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Alkali-activated Fly Ash-based Mortars for Green Applications in Architecture and Civil Engineering

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***Abstract*—Waste recycling is a compelling topic worldwide, especially in construction whose development is becoming highly unsustainable. Production and characterization of novel eco-composite alkali-activated mortars are reported. Specimens consist of a geopolymeric binder that uses biomass fly ash from a kraft pulp industry admixed with traditional construction silica sand in various proportions. Mix design is studied to investigate the effects of sand incorporation on mortars characteristics. Moreover, the effects of age and water addiction are analysed. Finally, a sustainable and reproducible manufacture is followed. The performed analyses indicate that the novel mortars can be used as structural material in construction and represent an efficient solution to reduce the environmental footprint associated with waste disposal.**

***Index Terms*—Construction, mortar, geopolymer, waste, sustainability.**

I. INTRODUCTION

Until the industrial revolution, construction was the principal human activity and still today it is one of the most active industrial sectors. As well as all the manufacture processes, also construction is subjected to specific restrictions and requirements that have occurred during time in various forms such as raw materials availability, technological overcoming imposed by obsolete techniques, or specific events. Recently, strict requirements are spreading out: novel market demands, regulations, sustainability issues, etc. [1]. Indeed, people are becoming highly sensitive to environmental and socio-economic issues such as depletion of natural resources, climate change, atmospheric pollution, etc..

One of the historically most common and efficient strategies to improve the constructive system was the selective reuse of disposed materials. Only after the 1973 Oil Crisis, with the accompanying 1973–74 stock market crash, people started to become aware of a real possible depletion of natural resources that, associated with the catastrophic forecasts for the planet “health”, has led the public conscience to a more accurate evaluation of the problem [2]-[3]. Finally, from the 1990s, some industrial sectors began to consider a viable and cost-effective solution both the whole product management - from manufacture to disposal – and the reuse, recycling, and valorisation of trashes, wastes, and by-products [4]-[5]. Transforming waste materials into useful products by reusing, recycling, or converting into an energy resource is of utmost importance. Indeed, many economic sectors, as construction, face the expanding problem of wastes and by-products that generates yearly an elevated loss of financial resources for treatment and disposal. Thus, industries are focusing on new technologies to transform low-quality, zero- or low-cost materials into high-value products with a surplus of financial resources and a consequent reduction in environmental impact associated with human activities.

This paper investigates production, mix design and characterization of novel geopolymeric mortars, formulated with industrial wastes, intended for applications in architecture and civil engineering. Wastes, namely fly ash (FA) from biomass combustion, derive from a local Kraft pulp industry and are here used as GP-binder precursor. Geopolymers (GP) are inorganic alkali-activated binders made of a reactive solid alumina-silicate source interacting with an alkaline solution [6]. Nowadays, they are claimed as one of the most viable and green alternative to Ordinary Portland Cement and are deeply investigated for diverse applications, mostly in construction [7]-[8]. Among the various advantages of GP, it is reported in literature their high resistance to

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chemicals, to fire loads, and to freeze and thaw cycling, a fast setting time with the formation of a stable gel, a low volumetric shrinkage, a remarkable mechanical performance, etc. [9]-[10]-[11]. Moreover, their manufacture is relatively simple and low-cost, and generates very low CO_2 emissions. The most used precursor in GP manufacture is metakaolin (MK) as a source of aluminium and silicon. MK can be partially substituted by other materials, such as industrial wastes, making GP-technology more sustainable. Many solid precursors have been explored so far: ground granulated blast furnace slags, FA, natural pozzolanic materials, calcined clays, etc.. Under an accurate mix design it is possible to engineer the novel GP-mortars with desired physical and chemical properties [12].

Structural applications in architecture and civil engineering is the key aim of this study. Thus, the specific variabilities are outlined in relation to specimens' mechanical performance (final GP-mortar classifiable at least as class M10, according to UNI EN 998-2). A complete physical characterization is also outlined in order to foresee any possible application.

II. MATERIALS AND METHODS

A. Precursors for Materials' Processing

In this work the GP-mortars have been produced by a mixture of MK and biomass FA as binder (source of aluminium and silicon). Benchmark MK is purchased as Argical™ M1200S from Univar®. Biomass FA partially substitute the MK, as previously discussed in [13]-[14]. The FA typology used in this work derives from a local Kraft pulp industry and are generated during the manufacture of bleached cellulose pulp. Manufacture involves an alkaline digestion of wood to extract the lignin. That is dissolved in a liquor which is heated to melt the inorganic components and burn the organic ones to generate steam, converted into electricity by a biomass thermoelectric power plant. FA is basically collected from exhaust gases passing through electrostatic precipitators. The alkaline activation is granted by a solution of sodium silicate (Quimialmel LDA, D40-PQ) and sodium hydroxide (ACS reagent, 97%; Honeywell) 10M dissolved in distilled water.

