REVISTA MATÉRIA V.27 N.01

ISSN 1517-7076 artigos e13138, 2022

Blasted copper slag as artificial fines in ecofriendly concrete

Felipe Alves de Oliveira[1], Cézar Augusto Casagrande[2], Érika Pinto Marinho[3], Lidiane Fernanda Jochem[2], Ana Cecília Vieira de Nóbrega[3,4]

[1]Federal University of Pernambuco (UFPE), Technologic Center of Campus Agreste (CAA), Av. Marielle Franco, s/n - Km 59 Nova Caruaru, CEP: 55014-900, Caruaru, PE, Brazil.
[2]Technological Federal University of Paraná (UTFPR), Academic Department of Civil Construction (DACOC), Rua Deputado Heitor Alencar Furtado 5000 Cidade Industrial, CEP: 81280340, Curitiba, PR, Brazil.
[3]Federal University of Pernambuco (UFPE), Graduate Program in Civil and Environmental Engineering (PPGECAM), Av. Marielle Franco, s/n - Km 59 Nova Caruaru, CEP: 55014-900, Caruaru, PE, Brazil.
[4]Federal University of Rio Grande do Norte (UFRN), Civil Engineering Department, Lagoa Nova, CEP: 59078970, Natal, RN, Brazil.
email: felip3_4lves@hotmail.com; cezarcasagrande@utfpr.edu.br; erika.pmarinho@ufpe.br; lidiane@utfpr.edu.br; anacecilianobrega@gmail.com

ABSTRACT

The present work assessed the feasibility of applying blasted copper slag (BCS) as addition to cementitious composites. Series with 0-15% of BCS were produced and characterized by compression strength, durability, spread and specific gravity. In fresh state, the workability was enhanced in until 250% when adding the slag. Besides, both mechanical strength and durability indicators of BCSR-added concrete were also improved. Although the greater strength at the ages of 7 and 28 days was achieved for the reference concrete, concretes containing 5% and 7.5% of BCSR also reached the expected resistance of 30 MPa at 28 days. Concretes containing 5% and 10% of the slag were the ones that less absorbed water. The reduction in capillary absorption reached 63% in comparison to the ref concrete for 5% BCS-modified concrete. The incorporation of BCS improved the performance of the reference concrete in terms of both mechanical strength and durability. So, the reuse of the BCS produced after abrasive blasting in concretes was viable and sustainable disposal alternative.

Keywords: Absorption, Concrete, Durability, BCS, Strength, Concrete ecofriendly.

1. INTRODUCTION

Copper slag is an industrial by-product of copper manufacturing, and it is usually applied in dry blasting processes of metal and concrete surfaces. It is estimated that for each ton of copper produced, approximately 2.2 tons of copper slag are generated. In Brazil, the production of copper slag in 2018 reached 385,762t [1]. After some reuse blasting cycles, an uninteresting power for the blasting process remains. This residue of the residue is called blasting copper slag residue (BCS), whose final destination is the landfill. The material was previously classified as non-inert waste; thus, the residue does not generate danger, being non-toxic [2].

Researchers report the reuse of both copper slag and blasting copper slag in Portland-based cementitious materials, whether replacing cement or sand in mortars [3], concretes [4], and pavers [5] when sand is replaced by copper slag. Increases in workability and in the specific mass of concrete are reported both when copper slag replaces cement [6], and when it replaces sand [4, 7, 8]. Dos Anjos et al. [2], with the replacement of the natural fine aggregate by the residue in proportions above 20%, report that there were significant improvements in the plasticity and cohesion of the concrete in the fresh state, dispensing with the amount of water previously necessary to make the mixture. However, a high tendency to segregate is also reported for high contents of copper slag due to its higher density and less water absorption [9].

Autor Responsável: Felipe Alves de Oliveira Data de envio: 26/11/2020 Data de aceite: 16/06/2021

10.1590/S1517-707620220001.1338

Improvements in compressive strengths, as well as lower absorption rates compared to reference concretes were also obtained when copper slag replaced sand [4, 7]. When cement is replaced by copper slag, increased strength over time equal to or greater than standard and durable concretes were also reported, but associated with greater fragility [10]. In terms of post-blast copper slag residue, an increase in workability are also reported due to the glassy and smoother surface of the grains compared to sand [7, 8]. The high specific mass, higher than sand, which contributes to a greater slump [2, 7]. For the hardened state, the authors report a slight reduction of 5.5% in the resistance to axial compression when replacing 20% of the fine aggregate with copper slag after blasting. However, other researchers observed that the resistance to axial compression of concrete increased by 8.7% when to 15% replacement of post-blasted copper slag by cement [2, 10].

