

## Assessment of geopolymers with Construction and Demolition Waste (CDW) aggregates as a building material

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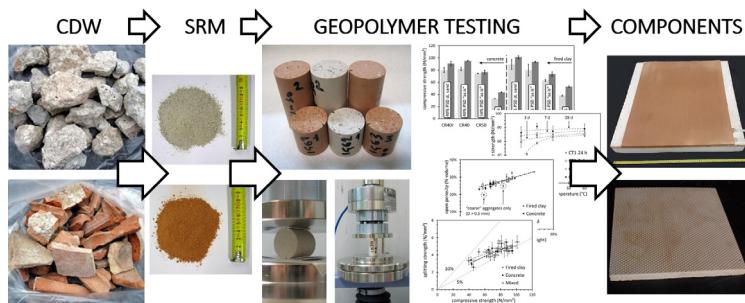
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### HIGHLIGHTS

- Geopolymer mixtures with CDW aggregates were extensively characterized from a mechanical and physical standpoint.
- Their potential as a building material was explored through the investigation of selected parameters.
- Aspects related to a possible exploitation at industrial level were investigated as well.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The paper presents the assessment of metakaolin-slag-potassium-silicate geopolymer mixtures containing concrete and fired clay aggregates from Construction and Demolition Waste (CDW). An extensive characterization was carried out from a mechanical and physical standpoint, aimed at exploring their potential as a building material and their suitability for exploitation at industrial level. Based on the obtained experimental results, geopolymers with CDW showed promising properties for use in building elements even with 50% of aggregates and more, although further aspects need dedicated investigations.

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### 1. Introduction

Construction and Demolition Wastes (CDWs) typically comprise inert mineral materials (concrete, bricks, tiles and ceramics, etc.), with smaller amounts of other components (e.g. wood, glass, plasterboard, bituminous mixtures and tar) [1]. CDWs are one of

the main sources of waste in Europe, according to official data released by the European Union (EU) [2]. Although estimations may vary, due to illegal dumping and to different waste definitions and reporting mechanisms in force in various Countries [3], CDWs approximately represent one third of the total waste generated by economic activities and households, which in EU-28 are about 2.5–3 billion tonnes per year [2]. Thus, the European CDWs stream is about 0.8–1 billion tonnes per year. As underlined by Peng et al. [4], the recycling of CDWs is of primary importance for several reasons: CDWs are heavy and bulky, thus undesirable for landfill disposal; many of them are potentially very relevant for recovery and

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reuse; their recycling is environmentally significant since it would reduce the consumption of energy and natural resources, the emission of CO<sub>2</sub>, and would promote the achievement of recycling goals (70% by weight in the European Union, according to the Waste Framework Directive [5]) and the preservation of valuable space in landfills. Incidentally, it is worth mentioning that a lack of harmonisation still exists in EU, with End-of-Waste (EoW) criteria not fully developed or consistent across different Countries [6].

Currently, two of the main destinations of recycled CDWs are: unbound aggregates for road sub-bases [7] and bound aggregates for concrete mixes [8–10], the latter being a higher added value recycling pathway. According to Nixon [10], just after the Second World War the use as aggregate in fresh concrete of brick debris left by intensive bombardments was documented, and later on concrete rubble coming from demolished fortifications was included as well. Conversely, after that period of intensive rebuilding, there was little research interest until the Seventies, when the increasing availability of CDWs and the expected future scarcity of natural aggregates promoted more systematic investigations on recycled aggregates. Recent studies demonstrated that the production of structural Recycled Aggregates Concrete (RAC) with properties comparable to those of standard concretes is feasible through a careful optimization of CDWs typologies [11,12], grading [13] and mixing approach [14]. This is mainly due to an improved refinement of the Interfacial Transition Zone (ITZ) between old aggregates and the new cementitious matrix [15,16]. Nevertheless, the use of RAC is restrained by several drawbacks. It is worth mentioning, among them, the inferior mechanical properties and the greater drying shrinkage generally exhibited by RACs in comparison to concrete made with virgin aggregates, their lower resistance to carbonation and chloride penetration, and the still low cost of natural aggregates [9–11].

A promising alternative recycling option appears to be offered by Alkali Activated Materials (AAM) and geopolymers binders, incorporating CDWs as either inert aggregates or partially reactive materials. Since AAM/geopolymers were shown to present great flexibility in using numerous types of different industrial wastes and by-products [17,18], the use of CDWs in these binders has been extensively investigated recently, with encouraging results. Concrete and/or fired clay waste aggregates were studied in [19–23]. Concrete, brick, glass and ceramic tile waste in geopolymer binders were investigated also by [24–26], while brick waste aggregates alone were specifically studied in [27] and [28], and ceramic waste aggregates were tested in [29] and [30]. These papers testify both the interest and the potential of AAM/geopolymer binders in the recycling/reuse of CDWs.

Within this context, a research was developed in the framework of the H2020 European project “InnoWEE – Innovative pre-fabricated components including different waste construction materials reducing building energy and minimising environmental impacts”, focused on the development of architectural components (i.e. prefabricated panels for insulation, ventilated façades and radiant heating/cooling) made with geopolymer mixtures embedding CDWs. The present work presents the assessment of metakaolin-slag-potassium-silicate mixtures containing concrete and fired clay aggregates derived from CDWs. The extensive mechanical and physical characterization herein reported aimed at exploring their potential as a building material and their suitability for exploitation at industrial level. It is worth noting that the term “geopolymer” was used instead of the more general “AAM”, according to Provis et al. [31], due to the primary role of the aluminosilicate and highly coordinated binding phase.

Several parameters were selected for the study, among the numerous variables that may affect the behaviour and the performance of mixtures. The test program was focused not only on mechanical performance and physical properties, but also on

aspects that may influence the exploitation in industrial processes. The experimentation was obviously not exhaustive, because the subject is very wide and there are challenging aspects [32,33] (e.g. drying shrinkage, efflorescence, freeze-thaw in presence of salts, lacking of effective superplasticizing agents, etc.), whose investigation is currently at a preliminary stage. Nonetheless, the aspects presented in the following sections were assumed to be of primary importance at the first stage of the assessment process.

## 2. Experimental program

The experimentation involved the thorough testing of 41 geopolymer mixtures with CDW aggregates, whose detailed features are provided apart as [supplementary data](#), for the sake of brevity. The mechanical performance of each mixture was evaluated in compression, at 7 days and 28 days of age, and in splitting at 28 days (some of them also at 7 days), except those aimed at investigating the effects of curing temperatures, which were tested only in compression but at the additional ages of 24 h and 3 days (two of them also at 3 and 6 months). Bulk and material density, open porosity and water absorption of each mixture were also measured after at least one month of curing.

In order to optimize time and material consumption, 3 repetitions for each test were envisaged, for overall 300 compression tests, 168 splitting tests and 123 measures of bulk density, material density, open porosity and water absorption. The test matrix is shown in [Table 1](#), where mixtures are grouped by scope. It is to be noted that the original labelling of mixtures was herein revised to improve clarity, thus the present labels might not match those apparent in photos. Groups are sorted in logical order, but they do not reflect the chronological sequence of testing. Details about materials, sample preparation and test methods are reported in the following sections, along with specifications of the investigated parameters. It is to be noted that, for the sake of clarity, aggregate contents are expressed throughout the paper as a percentage of the overall dry weight of the mixture, differently from the common practice of concrete and mortars, where aggregates are usually indicated by the ratio with the binder.

### 2.1. Materials and specimen preparation

#### 2.1.1. Binder

The geopolymer binder was prepared by mixing commercial metakaolin (MK: Argical MK 36), with median particle size 8.6 µm, and commercial furnace slag (SL: Minerali Ind. LV 425), with median particle size 9 µm, as reported in their datasheet. The quantitative chemical analysis of the reagents by Energy Dispersive X-ray Spectrometry (EDS), carried out with a FEI Quanta 200F FEG-ESEM equipped with an EDAX Genesis EDS system, is reported in [Table 2](#). Two types of potassium-silicate activator with a modulus SiO<sub>2</sub>/K<sub>2</sub>O of either 1.26 (dens. 48.3%, type A) or 1.88 (dens. 44.1%, type B) were prepared by mixing LUDOX® TM-50 colloidal silica and KOH pellets (both from Sigma-Aldrich) with distilled water at least 24 h prior to use. Based on the chemical composition of the reagents, the generic SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios of the activator and the solid precursors were comprised between 4.4 and 4.8, while K<sub>2</sub>O/SiO<sub>2</sub> ~ 0.35 and K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ~ 0.84.