Natural siliceous sand is used as thin aggregate and has been furnished by Saint-Gobain Weber Portugal.

B. Mortars Manufacture

The followed manufacture procedure is simple, reproducible, low-cost, and is completely performed at ambient conditions (20 ℃, 65% RH). That avoids any supply of external heat and, consequently, generates a more sustainable and cost effective process.

Specimens were prepared as follows: a) mixing of MK and FA for 1 min to ensure a uniform mixture; b) homogenization of sodium silicate with sodium hydroxide at 50 rpm for 5 mins; c) mixture of the alkaline solution with FA and MK at 100 rpm for 9 mins; d) admix aggregates and mix for 1 min to ensure a uniform dispersion; e) pouring the slurry into standard metallic moulds and vibrate for 2 mins on a vibrating table to assure compaction; f) sealed with plastic film for 24 hrs at ambient conditions; g) demolding hardened samples and curing at the same ambient conditions.

C. Specimens Characterization

The mineralogical composition was evaluated by X-ray diffraction using a Rigaku Geigerflex D/max-Series instrument. The chemical composition was evaluated by X-ray fluorescence (Panalytical Axios spectrometer). FA are mainly composed by SiO_2, CaO, and Al_2O_3 (total ≈ 70%); MK by SiO_2 and Al_2O_3 (total ≈ 99%).

Density has been measured as 2.28 g/cm^3 for FA; 2.32 g/cm^3 for MK, and 2.62 g/cm^3 for sand. Particle size distribution was determined by laser diffraction (Coulter LS230 analyser, Fraunhofer method and Polarization Intensity Differential Scattering). Table I shows the particle size distribution of FA, MK, and sand respectively. The specific surface area was estimated by BET in 3.97 m^2/g for FA, 16.30 m^2/g for MK, and 0.57 m^2/g for sand.

TABLE I. PARTICLE SIZE DISTRIBUTION OF FA, MK, AND SAND

μm	Fly ash %<	Metakaolin %<	Sand %<
10	3.73	0.83	477.40
25	13.32	2.17	622.10
50	34.17	4.30	814.50
75	61.30	7.86	1031.00
90	105.31	13.07	1244.00
mean	49.28	5.71	841.20

GP-mortars manufacture and characterization were performed according to "testing methods for mortar for masonry". Accordingly, specimens were produced following the standard dimensions 40x40x160 mm. The consistency of the fresh GP-mortars was estimated by flow table test, according to EN 1015-3:1999. Bulk density was calculated as the average from three specimens. The microstructure was investigated by scanning electron microscopy (Hitachi S4100). Water absorption by immersion was evaluated using the Archimedes principle, following EN 1015-18:2004, data were reported as the average from three tests. The coefficient of water absorption by capillarity was measured according to the same standard. Mechanical performance was determined according to EN 1015-11:2007 and EN 998-2:2016 (compressive strength ≥10 MPa, at least class M10, for structural applications). Therefore, the characteristics of the hardened mortars were determined. For each formulation, compressive strength (CS) and bending resistance (BR) were measured at 28 days of curing using an automatic hydraulic press (Shimadzu, AG-A) running at a displacement rate of 0.5 mm/min; data were reported as the average from four tests randomly taken from the batch. Deflection and shortening were calculated according to standards. The water/solid (w/s) and water/cement (w/c) ratios were also calculated.

D. *Mortars' Mix Design*

The mix design aims to engineer the novel GP-mortars with a solid mechanical performance to be used as ordinary lime/cement mortars replacement in architecture and civil engineering applications. Table II reports, according to EN 998-2:2016, the mortar categories and the relative final breaking points intended for masonry applications. The minimum admissible category for structural application is M10 (CS ≥10 MPa).

TABLE II. MORTARS FOR MASONRY CATEGORIES

category	break point at 28 days	
	N/cm^2	Kg/cm^2
M1	1	10
M2.5	2.5	25
M5	5	50
M10	**10**	**100**
M15	15	150
M20	20	200
M d*	>25	>250

* category declared by the producer.

