

# Heat of hydration in concrete

by Erik Rastrup, M.Eng.F.\*

## SUMMARY

*The paper traces the development of a function between time and temperature, which makes it possible to refer the process of hardening of concrete at varying temperature to hardening at constant temperature.*

*It is further shown that it is possible to predetermine the temperature of concrete during hardening when properties of concrete, sizes and shape of the specimen, insulation and external temperature are known. The time temperature function can also be applied to the development of strength. The validity of the theory is demonstrated by the results of tests upon 27 American and 3 Danish cements.*

## Introduction

The setting and hardening process in concrete is accompanied by the development of heat, the so-called heat of hydration. This heat has no significant influence on the quality of the concrete except when it occurs in large masses, as in dams, or is placed in cold weather.

In mass concrete, the heat developed during hardening should be limited so that the temperature stresses do not exceed the tensile strength developed by the concrete. This is accomplished by removing the excess heat, by pre-cooling the materials or through the use of low-heat cement.

When concreting takes place in cold weather the problem is the opposite, i.e. to keep the concrete warm as long as possible. This is necessary since the strength development of the concrete is sensitive to the temperature at which setting and curing take place. Thus it is important to trap the heat of hydration as long as possible in order to obtain the greatest possible strength before the concrete is subjected to frost.

In order to predict the variation in temperature of concrete during the period immediately after placing, it is necessary to know the dependency of the heat of hydration upon the time after mixing, the temperature of the concrete, the type of cement, and the mix proportions of the concrete including the water/cement ratio. The heat development in a short interval will further depend upon the actual temperature of the concrete and the stage of hydration.

## Analytical development of time-temperature functions for the heat of hydration

### PERFECT INSULATION (NO EXTERNAL INFLUENCE)

In heavy constructions, such as dams, the concrete at the centre of the structure may be considered completely insulated, the only source of heat being the heat of hydration. This condition is valid only for the relatively short time interval during which most of the heat of hydration is developed. These conditions have been simulated in the laboratory by the use of an adiabatic calorimeter. By this procedure a concrete test specimen is caused to set without absorbing heat from or dispersing heat to the surroundings. The temperature of the concrete will then be proportional to the "adiabatic heat of hydration". This can be expressed by the equation

$$Vc_bR_b d\theta = VCdQ \dots\dots\dots(1)$$

whence

$$R_b c_b d\theta = CdQ \dots\dots\dots(1a)$$

which states that the temperature rise  $d\theta$  during the time interval  $dt$  multiplied by the specific heat of the concrete, is equal to the heat of hydration of the concrete developed during the same time interval.

\*Civil engineer, Construction Department, Carlsberg Breweries, Copenhagen.

In the preceding equations

$V$  = volume of concrete (cu.m.)

$c_b$  = specific heat of concrete (kcal/kg°C)

$R_b$  = density of concrete (kg/cu.m.)

$C$  = cement content of concrete (kg/cu.m.)

$Q$  = heat of hydration of concrete (kcal/kg of cement)

$\theta$  = temperature of concrete (°C)

$t$  = hardening time of concrete (hours)

If the cement content and specific heat are considered constant, integration of equation (1a) gives

$$\theta - \theta_0 = \frac{C}{R_b c_b} Q \dots\dots\dots (2)$$

where  $\theta = \theta_0$  and  $Q_0 = 0$ , when  $t = 0$ .

Equation (2) states that the temperature rise and the heat of hydration are proportional;  $Q$  is normally a function of time and temperature, but since in this case the temperature is a function of  $Q$ ,  $Q$  will only depend upon time.

The formula commonly used for the heat of hydration under adiabatic conditions is

$$Q = E(1 - e^{-\alpha t}) \dots\dots\dots (3)$$

where  $E$  and  $\alpha$  are constants depending upon the mix proportions and the type of cement, and  $e$  is the base of the natural logarithms.<sup>(1,2,3,4)\*</sup>

Equations developed by Fourier for heat transmission make it possible to predict the temperature at any time and place in a concrete test specimen during hardening.<sup>(1)</sup>

$$\frac{\partial \theta}{\partial t} = \frac{\lambda}{R_b c_b} \left( \frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} + \frac{\partial^2 \theta}{\partial z^2} \right) + \frac{1}{R_b c_b} \frac{\partial Q}{\partial t} \dots\dots (4)$$

where  $\lambda$  = thermal conductivity (in this case considered constant in all directions).

$\left. \begin{matrix} x \\ y \\ z \end{matrix} \right\}$  = co-ordinates of any point

$\frac{\partial Q}{\partial t}$  = the heat of hydration developed in unit of

volume and time. From equation (3)

$$\frac{\partial Q}{\partial t} = \alpha E e^{-\alpha t}$$

Solution of the equation requires a knowledge of the initial temperature and boundary conditions.

#### IMPERFECT INSULATION (EXTERNAL INFLUENCE)

The assumptions of perfect insulating properties of the concrete do not apply to concrete in slender constructions or to concreting in cold weather. Under these conditions the heat of hydration will also be dependent upon the temperature conditions outside the concrete specimen. The presence of this condition suggests the

use of a well-known axiom from physical chemistry which states: the reaction velocity is doubled if the temperature at which the process is taking place is increased by 10°C. This leads to the following arguments.

If at constant temperature  $\theta_a$  a certain process will last  $t = \tau_a$  units of time, then at constant temperature  $\theta = \theta_a + 10n$  the same process will last  $t = \frac{1}{n} \tau_a$  units of time.

By eliminating  $n$  we obtain

$$\tau_a = 2^{(\theta - \theta_a)/10} t \dots\dots\dots (5)$$

If a time-temperature function such as (5) exists, it is possible to compare a known process at a known constant temperature with the same process at any arbitrarily chosen constant temperature by inserting the temperature into the formula.

If the process takes place at a varying temperature the time-temperature function can be used for a comparison with the same process at a known constant temperature by dividing the time into small increments  $\Delta t$ , and assuming the process to have a constant temperature throughout the small increment. The length of time the varying temperature process will last converted to time at constant temperature  $\theta_a$  can be determined by a summation of the increments which gives

$$\tau_a = \sum_0^t 2^{(\theta - \theta_a)/10} \Delta t \dots\dots\dots (6a)$$

or

$$\tau = \int_0^t 2^{(\theta - \theta_a)/10} dt \dots\dots\dots (6b)$$

The series of experiments described in this paper provides empirical evidence for the existence of such a time-temperature function. If values of the heat of hydration of a concrete at a constant temperature  $\theta_a$  are available, the time-temperature function enables the temperature at an arbitrary moment in a hardening concrete specimen to be computed, because the time-temperature function combined with the relation between the heat of hydration and time at a constant temperature takes into account that part of the process which has already taken place.

