NOVEL LOW-CARBON TILES OBTAINED WITH THE GEOPOLYMER TECHNIQUE

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ABSTRACT

Geopolymers are amorphous materials obtained from aluminosilicate precursors and alkaline activators in the liquid or solid state. Starting from 2000, geopolymers have attracted increasing research interests, especially in the construction material sector, where their use as a possible replacement for Portland cement has been extensively investigated. Geopolymers have also been developed as repair materials, protective coatings and low-cost ceramic-like materials. The main advantages of geopolymer development are the use of industrial by-products, e.g., fly ash from coal combustion and ground granulated blast furnace slag from iron-making production, which could be locally available, and curing at low temperature (< 100° C). So far, the most widely investigated forming technique for geopolymers has been the casting method where at least 20 wt% of water is necessary to satisfy the processability. However, few studies in the scientific literature have investigated extrusion and pressing as alternative forming strategies, in particular for producing ceramic-like materials.

This study aims to develop geopolymeric tiles obtained by pressing forming techniques. Metakaolin and industrial waste locally supplied by ceramic tile production plants (i.e., porcelain stoneware rectifying and glaze lapping powders) have been used as raw materials. Different activators and mix designs have been tested to optimize final product performance. In particular, anhydrous and liquid sodium silicate as well as a blend of sodium hydroxide and sodium silicate have been investigated as alkaline activators. The effect of different activator concentrations and increasing amount of ceramic waste in the mix have also been assessed. Finally, different pressing pressure values up to 50 MPa have been tested in the present study. The main results in terms of water absorption and microstructural observations indicate that the geopolymeric technology is a promising route in terms of environmental sustainability and final product performances.

1. INTRODUCTION

Geopolymers and alkali activated materials (AAMs) are aluminosilicate materials with different calcium concentrations characterized by a three-dimensional structure that is formed as a result of a reaction called geopolymerization [1,2]. This reaction occurs when an amorphous aluminosilicate precursor, such as metakaolin, fly ash or ground granulated blast furnace slags (GGBS), is mixed with an alkaline source, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), and/or sodium silicate (Na_2SiO_3) [3]. The prefix "geo" refers to the fact that these are not organic polymers, but they have a similar chemical composition to some minerals, such as zeolites. The great difference between natural zeolites and geopolymers is that they are almost totally amorphous composites [4]. Both geopolymers and AAMs represent innovative and sustainable building materials because of their low percentage of carbon dioxide (CO_2) emissions compared to traditional cementitious binders and ceramic materials. The low CO_2 emissions are mainly related to the fact that precursors are often sourced from industrial by-products and geopolymerization takes place at low temperatures (e.g., < 100 °C) [5]. Nevertheless, geopolymers and AAMs exhibit, when the mix designs are optimized, mechanical, microstructural and durability properties comparable to traditional building materials [6]. Firstly, geopolymers and AAMs have been largely investigated as possible replacement of hydraulic binders such as traditional ordinary Portland cement, yielding excellent results. More recently, geopolymers and AAMs seem to be promising materials for the production of ceramic-like materials, such as foams, tiles and bricks.

In addition, the production of geopolymers and AAMs is very versatile, as they can be formed by applying different forming methods, such as casting (the most common one), extrusion and pressing. Comparing casting and pressing forming techniques, Shee-Ween et al. [7] demonstrate that the casting method induces inferior performances of the hardened materials in terms of microstructural and mechanical properties compared to pressed ones. This is due to the high percentage of liquid activating solutions that produce higher porosity, consequently reducing bulk density and thus compressive and flexural strength. On the contrary, forming by pressing can be carried out either through hot or cold pressing. Prasanphan et al. [2] show that pressed geopolymers absorb less water, have a higher bulk density, and tend to have lower apparent porosity compared to cast geopolymers. In addition, it is shown that to produce pressed geopolymers, adding 24 - 26 wt% of activating solutions is sufficient to reach a mechanical strength in the range of 26.9 - 27.7 MPa. In the case of cast geopolymers, the presence of activating solution is much higher (i.e., 46 - 52 wt%) and the compressive strength is consequently much lower, about 14.5 - 22.3 MPa [8].

