ACTIVATION OF RED KAOLIN CLAY AS A POZZOLANIC MATERIAL

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ABSTRACT

This work included two stages; in the first stage the optimum burning temperature to convert red kaolin clay to metakaolin was investigated. The red kaolin was burnt in a different temperature (800, 850, 900, 950, 1000, and 1050) ºC for one hour. Many tests was carried out on the cement containing (8)% of calcined kaolin such as normal consistency, setting time, soundness, compressive strength at (3, 7, and 28) days, and pozzolanic activity index at (7, and 28) days. The results show that the optimum burning temperature to convert kaolin clay to metakaolin is (900) ºC.

In the second stage the effect of replacing the red kaolin calcined at (900) ºC at a (5, 8, and 10) % by weight of cement on compressive strength of cement mortar at (3, 7, and 28) days, and compared the results with reference mix. The results shows that the mortars contains red kaolin have compressive strength less than the reference mix at (3, and 7) days, but it shows slightly increasing in the compressive strength at (28) day about (100.8, 102.5, and 103.4) % for the mixes containing (5, 8, and 10) % of red kaolin respectively. The results also showed that the mortar containing (10)% red kaolin gives higher compressive strength compared with the mortar containing (5, and 8)% red kaolin at (28) day.

KEYWORDS: **Kaolin, red kaolin, cement, pozzolana, burning temperature**.

تفعيل اطيان الكاؤولين الاحمر واستخدامها كمادة بوزولانية

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الخلاصه

تضمن العمل في هذا البحث على مرحلتين، المرحلة الاولى تم فيها ايجاد افضل درجة حرارة لحرق الكاؤولين الاحمر وتحويله الى ميتاكاؤولين حيث تم حرقه بدرجات حرارة مختلفة (٨٠٠، ٨٥٠، ٩٠٠، ٩٥٠، ١٠٠٠، و ١٠٥٠) °م لمدة ساعة واحدة.تم اجراء العديد من الفحوصات للسمنت الحاوي على (٨) % من الكاؤولين المحروق مثل فحص القوام القياسي وزمن التجمد والثبات ومقاومة الانضغاط باعمار (٣، ٧و ٢٨) يوم ودليل الفعالية البوزولانية بعمر (٧و ٢٨) يوم وقد تبين من خلال هذه الفحوصات بان افضل درجة حرارة حرق لتحويل الكاؤولين الاحمر الى ميتاكاؤولين هي (٩٠٠) °م.

اما في المرحلة الثانية فقد تم دراسة تاثير تعويض الكاؤولين الاحمر المحروق بدرجة حرارة (٩٠٠) °م بنسب (٥و ٨و ١٠) % من وزن السمنت على مقاومة الانضغاط لمونة السمنت باعمار (٣و ٧و

٢٨) يوم ومقارنتها بالمونة القياسية وقد تبين ان المونة الحاوية على الكاؤولين الاحمر المحـــروق بدرجـــة حرارة (٩٠٠) °م تعطي مقاومة انضغاط اقل من المونة القياسية في الاعمار المبكرة (٣ و ٧) ايـــام لكنهـــا تعطي زيادة طفيفة بالمقاومة مقدارها (١٠٠.٨ ١٠٢.٥، و ١٠٣.٤)% للخلطات الحاوية على (٥ ، ٨ و ١٠)% من الكاؤولين الاحمر المحروق على التوالي بعمر (٢٨) يوم. وكذلك بينـــت النتـــائج ان المونـــة الحاوية على (١٠) % من الكاؤولين الاحمر تعطي مقاومة انضغاط اعلى من الخلطات الحاوية علـــى (٥ و ٨) % بعمر (٢٨) يوم.

