Leaching of alkali-activated tungsten mining waste materials by electrical conductivity and DRX

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Abstract. The production of Portland cement leads to high energy and natural resource consumption, as well as relevant emission of CO_2 into the atmosphere. Thus, this research work intends to contribute to the study of Portland cement alternative alkali activated binders, which utilization can contribute to counteract to this status. Different samples of alkaline activated binders using different combinations of tungsten mining waste from Panasqueira Mines, milled glass and metakaolin were made. Compression tests were performed at 3, 7, 14 and 28 days of curing. For evaluating reactivity chemical leaching was measured. For such, conductivity tests were carried out simultaneously with pH measurement, SEM-BSE and ATR-FTIR analysis. Electrical conductivity tests enabled to preliminary identify the chemical leaching for different precursors. Additionally, by SEM-BSE it was possible to observed reacted and non-reacted particles, and the reactivity extend was confirmed by ATR-FTIR.

Keywords: Alkali-activated, mining waste, milled glass, metakaolin, electrical conductivity

1. Introduction

Having in mind the objectives of the United Nations for Sustainable Development, particularly to reduce depletion of natural resources and to increase recycling of waste, this research work intends to contribute to the study of Portland cement alternative alkali activated binders. First, the alkali-activated materials (AAM) technology brings a new type of cementing materials that don't produce CO_2 emissions like the case of Portland cement (PC) industry [1, 2]. Secondly, this technology enables the reuse of fine particles from mud tailings as precursor materials, being very promising from a technical, environmental and economic point of view [3, 4]. Besides, the alkaline activation of aluminosiliceous industrial by-products is widely known to yield binders whose properties make them comparable to or even stronger and more durable than ordinary Portland cement [5, 6]. Moreover, several non-conventional waste materials are re-used nowadays as precursors in the alkaline activation, that can be blended/combined with mining waste mud tailings with promising results [7].

In this study, the reactivity of AAM's with different composition was evaluated by chemical leaching based on electrical conductivity measurements SEM-BSE and ATR-FTIR analysis. Electrical conductivity tests enabled to preliminary identify the chemical leaching for different precursors proportions. Additionally, by SEM-BSE it was possible to observed reacted and non-reacted particles, and the reactivity extend was confirmed by FTIR.

The main waste materials used in this investigation consisted of tungsten mine waste mud (TMW) from Panasqueira mine in Covilhã, Portugal and milled waste glass (WG) from local municipal deposits. Some mixes also contained metakaolin that was provided by the German chemical company BASF

Specimens to be tested were made with the following precursor's quantities combined together: 20%, 50% and 80% of tungsten mining waste mud, 10%, 50%, 80% and 100% of milled waste glass; 80% and 100% of metakaolin.

Compressive strength tests for different mixtures were carried on at 3, 7, 14 and 28 days of curing.

2. Experimental procedure

2.1 Materials

The main materials used in this investigation consisted of tungsten mine waste mud (TMW) from Panasqueira mine in Covilhã, Portugal, milled waste glass (WG), sodium hydroxide (NaOH) (SH), and sodium silicate (Na_2SiO_3) (SS).

WG was produced after milling for 6 hours using a ball mill. Both TMW and WG were used with particle size lower than 500μm, obtained by sieving analysis. The chemical composition of the TMW and WG was obtained by SEM-EDS. Table 1 shows the average values of TMW and WG chemical composition. Grain size distribution analysis was made for TMW and WG by laser diffraction analysis. The TMW has a mean particle size of 12,1 μm while the WG has a mean particle size of 39,7 μm.

Table 1. Chemical composition (wt.%) TMW and WG determined by SEM-EDS

Chemical compound	TMW	WG
SiO_2	49,33	73,93
Al_2O_3	16,28	0,00
Fe_2O_3	13,67	0,40
SO_3	8,93	0,00
K_2O	4,38	0,69
Na_2O	0,64	9,72
CaO	0,83	12,83
MgO	4,93	0,00
TiO_2	1,00	0,00

Sodium hydroxide solution was prepared by dissolving sodium hydroxide pellets (98% purity obtained from Fisher Scientific, Schwerte, Germany) in deionized water and allowed to cool before use. Sodium silicate (obtained from Solvay SA, Póvoa de Santa Iria, Portugal) had a SiO_2/Na_2O = 3,23 (8.60% by weight Na_2O, 27,79% by weight SiO_2, 63,19% by weight H_2O, and 0,4% by weight Al_2O_3).