#### 2.1.2. Aggregates

Aggregates used in geopolymer mixtures were obtained from the in-house grinding of concrete and fired clay scraps, both coming from two different sources. In the first phases (mixtures belonging to Group 1 – blend of aggregate types, and Group 2 – curing temperature), wastes with known origin were used, labelled CRO and FC0. Then, they were replaced by wastes (CR1 and FC1)

**Table 1**

Test matrix of geopolимер mixtures, grouped by scope (in brackets those that appear more than once).

| Mixtures   | Compression |     |     |      |                |                | Splitting<br>7 d                 | Others* |      |
|--|-------------|-----|-----|------|----------------|----------------|----------------------------------|---------|------|
|  | 24 h        | 3 d | 7 d | 28 d | 3 m            | 6 m            |                                  | 28 d    | >1 m |
| <i>Group 1: Blend of Waste types</i>                                   |             |     |     |      |                |                |                                  |         |      |
| BW1, BW2, BW3, BW4, BW5  | –           | –   | all | all  | –              | –              | –                                | all     | all  |
| <i>Group 2: Curing Temperature</i>                                     |             |     |     |      |                |                |                                  |         |      |
| CT1-AT, CT1-30°, CT1-40°, CT1-60°, CT2-AT, CT2-40°, CT2-60°            | all         | all | all | all  | CT1-AT, CT2-AT | CT1-AT, CT2-AT | –                                | –       | all  |
| <i>Group 3: waste amount of concrete (CR) and fired clay (FC)</i>      |             |     |     |      |                |                |                                  |         |      |
| CR40, CR40r, CR50, CR60, FC40, FC50, FC60                              | –           | –   | all | all  | –              | –              | CR60, FC60                       | all     | all  |
| <i>Group 4: Particle Size Distribution</i>                             |             |     |     |      |                |                |                                  |         |      |
| PSDcr-f, PSDcr-g, PSDcr-i, PSDcr-r, PSDfc-f, PSDfc-g, PSDfc-i, PSDfc-r | –           | –   | all | all  | –              | –              | all                              | all     | all  |
| <i>Group 5: metakaolin:slag ratio</i>                                  |             |     |     |      |                |                |                                  |         |      |
| (CR40), CR40-1:2, CR40-1:3, (FC40), FC40-1:2, FC40-1:3                 | –           | –   | all | all  | –              | –              | CR40-1:2, FC40-1:2               | all     | all  |
| <i>Group 6: reduction of base amount</i>                               |             |     |     |      |                |                |                                  |         |      |
| (CR40), CR40-15%, CR40-30%, (FC40), FC40-15%, FC40-30%                 | –           | –   | all | all  | –              | –              | CR40-15% & -30%, FC40-15% & -30% | all     | all  |
| <i>Group 7: Preparation Temperature during mixing</i>                  |             |     |     |      |                |                |                                  |         |      |
| PT0, PT1, PT2, PT3, PT4  | –           | –   | all | all  | –              | –              | all                              | all     | all  |

“others” indicates dry bulk density, material density, open porosity and water absorption.

**Table 2**

Elemental Analysis by oxides (% weight) of metakaolin (MK) and furnace slag (SL).

| Material | Al <sub>2</sub> O <sub>3</sub> | CaO   | Fe <sub>2</sub> O <sub>3</sub> | K <sub>2</sub> O | MgO | SiO <sub>2</sub> | SO <sub>3</sub> | TiO <sub>2</sub> |
|----------|--------------------------------|-------|--------------------------------|------------------|-----|------------------|-----------------|------------------|
| MK       | 39.08                          | –     | 1.78                           | 0.94             | –   | 56.16            | –               | 2.04             |
| SL       | 9.31                           | 44.36 | 0.57                           | 0.71             | 6.2 | 36.48            | 1.55            | 0.83             |

supplied by the company involved in the InnoWEE project, which can be considered representative of actual waste streams generated by selective demolition of ordinary buildings.

CR0 derived from residual cubic test specimens of Ordinary Portland Cement (OPC) concrete in class C30/37 according to [34], whereas FC0 derived from commercial red soft-mud bricks with a declared compressive strength  $f_b$  [35] of 18 N/mm<sup>2</sup>, produced by a local brick industry. Further data are not disclosed, being them covered by official testing certifications delivered to the proprietary industry. However, the main aim was only to collect selected and tested representative average waste with known compressive strength. Conversely, concrete waste CR1 and fired clay waste FC1 came from non-hazardous CDWs obtained by selective demolition processes and classified as 17.01.01 (concrete) and 17.01.02 (bricks), according to the European List of Wastes [36], for which is impossible pointing out the initial compressive strength. Images of CR1 and FC1, before and after milling, are shown in Fig. 1.

As a general indication, concrete with a compressive strength of 35 N/mm<sup>2</sup> was referred to as “high-strength” in the 1950s, and products with compressive strengths exceeding 60 N/mm<sup>2</sup> have become commercially available in the early 1970s [37], but they did not affect most of the ordinary low and medium rise buildings; nowadays, a reasonable strength limit for ordinary concrete can be assumed at 50 N/mm<sup>2</sup> according to Eurocode 2 [34], although not explicitly mentioned. Concerning fired clay bricks, their normalized strength rarely exceeds 40–50 N/mm<sup>2</sup> even in modern extruded units [38].

The mineralogical quantitative phase analyses (QPA) was performed through X-ray powder diffraction (XRPD) with a Bragg-Brentano 00 diffractometer (PANalytical X'Pert PRO) equipped with a real time multiple strip detector (X'Celerator by Panalytical). It revealed (Table 3) that the main components of CR1 were calcite, quartz (especially in “coarser” fractions) and amorphous (prevail in finer fractions), whereas the composition of FC1



Fig. 1. Waste before and after milling: (a) concrete CR1, and (b) fired clay FC1.

**Table 3**  
Mineralogical composition of waste aggregates CR1 and FC1 (% weight).

| Waste           | Particle size fraction (mm) | Calcite | Dolomite | Carbonate-AFm | Gypsum | Ettringite | Quartz | Albite | Microcline | Anorthite | Diopside | Muscovite | Clinohlore | Hematite | Amorphous |
|-----------------|-----------------------------|---------|----------|---------------|--------|------------|--------|--------|------------|-----------|----------|-----------|------------|----------|-----------|
| CR1 Concrete    | <0.063                      | 29.4    | 28.0     | 1.5           | 0.3    | 0.9        | 9.6    | 3.0    | 1.5        | 0.0       | 0.0      | 1.8       | 1.2        | 0.0      | 22.8      |
|                 | 0.063–0.125                 | 27.4    | 29.1     | 1.5           | 0.3    | 1.1        | 12.6   | 3.6    | 1.9        | 0.0       | 0.0      | 1.4       | 1.5        | 0.0      | 19.5      |
|                 | 0.125–0.25                  | 28.4    | 27.9     | 0.9           | 0.5    | 1.0        | 15.1   | 4.0    | 2.6        | 0.0       | 0.0      | 1.9       | 1.3        | 0.0      | 16.4      |
|                 | 0.25–0.5                    | 28.9    | 22.0     | 1.2           | 0.3    | 1.0        | 18.7   | 4.6    | 2.3        | 0.0       | 0.0      | 1.3       | 1.6        | 0.0      | 18.1      |
|                 | 0.5–1                       | 29.2    | 21.1     | 0.4           | 0.3    | 0.5        | 19.8   | 5.2    | 2.8        | 0.0       | 0.0      | 1.9       | 1.8        | 0.0      | 17.0      |
|                 | 1–2                         | 28.4    | 27.4     | 0.5           | 0.3    | 0.0        | 18.8   | 4.6    | 2.6        | 0.0       | 0.0      | 1.4       | 1.6        | 0.0      | 14.7      |
|                 | 2–4                         | 28.4    | 27.4     | 0.5           | 0.3    | 0.0        | 18.8   | 4.6    | 2.6        | 0.0       | 0.0      | 1.4       | 1.6        | 0.0      | 14.7      |
| FC1 Clay bricks | <0.063                      | 1.0     | 1.1      | 0.0           | 0.6    | 0.0        | 24.4   | 7.1    | 9.3        | 6.7       | 7.1      | 4.7       | 0.0        | 3.3      | 34.6      |
|                 | 0.063–0.125                 | 1.2     | 1.1      | 0.0           | 0.3    | 0.0        | 30.0   | 6.8    | 9.5        | 5.3       | 6.3      | 5.1       | 0.0        | 2.9      | 31.5      |
|                 | 0.125–0.25                  | 1.8     | 2.1      | 0.0           | 0.6    | 0.0        | 29.9   | 7.5    | 6.7        | 6.3       | 4.3      | 4.3       | 1.2        | 2.8      | 28.3      |
|                 | 0.25–0.5                    | 2.8     | 2.3      | 0.0           | 0.5    | 0.0        | 25.8   | 8.1    | 7.5        | 5.2       | 7.4      | 4.2       | 1.4        | 3.1      | 31.7      |
|                 | 0.5–1                       | 2.5     | 2.0      | 0.0           | 0.5    | 0.0        | 24.9   | 8.6    | 7.4        | 4.6       | 8.1      | 3.9       | 0.0        | 3.0      | 34.6      |
|                 | 1–2                         | 3.1     | 2.3      | 0.0           | 0.8    | 0.0        | 25.5   | 7.7    | 8.4        | 7.4       | 8.7      | 4.7       | 0.0        | 2.6      | 29.0      |

was predominantly of quartz and amorphous. It is to be noted that the milling process had a certain influence on the composition of separated particle size fractions, although lesser than expected and occurring mostly on concrete waste, with harder substances like quartz and feldspars prevailing in coarser fractions. The bulk chemical compositions of CR1 and FC1, carried out by X-ray fluorescence spectroscopy (XRF) on a WDS Philips PW2400 spectrometer, are reported in Table 4, whose results are basically consistent with the mineralogical analysis. CR1 revealed a composition typical for aged concrete, with dominant CaO and SiO<sub>2</sub> related to both the hydrated cement paste and the aggregate phases, associated MgO and Al<sub>2</sub>O<sub>3</sub> mainly related to the inert fraction and minor amounts of the remaining major chemical constituents. The loss on ignition is relevant, and consistent with the observed high amount of carbonate phases. The composition of FC1 is typical of bricks and ceramic materials prepared from carbonate-rich base clays, with dominant SiO<sub>2</sub>, associated Al<sub>2</sub>O<sub>3</sub>, CaO and Fe<sub>2</sub>O<sub>3</sub> and minor amounts of the other major chemical constituents. The loss on ignition is lower than 10%, mainly related to calcination processes of the residual carbonate phases.

