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Cement slurries for sealing casing in boreholes with increased risk of gas migration

Zaczyny cementowe do uszczelniania otworów o podwyższonym ryzyku migracji gazu

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ABSTRACT: A cement job is one of the most important operations carried out during the drilling of wells. Further functioning of the well depends on the correct execution of the cement job (for instance, in case of a failed cement job, further hydrocarbon deposit production may turn to be difficult or simply impossible). The article presents the issues of the cement slurry technology deployed for sealing shallow boreholes with an increased risk of shallow gas migration. Oil and Gas Institute – National Research Institute has developed a number of cement slurry formulations characterized by properly adjusted density, gelling and bonding time, which will allow the creation of a tight barrier in the borehole annulus that prevents the production fluid from leaking to the surface. Properly modified (with the aid of natural rubber latex or nanosilica) cement slurries based on Portland cement CEM I 42.5 are suitable for use in cement jobs carried out in shallow drilling wells. Particularly advantageous technological parameters have been obtained for cement slurries containing about 0.5–1% nano-SiO_2. The optimal water-cement ratio for these formulas was at the level of about 0.50–0.52. Both latex-containing and nano- SiO_2-containing samples were characterized by a very advantageous course of the gelation plot (static build-up of gel strength). Their TT transition times amounted to several tens of minutes (which is a proof of high ability to prevent gas migration from shallow gas accumulations). Bonding times of the tested slurries can be successfully controlled using acceleration agents commonly used in the industry. Slurries that had been tested using the Vicat apparatus were characterized by a bonding time in the range from approximately 100 up to 280 minutes. As a result, depending on the anticipated length of the cementing job, the required bonding time can be appropriately adjusted. Compressive strength after 7 days of hydration was high (for samples with the addition of latex, they were about 22–23 MPa, for nano- SiO_2 slurries around 29–31 MPa). Due to their good technological parameters, the cement slurries developed at Oil and Gas Institute – NRI could be used in the process of cementing casing strings, e.g. in the Carpathian Foreland, where there is a shallow gas accumulation hazard.

Key words: cement slurry, cement sheath, gas migration, cement thickening.

STRESZCZENIE: Zabieg cementowania rur okładzinowych jest zaliczany do najważniejszych operacji przeprowadzanych podczas wykonywania otworu wiertniczego. Od jego prawidłowego przebiegu zależy dalsze funkcjonowanie odwiertu (np. w przypadku nieudanego cementowania rur późniejsza eksploatacja złoża może okazać się utrudniona lub wręcz niemożliwa).W artykule przedstawione zostały zagadnienia technologii zaczynów cementowych służących do uszczelniania płytkich otworów wiertniczych o podwyższonym ryzyku wystąpienia migracji gazu. W Instytucie Nafty i Gazu – Państwowym Instytucie Badawczym opracowano szereg receptur zaczynów cementowych charakteryzujących się odpowiednio dobraną gęstością, czasem żelowania i wiązania, co pozwala na wytworzenie w otworze wiertniczym szczelnej bariery uniemożliwiającej przedostawanie się medium złożowego na powierzchnię. Odpowiednio zmodyfikowane (za pomocą lateksu lub nanokrzemionki) zaczyny cementowe na bazie cementu portlandzkiego CEM I 42,5 z powodzeniem nadają się do zastosowania w pracach cementacyjnych prowadzonych w płytkich otworach wiertniczych. Szczególnie korzystne parametry technologiczne uzyskano dla zaczynów cementowych zawierających około 0,5–1% nano-SiO_2. Optymalny współczynnik wodno-cementowy kształtował się dla tych receptur na poziomie około 0,50–0,52. Zarówno próbki zawierające lateks, jak i te zawierające nano-SiO_2 cechowały się bardzo korzystnym przebiegiem krzywej żelowania (narastania statycznej wytrzymałości strukturalnej). Ich czasy przejścia (*transition time*) TT wynosiły kilkadziesiąt minut (co świadczy o wysokiej zdolności do zapobiegania migracji gazu z płytkich horyzontów produktywnych). Czasy wiązania badanych zaczynów można z powodzeniem regulować za pomocą powszechnie używanych w przemyśle środków przyspieszających. Testowane na aparacie Vicata zaczyny posiadały czasy początku wiązania w przedziale od około 100 do 280 minut. Powoduje to, że w zależności od przewidywanej długości zabiegu cementowania można odpowiednio dobrać wymagany czas wiązania zaczynu. Wytrzymałości na ściskanie po 7 dniach hydratacji przyjmowały wysokie wartości (dla próbek z dodatkiem lateksu wynosiły one około 22–23 MPa, dla zaczynów z nano-SiO_2 – około 29–31 MPa). Zaczyny

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cementowe opracowane w INiG – PIB z uwagi na swe dobre parametry technologiczne mogłyby znaleźć zastosowanie w procesie cementowania kolumn rur okładzinowych, np. na obszarze przedgórza Karpat, gdzie występuje duże ryzyko pojawienia się migracji gazu.

Słowa kluczowe: zaczyn cementowy, kamień cementowy, migracja gazu, wiązanie cementu.