2.2 Methodology

All sample preparation was carried on at room temperature (around 20ºC). Alkali activated binders (AAM) were produced by blending TMW with WG and MK, with different percentages. For the constituents of the AAB the following parameters were selected: Molarity of SH= 10M; Weight ratio of SS:SH=4 and Weight ratio of precursor/activator = between 2.8 to 3 (except for samples containing higher percentage of MK were lower ratio, between 1 to 2, was used). To produce AAB samples TMW, WG and MK were first mixed in dry state for about 3 minutes. The SS and SH were also mixed together for a period about 5 minutes. Then alkali-activator solution was stirred together with the dry mix for about 5 minutes.

The resulting AAM mixes were then placed in prismatic molds of different sizes (accordingly to different tests) and cured in oven at 60ºC for 24 hours, prior to testing. Most details of mix preparation and curing procedures were developed in previous studies [8, 9].

Reactivity of AAM's with different composition was evaluated by chemical leaching based on electrical conductivity measurements. For this procedure 2.5 x 2.5 x 2.5 cm cubic specimens were used, after being cured for 7 days. First, specimens to be tested were placed in a goblet containing distilled water at a constant level of 150 ml. Then the electrical conductivity was measured by means of a probe that recorded values from hour to hour until reaching a constant electrical conductivity value. Since the electrical conductivity changes with the number of free ions that migrated from the samples to the distilled water, the higher the sample conductivity, the lower the alkaline activation reactivity extent.

2.3 Mixtures composition

Table 2 presents the main mixtures composition used in this research by combining different precursors percentage (e.g. 20%, 50% and 80% of tungsten mining waste mud (TMW), 10%, 50%, 80% and 100% of milled waste glass (WG); 80% and 100% of metakaolin (MK)).

Table 2. Mixtures composition

Mixture label	TMW	WG	MK
20TMW-80WG	20	80	-
50TMW-50WG	50	50	-
80TMW-10WG-10MK	80	10	10
100WG	-	100	-
100MK	-	-	100

3. Results and discussion

3.1 AAMs compressive strength

Table 3 presents compressive strength results for each mixture obtained between 3 to 28 days curing.

The compressive strength is considered only indicative, since most specimens were produced without using any compaction.

Table 3. AAMs compressive strength (average values of six specimens)

Mixture label	3 days	7 days	14 days	28 days
20TMW-80WG	24,7	23,3	15,8	23,0
50TMW-50WG	12,5	19,6	18,4	22,1
80TMW-10WG-10MK	17,9	18,0	20,1	16,0
100WG	52,7	39,8	29,4	39,5
100MK	16,7	22,4	16,0	14,0

3.2 Electrical conductivity

Specimens to be tested for electrical conductivity were placed in a goblet containing distilled water at a constant level of 150 ml, as presented in Figure 1. The electrical conductivity consisted in measuring the quantity of free ions that migrated from the samples to the distilled water. The electrical conductivity allows us to know the number of free ions, but not which specific ions are leached. The alkali-activated samples have activated compounds and non-activated compounds. The free ions correspond to the inactivated elements present in the specimen, that is, the higher the conductivity measured on the water immersed specimen, the lesser the alkaline reaction extend.

Figure 2 presents a typical graph of electrical conductivity of the water immersed with 20TMW-80WG specimen.
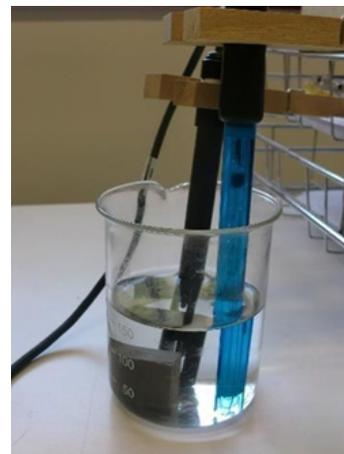

