Effect of elevated temperatures on alkali-activated tungsten mining waste based materials

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Abstract. Generally, alkali-activated materials (aka geopolymers) present good behaviour at high temperatures, but previous studies of geopolymers under elevated temperatures are, in most cases, focused on metakaolin or fly ash based geopolymers, making the information on geopolymers with mining waste mud almost inexistent. In this paper, were analysed geopolymers with different combinations of mining waste mud, waste glass powder, metakaolin and expanded cork in a total of 15 different mixtures using sodium hydroxide and sodium silicate as alkaline activators. Materials particle size used is under 500 µm for mining waste mud, waste glass powder. Some mixtures also included expanded granulated cork with particle size between 2 to 4 mm. Ten samples with 40 x 40 x 40 mm dimensions were used for the compression test, one sample for the TGA test, and one cube (100 x 100 x 60 mm) with a frustoconical hole (50 mm deep) and a 100 x 100 x 25 mm cover, for the cup test. All the mixtures were cured for 24h at a temperature of 60 ºC before being demoulded, and left at room temperature until they reach 7 days to be tested. On the 7th day, of each mixture, samples were placed in a static furnace before the compression test submitted to a temperature of 800 ºC during 2h. Then, the compression test was performed and the values before and after exposure to high temperatures were compared. Were recorded maximum gains of 724% and maximum losses of 100% in the compressive strength. This preliminary result shows the potentials of mining waste alkali-activated materials for elevated temperatures applications.

1 Introduction

Since several years that we have been looking for viable alternatives to ordinary Portland cement (OPC), because its production is one of the main responsible for the emission of gaseous pollutants into the atmosphere, in this case CO_2 (about 969 kg for each ton of clinker produced). According to Davidovits [1], geopolymers have very interesting characteristics (mechanical, chemical and durability) for construction and can be OPC alternative materials. In this work, we intend to demonstrate the potential of alkali activated tungsten mining waste based materials (AATMWM) when exposed to high temperatures and to compare with OPC. For this, several mixtures with different percentages of tungsten mining waste were tested for compression before and after being exposed to high temperatures, and were recorded the mass losses of each mixture by thermogravimetric analysis. Finally, the behaviour of each mixture was analysed for chemical resistance using K_2CO_3 as the attacking agent.

2 Materials and methods

2.1 Materials characterization

In the base mix, were used mining waste mud as a precursor, in this case mining waste mud (MD) from Panasqueira Mines, because they are rich in aluminosilicates. It was also used waste glass powder (GL) and metakaolin (MK), as precursors, to increase alkaline activation especially by adding SiO_2 since the MD is mainly composed of muscovite and quartz which have a low reactivity even after calcination (Pacheco, Torgal 2008c). The fineness of the MD and GL used were less than 500 µm. The chemical composition of the precursors was determined by x-ray (XRF) as indicated in table 1. Grain cork was added to the mixtures as lightweight aggregate.

Table 1 - Chemical composition of precursors

Chemical components	Constituants (%)		
	Mining waste mud	Glass powder	Metakaolin
SiO_2	46,67	68,13	52,28
Al_2O_3	17,01	2,8	42,99
K_2O	4,9	0,86	0,94
Na2O	0,85	12,52	0,32
CaO	0,69	10,52	-
SO_3	7,9	0,23	-
Fe_2O_3	15,47	2,9	1,49
MgO	4,83	2,04	0,47

As alkaline activators were used sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) whose chemical composition is presented in table 2. It was

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supplied by José Manuel Gomes dos Santos, Ltd. And LUXCITANIA, Ltd, respectively.

Table 2 - Chemical composition of activators

Chemical components	Constituants (g)	
	Sodium silicate	Sodium hydroxide
Na_2O	19,37	13,02
SiO_2	62,6	0
Al_2O_3	0,9	0
H_2O	142,32	43,27
K_2O	-	-
CaO	-	-

2.2 Mixtures

In this study, a total of 15 different mixtures were prepared (Table 3) where the precursor / activator ratio of 2.85 was always used except for mixtures MK20JN and 27JN055 where this ratio was 1.1 and 2.17, respectively.

