"EVALUATION OF METAKAOLIN FOR USE AS SUPPLEMENTARY CEMENTITIOUS MATERIAL"

,,تقييم الميتاكاؤلين لاستخدامه كمادة اسمنتية مضافة ،،

Dr. Ghalib M. Habeeb
Assist Prof.

Dr. Mahdi S. Essa
Assist Prof.

College of Eng.\ Babylon University

Esam M. Ali
M.Sc

Abstract

Three types of metakaolin were evaluated for use as supplementary cementitious materials in cement-based systems. The metakaolins were calcined at 745± 2 °C for three duration periods, (1/2, 1.0 and 1.5) hrs respectively. The water-to-cementitous ratio used was 0.40.

In this study, the early age properties of fresh self-compacting concrete and the mechanical properties of hardened concrete were examined. Early age evaluations aimed to determine the reactivity of metakaolin and its effect on mixture workability (slump-flow, T50, L-box, U-box and V-funnel). Compressive, tensile and flexural strengths and elastic modulus were measured at various concrete ages. Further more, two non-destructive test methods, ultra-sonic pulse velocity and Schmidt rebound hammer test were used at 7, 28 and 90 days. The results obtained from this study indicated that when the time of calcining metakaolin increased from (0.5 to 1.0) hrs and (0.5 to 1.5) hrs the compressive strength increased by (5-12) %, (12-18) %, (3-9) %, (16-21) %, (4-7) % and (12-16) % at 7,28 and 90 days respectively. Specimens in flexure, splitting, static modulus of elasticity, U.P.V and rebound number show similar behavior to those in compression.

الخلاصة:

ثلاث انواع من الميتاكاؤلين تم تقييمها للاستخدام كمواد اسمنتية مضافة الى منظومة عجينة الاسمنت. تم حرق الانواع الثلاثة بدرجة 745±2 °ملثلاث فترات تعرض مختلفة هي (2/1 ,1, 1.5) ساعة على التوالي. كانت نسبة الماء إلى المواد الإسمنتية المستخدمة في هذه الدراسة بمقدار 40 %. في هذه الدراسة تم فحص الخواص الطرية في الاعمار الاولى والخواص المتصلبة للخرسانة ذاتية الرص. تقييم الاعمار الاولى يهدف الى قياس فعالية هذه الاطيان(حرارة الاماهة) وتاثيرها على قابلية تشغيل الخلطة الخرسانية باستخدام فحص الانسياب, زمن الانسياب, الصندوق على شكل حرف L, الصندوق على شكل حرف U, القمع على شكل حرف V بينما تم فحص مقاومة الانضغاط, مقاومة الانشطار, مقاومة الانثناء ومعامل المرونة الثابت باعمار مختلفة بالاضافة الى طريقتان لا اتلافيتان هما: الموجات فوق الصوتية ورقم ارتداد المطرقة باعمار7 ،28 و 90 يوما على التوالي. لقد أثبتت النتائج المستحصلة من هذه الدراسة بأن زيادة فترة الحرق من 2/1 سا الى 1 سا ومن 2/1 سا الى 1.5 سا ستزداد مقاومة الانضغاط بمقدار (5-12) %,(12-18)%, (3-9)%,(16-21)%,(4-7)% و (12-16)% بعمر 7, 28 و90 يوما على التوالي. نماذج في حالة الانثناء, الانشطار, معامل المرونة الثابت, سرعة الموجات فوق الصوتية ورقم الارتداد تسلك نفس سلوك نماذج تحت الانضغاط.

Introduction:

The term kaolin is derived from the name of the Chinese town *Kao-ling*, which translates loosely to "high ridge" and is home to the mountain that yielded the first kaolins to be sent to Europe [High Reactivity Metakaolin: Engineered Mineral Admixture for Use with Portland cement, 2004]. The first documented use of MK was in 1962, when it was incorporated in the concrete used in the Jupia Dam in Brazil. It has been commercially available since the mid-1990s and currently costs approximately $500/ton [Zhang, 2004]. MK typically contains 50-55% SiO_2 and 40-45% Al_2O_3 [Poon, 2001]. Other oxides present in small amounts include Fe_2O_3, TiO_2, CaO, and MgO. MK is an amorphous pozzolan, with some latent hydraulic properties, that is well-suited for use as an SCM [Bensted, 2002].