NOMENCLATURE

10RM :	Mortar containing 10% red kaolin
5RM :	Mortar containing 5% red kaolin
8RM :	Mortar containing 8% red kaolin
HRM :	High reactivity metakaolin
HRWRA :	High range water reducing admixture
MK :	Metakaolin
P.A.I :	Pozzolanic activity index
Ref :	Reference cement mortar
SF :	Silica fume

INTRODUCTION

Kaolin clay is one of the raw materials of major importance for the ceramic and paper industry as well as for a number of auxiliary applications. There is an ongoing interest to apply kaolin clay in the construction industry as a raw material for the production of white cement clinker and as an artificial pozzolanic additive for concrete (in a form of metakaolin).

Kaolinite is composed of alternating layers of silicate (Si_2O_5) and gibbsite ($Al_2(OH)_4$). Kaolinite crystals are usually arranged in pseudohexagonal plates forming flaky aggregates and it has the same chemistry as its polymorphs halloysite, dickite and nacrite. Kaolin clay is formed as a result of the alteration of alumosilicates (feldspar, feldspathoid, spodumene, sillimanite) and volcanic glasses, sometimes altered by acidic hydrothermal solutions. Besides kaolinite, kaolin clay usually contains different minerals (such as quartz, feldspar, and calcite). It is mostly white, but it also can be grey, yellow or red. A recent development comprises the application of metakaolin as an artificial pozzolanic additive for concrete. The strength and durability of conventional cement-based materials can be significantly improved when additives based on thermally activated kaolin are used. Such additives are conventionally manufactured by firing high-grade purified kaolinite at 650-850 °C according to following reaction:

$$2SiO_2 \cdot Al_2O_3 \cdot 2H_2O \xrightarrow{650\text{-}850\ ^\circ C} 2SiO_2 \cdot Al_2O_3 + 2H_2O\uparrow \quad (1)$$

The main beneficial effect of metakaolin in concrete and cement systems is related to its high pozzolanic activity (its ability to react with portlandite, $Ca(OH)_2$ released during the hydration of portland cement). Due to its ability to improve the packing of the cement matrix the application of super-fine particles of metakaolin results in a microfiller effect [**Aydin Aras, et al**].

The particle density of metakaolin is lower than that of Portland cement. Thus, when metakaolin is used as a replacement for cement the volume of cementitious materialis increased. Reducing the sand content of the mix overcomes the effect of the increased volume of cementitious powder. [**Newman 2003**].

PREVIOUS RESEARCHES

Metakaolin is a reactive aluminosilicate pozzolan formed by purified kaolinite clays at a specific temperature range and by grinding it to a high fineness. Chemically, metakaolin encompasses as main constituents SiO_2 and Al_2O_3, and in smaller quantities Fe_2O_3, CaO, MgO, SO_3, Na_2O and K_2O. The efficiency of metakaolin as a pozzolan in cement and concrete is mainly governed by high content of SiO_2 and Al_2O_3. The high pozzolanic activity is also due to the large portion of small particles of metakaolin [**Krajei, et al, 2007**].

(Ali K. Ibrahim, 2005) investigates the optimum conditions to convert white kaolin clay to high reactivity metakaolin (HRM). This pozzolan is used with high range water reducing admixture (HRWRA) to produce high performance lightweight aggregate concrete. The mechanical properties of this type of concrete are studied. He found that the most suitable burning temperature required to convert the kaolin clay into HRM was 700 ^{0}C, and the optimum time of burning was 1 hour.

A. **Sadr Momtazi et al** studied the effect of Iran's metakaolin in enhancing the concrete compressive strength. In this study, four different type of metakaolin which one of them was made in UK and the others were from different part of Iran were used. Sixteen mortar mixtures with different amount of calcinating kaolin were made. The substitution proportion of metakaolin used was 5%, 10%, 15% and 20% by weight of cement. About 380 cylinders specimens were made to determine compressive strength. The results indicate that the replacing metakaolin (MK) up to 20% has noticeable effect on compressive strength in comparing with mixture without metakaolin. Also, shrinkage test was carried out on some specimens. The results show that shrinkage in specimens containing MK were almost the same as that in the pure cement specimens.

