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Effect addition of met kaolin and nano-metakaolin on mechanical properties and Kinetics of hydrothermal hydration of Portland cement clinker.

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Abstract This experimental study to investigate effect of metkaolin and nano-metakaolin on the mechanical properties and Kinetics of Hydration of autoclaved specimens made from OPCC, GGBFS, MK and NMK. The dry mixtures were prepared by thermal activation with the same initial water/solid cement (W/S) ratios of about 0.28 for 3minutes. Cylindrical specimens were moulded at a pressure of 50 kg/cm^2. Different hydrothermal reactions were studied by the hydrothermal treatment in an autoclaved at a pressure of 8 atm. of saturated steam for different time intervals of 0.5,2,6,12 and 24 hours. Various hydrothermal reactions were studied with respect to hydration kinetics, compressive strength of the hydration products. The kinetics of the hydrothermal hardening processes were studied via the determination of chemically combined water and free lime contents at the different autoclaved ages up to 24 hours. Were found incorporation of NMK in OPCC – GGBFS – MK – NMK blend is accompanied by increase in the compressive strength results of the autoclaved specimens made of this blend. The higher strength values of the hydrothermally hardened specimens made of autoclaved OPCC – GGBFS – MK-NMK blend are mainly attributed to the formation of calcium silicate hydrate CSH hydrates.

Keywords: Ground granulated blast-furnace slag, metakaolin, nano-metakaolin, Portland cement clinker, Kinetic, hydrothermal hardening.

تأثير اضافة الميتاكاولين والنانو ميتا كاولين على الخواص الميكانيكية وحركية تفاعل التهدرت الحراري لكلنكر الأسمنت البورتلاندي

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الملخص هذه دراسة معملية لمعرفة تأثير اضافة الميتاكولين والنانوميتاكاولين على الخواص الميكانيكية وحركية تفاعل التهدرت الحراري للعينات المعالجة بالأوتوكلاف والمحضرة من كلنكر الأسمنت البورتلاندي وخبث الأفران العالية المحبب والميتاكولين والنانوالميتاكولين تم تحضير المخاليط الجافة عن طريق التنشيط الحراري كانت نسبة الماء / الأسمنت الصلب تبلغ حوالي 0.28 لمدة 3 دقائق وشكلت العينات في صورة اقراص إسطوانية الشكل ذات قطر 2سم من خلال ضغطها في قالب إسطواني تحت ضغط 50كيلوجرام /سم^2 بإستخدام مكبس هيدروليكي .و تمت دراسة الخواص الميكانيكية للعينات بقياس قوة تحمل الانضغاط للعينات عند ازمنة مختلفة (0.5, 2, 6, 24,12 ساعة) ودرست حركية تفاعل التهدرت الحراري بتعين كل من محتوى الماء المتحد كيميائيا (الماء الغير المتطاير) والجير الحر (هيدروكسيد الكالسيوم الغير متحد) عند الأزمنة المختلفة من المعالجة بالأوتوكلاف أظهرت النتائج أن عند ادخال النانو ميتا كاولين على العينات المصنوعة من كلنكر الأسمنت البورتلاندي وخبث الأفران العالية المحبب وميتاكاولين والنانوميتاكاولين زادت وسجلت اعلى قيم لقوة تحمل الانضغاط للعينات ويعزى السبب بشكل أساسي إلى تكوين هيدرات سيليكات الكالسيوم (CSH) ، التي تتمتع بخصائص هيدروليكية قوية.

الكلمات المفتاحية: كلنكر الأسمنت البورتلاندي –خبث الأفران العالية المحبب–الميتاكولين –النانوالميتاكولين –حركية التهدرت الحراري.

Introduction

Several subsequent studies were reported regarding autoclaved building products obtained by steam curing of different mixtures including hydraulically active materials. Portland clinker is normally used as the main component in cement manufacturing. It is a mix of different oxides and silicates suitable for the production of low cost structural ceramics. Ordinary Portland Cement clinker is a mixture of compounds produced by burning limestone and clay together, in a rotary kiln, at a temperature of around 1450°C. Approximately 40% of cement plant CO_2 emissions are from the burning of fossil fuel to operate the kiln, 50% due to the manufacturing process and the remaining 10% are accounted for by indirect CO_2 emissions relating to transportation of the finished product and front-end production processes.[1] Blast furnace slag is a by-product obtained during the manufacture of pig iron in the blast furnace and is formed by combination of earthy constituents of iron ore with limestone flux. granulated slag having latent hydraulic properties. Such granulated slag when finely ground and combined with Portland cement, has been found to exhibit excellent cementitious properties, GGBS were used as a direct replacement for Portland cement, on a one-to-one basis by weight. It is used to make durable concrete structures in combination with ordinary Portland cement and/or other pozzolanic materials[2]. In general Ground slag has been used as a cementitious material in concrete since the beginning of the 1900s[3]. Metakaolin is one of the earliest known pozzolanic materials, it is the cementetious material used as an admixture to produce high strength concrete[4]. ***Manjit and Mridul*** [5] studied metakaolin from four kaolinitic clays collected from different sources in India. The metakaolin produced from these clays at 700–800°C show lime reactivity between 10.5 to 11.5 N/mm^2 which is equivalent to commercially available calcined clay Metacem-85. The microstructure of the metakaolin has been reported. The effect of addition of metakaolin up to 25% in the Portland cement mortars was investigated. An increase in compressive strength and decrease of porosity and pore diameter of cement mortars containing metakaolin (10%) was noted over the cement mortars without metakaolin. Results indicate better strength achievement in cement mortars containing 10% MK than the OPC mortars alone. The lime reactivity of the calcined clays or any pozzolana is studied by determining their capacity to react with lime in presence of water.

