Performance evaluation of cement mortars modified with metakaolin or ground brick

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ABSTRACT

The work analyzes the performance of mortars prepared with two metakaolin samples and ground calcined-clay brick. Complete stress–strain deformation response under compression, porosity, sorptivity, pore size distribution and resistance to penetration of chloride ions have been determined for mortars with up to 40% cement replacement. Continuum damage mechanics analyzes using a scalar model allowed to extract information on the mode of deformation leading to failure of the mortars during compressive loading. It is shown that not only the ultimate strength, but also the pre-peak deformation response is influenced by calcined-clay addition. The ultimate strength of the mortar mixture depended on the type of calcined-clay added, but in all cases mortars with addition were marginally more compliant during the elastic deformation stage and more brittle as fracture approached.

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1. Introduction

The incorporation of mineral additives can enhance the performance of mortars and concrete both in fresh and hardened states, improving their mechanical properties and durability. It can also reduce CO_2 emissions and energy consumption, while contributing to the reduction of the environmental impact associated to cement manufacture [1,2].

In Brazil, industrial byproducts, such as silica fume, fly-ash and blast-furnace slag, have comparatively limited availability when compared to the consumption of cement nationwide. This has led investigators to seek for alternative cementitious materials, such as thermally-activated (calcined) clay.

Clays most commonly used in the production of pozzolans are kaolinites, montmorilonites and ilites. Investigations conducted by a number of researchers showed that clays from the kaolinite group present the greatest pozzolanic activity after calcining when compared to those from other groups [3,4], so that a number of studies have been conducted that deal with the technical and environmental benefits from the use of metakaolin [5–8]. An additional possibility is the production of calcined-clay from wastes of the ceramics industry. This industry often produces calcined-clays that result from burning ilite-group clays, which are normally used in the production of common red-clay ceramic products, such as bricks and roofing tiles. The use of ceramic brick residues as partial cement replacement materials in mortars and concrete has been the subject of a number of recent studies [2,9–14]. Although their influence on the strength and other properties of mortars and concrete has been well studied, no work analyzes in enough detail their influence on the entire mechanical response of mortars and concrete in the hardened state.

The understanding and quantitative description of the effect of calcined-clays as partial cement replacements in the entire mechanical response of mortars and concrete is important, since it will allow predicting the deformability of the resulting structure. The stress–strain relationship, the modulus of elasticity and the rigidity of concrete at a certain age, depend on the elastic modulus of the cement paste and the aggregate, on the volume proportions of each phase and on the paste–aggregate interface [14].

Investigations conducted by Qian and Li [15] demonstrated that the replacement of up to 15% of cement by metakaolin resulted in increase in the elastic modulus of concrete. Studies have indicated that the presence of metakaolin leads to an increase in microhardness of cement matrices produced with a water/cementitious material ratio of 0.5, suggesting that metakaolin improves the toughness of the matrix [16]. Still, only a limited number of investigations have dealt with the role of calcined-clay in the deformation response of mortars and concrete.

An efficient framework to describe the deformation behavior and the rigidity of mortars and concrete is offered by models that describe the stress–strain response using a combination of damage mechanics and classical elasticity. The present work analyzes the deformability of mortars containing different types of

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calcined-clays using the scalar continuum damage mechanics model proposed by Løland [17], investigating also their porous structure, porosity and sorptivity.

2. Continuum damage modeling

Løland [17] proposed a model that describes strain–stress relationships which has been successfully applied to concrete under tensile and unconfined compressive stresses [17,18]. Damage mechanics combines the strain–stress relationship from linear elasticity with the definition of an effective elastic modulus in the constitutive equation

$$f = (1 - D)E^*\varepsilon \tag{1}$$

where E^* is Young's modulus of elasticity of the material in a state free of voids or cracks (undamaged and intact), D is the scalar damage variable, f are stresses and ε are strains. Løland [17] proposed that the damage variable may be related to strain by a power-law relationship

$$D = D_0 + A_0\varepsilon^\gamma \tag{2}$$

where D_0 is the initial damage at the onset of the unconfined compression test, and A_0 and γ are material-specific constants that must be determined empirically. This initial damage has been considered by Løland [17], in the case of concrete, to be essentially due (and therefore equivalent) to initial porosity. It also may be related to the nominal modulus of elasticity (the ordinary Young's modulus E) calculated from the initial linear part of the actual stress–strain relationship by

$$E = E^*(1 - D_0) \tag{3}$$

From the derivative of Eq. (1) equal to zero, the definitions of maximum stress f_c and the corresponding peak deformation ε_c, and by replacing (3) and (2) in (1), it gives [18]

$$f = \left[1 - \left(\frac{\varepsilon}{\varepsilon_c}\right)^\gamma \frac{1}{1+\gamma}\right]E\varepsilon \tag{4}$$

The critical amount of damage D_c may be given by

$$D_c = 1 - \frac{f_c}{E^*\varepsilon_c} \tag{5}$$

from which the constant γ, required to calculate the stress–strain relationship (Eq. (4)), is given by $\gamma = (1 - D_0)/(D_c - D_0) - 1$.

Values of the parameter γ and, therefore, D_c, in the present work were determined from fitting the stress–strain curves from individual tests using Eqs. (4) and (5).

D_c is the maximum amount of damage that the material sustains under loading and is still capable of withstanding stresses. Materials that present highly brittle behavior present low values of D_c, which means that small inelastic deformations and limited damage lead to its failure. On the other hand, materials that present high values of D_c are characterized by highly inelastic response, that is, are capable to withstand comparatively large inelastic deformations prior to fracture.

3. Experimental work

3.1. Materials

A Portland cement (PC) with mineral additive (85–91% by clinker; 3–5% by gypsum and 6–10% by filler, in weight) with 32 MPa of compressive strength at 28 days was used in preparing the mortars [19]. A summary of its chemical composition and some physical characteristics is presented in Table 1. The fine aggregate used was natural river sand with fineness modulus of 2.37 and specific gravity of 2.64 g/cm³. Naphthalene sulphonate formaldehyde-based superplasticizer was used to correct the workability of the blended mixes and tap water was used in all mixes.