The binder mix design was studied by the authors in [15]. In order to achieve a suboptimal mechanical performance, while maximising FA incorporation, the selected GP formulation is: solid part made of 70 wt% FA and 30 wt% MK; alkaline activator with a hydroxide/silicate ratio equal to 1:3. That formulation assures, after 28 days of curing, a break point of 22.15±1.22 MPa, and a bending resistance of 3.05±0.37 MPa. Those values made it classifiable as M20.

In this work, five different GP-mortar formulations have been produced. The amount of the admixed aggregate – siliceous sand – has been varied in order to evaluate its influence on the final properties. Table III shows the mix designs formulated for the novel GP-mortars. The calculated w/s ratio and average spread values are also reported.

TABLE III. MORTARS MIX DESIGN

N.	Ratio binder/aggregate	Binder [wt %]	Aggregate [wt %]	Ratio w/s	Spread [cm]
1	1:1	1	1	0.391	>30
2	1:2	1	2	0.261	26
3	1:3	1	3	0.196	21
4	1:4	1	4	0.156	15
5	1:5	1	5	0.130	10

III. RESULTS AND DISCUSSION

A. *Physical Characterisation*

The consistency of the fresh GP-mortars, estimated by flow table test, gives an indication of the materials workability. Consequently, the flow value (spread) was determined by measuring the mean diameter of the fresh mortars. If consistency is not at the desired level, then the mortar is applied with difficulty and might not show the required qualities once set. Indeed, if the material results too pasty, then cavities may form within its matrix leading to some anomalies, such as incongruous density, caused by the formation of large voids. When it is too liquid, then it may occur segregation and delay in setting and curing. This phenomena are clearly shown in Fig. 1 where the cross sections of the five produced mortars are presented. Voids may also cause cracks or reduce the final mechanical strength. Measured consistencies (spread) are reported in table III. Decreasing the w/s ratio, that is to say increasing the amount of the admixed aggregate, mortars become more pasty and, consequently, their workability decreases, and larger voids are formed. A suboptimal flow value ranges between 19 cm and 22 cm. It can be observed that only specimen n. 3 (ratio 1:3) responds to the requirement. For the GP-binder, the ratio water/cement (w/c) is constant and equal to 0.78.

Figure 1. Novel GP-mortars cross sections showing an increasing porosity in relation to aggregates amount.

The bulk density of the 28 days hardened GP-mortars are: GP – 1307 Kg/m^3; mortar ratio 1:1 - 1440 Kg/m^3; mortar 1:2 - 1771 Kg/m^3; mortar 1:3 – 1832 Kg/m^3; mortar 1:4 - 1921 Kg/m^3; mortar 1:5 - 1765 Kg/m^3. GP-binder is reported for comparison. It is observed that the overall bulk density increases with the relative amount of aggregates.

The 1: 5 formulation shows an anomalous behaviour that is caused by its very poor workability, which does not allow a good compactness.

The microstructure of the novel materials was investigated by SEM. Micrographs are shown in Fig. 2. The binder gel appears quite compact and dense (figure 2-A). The surface texture results rough but uniform and continuous. Some micro-formations of sodium salt are observed (Fig. 2-B). They are potentially highly dangerous for durability, however do not appear as efflorescence, neither after long aging time (specimens have been monitored up to six months) nor even after prolonged immersion in water.

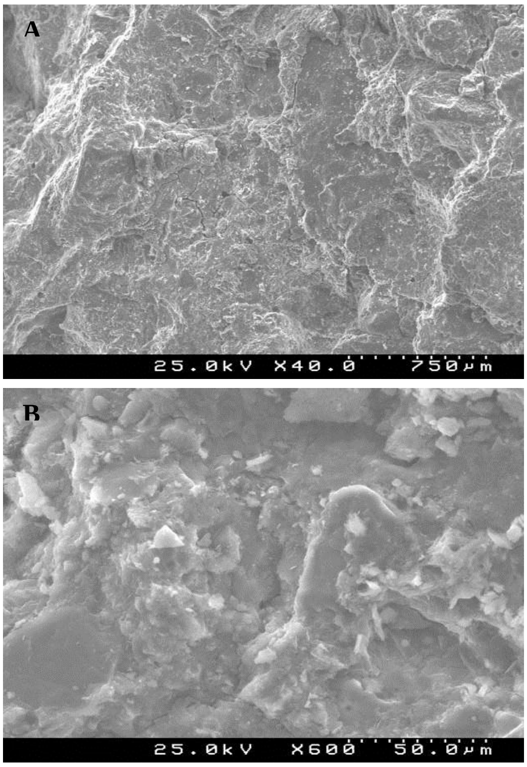

Figure 2. Micrographs at 750 µm and 50 µm, respectively A-B of the surface of the novel material. Only the specimen n. 3 (ratio 1:3) is reported. The overall gel results compact and uniform; it also completely covers the sands grains.

