Effect of High Temperature on the Physico - Chemical Properties of Cement Pastes Containing SilicaFume

[1]Abtisam M. Bazzaqah ,[2]Wegdan S.Al_harwi
[1]Chemistry Department, Faculty of Health Sciences , University of Zawia , Libya
[2]Chemistry Department, Faculty of Sciences , University of Zawia , Libya

الملخص:
تعتبر صناعة الإسمنت إحدى الصناعات الكبرى والاستراتيجية في ليبيا وكذلك الحال في عديد من دول العالم وتتجه الدول إلي الاهتمام بهذه الصناعة نظرا لتوجهها لإنشاء وتوفير مزيد من فرص العمل والاستثمار وإنعاش حركة الاقتصاد ولكنها كأي صناعة أخري لها من الجوانب ما هو سلبي خاصة علي الصعيد البيئي عندما يكون هناك غازات وجسيمات دقيقة (غبار) تطرح كنواتج عرضية من عملية التصنيع أهمها ما يطلق عليه غبار السيليكا ولغرض الاستفادة من هذه المخلفات والنواتج العرضية وتحقيق مردود بيئي واقتصادي ، تناولت هذه الدراسة تأثيردرجات الحرارة العالية علي الخواص الفيزيوكيميائية للعجائن الاسمنت المحتوية علي غبار السيليكا. تم تحضير اسمنت بورتلاندي عادي مع غبار السيليكا بنسب (**0,10,20,30**)بالوزن . عرضت العينات إلى درجات الحرارة بنسب **200,400,600,800** لمدة ساعتين بعد المعالجة جميع العينات بالرطوبة لمدة 28 يوما تم دراسة بعض الخواص الفيزيوكيميائية للعجائن الاسمنت وذلك بقياس قوة تحمل الضغط الميكانيكي ومحتوي الماء المتحد وكذلك استخدام جهار حيود الأشعة السينية. أهم النتائج المتحصل عليها ان عجائن الاسمنت المخلوط المحتوي على نسبة 10% غبارالسيليكا أعطت اعلي قوة تحمل للضغط الميكانيكي واظهرت معظم المخاليط المحتوية علي غبار السيليكا مقاومة كبيرة للحرارة حتي **600** م^{0}

Abstract . This study aimed to investigate the effect of heat treatment on the physic-chemical Properties of cement pastes containing Silica fume SF. Portland cement(OPC) has been partially replaced by 10% and 20, 30 Wt% SF .After curing The hardened cement pastes were dried at 100C^{0} for 24 hours subjected to thermal treatment at the rate of 4C^{0}/min and heated at temperature of 200,400,600,800 for 2hours then cooled to room temperature in air. Finally, their combined water content, compressive strength value were determined X-ray diffraction (XRD) analysis. The results showed that the blended cement containing 10 % SF and 90 % OPC give the highest compressive

strength values and the highest resistance to heat treatment up to 600 ^{o}C.

1. Introduction

Portland cement is the most common type of cement in general usage. It is a basic ingredient of concrete, mortar and plaster. English masonry worker Joseph Aspdin patented Portland cement in 1824. It was so named because of the similarity of its color to Portland limestone, quarried from the English Island (Portland) and used extensively in London architecture. It is artificial hydraulic agglomerate produced by burning a mixture of limestone and clays at high temperature approximately 1450°C (***1)***.

The major components of Portland cement clinker are lime (CaO), silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3) which combine to form the four phases of Portland cement, tricalcium silicate (alite, C_3S), β- diacalcium silicate, (belite, β-C_2S), tricalcium aluminate, (C_3A), and tetracalcium aluminate ferrite, (C_4AF) ***(2)***. The properties of Portland cement are mainly controlled by the relative properties of C_3S, β-C_2S, C_3A, and C_4AF in the cement clinker. For instance, high resistance to sulphate attack is attributed to low content of C_3A ***(3)***.

