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Cement & Concrete Composites 27 (2005) 125–130

Cement & Concrete Composites

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The effect of metakaolin on the corrosion behavior of cement mortars

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Accepted 13 February 2004

Abstract

In this paper the effect of metakaolin addition on the corrosion resistance of cement mortar is studied. A poor Greek kaolin with a low kaolinite content was thermally treated and the produced metakaolin (MK) was ground to the appropriate fineness. In addition, a commercial metakaolin (MKC) of high purity was used. Several mixture proportions were used to produce mortar specimens, where metakaolin replaced either sand or cement. Mortar specimens were then exposed to the corrosive environment of either partial or total immersion in 3.5% w/w NaCl solution. For the evaluation of the performance of metakaolin, the following methods were used: compressive strength, corrosion potential, mass loss, electrochemical measurements of the corrosion rate by the Linear Polarization method, carbonation depth and porosity. It is concluded that metakaolin improves the compressive strength and the 10% w/w addition shows the optimum contribution to the strength development. In addition, the use of metakaolin, either as a sand replacement up to 20% w/w, or as a cement replacement up to 10% w/w, improves the corrosion behavior of mortar specimens, while when metakaolin is added in greater percentages there is no positive effect.

Keywords: Metakaolin; Compressive strength; Corrosion behavior; Porosity

1. Introduction

The most common supplementary cementing materials (SCM) that are used in concrete, in addition to Portland cement, are fly ash, GGBS and silica fume. They save energy, conserve resources and have many technical benefits. Metakaolin, produced by controlled thermal treatment of kaolin, can also be used as a concrete constituent, since it has pozzolanic properties [1].

According to the literature, the research work on metakaolin is focused on two main areas. The first one refers to the kaolin structure, the kaolinite to metakaolinite conversion and the use of analytical techniques for the thorough examination of kaolin thermal treatment [2–10]. The second one concerns the pozzolanic behavior of metakaolin and its effect on cement and concrete properties [1,11–23]. Although there is disagreement on specific issues, the knowledge level is satisfactory and is being continuously extended.

The corrosion resistance of concrete influences its durability and finally its performance. The concrete performance depends mainly on the environmental conditions, the microstructure and the chemistry of the concrete. The two latter factors are strongly affected by the concrete components. It is obvious that the presence of metakaolin affects the concrete performance. The present work deals with the corrosion resistance of cement mortar with metakaolin, which is one of the most important parameters influencing concrete performance. This work forms part of a research project, which aims to exploit Greek kaolins in concrete technology.

2. Experimental

2.1. Materials and preparation of mortar specimens

The chemical analysis of Portland cement (PC: I/52.5) as well as the Bogue potential composition and the moduli of the clinker are given in Table 1.

A poor Greek kaolin with a low kaolinite content (K) was thermally treated at 650 °C for 3 h and the produced

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doi:10.1016/j.cemconcomp.2004.02.041

Table 1
Chemical analysis of PC and characteristics of clinker

Cement		Clinker	
Chemical analysis (%)		Bogue potential composition (%)	
SiO_2	21.54	C_3S	57.8
Al_2O_3	4.83	C_2S	18.1
Fe_2O_3	3.89	C_3A	6.2
CaO	65.67	C_4AF	11.8
MgO	1.71	Moduli	
K_2O	0.60	Lime saturation factor (LSF)	0.949
Na_2O	0.07	Silica ratio (SR)	2.47
SO_3	2.74	Alumina ratio (AR)	1.24
Cl^-	0.00	Hydraulic modulus (HM)	2.17
L.O.I.	0.90		

Table 2
Chemical analysis of kaolins (%)

	K	KC
SiO_2	65.92	47.85
Al_2O_3	22.56	38.20
CaO	0.36	0.03
MgO	0.02	0.04
Fe_2O_3	0.90	1.29
L.O.I.	8.60	12.30
SO_3	2.00	0.00

Table 3
Mineralogical analysis of kaolins (%)

	Kaolinite	Alunite	Quartz[a]	Illite
KC	96	–	–	3
K	52	5	41	–

[a] Quartz (mainly) + cristobalite.

