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Influence of low carbon cement and recycled aggregates on mortar fresh state and early hydration

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ABSTRACT

Calcined clay and limestone are promising clinker substitutes for production of new low carbon cements. Limestone calcined clay cement (or LC^3) can reduce carbon dioxide emissions by up to 40% and are made of raw materials which are abundant and globally available. Many studies have already examined the hydration behavior of calcined clay-based cements and linked it to early- and late-age strength development. However, very few works were dedicated to the analysis of mortars prepared with this type of binder and recycled sand. The introduction of construction and demolition waste as aggregate in combination with low-carbon cement would further decrease the environmental impact of building materials.
In this paper, the fresh state of mortar containing recycled sand and calcined clay in variable amounts was analyzed by means of flow table test. The pore size distribution of fresh mortar was identified using ^1H Time Domain Nuclear Magnetic Resonance (TD-NMR), that is a low field TD-NMR approach. The compressive strength of samples was also measured. Results show that mortar containing calcined clay immediately consumes part of the available capillary water with drastic consequences on its rheological behavior. Moreover, the recycled sand influences fresh properties and mechanical compressive strength. However, proper mix designs obtained by substituting the natural sand with recycled sand according to the occupied volume proved that mortar composed by low-carbon cement and recycled aggregate is still suitable for many applications contributing to the sustainability of construction materials.

KEYWORDS: *calcined clay, limestone, recycled sand, rheology, ^1H TD-NMR.*

1. Introduction

Concrete is the most widely used building material for infrastructures and habitations. Cement, concrete's key ingredient, has a dramatic carbon footprint as clinker production is responsible of about 7% of the global CO_2 emissions (WBCSD, 2009). For this reason, European Standard EN 197-5:2021 was published in May 2021 to allow formulation of cement of class CEM II/C-M containing from 50% to 64% of clinker, while previous version CEM II/B required minimum 65% of clinker. The properties of calcined clay limestone cement have been studied over last years in terms of chemistry and hydration, showing that this material has promising properties concerning cement reactivity and sustainability (K. L. Scrivener et al., 2018). However, workability studies on calcined clay cements showed that higher amount of admixture is required to provide rheological properties comparable to Ordinary Portland Cement (OPC) (Dhandapani et al., 2022). Another strategy to reduce concrete environmental impact is the use of recycled aggregates, i.e., obtained from construction and demolition waste. This has been extensively studied, highlighting that the high porosity of recycled aggregate makes them absorb more water than natural aggregates, making difficult the right estimation of the required effective water (Manzi et al., 2013). Indeed, recycled aggregates may be highly porous and sorptive, thus affecting some properties of concrete mixes like workability and mechanical strength (Thérené et al., 2020). Therefore, the combination of these aggregates with calcined clay-based binders, that provides a further step in improving concrete sustainability (Xing et al., 2023), arises important technical challenges as both components, the binder and the aggregate, significantly affect concrete workability and compressive strength. In this work, mortar containing calcined clay-based cement and recycled sand was studied to analyse rheological behaviour and mechanical strength properties. The amount of consumed water and the pore size distribution of mortar was quantified using the ^{1}H Time Domain Nuclear Magnetic Resonance (TD-NMR). The aim of this work is to show which technical adjustments are necessary to obtain a usable mortar composed of low carbon cement and recycled sand.

2. Materials

The materials to blend low carbon cements and aggregates were supplied by Heidelberg Materials AG, Germany. The binders and powders used in this study were: CEM I 52.5 R (CEM I), CEM II/A-LL containing 12% of limestone (CEM II), calcined clay from France (CC), and limestone (LS). The polycarboxylate ether-based superplasticizers (SP) was kindly provided by CHRYSO SAINT-GOBAIN R&D laboratory in Sermaises (France) and contains 22% of solid.

The Natural Sand (NS) was provided by Italcementi in Bergamo, Italy, while the Recycled Sand (RS) was provided by Heidelberg Materials and comes from construction and demolition waste. Characteristics of natural sand and recycled sand, measured according to EN 1097-6 standard, are reported in Table 1. Water absorption refers to the mass of the saturated and surface-dried aggregate in the air.

Table 1 – Characteristics of sands according to EN 1097-6 standard.

	Oven dried particle density (kg/m^3)	Water Absorption (%)
Natural Sand	2660 ± 20	0.44 ± 0.02
Recycled Sand	2274 ± 20	4.66 ± 0.23

Particle size distribution of sands was measured by quarting and sieving. The max diameter of NS is 4 mm while for RS is 2 mm.

3. Formulation

3.1 Binder

The two commercial cements, CEM I and CEM II, were used as reference binders. Other three binders were formulated according to the following proportions by mass: LC^3-50 2:1 with 50% of clinker, CC:LS=2:1, LC^3-50 1:1 with 50% of clinker, CC:LS=1:1 and LC^3-70 2:1 with 70% of clinker, CC:LS=2:1

3.2 Mortar

The mortar mixing and preparation were conducted in a Hobart mixer, according to standard EN 196-1:2016. The composition for mortars prepared with 100% NS was: (450 ± 2) g of binder, (1350 ± 5) g of NS, (225 ± 1) g of water. The composition for mortars prepared with 50% of NS and 50% of the same volume of RS was: (450 ± 2) g of binder, (675 ± 2) g of NS and (584 ± 2) g of RS (in oven dried condition), (252 ± 1) g of water. The amount of water was calculated by adding the effective water (225 g) and the water necessary to bring the RS to saturated surface dry conditions 27 g). The superplasticizer dosage was adjusted to provide target flowability.

