



## The Impact of Local Industrially Produced Metakaolin on Both Cement And Concrete Reinforcing Steel Physico-mechanical and Corrosion Resistance Properties



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### Abstract

Metakaolin (MK) is one of the innovative clay products developed in recent years. It is produced by the calcination of natural kaolin clay, thus, creating an amorphous, reactive product (MK). As a result of the high cost of pozzolanic materials investigation made the suitability of using such local MK as a pozzolanic material in concrete for constructional work unavoidable. The investigation disclosed that the industrially produced MK behaves as a pozzolanic material, thus, consuming part of the Ca(OH)<sub>2</sub> resulting from cement hydration forming extra – calcium silicate hydrate (CSH). For preparing cement mixes (for different utilizations – other than concrete) incorporating MK as cement replacement using physico- mechanical tests like Compressive strength, setting time, Differential thermal analysis (DTA) also using electrochemical measurements to test the corrosion resistance behavior, The significant results appear that 15% MK is the optimum dosage (yielding higher pozzolanic effect as well as filler effect). The dosage of 10% MK, as cement replacement ratio in plain (non-reinforced) concrete, is considered the optimum dosage, manifesting higher compressive strength as well as higher resistance to elevated temperatures. For reinforced concrete, 15% MK is the optimum ratio to be used, as a cement replacement, as long as maintaining the steel reinforcement passivity as well as counteracting the penetration of aggressive ions through concrete is concerned. The locally produced MK could be an excellent substitute for silica fume (SF) as a pozzolanic material in concrete.

**Keywords:** Metakaolin; Pozzolanic activity; SCM's; Corrosion resistance; Compressive strength; Durability; Passivation.

### 1. Introduction

Concrete is the most popular, versatile, and widely used building material worldwide. Over the last three decades, the construction industry has taken considerable strides forward regarding higher performing concrete materials. Scientists and engineers are continuously working for better concrete characteristics from the physical, mechanical and durability aspects with the help of innovative chemical admixtures and supplementary cementing materials (SCM'S) [1-4].

Egypt could be considered devoid of the suitable local industrial wastes that could be used as SCM'S (Particularly fly ash and blast furnace steel slag) Egypt could be considered devoid of the suitable

local industrial wastes that could be used as pozzolanic materials (particularly fly ash and blast furnace steel slag). Silica fume is rather expensive and is exported abroad. Fortunately, MK is now produced in Egypt by the calcination of raw kaolin during the manufacture of aluminium sulfate (alum) at "Aluminium Sulfate Company of Egypt – ASCE". The development in these materials is progressing rapidly. The most significant and indispensable ingredient of concrete is cement. The cement manufacturing process releases a significant amount of CO<sub>2</sub> emissions, a major contributor to the greenhouse effect and the global warming of the earth planet. The most effective way to decrease the CO<sub>2</sub> emissions of the cement industry is the substitution of

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a portion of the cement by (SCM'S). The usage of these materials in cement has dramatically increased along with the development of concrete industry due to considerations of reducing the cement content of concrete (hence energy and cost saving), in addition to, alleviating atmospheric pollution, improving workability, increasing strength and enhancing durability of concrete through SCM'S pozzolanic activity [5,6]. According to ASTM: C 618-92a [7]: "Pozzolanic are a broad class of siliceous or siliceous and aluminous materials which, in themselves, possess little or no cementitious value, but will, in finely divided form and in the presence of water, chemically react with calcium hydroxide liberated during cement hydration at ordinary temperatures to form additional compounds possessing cementitious properties" [8–10].

Silica fume and various mineral admixtures (pozzolanic), particularly, coal fly ash and ground granulated blast furnace steel slag have become staple ingredients that judiciously utilized in the production of concretes having particular strengths or where service environments, exposure conditions or life-cycle considerations dedicate the usage of specific concretes (e.g., high performance concrete – HPC) [11–14]. Metakaolin (dehydrated aluminium silicate –  $\text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2$ ) is one of the innovative clay products developed in recent years. It is produced by thermal activation (calcination) in the range of 500–800°C of previously refined raw kaolin clay (i.e., phyllosilicates or layer silicates) under carefully controlled conditions to create a disordered, amorphous, reactive (highly pozzolanic) product [15,16].

On the other hand, silica fume that has been initially considered as an industrial waste (of silicon mineral or ferrosilicon alloys production) has now become a world class product for which there is a constant demand as a (SCM) in the construction industry. This product is rather expensive. In Egypt, most of the collected silica fume (from the silicon and ferrosilicon industry) is exported abroad as its price is about 4-5 times the price of Portland cement [17]. Fortunately, metakaolin (MK), is now produced in Egypt, particularly, by the calcination of raw kaolin during the manufacture of aluminium sulphate (alum). Kaolin: is an aluminosilicates mineral composed mainly of kaolinite mineral which is [hydrated aluminum-disilicate  $\text{Al}_2\text{Si}_2\text{O}_5 (\text{OH})_4$  mixed with silica ( $\text{SiO}_2$ ) in the form of quartz mineral. At "Aluminum Sulfate Company of Egypt – ASCE", Abu Zaabal, Kaliobeya Governorate, natural kaolin (obtained from Abu Zinema Quarries, Southern Sinai) is refined, crushed, and collected in a silo. Then, such kaolin is transferred to a vertical kiln

where it is transformed to MK through calcining at 750°C for 2 hrs. Part of the formed MK is stored as fresh metakaolin. The other part of MK is conveyed to some sort of reactors where Al is leached out of MK by subjection to dilute  $\text{H}_2\text{SO}_4$  acid, thus, forming aluminium sulphate (alum). Previously, researchers worldwide have shown a lot of interest in MK as it has been found that it possesses high pozzolanic and micro filler characteristics. However, despite many recent studies, information about the properties of MK- modified cement and concrete (Plain or reinforced) is still limited. That thwarts its wide application. In Egypt, the deficiency, as results of high cost of pozzolanic materials made investigating the suitability of such local industrially produced MK as a (SCM) in concrete for constructional work unavoidable.

Accordingly, supplementary cementitious materials (SCMs), like metakaolin, increase the compressive strength of concrete in two ways: by acting as filler and reacting with CH crystals to produce secondary C-S-H. In a very alkaline environment, SCMs react with the CH to generate C-A-S-H, which reduces porosity and considerably increases the strength of the concrete [9]. SCMs often contain large concentrations of alumina-silica. Concretes containing MK have strong tensile and compressive properties. With more MK content, compressive strength was shown to rise significantly. Compressive strength had increased 51% over controls in samples with 15% replacement [10]. The compressive strength of cement containing five metakaolins up to 180 days was also examined by authors at [4]. After two days, it was found that Metakaolin had a significant impact on cement strength. It was found that Metakaolin, specifically at 28 and 180 days, had a significant favourable impact on cement strength after just two days. In general, 10% metakaolin content seems to be preferable to 20%. A summary of the research on the use of MK as a partial replacement for cement in mortar and concrete was presented by Siddique and Klaus [11]. According to the authors, MK improves cement paste/mortar/early concrete's age mechanical qualities as well as its long-term strength properties. Additionally, MK's partial replacement of cement lowers the water.

The current study has been planned with the target of investigating the suitability of the locally produced MK at ASCE for usage as a pozzolanic material upon replacing part of the cement in concrete. Its impact on the physico-mechanical properties of cement and concrete as well as retaining the passivity of steel reinforcement towards corrosion has been investigated.

## 2. Experimental

### 2.1. Materials utilized.

Industrially produced metakaolin (MK): The metakaolin used has been obtained from the metakaolin industrially produced at “Aluminium Sulfate Company of Egypt – ASCE” at Abu Zaabal, Kaliobeya Governorate. Table 1 presents the chemical composition of the industrially produced MK. Also, Fig. 1 presents the thermal gravimetric analysis (TGA / DTGA) of (a) raw kaolin and (b) raw kaolin after heat treatment at 750 °C for 2 hr. Cement and silica fume: Ordinary Portland cement (CEM 1 – 42.5N) has been supplied by Suez Cement Company, Suez, Egypt. Silica fume (SF) has been supplied by the “Silicon and Ferrosilicon Company”, Edfo-Aswan, Egypt. Table 1 gives the chemical composition of the Portland cement and silica fume. Figs. (2,3) presents the Particle size distribution and X-ray diffraction pattern (XRD) for silica fume.