metakaolin (MK) was ground to the appropriate fineness (20% residue at 13.6 μm). In addition, a commercial metakaolin (MKC) of high purity was used. The chemical analyses of kaolins are given in Table 2. The semi-quantitative mineralogical estimation of the materials is presented in Table 3. The estimation is based on the characteristic XRD peaks of each mineral, in combination with the bulk chemical analysis of the samples and has been presented in details in a previous work [6]. The Greek kaolin K mainly consists of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and quartz. K also contains K-alunite ($KAl_3(SO_4)_2(OH)_6$). KC contains kaolinite and a detectable amount of illite. It must be noted that KC is the raw kaolin used for the production of MKC. The fineness characteristics of the ground metakaolin as well as the MKC are given in Table 4.

For the evaluation of metakaolin cements properties, three blended cements were produced by replacing PC with 10% w/w MK (MK-10), 20% w/w MK (MK-20) and 20% w/w MKC (MKC-20) respectively.

For the corrosion measurements, six mortar mixes of PC with metakaolin were tested and compared to specimens with pure PC. Metakaolin replaced part of either PC or sand and the mortar mix proportions are given in Table 5. Specimens were constructed with shape and dimensions following previously established standards [24]. Mortar cylinders ($L = 100$ mm, $d = 40$ mm) (Fig. 1), into which the steel rebars (S500s, Tempcore) were axially embedded, were cast according to a procedure described in the literature [25]. The active (non-insulated) area of steel rebars was equal to 35 cm^2. After being demoulded, the specimens were cured in water for 1 day. Then they were immersed up to 20 mm height of the mortar cylinder in the corrosive environment, which was 3.5% w/w NaCl solution and remained there for up to 8 months.

3. Techniques

The compressive strength of the blended cements (EN 196-1) as well as the water demand and the setting time (EN 196-3) was determined.

The half-cell potential of the rebars was measured versus immersion time using a saturated calomel electrode (SCE) as a reference electrode.

The corrosion rate of reinforcing steel was determined by measuring the mass loss of the bars. Two specimens of each category were removed from the corrosive environment and treated according to ISO/DIS 8407.3, as described in a previous work [26]. The cleaned rebars were then weighed and the mass loss was calculated as the average value of the differences between initial and final weight.

Table 4
Metakaolin fineness characteristics

Sample	Fineness characteristics			Rosin–Rammler parameters	
	d_{20} (μm)	d_{50} (μm)	d_{80} (μm)	n	pp (μm)
MK	13.6	7.5	3.4	1.42	9.7
MKC	10.3	5.1	1.9	1.18	6.9

Table 5
Mortar mix proportions

Sample code	PC	MKC	MK	Sand	Water
PC	1.0	–	–	3.0	0.6
MKC-C20	0.8	0.2	–	3.0	0.6
MK-S10	1.0	–	0.1	2.9	0.6
MK-S20	1.0	–	0.2	2.8	0.6
MK-S30	1.0	–	0.3	2.7	0.6[a]
MK-C10	0.9	–	0.1	3.0	0.6
MK-C20	0.8	–	0.2	3.0	0.6

[a] With the addition of 0.06% Pozzolith 390N. Pozzolith 390N is a water reducing, plasticising admixture for the production of low slump loss, high workability concrete and it complies with the performance requirements of ASTM C-494 type B, D and G.

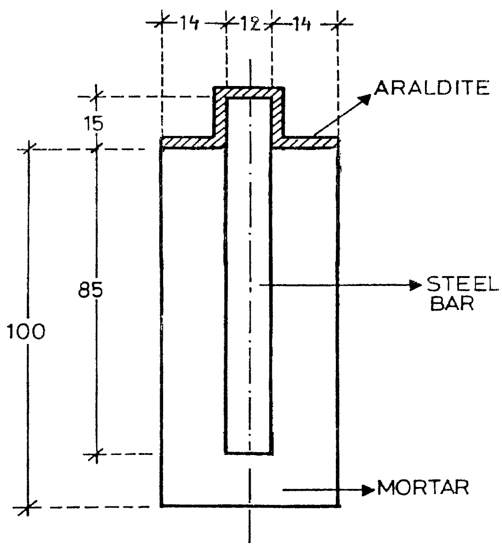

Fig. 1. Mortar specimen (mm).