The geopolymeric reactivity of CR1 and FC1 was investigated through the analysis of the leachates obtained after a 24 h leaching test in alkali solution 10 M KOH. The concentrations of Si and Al (Table 5), measured via inductively-coupled plasma mass spectrometry (ICP-MS) with an Agilent Technologies 7700× ICP-MS, suggested that both materials are active in alkali solution, thus prone to reaction in a hyper alkaline system. The fired clay FC1 resulted particularly active, with leaching values of Al more than three times higher with respect to the concrete CR1, and values of Si 50% higher. These results are anyway consistent with the overall content of Si and Al reported in Table 4. Considering standard geopolymeric precursors available in literature [39], it is possible to observe that CR1 is characterized by a leaching value of Al lower than fly ash, slag, metakaolin and zeolite, but higher or comparable to those of natural pozzolana and kaolin. Concerning Si, the obtained leaching value is lower than zeolite and metakaolin, significantly higher than kaolin, natural pozzolana and fly ash, and comparable with furnace slag. As for FC1, the leaching value of Al is higher than what obtained on all the tested precursors, with the exception of metakaolin, while the Si value is significantly higher than natural pozzolana, fly ash, slag and kaolin and comparable with the one of metakaolin and zeolite.

Crushed materials were screened with woven wire cloth sieves having a square mesh size complying with EN 933-2 [40] (apertures from 0.063 mm to 2 mm). Their Particle Size Distribution (PSD) was measured during the screening process. The various fractions were kept separated and mixed before use in two different fashions. The first distribution, used for CRO, FCO and for reference mixtures with CR1 and FC1, reproduced that of the standard sand for testing cements, which was directly measured on 12 packages of certified sand because the set of available sieves did not match the sizes provided by EN 196-1 [41]. The second distribution (labelled “as is”), which was specific for CR1 and FC1, represented the actual one produced by the hammer mill used for crushing the scraps, although particles with sizes above 2 mm and below 0.063 mm were not included, in analogy with the standard sand. The adopted PSDs are shown in Fig. 2, together with the upper and lower limit distributions used for studying the effects of granulometry.

#### 2.1.3. Preparation of binders and specimens

Geopolymer mixtures were prepared by stirring together in an 8 l planetary mixer metakaolin and alkali activator for about 3 min, before adding the furnace slag and stirring for further 2 min. Then, waste aggregates were mixed, and possible additional water was added to adjust workability and to keep a satisfactory thixotropic

**Table 4**

Bulk chemical composition of CR1 and FC1 (% weight), with the relative loss on ignition (LOI).

| Oxides: | SiO <sub>2</sub> | TiO <sub>2</sub> | Al <sub>2</sub> O | Fe <sub>2</sub> O <sub>3</sub> | MnO  | MgO   | CaO   | Na <sub>2</sub> O | K <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | Tot   | LOI  |
|---------|------------------|------------------|-------------------|--------------------------------|------|-------|-------|-------------------|------------------|-------------------------------|-------|------|
| CR1     | 38.03            | 0.23             | 5.01              | 1.80                           | 0.06 | 12.21 | 39.88 | 0.74              | 1.06             | 0.07                          | 99.09 | 31.3 |
| FC1     | 63.00            | 0.79             | 15.14             | 5.03                           | 0.08 | 3.22  | 8.52  | 1.00              | 2.57             | 0.11                          | 99.46 | 6.66 |

**Table 5**

Chemical composition of the leachates obtained in alkali solution for the analysed wastes.

| Element:        | Al     | Si      |
|-----------------|--------|---------|
| CR1 Concrete    | 16 ppm | 157 ppm |
| FC1 Clay bricks | 60 ppm | 229 ppm |

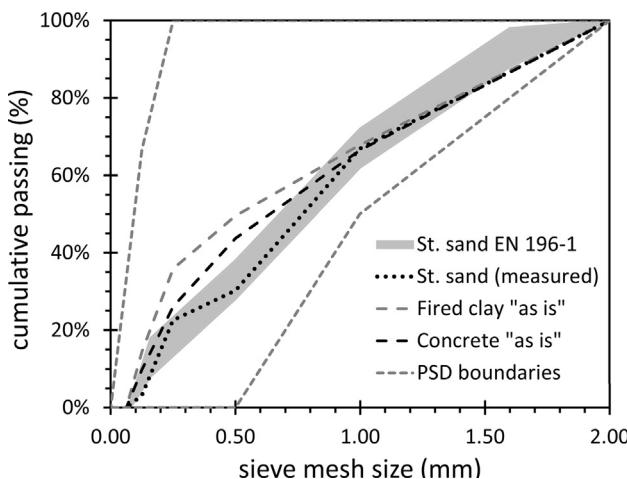


Fig. 2. Adopted Particle Size Distributions (PSDs).

behaviour. It is to be noted that the moisture content of ingredients (metakaolin, slag and waste) cannot be feasibly assessed at the moment of mixing, but raw materials were stored in rather constant conditions. Measures carried out between December and July provided an average moisture content of 0.2%, 0.4%, 1.0% and 0.6% for metakaolin, slag, concrete and fired clay aggregates, respectively, with fluctuations lower than 0.2% in any case. Those moisture contents were not taken into account in calculations. Details about mix ratios, due to their extensiveness, are presented as supplementary data. Nonetheless, as a general indication, the ranges of constituent materials were as follows, expressed for the sake of clarity as a percentage of the overall dry weight. Mixtures with 40% of waste aggregates and MK:SL 1:1: MK 21.9–23.8%; dry matter of the alkali activator 11.6–15.3%; total water including that of the alkali solution 16.4–21.2%. Mixtures with 50% of waste aggregates and MK:SL 1:1: MK 18.2–18.5%; dry matter of the alkali activator 12.7–14.3%; total water including that of the alkali solution 14.0–25.8%. Mixtures with 60% of waste aggregates and MK:SL 1:1: MK 14.8%; dry matter of the alkali activator 10.3%; total water including that of the alkali solution: 17.1–21.1%.

When ready, the geopolymer mixture was casted inside plastic pipes having a nominal internal diameter of 22 mm. Casting was promoted by external pneumatic ball vibrators that exploited the thixotropic behaviour of the mixtures. Pipes were further vibrated for a couple of minutes to enforce the expulsion of most air bubbles entrapped inside the mixture, then sealed with masking tape and placed in plastic bags, carefully sealed to avoid premature evaporation of water. Samples were kept for the subsequent 24 h either in a conditioned room at 20 °C (mixtures cured at ambient temperature – AT) or in an oven set at 30 °C, unless otherwise specified (see supplementary data). After one day, samples were demoulded and

placed until testing in a conditioned room at 20 °C inside their resealed plastic bag, which was opened after three days to allow cutting of specimens and to promote the evaporation of water.

## 2.2. Test methods

### 2.2.1. Compressive and splitting strength

The mechanical performance of the various geopolymer mixtures was measured through uniaxial compression tests and through splitting tests (also known as Brazilian tests). The main principles of standards EN 12390-3 [42] and EN 12390-6 [43] were adopted for the testing procedures.

Tests were performed with a universal multipurpose frame (Mattest Unitronic S205), equipped with a 50 kN load cell, on cylindrical specimens with a nominal diameter of 22 mm, and a nominal height of either 44 mm in compression or 22 mm in splitting. The size was a trade-off between representativeness of test results and economy of mixtures, and the upper bound of the diameter was limited by the maximum force that the machine could apply (i.e. 50 kN). Nonetheless, the minimum size of specimens was more than 10 times the maximum aggregate size  $D_{max}$  (2 mm), noticeably larger than the minimum value of 3.5 times required for concrete by EN 12390-1 [44], and of 5 times for mortars, as inferred by the combined provisions of EN 196 [41] and EN 13139 [45]. The actual sizes were measured with a resolution of 0.05 mm.

Compressive strength is assumed to be the most representative strength parameter for brittle and quasi-brittle materials like concrete, mortars and fired clay [46,47], which can be considered similar materials from a mechanical standpoint despite the chemical differences of the matrix, as well as AAM and geopolymers, as testified by most of the reported literature (e.g. see [19,20,24–31,33]). Indeed, the compressive strength is relevant to the extent that it identifies the class of concretes and mortars according to the European design standards [34,48]. The ratio between length and base of the specimen tested in compression should be equal to 2 [46] in order to obtain what is called “cylinder strength” [34] or “specified compressive strength” [49]. Otherwise, for lower ratios, the friction between the steel plates of the test machine and the faces of the specimen would affect the behaviour by producing a confinement effect of the specimen ends [50], resulting in greater values of strength that need to be normalized by proper reduction factors. In order to improve the contact between specimen and plates, for avoiding premature failures, either capping or grinding can be applied [42]: the latter method was chosen to smooth the faces of the specimen, due to the relevant expected values of strength, greater than 50 N/mm<sup>2</sup>, which would complicate the choice of suitable capping materials.

The splitting test was independently developed during the Forties by Carneiro in Brazil (hence the alternative name “Brazilian test”) and Akazawa in Japan, and is commonly used for obtaining an indirect evaluation of the tensile strength of brittle and quasi-brittle materials, like concrete and rocks [51,52], as well as clay bricks [53] and even masonry assemblages [54], being its simplest and reliable estimator [55]. The splitting failure is caused by a compressive force that induces a tensile stress across the diametral plane of loading [51], and the assumed strength [43] is generally the value of tension in the middle of the sample in correspondence

of the failure load, as derived from an elastic analysis. Due to the small size of specimens, packing strips (i.e. hardboard plates having a width of 0.1 times the diameter) were not used, but four layers of 80 g/m<sup>2</sup> paper were placed instead, in order to improve the contact with the steel plates of the machine. Soft putty for glass windows was stuck to the sides of the sample in order to keep it in position after being centred between the plates. The relation between splitting strength and actual tensile strength is complex and material dependent; nonetheless, as a general indication, for reduced characteristic lengths lesser than 300 mm the tensile strength is assumed to range between 85% and 98% of the splitting strength [56].