In this scenario, this article aims to evaluate the effects of partial replacement of cement by the post-blast copper slag residue in concrete, as a sustainable, and economical alternative with reduce environmental impacts.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

A CPV ARI Portland cement (equivalent to ASTM type III and high early strength, or EN CEM I 52.5, according to EN 197-1 standard [11]) was used. Table 1 presents the main physical characteristics and the chemical composition of the cement used, according to [12].

Table 1: Characteristics and composition of the CP V ARI and the copper slag [12].

CEMENT CP V PHYSICAL PROPERTIES	
Specific gravity ($g \cdot cm^{-3}$)	3.09
Clinker (wt. %)	98.5
Retained in sieve 0.075 mm (%)	< 0.22
Expansibility (mm)	< 2.0
d_{50} (μm)	15.9
Mineral addition (wt. %)	0-10
Initial setting (min.)	> 95
Final setting (min.)	< 180

CHEMICAL PROPERTIES		
Compound (%)	Cement	Copper slag
Fe_2O_3	1.83	61.22
SiO_2	20.4	25.21
Al_2O_3	4.90	3.73
CaO	65.4	2.39
ZnO	-	1.6
CuO	-	1.5
SO_3	3.6	1.2
K_2O	0.2	1.01
MoO_3	-	0.92
MgO	1.06	0.92
As_2O_3	-	0.18
P_2O_5	-	0.1
Cl	-	0.01
Loss of ignition	1.44	0.01

A natural sand (specific gravity of 2.62 g·cm^{-3}; fineness modulus 1.98) and an artificial crushed sand (specific gravity of 2.63 g·cm^{-3} and fineness modulus 2.61) were used as fine aggregates. A coarse crushed stone and a medium crushed stone, both with a specific mass of 2.71 g·cm^{-3} were used as aggregates, the granulometric distribution of all aggregates are presented in Figure 1.

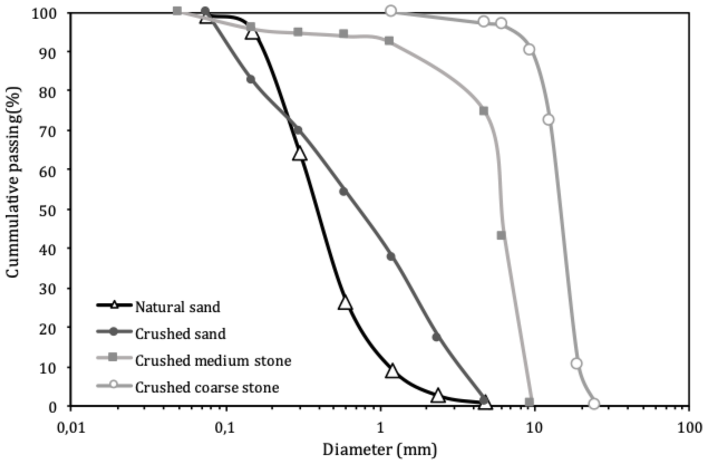


Figure 1: Particle size distribution of aggregates.

The BCS used in this work is a slag that was used in an industrial process of blasting for rusting remove, used during several cycles (Figure 2). After the cycles, the BCS has a reduced grain size distribution. The BCS was sieved in a 0.075 mm sieve. The BCS presented specific gravity of 3.81 g·cm^{-3} and it chemical composition is presented in Table 1.

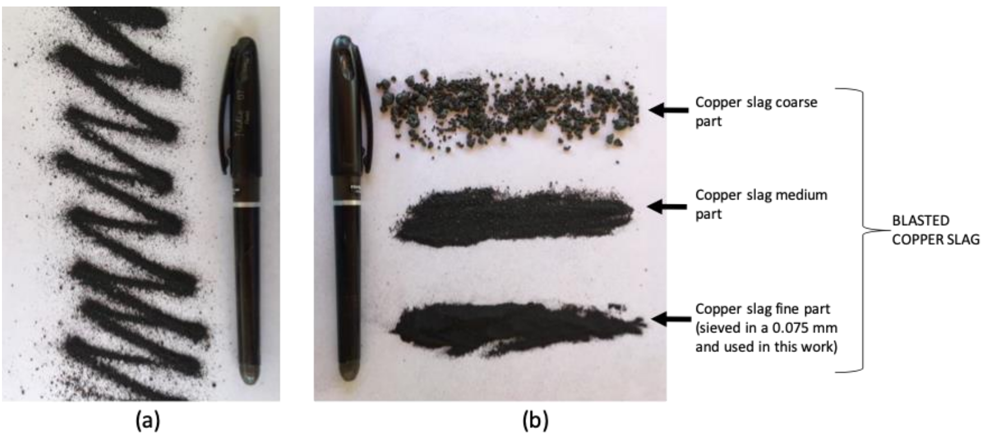


Figure 2: Copper slag.. (a) Blasted copper slag as received. (b) Sieved copper slag.

