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Effect on the heat of hydration, setting times and mechanical resistance adding fly ash and blast furnace slag in commercial cement mixtures

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Abstract. Commercial Portland cement is the most used construction material in the world, due its durability, versatility and economy generated in civil works, which follows a growth trend; however, a large amount of energy is required for its production, which generates a large amount of greenhouse gas emissions and air pollutants. Consequently, a large part of research has focused on mitigating these effects by partially replacing supplementary cementitious materials. Therefore, this research aims to evaluate the performance of commercial cement paste, partially replacing it with fly ash and blast furnace slag, characterized by scanning electron microscopy, X-ray fluorescence, surface area to establish variations of setting times and heat of hydration in hardening process. The results established that fly ash and blast furnace slag didn't generate sufficient capacities to develop stable cementation reactions and therefore higher strengths, due to their compositions surface area and the high content of alternative cements present in the commercial Portland cement since its manufacture. Nevertheless, the fly ash and blast furnace slag are alternatives in mitigating the environmental effect generated by commercial cements.

1. Introduction

Cement is the largest manufactured material used for construction in the world, additionally to being indispensable in buildings and infrastructure, cement is essential for economic development; however, this industry faces great challenges, due to high cost of energy resources, greenhouse gas emissions and air pollutants generated in its production process [1-2]. Thus, there are efforts by researchers and professionals in the construction industry to address this problem through the use of industrial by-products, in search of generating alternatives for the development of supplementary cementitious materials (SCM) [3], due to the similarity of hydration processes, production of hydrated calcium silicates and aluminates, and setting of cement mixtures, routinely specified in the manufacture of Commercial Portland Cement (CPC) [4,5]; consequently, these new cements contribute to the fight against the depletion of natural resources, the reduction of greenhouse gases and the elimination of solid waste [6-7]. Consequently, in Colombia, the new performance specification for hydraulic cement, NTC 121 of 2014 [8], adopted from the ASTM C-1157 standard [9], allows the compositional modification of cement or its components without restrictions provided it meets standards based on characteristics related to the performance of cement mixes; However, the reactivity of the SCM depends on the quality of the industrial processes, types of SCM and proportions implemented [8,9]. Therefore, the present investigation aims to add industrial waste such as fly ash (FA) and granulated blast furnace slag (GBFS) according to standard practices ACI 232.2R and ACI 233R [10,11], in different combinations and



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proportions, with the purpose of assessing their performance as SCM in the hydration, setting and mechanical resistance process with partial replacement of CPC, in search of clarifying controversies and disagreements in the effects of adding this kind of SCM in Colombian CPCs [4,12] and its use as alternative in mitigating the effects of manufacturing CPC.

2. Methodology

2.1. Materials

The CPC of general use is produced by Colombian cement companies [13]. FA and GBFS are produced and supplied by the thermoelectric power plant "Termopaipa" and by the steel company "Acerías Paz del Río" respectively. Before being used, GBFS was dehydrated and crushed, then sieved through a No. 60 sieve (250 μm stainless steel mesh).

2.2. Casting

270 paste cubes were developed following the ASTM C109 [14], corresponding to 30 combinations of CPC, FA and GBFS, using a water/cementing (a/c) ratio of 0.277, following the ASTM C187 [15]. A total of three samples are used for each mixture for each test age. 24 hours after mixing, the samples were unmolded and cured following the ASTM C192 [16].

2.3. Experimental methods

The scanning electron microscopy (SEM) was carried out by using Zeiss model EVO 420 equipment; nitrogen physisorption Analysis was performed at 77 K, following the Brunauer Emmett and Teller (BET) model for the determination of specific area, first sample cleaning was performed up to 373 K in Micromeritics ASAP 2010 equipment. For the determination of the specific surface area by ASTM C-204 [17], X-ray fluorescence spectrometry (XRF) was performed using the PANalytical MiniPal 2 device. As a starting point to know the proportions of the samples, a series of tests were performed on cement paste cubes, obtaining the optimal SCM mixtures. The compression resistance of 30 paste mixtures with different contents of CPC, GBFS and FA were evaluated mechanically at 3, 28 and 56 days after the casting. From the results obtained, four optimized mixtures were defined to be used in the preparation of samples. The optimized mixtures were evaluated by setting times according to ASTM C-191 [18] and the determination the heat of hydration by semi-adiabatic conditions followed the BS EN 196- 9 standard [19].

