

## **POZZOLANIC POTENTIAL OF CALCINED CLAY IN HIGH-PERFORMANCE CONCRETE**

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### **Abstract**

Supplementary cementitious materials (SCM) are required to improve the technical and environmental characteristics of high-performance concrete. They will substitute conventional binders to a greater extent than previously common. Calcined clays are considered to provide huge potential in this regard. Besides the well-known, highly reactive but relatively expensive metakaolin, which can be used in concrete only to a limited extent, calcined mixed layer clays are an alternative solution that appears to be very promising both in environmental and economic terms. In this study, the suitability and efficiency of a calcined mixed layer clay as SCM is compared to a metakaolin and a silica fume. The latter served as reference since it is the most common SCM used in high-performance concrete. The pozzolanic reaction kinetics and the formation of hydrate phases were specifically affected by the calcined clays' specific surface, their high water demand and did depend in addition on their aluminum content. These factors influence fresh and hardened concrete properties as well. The study investigates the impact of different calcined clays on microstructure and on strength, young's modulus of high performance concrete. The pozzolanic efficiency of calcined clay in blended pastes for high-performance concrete with low water-binder ratio was also determined by thermogravimetric analyses. Other than for metakaolin and silica fume the application of low-grade calcined mixed layer clays in concrete and mortar is especially interesting even for high substitution levels of up to 30 wt.% of cement due to their lower and retarding reactivity.

**Keywords:** supplementary cementitious material, bound water, hydration kinetics, microstructure, pozzolanic reaction

## 1. INTRODUCTION

The increasing use of binders with low clinker content requires effective and sufficient supplementary cementitious materials (SCMs) in future [1]. Calcined mixed layer clays with varying amounts of phyllosilicates, especially kaolinite, illite and mica, and a range of inert components (e.g. quartz and feldspar) are promising materials with great potential [2-5]. They are an attractive option for use in concrete at high cement substitution levels of up to 30 wt.% [6]. The low kaolinite content and physical properties like a high specific surface area and a comparatively high water demand (about 30 to 60 % higher than cement) are critically discussed aspects for use as SCM in high-performance concrete with low water-binder ratios [7, 8]. Dinakar et al. illustrate the impact of highly reactive metakaolin in high performance concrete [9]. The optimal substitution level is 10 wt.% of cement which is in the range that is common for silica fume [9, 10]. The pozzolanic reaction of calcined clays indicates C-(A)-S-H and AFm-phases including Strätlingite ( $C_2ASH_8$ ). The aluminate reaction plays an decisive role for the pozzolanic efficiency of calcined mixed layer clays [11]. A low  $C_3A$ -content in cement reduced for instance the reactivity of metakaolin according to Cyr et al. [12].

This study addresses the influences of aluminate level in calcined clays and the interaction with cement composition for pozzolanic reaction is compared with the purely siliceous reactivity of silica fume. The effects on microstructure, especially porosity, and mechanical characteristics were investigated in combination with three different cements and water-binder ratios of 0.4 and 0.6 on cement/blended pastes and concrete. Results reveal possibilities to control the properties of ecological high-performance concrete made with calcined clay as SCM.

## 2. EXPERIMENTAL INVESTIGATION

The first part of the investigation focuses on the pozzolanic reactivity of calcined clays in blended cement pastes with different cement substitution levels. This was accomplished using thermogravimetric analysis to determine bound water (20 to 400 °C) and portlandite consumption. Furthermore, microstructural analysis was performed following [13] by means of mercury intrusion porosimetry (MIP). The variables include differing cement types (ordinary Portland cement (OPC), Portland limestone cement (PLC), calcined clay content (10, 20 and 30 wt.% for calcined mixed layer clay, 20 wt.% for metakaolin. For PLC calcined clay content of 20 and 30 wt.%, a combination of 10 wt.% metakaolin with 20 wt.% of calcined mixed layer clay and the addition of 10 wt.-% silica fume were investigated. Water-binder ratio was 0.4 for OPC mixes and 0.6 for PLC mixes. PCE-based superplasticizer was added to the PLC mixes for adjusting the workability. Compressive strength of the OPC based binder matrices was tested on micro-prisms (10x10x40 mm<sup>3</sup>). Pure cement pastes served as references.

