CHLORIDE DIFFUSION RESISTANCE OF LIMESTONE CALCINED CLAY CEMENT (LC3) CONCRETE BASED ON CALCINED CLAY REACTIVITY

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Abstract:

This study investigated the chloride diffusion resistance of limestone calcined clay cement (LC3) concrete depending on the calcined clay reactivity. Two calcined clays with different reactivity were used to fabricate LC3 concretes. The replacement rate of calcined clay and limestone in binder was adjusted based on the reactivity in order to achieve similar compressive strength after 28 days of curing. The chloride diffusion resistance of LC3 concretes was evaluated using the bulk diffusion test protocol according to NT BUILD 443 (or ASTM C1556). Both LC3 concretes outperformed the reference general purpose cement concrete with significantly lower chloride diffusion coefficients. The chloride diffusion coefficients of the two LC3 concretes were similar despite the different replacement rates of calcined clay and limestone due to different calcined clay's reactivity. This result indicates that LC3 concrete chloride diffusion resistance is only marginally dependent on the type of calcined clay used if similar compressive strength can be obtained within the LC3 concretes by using an optimum replacement rate.

Keywords: calcined clay; LC3; limestone; low-carbon concrete; chloride diffusion; durability

INTRODUCTION

Limestone calcined clay cement (LC3) has been an emerging alternative for ordinary Portland cement (OPC) in an effort to reduce the CO_2 emission generated from cement production [1]. LC3 has demonstrated advantages in industry adoption due to the global availability of calcined clay and limestone. Moreover, a previous study indicated that the LC3 production cost is around 15% - 25% lower than that of OPC and blended cements [2]. The replacement of calcined clay and limestone in binder can compensate the low early strength when using other supplementary cementitious materials (SCMs) such as fly ash. The mechanical properties of LC3 were comparable to conventional OPC [3, 4]. Other durability properties of LC3 were reported in several previous studies [5-7]. It is widely accepted that LC3 materials outperformed in chloride diffusion resistance in comparison with OPC [8, 9]. The chloride diffusion is an important factor in evaluation of marine concrete structures as it determines the chloride-induced reinforcement corrosion and service-life of concrete structures. Calcined clay is a reactive SCM produced by calcination process of kaolinitic clay to 700 °C – 850 °C [10]. The reactivity of calcined clay is predominantly determined by kaolinite content in raw clays, influencing the performance in concretes. As a result, the influence of different reactivity of calcined clays on mechanical properties and chloride diffusion has not been fully investigated. In this study, the effect of different calcined clays on concrete performance in chloride environments was evaluated. Two different calcined clays with different reactivity were investigated. Due to calcined clay's different reactivity, different replacement rates in binder were selected to fulfil the requirement of Australian Standard AS 3600 for concretes used in the marine environment in terms of 28 days compressive strength. The chloride diffusion resistance test of different LC3 concretes was carried out using the chloride bulk diffusion protocol. The influence of different calcined clay types on the chloride diffusion was analysed and compared to conventional OPC concrete.

MATERIALS AND METHODOLOGY

Materials and Mix Design

Sydney sand and 10mm basalt were used as fine and coarse aggregate respectively. Binder comprised general purpose (GP) cement, calcined clay and limestone. GP cement contained 90 wt.% of ordinary Portland cement (OPC), 7 wt.% to 8 wt.% of mineral addition and 2 wt.% to 3 wt.% of gypsum according to Australian Standard AS 3792 [11]. Two calcined clays with different reactivity were used in this study. Calcined clays were denoted as "Flash calcined clay" and "Rotary kiln calcined clay" due to its production by flash calcination and rotary kiln calcination process [10]. Kaolinite content in raw clays prior to calcination process is an important factor to determine the reactivity of calcined clay [12, 13]. However, the calcined clays were received as industrial products and the kaolinite content was unknown to the authors. The amorphous content of calcined clay determined by Rietveld X-ray diffraction (XRD) can be an indicator for the reactivity. Flash calcined clay and rotary kiln calcined clay presented the amorphous content of 50.9 wt.% and 78.8 wt.% respectively. Limestone fulfilled the requirements to be utilised in concrete production. The chemical composition by X-ray fluorescence (XRF) and particle size distribution by laser diffraction of GP cement, calcined clays and limestone is shown in Table 1 and Figure 1 respectively.