Silica fume (SF) is composed of ultra-fine solid, amorphous glassy spheres of silicon dioxide (SiO_2) as a by-product of the manufacture of silicon or ferrosilicon SF particles were formed by oxidation and condensation of gaseous silicon suboxide (SiO) in reaction zone ***(4)***. Ferrosilicon is produced from quartz, coke and iron ore. Reaction of quartz at 2000°C, in the areas between electrodes submerged in the charge, results in the formation of silicon. Si and (SiO) vapors react with air to form SiO_2. Upon cooling SiO_2 fumes are condensed into very tiny spherical particles compose essentially of amorphous silica. Not all the silicon monoxide reacts with the carbon, some escape from the charge and rises to be burned in air. Small dusty amorphous SiO_2 particles of about 0.1 micron in size are formed and called silica fume. These are then blown out of the plant with the waste gases.

(5) stated that fire is one of the chemical processes stimulated by temperature in the particular phases of cement paste have a significant influence on the thermal deformations. Concrete subjected to elevated

temperatures may suffer loss in strength due to the development of micro cracks or phase transformations in the matrix. The prevailing mechanism depends on the type of aggregate as well as on the moisture content of concrete ***(6)*** studied the effect of firing temperature which varied from 100 to 600^{o}C for 3hrs on the phase composition and microstructure by DTA and SEM. The results show recrystallization and carbonation of $Ca(OH)_2$ as well as deformation of C-S-H and C_4AH_{13} phases. ***(7)*** studied the effect of high temperature on compressive and flexural strengths of ordinary and high-performance concrete. It was found that concrete strength decreases with temperature.

(8) was studied the effect of thermal treatment up to 800°C for three hours on the combined water content, compressive strength, phase composition and microstructure of the hardened Portland cement – silica fume pastes. Rehydration of the thermally treated cement pastes was carried out for various time intervals. Changes in the compressive strength, phase composition and microstructure upon rehydration of the thermally treated cement pastes were also investigated.

(9) studied the X-ray diffraction and DTA/TGA observation of the effect of elevated temperatures on the mineralogical changes occurring in the hydrated phases of concrete. It was found that, the changes in physical state of concrete were studied by measuring ultrasonic pulse velocity (UPV) and consequent deterioration in the compressive strength with temperature. SEM studies showed distinct morphological changes corresponding to deterioration of concrete exposed to higher temperatures ***(10)*** stated that high temperature may result in color changes along with significantly affecting the concrete's compressive strength, modulus of elasticity, concrete density and its appearance.

2. Materials and experimental program:

The materials used in this investigation were; ordinary Portland Cement (OPC) provided from Lafarge Cement Company, Egypt, Silica fume (SF) It is obtained from Ferro-Silicon Company, Egypt. Chemical compositions of the used Portland cement, SF are given in Table (1).

Table (1): Chemical Composition analysis of starting material (mass %).

Oxides (%)	Cement	Silica fume
SiO_2	20.14	99.80
Al_2O_3	4.72	0.20
Fe_2O_3	3.94	0.40
CaO	62.98	0.16
Na_2O	0.5	-
K_2O	0.27	0.03
Cl^-	0.04	-
MgO	1.77	0.09
SO_3	2.95	0.30
Ignition loss	0.91	-
Insoluble residue	1.50	-

Various cement mixes were prepared as shown in Table (2). The amount of OPC replaced by additives was 10, 20, 30 SF . The binder samples were manufactured in the moulds 20x20x20 mm. After curing, the samples were dried at 100°C for 24 hours and put into the furnace for heating to temperature levels of 200, 400, 600 ,800°C with a heating rate of not more than 4°C/min, then followed by constant heat process for 2 hours. After heating, the samples were cooled to room temperature and the volume compressive strength of binder were determined. and used the method of X-ray powder diffraction analysis (XRD)

Table (2): Mix composition, water/solid (w/s) and designations

Mix	**M_0**	**M_1**	**M_2**	**M_3**
OPC %	**100**	**90**	**80**	**70**
SF %	**-**	**10**	**20**	**30**
W/S(%)	**26**	**28**	**29**	**30**

3.Results and Discussion

3.1 Compressive strength

The results of compressive strength of the hardened OPC-SF blends hydrated for 28 days and heated for two hours at various temperatures are shown in Table (3) and also are represented graphically in Fig. (1).

