

# Chloride ingress and carbonation assessment of mortars prepared with recycled sand and calcined clay-based cement

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## ABSTRACT

A promising and economical route for the reduction of the environmental impact generated by Ordinary Portland Cement (OPC) and Construction and Demolition (C&D) waste could be possible using Recycled Sand (RS) with Limestone Calcined Clay Cement (LC<sup>3</sup>). This research study presents an experimental investigation based on the comparison between LC<sup>3</sup> and CEM II binders mixed with natural sand and two types of recycled sand (substitution rate 50 vol%). Mechanical and durability properties of the different mortars were examined through compression and flexural strength tests, capillary water absorption, Mercury Intrusion Porosimetry (MIP), fog chamber salt spray exposure and immersion in chloride solution condition to evaluate water-soluble and acid-soluble chloride contents, and carbonation assessment by natural and accelerated methods. According to experimental results, LC<sup>3</sup> containing 70 % of clinker and a calcined clay to limestone ratio of 2:1 exhibits superior compressive strength compared to CEM II for both natural and recycled sands and significantly enhances the resistance against chloride ions ingress and carbonation. These results demonstrate that LC<sup>3</sup> binder with 70 % clinker is a promising material to produce LC<sup>3</sup> blends with adequate durability against carbonation and chloride ions ingress, particularly when recycled sand is used as a source of fine aggregate.

## 1. Introduction

Sustainable development is a global issue, which aims to improve the infrastructure of our communities to enable comfortable living without significantly depleting natural resources and planet health. The escalating requirements for human life, such as access to clean water, unpolluted air, effective waste management, secure and efficient transportation systems for both individuals and goods, as well as the construction of residential and industrial structures, boost the need for careful management of the environmental impact and energy sources. The concrete industry stands as the highest consumer of natural resources, including water, sand, gravel, and crushed rock [1]. Consequently, the pursuit of sustainable concrete has emerged as a primary focus within the global construction sector [2]. The main objectives include the reduction in pollution and carbon dioxide emissions, efficient waste material usage, and the development of low-energy and long-lasting buildings [3]. Concrete is one of the most widely used materials globally after water and cement is its main component [4]. Which is accountable for emitting approximately 7 % of the global CO<sub>2</sub> into the

atmosphere [5]. A new approach for the development of binders with lower environmental impact is combining kaolinitic calcined clay and limestone powder with OPC, i.e. the manufacturing of the so-called limestone calcined clay cement (LC<sup>3</sup>) [6]. Numerous studies have been conducted to gain a deeper knowledge of LC<sup>3</sup> blend characteristics, demonstrating its great potential [7–9].

Additionally, the increasing demand for concrete involves a great impact on the associated natural resources like sand and coarse aggregate, especially considering that the growth in population and urbanization have contributed to an increase in the demand for river sand, especially in the Asian region [10]. River sand's global demand and consumption is approximately 32–50 billion tons per annum [11]. According to reports, natural sand consumption has surpassed its regeneration quantity, which has a significant effect on the coastal area's resident and their ecology [12]. Unfortunately, the sand from deserts is finer and is not suitable to be employed as a construction material, and the manufactured sand or crushed sand from the hard rock quarries causes a natural resources depletion as well. On the other hand, construction and demolition (C&D) waste constitute a growing

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**Table 1**

XRF Oxide compositional analysis of CEM I, CEM II and CC by X-ray Fluorescence (XRF). LOI=Loss On Ignition.

Chemical formula and LOI	CEM I (%)	CEM II (%)	Calcined Clay (%)
SiO <sub>2</sub>	19.24	18.12	60.24
CaO	62.69	61.44	0.98
Al <sub>2</sub> O <sub>3</sub>	5.12	4.80	25.79
Fe <sub>2</sub> O <sub>3</sub>	3.22	3.02	8.87
MnO	0.04	0.03	0.00
MgO	1.89	1.67	0.24
Na <sub>2</sub> O	0.07	0.06	0.00
K <sub>2</sub> O	1.02	1.04	0.17
SO <sub>3</sub>	3.32	3.24	0.05
P <sub>2</sub> O <sub>5</sub>	0.14	0.16	0.02
TiO <sub>2</sub>	0.29	0.28	1.26
LOI 1050 °C	2.49	5.74	2.36
Sum	99.51	99.60	99.99

**Table 2**

Physical properties of NS, RS1 and RS2.

Materials	NS	RS1	RS2
Density (g/cm <sup>3</sup> )	2.66	2.50	2.50
Maximum Size (mm)	4	2	4
Water absorption (%)	0.43	4.65	6.88
Blue methylene value (MB g of dye solution/kg of sand)	0.24	0.40	0.35
Chloride content (Cl <sup>-</sup> wt%)	0.019	0.029	0.026
Sulfate content (SO <sub>4</sub> <sup>2-</sup> wt%)	0.007	0.188	0.152
TOC (mg C/kg sand)	7.84	26.85	29.18

environmental menace [13,14]. Every year a huge quantity of waste from C&D activities is produced. In Europe, 820 million tons of C&D waste are generated by the building industry, accounting for 46 % of the total waste stream [15], and the disposal of such a huge quantity of C&D waste is a massive problem. The use of recycled sand (RS) manufactured from C&D waste is hence one of the mostly promising alternatives to the depletion of natural aggregates.

In this paper, the utilization of RS, as an ingredient of mortar in combination with an eco-friendly binder LC<sup>3</sup>, was investigated, having the potential to simultaneously minimize the problems described above. Besides determining the mechanical performance of the mortars prepared with RS and LC<sup>3</sup>, this study focuses on the durability of the newly developed materials, which is a key aspect not only for their long-term performance, but also for the minimization of their environmental impact on a life-cycle perspective.

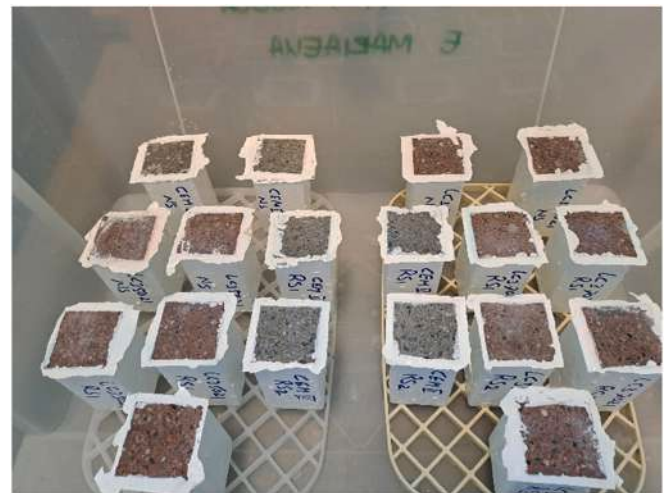
The durability of concrete structures is mainly threatened by reinforcement corrosion, with carbonation and chloride attack being the primary factors contributing to embedded steel corrosion due to de-passivation [16]. The interaction of hydration products with carbon dioxide decreases the pore solution's alkalinity, with consequent dissolution of the passive film that surrounds the steel [17]. Similarly,

**Table 3**

Formulation (mass in grams) of LC<sup>3</sup> and ordinary mortar (LS: Limestone, CC: Calcined clay, NS: Natural sand, RS1: Recycled sand1, RS2: Recycled sand2, SP: Superplasticizer).

Labels	Binder				Total Water		Sand			
	CEM I (g)	CEM II (g)	LS (g)	CC (g)	W <sub>eff</sub> (g)	W <sub>sand</sub> (g)	NS (g)	RS1 (g)	RS2 (g)	SP (g)
CEM II NS	-	450	-	-	225	0	1350	-	-	2.7
LC3-50-NS	237	-	71	142	225	0	1350	-	-	5.8
LC3-70-NS	332	-	39	79	225	0	1350	-	-	4.5
CEM II RS1	-	450	-	-	225	27	675	584	-	2.2
LC3-50-RS1	237	-	71	142	225	27	675	584	-	5.4
LC3-70-RS1	332	-	39	79	225	27	675	584	-	4.1
CEM II RS2	-	450	-	-	225	38	675	-	554	1.8
LC3-50-RS2	237	-	71	142	225	38	675	-	554	4.0
LC3-70-RS2	332	-	39	79	225	38	675	-	554	2.7

when the chloride ions concentration exceeds the threshold level around the steel bars, it may initiate local reinforcement corrosion [18,19]. Furthermore, it was found that free chloride ions, which are contained in pore solutions, are responsible for the initiation of corrosion, while bound chloride ions are chemically or physically bound by hydration products and show a different behavior [20,21]. The bound chlorides are unstable and can be affected by electrification, acidification, and carbonation [22]. Upon release, these bound chlorides can transform into free chloride, thus negatively affecting the durability of reinforced concrete [23]. The chloride binding capacity plays a crucial role in reducing deterioration caused by steel corrosion, making it essential to consider this capacity for forecasting the lifespan of reinforced concrete structures [24]. The chloride binding process is mainly influenced by the composition of the hydration products and porosity [25]. During physical chloride binding, because of the large specific surface area of C(-A)-S-H (calcium (aluminate) silicate hydrate), the chloride ions might be adsorbed to its surface [26,27]. On the other hand, the primary cause of chemical binding is the interaction of C<sub>3</sub>A, C<sub>4</sub>AF, or their hydrates with chloride ions, which results in the creation of Friedel's salt (Ca<sub>4</sub>Al<sub>2</sub>(OH)<sub>12</sub>Cl<sub>2</sub>·4 H<sub>2</sub>O) [27–29]. It was shown that the amount of chemically bonded chloride ions by Friedel's salt (FS) production is much larger in comparison to physically adsorbed chloride ions. Therefore, the ability of cement-based materials to bind chloride depends on the phases that contain alumina [28–30]. It has been suggested that adding alumina-rich Supplementary Cementitious Materials (SCMs) to concrete mixes is an effective method of increasing the chloride binding capacity [24,31–35]. Additionally, concretes containing SCMs potentially provide better durability properties by improving the pore structure [36,37]. Thus, several studies have documented the