Table 1
Physical properties and chemical composition of the Portland cement (PC), ground calcined-clay brick (GB), commercial metakaolin (MK1) and laboratory metakaolin (MK2)

	PC	GB	MK1	MK2
Specific gravity (g/cm³)	3.10	2.65	2.65	2.57
BET surface area (m²/g)	–	19.0	22.6	40.7
% passing on 45 µm sieve	80	62	100	100
Chemical composition (wt%)				
SiO_2	19.98	63.89	51.20	52.46
Fe_2O_3	3.12	7.73	4.00	2.06
Al_2O_3	3.70	25.49	35.30	44.24
CaO	62.80	0.29	2.62	Traces
MgO	3.10	0.04	0.40	Traces
Na_2O	0.07	Traces	Traces	Traces
K_2O	0.80	0.95	0.97	Traces
Ti_2O	Traces	Traces	0.41	1.28
MnO	Traces	Traces	0.16	Traces
Insoluble residue (%)	1.50	Traces	Traces	Traces

Three types of calcined-clays were used: (i) ground calcined-clay brick (GB); (ii) commercial metakaolin, designated here as metakaolin #1 (MK1) and (iii) a calcined-clay that was produced in the authors' laboratory and was designated metakaolin #2 (MK2).

Table 1 presents the chemical composition of the calcined-clays, which demonstrates that all of them meet the requirements specified by ASTM 618 C [20] for classification as Portland cement mineral additives.

The material used to produce the ground calcined-clay brick consisted of fragments of fired clay bricks that were calcined at about 850 °C and were discarded as waste in a local brick manufacturer. These were first crushed and then finely ground in a batch vibratory grinding mill. Fig. 1 compares the grading curves of GB and PC, which shows that both materials have about 50% of particles finer than 20 µm, whereas the ground calcined-clay brick presented a larger proportion of material in finer size ranges. The X-ray diffraction results are presented in Fig. 2, where quartz, hematite, sillimanite, microcline and illite were identified, besides amorphous material, in GB. Using Rietveld method the amount of amorphous material was estimated as 61% whereas the contents of quartz, hematite, sillimanite, microcline and illite were 27%, 5%, 2%, 2% and 1.5%, respectively.

The commercial metakaolin sample (MK1) was purchased from a Brazilian manufacturer and presented a median particle size of 3.0 µm (Fig. 1). The fineness of the pozzolan meets the requirements of ASTM 618 C since the percentage retained in the 45 µm sieve is smaller than 34%. X-ray diffraction results are presented in Fig. 2, which reveal the presence of amorphous material. Using Rietveld method the amount of amorphous materials was estimated as about 87%, whereas the contents of kaolinite, quartz, biotite and rutile were, respectively, 7%, 3%, 3% and
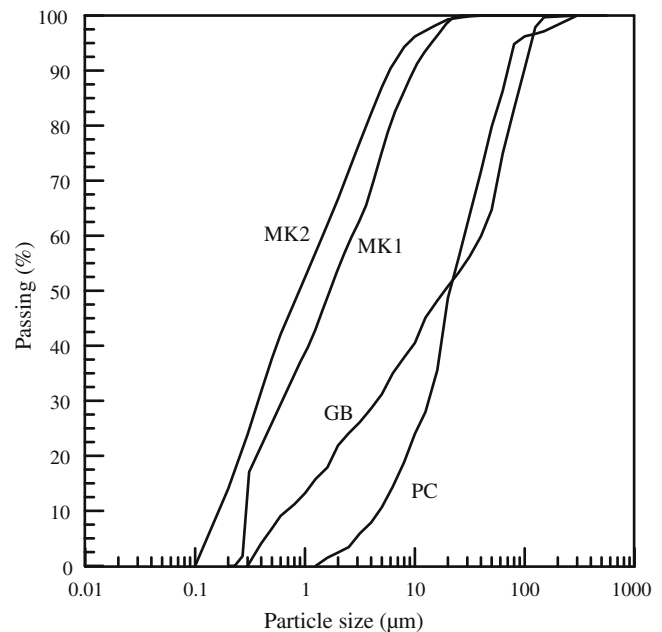

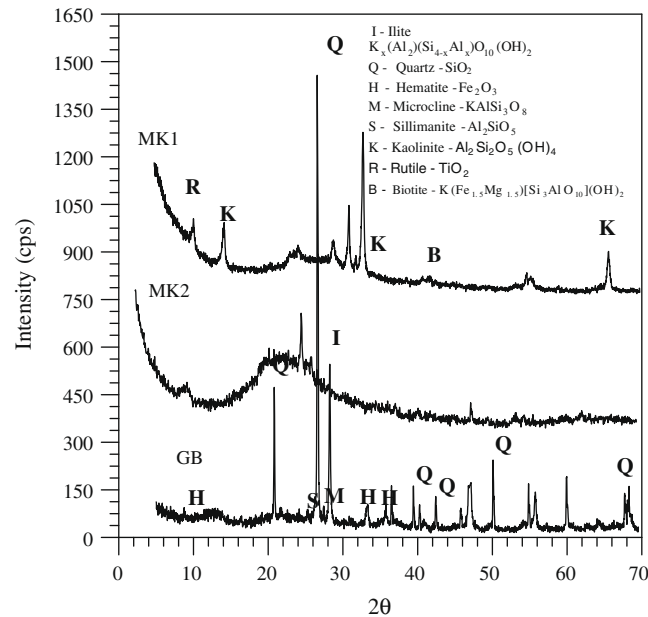**Fig. 1.** Grading curves of Portland cement and calcined-clays.

Fig. 2. X-ray diffraction patterns of calcined-clays.

<1%, approximately. The metakaolin presented a 3.8% weight loss between 105 and 1000 °C, which may be attributed to the presence of impurities in the raw material and/or deficient calcinations by the manufacturer.

