

Article

Influence of Hblock Fine-Grained Material on Selected Parameters of Cement Slurry

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Abstract: Fine-grained materials are used to seal the microstructure and improve the mechanical parameters of the formed cement sheath. They are used in cement slurries designed to seal casing columns at great depths and in geothermal boreholes to improve thermal conductivity. Such additions shorten the setting time and the transition time from the value of the initial time of the setting to the final of the setting. This allows the shortening of the time needed to bind the slurry and move on to further work. Additionally, it helps to eliminate the possibility of gaseous medium intrusion into the structure of the setting cement slurry. The goal of the work is to determine the influence of the Hblock fine-grained material on selected parameters of the cement slurry. Hblock is used in the research ranging from 1% to 20% (bwoc (bwoc—by weight of cement)), and the two types of cement most commonly used in the petroleum sector. Then the technological parameters of fresh and hardened cement slurries were tested. Research on rheological parameters, determined rheological models and flow curves are performed. On the basis of the obtained test results, the influence of the additive on the technological parameters of the cement slurry is discussed. The research results allow for further work and then the application of the fine-grained material in the petroleum sector.

Keywords: cement slurry; fine-grained material; borehole sealing efficiency; technological parameters



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1. Introduction

The column of casing pipes is sealing a cement slurry, which is a mixture of water, cement and additives or admixtures modifying the technological parameters of the cement slurry. Its properties are adjusted to the geological and technical conditions prevailing in the borehole where the hydration process takes place and the formation of a cement sheath in the annular space [1–3]. In this case, the decisive factor is the type of drilled geological layers, the final drilling depth, dynamic and static temperature, as well as formation pressure and fracturing pressure [4–7]. Therefore, it is necessary to adjust the parameters of the cement slurry properly. For this purpose, various types of chemicals, additives and fine-grained material are used, the use of which allows to obtain the parameters required for the given conditions and to obtain the highest possible tightness and durability of the cement sheath formed from the cement slurry [2,8,9]. However, the application of a new type of agent must be preceded by a test cycle, after which it is possible to determine the benefits or the impact of using a given additive [10,11]. Based on the analysis of the obtained results, it is possible to determine the suitability of the tested agent and then modify the slurry recipe for specific borehole conditions. The use of such an advantageously modified cement slurry contributes to the elimination of bad cementing. Such actions are necessary because poor cementation may result in complications and difficulties in liquidating possible outflows of the formation medium from the annular space [12,13]. Due to the high costs of additional works related to sealing, research on the impact and the possibility of using a new type of agents is a necessary element in the continuous improvement of the properties of drilling fluids.

The Role of Fine-Grained Material in the Technology of Cement Slurries

The use of hydraulic binders and modification of the properties of the developed cement slurries with the use of additives and mineral admixtures is an issue subject to a wide scope of research [14,15]. It is related to the pursuit of continuous improvement of technological parameters of cement slurries as a result of the use of a new type of agent. Thanks to this, it is possible to seal the matrix of the cement sheath formed in the annular space. Moreover, the modified cement slurry recipe has a more compact structure with a lower porosity value and a much lower gas permeability [2,16,17]. Such conditions make it possible to limit, and most often eliminate, gas migration through the cement sheath. Gas migration is a phenomenon that can occur both during the setting and hardening of the cement slurry, but also during the exploitation of the hole in which the slurry is in the solid state. After binding the cement slurry, the greatest risk of gas migration is in the capillary pore spaces, microcracks in the structure of the cement sheath or in the crevices formed [2,18–20]. Therefore, it is necessary to design a cement slurry recipe that, after setting, will be characterized by a lack of gas permeability. For this purpose, fine-grained material and admixtures in the form of mineral dust are used. By increasing the volume of the slurry and hydraulic activity, fine-grained material increases the tightness of the hardened cement slurry [21–23]. It is important because high permeability values of the cement sheath cause corrosion and decrease the mechanical parameters [2,24,25]. The mechanical strength, which is related to the microstructure of the cement sheath and the value of the total porosity, should also be taken into account. When designing the cement slurry recipe, its density is selected depending on the geological and technical conditions, and the mechanical strength decreases in proportion to the reduction in the cement slurry density. Therefore, in order to develop a cement slurry with a well-dense and gas-impermeable microstructure, macropores are filled with a solid substance of finer graining than that of the cement used [26–28]. As a result, it is possible to increase the value of the mechanical strength of the hardened cement slurry and shorten the transition time from the liquid phase to the solid phase. A very important parameter is also the setting time of the cement slurry and the transition time from the point of the beginning of the binding to the point of the end of the binding. It is one of the basic parameters allowing to pre-define whether the liquid cement slurry binds as quickly as possible before gas intrusion into the structure of the liquid cement slurry after being pushed into the cemented annular space. The shortest possible time between the value of the beginning of the setting and the end of the setting is important [29,30]. Fine-grained materials are commonly used in the building materials industry to improve selected technological parameters of fresh and hardened cement slurries. However, in the technology of cement slurries, these additives are treated with caution. This is due to the much more restrictive parameter values for slurries. The beneficial effect of fine-grained material used to improve the parameters of the hardened cement slurry may adversely affect the rheological parameters of the liquid slurry, which is related to the increase in the water needed for the designed slurry [31–34]. It is important in terms of the pumpability of the cement slurry during the cementing procedure. Therefore, the possibility of using fine-grained material is being investigated in terms of improving the parameters of both the liquid and hardened cement slurry. This is an innovative issue as fine-grain materials from the construction industry are rarely used in the oil industry. Such preliminary work allows to broaden the scientific horizons in this direction and open a new path in the technology of cement slurries.

