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EVALUATION OF MAGNESIUM SULPHATE ATTACK IN MORTAR-METAKAOLIN SYSTEM BY THERMAL ANALYSIS

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This paper reports an experimental study on the magnesium sulphate resistance of mortar specimens incorporating 0, 10 and 20% of metakaolin (MK). The evidence of the attack was evaluated through the content of calcium hydroxide (portlandite) and formation of magnesium hydroxide (brucite) by thermal analysis (thermogravimetric and derivative thermogravimetric analysis). The mechanical degradation of the mortar specimens was evaluated through splitting tensile tests after 200 days of exposition to the magnesium solution. The addition of metakaolin resulted in a reduction in the content of calcium hydroxide and in a smaller formation of brucite in comparison with reference mixture. A tensile strength loss of about 7% was observed for the metakaolin mortars submitted to the magnesium solution attack for 200 days.

Keywords: *metakaolin, mortar, sulphate attack, TG/DTG*

Introduction

Portland cement based materials when subjected to the attack of external magnesium sulphate may be seriously damaged due to the interaction between the hydrated cement paste and the magnesium sulphate solution [1, 2]. The interaction of magnesium sulphate with the calcium hydroxide (CH) present in the set cement paste generates magnesium hydroxide (brucite – $Mg(OH)_2$) and calcium sulphate (gypsum – $CaSO_4{\cdot}2H_2O$). The replacement of Ca by Mg in the hydrated calcium silicates (C–S–H) leads to the formation of M–S–H [2, 3]. These reactions can occur simultaneously causing expansion, cracking or spalling, softening and disintegration of the cementitious material [4].

Sulphate attack can be controlled using low-C3A portland cement and low water/cement ratios. The use the mineral admixtures such as metakaolin improves its sulphate resistance due to the reduction of matrix permeability and consume of the CH formed during calcium silicates hydration [5, 6].

The evaluation of the damage caused by the sulphate attack in cementitious materials are based on visual examination, changes in the mechanical properties or expansion of cement paste or mortars immersed in sulphate solutions [7, 8]. Analytical methods such as X-ray diffraction [9], scanning electron microscopy [10, 11] transmission X-ray microscopy [12] and X-ray microtomography [13] have also been used to evaluate the evidences of the magnesium sulphate attack on cement based materials but they can provide only qualitative information. The characterization of the products of magnesium sulphate attack (brucite, gypsum and M–S–H) by thermal analysis can give quantitative information on the magnitude of the sulphate attack and its combination with mechanical tests consists in a powerful methodology to determine the extent of the chemical and mechanical damage in cement based systems. In the present paper this approach is used to study the resistance to magnesium sulphate attack of mortar mixtures containing 0, 10 and 20% of metakaolin (MK) as Portland cement replacement (by mass).

Experimental

Materials

This study made use of a Portland cement, class CPII-F32 under Brazilian standards [14] (defined as containing: 85 mass%<clinker≤91 mass%; 3 mass%< gypsum<5 mass%; 6 mass%<filler< 10 mass%) and giving 32 MPa compressive strength at 28 days in the standard test. Its main chemical and physical characteristics are presented in Table 1.

The TG and DTG curves of the Portland cement are presented in Fig. 1a. It can be seen that the cement presents a slight mass loss between 380–440°C due to the dehydroxylation of the calcium hydroxide, which may be formed from the hydration of the free lime present in the clinker. Between 500–730°C the mass