The laboratory-produced metakaolin (MK2) was prepared from burning kaolin clay at 550 °C in a muffle furnace for 2 h, from an initial heating for 1 h at 80 °C followed by heating to 120 °C for 1.5 h. The particle size distribution of MK2 is presented in Fig. 1, which shows no residue in the 45 μm sieve, which allows to classify it also as an appropriate concrete mineral admixture (ASTM 618 C). The X-ray diffraction pattern (Fig. 2) shows the predominance of amorphous material, besides a small proportion of kaolinite and quartz, estimated by Rietveld analyzes as about 4%.

BET surface area measurements (Table 1) showed reasonably consistent results with particle size analyzes, with the highest surface area found for MK2 and the lowest for GB, while all surface areas significantly higher than those typically found, although not measured, for ordinary PC.

3.2. Mix proportions

Thirteen different mortar mixes have been prepared, with the ratio (in weight) of cementitious material to sand of 1:1.5 and the water/cementitious material ratio of 0.5 set for all tests. Mortar mixtures, where 10%, 20%, 30% and 40% of cement was replaced by calcined-clay samples (GB, MK1 or MK2), were prepared, besides a reference (control) mixture using only cement as binder (0% cement replacement). Mixing was performed in a bench-mounted mixer. The fine aggregate was first added, followed by a previously blended mix of cement and admixture (GB, MK1 or MK2). 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 mixes containing 20%, 30% and 40% of admixture in order to maintain a constant workability for all mixes, measured with the aid of the flow-table test. The superplasticizer dosage (in dry superplasticizer weight by mass of binder) for mixes containing 20% admixtures was 0.2% and for the mixes containing 30% and 40% admixtures was 0.3%.

3.3. Specimen preparation, curing and testing

For each mix, 12 specimens measuring 50 mm in diameter and 100 mm in length were cast in steel moulds and compacted by external vibration. Four specimens were tested under compression at the age of 28 days to determine the stress–strain curves until failure (in a 1000 kN Shimadzu® testing machine at a loading rate of 0.01 mm/min). Four additional specimens were used to determine the total porosity by the water absorption capacity test, and the remaining specimens were used for sorptivity tests.

After casting, the moulds containing the specimens were covered with a damp cloth and a polythene sheet in order to prevent water loss and, after 24 h, the specimens were demoulded and water-cured at 24 °C for 28 days.

The water absorption capacity test and the sorptivity test, based on the direct gravimetric method, were conducted according to the Brazilian standards NBR 9778 [21] and NBR 9779 [22], respectively, and were performed after 28 days curing.

Selected mixes were analyzed for chloride ion penetration and for measurements of pore size distribution. For each of the selected mixes two cylindrical specimens measuring 100 mm in diameter and 200 mm in length were cast for the chloride ion penetration tests. A disk measuring 100 mm in diameter and 50 mm of thickness was cut from the central part of each cylinder and tested according to ASTM 1202 [23] after 28 days of curing. Samples from the extremities of the cylinders were taken and used to conduct the pore size distribution measurements using the mercury intrusion porosimetry technique.

3.4. Packing density

The compressible packing model (CPM) [24] was used to characterize the packing density of the grain mixtures. In this model, the packing density (ϕ) depends on the size and shape of the grains, and on the method of packing adopted. The CPM allows making the transition from virtual packing density (β) to the actual packing density of the mixture, which is in accordance with the energy applied during placing. A scalar K, called compaction index, enables connecting β with ϕ. This scalar is strictly dependent on the protocol implemented for the particular mixture, such that as K tends to infinity, ϕ tends to β. The general form of the compaction index equation is given by [24]

$$K = \sum_{i=1}^{n} \frac{\frac{y_i}{\beta_i}}{\frac{1}{\phi} - \frac{1}{\beta^{(1)}}} \quad (6)$$

where n is the number of grain classes, y_i is the volumetric fraction and β_i the virtual packing density of the ith class, and $\beta^{(1)}$ is the virtual packing density when i is the dominant class. The values of index K are calculated for the binary mixtures in each placing process. The index K assumes a value of 4.5 when the compaction process is simple pouring, 6.7 for water demand and 9.0 when placing is by vibration followed by compression with 10 kPa of pressure. De Larrard [24] suggests determining the packing properties of sand and fine materials (cement and pozzolans) from the vibration and compaction tests ($K = 9$) and test used for measurement of water demand ($K = 6.7$), respectively.

4. Results and discussion

4.1. Packing, total porosity and porous structure

Fig. 3 shows the dry packing density ϕ of the mixtures, calculated using the CPM. It demonstrates that the replacement of cement by ground calcined-clay brick (GB) resulted in nearly no change in packing density. This is consistent with the similarity between the particle size distributions of GB and the PC (Fig. 1), although other factors are also known to affect packing. On the other hand, in the case of metakaolin samples (MK1 and MK2), increases in packing density of the dry mix are evident, which are
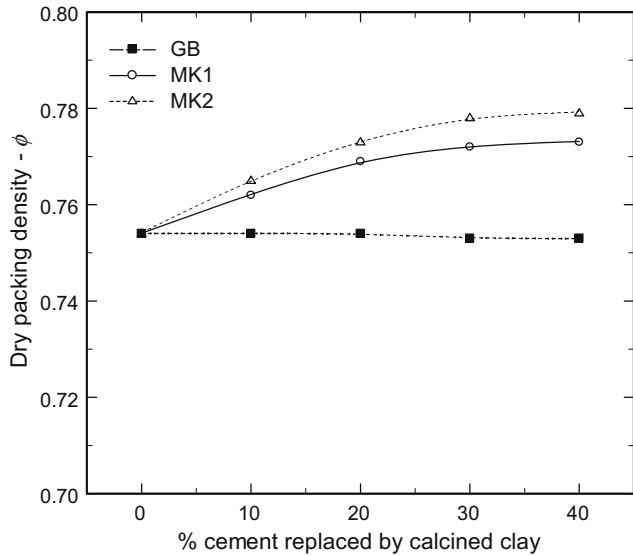
Fig. 3. Influence of proportion of cement replaced by each calcined-clay on the dry packing density of the mixes, calculated using CPM.

consistent with the finer size distribution of these pozzolanic materials, being even more significant for the finest pozzolan, MK2.

