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High-performance alkali-activated composites containing an iron-ore mine tailing as aggregate

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Abstract. High-performance cementitious composites have been developed to overcome the brittleness of mortars and concretes, thus improving the deformation and toughness of these materials under flexion and tension. Poli Vinyl Alcohol (PVA) fibres are employed in the production of such “Engineered Cementitious Composites” – ECC; the PVA fibres have a load-carrying capacity after the first crack (matrix failure), which changes the mechanical behaviour of the composites from brittle to ductile and significantly increases the ultimate strength. This deflection or strain-hardening behaviour is accompanied by a multiple cracking of the composites, which results from the design of a proper formulation, with correct amount of PVA fibres (usually 2% vol. fraction) and employment of a very fine sand (passing 0.6 mm). Recent developments in the area of ECC comprise the replacement of Portland cement (PC) matrices with alkali-activated materials (AAM). The idea is to produce composites with similar performance but with improved chemical durability and lower environmental impact. A more sustainable solution would consider the replacement of the fine sand with mine tailings in the production of ECC-AAM. Some tailings from the iron-ore mining activities in Brazil are significantly finer than those aggregates used for PC mortars and concretes; therefore, they cannot be employed in traditional PC-based materials. Nevertheless, those fine materials could replace the fine natural aggregate used in the production of ECC. This paper investigates the replacement of a natural quartz sand with an iron-rich mine tailing in PVA-reinforced AAM. Four composites were studied from a combination of two different matrices and 2 different aggregates. The matrices were obtained from the alkaline activation of metakaolin (MK) with sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH); silica fume (SF) was used to adjust their composition: SiO_2 / Al_2O_3 molar ratio equal to 3.0 or 3.8. The aggregates used were either natural quartz (passing 0.6 mm) or tailings produced during the mining activities of iron ore in the state of Minas Gerais, Brazil. The mine tailing studied is much finer than the natural sand (passing 0.3 mm) but it was used as received in the production of ECC-AAM. The aggregate to binder ratio was kept constant (equal to 1.0 in mass) irrespective of the type of aggregate. All mortars were reinforced with 2% vol. of PVA fibres; extra water was added to the mixes to maintain the same consistency for the composites. The mechanical properties investigated are compressive strength, flexural strength and toughness. The apparent dry density of the mortars was also assessed. The preliminary results presented in this paper indicate that iron-rich tailings may be effectively used in the production of ECC-AAM; however, durability tests are still necessary.

1 Introduction

Alkali-activated materials (AAM) can be defined as inorganic polymers obtained by the reaction between an aluminosilicate source (such as metakaolin, fly ash, blast furnace slag, silica fume, among others) and an alkaline activator solution [1–4]. Several studies point out that these materials may present several advantages to Portland cement (PC) composites, mainly in terms of lower carbon emissions [5, 6], early strength development [7], superior thermal [8, 9] and chemical durability [10–12]. Despite those advantages, AAM are inherently brittle materials and, similarly to PC matrices, may have their mechanical properties improved by fibre reinforcement. Increasing interest in the development of fibre-reinforced AAM has been recently reported, with the employment of a great variety of fibres. Poly vinyl alcohol (PVA) fibres stand up as a good option of reinforcement as they are highly stable in alkaline environment. Those fibres have already been used in the development Engineered Cementitious Composites (ECC) and alkali-activated composites, either presenting

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deflection or strain-hardening behaviour after first cracking under tensile stresses, followed by high ductility [13–15].

Increasing interest in AAM is directly related to their low environmental impact when compared to PC-based materials. Therefore, some studies aim to apply a wide variety of waste and tailings as aggregates or fine materials (precursors or fillers) in AAM [16–21]. Researches on the employment of mining by-products as substitutes for natural aggregates in AAM have increased in the recent decades [19–21]. This arises due to the significant increase in their generation and as an effort to prevent and mitigate the risks of waste accumulation and disposal in dams, as usual in Brazil [22–21]. This paper aims to investigate the effects of replacement of a natural quartz sand with an iron-rich mine tailing on the mechanical performance of two different PVA-reinforced alkali-activated mortars. The AAM were made from the alkaline activation of MK. Silica fume (SF) was used in order to alter the composition of the matrices (namely SiO_2/Al_2O_3 molar ratio) without significant changes in the composition of the activation solution (Na_2SiO_3 + NaOH).