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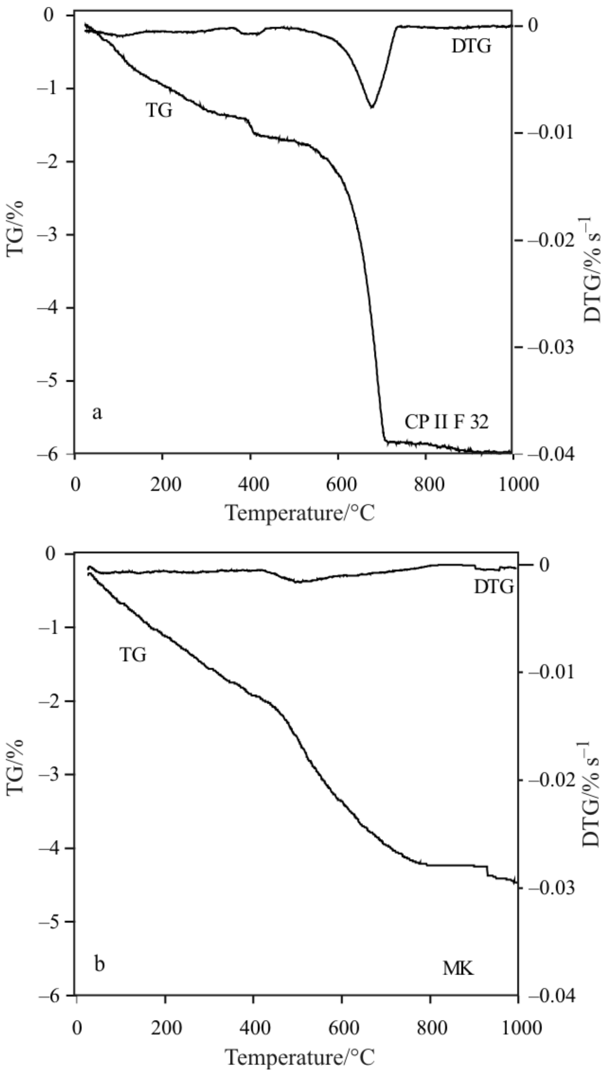

Fig. 1 TG and DTG curves of a – cement CPII F 32 and b – metakaolin

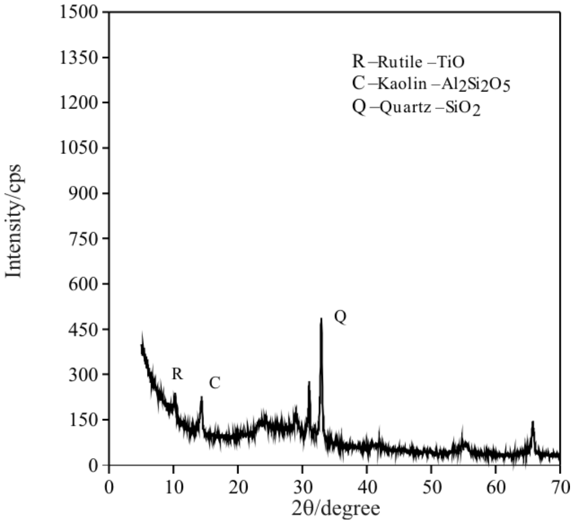

Fig. 2 X-ray diffraction pattern of metakaolin

loss is due to the decarbonization of $CaCO_3$ present in its composition. The mass loss between 105–1000°C was of about 5.4%.

The sand used was natural sand with fineness modulus of 2.37 and specific gravity of 2.64 g cm^{-3}. A naphthalene sulphonate formaldehyde-based superplasticizer (SP) with a total amount of solid particles of 40% was used to correct the workability of the blended mixtures. Tap water was used in all mixtures.

The used metakaolin (MK) was purchased from a Brazilian manufacturer and having a specific gravity of 2.65 g cm^{-3}, a specific surface area BET of 22.60 m^2 k g^{-1} and a median particle size of 3.0 μm. The chemical composition of the metakaolin pozzolan is presented in Table 1. X-ray diffraction results are presented in Fig. 2, which reveal the presence of amorphous material. Using the Rietveld method it was estimated that the amount of amorphous

Table 1 Physical and chemical properties of the Portland cement and metakaolin

	CP II F 32	Calcined-clay brick
Specific gravity/g cm^{-3}	3.10	2.65
Passing on 45 μm mesh/%	80	62
Chemical properties/mass%		
SiO_2	19.98	51.20
Fe_2O_3	3.12	4.00
Al_2O_3	3.70	35.30
CaO	62.80	2.62
MgO	3.10	0.40
Na_2O	0.07	Traces
K_2O	0.80	0.97
Insoluble residue/%	1.50	Traces

materials was about 87% whereas the contents of kaolinite, quartz, biotite and rutile were respectively 7, 3, 3 and <1%. Details about the principle of Rietveld analysis can be found in [15]. The metakaolin presented a 3.8% mass loss between 105–1000°C (Fig. 1), which may be attributed to the presence of impurities in the raw material and/or deficient calcinations by the manufacturer. The physical and chemical characteristics of the used metakaolin have shown that the material meets the specification requirements of ASTM 618 C (ASTM 1992) for Portland cement mineral additives.