These results were completed by running each month a potentiodynamic linear polarisation curve on two specimens of each category, using a 263A EG&G model potentiostat/galvanostat. The corrosion medium was 3.5% w/w NaCl solution. The reference electrode was a saturated calomel electrode. The auxiliary electrode consisted of two cylindrical graphite rods in contact with the working electrode (mortar specimen). Before each measurement the potential was recorded until it reached an almost stable value, which was the corrosion potential, E_{cor}. Then the linear polarization plot was performed in a range of about 40 mV. The scan rate was always 0.1 mV/s.

The carbonation depth of the specimens was determined by the phenolphthalein method recommended by RILEM CPC-18 on a vertical section of the specimen, after being removed from the corrosive environment.

Porosity of specimens was measured with the method of Mercury Porosimetry (CARLO ERBA 2000) and the mean pore size as well as the pore size distribution was determined.

4. Results and discussion

Fig. 2 presents the compressive strength of the tested samples. It is observed that the addition of metakaolin does not significantly alter the 1-day strength, but it has a very positive effect on the strength after 2 days and specifically at 28 days. As far as the metakaolin type is concerned, it is concluded that MK and MKC have a similar contribution on strength development. PC with 10% w/w MK (MK-10) showed the best results.

Table 6 presents the water demand of cement paste and the setting time of the tested samples. The term "water demand" is generally considered to be the quantity of water, which is required in order to prepare a cement paste of standard consistency as specified in EN 196-3. The blended cements demand significantly more water than the relatively pure cement and this phenomenon is attributed to the high fineness of metakaolin. The increase of the metakaolin content causes a significant increase of the water demand. PC with 10% w/w MK (MK-10) showed the lowest water demand, compared with the other blended cements. The initial and final setting time of metakaolin cements is higher than the setting time of pure cement.

The corrosion tendency of the reinforcing steel bars was estimated in all types of the mortar specimens, by the half-cell potential development versus the exposure time in the corrosive environment. Plots of this evolution are given for all specimens in Fig. 3. Initially the potential values of almost all specimens immersed in chloride environment equal −200 mV vs. SCE. Thereafter decay is observed to more negative values and finally after 8 months of exposure it differentiates between the various specimens. Consequently, mortar specimens can be separated in two categories:

1. Mortars PC, MK-S10, MK-S20 and MK-C10;
2. Mortars MKC-C20, MK-S30 and MK-C20.

It is well established [27] regarding the significance of the numerical value of the potentials that, if potentials over

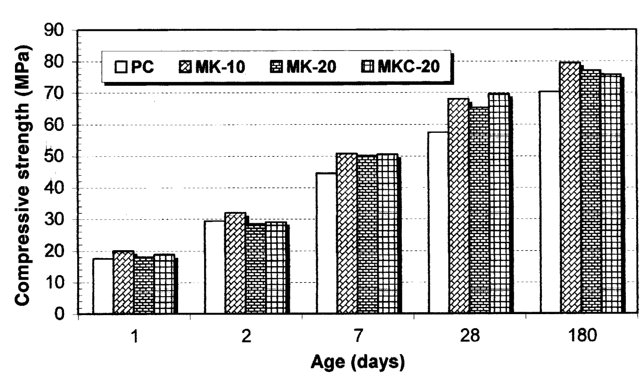

Fig. 2. Compressive strength of blended cements with metakaolin.

Table 6
Physical properties of blended cements with metakaolin

Sample	Water demand (%)	Setting time (min)	
		Initial	Final
PC	27.5	105	140
MK-10	32.5	155	180
MK-20	41.0	205	230
MKC-20	37.5	140	170

an area are numerically less than −0.200 V vs. SCE, there is a greater than 90% probability that there is no corrosion of the reinforcing steel bars at the time of measurement, whereas if potentials over the examined area fluctuate between −0.200 and −0.350 V vs. SCE, the corrosion activity of the reinforcing steel is uncertain. Finally, if potentials are numerically greater than −0.350 V vs. SCE, there is a greater than 90% probability that corrosion of reinforcing steel bars occurs.

