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**~~Viable and low cost alternative towards green liquor dregs~~
valorisation: In-depth investigation of the long-term strength and
leaching behaviour of inorganic polymer mortars containing green
liquor dregs**

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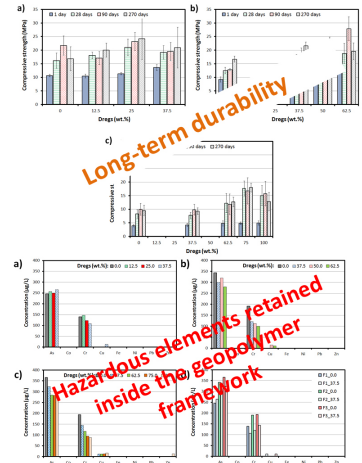
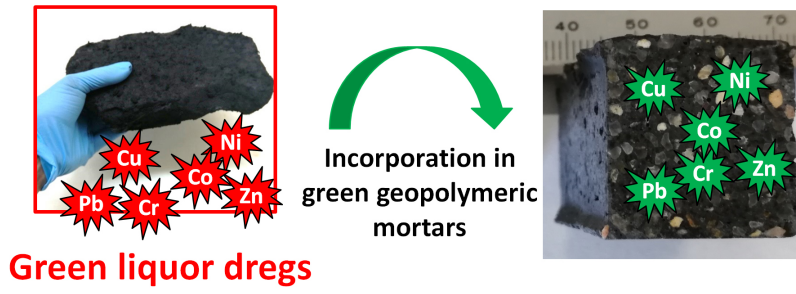
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Sustainable recycling strategy



ACCEPTED MANUSCRIPT

Abstract

Green liquor dregs are the most challenging waste stream coming from the pulp and paper industry. Despite tremendous efforts, there are not currently any viable recycling alternatives for this massively produced waste (2 Mt/year), which inevitably ends up in landfills. Urgent actions must be undertaken to tackle this. In this work, a substantial amount of dregs was incorporated into eco-friendly, waste-based inorganic polymer (geopolymer) mortars as fine filler. Then, and for the first time, the long-term strength performance (up to 270 days) and heavy metals leaching behaviour of the dregs-containing mortars was evaluated. The effect of the mixture composition and dregs incorporation content on the fresh- and hardened-state properties of the mortars was also studied. Dregs were found to increase the initial and final setting time of the slurries, thus extending the open time before their in-situ application. The use of dregs as fine filler effectively enhances the compressive strength of the mortars, and decreases their water absorption levels. These eco-friendly building materials showed excellent long-term performance, as their strength continuously increases up to the 270th day (after mixture), and no signs of efflorescence formation were detected. Moreover, the heavy metals leaching levels of the mortars were well below the contamination limits in soil, which demonstrates the feasibility of this recycling methodology.

Keywords: green liquor dregs; biomass fly ash; geopolymer; mechanical resistance; long-term performance; leaching.

1. Introduction

The pulp and paper sector is one of the most resource intensive, energy demanding and pollutant emitting manufacturing industries (Corcelli *et al.*, 2018; Sun *et al.*, 2018), and

production is still expected to increase in coming years (Corcelli *et al.*, 2018). In fact, recent data show that worldwide paper and board production has increased around 1.5% in 2017, reaching 420 Mt (CEPI, 2017), of which ~22% was produced in Europe. In 2016, the contribution of this industry to the EU economy reached €81 billion, while the number of paper and pulp employees was estimated to be 175,000 people (CEPI, 2016). These values show the huge economic impact of this industry in the EU context. On the other hand, this activity also generates a vast amount of wastes - 11 Mt/year in Europe (Monte *et al.*, 2009). Among the residues produced (e.g. biomass ash (Modolo *et al.*, 2018; Modolo *et al.*, 2015), grits (Saeli *et al.*, 2018), primary and biological sludge, lime mud (Modolo *et al.*, 2014)), green liquor dregs (Novais *et al.*, 2018c) are a major inorganic stream, for which there is not currently any viable and sustainable recycling methodology. Green liquor dregs are undissolved smelts from chemical recovery boilers mixed with weak white liquor created in kraft pulp production. This waste, whose global production was projected to reach 2 Mt in 2016 (Novais *et al.*, 2018c), is usually disposed of in landfills (Kinnarinen *et al.*, 2016), which raises serious environmental concerns due to the presence of hazardous metals such as Co, Cr, Cu, Cd, Ni, Pb and Zn in their chemical composition (Golmaei *et al.*, 2018a). However, it should be highlighted that some of these metals (e.g. Cu and Zn) are also known as nutrients in the soil (Pöykiö *et al.*, 2016).

Dregs are generated in the chemical recovery cycle employed to recover sodium hydroxide and sodium sulphide, this waste being formed in the dissolving tank where the weak white liquor and smelt from the chemical recovery boiler are mixed together. Recently, the possibility of extracting heavy metals from the dregs has been exploited using cyclones (Golmaei *et al.*, 2018a) or chelating agents (Golmaei *et al.*, 2018b), in order to allow their use as fertilizer or as a soil amendment. Despite the interesting

results of these investigations, the disposal of the highly-heavy metals concentrated dregs fraction when using cyclones (Golmaei *et al.*, 2018a) further intensifies their recycling challenge, while the use of chelating agents is complex (Golmaei *et al.*, 2018b), requiring the purification of the generated supernatant phase containing metal-chelating complexes, which could not only contaminate water resources, but would add cost to the papermaking process. Our strategy is less complex, allowing the direct use of this waste, without the need to perform expensive chemical treatments, in the production of eco-friendly and low cost building materials.

The incorporation of wastes into building materials is an excellent recycling methodology, decreasing the consumption of virgin raw materials, while at the same time preventing the landfill disposal of these wastes. However, the incorporation of some residues is particularly challenging, this being the case of the green liquor dregs. Dregs present very high pH (> 10) and alkaline and alkaline-earth oxide contents, which hampers their incorporation in cement or concrete. These features explain the reason why this massively produced waste remains yet unexplored. Despite this, some authors have attempted to use dregs as cement replacement in concretes and mortars (Martínez-Lage *et al.*, 2016), or as aggregate in road pavement construction (Modolo *et al.*, 2010; Pasandín *et al.*, 2016). Nevertheless, the properties of such dregs-containing materials were not suitable for the envisioned applications (hot-mix asphalt (Pasandín *et al.*, 2016) and concretes (Martínez-Lage *et al.*, 2016)). One exciting possibility could be the incorporation of dregs in the production of inorganic polymers (geopolymers), which are binder systems widely acknowledged as being an environmentally friendlier alternative to conventional Portland cement (Turner and Collins, 2013). The proof-of-concept has been recently demonstrated by the authors (Novais *et al.*, 2018c). This study showed the feasibility of using *as-received* dregs as fine fillers in the production

of a sustainable binder, without compromising the performance of the mortars. Indeed, an increase in both the flexural (up to 71%) and compressive strength (up to 34%) was achieved for the dregs-containing mortars in comparison with the reference. Nevertheless, the leaching behaviour and the long-term strength performance of the mortars was not considered.

In this work, and for the first time, the long-term strength performance and leaching behaviour of geopolymer mortars containing significant amounts of dregs was evaluated. This investigation is of the utmost importance to demonstrate that the hazardous elements present in the dregs composition are effectively retained inside the geopolymeric mortars and, therefore, that their incorporation in these mortars is a safer and environmentally better management strategy in comparison with their landfill disposal. This investigation represents a significant, and essential, step forward in comparison with the only previous study reported to date (Novais *et al.*, 2018c), reducing the existing knowledge gap regarding the long-term strength performance and leaching behaviour of these innovative materials. Moreover, the maximum dregs incorporation content was increased by a factor of 4, and the specimens were cured at ambient temperature (23 °C) instead of using 40 °C (Novais *et al.*, 2018c), this being a more sustainable and cost effective strategy. The influence of the mixture composition and dregs content on the fresh-state (workability and setting time of the mortars) and hardened-state properties (compressive strength, water absorption and heavy metals leaching) was also considered.

2. Experimental Conditions

2.1. Materials

A mixture of biomass fly ash waste (70 wt.%) and metakaolin (30 wt.%) was employed as a source of reactive silica and alumina in the geopolymer synthesis. The fly ash, produced by a Portuguese pulp mill, is a silica rich material; nevertheless, due to its low alumina content (13.5 wt.%; see Fig. 1), the use of minor amounts of an alumina source (in this case metakaolin) to attain proper molar ratios in the compositions is required. The biomass fly ash was collected from the bubbling fluidised combustor of the paper pulp mill, which burns wood biomass, mainly Eucalyptus forest waste. Metakaolin was supplied by Univar (Argical™ M1200S).

Green liquor dregs with lime mud precoat were supplied by the same pulp and paper plant (54 wt. % solids). This waste was used, without any chemical pre-treatment, as fine filler in the production of geopolymeric mortars. Prior to their addition to the geopolymer slurry, the dregs were dried, crushed in a mortar and sieved, in line with previous work from the authors (Novais *et al.*, 2018c). The particle size distribution of the crushed dregs is shown in Fig. 2. As observed, around 90 vol.% of the particles have sizes below 16 μm , the mean particle size being $\sim 6 \mu\text{m}$.

Two different activators were prepared using a mixture of sodium silicate ($\text{SiO}_2 = 28.77$ wt.% and $\text{Na}_2\text{O} = 9.13$ wt.%; Quimialmel) and 10 M sodium hydroxide solution (ACS reagent, 97%; Sigma Aldrich).

Sand with a particle size between 0.125 and 2 mm was used as aggregate in the production of the geopolymeric mortars.