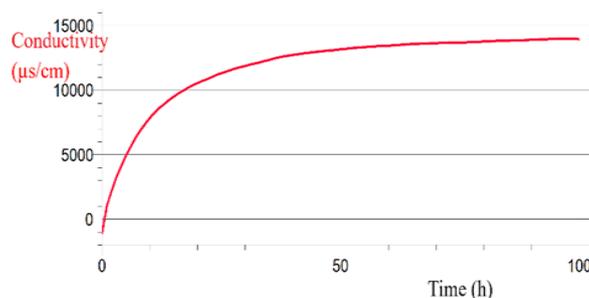Figure 1. Ongoing electrical conductivity testing

Figure 2. Electrical conductivity of the water immersed with the 20TMW-80WG specimen.

As can be observed in Table 4, the AAM specimen's electrical conductivity varies between 4122 and 17781µs/cm. The 100WG specimen presents the lowest

electrical conductivity value and the 50TMW-50WG specimen has the highest value.

The higher the electrical conductivity, the lesser the alkaline reaction extend. Thus, the 50TMW-50WG specimen is the one that presented a greater number of free ions in the distilled water, confirmed by the higher conductivity. The 50TMW-50WG specimen is the one with lowest alkaline activation reaction extend followed by 20TMW-80WG, 80TMW-10WG-10MK, 100WG and 100MK specimen.

There is a major disparity between electrical conductivity values obtained for the 100MK specimen and all the other specimens.

Table 4. AAMs Electrical conductivity

Mixture label	Conductivity values (μs/cm)	Number of hours to stabilize the sample
20TMW-80WG	14014	99
50TMW-50WG	17781	330
80TMW-10WG-10MK	12908	64
100WG	10000	66
100MK	4122	40

3.2 SEM-EDX analysis

Table 5 presents SEM-EDX analysis carried on for each specimen after being immersed in distilled water. From results, it can be observed that the alumina (Al) is in great content, 31.67% on 100MK specimen, which according to the conductivity test was the one that presented a greater alkaline activation extend, in contrast to the 50TMW-50WG specimen which, in turn, presents a higher silica (Si) content, 61.30%.

Table 5 also presents the weight percentage of other presents on the alkaline activated specimens, such as S, K, Ca, Ti, Fe, Zn, As and Cu.

Table 5. SEM-EDX analysis results

Element (%, wt.)	2T8G	5T5G	8T1G1M	1G	1M
Na	17,22	21,73	14,14	22,38	13,36
Al	4,37	6,66	16,61	2,21	31,67
Si	61,30	54,40	49,63	62,51	51,76
S	1,81	3,21	4,80	0,25	0,09
K	1,42	1,62	2,33	0,84	0,60
Ca	10,61	5,97	1,93	10,86	0,09
Ti	0,13	0,23	0,75	0,06	1,22
Fe	2,52	5,11	7,27	0,72	0,96
Zn	0,54	0,58	1,00	0,07	0,08
As	0,38	0,38	1,40	0,04	0,17
Cu	0,00	0,11	0,14	0,06	0,00

Mixtures short name:
20TMW-80WG – (2T8G); 50TMW-50WG – (5T5G)
80TMW-10WG-10MK – (8T1G1M)
100WG – (1G); 100MK – (1M)

3.3 SEM-BSE analysis

Figures 3 to 7 present typical backscattered electron imaging (SEM-BSE) micrographs of different specimens after being immersed in distilled water. It is possible to observe that the AAM mixtures with 20% or more of TMW and WG show some unevenness of the particles, and