**Fig. 1.** Sample preparation for salt fog chamber.

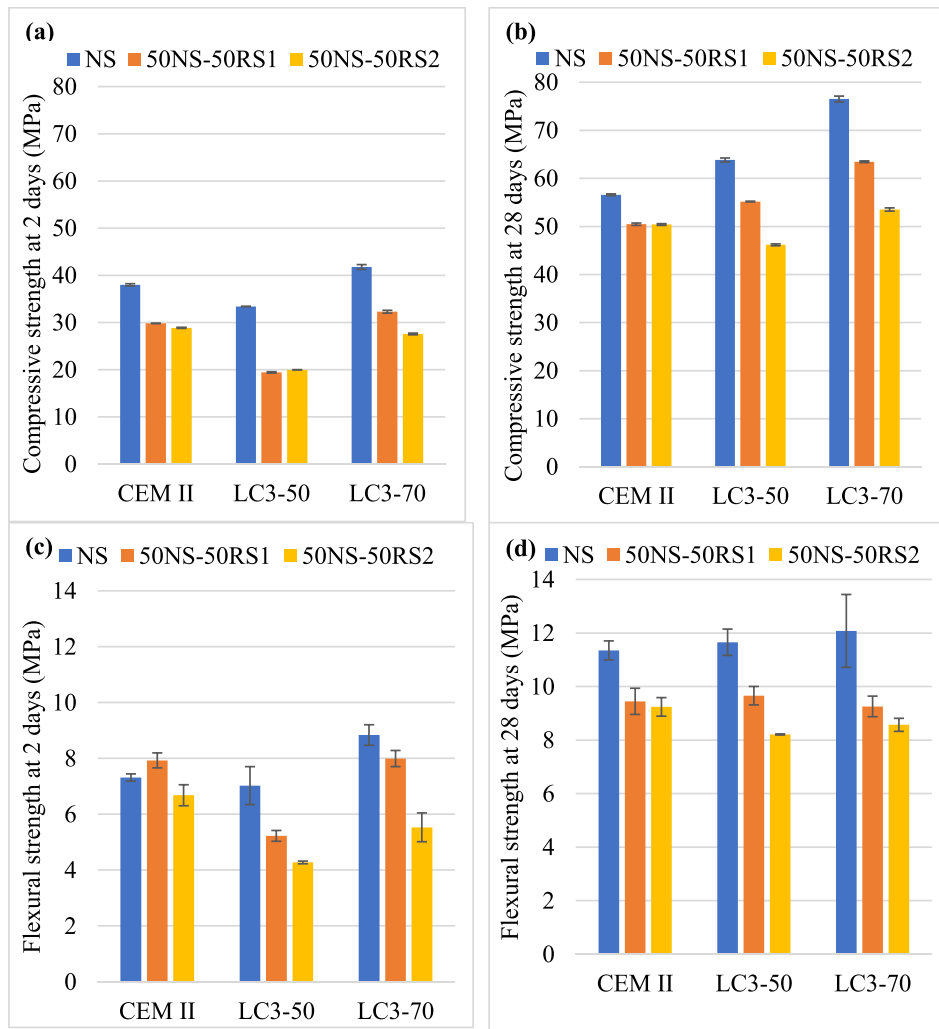


Fig. 2. - Mechanical strength obtained with different binders at various RS1 and RS2 substitution rates. (a) Compressive strength at 2 days, (b) Compressive strength at 28 days, (c) Flexural strength at 2 days, (d) Flexural strength at 28 days.

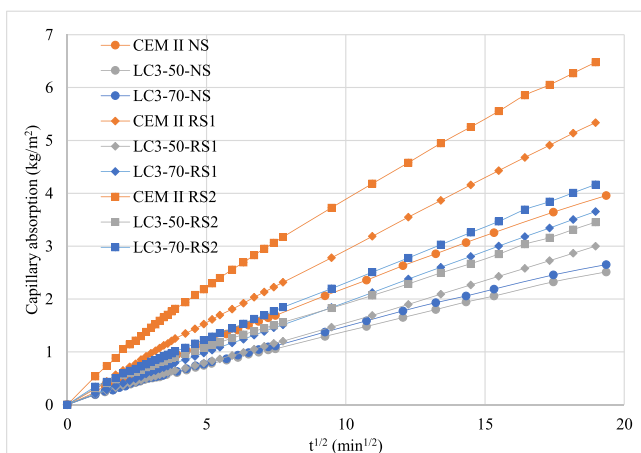


Fig. 3. -Capillary water absorption of mortars as a function of time for different binders and various RS substitution rate.

advantageous application of SCMs in chloride-contaminated reinforced concrete [38,39]. On the other hand, portlandite consumption during the pozzolanic process increases the corrosion susceptibility of concrete in terms of carbonation [40,41]. However, the mineral and admixture

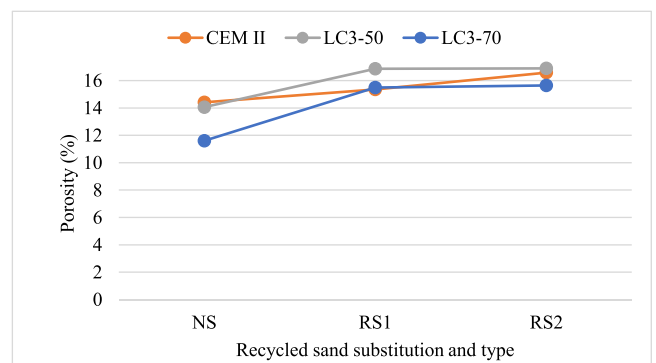


Fig. 4. Total Porosity as a function of recycled sand type (RS1 and RS2) measured by MIP.

types and their fineness have meaningful roles in the decreasing of carbonation depth [41].

The chloride ions ingress and carbonation reaction might be of great concern, especially regarding maritime buildings and deicing solutions in cold climates. Both CO<sub>2</sub> and chloride ions may permeate concrete under these exposure circumstances, either sequentially or concurrently. The combined influence of these two situations appears to speed up the

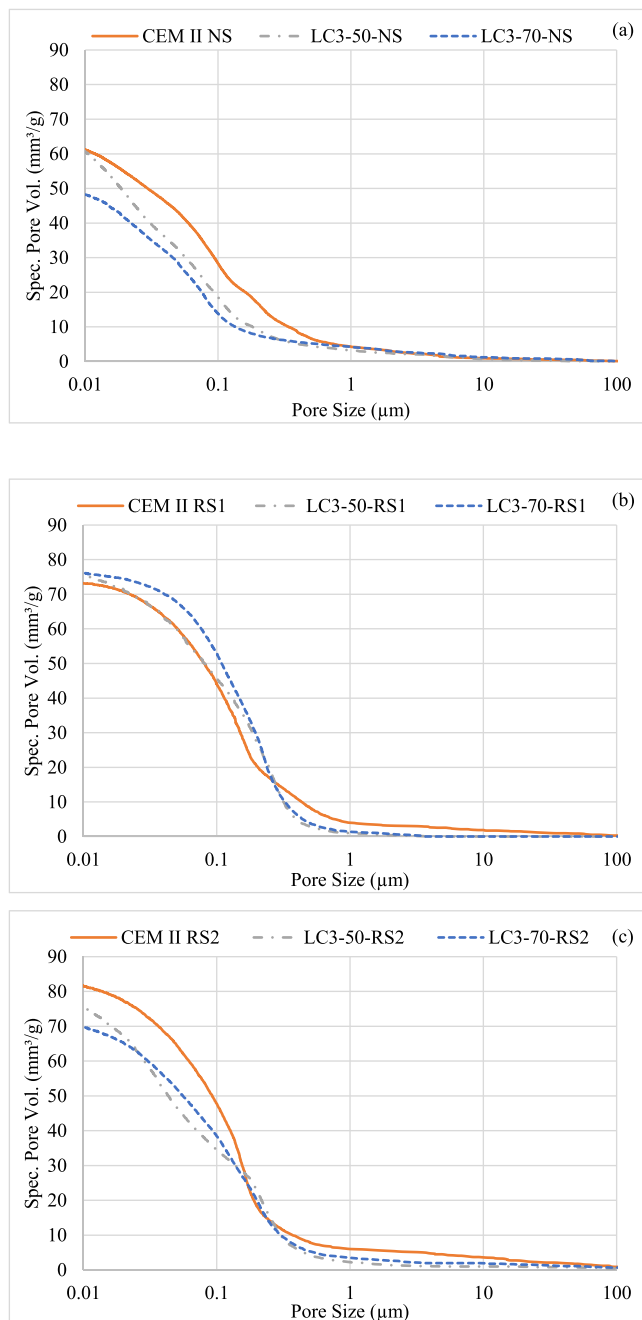


Fig. 5. Effect of different binders on the pore size distribution of mortars with NS (a), 50 % RS1 (b) and 50 % RS2 (c).