2.2. Mortars preparation

In this work, a total of thirteen formulations were prepared to evaluate the influence of the dregs incorporation amount and mixture composition on the geopolymeric mortar properties. The mixture composition of the prepared formulations is shown in Table 1. Considering preliminary work, in which the influence of the amount of fly ash to metakaolin, and sodium silicate to sodium hydroxide, on the geopolymer mechanical performance were studied, a reference composition (coded as F1_0.0 in Table 1) was established. Then, various amounts of dregs (up to 37.5 wt.%) were added to this composition to evaluate the influence of dregs incorporation content on the fresh- and hardened-state properties of the mortars. In this investigation, dregs were used as additives considering the binder (fly ash and metakaolin) mass. For example, in composition F1_37.5, 37.5 g of dregs were added to the mixture per 100 g of binder. Additionally, two other reference compositions (without dregs), coded as F2_0.0 and F3_0.0 (with differing amounts of sodium silicate and water), and seven other dregs-containing formulations, were prepared to evaluate the influence of mixture design on the maximum dregs incorporation content (see Table 1). In this regard, the maximum amount of dregs in the three reference compositions was limited by the spread on a flow table shown by the slurries (see discussion in *section 3.2.1*).

The geopolymeric paste preparation is described in detail in Ref. (Novais *et al.*, 2018a; Novais *et al.*, 2016c). Briefly, it involves three steps: i) homogenisation of the alkaline activators; ii) mixing of the aluminosilicate precursors (fly ash and metakaolin); and iii) mixture of the alkaline activators with the aluminosilicate precursors for 10 min. Then, the aggregate (sand), fine filler (dregs) and water (depending on the compositions) were added to the slurry and mixed for 2 min. Finally, the blend was poured to steel moulds, covered with a plastic film, and cured for 24 h at room temperature (23 °C; 65% relative

humidity). After this initial curing period, the specimens were demoulded and cured at room temperature until their mechanical characterisation.

2.3. Materials characterisation

The mineralogical composition of the mortars was evaluated by X-ray powder diffraction (XRD) (Rigaku Geigerflex D/mx-Series Instrument; Cu K_{α} radiation, 10–80° 2 θ , 0.02° 2 θ step-scan and 10 s/step). PANalytical X'Pert HighScore Plus software was then used to identify the different crystalline phases.

The morphology of the waste-based mortars was evaluated using optical analysis (Leica EZ4HD microscope), and the microstructure of the mortars was studied using scanning electron microscopy (SEM - Hitachi S4100).

Flow table tests were performed after mixing according to EN 1015-3 (2007) in order to evaluate the influence of the dregs content and mixture composition on the workability of the mortars.

The initial and final setting times of the pastes were determined using the Vicat needle according to NP EN 196-3. The Vicat needle measurements were conducted in a semi-conical paste over time (10 min intervals) at room conditions (23 \pm 1 °C and 65% RH). The fresh paste was cast into to a semi-conical mould, its surface evened and the needle positioned above its surface. To accurately determine small penetrations, a needle with a ring attachment was used, the final setting time being established when no visible mark was left by the ring, corresponding to a needle penetration smaller than 0.5 mm.

The compressive strength of the specimens cured for 1, 28, 90 and 270 days was measured, following the standard EN 1015-11:1999 but using smaller specimens (2 cm x 2 cm x 8 cm), at 0.5 mm/min using a Universal Testing Machine (Shimadzu, model

AG-25 TA). The water absorption of the mortars was evaluated on samples cured for 28 days. Three samples per batch were used, and the arithmetic mean value reported.

In order to evaluate the potential heavy metal leaching from the mortars, cuboid samples (2 cm x 2 cm x 8 cm), cured for 28 days, were immersed in 100 ml of distilled water at room temperature for 24 h. Afterwards, the water solution was analysed by inductively coupled plasma - optical emission spectrometry (ICP-OES, Horiba Jobin Yvon, Activa M) for As, Co, Cr, Cu, Fe, Ni, Pb and Zn. These elements were selected considering the wastes (biomass fly ash and dregs) chemical composition (see Fig. 1), determined by X-ray fluorescence (Philips X'Pert PRO MPD spectrometer). The leaching tests were intentionally performed under static conditions, and with monolithic samples, in order to mimic the materials' environment when in use (civil engineering applications). Leaching in acidic conditions, or the use of powdered samples, was not considered here, since these conditions are expected to give an overestimation of the heavy metals leaching (Izquierdo *et al.*, 2009). The use of monolithic samples (Bobirică *et al.*, 2018; Zhang *et al.*, 2016), static conditions (Ahmari *et al.*, 2013; Bobirică *et al.*, 2018; Zhang *et al.*, 2016) and water as immersion medium (Bobirică *et al.*, 2018; Zhang *et al.*, 2016) for evaluating geopolymer leaching potentials have been previously reported.

3. Results and discussion

3.1. Raw materials chemical composition

Fig. 1 presents the wastes (biomass fly ash and dregs) chemical composition determined by XRF, the most abundant oxides shown in Fig. 1a. For comparison, the metakaolin chemical composition was also included in the figure. Fly ash is a silica rich material (34.0 wt.%), also containing significant amounts of alumina (13.5 wt.%), which suggested the possibility of it being used as raw material in the production of inorganic

polymers that was recently demonstrated in the literature (Novais *et al.*, 2018a; Novais *et al.*, 2016c). Nevertheless, the use of an additional alumina source, in this case metakaolin, is necessary to ensure proper molar ratios in the compositions. Dregs are mainly composed of Na₂O (23.8 wt.%), CaO (15.2 wt.%), SO₃ (10.5 wt.%) and MgO (8.1 wt.%). However, soluble elements such as Na and K may be easily removed by a washing step, and in that case CaO would be the main component (as oxides). Besides these main oxides, dregs also contain significant amounts of heavy metals (see Fig. 1b) such as, copper, zinc, nickel, chromium, lead and cobalt, which raise environmental concerns regarding their incorporation in common applications (e.g. cement), hindering the recycling of the wastes. The presence of Cd in dregs chemical compositions has been reported by other authors (Golmaei *et al.*, 2018b; Golmaei *et al.*, 2017). However, this hazardous heavy metal was not detected in this study, or its concentration was below the XRF detection limit. In any case, the dregs heavy metals content should not be underestimated, and precaution is mandatory to ensure that benign strategies for the waste recycling are implemented.

The fly ashes also contain some heavy metals in their composition, but at a significantly lower amount (see Fig. 1b).

3.2. Mortars fresh-state characterisation

3.2.1. Workability tests

The incorporation of dregs into the geopolymer mortars is known to negatively affect the workability (Novais *et al.*, 2018c), this being the reason for the limited maximum dosage previously reported by the authors (25 wt.%). In this work, the mixture composition was tailored to allow the incorporation of a higher amount of dregs in the formulations. The maximum amount was defined by using the spread on a flow test

table. Fig. 3 presents images of the flow table after the tests, while the spread on table values are shown in Fig. 4. These figures clearly demonstrate the huge impact of both the mixture design and the dregs amount on the spread values. Amongst the three compositions prepared without dregs (see top images in Fig. 3), F3_0.0 showed the highest spread on the table (280 mm), followed by composition F2_0.0 (243 mm) and F1_0.0 (225 mm). This behaviour can be explained by the higher liquid to solid ratio of composition F3_0.0 (see Table 1). The addition of water, or the use of a higher amount of sodium silicate (containing 62.1 wt.% of H₂O), was found to decrease the viscosity of the pastes, and increase the flow table value by ~ 24 % in comparison with composition F1_0.0. These findings are in line with other investigations, which have shown the possibility of controlling the viscosity of the slurries by using water (Novais *et al.*, 2016a) and by the alkaline activators content (Fang *et al.*, 2018). Not surprisingly, the maximum possible amount of dregs incorporated into these compositions strongly differs, ranging between 37.5 and 100 wt.%. The latter corresponds to a fourfold increase in comparison with the previous study addressing the use of dregs in geopolymeric mortars (Novais *et al.*, 2018c). This is extremely relevant, as it may prevent the landfill disposal of a very significant amount of dregs. The observed decrease in the workability of the mortars when the dregs content in the composition rises is attributed to the increase in the solid content (dregs were used as additives).

The spread on table values of the studied compositions ranged between 280 and 137.5 mm, in line with those reported for lithomarge-based geopolymeric mortars (between 95.5 and 206 mm) (Kwasny *et al.*, 2018) and for fly ash- GGBS-based geopolymer mortar (between 87 and 189 mm) (Shang *et al.*, 2018). In this work, and considering the significant decrease in the workability of the mortars (up to 51 %) in comparison with the reference compositions (prepared without dregs), higher contents were not

considered. Nevertheless, optimised mixture design may allow the use of higher dregs incorporation contents into the compositions.

3.2.2. Setting time

Fig. 5a presents the Vicat needle penetration depth as a function of time for the geopolymeric slurries prepared without dregs (F1_0.0, F2_0.0 and F3_0.0). Despite the different mixture compositions (see details in Table 1), the initial setting time is similar for all of these formulations, but the final setting time ranged from 180 min to 220 min, respectively, for compositions F1_0.0 and F3_0.00. An increase in the soluble silica content is expected to promote faster geopolymerisation (Karakoç *et al.*, 2014; Lee *et al.*, 2016), and thus shorter setting. However, compositions F2_0.0 and F3_0.0 showed higher setting than their lower sodium silicate containing counterpart (F1_0.0). These results suggest that in these compositions the binder to activator ratio (B:A), rather than the sodium silicate content, is the prevailing factor controlling the setting of the slurries. One possible explanation for this interesting behaviour is the amount of calcium in the compositions: when the B:A ratio decreases, the calcium content will drop, thus explaining the longer setting observed for compositions F2_0.0 and F3_0.0. The role of calcium in geopolymer setting behaviour has been previously reported for metakaolin-based geopolymers (Chen *et al.*, 2018). The addition of calcium was found to enhance both the rate and the extent of metakaolin dissolution, which caused faster setting (Chen *et al.*, 2018).