Coarse and fine aggregates: Dolomite [CaMg(CO<sub>3</sub>)<sub>2</sub>] [D], It has been obtained from Attaka quarries, Suez, Egypt. Dolomite has been used as the coarse aggregate. The fine aggregate was local sand. Table 2 gives the chemical composition of the coarse and fine aggregates. Fig. 4 presents the X-ray diffraction pattern (XRD) for dolomite. The dolomite mineral (D) [Ca Mg (CO<sub>3</sub>)<sub>2</sub>] content is dominant with traces of calcite [CaCO<sub>3</sub>] and quartz [SiO<sub>2</sub>]. The mineralogical composition is in conformity to the chemical analysis of the aggregate. Fig. 5 shows the linear expansion of a mortar - bar due to the alkali – aggregate reaction of the coarse aggregate (dolomite). The expansion reached after 16 days (0.053%) is far enough from the specified expansion limit (0.1%) [18]. Table 3 gives the composition of the reinforcing steel used in the current study. Sea water used as a test medium in the current study has been obtained from Ein El-Sokhna coastal area, Suez Gulf, Red Sea, Egypt. Table 4 gives the chemical analysis of such sea water.

Table 1: Chemical composition of MK, ordinary Portland cement (OPC) and silica fume (SF).

Oxide Content	MK, %	CEM I 42.5N. %	SF, %
SiO <sub>2</sub>	62.37	21.50	94.86
Al <sub>2</sub> O <sub>3</sub>	31.60	3.47	0.69
Fe <sub>2</sub> O <sub>3</sub>	1.47	3.39	1.02
CaO	0.26	61.72	0.27
MgO	0.16	1.15	0.61
SO <sub>3</sub> <sup>-</sup>	0.15	2.57	0.21
L.O.I.	1.16	4.53	1.45
Na <sub>2</sub> O	0.13	0.30	0.31
K <sub>2</sub> O	0.12	0.30	0.35
TiO <sub>2</sub>	2.00	-	0.04
Cl	0.03	0.09	0.08
Total	99.45	99.87	99.98
Ins. Res	-	0.52	-
Na <sub>2</sub> OEq.	-	0.51	-
L.S.F	-	0.90	-
C <sub>3</sub> A	-	2.52	-
C <sub>3</sub> S	-	52.47	-
C <sub>2</sub> S	-	22.13	-
C <sub>4</sub> AF	-	11.51	-

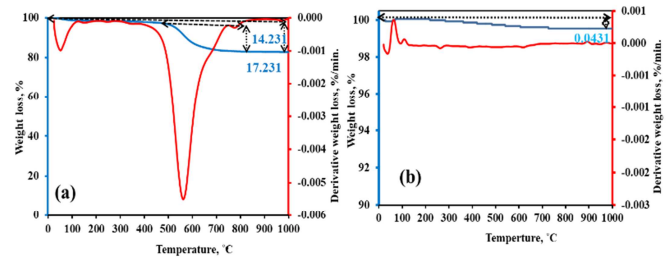


Fig. 1: Thermal gravimetric analysis (TGA / DTGA) of (a) raw kaolin and (b) raw kaolin after heat treatment at 750 °C for 2 hr.

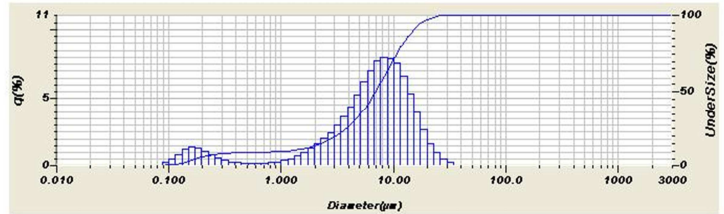


Fig. 2: Particle size distribution of silica fume

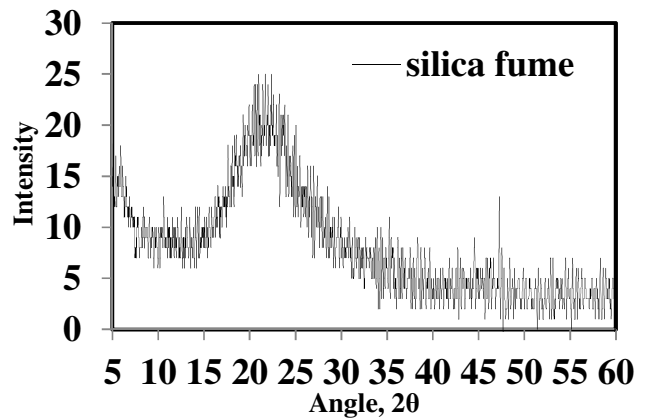


Fig. 3: XRD of silica fume

Table 2: Chemical composition of coarse dolomite and fine sand aggregates, (%).

Oxides, (%)	Dolomite	Sand
SiO <sub>2</sub>	1.67	94.40
Al <sub>2</sub> O <sub>3</sub>	0.08	2.03
Fe <sub>2</sub> O <sub>3</sub>	0.01	0.98
CaO	35.44	0.71
MgO	17.51	0.25
SO <sub>3</sub> <sup>-</sup>	0.13	0.30
Cl	1.01	0.08
Na <sub>2</sub> O	0.04	0.38
K <sub>2</sub> O	0.02	0.65
TiO <sub>2</sub>	0.01	0.13
P <sub>2</sub> O <sub>5</sub>	0.01	0.06
MnO	-	0.03
L.O.I.	45.99	0.74
Total	99.97	99.92

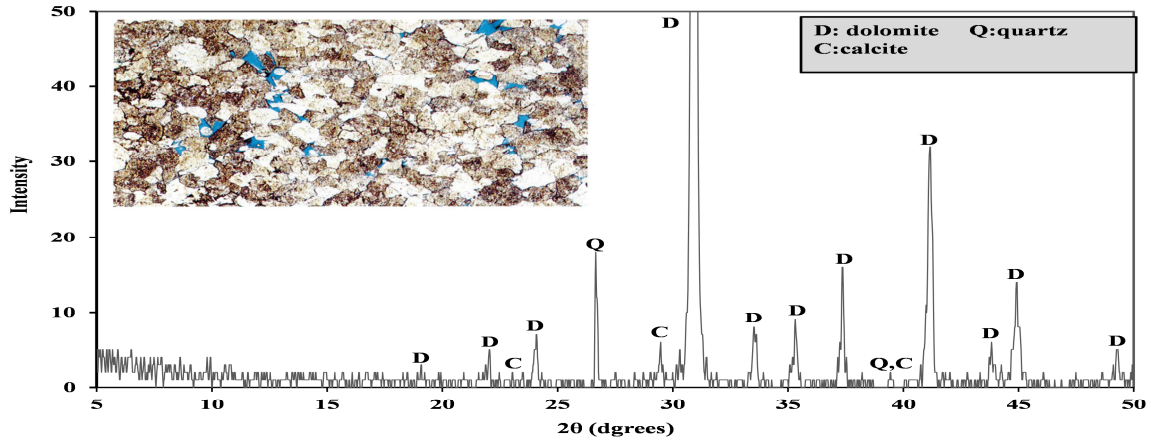


Fig. 4: X-ray diffraction pattern and microscopic patterns for dolomite coarse aggregate.

Table 3: Chemical analysis of reinforcing steel, (%)

Chemical analysis of Steel, (%)											
C	Si	Mn	P	S	Cr	Ni	Cu	Mo	Al	Fe	Total
0.088	0.063	0.590	0.015	0.021	0.124	0.125	0.253	0.022	0.011	98.60	99.535

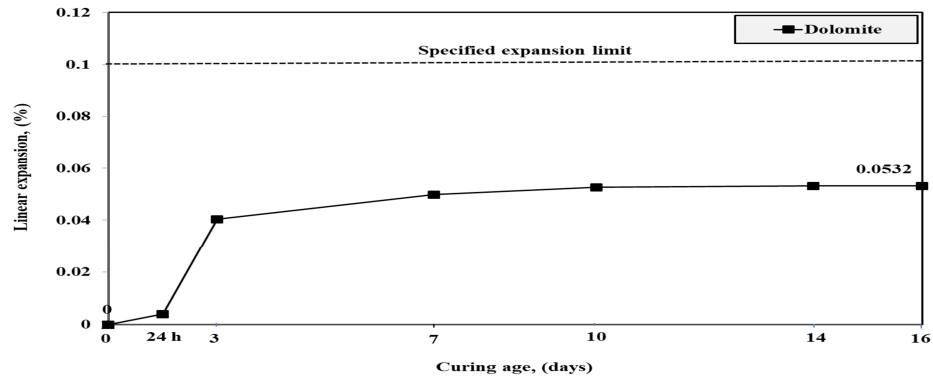


Fig. 5: Expansion values of concrete containing dolomite aggregate

Table 4: Chemical analysis (in Ppm) of sea water.