To explain the application of the time-temperature function to hardening concrete, an approximate solution is given for a slender construction. The calculation is based upon the following assumptions.

- At any instant the concrete has the same temperature everywhere in the specimen.
- The quantity of heat accumulated in the insulating layers does not influence the cooling or heating of the concrete.

\*The index numbers refer to the items in the list of references on page 90.

- (c) The surrounding air temperature is everywhere the same.
- (d) The specific heat of the concrete is not altered during the test.

By dividing the time interval into small increments  $\Delta t$  and, using the assumptions a, b, c, and d, the following argument can be used.

#### Boundary conditions

During the interval of time  $\Delta t$  the concrete will disperse the quantity of heat  $\Sigma kF(\theta - \theta_u)\Delta t$  to the surroundings. In this formula  $k$  is the coefficient of transmission of the individual insulating layers,  $F$  is the area of the insulating layers,  $\theta$  is the mean temperature of the concrete and  $\theta_u$  is the mean temperature of the surrounding air.

#### Conditions within the concrete mass

During the same interval of time  $\Delta t$  the concrete will develop the heat of hydration  $\Delta QCV$  and absorb the quantity of heat  $Vc_bR_b\Delta\theta$ . Since the quantity of heat dispersed must be equal to the difference between the amount developed and the amount absorbed, we have the equation

$$\Sigma kF(\theta - \theta_u)\Delta t = \Delta QCV - Vc_bR_b\Delta\theta \dots (7a)$$

If  $\theta = \theta_0$  and  $Q = Q_0$  at  $t = 0$  initial conditions

$$\sum_{t=0}^t [\Sigma kF(\theta - \theta_u)] \Delta t = CV(Q - Q_0) - Vc_bR_b(\theta - \theta_0)$$

Substituting

$$a = \frac{\Sigma kF}{Vc_bR_b} \dots \dots \dots (7b)$$

we obtain

$$\theta = \theta_0 + \frac{C}{c_bR_b}(Q - Q_0) - \Sigma_0(\theta - \theta_u)\Delta t \dots (8)$$

If  $Q = f(\tau_0)$  is determined at a constant temperature, for example  $0^\circ\text{C}$ , and the values  $\theta_0$  and  $Q_0$  are known, it is possible to calculate the temperature  $\theta$  step by step.

At the time  $\Delta t$ , we have from equation (6a)

$$\tau_{0.1} = 2^{\theta_0/10} \Delta t$$

and  $Q = f(\tau_{0.1})$

and from equations (7) and (8)

$$\begin{aligned} \theta_1 &= \theta_0 + \frac{C}{c_bR_b} [f(\tau_{0.1}) - Q_0] - a(\theta_0 - \theta_u)\Delta t_1 \\ \theta_2 &= \theta_0 + \frac{C}{c_bR_b} [f(\tau_{0.2}) - Q_0] - [a(\theta_1 - \theta_u)\Delta t_2 \\ &\quad + a(\theta_0 - \theta_u)\Delta t_1] \end{aligned}$$

and so on.

## Experiments conducted to verify the analytical result

The time-temperature function has been used for three

sets of calculations based on three series of experiments. The first series was performed by the American Portland Cement Association, and the other two series were planned by the Danish National Institute of Building Research and performed in co-operation with the Technical Information Office of Danish cement factories at the F. L. Smidth & Co. Ltd.'s Laboratory and the Laboratory of Building Technique of the Technical University of Copenhagen. These last two series were performed on Danish cements obtained direct from the factory. In their selection precautions were taken to ensure that all samples of each type came from the same charge. After their selection the cements were shipped in airtight containers to the two laboratories. Three Danish cements were investigated (Danish Portland cement, Danish Rapid cement and Danish Super Rapid cement), but only the tests on the Portland cement are described below.

#### TEST SERIES NO. 1

All data for the calculations in Test Series No. 1 were taken from the American Portland Cement Association's report entitled *Long-time study of cement performance in concrete*. The report describes an extremely thorough investigation of the heat of hydration of 27 different American Portland cements. In the investigation the heat of hydration was determined by both the heat of solution method and the calorimeter method.

The results obtained from experimental and calculated data for all the cements show good agreement with the author's hypothesis, and Figure 1 shows typical results. The temperature-time graph located below the heat of hydration versus time graphs is used in the following way: find the desired temperature on the vertical temperature scale; then proceed horizontally to the inclined line representing the desired value of time, and then proceed vertically to the curves.

In using the temperature-time graphs it is assumed that the concrete is hardening at constant temperature. In the graph the abscissa is the time

$$\tau_0 = 2^{\theta/10} t$$

and the ordinate is the heat of hydration  $Q$ . This corresponds to all the test results being referred to the constant hardening temperature  $\theta_a = 0^\circ\text{C}$ .

The determination of the heat of hydration by the heat of solution method was carried out at a constant temperature of  $21.1^\circ\text{C}$  ( $70^\circ\text{F}$ ),  $32.2^\circ\text{C}$  ( $90^\circ\text{F}$ ) and  $40.6^\circ\text{C}$  ( $105^\circ\text{F}$ ). The data based on the heat of solution method have been plotted as individual points, while the data based on the calorimeter tests have been connected by curves. This difference in plotting procedure is based on the almost complete independence of the heat of solution values, while the values obtained from the calorimeter tests are dependent upon the preceding ones. All the experiments were performed on neat cement paste with a water/cement ratio of 0.4 by weight.