2. Materials and Methods

2.1. Materials

CEM I 42.5R Portland cement was used to prepare slurries. The cement contained 3.22% SO₃ and 0.069% Cl⁻. The cement specific surface was 4200 cm²/g, the specific density was 3.09 g/cm³, and the alkalis content was (eq Na₂O) 0.61%. The tap water contained 0.064 mg/L NH₄ (ammonia), 2.95 mg/L NO₃ (nitrates), 0.048 mg/L NO₂ (nitrites), 29.2 µg/L Fe (iron), 5.81 µg/L Mn (manganese), and 344.0 mg/L CaCO₃ (calcium carbon-

ate). The second cement used for the tests was the German G class cement (Dyckerhoff). The specific surface area (measured by the Blaine method) is $2800 \text{ cm}^2/\text{g}$. The alkali content is kept at 0.89%, chloride at 0.061%, and sulphate at 3.23%. The loss on ignition is 3.03%, and the insoluble residue is 0.54%. The volume stability was found to be 0.44 mm.

Hblock is a fine-grained material with the name and chemical composition coded by the manufacturer, in which the dominant oxides are: CaO (35.81–37.53%) and Fe_2O_3 (26.52–32.45%). The share of MgO is 7.65%, Al_2O_3 3.62%, MnO 2.87%, and P_2O_5 1.07%.

2.2. Methods

To determine the effect of Hblock on selected technological parameters of the fresh cement slurry, the density test, rheological parameters of the cement slurry, and the slurry setting time test along with the transition time from the beginning of setting to the end of the setting are performed. Compressive strength tests and gas permeability tests are carried out for samples of hardened cement slurry.

2.2.1. Slurry Preparation

In order to determine the effect of Hblock on the parameters of the cement slurry, 10 recipes (5 slurries per one type of cement) were tested. The points of reference are two control recipes consisting of cement and water with a constant water-cement ratio. These are samples No. 1 and No. 6. Two types of cement materials are selected for research work: CEM I 42.5R Portland cement with a specific surface area of $4200 \text{ cm}^2/\text{g}$, and the C_3A content in clinker of approx. 7% and class G drilling cement. The specific surface area is $2800 \text{ cm}^2/\text{g}$, and the C_3A content in the clinker is approx. 3%. Modified slurries are 4 recipes containing the tested Hblock fine-grained material, the specific surface of which is $3200 \text{ cm}^2/\text{g}$. Starters 2 to 5 are made of CEM I 42.5R cement. Starters 7 to 10 were made on the basis of drill cement G. During the preparation of the cement slurry, a certain amount of water is measured with a measuring cylinder. The right amount of Hblock is dosed into the water. Water is poured into the mixer. The speed is then set to 1600 rpm, and mixing takes 5 min. After this time, the cement is poured into the mixing water mixture and mixed for another 25 min. Mixing at low speed is the same as mixing the slurry under the conditions of the well. The basic cement slurry, marked as No. 1 in Table 1, was prepared as a control sample. In order to eliminate the measurement error, the same water-cement coefficient of 0.46 was adopted for all recipes. In subsequent recipes of the cement slurry, increasing concentrations of Hblock in the amount of 1%, 3%, 6%, and 20% (bwoc) were used. Such action is aimed at checking the changes under the influence of the amount of the agent dosed to the starter. The slurry recipes are listed in Table 1 below, while the selected technological parameters are presented in Table 2. Table 3 summarizes the shear rate at 12 speed ranges from 600 rpm to 1 rpm, which corresponds to the shear rate from 1022.040 to 1.703 [1/s]. Table 4 summarizes the apparent viscosity values. On the other hand, Table 5 presents the rheological parameters of the tested slurries, described according to the presented rheological models.

Table 1. Recipes of cement slurries with the addition of Hblock agent (water-cement coefficient 0.46).

Type of Cement	Composition No.									
	1	2	3	4	5	6	7	8	9	10
Portland cement CEM I 42.5R, %			100.0							
Drilling cement G, %			-					100.0		
Hblok small-particle agent, %	-	1.0	3.0	6.0	20.0	-	1.0	3.0	6.0	20.0

The share of all measures is given in relation to the weight of cement (bwoc).

Table 2. Parameters of the tested cement slurrie.

Composition No.	Type of Cement	Temp. °C Hydration Pressure, MPa	Density	Cement Slurry Setting Time, min			Compressive Strength after 24 h of Hydration	Gas Permeability
				Initial Time of the Setting PW	Final Time of the Setting KW	Transition Time PW to KW		
				[kg/m ³]	[min]	[min]		
1	Portland cement CEM I 42.5R	30 °C 3 MPa	1890	338	532	194	15.5	0.245 ± 0.002
2			1900	269	343	74	20.0	0.043 ± 0.002
3			1910	278	340	62	24.5	0.032 ± 0.002
4			1920	272	344	72	17.5	0.021 ± 0.002
5			1960	339	382	43	25.5	0.013 ± 0.002
6			1870	322	538	216	14.5	0.337 ± 0.002
7	Drilling cement G		1880	401	546	145	17.5	0.126 ± 0.002
8			1890	400	513	113	18.0	0.042 ± 0.002
9			1910	387	532	145	15.0	0.033 ± 0.002
10			1970	451	555	104	16.0	0.021 ± 0.002

Table 3. Values of the compressive strength measurements for samples P1 to P10.

	Mesurement					Average Value
	1	2	3	4	5	
P1	16	15.8	14.7	15.5	15.5	15.5
P2	19.9	20	20.1	20	20	20
P3	24	24.5	25	24.5	24.5	24.5
P4	18.5	17	17	17.5	17.5	17.5
P5	24.6	25	26.9	25.5	25.5	25.5
P6	13	15	15.5	14.5	14.5	14.5
P7	17.8	17.3	17.4	17.5	17.5	17.5
P8	17	18	19	18	18	18
P9	15.5	15.6	13.9	15	15	15
P10	14.9	15.4	17.7	16	16	16

Table 4. Within-subject comparison (comparison of samples to baseline P1) Two-sample *t*-test for the mean.