3. Results

Micrographs SEM of the three cementitious materials used in this research are shown in Figure 1.

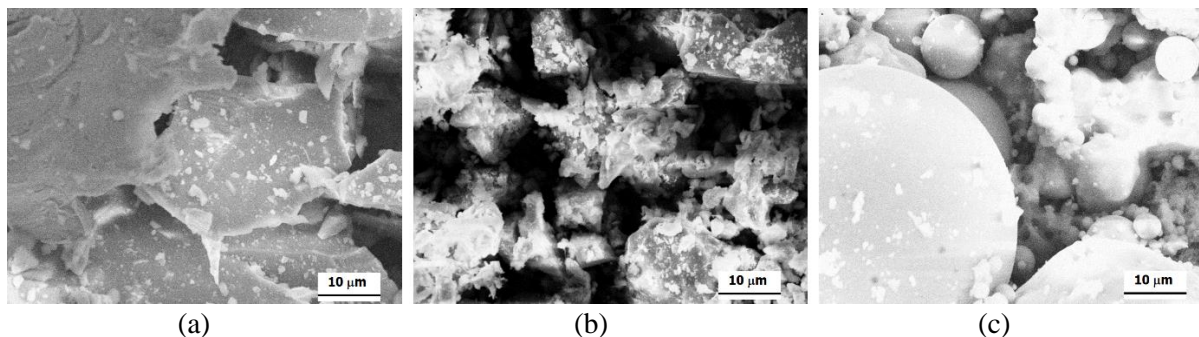


Figure 1. SEM micrographs of cements at 5000x. (a) CPC. (b) FA. (c) GBFS.

The SEM analysis allowed to establish typical microstructural characteristics of AF under study, such as its spherical shape, smooth surfaces and high surface area [20,21] and morphological characteristics of GBFS such as the larger particle size between cementants, angular shapes and sharp edges, presumably due to grinding [22]; this association of factors generates a decrease in surface area

and consequently reduction in reactivity, which depends on combining factors such as chemical composition, mineralogy and fineness, the latter affecting the degree of hydration, microstructure and porosity [23,24], which is consistent with the specific surface results performed according to ASTM C-204 [25], together with the physisorption analysis using the mathematical treatment proposed by BET; The results obtained are indicated in Table 1.

Table 1. Specific surface area by Blaine permeability device and physisorption analysis of cementitious materials.

Material	ASTM C-204		BET		
	Surface area (cm ² /g)	Density (g/cm ³)	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
CPC	4230	2.90	2.0	0.002	16.9
FA	4640	2.06	5.0	0.010	7.9
GBFS	1240	2.86	0.5	0.003	25.5

The specific surface analysis using Blaine and BET showed in Table 1, together with SEM, determined that GBFS has the lowest surface area, while FA has low density and high porosity, which is consistent with its high surface area and high pore volume, followed by CPC ; therefore, GBFS offers the most unfavorable conditions for hydraulic reactions from the point of view of the fineness of the material; on the other hand, FA with its high surface area and pore volume, generated less manageability in mixtures containing CPC + FA and consequently, less resistance in hardened state. In addition, the density values, obtained establish that CPC had been mixed with some mineral additives when compared to typical density of ordinary Portland cement (OPC) 3.15 g/cm³ [25], this was reduced to similar values to densities of the SCMs evaluated; likewise, the cementitious materials evaluated by X-ray fluorescence (XRF) exposed in Table 2.

Table 2. Cementitious materials oxides analysis (% by weight).

Component	CPC	FA	GBFS
SiO ₂	22.80±1.63	60.47±2.69	28.97±1.46
CaO	57.75±2.44	0.74±0.11	46.60±1.08
Al ₂ O ₃	10.87±0.29	26.11±10.81	18.15±3.69
MnO	1.07±0.38	-	1.90±0.00
Fe ₂ O ₃	2.55±2.52	6.58±0.60	1.75±0.23
SO ₃	3.07±0.38	-	1.43±0.63
NiO	-	-	0.37± 1.14
K ₂ O	0.54±0.84	1.54±0.14	-
TiO ₂	0.28±0.05	1.33±0.51	-

Five samples of each material were used, using the t-test and a confidence of 95% (p≤ 0.05).