Methods

Mix proportions

Mortar mixtures, where 10 and 20% of cement was replaced by metakaolin (MK) were prepared (mixes named M1MK10 and M1MK20) besides a reference (control) mixture using only Portland cement as binder (mix named M1MK0). The mixes were produced with the ratio by mass of 1 cementitious material: 1.5 sand. The water/cementitious material ratio was kept constant and equal to 0.5. Mixing was performed in a bench-mounted mixer. The fine aggregate was first added followed by a previously blended mix of cement and MK. After mixing for about 2 min water was slowly added and mixing was continued for a total of 5 min. Superplasticizer had to be added to the mix containing 20% of MK in order to maintain a constant workability (255±10 mm) for all mixes measured with the aid of the flow-table test. The superplasticizer dosage (in dry superplasticizer mass by mass of binder) for the mix containing 20% MK was 0.2%.

Specimen preparation, curing and testing

For each mix, ten specimens 50 mm in diameter and 100 mm in length were cast in steel moulds and compacted by external vibration. After casting, the moulds containing the specimens were covered with a damp cloth and a polythene sheet to prevent water loss and after 24 h the specimens were demoulded and water-cured at 24°C for 28 days. From the central part of each cylinder it was taken three disks of 50 mm in diameter×25 mm to evaluate the indirect tension strength of the mortars mixtures. Six disks of each mix were tested under splitting tensile loads after 28 days of curing in deionised water and the other six disks were tested after 200 days of exposition to a 5% MgS solution. The splitting tensile tests were carried out in a 1000 kN Shimadzu testing machine at a loading rate of 0.1 mm min^{-1}. The test set-up is shown in Fig. 3.

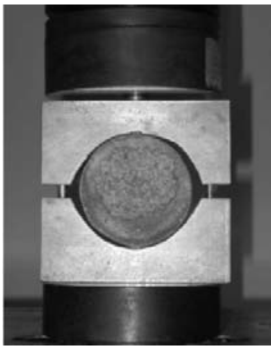

Fig. 3 Indirect tension testing set-up

The content of calcium hydroxide and brucite was evaluated by thermogravimetric analysis after 28 and 200 days of exposition. Samples of about 50 g were collected from the cylindrical specimens, grinded and sieved to have particles that were smaller than mesh 100 (149 μm). The samples were dried with acetone at the specified ages to stop hydration.

Thermal analyses were performed in a simultaneous TG/DTA Rigaku equipment, model TAS 100. The TG and DTG curves were obtained at a heating rate of 10°C min^{-1} from 35 to 1000°C and in 53 mL min^{-1} of nitrogen flow and in 8 mL min^{-1} of oxygen flow. Thermogravimetric analysis (TG) were performed from 35 to 1000°C in N_2 (53 mL min^{-1}) and in O_2 (8 mL min^{-1}) at a heating rate of 10°C min^{-1} in a simultaneous TG/DTA Rigaku, model TAS 100. The reference sample was alpha-alumina and a sample mass of about 15 mg was used in each analysis.

The content of calcium hydroxide (CH) and magnesium hydroxide (MgH) were determined from the ratio of the mass loss measured between the initial temperature (M_{tiCH} and M_{tiMgH}, respectively) and the final temperature (M_{tfCH} and M_{tfMgH}, respectively) and the mass loss at 1000°C ($M_{1000°C}$). The following dehydration and decomposition reaction and theoretical mass losses were considered:

$$\text{(R-1) } Ca(OH)_2 \rightarrow CaO + H_2O$$

$$\text{(mass loss = 24.34\%)}$$

$$\text{(R-2) } Mg(OH)_2 \rightarrow MgO + H_2O$$

$$\text{(mass loss = 30.88\%)} \qquad (1)$$

The content of CH and MgH were estimated using Eqs (2) and (3), respectively. The calculation of the CH and MgH content with reference to the final ignited mass of the sample ($M_{1000°C}$) allows a better evaluation of the non evaporable water of the hydrates [16–19]. The parameters CH and MgH were computed using the effective mass of Portland cement and metakaolin present in the mix, discounting the mass loss of each material.

$$CH = \frac{M_{tich} - M_{tfch}}{M_{1000℃}} \tag{2}$$

$$MgH = \frac{M_{tiMgh} - M_{tfMgh}}{M_{1000℃}} \tag{3}$$

Results and discussion

TG and DTG curves of the samples M1MK0, M1MK10 and M1MK20 after 28 days of curing in deionised water and after 200 days of exposition to a 5% MgS solution hydration are presented in Figs 4–6. Calcined cement mass basis (mass at 1000°C) was applied to thermogravimetric analysis (TG) data of the water cured and of the attacked cement mortars to calculate and compare, on a same basis, the mass losses due to dehydration or decomposition steps of the main phases of the water cured and attacked samples.

