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Comparison of Test Methods to Determine the Heat of Hydration of Cements and Cement Blends

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ABSTRACT:

This paper takes a critical look at test methods used to determine the heat of hydration of cements and cement blends. CEN/TC 51 N 467 heat of solution and CEN/TC 51 N 468 semi-adiabatic methods are discussed and compared with Adiabatic Calorimetry.

The findings show that the adiabatic calorimetry method is the most flexible, enabling the evaluation of temperatures at various depths in almost all concrete structures. The heat of solution test is the only method that can determine hydration rates, at intervals, over a long period of time.

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Comparison of Test Methods to Determine the Heat of Hydration of Cements and Cement Blends

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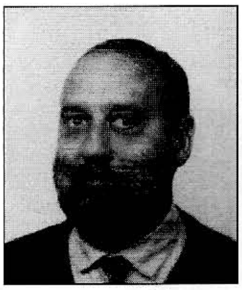

George Gibbon

George Gibbon obtained his MSc (Elec Eng) and PhD (Civil Eng) from the University of the Witwatersrand in 1990 and 1995 respectively. He worked at the Chamber of Mines Research Laboratories from 1974 to 1986 when he joined the University of the Witwatersrand as the Faculty Instrumentation Engineer and currently holds the position of Senior Lecturer in the Department of Electrical Engineering. During this time he has been involved with projects with the Cement and Concrete Institute, Blue Circle Cement, Ash Resources, PPC Cement and Slagment.

SYNOPSIS

This paper takes a critical look at test methods used to determine the heat of hydration of cements and cement blends. CEN/TC 51 N 467 heat of solution and CEN/TC 51 N 468 semi-adiabatic methods are discussed and compared with Adiabatic Calorimetry. The findings show that the adiabatic calorimeter method is the most flexible, enabling the evaluation of temperatures at various depths in almost all concrete structures. The heat of solution test is the only method that can determine hydration rates, at intervals, over a long period of time.

INTRODUCTION

As a result of both increased local competition and exposure to the international market, including joint projects such as the Lesotho Highlands scheme, the South African cement industry will be required to specify their cement products to international standards. The heat produced by the hydration process of cementitious materials will affect the mechanical properties of the concrete made with these materials in both mass concrete structures and where high ambient temperatures are experienced. Accurate measurement of this heat production with respect to time is required by design engineers, involved in such projects, to enable them to determine the most suitable concrete mix, production techniques and cooling systems that may be required for a particular structure.

THE HYDRATION PROCESS

Bye(1) describes the hydration process of Portland cement in terms of the heat liberation, by measuring the heat removed to keep the hydrating sample at 20°C, using a conduction calorimeter. An initial peak occurs, starting with the addition of the water, in excess of 200 W/kg after about 30 seconds and decreasing rapidly to a dormant period at about 1 hour after mixing. This initial peak is attributed to the wetting of the C_3S and the hydration of the gypsum, C_3A and any free lime in the sample (1,2). The physical change during this initial peak is an increasing stiffness which affects the workability and the time available for placement of concrete. The dormant period ends with an acceleration in heat evolution during which setting occurs with a peak in heat liberation between 9 to 10 hours. In some cements a third peak may be detected which varies considerably in both magnitude and the time at which it appears. These peaks are indicated on figure 1 in terms of power produced by an OPC mortar sample under adiabatic conditions.

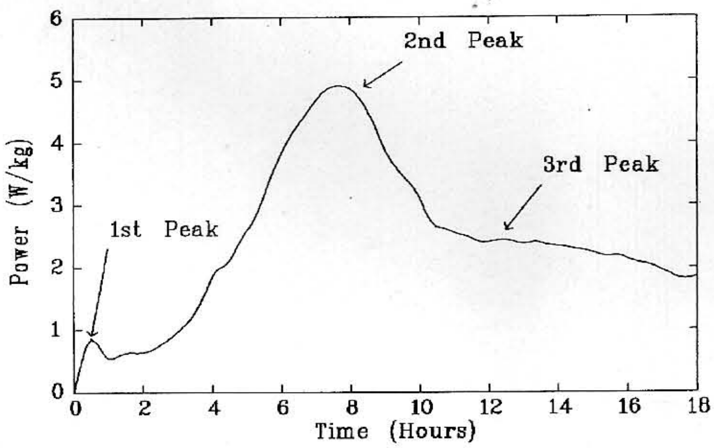

Figure 1: *Power Generated by the Hydration Reaction*

The hydration of cement is dependent on the following (3):

- Water:Cement ratio (w:c).
- Temperature (mixing, ambient and reaction).
- Intrinsic characteristics of the cement (composition and fineness).
- Moisture content of the mix during all stages of hydration.