Based in the Table 2, the CPC has a CaO and SiO₂ content greater than 80%, which are the main compounds for the development of calcium silicate hydrates and consequently favorable mechanical strengths [26,27]. The composition of AF is similar to other studies [26], with majority contents of SiO₂ and Al₂O₃, and contents less than 10% of CaO; Due to the above and its origin, as result of calcining bituminous coal in industrial processes for electric power generation, the FA is classified as a class F according to the standard specification for the use of coal fly ash in concrete ASTM C-618 [28]. On the other hand, the evaluated components of GBFS, determined that this is classified as basic slag with favorable hydraulic reactivity, due to the relationship of the network modifier with the network former CaO/SiO₂ is greater than 1 [29].

The results of the compressive strength of binary paste mixtures at 3.28 and 56 days can be seen in Figure 2 and Figure 3. For both SCM additions, the compressive strength is greater as the amount of the

CPC increases; In GBFC and FA ratio is directly proportional, however, the latter shows drastic decrease in residence from replacement.

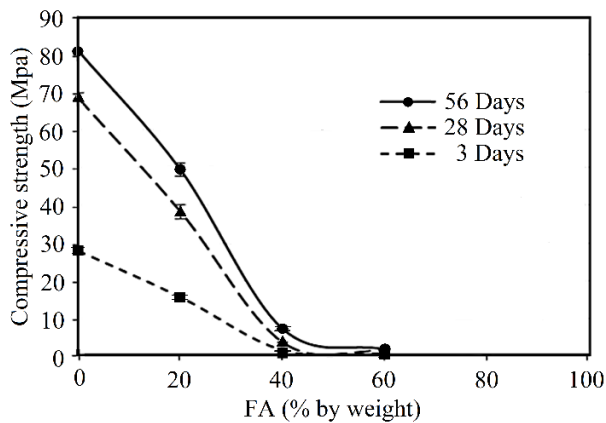


Figure 2. Compressive strength of CPC-GBFS pastes.

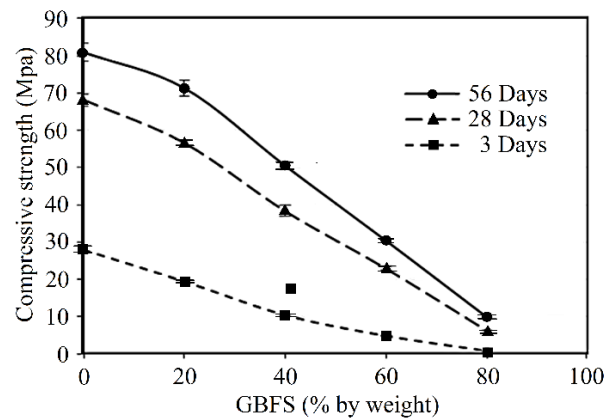


Figure 3. Compressive strength of CPC-FA pastes.

The same phenomenon is observed in ternary mixtures at 3, 28 and 56 *days*, shown in Figure 4. However, 5 combinations with CPC contents less than 20% and FA greater than 30% didn't form sufficient consistency for the process of curing and other resistances are proportional to the CPC content, and lower as the SCM content increases; nevertheless, the inclusion of GBFS showed better performance than FA; although, the combination of these two SCMs generated lower resistance than binary combinations with CPC.

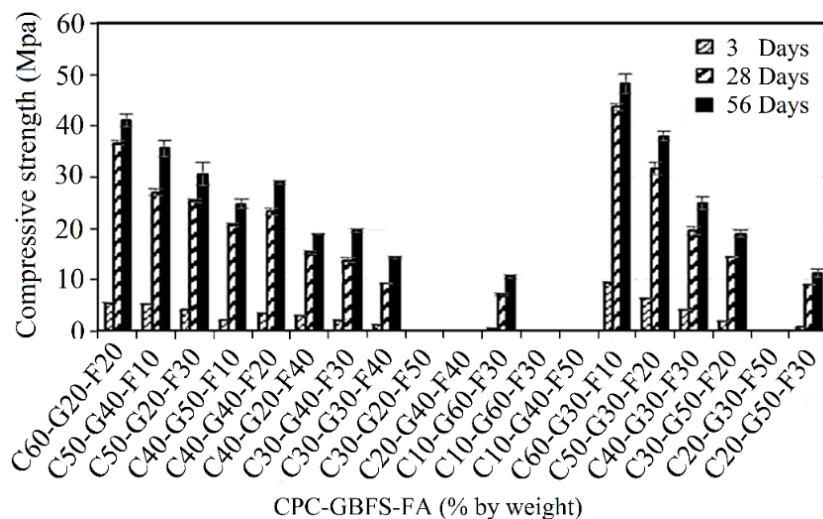


Figure 4. Compressive strength in paste cubes of CPC (C), GBFS (G) and FA (F).