All mixes show increase in the compressive strength on heating at 200^{o}C for 2 hours as a result of internal autocalving. This leads to accelerate the hydration process and hence more hydration products were formed. Therefore the compressive strength increases. On heating at 400^{o}C compressive strength values not change greatly. While as, on heating at higher temperature (600^{o}C) a significant decrease in the values of compressive strength for all samples can be observed. This can be attributed to the dehydration of the formed hydrates. At 800^{o}C a high drop in the values of compressive strength takes place for all samples. This is due to the high degree of dehydration at such high temperature. It can be noticed that most mixes have reasonable values of compressive strength at 600^{o}C. Mix M_1 which contains10% SF Shows relatively high values of compressive strength compared with the blank mix M_0.The mixes containing silica fume have higher values of compressive strength than the blank mix (M_0) after heating at 800^{o}C. This indicates that such mixes resist fire more than the blank.

Table (3): The compressive strength of OPC – SF blends with heating temperatures.

Mix. Temp °C	Compressive Strength Kg/cm^2				
	25°C	200°C	400°C	600°C	800°C
M0	350	367	370	363	126
M_1	365	380	390	335	150
M_2	310	377	387	334	190
M_3	300	390	395	280	158

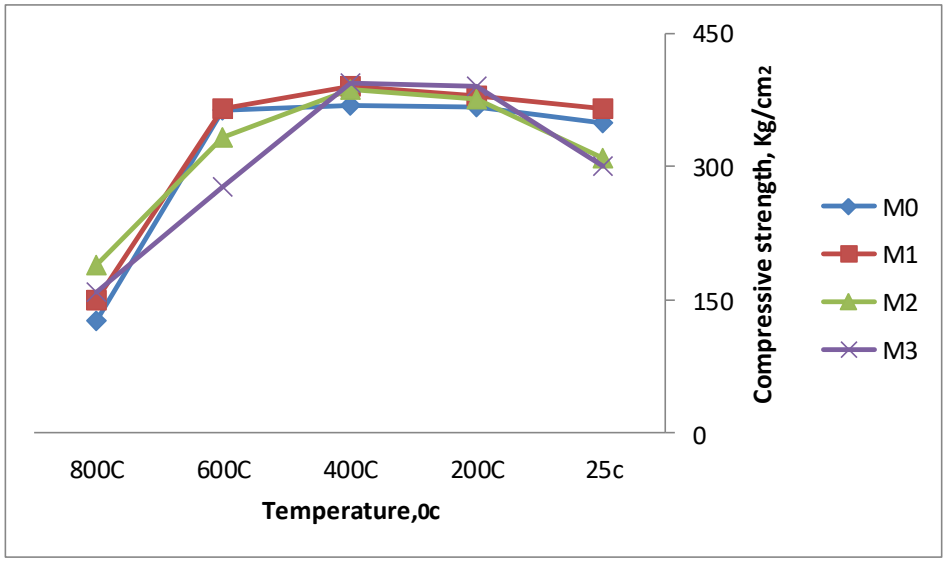

Fig. (1): Compressive strength of OPC-SF blends with heating temperatures.

3.2. Chemically combined water Wn% :

The change in the values of chemically combined water content of the hardened OPC-SF blends as a result of exposure to various temperature are given in Table (4). Also, these results are graphically represented din Fig. (2).

It can be noticed that the values of combined water content for all mixes increase by heating at 200^{o}C compared to those at 28 days. This is due to the increase of the degree of hydration as a result of internal autoclaving. A continuous decrease of the values of combined water can be noticed by increasing the temperature up to 800^{o}C. This can be attributed to the dehydration of the formed hydrates. Such results are in a good agreement with those of compressive strength.

Table (4): The combined water of OPC-SF blends with heating temperatures.

Mix. Temp °C	Combined Water Wn%				
	25°C	200°C	400°C	600°C	800°C
M0	16.22	19.19	12.63	6.81	3.50
M_1	16.31	18.52	11.88	6.88	5.72
M_2	15.30	19.76	11.96	5.32	3.32
M_3	14.22	18.74	12.72	6.41	2.70

