Effects of Calcined Clay as Low Carbon Cementing Materials on the Properties of Concrete

K-C Thienel, N Beuntner
University of the German Federal Army, Germany

Lias delta clay was calcined in a rotary kiln. It was ground leading to a surface area of 5700 m²/g and a mean particle diameter of 12,5 µm. The calcined clay was tested as a Type II addition in combination with different cements (CEM I, CEM II and CEM III) and two strength classes (32,5 and 42,5). In most tests calcined clay replaced 20 % of the cement. Additionally some tests went up to a replacement of 60 %. The parameters investigated were fresh concrete properties including bleeding, compressive strength of mortar samples and concrete cubes, depth of carbonation, chloride ingress, sulphate resistance and shrinkage. The addition of the calcined clay improves the stability of the fresh mortar and concrete. Bleeding is reduced significantly. Initial strength develops at a lower rate until seven days for most mixes containing calcined clay. Beyond this age mixes with a 20 % replacement exceed the strength of the companion pure cement mixes. This holds especially for mixes containing CEM II where in some cases even a replacement of 40 % leads to higher strength values at 28 days and beyond. A comparison was made of the non-renewable energy necessary to produce the calcined clay and the energy needed to produce the different types of cement. It reveals an ecological advantage for concrete containing a binder blend of cement and calcined clay. The possible advantage depends to a large extend on the k-value which can be considered for the calcined clay and the type of cement to be substituted. The tests prove a reasonable range for the k-value between 0,6 and 1,0.

Karl-Christian Thienel is professor and head of the Institute for Building Materials, University of the German Federal Army Munich, Germany. He received his diploma and Dr.-degree in civil engineering from TU Braunschweig. He was Alexander-von-Humboldt "Feodor-Lynen" stipendiary at ACBM, Northwestern University, Evanston, IL, and head of R&D at Liapor GmbH & Co. KG. He is chairman of CEN/TC 177 and member of CEN/TC 154 SC5. His research interests include lightweight concrete, lightweight aggregate, impact and micro cracking.

Nancy Beuntner is researcher at the Institute for Building Materials, University of the German Federal Army Munich, Germany. She studied civil engineering, especially technology of building materials at Bauhaus University Weimar, Germany. She worked from 2002-2008 as product manager and sales engineer at Rohrdorfer Baustoffgruppe, Germany.

Keywords: CO_2, Calcined clay, Strength, Type II addition, Workability

INTRODUCTION

Cement is a significant source of anthropogenic release of carbon dioxide. The CO_2 derives mainly from kiln fuel combustion, transport and distribution and decarbonating of limestone. The latter source is fairly constant. Thus one procedure to lower the release of carbon dioxide is reducing the clinker content of the cement by shifting the production from CEM I to CEM II or CEM III cements. Another approach is replacing cement partially in concrete mix design by Type II additions like fly ash, granulated blast furnace slag or silica fume. An alternative to these afore mentioned options provides the use of calcined clay either as reactive part of the cement [1] or as Type II addition in concrete [2].

Metakaolin is known as a very reactive calcined clay and has been in focus of many investigations [e.g. 3, 4, 5, 6, 11]. Its widespread use in concrete is prohibited mostly by its high price compared to other Type II additions. Suitable and less expensive clay qualities consist rather of a mixture of clay minerals, which range between the clays used in the ceramic industry and those required for the cement production [1] than of single type clay minerals. Thus it is worth taking a closer look at mixed clays.

The reactivity of any calcined clay depends on both its mineral composition and the calcination temperature [e.g. 1, 3 - 11]. In most cases these investigations used homogenous clay samples that were calcined at constant temperature and for a period of several hours. Furthermore these clays were ground prior to calcination ensuring a complete reaction to take place. If coarse crushed clay is fed into a rotary kiln it is exposed to varying temperatures on its journey through the kiln combined with temperature gradients due to the size of the chunks after crushing and in addition a varying degree of oxidation. This paper focuses on the impact of such calcined clay on various mortar and concrete properties and its inherent ecological potential.

MATERIALS AND METHODS

The calcined clay used was produced at the Liapor expanded clay plant in Pautzfeld, Bavaria, Germany. The source material originates from a Lias delta layer and is taken directly from the Liapor clay pit. Its chemical and mineral composition is given in Table 1. Coarse crushing is the only mechanical processing before feeding the raw clay into the rotary kiln. Maximum particle size of the raw clay is 100 mm. The clay passes the kiln within 35 minutes while being exposed to temperatures below 950 °C. After cooling the calcined clay is ground by means of a roller mill to its final grading. Figure 1 shows the particle size distribution of the calcined clay, which was obtained by laser granulometry. The mean particle diameter of the ground calcined clay is 12,5 µm, the diameter on cumulative 10 % is 5,3 µm and the diameter on cumulative 90 % is 21,4 µm. The resulting Blaine-surface area is 5700 m^2/g. Density was determined in a pycnometer to 2,57 g/cm^3.

Eight different cements coming from four different producers were included in the tests. They comprise the most common cements in the eastern part of Bavaria, Germany. The two CEM II/A-LL 32,5 R used come from different manufactures.

Two series of mortar tests were conducted. Composition of mortars and sample preparation and determination of strength were done according to EN 196-1 [12]. In both mortar series the replacement of cement by calcined clay was done on a mass by mass basis. Consistency was measured on a mortar flow table according to ASTM C230 [13]. In addition mortar was used to investigate sulphate resistance as described in [14].