The results of compressive strength in the binary and ternary combinations at 56 days of setting, are summarized and schematized in the ternary diagram shown in the Figure 5, which will help determine the mixtures with the highest resistance in order to establish the resistance variation Compression, hydration process and setting in time.

Based on the above, was possible to determine the mixtures with the highest compression resistance with the lowest CPC contents due to their higher cost; therefore, the higher the content of SCM, the final

cost will decrease and its environmental impact will be reduced [25]. Therefore, four combinations of CPC and SCM called a1, a2, a3 and a4 were chosen (Table 3).

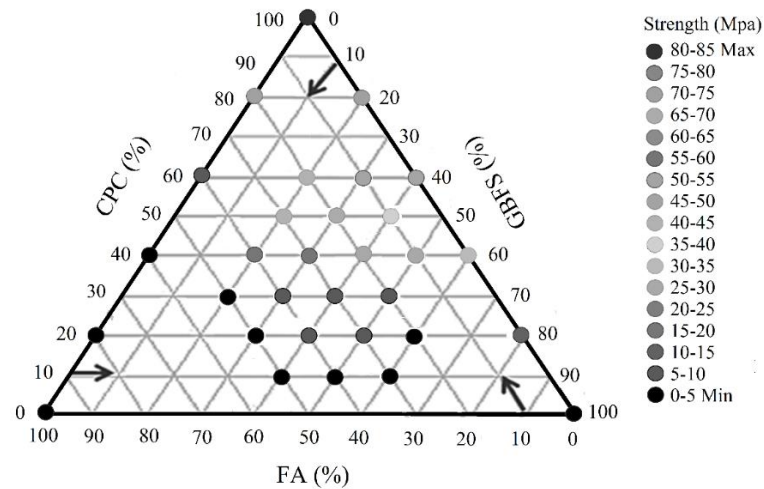


Figure 5. Compressive strength CPC-GBFS-FA combinations at 56 days.

Table 3. Cementing mixtures selected for resistance, hydration and setting tests.

Mix	Material
a1	100% CPC
a2	80% CPC + 20% GBFS
a3	80% CPC + 20% FA
a4	60% CPC + 30% GBFS + 10% FA

The evaluation of the setting times in mixtures was carried out according to the ASTM C 191 standard [18], through the recording of the changes in the penetration depth of Vicat needle during the first hours after mixing; the results are shown in the Figure 6.

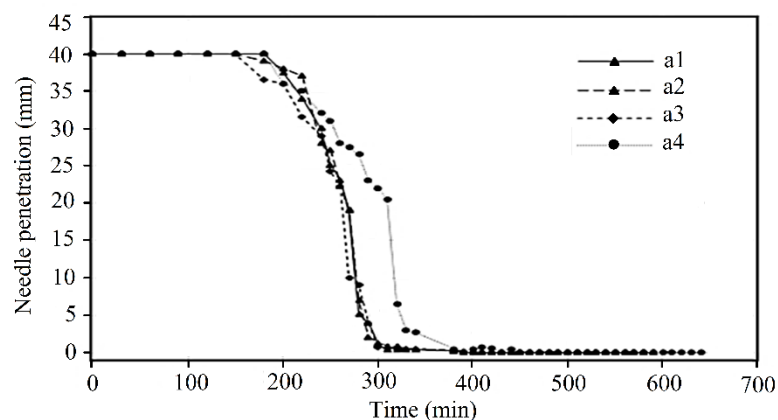


Figure 6. Variation of the needle penetration used for determining the setting times.

