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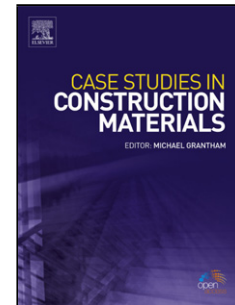
Title: Study of Heat of Hydration of Portland Cement Used in Iraq

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Study of Heat of Hydration of Portland Cement Used in Iraq

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Highlights:

1. heat of hydration was maximum in (COP-1) cement then (COP-2) and finally (COP-3) cement
2. Heat index were 93.6, 89.6 & 80.8 for (COP-1), (COP-2) and (COP-3) cement respectively.
3. heat of hydration were increase with increasing curing temperature.
4. heat of hydration was increase with increasing water to cement ratio.
5. The optimum heat of hydration was from (COP-1) cement.

Abstract

This study aims to obtain the heat generated from cement hydration, effect of chemical properties and curing temperature on heat of hydration.

Ordinary Portland cement used from different plants, which were north (COP-1), middle (COP-2) and south (COP-3) of Iraq. Two water to cement ratios (w\c) (0.4 & 0.6) and four levels of curing temperature (25°, 30°,40° and 50° Celsius) were used.

The experimental results showed that the optimum heat generation from hydration of cement was from (COP-1) cement, then (COP-2) cement and finally (COP-3) cement. Also the causes of variation were discussed.

Keywords: cement paste, heat of hydration, (COP-1), (COP-2) and (COP-3) cement.
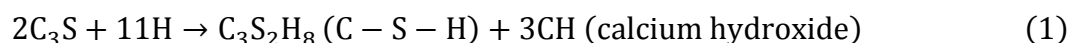
1. Introduction

When Portland cement is blended with water, heat will be generated. This heat is named the heat of hydration, and it is the product of the exothermic chemical reaction between cement and water.
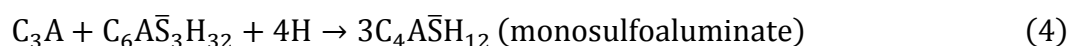
Ordinary Portland cement (OPC) is hydraulic cement and composed primarily of four kinds of minerals: "alite (C_3S), belite (C_2S), aluminate (C_3A), and aluminoferrite (C_4AF)". These four fundamental compounds specify the hydraulic characteristics of the cement because they assimilate for over 90 % of Portland cement (*Zhi Ge, 2005*).

Kim, 2010 stated that when these fundamental compounds and water are mixed together, hydration products will be produced. Calcium silicates are composed of (C_3S) and (C_2S). The two calcium silicates produce very analogous hydration reactions. Equations (1) and (2) depict the hydration reaction of calcium silicates. The fundamental hydration product are calcium silicate hydrate (C-S-H) and calcium hydroxide. C-S-H gel represents the role of a binder of the cement paste and ultimately has an influence on the strength and durability of concrete. C_2S and C_3S lead to produce a C-S-H gel of about 82 percent and 61 percent, sequentially. The

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maximum strength and durability of an elevated - C_2S cement would be greater than for one with an elevated proportion of C_3S.

$$2C_3S + 11H \rightarrow C_3S_2H_8 \ (C-S-H) + 3CH \ (\text{calcium hydroxide}) \tag{1}$$

$$2C_2S + 9H \rightarrow C_3S_2H_8 \ (C-S-H) + CH \ (\text{calcium hydroxide}) \tag{2}$$
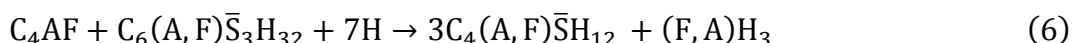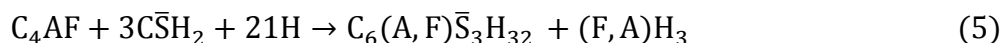
C_3A (tricalcium aluminate) interacts instantly with water. The swift hydration of C_3A can be delayed by the addition of gypsum. Therefore, the last hydration products alter with the gypsum quantity. The hydration outputs of C_3A are generally created ettringite in the headmost step and monosulfoaluminate posterior (Equation (3)). The deposition of ettringite shears in stiffening, setting, and early strength evolution. Ettringit becomes unsettled and is progressively transformed into monosulfoaluminate after the depletion of sulfate, (Equation (4)). monosulfoaluminate can mutate back to ettringite again if a new exporter of sulfate is added. C_3A (tricalcium aluminate) participates little to the strength of cement paste *(Kim, 2010)*

$$C_3A + 3C\overline{S}H_2 + 26H \rightarrow C_6A\overline{S}_3H_{32} \ (\text{ettringite}) \tag{3}$$

$$C_3A + C_6A\overline{S}_3H_{32} + 4H \rightarrow 3C_4A\overline{S}H_{12} \ (\text{monosulfoaluminate}) \tag{4}$$

The hydration of (C_3A) is identical to hydration products of tetracalcium aluminoferrite C_4AF, but the hydration reactions of C_3A are faster and include more heat.