Cl	SO <sub>4</sub> <sup>-</sup>	Total dissolved solids (T.D.S.)	Total alkalinity	Total suspended solids (T.S.S.)	PH
27.900	2.752	47.977	130	Nil	8.01

## 2.2. Mixing, casting, and curing

### 2.2.1. Preparation of cement pastes mixes.

Mixes of Portland cement incorporating dosages of MK at the ratios 5, 10, 15, 20 and 25% were prepared in order to determine the optimum MK ratio to be used with the cement. The water to solid ratio was varied according to the MK content in the mix (between 0.27 and 0.28, by mass). The paste was made – firstly – by hand mixing of the materials for 10 min. and, then, further mixing was carried out for 5 min. in a mixer. The mix with the MK ratio was always compared with the control (Portland cement – OPC). After mix preparation, the OPC/MK mixes were cast into one inch cubic moulds, vibrated for compaction and sealed with a lid to minimize any loss of evaporable water. The pastes were cured at room temperature for the first 24 hrs. at 100% relative humidity and  $23 \pm 2^\circ\text{C}$ . At the end of this moist curing period, the cubes were demoulded and cured in a water container till the time of testing.

### 2.2.2. Preparation of concrete mixes

The coarse and fine aggregates were mixed for 2 minutes. Half of the total volume of water was added. The materials were mixed for 3 minutes. The binder material (OPC + MK) at the mix proportions and superplasticizer were added to the aggregate in the mixing pan and mixing continued for 30 seconds. Then, the remaining water was added and mixing was continued for 3 minutes. The steel moulds were well prepared, sealed and were given a light coat of mould release agent. Fresh mixes were examined for their workability by the slump test [19]. Then, all concrete mixes were cast into the cubic steel moulds (10cm x 10cm x 10cm) by filling them with the mixes using a vibrating table. Then, the concrete surface was smoothed using a light metal float. Then, the moulds were covered by a plastic sheet and kept at room temperature ( $23 \pm 2^\circ\text{C}$ ) for 24 hours. After demoulding, the specimens were cured in tap water till the time of testing. Table 5 shows the mix proportions of concrete.

**Table 5** : The mix proportions of concrete kg per ( $1\text{m}^3$ )

Ingredients	OPC (0 %MK)	10 % MK	15 %MK	10% SF
Portland cement, CEM 1 - 42.5N	400	360	340	360
Metakaolin	-	40	60	-
Silica fume	-	-	-	40
Fine aggregate (sand)	632	632	632	632
Coarse aggregate (dolomite)	1264	1264	1264	1264
Superplasticizer	8	8	8	8
Water	140	140	140	140
Slump (mm)	10	10	10	10

### 2.2.3. Preparation of reinforcing steel

The reinforcing steel used in the present investigation was mainly mild smooth steel bars 8mm in diameter. The steel rods were mechanically polished to remove the firmly adherent mill scales on the steel surface and degreased with acetone, then, coated with wax so that a predetermined area was always exposed between the waxed areas [20, 21].

### 2.2.4. Preparation of steel in concrete electrodes

The concrete mixes were prepared according to the needed mix proportions. The reinforcing steel rods were centrally placed in cylindrical 5x10cm steel moulds and the active areas of the rods were completely covered by the prepared compacted mix. The specimens were cured for 24 (hrs.), after casting at room temperature, then, demoulded and continuously cured for 28 days in tap water, (then, in sea water) up to the testing ages.

### 2.2.5. Electrochemical measurements

Several electrochemical techniques are used to assess the corrosion risk of reinforcing steel in concrete, among them are:

- The galvanostatic anodic polarization (GAP) measurements.
- The corrosion rate measurement using the linear polarization resistance technique.

### 2.2.6. Electrochemical measurements

The anodic polarization experiments are conducted at a chosen applied constant current density of  $10\mu\text{A}/\text{cm}^2$  and the potential – time characteristics are observed. The shape of the polarization curves obtained belongs to one of three different types. Each type of curve characterizes the behavior of the steel in the medium under investigation [20-22].

- (i) For the polarization curve of steel in an inhibitive medium, the potential may increase rapidly, then after few minutes it becomes constant at potential values exceeding 600 mV VS SCE i.e. the oxygen evolution potential (Passivation potential). Thus, if the time is less than 7 minutes, the degree of inhibition is considered reasonably high, whereas, if the time is greater than 15 minutes, the degree of inhibition is comparatively low.
- (ii) The second type of polarization curves corresponds to the polarization of steel in a corrosive medium. The recorded potential values are slightly nobler during the early few minutes, and then

are reversed towards very active potential values. This is the behavior of typical corroding steel.

- (iii) The third kind of polarization curves shows at first a sharp rise in the potential until it reaches the oxygen evolution potential, followed by a decrease towards more active values. Such a case is described as a borderline case between corrosion and inhibition.

The galvanostatic anodic polarization technique proved to be a reliable accelerated test for predicting the corrosive or inhibitive nature of the medium surrounding the steel reinforcement. In this technique, the steel in concrete (working electrode) was made as an anode in a circuit using a counter platinum electrode as cathode. A constant current density of  $10 \mu\text{A cm}^{-2}$  was applied to the steel electrode and the corresponding potential was recorded as a function of time relative to saturated calomel reference electrode.

The cell used in all measurements consists of a beaker 500 ml, the working electrode (anode) as well as a counter platinum electrode (cathode) were put in the cell and the solution was poured into the cell till the concrete encasing the steel electrode was just covered with the solution. A saturated calomel electrode was used as the reference electrode. The calomel electrode was electrically connected to the cell by means of a plastic U-bridge, with a solution saturated silk wick running inside it, to a beaker containing the test solution which, in turn, was connected to the cell by another plastic U-bridge with a solution- saturated wick running inside it. All measurements were carried out using biologic SP-50 (potentiostat/ galvanostat) apparatus supported with EC-Lab software V 10.3 X package.

- **Linear polarization resistance ( $R_p$ )**

This technique has become a well – established method for determining the instantaneous corrosion rate of reinforcing steel in concrete. The polarization resistance measurement can be accomplished potentiostatically by changing the potential of the reinforcing steel by a fixed amount,  $\Delta E$ , and monitoring the current decay,  $\Delta I$ , after a fixed time. Alternatively, it can be done galvanostatically by applying a small, fixed current  $\Delta I$  to the reinforcing steel and monitoring the potential change,  $\Delta E$ , after a fixed time period. In each case the conditions are selected such that the change in potential,  $\Delta E$ , falls

within the Stern-Geary range of 20-50 mV [23]. The polarization resistance  $R_p$  of the steel is then calculated from the equation:

$$R_p = \Delta E / \Delta I \dots\dots\dots 1$$

From which the corrosion current  $I_{\text{corr}}$  can then be calculated:

$$I_{\text{corr}} = B / R_p \dots\dots\dots 2$$

Where B is the Stern-Geary constant. A value of 25mV (0.025V) has been adopted for active steel and 50 mV (0.05V) for passive steel. [24]. In order to determine the corrosion current density,  $I_{\text{corr}}$ , the surface area, A, of steel that has been polarized needs to be known:

$$I_{\text{corr}} = I_{\text{corr}} / A \dots\dots\dots 3$$

It is to be mentioned that, the modern computerized instruments for measuring the corrosion rate – as that used in the current study – exploits the linear polarization method to give a direct reading of the corrosion rate after supplying with specific data about the corroding metal (e.g. metal density) and the corrosion rate is expressed as (depth of corrosion per year). The  $R_p$  data enables a detailed assessment of the concrete structure condition and is a major tool in deciding upon the optimum remedial strategy to be adopted. Table 6 presents a broad criterion for corrosion that has been developed from field and laboratory investigations [24-26].

