Effect of temperature on the pozzolanic properties of Metakaolin produced from Iraqi kaolin clay

Asst. Prof. Dr. Amer M. Ibrahem — Diyala University, Iraq
Khalid A. Abdul Wahab — Asst. Lecturer in Civil Eng. Dep. Diyala University, Iraq

ABSTRACT

Non availability of pulverized fuel ash (PFA), silica fume and other types of high reactivity pozzolanic materials is a potential obstacle in reducing cement content specially in mass concrete mixes. Another option that can be considered is utilization of a super pozzolan called Metakaolin which is produced from conversion kaolin clay available in Dwekhla region in Iraq to Metakaolin. In this work a laboratory investigation were carried out to investigate the optimum calcination temperature and the optimum time of calcination at that calcination temperature required to convert kaolin clay to Metakaolin. The results show that, the optimum calcination temperature was 700C^{o} and the optimum time of calcination at that calcination temperature is one hour.

الخلاصة

إن عدم توفر رماد مسحوق الفحم ، أبخرة السيليكا أو المواد البوزولانية الأخرى ذات الفعالية العالية مما شكل عائقا في تقليل محتوى الأسمنت خصوصا في خلطات الخرسانة الكتلية. لذا كان من الواجب استخدام البديل المحلي الذي يمكن الاستفادة منه وتحويله إلى مادة بوزولانية عالية الفعالية وهو طين الكاؤولين الأبيض الذي تتوفر ترسبات و بكميات كبيرة منه في منطقة دويخلة في العراق وذلك عن طريق تحويله إلى مادة الميتاكاؤولين. في هذا البحث جرى التحري مختبريا عن درجة حرارة التكليس الضرورية وزمن التكليس الضروري لتحويل مادة طين الكاؤولين إلى الميتاكاؤولين ذا الفعالية البوزولانية. أظهرت النتائج إن درجة حرارة التكليس الضرورية هي ٧٠٠ درجة سيليزية وان زمن التكليس عند هذه الدرجة هو ساعة واحدة.

Introduction:

In order to reduce cement consumption we must use cementitious materials that are finely ground solid materials which are used to replace part of the cement in a concrete mixture. These materials react chemically with hydrating cement to form a modified paste microstructure. Also, they may improve concrete workability, mechanical properties, and durability. They may possess pozzolanic or latent hydraulic reactivity or a combination of these. The term pozzolan refers to a siliceous material, which, in finely divided form and in the presence of water, will react chemically with calcium hydroxide ($CaOH_2$) to form cementitious compounds. Pozzolans can be of natural or industrial origin. Metakaolin ((MK)) is an cementitious materials that conforms to ASTM C 618[1], Class N pozzolan specifications. (MK) is unique in that it is not the by-product of an industrial process nor is it entirely natural; it is derived from a naturally occurring mineral and is manufactured specifically for cementing applications. Unlike by-product Pozzolans, which can have variable composition, (MK) is produced under carefully controlled conditions to refine its color, remove inert impurities, and tailor particle size. As such, a much higher degree of purity and pozzolanic reactivity can be obtained [2]. (MK) has great promise as an cementitious materials, as it can improve many properties of concrete while also reducing cement consumption. The raw material input in the manufacture of Metakaolin is kaolin clay that could be brought from Dwekhla region which has the chemical composition show in table(1)[3]. Kaolin is a fine, white,. In general, clay minerals have been found from the decomposition of igneous rocks such as granite, which were them selves formed by solidification of molten materials from the interior of earth. Granite is composed of approximately equal proportions of the mineral; Mica ($K_2O.3Al_2O_3.6SiO_2.2H_2O$), Quarts ($SiO_2$), and Feldspar ($K_2O.Al_2O_3.6SiO_2$), of which the least stable when exposed to the action of water and air. It is from the decomposition of Feldspar in the presence of air and water over long periods of time that the kaolintic clays have been formed. All Potash and the part of the Silica in Feldspar have been dissolved away, the residue combining with water to give the clay mineral Kaolinite as shown in equation (1) [4].

$$K_2O.Al_2O_3.6SiO_2 \longrightarrow Al_2O_3.2SiO_2.2H_2O \quad \ldots\ldots\ldots\ldots(1)$$

Previous studies indicated that Kaolinite, after calcination at specific temperature and under controlled conditions, form Metakaolin ((MK)) that exhibits pozzolanic properties [5].

$$Al_2O_3.2SiO_2.2H_2O \longrightarrow Al_2O_3.2SiO_2 + 2H2O \quad \ldots\ldots\ldots\ldots..(2)$$

