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# Exploitation of poor Greek kaolins: Durability of metakaolin concrete

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ABSTRACT

In this paper the effect of metakaolin on concrete durability is investigated. A Greek kaolin of low kaolinite content was thermally treated at defined conditions and the produced metakaolin was finely ground. In addition, a commercial metakaolin of high purity was used. Eight mixture proportions were used to produce high performance concrete, where metakaolin replaced either cement or sand in percentages 10% or 20% by weight of the control cement content. Durability of metakaolin concrete was evaluated by means of resistance to chloride penetration, air permeability, sorptivity, porosity and pore size distribution. Metakaolin concrete exhibits significantly lower chloride permeability, gas permeability and sorptivity. The addition of metakaolin refines the pore system of concrete, leading to a decreased mean pore size and improved uniformity of the pore size distribution. The produced metakaolin, derived from the poor Greek kaolin, imparts similar behavior to that of the commercial metakaolin, with respect to the concrete durability.



## 1. Introduction

Metakaolin is the most recent mineral admixture to be commercially introduced to the concrete construction industry [1–3]. Unlike other pozzolans, it is a primary product, not a secondary product or by-product, produced by controlled thermal treatment of kaolin. This allows manufacturing process of metakaolin to be optimized, ensuring the production of a consistent pozzolanic material.

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 [4–12]. The second one concerns the pozzolanic behavior of metakaolin and its effect on cement and concrete properties [2,4,13–33].

Concrete durability depends mainly on the chemistry (cement hydration process), and the microstructure of the concrete. Metakaolin addition affects positively both factors; Metakaolin consumes rapidly and effectively the $Ca(OH)_2$ that is produced from the cement hydration process and additional to CSH, phases like $C_2ASH_8$ (stratlingite), $C_4AH_{13}$ and $C_3ASH_6$ (hydrogarnet) are produced. These pozzolanic products contribute to a total pore refinement [13,18,32]. The refined pore system results in a more compact concrete, through which transportation of the water and other aggressive chemicals is significantly impeded and therefore a decrease in the diffusion rate of harmful ions is reported [17,27,33,34].

This work forms part of a research project, which aims towards to the exploitation of poor Greek kaolins in concrete technology. Up to now, the optimization of the kaolin to metakaolin conversion [10,29,35], the study of the CH–metakaolin system [36], the effect of the crystallinity of the original kaolinite on the pozzolanic activity of metakaolinite [11,29], the properties and behavior of metakaolin cements [37], the effect of metakaolin on the corrosion behavior of cement mortars [30] and the evaluation of strength development of metakaolin concrete by means of *k*-value [38] have been carried out. In the present work, two metakaolins, a produced metakaolin originated from poor Greek kaolin and a commercial one of high purity, are examined and their effect on concrete durability is investigated.

## 2. Experimental

### 2.1. Materials

A poor Greek kaolin (K), originated from Milos Island, was used. In addition, a commercial (from Imerys Minerals) metakaolin (MKC) of high purity was also used as a reference material. The chemical analysis of the materials is given in Table 1. Concerning the commercial metakaolin, for comparison reasons, the characteristics of the commercial kaolin (KC), instead of MKC, are given. As can been seen from Table 1, K is a poor kaolin as it contains only 52% kaolinite.

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**Table 1**
Chemical and mineralogical analysis of kaolins.

| Material | $SiO_2$ | $Al_2O_3$ | CaO | MgO | $Fe_2O_3$ | L.O.I. | $SO_3$ |
|---|---|---|---|---|---|---|---|
| *Chemical analysis* (%)[a] | | | | | | | |
| KC | 47.85 | 38.20 | 0.03 | 0.04 | 1.29 | 12.30 | – |
| K | 65.92 | 22.56 | 0.36 | 0.02 | 0.90 | 8.60 | 2.00 |

| Material | Kaolinite | Alunite | Quartz[b] | Illite |
|---|---|---|---|---|
| *Mineralogical analysis* (%) | | | | |
| KC | 96 | – | – | 3 |
| K | 52 | 5 | 41 | – |

[a] EN-450, EN-196 and EN-451.
[b] Quartz (mainly) + cristobalite.