deterioration of reinforcement [42]. In general, the carbonation process decreases the permeability of the concrete matrix [43], but superficial cracks in concrete can also result from carbonation shrinkage, which increases the permeability of concrete [44]. Moreover, carbonation has the potential to favor the release of bound chloride ions into the pore solution, thus negatively impacting on the corrosion of steel bars [45, 46]. A research study was carried out on chloride-contaminated paste with a water-to-cement ratio of 0.5, exposed to a  $\text{CO}_2$  environment after 56 days of curing, and it was found that carbonation caused the release of bound chloride ions [47], which was attributed to the FS and C–S–H gel breakdown. Additionally, the decalcification of AFm and Aft phases contributed to incorporating aluminum into C–S–H, altering its surface charge [48]. The influence of supplementary cementitious materials on both carbonation and chloride attack becomes important when  $\text{CO}_2$  and

chloride ions are combined. Research indicates that carbonation leads to an increase in chloride ion concentration in fly ash mortars [49,50]. Another study investigated the effects of partial and total pre-carbonation on cement paste incorporating fly ash, slag, and metakaolin. It revealed that the quantity of calcium hydroxide (CH) in the mix plays a crucial role in mitigating the reduction in chloride binding capacity due to carbonation. Among the SCM blended mixtures, the mixture containing 25 % metakaolin exhibited the smallest decline in chloride binding capacity following partial carbonation. Therefore, the use of these materials should be carefully considered when incorporating SCMs [48].

Several studies have reported that  $\text{LC}^3$  blends show enhanced resistance against chloride attack [30,51], hence they could be a valid route to improve concrete durability, also in combination with recycled sand utilization. This study aims to fill the gap of knowledge regarding the durability of mortar with recycled sand and limestone calcined clay cement against the effects of chloride ions ingress and carbonation and compares the findings with ordinary mortar. In this regard, three binders (CEM II, LC3–50, and LC3–70) with natural sand (NS) and two types of recycled sand (RS1 and RS2, employed in 50 % volume replacement of NS) were used to prepare mortar samples. The initial focus was kept on the mechanical strength, and then the study was extended to evaluate the durability properties of the mortars through capillary water absorption, porosity assessment, chloride ion ingress through a salt fog chamber and immersed condition, and accelerated carbonation. Particular attention was given to investigate the chloride binding capacity of the different binders and the effect of RS presence. The findings of this investigation elucidate the potential of  $\text{LC}^3$  blends to compensate the technical gap related to recycled fine aggregates and promote calcined clay-based cements as an environmentally friendly alternative to traditional construction materials.

## 2. Materials and mixes

### 2.1. Materials and their characterization

In this study, commercial Portland cement type CEM II/A-LL 52.5 N, containing 12 % limestone was used as reference binder. To prepare  $\text{LC}^3$ , CEM I 52.5 R was used in combination with Calcined Clay (CC) and Limestone (LS). The kaolinitic content of clay before calcination is 40.6 % and the heat of hydration after calcination is 660 J/g at 7 days (R3 test according to the standard ASTM C1897 [52]). CEM I already contained the correct gypsum amount for setting regulation. The oxide compositions of CEM I, CEM II and CC were detected by X-ray fluorescence (XRF) analysis and are shown in Table 1.

These binders and powders were used in different ratios to manufacture the following binders:

- “LC3–50”, containing CEM I 52.63 wt%, CC 31.58 wt%, LS 15.79 wt%
- “LC3–70”, containing CEM I 73.68 wt%, CC 17.55 wt%, LS 8.77 wt%.

According to the standard EN 197, LC3–50 can be classified as CEM II/C-M, while LC-70 as CEM II/B-M. For the preparation of mortar, natural sand (NS) and two types of recycled sand (RS1 and RS2) were employed. Natural sand is a manufactured crushed sand from natural quartz rocks. The two recycled sands were produced using advanced concrete recycling techniques from demolished concrete in industrial trials. Similarly, to the conventional recycling process, advanced recycling trials begin with the removal of non-concrete materials, followed by primary crushing to reduce the demolished concrete into smaller pieces. A second step, often called selective separation, employs mechanical forces to separate the cement paste from the aggregates. After the selective separation stage, specialized equipment is used for monitoring and separating the different particle sizes, resulting in relatively clean fine and coarse aggregates, and recycled cement paste [53]. NS,

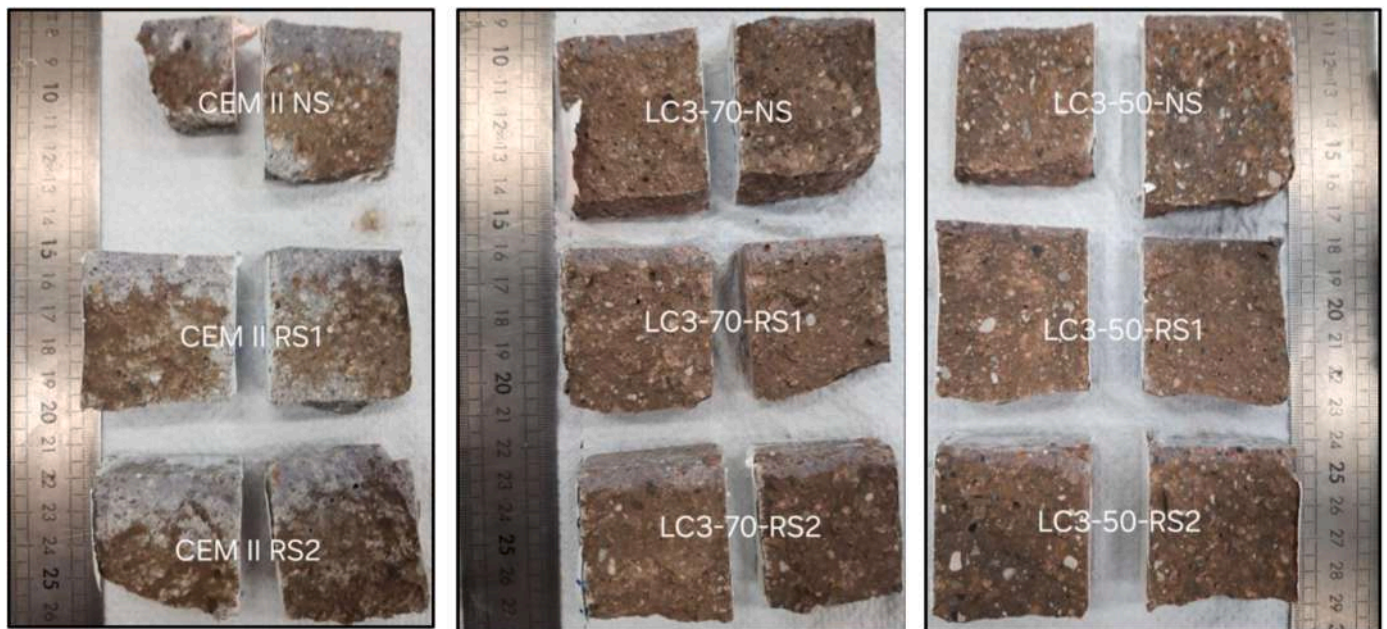


Fig. 6. Chloride penetration depth in the samples exposed to the salt fog chamber, measured by silver nitrate solution spray.

Table 4

Chloride penetration depth in the samples exposed to the salt fog chamber, measured by silver nitrate solution spray (samples in Fig. 5).

Mortars	Chloride penetration depth (mm) after salt fog chamber
CEM II NS	11.5 ( $\pm 0.3$ )
LC3-50-NS	3.8 ( $\pm 0.2$ )
LC3-70-NS	4.5 ( $\pm 0.1$ )
CEM II RS1	9.8 ( $\pm 0.2$ )
LC3-50-RS1	2.6 ( $\pm 0.1$ )
LC3-70-RS1	4.4 ( $\pm 0.2$ )
CEM II RS2	12.3 ( $\pm 0.5$ )
LC3-50-RS2	3.6 ( $\pm 0.0$ )
LC3-70-RS2	5.3 ( $\pm 0.1$ )

RS1, and RS2 were characterized using several methods Sieve analysis was performed following the EN 933-1 standard [54], while relative density and water absorption were measured following the EN 1097-6 standard [55]. Blue methylene tests were carried out according to the EN 933-9 standard [56]. Soluble chloride and sulphate contents were determined by ion chromatography (Dionex ICS 1000, ThermoFisher, US), after grinding, addition to boiling deionized water for 10 minutes under stirring and filtration. Total Organic Carbon (TOC) results were obtained through an analyzer TOC 5000 A, Shimadzu, Japan. The results are reported in Table 2. The recycled sands have lower density and higher water absorption and porosity compared to NS as expected. The aggregate chloride content is not specified in EN 12620 [57]. The water-soluble sulfate content of recycled aggregates is within the limit given by EN 12620 ( $< 0.2$  wt%) [57], and the French standard for methylene blue value was also fulfilled according to NF XP P 18-540 ( $\leq 1$  g/kg) [58]. The fluidity of mortars was adjusted using a polycarboxylate ether-based superplasticizer (SP), supplied by CHRYSO-SAINT GOBAIN laboratories, with a solid content of 22 %.