2 Materials and methods

2.1 Raw materials and formulation of the alkali activated composites

2.1.1 Materials

The AAM produced were obtained by the activation of metakaolin (MK) and silica fume (SF), supplied by Metacaulim do Brasil and Tecnosil ltda., respectively. The latter was used to partially replace MK and alter the composition of the matrices, as it is composed mainly of SiO_2. The aggregates employed were either natural quartz sand (passing 0.6 mm) (supplied by Moinhos Gerais, Brazil) or a mine tailing (passing 0.3 mm) from iron-ore mining in the state of Minas Gerais, Brazil. The chemical composition and x-ray diffraction pattern (XRD) of those precursors and aggregates are presented in Table 1 and Figure 1, respectively.

Table 1. Chemical composition of the solid precursors and mine tailing

Main oxides and physical properties	MK (%)	SF (%)	Natural Aggregate (%)	Tailing (%)
SiO_2	43.55	93.40	98.75	82.78
Al_2O_3	37.00	0.75	0.62	2.35
K_2O	-	1.25	0.1	0.1
CaO	0.05	0.23	-	-
MgO	0.05	-	-	-
Fe_2O_3	2.00	-	0.25	13.86
Specific gravity (g/m^3)	2.59	2.25	2.70	2.95
Mean particle size (µm)	2.12	0.37	-	-
Fineness modulus	-	-	1.03	0.14

MK is mostly amorphous and composed mainly of SiO_2 and Al_2O_3; some XRD peaks for quartz, illite and muscovite indicates impurities in the kaolin source, whereas the peaks for kaolinite show some incomplete dehydroxylation of kaolin during the calcination process. SF is predominantly composed of amorphous silica; the absence of Al_2O_3 will therefore increase the SiO_2/Al_2O_3 molar ratio of the matrices when SF replaces MK.

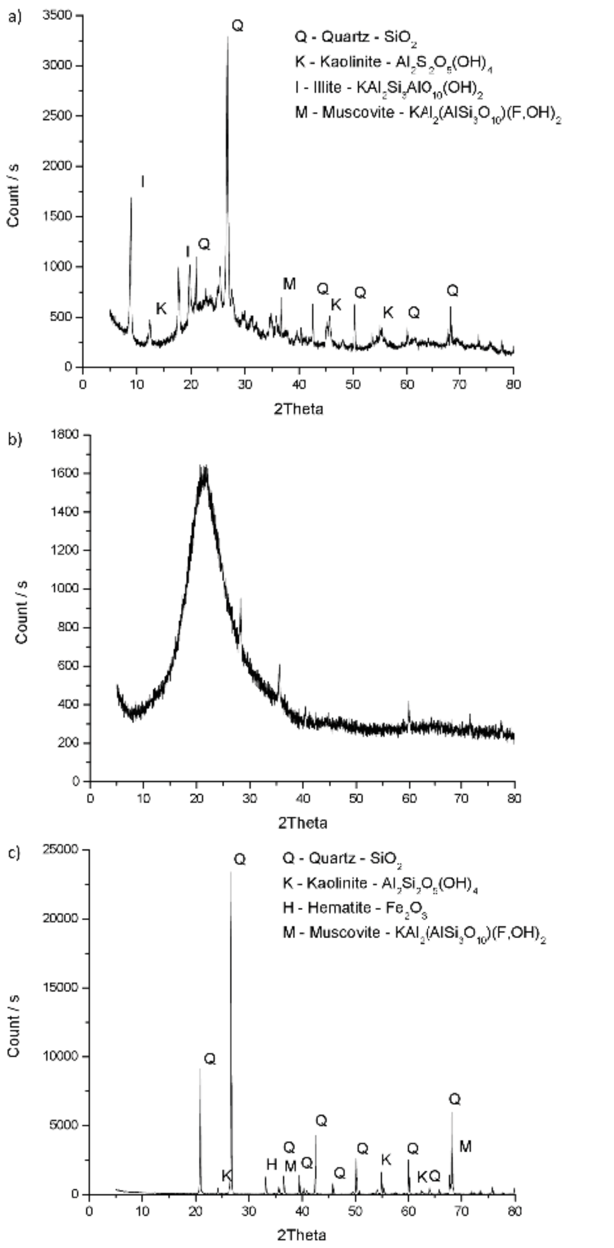

Figure 1. XRD pattern for (a) MK, (b) SF and (c) mine tailing.