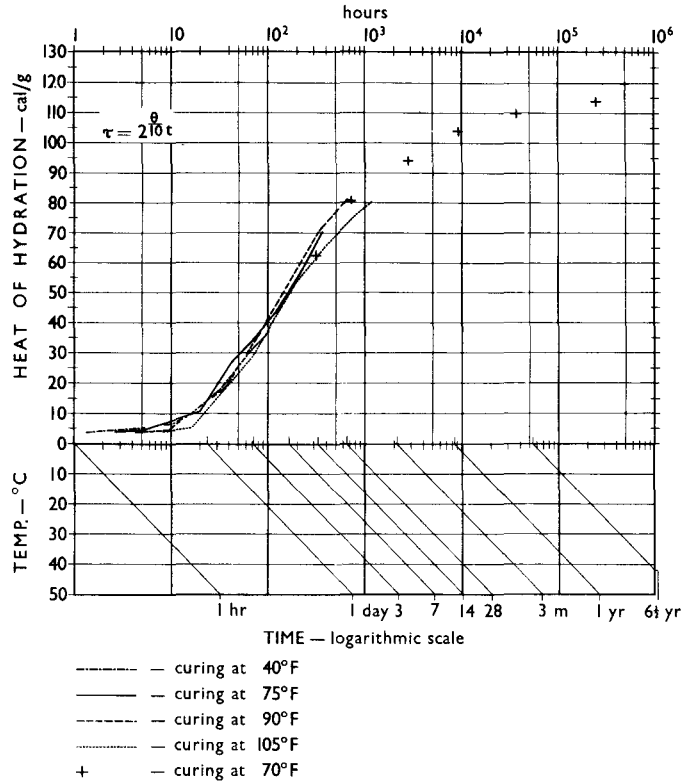


Figure 1: Heat of hydration plotted against the time-temperature function  $\tau = 2^{6/10} t$ . (Results of the Portland Cement Association.<sup>(5)</sup>)

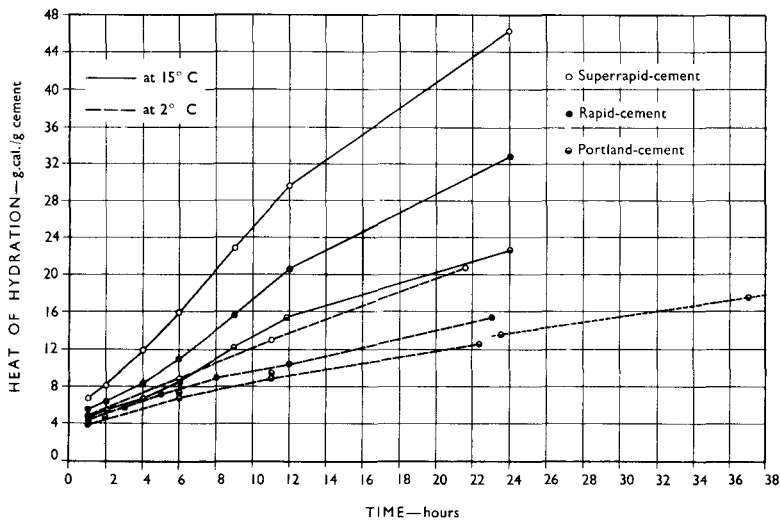


Figure 2: Heat of hydration of three Danish cements determined by the calorimeter method.

From Figure 1 it appears that the values for each temperature lie close to a hypothetical line which can be described as the curve for the heat of hydration at 0°C.

## TEST SERIES NO. 2

All data for the calculations in Test Series No. 2 were obtained at the Laboratory of F. L. Smidth & Co. Ltd. where an extensive series of experiments was performed on the heat of hydration of neat cement pastes with a water/cement ratio of 0.4 by weight. The greater proportion of these experiments were performed by the heat of solution method with the specimens stored at constant temperature. All determinations of the heat of solution were made in accordance with B.S.1370:1947 for low heat Portland cement.<sup>(6)</sup>

Since the determination of the heat of solution is very difficult for short curing times, the tests for hardening times up to 24 hours have been supplemented by direct determinations utilizing the calorimeter procedure.

The results from the experiments using the heat of solution method appear as the difference between the heat of solution  $A$  for unhydrated cement and the heat of solution  $B$  for hydrated cement. Thus the heat of hydration  $Q = A - B$  is measured in calories per gramme of cement.

Since the heat of solution of unhydrated cement has been measured many more times than the heat of solution for hydrated cement, the measurements of  $A$  have been used to determine the standard deviation of the individual test results. In Table 1 the standard deviations of the individual values of  $A$  have been used as the standard deviations of the hypothetical individual values of  $B$ . The standard deviation of the heat of hydration has then been computed from the formula

$$\sigma(Q) = \sqrt{[\sigma(\bar{A})]^2 + [\sigma(B)]^2}$$

The values of the heat of hydration for the Danish Portland cement as computed from  $Q = A - B$  appear in Table 2.

The experimental results obtained from the calorimeter measurements of the heat of hydration are indicated in Figure 2 which shows the heat of hydration plotted against time for both 2°C and 15°C. These results have also been plotted in Figure 3 in the same form as for Test Series No. 1. The curve indicated by the broken line in Figure 3 is the empirical equation<sup>(7)</sup>

$$Q = q + Ee^{-\alpha\tau_0^n} \dots\dots\dots(9)$$

in which the constants  $q$ ,  $E$ ,  $\alpha$  and  $n$  have been determined by the method of least squares. In the formula,

$$\tau_0 = 2^{0/10} t$$

and  $e$  is the base of the natural logarithm scale, Table 3 gives the values of the constants  $q$ ,  $E$ ,  $\alpha$  and  $n$  together with the resulting standard deviations of  $Q$ .

TABLE 1: The heat of solution for unhydrated ordinary Danish Portland cement.

$\bar{A}$ = mean value for heat of solution of unhydrated cement (cal/g)	610.4
$\sigma(\bar{A})$ = standard deviation from the mean $\bar{A}$	1.1
$\sigma(A) = \sigma(B)$ The unknown standard deviations of $B$ are set equal to the standard deviations of the individual values of $A$	4.0
$\sigma(Q) = \sqrt{[\sigma(\bar{A})]^2 + [\sigma(B)]^2}$ = standard deviation of $Q$	4.2

TABLE 2: Heat of hydration for Danish Portland cement in cal/g of cement (water/cement ratio = 0.4).

Curing temperature (°C)	Curing time (days)					
	2	3	5	7	14	28
2	—	30	—	33	45	66
5	—	22	—	47	—	67
15	—	39	—	61	—	80
25	—	51	—	69	—	84
45	77	77	78	77	—	—

TABLE 3: Constants in equation (9) (Danish ordinary Portland cement).

$q$ (cal/g)	$E$ (cal/g)	$\alpha$ (hr <sup>2</sup> )	$n$	$s(Q)$ (cal/g)
4.3	93.3	13.0	0.5	5.1

A comparison of the standard deviations ( $Q$ ) in Table 3 with the same standard deviation  $\sigma(Q)$  in Table 1 shows the two to be of the same magnitude.