Fig. 4 shows that replacement of up to 30% of cement by either one of the metakaolin samples (MK1 or MK2) resulted in a similar continuous reduction in total porosity. This may be attributed, at least in part, to improved packing of the mixtures (Fig. 3). Distinct behaviors were found for replacements of 40% cement by the metakaolin samples: whereas replacement by MK1 resulted in a further reduction in porosity, the same was not observed when MK2 was added. This behavior is demonstrated later in the paper to have important implications in both compressive strength and absortivity of these mixes when compared to the control sample.

In the case of ground calcined-clay brick (GB), Fig. 4 shows that, for all percentages of replacement, the mortar porosity is greater than that of the control sample. Although this change was not statistically significant for the 10% replacement, it was maximum for 20% replacement. This variation could not be directly explained by the packing density of the granular mix, since no change in packing was observed from replacement of PC by GB (Fig. 3).
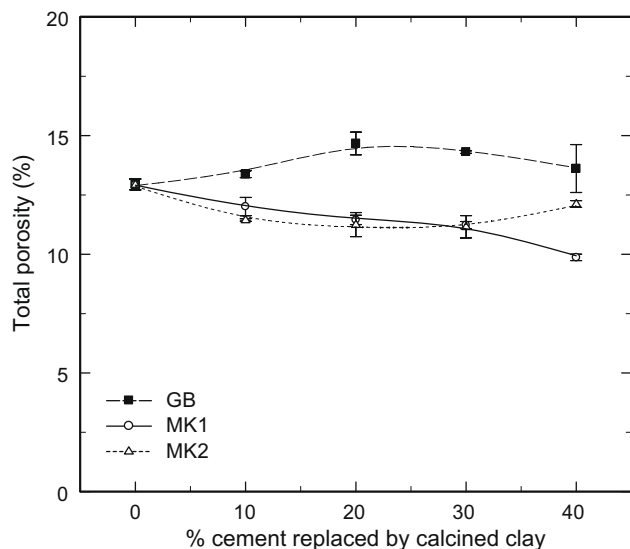

Fig. 4. Influence of proportion of cement replaced by each calcined-clay on total porosity.
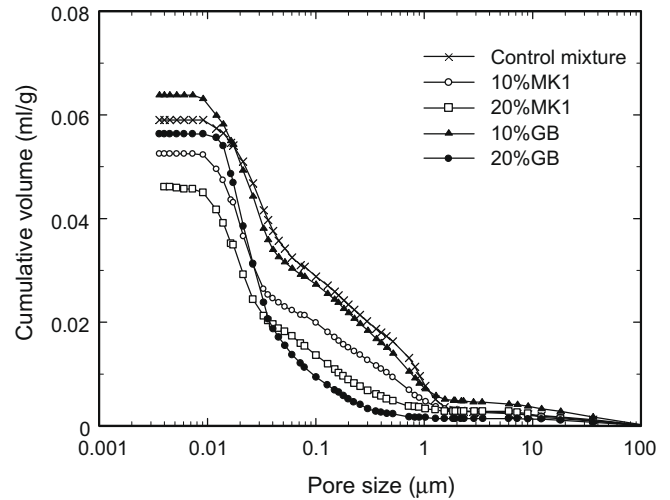

Fig. 5. Pore size distributions of the selected mortar mixtures.

Fig. 5 shows the cumulative increase in volume of mercury as a function of pore diameter in mixtures containing GB and MK1, as well as the control mixture. The pore structure of the mixtures was classified according to the International Union of Pure Applied Chemistry [25] and a summary is presented in Table 2. It is observed that when no calcined-clay is added (control mixture) the proportion of macropores in relation to the total porosity is the largest (54%), characterizing this mortar as one with predominance of larger-sized pores. With the partial replacement of cement by GB, a reduction in the proportion of macropores and an increment in the proportion of mesopores occurs (Table 2). This is particularly significant since no appreciable change in total porosity was observed as a result of replacing 10% Portland cement by GB (Table 2).

Porosities and porous structures found in mortars with MK1, MK2 and GB were also likely to be associated with differences in pozzolanic activities given the distinct proportions of amorphous material identified in the calcined-clay studied. However, a more direct assessment of their activity was possible through thermogravimetric analyzes of Portland cement pastes containing different proportions of the calcined-clays and cured for 28 days. The findings of that investigation, presented elsewhere [13], may be summarized as

- Mortars with 10% replacement of cement by GB presented nearly no change in the amount of non-evaporable water as the reference mixture. For higher levels of replacement, a gradual decrease in the proportion of non-evaporable water is observed, resulting in a reduction of about 15% for 40% replacement of cement by GB.
- An increase in the proportion of non-evaporable water is observed for all levels of addition of MK1 in comparison to the reference mixture. A maximum increase in the proportion of non-evaporable water is observed for 20% cement replacement by MK1, representing an increase of 35% in comparison to the reference mixture. For the case of the mixture with 40% cement replacement this increase is of only 3.3%.
- For 30% cement replacement by MK2 all hydroxides from cement Portland hydration were consumed and for mixtures with much less than 20% cement replacement, no CH exists in the mixture, so that from this level of replacement it can be stated that MK2 acts only as a filler, since no CH is left in the mix to make the pozzolanic reaction possible. This results in a reduction in the total volume of combined (non-evaporable) water.

Table 2
Distribution of pore sizes (%) of selected mixtures

Pore diameter d (nm)		% Cement replaced and admixture used				
		0%	10% GB	20% GB	10% MK1	20% MK1
Trapped air	$5000 < d < 50,000$	1.7	3.3	1.1	3.1	1.9
Macropores	$25 < d < 5000$	54.1	42.8	24.8	31.8	38.2
Mesopores	$1.25 < d < 25$	39.5	49.2	62.0	61.6	55.9
Micropores	$d < 1.25$	4.8	4.7	12.2	3.5	4.1

In this way, the higher porosities resulting from replacement of 20% and 30% Portland cement by GB were probably associated to the smaller total volume of hydrates that were formed in comparison to the matrix with only PC. Still, even with the increase in total porosity, the hydrates present in the mixture containing 20% GB, along with unhydrated GB particles, promoted a reduction in the proportion of macropores in the mixture, resulting in a finer porous structure (Table 2).