Table 1 Chemical and mineral composition of Lias delta clay in its original condition

CHEMICAL COMPOSITION		MINERAL COMPOSTION	
SiO_2	55 ± 2	Quartz	21 ± 2
Al_2O_3	25 ± 2	Illite	42 ± 2
Fe_2O_3	7 ± 2	Kaolinite	15 ± 2
CaO	4 ± 1	Chlorite	10 ± 2
K_2O	3.6 ± 0.5	Feldspar	5 ± 1
MgO	2.2 ± 0.2	Calcite	3 ± 1
TiO_2	1.2 ± 0.1		
SO_3	0.4 ± 0.1		
P_2O_5	0.3 ± 0.1		
NaO_2	0.1 ± 0.1		
MnO	0.1 ± 0.1		

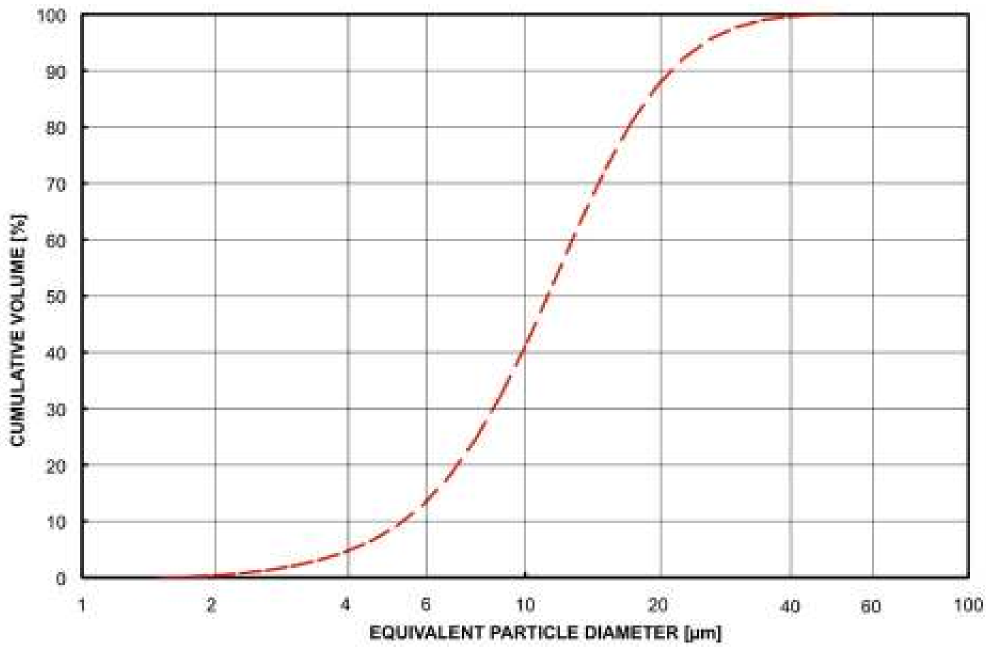

Figure 1 Particle size distribution of calcined clay by laser granulometry

The mortar tests were supplemented by concrete tests. The actual mix designs correspond “Concrete No 1a” (340 kg/m^3 CEM I 42,5R, w/c = 0,5) and “Concrete No 1b” (320 kg/m^3 CEM II/A-LL 32,5R, w/c = 0,6) [15]. The replacement rate was 20 % for “Concrete No 1a” and 25 % for the second one, which is identical to “Concrete No 2b” in [15]. The calcareous aggregate used originates from a local Munich pit and has a maximum size of 16 mm. Concrete compressive strength was tested on 15-cm-cubes. These tests should confirm the findings of the mortar tests. Additionally these concretes were taken to measure bleeding of fresh concrete using the so call “bucket-test” [16] and shrinkage at 20/65 on 150/300 mm cylinders. Depth of carbonation was determined at 14, 28, 56, 90 and 181 days. After demoulding the concretes were immersed in water until an age of 7 days. Afterwards they were stored in normal climate 20/65 [17]. Dry drilling was used the measure the chloride ingress after immersion in 3 % sodium chloride solution for 90 days. The effect of the calcined clay up on sulphate resistance was investigated after storing flat mortar prisms (40/10/160 mm^3) at 8 °C in a 4,4 % sodium sulphate solution and subsequent drying [14].

TEST RESULTS AND DISCUSSION

Mortar Tests

The first mortar series (Table 2) compared the effect of a 20 % replacement of five different cements upon the development of compressive strength R_c and flexural strength R_f resp. The second series (Table 3) investigated the effect of different replacement ratios (20 %, 40 % and 60 %) on compressive strength R_c.

Table 2 Data of first mortar series

CEMENT TYPE		CEM I 42,5R		CEM II/A-LL 32,5R		CEM II/B-S 42,5N		CEM II/B-P 32,5N		CEM III/A 32,5 N - LH/NA	
Cement content	% by mass	100	80	100	80	100	80	100	80	100	80
Spread	cm	14,8	14,6	16,2	14,8	15,9	14,1	11,8	11,5	14,1	13,6
ρ_f	kg/dm^3	2,28	2,24	2,19	2,26	2,23	2,26	2,24	2,25	2,26	2,23
$R_{f,1d}$	MPa	2,4	1,9	2,6	2,1	-	-	2,8	1,9	1,6	1,3
$R_{f,7d}$	MPa	7,2	6,4	5,7	4,9	5,5	5,5	6,3	5,5	6,7	5,8
$R_{f,28d}$	MPa	8,1	8,5	6,8	7,5	7,7	8,4	6,6	7,4	8,4	8,2
$R_{f,56d}$	MPa	9,1	9,5	8,0	7,2	7,8	8,4	8,9	8,2	6,0	4,4
$R_{f,90d}$	MPa	10,8	8,6	9,6	9,2	8,2	8,8	9,6	9,4	8,3	5,5
$R_{f,180d}$	MPa	10,9	9,1	8,8	9,3	-	-	8,5	9,3	10,3	7,4
$R_{f,365d}$	MPa	7,9	8,0	7,5	7,9	-	-	7,4	8,0	8,8	6,5
$R_{c,1d}$	MPa	14	11	5	5	-	-	15	12	8	7
$R_{c,7d}$	MPa	51	43	37	34	34	37	42	35	37	32
$R_{c,28d}$	MPa	66	65	48	54	54	60	52	52	44	48
$R_{c,56d}$	MPa	80	79	60	67	62	67	68	65	60	54
$R_{c,90d}$	MPa	81	80	60	68	65	69	69	66	73	60
$R_{c,180d}$	MPa	80	80	59	69	-	-	68	66	74	63
$R_{c,365d}$	MPa	80	83	59	71	-	-	70	69	73	64