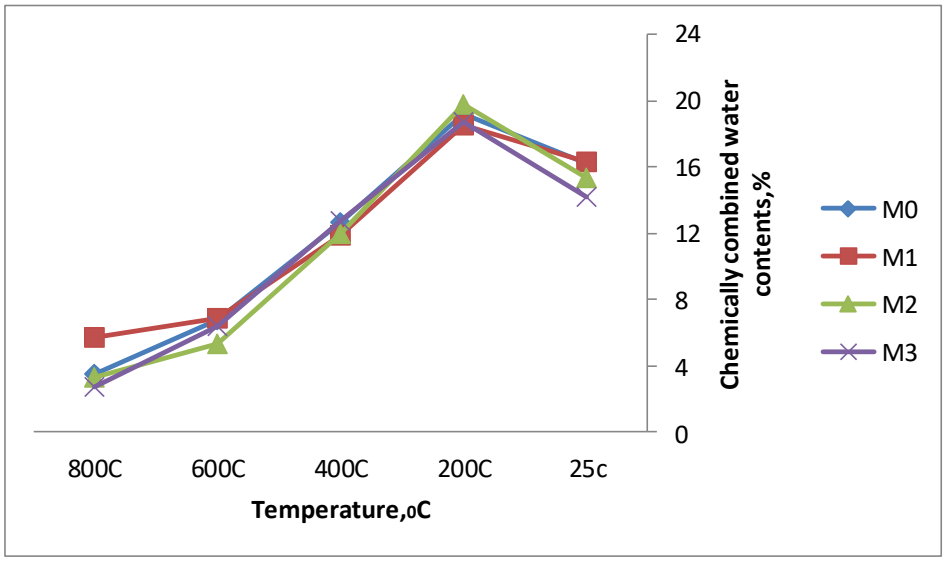

Fig. (2): Combined water of OPC –SF blends with heating temperatures.

3.3. X-ray diffraction analysis

The x-ray diffraction patterns of the hardened OPC-SF blends mixes M_1 and M_2 after heating at various temperatures are shown in Figs. (3, 4). It can be observed that the intensity of the peaks characteristic to CH decreases by heating at 400°C compared to that at 200°C. On

heating at 600 and 800^{o}C a nearly disappearance of the peaks of CH. This is due to dehydration process with rising temperature

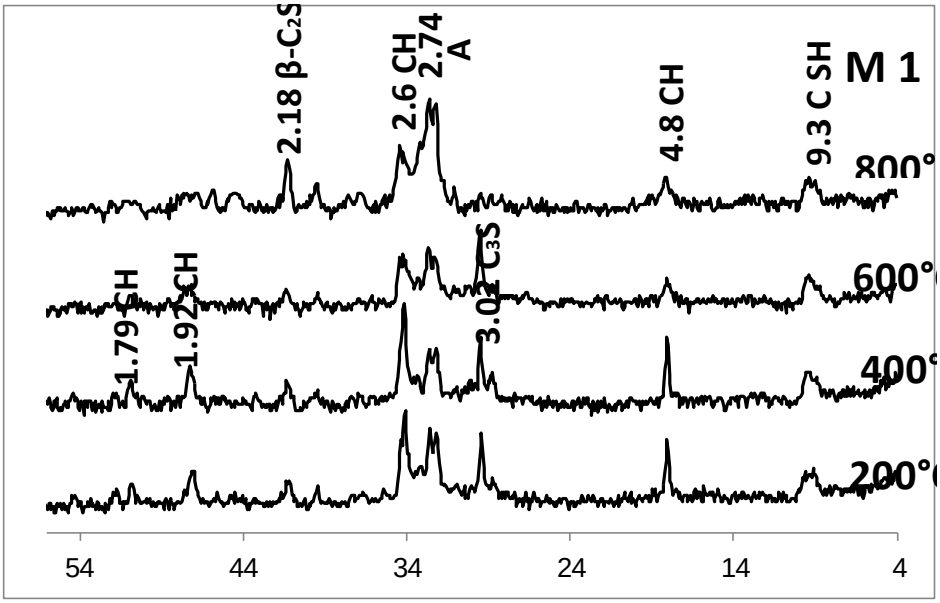

Fig. (3) :X-ray diffraction patterns of the mix. (90% OPC+ 10 % SF) at after 28day at