Table 1 – Chemical composition of GP cement, calcined clays and limestone

Chemical composition (wt.%)	GP cement	Flash calcined clay	Rotary kiln calcined clay	Limestone
SiO_2	19.74	70.42	48.15	0.36
Al_2O_3	4.70	22.34	41.63	0.11
Fe_2O_3	2.98	2.34	2.27	0.1
CaO	64.62	0.49	0.12	57.51
MgO	1.48	0.16	0.09	0.29
Na_2O	0.21	0.1	0.32	-
K_2O	0.64	0.19	0.05	-
TiO_2	0.31	1.1	3.39	-
SO_3	2.24	0.02	0.09	-
Loss on ignition (LOI)	3.18	1.76	3.21	42.61

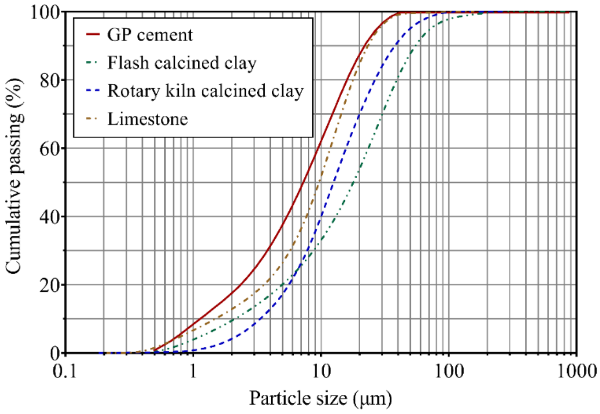

Figure 1. Particle size distribution of GP cement, calcined clays and limestone

Three concrete mix designs were fabricated in this study. Due to the requirement of concrete used in chloride environments from Australian Standard AS 3600 [14], the 28-day average compressive strength of concrete has to be higher than 45 MPa. Based on preliminary experiments and different reactivity of calcined clay, the replacement rate of GP cement was different between flash calcined clay and rotary kiln calcined clay. 20 wt.% of binder was replaced by flash calcined clay and limestone in LC3-L concrete whilst 44 wt.% of binder was replaced by rotary kiln calcined clay and limestone in LC3-H concrete. The ratio of calcined clay to limestone in the binder replacement was 2:1 by mass. A reference concrete (GPC concrete) was fabricated with 100 wt.% of GP cement in the binder. The mix design details were presented in Table 2 with all aggregate in saturated surface dry (SSD) condition. After 1 day of mixing, all concrete cylinders were demoulded and placed in water bath for 7 days at 23 ± 2 °C. The specimens were then stored in a controlled room with the temperature of 23 ± 2 °C and relative humidity (RH) of 50% until testing.

Table 2 – Mix design details

Materials (kg/m^3)	GPC	LC3-L	LC3-H
Coarse aggregate	1221	1221	1201.5
Fine aggregate	620.8	620.8	610.9
Total binder	388	388	388
GP cement	388	310.4	217.3
Flash calcined clay	0	50.44	0
Rotary kiln calcined clay	0	0	116.4
Limestone	0	27.16	54.3
Water/binder ratio	0.45	0.45	0.45
Water	174.5	174.5	174.5

Methodology

The compressive strength of concrete was determined using three 200 × 100 mm cylinders at 1, 3, 7, 14, 21 and 28 days of curing, following standard ASTM C39 [15]. The elastic modulus was measured at 28 days by ASTM C469 [16].

Chloride bulk diffusion test was conducted by following ASTM C1556 [17]. The concrete discs with 100 mm in diameter and 75 mm in height were exposed to 16.5% NaCl solution after 28 days of curing. Concrete powder was obtained after 35 days of exposure to NaCl solution. The total chloride content was determined according to ASTM C1152 [18] using potentiometric titration machine and demonstrated as wt.% of the concrete powder. The apparent chloride diffusion coefficient was calculated using total chloride content and exposure depth by a non-linear regression analysis with the least-square approach, as descried in ASTM C1556 [17].

