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APPLICATION OF HEAT FLOW CALORIMETRY TO THE STUDY OF OILWELL CEMENTS

P. N. Aukett and J. Bensted

BP RESEARCH, SUNBURY RESEARCH CENTRE, CHERTSEY ROAD, SUNBURY-ON-THAMES,
MIDDLESEX, TW16 7LN, ENGLAND

The majority of previous studies of the hydration of cements using heat flow calorimetry have been carried out isothermally. However, with oilwell cements the slurry is mixed on the surface at ambient temperature and then gradually increases in temperature as it is pumped down the well. A Setaram C-80 calorimeter has been used to simulate the temperature ramp in API oilwell cement test schedules. This approach has enabled cementing reactions to be studied for the first time under conditions approaching those encountered in the field, and has shown that the results obtained from isothermal experiments may be misleading.

Keywords: heat flow calorimetry, oilwell cement

Introduction

During the hydration of cement appreciable quantities of heat are evolved. Conduction calorimetry is a non-intrusive technique which allows the rate of heat evolution to be continuously monitored, giving valuable information on both the rate and nature of the chemical reactions that take place. The value of this approach has been illustrated by the widespread use of the Wexham calorimeter [1] in cement hydration studies. However, conduction calorimetry has not so far found extensive application with oilwell cements. This is partially explained by experimental limitations of the Wexham calorimeter:

(i) Experiments can only be carried out up to 95°C which does not allow the study of hydrothermal cementing reactions. Oilwell cements encounter temperatures of up to 180°C depending on the depth of the well.

(ii) It is difficult to mix water and cement in-situ, so the initial heat peak cannot be determined. Although not critical to an overall assessment of the reactivity of the cement, this peak provides valuable additional information on the reactions which are taking place.

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In this laboratory a Setaram C-80 calorimeter has been used to study cementing reactions at temperatures up to 180°C [2]. The reversal mixing cell allows both the initial heat peak from rapid solution, hydration and reaction to be determined in addition to the later peak during which thickening of the cement occurs. It is also possible with the C-80 to follow the temperature gradients used in API oilwell cement test schedules. These test schedules are designed to simulate the mixing of a cements slurry on the surface at ambient temperature followed by the passage of the slurry downhole. The temperature is increased linearly from the time of mixing to a maximum value which is then maintained. Although the corresponding pressure gradient cannot at present be simulated, such evidence as is available from field data suggests that the influence of temperature is correspondingly greater than the influence of pressure.

Experimental

A standard Setaram reversal mixing cell was used with a Setaram C-80 calorimeter. The cement (1 g) was placed in the lower half of the cell which was sealed with a loose fitting lid covered by a layer of mercury (2 ml). Distilled water was then floated on top of this layer of mercury (Fig. 1). The solid cement additives used in this study (borax and calcium lignosulphonate) were preblended with the cement. Experiments were carried out using a commercial Class G oilwell cement at a water/cement ratio of 0.44 (0.44 ml of water for 1 g of cement).

The calorimeter was preheated to the desired starting temperature and the cell was then placed into the calorimeter. It should be noted that for experiments over 100°C the cell is internally pressurised, as water will evaporate until liquid/vapour equilibrium is reached. This currently limits the maximum experimental temperature to 180°C. At this temperature the vapour pressure of water equals the maximum working pressure of the cell (10 bar). The reference cell in the calorimeter contained the same volume of mercury and 1 g of set cement.

Once thermal equilibrium had been reached, data collection was started and reaction initiated by rotating the calorimeter. This caused the loose fitting lid to fall away allowing the cement and water to mix. The calorimeter was rotated during the remainder of the experiment to ensure adequate mixing. At the moment of mixing a temperature programme was initiated as stipulated in API Schedule 5. This is the standard thickening test for Class G oilwell cements and is designed to simulate an 8000 ft well depth [3]. The temperature gradient is from 27° to 52°C in 28 minutes, then hold at 52°C.

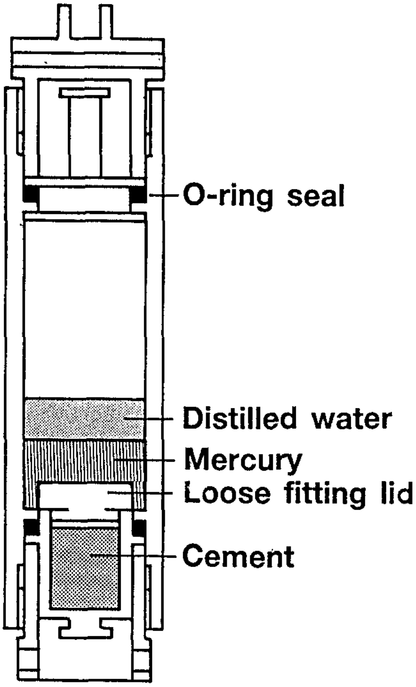

Fig. 1 Setaram reversal mixing cell

A blank measurement (see below) was carried out using the same temperature profile. This data was subtracted from the experimental data to correct for the baseline shift arising from the temperature programmed phase of the experiment. This is caused by the difference in heat capacity between the sample and reference cells.