B. *Water Sorptivity*

Water sorptivity was evaluated using two different methodologies. The first one foresees the full immersion of the specimens; the second one the capillary action. In both cases, the standard EN 1015-18:2004 has been followed.

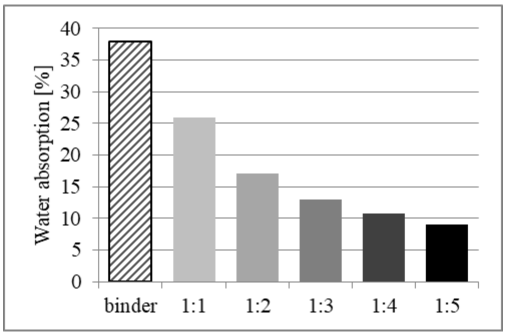

Figure 3. Water absorption by immersion.

Water absorption by immersion was evaluated using the Archimedes principle, as a percentage of $\Delta P/P$ of the hardened specimens that have been immersed in distilled water for 24 hrs. The results are shown in Fig. 3. The GP-binder water absorption resulted equal to 38%. That high value is due to a large number of small pores that are present in the gel, as reported by the authors in [15]. In GP-mortars, such porosity is filled up by the admixed sand. This effect is proportional to the amount of sand. As a consequence, the water absorption by immersion tends to decrease. In any case, it is observed that absorption by full immersion does not show high values, then allowing vast applications in construction. Indeed, only foundations or some parts subjected to particular harsh situations, such as proximity to water sources or presence of clay terrain, or completely immersed structure (*i.e.* bridges, piers, etc.) could be exposed to prolonged immersion (Fig. 4-5).

The test of water absorption by capillarity is performed by immersing one face, placed broken end downwards to a depth of 5-10 mm, in distilled water up to 90 mins. The increase in mass is measured at various stages. Fig. 6 shows the water absorption of the specimens expressed as mass percentage increase during time. Moreover, the coefficients of capillary were calculated.

As it is well known, the capillary action depends on the combination of surface tension and adhesive forces between the liquid and container walls, and propels the liquid upwards.

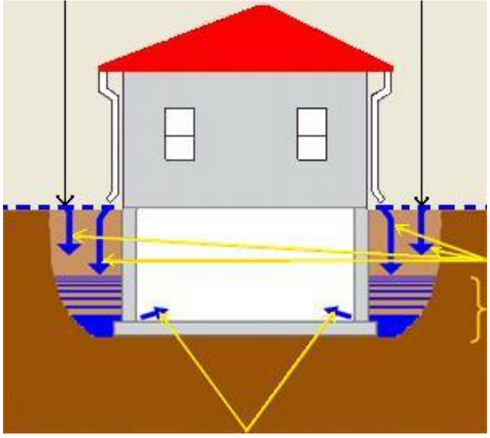

Figure 4. Basement subjected to complete immersion and seepage.

Figure 5. Modern and old building in London whose foundations are completely immersed in water

The absorption by capillarity of the GP-binder is higher than absorption of all mortars. As previously discussed, the GP-binder contains many small pores that are interconnected through the gel. This facilitates, and boosts, the water uprising action and, hence, a higher capillarity. In the produced GP-mortars, the fine aggregate tends to fills up the pores, then preventing the water to rise. As a consequence, smaller values are observed. Sample 1:5 shows again an anomalous behaviour due to the presence of voids that generates a contrasting action. From one side, they are not so large to completely prevent the capillary action, but are big enough to be completely filled up by the sand particles. The coefficients of water absorption by capillarity were calculated as: GP – 0.87 kg/(m^2 $min^{0.5}$); ratio 1:1 – 0.74 kg/(m^2 $min^{0.5}$); 1:2 – 0.38 kg/(m^2 $min^{0.5}$); 1:3 – 0.35 kg/(m^2 $min^{0.5}$); 1:4 – 0.28 kg/(m^2 $min^{0.5}$); 1:5 – 0.43 kg/(m^2 $min^{0.5}$). According to the physical general structure of the various mortars, and depending on the quantity of binder in the matrix, the coefficient C tends to diminish.