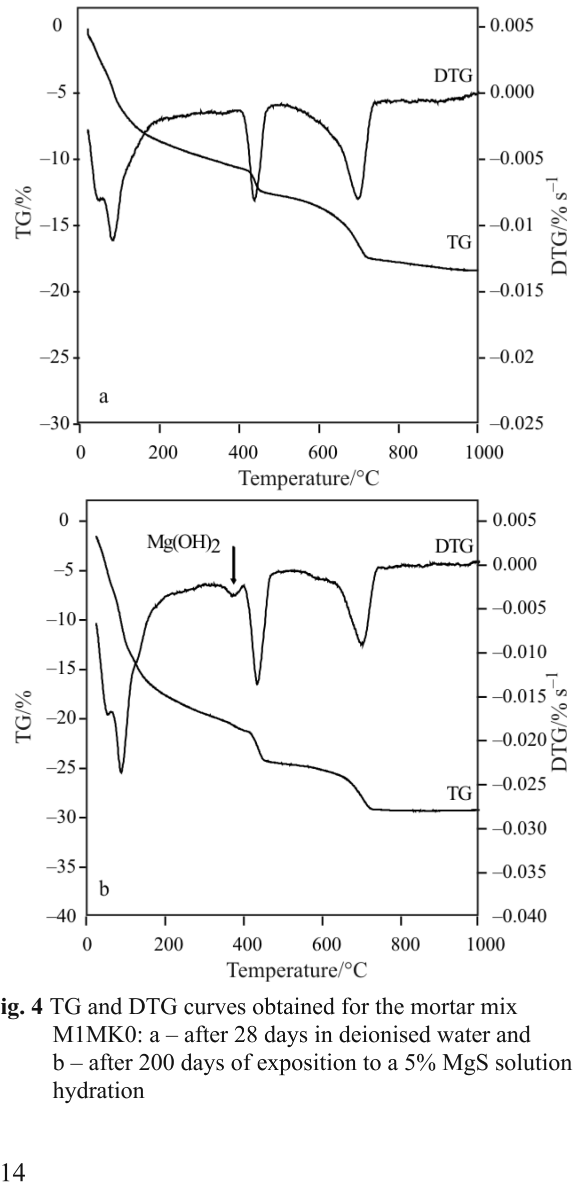

Fig. 4 TG and DTG curves obtained for the mortar mix M1MK0: a – after 28 days in deionised water and b – after 200 days of exposition to a 5% MgS solution hydration

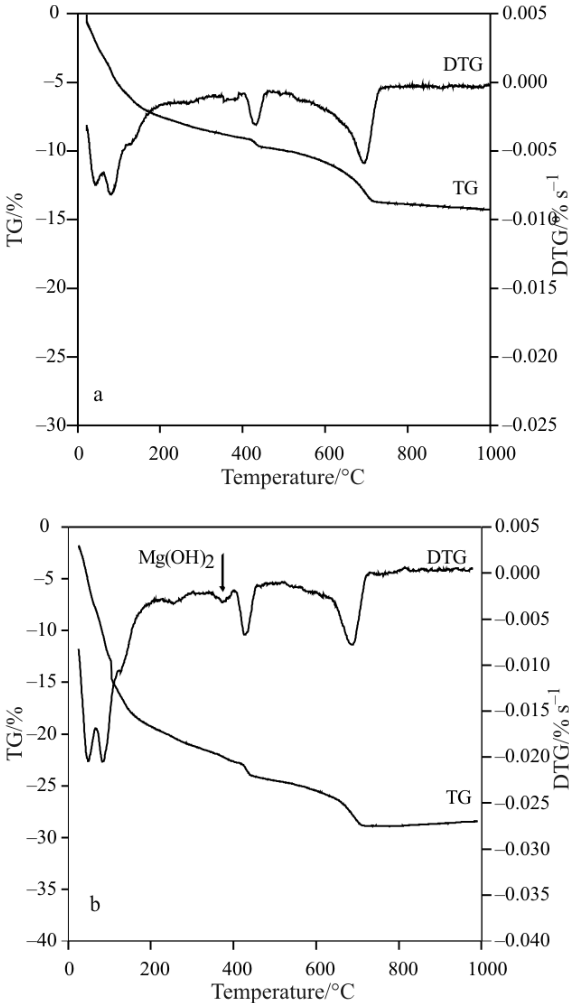

Fig. 5 TG and DTG curves obtained for the mortar mix M1MK10: a – after 28 days in deionised water and b – after 200 days of exposition to a 5% MgS solution hydration