All tests were carried out with the universal machine in displacement control. The rate of the movable transverse beam was 0.5 mm/min for compression and 0.3 mm/min for splitting, in order to ensure a quasi-static application of the load and a reasonable duration of about 3–5 min for most samples. The maximum load was recorded for calculating compressive strength  $f_c$  (Eq. (1), where  $P_{max}$  is the failure load and  $A_c$  is the cross-sectional area of the specimen on which the compressive force acts) and splitting strength  $f_{sp}$  (Eq. (2), where  $d$  and  $L$  are the average diameter and length in correspondence of the diametral plane under loading).

$$f_c = \frac{P_{max}}{A_c} \quad (1)$$

$$f_{sp} = \frac{2P_{max}}{\pi L d} \quad (2)$$

The displacement of the movable beam of the test machine was recorded as well, but was not used in any analysis because it is assumed not to be representative of the material behaviour, since it includes the contribution due to the deformation of the machine and to the contact areas.

### 2.2.2. Dry bulk density, material density, open porosity and water absorption

Dry bulk density, material density, open porosity and water absorption were measured according to the main principles of ASTM C20-00 [57]. Weighing operations were performed with a Mettler-Toledo BB2440 balance. Dry bulk density ( $\rho_b$ ) refers to the apparent density given by the ratio of the dry weight of the specimen divided by its exterior volume, including pores. Apparent material density ( $\rho$ ) refers to the ratio of the dry weight of the specimen divided by the volume of its impervious portions. The open porosity (OP) represents the amount of pores accessible by water expressed as a percentage of the specimen exterior volume. The water absorption (WA) is the ratio between the weight of water absorbed by the saturated specimen and the weight of the dry specimen. These parameters were measured in samples obtained by cutting disks about 10–15 mm thick from the cylinders with a nominal diameter of 22 mm used for compression and splitting tests. Specimens were immersed in water for 24 h and subsequently boiled in water for 2 h at least, in order to assure their complete saturation; then, their saturated weight ( $W$ ) was recorded. Their weight while suspended in water ( $S$ ) was measured as well, taking care to keep them immersed during the operations and to detract the weight of the hanging wire. Finally, their dry weight ( $D$ ) was obtained after drying in oven at 105–110 °C until constant weight (i.e. about 12–24 h).

## 3. Investigated parameters

### 3.1. Blends of waste aggregates.

Although CDWs suitable for reuse have to come from selective demolitions [58], a complete separation of concrete and fired clay

waste streams is not granted through the whole process from demolition to disposal/reuse. Indeed, from a practical standpoint, the great part of the ordinary buildings stock in Europe (from 60% to 90%, according to an inventory that involved 9 main Countries [59]) dates back to the second post-war period, when the most widespread construction system was (and still is) reinforced concrete frames with fired clay infill walls. In addition, from a health and safety point of view, concrete has known issues with the release of chromium contained in Ordinary Portland Cement (OPC) [60,61], and concrete wastes alone would unlikely meet the leaching requirements for recycled aggregates or even for landfill disposal in most EU Countries, which can be found in [62], unless mixed with other materials with a minor release. Consequently, the influence of aggregate types was studied by comparing the compressive strength of similar mixtures with different blends of concrete (CRO) and fired clay (FCO) waste in the following CRO-FCO ratios: 1:0; 3:1; 1:1; 1:3; and 0:1. The overall aggregate content was 40% of dry weight for all those mixture.

### 3.2. Temperature during the first 24 h of curing.

Curing temperature is known to influence the strength gain of geopolymers, since higher temperatures during the first phases of setting (up to 12–24 h according to [63]) promote the geopolymer reactions and improve the material quality. Conversely, keeping the curing environment warm for longer periods represents a cost in terms of required energy and storage area, thus the optimization of time and temperature is significant. As reference period of conditioning, 24 h (adopted also in [24]) was considered adequate to produce appreciable effects, and potentially compatible with industrial processes as well. The selected curing temperatures were 20 °C (also referred to as Ambient Temperature – AT), 30 °C, 40 °C and 60 °C. Compression tests were performed after 24 h, 3 days, 7 days and 28 days. The subset of mixtures cured at ambient temperature was tested also at 3 and 6 months. Mixtures incorporated either 40% or 50% of concrete CRO and fired clay FCO in 1:1 proportion.

### 3.3. Waste aggregates content.

The maximization of the aggregate content was investigated for the cost optimization and for the increase of CDW reuse. Three contents, expressed in terms of dry weight of the mixture, were selected for both concrete CR1 and fired clay FC1: (i) 40%, tested in preliminary trials and assumed as reference content; (ii) 50%; and (iii) 60%.

### 3.4. Particle Size Distribution (PSD) of aggregates

The distribution in size of aggregates, similarly to cement concrete and mortars, was assumed to affect the behaviour of both the fresh mixture (finer fractions generally require more water for achieving a suitable workability, due to their larger surface area) and the hardened material (in terms of strength, drying shrinkage, etc.). Since the beginning of the last Century, the importance of a correct grading of aggregates has been acknowledged not only for concrete [64,50], but also for mortars and stuccoes [65,66]. Given the maximum aggregate size ( $D_{max}$ ) lower than 2 mm, due to a practical requirement for casting thin panel layers (about 8–10 mm), the discussion about the PSD of aggregates might be of lesser importance. Nonetheless, the purpose of this point was investigating the suitability of ground aggregates as they result from milling, with minimum production steps, e.g. removal of finer dust, and providing possible ranges of acceptance for the aggregates. Indeed, a sieving process to separate size fractions of milled aggregates and, then, reassemble a specific grading

distribution, is feasible for research purposes but likely incompatible with a large-scale production. Moreover, a certain variability of PSD has to be taken into account, depending on the type of the hammer mill, the hardness of materials and even the milling time; possible dust reduction systems can influence the resulting product as well. Hence, the performance of mixtures with either CR1 or FC1 were compared and discussed, whose aggregates were either: (i) graded as a standard sand according to EN 196-1 [41], which has a maximum aggregate size of 2 mm; (ii) used as they resulted from the in-house milling; or (iii) graded with three limit distributions (either fines, intermediate particles, or “coarser” aggregates only).

The adopted limit distributions were as follows: (i) fines only:  $\frac{1}{3}$  between 0 and 0.063 mm,  $\frac{1}{3}$  between 0.063 and 0.125 mm,  $\frac{1}{3}$  between 0.125 and 0.25 mm; (ii) intermediate particles: 100% between 0.25 and 0.50 mm; (ii) “coarse” aggregates:  $\frac{1}{2}$  between 0.5 and 1 mm,  $\frac{1}{2}$  between 1 and 2 mm.

### 3.5. Metakaolin:Slag (MK:SL) ratio and reduction of alkali activator solution.

The cost of raw materials of geopolymer binders needs to be carefully considered when aiming at competitive products. For example, the cost of metakaolin is typically 3–4 times greater than that of ground blast furnace slags, and comparable with that of potassium silicate, depending on K-silicate modulus and concentration. For these reasons, compatibly with the desired mechanical performance, the amount of metakaolin and K-silicate should be optimized. Na-silicate activators, which are considerably cheaper than K-silicate, were dismissed due to their very large salt efflorescence exhibited in preliminary trials, which far exceeded that of K-silicate activators.

The reference recipe presented a metakaolin:slag (MK:SL) ratio of 1:1, whose effectiveness was proven in preliminary trials carried out by the authors. Although metakaolin generally presents great reactivity and promotes a quicker strength development if compared to slag [31], the cost ratio of the used materials was about 4:1. Consequently, the reference MK:SL proportion was modified into 1:2 and 1:3, in order to measure its influence on strength. Concerning the amount of K-silicate, although the proportion of the alkali activator was based on stoichiometric considerations (ratio K/Al  $\sim$  1 and Si/Al  $\sim$  2.5), preliminary trials suggested that part of the base did not react, intensifying leaching and salt efflorescence phenomena. Therefore, a reduction of 15% and 30% of the reference quantity of alkaline activator was tested to measure its effect on strength. Mixtures included 40% of either CR1 or FC1 aggregates, with the aim of intensifying the effects related to variations of the binder.

### 3.6. Influence on the open time of temperature during preparation.

The open time, which is an important parameter for the industrial applicability of geopolymer mixtures, was herein assumed as the time spanning from the end of mixing, which lasted about 10–12 min, and the beginning of setting with loss of thixotropy. This preliminary investigation stemmed from an unexpected short open time exhibited by a mixture prepared according to a recipe already tested in early springtime. The only significant difference in the boundary conditions was the room temperature, which the second time was relatively higher.

In order to clarify the impact of preparation temperatures on the open time, the following conditions were tested: cool room (19 °C) and ingredients (19–21 °C); warm room (28 °C) and ingredients (29–31 °C); warm room and ingredients, but with additional water; mildly cool room (21 °C) and ingredients (21–23 °C), with additional water; mildly cool room, and ingredients kept cold dur-

ing the mix (8–11 °C) through an ice bath of the vessel, with additional water. Mixtures were prepared with 50% of fired clay FC1 aggregates.

It is worth mentioning that viscosity was empirically adjusted to a suitable extent through water addition during mixing, although its evolution in time was measured on sample mixtures by means of a rotational viscometer (Brookfield DV2T with spindle nr. 7 and rpm = 0.2). According to preliminary trials, the suitability of the initial viscosity (i.e. just after the end of mixing, who lasted about 10 min in most cases) was found in the 1000–2500 Pa·s range. The end of the open time was conventionally set at about 6000 Pa·s for the sake of comparison, being the limit empirically related, for the tested mixtures, to loss of thixotropy and beginning of plastic behaviour unsuitable for the adopted casting procedures.

### 3.7. Influence of water content in the fresh mixture.

Water in the geopolymer reaction is reagent and solvent at the same time, and its quantity is critical for the final quality of geopolymer [67]. The water content of K-silicate activators was comprised between 51% and 55% as a consequence of previous trials by the authors, aimed at minimizing the addition of non-solvated water at the time of preparation of geopolymer mixtures. Additional water may be needed anyway to adjust workability to a suitable extent, according to the different behaviour of fired clay and concrete aggregates. Conversely, exceeding water leaves more pores in the binder and may affect the performance of the mixture. For these reason, the relation between water content of the fresh mixture and open porosity was investigated for all the tested mixtures, as well as possible relations between open porosity and compressive strength.