M.M. Morsy et al studied the effect of substitution of metakaolin (MK) by silica fume (SF) on thermal stability of Portland cement-MK blended pastes. The kaolinte was thermally activated at 850°C for 2 hours. The cement pastes were prepared using standard water of consistency. The pastes were kept in moulds at 20°C and 100% relative humidity for 24 hours and then hydrated for 28 days under water. The hydrated pastes were exposed for 2 hours to temperature 200, 400, 600 and 800°C. The pre-heated specimens were tested for compressive strength, thermal stability, and microstructure and phase composition. The thermal shock resistances were performed on cement pastes after hydration. The results of investigation showed that the compressive strength of pre-heated blended cement increases with temperature up to 400°C and then, it decreases as the pre-heated temperatures increase up to 800°C. The replacement of Portland cement, by 15% MK and 15% SF in cement pastes increases the thermal shock resistance by about 20 times than control.

MATERIALS

1- Cement

Ordinary Portland cement type (I) produced at Lebanon cement factory (Turabt Sabia) is used in this work. It was stored in a dry place (air-tight containers) to avoid exposure to atmospheric condition. The chemical composition and physical properties of cement are shown in **Tables (1) and (2)** respectively. Test results indicate that the adopted cement conform to the Iraqi specification No.5/1984.

2- Sand

Al-Ekadir natural sand was used as a fine aggregate. **Table (3)** and **Fig (1)**, illustrate the grading of sand used throughout this work. The grading of sand conforms to the requirement of ASTM C778-06.

3- Water

Tap water was used as mixing water for all mixes.

4- High Range Water Reducing Admixture

A modified condensation product of melamine and formaldehyde (Melment L10) was used as a high range water reducing admixture (HRWRA) of (5) % of weight of cement.

5- Red Kaolin Clay

The chemical composition of high reactivity metakaolin (HRM) is shown in **Table (4)**, it comprises nearly percent of (SiO_2 + Al_2O_3 + Fe_2O_3), which conforms to ASTM C618-05 class C pozzolan according to specification for natural and calcined pozzolans.

OPTIMUM BURNING TEMPERATURE OF RED KAOLIN CLAY

Kaolin is soft, white clay resulting from the natural decomposition of feldspars and other clay minerals. It occurs widely in nature. It is used for making porcelain and china, as a filler in the manufacture of paper and textiles and as a medicinal absorbent. Kaolinite is the principal mineral constituent of kaolin. When kaolin is heated to a temperature of 450 ºC dehydroxylation occurs and the hydrated aluminosilicates are converted to materials consisting predominantly of chemically combined aluminium, silicon and oxygen. The rate at which water of crystallization is removed increases with increasing temperature and at 600 ºC. Metakaolin is formed in kilns when kaolin is heated at a temperature between 700 ºC and 800 ºC. The calcined product is cooled rapidly and ground to a fine powder. The metakaolin formed in this way has a highly disorganized structure [**Newman, 2003**].

In the first stage many samples of red kaolin clay were burnt in a controlled temperature furnace at various temperatures (800, 850, 900, 950, 1000 and 1050) ^{0}C to determine the optimum temperature of calcinations. After calcinations process the kaolin clay was left to cool, then it was grounded to have high fineness metakaolin and mixed with cement in porcelain mill for 30 minutes to ensure HRM particles were thoroughly dispersed throughout the cement particles.

In this stage many tests such as normal consistency, setting time, soundness, compressive strength, and pozzolanic activity index, were investigated for each burning temperature. The pozzolanic activity index (P.A.I) was determined as follows, according to ASTM C311-05.

$$P.A.I = (A/B) \times 100 \qquad (2)$$

Where:

A: average compressive strength of test mix cubes.

B: average compressive strength of reference mix cubes.

Tables (5), and (6) and **figures (2), (3), and (4)** shows that the optimum burning temperature of the red kaolin clay is (900) ^{0}C, which is exhibited higher compressive strength and higher pozzolanic activity index compared with all other burning temperatures at (28) day.