In the second part of the investigation concentrated on compressive strength and Young`s modulus of high strength concrete. The SCMs were calcined mixed layer clay, a combination of calcined mixed layer with metakaolin and silica fume. Again, PCE-based superplasticizer was needed for adjusting the workability.

### 2.1 Materials and specimens

Two ordinary Portland cements (OPC1 and OPC2) and one Portland limestone cements (PLC) were used having a strength grade 42.5R and complying with DIN EN 197-1. Two calcined clays were selected: A commercially available metakaolin (Mk) and a calcined mixed layer clay (CT). The source material of CT originates from Amaltheen (black jura) in Southern

Germany and was calcined at 750 °C in a rotary kiln on industrial scale [6]. Silica fume (Sf) served as reference SCM for high-strength concrete mixes. The physical properties and chemical analysis of the cements, both calcined clays and silica fume are listed in Table 1.

Table 1: Physical and chemical compositions of investigated binders

	OPC1	OPC2	PLC	CT	Mk	Sf
Particle density [g/cm <sup>3</sup> ]	3.14	3.14	3.08	2.63	2.42	1.40
Specific surface area (BET) [m <sup>2</sup> /g]	1.23	1.08	1.24	5.3	14.1	-
Water demand [wt.%]	28	32	30	39	70	-
Loss of ignition [wt.%]	3.0	2.8	4.9	0.9	1.5	0.2
C <sub>3</sub> S [wt.%]	54.1	59.0	56.8			
C <sub>2</sub> S [wt.%]	20.1	14.0	8.5			
C <sub>3</sub> A [wt.%]	6.3	8.0	8.6			
C <sub>4</sub> AF [wt.%]	9.0	10.0	8.1			
SiO <sub>2</sub> [wt.%]	20.4	19.6	18.2	54.0	55.0	97.0
Al <sub>2</sub> O <sub>3</sub> [wt.%]	5.0	5.3	5.4	21.4	42.5	-
Fe <sub>2</sub> O <sub>3</sub> [wt.%]	3.1	3.5	2.9	9.0	0.5	-
CaO [wt.%]	60.8	61.4	61.1	4.3	0.1	-
MgO [wt.%]	1.8	1.7	1.9	2.0	0.1	-
SO <sub>3</sub> [wt.%]	3.0	3.4	3.2	2.0	0.1	-
Na <sub>2</sub> O <sub>eq</sub> [-]	0.6	1.2	1.1	3.0	0.5	-
TiO <sub>2</sub> [wt.%]	0.2	0.3	0.2	0.0	1.0	-
Cl <sup>-</sup> [wt.%]	0.06	0.08	0.07	0.01	0.01	< 0.10

Cement pastes were mixed in a Hobart type laboratory mixer for 5 minutes and cast into molds with a size of 10x10x40 mm<sup>3</sup> for testing compressive strength and in sealed plastic containers for analytical investigations. The latter samples were crushed after 2 and 28 days resp., and the hydration of 250 mg samples was stopped with acetone [14, 15]. The nomenclature of the specimens gives the type of cement followed by the replacement level and the type of SCM, e.g. (OPC1\_30CT).

Table 2 summarizes the high strength concrete compositions. The nomenclature system is identical to the one used for the paste specimens. Aggregates were river sand and crushed granite coarse. W/b ratio was 0.4. Workability was adjusted with a PCE-based superplasticizer (ACE 430).

Table 2: Concrete compositions

Components	PLC_10Sf	PLC_20CT	PLC_30CT	PLC_10Mk/20CT
Cement [kg/m <sup>3</sup> ]	297	264	231	231
SCM [kg/m <sup>3</sup> ]	33	66	99	33/66
Aggregate [kg/m <sup>3</sup> ]	2019	2030	2040	2038
Water [kg/m <sup>3</sup> ]	132	132	132	132
PCE [wt.% of cement]	1.6	3.5	6.5	6.5

Concrete was mixed in a pan-type mixer. The specimens were compacted on a vibration table and cured following DIN EN 12390-2. Compressive strength was tested on 150-mm-cubes according to DIN EN 12390-3. Young's modulus was measured on 150/300-mm-cylinders according to DIN EN 12390-13.