Fig. 5b illustrates the influence of the incorporation of dregs on the setting time of the mixtures. As depicted, dregs strongly delay both the initial and final setting of the compositions, the final setting time varying between 300 and 460 min. For example, a twofold increase was observed when adding 37.5 wt.% dregs in comparison with the

reference composition (F3_0.00). The reason for this major variation in the setting of the slurries suggests that the incorporation of the dregs modifies the geopolymerisation kinetics. Dregs act as filler - this means that they are not reactive, and do not contribute towards geopolymerisation (Novais *et al.*, 2018c). During mixing, dregs may partially or totally coat some fly ash and metakaolin particles, physically disrupting their reaction with the alkaline activators, thus extending the setting. A similar phenomenon has been reported for latex-containing geopolymer mortar (Lee *et al.*, 2016). The relationship between setting time and geopolymerisation kinetics has been studied in other investigations (Karakoç *et al.*, 2014; Temuujin *et al.*, 2009), shorter setting being connected with faster geopolymerisation. Temuujin *et al.* (2009) associated faster setting to the greater and more rapid dissolution of the milled fly ash particles that led to improved polymerisation and hardening of the gel phase, while Novais *et al.* (2018a) observed shorter setting when adding powdered aluminium to the compositions, possibly due to the increase in the quantity of soluble aluminate ions.

In any case, the longer setting times observed for the dregs-containing mortars increases the open time of the slurries before in-situ application.

Once again, a faster setting was observed for composition F1_37.5, while F2_37.5 and F3_37.5 showed slower setting times of 400 min and 460 min, respectively. The prolonged setting of composition F3_37.5 in comparison with F2_37.5 is attributed to the higher water content of the former (see details in Table 1). As stated above, a higher water content favours the dissolution of the raw materials, but is detrimental to polycondensation reactions. Indeed, Fig. 5b shows that the initial setting occurs earlier, suggesting a higher geopolymerisation rate (precursors dissolution) at this stage in comparison with F2_37.5. Nevertheless, after a few hours (~5 h) the geopolymerisation kinetics of these compositions changes, and suggests a weaker/slower polycondensation

(water releasing reaction) for F3_37.5 due to its higher initial water content. In line with the expected slower polycondensation rate, the final setting of this composition is achieved 60 min later than that observed for F2_37.5. These results show the possibility of tailoring the setting time of the mortars by the addition of dregs and by the water and activators content, which could be an advantage not only in geopolymer production, but most importantly for the transportation and storage of mixtures.

3.3. Mortars hardened-state characterisation

3.3.1. XRD and optical microscopy characterisation

The XRD characterisation of the biomass fly ash and the dregs was already described in detail in Ref. (Novais *et al.*, 2018c). Briefly, the fly ash contains quartz (SiO_2), calcite (CaCO_3) and illite ($((\text{K},\text{H}_{30})\text{Al}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O})$), while the most abundant crystalline phase observed in the XRD pattern of the dregs is pirssonite (a sodium calcium carbonate), along with minor amounts of calcite and magnesium oxide (Novais *et al.*, 2018c).

Fig. 6 presents the XRD patterns of some of the prepared mortars as an example. Quartz, coming from the aggregate (sand), is the dominant crystalline phase in all the XRD patterns. Nevertheless, in the dregs-containing mortars the presence of pirssonite is observed. This suggests that pirssonite is not involved in the geopolymerisation process, in line with our previous findings (Novais *et al.*, 2018c).

One common problem in the production of geopolymers is efflorescence formation (Xue *et al.*, 2018; Zhang *et al.*, 2018) due to the presence of unreacted alkalis within the geopolymer framework. When the geopolymers are exposed to wet conditions, the free alkalis may migrate to the surface of the specimens, reacting with carbon dioxide and giving rise to white salt deposits. This phenomenon hinders the widespread applications

of geopolymers, even if it is mainly an aesthetic problem rather than one that compromises their performance (Bai and Colombo, 2018). Although the dregs contain a substantial amount of sodium oxide (23.8 wt.%), none of the prepared mortars showed the presence of efflorescence even after water immersion followed by ambient drying, as clearly demonstrated by the optical microscopy and SEM micrographs of the mortar containing the highest quantity of dregs (F3_100.0), shown in Fig. 7 (the reference composition was also included for comparison). Optical micrographs of selected compositions are also provided in Fig. 8 to further demonstrate this. The absence of efflorescence in the compositions suggests that these mortars will present good long-term stability properties (this will be further discussed in *section 3.3.2*).

3.3.2. Compressive strength and water absorption measurements

The mixture composition (water and alkaline activators content), and the dregs incorporation content, are expected to promote changes in the compressive strength of the mortars. The differences between the compositions are illustrated in Fig. 9. For composition F1 (containing lower alkaline activator content and prepared without adding water), the incorporation of 25 wt.% dregs (F1_25.0) significantly enhances the compressive strength of the mortars over all time periods, leading to the highest value for this mortar of 21.0 MPa after 28 days (an increase of 30% over the 16.2 MPa of the reference F1). The highest dregs-containing mortar (F1_37.5) also reached a value of 19.2 MPa after 28 days (an increase of ~ 19 % more than the reference). These results confirm that the dregs are effectively acting as filler. This remark is corroborated by the water absorption of the mortars, shown in Fig. 10. As observed, the water absorption drops as the dregs content rises. For example, in composition F1_25.0 and F1_37.5 the water absorption reaches 9.3% and 8.7% water, respectively, while the dregs-free

mortar shows 10.1% (F1_0.0), suggesting that dregs effectively reduce the open porosity in the mortars.

The compressive strength of the dregs-containing composition increased to 24.2 MPa and 20.9 MPa after 270 days for F1_25.0 and F1_37.5, respectively, further enhancing their mechanical strength gains to ~44% and ~ 24 % in comparison with the reference F1_0.0. The latter also demonstrates the long-term strength performance of the mortars, as their strength still increases 9 months after synthesis.

The high standard deviation, observed for the dregs-containing compositions, associated with the limited number of tested specimens (three), hinders the definition of the optimum dregs content in order to reach the highest mechanical performance. This topic will be evaluated in future work. Nevertheless, results suggest that the use of higher dregs content without negatively affecting the mechanical performance of the specimens is feasible. This is particularly relevant when considering the current, and distressing, waste management strategy (landfill disposal) for these wastes.

As discussed in *section 3.2.1*, by changing the design/mixture of the formulations it was possible to enhance the amount of fine filler (dregs) present in the mixtures. In the compositions based on mortar F2 (see details in Table 1), the addition of dregs was also found to enhance their compressive strength, with the greatest addition giving the best results this time. At the 28th day, the compressive strength of the composition containing 62.5 wt.% dregs (F2_62.5) reached 18.8 MPa, while the reference (F2_0.0) presented only 12.5 MPa, this being approximately 50% lower. Once again, lower water absorption values as observed for the dregs-containing mortars, a drop from 10.6% (F2_0.0) to 6.8% (F2_62.5) being observed.

After 270 days in both compositions the strength has increased, but the difference between them was reduced to 17%, as values reached 19.6 and 16.7 MPa, respectively,

for the 62.5 wt.% dregs-containing and the reference mortar. Compositions F2_50.0 and F2_67.5 were the exceptions to the reported strength enhancement with ageing. In these compositions, a peak in compressive strength was observed after 90 days (27.9 MPa in the case of F2_62.5), and a decrease from the 90th to the 270th days was observed. In composition F2_50.0 the slight drop in strength from 19.1 to 18.0 MPa is statistically irrelevant, particularly considering the higher standard deviation of the results measured at the 270th day. The latter is attributed to the limited number of specimens tested, suggesting similar strength for both curing times. As for composition F2_67.5, the significant drop in strength cannot be exclusively attributed to the limited number of tested specimens, and may suggest a modification of the geopolymerisation products with ageing (Novais *et al.*, 2016b). Nevertheless, this unexpected behaviour conflicts with that observed for the other dregs-containing compositions.

Fig. 9c shows that the addition of water to the mixture is detrimental to the strength development of the mortars, with the reference composition (F3_0.0) reaching only 3.9 MPa 24 h after mixing, which is around 58% lower than that observed for composition F2_0.0 (prepared without adding water). As expected, the strength of the mortars increased with time, but only reaching 9.5 MPa after 270 days, which is still significantly lower (~43%) than that observed for composition F2_0.0 (16.7 MPa). The negative effect of water addition on the strength of the specimens development is clearly visible when comparing the compositions containing 37.5 wt.% dregs, the strength of composition F3_37.5 being 2.6 times lower than its non-water-containing counterpart (F2_37.5) after 24 h, with values of 4.2 and 10.9 MPa, respectively. These results are in line with the abovementioned setting time behaviour for these compositions, F3_0.0 reaching the final setting at longer times in comparison with F2_0.0. Despite this smaller gain in strength, the lower viscosity of the slurries allowed

the incorporation of higher amount of dregs, up to 100 wt.%. This was the main focus of this research, and is extremely relevant considering that the current management strategy for this waste is landfill disposal, which is environmentally and economically unsustainable. The composition with 75 wt.% dregs (F3_75.0) achieved 18.0 MPa after 270 days, close to the value reached with a lower addition of only 62.5 wt.% of this waste for F2_62.5. The composition containing the highest amount of dregs (F3_100.0) reached 12.8 MPa after 270 days, this being 35% higher than its dregs-free counterpart (F3_0.0).

The differing mechanical performances of the mortars, depending on the dregs amount or on the initial mixture composition, shows the possibility of using these eco-friendly materials for structural applications. As shown, the workability of the mortars is strongly affected by the dregs amount, which can be tuned by changing the mixture composition. Nevertheless, the addition of water to the compositions, to allow the incorporation of higher dregs content (up to 100 wt.%), will negatively affect their mechanical performance. In any case, the compressive strengths achieved after 28 days of 19.2 MPa for F1_37.5, 18.8 MPa for F2_67.5 and 15.0 MPa for F3_100.0 classifies these mortars as M15 according to EN 998-2 (2010).