Supplementary cementitious materials (SCMs) are finely ground solid materials that 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. In addition to their positive environmental impact, SCMs may improve concrete workability, mechanical properties, and durability. SCMs may possess pozzolanic or latent hydraulic reactivity or a combination of those. The term pozzolan refers to a silecious material, which, in finely divided form and in the presence of water, will react chemically with calcium hydroxide ($Ca(OH)_2$) to form cementitious compounds [Mindess, 2003; Sabir, 2001].

Metakaolin (MK) is an SCM that conforms to ASTM C 618-92, 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 [Brooks, 2001; Ding, 2002]. As such, a much higher degree of purity and pozzolanic reactivity can be obtained. MK has great promise as an SCM, as it can improve many properties of concrete while also reducing cement consumption.

The calcining temperature plays a central role in the reactivity of the resulting MK product. [Ambroise *et al]* studied the effects of calcining temperature on the strength development of MK-lime pastes. These authors found 700 °C to be optimal and later showed that calcination below this temperature results in a less reactive material containing more residual kaolinite. Above 850 °C, they reported, recrystallization began and reactivity declined, as kaolin had begun to convert to relatively inert ceramic materials, such as spinel, silica, and mullite [Bensted, 2002]. The heating process, illustrated by differential thermal analysis (DTA), is shown in Figure (1).

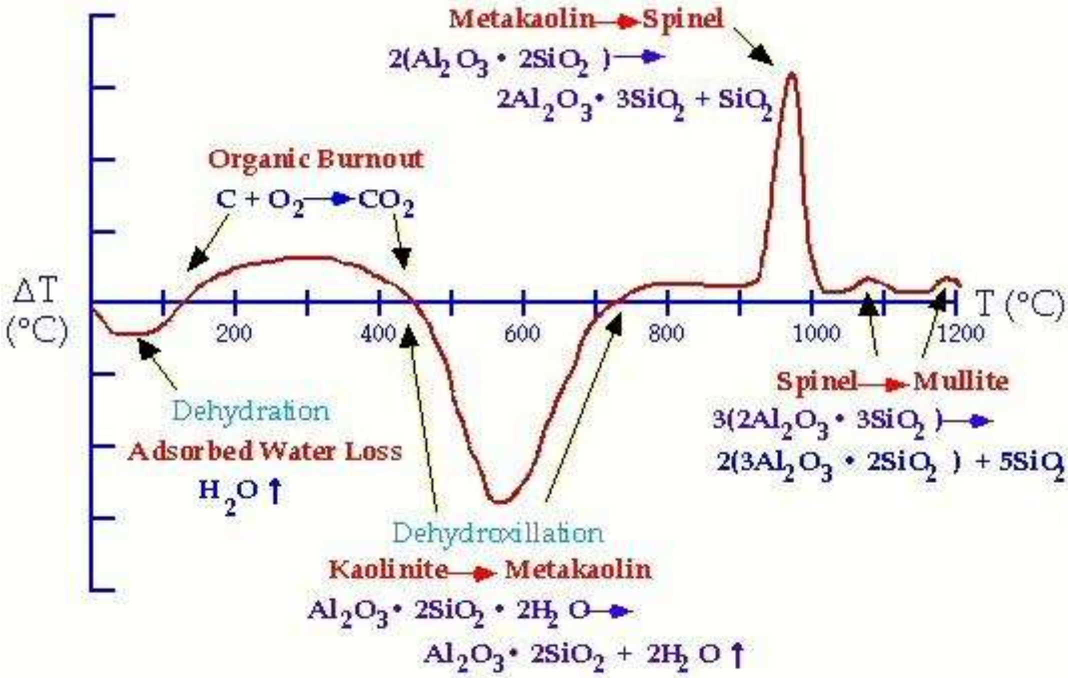


Figure (1): DTA thermogram of kaolin [DTA and TGA of Ball Clay and Kaolin, 2004] [10].

Research significance:

The calcining period plays a central role in the reactivity of the resulting MK product. The main purpose for this research is to evaluate the effect of time of calcining metakaolin on some of the mechanical properties of SCC. The investigated properties were 7, 28 and 90 days compressive strength, splitting tensile strength, flexural strength, static modulus of elasticity, Schmidt rebound hammer test and Ultra-sonic Pulse Velocity (U.P.V).