The natural aggregate (98.75% quartz, XRD not shown) has specific gravity of 2.70 g/cm^3 and fineness modulus equals to 1.03; it is a finer aggregate (PSD < 0.6 mm) as those commonly used in the production of engineered cementitious composites (ECC). The iron-ore tailing employed as aggregate results from the mining activities in the state of Minas Gerais, Brazil; it is composed of mainly quartz and hematite, with some XRDs peaks for kaolinite probably resulted from contamination (Fig. 1c). It is slightly denser than the natural sand (specific gravity of 2.95) due to the presence of hematite; it is also finer than the natural sand (fineness modulus of tailing = 0.14) but the objective of this paper was to use it as received without blending with another aggregate. The Particle size distribution of the natural sand and mine tailing aggregate are shown in Figure 2.

The activating solution was composed of a mix of sodium hydroxide (50% vol.) and sodium silicate solutions (Na_2O = 15.00%, SiO_2 = 31.79% and H_2O = 53.21%, in % wt.).

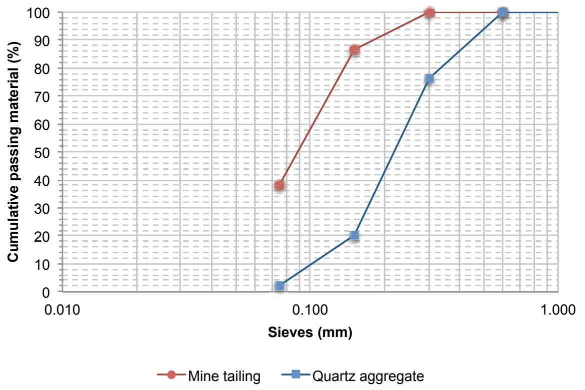

Figure 2. Particle size distribution of the natural (quartz) sand and iron-ore mine tailing.

The short PVA fibres supplied by Kuraray Japan (REC15) have the following properties: diameter: 40 µm; length: 8 mm; specific gravity: 1.3 g/cm^3; tensile strength: 1600 MPa; Young modulus: 41 GPa; elongation: 6%.

2.1.2 Methods

The mix design parameters used for the preparation of the AAM are shown in Table 2. Four composites were studied from a combination of two different matrices and 2 different aggregates. Two $[SiO_2]/[Al_2O_3]$ molar ratios were adopted: 3.0 and 3.8. The alkaline solutions consisted of a mixture of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH). Although Na_2SiO_3 to NaOH ratio (wt.) varied in each mix, the $[H_2O]/[Na_2O]$ molar ratio was kept constant in 12,80 for the mortars with natural aggregate and 13,44 for the mortars with the mine tailing aggregate. Solution to binder ratio was kept constant and equal to 1.0. All mortars were prepared with an aggregate to binder ratio of 1.0. The PVA fibres were employed at 2% vol. fraction in all composites. The alkali-activated mortars were named as follows: NAT for the reference mortars (with natural quartz sand) or MT for mortars with mine tailing as aggregates, both types followed by the $[SiO_2]/[Al_2O_3]$ molar ratio and the MK-SF wt. content (Table 2).

SF and NaOH were mixed 24 hours prior to use, in order to allow complete dissolution of the silica fume particles. The alkaline solutions (Na_2SiO_3 and NaOH or NaOH + SF) were mixed together on the day of casting to prepare the liquid component of the mixture. The alkaline activator was firstly added to the MK. The aggregate was then added while mixing for about 5 minutes. After that, the PVA fibres were gradually added while mixing until the mortar presented a homogeneous appearance.

The mortars were cast in 160x40x40 mm prismatic moulds for the determination of flexural strength and toughness and 100x50 mm cylindrical moulds for the determination of compressive strength, modulus of elasticity and apparent density. The specimens were exposed to ambient curing conditions until they reached the testing age (14 days).