In the P.C.A.'s report,<sup>(1)</sup> the heat of hydration results were used to compute the contributions of the individual clinker components to the heat of hydration. All heat of hydration results used were obtained by the heat of solution method at a constant temperature  $\theta = 21.1^\circ\text{C}$  ( $70^\circ\text{F}$ ) and curing periods of 3, 7 and 28 days, 3 months, and 1 and  $6\frac{1}{2}$  years. Three different empirical formulæ were used in the report in an attempt to determine the most satisfactory representation of the experimental data.

TABLE 4: Contribution of the individual clinker components to the heat of hydration (according to P.C.A.).

	3 days	7 days	28 days	3 months	1 year	½ years
<i>a</i>	0.54±0.08	0.51±0.11	0.91±0.07	1.07±0.04	1.22±0.04	1.20±0.07
<i>b</i>	0.01±0.09	0.04±0.13	0.29±0.07	0.53±0.04	0.74±0.04	0.65±0.08
<i>c</i>	1.51±0.38	3.43±0.55	3.44±0.31	3.60±0.18	3.70±0.18	3.85±0.32
<i>d</i>	0.20±0.34	0.94±0.48	1.30±0.27	1.37±0.16	1.63±0.16	1.55±0.28
<i>e</i>	8.92±4.12	4.34±5.94	-2.17±3.37	-7.16±1.91	-13.46±1.92	-8.28±3.44

TABLE 5: Chemical composition of the Danish Portland cements.

	per cent
SiO <sub>2</sub>	22.6
Al <sub>2</sub> O <sub>3</sub>	5.3
Fe <sub>2</sub> O <sub>3</sub>	2.0
CaO	65.0
MgO	1.2
SO <sub>3</sub>	1.4
Ignition loss	1.3
Insoluble and undetermined	1.2
Total	100.0

TABLE 6: Composition of clinkers in the Danish Portland cement according to Bogue's formula.

	per cent
CaSO <sub>4</sub>	2.4
C <sub>4</sub> AF = 4CaO, Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub>	6.0
C <sub>3</sub> A = 3CaO, Al <sub>2</sub> O <sub>3</sub>	10.6
C <sub>3</sub> S = 3CaO, SiO <sub>2</sub>	44.4
C <sub>2</sub> S = 2CaO, SiO <sub>2</sub>	31.3
Free CaO	1.5
MgO	1.2
Ignition loss	1.3
Insoluble and undetermined	1.3
Total	100.0

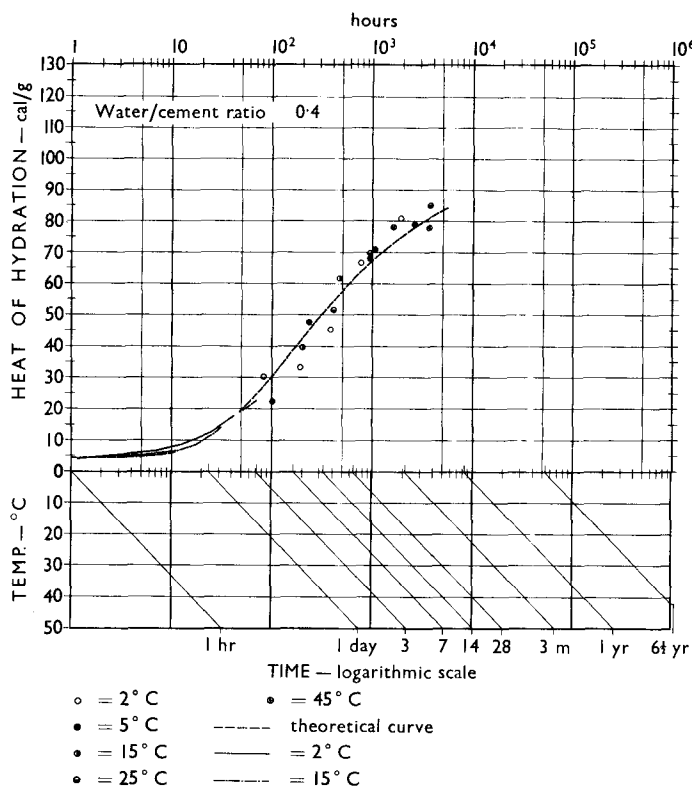


Figure 3: Heat of hydration of Danish Portland cement plotted against the time-temperature function.

TABLE 7: Heat of hydration of the Danish Portland cement at 21.1°C (70°F) computed from the P.C.A. figures in Table 4.

Curing time	3 days	7 days	28 days	3 months	1 year	6½ years
Heat of hydration (cal/g)	53±9	72±12	91±7	100±4	100±4	112±7

Table 4 gives the results obtained from the second P.C.A. formula (method 2 with 5 variables)

$$a(\%C_3S) + b(\%C_2S) + c(\%C_3A) + d(\%C_4AF) + e(\%SO_3) = \text{heat of hydration (cal/g) at a given age} \dots (10)$$

The composition of the clinkers of the Danish cements were determined by Bogue's method,<sup>(8)</sup> and the SO<sub>3</sub> contents were determined by chemical analysis.

The chemical composition of the Danish Portland cement is given in Table 5, and the compositions of the clinkers in Table 6.

Table 7 gives the values of the heat of hydration for the Danish cement computed from the values of Table 4. The standard deviations have been computed from the formula  $s(Q) = \sqrt{\sum s^2}$  where  $s$  = standard deviation multiplied by the percentage clinker component, or the deviations from Table 4 multiplied by the values from Table 6.

Table 8 gives the values of the heat of hydration for the Danish cements computed by the formula

$$Q = q + Ec^{-\alpha\tau_0^{-n}} \dots (9)$$

A comparison of Tables 7 and 8 indicates a reasonably good agreement, bearing in mind the relatively large standard deviations.

TABLE 8: Heat of hydration at 21.1°C (70°F) according to equation (9).

Curing time	3 days	7 days	28 days
Heat of hydration (cal/g)	49±4	62±4	78±4

## TEST SERIES NO. 3

In order to clarify the dependency of the heat of hydration on the water/cement ratio,<sup>(2)</sup> Test Series No. 3 was performed at the Technical University of Copenhagen on concrete having two different water/cement ratios. Concrete was cast in cork moulds and placed in the cold-storage chamber of the laboratory. The concrete contained 204 and 308 kg of cement per cubic metre of concrete and aggregates taken from the sea bottom.

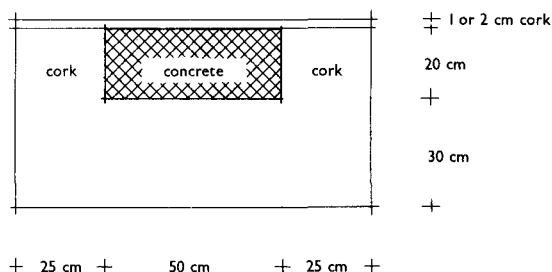


Figure 4: Cross-section of the cork mould used in Test Series No. 3.