Introduction

The cement job is one of the most critical operations carried out during the entire well construction process. The essential role of this process is played by cement slurry, which after being injected into the wellbore annulus starts thickening in course of time. The process of bonding may last from a few to several hours depending on the borehole conditions and slurry composition. The cement sheath formed after the slurry sets must be strong enough not to get cracked and to assure pressure integrity of the casing string system (including pressure formation integrity). In addition, the cement bond must be able to withstand the hydrostatic pressure occurred during the drilling of the hole, be resistant to changes in temperature and pressure in the borehole, as well as periodic loads resulting from various operations related to the production of hydrocarbons and others. For technological and economic reasons, obtaining a cement slurry with adequate early mechanical strength is extremely important. After the cement slurry has been injected into the annulus, the hydration process begins. A transition state is created between the liquid and the solid phase, i.e. gel structure. The hydrostatic pressure is also simultaneously reduced in the hole. During the disturbance of the pressure balance in the initial period of hydration, it may happen that gas or liquid enters the annulus, which may create a significant problem from the perspective of well control and further well production. Gas or liquid moving from the formation zone of higher pressure to the zone of lower pressure can cause a threat to the natural environment, and it may lead to a drop in production rate (Kremieniewski, 2011, 2014; Velayati, 2015).

The influence of static gel strength of the cement slurry (SGS, Static Gel Strength) on the possible occurrence of gas migration is described among others in papers both from abroad and from Poland (Crook and Heathman, 1998; Radecki and Witek, 2000; Rogers et al., 2004; Scott, 2015). The SGS (static gel strength) of the slurry, and the so-called TT (transition time) that are interdependent, determine the slurry's ability to prevent gas migration through the cement structure. The faster the SGS builds up, i.e. the shorter the TT transition time is (i.e. the gelling time of the slurry from the gel strength value of 50 Pa to the value of 250 Pa), the lower the probability of gas migration is. With an increase in the transition time, the risk of annular gas or fluid flow through and around the thickening cement sheath in the borehole increases (Dębińska, 2013; Kremieniewski, 2014). Ensuring the proper slurry bonding time (i.e., the time after which the cement slurry passes into the bonded cement sheath) plays an important role in prevention of gas outflows from the well.

Cement slurry bonding process

The hydration of cement slurry is a very complex process taking place in a mixture of cement and water (Kurdowski, 2010, 2014; Neville, 2000; Ridi, 2010). During the bonding and development of mechanical strength, a series of hydration reactions take place, which are crucial for the strength of the cement sheath. The plot of cement hydration is not a straight line in time. Initially, the process proceeds slowly, which allows for the proper placement of cement particles before setting.

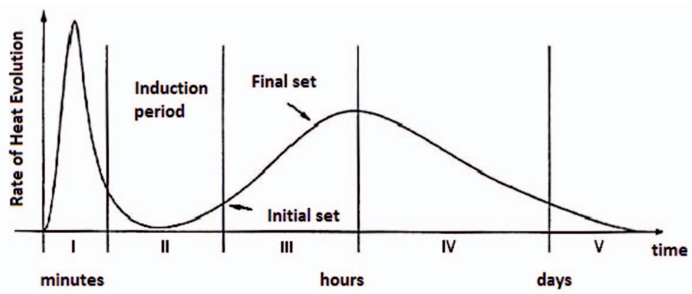

Fig. 1. Hydration curve for C_3S

Rys. 1. Krzywa kalorymetryczna hydratacji fazy C_3S

The C_3S grain hydration, due to its higher intensity compared to the C_2S grain hydration, is the main source of initial bonding and development of compressive strength in the hardened slurry. Furthermore, the hydration of C_2S grains is responsible for the final strength of the cement sheath. Both mechanisms emerge in a very similar way. Based on the C_3S grains, the hydration calorimetric graph (fig. 1) contains five stages of cement hydration that can be distinguished:

I – per-induction period – that lasts up to a few minutes with initial exothermic peak. Then the cement is rapidly hydrated immediately after contact with water. The initial film of C-S-H gel is formed on the C_3S grains.

II – induction period – there is a decrease in heat generation and slow precipitation of the C-S-H gel as well as an increase in the concentration of Ca^{2+} and OH^- ions. The $Ca(OH)_2$ sludge formed in the solution when full saturation is reached. That stage lasts approximately a few hours. There are two various types of theories of the induction period in literature, i.e.:

- protective barrier theory – according to it, the permeability of the formed C-S-H gel is low, which causes the inhibition of the subsequent hydration process and the initiation of the induction phase. According to one of the mechanisms, osmotic forces are formed in the C-S-H thin layer, which after a certain time lead to cracking of the C-S-H layer and formation of a significant amount of the secondary C-S-H gel. Then, the C-S-H gel film undergoes morphological changes that increase the permeability, making the water pass more easily into the layer and accelerating further hydration in result,
- delayed crystallization theory – precipitation of $Ca(OH)_2$ accelerates the hydration process. This theory covers various reversible mechanisms related to the induction period. According to one of the mechanisms, Ca^{2+} and OH^- ions migrate to a solution causing an increase in the lime saturation level. That leads to C_3S hydration delays due to the high concentration of Ca^{2+} ions.

III – acceleratory period – this is the most rapid period of hydration. The $Ca(OH)_2$ solution starts to crystallize and C-S-H builds up in areas occupied by water. Hydrates grow to form the structural integrity of the future cement sheath.

IV – deceleratory period – the porosity of the system decreases, the transport of ions and water through the C-S-H gel film is slowed down and the hydration intensity decreases.

V – steady period – the hydration process continues. The structure gets compacted, the porosity decreases and compressive strengths increases. This stage can last a very long time.