In the case of mixtures containing commercial metakaolin (MK1), besides promoting a reduction in the total porosity of the mixture (Fig. 3), hydrated products generated by the pozzolanic reaction between calcium hydroxide and MK1 also reduced the proportion of macropores. The increase in the proportion of mesopores of mixtures containing MK1 was about 41% higher than the control mixture. It is evident that mixtures containing MK1 presented practically the same porous structure, but different volumes (Table 2), since mixtures corresponding to 10% and 20% replacement of cement by commercial metakaolin (MK1) presented about 10% lower porosities than the control mixture.

4.2. Sorptivity

Figs. 6–8 show the cumulative weight gain as a function of time for mixtures containing GB, MK1 and MK2, respectively. In all cases, the water penetration depth (i) versus the square root of exposure time $t^{1/2}$ could be modeled by a bi-linear form.

Values of water sorptivity determined from the gradients of these plots during the final period of water exposure [26] are summarized in Fig. 9. The replacement of cement by all pozzolans studied resulted in reductions in sorptivity, being more significant in

Fig. 6. Sorptivity plots (i versus $t^{1/2}$) for the mortar mixes with additions of GB.

the cases of MK1 and MK2. These significant reductions in sorptivity found for MK1 and MK2 are associated to the combined effect of improved packing (Fig. 3), reduced porosity (Fig. 4) and refinement of the porous structure (Fig. 5) of probably unconnected pores, which hinder the flow of water. This refinement of the porous structure leads these mixtures to quickly reach saturation. In the case of GB the reduction in sorptivity is more gradual and is primarily the result of the refinement of the porous structure (Table 2), since no change in packing density of the granular mixture was observed (Fig. 3) and porosity even increased (Fig. 4). Indeed, reductions in sorptivity in spite of increases in total porosity of mortars and pastes containing pozzolanic materials have been previously observed by other researchers [27]. Therefore, GB resulted in a more refined porous structure, with pores of such smaller sizes, which hinder water penetration. Studies by O'Farrell et al. [28] confirmed the refinement of the porous structure of mortars containing ground calcined-clay brick. In the case of replacement of 40% cement by MK2, an increase in sorptivity was observed (Fig. 9), which is consistent with the increase in porosity also found in Fig. 4.

In the case of the initial period of exposure a general reduction in sorptivity was also observed with replacements of cement by the different admixtures, although the reductions were not as significant as in the final stage (inserts in Figs. 6–8). It is worth noting that the replacement of 10% cement by MK1 resulted in no change in sorptivity in comparison to the control mixtures. In the case of the mixtures containing 30% and 40% MK2 increases in sorptivity by 37% and 81%, respectively, in comparison the control mixture, were found. These occurred in spite of their even lower porosities when compared to the control mixture (Fig. 4). Still, sorptivities in the final (second) stage for 30% and 40% cement replacement by MK2 were lower than those of the control mixture, demonstrating that such additions lead to lower sorptivities of mortars at long exposures to water (Fig. 9).

4.3. Accelerated penetration of chlorides

Results from accelerated penetration of chloride ions of selected mixtures are presented in Table 3. The use of calcined-clay promoted a general reduction in the electric charge that passes through the sample. Replacement of cement by ground calcined-clay brick resulted in reduction from 1.5 to 6 times for mixtures containing 10% and 20% GB, respectively, whereas this reduction was even more significant, by 10 and 31 times for mixtures containing 10% and 20% MK1, respectively, in comparison to the control mixture. Since reductions in the electric charge that passes through the sample were observed for 10% and 20% cement replacement by GB, in spite of the relatively constant porosity (10% replacement) or even an increase in porosity (20% replacement) in comparison to the reference mixture (Fig. 4), it is concluded that the resistance to penetration of chloride ions is more directly associated to the refinement of the porous structure (Table 2).