The objective of this research was to produce SCC having the desirable properties in the fresh state to satisfy the SCC requirements by combining flow properties of matrix in fresh state, while preserving the strain hardening behavior.

The experimental program:

The compressive strength of concrete specimens was tested on 100 mm cubes; the splitting tensile strength was tested on cylinders with a diameter of 100 mm and a height of 200 mm, while 150 mm diameter and 300 mm height of cylinder specimens were tested for the modulus of elasticity, the flexural strength was tested on prisms of (100*100*400) mm for three types of metakaolin SCC mixes, namely **SI, SII**, and **SIII**. The proportions of concrete mixes are summarized in Table (1).

Table (1): Mix proportions (Kg/m^3).

Mix Notation	Cement (kg/m^3)	Filler (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)	w/p (%)	SP by wt of cement (%)
S	400	80	912	760	40	4

Materials:

1. Cement

Ordinary Portland Cement (O.P.C.) manufactured by the new cement plant of Kufa was used throughout this investigation. This cement complied with the Iraqi specification No.5/1984. The chemical composition and physical properties are presented in Tables (2) and (3).

Table (2): Chemical composition of the cement.

Oxide	**%**	**IQS No.5:1984**
CaO	60.79	
SiO_2	20.75	
Al_2O_3	6.20	
Fe_2O_3	3.00	
MgO	4.11	$\leq$5.0
SO_3	2.32	$\leq$2.8
Free lime	0.51	
L.O.I	2.00	$\leq$4.0
Compound Composition	**%**	**IQS No.5:1984**
C_3S	37.26	
C_2S	31.39	
C_3A	11.35	
C_4AF	9.12	
L.S.F	0.88	0.66-1.02

Table (3): Physical properties of cement.

Physical properties	Test results	IQS No.5:1984
Fineness, Blaine,cm^2/gm Setting time, Vicat method Initial; hrs: min Final ; hrs: min	3124 1:45 3:46	≥ 2300 ≥ 0.45 ≤ 10:00
Compressive strength MPa 3 days 7 days 28 days	 20 27 33	 ≥ 15 ≥ 23

2. Fine Aggregate

Natural sand from AL-Akaidur region was used. The physical and chemical properties of the sand are listed in Table (4). Its grading conformed to the IQS No .45/ 1984 zone three.

Table (4): Properties of fine aggregate.

Sieve size (mm)	Passing %	IQS No.45/1984 Limitations
10.00	100	100
5.00	100	89-100
2.36	94	60-100
1.18	84	30-100
0.60	66	15-100
0.30	37	5-70
0.15	3	0-15
Properties	**Results**	**IQS No.45/1984**
$S0_3$ %	0.432	≤ 0.5
Clay %	2.3	≤ 3.0
Specific gravity	2.65	
Absorption %	1.6	

3. Coarse Aggregate

The coarse aggregate was AL-Nibaee gravel with a maximum size of 20 mm was used. The coarse aggregate used in this research is complying with IQS No.45/1984 as shown in Table (5). The friction between the aggregate limits the spreading and the filling ability of SCC.

Table (5): Properties of coarse aggregate.

Sieve size In (mm)	**Passing %**	**IQS No.45/1984 Limitations**
40	100	100
20	100	100
14	97	90-100
10	84	50-85
5	6	0-10
pan	0	0
Properties	**Results**	**IQS No.45/1984**
Sulphate content SO_3 %	0.0799	≤ 0.1
Clay %	0.6	≤ 1.0
Specific gravity	2.64	
Absorption %	0.7	

4. Super-plasticizer

To achieve high workability needed to produce SCC, super-plasticizers (high range water reducers) were used. A super-plasticizer known as Ura-plast SF was used in producing SCC. According to ASTM C 494-92, this SP is classified as type F and G, because it has the capability of more than 12% water reduction for a given consistency and it has a retarding effect on the SCC. The typical properties of SP are shown in Table (6).

Table (6): Properties of Super Plasticizer.