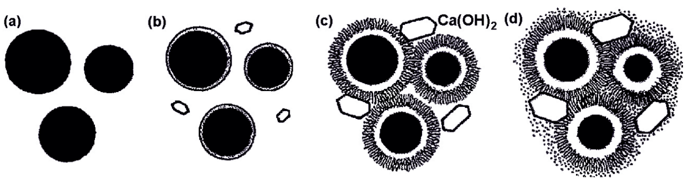

Fig. 2. Stages of cement hydration: a) cement grains are dispersed in water, b) formation of a C-S-H gel film in cement grains, c) breaking of the gel films under osmotic pressure and build up of secondary C-S-H gel, d) filling the pores in cement slurry after a longer time (full growth of C-S-H gel phase and calcium hydroxide)

Rys. 2. Etapy hydratacji cementu: a) ziarna cementu rozproszone są w wodzie, b) utworzenie warstwy żelu C-S-H na ziarnach cementu, c) rozerwanie warstw żelu pod ciśnieniem osmotycznym i narastanie wtórnego żelu C-S-H, d) wypełnienie porów w zaczynie po dłuższym okresie czasu (pełny wzrost fazy C-S-H i wodorotlenku wapnia)

Figure 2 shows the sequence of stages of cement hydration. This process consists in parallel reactions of anhydrous components with water. The C_3S tricalcium silicate is responsible for the formation of C-S-H gel and calcium hydroxide in the initial stage of hydration, while C_2S dicalcium silicate in the later stage of the reaction. Changes occur in the concentration of ions contained in the liquid phase during the hydration process causing variation in the speed of the process.

Hydration of aluminum particles, mainly C_3S, is the most active in the early phase of this process. Aluminum particles have a significant impact on the slurry rheology as well as on the mechanical strength of the formed cement sheath. Hydration of C_4AF is similar but slower than C_3A. The inter-phase reaction between non-hydrated molecules and water happens like in the first one. The aluminate hydrates do not form a protective barrier on the surface in contrast to silicate hydrates, therefore there is no induction period and the hydration process takes place very rapidly.

The Static Gel Strength of the Cement Slurry

The impact of SGS on the gas migration process is described in the standard (Isolating Potential Flow Zones During Well Construction API Standard 65 – Part 2, Second Edition, December 2010). Just after being pumped into the annulus, the cement slurry behaves as a liquid and maintains a constant hydrostatic pressure exerted on the formation and outbalancing the formation's pressure. Then, after the pumping of the slurry is stopped, the gelling process of the cement slurry occurs, i.e. static mechanical strength (SGS – Static Gel Strength) is built until the cement is completely set. The gelling process reduces the ability of cement slurry to maintain a hydrostatic pressure higher than the formation pressure, which can lead to gas intrusion into the annulus and its percolation through the slurry. The laboratory tests carried out in other foreign research institutes show that the SGS value of approximately 500 pounds/100 sq. feet, i.e. approx. 250 Pa, can block the gas flow from movement in the gelling slurry; this is called the SGS Limit Value. The below formula shows the relationships between SGS and maximum expected gas flow pressure loss (Crook and Heathman, 1998; Radecki and Witek, 2000):

$$P_{max} = \frac{SGS}{300} \cdot \frac{L}{D}$$

where:

P_{max} – maximum expected gas flow pressure loss [psi],

SGS – Static Gel Strength [lb/100 sq. feet],

300 – conversion factor for P_{max} [psi],

L – height of cement column [feet],

D – effective diameter of cement column (well bore diameter minus casing outside diameter) [in].

The hydrostatic pressure exerted by the cement column decreases while SGS increases. If the hydrostatic pressure drops below the reservoir pressure before the slurry reaches the appropriate SGS value, most likely the gas will start to penetrate through the cement slurry creating permanent channels. The Transition Time (TT) is defined in literature (Murray et al., 2004) as the time between the start of gel strength build up and the point when the SGS Limit Value (from 50 to 250 Pa, or approximately 100 to 500 lb/100 sq. feet) is reached. The delay in the onset of static mechanical strength allows the slurry to elongate the time slot when the hydrostatic pressure is higher than the formation pressure, and short TT transition times of less than 45 minutes can help in preventing formation fluid from migration and entry into the wellbore annulus.

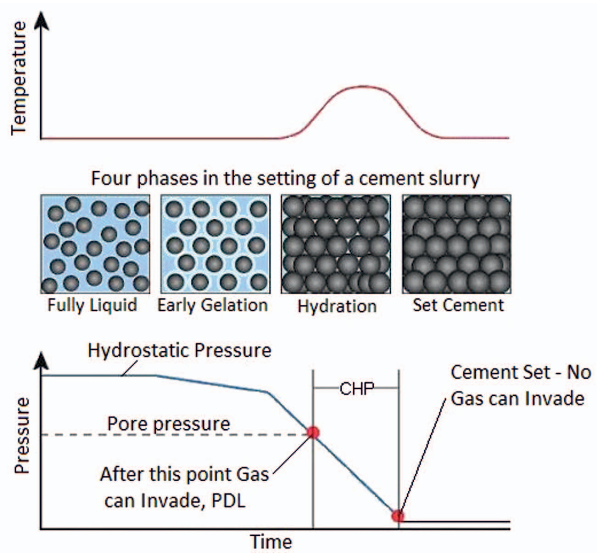

Fig. 3. Pressure changes during the setting of the cement slurry in the borehole

Rys. 3. Zmiany ciśnień podczas wiązania zaczynu cementowego w otworze

Figure 3 shows the pressure log during the cement slurry thickening in the wellbore. The short time of CHP (critical hydration period) restricts the migration of gas or liquid to the thickening slurry.