## 2.2. Mortars' formulations

The mortars were prepared using the three binders, namely CEM II, LC3-50, and LC3-70 (as described in Section 2.1), and the NS was substituted with RS1 and RS2 in a 50 vol%, according to the Table 3 formulations. It is important to mention that the volumetric method was

followed to replace natural sand with recycled ones, to take into account the difference in the bulk densities of the sands, and to ensure the same amount of cement paste volume fraction in the different mortars. Throughout the research study, the water-to-cement (w/c) ratio was constantly kept at 0.5 for all mix proportions, and the superplasticizer (SP) dosage was adjusted to reach target workability ( $21 \pm 1$  cm after 25 falls) on flow table for mortars. From Table 3 it can be observed that CEM I and CEM II required less amount of SP compared to LC<sup>3</sup> binders across all the substitution level of sand and the demands reaches up to 1.30 % for LC<sup>3</sup>-50-2:1 binder, which contains the highest amount of CC among all the binders, hence the CC has a negative effect on the workability and the SP demand for a targeted workability increases with the amount of CC [59,60]. Several authors have reported the same trend of the results and these findings are in the agreements with previous literature [9], and a recent study proposed that the impact of CC on SP dosage is due to the high specific surface area of calcined clay [61]. Of course, the recycled sands absorb a non-negligible amount of water, causing a significant and undesired reduction in the amount of available water in the fresh mixes. This was compensated by adding to the mixes the amount of water necessary to bring all the aggregates to the saturated surface dry condition, as currently done for concrete manufacturing in the case of recycled aggregates employment. Table 3 reports the mass of aggregates in dry condition, the mass of water necessary to bring them to saturated surface dry condition ( $W_{\text{sand}}$ ), and the mass of effective water ( $W_{\text{eff}}$ ), the latter corresponding to a water-to-cement ratio equal to 0.5.

## 2.3. Mortars' preparation and curing

The mixing and casting of the mortars was conducted at room temperature ( $25 \pm 2^\circ\text{C}$ ) in a Hobart mixer, according to EN 1015-11 [62] standard. Prismatic samples were prepared (size 160 mm  $\times$  40 mm  $\times$  40 mm) and the curing was carried out in a humid chamber at relative humidity  $> 95\%$ , according to EN 1015-11 [62].

## 3. Methods

### 3.1. Hardened state properties

The mechanical strength of mortars was evaluated according to EN

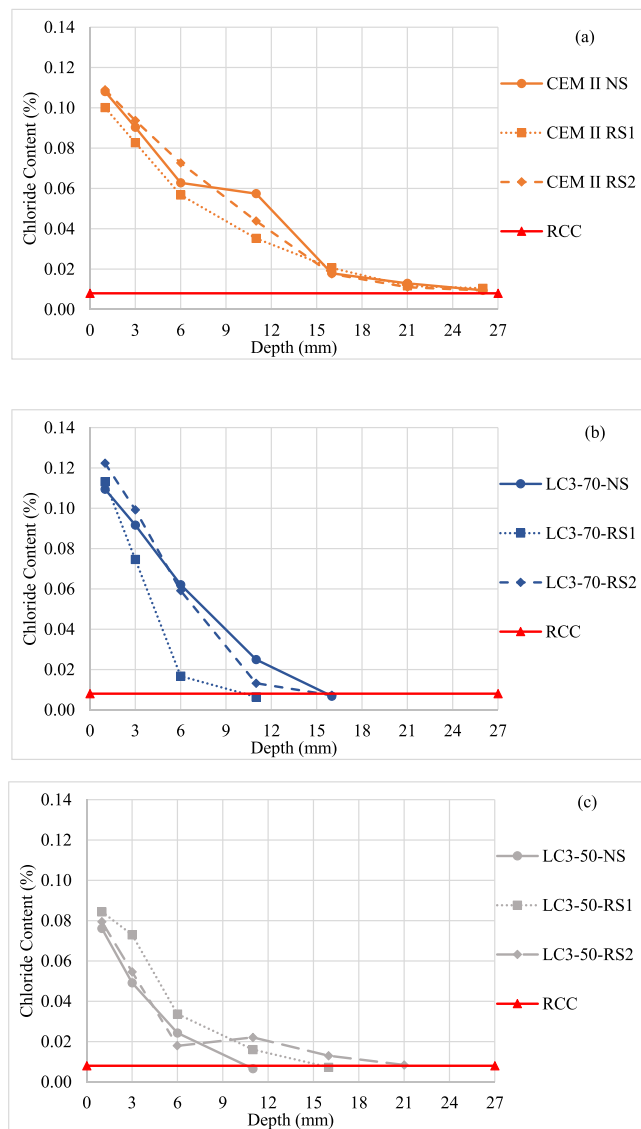


Fig. 7. Chloride penetration depth in the mortars after exposure to the salt fog chamber, measured by ion chromatography. CEM II with NS, RS1 and RS2 (a), LC3-70 with NS, RS1 and RS2 (b) LC3-50 with NS, RS1 and RS2 (c). RCC Reference chloride content of mortar exposed to the natural environment.

196–1 standard [63] at 2 and 28 days. The capillary water absorption test was carried out on mortars according to EN 1015–18 [64]. Moreover, the mercury intrusion porosimetry (MIP) was employed to characterize hardened mortars' pore structure. Samples of size 160 mm × 40 mm × 40 mm were prepared for all the binders with different fine aggregates and after 28 days of curing, the specimens were oven-dried at 110 °C for 24 hours. A fragment with a mass of 0.8–0.9 g was collected with the help of a chisel and hammer from the core of the sample to maintain sand to binder ratio same, and analyzed with a Thermo Scientific Pascal series mercury porosimeter (140 and 240) instrument. The size of the sample used for MIP analysis was considered suitable to obtain exploitable results for the assessment of the pore sizes, although a certain degree of variability in terms of binder to sand ration among the fragments analyzed could be present.

### 3.2. Durability tests

#### 3.2.1. Chloride resistance test

Mortar samples of size 160 mm × 40 mm × 40 mm were prepared for

the three binders with different fine aggregates and kept in a curing chamber for 28 days. Afterward, all the surfaces of the specimens were coated with epoxy except one surface of size 40 mm × 40 mm to ensure the one-directional penetration of chloride ions following the standard DD CEN/TS 12390–11:2010 [65] Fig. 1. The samples were kept for 28 days in a salt spray chamber [66], where the samples were constantly surrounded by a fog generated with a solution of 5 % NaCl to generate a relative humidity of 100 %. Salt spray tests are generally used for corrosion protection tests of metal alloys, usually with organic or inorganic coatings, according to EN ISO 9227:2022 [66]. In the procedure adopted in this study (Neutral salt spray test, NSS, according to EN ISO 9227), a neutral approximate 5 % sodium chloride solution is atomized under a controlled environment. The test is carried out in a cabinet where the conditions of homogeneity and distribution of the spray are met. The solution is not sprayed directly onto test specimens, but rather spread throughout the cabinet so that it falls naturally down to them, and the upper parts of the cabinet are designed so that drops of sprayed solution formed on its surface do not fall on the test specimens. It is important to recognize that the salt spray test does not guarantee a full reproducibility when performed in different laboratories [66], but in this study it was used mainly for comparative purposes to evaluate the performance of mortars prepared with different binders. Another set of samples was immersed in an aqueous solution of 3 % NaCl for 90 days. A final set of samples was put in deionized water for 90 days as reference.

The penetration depth of chloride ions in the mortar samples exposed to the different conditioning procedures was determined using the silver nitrate colorimetric method and by ion chromatography. For the colorimetric method, the samples were split in two using chisel and hammer, and a 0.1-M silver nitrate solution was applied by spraying. The depth of chloride penetration was visually assessed by the color difference. For ion chromatography, the specimens were cut into layers of different depth according to EN 12390–11:2010 [65] and ground to powder. After grinding, 1 g of the sample was mixed with 75 ml of deionized water and heated up under continuous stirring up to the boiling point, then the solution obtained by filtering (blue ribbon filter) was analyzed through ion chromatography (Dionex ICS-1000). The purpose of the test was the identification of the profile of chloride penetration in LC3 mortars in comparison to the reference mortar, so the extraction procedure through boiling water was considered effective and suitable for the purpose, although it might involve also the release of some bound chloride [67]. Other mortar specimens exposed to the salt fog chamber and immersed in saline solution were used to determine the acid-soluble chloride content by the test specified in EN 1744–5:2006 [68]. The samples to analyze were cut from the mortars specimens and had the following thickness: 2 cm depth from the exposed surface for LC3-70 and LC3-50 binders and 3 cm depth from the exposed surface for CEM II, for all types of sand employed in this research work. The same depth was considered as measured by ion chromatography for mortars after immersion in chloride solution. Similarly, the average value of the immersed condition chloride depth result obtained with ion chromatography was calculated over the same thickness used in the acid-soluble chloride test for the sake of comparison between water soluble chloride and acid soluble chloride content. The purpose of this test was not an exact quantification of the amount of bound chloride (some of them could be released also during the water extraction), but to understand if there was some chloride binding capacity of calcined clay, in comparison to CEM II.