Table 2. Formulation parameters

Formulation	SiO_2/ Al_2O_3	MK:SF	$[SiO_2]$/ $[Na_2O]$ in activator	Na_2SiO_3/ NaOH wt. Ratio	Type of aggregate
NAT 3.0 100MK-00SF	3.0	100:00	1.29	1.92	Natural
MT 3.0 100MK-00SF	3.0	100:00	1.29	1.76	Mine tailing
NAT 3.8 82MK-18SF	3.8	82:18	0.89	0.94	Natural
MT 3.8 82MK-18SF	3.8	82:18	0.89	0.88	Mine tailing

2.2 Characterisation

2.2.1 Compressive Strength and Modulus of Elasticity

Compressive strength tests were performed in conformity with the Brazilian standard ABNT NBR 7215 [24]; four specimens for each formulation were tested at the age of 14 days and the results were expressed in terms of the average and standard deviation.

The static modulus of elasticity of the mortars was determined as recommended by ABNT NBR 8522 [25]

2.2.2 Flexural Strength and Toughness

The modulus of rupture (MOR) of the mortars was determined in a 3-point flexural test, as described by ASTM C 293 [26]. Four prismatic (160 x 40 x 40) mm specimens were tested for each formulation. An electronic deflectometer with resolution of 0.001 mm and a maximum measurable deflection of 12.5 mm was used to measure the displacement of the specimens during the test. The average toughness of the AAM was calculated from the area under the load x mid-span deflection curves.

2.2.3 Apparent dry density

Apparent dry density was measured by dividing the mass of oven-dried samples by their volume (cylindrical samples).

3 Results

Table 3 shows the compressive strength and modulus of elasticity of the AAM. It is possible to see that the compressive strength results were quite variable, presenting large standard deviations. The mean values, however, show that the replacement of the natural sand with the mine tailing aggregate slightly reduced the compressive strength for both matrices. The reduction may be partially explained by the higher water demanded by the composites containing mine tailing as aggregate. The mortars with lower SiO_2/Al_2O_3 molar ratios presented higher mean compressive strength, although the standard deviation indicates no statistically significant differences between the figures.

The modulus of elasticity of the formulations containing 100% MK did not change with the aggregate type variation. However, the formulation with 82% MK and 18% SF presented a reduction in the modulus of elasticity when the mine tailing aggregate was used. Apparently, this matrix is more sensitive to the type of aggregate or to the variation of the amount of water used in its production. This behaviour needs to be further studied to permit better understanding.

Overall, the results suggest that the replacement of the natural quartz sand with the mine tailing aggregate is detrimental neither to the compressive strength nor to the modulus of elasticity of the mortars.

Table 3. Compressive strength and modulus of elasticity of the composites studied

Composite	Compressive Strength (Standard deviation) [MPa]	Modulus of Elasticity (Standard deviation) [GPa]
NAT 3.0 100MK-00SF	52.31 (6.01)	11.58 (0.59)
MT 3.0 100MK-00SF	44.45 (3.05)	11.58 (0.55)
NAT 3.8 82MK-18SF	49.50 (2.19)	11.88 (0.15)
MT 3.8 82MK-18SF	45.72 (2.96)	10.43 (0.43)

The results of apparent dry density measured for the four different mortars are shown in Table 4. The values of apparent dry density were higher when the mine tailing aggregate was employed, regardless of the matrix. Besides, the composites produced with 100% of MK presented higher apparent dry density than the ones produced with 82% of MK and 18 of silica fume. The apparent dry density of the mortars is partially a function of the specific gravity of the raw materials used; therefore, those results can be easily explained. As mentioned in Table 1, SF has specific gravity of 2.25 g/cm^3, while MK has specific gravity of 2.56 g/cm^3; the natural quartz sand has specific gravity of 2.70 g/cm^3 and the mine tailing of 2.95 g/cm^3. Thus, it makes sense that the apparent dry density of the mortars produced (i) decreases with higher SF content; (ii) increases with the replacement of the natural aggregate by the mine tailing. The changes in apparent dry density are always lower than 8%, which confirms that the employment of this mine tailing at this replacement level does not change the density of the products significantly.

Table 4. Apparent dry density of the studied composites

Composite	Apparent dry density (g/cm^3)
NAT 3.0 100MK-00SF	1,678
MT 3.0 100MK-00SF	1,750
NAT 3.8 82MK-18SF	1,612
MT 3.8 82MK-18SF	1,665

Figures 3 and 4 show the load (N) x mid-span (mm) deflection curves for the AAM studied after third-point loading tests. All the composites presented multi-cracking behaviour after bending tests typical from AAM containing 2% PVA fibres.

