Original Article

Developing a one-part geopolymer cement containing iron ore tailings from Minas Gerais state in Brazil

Ana Beatriz Moreira Silveira [1*]
Douglas Batista Mazzinghy [2]
Ricardo Augusto Martins Figueired [3]

Abstract

The growing perspective of mining tailings volume worldwide takes to a necessity of developing sustainable solutions to apply the concept of circular economy. Meanwhile, ordinary Portland cement (OPC) is the most consumed construction material globally, and its considerable CO_2 emission abundantly contributes to greenhouse effect. Geopolymers are environmentally friendly materials that can be used as a sustainable alternative to OPC. This study proposes the development of a geopolymer cement containing iron ore tailings (IOT) and investigates the influence of the water/solid (W/S) ratio on their uniaxial compressive strength (UCS). The best result had a W/S ratio of 0.37 and achieved strength of 62.7 MPa after 28 days curing at room temperature, which is considerable higher than the required in the worldwide OPC standards. Also, the binder in this study has higher compressive strength after one day of cure than the regular OPC should have in 28 days of cure, showing high early strength. The result can be optimized for better economic viability in the future and shows that IOT has potential to be applied as filler in geopolymer cements.

Keywords: Iron ore tailings; Geopolymer; Sustainability; Greener cement; Circular economy.

Desenvolvimento de cimento geopolimérico de uma parte contendo rejeitos de minério de ferro do estado de Minas Gerais no Brasil

Resumo

A perspectiva de crescimento do volume de rejeitos de mineração em todo o mundo leva à necessidade de desenvolver soluções sustentáveis, de forma a aplicar o conceito de economia circular. Enquanto isso, o cimento Portland comum é o material de construção mais consumido globalmente e sua considerável emissão de CO_2 contribui abundantemente para o efeito estufa. Os geopolímeros são materiais ecologicamente corretos que podem ser usados como uma alternativa sustentável ao cimento Portland comum. Este estudo propõe o desenvolvimento de um cimento geopolimérico contendo rejeito de minério de ferro e investiga a influência da razão água/sólido na sua resistência à compressão uniaxial. O melhor resultado teve razão água/sólido de 0,37 e atingiu resistência de 62,7 MPa após 28 dias de cura em temperatura ambiente, sendo consideravelmente mais alto do que o exigido pelos padrões internacionais para o cimento Portland comum. Além disso, o cimento neste estudo apresenta maior resistência à compressão após um dia de cura do que o Portland comum deveria ter em 28 dias de cura, apresentando alta resistência inicial. O resultado pode ser otimizado para uma melhor viabilidade econômica no futuro e mostra que os rejeitos de minério de ferro têm potencial para serem aplicados como material de enchimento em cimentos geopoliméricos.

Palavras-chave: Rejeitos de minério de ferro; Geopolímero; Sustentabilidade; Cimento verde; Economia circular.

1 Introduction

Over the years, a naturally drop in the number of new mineral deposits discoveries occurs. In addition, with the advancement of mineral exploration, there is a tendency of the available resources and reserves to decrease in terms of quality and ore contents, and consequently have higher waste/ore ratio. Also, on a global scale demand for the products

[1]*Departamento de Engenharia de Minas, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil.*
[2]*Programa de Pós-Graduação em Engenharia Metalúrgica, Materiais e de Minas, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil.*
[3]*Agência Nacional de Mineração, Belo Horizonte, MG, Brasil.*

**Corresponding author: anabmsilveira@gmail.com*

of the extractive industries is ever increasing. Extraction of the targeted resource results in the concurrent production of a significant volume of waste material, including tailings. As a result, the volume of mining tailings production is increasing, and most of them end in dam tailings, a worldwide used method for tailings disposal, which can fail, ensuing to environmental, human health and economic impacts [1].

Every 30 years, dams and mining pits worldwide have increased 10 times in volume and doubled in height. This rate grows exponentially, as shown in Figure 1. Currently, about 670,000 tons are generated per day and the expectation is that the mineral sector is going to generate approximately 1 million tons per day of tailings by 2030 [2].

The World Mine Tailings Failures (WMTF) database, which includes data for more than 100 years (1915 to 2019), comprises 356 records of disasters involving mining dams. The two most serious incidents involving mining dams in the 21st century took place in Brazil in the end of 2015 and beginning of 2019. Since they derived from mining production and tailings disposal processes, they can be primarily categorized as work accidents (WA) with impacts extending in space (hundreds of kilometers away from the event site) and time (i.e., ecological changes and contaminations which effects might last years and even decades). For these reasons they are also known as major accidents (MA). Moreover, for disrupting everyday life - with considerable (material, economic and environmental) damage, losses and impact on the health of the local populations, inasmuch as they surpass the response capacity of the directly involved communities, counties and regions - this type of accidents are also rated as disasters [3].