these mixtures also have high porosity. In the specimens that contain MK in its composition, these have a more homogeneous and denser structure, not showing as much disaggregation between the hydrated gel components of the mixture as was verified in those that do not have metakaolin in its composition. On the other hand, mixtures with metakaolin also presented the studied chemical elements more evenly distributed.
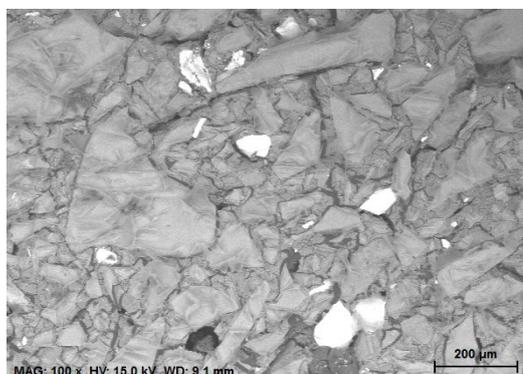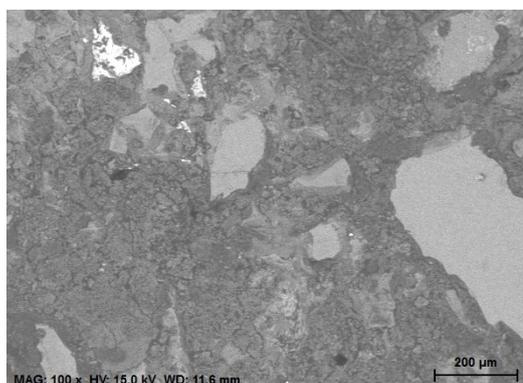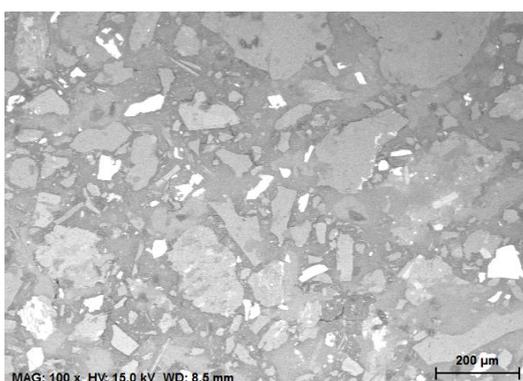

Figure 3. BSE 20TMW-80WG

Figure 4. BSE 50TMW-50WG

Figure 5. BSE 80TWM-10WG-10MK
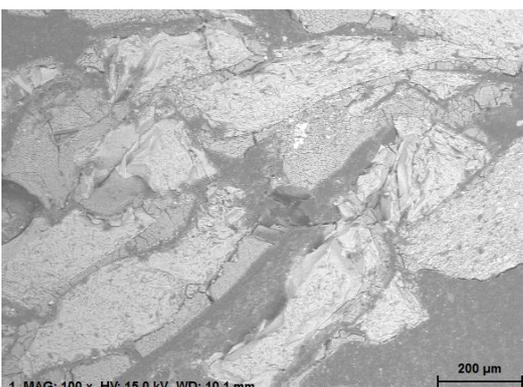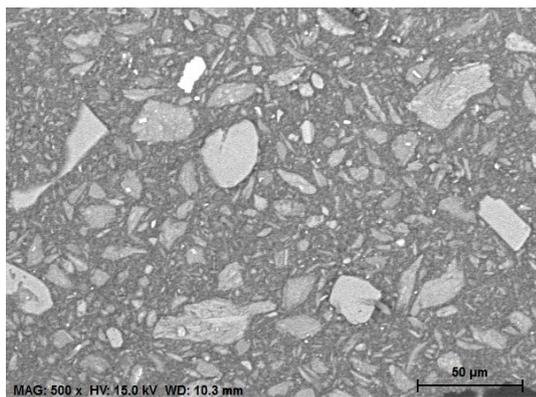

Figure 6. BSE 100WG

Figure 7. BSE 100MK

3.4 ATR-FTIR analysis

ATR-FITR (Fourier transform infrared spectroscopic technique) analysis for each specimen after being immersed in water for conductivity tests are presented in figures 8 and 9. Based on ATR-FTIR (Fourier transform infrared spectroscopic technique), we can determine the reaction rates, from the intensity variation of the bands related to the geopolymer gel network and the unreacted particles.

The 20TMW-80WG specimen has the highest value for an absorbance of about 0.090 and for a wavelength of about 3000 cm and between 1350 cm^{-1} and 600 cm^{-1} presents a succession of small peak zones that reach absorbance values between 0.015 and 0.030. The 50TMW-50WG specimen has the highest value for an absorbance of about 0.110 and for a wavelength of about 3000 cm and between 1350 cm^{-1} and 900 cm^{-1} presents a succession of small peak zones that reach absorbance values between 0.015 and 0.030. The 80TMW-10WG-10MK has a more pronounced peak. The peak is about 3000 cm^{-1}, for an absorbance of approximately 0.096. The 80TMW-20WG specimen has two more pronounced peaks, the first value is about 3000 cm^{-1} for an absorbance of about 0.036, and the second is about 1000 cm^{-1} for an absorbance of 0.028. The 100WG specimen has a more pronounced peak (3000 cm^{-1}), for which it has an absorbance of about 0.089 and, and the second is about 1000 cm^{-1} for an absorbance of 0.042. In turn, the 100MK also features two peaks that stand out, for which absorbance values of about 0.10 are presented for a wavelength of about 3000 cm^{-1} and an absorbance of 0.13 for a length of about 950 cm^{-1}, respectively.

