Sixth International Conference on Durability of Concrete Structures
18 - 20 July 2018
University of Leeds, Leeds, West Yorkshire, LS2 9JT, United Kingdom

Paper Number ICC21

Performance of Concrete Made with a Calcined Clay – Limestone-Portland Cement Exposed to Natural Conditions

Fernando Martirena, Ernesto Díaz, Dayran Rocha
Universidad Central de las Villas, CIDEM, Santa Clara, Cuba

Hamed Maraghechi, Karen Scrivener
Ecole Polytechnique Federal de Lausanne, EPFL, Lausanne Switzerland

ABSTRACT

This work presents the results of an investigation carried out to assess durability of concrete made with a calcined clay- limestone-Portland cement with 47% of clinker, hereafter named LC3, produced during an industrial trial in 2013. LC3 was used to cast concrete blocks and later expose them at a natural location at the northern coast of Cuba. Reference concrete was cast with Cuban Portland cement having 88% of clinker. Throughout three years (2015, 2016, 2017) concrete cores were systematically taken and the specimens were subjected to a testing program that included Formation factor, chloride profiling, surface resistivity, air permeability and carbonation depth. The studies proved that concrete made with the new binder presents a more refined capillary pore network, thus the movement of ions through the concrete matrix is slower than in normal PC concrete. Experimental measurement of the chloride profiles, Formation factor, surface resistivity and air permeability confirm an improvement of performance in the range of 2-3 compared to PC concrete. This is attributed to the presence of calcined clay in the new system and the synergy with limestone. For concrete exposed in coastal areas in hot & humid regions, carbonation is hindered by the high Relative Humidity, which saturates the pore system and reduces CO_2 diffusion. The use of LC3 in concrete in very aggressive –chloride- conditions could yield a better performance against steel corrosion, as the tests on surface resistivity have proven.

Keywords: pozzolan, cement, concrete, durability, chloride, carbonation

1.0   INTRODUCTION

Concrete is by far the most used material in modern civilization (Scrivener *et al.*, 2016). Most concrete is durable, but some aggressive conditions pose problems, particularly with corrosion of reinforcing steel due to chloride (The European Cement Association, 2014). For concrete placed in coastal areas in hot & humid tropical regions, the presence of chlorides becomes the main threat for durability (Scrivener, 2014).

The use of Supplementary Cementitious Materials, SCM, can contribute to mitigate the impact of chlorides in concrete, because of the improvement of the pore structure in concrete which hinders the ingress and transport of chloride ions through the matrix (Thomas *et al.*, 2012)

In recent papers the benefits of the synergy between kaolinitic calcined clay and limestone in Portland cement systems have been demonstrated. The main contribution to durability is the densely connected pore network, thus impacting on a reduced transport of ions through the matrix (Antoni *et al.*, 2012).

The realization of a full industrial trial for the production of concrete with this cement in Cuba in 2013 enabled the manufacture of reinforced concrete blocks that were laid at an exposure site on the northern coast of Cuba and were systematically tested for chloride and carbonation.

This paper presents the most recent results of the evaluation of concrete cores taken from the elements laid at the exposure site.

2.0   MATERIALS AND EXPERIMENTS

The limestone-calcined clay-Portland cement – identified as LC3- was produced at the cement plan Siguaney in Cuba during an industrial trial in August 2013. 25 MPa Concrete was made using Cuban calcareous aggregates. The series M381-LC3 was made with the ternary cement, with 47% clinker, while the series M32 was cast with Cuban Ordinary Portland Cement, type I with 88% of clinker, known as P35. Table 1 presents details of the mix design and the mechanical properties of the concrete made. More details are provided in reference (Vizcaino-Andres *et al.*, 2015).

Table 1: results of characterization of concrete mixes of the blocks laid at exposure site

ID	Cement kg/m^3	Slump cm	Strength MPa			porosity %
			3d	7d	28d	
M381-LC3	360	8	-	21	31.4	8.92
M32-PC	300	8	17.40	-	27.9	13.72

Concrete was placed on concrete blocks, which were laid at an exposure site at the northern coast of Cuba, see Fig. 1. The water accessible porosity value was measured according to norm ASTM C642. Relative Humidity (RH) oscillates around 80-95% and temperature around 25-35 ^{o}C throughout the year.