Irrespective of the type of aggregate, a higher SiO_2/Al_2O_3 molar ratio decreased the first peak and peak strength (Figure 5) with consequent increase in the deflection and toughness of the PVA-AAM.

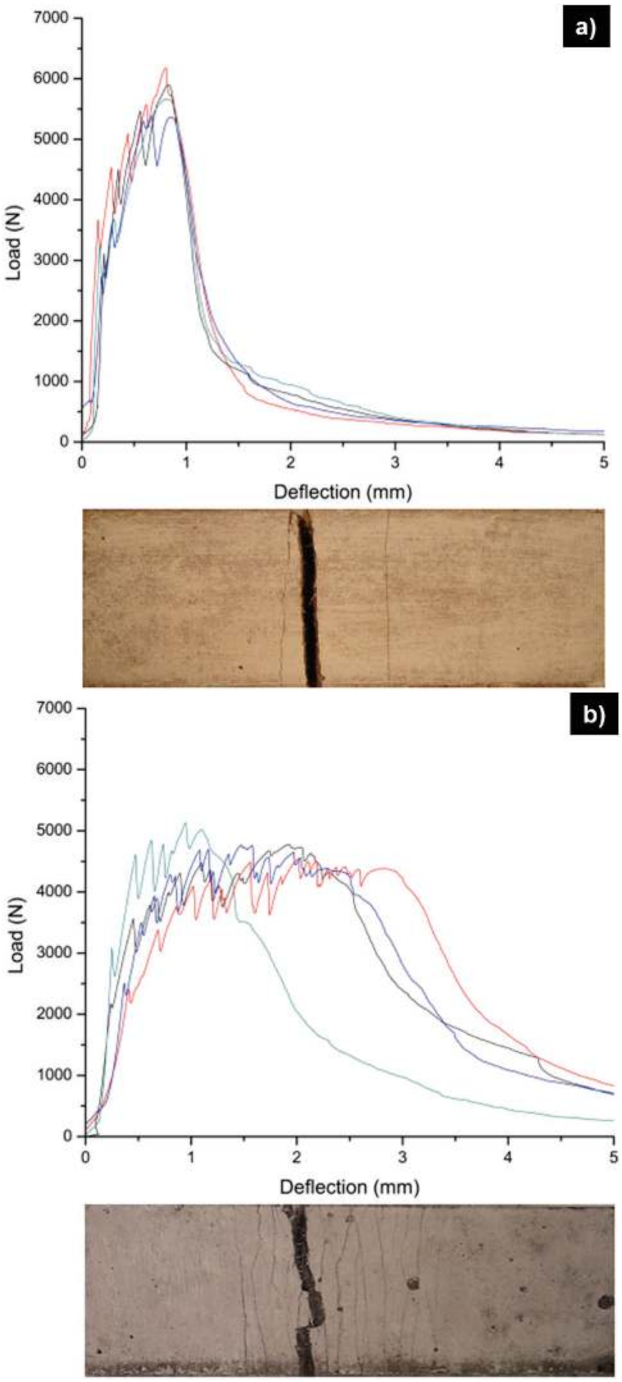

Figure 3. Load x mid-span deflection and cracked specimens for (a) NAT 3.0 100MK-00SF and (b) NAT 3.8 82MK-00SF mortars.

The employment of mine tailing as aggregate slightly increased the peak strength for a fixed SiO_2 / Al_2O_3 molar ratio; the toughness is not jeopardized when the mining tailing is used.