The semi-quantitative mineralogical estimation of the materials is presented in Table 1. 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 [11]. 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. In previous work [11] has also found that the contained kaolinite in Greek kaolin K is less ordered than the kaolinite in the commercial KC and this has a positive effect on MK reactivity (MK is the metakaolin originated from K).

Ordinary Portland cement (PC: I/55) of industrial origin was used for the production of the mixtures. The chemical analysis of PC and the characteristics of clinker are given in Table 2.

### 2.2. Metakaolin production

The optimum conditions of thermal treatment have been reported in previous works [35,36]. The kaolin K was thermally treated in a pro-pilot plant furnace at $T = 650\,^{\circ}C$ for 3 h. The complete transformation of kaolinite to metakaolinite was confirmed by X-ray diffraction. The metakaolinite content of the used metakaolins is 49% w/w and 95% w/w for MK and MKC, respectively (Table 3). The estimation is based on the chemical and mineralogical analysis of the kaolins (Table 1). In Table 3, the $SiO_2$ content (estimated from Table 1 data) and the active $SiO_2$ (measured according to EN 196-2) of the metakaolins are also given. The active silica is defined as the fraction of the $SiO_2$ that is soluble after treatment with hydrochloric acid and with boiling potassium hydroxide solution (EN 197-1).

The produced metakaolin MK was finely ground, using the AJ100 Aerojet Mill Minisplit Classifier of British Rema. The fineness characteristics of the ground metakaolin as well as the MKC are given in Table 4.

### 2.3. Concrete preparation and properties

The concrete production was carried out in a mixer of 50 l capacity. In addition to the control concrete mixture, four concrete mixtures were prepared for each metakaolin, where metakaolin replaced either cement or sand in percentages 10% or 20% by weight of the control cement content. The water content (tap water at 20 °C) for all specimens was kept constant (175 $kg/m^3$). Normal graded calcareous aggregates, including fine (37%), medium (21%) and coarse (42%) aggregates, were used. The coarse aggregate maximum size was 31.5 mm. For the control specimen, the water-to-cement ratio (W/C) was 0.5 and the aggregate-to-cement ratio (A/C) was 5.5. A common superplasticizer (CHEM SLP P by Domylco Ltd., type E and F of ASTM C494/C494M-08a) was used at appropriate percentages in order to retain the slump of the fresh concrete between 50 and 90 mm (class S2 of EN 206). The mixture proportions of all concrete specimens are summarized in Table 5 for cement and sand replacement, respectively. The main properties of fresh and hardened concrete are summarized in Table 6. For each age, three specimens (cubes of 150 mm) were tested for compressive strength and the mean value of these measurements is reported. The density of the fresh concrete varies from 2427 to 2453 $kg/m^3$.

**Table 2**
Chemical analysis of PC and characteristics of clinker.

| Cement | | Clinker | |
|---|---|---|---|
| *Chemical analysis* (%) | | *Mineralogical 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 | LSF | 0.949 |
| $Na_2O$ | 0.07 | SR | 2.47 |
| $SO_3$ | 2.74 | AR | 1.24 |
| $Cl^-$ | 0.00 | HM | 2.17 |

**Table 3**
Metakaolinite, $SiO_2$ and active $SiO_2$ content of metakaolins.

| | Metakaolinite (%) | $SiO_2$ (%) | Active $SiO_2$ (%) |
|---|---|---|---|
| MKC | 95 | 54.6 | 53 |
| MK | 49 | 72.1 | 30 |

**Table 4**
Metakaolin fineness characteristics.

| $d$ (μm) | Residue (%) | |
|---|---|---|
| | MK | MKC |
| *Particle size distribution* | | |
| 22.0 | 4.7 | 2.4 |
| 18.2 | 9.3 | 4.9 |
| 15.1 | 16.1 | 8.6 |
| 12.4 | 24.4 | 13.7 |
| 8.5 | 43.2 | 27.0 |
| 5.8 | 60.7 | 42.4 |
| 3.3 | 79.7 | 63.8 |
| 1.8 | 90.4 | 79.5 |
| 1.0 | 95.8 | 89.5 |
| 0.6 | 98.4 | 95.6 |
| *Fineness characteristics* | | |
| $d_{20}$ (μm)[a] | 13.6 | 10.3 |
| $d_{50}$ (μm) | 7.5 | 5.1 |
| $d_{80}$ (μm) | 3.4 | 1.9 |
| *Rosin–Rammler parameters* | | |
| n | 1.42 | 1.18 |
| pp (μm) | 9.7 | 6.9 |

[a] $d_i$: The diameter where $i$ % w/w of the particles (powder) are coarser.