TEST METHODS

Three different test methods for determining the heat of hydration of cementitious materials are discussed and their output compared.

Heat of solution method

The CEN/TC 51 N 467 (4) is a European standard, presently in final draft form, based on the heat of solution method. This test method is similar to the ASTM:C186-82 standard (5). The heat of hydration of hydraulic binders is determined by comparing the difference in the heat produced by an anhydrous and hydrated cement samples at different ages when they are mixed with a Nitric and Hydrofluoric acid mixture. The difference between the heat obtained from the samples gives the heat of hydration during the period that the hydrated sample has been hydrating. Hydration conditions which are arbitrarily specified for the test are:

- w:c ratio = 0,4
- Use of pure pastes
- 20°C temperature during the whole hydration process

The two drawbacks for this test method are that the sample is cured at a constant temperature (20°C) and the duration of preparing the samples and conducting the test (150 minutes). Curing the sample at a constant temperature does not represent the temperature conditions found in concrete structures and, as the hydration process is dependent on temperature, will not give accurate values for the heat liberation with respect to time. Evaluation of the hydration rate in the first 24 hours will be almost impossible because of the time required to conduct the test and the inability to quantify hydration during sample preparation, which includes crushing, homogenising and heating. The addition of pozzolanic materials with the Portland cement will reduce the accuracy of the results as pozzolanic materials are not completely soluble in the acid mixture (6). The heat of solution method is, however, the only method suitable for measuring the hydration process when the heat liberation drops to below the sensitivity of calorimeters using temperature measurement (1). This usually occurs between 3 and 7 days for OPC.

Semi-Adiabatic method

The CEN/TC 51 N 468 (7), also in final draft form, is based on the Langavant calorimeter method. A mixed sample of cement, sand and water is hydrated in a Dewar flask and the temperature of the sample together with ambient conditions are monitored during hydration. The specific heat of the sample and the flask, together with the calibrated heat loss of the system are used to calculate the heat produced during the test with respect to time.

The mix to be used is specified as:

- Binder = 360g
- Standard sand (EN 196-1) = 1 080g
- Distilled water = 180g

This is a w:c of 0,5 and an aggregate cement ratio (a:c) of 3:1.

The main drawback of this standard is that the heat loss from the system during hydration will prevent the test from determining the true heat of the hydration reaction, at temperatures in excess of those obtained during the test. This concern is valid for mass concrete structures where the conditions are almost adiabatic at depths greater than 0,5m (8). Comparison of results from the heat of solution and the semi-adiabatic methods is difficult as the different w:c ratios and curing temperatures used, produce different hydration reactions.

Adiabatic-calorimetry

As far as can be ascertained no standard has been defined for adiabatic calorimetry to determine the heat of hydration of cement although the process was first documented by Davey (9) in 1931.

With adiabatic calorimetry a sample (mortar or concrete) is allowed to hydrate in conditions where there is no heat transfer to or from the sample. The heat of hydration can then be calculated from the specific heat and the temperature increase of the sample.

Figure 2 shows a block diagram of a low cost, computer controlled adiabatic calorimeter (10,11).

An approximately 2kg sample of mortar or concrete is put into a plastic bottle which is then placed into the glass bottle. During a test the temperature of the water bath is kept to the same temperature as that measured by a temperature probe, placed in the sample, thus maintaining adiabatic conditions. If the same components, a:c and w:c ratios and specific heats as proposed for actual concrete mixes are tested, temperatures can be predicted for adiabatic conditions in concrete pours. The heat of hydration, with respect to time, for the binder used in the sample can also be determined at the temperature profile of the adiabatic test. As with the other two test methods discussed, this limits the rate of hydration determined to a specific curing temperature. Research into a method for using adiabatic calorimetry to determine the hydration reaction at any depth in any concrete structure was undertaken by the author.