(MK) is a reactive lime-pozzolan that reacts with free calcium hydroxide ($CaOH_2$), a pozzolanic reaction takes place whereby new cementitious compounds will contribute cementitious strength and enhanced durability properties to the system in place of the otherwise weak and soluble calcium hydroxide [6,7].

$$OPC + H_2O \xrightarrow{\textbf{Cement hydration process}} CSH + CH \quad \ldots\ldots\ldots\ldots\ldots.(3)$$

$$AS_2 + CH \xrightarrow{\textbf{Pozzolanic reactivity processes}} C_2ASH_8 + CSH \quad \ldots\ldots\ldots\ldots\ldots\ldots.(4)$$

Experimental Work:

1.Selection of the Suitable Calcination Temperature:

The kaolin clay is ground to a fine powder and burnt in a controlled temperature furnace at various calcinations temperature (550, 600, 650, 700 and 750 ºC) for a half hour depending on the DTA for the Iraqi kaolin clay brought from Dwekhla region that is shown in Figure (1)[8],. After that, the burnt clay was left to cool to the ambient temperature and then grinded for ten an hours by means of grinding mill in order to obtain high fineness. Then the cement was mixed with 20 % of (MK) as a partial replacement by weight of cement by means of grinding mill for a period of one hour. Several tests were performed for each calcinations temperature. The main properties of cement and Strength activity index (S.A.I) are presented in Tables (2) and (3) respectively. The fineness was determined by Blaine air permeability method in accordance with ASTM C204-84 [9], standard consistency, setting time, compressive strength and soundness tests were conducted in accordance with

B.S.12: part 2 [10]. The S.A.I with Portland cement was determined according to the ASTM C311-02 [11], as follows:

$$S.A.I = (A / B) \times 100 \qquad \text{……………………(5)}$$

Where

A = Average compressive strength of test mix cubes.

B = Average compressive strength of reference mix cubes.

2. Selection of the Suitable Time of Calcination:

Apart from the temperature of calcination it is well established that the time at the calcinations temperature also influences the reactivity of the pozzolana. The kaolin clay samples were burnt in a controlled temperature furnace so that the temperature increased gradually until 700 ºC and left for a period of (0.5, 1, 1.5, and 2 hours). The burnt clay left to cool to the ambient temperature then converted into very fine particles by using grinding mill. The cement was then mixed with the required quantity of (MK) by using grinding mill for a time of one an hour. Several tests were investigated for each time of calcination. The main properties of cement and S.A.I are presented in Tables (4)and (5) respectively.

Discussion:

The pozzolanicity of calcined clay is achieved by driving of the water molecules [12,13]. This process results in the formation of a quasi-amorphous material which is reactive with lime. When heat is applied firstly the absorbed water is removed and, as temperature is increased, the interlayer and hydrated water. The effect of heating is monitored using differential thermal analysis (DTA) shown in Fig.(1). The important endothermic peaks (reactions involving absorption of heat) at about 540 ºC is caused by de-hydroxylation or expulsion of combined water. The endothermic peaks are generally followed at higher temperature by exothermic peak (reaction involving emission of heat) at about 980 ºC caused by re-crystallization of the residual amorphous matrix to form high temperature silicates and oxides. The reactivity of the calcined clay with lime depends on the quasi-amorphous nature of the collapsed structure. Therefore an optimum calcinations temperature exists for each clay, at temperatures beyond the optimum, re-crystallization begins, while at temperature below the optimum the clay lattice structure is still intact [14]. From the point of view of strength, the optimum calcinations temperature for the kaolin is 700 ºC. It is obvious to note that the optimum temperature from lime-pozzolana strength point of view is not directly related to the decomposition temperature indicated by the endothermic peak. This is shown in Figures (2) and (3). It can be seen that the de-hydroxylation temperature is around 550 ºC; however the optimum temperature for strength is 700 ºC. On the basis of strength, the optimum time of calcination at 700 ºC is one hour. As shown in Figures (4) and (5), it is apparent that prolonged exposure to temperatures above the de-hydroxylation temperature promotes re-crystallization and hence loss in pozzolanic activity. The chemical composition of resulted MK shown in Table (6).