• The peak inserted in the range 3600-3700 cm^{-1} is relative to the OH group;
• The peak of the 3000 cm^{-1} at 2900 cm^{-1} refers to the axial deformation of the hydroxyl group of the water (stretching of the OH- group and the H-O-H bonds);
• Bands between 1350 cm^{-1} and 1450 cm^{-1}, are typical of CO_2- vibrations;
•The peak around 950 cm^{-1} is characteristic of a material rich in alumina. Alumina provides the conditions for a faster interaction between the dissolved part of silica and alumina, necessary for the formation of the tetrahedral gel net with high alumina content;
• Bands between 950 cm^{-1} and 1200 cm^{-1} result from the asymmetric stretching of Si-O bonds and the Si-O-Si and Si-O-Al bonds;

• The peak of 1000 cm^{-1} is indicative of large amounts of crystalline material (characteristic zeolite formation band displacement with disordered aluminosilicate precursors);
• Bands with characteristic values between 750 cm^{-1} and 850 cm^{-1} refer to the symmetrical stretching of Si-O-Si bonds;
• Bands between 950 cm^{-1} and 1200 cm^{-1} result from the asymmetric stretching of Si-O bonds and the Si-O-Si and Si-O-Al bonds;
• Bands with characteristic values between 750 cm^{-1} and 850 cm^{-1} refer to the symmetrical stretching of Si-O-Si bonds;
• Bands lower than 760 cm^{-1} are related to the ring structure of Al, which can give us knowledge through the comparison of formed zeolite phases.
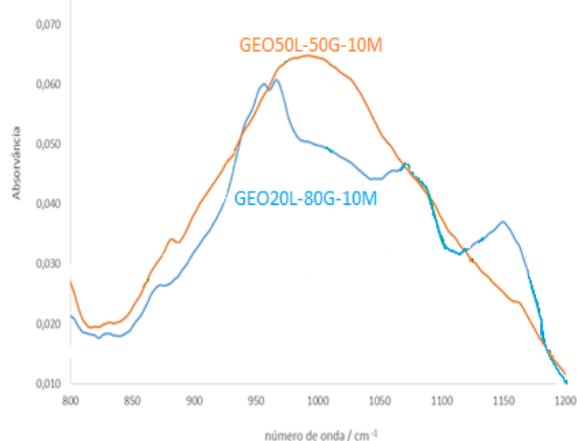

Figure 8. ATR-FTIR analysis for 50TMW-50WG (GEO50L-50G-10M) and 20TMW-80WG (GEO20L-80G-10M) specimens.

The introduction of metakaolin into the mixture gives rise to a more extensive formation of the three-dimensional structure. Comparing the results obtained with the 100MK specimen with those of the sample with introduction of only 10% metakaolin, 80TMW-10WG-10MK, it is possible to verify an increase in the formation of the three-dimensional structure. However, the shape of the curve, wide and poorly defined, also indicates the formation of a wide variety of other types of chemical bonds.
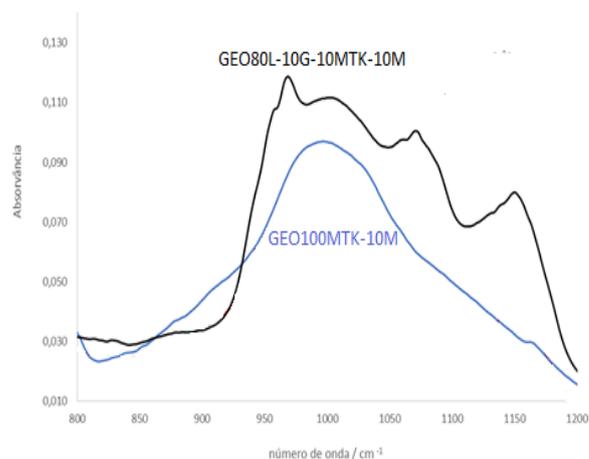

Figure 9. ATR-FTIR analysis for 80TMW-10WG-10MK (GEO80L-10G-10MTK-10M) and 100MK (GEO100MTK-10M) specimens.