COMPRESSIVE STRENGTH OF MORTARS

The effect of replacement of red kaolin burnt at (900) ºC as a (5, 8, 10) % by weight of cement on compressive strength of mortars was studied. (36) Specimens of (50) mm cube is cast and cured according to (ASTM C 109/C 109M – 05). The results shows that the reference mixes (Ref.) have higher compressive strength at (3 and 7) days compared with the mixes containing red kaolin Table (7) and Fig. (5), but at (28) day the mixes containing red kaolin exhibited slightly higher compressive strength than reference mix. The results also showed that the mix containing (10) % red kaolin (10RM) gives slightly higher compressive strength at (28) day compared with all other mixes. This is due to the reaction between the amorphous silica of the pozzolanic and the calcium hydroxide produced by the cement hydration reactions. In addition, the physical effect of the fine grains allows denser packing within the cement and reduces the wall effect in the transition zone between the paste and aggregate. In general, the pozzolanic effect depends not only on the pozzolanic reaction, but also on the physical or filler effect of the smaller particles in the mixture [**M.M. Morsy et al, 2008**].

CONCLUSIONS

1- The optimum burning temperature of red kaolin clay to gives best results with cement is (900) ºC.

2- Replacement of metakaolin slightly delays the setting time of cement paste.

3- The mortars containing red kaolin burnt at (900) ºC show slightly higher compressive strength than reference mortar at age (28) day although it have lower cement content.

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المواصفات العراقية القياسية (I.Q.S)رقم (١٩٦٩\٨) "فحص الثبات للسمنت بطريقة لي شاتليه".

المواصفات العراقية القياسية (I.Q.S)رقم(٥ \١٩٨٤) الاسمنت البورتلاندي.

Table (1) Chemical composition and main compounds of cement*

Oxides composition	Content %	Limits of (I.O.S.) No.5/1984
CaO	63.52	-
SiO_2	19.57	-
Al_2O_3	6.10	-
Fe_2O_3	3	-
MgO	1.25	$\leq$5.00
SO_3	2.73	$\leq$2.80
L.O.I.	2.36	$\leq$4.00
Insoluble residue	0.76	$\leq$1.5
Lime Saturation Factor, L.S.F.	0.95	0.66-1.02
Main compounds (Bogue's equations)		
C_3S	56.21	-
C_2S	14.00	-
C_3A	11.63	-
C_4AF	8.10	-

* Chemical analysis was conducted by National Center for Construction Laboratories and Researches.

Table (2) Physical properties of cement*

Physical Properties	Test results	Limits of (I.O.S.) No.5/1984
Specific surface area (Blaine method), m^2/kg	240	$\geq$230
Setting time (Vicate apparatus), Initial setting, h:min Final setting, h:min	 1:30 5:32	 $\geq$00:45 $\leq$10:00
Compressive strength, MPa 3 days 7 days	 23.40 34.62	 $\geq$15.00 $\geq$23.00
Soundness (Le-Chateler) method, mm	1.0	$\leq$10

*Physical analysis was conducted by National Center for Construction Laboratories and Researches.

Table (3) Grading of fine aggregate

Sieve size, mm	Cumulative % passing	**Limits of ASTM C778**
1.18	100	100
0.60	98	96-100
0.425	72	65-75
0.30	26	20-30
0.15	3	0- 4

Table (4) Chemical analysis of red kaolin clay

Oxide composition	Oxide content %
SiO_2	40.54
Al_2O_3	7.55
Fe_2O_3	3.97
TiO_2	0.53
Na_2O	1.03
K_2O	1.5
CaO	21.87
MgO	4.65
SO_3	0.25
L.O.I	16.35

*Chemical analysis was made by (State Company of Geological Survey and Mining).

