Various Durability Aspects of Calcined Kaolin-Blended Portland Cement Pastes and Concretes

M. Saillio, V. Baroghel-Bouny and S. Pradelle

Abstract The use of calcined clay, in the form of metakaolin (MK), as a pozzolanic constituent for concrete has received considerable attention in recent years, due to the lower CO_2 emission of this supplementary cementitious material compared to the production of a classic portland cement. Furthermore, concretes incorporating MK show some improve durability properties. In this paper, the durability of concretes and cement pastes with MK as partial replacement of cement (10 and 25 %) has been investigated in comparison with CEM-I materials one. Water porosity, chloride migration and diffusion, electrical resistivity and natural and accelerated carbonation tests have been performed. In addition, microstructural study is performed to better understand the results on the durability indicators. The cement pastes microstructure was characterized not only by usual techniques such as mercury intrusion porosimetry, XRD and TGA-DTA, but also by ^{29}Si and ^{27}Al NMR spectroscopy. For example, Friedel's salt (chemical binding) has been quantified by ^{27}Al NMR spectroscopy and XRD on cement paste. In addition, the progress of the durability properties for various water curing times has been investigated. Results show an evolution of the properties, as a function of the cement replacement degree by MK, such replacement increases durability against chloride penetration but decreases resistance to carbonation. The aluminate phases equilibrium is modified in concrete with metakaolin in comparison with a CEM-I one. Both chemical and physical chloride binding increases with MK replacement. In addition, since portlandite quantity decreases in cement materials with MK, these materials are less resistant to carbonation process for a same exposure condition (time and CO_2 concentration).

Keywords Concrete · Metakaolin · Durability · ^{29}Si and ^{27}Al NMR spectroscopy

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1 Introduction

Supplementary cementitious materials (SCMs) are included into concrete to substitute part of cement in order to reduce the carbon footprint. SCMs are mainly pozzolanic materials including industry waste such as ground granulated blast slag and fly ash. Metakaolin (MK) is known for having similar effects to improve strength and durability of concrete [1–4]. Metakaolin is produced by calcining kaolin at 650–800 °C and is mainly amorphous [4]. MK needs aqueous calcium hydroxide produced during clinker hydration to form C-S-H or C-S, Al-H gels [5]. In addition, MK induces a filler effect to the mixture [6].

This study focuses on the durability indicators of MK cement materials such as water porosity, apparent chloride diffusion coefficient ($D_{app,Cl}$), electrical resistivity. The resistance to the carbonation process (in replacement of gaz permeability as durability indicator) and chloride binding isotherms (CBIs) are also evaluated. In addition, microstructural study (XRD, thermal analyses and NMR) is performed to better understand the results on the durability indicators.

2 Experimental

Various concretes were mixed with the same clinker and granular squeleton using siliceous aggregates. The main constituents of the clinker are given in Table 1. The binder content is 300 kg/m^3 and the water to binder ratio (w/b is equal to 0.53 for all the mixtures. Studied binders are CEM I (OPC with 97 % clinker), CEM I + 10 % MK denoted CEM I MK(10 %) and CEM I + 25 % MK denoted CEM I MK(25 %). The partial replacement of CEM I by MK in binders is called here MK degree. Cement pastes with the same binders were also prepared with w/b equal to 0.50.

Many water-curing times are chosen (7, 28, 90, 180 and 365 days) in order to take into account the evolution of the microstructure as a function of the age. Sound samples (i.e. non-carbonated) will be denoted “reference” in the paper.

Various durability tests are performed on these concretes and pastes: water porosity, chloride migration and diffusion [7], electrical resistivity [8] and natural and accelerated carbonation tests [9]. In addition, chloride binding isotherms (CBIs) are obtained by equilibrium method [10]. Finally, microstructure is characterized by mercury intrusion porosimetry (MIP) [7], XRD [10], TGA-DTA [9] and ^{29}Si and ^{27}Al nuclear magnetic resonance magical angle spinning spectroscopy (NMR MAS) [10].