Table 3 Data of second mortar series

CEMENT TYPE		CEM II/A-LL 32,5R				CEM II/B-S 32,5R			CEM II/B-M (S-LL) 32,5R		
Cement content	% by mass	100	80	60	40	100	80	60	100	80	60
Spread	cm	17,3	16,7	14,5	12,9	17,5	15,7	14,2	17,0	14,9	14,1
ρ_f	kg/dm^3	2,23	2,28	2,26	2,23	2,24	2,23	2,21	2,23	2,28	2,27
$R_{c,7d}$	MPa	39	35	24	15	30	28	22	38	37	28
$R_{c,28d}$	MPa	49	50	48	36	41	50	44	48	54	49
$R_{c,56d}$	MPa	57	63	59	51	56	59	54	62	72	66
$R_{c,90d}$	MPa	66	75	75	63	58	70	63	57	72	66

Fresh Mortar and Concrete Properties

The addition of calcined changes already the fresh mortar properties. Workability of the three reference mortars differs hardly in the second test series (Table 3). An increasing content of calcined clay reduces the spread continuously. Differences between the three cements are significant at a replacement level of 20 %, but disappear at a level of 40 % replacement. Initial spread is smaller for the first mortar series. Again the replacement of 20 % cement by calcined clay reduced the spread (Table 2). The observed stiffening effect is due to a higher water demand of the calcined clay compared to the cements. Its stems mainly from the higher surface area provided by the calcined clay compared to the cements used. Consequently, the replacement of 20 % cement by calcined clay reduces bleeding of concrete significantly (Figure 2). A maximum value of 3 kg/m^3 is considered suitable for structural concrete. Below 2 kg/m^3 the concrete can be used for trafficked elements and below 1 kg/m^3 the mix is applicable for exposed concrete [16]. The improved water retention of mixes containing calcined clay is due to its higher water demand compared to the cements used. This effect may be attributed mainly to its higher surface area and partially to a different surface charge.

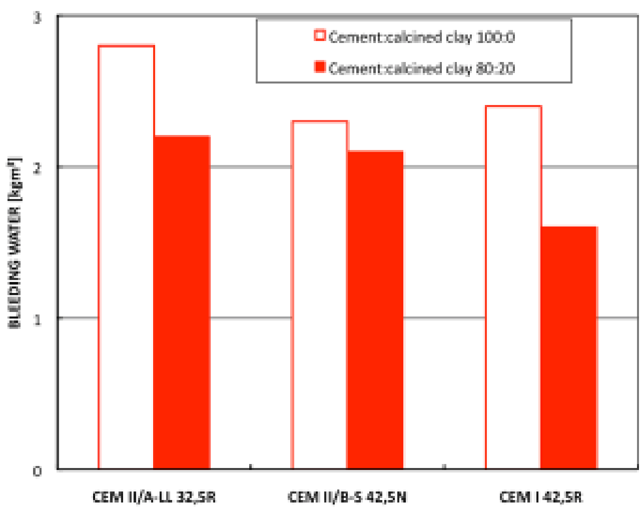

Figure 2 Effect of calcined clay content on bleeding of fresh concrete

Compressive Strength

The effect of a 20 % replacement on compressive strength was tested for all 8 cements. Results are given in Figure 3 as activity index. Thus strength measured with the mixes containing calcined clay can be compared directly with their references at each testing age. At the same time the potential can be evaluated of the combination of the calcined clay when used with different cement types. At a 20 % replacement level an activity index of 80 % stands for inert material while at 100 % the mixed binder can be denoted as efficient as the corresponding pure cement.

The activity index changes with mortar age. At one day the calcined clay acts mostly as inert material. A higher activity value at this age is rather due to the low strength of the reference mix (Table 2) and normal test scatter than a significant effect. At seven days differences between cement types show up. For CEM I, CEM II containing natural puzzolan and CEM III the effect of calcined clay becomes visible but is not very pronounced. On the other hand CEM II cements containing ground blast furnace slag approach or exceed the strength of the reference mixes at this age. The two CEM II/A-LL cements are in between the two other groups. At 28 days mortars containing 20 % calcined clay reach or exceed significantly the compressive strength of their corresponding references. CEM I and CEM II/B-P still represent the lower end while the others show no clear order. This does not change with increasing age except for CEM III/A. Its activity index decreases and levels off slightly above 80 %. This decline in due to a pronounced increase in compressive strength of the reference while the strength of the mix containing calcined clay remains constant (Table 2).