Main Action	**Concrete Super-plasticizer**
Subsidiary effect	Hardening retarder
Form	Viscous liquid
Color	Dark brown
Relative density	1.1 at 20 ^{0}C
Viscosity	128+/-30 cps at 20 ^{0}C
pH value	6.6
Transport	not classified as dangerous

5. Metakaolin

Metakaolin is a highly pozzolanic material produced by calcining the clay, using an oven at temperatures of (745± 2) ^{0}C. The particle size should not be more than 0.125 mm in order to achieve high workability and reactivity when added as a part of cement weight.

To evaluate the time of calcining metakaolin on mechanical properties of SCC, three types of metakaolin namely, “type I, type II and type III”, were used to enhance the workability of concrete. Type I was calcined for ½ hr, type II was calcined for 1.0 hr and type III was calcined for 1.5 hrs at the same temperature (745± 2) ^{0}C for all three types. All types shall conform to BS 8500-2, 4.4. The chemical composition of kaolin and the three types of metakaolin are shown in Table (7).

Table (7): Chemical composition of kaolin and metakaolin.

Oxide	Kaolin	Metakaolin Type I	Metakaolin Type II	Metakaolin Type III
SiO_2	57.27	68.84	71.88	74.00
Fe_2O_3	1.12	3.52	4.08	4.80
Al_2O_3	13.83	12.74	9.96	7.78
CaO	10.0	6.14	5.93	5.44
MgO	6.5	6.16	5.78	4.45
SO_3	1.32	0.86	1.02	1.28
L.O.I	14.06	1.40	1.29	1.27

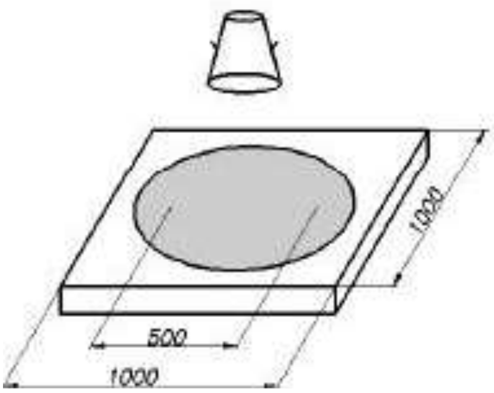
Test Procedures:

1. Fresh Tests

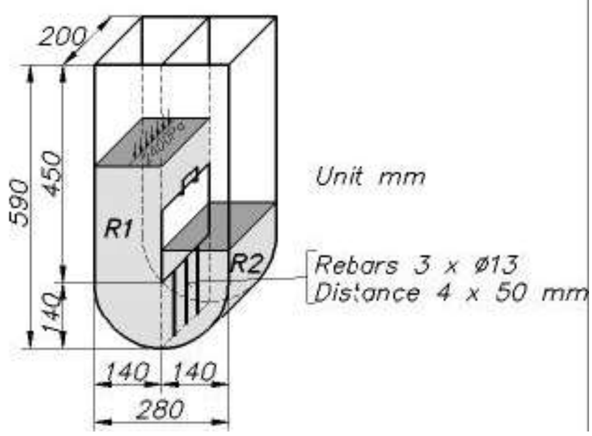
The workability of SCC is higher than the higest class of consistence described within EN 206 and can be characterized by the following properties:

•filling ability. •passing ability. •segregation resistance.

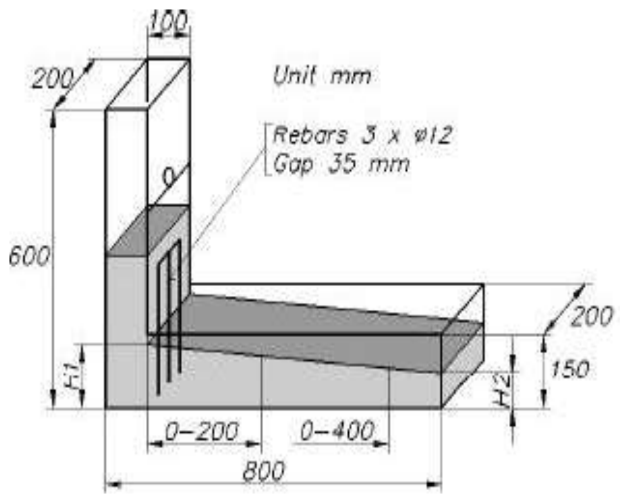
In order to evaluate the filling ability, passing ability and segregation resistance of the fresh concrete, slump-flow, T50 cm, U-box, L-box and V-funnel tests, as shown in Figure (2), were done according to EN 12350-05.