	P1	P2 – P1	P3 – P1	P4 – P1	P5 – P1
Average	15.5	20	24.5	17.5	25.5
Variance	0.245	0.005	0.125	0.375	0.755
Observations	5	5	5	5	5
Pearson's correlation		0.92857	0.92857	0.61859	0.9998
Difference of means according to the hypothesis		0	0	0	0
df		4	4	4	4
<i>t</i> Stat		17.92843	24.13988	9.035079	16.39565
P(T ≤ <i>t</i>) unilateral		2.84 × 10 ⁻⁵	8.73 × 10 ⁻⁶	0.000416	4.05 × 10 ⁻⁵
Test T unilateral		2.131847	2.131847	2.131847	2.131847
P(T ≤ <i>t</i>) bilateral		5.69 × 10 ⁻⁵	1.75 × 10 ⁻⁵	0.000831	8.1 × 10 ⁻⁵
Test <i>t</i> bilateral		2.776445	2.776445	2.776445	2.776445

2.2.2. Density of the Cement Slurry

Density is measured using a Baroid pressure balance (Figure 1) in accordance with EN-PN ISO10426-2 [35]. The balance consists of an arm with a slurry vessel on one side and a calibrated counterweight on the other. The weighing arm is equipped with a sliding weight and has a g/cm³ scale in the range of 0.8–2.75. The weight is read from the position of the sliding weight when the scale is leveled by the appropriate positioning of the bubble on the balance arm.

Table 5. Within-subject comparison (comparison of samples to baseline P6) *t*-test: pairwise pairing for the mean.

	P6	P7 – P6	P8 – P6	P9 – P6	P10 – P6
Average	14.5	17.5	18	15	16
Variance	0.875	0.035	0.5	0.455	1.115
Observations	5	5	5	5	5
Pearson’s correlation		0.92857	0.944911	0.61413	0.771966
Difference of means according to the hypothesis		0	0	0	0
df		4	4	4	4
<i>t</i> Stat		6.036327	22.13594	0.7706	4.918694
P($T \leq t$) unilateral		0.001899	1.23×10^{-5}	0.241967	0.003968
Test T unilateral		2.131847	2.131847	2.131847	2.131847
P($T \leq t$) bilateral		0.003798	2.47×10^{-5}	0.483935	0.007937
Test <i>t</i> bilateral		2.776445	2.776445	2.776445	2.776445

**Figure 1.** Baroid weight.

2.2.3. Rheological Parameters

The study of rheological properties is based on the determination of shear curves. The tests are performed for the following rotational speeds: 600, 300, 200, 100, 60, 30, 20, 10, 6, 3, 2, and 1 rpm. These values correspond to the shear rates ($\dot{\gamma}$): 1022,04; 511,02; 340.68; 170.34; 102.20; 51.10; 34.07; 17.03; 10.22; 5.11; 3.41; and 1.70 s^{-1} . The tests are carried out at a temperature of $20 \pm 2 \text{ }^\circ\text{C}$. The dosing liquid is tap water, free from contamination. The viscometer-Model 900 FANN (Figure 2) with coaxial cylinders is used to test rheological properties. To facilitate the calculations (Table 5), the numerical software “Rheo Solution” is used. The software is owned by the Faculty of Drilling, Oil and Gas of the AGH University of Science and Technology and is used in research and development [33,34].

**Figure 2.** Fann model 900 rotary viscometer.

2.2.4. Setting Time

The examination is performed with the use of an automatic six-chamber Vicat apparatus (Figure 3). The test is performed according to IS:4031-PART 4-1988 VICAT APPARATUS [36]. The measurement consists of determining the depth of immersion of the needle in the binding cement slurry. The points of the initial time of the setting and the final time of the setting are measured. The test is carried out continuously at the prescribed time. The camera is electronically controlled from a computer using software where the measurement conditions are set. The delay time after which the setting time test is to start is determined, and then the measurement is performed at specified time intervals ranging from 1 min to 20 min. Each subsequent measurement is carried out in a different place on the sample in order to avoid the needle sinking into the same place resulting in an incorrect value.



Figure 3. Automated Vicat apparatus.

On the basis of the obtained measurement results, a graph is drawn of the dependence of the depth of the needle plunging into the start of the needle to the binding time of the cement slurry (Figure 4). After each measurement, the needle returns to its base position, where it is cleaned and waits for the next measurement of a given sample or for the next sample. Up to 6 samples of different cement slurries can be measured at the same time. The samples are placed in a water bath that is temperature-controlled from 25 °C to 50 °C. When the initial time of the setting end is reached, further measurements are stopped, and the results are saved graphically.

2.2.5. Compressive Strength

Measurements are made on beams in accordance with the EN-PN ISO10426-2 [35] standard. The tests are performed using a Chandler Engineering model 4207 testing machine (Figure 5). After the cement slurry is prepared, it is placed in 4 cm × 4 cm × 16 cm molds. The molds are stored in water for 24 h in an autoclave at a temperature of 22 ± 2 °C and at atmospheric pressure.

2.2.6. Gas Permeability

The test is performed using a gas permeability meter. The measurement is the basic measure of the ability of a porous medium to transport the liquid and gaseous media it contains. The gas permeability meter (Figure 6) used in the test is used to measure the permeability of core or cement samples one inch in diameter and length (Figure 7). The sample is placed in a “modified Hassler” test cylinder [27]. Nitrogen is then supplied, and the differential pressure is measured at a constant flow velocity obtained. The flow velocity is measured with a calibrated flowmeter. The variables, when substituted for Darcy’s law, allow the permeability to be calculated in hardened cement slurry samples.