The specimens for the durability tests were cast in steel cylinders of 100 mm diameter and 200 mm height. The molds were stripped after 24 h and the specimens placed under lime-saturated water at 20 °C for 90 days. This long-term curing period under water ensures an advanced degree of both Portland cement hydration and pozzolanic reaction.

### 2.4. Durability tests

The AASHTO T277 rapid test method was followed to rank the chloride penetration resistance of concrete by applying a potential of 60 V (DC) and measuring the charge passed through the specimen. The tested concrete cores are slices 51 mm thick, cut from the middle of the initially 200 mm specimens and coated with watertight tape on the cylindrical surface.

The air permeability tests were applied to a concrete cylinder of 100 mm diameter and height varied between 45 mm and 50 mm. The specimens were oven-dried at 105 °C, until a weight change

**Table 5**
Concrete mix proportions.

| Sample | Content (kg/m$^3$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C | P | | Aggregates[c] | W | SP (%) | W/C | W/B |
| | | MKC | MK | | | | | |
| *Cement replacement* | | | | | | | | |
| PC | 350 | – | – | | 175 | 0.057 | 0.50 | 0.50 |
| MKC-CR10[a] | 315 | 35 | – | Fine: 720 | | 0.140 | 0.56 | |
| MKC-CR20 | 280 | 70 | – | Medium: 400 | | 0.170 | 0.63 | |
| MK-CR10 | 315 | – | 35 | Coarse: 800 | | 0.181 | 0.56 | |
| MK-CR20 | 280 | – | 70 | | | 0.400 | 0.63 | |

| Sample | Content (kg/m$^3$) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | P | | Aggregates | | | W | SP (%) | W/C | W/B |
| | | MKC | MK | Fine | Medium | Coarse | | | | |
| *Sand replacement* | | | | | | | | | | |
| MKC-SR10[b] | 350 | 35 | – | 685 | 400 | 800 | 175 | 0.145 | 0.50 | 0.42 |
| MKC-SR20 | | 70 | – | 650 | 400 | 800 | | 0.207 | | 0.45 |
| MK-SR10 | | – | 35 | 685 | 400 | 800 | | 0.222 | | 0.42 |
| MK-SR20 | | – | 70 | 650 | 400 | 800 | | 0.357 | | 0.45 |

[a] MKC-CR10: cement replacement, 10% by weight of the cement.
[b] MKC-SR10: sand replacement, 10% by weight of the cement.
[c] Fine aggregates: 100% w/w passing an 8mm sieve, 95% w/w passing a 4 mm sieve; medium aggregates: 100% w/w passing a 16 mm sieve, 1% w/w passing a 1 mm sieve; coarse aggregates: 100% w/w passing a 31.5 mm sieve, 40% w/w passing a 16 mm sieve.

of less than 0.1% over 24 h was observed [39]. The drying period of these specimens was 4–6 days. A modified commercial triaxial cell for 100 mm diameter specimens, operating to maximum cell pressure of 0.7 N/mm$^2$, was used for the determination of the gas ($N_2$) permeability of the specimens. The equipment used as well as the detailed procedure is described in a previous work [40].

The sorptivity test was applied to a concrete cylinder of 100 mm diameter and 125 mm height, oven-dried at 105 °C for 24 h. The equipment used as well as the detailed procedure is described in a previous work [40].

The concrete pore structure was studied using mercury intrusion porosimetry. More specifically, the total porosity of the specimens as well as their pore size distribution was measured with a Carlo Erba 2000 Hg porosimeter.

## 3. Results and discussion

Table 7 summarizes the experimental results for the chloride permeability, gas permeability, sorptivity, total porosity and mean pore size. The results given in Table 7 are average values of three different specimens.

The addition of metakaolin causes a significant increase of concrete resistance to chloride penetration. The charge passed (in the rapid chloride test) in metakaolin concrete varies from 180 to 820 C (Coulomb), while charge passed in PC concrete is 2460 C. Small differences are reported in between the two metakaolins, as far as the achieved reduction of chloride permeability is concerned. Moreover, these small differences become of minor significance when the total reduction on the chloride permeability is also considered. The concrete with MKC and 10% replacement of sand performs the higher resistance to chloride penetration.

