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STUDIES OF EARLY HYDRATION WITH CLASS G OILWELL CEMENT USING HEATFLOW CONDUCTION CALORIMETRY

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ABSTRACT

Examination of the early hydration of a production Class G oilwell cement by conduction calorimetry under temperature simulated API Schedule 5 and Schedule 8 conditions, using calcium lignosulphonate retarder and 'doped' additions of pure tricalcium silicate and tricalcium aluminate, has demonstrated significant changes in the precise course of hydration if one or more of these additions be present. Reasons for such changes are given.

INTRODUCTION

Previous studies of heatflow conduction calorimetry at temperatures up to 180 °C have indicated how useful the technique is for cement hydration studies, especially for oilwell and calcium aluminate (high alumina) cements [1], [2], [3], [4]. In particular, the technique has proved to be useful for simulating the temperature gradients used in API oilwell cement test schedules [1], [2], [5], [6].

In the present work, heatflow conduction calorimetry has been used to investigate how changes in the most reactive constituents, tricalcium silicate (alite) C_3S and tricalcium aluminate (aluminate or celite) C_3A (see Table 1), influence cement slurry reactivity during pumping downhole to form a cement sheath in the annular space between the metal casing (or liner) and the borehole walls, and also, for C_3S, in particular the advent of thickening (setting) and hardening in the annulus.

TABLE 1. CEMENT CHEMICAL NOMENCLATURE

Symbol	Chemical formulae
A	Al_2O_3
C	CaO
F	Fe_2O_3
H	H_2O
S	SiO_2
$C_3S \equiv$	$3CaO.SiO_2 \equiv Ca_3SiO_5$
$C_3A \equiv$	$3CaO.Al_2O_3 \equiv Ca_3Al_2O_6$
C-S-H	calcium silicate hydrate

(- the hyphens between C, S and H indicate that no specfic chemical composition is implied for this non-stiochiometric hydration product)

EXPERIMENTAL WORK

A Blue Circle HSR (high sulphate-resisting) Class G oilwell cement (see Table 3) was used as the basis for this investigation. Pure samples of C_3S and C_3A were prepared by direct synthesis [7] and checked for purity by X-ray diffraction. They were stored in vacuum desiccators prior to usage to avoid any surface carbonation [8], [9]. A proprietary calcium lignosulphonate retarder (CLS) in powered form was employed to regulate the hydration of cement slurries as appropriate. A water/cement ratio of 0.44 was chosen for these experiments, since this is the value employed in specification testing [5], [6]. The C_3S and/or C_3A 'doped' additions are considered to be part of the cement.

TABLE 2. API SCHEDULES 5 AND 8

(a) SCHEDULE 5

- Pressure increased uniformly from 6.9 MPa at 0 minutes to 35.6 MPa at 28 minutes (rate of increase 1.025 MPa/minute) and thence maintained at this value.
- Temperature increased uniformly from 27 °C at 0 minutes to 52 °C at 28 minutes (rate of increase 0.89 °C/minute) and thence maintained at this value.

(b) SCHEDULE 8

- Pressure increased uniformly from 12.1 MPa at 0 minutes to 92.3 MPa at 52 minutes (rate of increase 1.54 MPa/minute) and thence maintained at this value.
- Temperature increased uniformly from 27 °C at 0 minutes to 97 °C at 52 minutes (rate of increase 1.35 °C/minute) and thence maintained at this value.