2.2 Concrete composition and tests methods

The standard mix was designed for a target of compression strength of 30 MPa at 28 days of cement hydration, based on [13]. Then, the composition was produced where the cement was partially replaced by BCS in proportions of 5.0%, 7.5%, and 10% by weight, as presented in Table 2. For each mix evaluated, fifteen cylindrical concrete samples (10 cm in diameter and 20 cm in height) were prepared according to [14], molded according to [15] and cured immersed in water until the tests.

Table 2: Concrete proportion (unitary compound).

COMPOUND	REF	5.0%	7.5%	10.0%
Cement	1.00	1.00	1.00	1.00
Crushed coarse stone	2.15	2.26	2.32	2.39
Crushed medium stone	0.67	0.71	0.73	0.75
Sand	1.61	1.70	1.74	1.79
Crushed sand	0.70	0.73	0.75	0.78
Water	0.62	0.66	0.67	0.69
Copper slag	-	0.05	0.075	0.10

The concrete fresh state test was evaluated by slump test [16]; and, the dry specific gravity was carried out by the ratio between the mass of the dry specimen and the volume of the concrete in a temperature of 23°C. For hardened state, the compressive strength test was performed according [17], in triplicate, for the ages of 7, 28, and 63D. The durability testes were evaluated by absorption by capillarity [18] and absorption by total immersion [19] at 28 days of cement hydration.

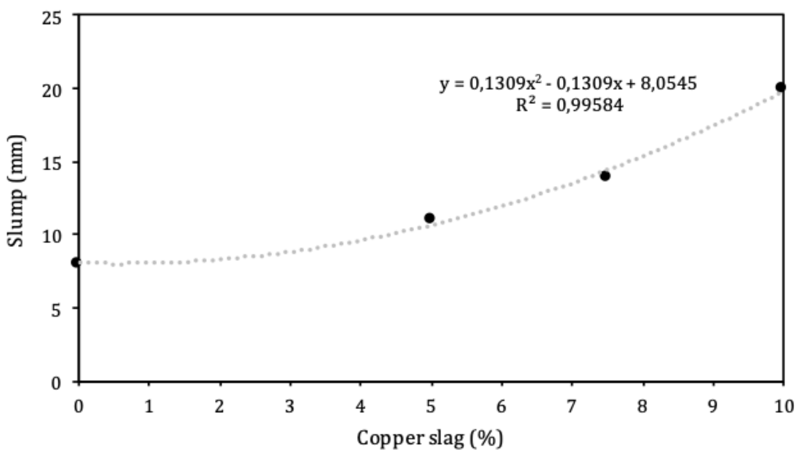
3. RESULTS AND DISCUSSION

3.1 Workability and physical properties

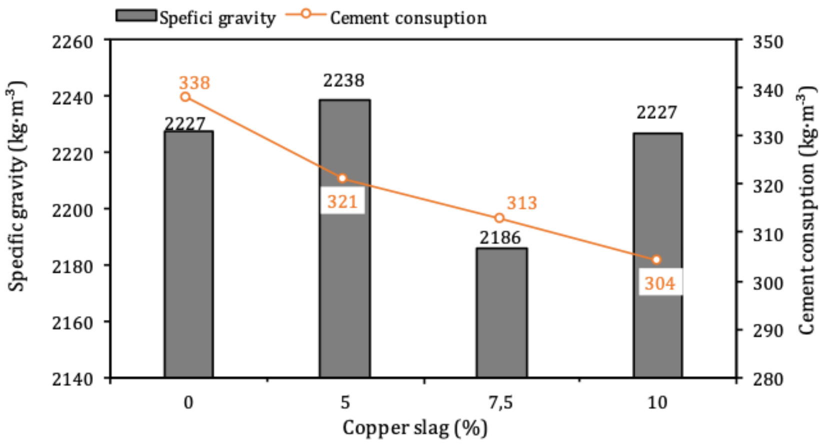
The Figure 3 presents the results of concrete fresh state, cement consumption and specific gravity. In general, as higher the slag in the mixture, also due the higher w/c ratio, higher was the workability for the concretes (Figure 3 (a)). The BCS promoted significant spreads in the consistency of the concrete for all evaluated percentages, going from 8 cm (REF) to 20 cm in the workability when 10% BCS replaced cement.

