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CHLORIDE-RELATED DURABILITY PROPERTIES OF MORTARS CONTAINING CALCINED CLAY

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Abstract

There is a need to decarbonise cement and concrete, and the use of supplementary cementitious materials is an efficient means of achieving this. But, supplies of traditional SCMs are not sufficient to achieve meaningful decarbonisation. Calcined clays have shown promise, but more work is required to understand their performance when blended at different levels with different cement types. Here cement blends containing calcined clay at 20 and 30% cement replacement with both CEM I and CEM II/A-L were evaluated. These blends have been tested in terms of compressive strength development, bulk conductivity, and chloride migration. The results indicate that incorporating calcined clay generally refines the pore structure, leading to lower conductivity and enhanced resistance to chloride penetration, although early-age strength development may be affected. The findings provide valuable insights into the potential of using calcined clays with CEM I and CEM II/A-L to improve the durability of concrete structures in chloride-rich environments.

Keywords: Calcined Clay, Durability, Bulk Conductivity, Diffusion, Migration, Sorptivity.

1. INTRODUCTION

Chloride-induced corrosion of steel reinforcement is a major cause of deterioration in reinforced concrete structures, particularly in marine environments and those exposed to de-icing salts [1, 2]. The penetration of chloride ions into concrete depends on several factors, including the permeability of the concrete, the chloride binding potential of the binder, the surface chloride concentration, and the temperature [3]. Supplementary cementitious materials (SCMs) are widely used to enhance the durability of concrete by modifying the pore structure which limits the diffusion of chloride ions [4, 5].

Calcined clays (CCs) have emerged as promising SCMs due to their availability and pozzolanic reactivity [6, 7]. Calcined clays react with calcium hydroxide (CH), a byproduct of cement hydration, to form additional calcium silicate hydrate (C-S-H) gel, which refines the pore structure and reduces the permeability of concrete [8, 9]. This pozzolanic reaction can lead to improved resistance to chloride ingress and enhanced long-term durability [10]. This study evaluates the influence of calcined clays on compressive strength, bulk conductivity, and chloride migration in mortars incorporating CEM I and CEM II/A-L with various replacement levels (30% and 20%) of calcined clays with different kaolinite contents. The results are analysed to assess the trend in chloride resistance and its relation to meta-kaolinite content of the calcined clays.

2. METHODOLOGY

Elemental composition was obtained by XRF, while the mineralogical composition was provided by the cement manufacturer for the cements and determined by XRD for the clays. Tables 1 and 2 provide the chemical and mineralogical composition of the materials used in the study. Five binders, as shown in Table 3, including CEM I 52.2N and Portland limestone cement i.e., CEM II/A-L 52.2N (BS EN 197-1 compliant, and found to contain 12.5% limestone) and three distinct calcined clay-based binder formulations produced with 30% and 20% clay replacement of cement, were used to investigate the effects of binder type on microstructure, hydration, and resistance to chloride ingress. The clays contained 70% and 50% kaolinite with R3 reactivity values of 700 and 480 J/gram of SCM respectively. Clay sources analysed pre-and post-calcination for CC1 and only post calcination for CC2 as it is commercially sourced calcined clay. Non-negligible LOI value can be traced for CC2 which could be from traces of carbonate impurities or decomposition of any other minerals. After calcination, the kaolinite was transformed into amorphous Metakaolinite, which is known to be pozzolanic, alongside minor amounts of residual quartz and anatase as reported in [11].

Table 1 : Chemical composition of all the cementitious materials, which will be determined by using a calibrated x-ray fluorescence equipment

Chemical Composition	CEM I (wt.%)	CEM II/A-L (wt.%)	CC1 (wt.%)	CC2 (wt.%)
SiO ₂	21.82	18.2	57.94	69.34
Al ₂ O ₃	3.89	4.69	33.59	22.59
Fe ₂ O ₃	1.33	2.95	4.07	2.89
CaO	64.78	64.64	0.22	0.81
MgO	0.76	1.04	0.10	0.27
SO ₃	3.57	2.80	0.01	0.08
K ₂ O	0.67	0.62	0.81	0.28
Na ₂ O	0.30	0.26	0.19	0.37
TiO ₂	0.17	-	1.46	1.24
Traces	0.65	4.81	0.40	0.26
Loss on Ignition (LOI)	2.20	N/A	1.30	1.90