Depending on the availability of gypsum, two possibility hydrates can be composed (Equations (5) and (6)).

$$C_4AF + 3C\overline{S}H_2 + 21H \rightarrow C_6(A,F)\overline{S}_3H_{32} + (F,A)H_3 \tag{5}$$

$$C_4AF + C_6(A,F)\overline{S}_3H_{32} + 7H \rightarrow 3C_4(A,F)\overline{S}H_{12} + (F,A)H_3 \tag{6}$$

($\overline{S}=SO_4$, $S=SiO_2$, $C=CaO$, $A=Al_2O_3$, $F=Fe_2O_3$, $H=H_2O$, $CH=Ca(OH)_2$)

Cement hydration is a robustly exothermal reaction that occurs in a number of phases *(Young 1985)*:

I. Speedy primary processes
II. Dormant (recumbent) period
III. Precipitation (acceleration) period
IV Delay (retardation) period
V. Long-range reactions

Mehta & Monteiro, 1993 stated that various parameters; namely, cement composition, fineness, temperature, and w/c ratio influence the heat of hydration of cement.

2. Materials and Methods

2-1: Cement

Three industrial Ordinary Portland Cement (OPC) (COP-1, COP-2, COP-3) according to (ASTM C150 Type 1) commercially available in Iraq market were tested for heat of hydration (HOH). These samples were carefully selected from three Iraqi regions and coded for this research as follow:

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Code:	Industrial Trade Name:	Region:
COP-1.	Cresta.	North of Iraq
COP-2.	Kufa	Middle of Iraq
COP-3.	Mabrouka.	South of Iraq

Test results indicated that the certified cement types were stratified to Iraqi specifications *(IQS No.5/ 1984)*.

The physical properties and chemical composition of these OPC were submitted in **Tables (2)** & **(1)** sequentially.

3. Experimental Set up

The heat of hydration of cement concerted in stratification with ASTM C 186, Standard Test Method for Heat of Hydration. The samples setup for effect of curing temperatures (25°, 30°, 40° and 50° C) , the samples were 500 gm constant weight with different water / cement ratio (40% & 60%). Each cement sample was tested in duplicate for heat of hydration up to 3 day and extrapolated for 7 days. High temperature rises had been observed with high water cement ratio mixture, **Table (3)** shows details of the reference mixes.

3.1 Apparatus and experimental procedure:

Calorimeter—The calorimeter, showed in Plate (1) consist of a 0.5-L (1-pt), wide-mouth vacuum jar, with cork stopper, or other suitable non-reactive stopper held in a suitably insulated container to keep the vacuum jar in position and to protect the jar from undue temperature fluctuations. The vacuum jar was coated on the interior with beeswax. As another means of protecting the vacuum jar, a plastic liner of suitable size were coated the interior of the jar.

Insulated Container—The container had an insulating layer of non-reactive fiber-glass, with 25 mm (1 in.) in thickness and encased the sides and bottom of the vacuum jar.

Thermometers—two thermometers were used Solution thermometer and Reference thermometer.

Funnel, Stirring Assembly, Storage, Mortar and Pestle, Drying Oven, maintained at 100 to 110 °C, Sieves, 150-μm (No. 100) and 850-μm (No. 20), Crucibles platinum 30-mL capacity with covers for loss on ignition determination, Muffle Furnace capable of maintaining a temperature of 900 to 950 °C, Analytical Balance and Analytical Weights, for weighing out calorimetric samples and for loss on ignition weighings.

A nicrome-wire coil, of 15 ohms resistance, connected through a variable resistance to a 220-volt alternating current line, provided the means of heating the water in the calorimeter jacket.

Mixer—a moderate-speed mechanical mixer (milk-shake type stirrer) capable of intimately mixing the cement and water to a uniform paste were used in this study.

3.2 Sampling and Test Specimens:

Preparation of Cement Paste—the cement and the mixing water were stored in a constant temperature room at 23.0 ± 2.0 °C (73.5 ± 3.5 °F) until the materials were at ambient temperature before preparation of the paste. The 150 g of cement and 60 mL of distilled water were mixed by means of a spatula, and then the mixture were vigorously stirred with a mechanical stirrer for 5 min. Approximately equal

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representative portions of the paste were placed in four or more plastic vials, the vials were filling to within about 13 mm (1⁄2 in.) of the top. Immediately after filling the vials, they closed with tight-fitting stoppers. The vials were stored in an upright position in a water bath at 23 ± 2.0 °C until the time of test.

Preparation of Partially Hydrated Sample—At the specified age of test, a vial of the partially hydrated sample was removed from storage and, during a 20-min initial stirring period of the calorimeter, the plastic was broken away from the sample and the entire sample were rapidly crushed with a mortar and pestle so that all the material were passed through a 850-μm (No. 20) sieve; then the sample were quickly placed in a well-stoppered weighing bottle.

3.3 Calibration:

Observations of the temperature differential between the liquid in the calorimeter vessel and the water in the surrounding jacket were made by means of a calibrated five-junction copper-constant differential thermoelement connected to a galvanometer with scale. The thermoelement junctions were placed in a 0.5-cm glass tube, sealed at one end, the tubes then filled with paraffin, one tube immersed in the liquid of the calorimeter vessel and the other tube in the water reservoir of the jacket. When the jacket temperature became too low, as indicated by the reading on the galvanometer scale, heat could be supplied by means of the heating coil in the jacket. If the jacket temperature became too high, cold water could be added to the jacket to bring about the necessary temperature drop.