C. Mechanical Performance

Generally speaking, mortars for masonry must show a compressive strength ≥10 MPa (at least class M10) in order to be suitable for structural applications in construction (table II). For each formulation, compressive strength (CS) and bending resistance (BR) were assessed at 28 days curing. Deflection and shortening were also calculated.

As discussed, the GP-binder formulation was engineered in order to guarantee a suboptimal waste incorporation and a good mechanical performance. Tests indicated that after 28 days of curing, the break point of the GP-binder is equal to 22.15±1.22 MPa, while the bending resistance is 3.05±0.37 MPa [15].

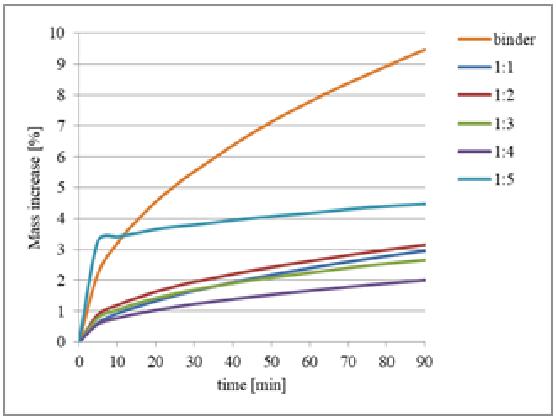

Figure 6. Water absorption by capillarity.

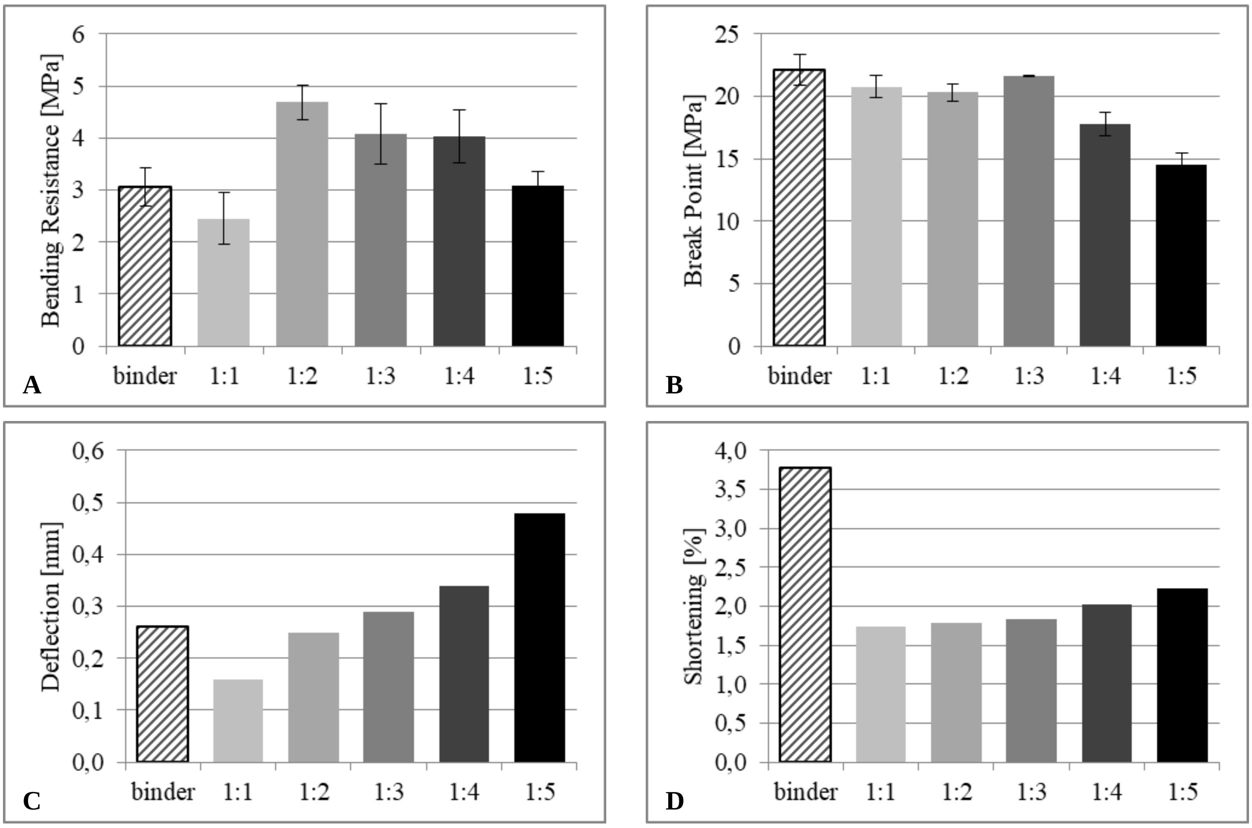

Figure 7. Novel GP-materials mechanical performance at 28 days curing. A: bending resistance; B compressive strength; C: deflection; D:

Fig. 7 shows the bending resistance (Fig. 7-A), compressive strength (Fig. 7-B), relative deflection (figure 7-C), and shortening (Fig. 7-D). Data are reported as the average of four tests of specimens randomly taken from the batch. It is observed that the final BR (Fig. 7-A) of GP-mortars ns. 2, 3, and 4 resulted higher than the one of the binder. The addition of sand improves the resistance to deformation to the external applied force. Mortar n. 5 showed a value close to the binder; the same could be observed for specimen n. 1 considering the calculated standard deviation. In detail, the calculated BR values are: ratio 1:1 – 2.45±0.49 MPa; ratio 1:2 – 4.69±0.33 MPa; ratio 1:3 – 4.08±0.58 MPa; ratio 1:4 – 4.03±0.52 MPa; and ratio 1:5 – 3.09±0.26 MPa. As a general trend, having reached the maximum value for the specimen n. 2, the bending resistance tends to decrease by enhancing the aggregate amount. On the contrary, the respective deflections (Fig. 7-C) increase, meaning that using larger amount of aggregates makes the material more deformable and less brittle.

According to the technology of construction, and for applications in civil engineering and architecture, that is not necessarily a positive factor since a high stiffness is required for all the inflexed horizontal elements, such as beams or slabs. Furthermore, deflections should be minimized for aesthetic reasons.

By limiting to masonry applications, the most important factor is the compressive strength. As it could be observed in figure 7-B, all the produced GP-mortars are suitable for structural applications in construction (class ≥ M10). The highest value was obtained for formulation n. 3, prepared with a binder/aggregate ratio equal to 1:3. Mortars n. 1 and 2 show similar values. There, it seems that aggregate contribution to compression strength is small, so the overall resistance is entrusted to the binder. By comparing GP-binder with mortars n. 1 and 2, a constant reduction is observed, which is exactly caused by the decreasing content of binder in the mixes. Mortars n. 4 and 5 show then a deep reduction in resistance. This is particularly evident for mortar n. 5. In detail, calculated CS values are: ratio 1:1 – 20.77±0.91 MPa; ratio 1:2 – 20.32±0.71 MPa; ratio 1:3 – 21.66±0.03 MPa; ratio 1:4 – 17.75±0.95 MPa; and ratio 1:5 – 14.54±0.93 MPa. According to UNI-EN-998-2, formulated GP-mortars n. 1, 2, and 3 are classifiable as M20; GP-mortar n. 4 as M15; GP-mortar n. 5 belongs to M10. Calculated shortenings (figure 7-D) demonstrate that the addition of thin aggregate improves the stiffness in compression of the material. Anyway, increasing the amounts of thin aggregates enhances the final deformability of the mortars. Calculated values range between 1.7% and 2.2%.

D. Effects Caused by Age and by Water

Traditional mortars (whether cementitious, lime-based, or others) harden and cure in presence of water gaining strength over time. This natural process can last years and usually generates hydrates. Furthermore, during hydration reaction the material can show a significant reduction in pore volume, caused by the natural evaporation of water along with its chemical consumption. Those factors usually result into a great volumetric shrinkage [16]-[17].

In GP-technology, geopolymerization occurs during hardening and curing. It is an exothermic process that can be theoretically split into three main stages: destruction, polymerization, and stabilization. The main reactions occur during the very first time, depending on precursors and curing conditions [12]-[18]. Thus, a high mechanical performance may be reached after a few days and continues increasing over time [8]-[19]. Geopolymerization does not form hydrates and the matrix structure, along with the pore size distribution, is refined throughout the hardening process [20]-[21]. As a consequence, the water/cement ratio in GP-mortars should be as lower as possible to obtain a low-porous material with a good mechanical performance. Furthermore, the use of a low liquid/solid ratio also reduces the tendency for efflorescence formation that raises concerns on durability.