Table 2 : Major mineralogical phases of CEM I, CEM II/A-L and calcined clays (wt%)

Cement mineralogical phases	CEM I (wt.%)	CEM II/A-L (wt.%)	Clay mineralogical phases	CC1 (wt.%)	CC2 (wt.%)
C ₃ S	56.97	54.3	Quartz	3.08	33.01
C ₂ S	20.36	13.5	Muscovite	6.66	2.04
C ₃ A	7.78	9.0	Amorphous content	86.97	56.83
C ₄ AF	2.04	6.4	Other minor phases	3.29	8.12
Anhydrite+ Gypsum +Bassanite	6.38	3.5			
Calcite	2.97	12.5			
Other minor phases	3.50	1.00			

Compressive strength (EN 196-1) and bulk conductivity (RILEM TC 298-EBD test protocol) were tested after hydration for 3, 7, 28, 56 days. Chloride migration was conducted as per NT Build 492 after curing for 28 and 90 days. The five binder combinations that were considered:

Table 3 : Binder combination of materials used

Binder Combination	Composition Details
CEM I	Portland Cement (52.2N)
CEM II/A-L	Portland Cement (52.2N)
CEM I + 30% CC1	70% CEM I + 30% CC1
CEM II/A-L + 30% CC1	70% CEM II/A-L + 30% CC1
CEM II/A-L + 20% CC1	80% CEM II/A-L + 20% CC1
CEM I + 30% CC2	70% CEM I + 30% CC2
CEM II/A-L + 30% CC2	70% CEM II/A-L + 30% CC2
CEM II/A-L + 20% CC2	80% CEM II/A-L + 20% CC2

Note: CC1- Commercial Calcined Clay- >70% kaolinite content, CC2- Commercial Calcined Clay - ~50% kaolinite content

3. RESULTS

3.1 Compressive strength

Figure 1 shows that the compressive strength development followed a consistent trend across all mixtures. CEM I and CEM II/A-L exhibited high early-age strengths at 3 days, respectively. The inclusion of calcined clays reduced early strengths due to dilution but enhanced long-term strength, particularly with CC1 (high kaolinite content), reaching 68.05 MPa when blended at 30% with CEM I at 56 days. Strength development in calcined clay-blended systems is related to the kaolinite content of the source clay. Higher kaolinite contents lead to a more reactive SCM, increased pozzolanicity and so to densification of the microstructure. Similar trends have been observed in previous studies, where increased pozzolanic activity enhances long-term performance [12,13].

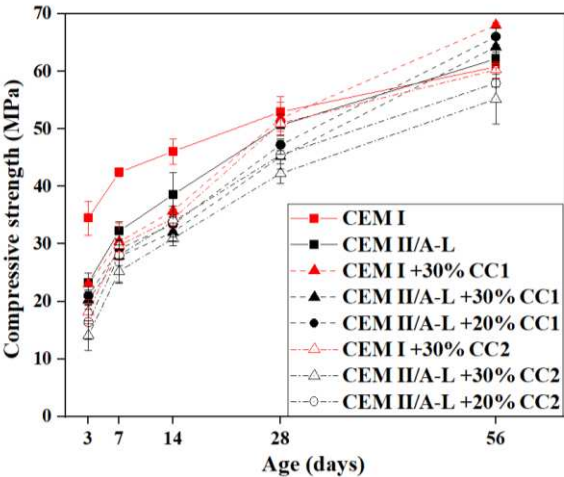


Figure 1 : Compressive strength development in cement mortar up to 56 days.

3.2 Bulk conductivity

The bulk conductivity results are shown in Figure 2. All samples showed a reduction in conductivity over time, as hydration progressed. The pure CEM I and CEM II/A-L samples showed a rapid decrease, reflecting their more rapid hydration. However, the clay blends all showed significantly lower conductivity, diminishing further with prolonged hydration. Comparing the blends, those containing the less reactive CC2 showed higher conductivity than those containing the more reactive clay. The reduction in conductivity with prolonged curing was also more gradual. This is a reflection of the continuous hydration of calcined clays and reflects compressive strength development [13].

While performance of the blends containing the more reactive CC1 were quite similar, there was quite a difference between the three mortars prepared with CC2. This could be because of a reduced synergistic interaction between limestone and kaolinite for lower kaolinite contents [14].