3.4 Determination of Heat Capacity of Apparatus:

The heat-capacity experiments were carried out in the following manner: The apparatus was assembled, the stirrers set in operation, and the temperature of the calorimeter vessel and the jacket adjusted to the same initial value of 23 ± 2° C. After equilibrium was established, observations of the calorimeter temperature were made in a 20 -minute "fore" period. After an initial stirring period of at least 20 min to allow the temperature of the system to become uniform, the temperature was recorded and then the prepared cement was immediately introduced through the funnel at a uniform rate. The temperature at 20 min and again at 40 min after beginning the introduction of the sample was recorded. The temperature rise in the first 20 min was including temperature rise due to the heat of solution of the sample and any heat gain or heat loss to the environment. This called the solution period. The temperature change during the second -20min period was due to heat loss or gain to or from the environment. It was used to correct the temperature rise in the solution period to give the actual heat of solution of the sample. The second 20-min period is called the correction period.

The corrected temperature rise was calculated as follows:

$$R_0 = \emptyset_{20} - \emptyset_0 \dots\dots\dots\dots\dots (7)$$
$$R = R_0 - (\emptyset_{40} - \emptyset_{20}) \dots\dots\dots\dots\dots (8)$$

Where:

R_0 = observed temperature rise, °C

$\emptyset_{20}$ = calorimeter temperature at the end of the solution period

$\emptyset_0$ = calorimeter temperature when sample was introduced

R = corrected temperature rise, °C

$\emptyset_{40}$ = calorimeter temperature at the end of the correction period.

The heat capacity of the calorimeter and contents was calculated as follows:

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$$C = \frac{W[1072+0.4(30-t)+0.5(T-t)]}{R} \dots\dots\dots\dots (9)$$

Where:

C = heat capacity, kJ/°C

W = mass of cement, g

t = final temperature of the calorimeter, °C (ø20 plus temperature, °C, at which the Beckmann thermometer reading is zero.

T = temperature of the cement (room temperature), °C, when introduced into the calorimeter

R = corrected temperature rise, °C.

3.5 Procedure

Calorimetric Procedure, Dry Cement—the heat of solution of the dry cement sample was determined according to the procedure described for the heat capacity determination.

Calorimetric Procedure, Partially Hydrated Sample— for the heat of solution of the partially hydrated sample followed the same procedure as for the dry cement but it was used a 4.18 -g calorimetric sample of the partially hydrated cement.

Loss on Ignition:

Portland cement—immediately before and after the calorimetric sample was being weighed out, a sample of similar amount was weighted into a platinum crucible for determination of loss on ignition, the used value was the average of the two determinations. The dry cement was ignited at 950 °C for 1 1⁄2 h. the crucible containing the sample was immediately placed in a desiccator and allowed to cool at room temperature; then the crucible quickly weighed. When determining the loss on ignition of the hydrated cement, first the weighed sample was dried in an oven at 100 to 110 °C for 1 h; then the sample placed in a muffle furnace at 950 6 50 °C overnight. The mass of the cement sample was reduced which was introduced into the calorimeter to the ignited mass basis for use in the final calculations as follows:

$$W_i = \left(\frac{A}{B}\right) W \dots\dots\dots\dots (10)$$

Where:

W_i= mass of calorimetric sample, on ignited basis, g

A = mass of ignited sample, g

B = mass of sample before ignition, g

W = mass of calorimetric sample, g.

The heat of solution of the dry cement was calculated as follows:

$$H_1 = \left(\frac{RC}{W_i}\right) - 0.8(T - t_d) \dots\dots\dots\dots (11)$$

Where:

H_1 = heat of solution of dry cement, kJ/kg

R = corrected temperature rise, °C

C = heat capacity, kJ/°C

W_i = mass of sample on ignited basis, g

T = room temperature, when sample is introduced, °C,

t_d = final calorimeter temperature at end of determination on dry cement, °C.

The heat of solution of the partially hydrated sample was calculated as follows:

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$$H_2 = \left(\frac{RC}{W_i}\right) - 1.7(T - t_h) - 1.3(t_d - t_h) \ldots\ldots\ldots\ldots\ldots (12)$$

Where:

H_2 = heat of solution of partially hydrated sample, kJ/kg

R, C, W_i, and T = the same definition above except that they related to the partially hydrated sample

t_d = the same numerical value as definition above.

t_h = final calorimeter temperature at end of determination on partially hydrated sample, °C.

The heat of hydration of the cement was calculated to the nearest kilojoule, as follows

$$H = H_1 - H_2 - 0.4(t_h - 25) \ldots\ldots\ldots\ldots\ldots (13)$$

Where:

H = heat of hydration of ignited cement, kJ/kg.

H_1 = heat of solution of dry cement.

H_2 = heat of solution of partially hydrated sample.

t_h = the same numerical value definition above.

4. Result and Discussion

Figures (1), (3), (5) & (7) show the heat flow with time at 0.4 water cement ratio and curing temperatures of 25°, 30°, 40° & 50° respectively.

Figures (2), (4), (6) & (8) show the heat flow with time at 0.6 water cement ratio and curing temperature 25°, 30°, 40° & 50° respectively.

From these figures it can be concluded that heat of hydration was maximum in (COP-1) cement then (COP-2) and finally (COP-3) cement, this is attributed to various parameters; namely, cement composition, fineness, temperature, and w/c ratio which influence the heat of hydration of cement, that was in agreement with *(Mehta & Monteiro, 1993)*.