Concrete with metakaolin exhibits lower gas permeability values compared with PC concrete. The gas permeability of the metakaolin concrete varies from 1.35 to $1.85 \times 10^{-16}$ m$^2$, while the PC concrete presents a gas permeability of $2.94 \times 10^{-16}$ m$^2$. As far as the comparison of the two metakaolins is concerned, similar effect on gas permeability reduction is reported. The concrete with MK and 10% replacement of cement shows the lower gas permeability.

The addition of metakaolin causes a relative decrease of concrete sorptivity. The sorptivity varies from 0.062 to 0.097 mm/min$^{0.5}$, while the PC concrete presents a sorptivity of 0.114 mm/min$^{0.5}$. Concrete specimens with commercial metakaolin (MKC) show the best behavior compared to MK concrete specimens and the concrete with MKC and 20% replacement of sand has the lower sorptivity.

The addition of metakaolin causes, in most cases, a decrease of concrete total porosity. The total porosity of metakaolin concrete varies from 7.2% to 11.2%, while the PC concrete presents a total porosity of 11.1%.

**Table 6**
Properties of concrete.

| Sample | Slump (mm) | Air content (%) | Compressive strength (N/mm$^2$) | | | |
|---|---|---|---|---|---|---|
| | | | 2 d | 7 d | 28 d | 90 d |
| PC | 70 | 1.4 | 38.1 | 49.0 | 55.8 | 67.0 |
| MKC-CR10 | 90 | 1.5 | 36.1 | 54.5 | 74.0 | 80.5 |
| MKC-CR20 | 60 | 1.0 | 34.3 | 57.4 | 75.6 | 85.3 |
| MK-CR10 | 50 | 1.5 | 42.5 | 59.4 | 79.9 | 91.4 |
| MK-CR20 | 70 | 1.0 | 34.0 | 54.5 | 77.4 | 86.3 |
| MKC-SR10 | 100 | 1.1 | 44.6 | 73.0 | 91.6 | 91.0 |
| MKC-SR20 | 60 | 1.0 | 45.4 | 67.1 | 81.5 | 82.9 |
| MK-SR10 | 70 | 1.1 | 46.6 | 63.3 | 81.4 | 90.9 |
| MK-SR20 | 40 | 1.0 | 49.7 | 69.7 | 83.7 | 94.8 |

**Table 7**
Chloride permeability, gas permeability, sorptivity, total porosity and mean pore size of specimens.

| Specimen | Chloride permeability [a](C) | Gas permeability ($m^2 \times 10^{-16}$) | Sorptivity ($mm \times min^{0.5}$) | Porosity (%) | Mean pore size (nm) |
|---|---|---|---|---|---|
| PC | 2460 | 2.94 | 0.114 | 11.1 | 96 |
| MKC-CR10 | 730 | 1.68 | 0.097 | 11.0 | 70 |
| MKC-CR20 | 240 | 1.45 | 0.089 | 11.2 | 55 |
| MK-CR10 | 690 | 1.35 | 0.080 | 7.2 | 74 |
| MK-CR20 | 760 | 1.60 | 0.067 | 10.3 | 62 |
| MKC-SR10 | 180 | 1.75 | 0.082 | 9.5 | 60 |
| MKC-SR20 | 530 | 1.56 | 0.062 | 9.9 | 70 |
| MK-SR10 | 820 | 1.71 | 0.065 | 8.3 | 62 |
| MK-SR20 | 390 | 1.85 | 0.092 | 10.4 | 64 |

[a] Expressed through the charge passed in the rapid chloride test.

Although the effect of metakaolin on concrete total porosity is not clear, its effect on the concrete mean pore size is impressive. The mean pore size of the metakaolin concrete varies from 55 to 74 nm, while the PC concrete presents a mean pore size of 96 nm. The concrete with MKC and 20% replacement of cement shows the lower mean pore size.

Figs. 1 and 2 present the pore size distribution of MKC and MK concrete, respectively. It is seen that in metakaolin concrete the curves are moved to the left of the PC concrete curve, resulting to a more compact and less porous material.

