dominated clays into smectitic and illitic clays. More different smectitic and illitic clays are needed to verify this approach. It is possible to calculate the parameters  $\alpha_i$  for each cement individually. High and very high correlations are obtained, but the values of the parameter differ considerably between the various cements. For a cement already used in this study, the expectable Activity Index of mortar prisms with a 20 wt% calcined clay blended cement could now be determined for a new clay using Eq. 1.

Fig. 8 shows how well the software calculations match the mortar prisms in form of regression lines between  $A_i$  as part of Eq. 2 and measured Activity Index. The weighting parameters from Table 9 are already inserted in the formulae of the axes and also used for the individual cements. The dashed lines are the Activity Index at 2 days and refer to the lower horizontal axis, while the solid lines are the Activity Index at 28 days and refer to the upper horizontal axis. The dashed lines are shorter than the solid lines because the same scaling was used for

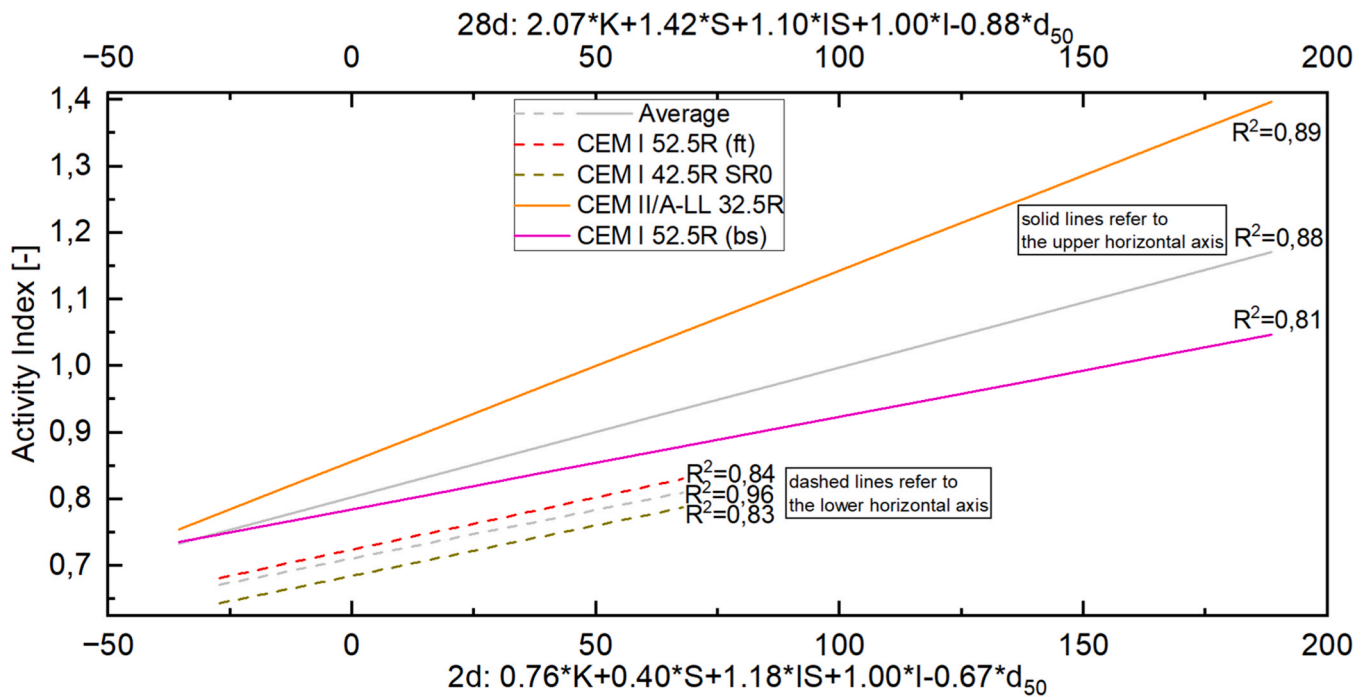


Fig. 8. Measured Activity Index of the mortar prisms with a replacement level of 20 wt% calcined clays as a function of the clay mineralogy and grinding fineness of the calcined clays. Dashed lines (2 days) refer to the lower horizontal axis and the solid lines (28 days) to the upper horizontal axis. The abbreviation "Average" stands for the average over all six cements. The weighting factors that were averaged for all 6 cements were also used for the individual cements.

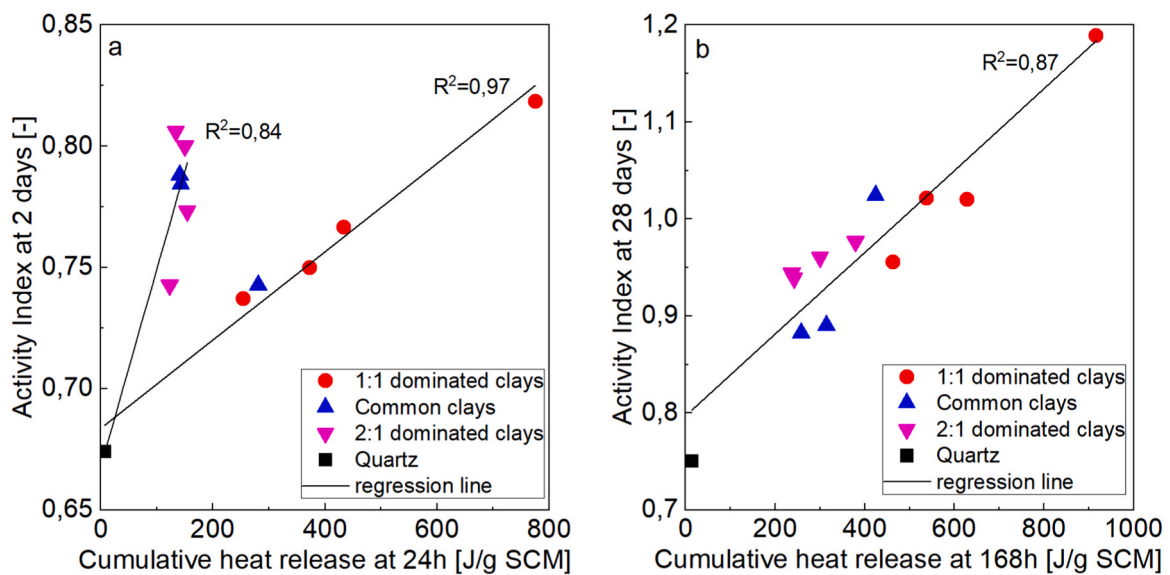


Fig. 9. Activity Index of the mortar prisms with a replacement level of 20 wt% calcined clays at 2 (a) and 28 days (b) averaged over all cements as a function of their cumulative heat release in  $R^3$  tests at 24 and 168 hours. Two regression lines formed for clays with a kaolinite content of more or less than 30 wt% with quartz in (a), one regression line formed for all clays and quartz in (b).

both axes and the weighting factors  $A_i$  are smaller at 2 days than at 28 days. A negative value on the horizontal axis occurs when the clay mineral content is low and the material only coarsely ground (low fineness). Quartz is the extreme and the start of the regression line.