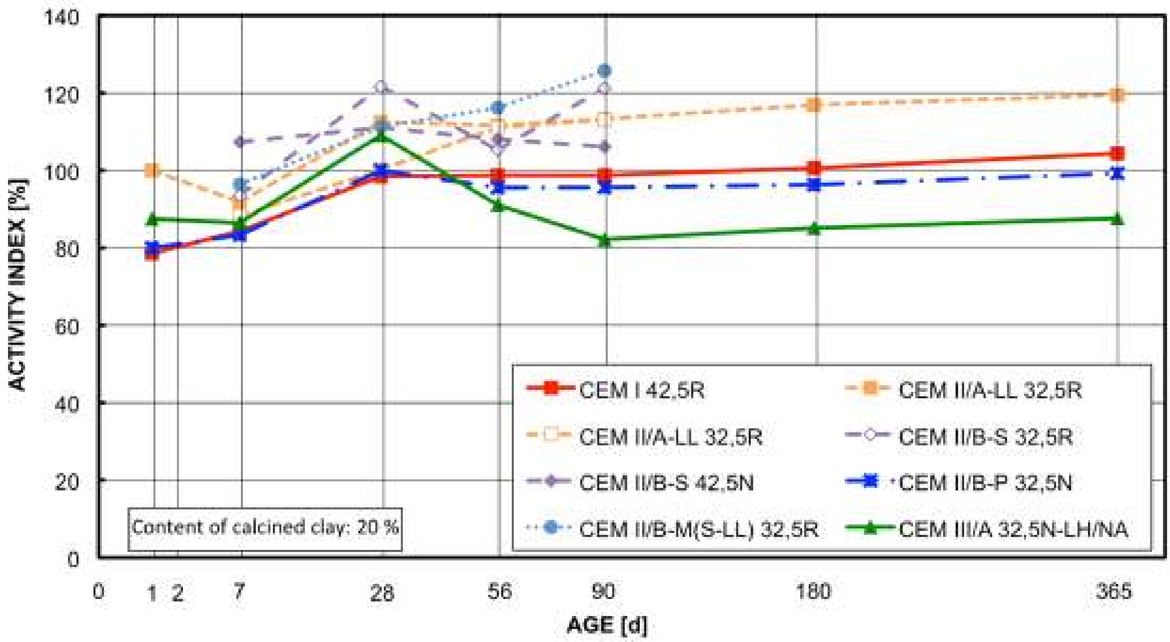

Figure 3 Development of the activity index based on compressive strength tests for a replacement of 20 % cement by calcined clay

Two strength classes (32,5 and 42,5) of CEM II/B-S were included in the tests. The results reveal that both strength classes benefit similarly from the addition of calcined clay.

A higher content of calcined clay does not change the basic observations (Figure 4). At 7 days the impact of the calcined clay is small for CEM II/A-LL and more pronounced for the two other cements. At 28 days and beyond all three combinations of cement and 40 % calcined clay reach or exceed the strength of their references.

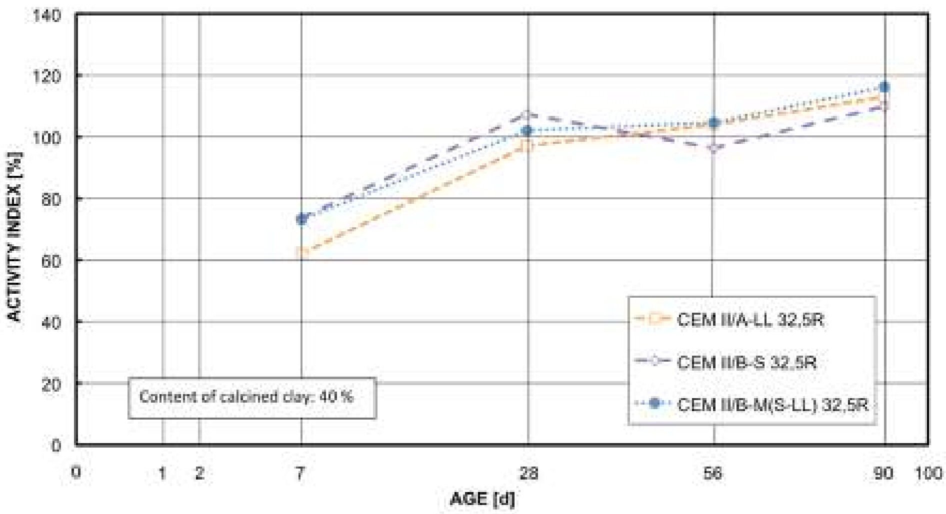

Figure 4 Development of the activity index based on compressive strength tests for a replacement of 40 % cement by calcined clay

Four cements were tested with a replacement of up to 60 % (Table 3). The activity index at an age of 28 days is given in Figure 5. It exhibits a most efficient replacement ratio in the range of 15 % to 25 %. Besides it proves that a one-by-one replacement of cement by calcined clay can be accomplished for the three CEM II cements up to a content of calcined clay of 40 % without jeopardizing strength.

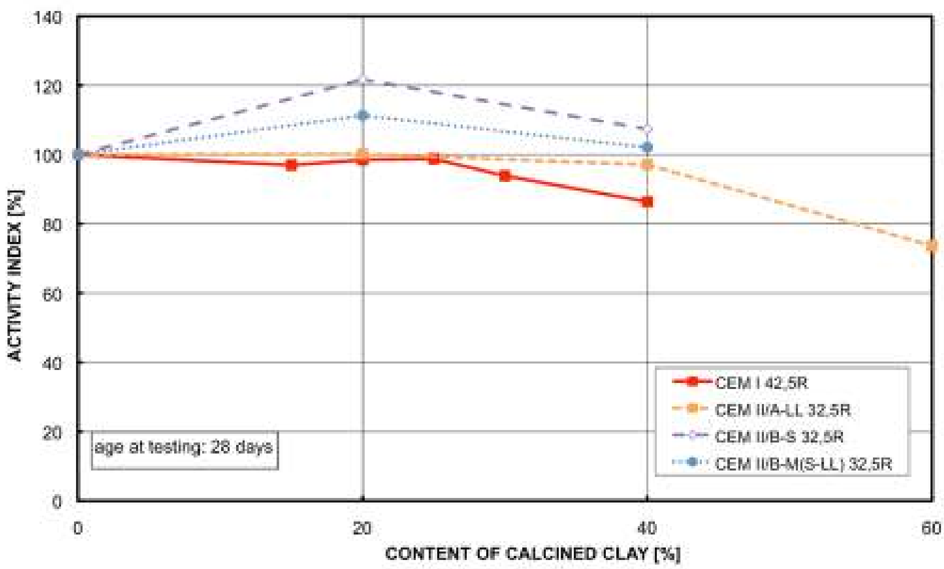

Figure 5 Effect of calcined clay content on the activity index at 28 days based on compressive strength tests

The general findings based on mortar tests are confirmed in concrete tests using two of the cements (Figure 6). At seven days no effect is visible yet. But, the impact of the calcined clay seems to be even more pronounced at 28 days and beyond.