Table (1) Chemical analysis of kaolinite clay

Oxide Composition	Oxide content (%)
SiO_2	53
AL_2O_3	32
Fe_2O_3	0.9
TiO_2	0.11
CaO	1.1
MgO	1.08
L.O.I	13

Table (2) Effect of calcination temperature on the properties of cement with 20% MK

Property	Cement with 20 % MK replacement Calcined for 1/2 hr.				
	550 ºC	600 ºC	650 ºC	700 ºC	750 ºC
Specific surface area (Blaine method) (m^2/kg)	990	880	775	560	1050
W/C for standard consistency	0.33	0.37	0.32	0.35	0.35
Setting time (Vicat's method) Initial setting time (hr:min) Final setting time (hr:min)	1: 25 4:45	1: 25 3:30	1:01 4:40	1:03 4:55	2:16 5:10
Compressive strength (MPa) (1:3 mortar) 3 days 7 days 28 days	24 33 40	29 36 45	26 38 44	31 42 50	32 42 46
Soundness (mm) (Le-chatelier method)	1	1	1	1	1
Soundness (%) (Autoclave method)	0.08	0.01	0.01	0.01	0.08

Table (3) Effect of calcinations temperature on S.A.I.

Property	Cement with 20 % MK replacement Calcined for 1/2 hr.				
	550 ºC	600 ºC	650 ºC	700 ºC	750 ºC
w/c.m required for flow(+,-) 5mL of control mixture.	0.55	0.60	0.56	0.57	0.58
strength activity index (%) (1:2.75) 7 days 28 days	91 91	87 100	92 98	98 102	96 98

Table (4) Effect of time of calcination on the properties of cement with 20 % HRM.

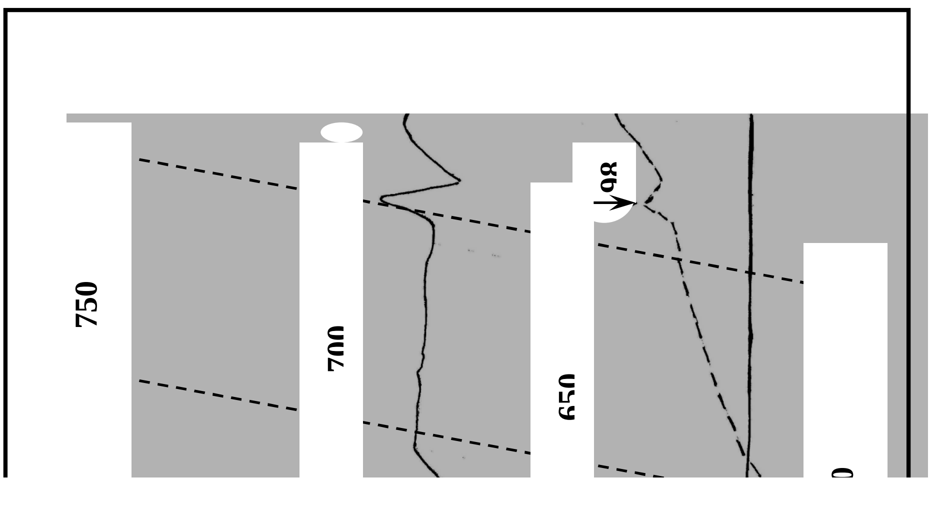
Property	Portland Cement	Cement with 20 % MK Calcined at 700 ºC.			
		1/2 hr.	1 hr.	1 1/2 hr.	2 hr.
w/c for standard consistency	0.30	0.33	0.32	0.30	0.29
Setting time (Vicat's method) Initial setting time (hr:min) Final setting time (hr:min)	1:14 2:40	1:40 2:50	1:15 3:00	1:03 3:20	1:17 2:35
Compressive strength (MPa) (1:3 mortar) 3 days 7 days 28 days	23 31 39	22 30 36	21 32 39	20 29 37	19 27 35
Soundness (mm) (Le-chatelier method)	1	1	1	1	1

Table (5) Effect of Time of Calcination on the S.A.I.

Property	Portland Cement	Cement with 20% MK Calcined at 700 ºC.			
		1/2 hr.	1 hr.	1 1/2 hr.	2 hr.
w/c.m required for flow(+,-) 5mL of control mixture.	0.66	0.69	0.69	0.69	0.69
strength activity index (%) (1:2.75)					
7 days	–	92	89	90	84
28 days	–	98	102	99	94

Table (6) Chemical analysis of resulted MK

Oxide Composition	Oxide content (%)
SiO_2	52.9
AL_2O_3	34.0
Fe_2O_3	1.29
TiO_2	1.13
CaO	0.26
MgO	0.16
Na_2O	0.43
SO_3	0.11
K_2O	0.40
L.O.I	7.91