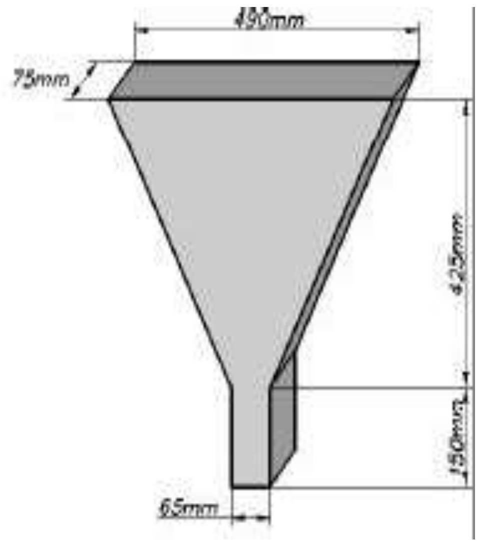
a. Slump-flow and T50.



b. U-box test.



c. L-box test.



d. V-funnel test.

Figure (2): Fresh concrete tests [13].

2. Hardened Tests

Compressive strength was carried out and tested according to BS 1881: part 116:1983. A total number of 36 cubes of 100 mm were tested by using a hydraulic compression machine of 2000 KN. All specimens were cured in water until testing age to investigate the effect of time of calcining metakaolin on mechanical properties of SCC. Each result of compressive strength obtained is the average for three specimens.

The splitting tensile strength was determined according to the procedure outlined in BS 1881: part 117: 1983. A total number of 24 cylinders (100*200) mm were tested. Cylinders were cast, demolded and cured in a similar way as the cubes. Each splitting tensile strength result was the average of strength for tow specimens.

Concrete prisms of dimensions (100*100*400) mm were cast according to BS 5328:4:1990 procedure. A total number of 24 prisms were tested. The prisms were cast, demolded and cured in a similar manner as the cubes. Modulus of rupture test according to BS 1881:118:1983 were performed using two-point load test.

The static modulus of elasticity was determined according to BS 1881:121:1983 specifications. A total number of 8 cylinders (150*300) mm were tested. A hydraulic compression machine of 2000 kN is used to apply a compression load until 40 % of the ultimate load. The proving rings used which have a gauge length of 200 mm and gauge with an accuracy of 0.01 mm, is made according to BS 1881:124:1988. The recorded results were the average of readings for tow cylinders.

Schmidt hammers were used to estimate the surface hardness of concrete specimens by recording the rebound number, which could be used as a measure of the concrete strength and percentage of voids. The test method is prescribed by BS 1881:202:1986 specifications.

This test is carried out according to BS 1881: part 203:1986, using the portable ultra-sonic non-destructive digital indicating tester (PUNDIT) to determine wave velocity in concrete specimens.

Results and discussion:

1.Fresh concrete

The results of the experimental work of this research are listed in Table (8), and figures (3) to (8). The properties of fresh concrete are presented in Table (8). These results show that the SCC used is complying with the requirements of SCC and is found to have a good consistency and workability at fresh state.

2.Compressive strength

Concrete cubes of 100 mm were tested at ages of 7, 28 and 90 days. Each value of tests results is the average of three specimens. Figure (3) shows that increasing the time of calcining metakaolin from (0.5 to 1.0) hr and (0.5 to 1.5) hrs leads to increase the compressive strength by (5-12) %, (12-18) %, (3-9) %, (16-21) %, (4-7) % and (12-16) % at 7,28 and 90 days respectively. This behavior can be explained by the densifing effect of metakaolin with a decrease in the porosity at early ages, while at later ages, in addition to the densifying effect of metakaolin by firing, a pozzolanic reaction with calicum hydroxide released from cement hydration and the filling effect in the voids among cement and other powder particles enhance the strength of concrete.

3.Splitting tensile strength

The results shown in Figure (4) shows that, when the time of calcining metakaolin increases from (0.5 to 1.0) hr and (0.5 to 1.5) hrs there is an increase in the splitting tensile strength by (5-10) %, (2-5) %, (6-16) %, (3-10) %, (8-10) % and (3-7) % at 7, 28 and 90 days respectively. At early ages, the higher splitting tensile strength is due to the better microstructure of the SCC, especially the smaller total porosity and more pore size distribution within the interfacial transition zone. While, at late ages, a pozzolanic reaction occures with calicum hydroxide released from cement hydration and filling voids among and between cement particles.