Morsy, et al., [6]. investigated the effects of high temperatures up to 800°C on the mechanical properties and microstructure of nano-metakaolin cement mortars. The blended cement used in this investigation is ordinary Portland cement (OPC) containing nano-metakaolin (NMK). The nano-metakaolin was prepared by thermal activation of nano-kaolin clay at 750°C for 2 hours. The compressive strengths were measured for blended cement mortar and compared with the strength of pure OPC mortar. It was found that after an initial increase in compressive strength at 250°C for the mortar specimens, the strength decreased considerably at higher temperatures. Pozzolans react chemically with calcium hydroxide liberated during cement hydration to form cementitious compounds. [7]. The large surface area of nano particles and their abundance due to their small size can facilitate the chemical reactions necessary to produce a dense cement matrix with more calcium silicate hydrate (CSH) and less calcium hydroxide contents. When nano particles are used as supplementary cementitious material (SCM) in concrete, various improvements can be attained, thereby leading to improved permeability and strength. The nano particles act as "nuclei" of hydration, possess pozzolanic behavior, and can fill the voids in the cement matrix. [8-9].

Tironi, et al., [10]. described five natural kaolinitic clays from different regions of Argentine, with different kaolinite content, different impurities and different degree of crystallinity were calcined in a fixed-bed electrical furnace at 700°C. This study confirmed that natural clays rather than pure kaolinite can be interesting pozzolanic materials when thermally activated. Some limited research has been conducted on altering kaolinite mineralogical properties, in turn potentially changing the reactivity of the SCM. The aim of the present work is focused on the study of the Effect of met kaolin and nano-metakaolin on the hydration mechanism of autoclaved specimens made from OPCC, GGBFS,MK and NMK.and determine their compressive strength, (chemically-combined) water and free lime contents at different hydration ages.

2. Experimental

2.1. Starting Materials:

Ordinary Portland Cement Clinker,(OPCC).

The OPCC was supplied from Ahlia Cement Company (Libya) with a Blaine surface area of 2945 cm^2g^{-1}.GroundGranulatedBlast-Furnace Slag,(GGBFS).The GGBFS used in this study was provided from Zletin Cement Company (Libya).Metakaolin,(MK)andnanometakaolin, (NMK).The MK used in this study was supplied from Middle East Company.the nano clay was fired at 750°C for 3 hours to obtain nano-metakaolin.

2.2. Processing and Methods

All mixtures were stirred using ethanol in order to assure a complete homogeneity of the mixture, and then dried at 80-100°C for 2 hours. The mixtures(A0 and AI) in table1 shows the percentage composition (OPCC:GGBFS)studied by Salima.[11]. Moreover table -1 shows the Percentage composition of the OPCC- GGBFS - MK dry mixtures.(BI-BIII)

Table (1): Percentage composition of OPCC- GGBFS - MK dry mixtures

The mixture	Composition (Wt.,%)			
	OPCC	GGBFS	MK	NMK
A0	100	-	-	-
AI	50	50	-	-
BI	50	45	5	-
BII	50	25	25	-
BIII	50	40	5	5

Various blended cement pastes were prepared from the different dry mixtures by mixing each dry mixture with water (Water/Solid ratio=0.27-0.28) and the cylindrical specimens having cm^2 diameter and about cm^2 height were mounded under a hydraulic pressure of $50kg/cm^2$. The specimens of each mixture, thus obtained, were first cured at 100% relative humidity at room temperature for 24 hours and cured under hydrothermal conditions in an autoclave at a pressure of 8 atm of saturated steam for(0.5,2,6,12 & 24)hours. At the end of each autoclaving period, the specimens were removed from the autoclave for dried overnight at 105^{0}C to remove the free water.