Mixture a1 and a2 have similar behaviors and holdings of setting times; however, the mixture a3 had an unstable behavior between 150 min and 250 min after setting, however these three mixtures have similar final setting times, around 300 min (5h). In addition, the mixture a4 showed instability and delay

in the process and fine setting time, about 30% compared to the other mixtures; therefore it is inferred that the effect of mixing FA + GBFS generates lower speed and intensity of hydration reactions, causing the delay in the beginning and end of setting.

The intensity of the reactions in the hydration process in the first 52 hours of setting are observed in the Figure 8 and Figure 9.

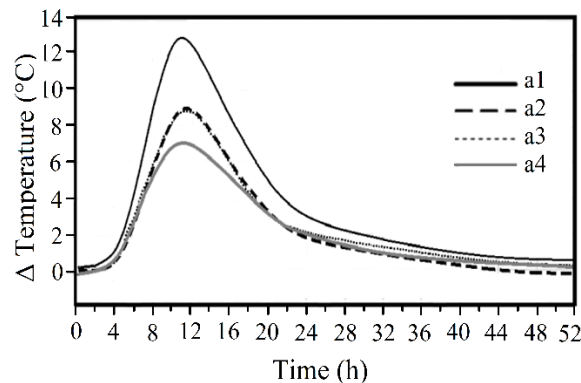


Figure 7. Temperature evolution.

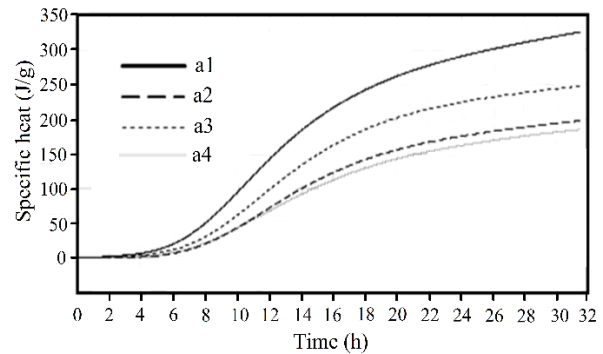


Figure 8. Specific Heat evolution.

The temperature variations represented in Figure 7 show similar maximum reaction times in all mixtures; however, the mixture a1 has the highest exothermic reaction due to a greater reactivity in the hydration process, which generates greater mechanical resistance, linked to the degree of hydration of the cement [30]. Mixtures a2 and a3 have similar exothermic temperatures and specific heat (Figure 8), however, these were reduced to $31\% \pm 7\%$ compared with a1; Similarly, the ternary mixture a4 reduced its heat of hydration up to 43% as shown in Figure 8. The above shows the relationship between heat of hydration and mechanical resistance, which is greater in the mixture a1.

4. Conclusions

The morphological, compositional and surface area characterization, together with the methodologies used for the elaboration of different combinations of mixtures between CPC, GBFS and FA determined the variation of setting times, heat of hydration and mechanical resistance. This SCM didn't generate enough mechanical resistance compared to the CPC due to the effect of the surface area on the manageability and setting times, related to the reduction of exothermic reactions, to the extent that the addition of SCM increases; nevertheless there are uncertainties generated by the high addition of SCM in the CPC since its manufacture. In addition, the GBFS generated an acceptable cementation activity, greater than the FA and the addition of SCM didn't affect the generation of exothermic reactions in the configuration process; therefore, the use of FA and GBFS are alternative to mitigate the effects of the manufacture of CPC in the environment.

References

- [1] Scrivener K L, *et al.* 2018 Eco-efficient cements: Potential economically viable solutions for a low- CO_2 cement-based materials industry *Cem. Concr. Res.* **114** 2
- [2] Uwasu M, *et al.* 2014 World cement production and environmental implications *Envir. Dev.* **10** 36
- [3] Kumar R P, *et al.* 2019 Industrial wastes as alternative materials to fine aggregates in triple blend self compacting Concrete a sustainable technological solution *IOP. Conf. Ser. Earth. Envir. Sci.* **268** p 8
- [4] Green C, *et al.* 2013 Characterization of physio-chemical processes and hydration kinetics in concretes containing supplementary cementitious materials using electrical property measurements *Cem. Concr. Res.* **50** 6
- [5] Sahani A, *et al.* 2018 An experimental study on strength development of concrete with optimum blending of fly ash and granulated blast furnace slag *Int. J. Appl. Eng. Res.* **13** 5700
- [6] Bilir T, *et al.* Effects of bottom ash and granulated blast furnace slag as fine aggregate on abrasion resistance of concrete *Sci. Eng. Comp. Mater.* **24** 261