Abla Zayed, 2013 mentioned that for cements of similar or small different in fineness, the higher the C_3A and/or C_3S content of cement, the higher heat generation.

Ferraro and et al, 2010 mentioned that standard specifications for Portland cement (ASTM C150 or AASHTO M85) assimilate a heat index to measure the amount of heat created by a Portland cement.

The heat index utilizes the phase composition of cement as the foundation for estimating its possibility for heat generation *(Abla Zayed, 2013)*.

$$\text{Heat index} = C_3S + 0.75C_3A \ldots\ldots\ldots\ldots\ldots (14)$$

Heat index for (COP-1) cement was maximum thus it had higher heat generation then (COP-2) and (COP-3) cement. Heat index= 93.6, 89.6 & 80.8 for (COP-1), (COP-2) and (COP-3) cement respectively.

From all figures, it could be concluded that the heat of hydration curve passed through three stages; increasing in the beginning then decreasing then increasing again.

Because ions dissolved in water react with C_3A and gypsum in dissolution stage, the reaction occurs right after contact with water. After primary hydration reactions pointedly reduces the rate of the reaction, the formation of ettringite produced in the second part of Stage I. This stage has little effect on concrete strength.

The system then enters Stage II (recumbent period). In this stage the concentration of ions in the solution progressively excesses along with the solution of solid phase. Cement concrete stays in the plastic state. This stage does not improve concrete strength. Whilst, it is important for workability and transportation of concrete because this stage permits concrete to be brought to a work site.

In precipitation stage (stage III), the alite (C3S) and belite (C2S) in the cement begin to hydration and liberation heat. In this stage concrete setting initiates and heat generation is quickly accelerated. The silicate arrives a peak rate of hydration at the terminus of the Stage III *(Steven, 2006)*.

Figures (13) & **(14)** showed that the heat of hydration increase(s) with increasing curing temperature, in agreement with *(Escalante-Garcia, 2003)* who stated that with the increase in temperature, the interaction of hydration rate increased.

Figure (9), (10), (11) and **(12)** show the effect of increasing in water cement ratio on heat of hydration at 25°, 30°, 40° & 50° curing temperature.
From these figures, it was concluded that the heat of hydration was increased with increasing water to cement ratio, that was in agreement with *(Danielson, 1962)* who stated that the water–cement ratio, influenced hydration kinetics, a higher water cement ratio led to a higher hydration rate.
Figure (15) & **(16)** show that the heat emitted from hydration of cement could be extrapolated up to 7 day by the equations (8) &(9) for (COP-1) cement, curing temperature=50° and water to cement ratio 0.4 & 0.6 respectively:

$$H_t = 3292.7 \, e^{-(10^{-4t})} \tag{15}$$

$$H_t = 3517.3 \, e^{-(10^{-4t})} \tag{16}$$

H_t= heat emitted from hydration of cement at given age, (j\g).
t= time in minute up to 7 days.

5. Conclusions

1. The optimum heat of hydration was from (COP-1) cement.
2. The heat of hydration increased with increasing water cement ratio.
3. The heat of hydration increased with increasing curing temperature.
4. The heat flow with time passed in three stage, rapid increasing in heat, dominated stage or little increasing in heat and increasing again stage