These findings align with literature reporting similar reductions in conductivity with calcined clay incorporation due to the refinement of pore structure [15]. Increased replacement levels generally led to higher conductivity, while the synergy between clay and limestone reduced conductivity.

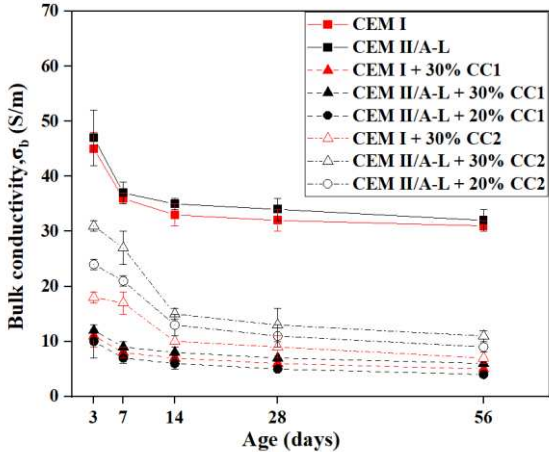


Figure 2: Bulk conductivity development in mortars to 56 days.

3.3 Chloride migration test

The chloride migration coefficients (Dnssm) are presented in Figure 3. The chloride migration results show that incorporating calcined clays significantly improved resistance to chloride ingress compared to CEM I and CEM II/A-L. Blends with 30% calcined clay, particularly CEM II/A-L + 30% CC1 and CEM II/A-L + 30% CC2, showed the greatest reductions in chloride migration, indicating enhanced durability. CC1 performed slightly better than CC2 overall, due to its higher reactivity. These findings align with literature highlighting the benefits of calcined clay-limestone blends (LC³ systems) in refining pore structure and reducing permeability, contributing to more durable and sustainable cementitious materials [11,16].

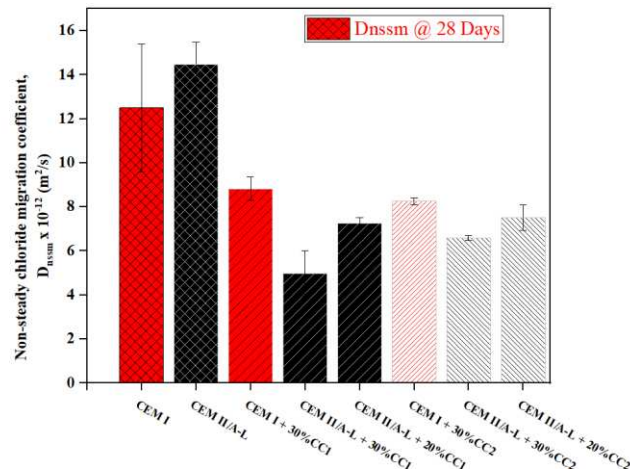


Figure 3: Chloride Migration for Mortars at 28 days.

4. CONCLUSIONS

This study investigated the influence of calcined clay as a partial cement replacement on the mechanical and durability characteristics of cementitious mortar, with a specific focus on chloride transport related properties.

1. The incorporation of calcined clay reduces early-age compressive strength up to 7 days but enhances long-term strength development. Similar strength development was observed for calcined clay blends of CEM I and CEM II/A-L .
2. Blending cement with calcined clay significantly reduces the bulk conductivity of mortars, indicating a refined pore structure and reduced ionic permeability. The extent of reduction varied at early ages with kaolinite content of the calcined clay source. CC1 with 70% kaolinite content showed significant reduction compared to CC2 containing 50% kaolinite content.
3. The addition of calcined clay substantially reduces the chloride migration coefficient, demonstrating improved resistance to chloride ingress, after curing for 28 days, i.e. in line with standard tests for assessing the durability of cementitious materials.

The results suggest that calcined clay is an effective SCM for enhancing the durability of cementitious materials used in chloride-rich environments. Ongoing work is focused on analysing concrete properties and the impact of calcined clay addition on bulk diffusion, wetting and drying resistance electrochemical performance in chloride environments. Also, future works will be done on the assessment of carbonation resistance and its potential impact on the corrosion of embedded steel reinforcement which tends to reduce with SCM addition.

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