In addition to the regression line of the Activity Index averaged over all cements, two regression lines of the Activity Index of individual cements are also shown as extremes in each case. The regression lines of CEM I 52.5 R (ft) and CEM II/A-LL 32.5 R have the maximum Activity Indexes and those of CEM I 42.5 R SR0 and CEM I 52.5 R (bs) the minimum Activity Indexes. The  $R^2$  coefficients of the individual cements are at a similar level to those averaged over all six cements even if the same weighting factors are used. The  $R^2$  coefficients of 0.96 and 0.88 (averaged over all cements) are already known from Table 9.

The correlation between the properties (mineralogy and fineness) of a calcined clay and the strength contribution in terms of Activity Index is given, but it is not possible to predict its performance with a new cement, because the scatter of the Activity Index of the blended cements is too large. At 2 days, the maximum deviations from the average over all cements are still relatively small, but at 28 days, especially with clay mineral-rich samples (right side of the Fig. 8), the cements have a dominant influence.

While the regression lines in Fig. 8 run parallel at 2 days, at 28 days they converge to the quartz reference point. For predicting the strength contribution of a calcined clay with a specific cement it is necessary that the Activity Index has already been measured for a known calcined clay with the same cement. This allows a regression line, which is either parallel (2 days) or runs through the quartz reference point (28 days), to be determined and the Activity Index of the calcined clay, for which the mineralogy and fineness must be known, to be read off.

#### 4.4. Correlation between cumulative heat release and compressive strength

Finally, measurements in the calorimeter are compared with the Activity Index of the mortar prisms. The cumulative heat release at 24 hours of 1:1 dominated clays determined in the  $R^3$  test correlates well with the early compressive strength of mortar prisms, in which the clays partially replaced cement [50]. Accordingly, the Activity Index at 2 days was compared with the cumulative heat release at 24 hours in Fig. 9a. The choice of more than 36 hours would lead a poorer correlation, due

to the changing development cumulative heat release between smectitic and illitic clays. As in the previous chapter, the Activity Index was averaged using all six cements. No significant correlation can be formed, if all clays are considered together, but when the clays are differentiated according to their kaolinite content into more or less than 30 %, high and even very high correlations are obtained ( $R^2$  coefficient of 0.84 and 0.97 resp.). At 2 days the gradient of the regression line of clays with less than 30 % kaolinite is greater because they have similar Activity Indexes as the clays with more than 30 % kaolinite despite lower cumulative heat release. The good correlation when using 1:1 dominated clays in [50] is confirmed, however, 2:1 dominated clays and also common clays are not on the same regression line. Thus, they must be considered separately. As mentioned, for common clays near 30 wt% kaolinite, the content of other clay minerals and grinding fineness play a decisive role.

Investigations on conventional SCMs (fly ashes, slags, natural pozzolans, silica fumes) and calcined clays showed that their cumulative heat release at 168 hours in the  $R^3$  test correlates well with the compressive strengths of mortars at 28 days whose cement was replaced by the respective SCMs [61,62]. Fig. 9b takes these points in time into account. A single regression line fits well all analysed clays. This is possible in contrast to Fig. 9a, since the mortar made with 1:1 dominated clays gain more in strength from second day onwards than the common and the 2:1 dominated clays. At the same time, common and 2:1 dominated clays start to release more heat from 24th hour onwards in relation to the cumulative heat release at 24 hours than the 1:1 dominated clays.

Only one cement for the strength tests was used in the studies on the  $R^3$  test from the cited literature [50,61,62]. App. 5a and b show the regression lines for each individual cement in our study analogous to Fig. 9a and b. The different courses make it clear that the Activity Index of a calcined clay blended cement cannot be predicted by measuring the cumulative heat release of the calcined clay in the  $R^3$  test. The performance of the calcined clays in a blend depends too much on the individual cements. Once a regression line has been created for a specific cement, the strength contribution of a new calcined clay in the same cement can be predicted unambiguous – at least at 28 days.

The following Fig. 10a and b use a single linear regression for all clays to predict the Activity Index at 2 days when measuring the hydration heat at 48 hours. They show this correlation for a CEM I 42.5 R and CEM II/A-LL 32.5 R resp. While there is a high correlation for

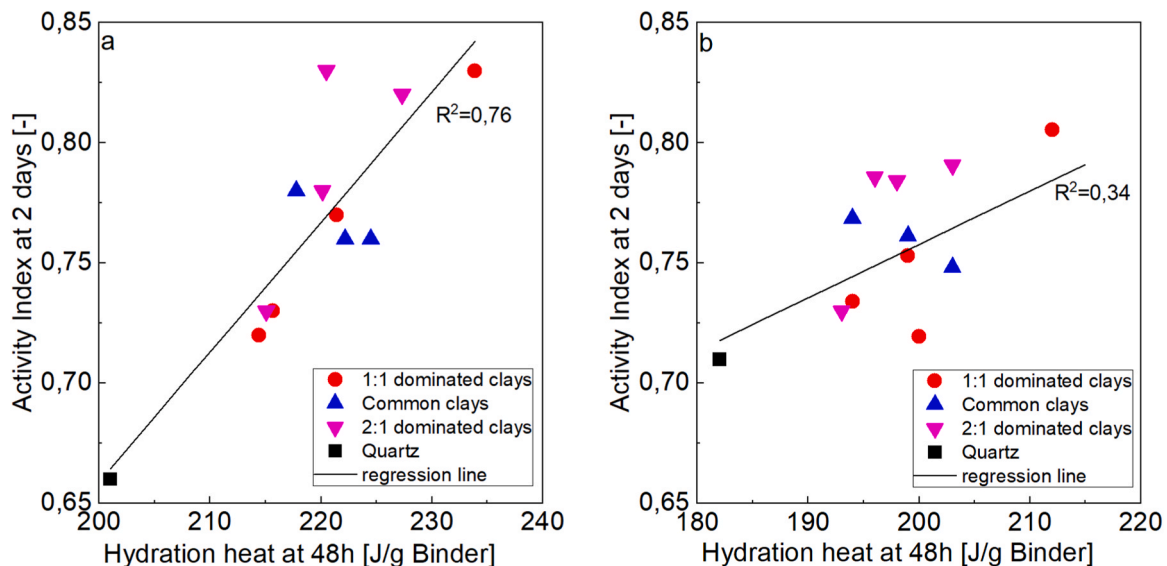


Fig. 10. Activity Index of the mortar prisms with a replacement level of 20 wt% calcined clays at 2 days for CEM I 42.5 R (a) and CEM II/A-LL 32.5 R (b) as a function of their hydration heat in corresponding cementitious system at 48 hours. Regression lines formed for all clays and quartz.

