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# Mix design and mechanical performance of geopolymers binder for sustainable construction and building material

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**Abstract.** Sustainability in construction is a major concern worldwide, due to the huge volume of materials and energy consumed by this sector. Associated supplementing industries (e.g. Portland cement production) constitute a significant source of CO<sub>2</sub> emissions and global warming. Valorisation and reuse of industrial wastes and by-products make geopolymers a solid and sustainable via to be followed as a valid alternative to Portland cement. In this work the mix design of a green fly ash-based geopolymers is evaluated as an environmentally friendly construction material. In the pursuit of sustainability, wastes from a regional kraft pulp industry are exploited for the material processing. Furthermore, a simple, reproducible, and low-cost manufacture is used. The mix design is hence optimised in order to improve the desirable mechanical performance of the material intended for structural applications in construction. Tests indicate that geopolymers may efficiently substitute the ordinary Portland cement as a mortar/concrete binder. Furthermore, valorisation and reuse of wastes in geopolymers is a suboptimal way of gaining financial surplus for the involved industrial players, while contributes for the implementation of a desirable circular economy.

## 1. Introduction

Construction is a crucial sector for the economy and is in continuous growing worldwide, especially in the developing countries. Over the past century, ordinary Portland cement (OPC)-based concrete has become the highest volume manufactured product on Earth due to its extraordinary versatility, reliable performance and low cost processing technology. Unfortunately, many recent studies have demonstrated that its production is highly unsustainable, as the very large volumes required to meet global demand lead to a huge consumption of (non-renewable) raw materials and energy, while generate enormous emission of greenhouse gases, and dust pollution [1]. The global CO<sub>2</sub> emissions attributed to the production of OPC contribute to around 5-8% according to the most recent data [2-4]. In particular, OPC manufacture responds for 80% of the overall CO<sub>2</sub> release, while the production of aggregates contributes with 20%. The overall emissions of the concrete industry contribute as much as 10% of the global CO<sub>2</sub> releases [5, 6]. Such a large amount is highly unsustainable. As a consequence, the development of novel and more sustainable construction and building materials, with reduced environmental footprint, is currently a major concern in the worldwide construction industry.

Nowadays, geopolymers (GP) are recognized to be a viable and sustainable alternative to OPC. The first studies on GP, with direct applications in civil engineering, date back in the 1950s in the former Soviet Union where Portland cement shortage was affecting the country following the IIWW. Hence, Prof. G. V. Glukhovsky began to study the binders used in the ancient Egyptian and Roman structures and discovered the possibility of producing a novel kind of binders exploiting low basic calcium or calcium-free alumina-silicate materials mixed with solutions containing alkali metals [7, 8].



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Subsequently, Prof. J. Davidovits developed and patented some binders obtained from the alkali-activation of metakaolin (MK) giving a strong boost to the scientific research [9].

GP are inorganic alkali-activated binders formed by the interaction of an alkaline solution with a reactive solid source of aluminium and silicon [10] that generates a three-dimensional structure of  $\text{SiO}_4$  and  $\text{AlO}_4$ . Many solid precursors have been explored so far: ground granulated blast furnace slags, fly ashes (FA), although a range of non-blast furnace slags, natural pozzolanic materials, and calcined clays. The use of aluminosilicate-based industrial wastes might reduce the greenhouse footprint, in comparison to traditional concretes. Furthermore, under an accurate mix design it is possible to engineer novel GP-materials with comparable, or superior, mechanical and chemical properties than OPC [11]. Additionally, GP manufacture is highly cost effective and sustainable, since preparation and curing might occur at room temperature and is simple and fast. Some benefits of GP-concrete are: short curing time, early strength gain, suitable pre-fabricated concrete products for fast-building construction, building securing, etc.. Moreover, the material shows excellent chemical resistance to harsh environment, to fire loads, and to abrasion, low shrinkage and thermal conductivity, etc. [12, 13]. All of that makes GP highly suitable either for construction materials and environmental uses. Many interesting applications were already reported in construction with potentials for future innovative developments. At present they include high strength concretes with good resistance to chloride penetration, fire and/or acid resistant coatings, and waste immobilization solutions for the chemical/nuclear industries. Other applications in construction, guaranteed by GP, are easy adhesion to fresh and old substrates of distinct nature (stone, steel, glass, etc.), high surface definition that might replicate mould patterns, and inherent protection of steel reinforcing. Finally, a great deal of research has been performing worldwide towards the structural behaviour of GP-concrete in load-bearing structural members such as reinforced concrete beams, columns, slabs, etc. [14, 15].