TABLE 3. ANALYTICAL DATA FOR THE CLASS G OILWELL CEMENT

Compound	%	API(%) [6]
C_3S	61.2	48 - 65
C_2S	15.1	—
C_3A	0.5	3 max
C_4AF	16.0	—
$C_4AF + 2 \times C_3A$	17.0	24 max
Na_2O Equivalent	0.33	0.75 max
SO_3	2.3	3.0 max
MgO	0.3	6.0 max
Loss on Ignition	1.1	3.0 max
Insoluble Residue	0.2	0.75 max
Free Lime	0.9	—
Surface Area	312 m^2/kg	

Experiments were carried out with the neat slurries as well as 5% by weight 'doped' additions of C_3S or C_3A and both with or without 0.3% by weight additions of CLS under temperature simulated API Schedule 5 conditions [6]. Similar experiments were carried out with the retarded slurries under the higher temperature simulated API Schedule 8 conditions [5], [6]. These experiments were undertaken in a Setaram C-80 heatflux calorimeter with a reversal mixing cell to prevent heat losses during initial hydration, as in earlier experiments [1], [2]. The second heat peak was quantified in terms of measuring the heat evolved and the height and position of the peak maximum.

RESULTS

The results of this investigation are given in Table 4 and illustrated in Figures 1-3.

DISCUSSION

The data obtained indicated not only the relative influences of more C_3S or more C_3A compared with the original cement, but showed interactive effects when both were increased by the same 5% (by weight of original cement) margin and also the relative influences of the CLS retarder. Given the long time scale of the experiment (64 hours) and the general broadness of the peaks, differences of 10 minutes or less for peak position and of 0.2 mW/g or less for peak height are not significant here. No assessment was made of the reproducibility of this technique.

When 5% pure C_3S was added to the Class G cement (test 2) more heat was evolved, giving a similar peak height but the same position here for the peak maximum at 3 hours 50 minutes, as compared with the neat Class G cement (test 1) under similar conditions.

TABLE 4. CONDUCTION CALORIMETRIC DATA

Test No.	Mix	2nd Heat Peak -ΔH (j/g)	Peak Height (mW/g)	Peak Maximum (hours-minutes)
(a)	API SCHEDULE 5			
1	C[1]	118.3	10.9	3-50
2	C+5% C_3S	131.5	11.0	3-50
3	C+5% C_3A	94.3	8.7	3-40
4	C+5% C_3S+C_3A	110.6	10.8	3-38
5	C+0.3% CLS[2]	169.1	2.3	8-26
6	C+0.3% CLS+5% C_3S	160.8	1.1	10-24[3]
7	C+0.3% CLS+5% C_3A	212.8	3.6	9-07
8	C+0.3% CLS+5% C_3S+5% C_3A	196.4	1.8	8-36
(b)	API SCHEDULE 8			
9	C+0.3% CLS	282.5	16.5	7-59
10	C+0.3% CLS+5% C_3S	183.1	12.8	9-16
11	C+0.3% CLS+5% C_3A	152.1	16.5	7-07
12	C+0.3% CLS+5% C_3S+5% C_3A	170.9	14.0	6-52

[1] C -HSR Class G oilwell cement

[2] CLS -Calcium lignosulphonate retarder (solid)

[3] 3rd heat peak of practically identical height 1.2 mW/g and peak maximum 18 hours and 58 minutes.

This clearly showed the dominant influence of calcium silicate hydrate C-S-H formation upon the second heat peak at a low C_3A level. When the cement was 'doped' with 5% pure C_3A, there was less heat evolved and a lower peak height than in either test 1 or test 2, presumably as a result of relatively less C_3S being present overall. This decrease is greater than the dilution factor here and indicates that interactive effects are arising, which require further investigation.

However, the peak maximum was advanced by only 10 minutes to 3 hours 40 minutes, most likely due to the effect of some more ettringite (AFt phase) being formed from the enhanced C_3A content. When both 5% C_3S and 5% C_3A were present (test 4) the heat evolved was similar to that with just 5% C_3S addition being present, with the peak height also being similar and the peak maximum being about the same as that with 5% C_3A present.

With CLS retarder present (test 5), the second heat peak was reduced in size, but spread out over a longer time span. Overall there was more heat evolved than in the absence of the retarder (test 2), but the peak height was much diminished and the peak maximum had appeared much later at 8 hours 26 minutes. This reduced peak height and retarded peak maximum could be ascribed to the effects of less C-S-H being formed.