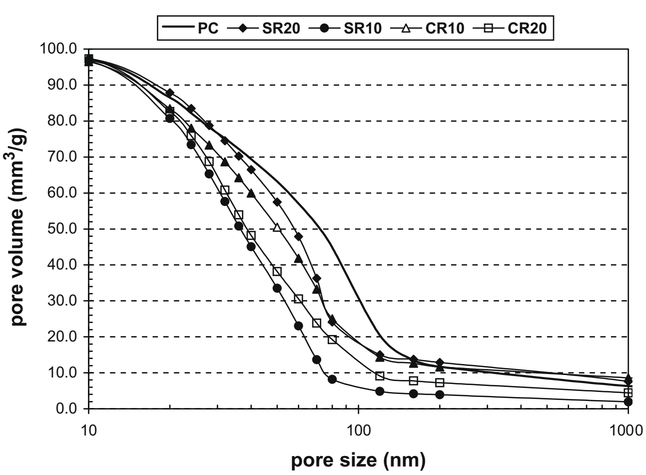


**Fig. 1.** Pore size distribution for concrete incorporating metakaolin MKC.

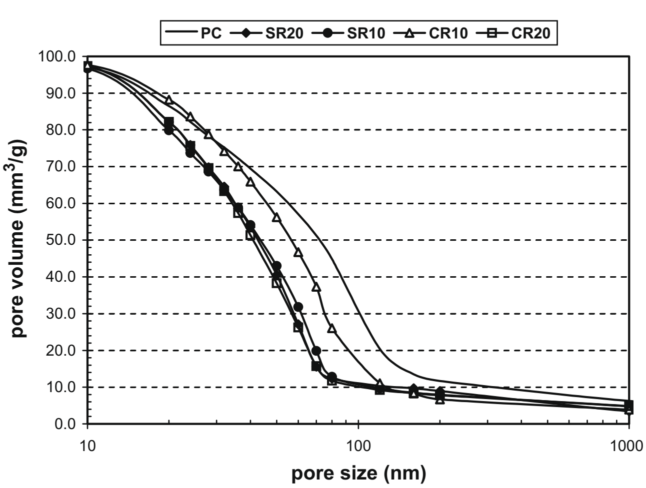


**Fig. 2.** Pore size distribution for concrete incorporating metakaolin MK.

In order to evaluate the pore size distribution of the specimens, Rosin–Rammler equation has been applied. Table 8 presents the uniformity coefficient ($n$) of the pore size distribution of the tested

**Table 8**
Rosin–Rammler uniformity coefficient of pore size distribution of concrete specimens.

| PC | MKC | | | | MK | | | |
|---|---|---|---|---|---|---|---|---|
| | SR20 | SR10 | CR10 | CR20 | SR20 | SR10 | CR10 | CR20 |
| 1.24 | 1.55 | 1.55 | 1.35 | 1.41 | 1.51 | 1.42 | 1.60 | 1.53 |

**Table 9**
Pore volume of specimens in selected size areas.

| Specimen | Pore volume ($mm^3$/g) | | |
|---|---|---|---|
| | <20 nm | >20 nm | >160 nm |
| PC | 7.0 | 44.8 | 7.0 |
| MKC-CR10 | 8.5 | 42.9 | 6.5 |
| MKC-CR20 | 9.1 | 43.2 | 4.1 |
| MK-CR10 | 3.7 | 27.5 | 2.6 |
| MK-CR20 | 8.2 | 37.8 | 3.9 |
| MKC-SR10 | 8.6 | 36.1 | 1.9 |
| MKC-SR20 | 5.7 | 40.8 | 6.4 |
| MK-SR10 | 7.3 | 29.0 | 3.1 |
| MK-SR20 | 8.6 | 39.2 | 4.6 |