#### 3.2.2. Carbonation Test

For the accelerated carbonation test, samples of size 160 mm × 40 mm × 40 mm were prepared for all the binders with different fine aggregates and kept in a curing chamber for 28 days. Then, the specimens were dried in ventilated oven at 110 °C for 24 hours. Half of the specimens was subjected to accelerated carbonation in a chamber with 5 % CO<sub>2</sub> (this concentration was established in the chamber every 3 days and then sealed) and relative humidity 75±3 % for 56 days. Considering

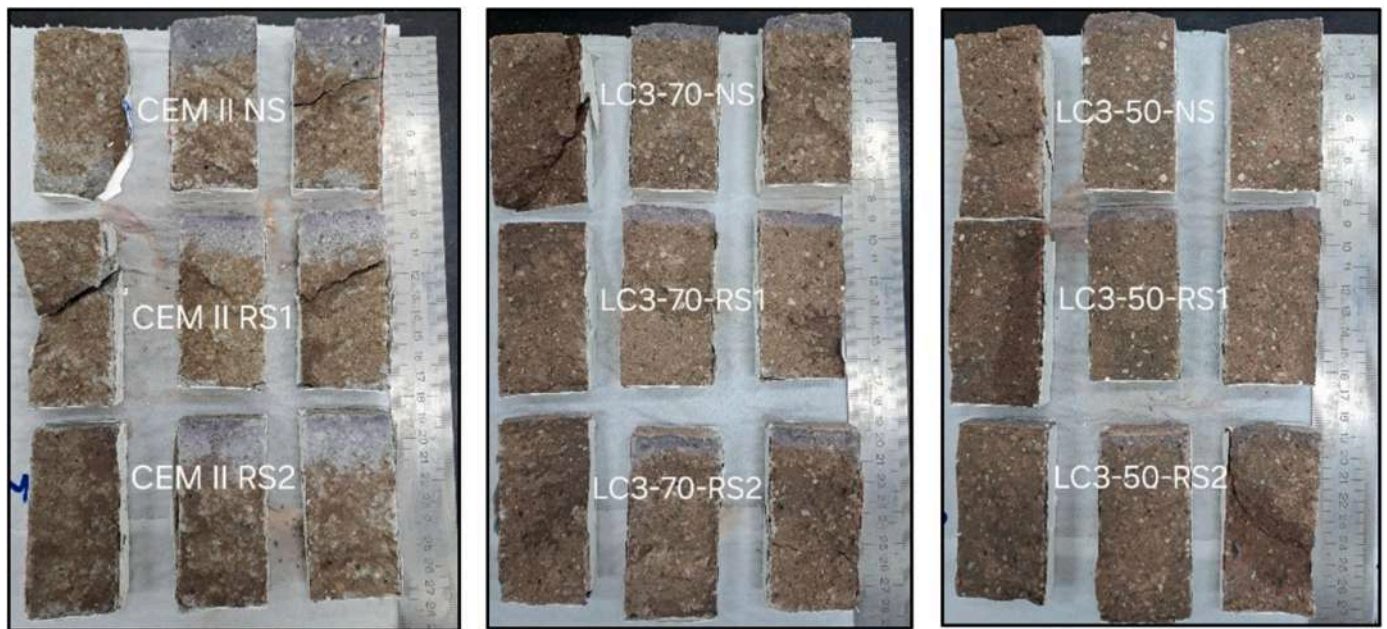


Fig. 8. Chloride penetration depth after mortars’ immersion in a NaCl solution, measured by silver nitrate solution. Sample on the left in each group are the mortars immersed in deionized water.

**Table 5**  
chloride penetration depth after mortars’ immersion in a NaCl solution, measured by silver nitrate solution (samples in Fig. 7).

Labels	Immersed condition chloride penetration depth (mm)
CEM II NS	22.3 (±0.3)
LC3-50-NS	6.2 (±0.1)
LC3-70-NS	7.9 (±0.2)
CEM II RS1	18.7 (±0.3)
LC3-50-RS1	5.9 (±0.1)
LC3-70-RS1	7.7 (±0.1)
CEM II RS2	24.8 (±0.7)
LC3-50-RS2	6.9 (±0.0)
LC3-70-RS2	8.9 (±0.4)

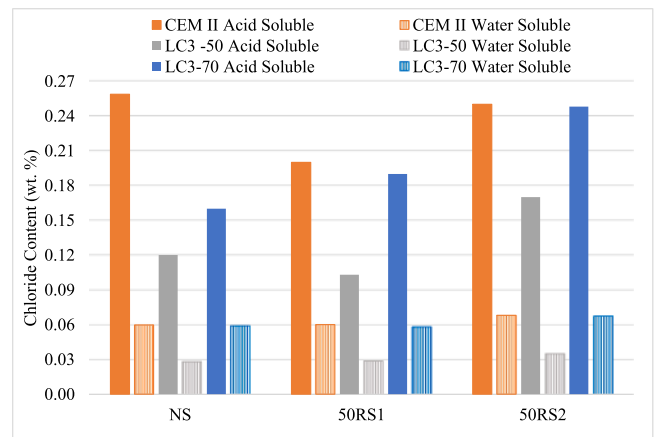


Fig. 10. water-soluble and acid-soluble chloride contents of different mortars after three months of immersion.

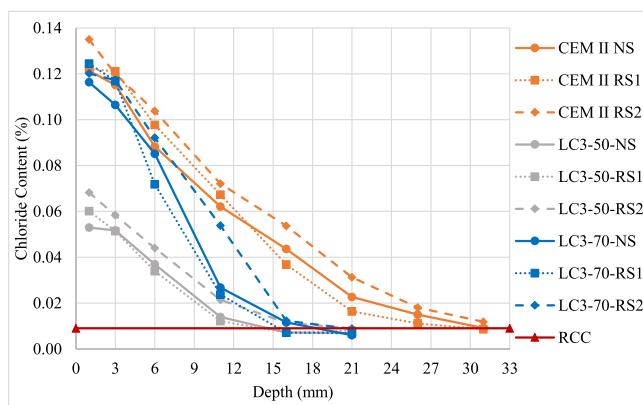
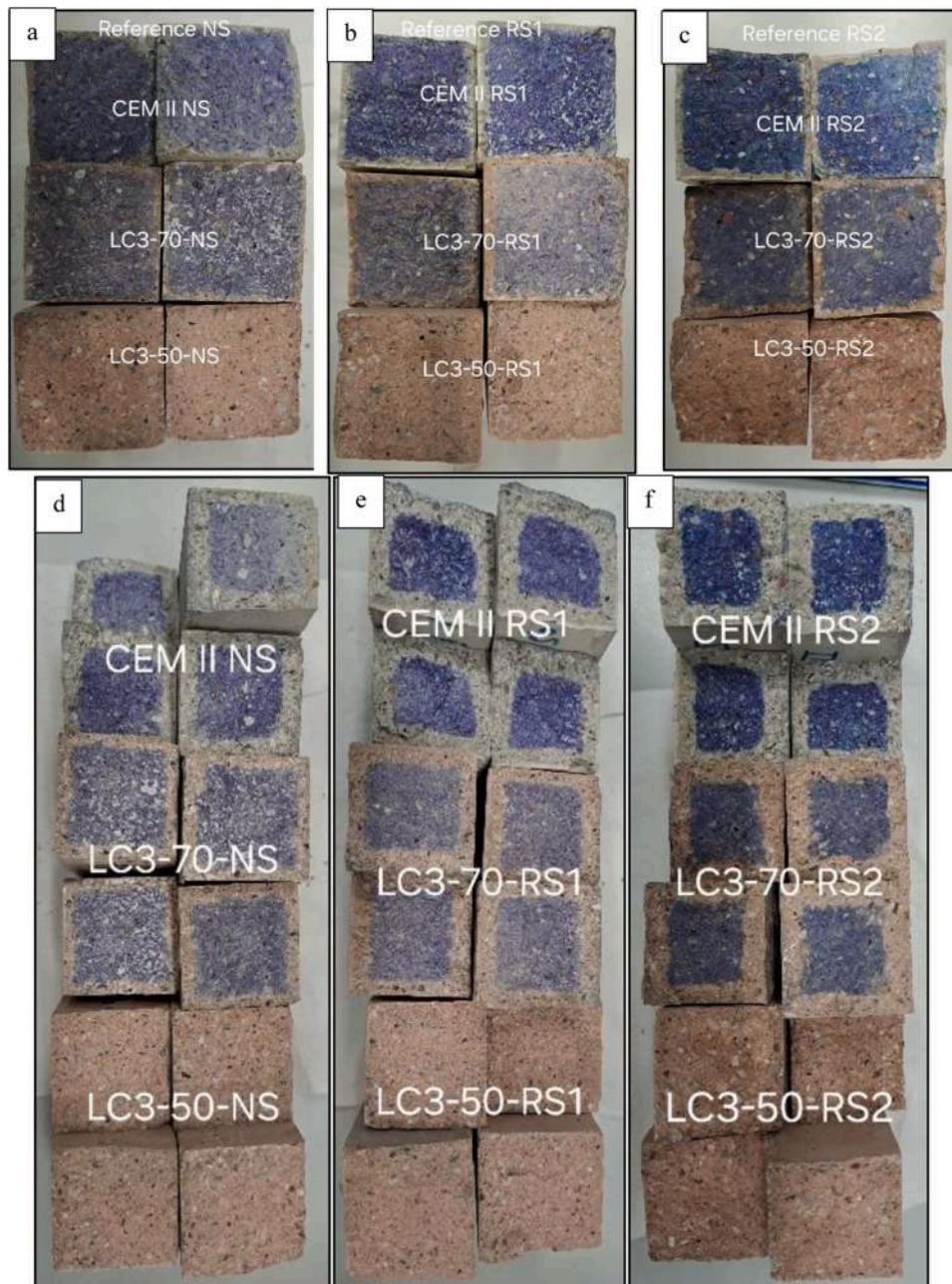