Based on the previous results, mortar n. 3 shows the best performance for applications in masonry. The main characteristics of the material are: w/s = 0.20; spread – 21 cm; bulk density - 1832 Kg/m^3; homogeneous structure with some pores; water absorption by immersion – 13.03 %; coefficient of water absorption by capillarity - 0.35 kg/(m^2 ·min$^{0.5}$); bending resistance - 4.08±0.58 MPa; deflection – 0.29 mm; break point - 21.66±0.03 MPa; shortening – 1.83 %.

In this section we will focus on the effects caused by aging. Understanding how the physical features might change during time is essential to indicate a suboptimal real application. That is crucial for the mechanical performance whose evolution could prevent a novel material from particular usages or may suggest more advisable applications. Furthermore, analysing such an evolution is essential to predict durability, *i.e.* issues linked to water sorptivity.

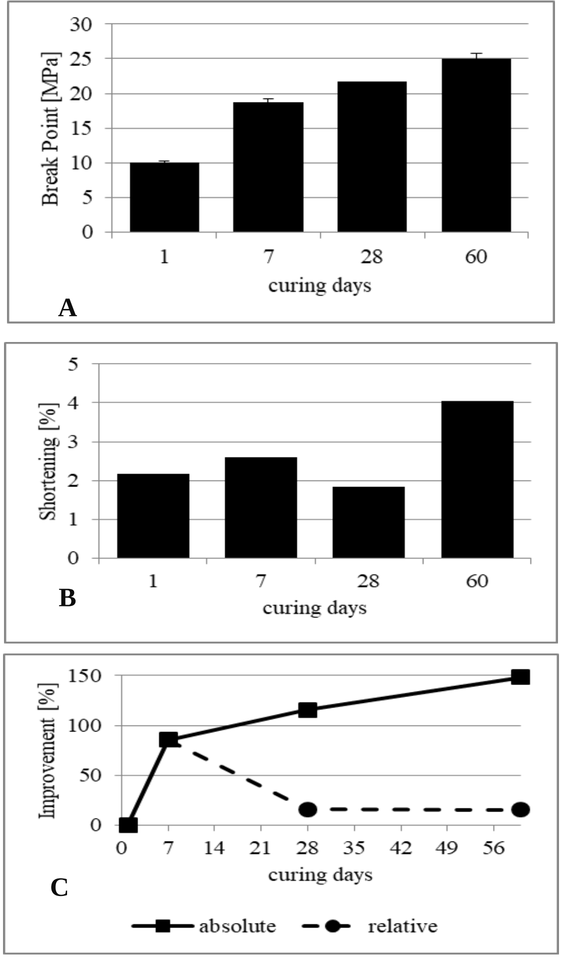

Figure 8. Mortar 1:3 mechanical performance: break point (A); shortening (B); compressive strength improvement % (C).

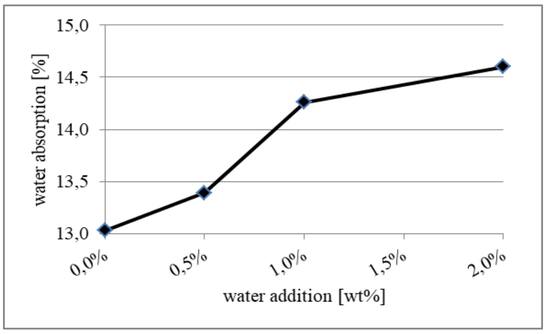

Figure 9. Water absorption by immersion vs. water addition.

We will also investigate the effects caused by adding water during manufacture. That is central in some applications where large amounts of aggregate, or also filler, are required reducing *de facto* the paste workability and, consequently, its real applicability. Indeed, adding water makes the mixture more liquid but, on the other hand, it could seriously affect the other properties, *i.e.* porosity or the mechanical performance.

Figure 8 shows the mechanical performance during aging. Figure 8-A shows the resistance to compression (CS) that is observed to increase over time. Day 0 represents the production date; day 1 when specimens were demolded. At this stage the material shows a break point of 10.05±0.23 MPa, already assuring the M10 classification. During the first 7 days there is a gain of 86% in CS values but then the rate slows down. At 28 days, as discussed, the break point is 21.66±0.03 MPa; at 60 days it is increased to 24.97±0.80 MPa, corresponding to a total improvement of ≈150%. At the same time the material becomes more deformable (figure 8-B). Figure 8-C represents the CS improvement rate.