## 2.2 Analytical investigation

Bound water and portlandite consumption were evaluated by thermogravimetric analysis (TGA) using a STA 449 F3 Jupiter (Netzsch) by measuring the weight loss in the temperature range 20-400 °C for bound water (H) and 450-550 °C for portlandite (CH) [13]. Porosity parameters are determined by mercury intrusion porosimeter Pascal 140/440 (Thermo Fisher Scientific). Results are the accessible porosity [vol.-%], the quantity of pores smaller than 30 nm [vol.-%], the median pore diameter [nm] and the threshold pore entry radius [nm] [16].

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

### 3.1 Evaluation of pozzolanic reactivity by bound water and portlandite consumption

The pozzolanic reactivity was determined by bound water and portlandite consumption after two and 28 days. The results are presented in Table 3. The bound water in the temperature range of 20-140 °C ( $H_1$ ) characterizes C-S-H phases and ettringite in cementitious systems [17]. The AFm phases typically show water loss over a wide temperature range of 140-400 °C ( $H_2$ ) [18].

The total bound water ( $H_{total}$ ) is higher after two days for the blended cement pastes containing Mk or silica fume than for those made with even higher replacement levels of CT. After two days higher values of  $H_1$  as compared to  $H_2$  indicate a more pronounced formation of C-S-H phases and ettringite than AFm. Nevertheless, the amount of  $H_2$  indicates a distinctive formation of AFm phases in blended binders with the alumina-rich SCMs used here already after two days.

In the following the aluminate reactions are intensified and after 28 days significantly more water is bound in AFm phases ( $H_2$ ) compared to C-S-H phases and ettringite ( $H_1$ ) in the mixes containing CT. With increasing alumina content in SCMs the formation of AFm phases is typical and becomes dominant in blended cement pastes. This holds especially for mixes based on PLC [19]. Portlandite consumption increases in the course of hydration and with increasing substitution levels of CT, but it remains significantly below the one measured for Mk. The portlandite consumption for the silica rich, highly pozzolanic silica fume in PLC\_10Sf is in the range of PLC\_20CT after 28 days. Especially, the Mk blended cements (OPC1/OPC2\_20Mk and PLC\_10Mk/20CT) show a significantly lower portlandite content of less than 6 g/100 g cement after 28 days which was already indicated after two days where 12 g CH/100 g cement and less were measured for OPC1\_20Mk and PLC\_10Mk/20CT.

Figure 1 provides for OPC based binders the compressive strength values of the micro-prisms as a function of the amount of bound water. In all systems, there is a good correlation between the amount of bound water and compressive strength. For alumina rich binders, containing Mk or CT, this phenomenon can be attributed to the AFm phases formed during hydration [9, 11, 12]. In consequence, AFm phases seem to have a strength-enhancing effect since they densify the paste. The influence of AFm phases upon volume stability might be significant in blended systems containing alumina rich SCMs, like calcined clays and can reduce drying shrinkage [20].

Table 3: Amount of bound water (H) and portlandite (CH) content after 2 and 28 days determined by TGA