It may be due to the spherical shape of the grains with a glassy surface [20], that results in a higher packing and dispersion effect [21, 22]. Similar to add and spherical sand to the concrete, that improves the rolling of the aggregates [23]. In parallel, a lower water retention due the less amount of the cement in the mixture. This results in more water available in the mixture to lubricate the aggregates, promoting more workability [2, 7, 8].

These results agree with the literature incorporating copper slag in concrete [4, 7, 8]. In the specific case of using blasted copper slag, Dos Anjos et al. [2] report significant improvements in the plasticity and cohesion of the concrete in the fresh state when replacing fine natural aggregate in proportions above 20%. So, dispensing it with the amount of water previously necessary to make the mixture. This behavior is essential for both fresh and hardened states because it can promote reductions in superplasticizer content and its possible effects of delaying the setting time. Increases in mechanical strength can also be achieved due to possible reductions in the water-cement ratio for concretes with similar workability [24].



(a)



(b)

Figure 3: Fresh and physical properties of the concretes: Workability in (a); Specific gravity and cement consumption in (b).

Other factor resulted due the slag incorporation is impact in the cement consumption. Is possible to note that as higher the slag amount, lower is the cement consumption. Achieved with lower values up to 34 $kg{\cdot}m^{-3}$ were obtained (Figure 3 (b)). However, the specific gravity is no direct dependent of the cement consumption, where the REF and 10% series presented similar specific gravity. This may be due the air incorporation in the mixture, that is affected by the powders added to cementitious matrixes [25].

3.2 Durability: Total water absorption and capillarity absorption

In the Figure 4 is presented the total water absorption by immersion of the concretes at 28D. In general, all the slag-added series presented lower values of water absorption in comparison with REF series. Nevertheless, the results of water absorption do not present a tendency, where the low amount of slag is achieved with 5% and then the values growth until 10%, value similar to REF series. This may be due the blasting copper slag incorporation did not significantly change the specific gravity of the samples, as presented in Figure 3 (b). In one way, this allowing its application without increasing the weight of the structure. One explanation is that both filler and tortuosity effects can interfere, and here there are a difference of filler between the samples, then the water percolation needs to seepage through more tortuous paths due to the barriers imposed by the BCS grains [7, 26]. A future better understanding is needed about possible actions of the BCS in hydration of the Portland cement and microstructural changes. There is a combination between the fines and the compaction of concrete when replacing fine aggregate with blasting copper slag after in proportion [2].

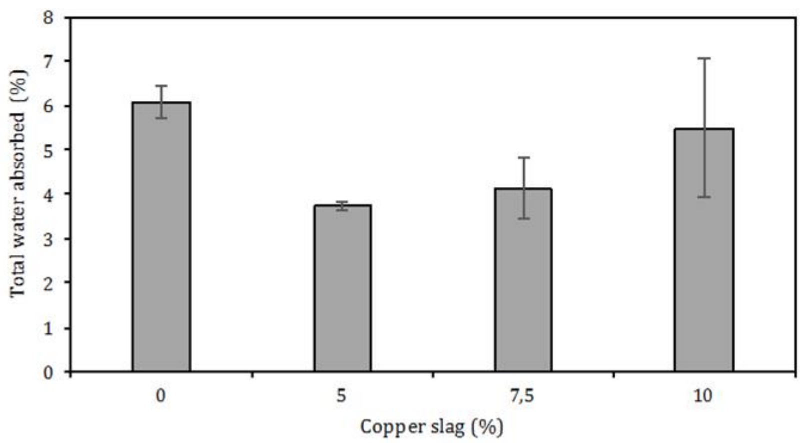


Figure 4: Total water absorption by immersion of concretes with 0%, 5%, 7.5% and 10% copper slag amount at 28D.

In the Figure 5 is presented the water absorption by capillarity of the concretes. In general, BCS-added concretes presented more water absorption by capillarity than ref series. Greater capillarity is expected slag-slag added concrete due the lower cement consumption, this leads to a more interconnected pores, impacting the cohesion and adhesion forces between water particles and concrete pores. For until 24 hours, all the slag-added concretes presented absorption higher than REF [27]. However, for 48 and 72h the 5 and 10% slag-added series presented lower values of water absorption, suggesting that the copper slag improved the cementitious matrix. This may be attributed to the higher specific gravity of this samples, that are similar or higher than REF series (Figure 3 (b)) [28].