This paper investigates the mix designs for GP-based binders intended for structural purposes, and formulated with industrial wastes. Regional wastes generated from a kraft pulp industry are exploited as precursors for the material processing. The specific variabilities are outlined in relation to the specimens' mechanical performance. Despite the key technological attributes and the most innovative applications, environmental and industrial cost saving issues are the main drivers for the uptake of the investigated technology. Valorisation and reuse of industrial wastes and by-products is a compelling business for governments and industries in order to respect the strict parameters and regulations imposed by the international frameworks, as the Paris Agreement from the Climate Conference COP21 (2015) or the EU Climate Action [16]. Such an issue is central, not only for cement companies but also for other industrial sectors where a large amount of wastes and by-products generates yearly an elevated loss of financial resources for treatment and disposal, reducing *de facto* the overall profit margins. This paper discusses the practical, technical, environmental, and commercial drivers, as well as how GP technology may form part of an overall "Green Concrete" industry.

## 2. Materials

The mix design aims to produce a GP binder to be used as lime or cement replacement in structural applications in construction (final mortar classifiable at least as class M10, according to UNI EN 998-2). GP have been produced by a mixture of MK and biomass FA as a source of alumino-silicates. The MK is purchased as Argical<sup>TM</sup> M1200S from Univar®. Its chemical composition was evaluated by X-ray fluorescence (Panalytical Axios spectrometer) (table 1). FA have been extensively investigated and exploited in GP production [17, 18] as a partial MK replaced in the formulations.

The typology used in this work comes from a regional kraft pulp industry. FA chemical composition was obtained by X-ray fluorescence (table 1), while the particle size distribution was determined by laser diffraction (Coulter LS230 analyser) (table 2). The specific surface area (estimated by BET) was measured in  $3.97 \text{ m}^2/\text{gr}$  for FA, and  $16.30 \text{ m}^2/\text{gr}$  for MK.

The alkaline activation was granted by a mixture made of a solution (10M) of sodium hydroxide (Na Hyd.) (reagent grade, 97%, Honeywell) dissolved in distilled water and sodium silicate (Na Sil.) (Quimialmel LDA, D40 - PQ).

**Table 1.** X-ray fluorescence of fly ash and metakaolin (left).**Table 2.** Particle size distribution of fly ash (right).

Oxides [wt%]	Fly ash	Metakaolin	$\mu\text{m}$	%<
SiO <sub>2</sub>	38.47	57.71	10	3.73
CaO	16.73	0.11	25	13.32
Al <sub>2</sub> O <sub>3</sub>	14.79	41.03	50	34.17
K <sub>2</sub> O	5.97	0.98	75	61.30
Fe <sub>2</sub> O <sub>3</sub>	5.94	1.77	90	105.31
MgO	3.44	0.29	mean	49.28
SO <sub>3</sub>	2.66	0.07		
Na <sub>2</sub> O	1.53	0.06		
P <sub>2</sub> O <sub>5</sub>	1.12	0.06		
TiO <sub>2</sub>	0.76	1.84		
MnO	0.50	0.01		
LOI	6.39	1.88		