Table 6: Corrosion risk for steel in concrete as assessed from polarization resistance, corrosion current density and corrosion rate measurements.

Corrosion risk	Polarization resistance, $R_p$ ( $\text{K}\Omega\cdot\text{cm}^2$ )	Corrosion current density, $I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	Corrosion rate ( $\mu\text{m}/\text{year}$ )
Very high	2.5-0.25	10-100	100-1000
High	25-2.5	1-10	10-100
Low/moderate	250-25	0.1-1	1-10
Passive	>250	<0.1	<1

### 2.2.7. Techniques utilized and apparatus.

The chemical analysis of the starting materials was carried out using X-ray fluorescence (XRF) technique for which a Philips Spectrometer PW 1400 using Rubidium Rb-K  $\alpha$ -radiation at 50KV and 50mA has been used. The samples were ground to pass a  $75\mu\text{m}$  sieve and pellets were prepared by the pressed method using manual press machine at 20 tons.

The crystalline and amorphous phases present in the industrially produced metakaolin were identified using the X-ray diffraction (XRD) technique using a Cu-K  $\alpha$  source. The differential thermal analysis (DTA) for Portland cement pastes incorporating different percentages of the industrially produced MK has been performed using a (DT-50) thermal analyser, Schimadzu-Tokyo, Japan. The particle size

distribution analysis of ground industrially produced MK has been carried out using a particle size distribution analyzer, Horiba La 950 – France. The setting time measurements were carried out following the procedure assigned by the Egyptian Standard Specification [27]. The compressive strength measurements were carried out using 5 tons German Bruf pressing machine with a load rate of 100 kg/min. The chemical analysis of reinforcing steel has been performed using the apparatus “Version 1.0 Spectromax – Stand (2008), Germany. Scanning electron micro photographs (SEM) were taken for selected samples using and Inspect (S) apparatus (FEI Company, Holland) equipped with an energy dispersive X-ray analysis (EDAX). Alkali-aggregate reaction test according to the mortar – bar method specified by [18], has been followed. Expansion has been calculated according to:

$$\text{Expansion \%} = \frac{L2 - L1}{L1} \times 100 \dots\dots 4$$

L=Moulds length.

L1=Sample length after soaking in water at 80°C for 24hrs.

L2= Sample length after soaking in 1 M NaOH solution at 80°C periodically till 14 days. Expansion is considered out of specification if exceeding 0.1% after soaking in alkali for 14 days.

### 3. Results and Discussion

#### 3.1. Characteristics of the industrially produced metakaolin

Table 1 gives the chemical analysis of the industrially produced metakaolin. It can be seen that, the SiO<sub>2</sub> content is high reaching (62.37%) and the alumina content reaches (31.60%). The Fe<sub>2</sub>O<sub>3</sub> content is low (1.47%). Also, CaO is low (0.26%). Table 1 reveals, also, the reduction in the loss on ignition (1.16%). It is worth mentioning that, as Table 1 indicates that, the chemical composition (oxide content) of MK is almost similar to that of ordinary Portland cement (OPC), a property that could afford the needed compatibility when metakaolin is used replacing part of the cement. Fig. 6 presents the XRD analysis of the industrially produced metakaolin. The XRD pattern reveals the transformation of the crystalline kaolinite mineral [Hydrated aluminum disilicate – Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (OH)<sub>4</sub>], which is the main component of raw kaolin, into an amorphous metakaolin. The silica of kaolin (as quartz mineral) still appears since it has high temperature resistance.

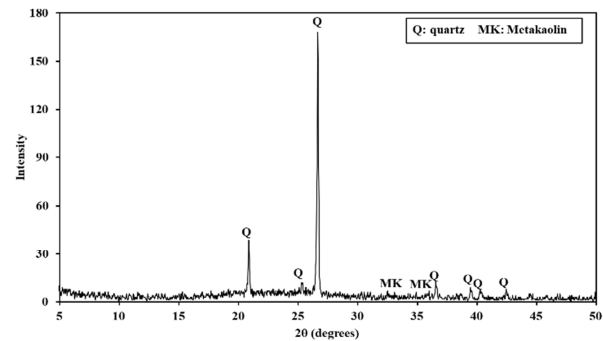


Fig.6: XRD pattern for metakaolin produced at (ASCE).

Metakaolin is industrially produced at (ASCE) having the particle size of (3mm). Therefore, for testing the produced metakaolin as a pozzolanic material, the company had to grind the produced metakaolin to a particle size close to that of the traditional pozzolanic materials (e.g. silica fume – SF) for increasing the surface area of the product and hence the reactivity of the produced metakaolin. Fig. 7 presents the particle size distribution analysis of the industrially produced metakaolin after grinding. It can be seen that:

- The median size (i.e. the value of 50% of the tested sample) = 3.950 μm
- The mean size (i.e. the average value of the sample) = 4.507 μm
- The mode size (i.e. the major diameter) = 5.471 μm

These results indicate the reasonable particle size of the industrially produced metakaolin since the mean size is about 4.5 μm. That size could close the pore structure upon using as a pozzolanic material in concrete (satisfying the micro - filler – effect).

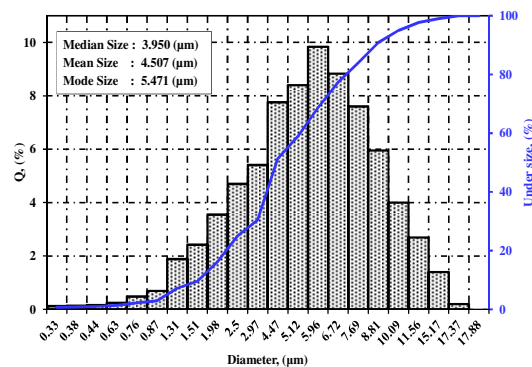


Fig. 7: Particle size distribution of industrially produced MK.

### 3.2. Pozzolanic activity

Pozzolanicity is one of the most important properties of supplementary cementing materials (SCM'S). As previously stated, it has been defined by [7] as "The ability of these materials to consume Portlandite mineral  $[\text{Ca}(\text{OH})_2 - \text{CH}]$  resulting from cement hydration forming extra calcium silicate hydrate (CSH)". Pozzolanicity of a SCM / cement paste at a particular percentage of the pozzolanic material and a specific curing age could be determined by the differential thermal analysis technique. This technique has been adopted in the present study for evaluating the Pozzolanicity of the metakaolin produced at "Aluminum Sulfate Company of Egypt – ASCE". Differential thermal analysis (DTA) has been performed for Portland cement pastes incorporating MK at the replacement percentages 0, 5, 10, 15, 20 and 25% after water – curing age of 28 days. Fig. 8 illustrates the results obtained. It can be seen that:

- An endothermic signal is always detected before reaching  $100^\circ\text{C}$ . This peak is basically related to the moisture absorbed by the sample from the environment.
- The endotherms observed in the temperature region  $100\text{-}200^\circ\text{C}$  are attributed to the process of calcium silicate hydrate (C-S-H) formation.
- The endotherms at the temperature range  $450\text{-}500^\circ\text{C}$  are due to the dehydroxylation of  $\text{Ca}(\text{OH})_2$ .
- The endotherms at the temperature near to  $700^\circ\text{C}$  are due carbonation of lime and  $\text{CaCO}_3$  (CC) formation.
- It is obvious that, as the cement replacement by MK increases from 5% up to 15%, C-S-H content increases at the expense of  $\text{Ca}(\text{OH})_2$ .
- Upon increasing the replacement dose to 20% MK, insignificant variation in the C-S-H and CH content has occurred relative to 15% MK replacement.
- Upon increasing the replacement dose to 25% MK, it seems that, the cementitious materials reactions between MK and OPC were slowed down (or close to completion).
- These results are in agreement with previous research studies [13,14].