different temperature

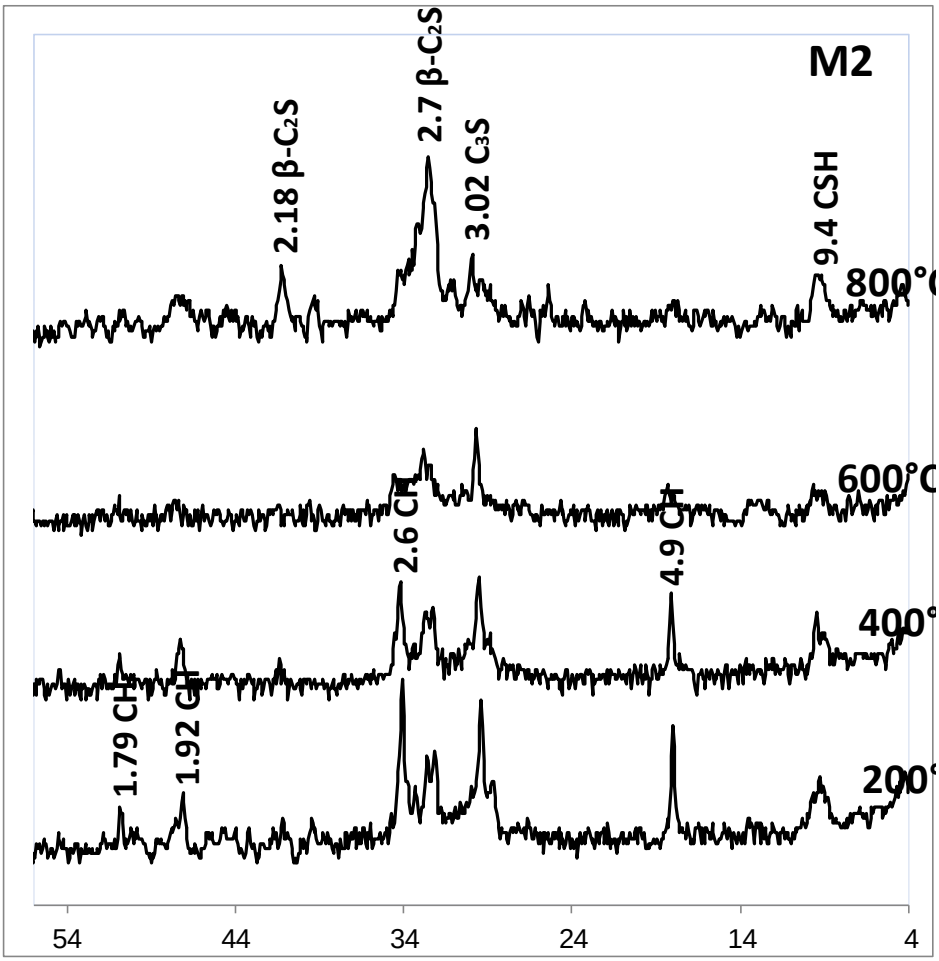

Fig. (4) :X-ray diffraction patterns of the mix. (80% OPC+ 20% SF) at after 28day at different temperature.