Determination of slurry thickening time

In order to determine the time after which the cement slurry stored under the assumed conditions starts to set and then form the bond, the Vicat's device (photo 1) is used. It allows to specify the waiting time for the slurry to bond in the borehole. The method consists of periodically measuring the depth of immersion of the Vicat needle in a setting cement slurry (Standard Test Method for the Time of Setting of Hydraulic Cement by Vicat Needle).

The apparatus used in Oil and Gas Institute – NRI enables automatic testing of six different samples of cement slurries (slurries are placed in special rings). Determination methodology follows the PN-EN 196-3:2016-12 *Metody badania cementu – Część 3: Oznaczanie czasów wiązania i stałości objętości*. The time delay between mixing the slurry and placing the special ring in the water should not be longer than 30 min. Advisably, the first test is taken after 1 hour from slurry mixing. According to the rate of slurry setting, the apparatus takes the subsequent tests automatically, every 8 to 24 minutes.

The results of the setting process of cement slurries are automatically recorded and stored in the form of tables and charts. The beginning of the slurry setting or initial setting (the green dotted line in the diagrams) is the time from the moment of mixing the slurry to the moment until the needle stops approximately 2 mm from the base. The final setting (the red dotted line in the diagrams) is the time from the moment of slurry mixing until the needle stops approximately 2 mm below the upper surface of the tested sample.

Photo 1. Computer-controlled Vicat needle apparatus with 6 measuring points

Fot. 1. Sześciokomorowy automatyczny aparat Vicat'a wraz z komputerem sterującym

Laboratory tests of slurries and cement sheaths

Laboratory tests aimed at developing compositions of cement slurries with short gelation and settig times for sealing systems for shallow wells were carried out at the Drilling Technology Department of Oil and Gas Institute – NRI in accordance with the following industry standards: PN-EN 10426-1 and 10426-2 *The oil and gas industry* – Cements and materials for cementing of drilling wells – parts 1 and 2: *Drilling cements research* (Rzepka and Stryczek, 2008; Stryczek and Gonet, 2001; PN-EN ISO 10426-1; PN-EN ISO 10426-2).

Compositions and test results of slurry recipes with required gelation times and quick setting are given in tables 1 and 2. All slurries intended for sealing shallow boreholes contained 3% of KCl and were prepared on the basis of Portland cement CEM I 42.5. Formulas marked with letters A and B contained additives in their composition, like a defoaming agent, an anti-filtration agent, a swelling agent, a liquefier as well as natural rubber latex and microcement. They differed only in the amount of the setting time accelerator used (composition A contained 2% and composition B – 3%). For preparation of formulas C and D, a 0.5% solution of nano-SiO_2 was used, introducing a defoaming agent and a liquefier (composition C did not contain a setting accelerator while in composition D the amount of accelerator was 1%). Formulas E and F were prepared based on a 1% solution of nano-SiO_2 and the other additives were the same as in the two previously described slurries. There was a 2% accelerator in formula E and a 3% one in formula F.

The densities of the tested slurries ranged from 1800 to 1840 kg/m^3, the test temperature was 25°C and the pressure was 5 MPa, which allowed the use of developed formulas for sealing the top intervals in the wellbores (e.g. from 0 to about 400 meters). Cement slurries (compositions A and B) obtained a transition time TT of 25 to 40 minutes (depending on the amount of the accelerator used) and their initial time of setting ranged from about 200 to 285 minutes. In slurries in which 0.5% nano-SiO_2 (C and D compositions) were used, TT transition times 41 and 46 minutes were obtained and initial times of thickening were from approximately 220 to approx. 265 minutes. The last two recipes (marked with the letters E and F) with 1% nano-SiO_2 gelled in less than 30 minutes (the transition time TT for the composition E was 29 minutes and for the composition F was equal to 23 minutes). The final times of thickening were obtained after 115 and 90 minutes, respectively. With regards to compressive strength after 2 days of hydration, nanosilica compositions had about 35% higher mechanical strength than the recipes without nano-SiO_2 (it should be noted that no significant mechanical strength improvement was observed for samples containing 1% of nano-SiO_2 compared to samples containing 0.5% of nano-SiO_2).

Charts 4 to 9 contain gelation logs for the six tested cement

Table 1. Compositions of tested cement slurries
Tabela 1. Składy testowanych zaczynów cementowych

Slurry mark/components [%] bwoc*	Slurry A	Slurry B	Slurry C	Slurry D	Slurry E	Slurry F
Water	40	40	52	52	50	50
Nanosilica nano-SiO_2	–	–	0.5	0.5	1	1
KCl**	3	3	3	3	3	3
Defoaming agent	0.5	0.5	0.3	0.3	0.3	0.3
Liquefier	0.3	0.3	0.2	0.2	0.4	0.4
Anti-filtration agent	0,1	0.1	–	–	–	–
Rubber latex stabilizer	1	1	–	–	–	–
Natural Rubber Latex	10	10	–	–	–	–
Swelling Agent	0.1	0.1	–	–	–	–
Accelerator	2	3	–	1	2	3
Microcement	10	10	–	–	–	–
Portland Cement CEM I 42,5	100	100	100	100	100	100

* bwoc – i.e. in relation to mass of dry cement
** KCl – in relation to mass of mixing water (bwow)

Table 2. Parameters of cement slurries and sheaths tested at 25°C
Tabela 2. Parametry zaczynów i kamieni cementowych testowanych w temperaturze 25°C