The concrete series with 7.5% of BCSR may have a poor granular packing that leads to the lowest compactness and densification of the matrix, resulting in the higher water absorption, in comparison with the series studied. Although the reference specimens absorbed less water in the first times, is verified an upward trend in absorption until the end of the test. The final lowest capillary water absorptions occurred for concrete specimens with 5% and 10% BCRS, contributing to the durability of concrete in severe environments. The geometry of the BCR associated with its capacity to fill empties and its high density could provide densification in the concrete matrix [7].

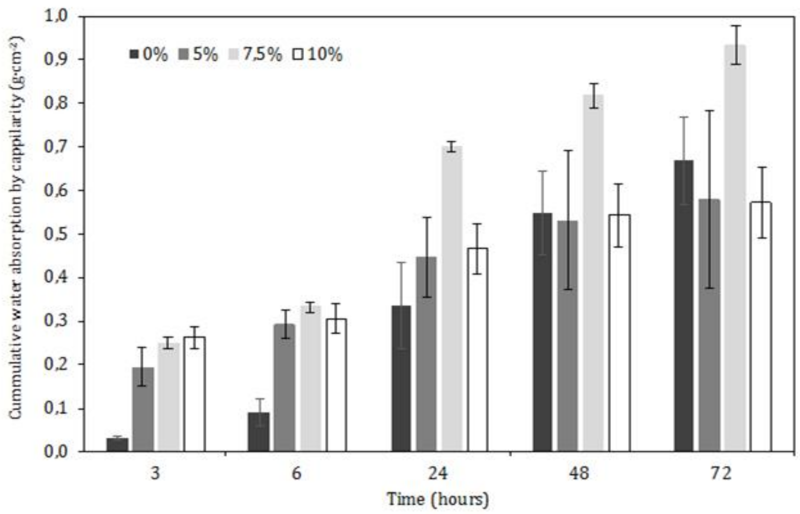


Figure 5: Capillary water absorption of concretes when cement was replaced by RECPJ at 0%, 5%, 7.5% and 10%, at 28 days.

In the Figure 6 is presented the correlation of the cement consumption and total water absorption and capillarity absorption. In general, as the higher was the cement consumption, the lower was the absorption by capillarity and the total water absorption. However, for total water, the reduction of water absorption is more effective for until 7.5%, from this amount of cement replacement, the matrix presented a lower capacity to improve the durability by water penetration [27].

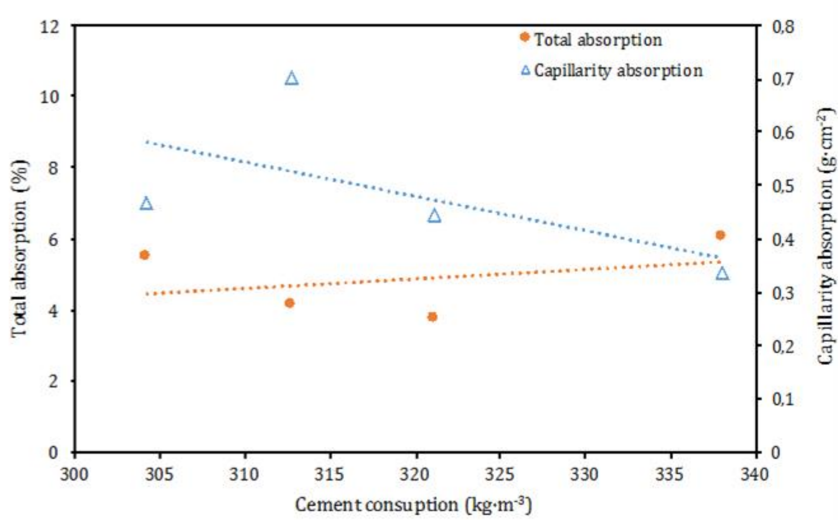


Figure 6: Correlation between cement consumption x total water absorption and capillarity absorption by immersion

3.3 Hardened state

Figure 7 presents the compression strength of the modified BCS-concretes with 0%, 5% and, 7.5% and 10% that were performed at 7, 28 and 63 days, achieving strengths higher than the expected 30 MPa at 63D, attributed due to its filer effect. In general, all samples presented lower strength as higher the slag amount in the mixture. In other hand, the 5% series presented similar behavior in comparison with REF series. At 7 days, there were the highest lost in strength (26.7% in average), due the lower cement amount as higher the slag presence. With lower cement and a power that do not react in lower ages, the strength tends to be more affected than in longer ages. At 28 and 63 days, the strength of the slag-added concretes lost lower strength in comparison with REF series (17.8% in average for 63 days) [29].