### 3.8. Evolution of strength during time.

Since the mechanical performance, from a standardisation standpoint, needs to be assessed at conventional ages, the reliability of 28-day testing was investigated, being a typical reference age for building materials [34,48,49]. For this purpose, two mixtures, incorporating either 40% or 50% of waste aggregates with blended CRO and FCO in 1:1 proportion, were tested in compression after 3 and 6 months. A second point was the assessment of a relation between the strength at 7 and 28 days of age for possibly estimating the resistance through early testing, which was considered of interest for reducing the time spanning between preparation and testing of mixtures.

### 3.9. Relation between splitting and compressive strength.

As usual for building materials [34,48,49], the ratio between tensile and compressive strength is extremely important, due to the difficult estimation of the former property. Possible correlations between compressive strength and splitting strength were investigated with the aim of obtaining a predictive formulation of the latter based on the measured compressive strength.

### 3.10. Comparison with natural aggregates

The presented geopolymer mixtures, given the maximum nominal aggregate size limited to 2 mm, might be assimilated to mortars, hence the behaviour of waste aggregates might be compared to sand. As a preliminary investigation, several mixtures with 50% to 55% in weight of fine siliceous sand, which is a typical aggregate for rendering, were tested. It is worth noting that a perfect match of mixtures with either siliceous sand or waste aggregates is very difficult from a practical standpoint, due to the nature of sand that has a negligible water absorption. This implies a generally different

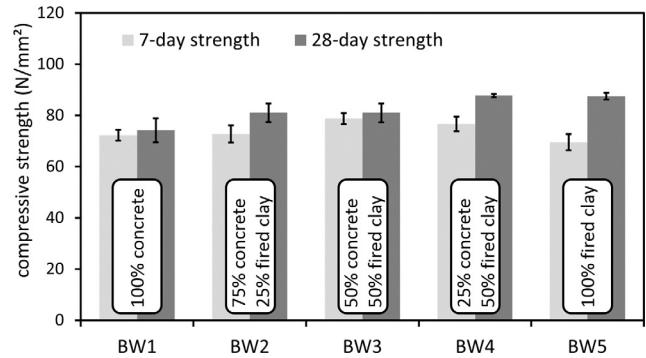
water content in the fresh mixture, which affects accordingly the properties of the hardened geopolymers, and allows mixtures with sand to increase further the aggregate content retaining a remarkable strength. Nonetheless, a rather close match in terms of mix ratio and water content was achieved in two cases with concrete waste aggregates only.

#### 4. Results and discussion

For the sake of brevity, detailed quantitative results are provided apart as [supplementary data](#). Typical failure modes of cylindrical test samples under compression and splitting tests are shown in [Fig. 3](#). Samples under compression failed either in explosive manner or in a less sudden mode, nonetheless without exhibiting any appreciable softening behaviour. Specimens of splitting tests failed in a brittle fashion along the loaded diametral plane. Considering the complete dataset, the Coefficients of Variation (CoVs) as well as their 95%-percentile were evaluated to obtain an estimate of the quality of data. Average CoVs for compression tests were lower than 4% and their 95-percentiles lower than 10%. These values suggest that results obtained with three samples per test are sufficiently representative for the current research. Mean and 95-percentile CoVs for splitting tests are greater but still satisfactory (less than 9% and 18%), given the intrinsic limited reliability of tests involving tensile properties of brittle and quasi-brittle materials [56]. Mean and 95-percentile CoVs of density, porosity and water absorption are even lower than those of compression tests. A dedicated discussion for each group of mixtures is reported in the following sections. Error bars reported in charts represent  $\pm$  one standard deviation.

##### 4.1. Blends of waste aggregates

Results in terms of compressive strength are shown in [Fig. 4](#). Samples with greater amounts of fired clay aggregates showed a higher 28-to-7 day strength ratio, presumably due to some residual pozzolanic reactivity of the fired clay, similarly to what was highlighted by the characterization of the second batch of wastes ([Table 5](#)) and as reported by other authors [68,69]. Geopolymer samples with blends of concrete and fired clay aggregates approximately behaved in an intermediate fashion, in between those with a single type of aggregate. Anyway, all mixtures exhibited a compressive strength at 28 days between 74 and 88 N/mm<sup>2</sup>, and the difference between the weakest and the strongest mixture did not exceed 15%. From a strength standpoint, the use of concrete and fired clay waste aggregates, either separated or blended together, appears suitable, as confirmed by tests carried out on samples with the second type of wastes.



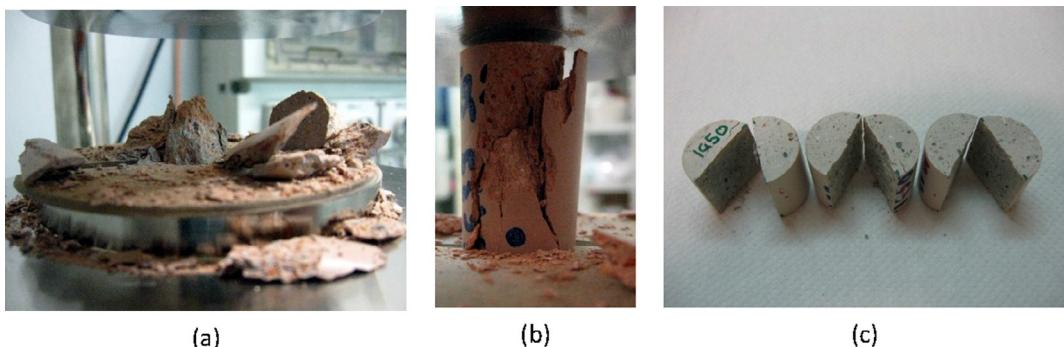
**Fig. 4.** Results of mixtures with blended aggregate types (40% dry weight of aggregate content).

##### 4.2. Temperature during the first 24 h of curing

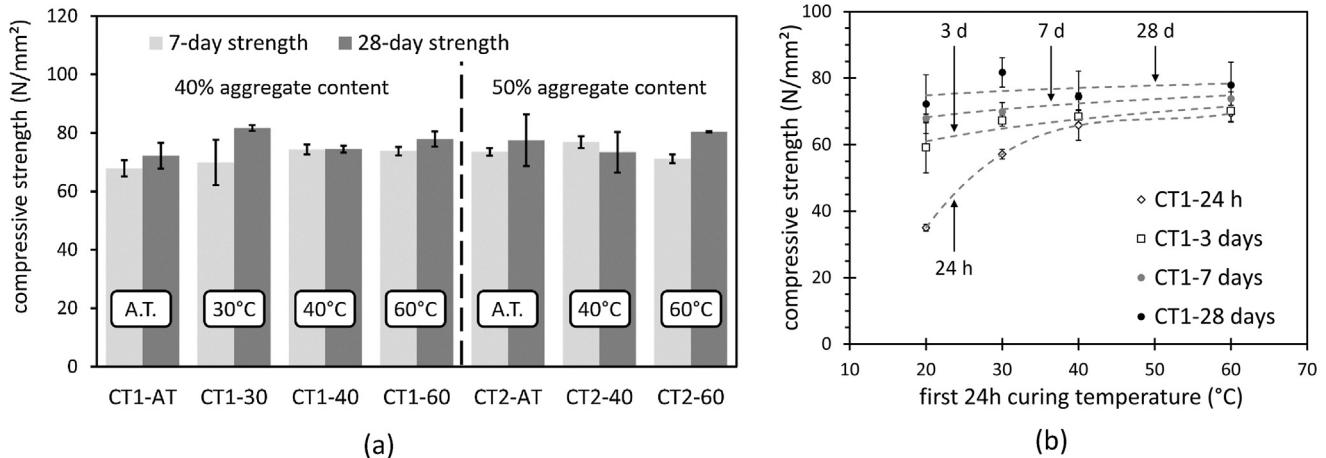
Compressive strengths measured at 7 and 28 days are shown in [Fig. 5a](#), whereas [Fig. 5b](#) compares the strength development from 24 h to 28 days as a function of the curing temperature. The effect was particularly evident in the early phases, and most of the strength gain was achieved in the range 20–40 °C. After 7 days, no remarkable improvement was noticed, provided that a certain fluctuation of values has to be taken into account when testing mechanical properties of brittle and quasi-brittle materials [70] and, consequently, the tested temperatures seemed not to affect sensibly the reference strength after 28 days. However, the compressive strength after 24 h was greater than 30 N/mm<sup>2</sup> in all cases, hence demoulding operations are assumed to be feasible even when curing is carried out at ambient temperature. Temperatures equal to or greater than 30 °C might be selected when a stricter control of curing conditions or shorter demoulding intervals are needed. Nonetheless, temperatures greater than 60 °C are supposed not to appreciably improve the strength, therefore the energy required for the initial curing can be limited.