Slurry mark / Determined parameter	Slurry A	Slurry B	Slurry C	Slurry D	Slurry E	Slurry F
Slurry density [kg/m^3]	1840	1840	1800	1800	1820	1820
Static Gel Strength 50 Pa [h:minutes]	0:03	0:16	0:27	0:07	0:22	0:11
Static Gel Strength 250 Pa [h:minutes]	0:43	0:41	1:13	0:48	0:51	0:34
TT Transition Time [minutes]	40	25	46	41	29	23
Initial Time of Thickening [minutes]	285	200	265	220	115	90
Final Time of Thickening [minutes]	370	375	330	290	305	170
Cement sheath compressive strength after 2 days of hydration [MPa]	22,3	22,5	29,6	29,9	30,4	30,8

slurries (green lines show the SGS build up process – in the upper right corner there is information about the slurry obtaining the appropriate SGS value and TT Transition Time). Charts 10 to 15 show the gelation logs of the tested slurries. The green lines in the charts indicate the initial time of thickening and the red lines – the final time of thickening.

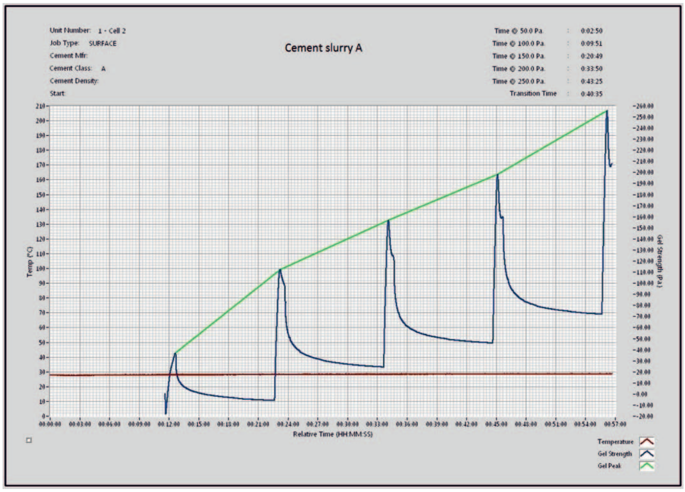

Fig. 4. Static gel strength development for cement slurry marked A
Rys. 4. Narastanie SGS dla zaczynu oznaczonego symbolem A

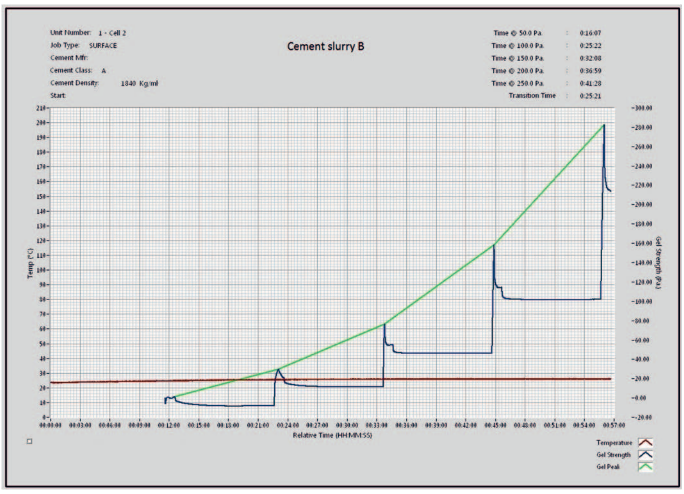

Fig. 5. Static gel strength development for cement slurry marked B
Rys. 5. Narastanie SGS dla zaczynu oznaczonego symbolem B

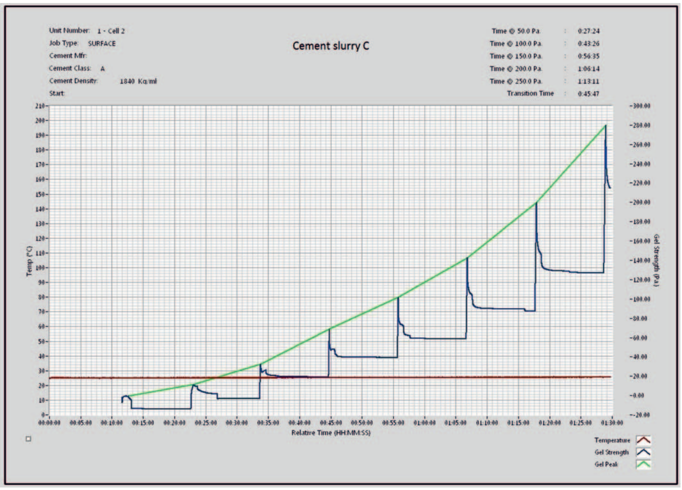

Fig. 6. Static gel strength development for cement slurry marked C
Rys. 6. Narastanie SGS dla zaczynu oznaczonego symbolem C