Table (5) Properties of cement with 8 % HRM at various burning temperatures

Property	Cement with 8 % HRM replacement					
	800	850	900	950	1000	1050
w/c ratio for standard consistency	0.3125	0.305	0.3075	0.3075	0.315	0.315
Setting time[12]						
Initial setting, h:min	1:37	1:40	1:39	1:18	1:50	1:53
Final setting, h:min	5:48	6:13	5:50	6:08	5:45	5:43
Compressive strength, MPa						
3 days	21.53	20.75	22.15	21.08	21.57	19.66
7 days	30.37	31.88	33.64	30.13	29.32	29.75
28 days	39.39	42.16	43.62	40.93	40.77	39.03
Soundness (Le-Chatelier) method, mm	0.5	1.5	0.5	0.5	0.5	1.5
Soundness (Autoclave) method, %	0.26	0.23	0.23	0.25	0.6	0.27

Table (6) Pozzolanic activity index (P.A.I) at various burning temperatures

Property	Portland cement	Cement with 8 % HRM replacement					
		800	850	900	950	1000	1050
w/c ratio to give flow of 100-110 %	0.53	0.552	0.54	0.544	0.548	0.56	0.56
Pozzolanic activity index % at							
7 days	----	86.6	87.7	90.2	90.6	88.4	89.6
28 days	----	96.3	96.8	100.9	95.6	93.5	93.4
w/c ratio to give flow of 100-110 % with HRWRA	0.385	0.392	0.4	0.408	0.412	0.42	0.42
Pozzolanic activity index % with HRWRA at							
7 days	----	87.3	88.6	91.4	87.1	89.1	85.2
28 days	----	92.8	98.6	102.3	94.4	91.6	92.8

Table (7) Compressive strength of reference and red kaolin mortars

Mix symbol	Compressive strength, (MPa)		
	3 days	7 days	28 days
Ref.	23.40	34.62	42.54
5RM	22.43	33.52	42.9
8RM	22.15	33.64	43.62
10RM	21.86	33.15	43.97