This source of gravel is commonly utilized in the production of concrete in the Copenhagen region.

The cork mould used in the experiments had a square base, a cross-section as shown in Figure 4, and either 1 or 2 cm of cork insulation on the top. Prior to each test the cork box was heated to room temperature and then placed in the cold-storage chamber immediately before concreting. This procedure was designed to eliminate as far as possible the influence on the concrete specimen of the cork cooling.

The investigation comprised both ordinary, Rapid and Super Rapid Portland cement, the data for tests using ordinary Portland cement being given in Table 9.

Table 10 gives the compositions of the concretes tested in Test Series No. 3.

The temperature of the concrete and the air temperature of the cold-storage chamber were measured by means of thermocouples with an estimated deviation of the individual measurements of 0.2°C. The concrete temperature in each experiment was measured at various locations in the concrete block and from the data of one of the experiments Figure 5 was plotted. The concrete temperatures were measured continuously from the time of mixing until the end of the experiment, when the concrete had the temperature 0°C.

The density of representative samples of the concrete was measured on test cylinders 30 cm high and 15 cm in diameter. The cylinders were weighed immediately after concreting and again after setting, and were then used for determinations of compressive strength. The

TABLE 9: The testing combinations used for Test Series No. 3.

Test No.		Cement content (kg/cu.m.)	Water/cement ratio	Thickness of top cork insulation (cm)	Air temperature (°C)
3	1	308	0.65	2	—20
9	11	308	0.65	2	— 5
6	5	308	0.65	1	—20
10	14	308	0.65	1	— 5
3	1	204	0.92	2	—20
9	11	204	0.92	2	— 5
6	5	204	0.92	1	—20
10	14	204	0.92	1	— 5

TABLE 10: The composition of the concrete tested.

Cement content (kg/cu.m.) <i>C</i>	Aggregate content (kg/cu.m.) <i>S</i>	Water content (kg/cu.m.) <i>V</i>	Water/cement ratio by weight	Slump (mean value) (cm)
204	1,978	188	0.92	3
308	1,862	200	0.65	5

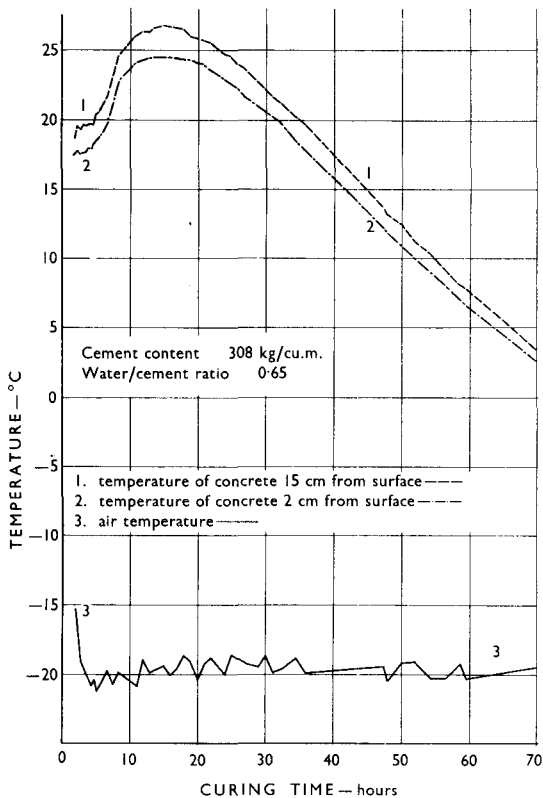


Figure 5: Typical temperature distribution in the concrete block during the test.

density measurements on the cylinders with the Portland cement gave the following results:

$$R_{b \text{ wet}} = 2,370 \text{ kg/cu.m.}$$

$$R_{b \text{ dry}} = 2,350 \text{ kg/cu.m.}$$

The 28 day compressive strengths as determined on the cylinders are given in Table 11.

TABLE 11: Compressive strengths of test cylinders.

Cement content (kg/cu.m.)	Compressive strength (kg/sq.cm.)
308	230 ± 10
207	160 ± 10

The specific heat  $c_s$  of the aggregate was determined at the Physical Laboratory of the Technical University of Copenhagen and was found to be  $0.200 \pm 0.005$  kcal/kg.°C.

The specific heat of the plastic concrete  $c_{b \text{ wet}}$  was computed directly from the contributions of the individual constituents according to the formula:

$$c_{b \text{ wet}} R_{b \text{ wet}} = c_c C + c_s S + c_v V \dots (11)$$

In equation (11)

$c_c$  = specific heat of the cement (kcal/kg.°C)

$c_s$  = specific heat of the aggregate (kcal/kg.°C)

$S$  = aggregate content (kg/cu.m.)

$c_v$  = specific heat of the water (kcal/kg.°C)

$V$  = water content (kg/cu.m.)



TABLE 12: Specific heat of the concretes used in Test Series No. 3 (Portland cement).

Cement content (kg/cu.m.)	Specific heat of concrete $\times$ density (kcal/cu.m. °C)			Specific heat of concrete (kcal/kg. °C)		
	wet	dry	mean	wet	dry	mean
204	624	584	604	0.263	0.249	0.256
308	634	583	609	0.267	0.248	0.258

In the evaluation of formula (11) the specific heats  $c_c$  and  $c_s$  were estimated at 0.20 kcal/kg. °C and  $c_v$  was taken as 1.0 kcal/kg. °C.

The specific heat of the set concrete  $c_{b \text{ dry}}$  was calculated in the same way as  $c_{b \text{ wet}}$  except that  $c_c$  was taken as equal to 0.1 (see references (2) and (3)) and the reduced water content resulting from the volume shrinkage was taken into account. The values of the specific heats for both the plastic concrete and the set concrete are listed in Table 12.