System	H <sub>total</sub> [%]	H <sub>1</sub> [%]	H <sub>2</sub> [%]	CH [%]	CH [g/100 g cement]
	2 d / 28 d	2 d / 28 d	2 d / 28 d	2 d / 28 d	2 d / 28 d
OPC1	12.7 / 16.2	7.9 / 8.2	4.8 / 8.0	11.4 / 17.3	19.2 / 22.7
OPC1_10CT	12.0 / 17.2	7.1 / 8.8	4.9 / 8.4	11.0 / 13.3	17.2 / 19.6
OPC1_20CT	10.6 / 17.6	6.1 / 8.7	4.5 / 8.9	6.5 / 10.2	11.6 / 16.2
OPC1_30CT	11.6 / 16.0	6.7 / 7.8	4.9 / 8.2	9.1 / 7.5	18.5 / 14.3
OPC1_20Mk	12.6 / 18.2	6.2 / 6.7	6.4 / 11.5	6.9 / 1.9	12.0 / 3.1
OPC2	12.9 / 16.7	7.9 / 8.3	5.0 / 8.4	9.1 / 20.3	12.7 / 26.5
OPC2_10CT	13.2 / 17.6	9.8 / 9.1	3.4 / 8.5	8.4 / 16.9	10.1 / 24.8
OPC2_20CT	10.9 / 18.2	5.7 / 9.4	5.2 / 8.8	6.1 / 14.3	10.8 / 23.5
OPC2_30CT	12.6 / 17.9	9.6 / 9.4	3.0 / 8.5	6.9 / 12.1	10.9 / 22.6
OPC2_20Mk	14.6 / 17.5	6.8 / 6.2	7.8 / 11.3	10.0 / 1.2	17.1 / 2.0
PLC_10Sf	13.7 / 17.6	8.7 / 11.6	5.0 / 6.0	10.3 / 7.4	16.0 / 11.6
PLC_20CT	13.5 / 17.9	8.4 / 10.6	5.1 / 7.3	8.4 / 6.4	14.7 / 11.2
PLC_30CT	10.8 / 17.9	6.1 / 10.9	4.7 / 7.0	7.3 / 4.0	14.6 / 8.1
PLC_10Mk/20CT	13.7 / 17.5	8.4 / 10.8	5.3 / 6.7	6.0 / 2.9	12.0 / 5.8

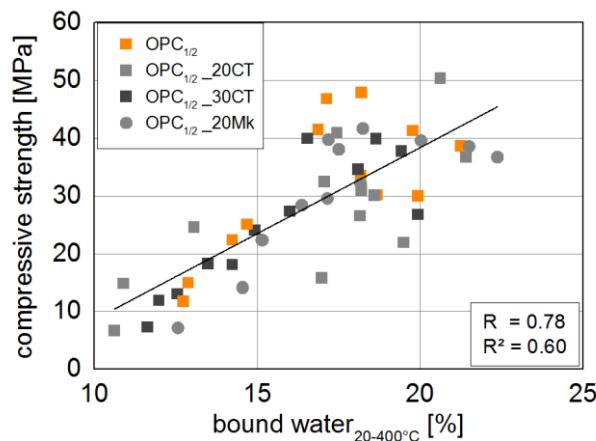


Figure 1: Compressive strength [MPa] related to the amount of bound water [wt.%]

### 3.2 Porosity

For blended binders, the accessible porosity decreases with increasing substitution levels of SCMs after 28 days of hydration (Table 4). The volume of pores below a pore size of 30 nm increases slightly for OPC systems blended with CT. The effect is more pronounced for binders containing Mk. The pore volumes below a pore size of 30 nm in the PLC systems exhibit a similar trend. After 28 days, the median pore diameter of systems containing Mk has decreased even to less than 20 nm, as already stated e.g. by [21, 22]. The silica fume containing binder has a median pore diameter of 4.7 nm which is hardly surprising due to the high specific surface area of Sf. A comparable low value was obtained for the Mk/CT blended PLC system. In terms of durability, the threshold pore entry radius [16] is a significant parameter to evaluate the possible threat of transportation mechanisms. It decreases with increasing substitution level of CT and provides the lowest values for OPC systems containing Mk. The threshold for the blended PLC systems was even lower. The results confirm a significant refinement of

microstructure due to the SCMs used. The modification of porosity originates from differences in hydration products and is also valid for blended binders with 20 and 30 wt.% of CT.

Table 4: Porosity parameters determined by MIP after 28 days of hydration

System	Accessible porosity	Pore size < 30 nm	Median pore diameter	Threshold pore entry radius
	vol.-%	vol.-%	nm	nm
OPC1	37.3	15.9	41.0	110
OPC1_10CT	35.6	13.9	49.5	105
OPC1_20CT	37.0	17.5	50.1	70
OPC1_30CT	36.8	18.6	29.2	75
OPC1_20Mk	34.8	22.6	20.0	30
OPC2	37.3	16.7	38.3	150
OPC2_10CT	36.5	16.8	39.2	110
OPC2_20CT	36.1	18.5	28.4	115
OPC2_30CT	36.8	17.3	34.0	116
OPC2_20Mk	34.8	22.6	20.0	80
PLC_10Sf	22.3	12.1	4.7	64
PLC_20CT	24.4	15.3	28.3	52
PLC_30CT	23.3	18.5	21.9	37
PLC_10Mk/20CT	11.4	21.3	7.2	28