In the case of mixtures containing commercial metakaolin (MK1), the significant reductions in chloride ion penetration probably resulted from the combined effect of segmentation (reduction
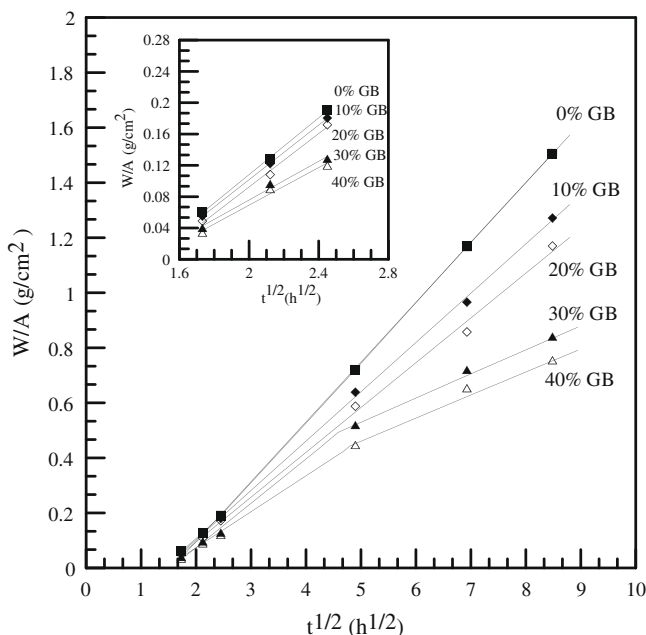
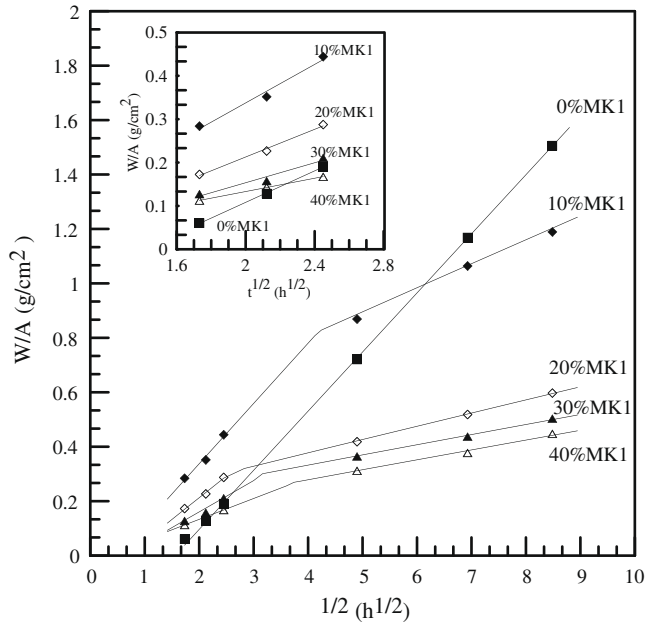**Fig. 7.** Sorptivity plots (*i* versus $t^{1/2}$) for the mortar mixes with additions of MK1.
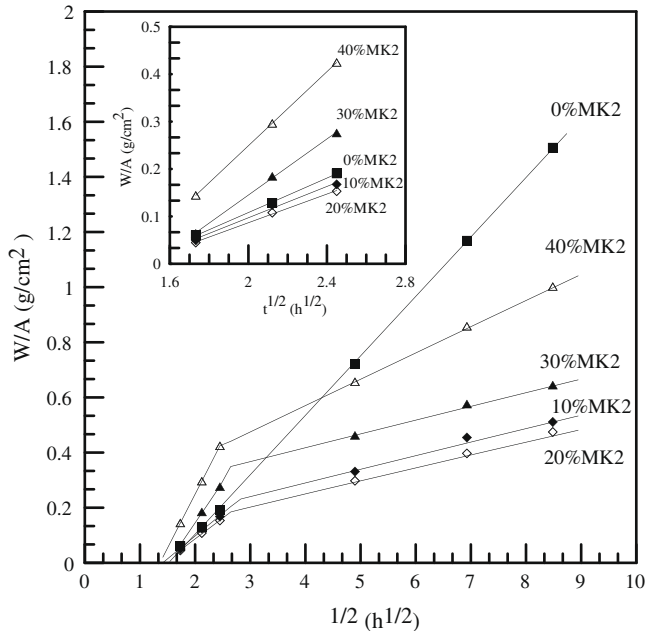

Fig. 8. Sorptivity plots (*i* versus $t^{1/2}$) for the mortar mixes with additions of MK2.

in total porosity) and refinement of the porous structure produced by the replacement of cement by MK1, increasing the amount of mesopores (Table 2) and hindering the ionic transport.

4.4. Mechanical response

Typical stress–strain relationships for the mortar mixtures tested are presented in Figs. 10–12 and a summary of results of the influence of calcined-clay additions on the compressive strength of the mortars is shown in Fig. 13.

The influence of cement replacement by ground calcined-clay brick (GB) on the compressive strength of mortars can be analyzed in two stages: up to 20%, where nearly no (statistically significant)
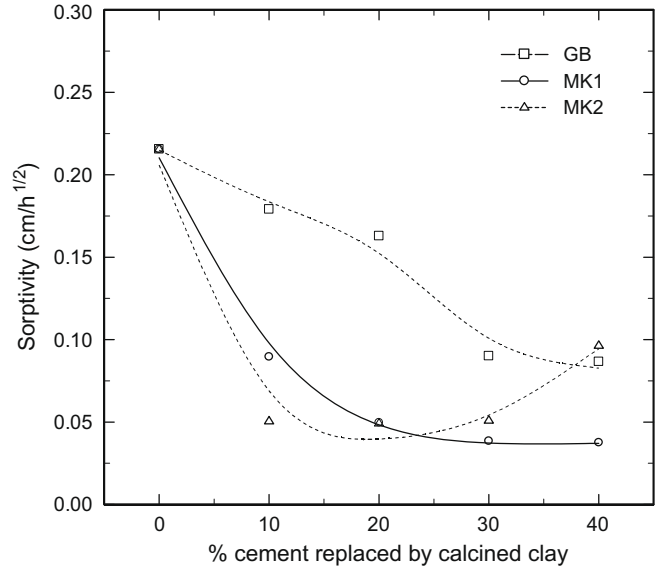

Fig. 9. Influence of proportion of cement replaced by each calcined-clay on sorptivity in the final stage.

effect is observed (Fig. 13), and at higher levels of replacement (30% and 40%), where a significant reduction in strength is observed in comparison to the control mixture. Since the packing density of the dry mix did not change with the replacement of PC by GB (Fig. 3), then it is possible to infer that the amount of hydrates formed by the pozzolanic reaction from replacement of up to 20% cement by GB was high enough so that it was able to maintain a constant compressive strength. However, with higher replacement levels, the amount of hydrates resulting from the pozzolanic reaction was probably insufficient to allow maintaining a constant compressive strength, so that the excess of unreacted GB was only able to contribute in strength due to its physical filler effect.

For mixtures where cement was replaced by metakaolin (MK1 and MK2) increases in compressive strength were observed for all levels of replacement studied, when compared to the reference mixture, although they were more modest when cement was replaced by MK1. Optimal results were obtained for 20% replacement of cement by metakaolin, representing increases in 39% and 18% for MK2 and MK1, respectively. This increase may be explained by the greater formation of hydrates under these conditions, already observed from thermogravimetric analyzes [13]. At higher levels of replacement (30% and 40%), higher compressive strengths than those of the reference mixture were observed, but reductions in relation to the strengths obtained at 20% replacement resulted. This may be associated with the fact that the more limited availability of calcium hydroxide from the smaller proportion of cement added becomes the limiting factor in the formation of new hydrates. As a result, the unreacted metakaolin can act only as filler.