Table 1 Chemical composition of the cement and SCM tested (%) and mineralogical composition of the CEM I from BOGUE calculation (%)

	CaO	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	MgO	Na_2O	K_2O	MnO	SO_3	C_3S	C_2S	C_3A	C_4AF
CEM I	62.53	19.54	2.90	4.98	0.30	0.84	0.30	0.82	0.09	2.97	51.23	28.32	9.90	8.81
MK	0.00	66.29	4.29	21.30	1.12	0.25	0.84	0.49	0.00	0.08				

3 Results and Discussion

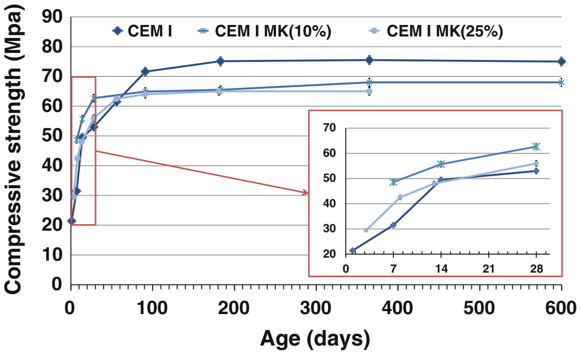
3.1 Compressive Strength and Durability Indicators

At the young age (see Fig. 1), CEM I MK(10 %) concrete has a higher compressive strength than others concretes (an increase of 50 % in comparison of CEM I concrete) which is consistent with previous studies [11]. MK concretes reach theirs stabilization value within 28 day. The high reactivity of MK at young age is related to their aluminate phases and their high surface area. MK pozzolanic reactions consume portlandite and produce C-S-H and C-S,Al-H denser [12]. Furthermore, MK also plays an accelerator on hydration of C_3S by the nucleating effect due to the increase of fines in a cementitious matrix [6]. The filler effect could have an impact in increasing the compactness of concrete, and thus improving the mechanical properties [1]. However, at the long term, the maximum compressive strength of MK concrete (65 MPa) is still lower than the CEM I concrete (80 MPa). A MK degree of 25 % in binder improves slightly the strength properties at early age compared to CEM I concrete; it seems that there is an optimum in terms of the MK degree. This optimum (between 10 and 25 %) is also being studied to establish a European standard. In France, it is the new standard issued in March 2010, the NF P 18-513 that governs this type of addition.

Water porosity of CEM I MK(25 %) concrete decrease slightly (see Fig. 2 in left) in comparison to CEM I one, but the measurement uncertainties (not figured here) are relatively close. For cement pastes, the tendency is clearer: CEM I MK (25 %) porosity is very low porosity compared to CEM I one and evolve to less porosity with water-curing time in concordance with other results [12]. Here, cement paste porosity is a negative linear function of MK degree (see Fig. 2) confirmed by two methods (water porosity and MIP) for each water-curing time.

Less porosity has consequences on other durability properties such as chloride diffusion. Indeed, it appears in Fig. 3 that chloride apparent coefficient ($D_{app,Cl}$) of MK concretes decrease compared to CEM I one. These results obtained by migration tests are similar to those obtained by diffusion tests (respectively 12; 7

Fig. 1 Compressive strength of concretes in function of water-curing time



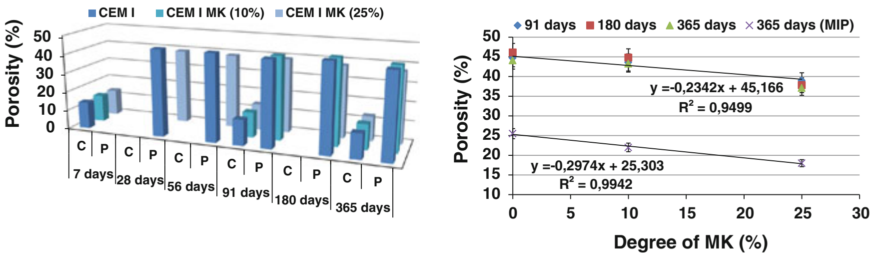


Fig. 2 Water porosity of paste (P) and concrete (C) in function of water-curing time. In *right*, comparison between water porosity and porosity obtained by MIP for cement pastes