### 3. Geopolymeric binder manufacture and characterisation

Specimens were manufactured by a simple and reproducible mechanical process performed at environmental temperature (20°C) to avoid any supply of external heat and, consequently, reducing the costs. GP specimens were prepared as follows: a) homogenization of the Na Hyd. solution and the Na Sil. at 50 rpm for 5 mins; 2) mixture of the alkaline solution with the FA and MK at 100 rpm for 10 mins; 3) pouring the slurry into cubic (30x30x30 mm) plastic moulds sealed with a plastic film for 24 hours (20°C, 65% RH); 4) demoulding hardened samples and curing at room conditions up to 28 days. For each formulation, the compressive strength (CS) was determined using an automatic hydraulic press (Shimadzu, AG-A) according to UNI EN 1015-11:2007 and ASTM C109 up to 28 days. Data were reported as the average from four tests. For scanning electron microscopy analysis (SEM) a microscope (Hitachi S4100) equipped with energy-dispersive spectroscopy (EDS) was used. Water absorption was evaluated as a percentage of  $\Delta W/W_1$  ( $W$ =weight) by specimens immersion in distilled water for 24 hrs once they had been previously dried to constant mass (UNI EN 1015-18:2004).

### 4. Mix design: optimization of fly ash amount and alkaline activators ratio

GP mix design was outlined to engineer the novel binder with a solid mechanical performance (structural application in construction, maximisation of breaking point in compression) along with a suboptimal incorporation of the industrial wastes. FA have been exploited in various quantities for partial replacement of MK; different alkaline activators' ratios have been investigated as well. The performed analyses and mechanical tests lead to a suboptimal GP-based binder composition.

Traditional binders (whether cementitious or lime-based) harden in contact with water generating hydrates (a process that may last years in the case of lime products). Furthermore, they show a large reduction in pore volume due to the consumption of water during the hydration reaction, with a subsequent great volumetric shrinkage [19]. On the contrary, GP-based binders do not form hydrates and the pore size distribution is refined throughout the hardening process [20, 21]. As a consequence, the ratio water/binder in GP should be as lower as possible to obtain a non-porous binder with a good mechanical performance. The use of a low liquid/solid ratio also reduces the tendency for efflorescence formation. Furthermore, the molar oxide ratios SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>, and Na<sub>2</sub>O/SiO<sub>2</sub> should range within the Davidovits limits [9] returning also a good indication of such a possible on-going disastrous phenomenon that raises concerns on the possible materials durability.

MK is the most used precursor in GP production due to its relatively low cost along with the capability to develop high strength products [22, 23]. FA have been found to be a valid alternative source of aluminium and silicon to MK and can be successfully employed.

Different mixes of MK/FA were designed in order to study the effect of the FA content on the GP final breaking point (table 3a). Afterwards, having set a suboptimal FA amount, to optimise the best

alkali activators' ratio different ratios of Na Hyd. solution and Na Sil. were tested (table 3b). Subsequently, considering that larger FA particles might not be highly reactive, also due to their organic nature, a set of them was sieved at 75 µm and 125 µm (table 3c). These fractions were then used. That is aimed to maximise FA incorporation, along with reducing the samples' overall porosity.

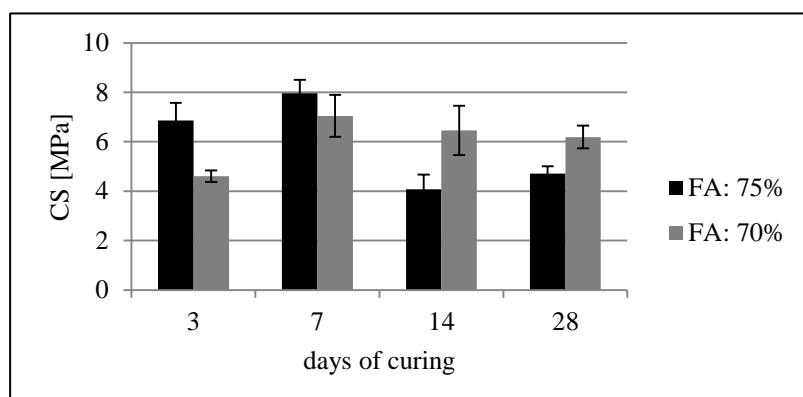
**Table 3.** Mix design (in weight) of geopolymeric binders for structural applications.