From the foregoing results of DTA, it is evident that, the industrially produced MK at (ASCE)

behaves as a pozzolanic material, thus, consuming  $\text{Ca}(\text{OH})_2$  that results from cement hydration forming extra C-S-H (The phase that is mainly responsible for strength development of the MK/cement mix). Accordingly, such industrially produced MK satisfies the definition of "Pozzolanic materials" as defined by [7]. 10% or 15% MK dosage could be the (optimum) cement replacement dosage.

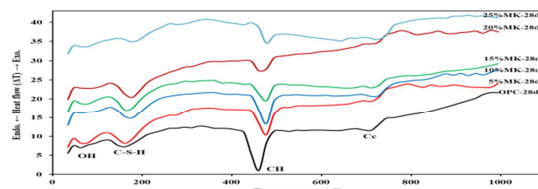


Fig. 8: DTA Patterns for Portland cement incorporating MK at the replacement dosages 0, 5, 10, 15, 20 and 25% after 28 days of water – curing.

### 3.3. Usage of the industrially produced MK as a partial cement replacement material and its effect on the physico-mechanical properties of the hardened cement mix

As the produced MK behaves as a pozzolanic material, the following part of the study investigates its effect on the physico-mechanical properties of cement and its role in producing extra components that could enhance the mechanical properties of cement (and hence concrete).

#### 3.3.1. Water consistency

Fig. 9 gives the results of the water of consistency for the mixes of Portland cement incorporating MK replacement percentages increasing from 5% up to 25 (by mass) relative to MK- free cement. The results indicate that the water needed for consistency (workability) increases as the MK percent increases in the cement paste relative to the MK - free paste.

#### 3.3.2. Setting time

Fig. 9 presents, also, the initial and final setting times for OPC pastes incorporating MK replacement of percentages from 5 to 25% relative to the MK-free cement paste (control sample). The results show clearly that, the initial and final setting times decrease upon MK inclusion in cement up to 15%, thereafter, the setting times slightly increase up to 25% MK in the cement paste. These results are in conformity with the results obtained by previous studies [28] where they found that: cement blended with MK in a quantity of 5-25%, by mass, showed lower setting times (initial and final), than that of control cement. In other words, they accelerated the initial and final setting times. Essentially, one of the most important factors that cause the decrease in the setting time is the higher surface area of metakaolin.



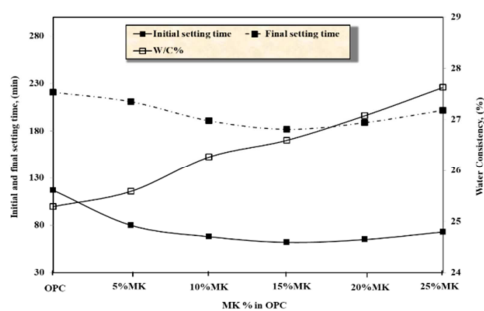


Fig. 9: Water of consistency and setting times (initial and final) of (5-25%) MK/OPC mixes compared to control OPC.

### 3.3.3. Compressive strength

Fig. 10 presents the compressive strength results of MK/OPC hardened pastes including MK at the cement replacement ratios: 0, 5, 10, 15, 20 and 25% MK after water curing ages of 2, 7, 14, 28 and 56 days. Where it could be seen that:

- All MK/OPC pastes (5-25%) after 2 days of curing show reduction in early strength relative to the OPC control sample. This behavior reveals that, the pozzolanic reaction still did not show its effect up to this curing age (2 days). Such finding is in agreement with the results indicated by previous studies [28].
- The compressive strength of the hardened pastes increases relative to the control sample up to the inclusion of 15% MK, where the compressive strength increases by 10, 17 and 22% upon replacing the cement by 5, 10 and 15% MK, respectively, after 28 days of water curing. The increase in the compressive strength reaches 10, 19 and 26%, respectively, after 56 days of curing.
- The increase in the MK ratio in the cement paste to 20 and 25% results in reduction in the paste strength.
- These results, as far as the compressive strength property is concerned, show that:
  - The paste that gives the highest value in compressive strength, relative to the control paste, (after 28 days curing) is that incorporating 15% MK, where the strength increase reaches 22%. The strength increase for the paste incorporating 10% MK reaches 17%.
  - The present results are in agreement with the results reached by previous investigations, where some reported that 10% MK is the best cement replacement ratio affording the

highest effect on compressive strength [113,29–31]. Other researchers indicated that 15% MK cement replacement is the best percent for enhancing the compressive strength of the hardened cement paste [16,26].

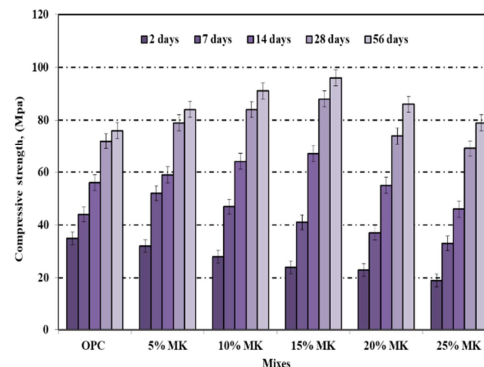


Fig. 10: Compressive strength of 5 to 25% MK/OPC mixes compared to control OPC.

### 3.3.4. Characteristics of cement pastes incorporating 10% and 15% MK dosages

The preceding part of the study declared that, the best MK percentages, as far as the compressive strength of the hardened paste is concerned, are 10% MK/OPC and 15% MK/OPC. These pastes yield strength enhancement reaching 17% and 22%, respectively. Accordingly, the coming part of the study will investigate the characteristics of the cement pastes incorporating such MK percentages (i.e. 10% and 15% MK). As silica fume (SF) (Particularly at 10% dosage) is the most prevailing pozzolanic SCM in concrete industry worldwide, it deemed of interest to compare its impact on cement paste characteristics with those pertaining to the cement paste incorporating 10% and 15% MK.

#### 3.3.4.1. Chemical composition

Table 7 gives the chemical composition for hardened cement pastes incorporating 10% and 15% MK compared to the paste containing 10% SF and the control (SCM-Free) cement paste after 28 days of water curing. It can be seen that, the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  % increase with the increase in the MK content of the cement paste, reaching 20.20%  $\text{SiO}_2$ , and 6.50%  $\text{Al}_2\text{O}_3$  for the 15% MK/OPC paste. For SF/OPC,  $\text{SiO}_2$  reaches 22.10% and  $\text{Al}_2\text{O}_3$  reaches only 2.90%. It is worth noting that,  $\text{Fe}_2\text{O}_3$  % reaches a minimum value (3.41%) for the paste incorporating 15% MK. Such

property could be an advantage for MK (particularly 15% percent). Daux, et al, [32] showed that the rate of dissolution of iron in the highly alkaline medium (as in case of fresh concrete) is higher than that of aluminium and silicon. Consequently, iron will remove the OH<sup>-</sup> ions from the medium precipitating Fe(OH)<sub>2</sub>, thus, lowering the medium alkalinity and slowing dissolution of the remaining components. In addition, iron hydroxide [Fe(OH)<sub>2</sub> or Fe(OH)<sub>3</sub>] flocculates to form a colloidal gelatinous precipitate. The iron oxide gel absorbs because of its water demand a certain amount of mixing water thus increasing in volume offering internal stresses in the (concrete) mix.