2.3. Compressive Strength Determination

The mechanical properties of the hydration products were determined via the determination of the compressive strength at different ages of autoclaving. The average value was recorded as $Kg.cm^{-2}$. This test was performed using a Ton industric machine (West Germany) for maximum load of 60 tons.

2.4. Kinetics of Hydration

The kinetics of hydration process were studied via determination of chemically-combined water (Wn, %).Two representative samples of the dried specimens, exact about 1g each, were weighted in porcelain crucibles and ignited for one hour at 1000˚C in an adjustable muffle furnace, cooled in a desiccator and then weighted. The chemically-combined water content calculated as Wn (%) using the following equation:

$$Wn\ (\%) = [(W_1 - W_2) / W_2] \times 100$$

W_1: is the weight of the dried sample before ignition (g) and W_2: is the ignited weight of sample (g).The free lime (CaO, %) contents for the hardened specimens at different autoclaving time was determined by the titration method. free CaO present in the hardened sample will react with dry glycerol with the formation of calcium–glycerate. The glycerate is treated with an alcoholic solution of ammonium acetate. In the solution only calcium glycerate would be present, free CaO, will react with glycerol and consequently would not present in solution.The contents were titrated with a standardized alcoholic ammonium acetate solution until the pink colour was disappeared. Heat again, if the pink colour reappears, complete the titration with ammonium acetate solution until no further appearance of pink colour takes place. free CaO present in the hardened sample will react with dry glycerol with the formation of calcium–glycerate. The glycerate is treated with an alcoholic solution of ammonium acetate. In the solution only calcium glycerate would be present, free CaO, will react with glycerol and consequently would not present in solution.

2.5 Scanning electron microscopy (SEM):

Scanning electron microscope, (SEM), has been used to study the morphology and micro-structure of NMK JSM-5410 Scanning electron microscope was used in this investigation. The SEM micrographs shown in Fig.(1) display the presence of NMK particles (<1 μm) having an almost hexagonal shape with varying crystal sizes ranging from 50 nm to 950 nm with the predominance of NMK particles having sizes of 50 – 200 nm.

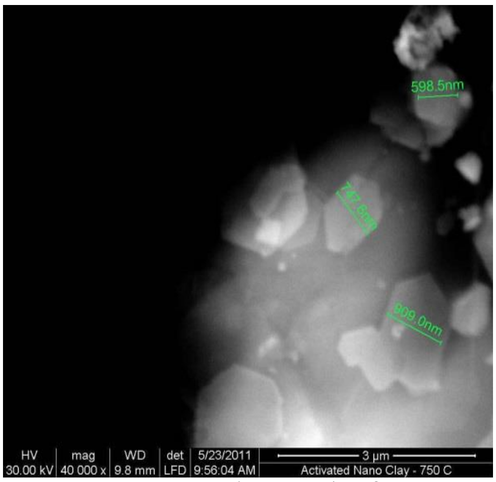

Fig.(1): SEM micrograph of NMK

3- RESULTS AND DISCUSSION

3.1. The Compressive Strength

The mechanical properties of the hydration products were determined via the determination of the compressive strength at different ages of autoclaving.

The results of compressive strength, non-evaporable (chemically-combined) water and free lime contents of these series of mixes (B1-BIII) are given in tables (2 - 4)

The results of compressive strength for the autoclaving specimens made from, 50/45/5 and 50/25/25 of OPCC/GGBFS/MK, respectively, (mixes BI- BII) are given in tables .(2-3). As show in the values the same trend of increasing the compressive strength values with increasing the autoclaving ages up to 24 hours as in mixes BIII is observed, but with slight lower strength values up to 12 hours of autoclaving. After 24 hours autoclaving all the mixes give a comparable strength values as mix BIII. The compressive strength values

obtained for theses mixes are a net result of two processes; the progress of hydration reaction of the OPCC and the pozzolanic reaction between the lime liberated from the clinker hydration and silica present in GGBFS and MK . Both reaction leads to formation of hydration products (mainly as nearly amorphous or micro crystalline CSH), which have good hydraulic properties and acts as good binding centers between the cement grains.

The results of compressive strength for autoclaved specimens made of mix BIII (50% OPCC+40% GGBFS +5% MK+5% NMK) are show in table.(4).The compressive strength results indicate a gradual continuous increase up the final ages of autoclaving(24 hours),with a notable higher values as compared to mix AI (50% PCC + 50% slag). These results can be explained in term of the progress of hydration reaction of the clinker and the pozzolanic interaction between the lime liberated from the clinker hydration and the amorphous silica present in both slag, MK and NMK leading to the formation of additional amounts of hydration products mainly as calcium silicate hydrate C-S-H which have good hydraulic characteristics and acts as good binding centres between the cement grains. Presence of 5% MK and 5% NMK causes the formation of additional amounts of calcium silicate hydrate C-S-H as compared to mixAI,[11]

Table(2):Some physicochemical characteristics of autoclaved specimens made from 50% OPCC,45% GGBFS and 5% MK (mix BI).