Thus, from the development of the half-cell potentials of the steel rebars, it is clear that for the first category of specimens a better performance in corrosion resistance is expected than that of the second ones.

Among the laboratory tests, measurement of the mass loss versus the exposure time provides the ability of a rather correct prediction of a construction lifetime. The plots of these measurements for all types of specimens tested are presented in Fig. 4, which reveals that the mass loss increases with increasing exposure time. It must be noted that 100 mg mass loss equals to about 0.1% of the steel rebar mass. Mortars MK-S10, MK-S20 and MK-C10 exhibit improved anticorrosive properties, which lead to better corrosion performance of the steel rebars, whereas MKC-C20, MK-S30 and MK-C20 present greater mass losses. These results are in accordance with the relevant ones from the corrosion potential measurements.

These results are validated by the corresponding electrochemical measurements of the corrosion rate according to the Linear Polarization method (Fig. 5), where the electrochemical mass loss was calculated from the corrosion current with the Faraday law. Mortars MK-S30 and MK-C20 present the worst anticorrosive properties.

Comparing the pore characteristics of mortars PC and MK-S20, it seems that they have a similar total porosity (PC: 7.3%, MK-S20: 7.8%). In contrast, the mortar with metakaolin shows a significantly lower mean pore size (PC: 80 nm, MK-S20: 64 nm). The improved pore size distribution of MK-S20, compared to that of PC, is also confirmed from Fig. 6, that presents the cumulative pore size distribution of these samples.

Mortars PC, MKC-C20, MK-S10, MK-S20 and MK-C10 presented no carbonation after 8 months of exposure to the corrosive environment, whereas mortars MK-S30 and MK-C20 had a carbonation depth of approximately 2 mm.

From all measurements performed in this work, it is obvious that the addition of metakaolin in percentages up to 20% w/w improves the strength development.

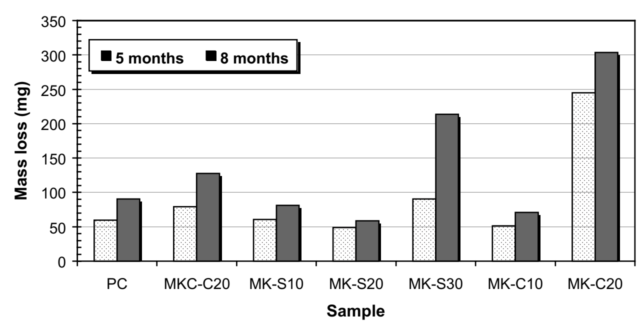

Fig. 4. Mass losses of mortar specimens immersed in 3.5% NaCl solution.

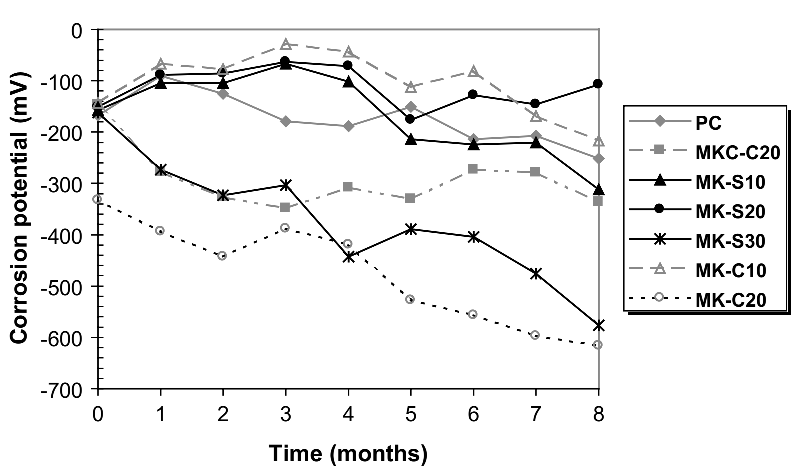

Fig. 3. Corrosion potentials of mortar specimens immersed in 3.5% NaCl solution.