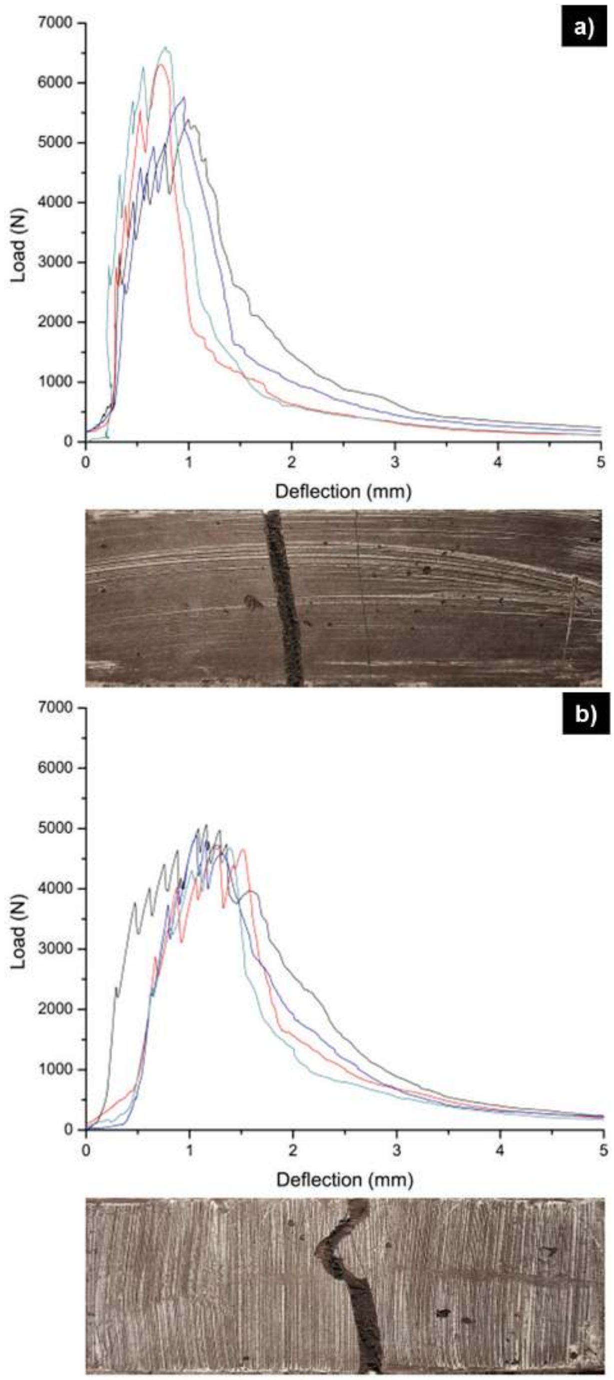

Figure 4. Load x mid-span deflection and cracked specimens for (a) MT 3.0 100MK-00SF and (b) MT 3.8 82MK-00SF mortars.

Overall the results show that the mine tailing used does not affect the mechanical behaviour in flexion significantly; the composition of the matrix appears to play a major role in the adhesion with fibres and toughness.

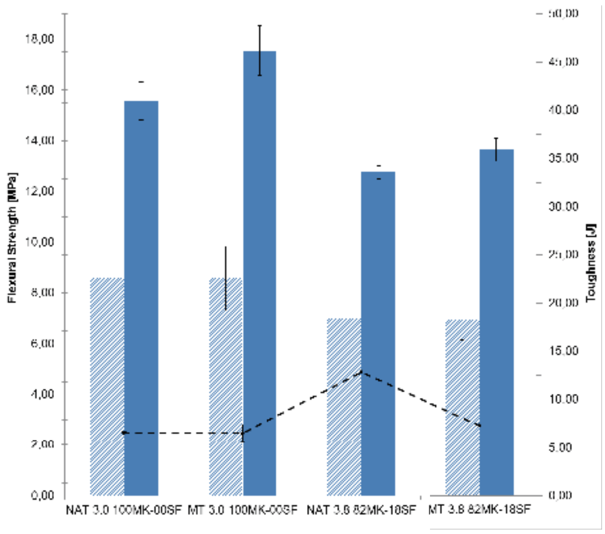

Figure 5. Average first peak (dashed bars), peak strength (solid bars) and toughness (line) of the four different AAM.

4 Conclusions

This study investigated the mechanical properties (compressive and flexural strength) of PVA-reinforced AAM containing either natural quartz aggregate or an iron-ore mine tailing. Irrespective of the type of aggregate used (natural or tailing), satisfactory results were obtained for matrices designed with SiO_2 / Al_2O_3 of 3.0 or 3.8. Overall, the employment of mine tailing slightly reduce the compressive strength, but the flexural strength and toughness is not affect; they are rather a function of the matrix composition.

The results presented in this paper indicate that iron-ore tailings may be effectively used in the production of ECC-AAM, with little or no processing (may be used as received). It is important, however, to investigate the durability-related properties of those AAM.

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