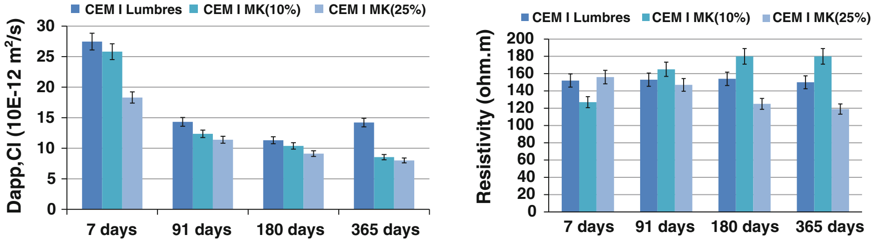


Fig. 3 Chloride apparent coefficients (in *left*) obtained by chloride migration and resistivity (in *right*) of concretes in function of water-curing time

and 1.10E-12 m^2/s for respectively CEM I, CEM I MK(10 %) and CEM I MK (25 %). Nevertheless, the observed differences are larger in these tests for MK cementitious materials. For example, a factor 5 is reached for $D_{app,Cl}$ of CEM I MK (25 %) obtained by migration and diffusion tests. In general, it is considered [7] that $D_{app,\ Cl}$ obtained by the migration depends only on the porous network. Indeed, during the migration test, interactions (between chloride and cementitious matrix) are very weak and can be often neglected. In contrast, $D_{app,\ Cl}$ from diffusion tests depends in part on these interactions and also the porous network which explain why $D_{app,\ Cl}$ obtained by the migration are higher to $D_{app,\ Cl}$ obtained by diffusion tests. Consequently, CEM I MK(25 %) seems to have a higher capacity for chloride binding which is confirmed by CBIs presented in Fig. 4. There is also linear relationship between chloride binding and MK content.

Resistivity tests show contrasted results (see Fig. 3 in right) in opposite to some other studies [2]. Here, it seems that CEM I MK(10 %) concrete has the best resistivity for 365 days of water curing time.

For cement pastes, portlandite amounts decrease when MK degree increases (see Fig. 5 in left) because it is only produced by the clinker and CEM I MK(25 %) contains less clinker than CEM I (dilution effect). In addition, the pozzolanic reactions in MK pastes consume portlandite. In order to separate the effect of the dilution and the consumption of portlandite due to pozzolanic reactions, the mass proportion of portlandite compared to the clinker is calculated. It is 22 % for CEM I

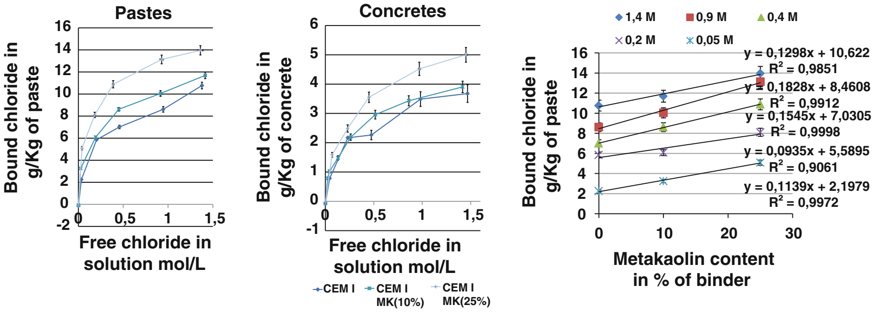


Fig. 4 Concretes and cement pastes CBIs (in *left*) and chloride binding of cement pastes in function of MK content (in *right*) obtained by equilibrium method