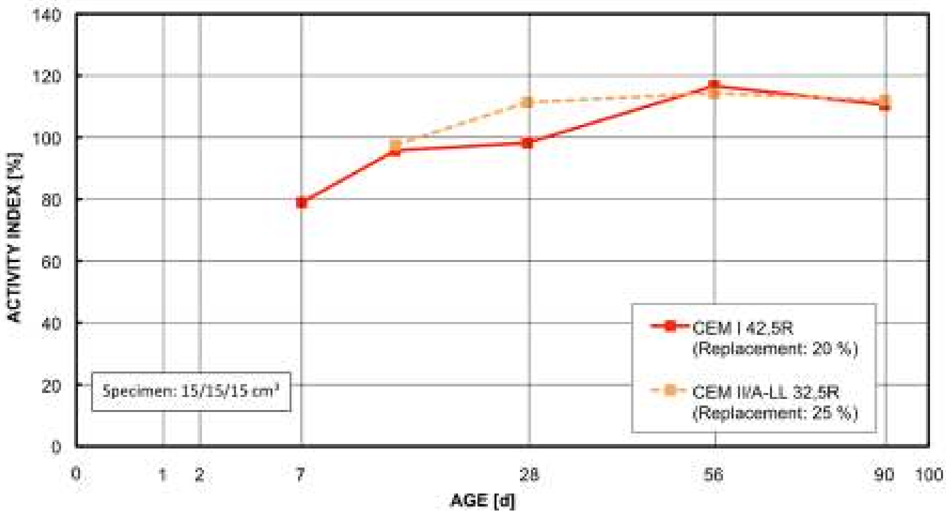

Figure 6 Development of the activity index of concrete based on compressive strength

The impact of the calcined clay on compressive strength can be attribute partially to its higher water demand. Thus less water is available for the cement. Secondly the calcined clay provides alkali soluble silicon and aluminium ions, which contribute to its puzzolanic reactivity and will form additional calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) phases [6 - 11]. Obviously this process of releasing the ions is faster than the similar process that takes place when fly ash is used as Type II addition [18]. Due to the higher release rate calcined clay starts being effective as early as seven days.

Flexural Tensile Strength

The use of the calcined clay is less beneficial on the flexural tensile strength. Especially CEM I and CEM III seem to exhibit no or even an detrimental effect compared to the reference mixes (Figure 7). This effect visible on the activity index is more due to an increased flexural strength of the reference mixes rather than a strength reduction of the mixes containing calcined clay (see Table 2). The overall picture is similar to the one seen for the compressive strength results. The calcined clay is more effective in combination with CEM II than with CEM I or CEM III.

Shrinkage

The impact of calcined clay on shrinkage was tested on two concretes. A 20 % replacement of cement by calcined clay reduced slightly shrinkage in both cases beyond 90 days. Again the effect is more obvious in case of CEM II/A-LL 32,5R.

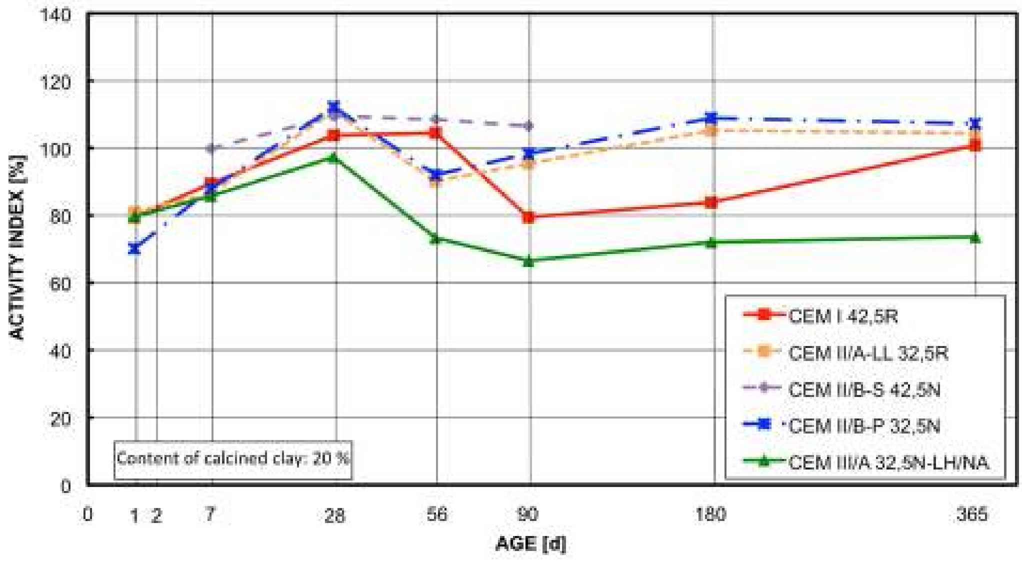

Figure 7 Development of the activity index based on flexural tensile strength tests for a replacement of 20 % cement by calcined clay

