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## The effect of matrix composition and calcium content on the sulfate durability of metakaolin and metakaolin/slag alkali-activated mortars

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### ABSTRACT

The work in hand presents the results of an experimental research on the effect of different precursors (binders) used in alkali-activated materials (AAM) and its composition (i.e.  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio) on their sulfate durability. A reference matrix is formed from the activation of metakaolin (MK); this matrix was modified by the partial replacement of MK with either 20 wt% silica fume (SF) or 20 and 40 wt% blast furnace slag (BFS), so that the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of calcium-free and calcium-rich AAM changed from 3.0 to 3.9. The properties assessed prior to the durability testing were: density (pycnometry), compressive strength, capillary sorption and oxygen permeability. The sulfate durability was investigated by exposing the matrices to a magnesium sulfate solution for 30, 90 and 180 days of attack, after which the residual compressive strength was determined. The reductions in strength after each period of testing were correlated with variations in the pH of the sulfate solutions and with geometry changes (expansion) measured in cylinders exposed to the durability tests. X-Ray diffraction was used to determine the minerals formed onto the surface of the samples after magnesium sulfate attack. The results show that the MK-based AAM present a higher resistance to magnesium sulfate attack. Furthermore, the partial replacement of MK with BFS is responsible for reductions in the mechanical properties after attack to sulfate. This is associated with the formation of ettringite and gypsum in the presence of calcium from BFS, besides the loss of alkalinity from the migration of alkali ( $\text{Na}^+$ ) to the solution.

### 1. Introduction

Alkali-activated materials (AAM) have been studied as alternative binders to Portland cement due to their lower environmental impact, fast strength development and higher chemical and thermal durability. AAM are obtained from the alkaline activation of one or more sources of alumina ( $\text{Al}_2\text{O}_3$ ) and silica ( $\text{SiO}_2$ ), such as metakaolin (MK) [1–4] fly ash [5,6], blast furnace slag [7–9], or mixtures of these materials [10–13]. AAM can be divided into two groups according to the chemical composition of the solid precursor materials [14]. The first group refers to precursors (aluminosilicates) with low CaO content that give rise to a N-A-S-(H) ( $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ ) gel [15]. The materials obtained with the precursors of this group are usually referred to as geopolymers [16]. The second group comprises precursors containing not only  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , but also significant amounts of CaO, producing both N-A-S-(H) and C-A-S-H ( $\text{Ca}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ ) gels from alkaline activation [17–20].

The employment of low-CaO/CaO-free or calcium-rich AAM as binders in mortars and concretes depends mainly on their long-term

durability. Sulfate attack is an issue in Portland-cement based concretes due to the chemical reaction that occurs between the sulfates that will combine with C-S-H, CH and  $\text{C}_3\text{A}$ , forming expansive hydrates (gypsum, ettringite and thaumasite), resulting in the formation of microcracks and loss of mechanical resistance [21,22].

Studies on the durability of AAM exposed to sodium and magnesium sulfate solutions have been carried out over the years [23–27]. It was reported that alkali-activated MK presented some initial reductions in the mechanical strength after exposure to 4.4 wt%  $\text{Na}_2\text{SO}_4$  solution due to an alkali removal from the structure [5]. However, samples continued to react and strength gains were reported after 90-days of exposure as a consequence of formation of zeolitic products that could be filling the porous spaces in the microstructure. Thokchom et al. [24] studied low-calcium alkali-activated fly ash (Class F PFA) under  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  attack (5%  $\text{Na}_2\text{SO}_4$ , 5%  $\text{MgSO}_4$ , and 5%  $\text{Na}_2\text{SO}_4 + 5\%$   $\text{MgSO}_4$ ); in general, the stability of AAM was higher when  $\text{MgSO}_4$  was used, as the diffusion of Mg into the AAM structure appeared to compensate the migration of alkalis from the samples [23]. The reductions on the mechanical strength presented for sodium silicate-activated PFA

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after sulfate exposure is said to be related to the formation of ettringite, although cracks were only visible on SEM analysis [23,24].

In general, low-CaO or CaO-free AAM tends to be more durable due to the non-formation of calcium hydroxide, which is highly susceptible to sulfate attack [25]. Indeed, the durability of AAM is linked to the presence of calcium in the systems [26]; calcium can react with  $\text{SO}_4^{2-}$  ions, producing ettringite that results in the formation of microcracks, reducing the mechanical strength of the material. The degradation mechanisms of the AAM are associated with the nature of the cation that accompanies the sulfate anions: exposure to  $\text{Na}_2\text{SO}_4$  solutions contributes to the structural evolution of the binding and densification phases of the system; in contrary, solutions of  $\text{MgSO}_4$  cause decalcification of the C-A-S-H resulting products of the alkaline activation of blast furnace slag [27].

Although there is some valuable information on sulfate durability of AAM in the literature, the effect of the composition of the matrix (in terms of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio) is little explored. This work evaluates the influence of modifications in the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio on the mechanical and durability properties of alkali-activated materials exposed to a magnesium sulfate solution. The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios are altered by the partial replacement of MK (the main source of aluminosilicates) with 20% and 40% blast furnace slag (BFS) or 20% silica fume (SF). Thus, the effect of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio on the sulfate durability is studied for both calcium-rich and calcium-free AAM.

## 2. Materials and methods

### 2.1. Raw materials and formulations of alkali-activated mortars

The AAM studied are based on the alkaline activation of metakaolin (MK), silica fume (SF) and blast furnace slag (BFS), respectively supplied by Metacaulim do Brasil Ltda, Tecnosil Ltda and IBEC Central. The alkaline solution used as activator was composed of a mixed NaOH (50 vol%) and sodium silicate solution ( $\text{SiO}_2 = 31.8\%$ ;  $\text{Na}_2\text{O} = 15.0\%$ ;  $\text{H}_2\text{O} = 53.2\%$ ). River sand aggregate (particle size < 1.18 mm) was used in the production of the mortars.