In the present study, a preliminary investigation on the optimization of the mix designs to produce metakaolin-based geopolymers by pressing is reported with the final aim of producing a ceramic-like material. Different activators (anhydrous and liquid sodium silicate, sodium hydroxide and their blend), pressing pressures ranging from 20 and 50 MPa, and curing temperatures (room temperature, 50 and 70 °C) have been investigated and the relevant samples have been characterized from the microstructure point of view.

2. EXPERIMENTAL

2.1. MATERIALS

To prepare geopolymeric samples obtained by the pressing forming technique, metakaolin (MK) was used as a precursor, sodium silicate (SS) in anhydrous and liquid form, and sodium hydroxide (NaOH) as activators. In further detail, MK powders (Argicem) were supplied by Argeco Développement, a French company that calcinates kaolin with a rapid process that lasts at most a few tenths of second [9]. The chemical composition of this MK is reported in Table 1. In a previous study, it was reported that the amorphous content of silica in this MK is only 29% [9] and this percentage was considered as reactive concentration when mix designs were prepared. As regards the alkaline activators, NaOH pellets (sourced from Sigma Aldrich, ACS reagent) were used to prepare solutions at different concentrations. NaOH solutions were cooled to room temperature before their use. Both solid (anhydrous powder (ASS) provided by Alfa Aesar) and liquid (Reoflux B (RF) supplied by Ingessil srl, Italy) sodium silicate (Na_2SiO_3) have been used in this study. Anhydrous SS has a density of 1.1 g/cm^3 and its chemical composition is reported in Table 2. To improve its reactivity, it was milled in a ceramic jar with a solids-to-alumina ball ratio of 1:2 for 30 minutes, as described in a previous study [10]. The composition of liquid SS is also reported in Table 2.

	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe_2O_3	Others
MK	72.0	22.1	< 0.1	0.3	0.4	< 0.1	1.6	3.6

Table 1: *Chemical composition in wt% of Argicem MK measured by ICP-OES.*

	SiO_2	Na_2O	H_2O	Others	SiO_2/Na_2O
ASS	46.7	50.4	-	2.9	0.9
RF	29.2	14.2	56.6	-	2.1

Table 2*: Chemical composition in wt% of anhydrous and liquid sodium silicate.*

2.2. SAMPLE PREPARATION

The geopolymeric specimens were obtained by varying precursors and activators. All the tested mixes are listed in Table 3. The sample nomenclature used in this study was chosen on the basis of the type of activators used and the other process parameters, such as the liquid-to-precursor (L/P) ratio that ranged between 0.18 and 0.25. In particular, "OP" stands for "one-part geopolymer," "TP" stands for "two-part geopolymer," "ASS" stands for "anhydrous SS", "RF" stands for liquid SS. Sample preparation differs depending on whether geopolymers were prepared from ASS (OP) or liquid activating solutions (TP). In the case of OP geopolymers, MK was combined with the ASS by mixing the powders inside a plastic bag. After that, the powder was placed on a tray and hydrated by spraying distilled water. Then, it was mixed from time to time to increase the homogeneity of the compound. Conversely, in the case of TP geopolymers, the activating solutions were mixed and diluted with distilled water in a beaker and stirred until complete dissolution was reached.

Activating solutions were cooled at room temperature before their use. Lastly, depending on the viscosity of the activating solutions, it was decided to either spray or pour them with a plastic dropper onto the tray containing the dispersed MK powder. When the semi-wet powder reached the right consistency, it was poured inside a cylindrical stainless-steel mould ready to be pressed. The mould with a diameter of 36 mm and a height of 14 mm, was filled with about 9 g of geopolymeric semi-wet powder. Pressing was performed by applying a pressure of 20, 30, 40 and 50 MPa and 5 specimens were prepared for each mix design. After ejection from the mould, the pressed samples were laid on Teflon slabs and wrapped in plastic film for curing in sealed conditions. Samples were subjected to different curing conditions: room temperature (RT), 50 or 70 °C for 24 h.