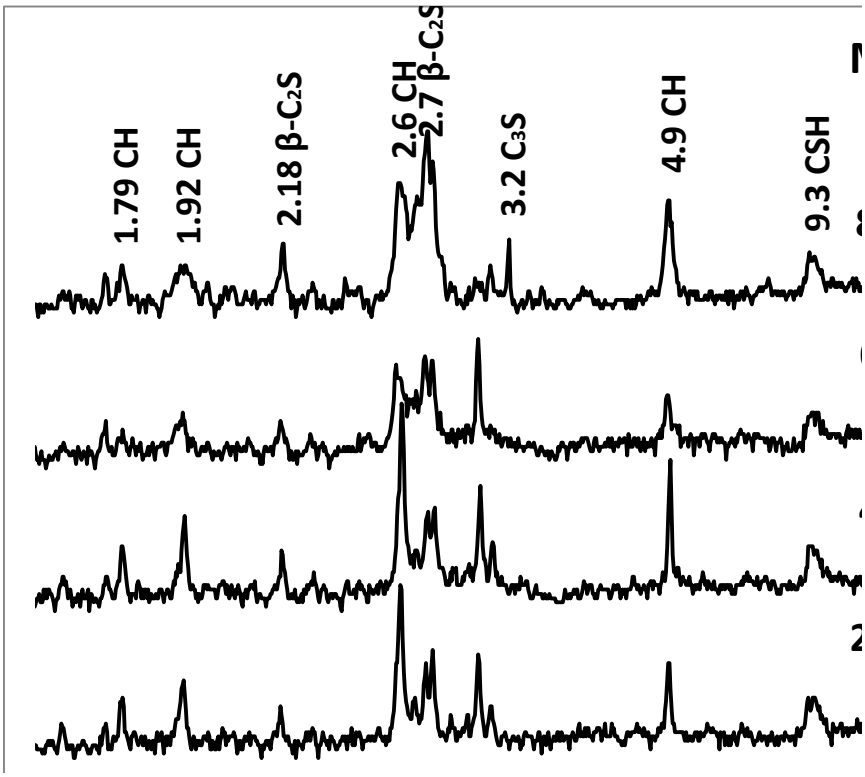

Figure (5) XRD pattern of hydration product formed after 28 day at different temp. of the Mix. (100% OPC).

4. Conclusions

Based on the empirical results, some conclusions are drawn as follows:

1. The mixes containing silica fume have higher values of compressive strength than the blank mix (M_0) after heating at 800^{o}C. This indicates that such mixes resist fire more than the blank.
2. A continuous decrease of the values of combined water can be noticed by increasing the temperature up to 800^{o}C.

3. The X-ray diffraction analysis results indicate that there is It can be observed that the intensity of the peaks characteristic to CH decreases by heating at 400^{o}C compared to that at 200^{o}C. On heating at 600 and 800^{o}C a nearly disappearance of the peaks of CH. This is due to dehydration process with rising temperature.

4. Mix M_1 which contains10% SF Shows relatively high values of compressive strength compared with the blank mix M_0**.**

5. Mix M_1containing 10 % SF give high resistance to heat tell 600 °C better than the blank (M0).

References:

1. **Varas ; M. J., Alvarez de Burgoo and fort; R., "**The origin and development of natural cements: the Spanish experience" Construction and Building Materials, Vol. 21, pp. 436 -445 (2007)

2. **Taylor; H .F .W., "**The chemistry of cement " Academic Press, Inc., London, Vol. II PP 88 (1990).

Taylor; H. F. W., "Cement Chemistry" , Academic Press Limited., London PP 195 (1990) .

3. **Shondeep; L. S., and Harsh; S., "**Mineral admixtare in cement and concrete" , 1st Ed. New Dalhi, Indian, Vol.4, PP. 91-102, (1993).

4. **Malhotra; V. M ., Ramachandran; V. S., Feldman; R. F., and Aitchin; P. C.,** "Condensed silica fume in concrete", C . R. C Press lnc . Boca Raton , Florida Chapter 9 , PP , 46 (1987**)**

5. **Kropp; J., Seeberger; J., and Hilsdorf; H.,** "Chemical and physical properties of cement paste and concrete after hydrothermal exposure", ACISP, Vol. 91 , PP 20 – 21 (1986).

6. **Morsy; M. S., Galal; A. F., and Abo-El-Enein; S. A.,** "Effect of temperature on phase composition and

microstructure of artificial pozzolana-cement pastes containing burnt kaolinite clay″,Cement and Concrete Research, Vol.28 PP 1157,(1998)

7. **Husem; M.,** ″The effects of high temperature on compressive and flexural strengths of ordinary and high - performance concrete″ , fire Safety journal , Vol. 41 PP 155-165,(2006)

8. **Hekal; E.E.,** ″Effect of silica fume on physico – chemical and mechanical properties of Hardened cement pastes :II- Dehydration – Rehydration of the Hardened cement pastes ″ proceedings of nineteenth international conference on cement microscopy, Cincinnati, Ohio, USA, April 27- May 1 (1997).

9. **Handoo; S.K., Agarwal; S., and Agarwal; S. k.,″** physicochemical, mineralogical, and morphological characteristics of concrete exposed to elevated temperatures ″, Cement and Concrete Research , Vol. 32 PP 1009-1018(2002)

10. **Morsy; M . S., Rashad; A. M. and EL – Mouhy; H. A.,** ″Effect of elevated temperature on physic – mechanical properties of met kaolin blended cement mortar″, structural Engineering and mechanics , Vol , 31 , PP,1-10 (2009)