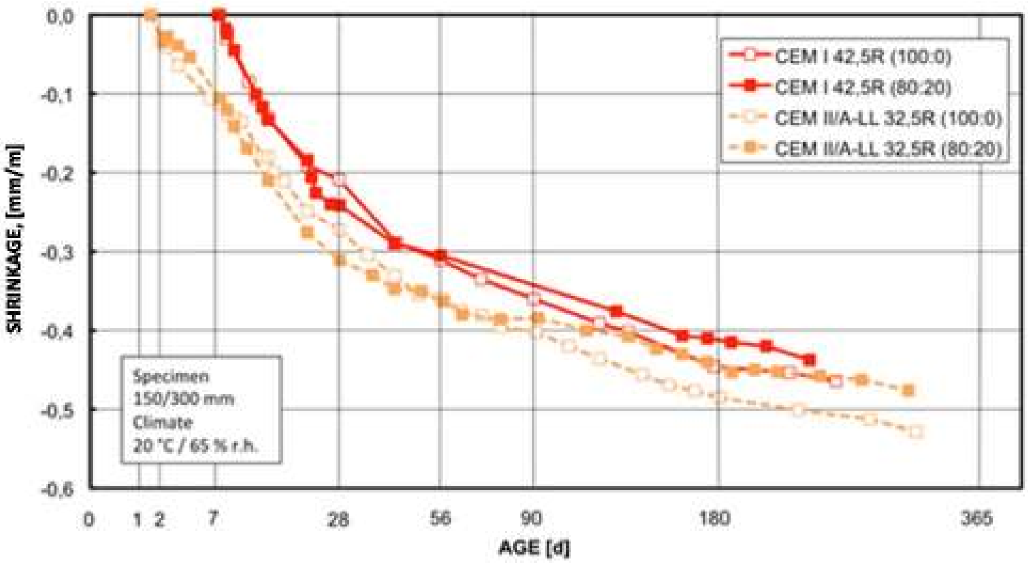

Figure 8 Shrinkage of concretes using cement only or a replacement of 20 % of these cements by calcined clay

Durability

Depth of carbonation tends to be slightly higher for concrete containing 25 % calcined clay (Figure 9). Considering the normal scatter of these measurements the difference is rather insignificant.

The ingress of chlorides was measured on concrete made with CEM I 42,5R. The concrete containing 20 % calcined clay exhibits hardly any difference compared to the reference concrete (Figure 10).

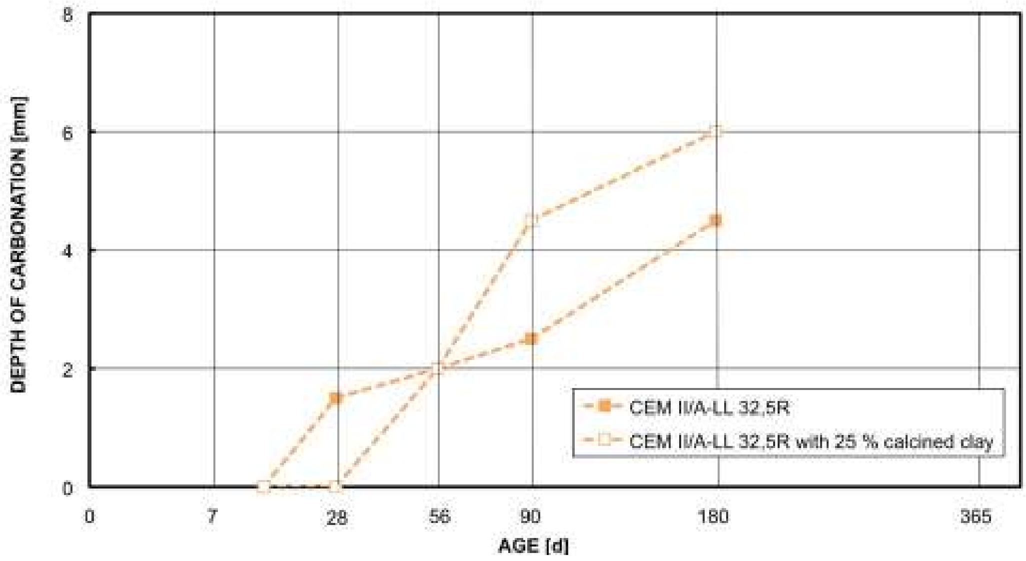

Figure 9 Depth of carbonation of concrete made with cement only or with a replacement of 25 % cement by calcined clay

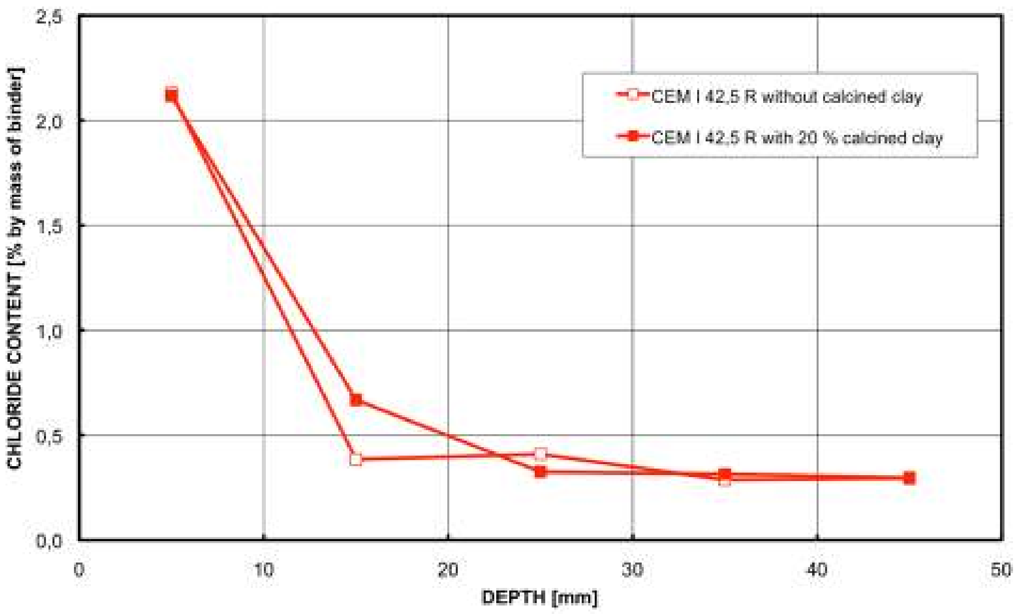

Figure 10 Chloride ingress in concrete made with cement only or with a replacement of 20 % cement by calcined clay

Length change due to sulphur attack increases at a slightly lower rate compared to the reference (Figure 11). Nevertheless the replacement of 20 % CEM I 42,5 R by calcined clay is not sufficient to limit the expansion to 0,5 mm/m at 56 days as required for a sulphate resistant binder [14].