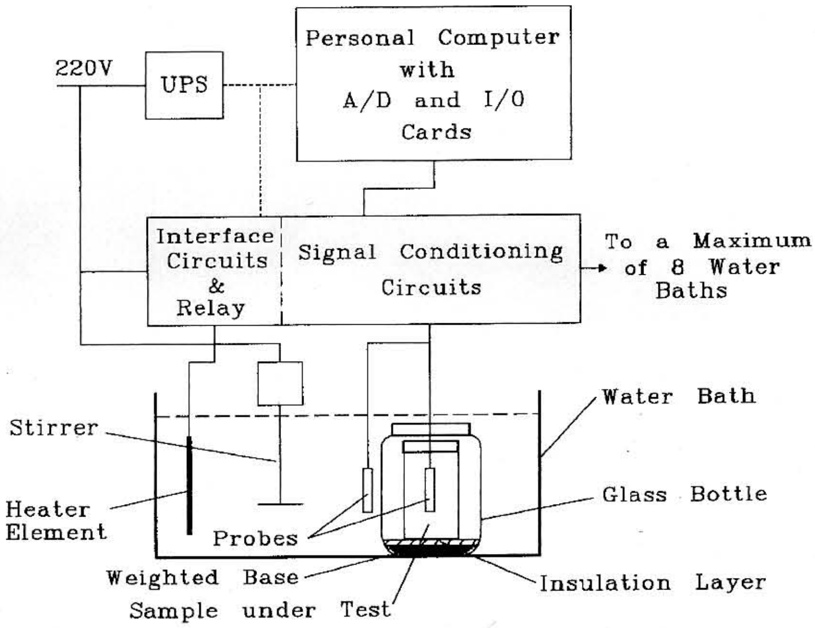

Figure 2: *Adiabatic Calorimeter*

The relationship between the curing temperature and the hydration reaction is defined in equation 1 (3).

$$\frac{1}{T} \alpha \log_{10} q \qquad (1)$$

where

T=Curing Temperature (K)
q=Heating Rate (J/kg K)

A test procedure has been developed where the cementitious material is mixed with washed silica sand, with particle sizes from 0,075 to 1,5mm, and water with an a:c ratio of 3:1 and a w:c ratio of 0,6. This mortar is then blended with silica stone (4-9mm) to provide for a:c ratios up to 12:1.

Three tests which were conducted under adiabatic conditions with the same binder and w:c ratio but with differing a:c ratios as shown in table 1.

Because of the different a:c ratios curing takes place at different temperature profiles, shown in figure 3, which results in the power and heat calculated as shown in figures 4 and 5. From this information and equation 1 the hydration rate at any temperature can be determined and used with the thermal conductivity in a heat model (10,12) to determine the expected temperature at any position within a concrete structure. For example, predicted temperatures were verified (to within 2°C) at the Katse and Muella dams in the Lesotho Highlands Water Scheme. Temperature matched curing (TMC) (13,14,15)

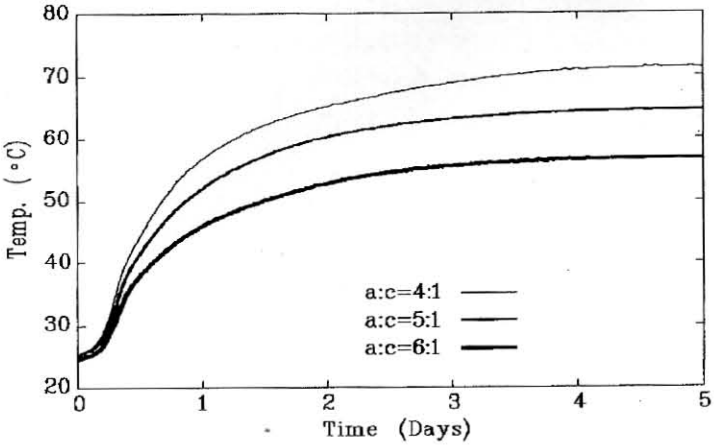

Figure 3: *Temperature Profiles (OPC SABS-471)*

Table 1: *Test Mixes*

	Mix 1	Mix 2	Mix 3
Binder	337,5g	270g	225g
Aggregate	1,35kg	1,35kg	1,35kg
Water	168g	135g	112g
w:c	0,5g	0,5	0,5
a:c	4:1	5:1	6:1