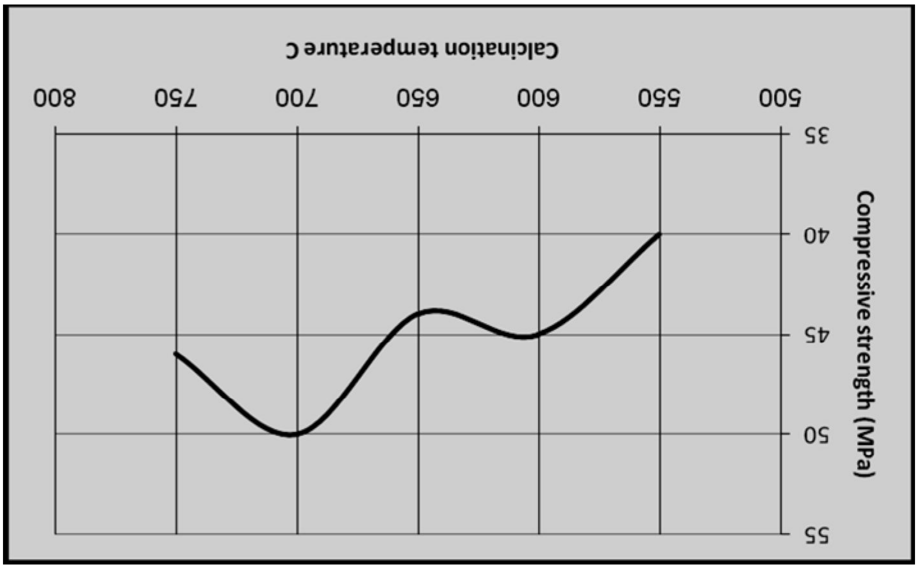


Figure (2) Effect of calcination temperature on compressive strength at age of 28 days.

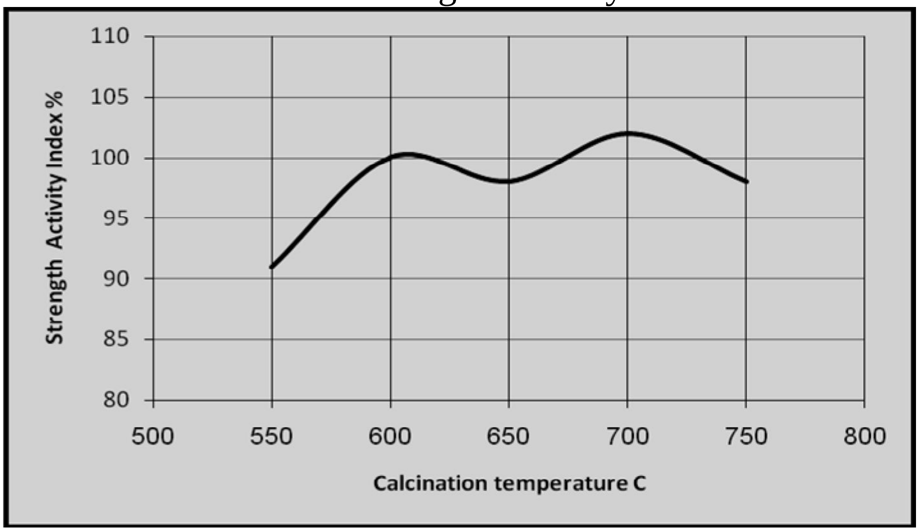


Figure (3) Effect of calcination temperature on P.A.I at age of 28 days.

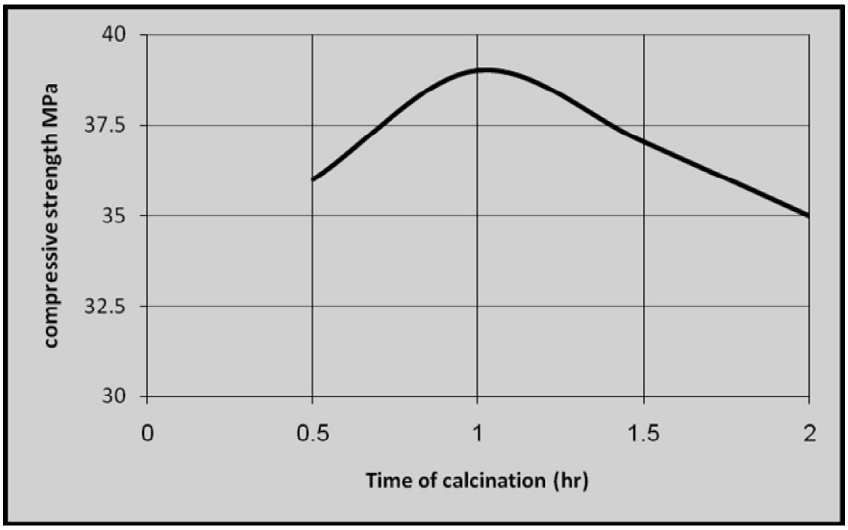


Figure (4) Effect of time of calcination on compressive strength at age
of 28 days.

