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GELATION OF OILWELL CEMENT

GELIRANJE CEMENTA ZA NAFTNE VRTINE

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Gelation of a cement slurry is one of the most serious problems occurring in well cementing. It appears as a premature viscosification or as gel strength build-up of the cement slurry in the well. The problem may be so severe to cause job failure. The main scope of this research was to prove and define some possible reasons for the gelation of the well cement. Samples of class G oilwell cements (Salonit Anhovo) were tested in the pressurised consistometer. With this method gelled were separated from non-gelled cements. A comparison between cement clinkers, used in this investigation, was made on the basis of XRD analysis. The influence of triethanolamine (TEA) on cement slurry behaviour was determined in order to establish whether the gelation was due to the contamination of cement with TEA during grinding. IR spectroscopy and thermogravimetry (TG) were used for the assessment of the hydration degree of gelled cement and compared with data for non-gelled cement.

Key words: oilwell cement, hydration, triethanolamine, gelation, XRD, IR, TG

Geliranje je pogost problem cementiranja naftnih vrtin. Ka‘e se kot prezgodnje pove~anje viskoznosti ali prezgodnje strjevanje cementne paste v vrtini. Geliranje lahko ogrozi celo izvedbo dela na vrtini. Glavni namen opisanih raziskav je bil ugotavljanje in definiranje nekaterih mo‘nih vzrokov za geliranje cementa. Nekaj vzorcev cementov za naftne vrtine (tip G, Salonit Anhovo) smo testirali v visokotla~nem konsistometru. S to metodo smo lo~ili cemente, ki gelirajo, od tistih, ki se strjujejo normalno. Za klinkerje, ki ustrezajo predhodno testiranim cementom, smo posneli pra{kovne difraktograme in jih primerjali med sabo. Preiskali smo vpliv trietanolamina na geliranje, da bi ugotovili, ali lahko geliranje cementa nastopi zaradi kontaminacije s tem pospe{evalcem mletja v mlinu. S tehnikama IR spektroskopije in termogravimetri~ne analize smo sledili hidratacijo cementa, ki gelira, primerjalno s cementom, ki ne gelira.

Klju~ne besede: cement za naftne vrtine, hidratacija, trietanolamin, geliranje, XRD, IR, TG

1 INTRODUCTION

During the 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 to allow its injection under specific well conditions (pumping times from 2 to 6 hours, temperatures up to 350°C, and pressures up to 200 MPa). Various additives are available in order to achieve the above requirements[1].

Class G oilwell cement is used as a basic well cement and, mixed with additives, covers a wide range of well depths and temperatures. It is produced by grinding of Portland cement clinker and one or more of the forms of calcium sulphate as an interground addition.

Gelation can be defined as a premature viscosification or a gel strength build-up of the cement slurry. The gelled slurries can be divided into four distinct categories: primary, secondary, tertiary, and quaternary gel. Tertiary and quaternary gels are likely to become unpumpable before the end of the slurry's placement, and they can be detected during the thickening time test as an increase of consistency[2].

2 EXPERIMENTAL PART

Thickening time experiments were carried out on Class G oilwell cements produced in Salonit Anhovo cement factory. Experimental conditions were as follows:

1. 90°C was reached in 30 min from room temperature
2. 35 Mpa was achieved in 30 min from normal pressure.

These conditions were maintained throughout the test. See **figure 1**.

Slurries were prepared according to API Spec. 10A standard[3]. Additives and quartz flour were added to cements in the following proportions by weight of cement:

cement	100%
quartz flour	35%
fluid loss additive Halad 22A	0,9%
dispersant CFR-2	0,25%
retarder HR-12	0,4%
water	56%

Clinker samples used were analysed by X-ray powder diffraction. Diffractograms were compared to find eventually differences in structure of the main cement minerals.

Different concentrations of TEA (0,01 wt.% - 0,03 wt.%) were added to slurries which normally exhibited no gelation. Thickening time experiments were carried out for a variety of concentrations of TEA and the influence of this additive on gelation was evaluated.

Hydration studies were performed on two cements, one of them exhibiting gellation. Slurries were cured in the consistometer for 100 min. Immediately after that hydration was stopped by means of acetone drying. Samples were kept in a desiccator over silica gel until used. IR spectroscopy studies were carried out on samples from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. TG analyses (from 25 to 800°C; 10 °/min) were performed to evaluate the degree of hydration during the test.

3 RESULTS AND DISCUSSION

Thickening time experiments detected 3 of tested cements having tertiary gelling behaviour under experimental conditions (see **table 1**).

Table 1: Gelation of cement samples

Sample	Clinker production	Gelation
A	Aug. 95	no
B	Aug. 94	yes
C	Aug. 95	no
D	Aug. 94	yes
E	Jan. 95	no
F	Jan. 95	no
G	Aug. 94	yes

It was established that all of gelled cements were prepared from the clinker produced within the same production period. This was a strong evidence that in our case gelation was somehow connected to the clinker production rather than to other steps in cement manufacture and handling.

No significant differences in the structure of cement clinkers, used in this study, was found by X-ray powder diffraction studies. It was therefore concluded that the clinker structure itself was not the reason for gelation.