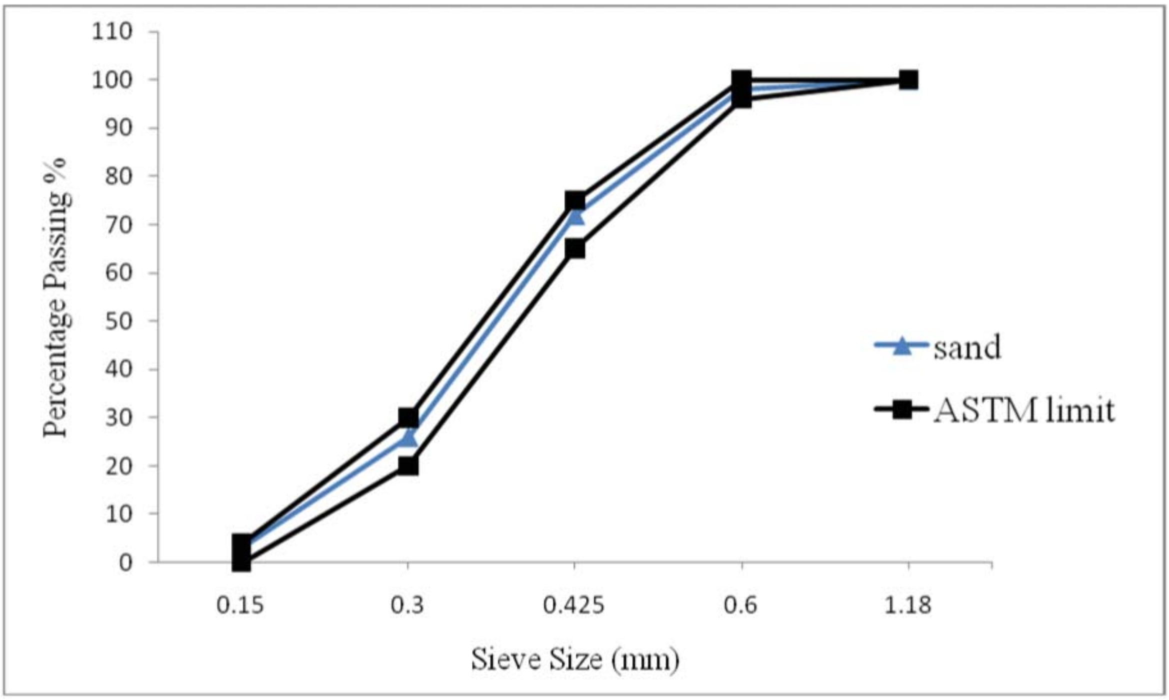

Fig (1) Grading of sand

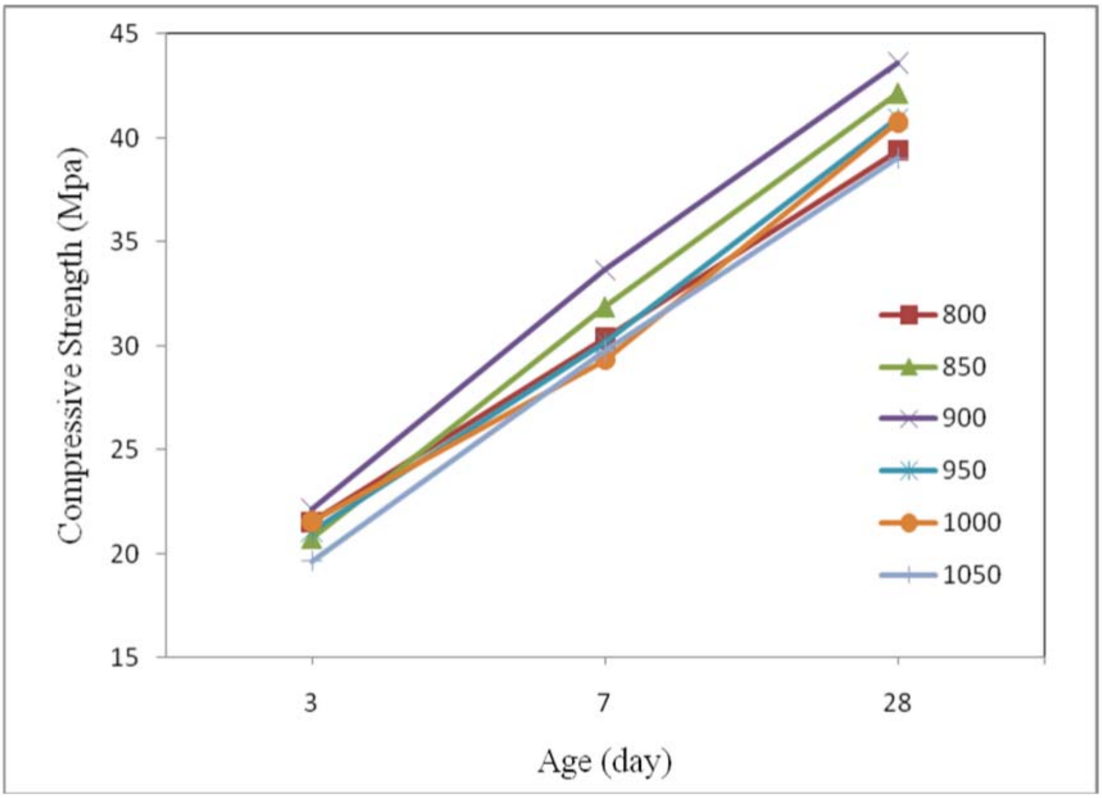

Fig (2) Compressive strength of cement mortars containing (8) % of red kaolin burnt at different burning temperatures.