Fig. 1: exposure site at the northern coast of Cuba

The experimental program carried out was the following:

- Formation factor: it the resistivity of the sample, divided by the resistivity of the pore solution. Migration cells were used to measure conductivity. For the calculation of the Formation factor the composition of the solution in concrete was fixed according to the recommendations of the literature based on the concentration of OH-, K+ and Na+ (Snyder et al., 2003).
- The formation factor was calculated using the initial current measurement (t=0) to guarantee that the ion composition of the solution was not changed.
- Measurement of surface resistivity of fully saturated concrete cores. A four-point probe was used -Wenner probe-; four equally spaced electrodes are placed on the concrete surface. An AC current is injected through the outer two electrodes, and the voltage drop is measured between the two inner electrodes (Angst and Elsener, 2014).
- Chloride profiling of concrete cores; the outer 50 mm ring was cut from the core and total chloride content was measured after acid dissolution and titration using AgNO$_3$.
- Measurement of air permeability of concrete cores using the Torrent method: it measures the coefficient of air-permeability kT with the PermeaTORR instrument (S. 262/1:2913, 2013) The coefficient of air-permeability kT (10-16 m²) is calculated as function of the increase in pressure recorded in the measuring chamber.

- Carbonation depth, measured by spraying the exposed surfaced with phenolphthalein. Cores of the elements were taken. The cores were split in two parts so have the carbonated part exposed.

3.0 DISCUSSION OF RESULTS

3.1 Formation factor

Cores of concrete were taken, slices 100 x 27 mm were prepared (with replica) and placed at the accelerated migration cell, with a voltage applied to accelerate ions transport through the concrete matrix. Based on the data from measurement of current, the formation factor was calculated according to the equation (1):

$$\Upsilon = \frac{\sigma_p}{\sigma_b} \tag{1}$$

where:

σp : Electrical conductivity of the pore solution

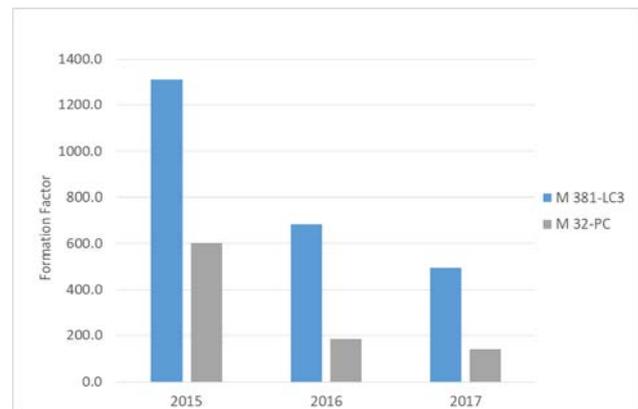σb: Electrical conductivity of the matrix (solid and solution)

Fig. 2. Formation factor of concrete tested at 2015, 2016, 2017

Figure 2 presents the results of the measurement of the Formation factor at both concrete series throughout a period of three years (2015, 2016, 2017). The Formation factor describes the transport properties of the concrete matrix (Snyder, 2001). The higher it gets the slower the movement of the ions through the matrix.

Results confirm the beneficial effects of having calcined clays in the composition of cement, which despite its low clinker content has a Formation factor greater in a factor 2-3 times higher compared to concrete made with Portland cement. This trend remains throughout all measurements.

3.2 Surface Resistivity

Measuring the surface resistivity of concrete enables assessment of microstructure and transport properties; in addition, concrete resistivity has been

suggested to correlate with the rate of reinforcement steel corrosion (Angst and Elsener, 2014).