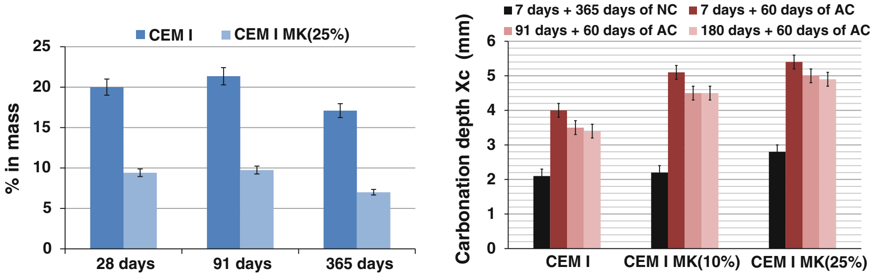


Fig. 5 % in mass of portlandite (in *left*) in cement pastes and carbonation depth (in *right*) measured by phenolphthalein tests on concretes after various water-curing times and natural (NC) or accelerated carbonation (AC) (1.5 % CO_2, 65 % RH and T = 20 °C)

and 14 % for CEM I MK(25 %). Therefore, large amounts of portlandite are consumed by pozzolanic reactions in these materials. The main consequence is that MK cementitious materials are less resistant than CEM I ones against a same carbonation treatment (see Fig. 5) confirming results [4].

3.2 *Microstructure*

Pore size distribution of cement pastes obtained by MIP is presented in Fig. 6. The main peak of the distribution decreases whereas MK degree increases. It can due to the filler effect [6]. Additionally, C-S,Al-H denser forms inside the porous during the pozzolanic reactions. This can explain the better results of CEM I MK(25 %) $D_{app, Cl}$ obtained by migration compared to CEM I one (see Fig. 3).

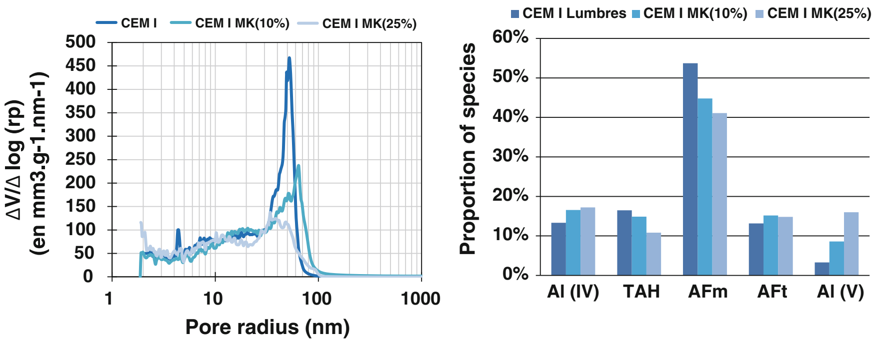


Fig. 6 Pore size distribution obtained by MIP (in *left*) and proportion of Al species obtained by ^{27}Al MAS NMR (in *right*). Al(IV) aluminum substituted for silicon in C-S-H chains and residual anhydrous cement. Al(V) aluminum substituted for calcium in the C-S-H interlayers or present in non-hydrated phases or in MK. TAH : amorphous/disordered aluminum hydroxide or a calcium aluminate hydrate

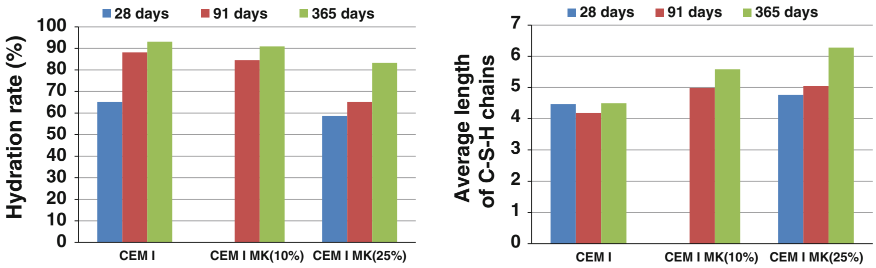


Fig. 7 Hydration rate (in *left*) and average length of C-S-H chains obtained by ^{29}Si MAS NMR for various water-curing time

Equilibrium of aluminates phases in cement pastes is presented in Fig. 6. There are more AFt phases (respectively less AFm phases) in MK cement pastes than in CEM I. Furthermore, MK cement pastes contains more Al(IV) and Al(V) due to residual MK but also to Al incorporated in C-S-H during pozzolanic reactions.