Sample name	MK	ASS	RF	NaOH	NaOH 8M	Additional water	L/P ratio
OP_ASS_0.18	68.2	19.8	-	-	-	12.0	0.18
OP_ASS_0.23	65.9	19.1	-	-	-	15.0	0.23
TP_NaOH_0.18	71.0	-	-	13.4	-	15.6	0.18
TP_NaOH_0.23	68.4	-	-	12.9	-	18.7	0.23
TP_RF_0.25	70.1	-	13.4	-	-	15.6	0.25
TP_RF_NaOH_0.18	73.8	-	19.3	-	7.0	-	0.18
TP_RF_NaOH_0.23	68.6	-	25.1	-	6.3	-	0.23

Table 3: *Metakaolin-based geopolymer mixture composition in wt%.*

2.3. CHARACTERIZATION

After 7 days of curing, all samples were measured (diameter: 36 mm, thickness: 4.6 mm), weighed, and then placed in an oven at a temperature of 100 °C for complete drying. Dry mass was determined to measure geometric density and water absorption. All the testing was carried out on at least 3 samples for each mix design.

Geometric density is used to give a descriptive parameter of the level of sample compactness, and it is measured by the equation (1):

$$\rho_G = m_d/V\ [\mathrm{g/cm^3}] \qquad (1)$$

where m_d is the dry mass and V is the geometric volume of the samples.

The water absorption test was carried out on the same three samples used for density measurement. Samples were brought to saturation after being soaked for at least 24 h in distilled water. After 24 h, they were weighed and again placed in water until saturation was completed (weight variation lower than ±1%). Water absorption was calculated by equation (2):

$$\mathrm{WA\%} = \left(\frac{m_{ssd} - m_d}{m_d}\right) \times 100\ [\%] \qquad (2)$$

where m_{ssd} is the mass of the samples in saturated-surface-dry condition and m_d is the dry mass.

Weight stability of the samples after being soaked in water was determined by again drying the water-saturated samples for a further 24 h at 100 °C. Weight stability was determined with equation 3 where m_d is the initial dry mass, and m_{d2} is the dry mass obtained after water saturation.

$$\Delta W = \left(\frac{m_d - m_{d2}}{m_d}\right)\ [\%] \qquad (3)$$

Lastly, the microstructure of the sample surfaces was observed using the Olympus SZX10 stereoscopic microscope.

3. RESULTS AND DISCUSSION

Figures 1 – 3 report all the results in terms of geometric density, water absorption and weight stability after water saturation of all the pressed samples cured at room temperature (RT), 50 and 70 °C for 24h, respectively.

The L/P ratio is a fundamental parameter for the processability of the semi-wet powder, especially when liquid activators are used (e.g., TP_RF_NaOH_0.18/0.23 mixes). In particular, an L/P ratio of 0.23 for the blend of NaOH and RF results in an excess of humidity in the mix, making it unsuitable for pressing. This means that this mix design is not optimized for this specific forming techniques. The most promising mixes have been obtained when a blend of NaOH and RF solutions was applied considering the L/P ratio equal to 0.18 (TP_RF_NaOH_0.18) and when only RF is applied (TP_RF_0.25). For this latter sample, a higher L/P ratio (equal to 0.25) is necessary due to the high viscosity of RF. In general, when RF has been used as an activator, the relevant samples show for all the tested conditions the best results in terms of microstructure, therefore its presence is fundamental for producing the most optimized pressed geopolymers.

Regarding curing temperatures, 50 °C is the temperature that mostly optimizes the investigated properties of the final products. In particular, samples cured at 50 °C exhibit slightly higher geometric density and consequently lower water absorption and mass loss after water saturation. This means that 50 °C as curing temperature promotes a higher geopolymerization degree with a more efficient consolidation process.

