Pergamon

Cement and Concrete Research 30 (2000) 1709–1713

CEMENT AND CONCRETE RESEARCH

Tertiary gelation of oilwell cement

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Received 6 October 1998; accepted 22 August 2000

Abstract

The aim of this research was the investigation of the origin of the oilwell cement slurry gelation problem which can appear during well-cementing operations. In this study, the relations between the development of consistency of cement slurry, the hydration process and surface growth in the paste were studied for several commercial oilwell cements. The effect of gypsum content on the consistency of cement slurry was evaluated. In order to relate the hydration process and the consistency development, the hydration of cements was followed by thermogravimetric analysis (TGA), X-ray diffraction and by proton NMR spectroscopy. A comparison between the results obtained and some published data is presented. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Rheology; Hydration; Oilwell cement

1. Introduction

During oilwell cementing, the cement slurry is placed and hardened in the annulus between the metal casing and the formation. Hardened cement isolates different zones within the wellbore and supports the casing. Cement slurry must thus remain pumpable for sufficient time so as to allow its placement under specific well conditions.

Gelation is one of the most serious problems that can appear during oilwell cementing. It can be defined as a premature increase of viscosity or a gel strength buildup of the cement slurry. The physico-chemical basis of gelation is very complex and, consequently, there is a broad spectrum of conditions under which gelation can occur. Factors involved include chemical composition of cement, its microstructure, the water quality, the types of additive used and the temperature to which the slurry is exposed.

Four different types of gelation can generally be defined and their properties have been described in the literature [1]. The so-called tertiary gel can be detected by the test in pressurized consistometer. Normally, the cement slurry possesses low consistency for most of the time during the test and only increases at the beginning of the actual setting process. However, in the case of tertiary gelation, a distinct premature increase of viscosity can be observed. Consistency may rise to over 40 Bearden units (Bc), while the slurry does not begin to set until much later (several hours).

The goal of this research was to find some relations between cement hydration process and the rheological behavior of cement slurry. Since the problem was very complex, there was only a hope for some approximate relations.

2. Experimental

The time dependence of consistency was measured by using the EG&G Chandler Engineering Pressurized Consistometer, model 7-25-10. Each measurement was performed on a fresh slurry prepared in a mixer following the API Specification 10A standard procedure [2]. Additives and quartz flour were added to the cement in the following proportions by weight of cement: quartz flour, 35%; fluid-loss additive, 0.9%; dispersant, 0.25%; retarder, 0.4%; and water, 56%. Measurements were performed at 90°C and 35 MPa. Temperature and pressure were reached in 30 min and were maintained to the end of the test.

In order to evaluate the degree of cement hydration during the test in the consistometer, in some of slurries,

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0008-8846/00/$ – see front matter
PII: S0008-8846(00)00414-2

the hydration was stopped by means of the acetone drying. After 100 min, the test procedure was stopped and immediately after that the slurry was mixed with acetone. Slurry was vacuum-filtered and the residue was dried at 40°C. Samples were stored in tightly closed containers and stored in a desiccator before analysis. For the evaluation of the degree of cement hydration, thermogravimetric analysis (TGA) was used. TGA was performed in the temperature interval from 25°C to 700°C at a heating rate 10°C/min in dynamic helium atmosphere (50 ml/min). Samples were dried at 105°C prior to TG analysis.

The degree of C_4AF hydration was estimated by X-ray diffraction analysis (XRD). Diffractograms were obtained for 100-min hydrated and for unhydrated samples after selective dissolution of silicate phases by salicylic acid/methanol extraction procedure. $MgO{\cdot}Fe_2O_3$ (MF) was used as internal standard. The degree of C_4AF hydration was estimated by comparison of peak areas of 33.8° 2θ reflection for samples before and after hydration. The same procedure was used by other authors in the past [3].

NMR relaxation is one of the very few methods suitable for non-destructive measurement of a solid–water interface area in slurries. This technique has also been extensively used for the study of the hydration of cement [4–8]. It is well known that the spin–lattice NMR relaxation rate of mobile water molecules increases near a liquid–solid interface. Under conditions of rapid exchange between two populations of spins, one related to free water (designated F), and the other to adsorbed water (designated A), the observed effective spin–lattice relaxation rate $1/T_{1\mathrm{ef}}$ results from an averaging of the two limiting rates of relaxation:

$$\frac{1}{T_{1\mathrm{ef}}} = p_\mathrm{F}\frac{1}{T_{1\mathrm{F}}} + p_\mathrm{A}\frac{1}{T_{1\mathrm{A}}} \tag{1}$$