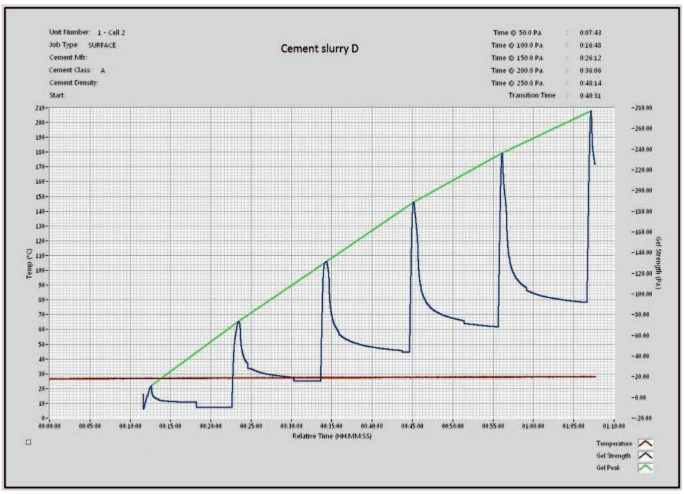

Fig. 7. Static gel strength development for cement slurry marked D
Rys. 7. Narastanie SGS dla zaczynu oznaczonego symbolem D

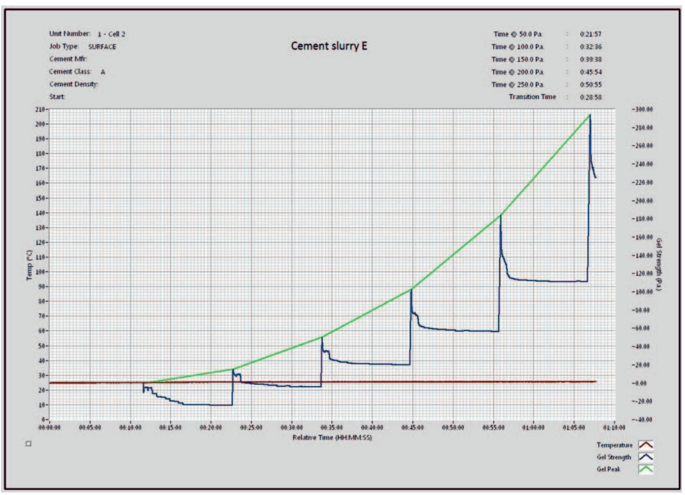

Fig. 8. Static gel strength development for cement slurry marked E
Rys. 8. Narastanie SGS dla zaczynu oznaczonego symbolem E

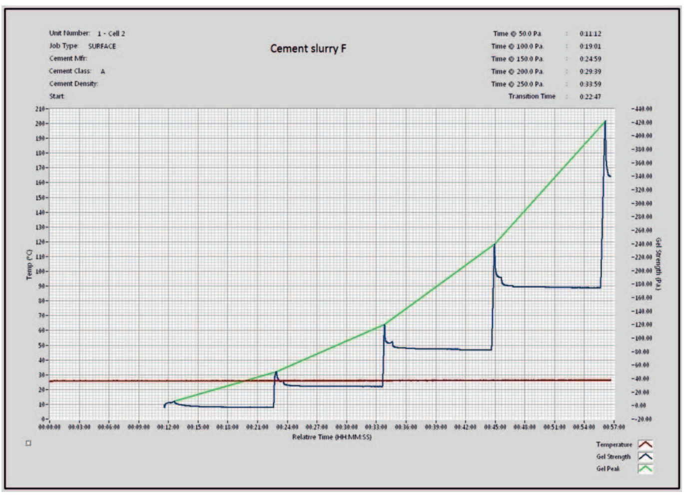

Fig. 9. Static gel strength development for cement slurry marked F
Rys. 9. Narastanie SGS dla zaczynu oznaczonego symbolem F