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Plate (1): Calorimeter Apparatus
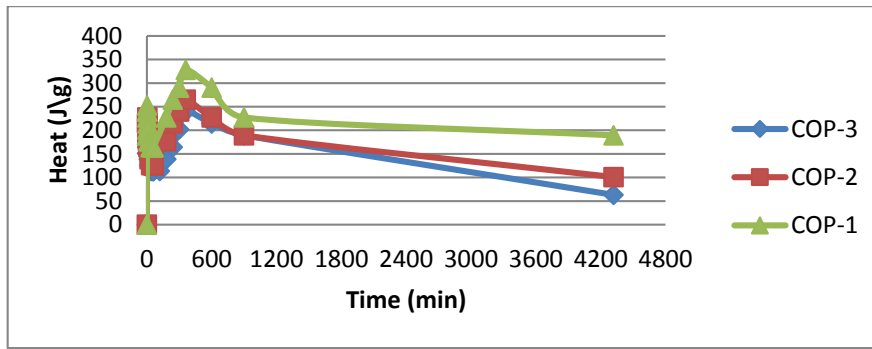
Figure (1): Heat flow –time (water cement ratio=0.4, curing temperature=25°)
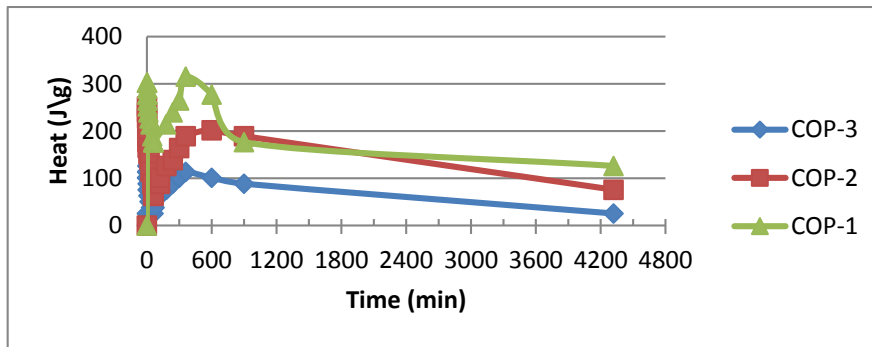
Figure (2): Heat flow –time (water cement ratio=0.6, curing temperature=25°)
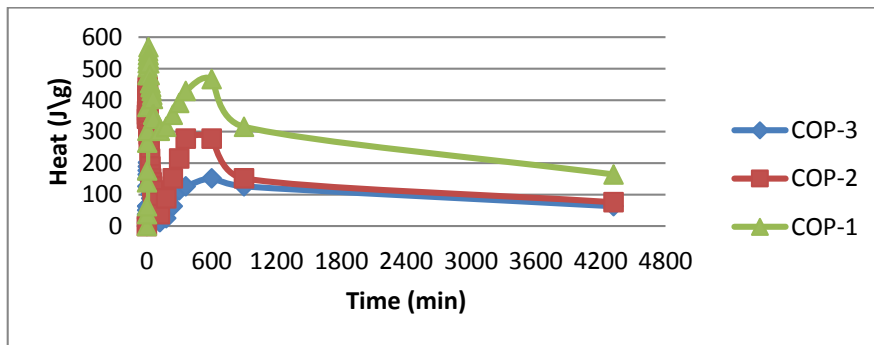
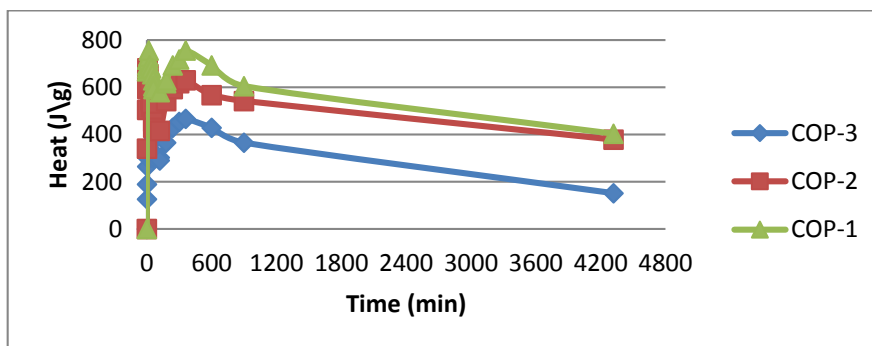**Figure (3):** Heat flow –time (water cement ratio=0.4, curing temperature=30°)

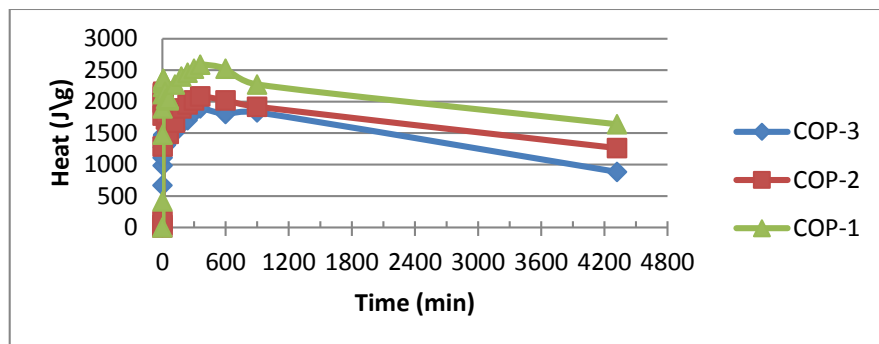**Figure (4):** Heat flow –time (water cement ratio=0.6, curing temperature=30°)