Figure 3 presents the results of measuring surface resistivity in both series in 2016 and 2017. Again, the surface resistivity of concrete made with calcined clays, despite having only 47% of clinker, is 3 times higher than the one for concrete made with PC with 88% of clinker. The reason for this performance can be attributed to the presence of calcined clays, whose contribution is the reduction of the average pore size, and thus reduces the possibility of ions moving through the pore structure (Antoni *et al.*, 2012). In terms of corrosion risk, the performance of LC3 concrete is also better than PC concrete.
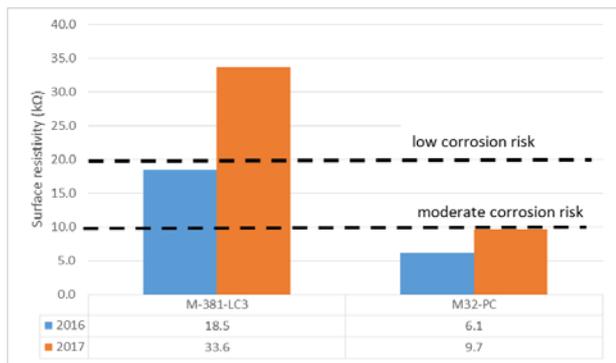
Fig. 3. Results of measuring surface resistivity in saturated concrete cores in 2016 and 2017

3.3 Chloride profiling

Acid-soluble chloride content of the concrete cores were tested according to ASTM C 152/C1152M to obtain the total chloride concentration profiles. Figure 4 presents the results, which are coherent with the previous measurements presented. At the same depth concrete made with LC3 has a lower chloride concentration, normally in a factor of 2.
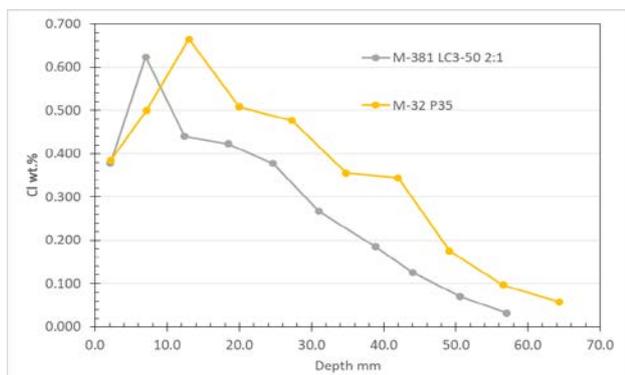

Fig. 4. Chloride profiles of concrete cores after two years of exposure under natural conditions

3.4 Air permeability

Figure 5 presents the results of measuring air permeability measure in concrete cores taken at three ages (2015, 2016, 2017). kT in series M381-LC3

qualifies as a low permeability concrete (Jacobs *et al.*, 2012) whereas the series M32-PC has moderate permeability. Air permeability in PC concrete is on the average 3 times higher than in LC3 concrete. This could clarify the performance observed while measuring the Formation factor and surface resistivity above; the main contribution of calcined clays is the refinement of the pore structure.
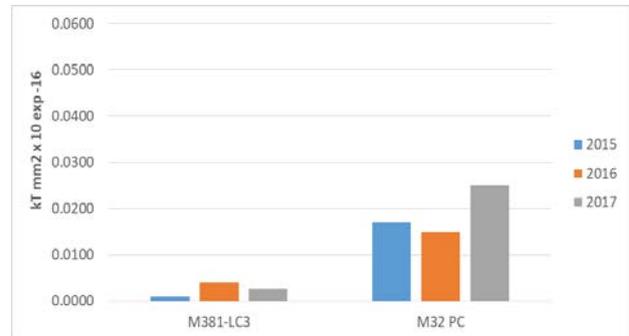
Fig. 5. Results of measuring air permeability in concrete cores at 2015, 2016 and 2017