Results for samples based on ASS, exhibit contradictory outcomes. Regardless of the selected curing temperature, the OP series exhibit the highest density values and consequently the lowest water absorption values. However, the reported plots show how the mixes OP_ASS_0.18 and OP_ASS_0.23 are highly unstable in terms of weight stability. This is due to the fact that ASS is unable to completely dissolve during geopolymerization and thus its reaction with metakaolin is incomplete. Unreacted ASS remains as floccules/flakes in sample bulk and surfaces. When these samples are tested for weight stability, the mass loss determined after water immersion is strongly influenced by unreacted ASS that is finally dissolved during the test. Moreover, OP geopolymers exhibit closed porosity as reported in Figure 4 for samples OP_ASS_0.18 and OP_ASS_0.23.

Microstructural observation of the surface of the samples pressed at 20 MPa and cured at 50 °C for 24h is reported in Figure 4. The difference between the surfaces of the OP samples and that of the TP samples is evident. In the first case, pores left by the dissolution of the ASS, following the water absorption test, are clearly visible, while in the TP samples the microstructure appears more homogenous and compact.

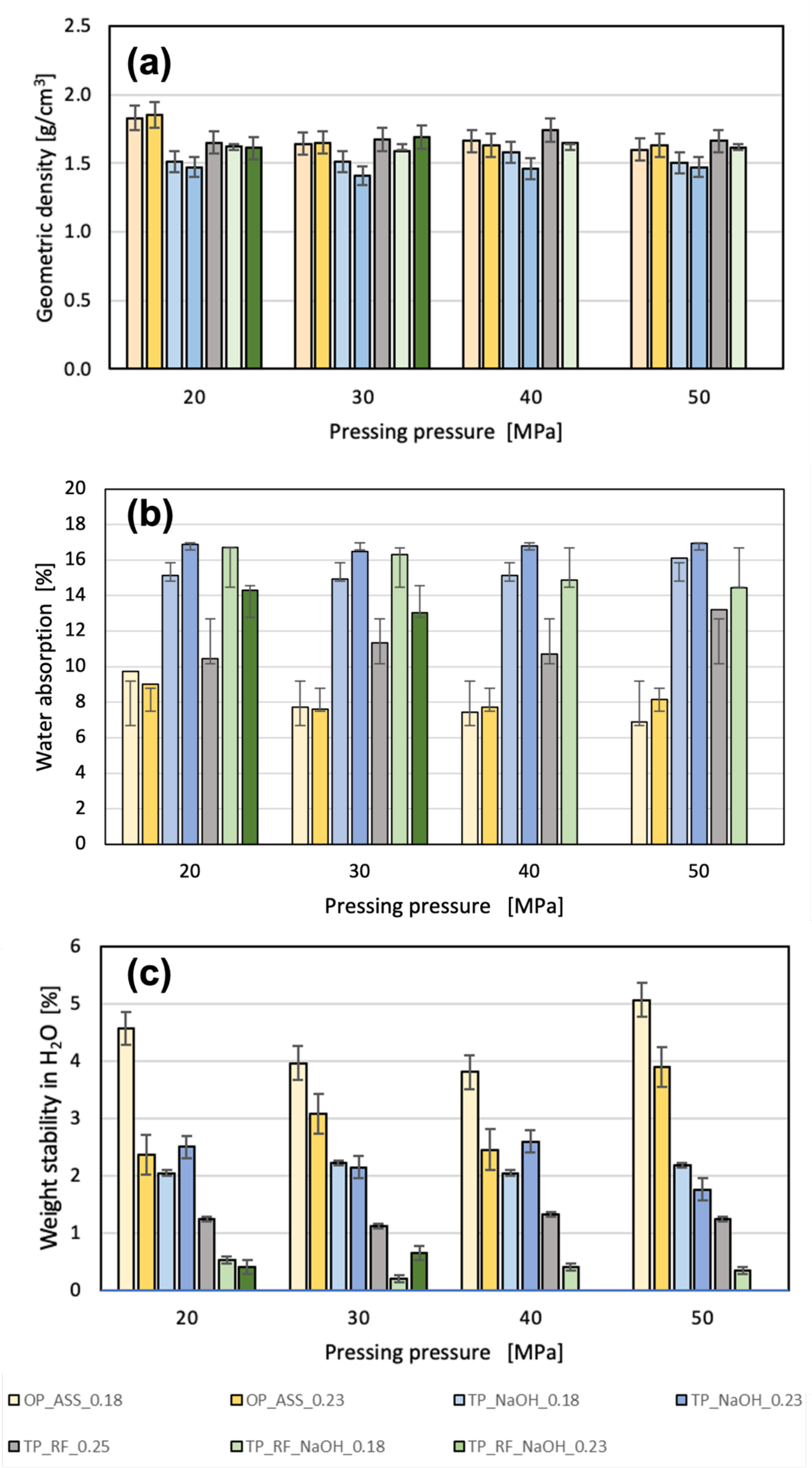

Figure 1: *Geometric density (a), water absorption (b) and weight loss (c) of all the samples cured at room temperature for 7 days.*