Fig. 1 presents the LASER particle size distribution for MK, SF and BFS; it shows that SF is thinner than MK, and BFS is coarser than MK. Thus, it is expected that the substitution of MK by SF and BFS affect the workability of MK/SF and MK/BFS alkali-activated mortars. Table 1 shows the precursors chemical compositions (main oxides) for the same raw materials, whereas Fig. 2 shows their XRD diffraction patterns. Silica fume is predominantly composed of amorphous  $\text{SiO}_2$ ; its employment as MK replacement does not add calcium to the matrices, but alters the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio due to the extremely low  $\text{Al}_2\text{O}_3$  content in the first. MK and BFS are mostly amorphous as well; MK contains small

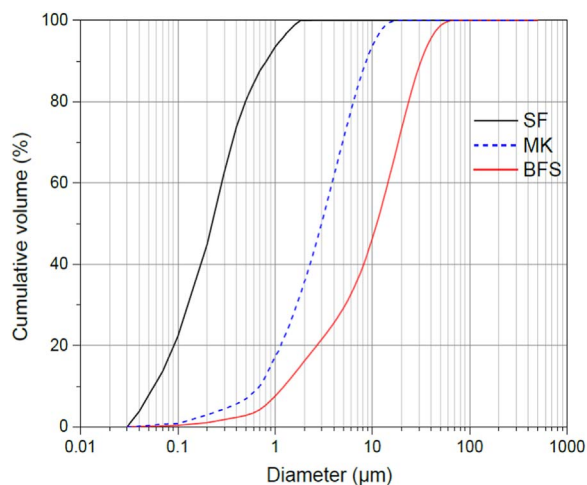


Fig. 1. LASER particle size distribution for MK, SF and BFS.

Table 1

Chemical compositions of metakaolin (MK), blast furnace slag (BFS) and silica fume (SF).

Oxides (%)	MK	BFS	SF
$\text{SiO}_2$	55.9	45.2	95.1
$\text{Al}_2\text{O}_3$	43.0	10.8	0.7
CaO	0.1	32.7	0.4
$\text{Fe}_2\text{O}_3$	0.5	2.3	1.1
MgO	–	5.4	0.8
MnO	–	1,38	0,05
$\text{K}_2\text{O}$	0,17	0,93	1,33
$\text{SO}_3$	0,04	0,44	0,30
$\text{TiO}_2$	0,06	0,43	–

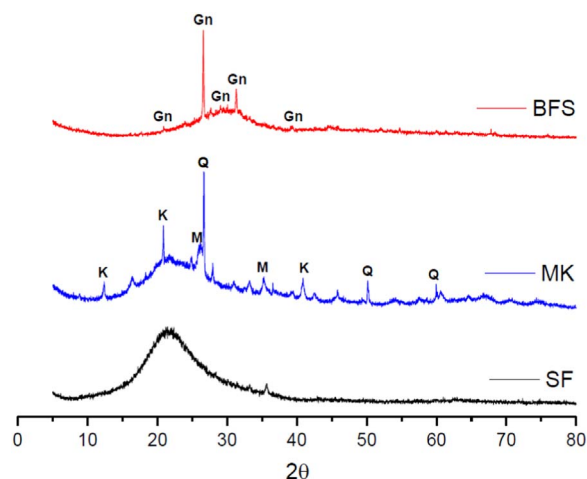


Fig. 2. XRD diffraction patterns for the starting materials, MK, SF and BFS. Q = quartz; K = kaolinite; M = muscovite; Gn = gehlenite.

peaks of quartz and muscovite, which are normal impurities in kaolins and metakaolins. The kaolin peaks indicate that a small fraction of kaolinite did not transformed into MK during the calcination process. BFS presents some crystalline peaks for the mineral gehlenite, which is usually found in pig iron slags. The replacement of MK with BFS also increases the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio, as the  $\text{Al}_2\text{O}_3$  content is also lower in the latter (10.8% against 43.0% in MK); however, the employment of BFS introduces calcium in the matrices, given the high content of CaO (32.7%) in this precursor.

Four different matrices were studied (Table 2); the reference matrix is composed of the alkali-activation of MK, designed to present a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio equal to 3.0 (F3.0-100MK). The second matrix (F3.0-80MK20BFS) has the same silica/alumina molar ratio (3.0), but with the replacement of MK with 20 wt% of BFS; being produced, therefore, with a source of calcium (BFS). The other two matrices were produced with a higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio i.e. 3.9, achieved by replacing MK with either 20 wt% SF (F3.9-80MK20SF) or 40% BFS (F3.9-60MK40BFS). The formulation codes refer to the designed  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio followed by the proportion (in mass) between the precursors. It is possible to perceive that the formulations were designed to assess changes due to (i) the effect of calcium content on matrices with same  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ; (ii) different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (3.0 and 3.9) on both Ca-free and Ca-rich matrices.

It is also important to note that the  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  molar ratio was fixed for all matrices (equal to 11.0); this was experimentally established to allow the production of self-compacting mortars without segregation (which occurred for matrices containing BFS and  $\text{H}_2\text{O}/\text{Na}_2\text{O} > 11.5$ ). A constant  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  molar ratio is important to compare the durability-related properties, given that  $\text{H}_2\text{O}$  does not take part of the alkali-activation per se [14]; it only provides a media so that the alkalis can reach the precursors properly.

The amounts of precursors and the composition of the alkaline

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