RESULTS AND DISCUSSION

Compressive strength and elastic modulus

The compressive strength development of GPC and LC3 concretes is shown in Figure 2. Due to the different reactivity of the calcined clays as previously discussed in section 2.1, different replacement rates were used between LC3-L and LC3-H to achieve similar compressive strength after 28 days of curing. In Figure 2, the LC3 concretes (LC3-L and LC3-H) presented higher compressive strength than the GPC concrete from 1 to 3 days whilst the GPC concrete showed the highest compressive strength from 7 to 28 days after curing, achieving 52.3 MPa at 28 days. LC3-L and LC3-H concretes had relatively comparable compressive strength value until 3 days after curing and LC3-H concrete exhibited higher values from day 7 to 21. At 28 days after curing, LC3-L and LC3-H reached the compressive strength of 49.33 MPa and 49.66 MPa respectively, which is around 5% less than GPC concrete value. Previous studies reported the effect of different calcined clay reactivity to the compressive strength. Avet and Scrivener [13] indicated that the higher reactivity of calcined clay produced higher compressive strength, especially after 3 days of hydration when using the same replacement rate. Tironi et al. [19, 20] showed that similar compressive strength was maintained between LC3 and GPC mortars by using 20 wt.% binder replacement rate of calcined clay with 40 wt.% amorphous content and limestone, which is consistent with this study using flash calcined clay. In addition, Tironi et al. also concluded that different binder replacement rates were required to obtain similar compressive strength among calcined clays with different reactivity [19, 20].

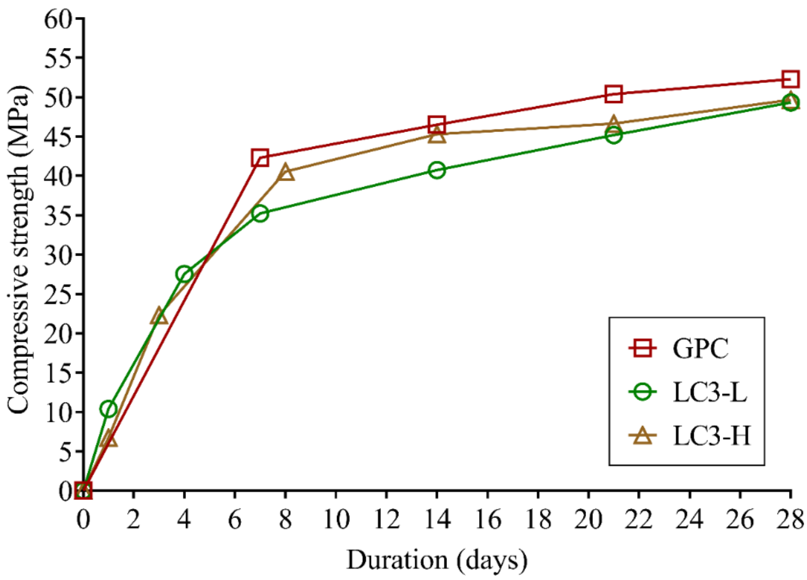

Figure 3. Compressive strength developments of concretes

The elastic modulus after 28 days of curing is shown in Table 3. LC3 concretes had higher elastic modulus than that of GPC concrete. LC3-L and LC3-H concretes obtained values of elastic modulus at 34.5 GPa and 41.0 GPa, which was 10.9% and 31.8% higher than GPC elastic modulus respectively. LC3 concretes elastic modulus values indicate the benefits of using LC3 concretes in structural applications with high elastic modulus as a requirement. A previous study also revealed higher elastic modulus of LC3 concretes compared to OPC concrete with a replacement rate at 50 wt.% [21].

Table 3 – Elastic modulus of concrete after 28 days of curing

Concrete types	Elastic modulus (GPa)
GPC	31.1
LC3-L	34.5
LC3-H	41.0

Bulk diffusion test and apparent chloride diffusion coefficient

The total chloride content profiles of the three concretes are presented in Figure 4. LC3 concretes exhibited higher total chloride content near the exposure surface than that of reference concrete. LC3-L and LC3-H had higher chloride content in comparison with GPC concrete from exposure surface to 9 mm and to 5 mm depth respectively. Within LC3 concretes, LC3-L showed higher chloride content than LC3-H concrete until 15 mm exposure depth. Chloride content of LC3-based concretes became negligible after 15 mm. The GPC concrete gradually reduced its chloride content from exposure surface. At 25 mm of exposure depth, GPC concrete showed the highest total chloride content.