Fig. 14 shows that the increase in replacement of cement by the calcined-clays results in a continuous decrease in the elastic mod-

Table 3
Chloride ion penetration of selected mortar mixtures

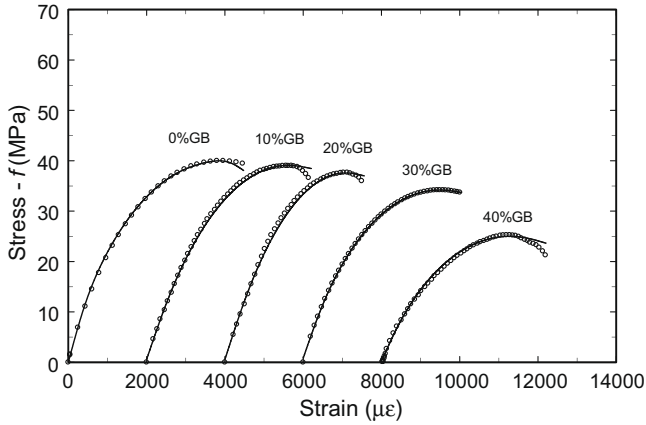| Admixture	% Cement replacement	Chloride ion penetration (Coulombs)	Classification (ASTM C 1202, 1992)
–	0	13,487	High
GB	10	8460	High
	20	2111	Moderate
MK1	10	1301	Low
	20	432	Very low

Fig. 10. Typical stress–strain relationships for mortar mixes with additions of ground calcined-clay brick (GB). Experimental data represented with symbols and fitted results to Eq. (4) with lines (all tests start from zero strain).
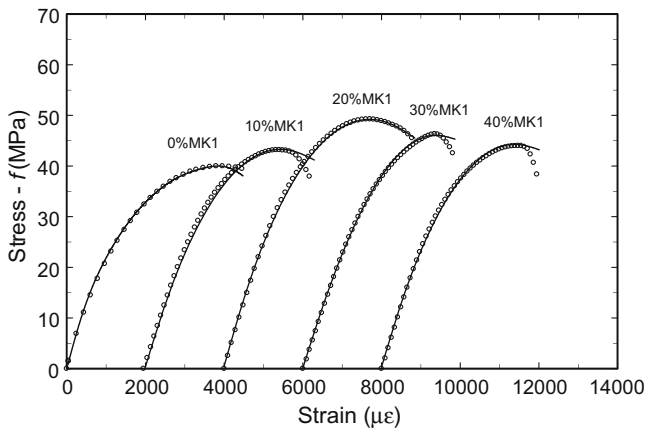

Fig. 11. Typical stress–strain relationships for mortar mixes with additions of metakaolin 1 (MK1). Experimental data represented with symbols and fitted results to Eq. (4) with lines (all tests start from zero strain).

ulus of the mortars, reaching reductions of up to 10% in comparison to the control mixture. Such decrease is, however, not statistically significant (at 95% confidence) for replacements of up to 20% by all calcined-clays studied. The reduction in the elastic modulus of
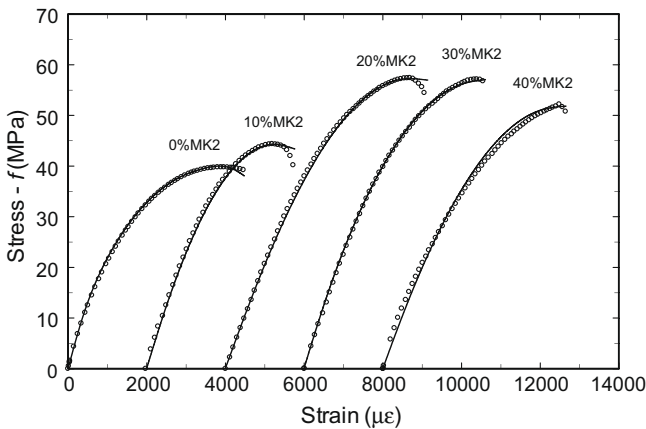

Fig. 12. Typical stress–strain relationships for mortar mixes with additions of metakaolin 2 (MK2). Experimental data represented with symbols and fitted results to Eq. (4) with lines (all tests start from zero strain).
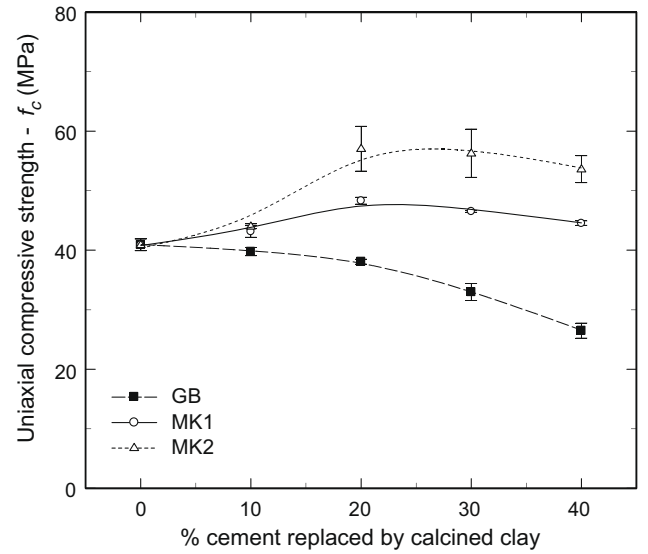

Fig. 13. Influence of proportion of cement replaced by each calcined-clay on uniaxial compressive strength of cement mortars.

Portland cement mortars with calcined-clay additions may be probably attributed to the lamellar structure of the clays, which are more deformable under loading. This is associated with the fact that both kaolinite and ilite, even after being calcined at temperatures as high as 550 °C and 850 °C, respectively, retain their lamellar residual structure [3,29]. Shear stresses can cause sliding of one layer over another, resulting in greater deformability of the clays and materials that contain appreciable amounts of them. This behavior is likely to have influenced the elastic modulus of deformation of mortars containing calcined-clays, being more significant for mixtures with higher levels of cement replacement.