The values of the cooling constant  $a$  which has the units (hours)<sup>-1</sup> were determined from tests on hardened concrete samples. In the calculations the heat of hydration in equation (13) was set equal to zero to account for the hardened concrete and the remaining data were obtained from the experiments. Using these values of  $a$  the heat of hydration was determined by means of equation (13) and the time of duration of the similar process at 0°C was calculated from

$$\tau_0 = \sum_0^t 2^{0/10} \Delta t$$

This is equation (6a) referred to the constant hardening temperature  $\theta_a = 0^\circ\text{C}$ . A revision of the experimental values of the cooling constant was necessary to correct for the smaller values of the specific heat and density which occur in the hardened concrete. Values of  $a$  were found to be:

1 cm cork:  $a = 0.0243 \text{ hr}^{-1}$  revised to  $a = 0.0234 \text{ hr}^{-1}$

2 cm cork:  $a = 0.0164 \text{ hr}^{-1}$  revised to  $a = 0.0158 \text{ hr}^{-1}$

It has been shown above that it is possible to compute step by step the temperature within the concrete mass using certain assumptions and knowing the heat of hydration as a function of time at constant temperature.

In the experiments described above the temperature was recorded, and using the same assumptions as before the formula (7a) can be solved with regard to  $\Delta Q$ .

$$\Delta Q = \frac{c_b R_b}{C} \left[ \Delta \theta + \frac{\Sigma k F}{V c_b R_b} (\theta - \theta_u) \Delta t \right]$$

Substituting

$$a = \frac{\Sigma k F}{V c_b R_b}$$

$$\Delta Q = \frac{c_b R_b}{C} \left[ \Delta \theta + a(\theta - \theta_u) \Delta t \right] \dots \dots (12)$$

Summing the intervals from  $t = 0$  to  $t = t$ :

$$Q = \frac{c_b R_b}{C} \left[ (\theta - \theta_0) + a \sum_0^t (\theta - \theta_u) \Delta t \right] \dots (13)$$

As the physical data were determined independently and the temperatures recorded continuously, the heat of hydration can be computed from equation (13) as a function of time at the varying temperature  $\theta$ .

Using

$$\tau_0 = \sum_0^t 2^{0/10} \Delta t$$

the heat of hydration  $Q$  may be plotted as a function of  $\tau_0$ —the hardening time at constant concrete temperature  $\theta = 0^\circ\text{C}$ —as shown on Figure 6. This procedure has previously been used in Test Series Nos. 1 and 2.

The values for the two water/cement ratios are plotted separately. From an examination of the graphs it is evident that the values are in good agreement and that a time function similar to formula (6) exists. It can further be seen that the heat of hydration per kilogram of cement increases with the water/cement ratio (see Figure 7), which is in agreement with the results of the U.S. Department of the Interior Bureau of Reclamation in their investigation of Portland cement on the Boulder Canyon Project.<sup>(2)</sup>

In the computation of  $Q$ , variations of the specific heat or the density have been neglected, since the determination of these factors would involve a whole new test series. The error introduced by this omission may have the magnitude

$$\Delta Q = \frac{\Delta(c_b R_b) \theta}{C} = \frac{(624 - 584) \times 15}{204} = 2.9 \text{ kcal/kg} \quad (14)$$

The data used to determine  $\Delta Q$  from equation (14) were taken from Table 12 for Portland cement with a cement content of 204 kg/cu.m.

### The dependency of concrete strength on hardening time and temperature

From the preceding discussion, in which it has been shown that a time-temperature function must exist, and from the results reported by Verbeck<sup>(5)</sup> and Powers,<sup>(8)</sup> it is possible to establish that the time-temperature function which applies to the heat of hydration of a

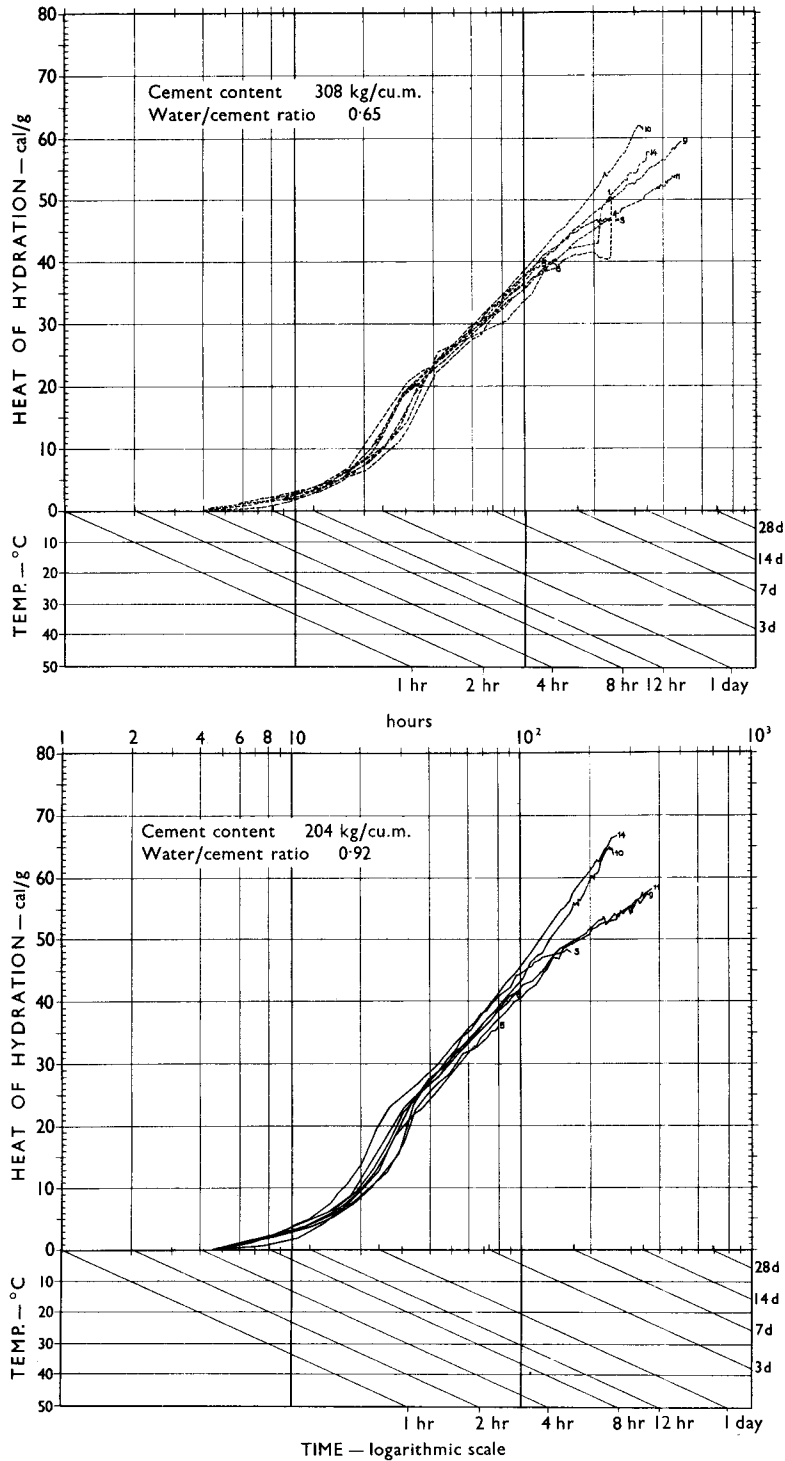


Figure 6: Heat of hydration of Danish Portland cement plotted against the time-temperature function, determined by Test Series No. 3.