3.3.3. Leaching behaviour of the waste-based geopolymeric mortars

The specimens leaching behaviour in water medium was evaluated at the 28th day and the results are shown in Fig. 11. Results show that despite the significant heavy metals content of the dregs (see Fig. 1) (e.g. 0.31 wt.% Cu), these hazardous elements do not leach, or show poor leachability (below 400 µg/L), from the dregs-containing geopolymeric mortars. In fact, Pb, Ni, Fe and Co were not detected in any of the water solutions coming from the dregs-containing mortars. These results are in line with

previous investigations showing the possibility of using these innovative binders to efficiently encapsulate/retain hazardous species in their structure, namely heavy metals (Zhang *et al.*, 2008; Novais *et al.*, 2016d) and dyes (Novais *et al.*, 2019). Moreover, previous studies addressing the sequential leaching of heavy metals from dregs showed that most of the heavy metals are poorly soluble in water (ultrapure acidified water; pH = 4.8), their leachability ranging from 0.5 to 2 mg/kg (Nurmesniemi *et al.*, 2005), thus in line with our results.

Nevertheless, other toxic elements were found to leach, the amounts depending on the dregs content in the mortars, as well as the mixture design (water and alkaline activators content). Regardless of the composition, arsenic was the most leachable element, followed by chromium and copper. Dregs do not contain As in their chemical composition; however, this element is present in the biomass fly ashes used as the aluminosilicate source. Indeed, the highest leaching values were observed for the mortars without dregs (F1_0.0, F2_0.0 and F3_0.0), while the dregs-containing mortars presented generally lower As leaching, which may be attributed to the lower open porosity of these specimens (see Fig. 10). Likewise, the chromium leaching values were found to decrease as the dregs amount in the mortars rises.

The trend for copper leaching differs from that observed for arsenic and chromium. This element was not observed in the water solution coming from the dregs-free mortars, and its presence in the water solution of the dregs-containing mortars can be attributed to the dregs. Interestingly, the occurrence of Cu in the water solutions was found to be dependent not only on the dregs content, but also on the mixture composition. In the compositions prepared with the lowest alkaline activator and without using water (F1), Cu was detected only in the highest dregs-containing mortar (F1_37.5). As for F2 compositions, this element was detected only when the dregs content exceeded 50 wt.%

(F2_50.0). Interestingly, copper was detected in all the dregs-containing mortars when water was added to the mixture composition (F3). This demonstrates that the lower geopolymerisation extension of these compositions, demonstrated by their lower compressive strength in comparison with their non-water containing counterparts (F2), exerts a negative impact on the ability of the geopolymers to retain heavy metals in their framework. These results are in line in those reported by Li *et al.* (2018) for lead-zinc containing fly ash geopolymers. In their study, the heavy metals leaching was dominated by the amount of lead-zinc slag added to the compositions, with higher amounts leading to lower compressive strength and higher heavy metals leaching from the specimens. The use of geopolymers for heavy metals encapsulation/immobilisation is widely recognised as a promising alternative for hazardous waste management (Novais *et al.*, 2018b; Toniolo *et al.*, 2017). Heavy metals can be physically and/or chemically retained in the framework of the geopolymers. Moreover, the intrinsically alkaline nature of these binders further contributes to the inhibition of the heavy metals mobility (Izquierdo *et al.*, 2009), which explains the low leaching values observed for the dregs-containing mortars.

As for Zn, this element was only detected (14 $\mu\text{g/L}$) in the water solution coming from the highest dregs-containing mortar (F3_100.0), which may limit the maximum admissible amount of dregs in the formulations. Despite all this, the maximum concentrations of As (366 $\mu\text{g/L}$), Cr (195 $\mu\text{g/L}$) or Cu (18 $\mu\text{g/L}$) leached from the mortars are much smaller than the contamination limits in soils, which are 5.6 ppm, 212 ppm and 45 ppm, respectively (Zhang *et al.*, 2016). The leaching values are also significantly lower than those defined in the Universal Treatment Standards list (5 ppm for As, 4.3 ppm for Zn and 0.6 ppm for Cr) (Universal Treatment Standards, 2012),

which demonstrates the feasibility of using these eco-friendly materials in structural applications.

The solution pH is known to affect the heavy metals mobility. However, no attempt was made to control the expected increase in the pH of the solutions when immersing the geopolymers, due to the release of free alkalis from the geopolymer framework (Novais *et al.*, 2018b; Novais *et al.*, 2019), since this study aims to evaluate the heavy metals leaching under a realistic application scenario. A strong increase in the pH of all solutions was observed after the leaching tests. The final pH ranged between 9.4 and 9.7 for the reference compositions (without dregs), while slightly increasing (ranging from 9.6 to 10.0) for the dregs-containing mortars, which is attributed to the high alkalinity of this waste. The minor differences between the pH of the solutions observed for the reference compositions and the dregs-containing mortars are not expected to play a major role on the heavy metals mobility, which seems to be controlled by the compressive strength and open porosity of the specimens. Nevertheless, future work will evaluate the influence of the solutions pH in the heavy metals leaching.

To further characterise the specimens leaching behaviour, the heavy metals leaching ratio (amount of heavy metal leached from the sample (mg/g) divided by the pollutant initial concentration in the starting block (mg/g)) was determined, and results are shown in Fig. 12. Results show minor heavy metals leaching in comparison with the initial concentration of these pollutants in the specimens. Once again, the most leached element was As, a maximum of 1.09% being observed for the composition F3_0.0. The second most leached element was Cr (up to 0.16%); however, the leaching was roughly one order of magnitude lower than that observed for As. The leaching ratio of all other heavy metals was irrelevant, the maximum values being 0.00065% for Cu (F3_37.5) and 0.0048% for Zn (F3_100.0).

Despite these promising results, an exhaustive evaluation of the leaching behaviour of the specimens in more demanding conditions (e.g. acidic medium; longer immersion periods; powdered specimens) is required to fully support the findings obtained from water immersion tests. This will be considered in future work.

4. Conclusions

In this study, two industrial wastes generated on a massive scale globally were used to produce eco-friendly geopolymeric mortars, which may increase the sustainability of the construction sector, and simultaneously mitigate the paper and pulp industry carbon footprint.

Then, and for the first time, the long-term strength performance and the heavy metals leaching behaviour of dregs-containing waste-based geopolymer mortars was evaluated. Dregs affect both the fresh- and hardened properties of the mortars. Their addition to the geopolymeric slurries decreases the workability, while extending the initial and final setting time of the specimens. The compressive strength of the dregs-containing compositions was significantly higher than their dregs-free counterparts, since the dregs act as fine filler decreasing the mortars water absorption levels. The highest dregs-containing mortar (F3_100.0) reached 12.8 MPa compressive strength at the 270th day, which is 35% higher in comparison with the reference. In general, the compressive strength of the specimens increased with ageing, which suggests the formation of stable geopolymeric products. This remark is corroborated by absence of efflorescence in the specimens. Moreover, the leaching tests performed on the mortars demonstrated that the hazardous elements present in the dregs compositions (e.g. Pb, Ni, Co) are effectively retained inside the geopolymer framework. While minor concentrations of Cr (below 195 µg/L) and Cu (below 18 µg/L) were found to leach from the specimens, these

values are still well below the contamination limit in soils. These results allow the use of these eco-friendly waste-based materials for structural applications allowing the reuse of an impressive amount of dregs (up to 194 kg/ ton of geopolymeric mortar). This innovative strategy is a step forward to achieve a circular economy, and besides the obvious environmental advantages in comparison with the current management strategy for these wastes (landfill disposal), this approach (upcycling industrial waste streams to produce high added value products) may also attribute value to these unexplored residues.

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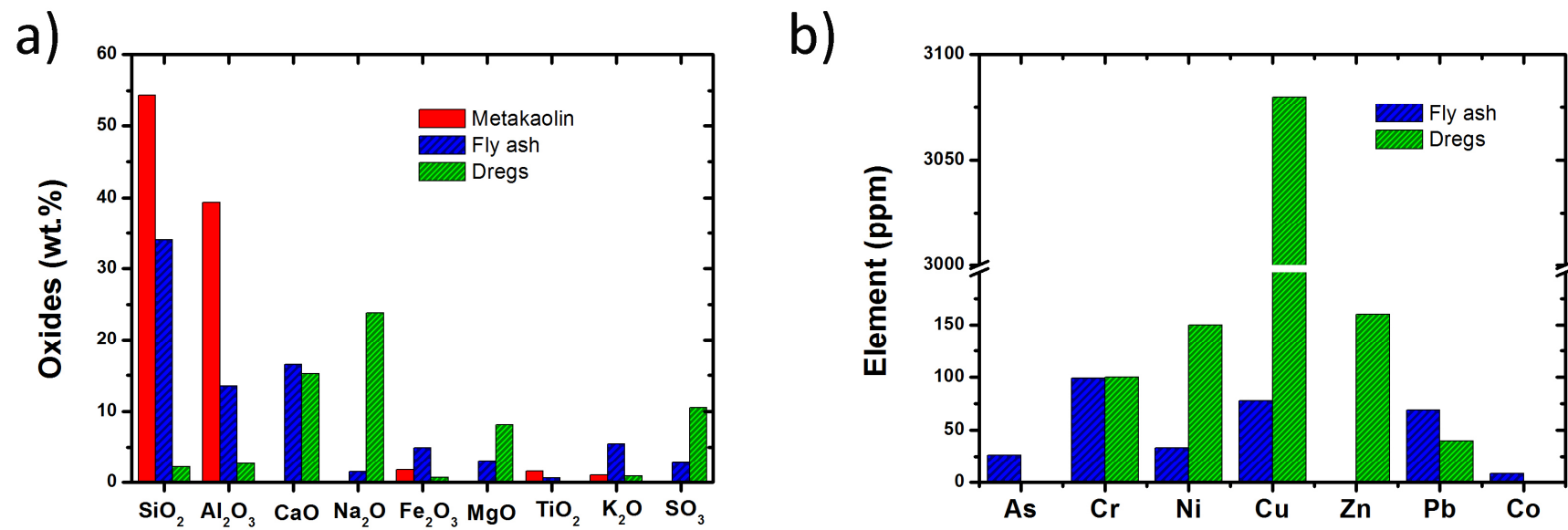


Fig. 1 Chemical composition of metakaolin, fly ash and dregs: a) most abundant oxides, and b) heavy metals.