Fig. 9. Chloride penetration depth in the mortars after immersion in chloride solution, measured by ion chromatography. RCC= Reference chloride content of mortar immersed in deionized water.

that different standard methods suggest different CO<sub>2</sub> concentrations in accelerated carbonation tests and that various experiments reported in the literature have used widely varying CO<sub>2</sub> levels for accelerated tests, mostly between 4 % and 10 %, a concentration of 5 % was selected in this study [69]. The other half of specimens was left in open laboratory

environment at temperature 20±2°C and relative humidity 50±5 %, for comparison. After completion of the test, the specimens were taken out from the carbonation chamber, and the depth of carbonation was measured by spraying the surface of a freshly broken mortar prism with a pH indicator that contains 1 g of thymolphthalein in 70 ml ethanol and 30 ml of deionized water. This indicator was recently proposed as a substitute for phenolphthalein, the latter one being carcinogenic. Using this indicator, the non-carbonated part of the specimen, where the mortar is still highly alkaline and pH is higher than 9 [70], turns blue, while in the carbonated part no color change occurs. To cross-check the obtained results, only for the mortars manufactured with NS, an ex-situ leaching method was employed for the pH measurement [71]. In brief, 5 g of mortar were collected from the core of the samples exposed to natural carbonation, ground and mixed with 50 ml of water and stirred for 24 hours, then pH was measured through a pH-meter (VWR pHEnominal). After this measurement, the dispersion was covered and kept for additional 24 hours without stirring, and the pH was measured again. After analyzing the results (see Section 4.6), the assessment of the carbonation depth was repeated by spraying a solution of



**Fig. 11.** Results of the test with the thymolphthalein pH indicator. Carbonation depth under natural conditions: (a) different binders with NS, (b) different binders with RS1, (c) different binders with RS2. Carbonation depth under accelerated conditions: (d) different binders with NS, (e) different binders with RS1, (f) different binders with RS2.

phenolphthalein (1 g of phenolphthalein in 70 ml ethanol and 30 ml deionized water) over a freshly broken surface of the mortar samples, according to EN 14630:2007 [72]. In this case, the indicator turns from colorless to purple in the non-carbonated part of the specimen.

## 4. Results and discussions

### 4.1. Mechanical test

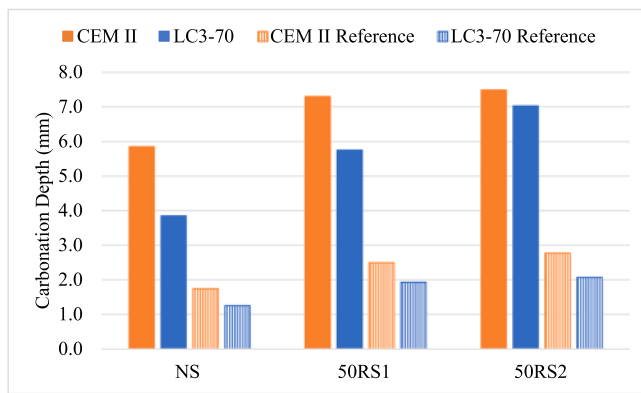
The compressive and flexural strength of mortars with different binders and sands (NS, RS1 and RS2, the latter two at 50 vol% replacement rate) are shown in Fig. 2 with respect to curing age (2 and 28 days).

Focusing on the effect of the binders alone (data for NS in Fig. 2), it can be observed that at 2 days the mechanical strengths of mortars with

LC<sup>3</sup> binders are slightly worse (LC3-50) and slightly better (LC3-70) than CEM II, however the variation is rather limited. On the contrary, mortars with LC<sup>3</sup> are much better than mortar with CEM II at 28 days, especially considering compressive strength in Fig. 2(a) (+ % 12 for LC3-50 and +35 % for LC3-70). This is because of the slow early-stage hydration process of LS and CC compared to OPC [73-75]. As the hydration of the binders progresses, the effect of the pozzolanic reaction of CC with portlandite enhances the strength development [6,7,76], overperforming CEM II.

Focusing on the effect of recycled sands, for each binder an identical trend of compressive and flexural strength reduction with recycled sand employment can be observed, as expected due to the porosity of RS1 and RS2 (see Table 2, where the higher porosity of RS1 and RS2 is visible from their higher water absorption compared to NS). However, when comparing the 28-day compressive strength values for NS and RS, the





**Fig. 12.** Carbonation depth of the different mortars after accelerated and natural (reference) carbonation, measured by the thymolphthalein pH indicator. LC3-50 was not reported, as it resulted fully carbonated.

**Table 6**

pH of the mortars with different binders and NS, exposed to the natural carbonation, measured by ex-situ leaching method (the samples were collected at the center of the prisms).

Mortar	Solid-to-water ratio	pH after 24 hours stirring	pH after further 24 hours in a static condition
CEM II-NS	1:10	13.0	13.0
LC3-50-NS	1:10	12.3	12.2
LC3-70-NS	1:10	12.9	12.8

LC3-70 binder exhibits superior mechanical strength compared to CEM II and LC3-50. LC3-70-RS1 compressive strength improved by 25 % compared to CEM II-RS1 and LC3-70-RS2 by 6 % compared to CEM II-RS2 respectively. Interestingly, Fig. 2(b) clearly shows the superior compressive strength of the LC3-50 binder in comparison to CEM II for NS and 50 % RS1 substitution, while LC3-70 exhibits higher compressive strength than CEM II for all samples with recycled sand replacement. This seems due to the lower porosity and refined pore size distribution of LC3-70 mortar compared to the reference mortars, as discussed below in Section 4.3. Fig. 2(c) and (d) report the 2- and 28-day flexural strength values, indicating that LC<sup>3</sup> binders give comparable flexural strength to CEM II for both types of RS and NS. However, also in this case the flexural strength decreases when RS substitutes NS, for each binder type, hence the results confirm that mechanical strength is impacted by sand substitution. However, it is noteworthy that at 28 days mortars with CEM II are affected by the substitution with recycled sand but without a particular difference between RS1 and RS2, while the mortars with LC<sup>3</sup> binders are also affected by sand quality (which is worse for RS2 than for RS1).

#### 4.2. Capillary water absorption

Capillary water absorption as a function of time can be used as an indication of open porosity and pores' connectivity [77], being a helpful parameter for the prediction of materials' durability, as all the deterioration processes are related to the presence of moisture in materials. A positive reduction in the capillary water absorption rate has been observed for binders containing calcined clay and limestone [59]. Fig. 3 shows the capillary water absorption curve of mortars manufactured with different binders and in combination with different recycled sands (RS1 and RS2). It was observed that mortars made with CEM II exhibited higher water absorption rates than mortars with LC<sup>3</sup>, regardless the sand type. Of course, the water absorption rate of CEM II mortars increased