From the DTG curves the following main mass loss can be identified: (*i*) the mass loss between 100 and 300°C is due to the dehydration of the tobermorite and ettringite phases present in the cement matrix [4]; (*ii*) between 300 and 400°C occurs the dehydration of brucite (magnesium hydroxide); (*iii*) the mass loss between 400 and 460°C is related to the dehydroxylation of the portlandite (calcium hydroxide); (*iv*) the mass loss between 500 and 700°C corresponds to the calcium carbonate phase decomposition [18]. The main focus of the present paper was to evaluate the influence of the MK addition on the decomposition of brucite and portlandite phases.

Portlandite content before and after aging

The variation of the calcium hydroxide is presented in Fig. 7. It can be seen that the MK addition reduced significantly the CH content of the reference Portland cement mixture after 28 days of cure in deionised water. For example, the CH content of mixtures M1MK10 and M1MK20 is, respectively, 56 and 79% less than that presented by the mixture M1MK0. This behaviour is attributed to the pozzolanic reaction between the CH and the MK that results in an increase in the silicates and aluminates hydrates phases in the mixtures. A similar trend was observed for the mechanical test results. The splitting tensile strength (Table 2) is increased by about 13.2 and 15.6% when respectively, 10 and 20% of MK are present in the mixtures.

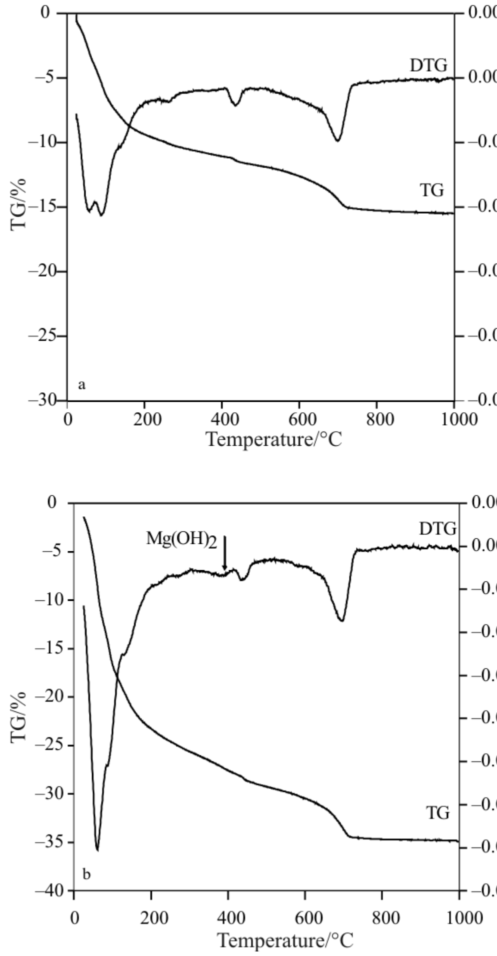

Fig. 6 TG and DTG curves obtained for the mortar mix M1MK20: a – after 28 days in deionised water and b – after 200 days of exposition to a 5% MgS solution hydration

After 200 days of exposure to the magnesium sulphate solution the CH content was reduced for all mixes. The reduction reached 21.6, 30.8 and 39.7% for the mixtures M1MK0, M1MK10 and M1MK20, respectively, in comparison with the control mixes. Observe that the mixture containing a higher content of metakaolin suffered a more severe attack. This occurs due to the dissolution of calcium and hydroxyl ions from the system leading to a possible decrease in the alkalinity of the medium and to the formation of potentially expansive compounds such as ettringite or gypsum [20].