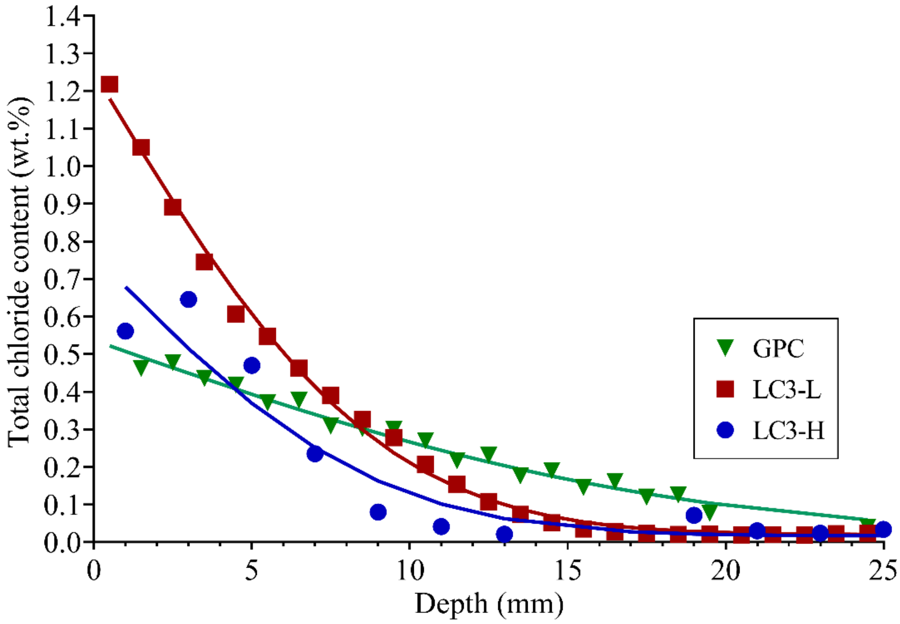

Figure 4. Total chloride profile of concretes

Table 4 presents the apparent chloride diffusion coefficient of concretes after 35 days exposed to NaCl 16.5% solution based on the total chloride profile in Figure 4. The GPC concrete had the highest chloride diffusion coefficient at 34.42×10^{-12} m^2/s. By contrast, LC3 concretes exhibited significantly lower chloride diffusion coefficients than reference concrete. To be specific, LC3-L and LC3-H concretes presented four times lower values of chloride diffusion coefficients at 8.18×10^{-12} m^2/s and 7.97×10^{-12} m^2/s respectively. The overperformance of LC3 concretes against chloride diffusion can be attributed to the refinement of pore structure and better chloride binding capacity. Consistent with this study, a previous study also reported significantly lower chloride diffusion coefficient of LC3 concretes than that of OPC concrete [22]. Moreover, Maraghechi et al. [9] and Sui et al. [23] revealed that LC3-based materials had higher chloride binding capacity and refined pore structure, contributing to the low apparent chloride diffusion coefficient of LC3 concretes.

Table 4 – Apparent chloride diffusion coefficient of concretes

Concrete types	Apparent chloride diffusion coefficient ($\times 10^{-12}$ m^2/s)
GPC	34.42
LC3-L	8.18
LC3-H	7.97

Importantly, the chloride diffusion coefficient values confirm that the high chloride diffusion resistance of LC3 concretes may be obtained by using an optimum calcined clay and limestone replacement rate. Specifically, LC3-L and LC3-H concretes had chloride diffusion coefficient of 8.18×10^{-12} m^2/s and 7.97×10^{-12} m^2/s respectively, regardless the reactivity of the different calcined clays. Similarly, the relatively similar 28-day compressive strength of LC3 concretes could be achieved by optimising the calcined clay and limestone replacement level based on calcined clay reactivity. As a result, potential performance-based criteria in chloride environments can be established for LC3 concretes based on calcined clay's reactivity, compressive strength and chloride diffusion coefficient and further study is recommended to provide comprehensive criteria.

CONCLUSION

Similar compressive strength after 28 days of LC3 concretes using calcined clay with different reactivity could be obtained by using appropriate replacement rates of calcined clay and limestone in the binder. In this study, 20 wt.% of flash calcined clay and limestone could replace 20 wt.% binder in concrete mixture achieving similar compressive strength to that of concrete containing 44 wt.% of rotary kiln calcined clay and limestone. In addition, the early-age compressive strength of LC3 concretes was comparable to GPC concrete.

LC3 concretes presented more than four times lower apparent chloride diffusion coefficient in comparison with reference concrete. The outperformance of LC3 concretes can be explain by better chloride binding capacity and refinement of pore structure. Moreover, similar chloride diffusion coefficient can be obtained when using an optimum replacement rate of calcined clay and limestone depending on calcined clay reactivity.

Results indicate that performance-based criteria for using LC3 concretes in chloride environments can be established depending on the reactivity of calcined clay to design compressive strength and chloride diffusion coefficient.