Therefore, it is a critical practice to store the tailings in ponds or impoundments behind dams. However, tailings dams can fail, resulting in the discharge of significant quantities of tailings into the natural environment, thereby causing grievous casualties and serious economic losses [4]. In the face of this scenario, it is necessary to create sustainable solutions to deal with all this volume of mining tailings, in which civil construction would have potential applications to sensibly take advantage of it.

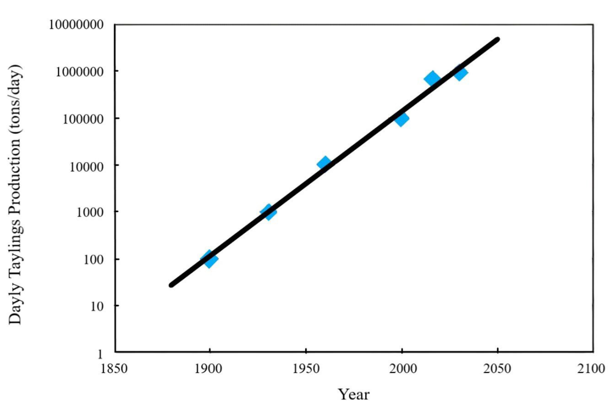

Figure 1. Tailings production rate evolution in the world [4].

Portland cement nowadays is the most-consumed construction material worldwide [5]. The manufacture of Portland cement used in the production of concrete emits large amounts of CO_2 into the atmosphere, contributing to the increase of the greenhouse effect. The environmental impact generated by the mineral exploitation activity is a problem of easy verification, especially in open pit mines [6]. Consequently, the development of alternative low-carbon binders is recognized as one option to reduce CO_2 emissions and geopolymers are promising materials in this regard [7].

The term 'geopolymer' was coined in the 1970s by the French scientist Joseph Davidovits and applied to a class of solid materials synthesized by the reaction of an aluminosilicate powder with an alkaline solution [8]. The reaction mechanism of geopolymer or geopolymerization is an exothermic phenomenon due to polycondensation. Initially the dissolution of Al and Si in alkaline medium occurs, with the formation of aluminate and silicate species until the equilibrium of this reaction is reached. The high pH of the solution, concomitant with the presence of the then dissolved species, favors the formation of a matrix gel, and given the exothermic nature of the reaction, as water is released, it becomes a three-dimensional network of silica-aluminate structure, and with the spatial reorganization of this gel, it reaches the hardening or polymerization step [9]. The geopolymerization process is shown in Figure 2.

Every year, the intense industrial and mining activities around the world generate large quantities of wastes, which pose several difficulties and concerns in their treatment and disposal. Therefore, product and waste management (including the reuse, recycling, and valorization of wastes and by-products) has recently become a cost-effective solution to transform high volume, low quality, zero or low-cost materials into high-value products, with a view to improving circular economy [11,12].

Geopolymers are a sustainable and environmentally friendly replacement for ordinary Portland cement as they lead to a reduction in carbon footprint [13]. This study proposes the development of a geopolymer cement containing iron ore tailings as a sustainable alternative for the OPC and investigates the influence of water/solid ratio on their compressive strength resistance.

2 Experimental procedure

Traditional two-parts methodology comprehends a solid precursor plus an alkaline solution, which is less practical in many applications [14]. On the other hand, one-part (or just add water) involves a dry mix that consists of a solid aluminosilicate precursor, a solid alkali source, and possible admixtures to which water is added, similar to OPC preparation [2]. Hence, the one-part method is more potentially capable of competing on an equal footing with Portland cement technology [14]. The geopolymers in this study were prepared by one-part methodology and the water/solid ratio (W/S) varied between 0.37 and 0.43. Figure 3 shows the experimental procedures done in this study.

2.1 Materials

The precursor used in this study was a commercial metakaolin (MK). The solid activators used were Micro Pearl sodium hydroxide (NaOH, purity ≥ 97%) and sodium silicate powder (Na_2O = 25.28% and SiO_2 = 53.35%). The filler used was iron ore tailings (IOT) from flotation process, from Minas Gerais state in Brazil.