Portland cement, it is low for Portland limestone cement. One hypothesis for the different correlations is the influence of limestone, which ensures in combination with calcined clays the increased formation of AFm phases. It is possible that the strength contribution of AFm phases is not related to their heat release.

The values of the hydration heat of the 2:1 dominated clays in Fig. 10a and b are on the same level as those of the 1:1 dominated clays. In App. 7a and b this relationship is shown as a function of the kaolinite content. A clear regression is not possible across all clays using kaolinite content and hydration heat at 48 hours in cementitious system, as is the case between kaolinite content and cumulative heat release at 24 hours in the  $R^3$  test (App. 6a). App. 6b shows that this single correlation also exists at 168 hours in  $R^3$  test. Investigations of 1:1 dominated and 2:1 dominated and common clays in [19] also show a linear correlation between cumulative heat release and kaolinite content.

The inhibition of alite hydration by metakaolinite at an early age is also recognisable when comparing App. 6a with App. 7a and b. Although the cumulative heat release of the 1:1 dominated clays is in the cement-free  $R^3$  test (App. 6a) many times higher than in the other clays, the 1:1 dominated clay blended cements achieve similar hydration heats as cements blended with common clays or 1:1 dominated clays (App. 7a and b). The high reactivity of the 1:1 dominated clays in the  $R^3$  test does not occur in their blended cements because less heat is released from the reduced alite hydration.

## 5. Conclusion

In this study, eleven different clays were analysed in order to identify the influence of the type of clay mineral on its compressive strength contribution and to estimate the individual compressive strength contribution of calcined clays.

The huge variety of clays requires categorizing them into groups with the same properties. The performance of the calcined clays differs to such an extent that they cannot be generalized. In compressive strength tests, a separation into 1:1 dominated, illitic, smectitic and common clays turned out to be necessary. Illitic and smectitic clays behave too differently to be considered together as 2:1 dominated clays.

2:1 dominated and common clays have proven that they also have their legitimacy as SCM alongside 1:1 dominated clays. The kaolinite content is not solely the decisive criterion for assessing the performance of a calcined clay in the cementitious system especially not for the early age strength. The investigated illitic clays lead to a higher strength at 2 days in blended cement than 1:1 dominated clays. The pozzolanic reaction of smectitic clays develops at a slower speed, but is clearly recognizable and even surpassing that of illitic clays at 28 days. The 1:1 dominated clays provide the highest strengths at 28 days. The widely available common clays perform well at 2 and 28 days in terms of strength, making them a reasonable alternative to conventional SCMs. After 28 days, the combination of calcined clays (especially 1:1 dominated clays) with limestone powder stand out in their performance compared to those without limestone powder, making this combination a viable option for the cement and concrete industry. The strength contribution of a calcined clay depends on the cement used. The Activity Index of a calcined clay blended cement differs less at 2 days and more at 28 days between the various cements.

The clay mineralogy correlates well with the compressive strength of mortar made with their blends, taking into account its fineness of grinding. However, this correlation is dependent on the cement, because a calcined clay in different cements delivers different Activity Indexes. As soon as the parameters of the variables (clay minerals, grinding fineness) are known for a cement, the expected strength contribution

could be estimated of a new clay in blends with this cement. If the parameters of the variables for a cement are not determined, it is difficult to predict the strength contribution of any calcined clay.

The  $R^3$  test of calcined clays has a high correlation with the mortar compressive strengths of calcined clays blended cement at 28 days. Taking the cement dependency into account, the strength can be predicted for this point in time. For the 2-day strength values it is necessary to differentiate on basis of the primary phase content. 1:1 dominated clays have a high cumulative heat release in the  $R^3$  test and lie on a different regression line than 2:1 dominated clays. When only measuring the cumulative heat release of a calcined clay in the  $R^3$  test, the Activity Index of its blend at 2 days cannot be predicted. This can be remedied by measuring the hydration heat of a blended cement. A single regression line for all calcined clays results for the dependence of the Activity Index at 2 days on the hydration heat. The correlation with a Portland cement is high, but with a Portland limestone cement it is too poor for a clear prediction.

As the strength contribution of the calcined clays varies depending on the cement used, a further study is required to make a statement about the influence of the cement on the reaction of the calcined clays. The addition of sulphate carrier in calcined clay blended cements will change their strengths especially at 2 days, so that in a further study the impact of sulphate carrier on the strength contribution of different clay minerals will be analysed.

As the positive results became clear in the course of this work, it was decided to start a project with an industrial partner in which the findings of this paper are used in practice on a large scale. The promising findings will be published in near future.

## CRediT authorship contribution statement

**Nancy Beuntner:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization. **Christian Thienel:** Writing – review & editing, Supervision. **Maximilian Panzer:** Writing – original draft, Visualization, Validation, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sebastian Scherb:** Writing – review & editing, Methodology.

## Declaration of generative AI and AI-assisted technologies in the writing process

The authors declare that they did not use generative AI or AI-assisted technologies in the writing process of this paper.