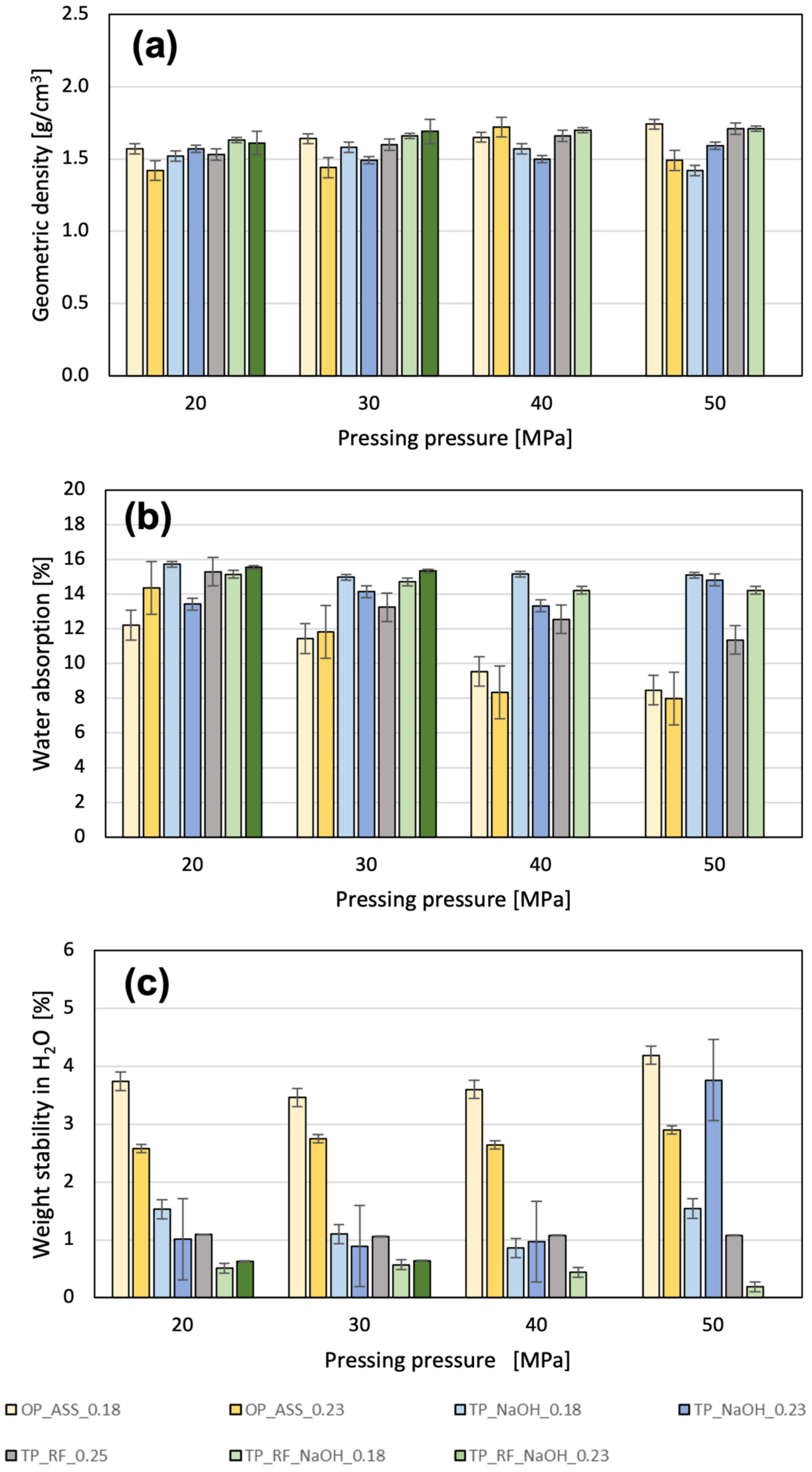

***Figure 2**: Geometric density(a), water absorption (b) and weight loss (c) of all the samples cured at 50 °C for 24h.*