4.Flexural strength

From the results shown in Figure (5) it can be seen that increasing the time of calcining metakaolin from (0.5 to 1.0) hr and (0.5 to 1.5) hrs leads to increase the flexural strength by (8-19) %, (20-34) %, (14-24) %, (26-37) %, (22-31) % and (33-39) % at 7, 28 and 90 days respectively. This is caused by the better microstructure of the SCC, especially the smaller total porosity and the better pores distribution within the interfacial transition zone at early ages when increasing the time of calcining metakaolin as it becomes more soft and viscous. At later ages (28 days and more), a pozzolanic reaction occures between pozzolana in metakaolin and calicum hydroxide $Ca(OH)_2$ released from cement hydration which fills voids among and between cement particles.

5.Static modulus f elasticity

Figure (6) shows the relationship between the time of calcining metakaolin and the static modulus of elasticity at 28-days. It can be seen that increasing the calcining time from (0.5 to 1.0) hr and (0.5 to 1.5) hrs results to increase the static modulus of elasticity by (1-4) % and (5-10) % respectively. This is due to both, increasing the softness of metakaolin by calcining at early ages and to the pozzolanic reaction at later ages.

6.Ultrasonic Pulse Velocity

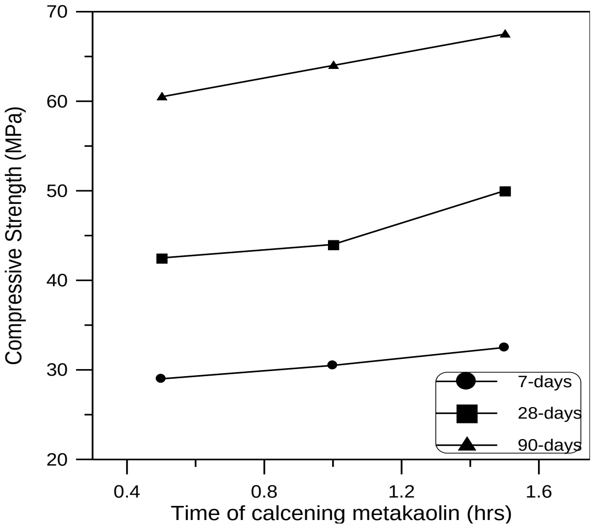
Figure (7) shows that increasing the time of calcining metakaolin from (0.5 to 1.0) hr and (0.5 to 1.5) hrs leads to increase the pulse velocity by (1-2) %, (1-4) %, (1-6) %, (3-8) %, (1-4) % and (2-6) % at 7, 28 and 90 days respectively. This is caused by the more softness of metakaolin by calcining at early ages, (to 7-days) and to the pozzolanic reaction with calicum hydroxidate at later ages (28 and more). It is clear that different types of filler help to improve the structure of the mortar aggregate interface, to get high density as that of the bulk mortar due to the continued hydration and dissolution of different filler particles and then increase the density of the SCC specimens.

7.Rebound number results

From the results shown in Figure (8) it is clear that increasing the time of calcining metakaolin from (0.5 to 1.0) hr and (0.5 to 1.5) hrs increases the rebound number by (6-9) %, (9-14) %, (5-9) %, (12-16) %, (5-6) % and (6-11) % at 7, 28 and 90 days respectively. This is due to the densifying effect of metakaolin which increses by increasing the duration of firing process on metakaolin at early ages, on the other hand, at later ages the pozzolanic reaction with calicum hydroxidate and filling effect of voids among and between cement particles. This trend is similar to what was detected by [Klaus H. et al] and [William D].

Table (8): Fresh concrete results.