## 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.

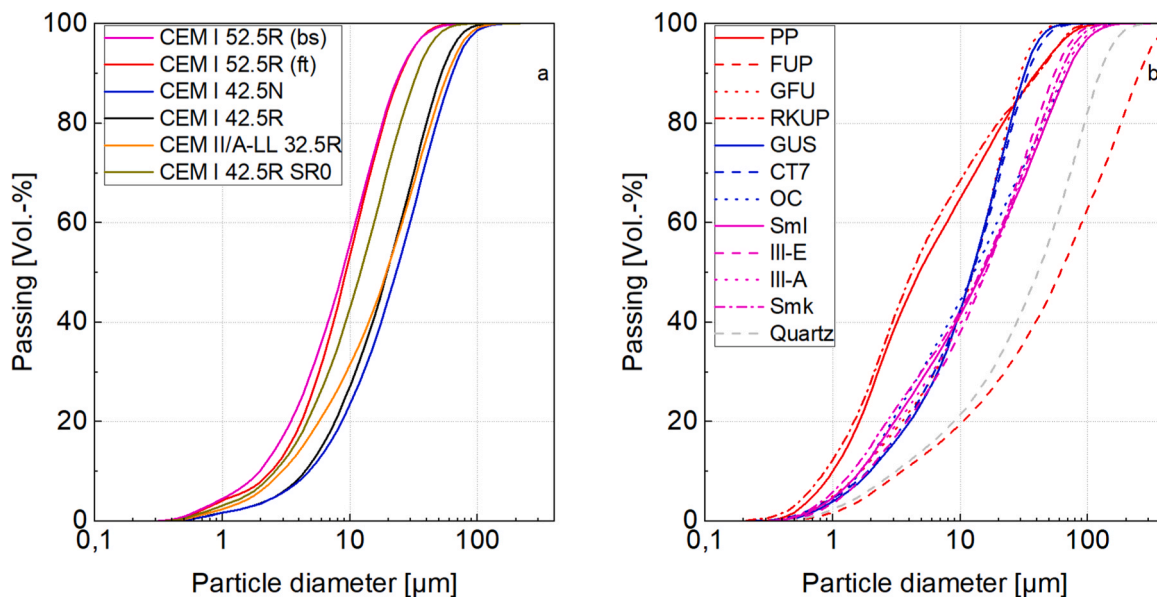
## Data Availability

Data will be made available on request.

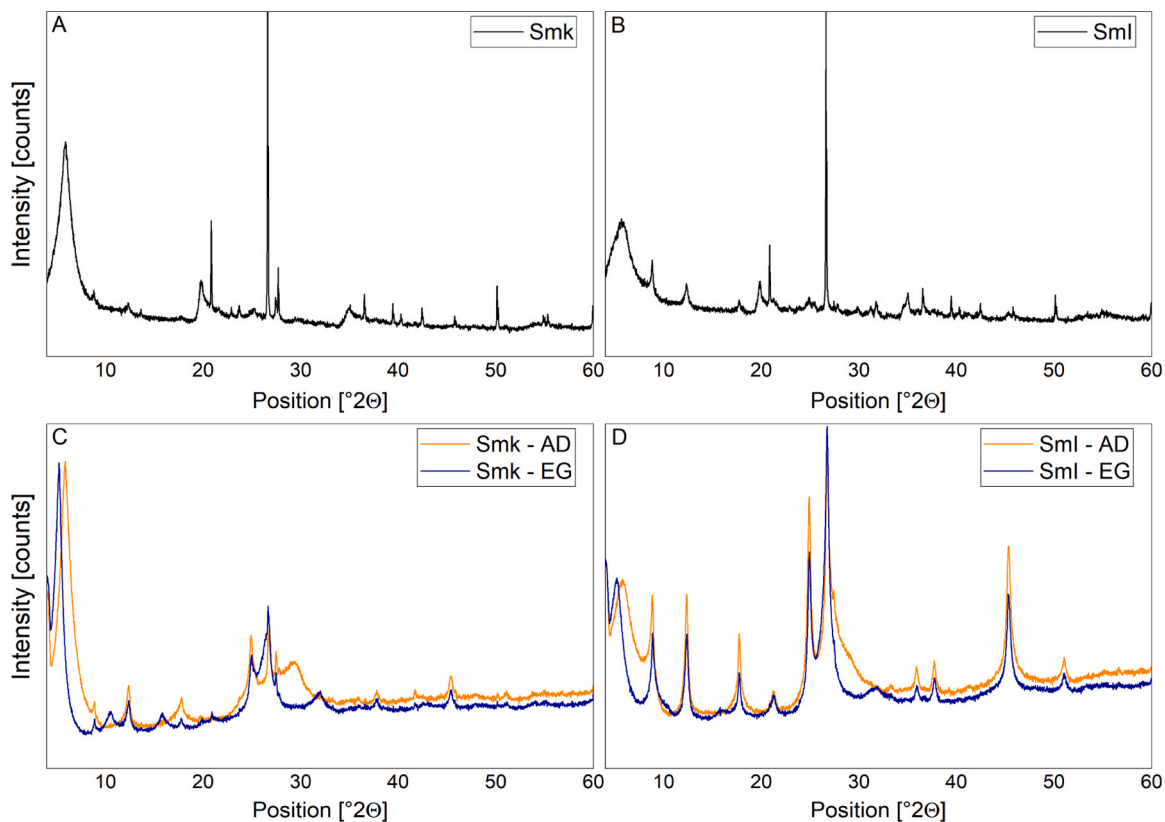
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Appendix



App. 1. Particle size distribution of cements (a) and calcined clays (b).



App. 2. XRD patterns of the raw clays Smk and SmI after side-loading preparation (A and B) and on oriented mounts of the < 2 μm fraction (C and D), AD means air dried and EG glycolated.

**App. 3**

Compressive strengths of mortar prisms with a replacement level of 20 wt% calcined clays in different cements at 2 and 28 days.

Calcined clay	CEM I 52.5 R (bs) f [N/mm <sup>2</sup> ]		CEM I 52.5 R (ft) f [N/mm <sup>2</sup> ]		CEM I 42.5 N f [N/mm <sup>2</sup> ]		CEM I 42.5R f [N/mm <sup>2</sup> ]		CEM II/ A-LL 32.5 R f [N/mm <sup>2</sup> ]		CEM I 42.5 R SR0 f [N/mm <sup>2</sup> ]	
	2d	28d	2d	28d	2d	28d	2d	28d	2d	28d	2d	28d
PP <sup>1</sup>	33.4	74.6	37.5	78.5	15.4	66.6	20.2	65.8	16.5	70.3	22.0	63.2
FUP <sup>1</sup>	32.0	67.9	34.0	69.7	14.4	55.9	17.7	51.5	14.7	58.5	20.4	54.2
GFU <sup>1</sup>	31.2	61.9	32.6	63.5	13.9	54.0	17.5	48.8	15.0	56.4	20.3	52.8
RKUP <sup>1</sup>	32.2	66.7	34.0	68.3	14.6	57.0	18.7	54.8	15.4	61.3	20.7	52.3
GUS <sup>2</sup>	30.5	58.3	34.0	58.7	14.4	50.1	18.5	46.0	15.3	52.6	18.6	48.8
CT7 <sup>2</sup>	33.2	68.3	34.4	65.6	15.6	59.2	19.0	57.5	15.8	54.9	21.2	56.7
OC <sup>2</sup>	33.7	62.0	35.3	57.4	15.2	49.5	18.5	47.7	15.6	47.4	21.0	49.1
Sml <sup>3</sup>	32.4	63.8	34.8	64.2	14.4	52.1	19.0	49.3	16.1	56.0	20.2	54.2
III-E <sup>3</sup>	33.2	61.9	36.6	63.5	15.0	52.0	19.9	49.3	16.2	52.0	20.9	53.8
III-A <sup>3</sup>	33.0	62.3	36.6	62.8	15.4	51.8	20.2	49.3	16.1	52.2	21.3	54.2
Smk <sup>3</sup>	30.6	64.4	34.4	66.3	14.3	55.4	17.7	52.6	15.0	53.4	20.5	53.9
Quartz	27.1	52.8	30.0	51.2	13.1	42.6	16.0	41.1	14.6	39.0	17.6	40.1