2.2 Mix proportions and procedures

The formulation of the geopolymer in this study was obtained through previous exploratory tests, where the quantities of the materials used are shown in Table 1. These tests also led to the production of 3 tests varying the W/S ratio in 0.37, 0.40 and 0.43, due to flowability. First, precursor and activators were mixed. Then, water was added and it was mixed for 2.5 min in mechanical mixer, and then the filler was added, and it kept mixing for more 7.5 min.

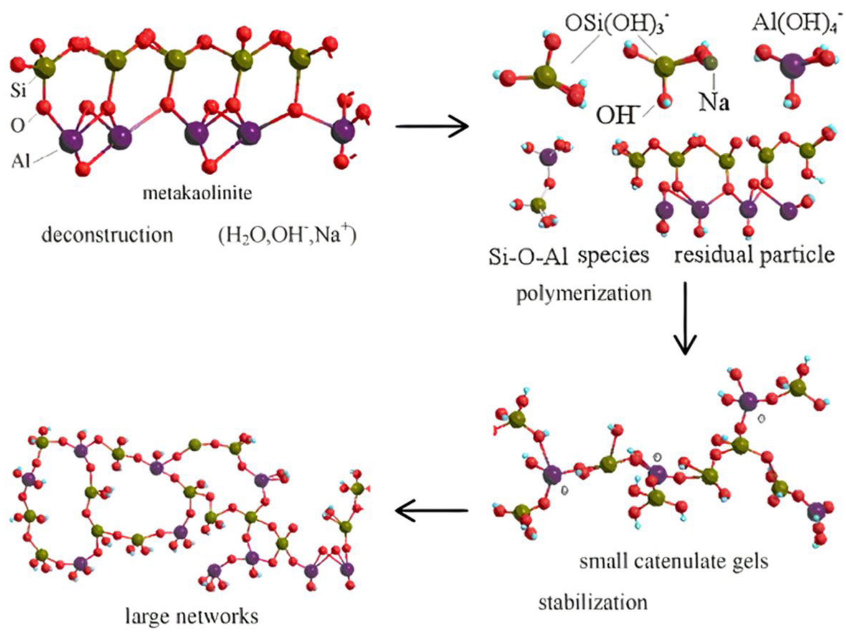

Figure 2. Sketch of the geopolymerization process, including the deconstruction of metakaolinite (MK) by alkalination, the polymerization of generated alumina/silica-hydroxy species and the stabilization of fresh formed structures [10].

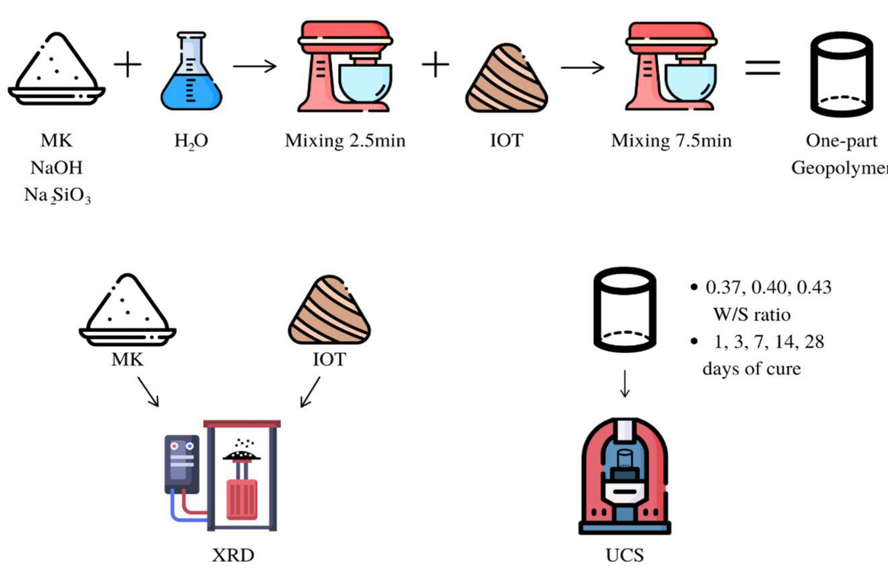

Figure 3. Experimental procedure.

3 Results and discussion

The chemical composition of precursor and filler are listed in Table 2. These materials were also characterized through X-ray diffractometry (XRD) with a PANalytical X'Pert APD diffractometer using copper radiation (CuKα) before the reaction and are shown in Figures 4 and 5. In Figure 5, precursor presented a majority of amorphous phase, although also presented minor amounts of crystalline species such as quartz, feldspar, muscovite and kaolinite, the latter indicating incomplete dihydroxylation of the original kaolin. While in Figure 5, filler's main crystalline peaks are quartz, hematite, and goethite.