where p_F and p_A are the relative weight fractions of free and adsorbed water, respectively, and $1/T_{1\mathrm{F}}$ and $1/T_{1\mathrm{A}}$ represent their characteristic rates of relaxation. At constant solid/water ratio, the relative fraction of adsorbed water is proportional to the external surface area of the solid and we can write:

$$p_\mathrm{A} = \rho S\lambda\frac{m_\mathrm{S}}{m_\mathrm{W}} \tag{2}$$

where ρ is the water density, S the specific surface area of the solid, λ the thickness of the adsorbed water layer, m_S the mass of solid and m_W the mass of water in the paste. Because p_F and p_A sum to unity, we can rearrange Eqs. (1) and (2) as follows:

$$\frac{1}{T_{1\mathrm{ef}}} = \frac{1}{T_{1\mathrm{F}}} + \rho\lambda S\frac{m_\mathrm{S}}{m_\mathrm{W}}\left(\frac{1}{T_{1\mathrm{A}}} - \frac{1}{T_{1\mathrm{F}}}\right) \tag{3}$$

The linear relationship between effective relaxation rate and solid–water interface surface area is evident in Eq. (3). This relationship enables us to follow the development of new surface during cement hydration process.

The measurements of $T_{1\mathrm{ef}}$ in cement slurries were carried out by using a coherent pulse NMR spectrometer, model MRS6 Industrial NMR Analyzer, designed by J. Stefan Institute, Ljubljana, Slovenia. Cement slurry was prepared as described earlier and was placed in a glass tube. Immediately after that, the glass tube was closed with a rubber stopper. The hydration was carried out for different time periods in the thermostat at 90 ± 1°C. It was impossible to maintain this temperature in the measuring device, so the temperature was 20°C during measurement. After curing, samples were cooled down with a stream of cold water and thermostated at 20 ± 0.5°C for 5 min before relaxation rate measurements were performed.

3. Results and discussion

3.1. Chemical compositions of cements

Chemical compositions of some class G oilwell cements are shown in Table 1. Cements that exhibited gelation under

Table 1
Chemical compositions of cements (%)

	MgO	SO_3	Loss on ignition	Insoluble residue	C_3S	C_3A	$C_4AF + 2{*}C_3A$	Total alkali content (Na_2O equivalent)	Free lime
C-1	1.73	2.21	0.82	0.46	63.67	2.98	19.43	0.73	0.49
C-2	1.58	2.19	0.73	0.37	61.17	2.68	19.37	0.71	0.53
C-3	1.52	2.03	0.81	0.47	62.74	2.52	18.62	0.71	0.37
C-4	1.29	2.21	0.69	0.72	53.74	1.95	18.31	0.69	0.28
C-5	1.81	2.38	0.86	0.52	53.21	2.18	19.17	0.69	0.44
C-6	1.56	1.93	0.56	0.27	47.35	2.17	18.74	0.73	0.32
C-7*	1.49	1.68	0.70	0.61	61.82	2.08	18.63	0.66	0.60
C-8*	1.60	1.63	0.74	0.64	61.39	2.07	18.48	0.66	0.55
C-9*	1.53	1.91	1.03	0.67	63.50	1.92	18.31	0.69	0.47
C-10*	1.57	1.83	0.81	0.57	62.52	1.83	18.42	0.66	0.52
C-11*	1.51	1.90	0.79	0.67	62.25	2.23	18.20	0.67	0.52
C-12*	1.47	1.78	0.74	0.58	62.50	2.35	18.92	0.73	0.55
C-13*	1.54	1.79	0.80	0.57	62.78	2.27	18.95	0.74	0.58

* Denotes cements suffering from gelation problem.

specified conditions are marked with an asterisk (group A), while others did not (group B).

Chemical composition itself is rarely the only cause for oilwell cement gelation. High C_3A, free lime content, and low sulfate content have been most frequently mentioned among the main chemical factors affecting gelation [1,9]. However, in this study, the chemical composition of cements was taken into account to elucidate the eventual dependence of gelation on the chemical composition. XRD studies were also performed in order to find any differences in crystal structures of main cement minerals in these cements, but no significant differences were found. Particle size distributions of cements used, as determined by laser granulometric analysis, were also very similar. There were no significant differences in chemical composition between the two groups considered, except that there was significantly lower content of SO_3 in group A cements. X-ray diffraction of all samples indicated the presence of sulfate manly as hemihidrate, the traces of syngenite were evident. The fact that there was such a difference in SO_3 content between the two groups leads to the conclusion that maybe sulfate level plays an important role in gelation problems under specified conditions. In order to prove this assumption, 1.2 wt.% of calcium sulfate dihydrate (calcium sulfate precipitated, p.a. grade, Kemika, Zagreb) was added to one cement from group A (sample C-7). Thus, the total content of SO_3 in this blended cement was 2.2%. The mixture was homogenized prior to slurry preparation. Test in the pressurized consistometer was then performed for two slurries with and without added sulfate and the comparison of the two consistograms is shown in Fig. 1. The consistogram of cement C-6 is also shown as a reference.