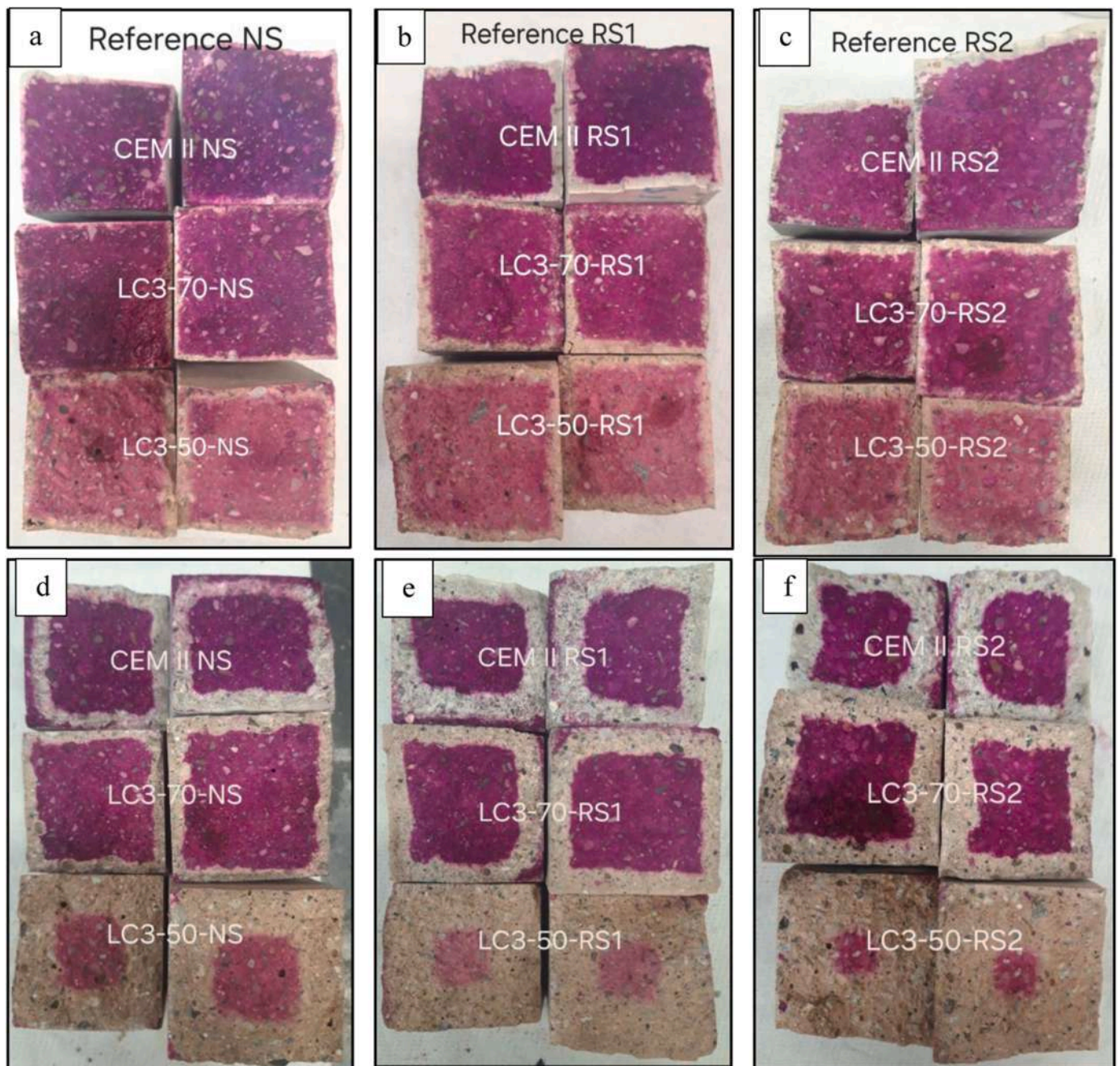
passing from NS to RS1 to RS2, and reached the value of 6.48 kg/m<sup>2</sup> for RS2 after 6 hours. These findings and observations can be correlated with the statement that the capillarity of mortar is not only related to the overall porosity of mortar but to interconnected pores present in the microstructure (see Fig. 4) [78], as LC3-50 binder has higher or comparable porosity with respect to CEM II. Furthermore, these findings highlight the critical role of the binder composition in determining capillary water absorption. For example, CEM II NS has a higher value of capillary water absorption after 6 hours (3.95 kg/m<sup>2</sup>) compared to LC3-50-RS2 (3.45 kg/m<sup>2</sup>) and LC3-70-RS1 (3.65 kg/m<sup>2</sup>), even if recycled sand is employed for the mortar production. This classification highlights the potential of LC<sup>3</sup> to mitigate the negative effects on durability associated with variations in sand type and substitution, providing improved performances in comparison to CEM II.

#### 4.3. Porosity assessment

The total porosity and pore size distribution of mortars obtained by MIP are presented in Fig. 4 and Fig. 5(a, b, and c) respectively. Fig. 4 demonstrates that up to 30 % replacement rate of LC<sup>3</sup> reduced the total porosity and beyond 30 % the total porosity rapidly increased and reached almost 17 % for LC3-50-RS2 which is comparable to CEM II RS2. Moreover, the total porosity of LC3-70 is lower compared to CEM II at all substitution levels of NS with RS1 and RS2. However, the recycled sand increases the total porosity. From Fig. 4 it can also be observed that porosity greatly depends on the quality of recycled sand. The RS2 produced more porous mortar as compared to NS and RS1. Similarly, Fig. 5 (a, b, and c) showed that mortar with LC<sup>3</sup>s refines the micropore size distribution and exhibits, for NS and RS2, the finest pores over the 3 binders, while CEM II displays the largest ones. The situation is slightly different for RS1 (Fig. 5b) where the three binders have comparable fine pores (below 0.02 μm). However, CEM II display higher volume of large pores (over 0.3 μm) also with RS1. Furthermore, since the analyzed samples were approximately 1 g, the ratio of binder, NS, and recycled sand may slightly vary from the original mortar composition, which could introduce some uncertainty. Nevertheless, a clear trend of the influence of the aggregate type and the classification of binders can be identified. This observation potentially explains the differences detected in the measured capillary absorption and mechanical strength [79,80]. These findings collectively contribute to a deeper understanding of the complex interplay between materials and water absorption, shedding light on potential improvements in cement and mortar formulations. Besides, according to literature, the pore structure was reported to become more refined with the aging of the samples for binders with higher kaolinite content up to a certain limit, which ultimately contributes to higher strength development at a later age compared to OPC binders [7]. Hence the presence of CC produces mortars with a denser microstructure and increases the overall performance of the LC3-70 binder in comparison to all the examined binders at a later age (28 days properties).

#### 4.4. Chloride ingress

The permeability and chloride-binding capability of binders have a major impact on the diffusion of chloride ions in cement-based materials and on the lifespan of reinforced concrete. Fig. 6 provides the aspect of the samples exposed to the salt fog chamber after the spraying of the silver nitrate solution, while Table 4 reports the Cl<sup>-</sup> penetration depths measured on the same samples with a vernier calliper. The mortars with CEM II binder have the least resistance to chloride ions penetration compared to those with LC<sup>3</sup> binders. The amount of chloride ions penetrated in the mortars after exposure to the salt fog chamber was measured by ion chromatography and the results are reported in Fig. 7 (a, b and c). The concentration of Cl<sup>-</sup> in both CEM II and LC3-70 mortars was higher than in LC3-50 near the specimens' surface, and the depth of the chloride ions penetration varied depending on the binder. The use of



**Fig. 13.** Carbonation depth of the mortars measured by the phenolphthalein indicator. After natural carbonation: (a) different binders with NS, (b) different binders with RS1, (c) different binders with RS2. After accelerated carbonation: (d) different binders with NS, (e) different binders with RS1, (f) different binders with RS2.

LC<sup>3</sup> reduced the chloride ion penetration depth by 57 % for LC3-50-NS and 38 % for LC3-70-NS compared to CEM II-NS. A similar reduction was observed when RS1 and RS2 were employed. In general, the chloride ions penetration depth and concentrations have been reduced by increasing the calcined clay percentage in the formulated cements. This could be attributed to the lower permeability of mixtures (See section 3.6) and higher alumina content of the system. Therefore, LC3-50 having 31.58 wt% of CC and LC3-70 having 17.55 wt% of CC have shown higher resistance to chloride ions ingress in terms of both concentration and penetration depth among all the examined mixture of different binders with different recycled sands.

Similarly, the chloride ingress test was carried out by immersion of the mortar samples in a 3 % NaCl solution and the ions penetration depth was assessed through silver nitrate solution and ion

chromatography. Fig. 8 provides an image of the samples, while Table 5 reports the Cl<sup>-</sup> penetration depth measured in the same samples with a vernier calliper. From Fig. 8 and Table 5, it is clear that mortars with CEM II suffered the highest penetration depth compared to those with LC<sup>3</sup> binders. Fig. 9 shows the chloride ion amounts at different depths obtained through ion chromatography. LC<sup>3</sup> binders provided higher resistance to ions penetration compared to CEM II binder, reducing the chloride contaminated depth by about 42 %. Fig. 9 also shows that the type of sand does not have a significant influence on the depth of chloride penetration and seems to only slightly affects their concentration.

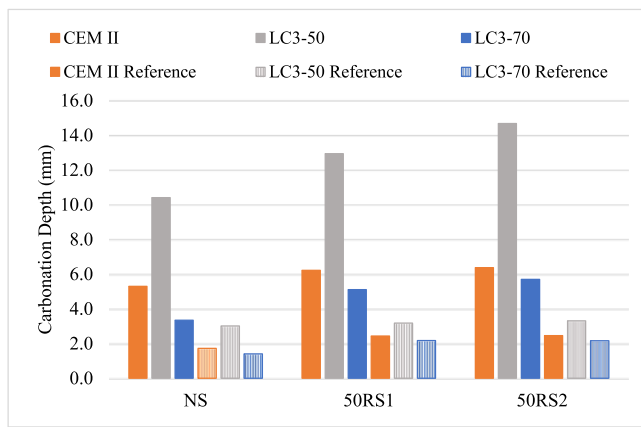


Fig. 14. Carbonation depth of the different mortars after accelerated and natural (reference) carbonation, measured by the phenolphthalein pH indicator.