REFERENCES

[1] K. Scrivener, F. Martirena, S. Bishnoi, S. Maity, Calcined clay limestone cements (LC3), Cement and Concrete Research, 114 (2018) 49-56.
[2] Y. Cancio Díaz, S. Sánchez Berriel, U. Heierli, A.R. Favier, I.R. Sánchez Machado, K.L. Scrivener, J.F. Martirena Hernández, G. Habert, Limestone calcined clay cement as a low-carbon solution to meet expanding cement demand in emerging economies, Development Engineering, 2 (2017) 82-91.
[3] M. Antoni, J. Rossen, F. Martirena, K. Scrivener, Cement substitution by a combination of metakaolin and limestone, Cement and Concrete Research, 42 (2012) 1579-1589.
[4] F. Avet, L. Sofia, K. Scrivener, Concrete Performance of Limestone Calcined Clay Cement (LC3) Compared with Conventional Cements, Advances in Civil Engineering Materials, 8 (2019) 275-286.
[5] M.S.H. Khan, Q.D. Nguyen, A. Castel, Performance of limestone calcined clay blended cement-based concrete against carbonation, Advances in Cement Research, 32 (2020) 481-491.
[6] Q.D. Nguyen, A. Castel, Reinforcement corrosion in limestone flash calcined clay cement-based concrete, Cement and Concrete Research, 132 (2020) 106051.
[7] Q.D. Nguyen, T. Kim, A. Castel, Mitigation of alkali-silica reaction by limestone calcined clay cement (LC3), Cement and Concrete Research, 137 (2020) 106176.
[8] Q.D. Nguyen, M.S.H. Khan, A. Castel, Chloride Diffusion in Limestone Flash Calcined Clay Cement Concrete, ACI Materials Journal, 117 (2020).
[9] H. Maraghechi, F. Avet, H. Wong, H. Kamyab, K. Scrivener, Performance of Limestone Calcined Clay Cement (LC3) with various kaolinite contents with respect to chloride transport, Materials and Structures, 51 (2018) 125.

[10] R. San Nicolas, M. Cyr, G. Escadeillas, Characteristics and applications of flash metakaolins, Applied Clay Science, 83 (2013) 253-262.
[11] AS 3972: General purpose and blended cements, Standards Australia, Sydney, Australia 2010.
[12] Q.D. Nguyen, M.S.H. Khan, A. Castel, Engineering Properties of Limestone Calcined Clay Concrete, Journal of Advanced Concrete Technology, 16 (2018) 343-357.
[13] F. Avet, K. Scrivener, Investigation of the calcined kaolinite content on the hydration of Limestone Calcined Clay Cement (LC3), Cement and Concrete Research, 107 (2018) 124-135.
[14] AS 3600: Concrete structures Standards Australia, Sydney, Australia, 2018.
[15] ASTM C39/C39M-18: Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens, ASTM International, West Conshohocken, PA, 2018.
[16] ASTM C469/C469M-14: Standard Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression, ASTM International, West Conshohocken, PA, 2014.
[17] ASTM C1556-11a(2016): Standard Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion, ASTM International, West Conshohocken, PA, 2016.
[18] ASTM C1152 / C1152M-04(2012)e1: Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete, ASTM International, West Conshohocken, PA, 2012.
[19] A. Tironi, C.C. Castellano, V.L. Bonavetti, M.A. Trezza, A.N. Scian, E.F. Irassar, Kaolinitic calcined clays – Portland cement system: Hydration and properties, Construction and Building Materials, 64 (2014) 215-221.
[20] A. Tironi, A.N. Scian, E.F. Irassar, Blended Cements with Limestone Filler and Kaolinitic Calcined Clay: Filler and Pozzolanic Effects, Journal of Materials in Civil Engineering, 29 (2017) 04017116.
[21] Y. Dhandapani, T. Sakthivel, M. Santhanam, R. Gettu, R.G. Pillai, Mechanical properties and durability performance of concretes with Limestone Calcined Clay Cement (LC3), Cement and Concrete Research, 107 (2018) 136-151.
[22] R.G. Pillai, R. Gettu, M. Santhanam, S. Rengaraju, Y. Dhandapani, S. Rathnarajan, A.S. Basavaraj, Service life and life cycle assessment of reinforced concrete systems with limestone calcined clay cement (LC3), Cement and Concrete Research, 118 (2019) 111-119.
[23] S. Sui, F. Georget, H. Maraghechi, W. Sun, K. Scrivener, Towards a generic approach to durability: Factors affecting chloride transport in binary and ternary cementitious materials, Cement and Concrete Research, 124 (2019) 105783.