##### 4.3. Waste aggregates content

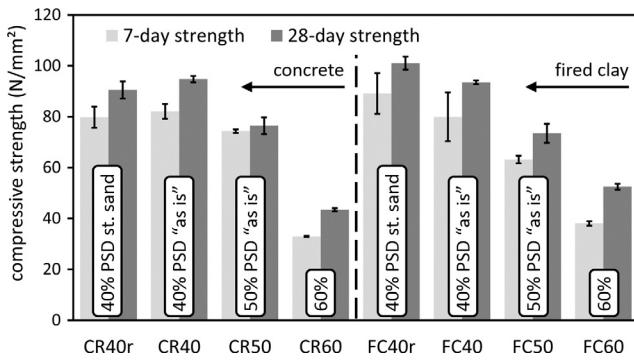
Concrete and fired clay aggregates were studied separately, with either a grading curve that matched the PSD of standard sand [41], taken as reference for the 40% content, or with the PSD that resulted from the in-house milling (labelled “as is”), without particles smaller than 0.063 mm. [Fig. 6](#) shows the compressive strength measured at 7 and 28 days of age. Using the “as is” grading did not affect significantly the strength: at 28 days, the difference was lesser than 7% for both concrete and fired clay aggregates. The negligible influence of the “as is” grading curve was initially not



**Fig. 3.** Typical failure modes in compression: (a) explosive, with disintegration of the sample, (b) less sudden; and (c) typical failures in splitting along the loaded diametral plane.



**Fig. 5.** Effect of curing temperature during the first 24 h: (a) comparison of results, and (b) evolution of strength.



**Fig. 6.** Results for aggregate content increasing from 40% to 60%.

granted, due to the slightly larger amounts of finer particles, in comparison with that of standard sand (Fig. 2), which however does not lie very far. Conversely, the reduction of strength was noticeably (about 20%) for both the input CDW when moving from 40% to 50% of aggregates content, and was remarkable for 60% content (about 55% and 45% for concrete and fired clay waste, respectively).

The slightly different trends of concrete and fired clay aggregates might be partly explained by considerations about the water content of the fresh mixture, and the different features of the aggregates, in terms of porosity and related water absorption. The apparent porosity of clay bricks can reach 40%, according to their type and constituent materials [71–73]; values measured by the authors for siliceous extruded and soft mud bricks used in [74], which are likely to cover the range of available fired clay waste, were approximately 25% and 35%, respectively. On the other hand, the order of magnitude of the apparent porosity of ordinary concretes is about 9–16% [75,76]. The different porosity reflects the greater water demand when fired clay aggregates are included in geopolymer mixtures: for example, the water content of mixture FC40r was about 11% greater than CR40r. It is underlined again that the dilution of the alkaline activators was tuned to minimize the addition of non-solvated water during mixing. CR40r and CR40 were fluid enough with no extra water, and CR50 required only a minor addition (0.2% of dry weight) to achieve a satisfactory workability, thus suggesting that the water intake due to the base was slightly exceeding for lower concrete aggregates contents. Indeed, although the water content of fresh CR50 is lower if referred to the overall weight (14.0% compared to 16.4%), there is a slight increase if that quantity is referred to the amount of matrix, which decreased from 60% to 50%. With 60% of concrete aggregates, the

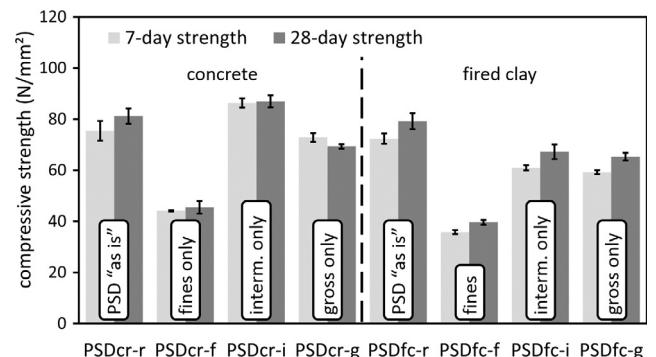
increase of water content was 4.1%, compared to the water content of CR40r. Conversely, all the mixtures with fired clay aggregates required extra water, leading to water contents that were progressively increased by 9.2%, 10.0% and 15.5% with reference to the FC40r mixture.

Although water is known to increase porosity and, consequently, affect the resistance of geopolymer binders [67], similarly to most of the engineering materials [77], it might be inferred that the larger water demand of mixtures with fired clay aggregates was balanced by their greater porosity and water absorption. They might have retained part of the water reducing its amount in the binder and, thus, levelling the initial difference with concrete mixtures and even promoting a more gradual setting of the geopolymer binder.

#### 4.4. Particle Size Distribution (PSD) of aggregates

It is to be noted (Table 3) that the milling process determined a slightly different composition of the various particle size fractions, especially in the case of concrete aggregates, which derive from a material inhomogeneous at centimetric scale. In particular, finer particles of concrete ( $D_{max} \leq 0.25$  mm) presented a higher content of carbonate phases, while coarser particles ( $D_{max} > 0.5$  mm) were richer in quartz, albite and microcline, which are minerals with greater hardness (about 6–7 in Mohs scale). Conversely, fired clay size fractions presented lesser difference, except for a slightly larger content of carbonate phases in coarser particles ( $D_{max} > 0.5$  mm).

Results in terms of compressive strength are shown in Fig. 7. Compared to the reference mixtures, the use of fine aggregates only (i.e. with  $D_{max} \leq 0.25$  mm) implied a remarkable increment of water content to achieve a suitable workability, approximately



**Fig. 7.** Effects of Particle Size Distribution of aggregates on compressive strength.

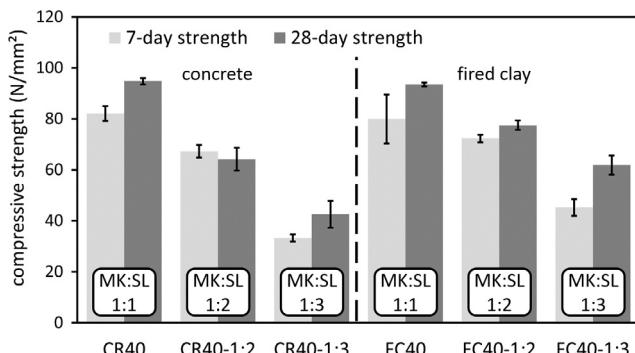
between 30% (fired clay) and 40% (concrete), with a consequent relative increase of porosity equal to 17% and 25% for fired clay and concrete waste, respectively. This might justify a strength loss that almost reached 50%. Conversely, the use of “coarse” aggregates only (i.e. with nominal size comprised between 0.5 and 2 mm) required less water than the reference mixtures, and determined a decrease in porosity (approximately 10–15% for fired clay and concrete, respectively) with a strength loss of about 15–17%. The use of the intermediate aggregate size fraction ( $D_{max}$  between 0.25 and 0.5 mm) seemed even beneficial in the case of concrete, while the behaviour did not differ sensibly from samples with coarser aggregates in the case of fired clay. The removal of a reasonable amount of finer fractions (i.e. with  $D_{max}$  comprised between 0.063 and 0.25 mm), which represented about 25% and 35% in weight of the “as is” distribution of concrete and fired clay aggregates, seemed more detrimental for fired clay, likely due to their residual reactivity that might contribute to the geopolymer reaction.

#### 4.5. Metakaolin:Slag (MK:SL) ratio and reduction of alkali activator solution

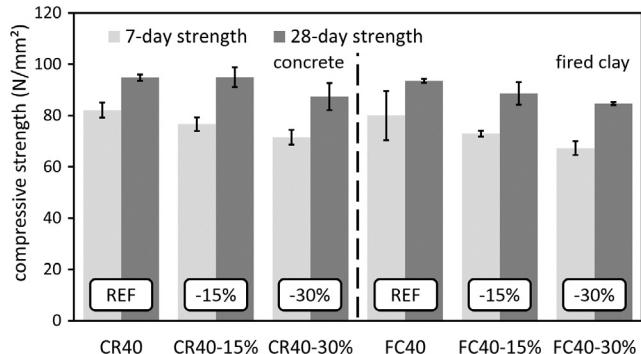
**Fig. 8** shows the effect on compressive strength of MK:SL ratios that changed from 1:1 to 1:2 and 1:3. The progressive decrease of strength is apparent for both the aggregate types (approximately 30% and 55% for concrete, 20% and 35% for fired clay), but more remarkable in the case of concrete waste. Result can be explained by the lower reactivity of the slag, compared to the used metakaolin, and might support again the slightly greater residual pozzolanicity of fired clay aggregates, likely responsible for the lower loss of strength.

**Fig. 9** shows the effect on compressive strength of the reduction, referred to the starting mixture, of the K-silicate activator. The decrease of up to 30% by weight resulted in only a slight decrease (about 10%) of compressive strength. It is to be noted that the missing alkaline activator was replaced by metakaolin and slag (for the dry part) to keep the same aggregate content ratio, and by water, to retain the fluidity of the mixture. The slightly greater amount of powder required more extra water to achieve a suitable viscosity (see also Sections 2 and 4.6). The water content was slightly increased (adding 0.4% and 0.7% of dry weight) for concrete aggregates, which however resulted in approximately the same porosity of all the three mixtures (about 26%), while fired clay aggregates required more extra water (0.9% and 1.3%), which determined an approximately comparable increase of porosity (from 28% to 29%).

Results confirmed that the stoichiometric ratios adopted for calculating binder components, based on the assumption that all the Al was available for the geopolymer reaction, need to be empirically adjusted to take into account the specific features of the used materials, reducing non-reacted quantities that might affect efflorescence and leaching in water of soluble salts.



**Fig. 8.** Results for various Metakaolin:Slag (MK:SL) ratios.



**Fig. 9.** Effect of K-silicate base reduction on compressive strength.

#### 4.6. Influence on the open time of temperature during preparation

The controlled conditions and the measured open time are reported in **Table 6**, while **Fig. 10** shows the measured compressive strength at 7 and 28 days of age. Temperature appears to have a remarkable effect on the open time, which might be dramatically reduced when the preparation is carried out in a room without conditioning. As a preliminary indication, limited to this family of metakaolin-slag mixtures, the temperature of both room and ingredients should not exceed 20–21 °C for a reasonably long open time. Conversely, the addition of water, while effective in reducing the viscosity, did not seem to affect the open time. With reference to the measured strength, temperature might have affected the early strength (at 7 days), but the long term values appeared consistent with the amount of water in mixtures, which was slightly greater (+0.2%) in PT1 and sensibly greater (+0.6%) in PT2–4, compared to the reference PTO. Possible other options to increase the open time might be considered, e.g. the use of fly-ash or the addition of retardants like boron, but they would affect the recipe and its properties.