The results indicate that lack of sulfate content in cement may cause gelation in certain special conditions even when the cement conforms to the API Spec 10A standard requirements for class G oilwell cement. It is well known that cements exist with even lower sulfate content and still behave normally. Hence, the need of sulfate content individually depends on other clinker properties. Therefore, it is extremely important to properly adjust the amount of gypsum added into the cement in order not only to meet API standard requirements but also to obtain good performance in more severe conditions.

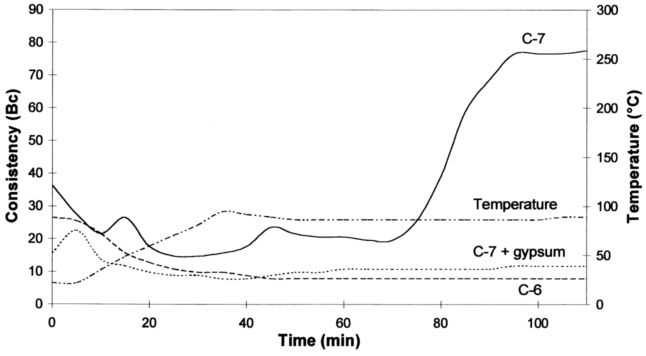

Fig. 1. Consistograms of cement pastes prepared from cement C-6, C-7 and from C-7 with the addition of $CaSO_4{\cdot}2H_2O$. Consistency of slurry is expressed in Bearden units (Bc) as defined in Ref. [2].

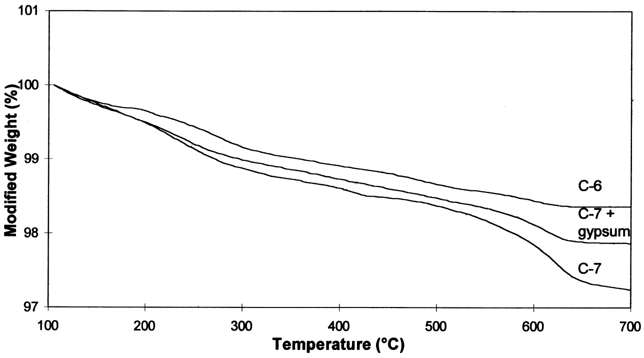

Fig. 2. TG curves of partially hydrated cement samples (dried for 2 h at 105°C).

3.2. TGA of hydrated samples

TG analysis on two different samples (cements C-6 and C-7) after 100 min of hydration in the pressurized consistometer were performed. Additionally, TG analysis of 100-min hydrated sample with $CaSO_4{\cdot}2H_2O$ addition was carried out. TG curves of partially hydrated cements are represented in Fig. 2.

It is clearly seen that the highest mass loss occurs for sample C-7, while for the other two the losses are lower. It was therefore concluded that the addition of calcium sulfate dihydrate to cement C-7 slows down the hydration process and prevents gelation. In addition, the early hydration of cement C-6 was slower compared to cement C-7. The conclusion was therefore made that gelation is in fact connected to the early hydration rate of cement. To clarify hydration process in cements C-6, C-7 and C-7 with gypsum addition, $Ca(OH)_2$ content was determined in these samples after 100 min of hydration. Titration with 0.1 M HCl after extraction of $Ca(OH)_2$ in anhydrous ethylene glycol was used. C-6 contained 0.4%, C-7 0.9%, and C-7 with gypsum addition 0.8% of $Ca(OH)_2$. These results could only partly explained differences observed in TG curves. In addition, DTG indicated that there were several decomposition processes involved in mass loss between 500°C and 700°C, where differences between TG curves were largest. Therefore, there was no simple explanation for the differences in TGA results, and one could only take these results as approximate measure of the hydration degree of samples.