4. Methods

4.1 Mortar test

The mortar flow was measured immediately after mixing by flow table test according to EN 1015-3 standard specification. A mortar spread diameter between 20 and 22 cm was targeted by using an appropriate superplasticizer dosage to obtain a mortar which is neither too sticky, nor too liquid, in order to allow a good flow and avoid segregation. The mechanical compressive strength was measured at 2d according to the EN 196-1 standard.

4.2 Water detection by ^1H TD-NMR

The objective of ^1H TD-NMR measurements was to detect the amount of the capillary, interhydrate and interlayer water in mortar. NMR equipment allows the detection of the transverse (T_2) relaxation curves and the computed values of T_2 provide information about water confinement in cement matrix and porous media in general. The instrumental setup is composed of a permanent magnet (ESAOTE, Genova, Italy) with a magnetic field $B_0 \approx 0.2$ T (corresponding to ^1H Larmor frequency ≈ 8 MHz), a 25 mm probe, and an NMR console (Stelar s.r.l., Mede, Italy). Relaxation T_2 curves were detected using the Carr–Purcell–Mei-boom–Gill (CPMG) sequence with 512–2048 number of echoes, depending on the mobility of water in the sample microstructure, with an echo time of 60 µs and 100-500 scans. Data acquisitions were conducted at 1 hour of hydration and two repeated measurements were performed on each sample or around 20 g. The T_2 quasi-continuous distribution was computed by the software UpenWin (Borgia et al., 2000), developed by the group at the University of Bologna, to verify the presence of specific peaks, while for multi-exponential non-linear fitting a script in Psi-Plot was implemented (*Poly Software International, USA*, n.d.). For tri-exponential fitting, the T_2, the corresponding assignment and pore size are as follow, according to previous studies carried out on white cement (K. Scrivener et al., n.d.):

- Capillary water pore size ≈ 1000 nm T_2 8-10 ms
- Interhydrate water pore size 10–20 nm T_2 1-2 ms
- Interlayer water pore size 3−5 nm T_2 0.1-0.2 ms

5. Results

The superplasticizer dosage to obtain target workability and the water distribution in the different pore classes of the mortar at 1 hour hydration are shown in Table 2.

Table 2 – Summary of results obtained with mortar flow test and TD-NMR.

Sand	Binder	Average mortar spread diameter (cm)	SP dosage for target workability (g SP/g binder)	Capillary water – 1 µm pores (%)	Interhydrate water – 10-20 nm pores (%)
NS	CEM I	21.3	0.6%	68	32
	CEM II	21.0	0.6%	54	46
	LC^3-50 2:1	20.7	1.3%	27	73
	LC^3-50 1:1	21.4	1.1%	36	64
	LC^3-70 2:1	21.8	1.0%	42	58
RS	CEM I	21.8	0.5%	69	31
	CEM II	20.9	0.5%	50	50
	LC^3-50 2:1	20.8	1.2%	29	71
	LC^3-50 1:1	20.4	1.0%	29	71
	LC^3-70 2:1	20.7	0.9%	35	65

It has to be noticed that SP dosage increases linearly with the amount of calcined clay in the binder. The results also show that, if the sand substitution is carried out by volume (i.e., not altering the binder to aggregate ratio in the material) and the water absorption by the recycled sand is properly compensated, the amount of SP additive necessary to obtain a sufficiently fluid mortar is basically the same when using natural and recycled sand, or even slightly lower SP for the mortars containing RS. This result is not controversial if it is considered that in literature studies the aggregate substitution is usually calculated by mass (Faleschini et al., 2014). The TD-NMR results highlight that a significant amount of capillary water, i.e. pores of nearly 1 µm size, is consumed by cement containing calcined clay after only 1 hour of hydration, generating voids of 10-20 nm assigned to interhydrate water, as showed by (Ferrari et al., 2023). This highlights a specific consumption of water by calcined clay that directly affect workability. Unexpectedly, no significant difference in porosity between mortars containing NS and RS is detectable in these preliminary experimental conditions. This new approach is still under investigation to possibly highlight differences between natural sand and recycled aggregates.

Compressive strength measured at 2 days of curing is reported in Table 3.

Table 3 – Compressive strength values at 2 days (MPa).

Sand	CEM I	CEM II	LC^3-50 2:1	LC^3-50 1:1	LC^3-70 2:1
NS	50	38	33	29	42
RS	36	30	19	19	32

Recycled Sand has a strong impact on mechanical strength development, although the values obtained with the LC^3-50 cements and RS can be considered still acceptable, as they are above the minimum value of 18 MPa prescribed by EN 197-1 standard for 42.5R or 52.5N cements.

6. Conclusions

This paper demonstrates that the combination of low carbon cement and recycled sand may lead to mortars with good rheological properties as well as acceptable early compressive strengths. The approach proposed showed that a substitution of 50 % of sand particles according to their volume, instead of their mass, is a successful strategy to limit the impact of recycled aggregate on mortar rheology. Moreover, the consideration of effective water, related to water absorption of recycled material, helps to adjust superplasticizer dosage with almost no change in comparison to the standard mortar.
Further investigations by TD-NMR highlighted that calcined clay consumes high amount of water directly impacting mortar workability and consequent superplasticizer dosage. However, the interaction between water and recycled aggregates still needs to be more investigated.

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