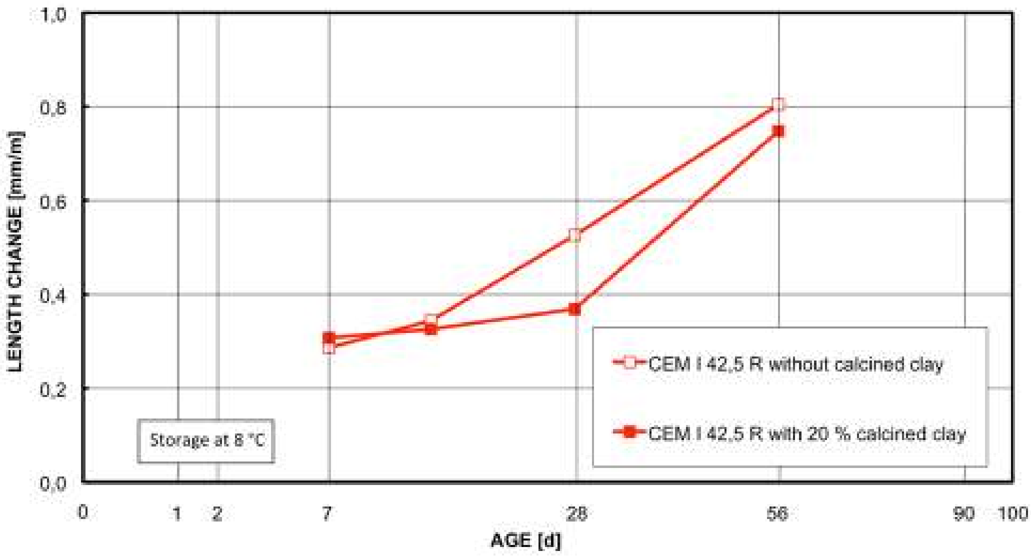

Figure 11 Length change due to sulphur attack of concrete made with cement only or with a replacement of 20 % cement by calcined clay

ECOLOGICAL ASPECTS

The production of calcined clay consumes less energy than the production of cement clinker. Information is given in Table 3 about the non-renewable primary energy needed for the different cement types and the calcined clay used. The overall average CO_2 release caused by clinker production in Germany adds up to 0,78 ton CO_2 per ton of Portland cement clinker [19]. Decarbonating the carbon content in the Lias delta clay yields 0,022 ton CO_2 per ton of calcined clay.

Table 3 Clinker content and non-renewable primary energy consumption of binders [20, 21, 22]

	CLINKER CONTENT [%]	NON-RENEWABLE PRIMARY ENERGY (MEAN VALUE) [MJ/t]
CEM I	95 - 100	4355
CEM II/B-M	65 - 79	3220
CEM III/A	35 - 64	2156
Calcined clay	-	1731

The possible quantity of non-renewable primary energy and CO_2 to be saved per m^3 of concrete due to replacing cement by calcined clay depends on the type of cement and the k-value considered for the calcined clay. The k-value approach considers a cementing equivalence value to Type II additions. Typical values for common Type II additions are 0,4 (fly ashes) [23], 0,6 (blast furnace slag) [24] and 1,0 (silica fume) [23]. Different k-values presuppose different quantities of calcined clay needed for replacing cement, which in turn has a direct impact on the ecological balance. The result can be compared best, if a typical ready-mix concrete is taken as an example. A first estimate shall start with replacing 50 kg cement per m^3 of concrete. This quantity corresponds to the difference between the minimum cement content (320 kg/m^3) and the minimum cement content if Type II additions are considered (270 kg/m^3) [23]. Such concrete is suitable for exposure classes: XD2, XD3, XF2, XF3, XF4, XA2, XA3, XM2 und XM3 [23]. The production of a ready-mix concrete consumes typically 1350 MJ/m^3 to 1792 MJ/m^3 non-renewable primary energy and 0,124 to 0,243 t_{CO_2}/m^3 [15].

The comparison given in Table 4 highlights the saving potential with respect to non-renewable primary energy and CO_2 due to replacing cement by calcined clay. The quantities of calcined clay given in the heading of Table 4 are the replacements needed for 50 kg/m^3 of cement for the corresponding k-value. Even a low k-value of 0,4 will reduce the CO_2 emission by up to 14 %, but up to 12 % more energy will be required. Taking into account the full potential of the calcined clay used in this investigation a k-value of 1,0 is not far from being realistic. Thus a CO_2 reduction can be accomplished close to 15 % combined with savings in non-renewable primary energy of 6 to 8 %. This holds for a partial replacement of CEM I. Benefits will be smaller in case of CEM III.

Table 4 Possible savings per m^3 of concrete in non-renewable primary energy and CO_2 due to replacing cement by calcined clay

	K-VALUE: 0,4 (≙ 125 kg/m^3)		K-VALUE: 0,6 (≙ 80 kg/m^3)		K-VALUE: 1,0 (≙ 50 kg/m^3)	
	Energy [MJ/m^3]	CO_2 [t/m^3]	Energy [MJ/m^3]	CO_2 [t/m^3]	Energy [MJ/m^3]	CO_2 [t/m^3]
CEM I	- 49,8	0,035	46,6	0,036	110,8	0,037
CEM II/B-M	-106,5	0,025	-10,2	0,026	54,0	0,027
CEM III/A	-159,7	0,017	-63,4	0,018	0,8	0,018

CONCLUSIONS

Initial strength develops at a lower rate until seven days for most mixes containing calcined clay. At higher ages mixes with a 20 to 25 % replacement reach and exceed significantly the strength of the companion pure cement mixes. This holds especially for mixes containing CEM II where in some cases even a replacement of 40 % led to higher strength values beyond 28 days. The efficiency of the calcined clay as a Type II addition ranges in between granulated blast furnace slag and metakaolin. The inclusion of cement by calcined clay reduces consistency, bleeding and shrinkage. The effect on durability aspects is negligible. Besides the positive impact on strength the replacement of cement by calcined clay will yield ecological benefits. Considering a k-value close to 1,0 will help saving non-renewable primary energy and reduce the average CO_2 release of concretes utilizing this calcined clay as Type II addition.