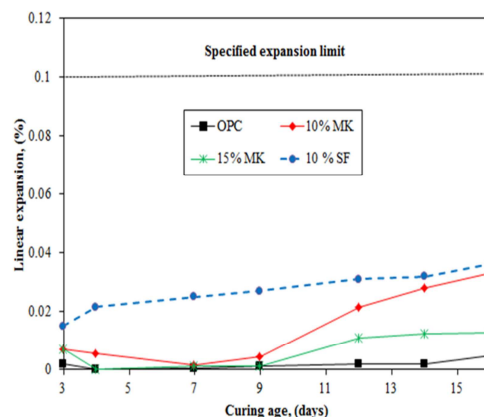
**Table 7:** Chemical composition of OPC containing 10, 15% MK and 10% SF after 28 days of tap water curing compared to MK-free cement

Oxides, (%)	MK-free OPC	10% MK	15% MK	10%SF
SiO <sub>2</sub>	14.00	18.00	20.20	22.10
Al <sub>2</sub> O <sub>3</sub>	3.17	5.38	6.50	2.90
Fe <sub>2</sub> O <sub>3</sub>	4.05	3.81	3.41	3.57
CaO	54.38	49.70	47.80	52.50
MgO	0.95	0.78	0.78	0.72
SO <sub>3</sub> <sup>-</sup>	2.54	2.33	2.27	2.80
Cl <sup>-</sup>	0.12	0.12	0.15	0.11
Na <sub>2</sub> O	0.21	0.19	0.25	0.35
K <sub>2</sub> O	0.25	0.21	0.26	0.23
TiO <sub>2</sub>	0.37	0.62	0.75	0.42
P <sub>2</sub> O <sub>5</sub>	0.14	0.13	0.13	0.10
MnO	0.11	0.07	0.13	0.12
L.O.I	19.20	18.21	17.00	13.80
Total	99.96	99.88	99.96	99.97

### 3.3.4.2. Linear expansion due to alkali-silica reaction (ASR) by MK

Since MK possesses high reactivity towards cement hydration products, it was necessary to measure the expansion due to the reaction of silica in MK and alkalis in the surrounding medium (i.e. ASR). Fig. 11 shows the expansion values due to ASR for the Portland cement mixes incorporating 10% SF/OPC mix is included for comparison. Fig. 11 reveals that the expansion values due to the presence of MK in the cement mix are far enough relative to the value specified by the standard specification [33] (i.e. 0.1%). The expansion value for the mix 15% MK /OPC reaches 0.033% which is, even, less than that pertaining to the mix 10% SF/OPC (0.036%). Such low expansion values by ASR due to the presence of MK in the cement mix have been confirmed by several researchers [34]. They explained that, for alkali silica reaction (ASR) to occur and produces a swelling gel, essential ingredients are soluble Ca<sup>++</sup> and OH<sup>-</sup>, active silica and water. Soluble alkali metal ions are also

necessary. If metakaolin is used, it will reduce the concentration of Ca(OH)<sub>2</sub> in the cement paste to a sufficiently low level and any ASR gel produced is not expansive and no cracking occurs. Also, it has been found that, aluminum in SCM's reduces the solubility of silica in alkaline solutions restricting ASR expansion [14].



**Fig. 11:** Expansion values due to alkali-silica reaction of cement pastes incorporating 10, 15% MK and 10% SF dosage relative to MK-free cement paste.

### 3.3.4.3. Variation in cement paste alkalinity (pH) due to cement replacement by MK

The alkalinity, and hence the PH value of the medium, is the most liable factor to affect the corrosion behavior of reinforcing steel. It has been found that, complete protection from corrosion for reinforcing steel is obtained at and above PH 11.5 for the medium in the direct vicinity of the reinforcing steel [35]. Below this critical PH value, the steel passivity is impaired and corrosion of reinforcing steel will insure. The corrosion products cause internal stresses in concrete leading to cracking and spalling and finally premature deterioration of the reinforced concrete structure. Therefore, it was necessary to test the effect of cement replacement, partially, by 10% and 15% MK on the cement alkalinity (PH-value for water cement extract). Fig. 12 shows the results of PH measurements. It can be seen that, generally, insignificant reduction in PH-value occurs upon incorporating MK in the cement pastes. It is evident that the mix 15% MK/OPC gives higher PH value (12.7) relative to the mix 10% MK/OPC (12.4) and also to the mix 10% SF/OPC (12.5). This could be due to the higher alkali content (Na<sub>2</sub>O & K<sub>2</sub>O) and lower Fe<sub>2</sub>O<sub>3</sub> content in the mix 15% MK/OPC relative to the mix 10% MK/OPC.

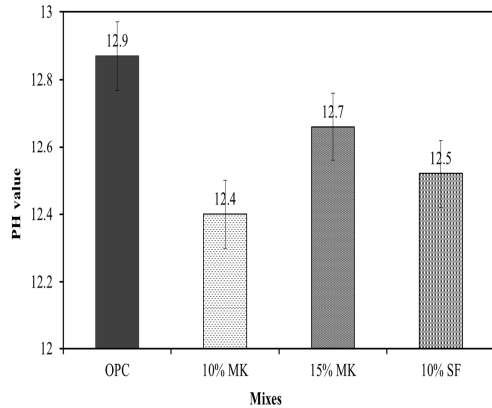


Fig. 12: Alkalinity of the water extract (PH) for cement pastes incorporating 0, 10 and 15% MK and 10% SF.

### 3.3.4.4. Microscopic investigation

Microscopic analysis using scanning electron microscope (SEM) has been carried out on samples of the hardened cement pastes incorporating 10% and 15% MK after water - curing for 28 days together with a sample of MK – free cement and a 10% SF/OPC mix sample. Fig. 13 shows the results of such microscopic study. It is evident that Portlandite mineral  $\text{Ca}(\text{OH})_2$  content (white spots) decreases as the MK content in the mix increases. This is due to the consumption of part of  $\text{Ca}(\text{OH})_2$  in the pozzolanic reaction. It can be seen, also, that the effect of the mix 15% MK /OPC on  $\text{Ca}(\text{OH})_2$  reduction is almost comparable to the effect of 10% SF/OPC

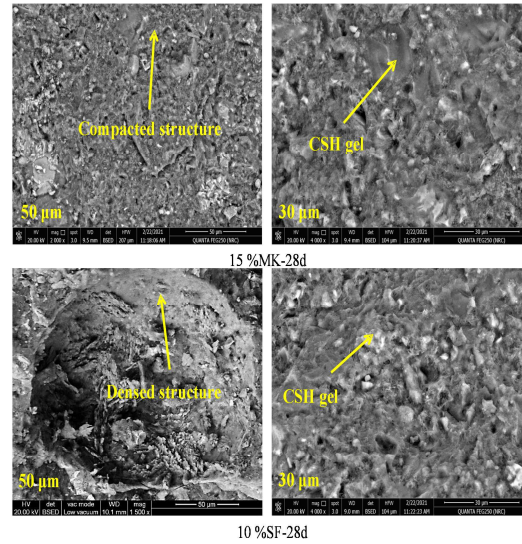


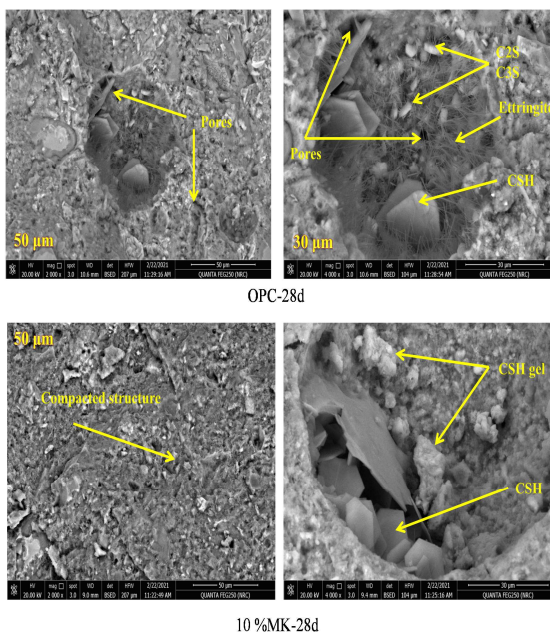
Fig. (13): SEM images for cement pastes Incorporating 0, 10 and 15% MK and 10% SF, after curing in tap water up to 28 days

### 3.3.5. Physico-mechanical properties and durability of concrete containing 10% and 15% MK as cement replacement

#### 3.3.5.1. Compressive strength of concrete containing 10% and 15% MK

The main criterion that tends to be used to assess concrete durability is the compressive strength [36]. In the current study, concrete compressive strength has been, also, considered as a reasonable indicator in evaluating the durability of concrete incorporating the dosages 10% and 15% MK.