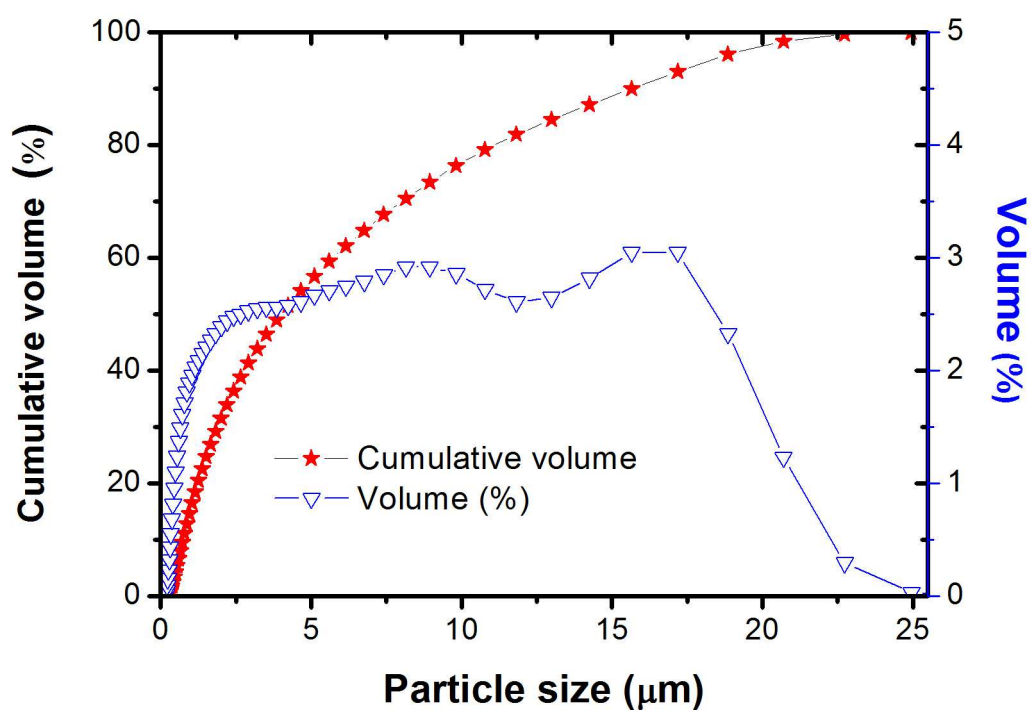


Fig. 2 Particle size distribution of the crushed green liquor dregs.

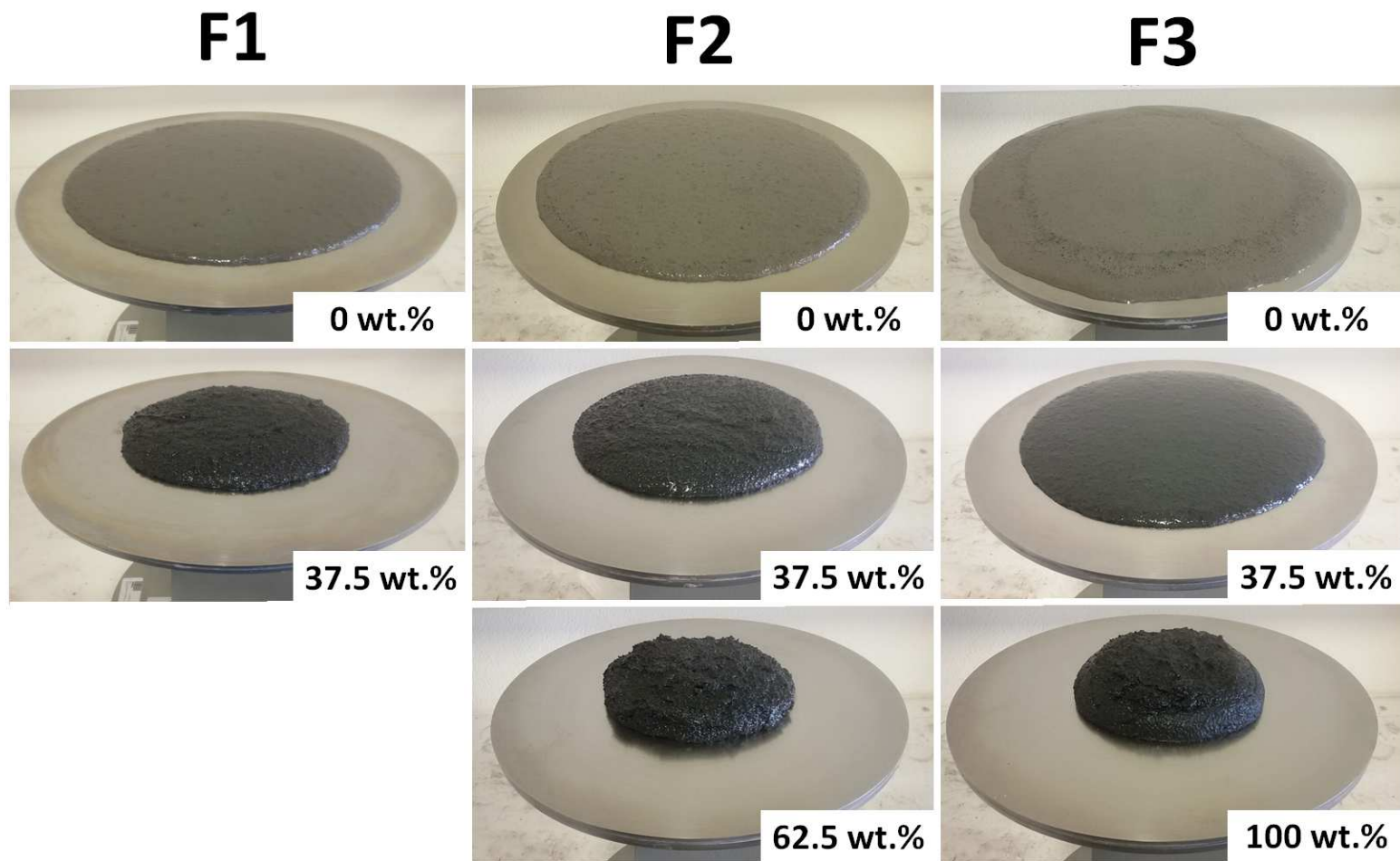


Fig. 3 Influence of the mixture composition and dregs incorporation content (regarding the aluminosilicate precursors) on the mortars' spread on table behaviour of the mortars.

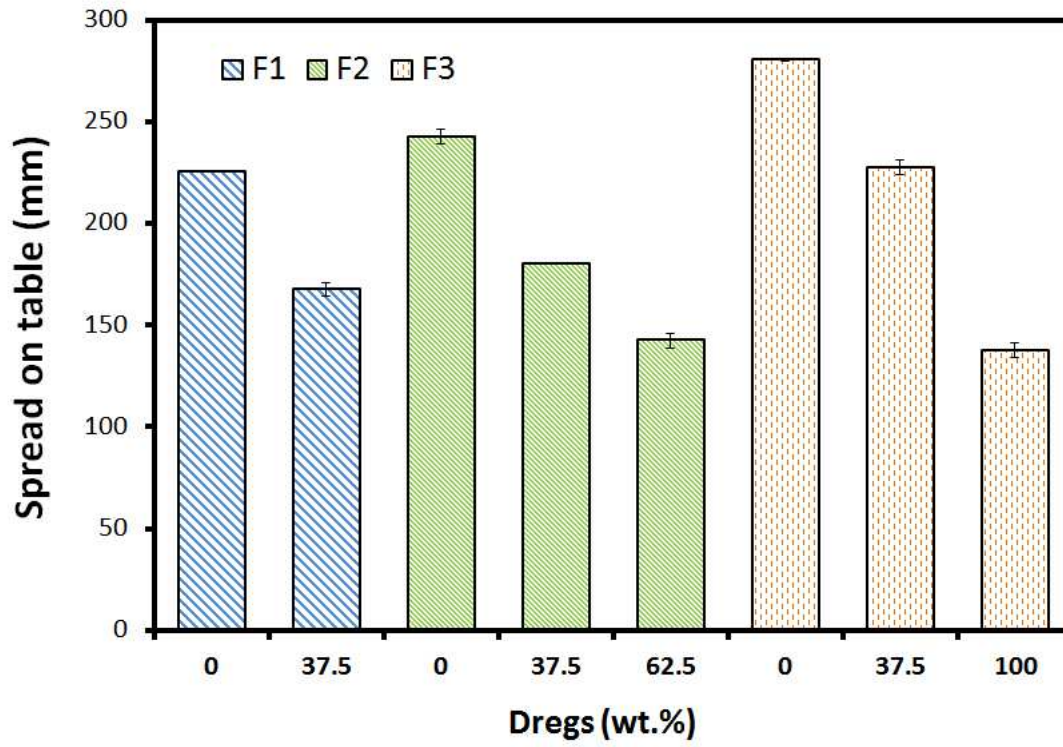


Fig. 4 Influence of mixture composition and dregs incorporation content on the workability of the mortars.