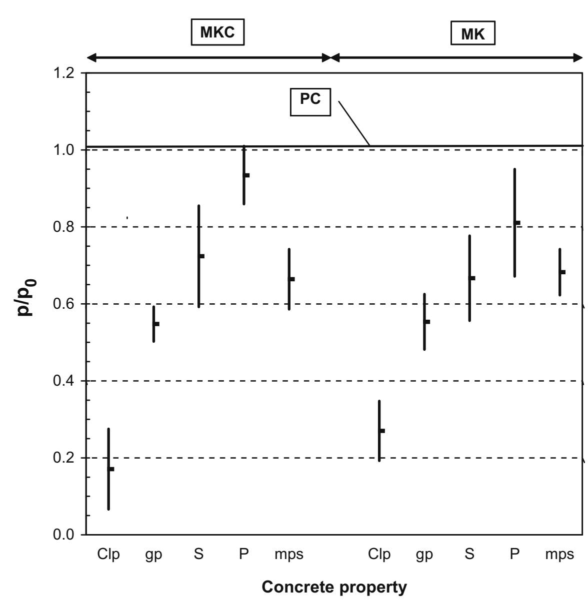


**Fig. 3.** The effect of metakaolin on concrete durability ($p$: value of a specific property of metakaolin concrete, $p_0$: value of the same property in PC concrete, Clp: chloride permeability, gp: gas permeability, $S$: sorptivity, $P$: total porosity, mps: mean pore size).

specimens. As ($n$) is increased, the pore size distribution becomes more uniform. Uniformity coefficient ($n$) ranges from 1.35 to 1.60 for metakaolin concrete, while the PC concrete has a ($n$) value of 1.24. The more uniform pore size distribution of the metakaolin concrete, along with the lower mean pore size mentioned above, leads to more durable concrete.

Table 9 presents the pore volume in selected size areas. According to the literature [17,19,41], pores with size less than 20 nm do not influence concrete properties, pores with size more than 20 nm have a negative effect on concrete strength development and pores with size more than 160 nm have a negative effect on concrete penetrability. Metakaolin addition results to a lower volume of pores, sizing more than 20 and 160 nm, compared to PC concrete (Table 9).

In order to indicate more clearly the contribution of the metakaolin to the concrete durability, the ratio ($p/p_0$) has been used, where $p$ is the value of a specific property of metakaolin concrete and $p_0$ is the value of the same property in PC concrete. Fig. 3 presents the ($p/p_0$) values of the applied durability tests. It must be noted, that the $p$ value is the mean value of the four tested mixtures for each metakaolin. In Fig. 3 the deviation of the mean value is also given. The ($p/p_0$) values presented in Fig. 3, show that the metakaolin addition has a positive effect on all the studied concrete properties. Metakaolin affects especially the chloride permeability and the gas permeability of the concrete. It is also concluded from Fig. 3, that the produced metakaolin MK as well as the commercial one imparts a similar behavior with respect to the concrete durability.

All the above results show that the metakaolin coming from poor Greek kaolin as well as the commercial metakaolin of high purity have a positive effect on concrete properties. Although the two metakaolins have significantly different mineral composition, small differences of concrete properties, like resistance to chloride penetration, gas permeability, sorptivity, total porosity and mean pore size are reported. It seems that the kind of replacement (sand or cement) and the percentage of metakaolin in concrete, affect the concrete properties in a greater extend than the kind of metakaolin. Metakaolin from poor Greek kaolins has a contribution to concrete properties comparable with the commercial metakaolin of high purity. This may be attributed to the following reasons: (a) as it has been published elsewhere [11], the two metakaolins have almost the same pozzolanic reactivity (on the basis of Chapelle test). This is due to the fact that Greek kaolin contains less ordered kaolinite and less ordered kaolinite is transformed to more reactive metakaolinite, (b) the Greek metakaolin contains 41% w/w quartz, which acts as an aggregate – very compact structure compared to the cement paste, no pores – and has a positive effect on porosity and permeability properties of the concrete, (c) as already mentioned, the two main components of Greek metakaolin is quartz and metakaolinite. Metakaolinite has a higher grindability (easier ground) than quartz and therefore metakaolinite is concentrated in the finer fractions of the material. This fact has a positive effect on the rate of the pozzolanic reaction. Further research is on progress in order to have a thorough insight on the behavior of Greek metakaolins as concrete components.

## 4. Conclusions

The following conclusions can be drawn from the present study:

- The produced metakaolin, derived from a poor Greek kaolin, imparts similar behavior to that of the commercial metakaolin, with respect to the concrete durability.
- Metakaolin concrete, compared to PC concrete, exhibits significantly lower chloride permeability, gas permeability and sorptivity.
- The addition of metakaolin refines the pore system of concrete, leading to a decreased mean pore size, improved uniformity of the pore size distribution and decreased volume of pores with size more than 160 nm.
- The above improved properties would improve the durability of the concrete with respect to most forms of attack.

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