#### 4.7. Influence of water content in the fresh mixture

**Fig. 11** shows a fairly linear correlation between porosity and total amount of water in the formulation. Clearly, the overall open porosity includes both that of the binder and that of the aggregates, and they cannot be feasibly separated. As previously noted, samples with fired clay aggregates required generally more water than those with concrete aggregates, due to the intrinsically higher porosity of fired clay (20–40%) compared to concrete (10–15%). Interestingly, these values are close to the porosity values of samples with “coarse” aggregates only, suggesting that, in this case, water absorption and porosity are controlled more strongly by the properties of the aggregates than in case of finer aggregates.

In **Fig. 12** the compressive strength of the same samples is plotted as a function of open porosity, confirming a general trend of decreasing compressive strength with increased sample porosity, even though masked by a large data scatter related to the various modifications introduced in the mixtures.

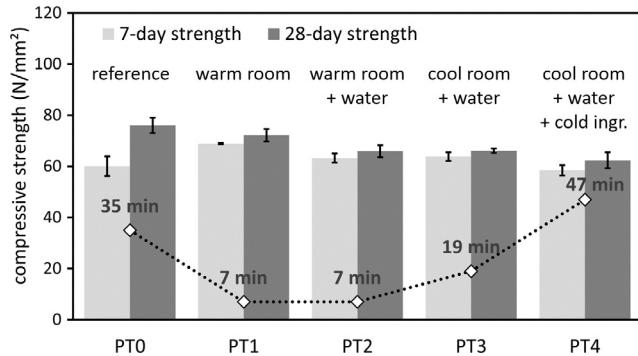
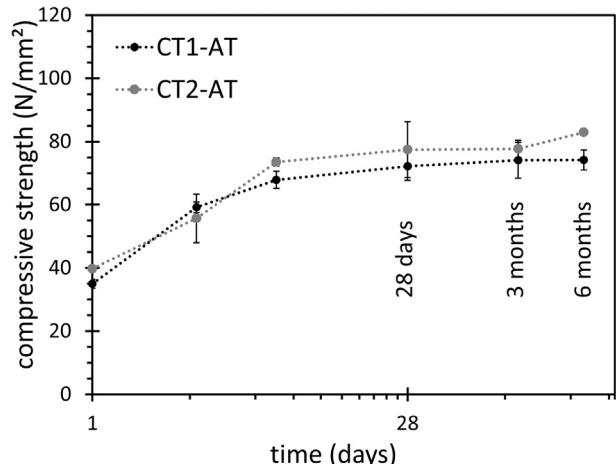
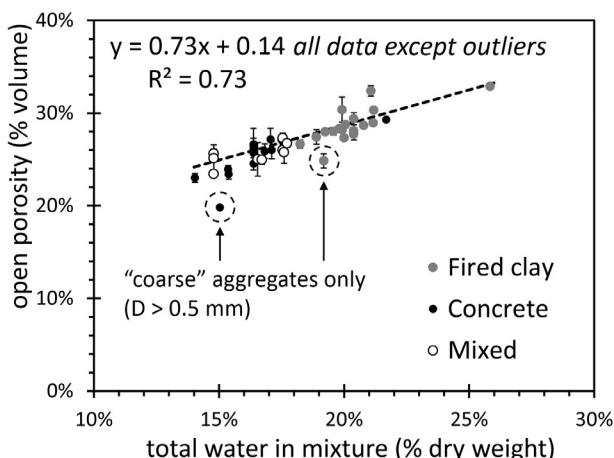
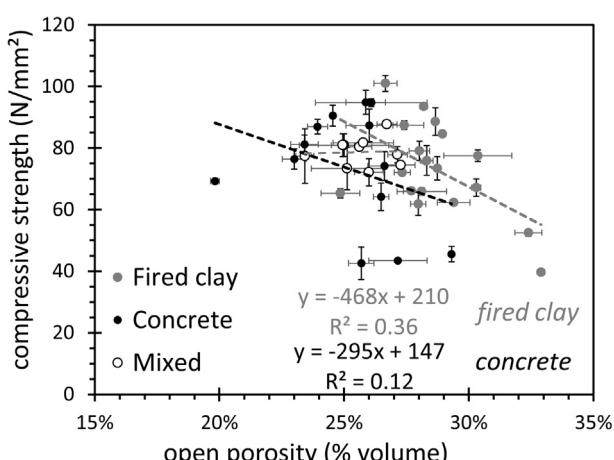
#### 4.8. Evolution of strength during time

**Fig. 13** shows the evolution of compressive strength along time for samples cured at ambient temperature, spanning from 24 h to 6 months of age. At 28 days of age, specimens achieved more than 90% (i.e. 97% for CT1-AT and 93% for CT2-AT) of the strength measured after five additional months. It is to be noted that the 28-day strength of CT2-AT had an unusually large variability and might be underestimated. Results suggested that 28 days can be

**Table 6**

Preparation conditions and open time of the tested mixtures.

| MIXTURE | Ambient temperature | Temp. of ingredients during mixing | Temp. at the end of the open time | Water content % dry weight | Open time |
|---------|---------------------|------------------------------------|-----------------------------------|----------------------------|-----------|
| PT0     | 19 °C               | 19–21 °C                           | 22.5 °C                           | 19.8%                      | ~35 min   |
| PT1     | 28 °C               | 29–31 °C                           | 32 °C                             | 20.0%                      | ~7 min    |
| PT2     | 28 °C               | 29–31 °C                           | 31.5 °C                           | 20.4%                      | ~7 min    |
| PT3     | 21 °C               | 21–23 °C                           | 25 °C                             | 20.4%                      | ~19 min   |
| PT4     | 21 °C               | 8–11 °C                            | 18.5 °C                           | 20.4%                      | ~47 min   |

**Fig. 10.** Strength and open time for different conditions during preparation.**Fig. 13.** Evolution of compressive strength over 6 months for mixtures CT1-AT and CT2-AT.**Fig. 11.** Relation between open porosity and water added to the fresh mixture.**Fig. 12.** Compressive strength plotted versus the open porosity (trends are qualitative).

reasonably assumed as reference age also for this family of geopolymmer materials. This outcome was confirmed by tests carried out on similar mixtures, prepared outside the scope of this paper, which provided a 28-day-to-6-month strength ratio comprised between 91% and 97%.

Concerned the feasibility of early testing for a reliable estimation of strength, it is worth noting that an increment of strength from 7 to 28 days was not unexpected [31], and was observed in several cases by other authors for Alkali-Activated Cements (AACs) and Hybrid Cements (HYCs) with concrete waste [19] and red clay brick waste [27,28]. With reference to the mixtures tested in this work, Fig. 14a shows an apparent linear correlation when the 28-day compressive strength is plotted versus the 7-day compressive strength. The least square regressions, calculated on a set of data that excluded PT1 to PT4 mixtures, provided a strength ratio of 1.09 and 1.18 for concrete and fired clay, respectively. It can be observed once more that samples with fired clay aggregates developed on average a slightly higher strength in time compared to samples with concrete aggregates, suggesting that some slower pozzolanic reactivity [68,69] contributed to the long-term strength, consistently also with the greater release in alkali solution of Al exhibited by fired clay waste, compared to concrete waste (see Section 2.1.2), and with other results above discussed (see Sections 3.1, 3.4, and 3.5). Conversely (Fig. 14b), the splitting strength does not reveal any significant correlation, partly due to its intrinsic variability as indicator of tensile properties that might have hindered the observation of a clear trend.

#### 4.9. Relation between splitting and compressive strength

As expected, the splitting-to-compressive strength ratio tends to reduce for greater compressive strengths, as can be seen in Fig. 15a, and most values are comprised in the range 5–10%. Although the average splitting-compressive strength ratio was

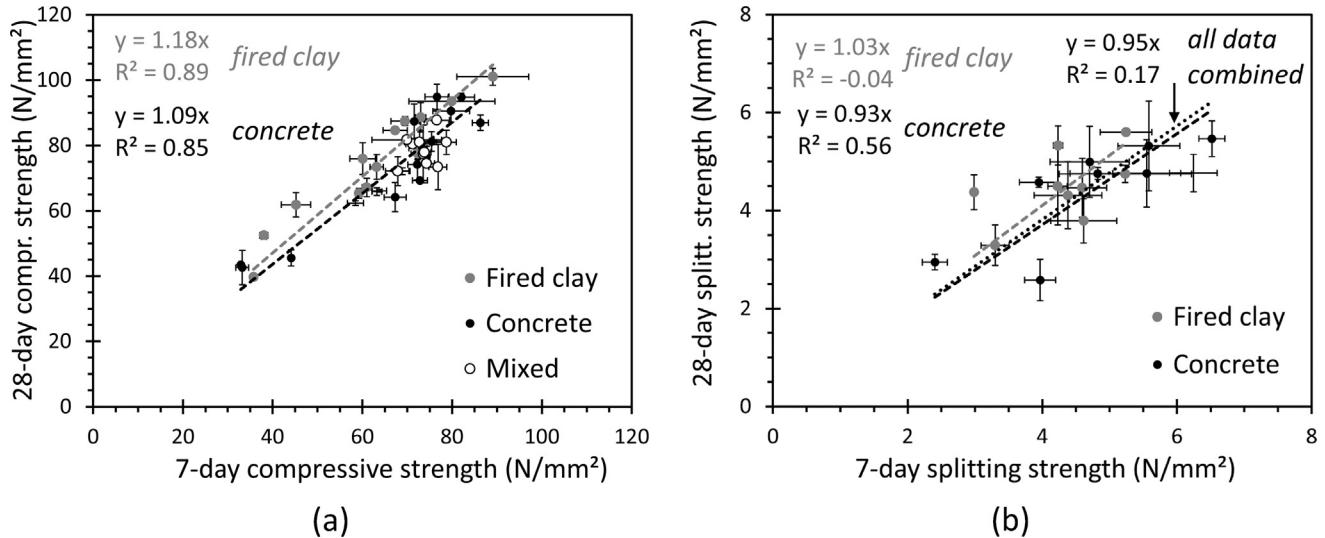


Fig. 14. Values measured at 7 and 28 days for: (a) compressive strength, and (b) splitting strength.