Table 3 - Mixtures composition

	Precursors (g)			Activators (g)		Aggregates (g)
Mixture	Mining waste mud	Glass powder	Metakaolin	Sodium silicate	Sodium hydroxide	Cork (granulated expanded)
MD16JN	4437,85	-	-	1167,86	389,29	-
MK20JN	-	-	2278,03	1553,20	517,73	-
20JN811	2144,69	219,09	227,80	682,00	227,33	-
GL21JN	-	2190,93	-	576,56	192,19	-
22JN820	2309,66	471,89	-	731,99	244,00	-
22JN802	2309,66	-	490,65	736,93	245,64	-
23JN52525	1391,99	568,80	591,41	671,63	223,88	-
23JN811C1	2004,46	204,77	212,91	637,40	212,47	11,34
27JN055	-	1137,60	1182,83	812,33	255,93	-
29JN552718	1497,16	600,65	416,35	661,62	220,54	-
30JN552718C1	1347,44	540,59	374,72	595,46	198,49	11,09
4JL811C2	1742,15	177,97	185,05	553,99	184,66	22,18
5JL622	1633,26	444,93	462,62	668,63	222,88	-
6JL552718C2	1197,73	480,52	333,08	529,30	176,43	22,18
11JL622C1	1469,94	400,44	416,35	601,77	200,59	11,09

2.3 Mixtures preparation

Initially, the precursors were mixed, manually and dry, together with the aggregates until a uniform mixture was obtained. The activators were then blended, in this case sodium silicate and sodium hydroxide, for approximately 5 minutes using a magnetic mixer. The precursors were combined with the activators using an electric mixer at an average speed for approximately 2 to 3 minutes and about 1 minute at full speed.

2.4 Curing regime and elevated temperature exposure

The specimens were cured for 24 hours at a controlled temperature of approximately 60 °C, then removed from respective moulds, then allowed to cool to room temperature until tested.

For the elevated temperature exposure was used a static furnace (muffle) with a maximum temperature of 1100º C. The specimens were subjected to temperatures up to 800º C, with an increase of 3.4º C / min, for 2 hours. After completion of the 2 hours' cycle, the specimens had a natural cooling inside the muffle until they reached 100 º C at which time they were withdrawn and placed at room temperature until tested.

2.5 Compressive strength

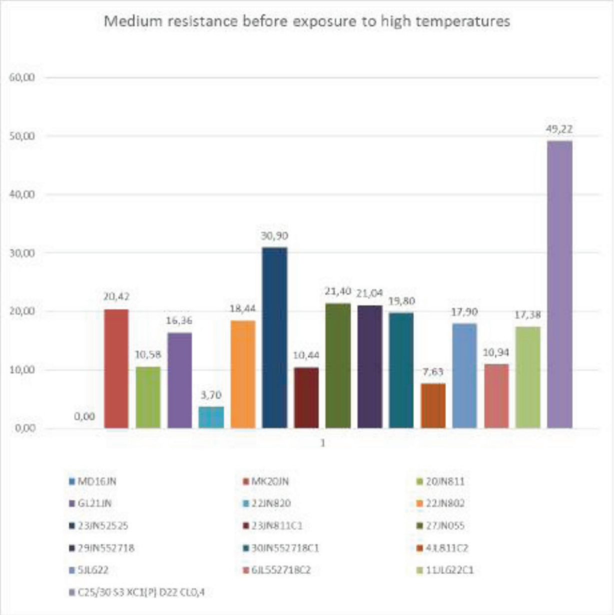
For the analysis of compressive strength were used a hydraulic press ELE 3000kN and testing was according to EN 1015-11 for 40x40x40 mm cubic specimens. This equipment is provided y DECA-UBI in the construction laboratory.

2.6 Thermogravimetric analysis

To analyse the mass losses of the test specimens when exposed to high temperatures, the thermogravimetric test was used with the TGA Q50 equipment, available at the DECA-UBI materials laboratory, where the same 15 mixtures were analysed.

2.7 Cup test

In this test were made specimens with dimensions of 100 x 100 x 60 mm with a small hole of 40 mm at the base and 50 mm at the surface of the mould and still others with dimensions of 100 x 100 x 25 mm, with the mixtures indicated in section 2.2. Following the curing, as indicated in point 2.4, and following an ASTM C454, with some changes, was placed a mixture of K_2CO_3 (potassium carbonate) granulated on the hole of the sample. The hole is checked with the 100 x 100 x 25 mm sample and use a refractory mass to make a connection between test pieces. Hardened mortars were left to cure for 24 hours at a temperature of 60 ° C and only then was the specimen placed in the muffle at a temperature of up to 800 ° C with a temperature rise of 200 ° C / h for 5 hours. At the end of the 5 hours cycle the specimens had a natural cooling inside the muffle up to 100 ° C at which time they were withdrawn and placed at room temperature until they were cut to see what changes have been caused by the presence of K_2CO_3.