The hydration rate obtained by ^{29}Si NMR (ref) is presented in Fig. 7. For each water-curing time, hydration rate of MK cement pastes stays inferior to CEM I one. By combination of microstructural techniques (DRX, TGA and NMR), the anhydrous phases remaining are evaluated at 8 % in mass in CEM I MK(25 %) after one year of water-curing, against 3 % in CEM I.

Average length of C-S-H chains (obtained by ^{29}Si NMR,) presented in Fig. 7 is longer in MK cement pastes than CEM I. It appears that C-S-H chains polymerise in MK cement pastes. It is probably due to the presence of Al substituted to Si in C-S-H from pozzolanic reactions of MK.

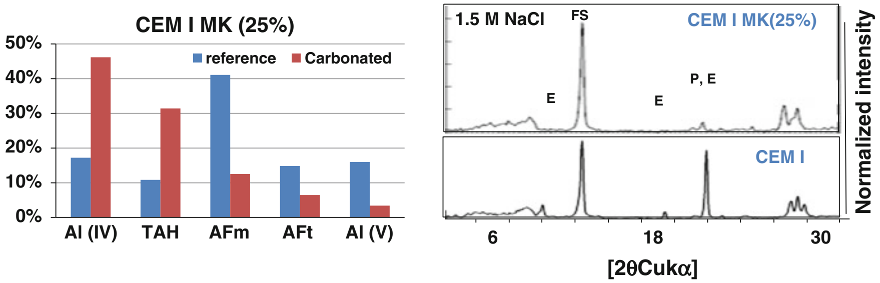


Fig. 8 Proportion of Al species obtained by ^{27}Al MAS NMR (in *left*) and diffractogramms (in *right*) of crushed pastes in contact of NaCl solution (1.5 M). E ettringite, FS Friedel's salt, P portlandite

The microstructure has been investigated after exposure to chloride or after carbonation and only the most remarking results are presented here.

Concerning carbonation, a partial treatment (3 days 1.5 % CO_2 and 65 %RH) was applied on crushed pastes. Almost no difference is observed for CEM I before and after the carbonation treatment. In opposite, after carbonation, CEM I MK (25 %) shows a lower portlandite amount (5 % instead of 8 %), a new equilibrium of aluminate phase (see Fig. 8), a higher decalcification (C/S is 0.5 instead 0.9) and polymerisation of C-S-H chains. Consequently, for a same carbonation treatment (condition exposure and duration), MK cementitious materials are less resistant to carbonation than CEM I confirming the results presented in Sect. 3.1 and the modification of aluminate phase equilibrium and C-S-H decreases the binding capacities as reported in [10].

Concerning chloride ingress, crushed pastes were put in contact to various NaCl solutions then analysed by ^{27}Al NMR and XRD. For a same NaCl concentration of the solution (see Fig. 8), CEM I MK(25 %) produces more Friedel's salt than CEM I and physical binding (accessed by combination of NMR and CBIs results) is also higher confirming results presented in Sect. 3.1. More binding means more resistant to chloride ingress for MK cementitious materials for example in marine environment. However, in case of a multiple aggression, such as carbonation then chloride ingress, MK cementitious materials lose this advantage.

4 Conclusions

In term of durability properties, MK concretes exhibit advantages compared to CEM I concretes. A decrease in porosity is recorded and the apparent coefficient of chloride ion diffusion. However, their lower Portlandite content makes them more sensitive to carbonation. Water porosity and chloride binding clearly evolve (according to a linear trend) with MK content of the binder within the range studied (0–25 %).

Further investigation of the microstructure yields a better understanding of these advantages and disadvantages concerning carbonation and chloride ingress. The finer pore network and the largest capacity to bind chlorides improves $D_{app,\ Cl}$ compared to CEM I materials. Consequently, MK cement materials can be used in marine environment. However, compared to CEM I mixture, their lower Portlandite amount increases carbonation progress which results in a rearrangement of the aluminate phases and a decalcification/polymerization of C-S-H (which both decreases chloride binding). In presence of CO_2 or in case of multiple aggression (carbonation and chloride environment), the use of MK cement materials has to be limited.

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