<sup>1</sup>1:1 dominated clay <sup>2</sup> common clay <sup>3</sup> 2:1 dominated clay

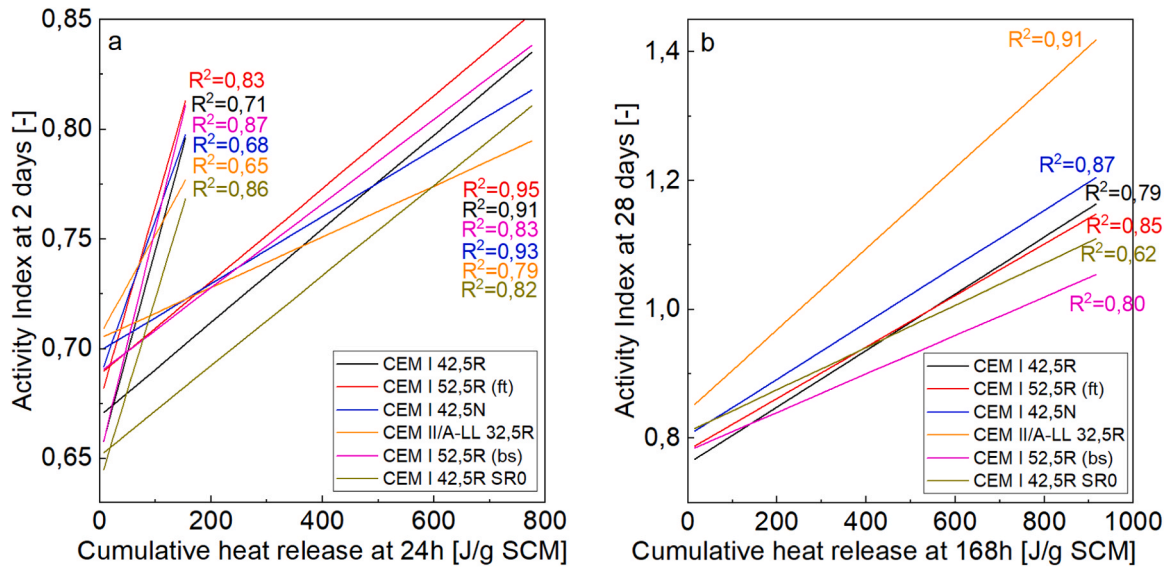


## App. 4

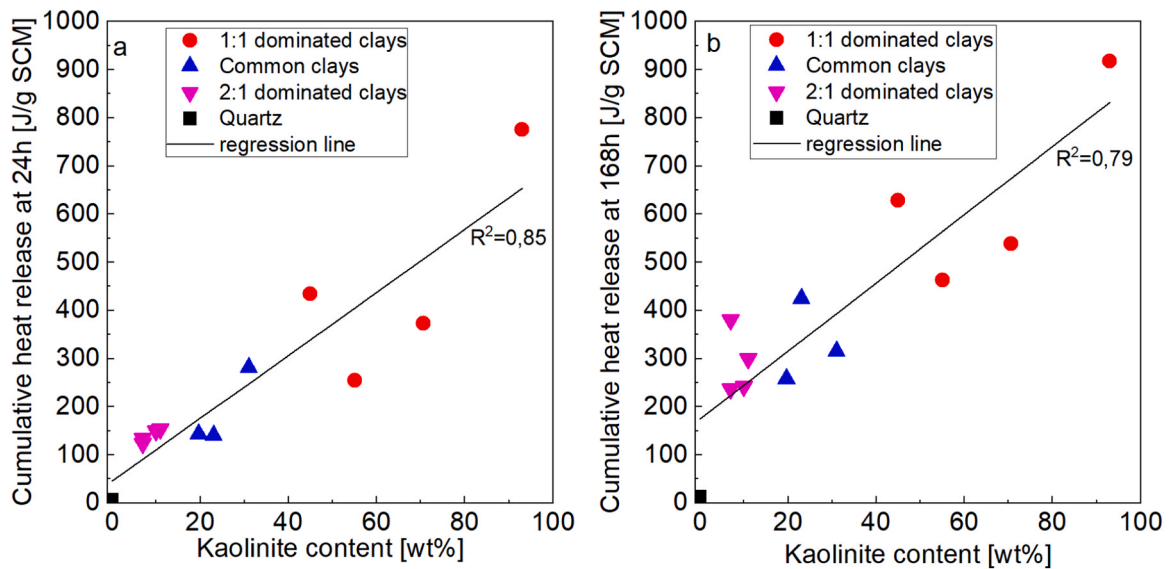
Activity indexes of mortar prisms with a replacement level of 20 wt% calcined clays in different cements at 2 and 28 days.