### 3.3 Compressive strength and Young`s modulus in concrete

**Error! Reference source not found.** presents compressive strength and modulus of elasticity of high performance concretes with different substitutions levels of SCMs at an age of 28 days. Concretes made with calcined clays yield comparable strength results as the reference high strength concrete made with silica fume even though high amounts of superplasticizer were necessary for the calcined clay mixes. It is interesting that it is possible to obtain the same strength with 30 wt.% of pure or mixed calcined clays as with 10 wt.% of silica fume. Such a high replacement level is needed in future for a more ecological mix design.

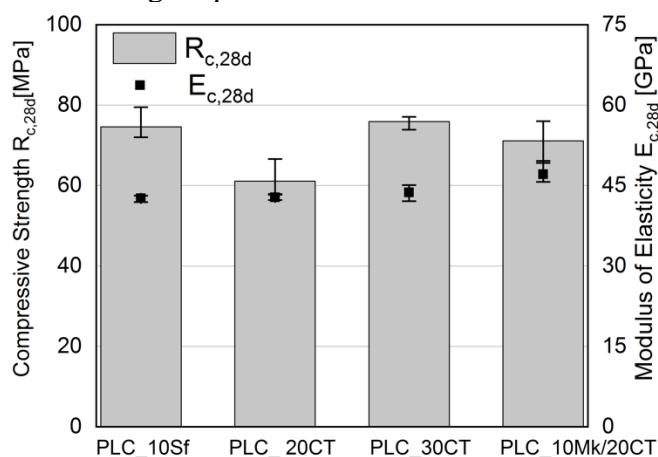


Figure 2: Compressive strength ( $R_{c,28d}$ ) and modulus of elasticity ( $E_{c,28d}$ ) after 28 days

The modulus of elasticity is in the same range of about 43 GPa for PLC\_10Sf, PLC\_20CT and PLC\_30CT and is slightly higher for the combined calcined clay substitution in

PLC\_10Mk/20CT. Furthermore, positive synergetic effects between the calcined clays and limestone in the PLC may have an impact which result in a preferred formation of strength-enhancing AFm phases according to Antoni et al. [23]. In addition, a higher alkali and C<sub>3</sub>A content of the PLC both promote the pozzolanic reactivity and confirms the findings of Cyr et al. [12] for metakaolin blended cements.

#### **4. FURTHER RESEARCH**

The poor workability of high strength concretes with a high substitution level of calcined clays due to the latter's high water demand represents the biggest challenge so far. It is indispensable to test the interaction of calcined clays with superplasticizers. The investigations show that high concrete strength can be achieved with PLC blended with calcined clays. The combination of calcined mixed layer clays with other composite cements should be evaluated in further investigations.

#### **6. SUMMARY AND CONCLUSIONS**

Based on the results of this investigation the following conclusions are drawn:

1. The investigated calcined mixed layer clay exhibits a high pozzolanic reactivity comparable to other highly reactive SCMs. Its benefit consists in higher substitution rates becoming possible than recommendable with common SCMs like metakaolin and silica fume. With an increasing alumina content in blended binders, the aluminate reaction is preferred over the well-known pozzolanic reaction which is until now often primarily seen as silicate reaction only.
2. The favored AFm phase formation leads to an increasing volume of hydrate phases, resulting in higher density of the microstructure and pore structure refinement. Both effects contribute to an increased compressive strength of blended binders.

Environmentally friendly high strength concrete can be achieved with low water-binder ratio and a cement replacement of up to 30 wt.% by calcined mixed layer clays. Properties of concretes with 30 wt.% of calcined mixed layer clays or mixes of CT with metakaolin are comparable to concrete made with 10 wt.% of silica fume, even though necessary dosages of superplasticizer may exceed dosages recommended by producers.

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