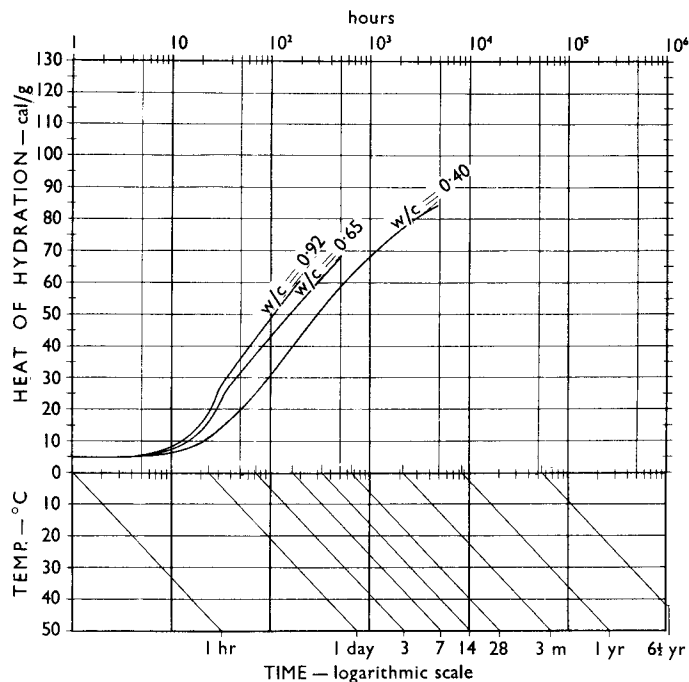


Figure 7: Heat of hydration of Danish Portland cement plotted against the time-temperature function for three water/cement ratios.

cement must also apply to the strength development of the cement.

In their reports, Verbeck and Powers both measured the extent of hardening by the amount of non-evaporable water present in the concrete. The non-evaporable water which is represented by  $w_n$  is the water that is retained by a sample of cement paste after it has been dried at 23°C to constant weight in an evacuated desiccant. According to Verbeck's findings the relationship between the heat of hydration and the non-evaporable water may be expressed by

$$Q = 500w_n \dots\dots\dots(15)$$

Powers demonstrated by experiments that the strength of mortar is a function of the ratio  $\frac{w_n}{w_o}$ , where  $w_n$  is the non-evaporable water and  $w_o$  is the water/cement ratio. This relationship can be expressed by the formula

$$\sigma = \alpha x^\beta \dots\dots\dots(16)$$

in which  $\sigma$  = the compressive strength in kg/sq.cm.

$$x = \frac{\gamma w_n}{\delta w_n + w/c} \dots\dots\dots(17)$$

and  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  are constants which depend upon the composition of the cement and the type of aggregate. The values of the strength found by Powers<sup>(9)</sup> show good agreement with Danish experience.

If a given concrete specimen is now considered, the following relationships will apply during the hardening: Since  $\sigma = f_1(w_n)$      $w_n = f_2(Q)$      $Q = f_3(\tau)$  then  $\sigma = f_3(\tau) \dots\dots\dots(18)$

where  $\tau = f_3(\theta, t) = \int_0^t 2^{(\theta - \theta_a)/10} dt$

Thus the strength development of the concrete is a function of the same time-temperature relationship as the heat of hydration.

SAUL'S TIME-TEMPERATURE RELATIONSHIP

Saul<sup>(10)</sup> suggested the use of a "maturity" figure, which is the product of time and concrete temperature plus 10°C

$$M = \Sigma(\theta + 10)\Delta t \dots\dots\dots(19)$$

to relate strength with the stage of hardening. The use of

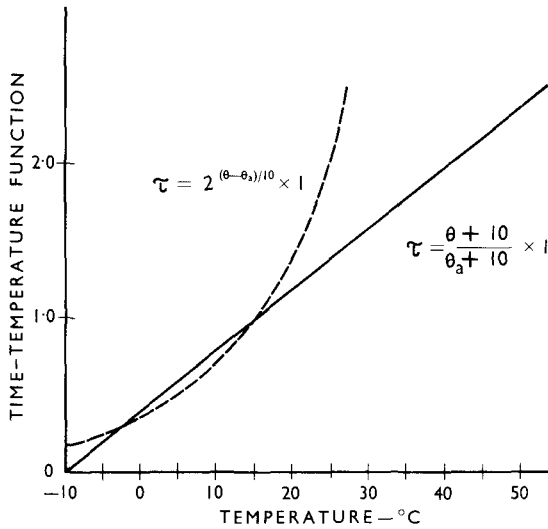


Figure 8: Comparison between Saul's time-temperature function and that suggested by the author.

this maturity figure gives the following time-temperature function:

$$\tau = \frac{\Sigma(\theta + 10)\Delta t}{(\theta_a + 10)} \dots\dots\dots(20)$$

In equation (20),  $\theta_a$  is the constant temperature to which the process is referred and  $\tau$  is the time of hardening at this temperature  $\theta_a$  expressed in the same units as  $t$ .

In Figure 8 Saul's time-temperature function and the relationship developed by the author—equation (6b)—are plotted for a unit value of time and with  $\theta_a = 15^\circ\text{C}$ . These curves indicate that agreement between the two formulae is good only for concrete temperatures below 20–25°C.

Figure 9 shows a comparison between the values of the heat of hydration of the American cement shown in Figure 1 for five different curing temperatures as determined by the Saul formula and by equation (6b). In Figure 9 the values given by equation (6b) align themselves around a hypothetical curve more closely than the values given by Saul's formula. However, it must be borne in mind that these curves are for values over the temperature range  $+2^\circ$  to  $+45^\circ\text{C}$  only. Beyond this range it is possible that more suitable time-temperature functions may exist.