$Mg(OH)_2$ content after aging

The variation in the magnesium hydroxide content is also presented in. After 200 days of exposure to the magnesium sulphate solution it can be observed the

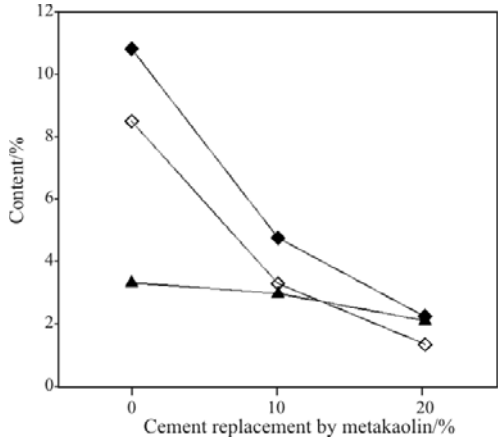

Fig. 7 Variation of the $Ca(OH)_2$ and $Mg(OH)_2$ content with the Portland cement replacement by metakaolin
◆ – Ca $(OH)_2$, 28 days in deionised water;
◇ – Ca $(OH)_2$, 200 days of sulphat solution;
▲ – $Mg(OH)_2$, 28 days in sulphat solution

Table 2 Values of tensile strength (f_t), coefficient of variation (*CV*) and relative strength for the mortar mixes immersed to deionised water (f_{tw}) and in a 5% MgS solution ($f_{t\ 5\%\ MgS}$)

Time of immersion/day	Mix	Tensile strength (MPa)–(*CV*/%)		
		f_{tw}	($f_{t\ 5\%\ MgS}$)	$f_{t\ 5\%\ MgS}/f_{tw}$
Prior to immersion*	M1MK0	3.33–(3.03)	–	–
	M1MK10	3.77–(0.80)	–	–
	M1MK20	3.85–(2.20)	–	–
200	M1MK0	4.33–(5.15)	3.83–(0.84)	0.88
	M1MK10	4.34–(1.80)	4.66–(6.61)	1.07
	M1MK20	4.71–(2.88)	4.38–(6.79)	0.93

*Values of tensile strength of the specimens cured in water at 24°C for 28 days formation of 3.3% of $Mg(OH)_2$ for the mixture of M1MK0. These increase in the content of $Mg(OH)_2$ is an indication of the intensity of the chemical attack in the matrix due to the reaction between the magnesium sulphate with the calcium hydroxide. The formation of $Mg(OH)_2$ in the mixes containing metakaolin was in a less proportion. For example, the mixture M1MK10 presents a 3.0% content of $Mg(OH)_2$ whereas the mixture M1MK20 presents 2.1% of $Mg(OH)_2$ after aging. The reduction in the level of $Mg(OH)_2$ formation occurs due to the consume of CH by the MK with a consequent increase in the volume of CSH products.

Mechanical damage due to the sulphate attack

The results presented in Table 2 indicate that after 200 days of exposure to the magnesium sulphate solution the OPC reference mixture presents a strength loss of about 12% in comparison with the results obtained for the specimens cured in deionised water for the same period. This damage has been attributed to the replacement of Ca in C–S–H by Mg leading to a reduction in the mixture cementing properties [3].

The M1MK10 specimens exposed to a 200 days sulphate attack presented a tensile strength slightly higher (increase of about 7%) than that of the specimens kept in deionised water for the same period. For the same period of exposition the samples of mix M1MK20 presented a strength loss of about 7%. This strength reduction may be related with the fact that in cement based materials with low amount of the CH it can occur a high rate of decalcification of C–S–H producing gypsum, non-cementing M–S–H phase, brucite and hydrated silica gel. A second mechanism to explain a similar strength reduction is described by [21]. According to the author, the formation of salts crystals in the fine pore structure of cement-metakaolin systems exerts considerable pressure that result in a higher deterioration of the material.

Conclusions

The use of thermoanalytical techniques for monitoring the evolution of brucite formation and portlandite content during a magnesium sulphate attack to cementitious materials has proven to be a powerful tool to give quantitative information regarding to the magnitude of the deterioration.

Regarding to the influence of metakaolin addition in the resistance to sulphate attack of Portland cement mortar mixes the results indicated that its presence consumes calcium hydroxide and generates a smaller quantity of brucite in comparison with reference mixture. This addition, however, does not avoid the strength loss of the Portland cement mixture with aging. For example, a tensile strength loss of about 7% was observed for the metakaolin mortars submitted to the magnesium solution attack for 200 days.

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