Calcined clay	CEM I 52.5 R (bs)			CEM I 52.5 R (ft)			CEM I 42.5 N			CEM I 42.5 R			CEM II/A-LL 32.5 R			CEM I 42.5 R SR0			Average of all cements		
	2d-AI	28d-AI	Δ AI	2d-AI	28d-AI	Δ AI	2d-AI	28d-AI	Δ AI	2d-AI	28d-AI	Δ AI	2d-AI	28d-AI	Δ AI	2d-AI	28d-AI	Δ AI	2d-AI	28d-AI	Δ AI
PP <sup>1</sup>	0.82	1.05	0.24	0.85	1.15	0.30	0.81	1.21	0.40	0.83	1.20	0.37	0.81	1.41	0.60	0.80	1.12	0.32	0.82	1.19	0.37
FUP <sup>1</sup>	0.78	0.96	0.18	0.77	1.02	0.24	0.76	1.01	0.25	0.73	0.94	0.21	0.72	1.17	0.45	0.74	0.96	0.22	0.75	1.01	0.26
GFU <sup>1</sup>	0.76	0.87	0.11	0.74	0.93	0.18	0.73	0.98	0.25	0.72	0.89	0.17	0.73	1.13	0.39	0.74	0.93	0.20	0.74	0.96	0.22
RKUP <sup>1</sup>	0.78	0.94	0.15	0.77	1.00	0.23	0.77	1.03	0.26	0.77	1.00	0.23	0.75	1.23	0.47	0.75	0.93	0.17	0.77	1.02	0.25
GUS <sup>2</sup>	0.74	0.82	0.08	0.77	0.86	0.09	0.76	0.91	0.14	0.76	0.84	0.08	0.75	1.05	0.30	0.68	0.86	0.19	0.74	0.89	0.15
CT7 <sup>2</sup>	0.81	0.96	0.15	0.78	0.96	0.18	0.82	1.07	0.25	0.78	1.05	0.27	0.77	1.10	0.33	0.77	1.00	0.23	0.79	1.02	0.24
OC <sup>2</sup>	0.82	0.87	0.05	0.80	0.84	0.03	0.80	0.89	0.09	0.76	0.87	0.11	0.76	0.95	0.19	0.76	0.87	0.11	0.78	0.88	0.10
Sml <sup>3</sup>	0.79	0.90	0.11	0.79	0.94	0.15	0.76	0.94	0.19	0.78	0.90	0.12	0.78	1.12	0.34	0.74	0.96	0.22	0.77	0.96	0.19
III-E <sup>3</sup>	0.81	0.87	0.06	0.83	0.93	0.10	0.79	0.94	0.15	0.82	0.90	0.08	0.79	1.04	0.25	0.76	0.95	0.19	0.80	0.94	0.14
III-A <sup>3</sup>	0.81	0.88	0.07	0.83	0.92	0.09	0.81	0.94	0.13	0.83	0.90	0.07	0.79	1.04	0.26	0.78	0.96	0.21	0.81	0.94	0.14
Smk <sup>3</sup>	0.75	0.91	0.16	0.78	0.97	0.19	0.75	1.00	0.25	0.73	0.96	0.24	0.73	1.07	0.34	0.74	0.95	0.21	0.75	0.98	0.23
Quartz	0.66	0.74	0.08	0.68	0.75	0.07	0.69	0.77	0.08	0.66	0.75	0.09	0.71	0.78	0.06	0.64	0.71	0.06	0.67	0.75	0.07
Average of:																					
1:1 dominated clays	0.79	0.95	0.17	0.78	1.03	0.24	0.77	1.06	0.30	0.76	1.01	0.25	0.75	1.23	0.48	0.76	0.98	0.23	0.77	1.05	0.28
Common clays	0.79	0.89	0.09	0.78	0.89	0.10	0.79	0.96	0.16	0.77	0.92	0.15	0.76	1.03	0.27	0.74	0.91	0.18	0.77	0.93	0.16
2:1 dominated clays	0.79	0.89	0.10	0.81	0.94	0.13	0.78	0.96	0.18	0.79	0.92	0.13	0.77	1.07	0.30	0.75	0.96	0.21	0.78	0.96	0.18

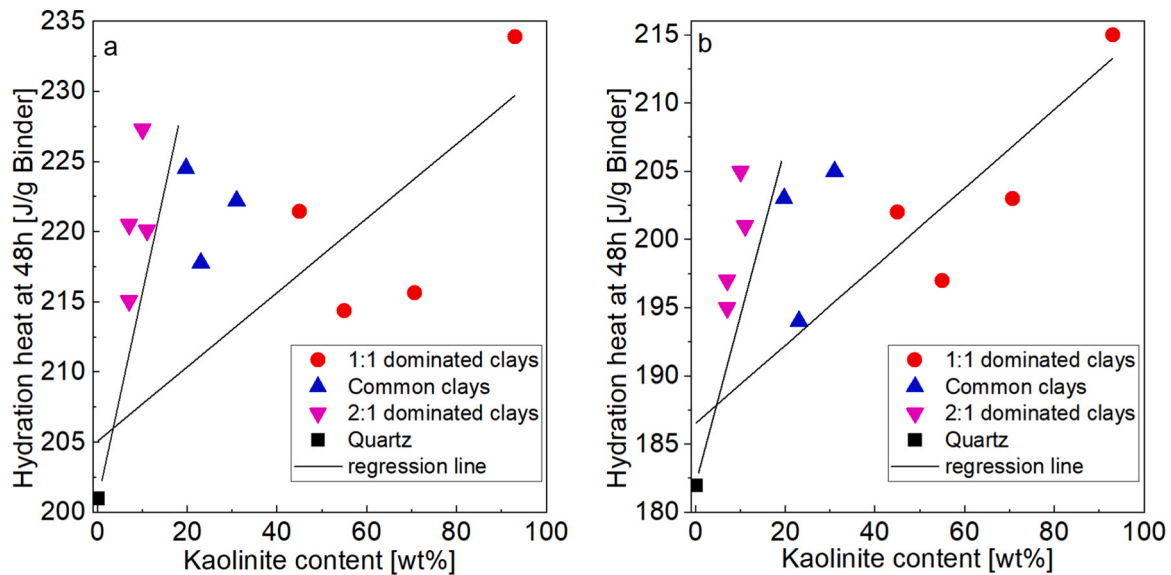
<sup>1</sup> 1:1 dominated clay <sup>2</sup> common clay <sup>3</sup> 2:1 dominated clay



App. 5. Activity Index of the mortar prisms with a replacement level of 20 wt% calcined clays in different cements at 2 (a) and 28 days (b) as a function of their cumulative heat release in R<sup>3</sup> tests at 24 and 168 hours. Regression lines of the measured values for all clays and quartz.



App. 6. Cumulative heat release of calcined clays in R<sup>3</sup> tests at 24 (a) and 168 hours (b) as a function of their kaolinite content. Regression lines are formed for all clays and quartz.



**App. 7.** Hydration heat of calcined clays in cementitious system at 48 hours for CEM I 42.5 R (a) and CEM II/A-LL 32.5 R (b) as a function of their kaolinite content. Two regression lines are formed for clays with a kaolinite content of more or less than 30 wt% in each case with quartz.