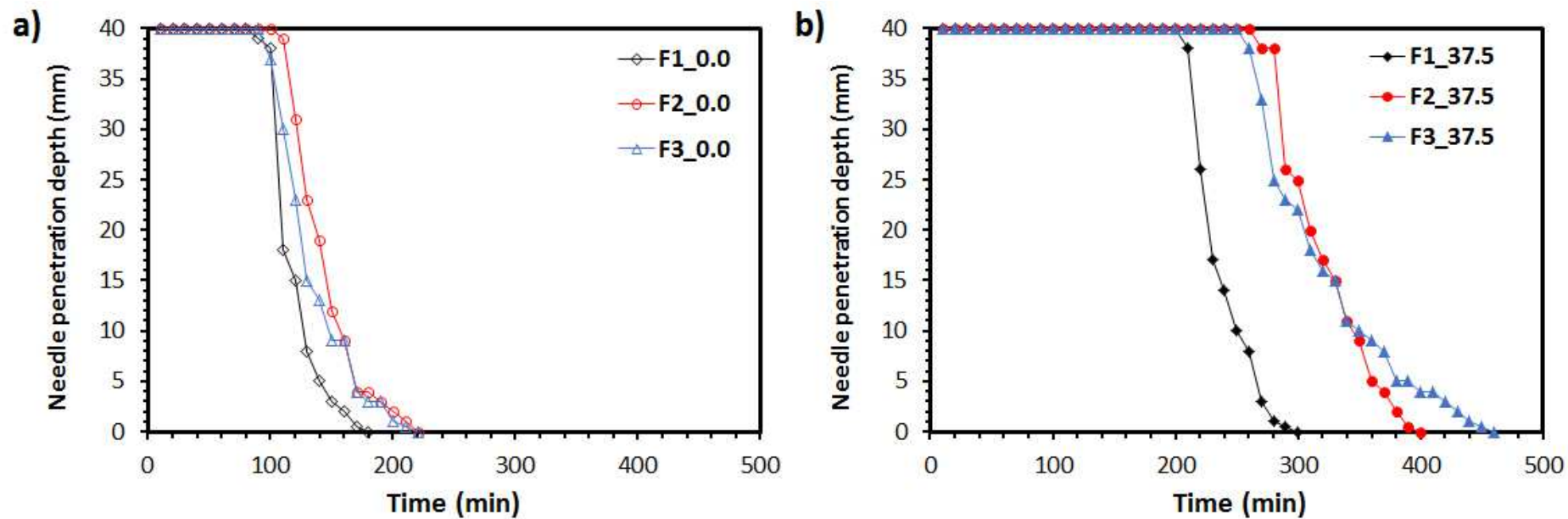


Fig. 5 Vicat needle penetration depth as a function of time for compositions prepared a) without dregs (reference specimens) and with b) 37.5 wt.% dregs.

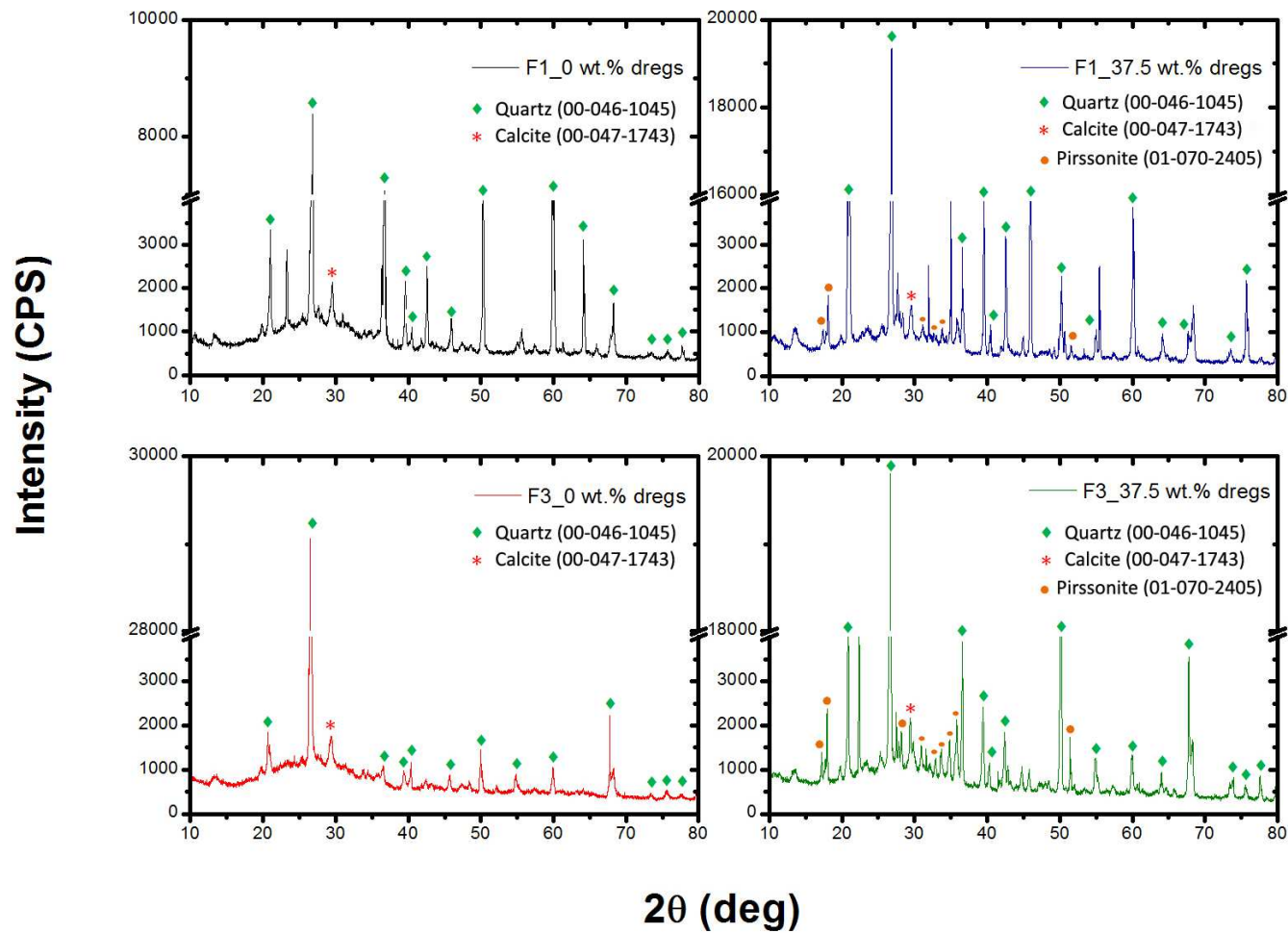


Fig. 6 Influence of mixture composition on the XRD patterns of waste-based mortars produced using dregs as fine filler.

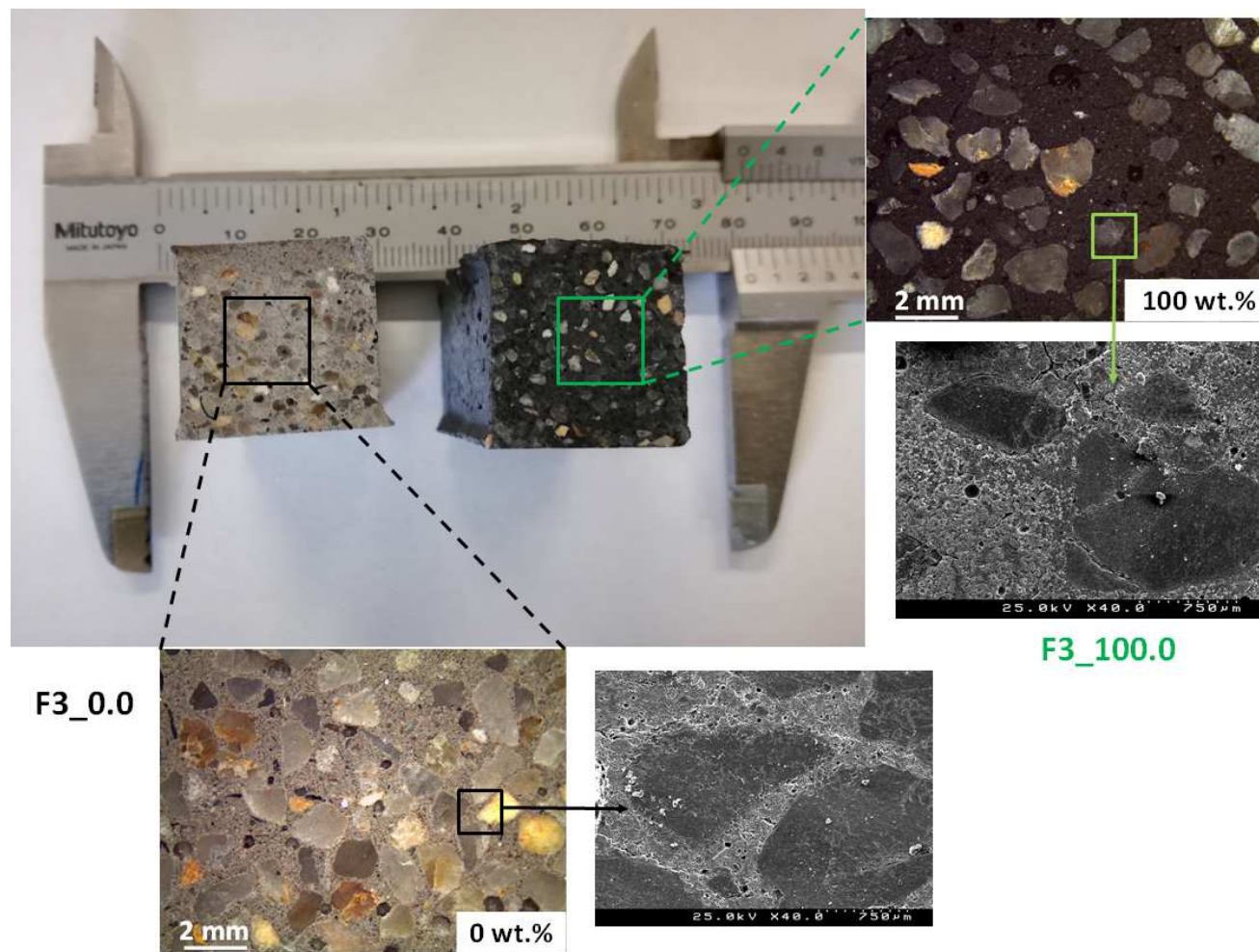


Fig. 7 Digital photograph of a geopolymeric mortar prepared without dregs (F3_0.0) and with 100 wt.% dregs (F3_100.0) illustrating the absence of efflorescence formation.