Uniaxial compressive strength tests were performed with cylindrical specimens of dimensions 21 x 42 mm at 1, 3, 7, 14 and 28 days of cure in room temperature. In total, 6 specimens per day of test were produced per test and the results shown are the average of the results. Figure 6 and Table 3 present compressive strength of the 3 tests between 1 and 28 days.

Table 1. Formulation of geopolymers considering weight proportions

Formulation	Dosage	Molar ratio
IOT	50%	**SiO_2 / Al_2O_3**
MK	35%	2.96
Na_2SiO_3	12%	**Na_2O / SiO_2**
NaOH	3%	0.20

Table 2. Chemical analysis of metakaolin (MK) and iron ore tailings (IOT) [15, 16, 17]

Material	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3
MK (%)	55.4	42.3	0.4	0.5	0.1	0.2	0.7	0.1	0.1
IOT (%)	76.3	0.2	22.6	0.1	0.4	0.1	-	-	0.1

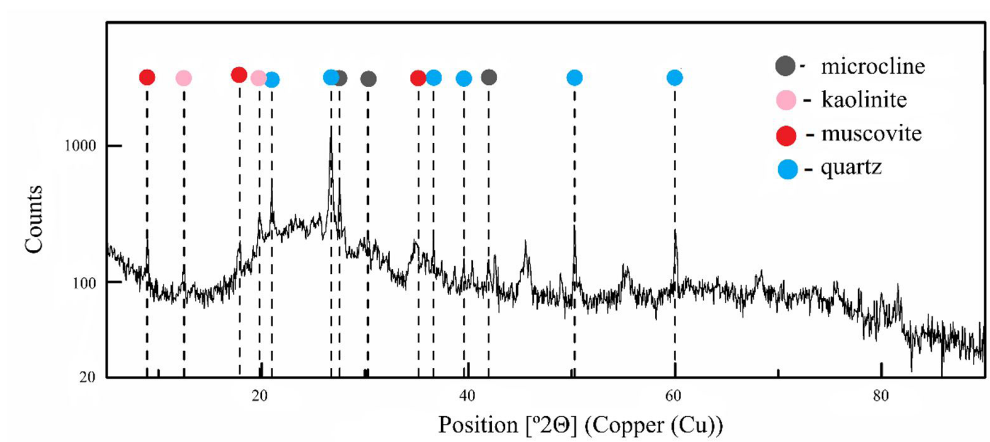

Figure 4. X-ray diffraction pattern of metakaolin (MK).

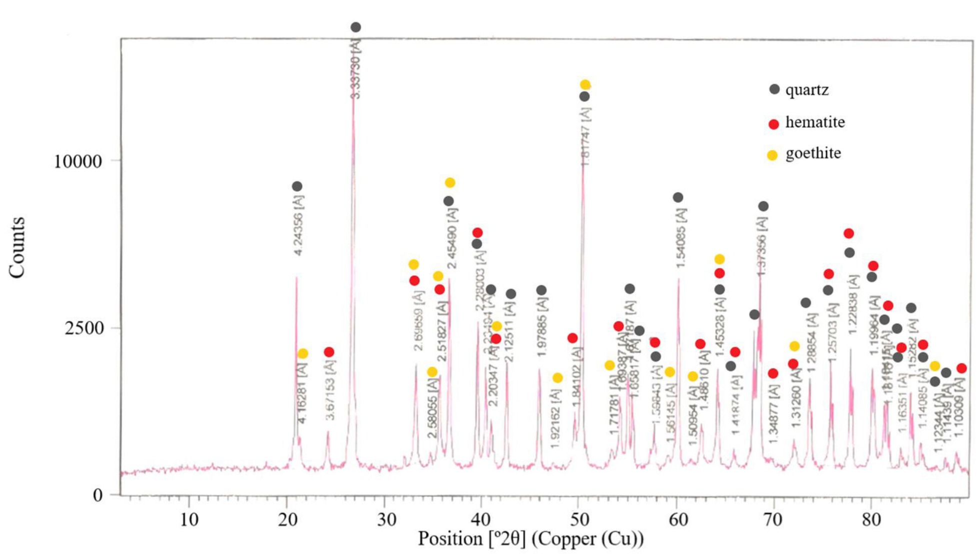

Figure 5. X-ray diffraction pattern of iron ore tailings (IOT).