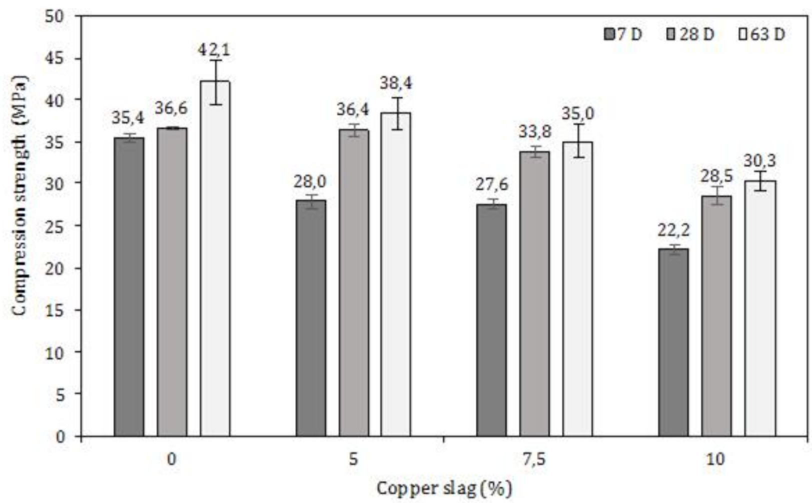


Figure 7: Compressive strength of concretes with 0, 5, 7.5 and 10% of cement replacement by BCS, at 7, 28 and 63 D.

Although acceptable strength values (28.52 MPa) could also be obtained when the BCSR replaced 10% cement, strengths can still be improved by reducing the used water/cement ratio due to spread consistencies. In this way, performance can grow up and exceed the minimum valued strengths at 28 days. Losses can be directly associated with the cement removal in more significant amounts since it has binder properties in the mixture [30, 31].

As can be seen in Figure 7, distinct improvements were achieved along the time (7 - 28, and 7 - 63 days) when BCS is present or not. Then, pozzolanic reactions, C-S-H nucleation effects, or new distinct phases can occur due to the presence of the BCS filler. Future tests are necessary to monitor the hydration reactions over time, both in early and advanced ages. Different replacement of the cement mass by BCS is also suggested.

The Figure 8 presents the binder index of the concrete mixtures produced at 7, 28 and 63D of cement hydration. Is possible to note that the higher the time of cement hydration, lower was the binder index, this is expected once the higher is the strength of the composite. Mainly due the loss in the binder capacity as higher the slag amount in the mixture. Also, is noted that in higher ages of hydration, the BCS-concrete presented a similar binder index compared to REF series. This is due the lower amount of cement consumption by volume, even showing lower strength in this added mixtures. This behavior similar to ref series is associated to a higher cement efficiency hydration [32]. This means that the amount of the cement present in the mixture was hydrated in higher degree than no-added series.

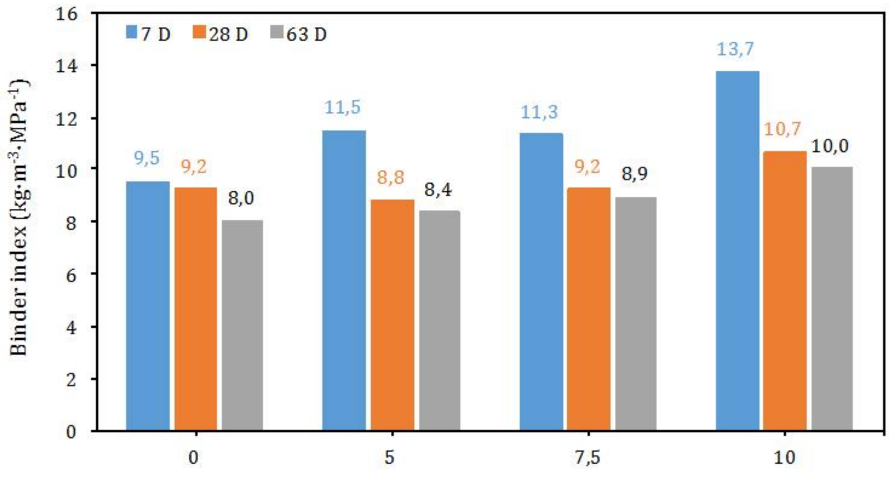


Figure 8: Binder index of the concretes (values lower than reference is better).