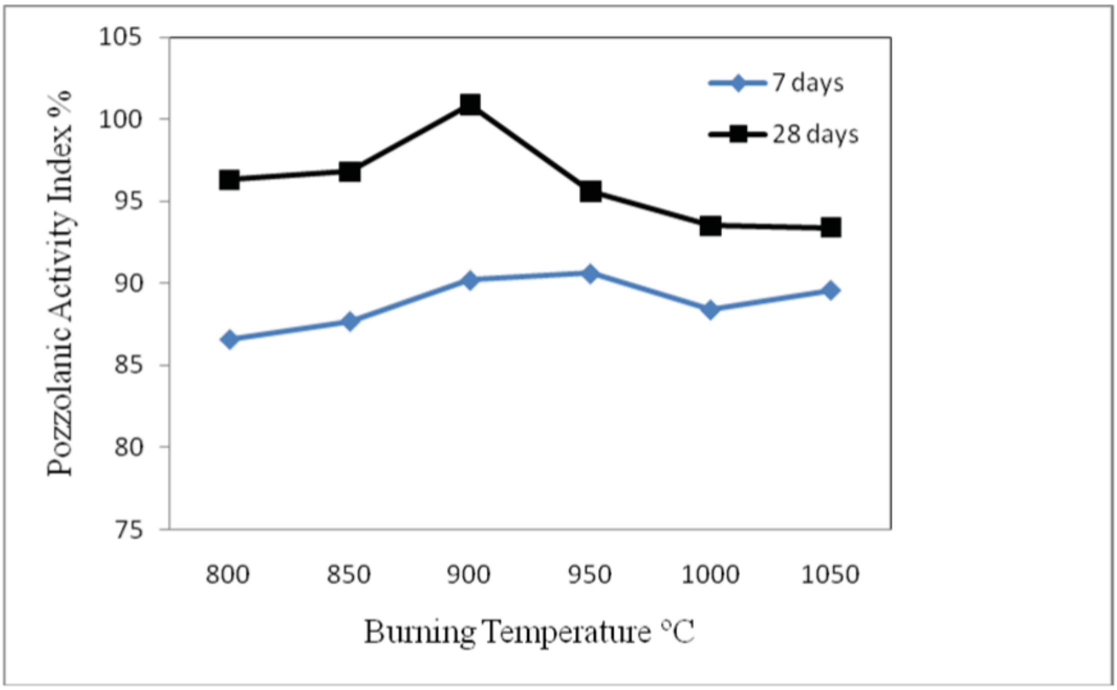

Fig (3) Pozzolanic activity index of cement mortars containing (8) % of red kaolin burnt at different burning temperatures.