Phase	Composition	MK	FA	Sodium hydroxide	Sodium silicate	note
(a)	I (75%)	1	3.0	2	2	
	II (72.97%)	1	2.7	2	2	
	III (70.59%)	1	2.4	2	2	
	IV (67.74%)	1	2.1	2	2	
	V (64.29%)	1	1.8	2	2	
	VI (60%)	1	1.5	2	2	
(b)	A	1	2.33	2	2	
	B	1	2.33	1.5	2.5	
	C	1	2.33	1	3	
	D	1	2.33	0.5	3.5	
(c)	C1	1	2.33	1.5	2.5	d<75 µm
	C2	1	2.33	1.5	2.5	75<d<125 µm
	C3	1	2.33	1.5	2.5	d<125 µm

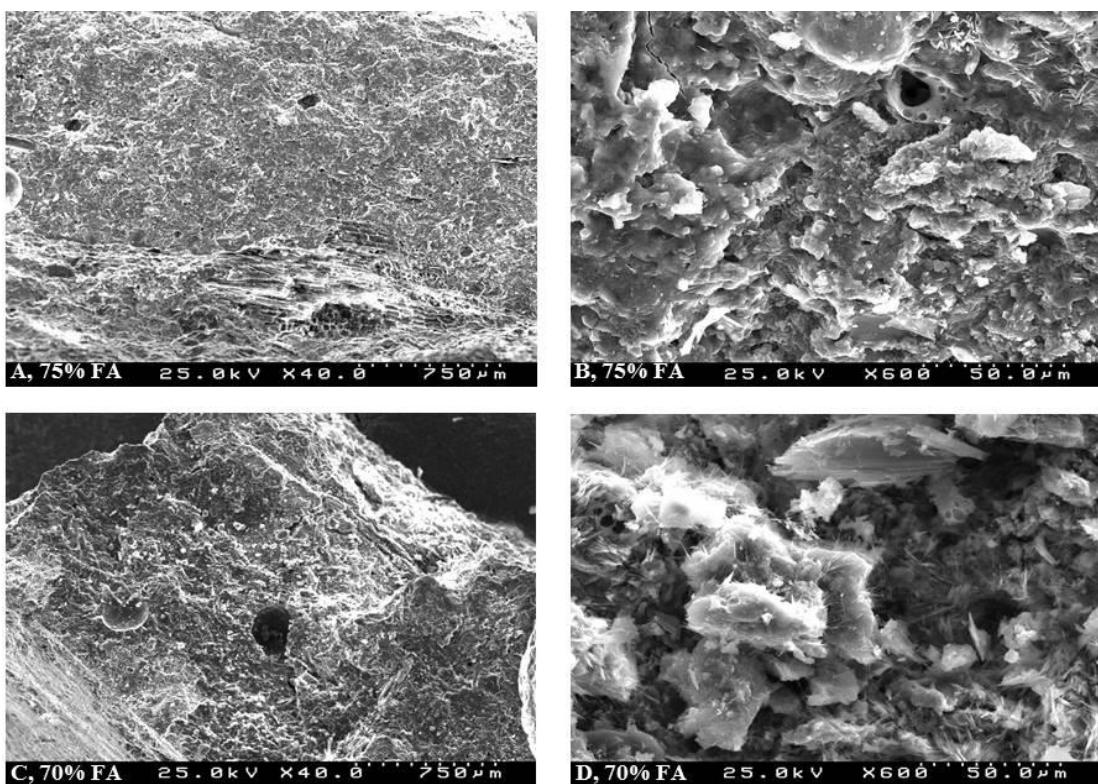
## 5. Results and discussion: mechanical performance

For each formulation, the CS, along with the mechanical performance, was determined up to 28 days curing. Data were reported as the average from four tested cubes randomly taken from the batch.