Mix notation	Slump-flow (mm)	T50 Sec.	U_1-U_2 (cm)	H_2/H_1 (%)	V-time Sec.
Limitations	600-800	*2-5*	0-3	80-100	5-15
SI	680	3.8	0.6	83	9.5
SII	674	4.0	0.8	82	10
SIII	668	4.2	1.0	82	10.5



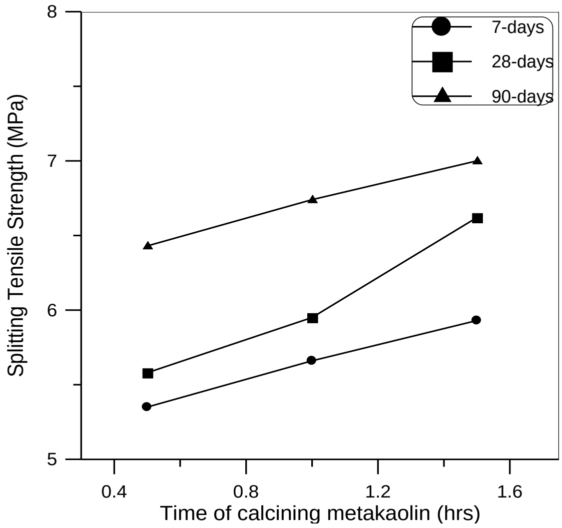
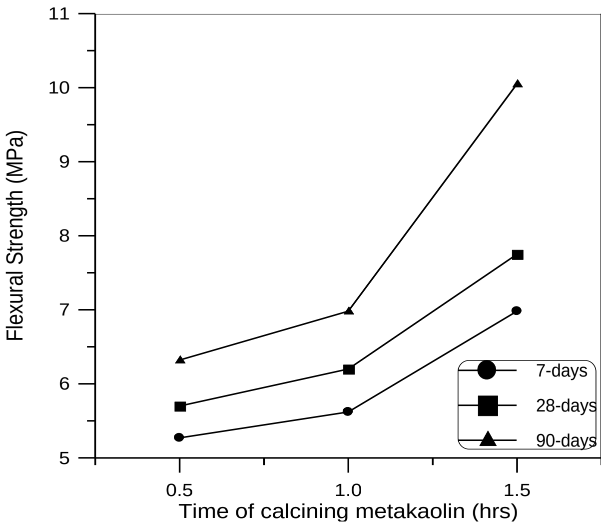


Figure (3): Effect of time of calcining metakaolin on compressive strength.

Figure (4): Effect of time of calcining metakaolin on splitting tensile strength.



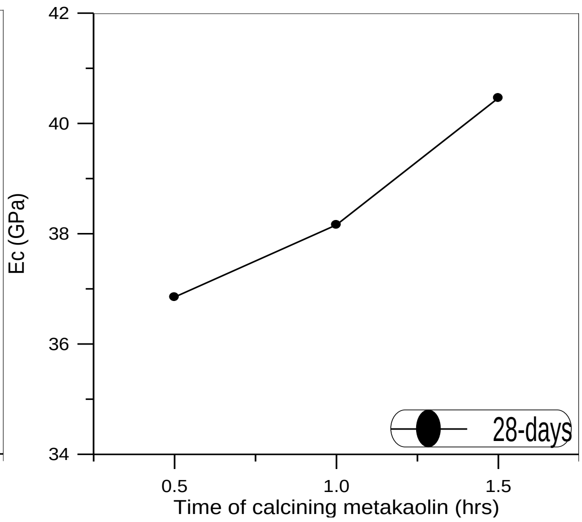


Figure (5): Effect of time of calcining metakaolin on flexural strength.

Figure (6): Effect of time of calcining metakaolin on Ec .

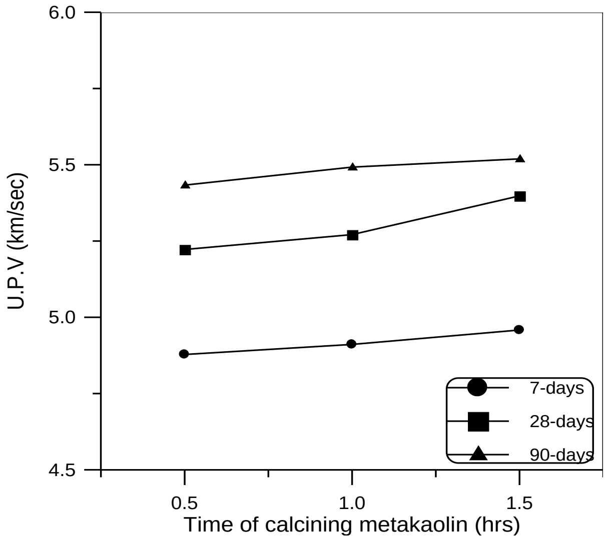


Figure (7): Effect of time of calcining metakaolin on U.P.V..