Table 3. Results of uniaxial compressive strength tests

Test W/S ratio	Compressive Strength (MPa)				
	1 day	3 days	7 days	14 days	28 days
0.37	43.8	46.5	53.4	57.0	62.7
0.40	32.8	38.1	43.5	46.5	49.6
0.43	27.8	37.4	39.5	44.0	45.5

Table 4. American, Brazilian and European Standards for Ordinary Portland Cement (OPC)

Standard	Class	Compressive Strength		
		3 days	7 days	28 days
American - ASTM C 150 [15]	25	10	17	28
Brazilian - ABNT NBR 16697 [16]	32	10	20	32
European - EN-197-1 [17]	40	10	16	32.5

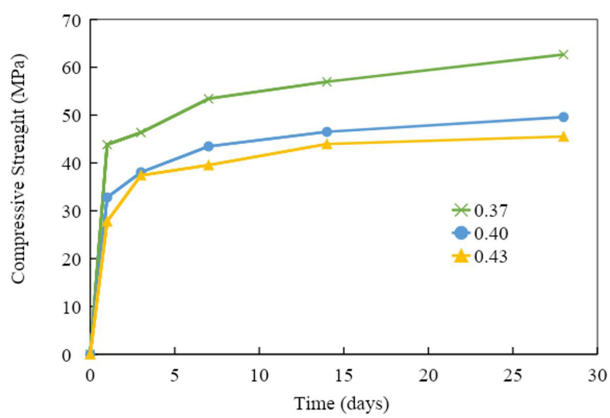

Figure 6. Compressive strength (MPa) x time (days) of 3 tests varying W/S ratio.

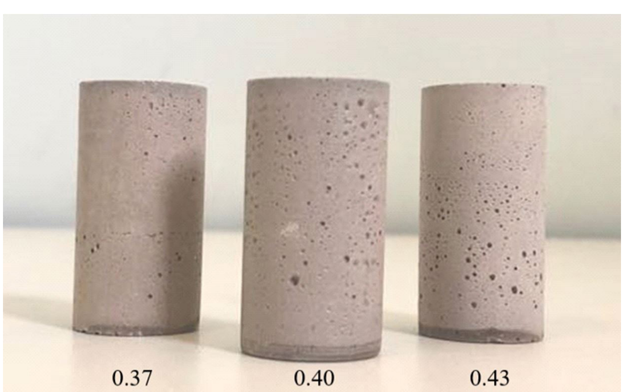

Figure 7. 0.37, 0.40 and 0.43 specimens, respectively, at 28 days.

Figure 7 shows the specimens at 28 days. It is worth mentioning that although IOT have a reddish coloration, the specimens have a color similar to that of the OPC. Also, the lower the W/S ratio, the less porous the specimens are.

There is a tendency to increase the efficiency of the cement reaction as the water dosage decreases, until a certain point, due to flowability. The test that has lower W/S ratio (0.37) presented the best result: 62.7 MPa at 28 days, which is significantly higher when compared to the other tests (49.6 MPa and 45.5 MPa at 28 days). Therefore, in this case, the higher the W/S ratio, the lower the geomechanical quality of the binder. According to the American, Brazilian and European Standards for OPC, cement should have the compressive strength patterns shown in Table 4, which are lower than the ones achieved in this study.

4 Conclusion

This study proposed a sustainable alternative for ordinary Portland cement (OPC), which would be an appropriate way to deal with current volume and tailings disposal issues. All the tests fit satisfactorily current OPC standards for compressive strength. The formulation considered the following weight proportions: 50% of IOT, 35% of MK, 12% of Na_2SiO_3 and 3% of NaOH. The best result had a W/S ratio of 0.37 and achieved 62.7 MPa of compressive strength at 28 days. Besides exceeding the minimum value of all the analyzed standards, the results showed that the binder proposed in this study has shorter cure time capacity (46.3 MPa at 3 days versus 10 MPa at 3 days for OPC), and this could be studied for other industrial and civil construction applications that require high early strength cements.

As suggestions for future research, tests could be done to ensure compressive strength will not decrease in time longer than 28 days. Also, economic evaluation of the formula compared to OPC could be done, and even an optimization of the formula to make it more economically viable, however keeping standards compliance.

Acknowledgements

Errol Flynn da Silveira and Professors Roberto Galery, Maria Teresa Paulino Aguilar and Paulo Roberto Brandão are thanked for their support in this work.