Fig. 14 gives the results of compressive strength for concrete incorporating 10% and 15% dosages of MK as cement replacement after water curing for intervals up to 90 days. The results pertaining to concrete- free of MK and that for concrete containing 10% SF have been included for comparison. The results of compressive strength increase for the concrete containing 10% MK relative to the control sample (containing 0.0%MK). Also, the concrete containing 10% MK increases relative to the concrete containing 15%MK. Taking into consideration the compressive strength results obtained after 28 days water curing, we notice that the compressive strength of concrete containing 10% MK increases by 27% relative the concrete free of MK while the concrete containing 15% MK increases by 15%. Accordingly, the dosage of 10% MK as a cement replacement in concrete is the optimum dosage as far as the compressive strength is concerned, upon using in plain concrete (No steel reinforcement). It is to be noticed that the



increment in compressive strength upon using SF reaches 31% relative to the control concrete. These results agree with the results obtained by Dinakar, P., et al., [37]. The reduction in compressive strength for 15% MK dose in concrete compared to 10% MK has been explained as the result of concrete “dilution effect”. The dilution effect is the result of replacing a part of cement by equivalent quantity of MK and the resulting variation in some physical

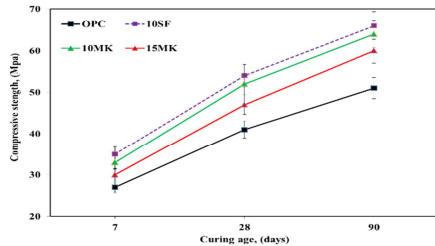


Fig. 14: Compressive strength of concrete containing 0,10, 15% MK and 10% SF after curing in tap water up to 90 days.

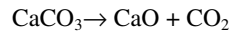
properties of concrete.

### 3.3.5.2. Effect of elevated temperatures on the compressive strength of MK concrete

Elevated temperature is one of the most important physico-mechanical factors that could affect concrete causing its deterioration and premature failure. Concrete constructions could be subjected to elevated temperature as in hot climate countries or upon exposure to high temperature during its service. Such circumstances give a necessity to investigating the effect of MK in concrete upon its resistance to elevated temperature and maintaining its endurance. Consequently, the effect of high temperature on the compressive strength of concrete incorporating MK at the cement replacement dosages of 10% and 15% relative to the concrete free of MK has been investigated. The results pertaining to concrete incorporating 10% SF as the cement replacement have been included for comparison. The U.S. Nuclear Regulatory Commission, Washington, DC [38] investigated the effect of increasingly temperature degrees on the chemical reactions taking place in Portland cement concrete. The exposure temperatures and their effects are as follows:

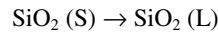
- A. 100°C: loss of evaporable water (H<sub>2</sub>O).
- B.100-850°C: Dehydration of cement hydrates (In conjunction with water evaporation).  
 $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} \longrightarrow 2\text{CaO} \cdot \text{SiO}_2 + \text{CaO} \cdot \text{SiO}_2 + 3\text{H}_2\text{O}$
- C.400-600°C: Dehydration of calcium hydroxide (Portlandite).  
 $\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$
- D. 574°C : Crystalline transformation from  $\alpha$  to  $\beta$ -quartz  
 $\text{SiO}_2 (\alpha) \rightarrow \text{SiO}_2 (\beta)$

E. 600-900°C: Decomposition (decarbonation) of calcium carbonate.



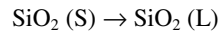
F. 1200-1500°C: Melting of Portland cement.

G.  $1423 \pm 50^\circ\text{C}$ : Melting of quartz.



F. 1200-1500°C: Melting of Portland cement.

G.  $1423 \pm 50^\circ\text{C}$ : Melting of quartz.



H.  $> 1423^\circ\text{C}$ : Melting and decomposition of aggregates.

The Response of concrete in terms of strength loss has been divided into three ranges: 20 to 400 °C, 400-800 °C and above 800 °C.

In the first range: it was noted that normal strength concretes (< 50MPa) exhibit a slight loss of strength (about 15%) whereas higher strength concretes (80-100MPa) maintain their strengths. In the second range: both concretes lose most of their original strength, especially above 600 °C (in this range, dehydration of calcium-silicate hydrate gel is most significant). In the third range: only a small fraction of the original concrete strength remains. In the present study, Fig. 15 declares the effect of concrete exposure to increasing temperature (25°C-700°C) on the compressive strength of concrete containing 0, 10 and 15% MK. Also, Table 8 presents the compressive strength values for the concrete incorporating 10% and 15% MK upon temperature increase relative to the control value (at room temperature 25°C). The Table presents, also, the increase percent in the compressive strength of concrete containing 10% and 15% MK relative to the MK-Free concrete. The strength values obtained upon using 10% SF as the cement replacement is included both Table 8 and Fig.15.

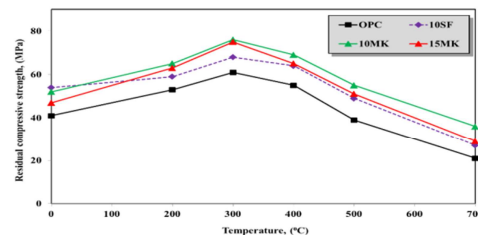


Fig.15: Residual compressive strength of concrete containing 0, 10 and 15% MK and 10% SF and exposed to elevated temperatures up to 700 °C.

These results demonstrate, clearly, the following:

- Generally, the compressive strength of concrete increases as the exposure temperature rises till 300°C after which the concrete strength decreases with the temperature rise till 700°C.
- At all temperatures, the concrete containing 10% MK gives higher compressive strength

values relative to concrete containing 15% MK and that of MK-Free.

- At the maximum exposure temperature (i.e. 700°C), the strength loss for the concrete containing 10% MK reaches 32% relative to the strength value at room temperature (i.e. 25°C), while the strength loss for the concrete incorporating 15% MK reaches 38%.
- The results summarized in Table 8 reveal that, the MK dosage (10%) is the best regarding the elevated temperature endurance and maintaining higher compressive strength as compared to the MK dosage (15%) and that for MK-free concrete.
- In all cases, the concrete containing MK as a partial cement replacement in concrete shows higher heat resistance than the concrete incorporating silica fume (SF).

**Table 8:** Residual compressive strength of concrete containing 0, 10, 15 % MK and 10 % SF

Mixes	Residual compressive strength, (MPa)									
	0 °C (= 25 °C)	200 °C	300 °C	% increase compared to 0 °C	400 °C	% increase compared to 0 °C	500 °C	% increase compared to 0 °C	700 °C	% increase compared to 0 °C
OPC	41	53	61	+49%	55	+34%	39	-4%	29	-74%
10%MK	52	65	76	+46%	69	+33%	55	+5%	35	-32%
% increase compared to OPC	+27%	+22%	+25%		+25%		+42%		+74%	
15%MK	47	63	75	+99%	65	+38%	51	+7%	29	-38%
% increase compared to OPC	+15%	+19%	+23%		+19%		+31%		+43%	
10%SF	54	58	68	+26%	64	+18%	49	-9%	27	-50%
% increase compared to OPC	+31%	+10%	+11%		+16%		+27%		+31%	

### 3.3.5.3. Effect of MK, as a partial cement replacement in reinforced concrete on the corrosion behavior of steel reinforcement

The current study is investigating the suitability of MK that is produced locally in Egypt for the first time for usage as a pozzolanic material in concrete. Therefore, it deemed necessary to investigate all aspects that could help to evaluate the propensity of such new industrial product for usage in reinforced concrete.

Since corrosion of steel reinforcement in concrete is the most serious problem that can afflict a concrete structure yielding to its deterioration and probably premature failure. Therefore, the coming part of the study will investigate the effect of using the dosages 10% MK and 15% MK, as cement replacement, in reinforced concrete upon maintaining the steel passivity and withstanding the effect of aggressive surrounding environments. Several electrochemical

measurements are used for evaluating the risk of steel corrosion in concrete. Of the most important measurements are:

- The anodic polarization measurement, and
- The corrosion rate measurement by the linear polarization resistance technique.

These methods proved to be reliable tests for predicting the corrosive or inhibitive nature of the medium surrounding the steel reinforcement.

#### a. Anodic polarization measurement

Fig. 16 presents the results of the anodic polarization measurements for reinforcing steel in concrete incorporating the dosages 0, 10 and 15% MK, as partial cement replacement, after curing in tap water for 28 days. Several research studies [39, 40] reported the limits for maintaining the steel passivity in concrete in the surrounding environment as:

Passivation potential > 600 mV (SCE).

Time to reach passivation 0.0 up to 15 min.