The greater heat evolution suggested that the other phases like C_3A and C_4AF were re-

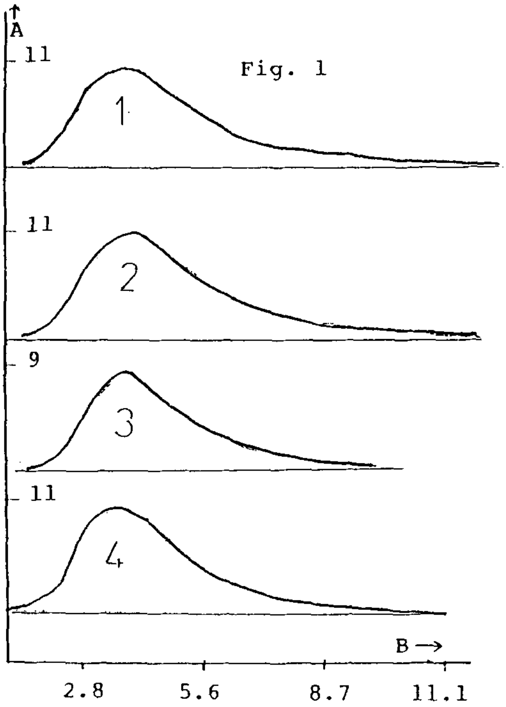
Fig. 1

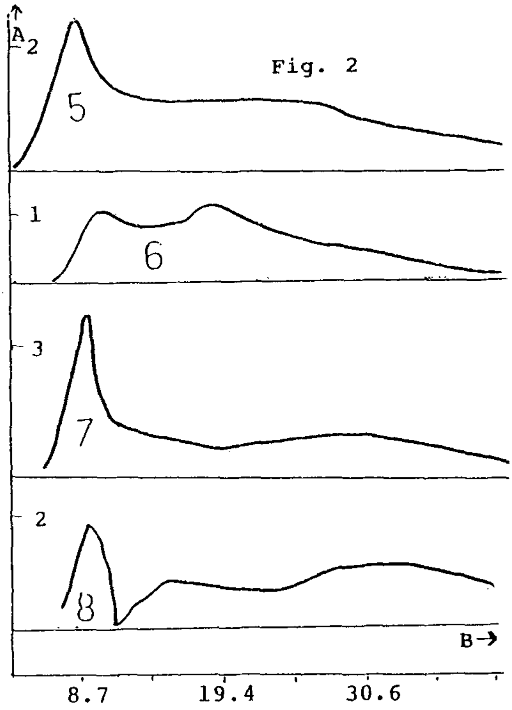
Fig. 2

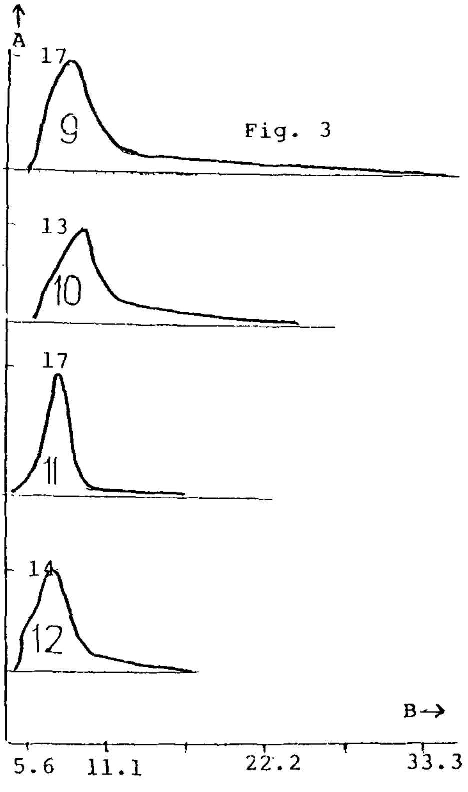
Fig. 3

Conduction Calorimetric Curves:

1. API Schedule 5 conditions without CLS retarder.
2. API Schedule 5 conditions with CLS retarder.
3. API Schedule 8 conditions with CLS retarder.