## References

- Müller, N. and J. Harnisch, *A Blueprint for a Climate Friendly Cement Industry – How to Turn Around the Trend of Cement Related Emissions in the Developing World*, Report prepared for the WWF-Lafarge Conservation Partnership, Editor. 2008: Nürnberg, p. 94.
- M. Schneider, et al., Sustainable cement production—present and future, *Cem. Concr. Res.* 41 (7) (2011) 642–650.
- T. Østnor, Alternative pozzolans as supplementary cementitious materials in concrete, *SINTEF* (2007) 25.
- S.S. Berriel, et al., Assessing the environmental and economic potential of Limestone Calcined Clay Cement in Cuba, *J. Clean. Prod.* 124 (2016) 361–369.
- A.K. Chatterjee, Pozzolanicity of Calcined Clay, in: K. Scrivener, A. Favier (Eds.), *1st International Conference Calcined Clays for Sustainable Concrete*, Springer Netherlands: Lausanne, 2015, pp. 83–89.
- A. Tironi, et al., Incorporation of Calcined Clays in Mortars: Porous Structure and Compressive Strength, *Procedia Mater. Sci.* 1 (2012) 366–373.
- Y. Sun, et al., Development of a novel eco-efficient LC2 conceptual cement based ultra-high performance concrete (UHPC) incorporating limestone powder and calcined clay tailings: Design and performances, *J. Clean. Prod.* 315 (2021) 128236.
- A. Muhammad, K.-C. Thienel, S. Scherb, Calcined Clays from Nigeria - Properties and Performance of Supplementary Cementitious Materials Suitable for Producing Level 1 Concrete, *Materials* 16 (7) (2023) 2684.
- N. Beuntner, R. Sposito, in: H.-J. Walther (Ed.), *Reduction of CO<sub>2</sub> emissions by means of calcined clays - a challenge for concrete technology (CO<sub>2</sub>-Reduzierung durch calcinierte Tone - eine betonologische Herausforderung?)*, in *64<sup>th</sup> BetonTage*, Bauverlag, Neu-Ulm, Germany, 2020, p. 21.
- F. Martirena, Practical experiences in the use of a combination of calcined clay and limestone as clinker substitute in cement, *ce/Pap.* 6 (6) (2023) 382–385.
- A. Alujas Diaz, et al., Properties and occurrence of clay resources for use as supplementary cementitious materials: a paper of RILEM TC 282-CCL, *Mater. Struct.* 55 (2022) 139.
- R. Fernandez, F. Martirena, K.L. Scrivener, The origin of the pozzolanic activity of calcined clay minerals: a comparison between kaolinite, illite and montmorillonite, *Cem. Concr. Res.* 41 (1) (2011) 113–122.
- S. Hollanders, et al., Pozzolanic reactivity of pure calcined clays, *Appl. Clay Sci.* (2016) 552–560.
- T. Sowoidnich, et al., Reaktivitätsuntersuchungen von calcinierten Tonen mit geringem Metakaolingehalt, *ce/Pap.* (2023) 400.
- N. Werling, et al., Solubility of Calcined Kaolinite, Montmorillonite, and Illite in High Molar NaOH and Suitability as Precursors for Geopolymers, *Clays Clay Miner.* 70 (2022).
- A. Trümer, *Calcinierte Tone als Puzzolane der Zukunft - Von den Rohstoffen bis zur Wirkung im Beton*, in *Fakultät Bauingenieurwesen*, Bauhaus-Universität Weimar, (2020) XXI.
- C. He, B. Osbaeck, E. Makovicky, Pozzolanic reactions of six principal clay minerals: activation, reactivity assessments and technological effects, *Cem. Concr. Res.* 25 (8) (1995) 1691–1702.
- R. Snellings, et al., Paper of RILEM TC 282-CCL: mineralogical characterization methods for clay resources intended for use as supplementary cementitious material, *Mater. Struct.* 55 (5) (2022) 149.
- M. Maier, N. Beuntner, K.-C. Thienel, Mineralogical characterization and reactivity test of common clays suitable as supplementary cementitious material, *Appl. Clay Sci.* 202 (2021) 105990.
- S. Scherb, et al., Reaction kinetics during early hydration of calcined phyllosilicates in model cement systems, *Cem. Concr. Res.* 175 (2024) 107356.
- T. Sowoidnich, et al., The impact of metakaolin on the hydration of tricalcium silicate: effect of C-A-S-H precipitation, *Front. Mater.* 10 (2023).
- N. Beuntner, *Zur Eignung und Wirkungsweise calcinierter Tone als reaktive Bindemittelkomponente in Zement (On the suitability and mode of action of calcined clays as reactive binder components in cement)*, in *Fakultät für Bauingenieurwesen und Umweltwissenschaften*, Univ. ät der Bundeswehr München: Neubib. (2017) 207.
- M. Antoni, et al., Cement substitution by a combination of metakaolin and limestone, *Cem. Concr. Res.* 42 (12) (2012) 1579–1589.
- J. Tang, et al., Synergistic effect of metakaolin and limestone on the hydration properties of Portland cement, *Constr. Build. Mater.* 223 (2019) 177–184.
- I.M.R. Bernal, et al., Early-age reactivity of calcined kaolinitic clays in LC3 cements: a multitechnique investigation including pair distribution function analysis, *J. Sustain. Cem.-Based Mater.* 12 (2023) 721–735.
- H. Maraghechi, et al., Performance of Limestone Calcined Clay Cement (LC3) with various kaolinite contents with respect to chloride transport, *Mater. Struct.* 51 (5) (2018) 125.
- C. He, E. Makovicky, B. Osbaeck, Thermal stability and pozzolanic activity of calcined illite, *Appl. Clay Sci.* 9 (5) (1995) 337–354.
- C. He, E. Makovicky, and B. Osbaeck, *Thermal treatment and pozzolanic activity of Na- and Ca-montmorillonite*, *Appl. Clay Sci.* 10 (5) (1996) 351–368.
- C. He, E. Makovicky, and B. Osbaeck, *Thermal stability and pozzolanic activity of calcined kaolin*, *Appl. Clay Sci.* 9 (3) (1994) 165–187.
- N.S. Msinjili, et al., Comparison of calcined illitic clays (brick clays) and low-grade kaolinitic clays as supplementary cementitious materials, *Mater. Struct.* 52 (5) (2019) 94.
- T. Danner, G. Norden, H. Justnes, Calcareous smectite clay as a pozzolanic alternative to kaolin, *Eur. J. Environ. Civ. Eng.* (2019) 1–18.
- T. Danner, *Reactivity of Calcined Clays*, in *Faculty of Natural Science and Technology, Department of Natural Sciences and Engineering*, NTNU: Trondheim (2013) 229.
- A. Ito, R. Wagai, Global distribution of clay-size minerals on land surface for biogeochemical and climatological studies, *Sci. Data* 4 (1) (2017) 170103.
- DIN EN ISO 17892-3, *Geotechnical investigation and testing - Laboratory testing of soil - Part 3: Determination of particle density*. 2015, Beuth-Verlag: Berlin, Germany. p. 21.
- DIN ISO 9277, *Determination of the specific surface area of solids by gas adsorption - BET method*. 2003, Beuth-Verlag: Berlin, Germany. p. 19.
- DIN 66145, *Darstellung von Korn-(Teilchen-)größenverteilungen RRSB-Netz / Graphical representation of particle size distribution; RRSB-grid*. 1976. p. 3.
- DIN EN 196-3, *Prüfverfahren für Zement - Teil 3: Bestimmung der Erstarrungszeiten und der Raumbeständigkeit (Methods of testing cement - Part 3: Determination of setting times and soundness)*. 2017, Beuth-Verlag: Berlin, Germany. p. 17.
- DIN EN 196-6, *Prüfverfahren für Zement - Teil 6: Bestimmung der Mahlfeinheit (Methods of testing cement - Part 6: Determination of fineness)*. 2019, Beuth Verlag: Belrin, Germany. p. 21.
- DIN EN 196-1, *Prüfverfahren für Zement - Teil 1: Bestimmung der Festigkeit (Methods of testing cement - Part 1: Determination of strength)*. 2016, Beuth-Verlag: Berlin, Germany. p. 31.