Graphic 1 - Compressive strength results before the exposure to high temperatures

3 Results and discussions

3.1 Compressive strength

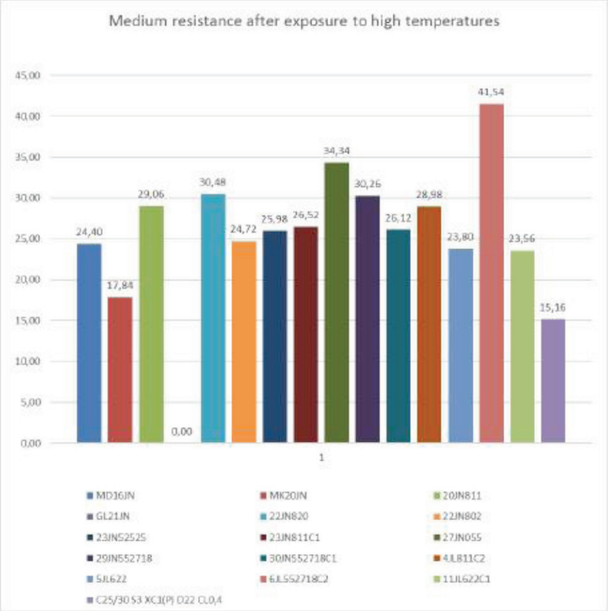
The graphics 1 and 2 show the results obtained for each mixture before and after being exposed to high temperatures. Observing the results, we see that the highest resistance before being exposed was 30,9 MPa in the 23JN52525 specimen and the highest resistance after being exposed to high temperatures was 41,5 MPa in the 6JL52718C2 specimen. As can be observed, there was a great increase in compressive strength in all the mixtures, except for the mixtures MK20JN, GL21JN and 23JN52525 where a resistance loss of 13%, 100% and 16% was resisted respectively. But it should be noted that the greater increase was observed in the 22JN820 blend with an increase of 724%.

3.2 Thermogravimetric analysis

Table 4 shows the results of mass losses of all mixtures and the mass loss of the precursors, except for the glass mixture for which was not possible to measure the mass loss since there was a risk of damaging the equipment when the glass enters in fusion. The average mass loss is of the order of 8.98%, with the largest recorded loss of 13.67% in the MK20JN mixture and the lowest recorded loss of 1.76% in the metakaolin mixture.

3.3 Cup test

In this test, the analysis that was done was a visual observation of the damages caused by the presence of K_2CO_3 as can be observed in fig. 1.



Graphic 2 - Compressive strength results after the exposure to high temperatures

The presence of K_2CO_3 had a significant impact on the internal degradation of the specimens. There was a very visible carbonation in the zone in direct contact with the chemical that caused the slit openings in all the specimens due to the expansion effect caused by the carbonation process.

Table 4 - TGA results

Mixture	Weigth loss (%)
Mud	5,73
Metakaolin	1,76
MD16JN	7,99
MK20JN	13,67
20JN811	11,08
GL21JN	7,45
22JN820	8,71
22JN802	8,82
23JN52525	8,67
23JN811C1	8,69
27JN055	10,03
29JN552718	10,92
30JN552718C1	10,68
4JL811C2	8,86
5JL622	9,93
6JL552718C2	11,07
11JL622C1	8,59
C25/30	9,60

4 Conclusion

1- The results of the resistance test show that AATMWM has an excellent performance when exposed to high temperatures and compared with OPC, whose resistance after exposure to high temperatures had a decrease of 69 %, are a very viable solution. On the other hand, the excessive presence of MK in the mixtures proved to be detrimental to the resistance after exposure to high temperatures. The cork, as a light aggregate, proved to be beneficial, helping to increase the resistance of the mixtures after exposure to high temperatures.

2- The TGA results showed that the mass losses in the AATMWM are very similar in all mixtures and even the OPC shows a mass loss within the expected values. On the other hand, the mixture of metakaolin (MK20JN), which showed the greatest loss of mass (13.67%), again demonstrated the weaknesses of the excessive use of metakaolin in the mixtures. According to previous [2] research, the increased moisture loss of the metakaolin-based mixtures causes damage to the internal matrix of the mixtures consequently a lower strength.

3- The cup test showed some AATMWM weaknesses for chemical attacks causing a visible internal and external degradation. Once again, the mixtures with more metakaolin were those that presented greater degradation.

Figure 1 - Cup test sample after testing

5 References

[1] J. Davidovits, “Geopolymers: inorganic polymeric new materials,” *J Therm Anal*, 1991.

[2] D. L. Y. Kong, J. G. Sanjayan, and K. Sagoe-crentsil, “Comparative performance of geopolymers made with metakaolin and fly ash after exposure to elevated temperatures,” vol. 37, pp. 1583–1589, 2007.

[3] D. L. Y. Kong and J. G. Sanjayan, “Cement and Concrete Research Effect of elevated temperatures on geopolymer paste , mortar and concrete,” *Cem. Concr. Res.*, vol. 40, no. 2, pp. 334–339, 2010.

[4] P. D. Æ. A. Ferna and G. C. L. Æ. A. P. Æ. J. S. J. Van Deventer, “Geopolymer technology : the current state of the art,” no. 4, pp. 2917–2933, 2007.