Age of hydration (hrs.)	Wn (%)	CaO (%)	Compressive strength (kg/cm²)
0.5	4.60	1.09	406.10
2	5.60	1.20	578.20
6	6.85	1.02	643.20
12	7.30	0.86	675.70
24	8.20	0.53	732.50

Table(3):Some physicochemical characteristics of autoclaved specimens made from 50% OPCC,25% GGBFS and 25% MK (mix BII).

Age of hydration (hrs.)	Wn (%)	CaO (%)	Compressive strength (kg/cm²)
0.5	4.90	0.89	347.60
2	5.58	0.67	438.50
6	6.54	0.56	526.20
12	7.05	0.36	578.20
24	7.88	0.22	740.60

Table(4):Some physicochemical characteristics of autoclaved specimens made from50%OPCC, 40% GGBFS 5% MK and 5% NMK (mix BIII).

Age of hydration (hrs.)	Wn (%)	CaO (%)	Compressive strength (kg/cm²)
0.5	5.30	0.55	407.46
2	5.84	0.49	474.30
6	7.25	0.47	506.80
12	7.93	0	629.50
24	850	0	769.87

On the ether hand the kinetics of hydration were studied via two methods determination of chemically-combined water (Wn, %).and free lime contents at different ages of autoclaving.

Chemically-Combined Water Content, Wn,%

The results of non-evaporable (chemically combined) water content for the autoclaved mixes made from,50/45/5 and 50/25/25 of OPCC/GGBFS/MK, respectively, (mixes BI- BII) are given in tables.(2-3). All the mixes give the same trend and also a comparable values as that of mix(BIII). These results is explained in terms of the progress of the hydration reaction, and formation of hydration products having good hydraulic properties and lower water contents.

The results of non-evaporable (chemically combined) water content for autoclaved specimens made from 50% OPCC - 40% slag - 5% MK and 5% NMK, are given in tables.(4). indicate a continuous gradual increase with increasing the age of autoclaving. The values obtained for combined water for these specimens are in comparable to that of the autoclaved specimens made of mix AI and lower than that of the autoclaved specimens made from neat OPCC (mix A0)[11] . These results is attributed to the progress of hydration reaction and formation of hydration products having good hydraulic properties and with lower water content.

The Free Lime Contents

The free lime contents for autoclaved specimens made from mixes BI-BII are show in tables. (2-3).The free lime contents for mixes BII and BIII show a continuous decrease during all ages of autoclaving up to 24 hours. These decrease attributed to the consumption of the lime liberated from the clinker hydration via the pozzolanic reaction with the silica present in GGBFS and MK. The free lime contents for autoclaved specimens made from mixe BIII are show in table. (4).The free lime contents for mixe BIII show a continuous decreases till reached zero after 12 and 24 hours of autoclaving. These decrease attributed to the consumption of the lime liberated from the clinker hydration via the pozzolanic reaction with the silica present in GGBFS, MK and NMK.

Conclusion

1. The autoclaved specimens made of OPCC (50%) –GGBFS(25%)-MK(25%)blend (mix BII) possess of lower compressive strength values than those of the specimens made of OPCC–GGBFS-MK or/and NMK (mix BI&BIII) at all ages of hydration. However, the incorporation of, meta kaolin (MK) and nano-meta kaolin MK (NMK) at the expense of slag leads to an enhancement in the compressive strength values at all autoclaving ages for the specimens made of OPCC – GGBFS – MK-NMK blends (mixes BI, BII and BIII).
2. The decrease in the compressive strength values is mainly due to the formation of hydration products having weaker hydraulic properties, mainly as hydrogarnet – like hydrate (C3ASH4), at the expense of calcium silicate hydrates (CSH) which possess stronger hydraulic character.
3. The incorporation of NMK in OPCC – GGBFS – MK – NMK blend (mix BIII) is accompanied by increase in the compressive strength results of the autoclaved specimens made of this blend. The higher strength values of the hydrothermally hardened specimens made of autoclaved OPCC – GGBFS – MK-NMK blend (mixes BIII) are mainly attributed to the formation of calcium silicate hydrates CSH hydrates at all ages of autoclaving.
4. The results of hydration kinetics, as obtained from non – evaporable water (Wn,%) and free lime (CaO,%) contents are in agreement with the result of compressive strength development of the autoclaved OPCC – GGBFS-MK or/and NMK pastes.

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