Results and discussion

Experimental considerations

Selection of an appropriate reference cell and blank measurement is essential in obtaining reliable data, particularly for temperature programmed experiments. It is desirable to match the thermal capacity of the reference and sample cells and for the blank measurement to match the actual experiment as closely as possible. Since in these experiments the initial components are consumed to form new materials the heat capacity of the system will change with time. Only the extremes are accessible as reference systems, i.e. unmixed water/cement and set cement. For the majority of the experiment the heat capacity of the reaction mixture is expected to be closest to set cement. Therefore, set cement was used in the reference cell for all experiments including the blank measurement.

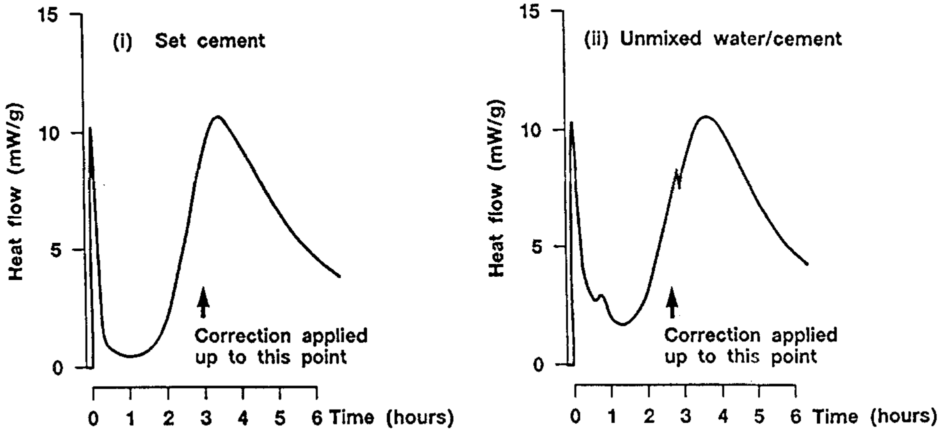

Fig. 2 Comparison of blank experiment corrections

In contrast, it is not clear which reference system should be placed in the sample cell for the blank measurement. Taking into account both how long the temperature programmed phase lasts and also the time constant of the calorimeter, a correction is only required for the first 2-3 hours of the experiment. During this time the cement will remain as a slurry, i.e. chemically and physically intermediate between the two possible reference systems. Figure 2 compares the corrected result obtained using

(i) a set cement and

(ii) an unmixed water/cement for the blank measurement.

It can be seen that the set cement provides an acceptable correction. In contrast, the unmixed water/cement causes a discontinuity in the heat flow curve at a point at which the correction should no longer be required. This is probably because in the unmixed system there is a significant endotherm from evaporation of water. This is not present in the actual experiment as the majority of the water will be chemically bound to components of the cement. A large difference in heat capacity between the unmixed and mixed system may also be responsible.

Comparison of temperature simulations with isothermal experiments

In Fig. 3 the heat flow curve obtained for a class G oilwell cement using the API Schedule 5 simulation is compared with the heat flow curve obtained from an isothermal experiment at 52°C. Qualitatively the curves are similar, exhibiting the usual two peaks separated by a short plateau region [2]. Thickening of the cement occurs on the rising edge of the second peak. However, the time at which the second peak occurs is significantly advanced for the API Schedule 5 simulation. This can be explained by the lower initial temperature. The extent of reaction on mixing is lower (the area of the first peak is reduced from 12.1 to 5.8 $J \cdot g^{-1}$), therefore the further reaction usually observed on mixing for the isothermal experiment appears at a later time once the cement has been heated to 52°C.