The preliminary phase (a) was performed in order to define the best amount of FA to substitute MK, aiming to optimize CS values. Thus, the ratio FA/MK has been varied from 3:2 (60%) to 3:1 (75%). Figure 1 reports the CS values of specimens containing 75% and 70% FA. The CS variation is not linear during curing due to the progress of the reactions of geopolymerisation and densification changes of the gels. The final best performance was achieved for a 70% incorporation of FA, corresponding to  $6.19 \pm 0.46$  MPa. This formulation was then explored in the following steps. Water absorption and apparent bulk density have been calculated respectively as 31.12 % and  $1405 \text{ kg/m}^3$  for the 75% FA sample, and 32.97 % and  $1265 \text{ kg/m}^3$  for the 70% FA sample. Figure 2 shows the micrographs of the two specimens. 70% FA appears to be more compact and presents many needle-shaped formations of sodium salt that enhance the bonding character of the whole structure; hence a superior compressive strength was obtained. However, such formations thereafter appear as efflorescence after immersion in water - as will be discussed - generating issues on durability.

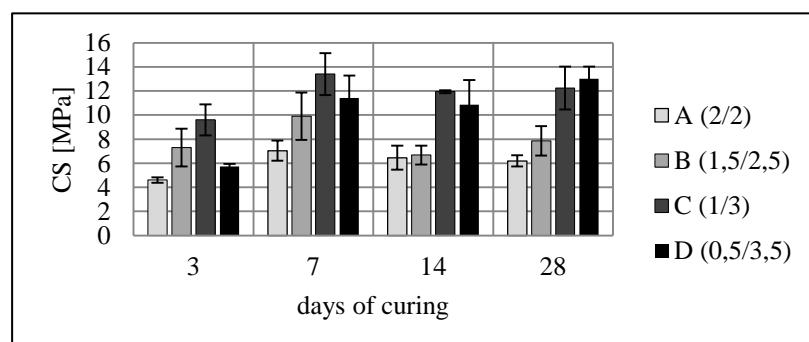


**Figure 1.** Compressive strength at 3, 7, 14 and 28 days curing for 75% e 70% fly ash content.



**Figure 2.** Micrographs at 750  $\mu\text{m}$  and 50  $\mu\text{m}$ , respectively A-B for 75 % FA (top images), and C-D for 70 % FA (bottom images).

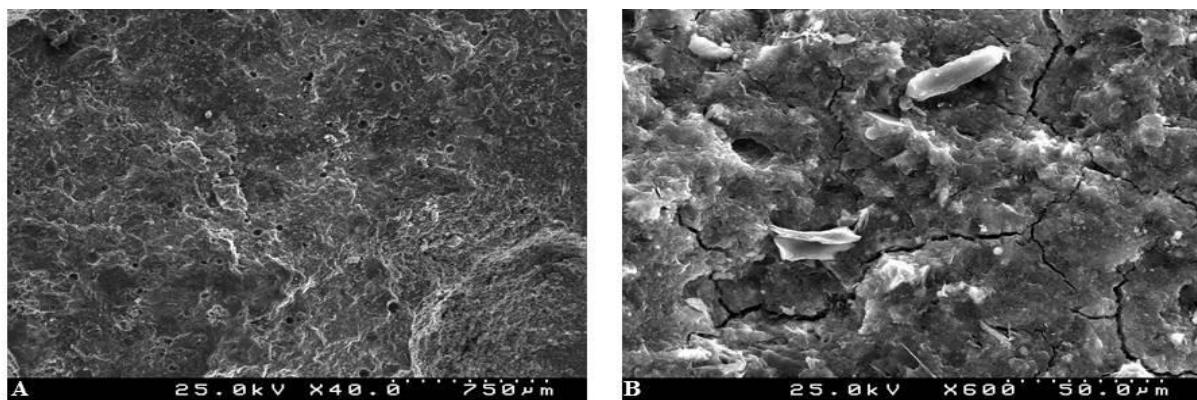
Phase (b) is aimed to optimise the alkali activator formulation (Na Hyd. / Na Sil. ratio). Figure 3 shows the CS values of the specimens cured up to 28 days. As a result, the decrease of such a ratio enhances the mechanical strength. Values for 28-day cured samples are: A –  $6.19 \pm 0.46$  MPa, B –  $7.86 \pm 1.23$  MPa, C –  $12.24 \pm 1.79$  MPa, and D –  $13.01 \pm 1.01$  MPa. Values of the water absorption are: A – 31.12 %, B – 32.97 %, C – 38.73 %, and D – 26.59 %. Figure 4 shows the SEM pictures of mix C, revealing the presence of a larger number of small pores, in comparison to composition A (figure 2, C-D). Anyway, the overall gel looks denser, hence explaining the better mechanical performance. Table 4 reports the theoretical molar ratios of the four prepared mixes. Noteworthy that decreasing Na<sub>2</sub>O to Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> ratios causes CS increase. Mix A contains the highest Na<sub>2</sub>O concentration, responsible for the efflorescence appearance, as already stated. The usability of this material is then questionable. No efflorescence has been observed when Na Hyd. decreases. At the same time, a better slurry workability is achieved by increasing the H<sub>2</sub>O content in the mixture. Although composition D shows the highest CS, at the same time it is highly cost ineffective as Na Sil. is more expensive than Na Hyd. It is also the least environmental interest. By balancing all observations, composition C represents the best compromise between mechanical performance and environmental/financial sustainability.