The continuous line indicates the overall improvement % calculated at each curing stage in relation to the first measurement (1 day); the dot line indicates the improvement % during the various stages. A fast increasing rate was measured during 1-7 days, meaning that the most of the geopolymerization reaction has occurred in this period; a slowing down was calculated during the following period, 7-28 days, indicating that residual reaction is still in progress; finally, a slow increase is observed by aging till the 60th day.

Table IV shows the re-mix design of the mortar 1:3, testing distinct water amounts for its preparation. Figure 9 shows the values of water absorption by immersion of samples cured for 28 days; their mechanical performance is shown in Fig. 10.

TABLE IV. MORTARS MIX DESIGN

N.	Ratio binder/aggregate	Water [wt %]	Ratio w/s	Spread [cm]
3	1:3	0.0	0.196	21.0
3-a	1:3	0.5	0.201	21.5
3-b	1:3	1.0	0.206	22.5
3-c	1:3	2.0	0.216	24.6

As expected, values of spread on table (table IV) increase by using higher water content (wt%) in the mixture, meaning that material becomes more fluid and workable. Nevertheless, nor segregation has been observed, neither delays in setting time, or efflorescence formation. Indeed, after one day curing, all the specimens were completely hardened and could be easily demolded. According to literature [22]-[23]-[24], addiction of extra water to GP-mortars will increase the porosity of the material, since no hydration reactions are occurring along the time. This explains the improvement of water absorption values (figure 9), and the mechanical resistance lowering (figure 10) together with the larger deformability. Anyway, the behaviour in the elastic region is not affected that much by the quantity of added water.

IV. CONCLUSIONS

This paper describes the development of geopolymeric mortars for applications in architecture and civil engineering, using biomass fly ash as binder major solid component and sand as thin aggregate. Five different formulations, prepared with distinct binder/aggregate ratios, have been tested in order to study the effects of aggregate proportion on the properties.

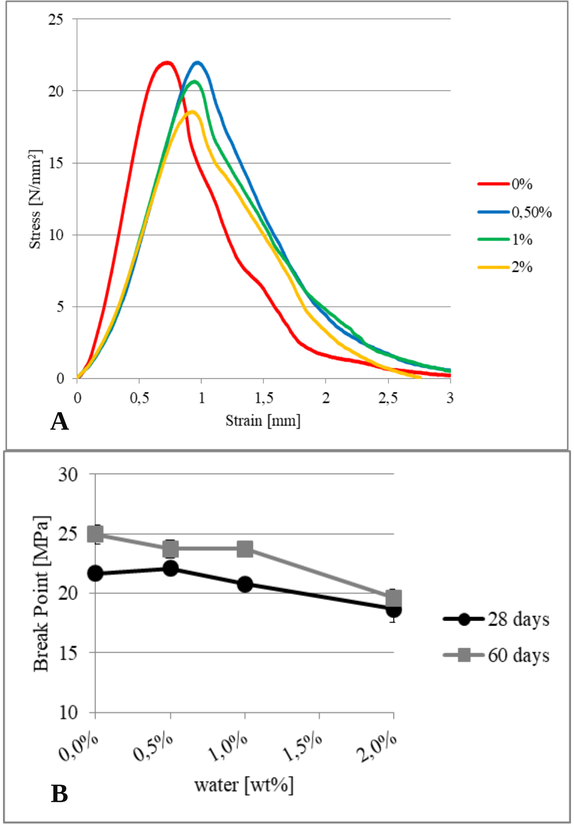

Figure 10.Mortars mechanical performance to water addition. Stress-Strain diagram at 28 curing day (A); CS at 28 and 60 days.

All formulated mortars are suitable for structural applications in construction, being classifiable at least as class M10. The optimal achieved binder/aggregate ratio resulted 1:3 with a 28-day compressive strength equal to 21.66±0.03 MPa (M20). This formulation was then studied in more detail, considering aging and fresh consistency by changing the water content in the mixture. Its compressive strength increased over time, reaching 150% improvement after 60 days curing. Adding more water made the mortar more porous, leading to higher water absorption and lowering the compressive strength. Anyway, the mechanical behaviour is only slightly influenced in the elastic region.

All considering, the biomass fly ash from the kraft pulp industry can be opportunely reused to produce alkali-activated mortars intended for an environmentally friendly construction material. Furthermore, in the pursuit of sustainability, manufacture can be conducted at room conditions, avoiding any external source of energy, by a simple, reproducible, and low-cost methodology.

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