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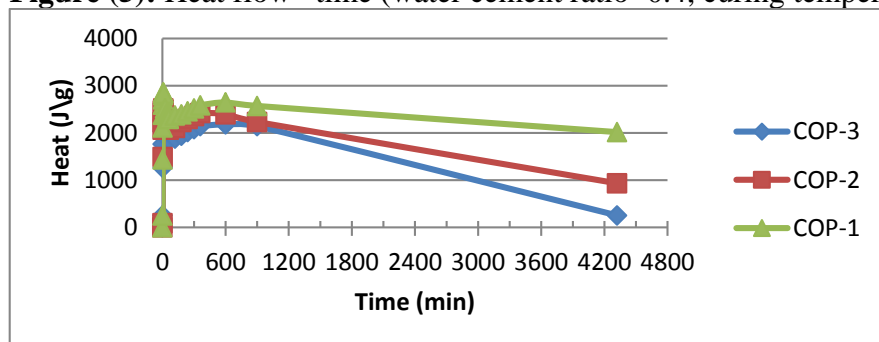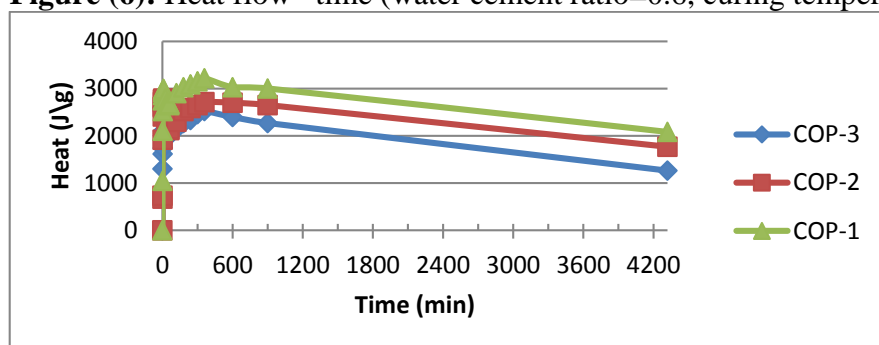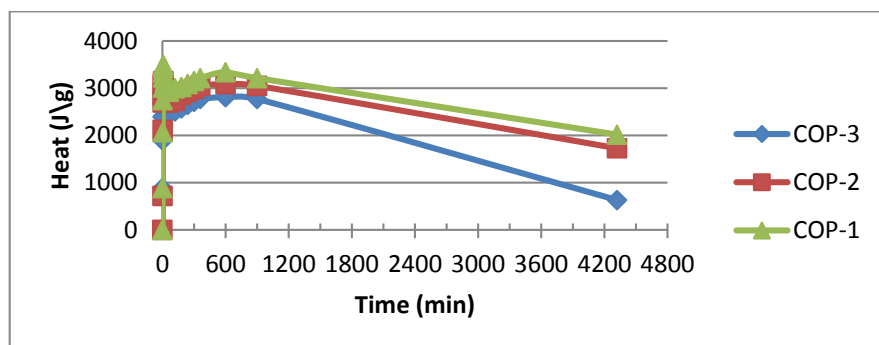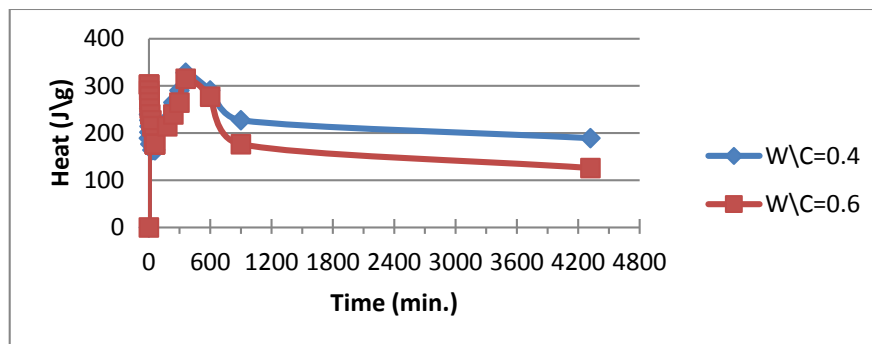**Figure (5):** Heat flow –time (water cement ratio=0.4, curing temperature=40°)

Figure (6): Heat flow –time (water cement ratio=0.6, curing temperature=40°)

Figure (7): Heat flow –time (water cement ratio=0.4, curing temperature=50°)

Figure (8): Heat flow –time (water cement ratio=0.6, curing temperature=50°)

Figure (9): Effect change in water cement ratio on heat of hydration at 25°
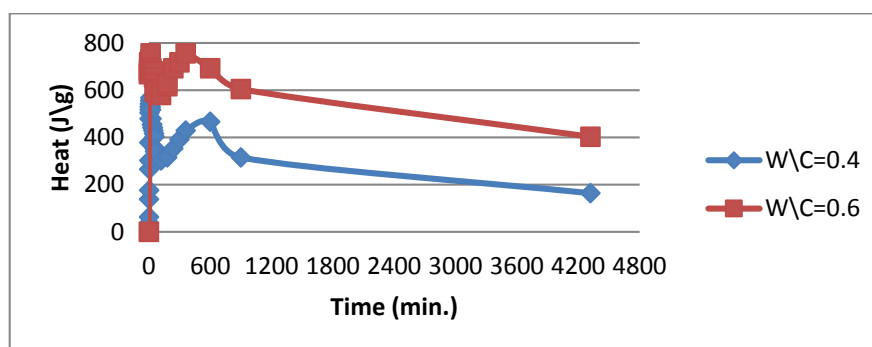curing temperature – Cresta cement

Figure (10): Effect change in water cement ratio on heat of hydration at 30°
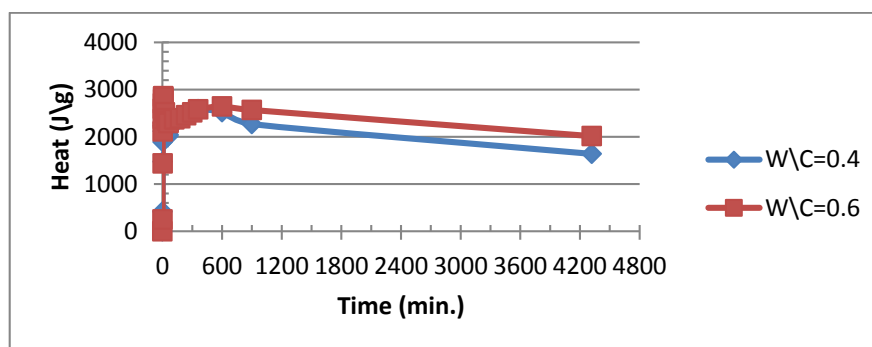curing temperature – Cresta cement