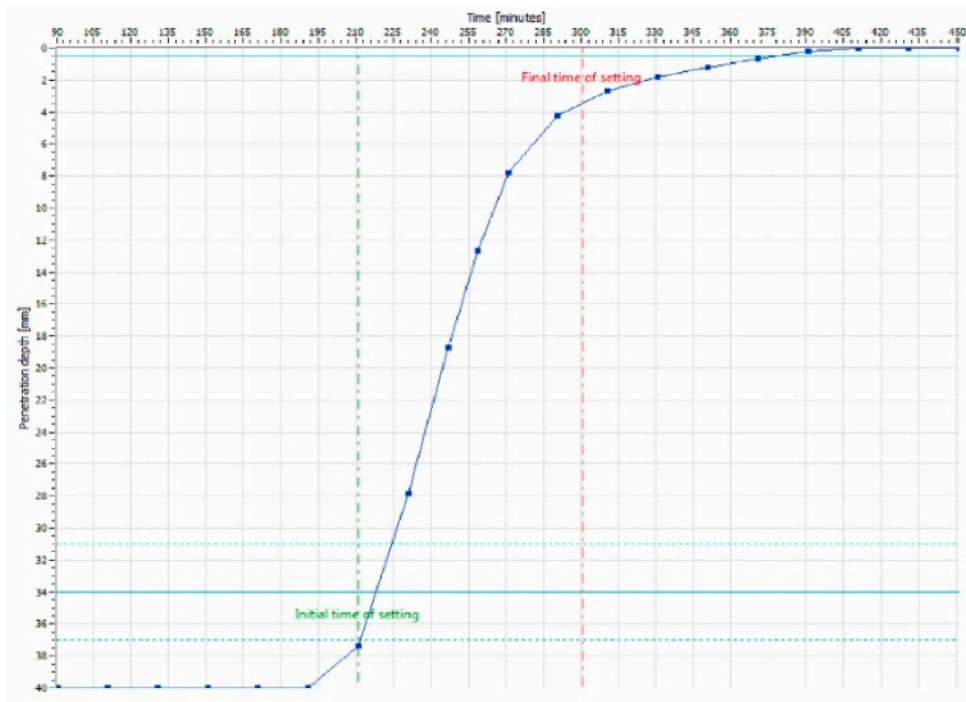


Figure 4. Graph of the dependence of the needle immersion depth in initial time of the setting as a function of time.



Figure 5. Chandler Engineering testing machine.



Figure 6. OFITE gas permeability meter.



Figure 7. A sample of hardened cement slurry for gas permeability testing.

3. Results and Discussion

The presence of the fine Hblock agent causes the density of the slurry to increase. When analyzing the P1 sample prepared on the basis of CEM I 42.5R cement, the density increased by 10 kg/m^3 after adding 1% Hblock compared to the sample without Hblock addition. The addition of 3% Hblock increases the density by 10 kg/m^3 compared to the previous sample. The next amount of 6% Hblock in sample P4 is a further increase in density by 10 kg/m^3 compared to sample P3, which has 3% Hblock. On the other hand, the use of 20% Hblock in sample P5 causes an increase in density by 40 kg/m^3 compared to sample P4.

However, when analyzing the P6 sample prepared on the basis of class G cement, the same trend is visible, but for some time. So 1% Hblock in sample P7 causes an increase in density by 10 kg/m^3 compared to the sample without the addition of Hblock, i.e., P6. The addition of 3% Hblock in sample P8 increases the density by 10 kg/m^3 compared to sample P7. However, the amount of 6% Hblock in sample P9 increases the density by 20 kg/m^3 compared to sample P8, which has 3% Hblock. On the other hand, the use of 20% Hblock in sample P10 causes an increase in density by 60 kg/m^3 compared to sample P9.

On the basis of the above, the increase in density is more evident in the formula of the slurry prepared on the basis of G drilling cement than in the case of the CEM I 42.5R Portland cement grout (Figure 8). At the maximum 20% concentration of the Hblock agent in the CEM I 42.5R cement-based slurry, an increase in density by 70 kg/m^3 compared to the control recipe can be seen, while in the case of the cement-based slurry, the increase in density is 100 kg/m^3 at only a concentration of 20% Hblock (Table 2). This is due to the larger grain diameter of class G drilling cement than CEM I 42.5R class cement, which is related to a better filling of the microstructure of the G cement-based cement slurry.

It should be noted here that the P1 sample has a density of 1890 kg/m^3 , and the base sample, made on the basis of G cement, has a density of 1870 kg/m^3 . The difference of 20 kg/m^3 more in sample P1 compared to sample P2 results from the greater specific surface area, which for cement in sample P1 is $4200 \text{ cm}^2/\text{g}$, while cement G used in sample P2 has a specific surface area of $2800 \text{ cm}^2/\text{g}$.

The addition of 1% Hblock fine-grained material to the composition of the CEM I 42.5R Portland cement-based cement (sample No. 2) accelerates the setting, as shown in Figure 9. The setting time is shortened by 69 min, while the setting time is shortened by 189 min (Table 2). A further increase in Hblock concentration (values 3% and 6%) does not cause a significant difference in the setting time of the slurry; only at a 20% concentration of the agent (sample P5) is an extension of the thickening time visible compared to the previous sample (P4). However, this value is lower than the base sample (P1). When analyzing the slurries based on drilling cement G, it can be seen that the presence of the Hblock agent in the slurry results in an upward trend for the analyzed values of the slurry setting time (Figure 9). This effect is a result of the larger grain diameter of class G cement than CEM I 42.5R cement.

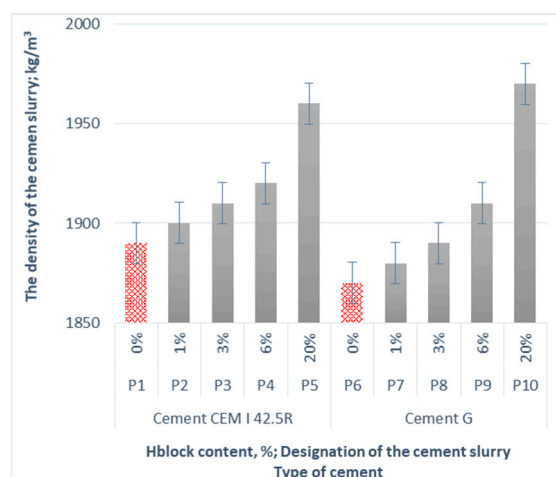


Figure 8. Summary of the density of the tested cement slurries.