Figs. 10–12 show that not only the initial rigidity and the ultimate stress vary with the addition of calcined-clays, but also the deformation behavior leading to failure of the mortar samples. The stress–strain responses were individually fitted to Loland´s continuum damage model (Eqs. (4) and (5)) and a summary of the critical damage values is presented in Fig. 15, which shows
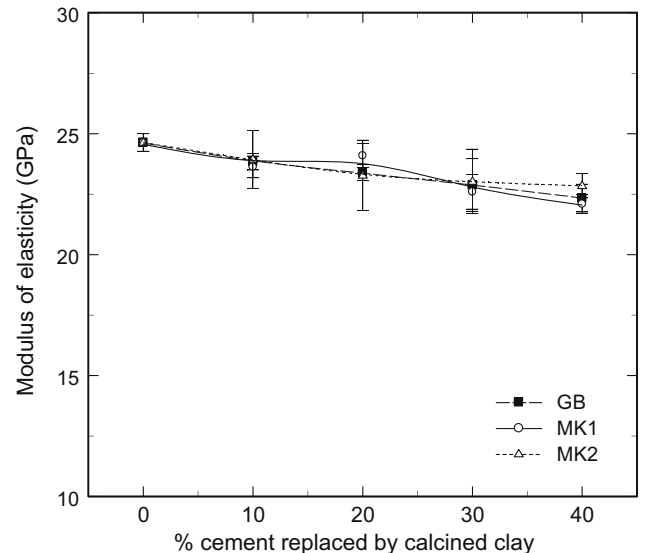

Fig. 14. Influence of proportion of cement replaced by each calcined-clay on modulus of elasticity of mortars.
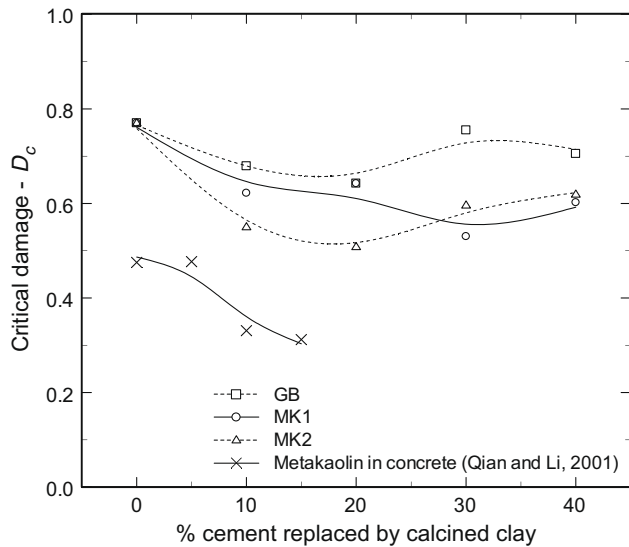
Fig. 15. Influence of proportion of cement replaced by each calcined-clay on critical damage of mortars. Also included in the figure are critical damage values estimated from data on high-performance concrete with different levels of addition of metakaolin [15].

its variation as a function of % replacement of cement by calcined-clays. In all cases, the replacement of Portland cement by calcined-clay resulted in a mortar that had a more brittle response (lower critical damage). The figure also shows that replacements as small as 10% of cement cause a significant change in deformation response of the mortars, being highest for 20% additions. Such increase in brittleness was, however, less significant for mortars with replacement of cement by GB.

Recent work by the authors [30] showed that brittleness in the stress–strain response increases with the presence of increasing amounts of filler and with a reduction in porosity, given that the greater voids-filling capacity of these particles limit the space available for the material do withstand deformations elastically. Given the modest, although significant, increase in brittleness with additions of GB, in spite of the higher porosities of the mortars (Fig. 3), it is likely that the porous structure also influences the capacity of the material to store strain energy elastically. The more significant change in deformation response to brittle in the case of metakaolin additions (MK1 and MK2) is another evidence of the joint influence of total porosity and pore size distribution. The increase in inelastic behavior and less brittle response for greater additions of calcined-clays (30% and 40%) may also be attributed to the plasticity of the calcined-clays.

Finally, Fig. 15 also shows values of critical damage estimated using Eqs. (3) and (5) from data published by Qian and Li [15] for high-performance concretes with replacements of up to 15% of cement by metakaolin. It is evident that replacements as small as 10% of cement by metakaolin cause a significant change in the critical damage values and, therefore, in a more brittle fracture response of the high-performance concretes, similar to what was found in the present work for the mortars with the various additions of calcined-clays.

5. Conclusions

Mortars with up to 20% cement replaced by a high-purity metakaolin (MK2) presented higher uniaxial compressive strengths when compared to those prepared using the same levels of cement replacement by a commercial and impure metakaolin (MK1). However, no statistically significant difference was found

in porosity, modulus of elasticity, sorptivity and deformation behavior up to this level of replacement in regard to metakaolin used.

Replacements of cement in mortars by calcined-clays resulted in a refinement of the porous structure, with reductions in the proportion of macropores and modulus of elasticity of the mortars in the hardened state. Although this resulted also in reduction in total porosity and increase in uniaxial compressive strength of mortars containing metakaolin (both commercial, MK1, and laboratory-made, MK2), an increase in total porosity and a reduction in strength was observed with the increase in the amount of cement replaced by ground calcined-clay brick (GB). This effect, however, was not significant for replacements as low as 10% of cement by GB.

General reductions in sorptivity in both initial and final stages and increases in resistance to penetration of chlorite ions were observed from additions of calcined-clays. Exceptions were results from initial sorptivity measurements after replacements of 30% and 40% cement by MK2, where a significant increase was observed in comparison to the control sample (with no additions). The reduction in chloride ion penetration was more significant with similar amounts of replacement by MK1 than GB.

Reasonably small additions (10%) of calcined-clays that had no statistically significant effect on compressive strength or modulus of elasticity had a marked effect on the deformation response of cement mortars. This becomes even more significant for 20% replacements of cement by calcined-clays, which resulted in mortars that were more brittle and less amenable to inelastic deformation just prior to fracture. This appears to partially compensate the reduction in modulus of elasticity that was associated with the replacement of cement by calcined-clays, so that the toughness of mortars becomes predominantly determined by their ultimate compressive strength.

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