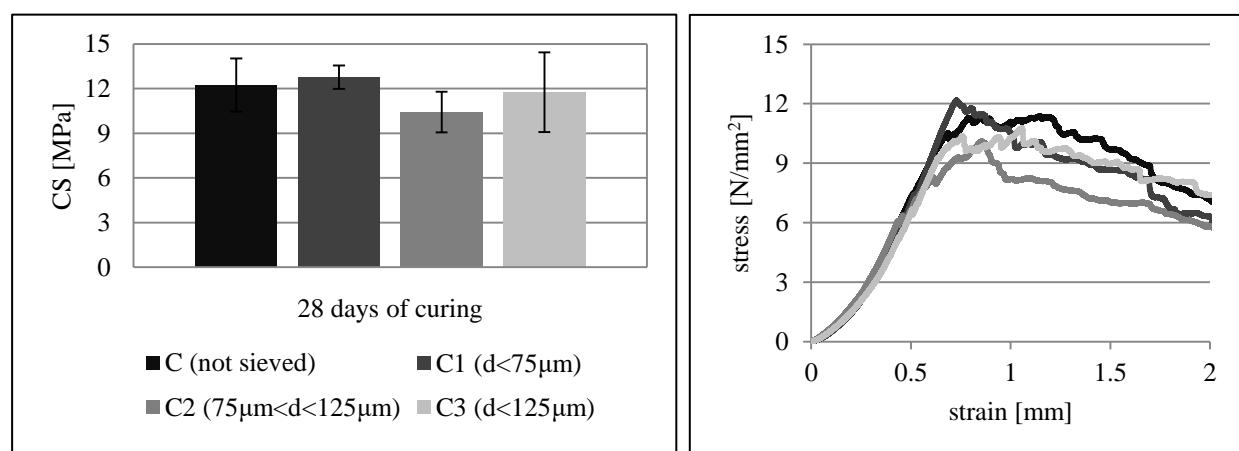
**Figure 3.** Compressive strength at 3, 7, 14 and 28 days curing for mix designs phase (b), A, B, C, and D. Ratios (Na Hyd./Na Sil.) are indicated.

**Table 4.** Theoretical molar ratios for phase (b) mix design.

	A 100/0	B 100/0	C 100/0	D 100/0	Davidovits limit
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	4.58	4.92	5.27	5.61	3.30 – 4.50
Na <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	1.69	1.50	1.31	1.12	0.80 – 1.60
Na <sub>2</sub> O/ SiO <sub>2</sub>	0.37	0.30	0.25	0.20	0.20 – 0.48
H <sub>2</sub> O/Na <sub>2</sub> O	12.9	14.2	15.9	18.2	10 – 25