3.5 Carbonation

Figure 6 presents the results of measuring carbonation depth on concrete cores for both series. There are no major differences in carbonation depth of both series, probably due to the high Relative Humidity of the zone where concrete blocks are exposed, normally above 80%, thus the capillary pore system is fully saturated and CO_2 cannot diffuse properly (a Costa, 2001).
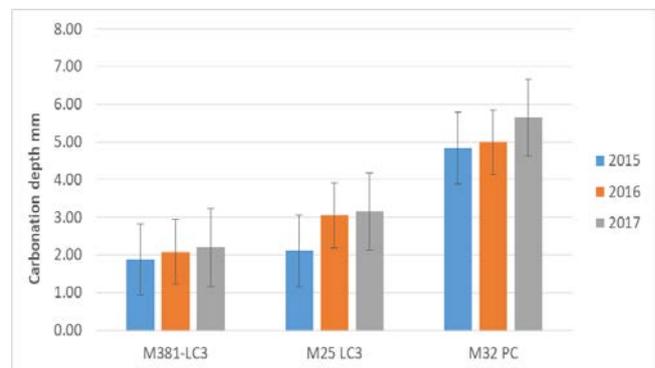
Fig. 6. Carbonation depth measured on concrete cores, 2015-2017

4.0 CONCLUDING REMARKS

Concrete made with a calcined clay-limestone-Portland cement presents a more refined capillary pore network, thus the movement of ions through the concrete matrix is slower than in normal PC concrete. Experimental measurement of the Chloride profiles, Formation factor, surface resistivity and air permeability in cores taken from concrete exposed under natural conditions confirm an improvement of performance in the range of 2-3 compared to PC

concrete. The reason for this improvement is attributed to the presence of calcined clay in the LC3 system, which through a synergetic reaction with limestone enables a denser microstructure.

For concrete exposed in coastal areas in hot and humid regions chloride is the main concern in terms of durability, since carbonation is hindered by the high Relative Humidity which saturates the pore system and reduces CO_2 diffusion through the system. The use of LC3 in concrete in very aggressive –chloride- conditions could yield a better performance against steel corrosion, as the tests on surface resistivity have proven.

Acknowledgement

References

a Costa, J. Appleton, Concrete Carbonation and Chloride Penetration in a Marine Environment, Concr. Sci. Eng. 3 (2001) 242–249.

U.M. Angst, B. Elsener, On the Applicability of the Wenner Method for Resistivity Measurements of Concrete, ACI Mater. J. 111 (2014). doi:10.14359/51686831.

M. Antoni, J. Rossen, F. Martirena, K. Scrivener, Cement substitution by a combination of metakaolin and limestone, Cem. Concr. Res. 42 (2012) 1579–1589. doi:10.1016/j.cemconres.2012.09.006.

The European Cement Association, The role of CEMENT in the 2050 LOW CARBON ECONOMY, 2014.

F. Jacobs, A. Leemann, T. Teruzzi, R. Torrent, E. Denarie, Specification and site control of the permeability of the cover concrete : The Swiss approach Dedicated to Professor Dr . Bernhard Elsener on the occasion of his 60th birthday, Mater. Corros. 63 (2012) 1127–1133. doi:10.1002/maco.201206710.

S. 262/1:2913, Bauwesen Betonbau – Ergänzende Festlegungen, 2013.

K.L. Scrivener, Options for the future of cement, Indian Concr. J. 88 (2014) 11–19.

K.L. Scrivener, V.M. John, E.M. Gartner, Eco-efficient cements: POtential, economically viable solutions for a low CO2, cement based materials industry, 2016.

K.A. Snyder, The relationship between the formation factor and the diffusion coefficient of porous materials saturated with concentrated electrolytes : theoretical and experimental considerations, Concr. Sci. Eng. 3 (2001) 216–224.

K.A. Snyder, X. Feng, B.D. Keen, T.O. Mason, Estimating the electrical conductivity of cement paste pore solutions from OH À , K + and Na + concentrations, 33 (2003) 793–798. doi:10.1016/S0008-8846(02)01068-2.

M.D.A. Thomas, R.D. Hooton, A. Scott, H. Zibara, The effect of supplementary cementitious materials on chloride binding in hardened cement paste, Cem. Concr. Res. 42 (2012) 1–7. doi:10.1016/j.cemconres.2011.01.001.

L. Vizcaíno-Andrés, S. Sánchez-Berriel, S. Damas-Carrera, A. Pérez-Hernández, K. Scrivener, M.-H. Fernando, Industrial trial to produce a low clinker , low carbon cement, Mater. Construcción. 65 (2015). doi:http://dx.doi.org/10.3989/mc.2015.00614.