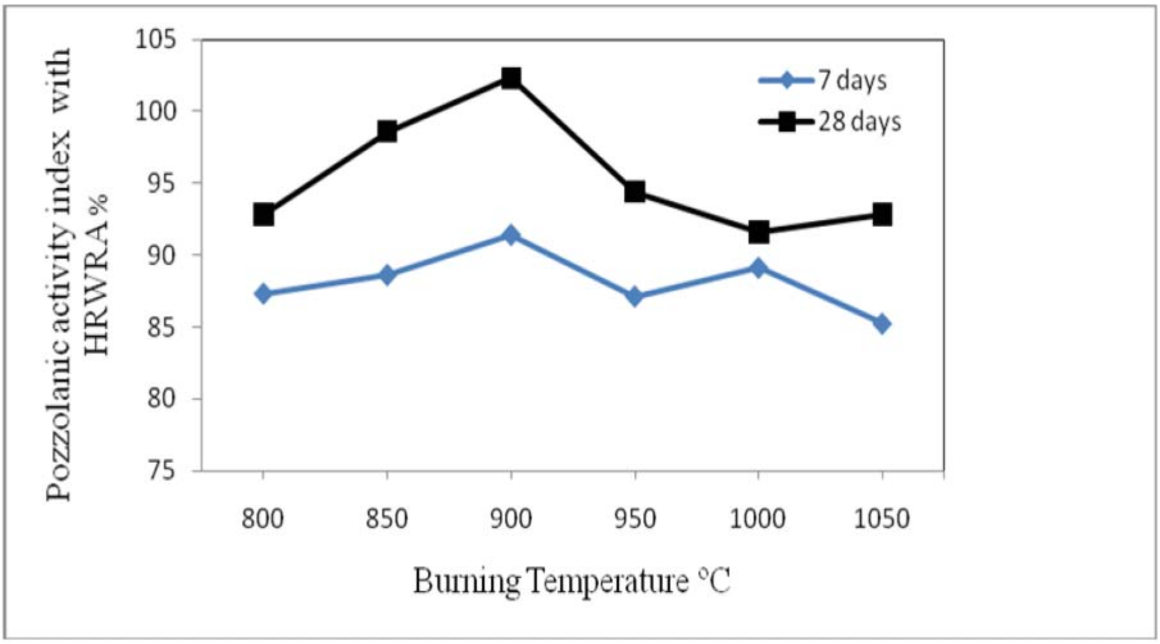

Fig (4) Pozzolanic activity index of cement mortars containing HRWRA and (8) % of red kaolin burnt at different burning temperatures.

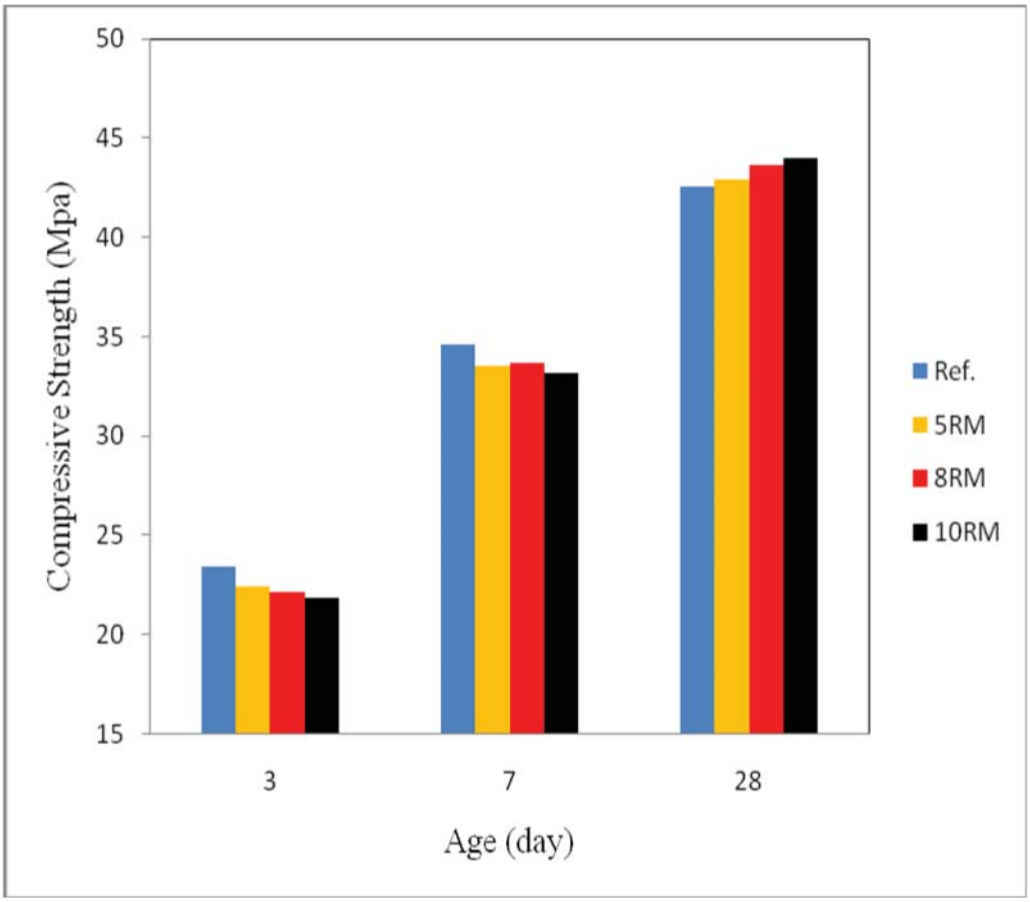

Fig (5) Compressive strength of reference and red kaolin mortars.