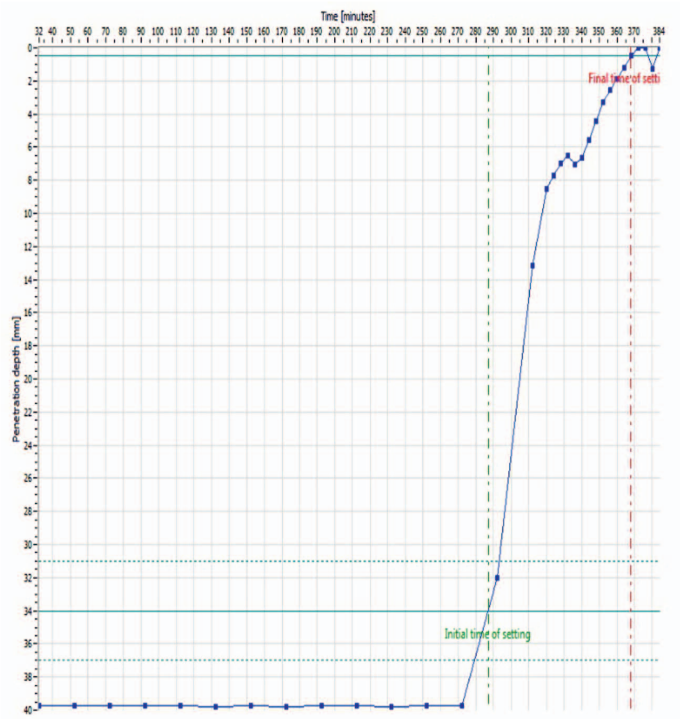

Fig. 10. Thickening time plot for cement slurry A

Rys. 10. Krzywa procesu wiązania zaczynu A

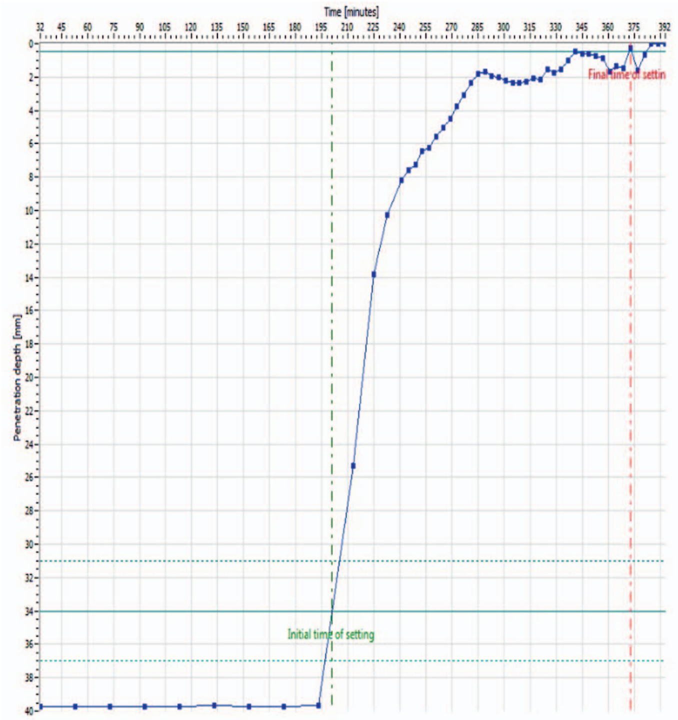

Fig. 11. Thickening time plot for cement slurry B

Rys. 11. Krzywa procesu wiązania zaczynu B

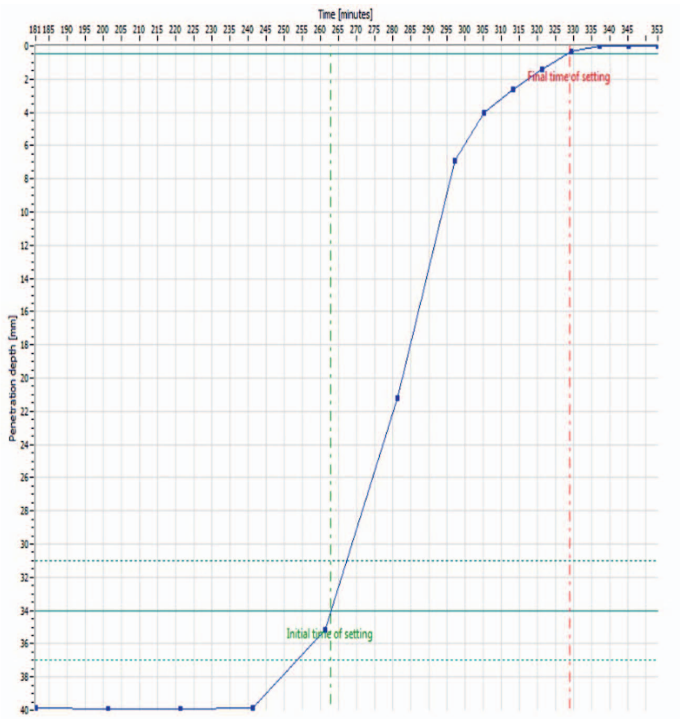

Fig. 12. Thickening time plot for cement slurry C

Rys. 12. Krzywa procesu wiązania zaczynu C

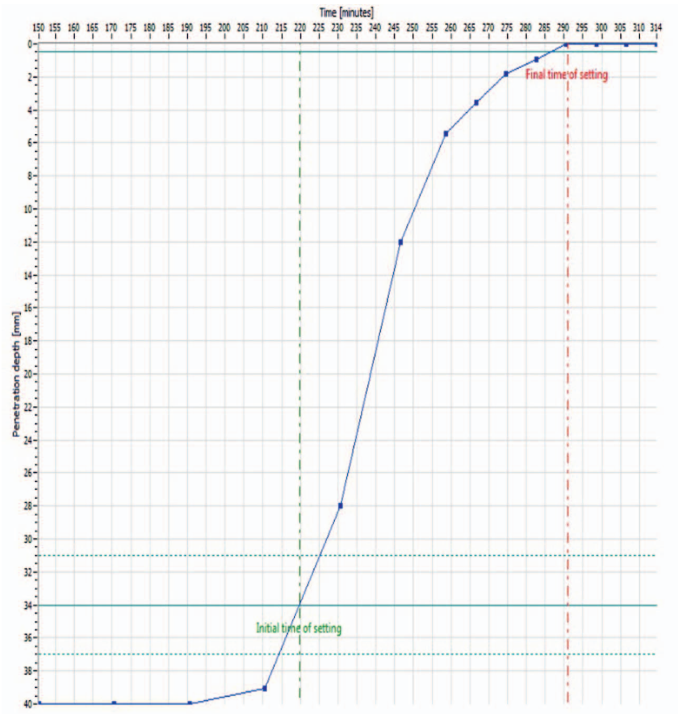

Fig. 13. Thickening time plot for cement slurry D

Rys. 13. Krzywa procesu wiązania zaczynu D

Conclusions

The following conclusions have been drawn after the performed research and analysis of cement slurries and cement sheaths:

1. To avoid the migration of gas from shallow gas accumulations in drilling wells, one should, among others, use cement slurry with quick gelling times (less than about 40–45 minutes) and a setting time properly selected for the borehole conditions is advisable. This is defined in the