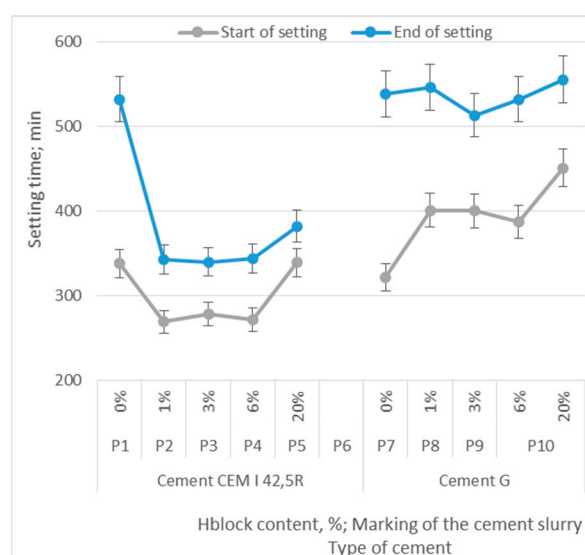


Figure 9. Summary of the setting time values of the tested cement slurries.

The transition time of the tested recipes was significantly shorter in the case of CEM I 42.5R Portland cement slurries than in the case of G cement-based slurries (Figure 10).

The transition from the value of the beginning of the setting to the end of the setting for the base slurry (sample P1) is strongly stretched in both time and amount to 194 min, as shown in Figure 11.

On the other hand, after using the Hblock agent, much shorter values were obtained in the range from 43 min for the P5 sample to 74 min for the P2 sample. The short transition time from the value of the beginning of the setting to the value of the end of the setting for the P5 cement slurry is shown in Figure 12 and Table 2.

In the case of G cement-based slurry, a reduction in the value of the transition time between the initial time of the setting and the final time of the setting is also obtained. However, this change takes place to a lesser extent than in the previous group of slurries. The cement G-based control slurry has a transit time of 217 min, while the Hblock-containing slurries have transition times ranging from 104 min (sample P10) to 145 min (samples P7, P9). When analyzing the changes in the value of the transition time of the slurries containing the Hblock agent (Figure 10), the most favorable change is visible when using the 1% Hblock concentration in relation to the cement mass.

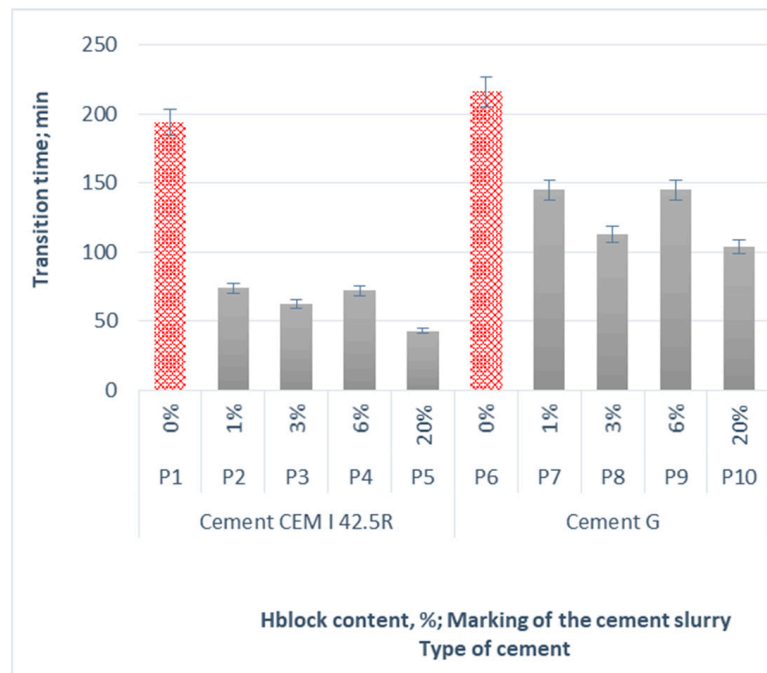


Figure 10. Summary of the values of the transition time from the initial time of the setting to final time of the setting of the tested cement slurries.

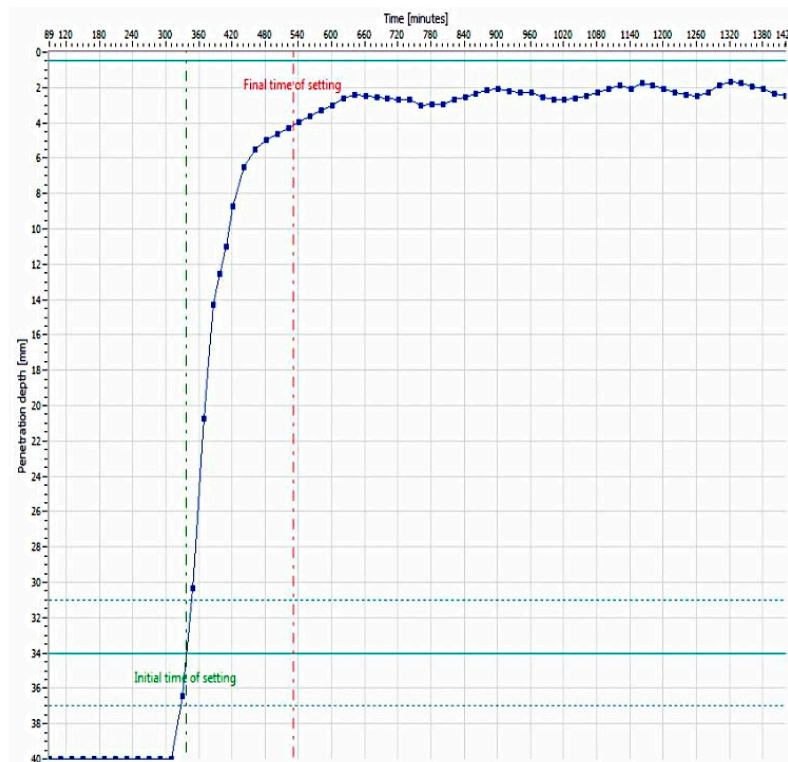


Figure 11. The setting process of the cement slurry based on CEM I 42.5R Portland cement (long transition time); Composition No. 1.