References

1 Kossoffab D, Dubbinb WE, Alfredsson M, Edwards SJ, Macklin MG, Hudson-Edwards KA. Mine tailings dams: Characteristics, failure, environmental impacts, and remediation. Applied Geochemistry, Elsevier. 2014;51:229-245. http://dx.doi.org/10.1016/j.apgeochem.2014.09.010.

2 Lyu Z, Chai J, Xu Z, Qin Y, Cao J. A comprehensive review on reasons for tailings dam failures based on case history. Advances in Civil Engineering. 2019;2019: 4159306 . http://dx.doi.org/10.1155/2019/4159306.

3 ÁVILA, J. A disposição de rejeitos sem barragens. 2011. VII Congresso Brasileiro de Geotecnia Ambiental (REGEO 2011). 21 a 24 de novembro de 2011, UFMG, Belo Horizonte, Minas Gerais, Brasil.

4 Freitas CM, Silva MA. Work accidents which become disasters: mine tailing dam failures in Brazil/Acidentes de trabalho que se tornam desastres: os casos dos rompimentos em barragens de mineracao no Brasil. Revista Brasileira de Medicina do Trabalho. 2019;17(1):21-29.

5 Bastos G, Patiño-Barbeito F, Patiño-Cambeiro F, Armesto J. Admixtures in cement-matrix composites for mechanical reinforcement, sustainability, and smart features. Materials. 2016;9(12):972. http://dx.doi.org/10.3390/ma9120972.

6 Magalhães LF, de Souza Morais I, dos Santos Lara LF, de Resende DS, Menezes RMRO, Aguilar MTP, et al. Iron ore tailing as addition to partial replacement of portland cement. Materials Science Forum. 2018;930:125-130. http://dx.doi.org/10.4028/www.scientific.net/msf.930.125.

7 Luukkonen T, Abdollahnejad Z, Yliniemi J, Kinnunen P, Illikainen M. One-part alkali-activated materials: a review. Cement and Concrete Research, Elsevier. 2018;103:21-34. http://dx.doi.org/10.1016/j.cemconres.2017.10.001.

8 Davidovits J. Geopolymer chemistry and applications. 2nd ed. Saint-Quentin, France: Institut Géopolymère; 2008.

9 Pinto AT. Binding Systems Obtained by Alkali Activation of Metakaolin/Sistemas ligantes obtidos por activação alcalina de metacaulino [doctoral thesis]. Portugal: Universidade do Minho; 2004.

10 Yao X, Zhang Z, Zhu H, Chen Y. Geopolymerization process of alkali–metakaolinite characterized by isothermal calorimetry. Thermochimica Acta, Elsevier. 2009;493(1-2):49-54. http://dx.doi.org/10.1016/j.tca.2009.04.002.

11 Saeli M, Tobaldi DM, Seabra MP, Labrincha JA. Mix design and mechanical performance of geopolymeric binders and mortars using biomass fly ash and alkaline effluent from paper-pulp industry. Journal of Cleaner Production, Elsevier. 2019;208:1188-1197. http://dx.doi.org/10.1016/j.jclepro.2018.10.213.

12 Figueiredo RAM, Silveira ABM, Melo ELP, Costa GQG, Brandão PRG, Aguilar MTP, et al. Mechanical and chemical analysis of one-part geopolymers synthesised with iron ore tailings from Brazil. Journal of Materials Research and Technology, Elsevier. 2021;14:2650-2657. http://dx.doi.org/10.1016/j.jmrt.2021.07.153.

13 Oderji SY, Chen B, Ahmad MR, Shah SFA. Fresh and hardened properties of one-part fly ash-based geopolymer binders cured at room temperature: Effect of slag and alkali activators. Journal of Cleaner Production, Elsevier. 2019;225:1-10. http://dx.doi.org/10.1016/J.JCLEPRO.2019.03.290.

14 Provis JL, van Deventer JSJ. Geopolymers: structure, processing, properties and industrial applications. Cambridge: Woodhead Publishing Limited; 2009.

15 American Society for Testing and Materials. ASTM C150: standard specification for portland cement. West Conshohocken: ASTM; 2017.

16 Associação Brasileira de Normas Técnicas. ABNT NBR 16697: Cimento Portland — Requisitos. Rio de Janeiro: ABNT; 2018.

17 European Committee for Standardization. EN-197-1: Cement - Part 1: Composition, specifications and conformity criteria for common cements. Brussels: CEN; 2011.

Received: 12 Jan. 2021
Accepted: 9 Oct. 2021