Figure (11): Effect change in water cement ratio on heat of hydration at 40°
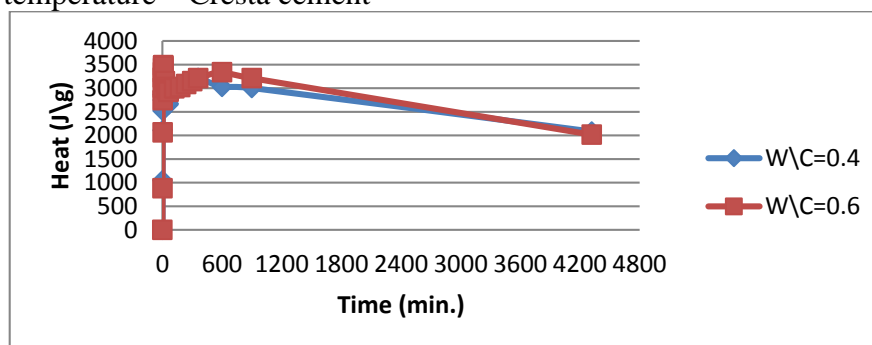curing temperature – Cresta cement

Figure (12): Effect change in water cement ratio on heat of hydration at 50°
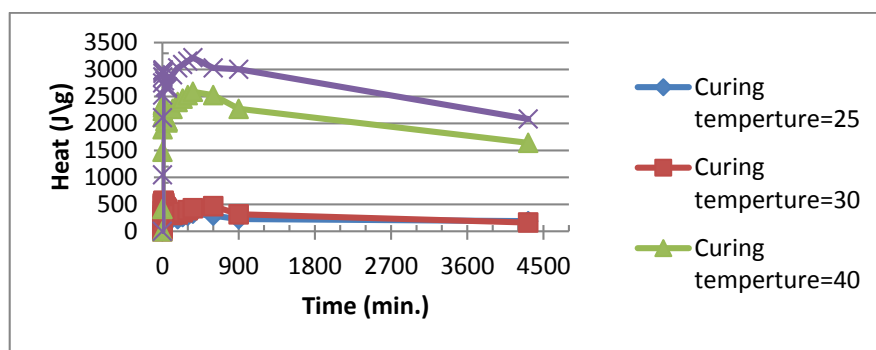curing temperature – Cresta cement

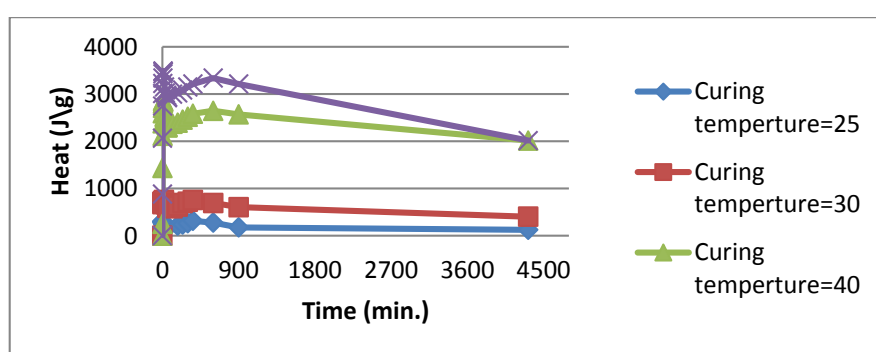**Figure (13):** Effect curing temperature on the heat of hydration at 0.4 water to cement ratio – Cresta cement

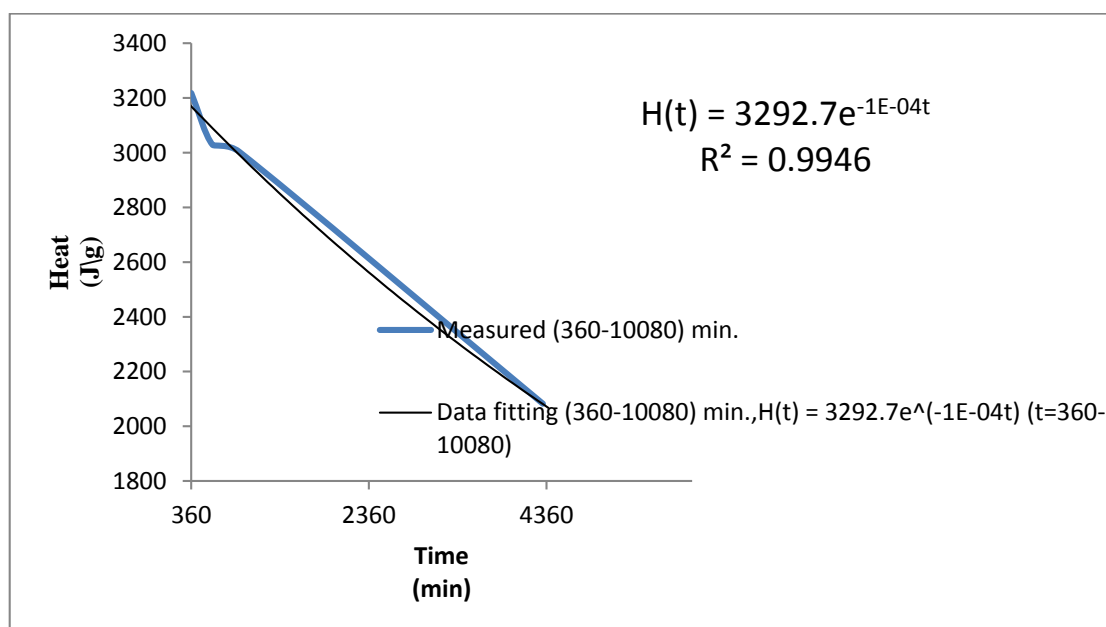**Figure (14):** Effect curing temperature on the heat of hydration at 0.6 water to cement ratio – Cresta cement