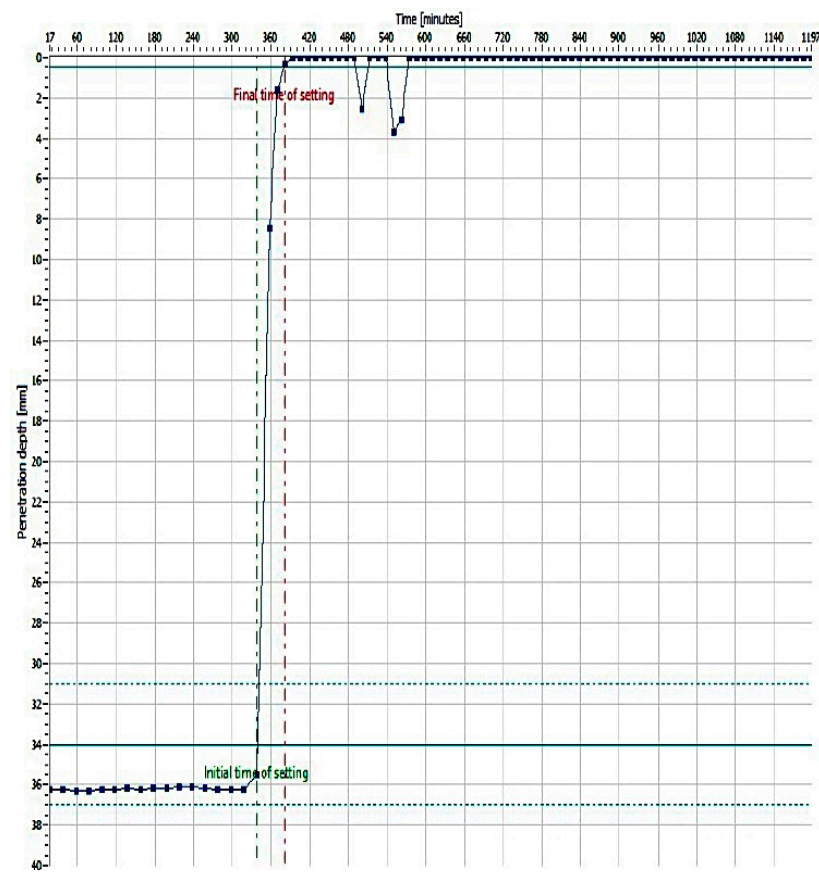


Figure 12. The setting process of the cement slurry with the addition of 20% Hblock (short transition time) Composition No. 5.

The addition of Hblock in the tested cement slurries has a beneficial effect on the improvement of the mechanical parameters of hardened cement slurries. When analyzing the results of compressive strength tests after 24 h of hydration for the cement-based CEM I 42.5R slurry, an increase in the range from 17.5 MPa (sample P4) to 25.5 MPa (sample P5) compared to the base value of 15, 5 MPa for the P1 hardened cement slurry (Figure 13, Table 2). For slurries based on G drilling cement, an increase in the value of compressive strength is also visible, but to a lesser extent. From the value of 14.5 MPa for the base cement slurry (sample P6), the strength value increased to 18 MPa for the P8 slurry containing 3% Hblock. A further increase in the concentration of the tested agent does not improve the value of the compressive strength (Figure 13). The most favorable concentration range is visible, ranging from 1% to 3% of Hblock (marked in Figure 13). It significantly improves the compressive strength of the hardened cement slurry based on the analyzed cement.

Statistical Analysis of the Value of Compressive Strength

Based on the obtained results, a statistical analysis is performed, taking into account the variability of the data. Table 3 presents the measurement values. However, in Tables 4–6 the uncertainties of measurement and calculated values are estimated. They come from direct measurements based on the accuracy of the measuring devices. Value uncertainties are estimated from the calculated standard deviations from the mean, and a pairwise *t*-test for the mean is estimated from the appropriate formulas.

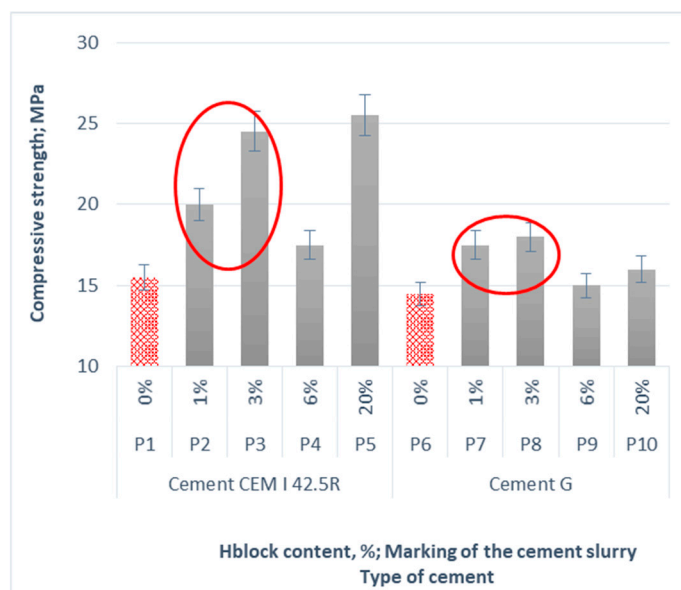


Figure 13. Compressive strength values of the samples of hardened cement slurries.