4. CONCLUSIONS

Considering the results obtained in the research, the incorporation of blasted copper slag replacing the cement in concrete is a viable alternative. The BCS discard in the environment is reduced, as well as the use of cement minimized. Based on the laboratory test results, the following conclusions were drawn:

There was a progressive increase in workability for concretes with blasted copper slag (BCSR), acting as a kind of natural plasticizer.

Replacement of cement by BCSR up to 7.5% did not significantly affect compressive strengths, keeping then into the original design of 30 MPa concretes at 28 days. Otherwise, the strength was reduced by about 4.94% when the cement replacement was increased by 10% replacement. However, this can be circumvented with reductions in the water-cement ratio, since the fresh state's properties allow such a reduction.

The replacement of cement by the BCSR did not significantly increase the specific mass regardless of the content. The standard deviation for all samples with replacement between 0 and 10% was 8.97 kg/m³.

Regardless of the absorption by total immersion, modified 5% and 7.5% BCSR-concretes showed better performances. Also, concretes containing 5 and 10% of BCSR performed well in capillarity absorption, with a reduction in total absorption of 63.14% and 31.69%, respectively, compared to standard concrete.

Was possible to note that the 5 to 7% of cement replacement by BCS is efficient in was of cement hydration efficiency.

Finally, the results of this study contribute to increasing recycling rates of BCS, using them in cementitious matrixes with-out losing their final properties. However, more research should be made for copper slag addition or field storage. This material is a waste and has to be investigated by leaching and other complexes processes among additional chemical reactions between the environment and the cementitious matrix.

5. ACKNOWLEDGMENT

The authors would like to acknowledge the Laboratory of Civil Construction and Structures of the Federal University of Pernambuco for the support during the experimental program. We also would like to acknowledge the Brazilian governmental research agencies Coordination for the Improvement of Higher Education Personnel (CAPES) and the National Council for Scientific and Technological Development (CNPq) for the financial support to laboratories involved in the research.

6. REFERENCES

[1] AGN ABRASIVOS, A Escória Granulada - http://agnabrasivos.com.br/a-escoria-granulada/, 2019.

[2] DOS ANJOS, M.A.G., SALES, A.T.C., ANDRADE, N., "Blasted copper slag as fine aggregate in Portland cement concrete", *Journal of Environmental Management*, v. 196, pp. 607-613, 2017.

[3] AL-JABRI, K.S., AL-SAIDY, A.H., TAHA, R., "Effect of copper slag as a fine aggregate on the properties of cement mortars and concrete", *Construction and Building Materials*, v. 25, n. 2, pp. 933–938, 2011.

[4] AL-JABRI, K.S., HISADA, M., AL-ORAIMI, S.K., *et al*., "Copper slag as sand replacement for high performance concrete", *Cement and Concrete Composites*, v. 31, n. 7, pp. 483-488, 2009.

[5] RESENDE, C.M.A., *Estudo da viabilidade de incorporação de escória de cobre como agregado fino em produtos de construção*, B.m., Universidade do Porto, 2009.

[6] NAJIMI, M., SOBHANI, J., POURKHORSHIDI, A.R., "Durability of copper slag contained concrete exposed to sulfate attack", *Construction and Building Materials*, v. 25, n. 4, pp. 1895-1905, 2011.

[7] MOURA, W.A., MOLIN, D.C.C.D., "Influência da adição de escória de cobre em características relacionadas à durabilidade do concreto", *Ambiente Construído (Online)*, 2004.

[8] WU, W., ZHANG, W., MA, G., "Optimum content of copper slag as a fine aggregate in high strength concrete", *Materials and Design*, v. 31, n. 6, pp. 2878-2883, 2010.

[9] SHI, C., MEYER, C., BEHNOOD, A., Utilization of copper slag in cement and concrete, 2008.

[10] ARINO, A.M., MOBASHER, B., "Effect of ground copper slag on the strength, and toughness of cementations mixtures", *ACI Materials Journal*, v. 96, n. 1, pp. 68-75, 1999.

[11] AENOR., Asociación Española de Normalización y Certificación - UNE-EN 197-1 - Cemento - Parte1: Composición, especificaciones y criterios de conformidad de los cementos comunes, 2011.

[12] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, NBR 16697 - Cimento Portland – Requisitos, 2018.

[13] HELENE, P., TUTIKIAN, B.F., "Dosagem dos Concretos de Cimento Portland", In: Concreto: Ciência e Tecnologia, São Paulo, Brasil: Ibracon, 2011.