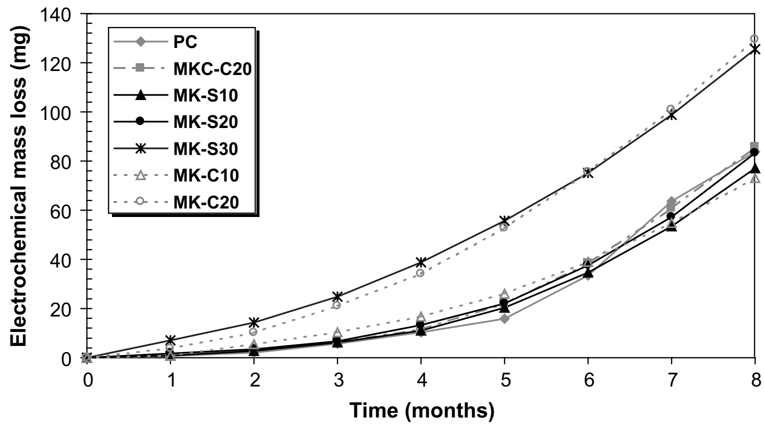

Fig. 5. Electrochemical mass loss of mortar specimens immersed in 3.5% NaCl solution.

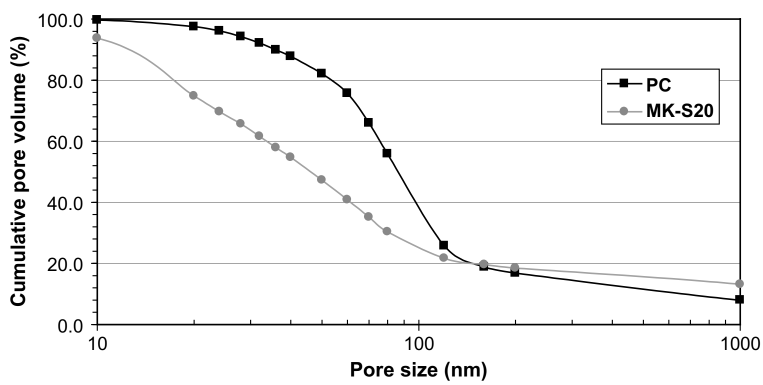

Fig. 6. Cumulative pore size distribution of mortar specimens PC and MK-S20.

Concerning the corrosion, the use of metakaolin, either as sand replacement up to 20% w/w, or as a cement replacement up to 10% w/w, improves the corrosion behavior of mortar specimens. Higher percentages of metakaolin decrease the corrosion resistance of the specimens. This phenomenon is mainly attributed to the pH decrease of the pore solution, due to the pozzolanic reaction and the following consumption of the $Ca(OH)_2$. By measuring the porosity of mortar samples performed on a Mercury Porosimeter, it comes out that mortar samples with metakaolin have the same total porosity as the PC samples, but they present a lower mean pore size and an improved pore size distribution. This fact comes in accordance with the opinion that when an active substance is added to mortar, there is an upper limit on its addition, above which it stops being active [28]. Consequently, the addition of metakaolin in high percentages does not lead to a further reduction of mean pore size. In addition, mortars with 20% cement replacement and 30% sand replacement demand the use of a greater w/c ratio. This provokes an increase in total porosity, which results in a reduction of the beneficial effect of metakaolin.

5. Conclusions

The following conclusions can be drawn from the present study:

- Both the produced and commercial metakaolin indicate a similar behavior concerning the strength development and the corrosion resistance.
- The metakaolin improves the compressive strength and the 10% w/w addition shows the optimum contribution to the strength development.
- The use of metakaolin, either as a sand replacement up to 20% w/w, or as a cement replacement up to 10% w/w, improves the corrosion behavior of mortar specimens. Higher percentages of metakaolin decrease the corrosion resistance.

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