3.3. XRD analysis of hydrated samples

Since various contents of gypsum were involved in our case, it seems possible that the hydration of interstitial phases was accelerated during gelation. Similar phenomenon was described in the literature in connection with the influence of triethanolamine (TEA) on cement hydration [10]. Induction of tertiary gelation by TEA was reported, and it was suggested that the gelation was caused by accelerated hydration of interstitial phases. It is also well known that TEA may accelerate C_3A hydration [10–12]. The appearance of gelation after TEA addition was also observed in our laboratory. It is therefore reasonable to assume that, at least in some cases, gelation is related to the accelerated hydration of interstitial phases. Results of C_4AF hydration degree obtained by XRD analysis in samples C-6, C-7 and C-7 with gypsum addition were in agreement with this hypothesis. After 100 min of hydration in pressurized consistometer about 17% of C_4AF was consumed in the case of C-7, while in other two samples, less than 7% of C_4AF reacted. It was impossible to estimate the hydration degree of C_3A by the same procedure, because the reflections were too weak, thus indicating that C_3A was present only in small amounts in these samples. Nevertheless, the results would most likely be similar as in case of C_4AF.

3.4. Surface area development followed by NMR relaxation rate measurements

The hydration of two cements (C-6 and C-7) was followed by proton NMR relaxation rate measurements. The dependence between relaxation rate and hydration time for the cements is shown in Fig. 3.

Nothing unusual can be seen in the behavior of cement C-6. The relaxation rate was almost constant until the setting process started and then a rapid increase was observed. On the other hand, the relaxation rate in the slurry prepared from cement C-7 was moderately increased after approximately 100 min of hydration, long before the setting was started. There is certain similarity between consistogram and NMR hydration curve of cement C-7. The rise of consistency of the cement slurry occurs simultaneously with the increase in proton relaxation rate and thus also with the increase in surface area. Measurements of BET (N_2) surface area were also performed on 100-min hydrated and unhydrated samples and the results were consistent with NMR measurements. Generally, BET surface area increased with hydration and the greatest increase was observed for C-7 (BET values of C-6 increased from 0.8 to 1.1 m^2/g, of C-7 from 0.6 to 1.9 m^2/g, and of C-7 with gypsum addition from 0.8 to 1.4 m^2/g during 100 min of hydration.). It is reasonable to conclude that consistency of the slurry increases through the development of new surface areas and reduced mobility of water, both of which are the consequence of increased hydration rate. This is in agreement with the results of TG analysis of partially hydrated samples discussed previously.

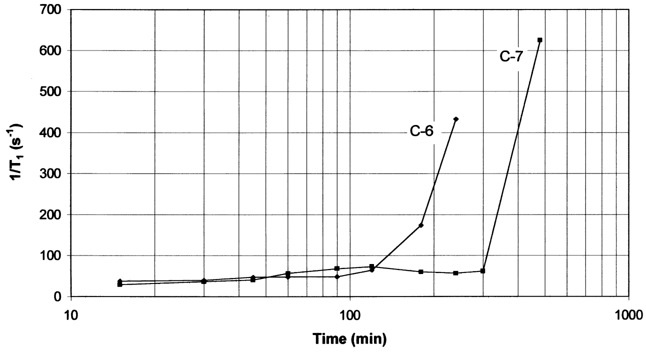

Fig. 3. Spin–lattice relaxation rate as a function of hydration time.

Since relaxation rate does not depend only on cement/water interface area, it is not easy to determine the absolute value of cement surface area. However, it is more meaningful to consider relative changes in each paste separately and to connect this with consistency development in the slurry. The conclusion is that there are significant differences between the behaviors of the two cements, considering both development of consistency and NMR relaxation measurements. It is possible to associate these two effects in order to better understand the nature of gelation. Probably, at the same time, as new surfaces develop in the paste, the number of connections between particles increases and agglomeration appears. This phenomenon reduces the mobility of water in the paste and causes the increase of the consistency of the slurry.

4. Conclusion

Relationships between cement hydration process, development of surface area and consistency changes during the test in the pressurized consistometer were evaluated with regard to oilwell cement gelation problem. The connection between surface area evolution and consistency of cement slurry was observed. The consistency was related to the degree of cement hydration. It was concluded that gelation was connected to the premature development of surface area in the paste, which was caused by accelerated hydration of cement. Chemical compositions of some commercial oilwell cements were taken in the account as possible causes for the appearance of gelation. Significantly lower content of SO_3 was found in cements that showed gelation, but no other important differences in cements were observed. The influence of $CaSO\cdot 2H_2O$ content on consistency development was tested by the addition of $CaSO_4\cdot 2H_2O$ into the cement that normally exhibited gelation in specified conditions. It was found that $CaSO_4\cdot 2H_2O$ significantly influenced the consistency of cement paste, and the lack of sulfate in the cement might, in some cases, cause gelation problems. The problem of gelation is very complex, and there are other possible reasons for its occurrence. However, this paper offers some findings that may be helpful in elucidating the very nature of the problem.

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