- [7] Gartner E and Sui T 2018 Alternative cement clinkers *Cem. Concr. Res.* **114** 27
- [8] Instituto Colombiano de Normas Técnicas y Certificación (ICONTEC) 2014 *Especificación de desempeño para cemento hidráulico, Norma Técnica Colombiana, NTC-121* (Colombia: ICONTEC) p 34
- [9] American Society of Testing Materials (ASTM) 2017 Standard performance specification for hydraulic cement (USA: American Society of Testing Materials) p 8
- [10] American Concrete Institute (ACI) 2002 *ACI 232.2R-96 Use of fly ash in concrete* (USA: American Concrete Institute) p 34
- [11] American Concrete Institute (ACI) 2003 *ACI 233R-03 Slag cement in concrete and mortar* (USA: American Concrete Institute) p 34
- [12] Aroghel-Bouny V, *et al.* 2011 Easy assessment of durability indicators for service life prediction or quality control of concretes with high volumes of supplementary cementitious materials *Cem. Concr. Comp.* **33** 832
- [13] American Society of Testing Materials (ASTM) 2015 *Standard specification for Portland cement, ASTM C-150* (USA: American Society of Testing Materials) p 6
- [14] American Society of Testing Materials (ASTM) 2016 *Standard test method for compressive strength of hydraulic cement mortars, ASTM C-109* (USA: American Society of Testing Materials) p 6
- [15] American Society of Testing Materials (ASTM) 2016 *Standard test method for normal consistency of hydraulic cement, ASTM C-187* (USA: American Society of Testing Materials) p 6
- [16] American Society of Testing Materials (ASTM) 2018 *Standard practice for making and curing concrete test specimens in the laboratory, ASTM C-192* (USA: American Society of Testing Materials) p 6
- [17] American Society of Testing Materials (ASTM) 2018 *Standard test method for fineness of hydraulic cement by air permeability apparatus, ASTM C-204* (USA: American Society of Testing Materials) p 8
- [18] American Society of Testing Materials (ASTM) 2018 *Time of setting of hydraulic cement by vicat needle, ASTM C-191* (USA: American Society of Testing Materials) p 10
- [19] British Standards Institution (BSI) 2010 *Methods of testing cement heat of hydration semi-adiabatic method, BS EN 196-6* (London: British Standards Institution)
- [20] Kutchko B G and Kim A G 2006 Fly ash characterization by SEM-EDS *Fuel* **85** 2537
- [21] Zyrkowski M, *et al.* 2016 Characterization of fly-ash cenospheres from coal-fired power plant unit *Fuel* **174** 49
- [22] Kumar R, *et al.* 2005 Hydration of mechanically activated granulated blast furnace slag *Metall Mater Trans B* **36** 873
- [23] Wang P Z, *et al.* 2005 Effect of fineness and particle size distribution of granulated blast-furnace slag on the hydraulic reactivity in cement systems *Adv. Cem. Res.* **17** 161
- [24] Arel H Ş 1998 The effect of lignosulfonates on concretes produced with cements of variable fineness and calcium aluminate content *Constr. Build. Mater.* **131** 347
- [25] Gutiérrez-Junco O J, *et al.* 2018 *Concreto con cemento Portland comercial, escoria y ceniza, apreciaciones frente a un cambio de normativa* (Tunja: Editorial UPTC) p 330
- [26] Hewlett C and Liska M 2019 *Lea's chemistry of cement and concrete* (Oxford: Elsevier) p 870
- [27] Wiesław K 2014 *Cement and concrete chemistry* (Kraków: Springer) p 705
- [28] American Society of Testing Materials (ASTM) 2010 *Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete, ASTM C-618* (USA: American Society for Testing and Materials) p 6
- [29] Winnefeld F 2014 Influence of slag composition on the hydration of alkali-activated slags *J. Sustain Cem. Mate.* **4** 85
- [30] Mehdipour I and Khayat K 2017 Elucidating the role of supplementary cementitious materials on shrinkage and restrained-shrinkage cracking of flowable eco-concrete *J. Mater. Civ. Eng.* **30** 1