[14] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, NBR 12655 - Concreto de cimento Portland- Preparo, controle e recebimento – Procedimento, 2015.

[15] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, NBR 5738 - Concreto - Procedimento para moldagem e cura de corpos de prova, 2016.

[16] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, NBR 67 - Concreto - Determinação da consistência pelo abatimento do tronco de cone, 1998.

[17] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, NBR 5739 - Concreto - Ensaio de compressão de corpos de prova cilíndricos, 2018.

[18] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, NBR 9779 - Argamassa e concreto endurecidos - Determinação da absorção de água por capilaridade, 2012.

[19] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS, NBR 9778 - Argamassa e concreto endurecidos - Determinação da absorção de água, índice de vazios e massa específica, 2005.

[20] JOCHEM, L.F., CASAGRANDE, C.A., ONGHERO, L., *et al.*, "Effect of partial replacement of the cement by glass waste on cementitious pastes", *Construction and Building Materials*, p. 121704, 2020.

[21] JOCHEM, L.F., CASAGRANDE, C.A., ROCHA, J.C., "Effect of lead in mortars with recycled aggregate and lightweight aggregate", *Construction and Building Materials*, v. 239, p. 117702, 2020.

[22] CASAGRANDE, C.A., REPETTE, W.L., HOTZA, D., "Effect of environmental conditions on degradation of NOx gases by photocatalytic nanotitania-based cement mortars after long-term hydration", *Journal of Cleaner Production*, v. 274, p. 123067, 2020.

[23] MATOS, P.R., PILAR, R., CASAGRANDE, C.A., *et al*., "Comparison between methods for determining the yield stress of cement pastes", *Journal of the Brazilian Society of Mechanical Sciences and Engineering*, pp. 1–13, 2019.

[24] JOCHEM, L.F., APONTE, D., BIZINOTTO, M.B., *et al*., "Effects of pre-wetting aggregate on the properties of mortars made with recycled concrete and lightweight aggregates", *Matéria (Rio de Janeiro)*, v. 24, n. 2, 2019.

[25] CASAGRANDE, C.A., JOCHEM, L.F., ONGHERO, L., *et al*., "Effect of partial substitution of superplasticizer by silanes in Portland cement pastes", *Journal of Building Engineering*, v. 29, p. 101226, 2020.

[26] JOCHEM, L.F., ROCHA, J.C., CHERIAF, M., "The Influence of Fine Sand from Construction-Demolition Wastes (CDW) in the Mortar Properties", *Key Engineering Materials*, v. 600, pp. 357–366, 2014.

[27] CASAGRANDE, C.A., SANTOS, D.D., JOCHEM, L.F., *et al*., "Evaluation of coppe slag as aggregate addition on properties of cementitious matrix", *Matéria (Rio de Janeiro)*, v. 25, n. 4, 2020.

[28] CASAGRANDE, C.A., JOCHEM, L.F., REPETTE, W.L., *et al*., "Evaluation of nano-TiO2 on properties of cementitious mortars", *Matéria (Rio de Janeiro)*, v. 25, n. 4, 2020.

[29] MAHARISHI, A., SINGH, S.P., GUPTA, L.K., *et al*., "Strength and durability studies on slag cement concrete made with copper slag as fine aggregates", *Materials Today: Proceedings*, v. 38, pp. 2639–2648, 2021.

[30] BHOI, A.M., PATIL, Y.D., PATIL, H.S., *et al*., "Feasibility Assessment of Incorporating Copper Slag as a Sand Substitute to Attain Sustainable Production Perspective in Concrete", *Advances in Materials Science and Engineering*, v. 2018, pp. 1–11, 2018.

[31] RAMAN, J.V.M., RAJESH, R., VELSWARAN, P.S., "Study on Strength of High Performance Concrete by Partial Replacement of Fine Aggregate by Copper Slag", *International Journal of Applied Engineering Research*, v. 14, n. 11, pp. 2795–2798, 2019.

[32] DE MATOS, P.R., PRUDÊNCIO JR., L.R., PILAR, R., *et al*., "Use of recycled water from mixer truck wash in concrete: Effect on the hydration, fresh and hardened properties", *Construction and Building Materials*, v. 230, p. 116981, 2020.

ORCID

Cézar Casagrande	https://orcid.org/0000-0002-4293-6574
Lidiane Jochem	https://orcid.org/0000-0001-6679-2897
Ana Cecília	https://orcid.org/0000-0003-1118-1911
Érika Marinho	https://orcid.org/0000-0001-7405-0877
Felipe Alves	https://orcid.org/0000-0002-0929-0601