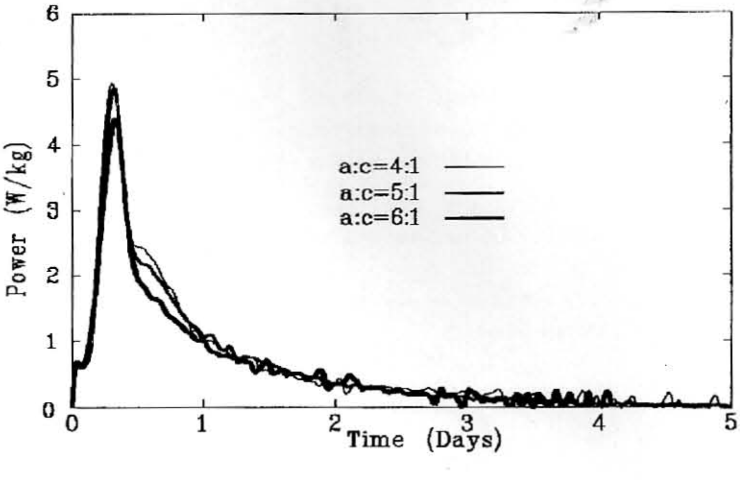

Figure 4: *Power Generated (OPC SABS-471)*

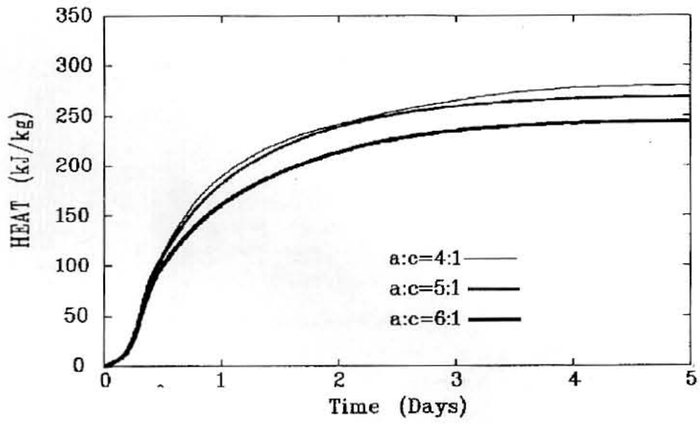

Figure 5: *Heat Generated (OPC SABS-471)*

can also be undertaken with these temperature profiles and the physical properties of the in-situ concrete determined.

CONCLUSION

The CEN/TC 51 N 467 heat of solution and CEN/TC 51 N 468 semi-adiabatic methods discussed in this paper provide information on the heat liberated during hydration of hydraulic binders. The results from the heat of solution test are limited by a constant curing temperature and an inability to determine the reaction rate at early stages of hydration. It is the only test which can determine low rates of hydration (after 7 days).

The semi-adiabatic test allows the hydration rate to be determined at varying temperatures but it has a limited maximum temperature due to heat being lost through the system. If other w:c and a:c ratios are used temperature profiles could be varied from those obtained when using the standard mix proportions.

The tests described using the adiabatic test procedures allow for the determination of the heat of hydration at any temperature profile within a concrete structure. The tests would be conducted with a w:c ratio usually selected to obtain the desired strength or durability for a particular structure. The adiabatic calorimeter method is a low cost option when based on the computer controlled calorimeter described, capable of monitoring up to eight samples in separate water baths and controlling the temperature of each bath. Thus tests comparing w:c ratios, a:c ratios or different binders can be conducted simultaneously reducing the time required to obtain the input information required for the design of concrete structures.

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