It is known, that TEA induces gelation in combination with some other additives in oilwell cements. It has been also suggested, that gelation is the consequence of accelerated hydration of C_3A and C_4AF by TEA[4]. The results of our trial experiments were as follows:

- 0.01% TEA no gelation after 3 h
- 0.02% TEA gelation occurred at 100 min
- 0.03% TEA gelation occurred at 60 min. (% by weight of cement)

It is evident that TEA may induce gelation and the time of appearance is related to the TEA concentration. The concentration of TEA that induces gelation is evidently too high to be caused only by contamination of cement during the grinding. It is thus very unlikely that the gelation of cements investigated in this study would be the result of contamination by TEA.

The course of hydration of cement can be followed by observation of changes in IR spectra. Their most prominent changes during the hydration process are the following:

1. shift of the band from 925 to 970 cm^{-1} due to silicate groups condensation
2. changes in the region between 1100-1170 cm^{-1} due to ettringite and monosulphate formation
3. changes of broad water vibration band at 3200-3700 cm^{-1} and around 1650 cm^{-1}, among these a strong, sharp peak at 3640 cm^{-1} due to the stretching vibration of OH from $Ca(OH)_2$.

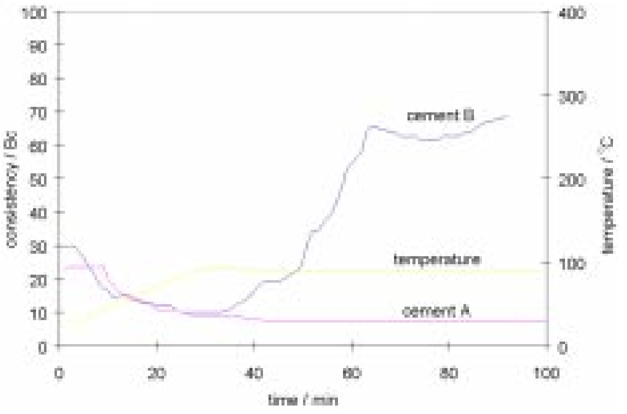

Figure 1: Consistograms of cements A and B
Slika 1: Konsistograma cementov A in B

The peak at 3640 cm^{-1} is very useful for the diagnosis of the initiation of C_3S/C_2S hydration[5]. **Figure 2** shows IR spectra for cements A and B after 100 min hydration in the pressurised consistometer. While the cement A shows no significant peak at 3640 cm^{-1}, the cement B shows a small peak at that position indicating the onset of hydration process of silicate phases in the cement. Other bands are quite similar in both spectra.

IR and TG results are consistent with each other. The weight loss in the temperature interval 25-800°C was 1.9 wt.% for the cement A and 3.3 wt.% for the cement B. This suggests that the appearance of gelation is connected to the early hydration process of C_3S and C_2S in the cement. It has been reported that thickening is caused by the onset of significant calcium silicate hydrate formation, which severely reduces the mobility of water in cement slurry[6]. It has been also suggested that appearance of gelation in the presence of TEA is connected to the accelerated hydration of the interstitial phase which is mostly composed of brownmillerite, tricalcium alumi-

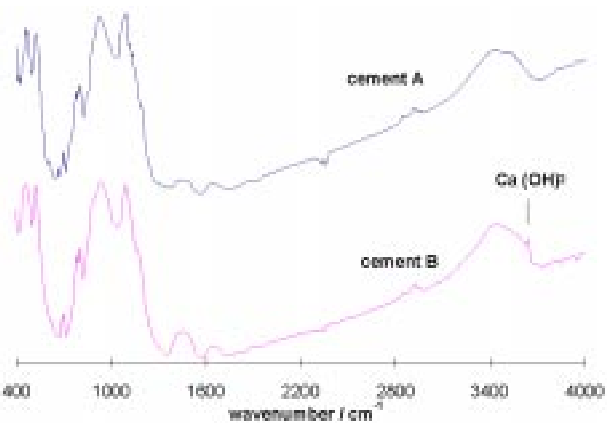

Figure 2: IR spectra of cements A and B
Slika 2: IR spektra cementov A in B

nate and glass[4]. It is reasonable to assume that in most cases gelation is due to the reduced mobility of water, which is the result of the hydration process.

4 CONCLUSIONS

1. It is evident, from the systematic testing of cements, that gelation in the investigated case is related to the clinker production process rather than to other steps in cement manufacture.
2. The influence of TEA on gelation of oilwell cements was ascertained. Results are in agreement with previously published data. The possibility that the gelation of cement occurred due to its contamination with TEA during grinding was excluded.
3. The onset of significant hydration of silicate phases was observed in the case of gelation, while in normal slurries the hydration was not observed at the same curing time. It is therefore suggested, that the gelation is due to the reduction of water mobility in the cement slurry. Reduced mobility results from the process of hydration.

5 REFERENCES

[1] E. B. Nelson: Well Cementing, Schlumberger Educational Services, Houston, Texas (1990)

[2] J. Kieffer, P. Rae, How Gelation Affects Oil Well Cements, *Petroleum Engineer International*, May (1987) 46-

[3] Specification for Well Cements, API Specification 10A Twenty-second Edition, January (1995)

[4] R. Oberste-Padtberg: The Effect of Triethanolamine on the Hydration Behaviour of Oil-Well Cements, *Il Cemento*, 84 (1987) 223-

[5] J. Bensted, S. P. Varma: Some Applications of Infrared and Raman Spectroscopy in Cement Chemistry, *Cement Technology*, September/October (1974) 440-

[6] J. Bensted: Thickening Time Investigation of Class G Oilwell Cement, *Il Cemento*, 82 (1985) 27-