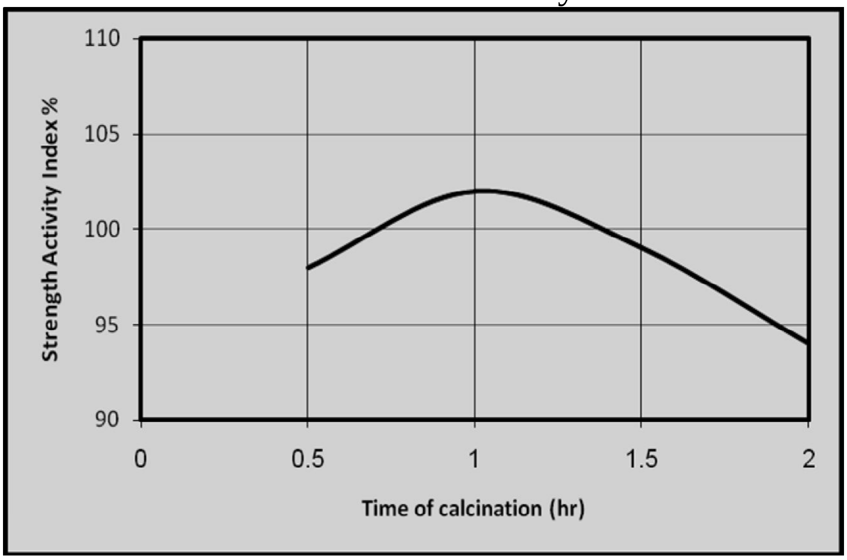


Figure (5) Effect of time of calcination on P.A.I.

Conclusions:

1- The Iraqi kaolin clay brought from Dwekhla region could be used as pozzolanic materials after convert it to Metakaolin.
2- It was found that optimum temperature used to converting Iraqi kaolin clay to Metakaolin is 700C^o .
3-The optimum required duration time at 700C^o for converting Iraqi kaolin clay to Metakaolin is one hour.

Notations:

MK = Metakaolin

DTA =Differential Thermal Analysis

S.A.I = Strength Activity Index

References:

1. ASTM C618, "Standard Specification for Chemical Admixtures for Concrete", Annual Book of ASTM Standards, V. 04.02, 1989, pp. 291-293.
2. Justice, J. M., " Evalution Of Metakaolin For Use As Supplementary Cementitious Materials ", MSc. Thesis, Georgia Institute of Technology, April, 2005, www.Google.com.
3. كريم، حسين حميد، خالد أحمد، هشام " مواصفات المواد الخام المستخدمة في الصناعات الإنشائية " ، الجامعة التكنولوجية، أب، ٢٠٠١ .
4. Rayan, W. "Properties of Ceramic Raw Materials", Pergamum Ltd., Second Edition, 1978, p. 113.
5. Sayamipuk, S. and Nimityongskul, P., "Strength and Durability of Mortar Containing Metakaolin from Thailand", WWW.Google.Com, 2000, p. 7.
6. Advanced Cement Technology, LCC, "High Reactivity Metakaolin (HRM) Engineered Mineral Admixture for Use with Portland Cement", WWW.Sales@Metakaolin.Com, 2002, p. 5.

7. Chakravorty, A.K. and Ghosh, D.K., “Kaolinite-Mullite Reaction Series: The Development and Significance of a Binary Aluminosilicate Phase”, J.Am.Ceram.Soc., V. 74, No. 6, January 1991, pp. 1401-1406.
8. الشركة العامة للمسح الجيولوجي و التعدين .
9. ASTM C204-84, “Standard Test Method for Fineness of Portland Cement by Air Permeability Apparatus”, Annual Book of ASTM Standards, V. 04.01, 1989, pp. 157-162.
10. B.S.12: Part 2, “Method for Determination of Setting Time and Soundness”, British Standards Institution, 1971.
11. ASTM C311-٠٢, “Standard Test Method for Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland Cement Concrete”, Annual Book of ASTM Standards, V. 04.02, ٢٠٠٢.
12. Lea, F.M, “The Chemistry of Cement and Concrete”, Third Edition, London, 1976, p. 727.
13. Mehta, P.K., “Concrete Structure, Properties and Materials”, Prentice-Hall, Inc., New Jersy, 1986, p. 450.