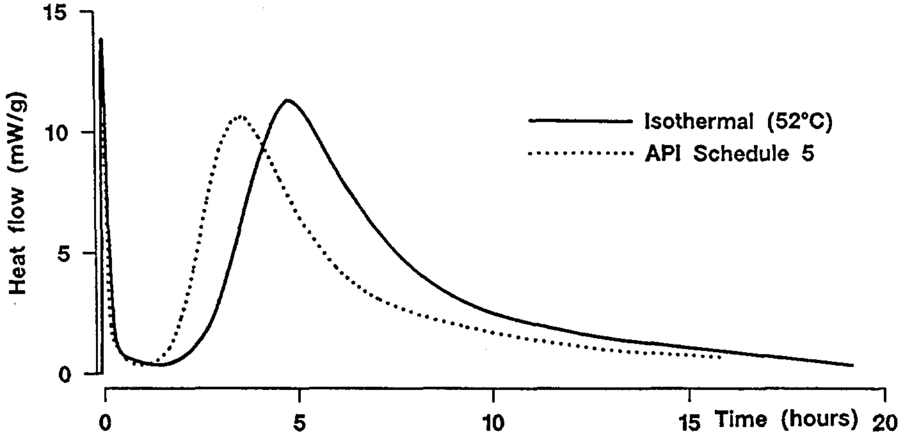

Fig. 3 Heat flow curves for class G oilwell cement

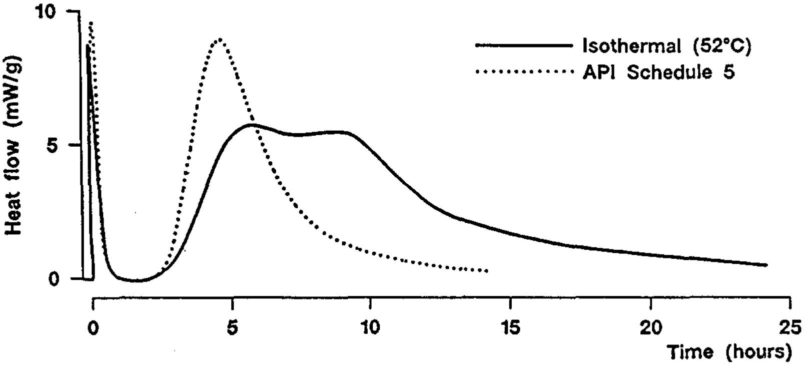

Fig. 4 Heat flow curves for class G oilwell cement +0.3% borax

This advancement of the second heat peak is even more apparent when 0.3 wt% borax ($Na_2B_4O_7$) is added as a retarder (Fig. 4). In contrast, with 0.3 wt% calcium lignosulphonate the effect is less marked (Fig. 5). Differences such as this illustrate that conclusions regarding the reactivity of a cement or on the effect of additives on reactivity may be misleading when based on isothermal experiments alone.

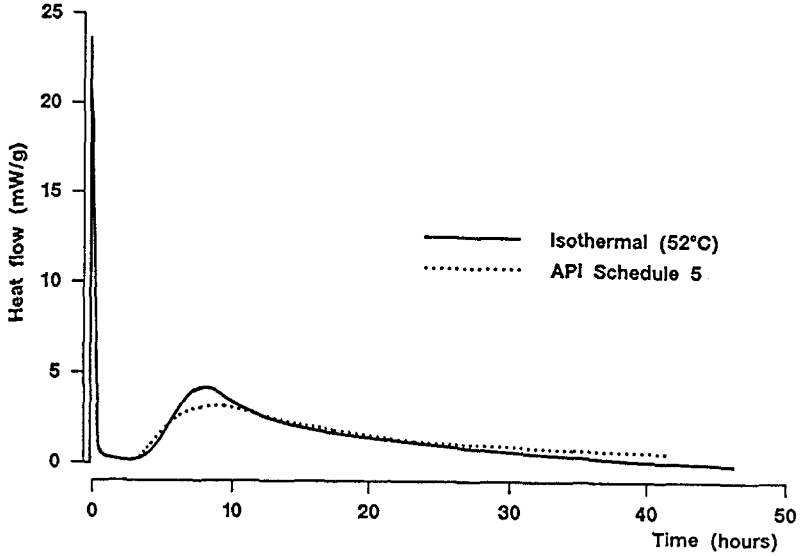

Fig. 5 Heat flow curves for class G oilwell cement +0.3% calcium lignosulphonate

Conclusion

This approach enables oilwell cements to be studied for the first time under conditions approaching those encountered in the field. The various cementing reactions will occur at different rates at different temperatures, and it has been shown that the reactivity of cement/additive combinations are difficult to predict from isothermal experiments. Reliable simulation experiments allow the most suitable cement and additives to be recommended for a particular application with greater confidence than is possible at present.

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Zusammenfassung — Die Mehrzahl der bisherigen Untersuchungen der Hydratation von Zement unter Anwendung der Wärmeflußkalorimetrie wurden unter isothermen Bedingungen durchgeführt. Mit Zement für Erdölbohrungen wird der Rohschlamm jedoch an der Oberfläche bei Umgebungstemperatur gemischt und nimmt dann, während er die Bohrung hinuntergepumpt wird, laufend an Temperatur zu. Zur Simulation des Temperaturanstieges in API Zement für Erdölbohrungen wurde ein Setaram C-80 Kalorimeter verwendet. Dies gestattet es erstmals, die Zementierungsreaktionen unter den gleichen Bedingungen wie in der Praxis zu untersuchen. Es zeigte sich, daß die aus isothermen Experimenten erhaltenen Ergebnisse irreführend sein können.