Fig. 16 gives the values for passivation potential and time to reach passivation for steel in concrete containing 10% and 15% MK relative to the steel in MK-free concrete after tap water curing for 28 days. The values obtained upon using 10% SF, as the partial cement replacement, are included in the figure for comparison. The steel in concrete containing 15% MK gives the highest passivation potential value (696 mV), also, this value is reached after the elapse of, only, (5.4 min). It is worth noting that, such passivation potential is even higher than that obtained for the steel in concrete containing 10% SF (668 mV) and the time to reach passivation is shorter than that obtained for steel in concrete containing SF (6.4min). The anodic polarization measurements have also been carried out upon using sea water – as the concrete surrounding medium. Fig. 17 presents the results obtained. The steel in concrete containing 15% MK keeping the highest passivation potential value (665 mV) that is reached after the elapse of (6.4 min). From these measurements it is evident that 15% MK is the most reasonable dosage, as cement replacement, in reinforced concrete for maintaining steel passivity against corrosion that could ensue due to the penetration of aggressive ions from the surrounding medium through the concrete.

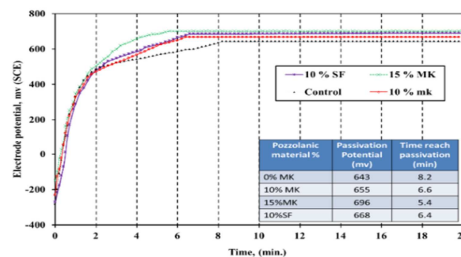


Fig. 16: Anodic polarization behavior of steel in concrete, after curing in tap water for 28 days.

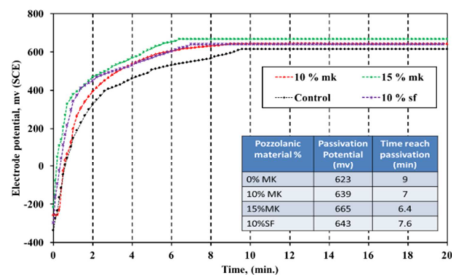


Fig. 17 : Anodic polarization behavior of steel in concrete, after curing in sea water for 28 days.

### b. Linear polarization resistance and corrosion rate measurements:

This technique has become a well-established method for determining the corrosion rate of steel reinforcement in concrete exposed to different surrounding media. Such technique has been applied in several research studies [25,26,41]. These extensive studies determined the limits for the corrosion rate ( $\mu\text{m}/\text{year}$ ) of the steel reinforcement and the estimated corrosion risk at each corrosion rate range as given in Table 6. Table 9 presents the results of determining the corrosion rate of reinforcing steel in concrete incorporating the dosages 0, 10 and 15% MK, as cement replacement, after curing in tap water for 28 days. The results of the corrosion rate measurements of steel in concrete containing 10% SF are included for comparison. Generally, the steel in the concrete cured in tap water exhibits very low corrosion rate maintaining its passivity ( $<1\mu\text{m}/\text{year}$ ). Yet, the steel in concrete containing 15% MK exhibits the least corrosion rate value ( $0.466\mu\text{m}/\text{year}$ ) relative to the steel in concrete containing 10% MK ( $0.563\mu\text{m}/\text{year}$ ), and that in concrete free of MK ( $0.669\mu\text{m}/\text{year}$ ). The reinforcing steel in concrete containing 10% SF exhibits a corrosion rate reacting ( $0.515\mu\text{m}/\text{year}$ ) [i.e. slightly higher than the value pertaining to steel in 15% MK-concrete]. The results presented in Table 10 demonstrate the efficiency of the concrete incorporating 15% MK in yielding the least corrosion rate ( $0.775\mu\text{m}/\text{year}$ ) upon exposure to sea water as the surrounding environment. While the corrosion rate reaches ( $0.945\mu\text{m}/\text{year}$ ) for the steel in concrete containing 10% MK and ( $1.171\mu\text{m}/\text{year}$ ) for the steel in MK-free concrete. It can be seen that, the corrosion rate reaches ( $0.851\mu\text{m}/\text{year}$ ) for the steel in concrete containing 10% SF.

From the foregoing results, it is explicit that, 15% MK is the optimum ratio to be used, as a cement replacement, in reinforced concrete as far as maintaining the steel reinforcement passivity is concerned and withstanding the penetration of aggressive ions through concrete to harm the steel reinforcement. It is worth noting that, 15% MK is, even, more efficient than 10% SF upon yielding a

lower corrosion rate for reinforcing steel in concrete. Such 15% MK efficiency in preserving the steel passivity could be attributed to:

- The high alkalinity of the concrete surrounding the steel reinforcement due to the formation of  $\text{Ca}(\text{OH})_2$  during cement hydration as well as containing, relatively, high percent alkalis ( $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ).
- Also, the concrete containing 15% MK gives the least  $\text{Fe}_2\text{O}_3$  content, thus, yielding lower  $\text{Fe}(\text{OH})_2$  formation, enhancing the alkalinity around the steel reinforcement.
- Since Al metal is one of the corrosion resistant elements, therefore its high content in 15% MK-concrete (as  $\text{Al}_2\text{O}_3$ ) assists counteracting the effect of aggressive ions in the surrounding medium.

Table 9: corrosion rate for steel in concrete after curing in tap water for 28 days.

Concrete content	Electrochemical Measurements		
	Polarization resistance, $R_p$ ( $\text{k}\Omega\cdot\text{cm}^2$ )	Corrosion current density, $I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	Corrosion rate, ( $\mu\text{m}/\text{year}$ )
Control	195	0.183	0.669
10% MK	240	0.125	0.563
15% MK	282	0.092	0.466
10% SF	239	0.109	0.515

Table 10: corrosion rate for steel in concrete after curing in sea water for 28 days.

Concrete content	Electrochemical Measurements		
	Polarization resistance, $R_p$ ( $\text{k}\Omega\cdot\text{cm}^2$ )	Corrosion Current density, $I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	Corrosion rate, ( $\mu\text{m}/\text{year}$ )
Control	84	0.577	1.171
10% MK	99	0.342	0.945
15% MK	123	0.253	0.775
10% SF	108	0.316	0.851

## 4. Conclusions

- The raw kaolin from Abu-Zinema quarries, Southern Sinai, Egypt is suitable for the production of pozzolanic metakaolin by calcination.
- The industrially produced metakaolin has to be grind to reach the size of the traditional SCM's (e.g. silica fume -  $<10\mu\text{m}$  in size) to increase the reaction surface area and hence the metakaolin reactivity.

- Usage of metakaolin as cement replacement in Portland cement pastes accelerates the initial and final setting times compared to metakaolin – free pastes.
- Usage of metakaolin as a pozzolanic material in cement pastes causes insignificant expansion far below the value specified by the standard specifications (i.e. 0.1%). Also, such usage does not affect the cement alkalinity, maintaining the pH value higher than the critical value (pH 11.5).
- Upon preparing cement mixes (for different utilizations other than concrete) incorporating metakaolin as cement replacement, 15% MK is the optimum dosage (yielding higher pozzolanic effect and filler effect).
- The dosage of 10% metakaolin, as cement replacement ratio in plain (Non reinforced) concrete is considered the optimum dosage.
- The plain concrete containing 10% metakaolin, as cement replacement, manifests higher compressive strength relative to the concrete containing 15% metakaolin or that metakaolin — free. Also, it shows higher resistance to elevated temperatures, retaining higher compressive strength.
- 15% metakaolin is the optimum ratio to be used, as a cement replacement, in reinforced concrete as long as maintaining the steel reinforcement passivity as well as counteracting the penetration of aggressive ions through concrete is concerned.
- The locally produced metakaolin could be an excellent substitute to silica fume (which is being exported from Egypt) as a pozzolanic material in concrete.
- Since metakaolin production is based on calcination of a natural raw material (kaolin) therefore, the slight increase in cost (relative to the usage of industrial wastes such as slag or fly ash as pozzolanic materials) due to energy requirement for the production process is marginal compared to the improvement in the engineering properties of concrete (high mechanical properties, durability, heat resistance and steel corrosion protection), besides, reduction in environment pollution (due to reduction in cement usage).

## 5. Conflict of Interest

“There are no conflicts to declare”.

## 6. References

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