Table 6. Among-subject comparison (comparison of samples with the same amounts of Hblock) *t*-test: pairwise pairing with two samples for the mean.

	P1 – P6	P2 – P7	P3 – P8	P4 – P9	P5 – P9
Average	14.5	20	17.5	17.5	25.5
Variance	0.875	0.005	0.375	0.375	0.755
Observations	5	5	5	5	5
Pearson’s correlation	0.75593	0.75593	0.86603	0.453921	0.999989
Difference of means according to the hypothesis	0	0	0	0	0
df	4	4	4	4	4
<i>t</i> Stat	−1.65748	22.82177	−0.87706	8.287419	113.5467
P(T ≤ <i>t</i>) unilateral	0.086381	1.09 × 10 ^{−5}	0.214987	0.000579	1.8 × 10 ^{−8}
Test T unilateral	2.131847	2.131847	2.131847	2.131847	2.131847
P(T ≤ <i>t</i>) bilateral	0.172762	2.18 × 10 ^{−5}	0.429973	0.001157	3.61 × 10 ^{−8}
Test <i>t</i> bilateral	2.776445	2.776445	2.776445	2.776445	2.776445

On the basis of the mean equality test for $\alpha = 0.05$, the T-Student’s statistic is calculated and compared with the data from the distribution. When analyzing the within-subject comparison for samples P1 – P6 made on the basis of CEM I 42.5R cement (Table 4), all Tstat values are in the critical area and range from 9.03 to 24.14, assuming a two-sided T-test of 2.78. Therefore, the samples are statistically different.

The second comparison in Table 5 for the samples (P7 – P10) based on drill cement G shows that only sample P9 is statistically similar to the base samples (P9 – P6) null hypothesis. However, the remaining samples are statistically different.

However, in the among-subject analysis (Table 6), where samples prepared on different types of cement are compared, it can be seen that the P1 – P6 base samples and samples with 3% Hblock additive (P3 – P8) show statistical similarity. The 3% Hblock amount may be the optimal dosing value to achieve the required mechanical performance.

The gas permeability of the analyzed cement slurries decreased from 0.245 mD (sample P1) to 0.043 mD (sample P2) after using 1% Hblock in the case of CEM I 42.5R Portland cement slurries and from 0.337 mD (sample P6) to the value of 0.042 mD (sample P8). The obtained values are summarized in Table 2.

Analyzing the influence of the Hblock agent on the rheological parameters of the cement slurry prepared on the basis of CEM I 42.5R Portland cement, an increase in the

yield point after the application of the Hblock additive can be seen. The base slurry P1 had the value of the yield point equal to 6.1 Pa, described by the Herschel–Bulkley model; the introduction of 1% Hblock causes the increase in the yield limit HB to 10.08 Pa, while the 3% Hblock reduces the yield limit to 5.8 Pa. Increasingly larger amounts of the tested agent cause an increase in the yield point value, which can be seen in Figure 14,. The addition of Hblock also increases the consistency coefficient according to the Herschel–Bulkley model. The control slurry (P1) has a consistency coefficient HB of 9.59 Pa sⁿ. After introducing Hblock into the cement slurry, the HB consistency coefficient increases in the range from 12.29 Pa sⁿ to 31.21 Pa·sⁿ. Significantly lower values of the discussed rheological parameters were obtained for the cement slurry prepared on the basis of drilling cement G (Figure 15, Tables 7–9).

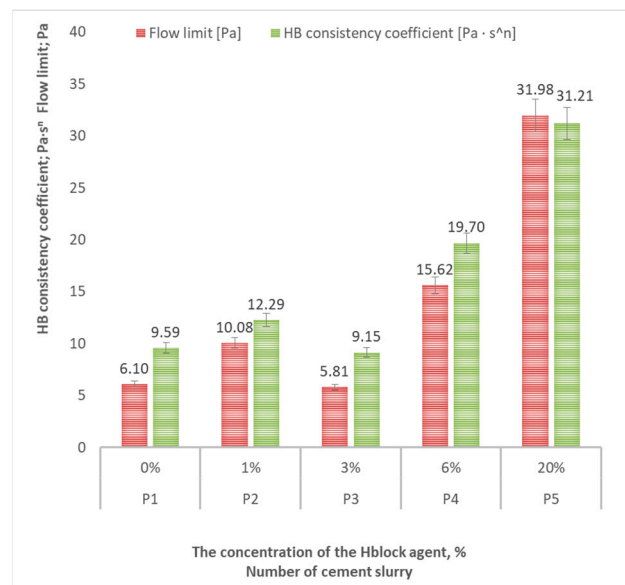


Figure 14. Summary of selected test results for rheological parameters of cement slurries (cement class CEM I 42.5R).

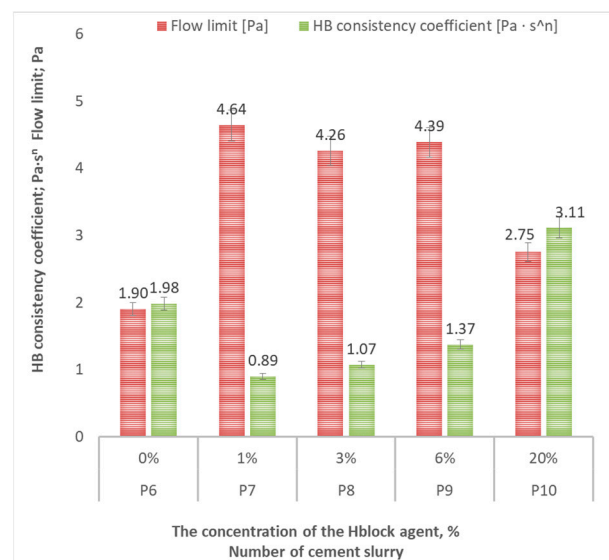


Figure 15. Summary of selected test results for rheological parameters of cement slurries (cement class CEM G).