- [40] R. Sposito, N. Beuntner, K.-C. Thienel, Characteristics of components in calcined clays and their influence on the efficiency of superplasticizers, *Cem. Concr. Compos.* 110 (2020) 103594.
- [41] D.M. Moore, R.C.J. Reynolds, X-Ray Diffraction and the Identification and Analysis of Clay Minerals. Geological Magazine, 2 ed., Cambridge University Press, Oxford, New York, 1997, p. 322.
- [42] J. Bergmann, P. Friedel, R. Kleeberg, BGMN – a new fundamental parameter based Rietveld program for laboratory X-ray sources, its use in quantitative analysis and structure investigations, *Comm. Powder Diffr. Newsl.* 20 (1998) 5–8.
- [43] N. Doebelin, R. Kleeberg, Profex: a graphical user interface for the Rietveld refinement program BGMN, *J. Appl. Crystallogr.* 48 (5) (2015) 1573–1580.
- [44] H.M. Rietveld, Line profiles of neutron powder-diffraction peaks for structure refinement, *Acta Crystallogr.* 22 (1) (1967) 151–152.
- [45] H.M. Rietveld, An Algol Program for the Refinement of Nuclear and Magnetic Structures by the Profile Method, in *RCN, React. Cent. Ned.* (1969).
- [46] M. Hunger, H.J.H. Brouwers, Flow analysis of water–powder mixtures: Application to specific surface area and shape factor, *Cem. Concr. Compos.* 31 (1) (2009) 39–59.
- [47] DIN EN 17979 - Entwurf, Reaktivität von Zementbestandteilen - Verfahren zur Bestimmung der Hydratationswärme und des chemisch gebundenen Wassers (Reactivity of cement constituents - Heat of hydration and bound water methods), Beuth-Verl. GmbH: Berl., Ger. (2023) 31.
- [48] G. Kundt, H. Krentz, *Ä. Glass, Epidemiologie und Medizinische Biometrie (Epidemiology and Medical Biometry)*. Berichte aus der Statistik, Shaker Verlag, Aachen, 2011, p. 246.
- [49] R. Sposito, et al., *Early hydration behavior of blended cementitious systems containing calcined clays and superplasticizer*, in *15<sup>th</sup> International Congress on the Chemistry of Cement*, in: J. Gemrich (Ed.), Research Institute of Binding Materials Prague: Prague, Czech Republic, 2019, p. 10.
- [50] F. Avet, et al., Development of a new rapid, relevant and reliable ( $R^3$ ) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays, *Cem. Concr. Res.* 85 (2016) 1–11.
- [51] Hesse, C., *Der Reaktionsverlauf der frühen Hydratation von Portlandzement in Relation zur Temperatur*, in *Naturwissenschaftliche Fakultät*. 2009, Friedrich-Alexander-Universität Erlangen-Nürnberg.
- [52] Maier, M., S. Scherb, and K.-C. Thienel, *Sulfate consumption during the hydration of Alite and its influence by SCMs*, in *Vortrag auf der 21. Internationale Baustofftagung ibausil, 13.-15. September 2023 in Weimar*. 2023.
- [53] DIN EN 197-1, *Zement - Teil 1: Zusammensetzung, Anforderungen und Konformitätskriterien von Normalzement (Cement - Part 1: Composition, specifications and conformity criteria for common cements)*. 2011, Beuth-Verlag: Berlin, Germany. p. 8.
- [54] T. Hanein, et al., Clay calcination technology: state-of-the-art review by the RILEM TC 282-CCL, *Mater. Struct.* 55 (3) (2022) 29.
- [55] P. Lawrence, M. Cyr, E. Ringot, Mineral admixtures in mortars effect of type, amount and fineness of fine constituents on compressive strength, *Cem. Concr. Res.* 35 (6) (2005) 1092–1105.
- [56] T. Matschei, F.P. Glasser, The influence of limestone on cement hydration, *ZKG Int.* 59 (12) (2006) 78–86.
- [57] B. Lothenbach, M. Zajac, Application of thermodynamic modelling to hydrated cements, *Cem. Concr. Res.* 123 (2019) 105779.
- [58] A. Tironi, et al., Kaolinitic calcined clays – Portland cement system: Hydration and properties, *Constr. Build. Mater.* 64 (2014) 215–221.
- [59] M. Maier, et al., Particle characteristics of calcined clays and limestone and their impact on the early hydration and sulfate demand of blended cement, *Cem. Concr. Res.* 154 (106736) (2022) 15.
- [60] A. Tironi, et al., Kaolinitic calcined clays: Factors affecting its performance as pozzolans, *Constr. Build. Mater.* 28 (1) (2012) 276–281.
- [61] X. Li, et al., Reactivity tests for supplementary cementitious materials: RILEM TC 267-TRM phase 1, *Mater. Struct.* 51 (6) (2018) 151.
- [62] D. Londono-Zuluaga, et al., Report of RILEM TC 267-TRM phase 3: validation of the  $R^3$  reactivity test across a wide range of materials, *Mater. Struct.* 55 (5) (2022) 142.