## Conclusions

1. In the preceding report it has been shown that the heat of hydration of a variable temperature process

can be compared with the same process at a pre-determined constant temperature by means of the time-temperature function

$$\tau_a = \int_0^t 2^{(\theta - \theta_a)/10} dt$$

2. By means of a test series conducted with three different values of water/cement ratio, it is shown that the heat of hydration per kilogram of cement at a given value of the time-temperature function varies with the water/cement ratio.
3. Using data from reports by Verbeck and Powers, the author has extended the use of his time-temperature function, developed as a heat of hydration relationship, to include the strength development of concrete.
4. When size, shape and insulation of a concrete specimen are known, together with mix proportions and properties of the cement (especially with regard to development of heat of hydration as a function of time at a constant temperature), it is possible to predict the temperature curve during hardening.
5. If the temperature is recorded during hardening, and the above-mentioned properties are known with the exception of the heat of hydration as a function of time, the latter can be computed and converted to relate to constant temperature.

## REFERENCES

- (1) CARSLAW, H. S. and JAEGER, J. G. *Conduction of heat in solids*. Oxford. The Clarendon Press. 1947. pp. 386.
- (2) Investigations of Portland cements. Denver. United States Department of the Interior, Bureau of Reclamation. 1949. Boulder Canyon Project, Final Reports. Part VII. Cement and Concrete Investigations. Bulletin No. 2. pp. 529.  
Thermal properties of concrete. Bulletin No. 1. pp. 154.  
Cooling of concrete dams. Bulletin No. 3. pp. 236.  
Mass concrete investigations. Bulletin No. 4. pp. 255.
- (3) LÖFQUIST, B. Temperatureffekter i hårdnande betong. Stockholm. Tekniska meddelanden från Kungl. Vattenfallsstyrelsen. Series B. No. 22. 1946. Vol. 1. 1st July. pp. 195.
- (4) HIRSCHFELD, K. Die Temperaturverteilung im Beton. Berlin. Springer-Verlag. 1948. pp. 154.
- (5) VERBECK, G. J. and FOSTER, C. W. Long-time study of cement in concrete. Chapter 6. The heats of hydration of the cements. *Proceedings of the American Society for Testing Materials*. 1950. Vol. 50. pp. 1235–1262.

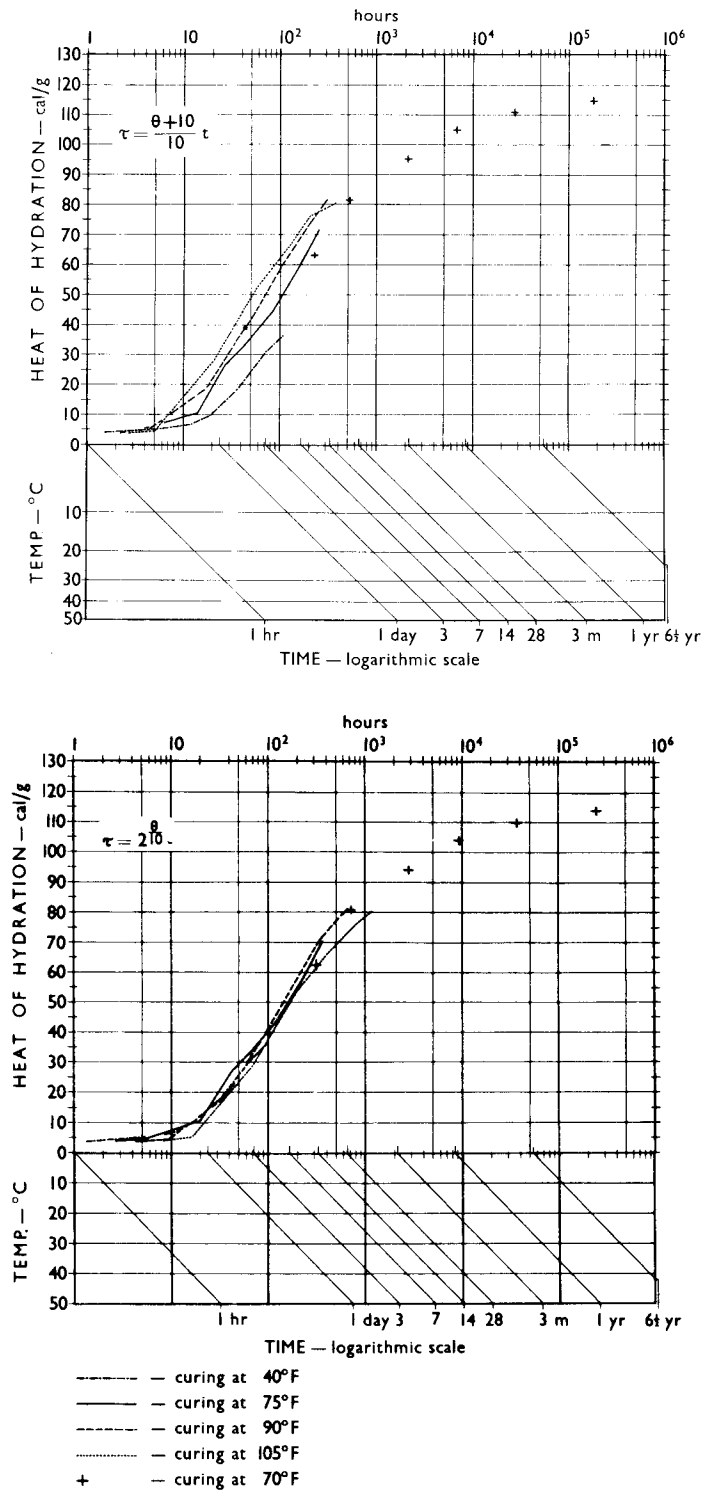


Figure 9: Heat of hydration plotted against the two time-temperature functions. (Results of the Portland Cement Association.<sup>(5)</sup>)

- (6) Low heat Portland cement. London. British Standards Institution. British Standard No. 1370:1947. pp. 36.
- (7) HALD, A. *Statistiske metoder med eksempler paa anvendelser indenfor tekniken*. Copenhagen. Det private Ingeniørfond. 1948. pp. 654.
- (8) BOGUE, R. H. *The chemistry of Portland cement*. New York. Reinhold Publishing Corporation. 1947. pp. xv, 572.
- (9) POWERS, T. C. *The air requirements of frost-resistant concrete*. Chicago. Portland Cement Association. Research Laboratory Bulletin No. 33. 1949. pp. 28.
- (10) SAUL, A. G. A. Principles underlying the steam curing of concrete at atmospheric pressure. *Magazine of Concrete Research*. 1951. Vol. 2, No. 6. March. pp. 127-135.