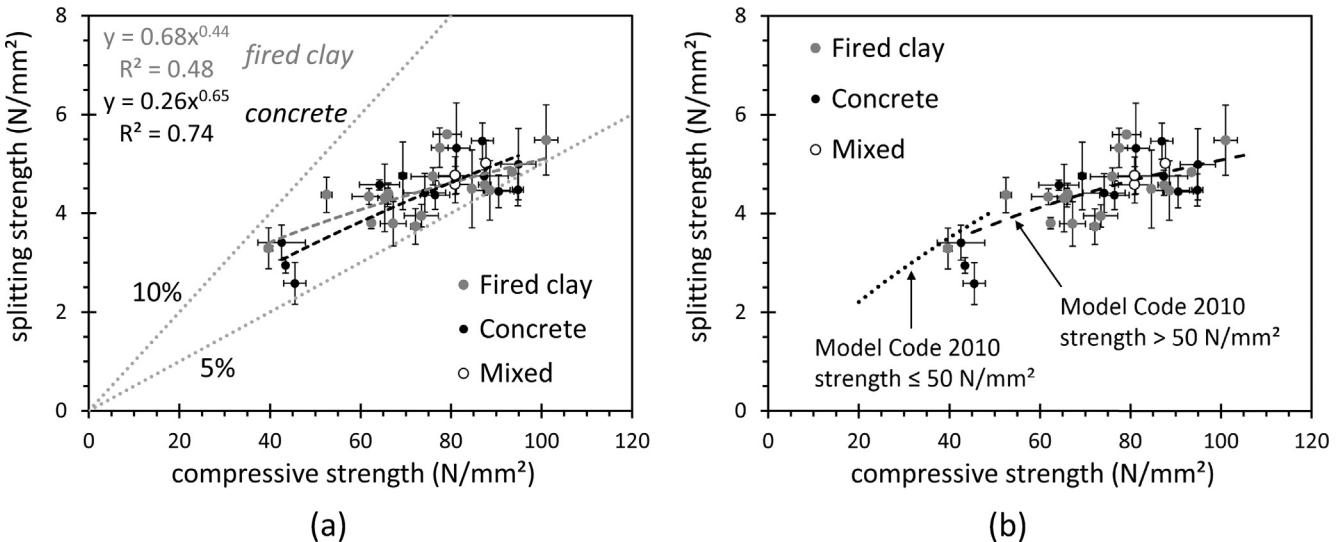


Fig. 15. Splitting vs. compressive strength measured at 28 days.

Table 7

Comparison of performance of mixtures with either concrete waste or fine siliceous sand aggregates.

| Property                                  | CR50  | corresp. mix with sand | Δ    | PSDcr-r | corresp. mix with sand | Δ    |
|---|-------|------------------------|------|---------|------------------------|------|
| Compressive strength (N/mm <sup>2</sup> ) | 76.5  | 79.3                   | +4%  | 81.2    | 89.7                   | +10% |
| Splitting strength (N/mm <sup>2</sup> )   | 4.4   | 6.6                    | +50% | 5.3     | 6.0                    | +13% |
| Bulk density (kg/m <sup>3</sup> )         | 1970  | 2040                   | +4%  | 1940    | 2000                   | +3%  |
| Porosity (% volume)                       | 23.0% | 15.8%                  | -31% | 23.4%   | 16.5%                  | -29% |
| Water absorption (% mass)                 | 11.7% | 7.7%                   | -34% | 12.0%   | 8.2%                   | -32% |

about 6% regardless the aggregate type, an empirical power law regression appears to describe adequately the observed trends, with a slight difference between concrete and fired clay aggregates, which resulted in the calculated exponents 0.65 and 0.44, respectively, which are consistent with those proposed for concrete [55]. For the sake of comparison, data are plotted (Fig. 15b) against the curves proposed by Model Code 2010 [78] for the estimation of concrete tensile strength (Eq. (3), where  $f_{ctm}$ ,  $f_{ck}$  and  $f_{cm}$  are the

mean tensile, characteristic compressive and mean compressive strength of concrete, respectively). Interestingly, the expression provided for grades greater than C50 (i.e. with characteristic compressive strength >50 N/mm<sup>2</sup>) appears to fit satisfactorily the experimental data.

$$f_{ctm} = 0.3 \cdot f_{ck}^{0.3} \quad (\text{grades } \leq 50); \\ f_{ctm} = 2.12 \cdot \ln(1 + 0.1 \cdot f_{cm}) \quad (\text{grades } > \text{C50}) \quad (3)$$

#### 4.10. Comparison with natural aggregates

As shown in Table 7, mixtures with siliceous sand, compared to concrete waste aggregates, exhibited as expected a greater compressive and tensile strength, and a higher apparent density as well. On the other hand, porosity and water absorption were sensibly greater in mixtures with waste aggregates.

Further preliminary data, which cannot be herein presented in detail, confirmed in general these results. Geopolymers with fine siliceous sand showed practically no strength increment from 7 to 28 days, and presented a different behaviour also in terms of splitting vs compressive strength, with a correlation satisfactorily depicted by a straight line ( $f_{sp} \approx 0.07 \cdot f_c$ , with  $R^2 \approx 0.73$ ) or by a power law with exponent closer to 1 than to 0.5 ( $f_{sp} \approx 0.15 \cdot f_c^{0.83}$ , with  $R^2 \approx 0.83$ ). For the sake of comparison, ranges of average compressive and splitting strength, bulk density, open porosity and water absorption, measured in mixtures with 50-to-55% of fine siliceous sand aggregates, were 78–107 N/mm<sup>2</sup>, 5.4–7.9 N/mm<sup>2</sup>, 1940–2110 kg/m<sup>3</sup>; 12.3–22.4%; and 5.8–11.5%, respectively. The corresponding ranges, obtained for mixtures with 50% of waste aggregates, were 40–87 N/mm<sup>2</sup>; 2.6–5.6 N/mm<sup>2</sup>; 1680–2000 kg/m<sup>3</sup>; 19.8–32.9%; and 9.9–19.6%, respectively.

## 5. Conclusions

The mechanical and physical characterization of metakaolin-slag-potassium silicate geopolymers with 40-to-60% of CDW aggregates, although not exhaustive, provided encouraging results and pointed out interesting aspects related to their possible exploitation as a building material.

Concrete and fired clay aggregates determined slightly different results, while a blend of them led to intermediate properties. Mixtures with fired clay, despite their generally greater open porosity, showed performances in line with those with concrete aggregates, but with a higher increment of strength from 7 to 28 days (18% for fired clay and 9% for concrete, in average), probably related to their residual pozzolanicity.

Higher temperatures of curing, as expected, accelerated the strength gain. After 24 h, 40 °C and 60 °C provided about 90% of the 28-day strength, while 20 °C provided about 50% and 30 °C about 70%. Therefore, a range of 30–40 °C kept for 24 h could be a reasonable trade-off when curing conditions need a stricter control. Higher temperatures might be suitable for demoulding after curing periods shorter than 24 h.

With reference to the PSD of aggregates, typical distributions produced by hammer mills were tested and proved acceptable, provided that an unlikely exceeding preponderance of finest fractions can be excluded. Conversely, the increment of CDW aggregates from 40% of dry weight to 50% and 60% led to a strength loss (approximately 20% and 55% for concrete and 20% and 45% for fired clay), but with average values not lesser than 40 N/mm<sup>2</sup> and 50 N/mm<sup>2</sup> respectively.

The reduction of metakaolin:slag ratios from 1:1 to 1:2 and 1:3 resulted in a strength loss as well (about 30% and 55% for concrete, 20% and 35% for fired clay), but geopolymers with fired clay were less affected.

Temperatures of room and ingredients, during preparation and casting processes, affected sensibly the open time of mixtures, pointing out the importance of avoiding exceedingly warm conditions. For example, working at 28–30 °C lead to a decrease of 80% of the open time available at about 20 °C.

The open porosity, which affects the strength, is positively correlated to the water content of the fresh mixture. This aspect should be taken into account when increasing the water content to improve workability.

Based on additional tests carried out at 3 and 6 months, strength at 28 days can be assumed as a reasonable reference value, as usual for building materials. The relation between the compressive strength measured at 7 and 28 days of age showed an almost linear correlation, and, if early testing is needed, the 28-day strength can be preliminarily estimated as 109% and 118% of the 7-day strength for mixtures with concrete or fired clay aggregates, respectively.

The relation between splitting and compressive strength, as expected, was non-linear and reasonably depicted by a power function, whose exponent is slightly less of the square root (approximately 0.45) for fired clay mixtures, and slightly more (approximately 0.65) for concrete ones. Interestingly, the relation that correlates tensile and compressive strength of concrete provided by Model Code 2010 [78] in the case of grades > C50 seemed to fit satisfactorily data on the tested geopolymers.

Finally, a preliminary testing of mixtures with fine siliceous sand aggregates, instead of waste ones, showed, as expected, that the former exhibit a generally greater compressive and tensile strength, and a higher apparent density as well. On the other hand, porosity and water absorption were sensibly greater in mixtures with waste aggregates.

## 6. Conflict of interest

None.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.conbuildmat.2018.06.018>

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