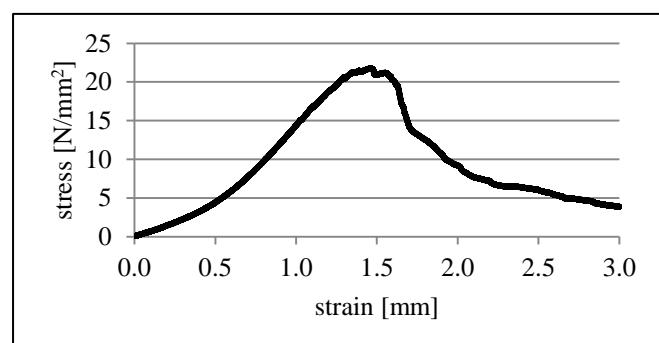
**Figure 4.** Micrographs at 750  $\mu\text{m}$  and 50  $\mu\text{m}$ , respectively A and B, for the mix design C.

As already mentioned, phase (c) aims to study the effect of FA particle size. Finer particles tend to show higher reactivity, while improving the compactness of the samples. Both effect should increase the mechanical strength and reduce the penetration of aggressive external agents that affects the durability, as observed for ordinary artificial stone materials [24]. The use of finer materials demands extra water to correctly mix the components and adjust the rheology of the system. The water content should be carefully controlled, since an excess will create an extra volume of pores after curing. Figure 5 shows CS and the mechanical behaviours of mixes C<sub>n</sub> using sieved FA. Tests clearly show that even if there is a slight improvement using sieved FA ( $d < 75 \mu\text{m}$ ), 12.77 MPa against 12.24 MPa, then the deviation is not that large to justify an extra employment of energy, and financial resources, to mill and sieve the material. Analogously, the overall mechanical performance, at least in the elastic region, is similar, meaning that FA particles size has a little influence in the overall behaviour.

**Figure 5.** Compressive strength at 28 days curing for mix designs phase (c): left: break point; right: mechanical performance.

## 6. Standard mechanical tests

All the above discussed factors constitute the basis for a further test according to the standard UNI EN 1015-11:2007. Thus, geopolymers specimens were produced with formulation C in standard dimensions (40x40x160 mm). The standardized procedure prescribes that a mortar, in order to be classifiable as a structural material, might show a compressive strength at least equal to 10 MPa, class M10 according to UNI EN 998-2. The new performed mechanical tests have revealed a final breaking point equal to  $22.15 \pm 1.22$  MPa at 28 days curing. The final resistance to bending was also measured returning  $3.05 \pm 0.37$  MPa. Figure 6 shows the mechanical performance of the optimized geopolymeric binder at 28 days curing, following the prescribed standardized procedure. All considering, such a geopolymers, under the discussed formulation C, could be classifiable equal to a class M20 mortar.



**Figure 6.** Mechanical performance of the optimized geopolymeric binder at 28 days curing, following the standard procedure.

## 7. Conclusion

This work analysed the possibility of producing novel geopolymers binders by valorising and reusing some industrial wastes, such as the fly ash, from a regional kraft pulp industry. Different mix designs have been tested in order to optimise the final mechanical performance of the binder intended for structural applications in construction and a sustainable replacement of the ordinary Portland cement. Based on the investigation carried out, it is concluded that, with these particular wastes, the incorporation of 70% fly ash in the geopolymers paste assures the best 28 days compressive strength. Furthermore, fly ash does not need any particular treatments, such as sieving, and can be incorporated as produced. Indeed sieving does not cause any relevant effects on the final compressive strength. The best alkaline activator presents a ratio sodium hydroxide/sodium silicate equal to 1:3 leading to a break point equivalent to  $12.24 \pm 1.79$  MPa, corresponding to the mix design C.

Moreover, the mechanical tests have been repeated following the standard for mortars, leading to a break point equivalent to  $22.15 \pm 1.22$  MPa and a bending resistance equal to  $3.05 \pm 0.37$  MPa. All these values are suitable for structural applications in construction, with a classification equal to M20.

All considering, the wastes from the kraft pulp industry can be opportunely reused to produce a green fly ash-based geopolymers intended for an environmentally friendly construction material. Furthermore, in the pursuit of sustainability, manufacture is performed at environmental temperature and is simple, reproducible, and low-cost leading to a surplus of profit margins for the industry.

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