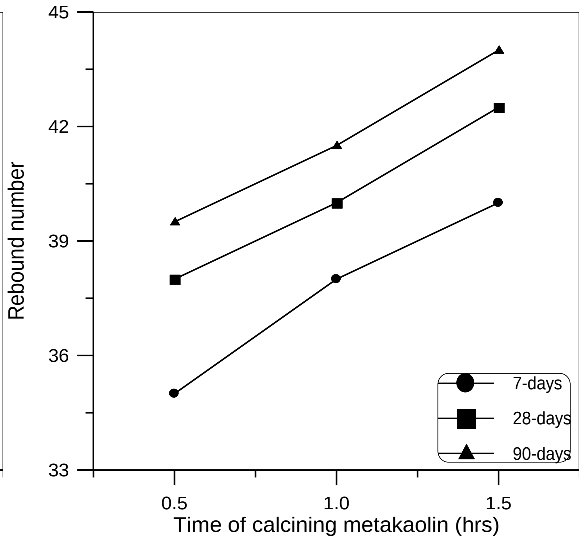


Figure (8): Effect of time of calcining metakaolin on rebound number.

Conclusions:

Based on the tests results of the present study the following conclusions can be drawn:-

1.When the time of calcining metakaolin increases from (0.5-1.5) hrs the slump-flow decreases insignificantly by (0.5-3) % while T50 cm increases by (3-27.5) %.

2.Increasing the time of calcining metakaolin from (0.5-1.5) hrs increases the compressive strength by (7, 14.3 and 10.6) % at 7, 28 and 90 days respectively.

3.Specimens in flexure, splitting, U.P.V and rebound number show similar behavior to those in compressive.

4.Increasing the time of calcining metakaolin from (0.5-1.5) hrs increases the Ec by (1-10) %.

References

1.High Reactivity Metakaolin: Engineered Mineral Admixture for Use with Portland Cement,AdvancedCementTechnologies,http://www.metakaolin.com/Operation%20 Description.htm, accessed September 2004.

2.Zhang, Z.Z., personal communication with J.M. Justice, September 2004.

3.Poon, C.S., Lam, L., Kou, S.C., Wong, Y.L. and Wong, R. (2001), Rate of pozzolanic reaction of metakaolin in high-performance cement pastes, *Cement and Concrete Research*, 31(9): 1301-1306.

4.Bensted, J. and Barnes, P. (2002), *Structure and Performance of Cements, 2nd ed.*, New York: Spon Press.

5.Mindess, S., Young, F.J. and Darwin, D. (2003), *Concrete, 2nd ed.*, Upper Saddle River: Prentice Hall .

6.Sabir, B.B., Wild, S. and Bai, J. (2001), Metakaolin and calcined clays as pozzolans for Concrete: a review, *Cement and Concrete Composites*, 23(6): 441-454.

7.Brooks, J.J. and Johari, M.A.M. (2001), Effect of metakaolin on creep and shrinkage of Concrete, *Cement and Concrete Composites*, 23(6): 495-502.

8.Ding, J.T. and Li, Z.J. (2002), Effects of metakaolin and silica fume on properties of concrete, *ACI Materials Journal*, 99(4): 393-398.

9.Ambroise, J., Murat, M., Pera, J. (1985), Hydration reaction and hardening of calcined clays and related minerals: V. Extension of the research and general conclusions, *Cement and Concrete Research*, 15: 261-268.

10. DTA and TGA of Ball Clay and Kaolin, http://cems. Alfred. Edu/ courses/ ces101 /firing/ tc.html, accessed November 2004.
11. Klaus H., and Yvette K.," A data Base for the Evaluation of Hardened properties of SCC", LACER Journal, No.7, 2002, pp.(123-134).
12. William D.," Materials Science and Engineering: An Introduction", The University of Utah, 5th Edition, 1999, pp.(381-443).
13. Ali M. E. "Effect of Type of Filler and Water to Powder Ratio on Some Mechanical Properties of Self-Compacting Concrete" M.Sc Thesis, Babylon University, 2006.