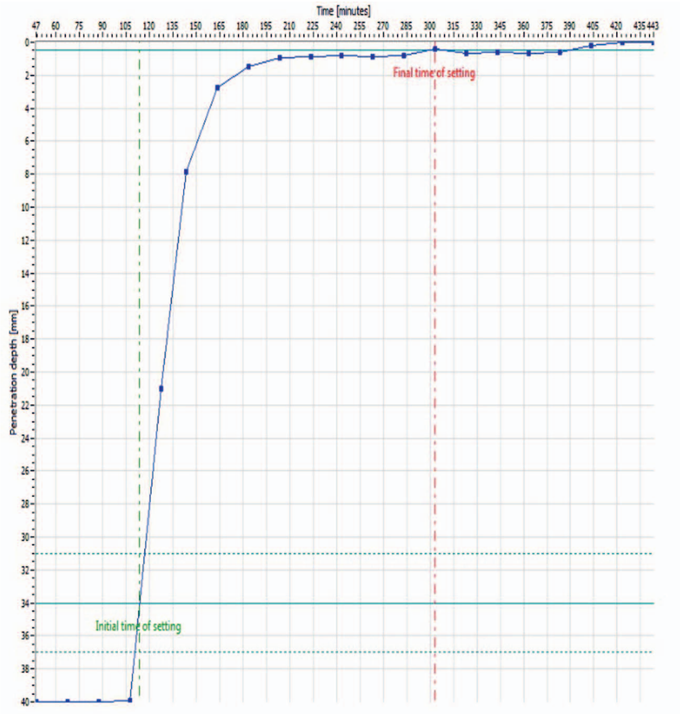

Fig. 14. Thickening time plot for cement slurry E
Rys. 14. Krzywa procesu wiązania zaczynu E

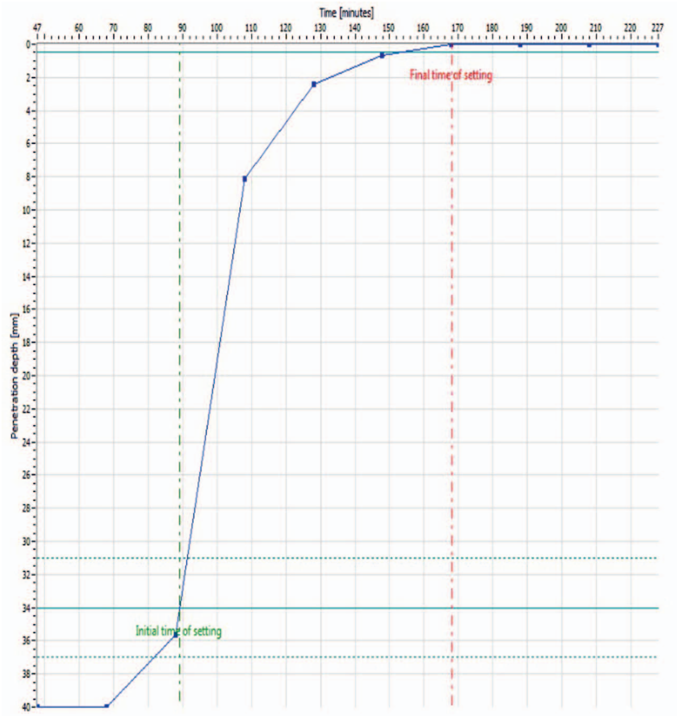

Fig. 15. Thickening time plot for cement slurry F
Rys. 15. Krzywa procesu wiązania zaczynu F

standard API STANDARD 65. It allows to produce a tight barrier in the borehole annulus that prevents the formation fluid from leaking to the surface.

2. Properly modified (with latex and nanosilica additives) cement slurries based on Portland cement CEM I 42.5 can be successfully deployed in cement jobs in top sections of drilling wells with increased risk of shallow gas migration.
3. The cement slurry formulas included in this paper have the appropriate technological parameters. Some of them, especially those with extended setting time and extended transition time TT, can be used for sealing deeper intervals (i.e. up to approx. 400 m), and others (these with short setting time equal approximately to 2 hours) and TT below 30 minutes are better suited for sealing the top section of the well (e.g. from 0 to approx. 150 m).
4. Particularly advantageous technological parameters have been obtained for cement slurries with densities of approx. 1800–1820 kg/m^3 containing about 0.5–1% nano-SiO_2. The optimal water-cement ratio was around 0.50–0.52 for them.
5. Samples containing 10% latex and those containing 0.5% and 1% nano-SiO_2 were characterized by a very favorable course of the setting plot (static build-up of mechanical strength). Their TT transition times were several tens of minutes (which proves their high ability to prevent gas migration from shallow gas accumulations).
6. The setting times of the tested slurries can be successfully controlled using accelerators commonly used in the industry. The slurries tested on the Vicat apparatus had an initial setting time ranging from approximately 100 to 280 minutes. That provides, depending on the anticipated duration of the cement job, that the appropriate thickening time of slurry can be successfully adjusted.
7. Compressive strength after 7 days of hydration was high. For samples with the addition of natural rubber latex (compositions A and B), these were approx. 22–23 MPa for slurries of 0.5% nano-SiO_2 (compositions C and D) – about 29–30 MPa, and for slurries with the addition of 1% nano-SiO_2 (compositions E and F) – around 30–31 MPa.
8. Slurries containing appropriate additions of nanomaterials, due to their good technological parameters, could be used in the cementing process of casing strings, e.g. in the Carpathian Foreland.

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Legal and normative acts

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PN-EN ISO 10426-2 Przemysł naftowy i gazowniczy – Cements and accessories for cementing boreholes – part 2: Testing of cements for drilling applications.

PN-EN 196-3:2016-12 Metody badania cementu – Część 3: Oznaczanie czasów wiązania i stałości objętości.

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