Pergamon

Cement and Concrete Research, Vol. 25, No. 2, pp. 240-242, 1995

0008-8846/95 $9.50+.00

0008-8846(95)00002-X

S-CURVE EFFECT IN OILWELL CEMENT COMPRESSIVE STRENGTH DEVELOPMENT UNDER HYDROTHERMAL CONDITIONS

John Bensted*
BP International Ltd, Sunbury Research Centre, Sunbury-on-Thames,
Middlesex, TW16 7LN, United Kingdom

(Communicated by D.M. Roy)
(Received June 24, 1994)

An oilwell cement formulation produced for cementing a deep liner under high pressure and temperature conditions performed satisfactorily in simulated tests like thickening time, free fluid, rotational viscometry, but gave an unexpected retrogression in the compressive strength measured at 12 hours, which disappeared at 20 hours and beyond, when normal strength growth had resumed. Reasons for this transient strength retrogression, which can be called S-curve behaviour from the S-shape of the strength vs time curve obtained, have been addressed.

The cement formulation is reasonably typical of the type employed for high pressure and temperature well sections, and was designed for a 16000 ft (4880 m) liner under API Schedule 30L8 conditions[1] where the bottom hole circulating and static temperatures[2] were 171°C and 193°C respectively. See Table 1.

TABLE 1 : LINER CEMENT FORMULATION
For convenience here, all additives are given as % by weight of cement (BWOC).

Material	%BWOC
HSR Class G Cement	-
Silica Sand	35.0
Haematite Weighting Agent	45.7
Proprietary Dispersant	2.0
Proprietary Fluid Loss Controller	1.5
Microsilica Slurry (50% in water)	18.6
Proprietary High Temperature Retarder	2.3

Freshwater to 18.7 lb/U.S. gallon (2.24 kg/l)

As well as HSR Class G oilwell cement, the formulation contained 35% silica sand to prevent strength retrogression under hydrothermal conditions, haematite weighting agent to thwart any blow out, a suitable dispersant to permit satisfactory mixing and pumping into position in the annulus, a fluid loss controller to minimise any slurry loss into the rock formations downhole, microsilica

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* Present address: Industrial Materials Group, Department of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX

(condensed silica fume) to act as a bed to stop settlement within the slurry, and a suitable retarder to allow an adequate thickening time for pumping[3,5].

The results are shown in Table 2. The thickening time and zero operating free fluid[1] indicate an adequate placement time and that the slurry ingredients should not settle out during placement. The rheological data show that the slurry is sufficiently fluid for pumping into position downhole. With the Schedule 10Sg8 compressive strengths carried out at the bottom hole static temperature of 193°C, significant strength is obtained at 5 hours and afterwards follows the pattern shown in Figure 1 as curing time rose.

TABLE 2: CEMENTING DATA

Schedule 30L8 Thickening Time	249 minutes
Operating Free Water	0 ml

Rheological Data (Rotational Viscometry)[1,5]

r.p.m.	dial reading	r.p.m.	dial reading
600	300	100	96
300	225	6	29
200	159	3	28

10 sec gel str 92 Pa
10 min gel str 167 Pa
PV 0.176 Pa.s
YP 21 Pa

str- strength, PV- plastic viscosity, YP- yield point

CT (hours)	CS (MPa)	CT (hours)	CS (MPa)
5	2.8	16	23.4
8	24.9	20	26.5
12	22.1	24	35.2

CT- curing (hydration) time.
CS- Schedule 10Sg8 compressive strength.

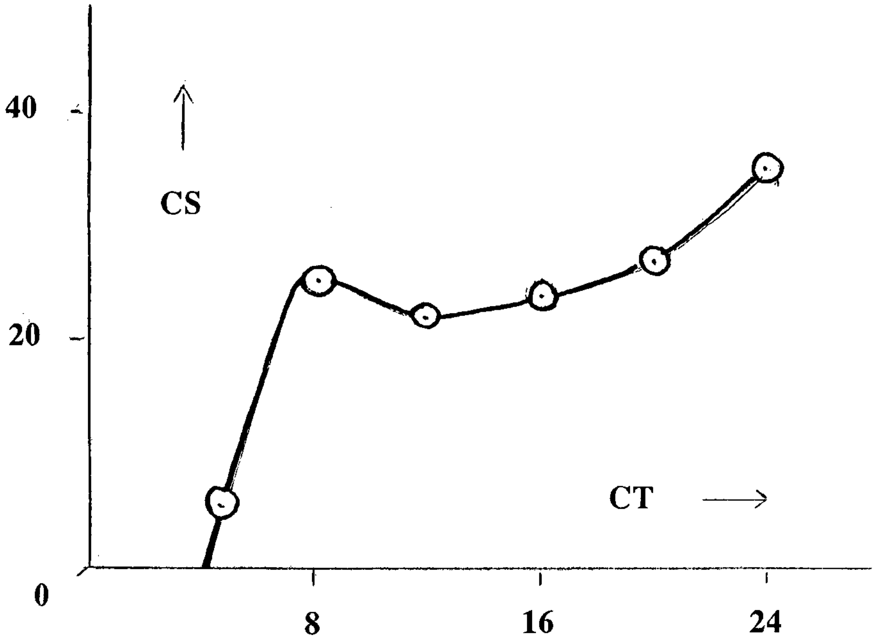

FIGURE 1: GRAPH OF CURING TIME (hours) vs API SCHEDULE 10Sg8 COMPRESSIVE STRENGTH (MPa)

X-ray diffraction studies were carried out on freeze-dried specimens, that were dried out immediately following the strength measurements that had been stored under nitrogen to stop carbonation of the small dried out samples. From this work the reasons for the S-curve effect of compressive strength vs curing time became apparent. (This S-curve effect is not related to the S-curve effect of thickening time vs retarder addition, which has previously been described[6]).

At 5 hours formation of poorly crystalline calcium silicate hydrate C-S-H (II) had just formed, whilst at 8 hours much more was observed as the strength rose rapidly. At 12 hours there was also alpha-dicalcium silicate hydrate α-C_2SH, which corresponded to a relatively small but significant strength reduction. Moreover at 16 hours there was evidence for the presence of some tobermorite $C_5S_6H_5$ as well, a trend which continued at 20 hours, where the strength had risen a little more. At 24 hours a relatively large increase in tobermorite relative to α-C_2SH corresponded to a big strength rise.

The strength behaviour observed can be attributed to microsilica reacting much quicker than silica sand, forming the C-S-H before producing α-C_2SH, since at 9.3% BWOC, there was insufficient to form strength giving tobermorite, which had to wait for silica sand to start reacting significantly, since it was present here in quantities beneficial for tobermorite formation under prevailing hydrothermal conditions (35% BWOC). The formation of the characteristically large crystals of α-C_2SH is known to be a cause of strength retrogression in oilwell cements under hydrothermal conditions[4,7].

Thus, the S-curve behaviour of compressive strength with curing time observed under high pressure and high temperature conditions for a given HSR (high sulphate-resistant) Class G oilwell cement in a 16000 ft (4880 m) liner formulation can be explained on the basis of high early reactivity of the finely-divided microsilica bed and the much lower commensurate reactivity of silica sand in the slurry under the simulated downhole conditions employed here. The minimum in the strength curve found in these experiments was well above the safety margin and would not per se give rise to any real problems in practical usage under these conditions.

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