4. Conclusions

In this study the reactivity of AAM's with different composition was evaluated by chemical leaching based on electrical conductivity measurements SEM and FTIR analysis. Electrical conductivity tests enabled to preliminary identify the chemical leaching for different precursors. Additionally, by SEM-BSE it was possible to observed reacted and non-reacted particles, and the reactivity extend was confirmed by ATR-FTIR.

Based on the results of this study, to following conclusions can be given:

- The 100WG specimen presented the highest compressive strength at 28 days (39.5 MPa), however compressive strength is considered only indicative, since most specimens were produced without using any compaction;
- The water immersing the 50TMW-50WG specimen was the one with the highest conductivity value, and therefore, of the 5 specimens analyzed, the one with the highest alkaline leaching; The higher the electrical conductivity, the lesser the alkaline reaction extend. Thus, the 50TMW-50WG specimen was the one that presented a greater number of free ions in the distilled water, confirmed by the higher conductivity;
- The 100MK specimen (100% metakaolin) is the one with the lowest electrical conductivity value, and therefore, the one with the lowest number of free ions and hence it can be said that it had greater alkaline activation extend; It was also the specimen with the highest alumina content, about 31.67%, after water immersion;
- The specimens with lower conductivity values (100MK and 100WG) presented two characteristic peaks in the FTIR-ATR analysis, between 950 cm^{-1} and 1200 cm^{-1} result from the asymmetric stretching of Si-O bonds and the Si-O-Si and Si-O-Al bonds.

The electrical conductivity testing can be used as a preliminary method to determined the reactivity extend of alkali-activated materials (AAMs).

Acknowledgement

References

[1] J. Davidovits, Global Warming Impact on the Cement and Aggregates Industries, World Resour. Rev. 6 (1994) 263–278.

[2] J.L. Provis, J.S.J. van Deventer, Geopolymers - Structure, Processing, Properties and Industrial Applications, Woodhead Publishing Limited, 2009.

[3] F. Pacheco-Torgal, J.P. Castro-Gomes, S. Jalali, Utilization of mining wastes to produce geopolymer binders, in: J.L. Provis, J.S.J. van Deventer (Eds.), Geopolymers - Struct. Process. Prop. Ind. Appl., Woodhead Publishing Limited, 2009: pp. 267–293.

[4] I. Silva, J.P. Castro-Gomes, A. Albuquerque, Effect of immersion in water partially alkali-activated materials obtained of tungsten mine waste mud, Constr. Build. Mater. 35 (2012) 117–124.

[5] A. Palomo, P. Krivenko, I. Garcia-Lodeiro, E. Kavalerova, O. Maltseva, A. Fernández- Jiménez, Activación alcalina: Revisión y nuevas perspectivas de análisis, Mater. Construcción. 64 (2014) e022.

[6] J.L. Provis, A. Palomo, C. Shi, Advances in understanding alkali-activated materials, Cem. Concr. Res. 78 (2015) 110–125.

[7] N. Sedira, J. Castro-Gomes, G. Kastiukas, X. Zhou, A. Vargas, A review on mineral waste for chemical-activated binders: mineralogical and chemical characteristics, Min. Sci. 24 (2017) 29–58.

[8] G. Kastiukas, X. Zhou, J. Castro-Gomes, Preparation conditions for the synthesis of alkali-activated binders using tungsten mining waste, J. Mater. Civ. Eng. 29 (2017).

[9] Castro-Gomes, J., Magrinho, M., Sedira, N., Humber, P., Beghoura, I., Manso, M., … Silva, R. (2017). Alkali-activation of tungsten mining waste mud blended with waste glass: reactivity, performance and innovative applications. International Congress on Engineering UBI, Covilha, Portugal, 253–261.