#### 4.5. Water soluble versus acid soluble chloride content

The results obtained in the previous paragraph clearly indicate that the use of LC<sup>3</sup> decreases the penetration of chloride in mortars in terms of both depth and amount, determined by ion chromatography, i.e., in terms of water-soluble chloride. This effect might be due to a refining of the pore microstructure of the mortars, positively impacting on the diffusivity of ions, or to some chloride binding capacity of LC<sup>3</sup>. To investigate this latter effect, which might be ascribed to the extremely high specific surface area of CC [81], the mortars exposed to immersion in the NaCl saline solution were investigated for the measurement of the amount of acid-soluble chlorides in the contaminated layer, i.e. in the first 3 cm of CEM II mortars and in the first 2 cm of LC<sup>3</sup> mortars. The results are reported in Fig. 10, in comparison with the amounts of water-soluble chloride calculated by averaging the results obtained by IC on the same thickness (Fig. 9). It should be noted that, in most studies, the acid-soluble chloride content is regarded as the total amount of chloride penetration into concrete, specifically the sum of the free chloride ions, physical absorption, and chemical combination [82]. Similarly, the water-soluble chloride content represents the amount of free chloride ions in the pore solutions [83] and a negligible amount of binding chloride which might be released during the heating process of the sample [67]. From Fig. 10, it can be observed that mortars with LC3-50 exhibit significantly less chloride, including acid-soluble and water-soluble, compared to mortars CEM II and LC3-70. The first scope of determining the acid-soluble chloride was to investigate and compare the binding capacity of CC with CEM II and from Fig. 10, it can be observed that there is an identical difference between acid and water soluble chloride content across all the samples. Thus, the significantly lower acid-soluble and water-soluble chloride content of LC3-50 mortar can be explained by its lower capillary water absorption and the refinement of pore structure and pore solution [84]. From Fig. 10, it can also be observed that water-soluble chloride is barely affected by the employment of RS, while the acid-soluble chloride seems more variable, although a clear trend could not be found. The experimental results in this research work confirm that high chloride diffusion resistance can be achieved with the employment of calcined clay and limestone.

#### 4.6. Carbonation depth

Fig. 11 (a, b, and c) shows the carbonation depth of the mortar sample exposed to natural environment for 2 months. The type of binder plays an important role in the resistance to carbonation. Among the three binders, LC3-70 showed more resistance than CEM II and only a few millimeters of carbonation depth were observed, while LC3-50 was fully carbonated, as reported in Fig. 12. Similarly, the recycled sand has

a negative effect on the carbonation depth and passing from NS to RS1 and RS2 an increasing depth has been observed, as summarized in Fig. 12. These results can be attributed to the higher porosity and permeability of the mortars with recycled sands.

Fig. 11 (d, e, and f) show photos of the thymolphthalein indicator test performed on mortar specimens exposed to 5 % CO<sub>2</sub> for 2 months, i.e. to accelerated carbonation. The binders showed a similar trend of resistance to carbonation compared to natural conditions and the results confirm that LC3-70 binder gave higher resistance compared to CEM II, while LC3-50 was fully carbonated. This is a very interesting result, because the refinement in the mortars' microstructure would suggest a better behavior for LC3-50 mortar, which was not observed. Additionally, the type of sand also plays an important role in resistance to carbonation, likely owing to the fact that the porosity of recycled sands is higher than that of NS and hence offer less resistance to CO<sub>2</sub> penetration. From Fig. 12 it can be observed that mortars with recycled sands suffer a deeper carbonation in comparison to NS, and in fact the carbonation depth of CEM II-RS1 and CEM II-RS2 mortars increased up to 25 % and 28 % compared to CEM II-NS. Similarly, the carbonation depth of LC3-70-RS1 and LC3-70-RS2 mortars increased by 49 % and 82 % compared to LC3-70-NS. These findings indicate that LC3-70 binder is more affected by sand quality than CEM II.

Concerning the fact that the mortars with LC3-50 binder were fully carbonated across all types of sand and in both conditions (natural exposure and accelerated carbonation), there seem to be two possible explanations. The first one is that the high content of CC and LS reduces the pH of the mortar, probably even before carbonation. To investigate this hypothesis, the pH of the mortars manufactured with NS and exposed to natural carbonation was determined, collecting the samples from the core of the prisms and using the 'ex-situ leaching method', and the results are reported in Table 6. It can be observed that the pH varies according to the clinker's content in binders, but this variation is very limited, as there is not much difference in the pH for different binders in both measurement times (i.e., after 24 hours of stirring and after additional 24 hours in static condition), hence this first hypothesis was discarded. The second possible explanation is that the thymolphthalein indicator somehow interacted with the calcined clay in the samples, altering their appearance in Fig. 10. To investigate this hypothesis, a test with a different pH indicator was conducted on mortar samples. The specimens were split again and sprayed with phenolphthalein solution. The results obtained are shown in Fig. 13 (natural and accelerated carbonation), which confirms that the thymolphthalein pH indicator is not effective for LC<sup>3</sup> binder having up to 50 % replacement of OPC. A summary of the carbonation depths measured by phenolphthalein is reported in Fig. 14. The results confirm that LC3-70 binder exhibits more resistance to carbonation compared to CEM II and LC3-50 across all types of sands utilized for mortar production. Conversely, LC3-50 exhibits the lowest resistance to carbonation, although the carbonation was not complete as apparently resulted from the previous test, and a carbonation depth of about 10 mm was measured in the case of NS after accelerated carbonation. When NS was replaced by RS, the carbonation depth increased and reached up to 15 mm with RS2 replacement. This could be attributed to the lower portlandite amount in LC3-50, due to the low clinker content from the beginning present in the LC3-50 [85]. However, this result can have significant implications for the use of LC3-50 in reinforced concrete structures, hence additional investigation on the corrosion susceptibility of steel in contact with LC<sup>3</sup> binder will be necessary to properly assess the behavior of this binder.

## 5. Conclusions

This study deals with the performances of mortars prepared with a combination of LC<sup>3</sup> with two types of recycled sands, in comparison to mortars prepared with limestone Portland cement (CEM II) and natural crushed sand. The recycled sands were employed in the mortars with a percent of substitution of natural sand equal to 50 % by volume. The

obtained results can be summarized as follows:

- Mortars prepared with LC<sup>3</sup> binders require significantly higher doses of SP compared to traditional OPC mixtures to achieve target workability and shows relatively slow strength development, especially at early curing time (2 days) and at lower clinker amount (LC3–50). However, at 28 days, the mechanical properties of mortars with LC<sup>3</sup> binders are superior to those with CEM II, for natural sand, RS1 and RS2, except for the combination of LC3–50 and RS2 (i.e., the lowest amount of clinker and the worst recycled sand). Notably, the mortars with LC<sup>3</sup> and recycled sand RS1 (50 % replacement) exhibit compressive strengths comparable or even higher than the mortar prepared with CEM II and natural sand. This is a very encouraging result, which suggests that LC<sup>3</sup> binders have the potential to mitigate the negative impact of substituting part of natural sand with recycled ones, provided that such substitution is carried out by volume not to alter the amount of binder paste per unit volume.
- LC3–70 binder exhibited lower capillary water absorption rates across all the substitution levels of natural sand with recycled ones compared to CEM II. This is extremely important, suggesting an improved durability of the materials prepared with LC<sup>3</sup>.
- LC<sup>3</sup> binder has a positive impact on the pore size distribution of the mortars produced, which exhibited refined pores. In particular, LC3–70 binder also allowed to obtain mortar with lower total porosity compared to CEM II and LC3–50.
- The chloride resistance of mortars with LC<sup>3</sup> binders increases as limestone and calcined clay amounts increase and the depth of chloride ingress was found to decrease by about 42 % in comparison to CEM II mortar. This result is basically unaffected by the partial substitution of natural sand with recycled ones, indicating that the binder is the component which plays the key role in resistance to chlorides.
- LC3–70 binder has shown the potential to reduce carbonation depth in comparison to the reference binder CEM II. However, the LC3–50 binder exhibited less resistance against carbonation and this will require further tests to assess whether the limited amount of clinker in the cement (50 %) may affect the corrosion behavior of steel reinforcement. Apparently, the pH of the non-carbonated mortars is comparable for all the binders investigated, but also in this case further investigation seems necessary to follow the pH evolution during curing.
- Thymolphthalein pH indicator seems not effective for the assessment of the carbonation depth of the mortars with limestone calcined clay cements, so it is recommended to use phenolphthalein as a pH indicator for LC<sup>3</sup> binder, particularly when the clinkers replacement is high (50 %).

This study demonstrates that the use of LC<sup>3</sup> binders in mortars not only improves mechanical properties and durability, but also enhances resistance to chloride ingress and carbonation, although the clinker substitution rate is a delicate point to consider for corrosion behavior of steel reinforcements. Moreover, in combination with recycled sand, these low-carbon cements specifically enhance the performances of mortars, providing a valid and sustainable alternative to the commercial cement mostly used nowadays in construction.

#### CRediT authorship contribution statement

**Lucia Ferrari:** Project administration, Methodology, Investigation. **Ahmad Jan:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation. **Nikola Mikanovic:** Writing – review & editing, Validation. **Elisa Franzoni:** Writing – review & editing, Supervision, Software, Resources, Project administration, Methodology, Formal analysis, Conceptualization. **Mohsen Ben-Haha:** Writing – review & editing, Validation.

#### Declaration of Competing Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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#### Data availability

Data will be made available on request.

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