Axes of Curves:

A. Heat Flow (mW/g).

B. Hydration Time (hours).

acting more, presumably because as less C-S-H was being formed there was more room for hydrates like ettringite $C_3(A,F).3CaSO_4.32H_2O$ to form these phases [10]. Certainly at this early stage of hydration there is ample room for any kind of precipitation. Nevertheless, a greater rate of ettringite deposition was recorded qualitatively by infrared spectral examination of similar cement samples hydrated under comparable conditions and dried out at various fixed time periods (to be published). When 'doped' with 5% C_3S, there was even less heat evolved and greater retardation (test 6), presumably because the extra C_3S was being retarded and extra unretarded clinker mineral of this type occupied space that prevented as much ettringite being formed as in test 5. With 5% C_3A addition, more heat was evolved and there was a greater peak height, most likely due to more ettringite formation here, but the peak maximum of 9 hours 07 minutes was retarded in comparison with that of test 5.

This situation would have arisen from the relative diminution of total C_3S content in the overall cementitious mix of test 7, since C_3S hydration is the prime contributor to thickening time and to the emergence of the second heat peak. When both 5% C_3S and 5% C_3A were added to the cement and retarder (test 8), the heat evolved and peak height were lower than for test 7, because of the relative diminution of C_3A compared with test 7. However, as observed earlier with test 4, the peak maximum was brought forward, significantly so in this instance to 8 hours 36 minutes, suggesting that increasing both C_3S and C_3A produces a mutual symbiotic relative acceleration of the hydration of both phases.

Similar relative effects were observed under Schedule 8 conditions in respect of peak height and peak maximum, which were respectively enhanced and brought forward under the higher temperature conditions pertaining here compares with those of Schedule 5 (Table 2). However, although more heat was, as expected, evolved in tests 9 and 10 in comparison with the situation in tests 5 and 6 respectively, less total heat was evolved in the presence of C_3A for tests 11 and 12, especially in test 11 in comparison with tests 7 and 8 respectively.

This was probably due to the 'threshold effect' of extended thickening time during the temperature ramping up at 60 °C and 80 °C caused by an initial 'burst' of ettringite formation from C_4AF prior to the advent of the second heat peak, which obstructed C_3S hydration. The threshold effect has been described in detail elsewhere [11]. The symbolic effect of the peak maximum being brought forward when the 'doped' C_3S and C_3A were both present was again apparent in test 12.

Thus, even at the 5% level changes in the phase composition for C_3S and/or C_3A have a significant effect upon the hydration behaviour of Class G oilwell cement. Such changes obviously influence thickening time, which arises on the low time side of the second heat peak, and the rheological development of the cement slurry as it is pumped into position downhole. The heat evolution pattern is complicated by the complexity of the hydration behaviour under the conditions examined.

CONCLUSION

Heatflux conduction calorimetry is a very discerning method for studying cement hydration behaviour, such as Class G oilwell cement. It has been shown to be very useful for revealing changes in the pattern of heat evolution and this in the precise course of hydration when changes are made to the relative levels of C_3S and C_3A in the cement. From the relative levels of heat evolution from the second heat peaks, it is clear that changes in the respective levels of C_3S and C_3A in the oilwell cement influence each other's hydration behaviour. C_3S does not hydrate effectively independently of C_3A during early hydration and vice versa. Although the pressure effects of API Schedules 5 and 8 could not be simulated by the calorimeter employed, the influence of temperature, which was able to be simulated, is likely to have a more profound effect upon the hydration chemistry than changes in pressure. The temperature simulation API Schedule 5, for example, is readily discernible by heatflux conduction calorimetry from that carried out isothermally at 52 °C [2]. This technique is particularly useful for investigating the hydration of oilwell cements and thus complementing the usual laboratory specification testing and other test data [5], [6].

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