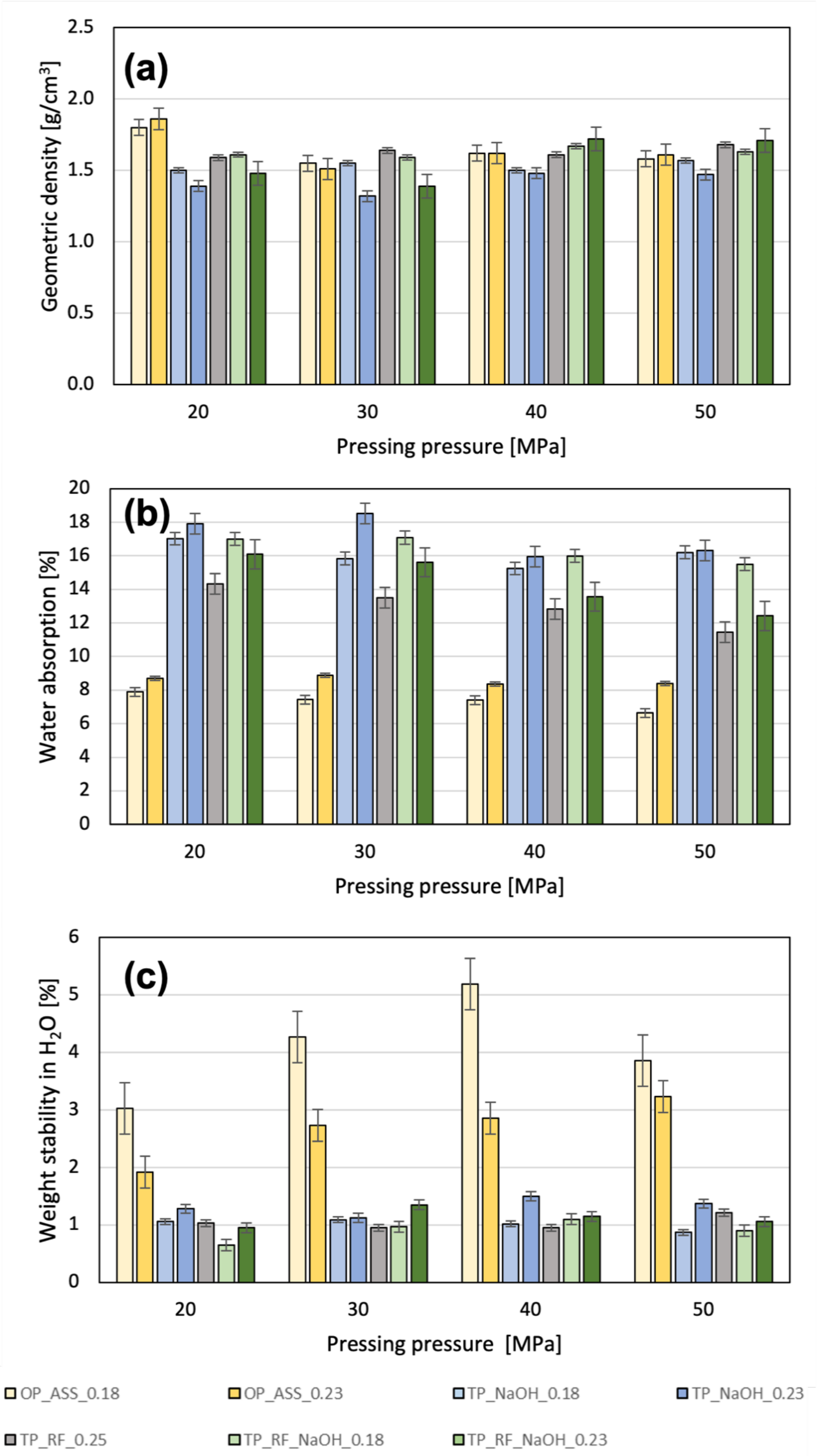

Figure 3: *Geometric density(a), water absorption (b) and weight loss (c) of all the samples cured at 70 °C for 24h.*

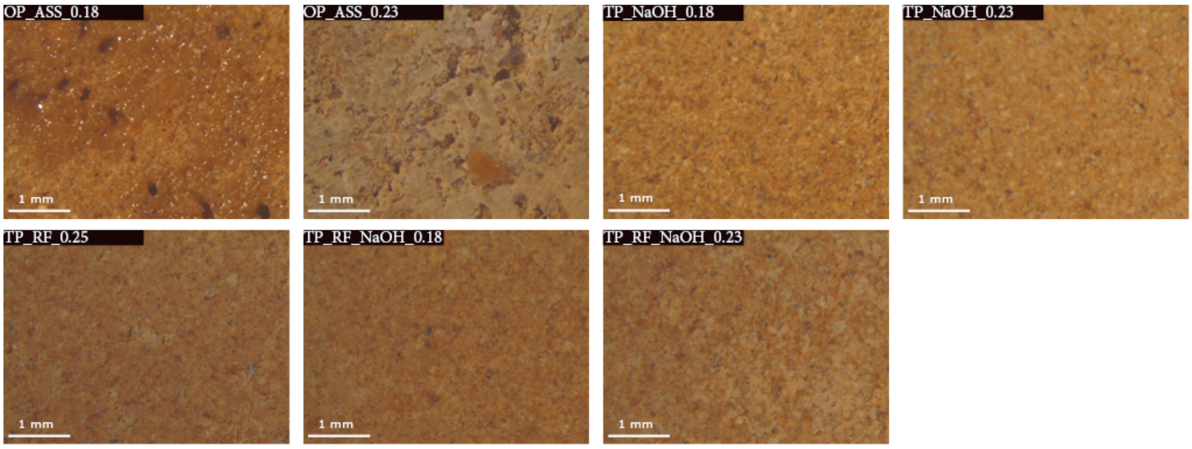

Figure 4: *Microstructural observations performed by optical microscopy of all the geopolymers pressed at 20 MPa and cured at 50 °C.*

4. CONCLUSIONS

This study represents a preliminary data set on the mix design optimization for the application of pressing as a forming method to produce metakaolin-based geopolymers.

The influence of process parameters (different types and concentrations of alkaline solutions, different liquid-to-precursor (L/P) ratios, different pressing pressure values and curing conditions) have been examined.

The main conclusions can be summarized as follows:

- The L/P parameter is of fundamental importance in the optimization of the mix design for pressing as a forming technique. Samples with L/P = 0.18 are the best for obtaining weight stability, high density and low water absorption value;
- The best curing temperature is 50 °C;
- The activator that seems most promising to produce pressed geopolymeric samples with the best performance features is liquid sodium silicate solution.

Further investigations are currently ongoing to analyse the mechanical performances of the most promising mix designs.

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