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

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 dif-
f erent 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). V arious additives
are available in order to achieve the above requirements1.

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 viscosifica-
tion or a gel strength build-up of the cement slurry. The
gelled slurries can be divided into four distinct catego-
ries: primary, secondary, tertiary, and quaternary gel. T er-
tiary and quaternary gels are likely to become unpumpa-
ble before the end of the slurry’s placement, and they can
be detected during the thickening time test as an increase
of consistency2.

2 EXPERIMENTAL PART

Thickening time experiments were carried out on
Class G oilwell cements produced in Salonit Anhovo ce-
ment 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 pres-
   sure.

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

Slurries were prepared according to API Spec. 10A
standard2. A dditives and quartz flour were added to ce-
ments 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 pow-
der 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 influ-
ence of this additive on gelation was evaluated.

Hydration studies were performed on two cements,
one of them exhibiting gelation. Slurries were cured in the
consistometer for 100 min. Immediately after that
hydration was stopped by means of acetone drying. Sam-
ple 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**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clinker production</th>
<th>Gelation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Aug. 95</td>
<td>no</td>
</tr>
<tr>
<td>B</td>
<td>Aug. 94</td>
<td>yes</td>
</tr>
<tr>
<td>C</td>
<td>Aug. 95</td>
<td>no</td>
</tr>
<tr>
<td>D</td>
<td>Aug. 94</td>
<td>yes</td>
</tr>
<tr>
<td>E</td>
<td>Jan. 95</td>
<td>no</td>
</tr>
<tr>
<td>F</td>
<td>Jan. 95</td>
<td>no</td>
</tr>
<tr>
<td>G</td>
<td>Aug. 94</td>
<td>yes</td>
</tr>
</tbody>
</table>

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\(_3\)A and C\(_4\)AF by TEA. The results of our trial experiments were as follows:
- 0.01% TEA no gelation after 3 h
- 0.02% TEA gelation occurred at 60 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)\(_2\).

The peak at 3640 cm\(^{-1}\) is very useful for the diagnosis of the initiation of C\(_3\)S/C\(_2\)S hydration. **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\(_3\)S and C\(_2\)S 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. 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](image-url)
nate and glass. 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