Figure (15): measured and extrapolated 7 day heat of hydration – Cresta cement (w\c=0.4 & curing temperature=50°)
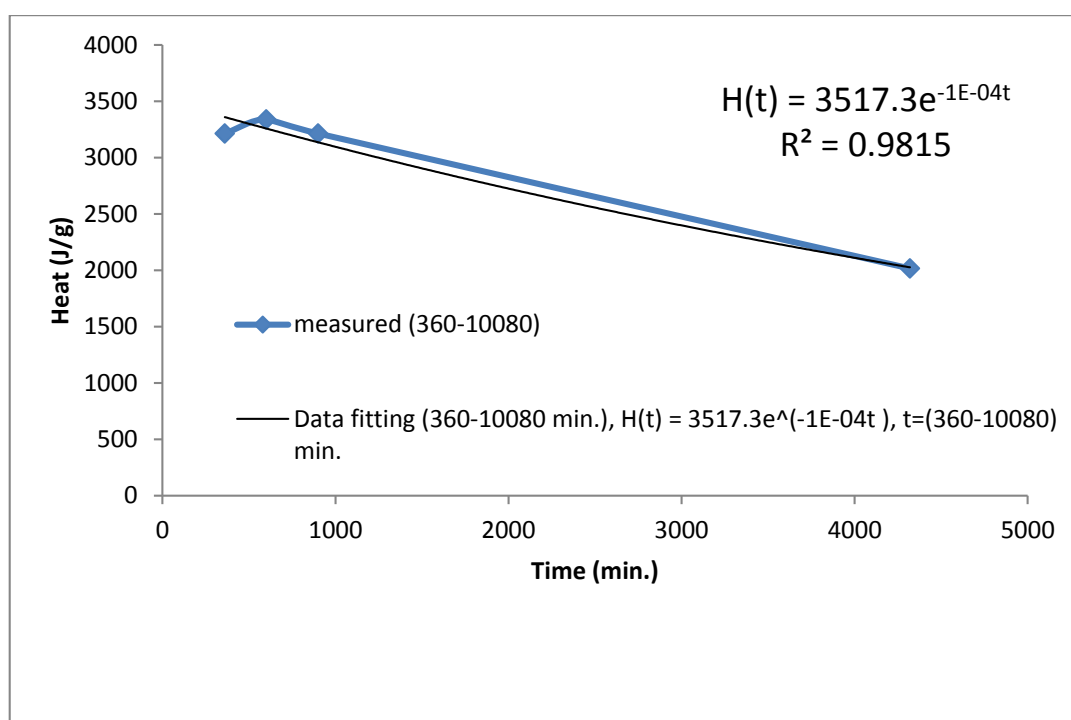
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Figure (16): measured and extrapolated 7 day heat of hydration – Cresta cement (w\c=0.6 & curing temperature=50°)

Table (1): Chemical composition of cement

Compound composition	Chemical composition	Percentage by weight			Limits of IQS 5:1984
		COP-1	COP-2	COP-3	
Lime	CaO	62	60.77	61.32	_
Silica	SiO$_2$	19.66	19.35	19.34	_
Alumina	Al$_2$O$_3$	5.48	5.2	4.78	_
Iron oxide	Fe$_2$O$_3$	3.72	3.6	4.68	_
Magnesia	MgO	2.87	2.95	2.65	<5
Sulfate	SO$_3$	2.2	2.5	1.96	<2.8
Free lime	Free CaO				
Loss on ignition*	L.O.I	3.55	1.15	3.89	<4
Insoluble residue	I.R	1.39	0.2	0.52	<1.5
Lime saturation factor	L.S.F		0.5		0.66-1.02
Main compounds (Bogue's equation) percentage by weight of cement					
		COP-1	COP-2		COP-3

Tricalcium silicate (C_3S)	54.5088	53.0569	58.1884
Dicalcium silicate (C_2S)	15.32456	15.5296	11.63175
Tricalcium aluminate (C_3A)	8.2352	7.696	4.7578
Tetraclcium aluminoferrite (C_4AF)	11.3088	10.944	14.2272

Table (2): Physical properties of cement

Physical properties	Test results			Limits of (IQS NO.5 /1984)
	COP-1	COP-2	COP-3	
Setting time (Vicat's Method) Initial, (min) Final, (min)	135 480	124 420	75 300	$\geq$ 45 min $\leq$ 600 min
Fineness (Blaine Method) ,m^2/kg	305	307	310	$\geq$ 230 m^2/kg

 * None of the cement types had interground limestone.

Table (3): Proportions of reference mixture

Water/cement ratio	Cement (g)	Water (ml)
0.4	500	200
0.6	500	300