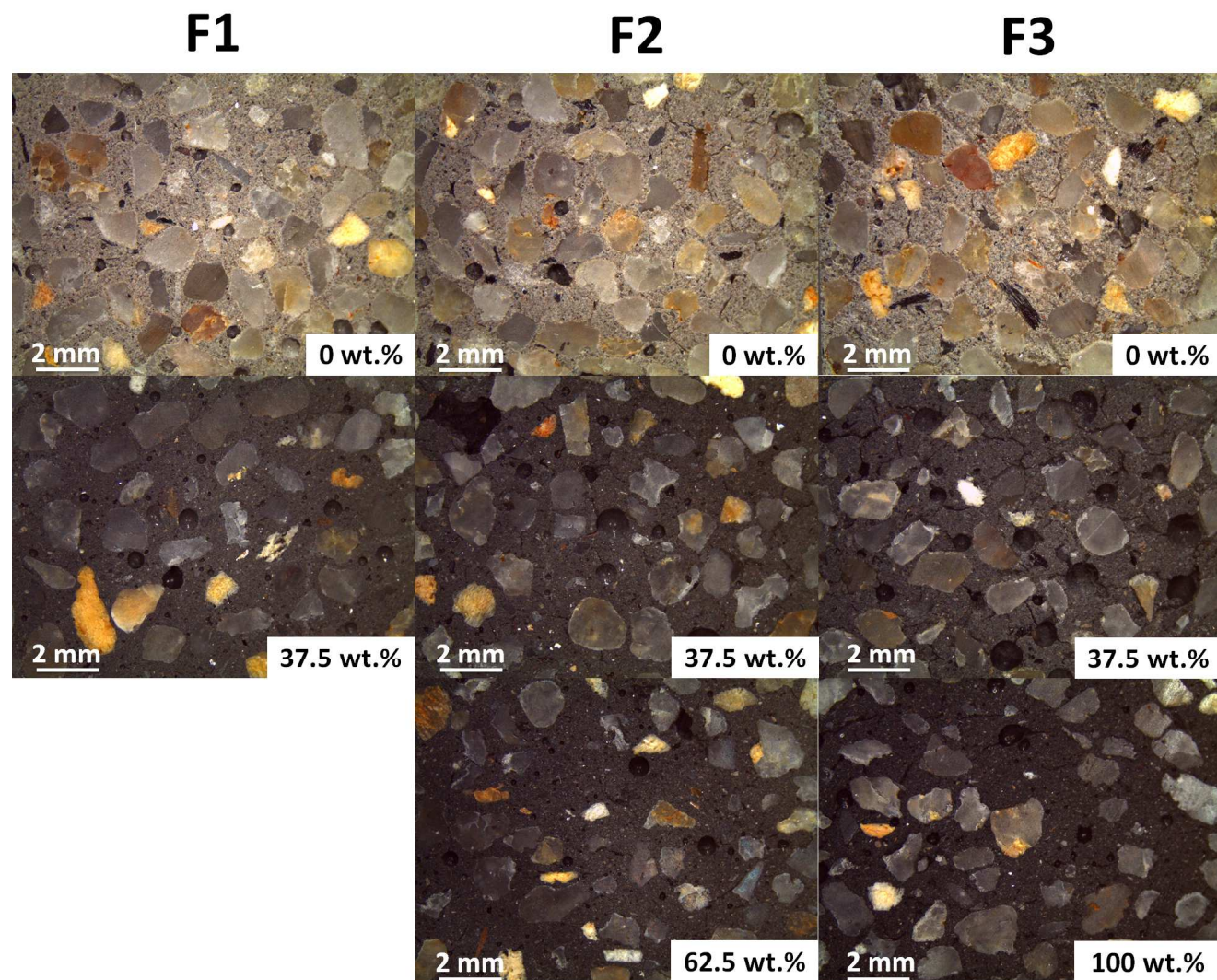


Fig. 8 Optical micrographs of distinct mortars (with or without using dregs as fine filler) cured for 28 days.

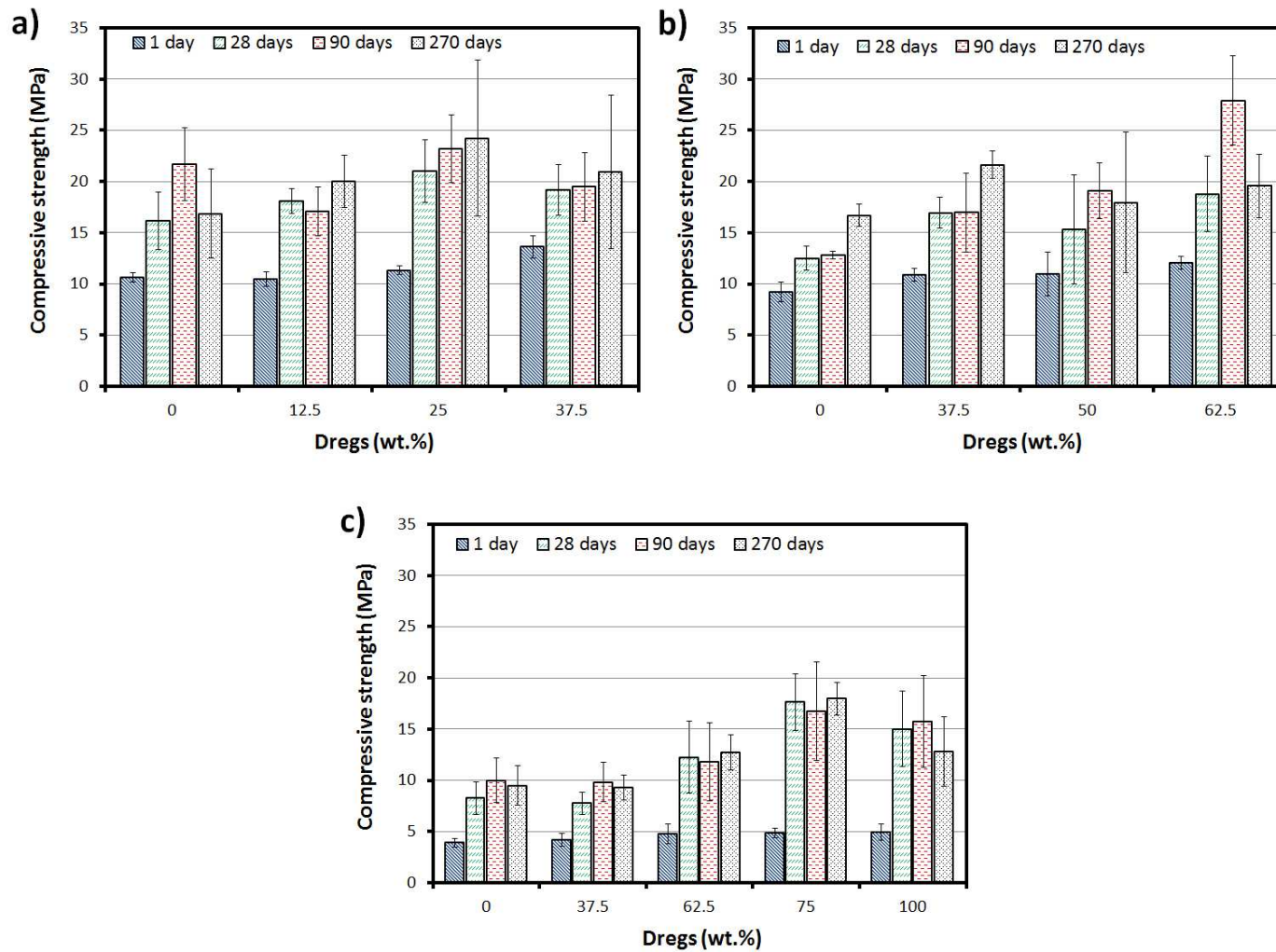


Fig. 9 Compressive strength of the distinct mortars upon curing prepared with composition: a) F1, b) F2 and c) F3.

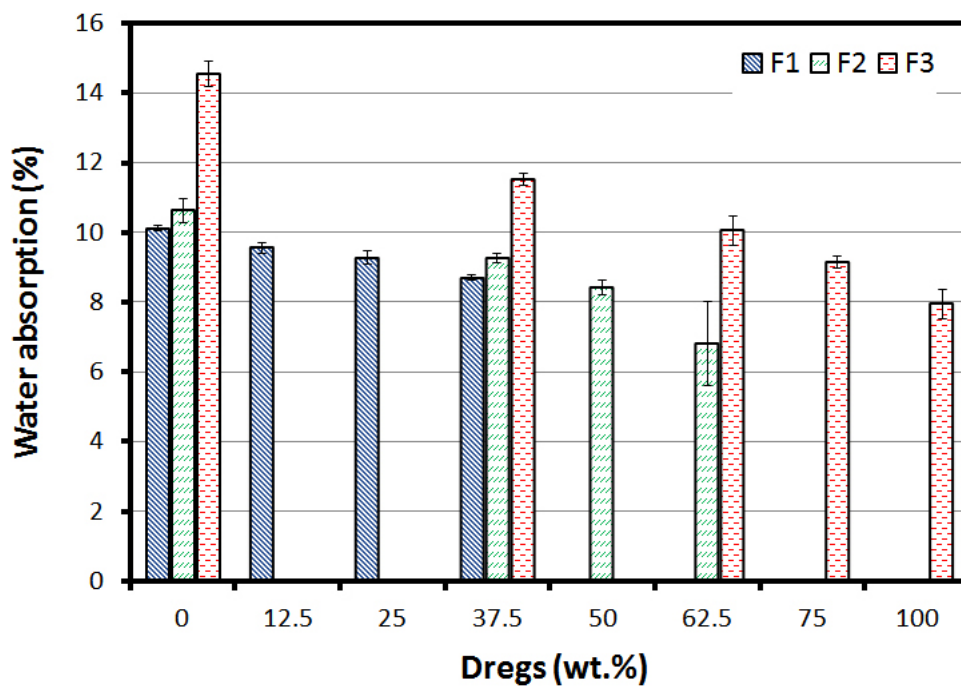


Fig. 10 Water absorption of fly ash-based geopolymer mortars (cured for 28 days).