ACKNOWLEDGEMENTS

The authors like to thank Liapor GmbH & Co. KG for the supply of the calcined clay.

REFERENCES

1. VEREIN DEUTSCHER ZEMENTWERKE E.V. (VDZ). Clay as pozzolanic main constituent of cement, VDZ-Activity Report 2007 – 2009, pp 51-52.

2. SCHRENK, J, WENDA, R. Improvement of the properties of cementitious systems. Application of clay powder containing metakaolin, BFT International, No. 4, 2006, pp 24-36.

3. JONES, R T. Metakaolin as a pozzolanic addition to concrete, Structure and Performance of Concrete, Eds. J Bensted and P Barnes, 2nd Edition, 2002, pp 372-397.

4. AMBROISE, J, MARTIN-CALLE, S, PERA, J. Pozzolanic behaviour of thermally activated kaolin. Fly Ash, Silica Fume, Slag and natural Puzzolans in Concrete, Ed. V M Malhotra, ACI SP132-40, 1992, pp 731-748.

5. WILD, S, KHATIB, J, M, JONES, A. Relative strength, pozzolanic activity and cement hydration in superplasticised metakaolin concrete. Cement and Concrete Research, Vol. 26, No. 10, 1996, pp 1537-1544.

6. HE, C, MAKOVICKY, E, OSBÆK, B. Thermal stability and pozzolanic activity of calcined kaolin. Applied Clay Science, Vol. 9, No. 3, 1994, pp 165–187.

7. HE, C, MAKOVICKY, E, OSBÆK, B. Thermal stability and pozzolanic activity of calcined Illite. Applied Clay Science, Vol. 9, No. 5, 1995, pp 337–354.

8. HE, C, MAKOVICKY, E, OSBÆK, B. Thermal stability and pozzolanic activity of sepiolite. Applied Clay Science, Vol. 10, 1996, pp 337–349.

9. HE, C, MAKOVICKY, E, OSBÆK, B. Thermal stability and pozzolanic activity of Na- and Ca-montmorillonite. Applied Clay Science, Vol. 10, 1996, pp 351–368.

10. HE, C, MAKOVICKY, E, OSBÆK, B. Thermal stability and pozzolanic activity of raw and calcined mixed-layer mica/smectite. Applied Clay Science, Vol. 17, 2000, pp 141–161.

11. FERNANDEZ, R, MARTRENA, F, SCRIVENER, K, L. The origin of the pozzolanic activity of calcined clay minerals: A comparison between kaolinite, illite and montmorillonite. Cement and Concrete Research, Vol 41, No. 1, 2011, pp 113-122.

12. EN 196-1. Methods of testing cement - Part 1. Determination of strength, 2005.

13. ASTM C230M – 08. Standard Specification for Flow Table for Use in Tests of Hydraulic Cement, 2008.

14. WITTEKIND, W. Sulfatbeständige Zemente und ihre Prüfung (in German) (Sulfate resistant cements and their testing). Zement-Kalk-Gips Vol. 13, No. 2, 1960, pp 565-572

15. European Organisation for Technical Approvals EOTA. CUAP Natural calcined pozzolana as Type II addition. 2005, p 17.

16. DEUTSCHER BETON- UND BAUTECHNIK-VEREIN E. V. Special testing methods for fresh concrete (in German), DBV-Merkblatt, 2007, p 24.

17. RILEM RECOMMENDATIONS. CPC-18 Measurement of hardened concrete carbonation depth, Materials and Structures, Vol. 21, No. 6, 1988, pp 453-455.

18. SYBERTZ, F. Beurteilung der Wirksamkeit von Steinkohlenflugaschen als Betonzusatzstoff (in German) Assessment of the Effectiveness of Coal Fly Ash as a Concrete Addition, Beuth Verlag, 1993, p 111.

19. MCKINSEY&COMPANY. Änderung der europäischen Richtlinie zum Emissionshandel: Auswirkungen auf die deutsche Zementindustrie (in German) (Changes in the European guideline for emission trading: Impact on the German cement industry), Düsseldorf, 2008, p 33.

20. DIN 197-1. Cement - Part 1. Composition, specifications and conformity criteria for common cements, 2004.

21. BUNDESVERBAND LEICHTBETONZUSCHLAG (BLZ). Ganzheitliche Bilanzierung von Blähton und Blähschiefer (in German) Holistic balance study of expanded clay and expanded shale (internal document), 1995.

22. EYERER, P, REINHARDT, H.-W. Ökologische Bilanzierung von Baustoffen und Gebäuden: Wege zur ganzheitlichen Bilanzierung (in German) (Ecological Balance study of building materials and buildings: Ways to holistic balancing). Birkhäuser, Berlin, 2000, p 233.

23. DIN 1045-2. Tragwerke aus Beton, Stahlbeton und Spannbeton – Teil 2: Beton – Festlegung, Eigenschaften, Herstellung und Konformität – Anwendungsregeln zu DIN EN 206-1 (in German) (Concrete, reinforced and prestressed concrete structures – Part 2: Concrete –Specification, properties, production and conformity – Application rules for DIN EN 206-1), 2008, p 62.

24. EHRENBERG, A. Hüttensandmehl als Betonzusatzstoff – Aktuelle Situation in Deutschland und Europa (in German) (Ground blast furnace slag as concrete addtion – Actual situation in Germany and Europe). Beton-Information No. 3/4, 2010, pp 48-63.