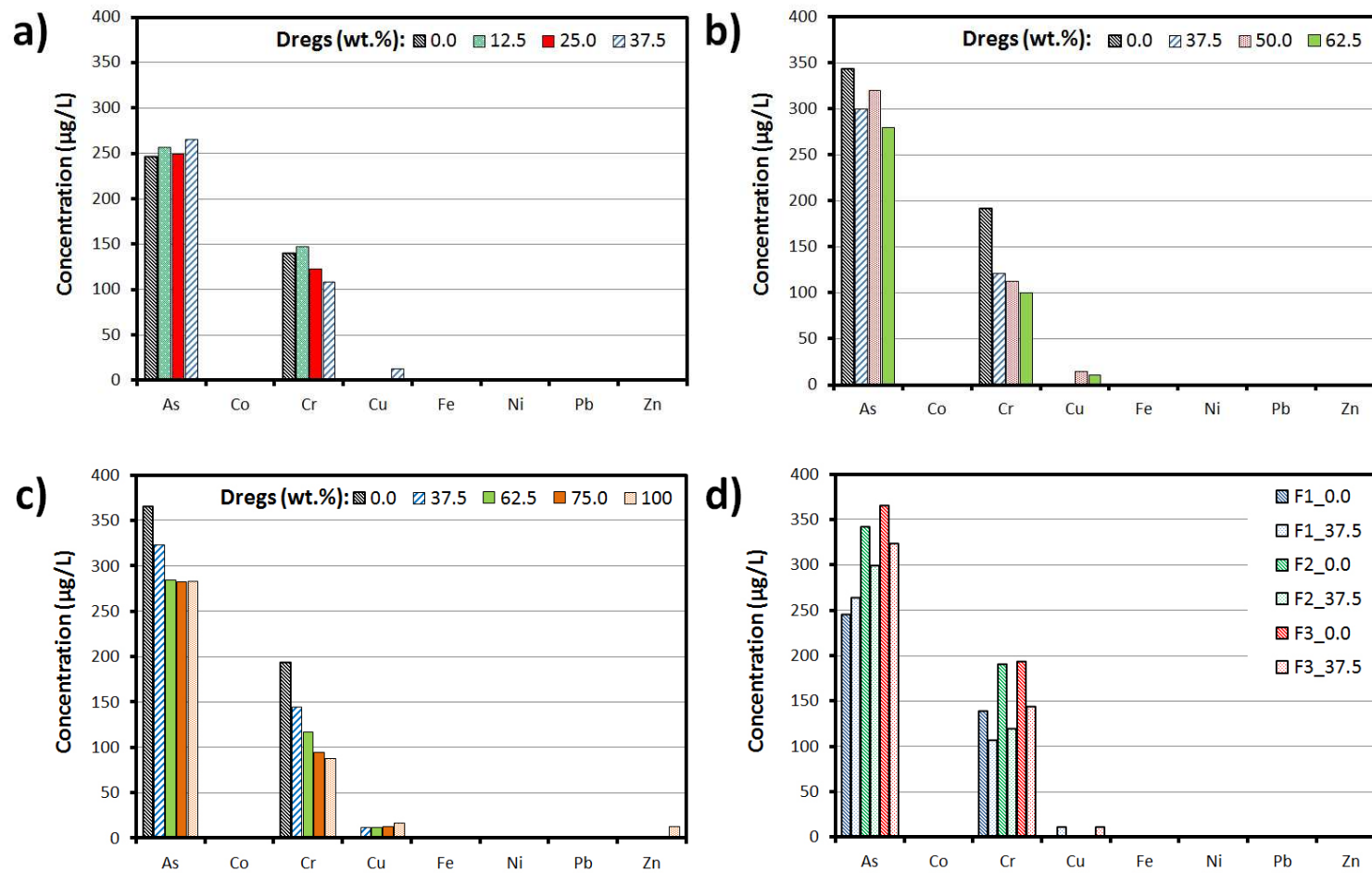


Fig. 11 Heavy metals leaching behaviour of the mortars after immersion in distilled water for 24 h: a) F1, b) F2, c) F3. Fig. 11d shows a comparison between the distinct compositions (F1, F2 and F3) without and with 37.5 wt.% dregs.

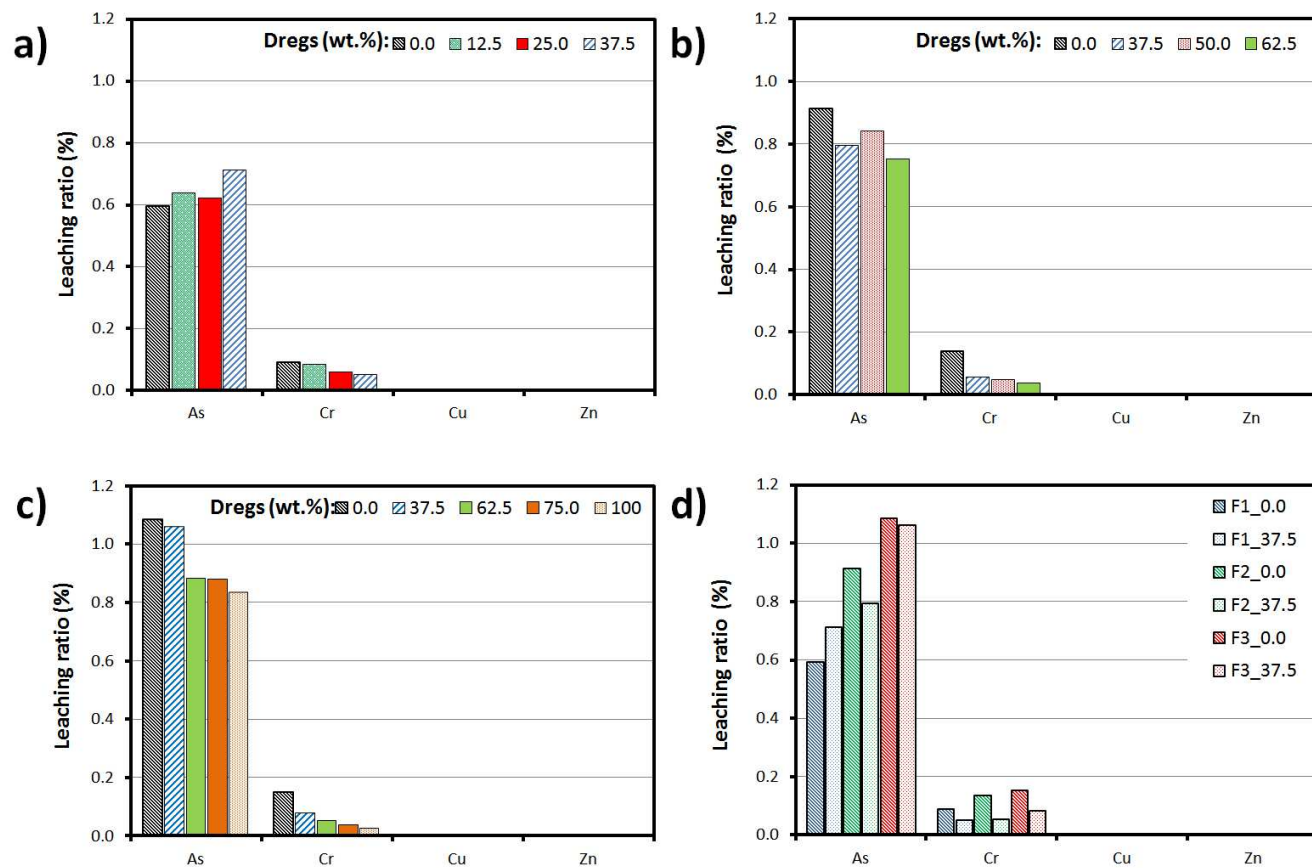


Fig. 12 Heavy metals leaching ratio from the various mortars after water immersion (24 h): a) F1, b) F2, c) F3. Fig. 12d shows a comparison between the distinct compositions (F1, F2 and F3) without and with 37.5 wt.% dregs.

Table 1 Mixture composition of the waste-based geopolymeric mortars.

| Sample name | Mixture proportion (g) | | | | | | |
|-------------|------------------------|---------|-------|-----------------|------|------------------|------|
| | Metakaolin | Fly ash | Dregs | Sodium silicate | NaOH | H ₂ O | Sand |
| F1_0.0 | | | 0.0 | | | | |
| F1_12.5 | 30 | 70 | 12.5 | 75 | 25 | - | 200 |
| F1_25.0 | | | 25.0 | | | | |
| F1_37.5 | | | 37.5 | | | | |
| F2_0.0 | | | 0.0 | | | | |
| F2_37.5 | 30 | 70 | 37.5 | 84 | 25 | - | 200 |
| F2_50.0 | | | 50.0 | | | | |
| F2_62.5 | | | 62.5 | | | | |
| F3_0.0 | | | 0.0 | | | | |
| F3_37.5 | | | 37.5 | | | | |
| F3_62.5 | 30 | 70 | 62.5 | 84 | 25 | 7.5 | 200 |
| F3_75.0 | | | 75.0 | | | | |
| F3_100.0 | | | 100.0 | | | | |

Highlights

- Eco-friendly geopolymer mortars containing green liquor dregs were synthesised.
- For the first time the durability and leaching behaviour of dregs-containing mortars was studied.
- Dregs effectively enhanced mortars' compressive strength (up to 44%).
- Samples' compressive strength increased with ageing demonstrating their durability.
- Mortars' heavy metals leaching levels were below the contamination limits in soil.