Table 7. Results of measurements and calculated values of shear stress for slurries.

Shear Rate, s ⁻¹	Shear Stress, Pa									
	Composition No.									
	1	2	3	4	5	6	7	8	9	10
1.703	8.176	6.643	6.643	9.709	10.220	3.577	3.577	3.066	3.577	5.110
3.407	10.220	8.687	8.687	12.775	14.308	4.599	4.599	4.599	5.621	7.665
5.110	12.775	10.731	10.731	15.330	17.374	5.621	6.132	6.643	7.154	8.687
10.220	17.885	15.841	15.841	21.462	24.017	9.198	9.198	9.709	10.220	12.775
17.034	23.506	21.462	21.462	30.149	32.704	12.264	12.775	12.775	13.286	16.863
34.068	33.215	32.193	32.193	42.924	44.968	16.863	15.330	17.374	19.418	26.061
51.102	42.924	43.946	45.479	58.254	55.699	18.907	16.863	18.396	21.462	30.660
102.204	65.408	55.699	55.188	71.029	85.337	25.039	24.528	24.528	26.572	38.325
170.340	79.716	65.408	63.875	81.249	102.200	31.682	27.083	30.660	33.215	46.501
340.680	104.244	84.315	81.249	100.156	131.327	44.457	38.325	43.946	45.990	64.386
511.020	121.618	100.156	92.491	116.508	155.344	55.188	51.100	56.210	57.743	80.227
1022.040	170.674	134.393	130.816	157.388	174.762	81.760	80.738	89.425	87.892	120.085

Table 8. Results of measurements and calculated values of apparent viscosity for slurries.

Shear Rate, s ⁻¹	Apparent Viscosity, Pa·s									
	Composition No.									
	1	2	3	4	5	6	7	8	9	10
1.703	4.7998	3.8998	3.8998	5.6998	5.9998	2.0999	2.0999	1.7999	2.0999	2.9999
3.407	2.9999	2.5499	2.5499	3.7499	4.1998	1.3499	1.3499	1.3499	1.6499	2.2499
5.110	2.4999	2.0999	2.0999	2.9999	3.3999	1.1000	1.2000	1.2999	1.3999	1.6999
10.220	1.7499	1.5499	1.5499	2.0999	2.3499	0.9000	0.9000	0.9500	1.0000	1.2500
17.034	1.3799	1.2600	1.2600	1.7699	1.9199	0.7200	0.7500	0.7500	0.7800	0.9900
34.068	0.9750	0.9450	0.9450	1.2600	1.3199	0.4950	0.4500	0.5100	0.5700	0.7650
51.102	0.8400	0.8600	0.8900	1.1400	1.0900	0.3700	0.3300	0.3600	0.4200	0.6000
102.204	0.6400	0.5450	0.5400	0.6950	0.8350	0.2450	0.2400	0.2400	0.2600	0.3750
170.340	0.4680	0.3840	0.3750	0.4770	0.6000	0.1860	0.1590	0.1800	0.1950	0.2730
340.680	0.3060	0.2475	0.2385	0.2940	0.3855	0.1305	0.1125	0.1290	0.1350	0.1890
511.020	0.2380	0.1960	0.1810	0.2280	0.3040	0.1080	0.1000	0.1100	0.1130	0.1570
1022.040	0.1670	0.1315	0.1280	0.1540	0.1710	0.0800	0.0790	0.0875	0.0860	0.1175

Table 9. Rheological parameters of cement slurries.

Rheological Model	Rheological Parameters	Composition No.									
		1	2	3	4	5	6	7	8	9	10
Newton's model	Newton's dynamic viscosity, Pa·s	0.2022	0.1625	0.1559	0.1917	0.2281	0.0933	0.0891	0.0988	0.988	0.1368
	Correlation coefficient, -	0.8231	0.7599	0.7812	0.6736	0.6622	0.8717	0.8953	0.9047	0.8765	0.8624
Bingham's model	Plastic viscosity, Pa·s	0.1600	0.1240	0.1202	0.1403	0.1677	0.0756	0.0730	0.0817	0.0799	0.1100
	Flow limit, Pa	27.2736	24.8480	23.0535	33.2245	38.9787	11.4776	10.3816	10.9878	12.1882	17.3186
	Correlation coefficient, -	0.9428	0.9276	0.9346	0.9162	0.8868	0.9679	0.9801	0.9801	0.9742	0.9661

Table 9. Cont.

Rheological Model	Rheological Parameters	Composition No.									
		1	2	3	4	5	6	7	8	9	10
Ostwald–de Waele’s model	Coefficient of consistency, Pa·s ^s	5.2967	5.2854	5.2419	8.0588	8.3847	2.7714	2.8778	2.7498	3.2356	4.2045
	Exponent, -	0.4929	0.4841	0.4740	0.4442	0.4685	0.4840	0.4628	0.4895	0.4649	0.4797
	Correlation coefficient, -	0.9962	0.9865	0.9920	0.9844	0.9740	0.9983	0.9882	0.9929	0.9920	0.9973
Casson’s model	Casson’s viscosity, Pa·s	0.1146	0.0866	0.0830	0.0915	0.1184	0.0519	0.0477	0.0554	0.0523	0.0748
	Flow limit, Pa	11.7086	11.2039	10.5368	16.5485	17.6915	5.2151	5.0616	5.0643	5.9163	7.9848
	Correlation coefficient, -	0.9652	0.9539	0.9600	0.9483	0.9217	0.9852	0.9928	0.9926	0.9893	0.9839
Herschel–Bulkley’s model	Flow limit, Pa	6.1029	10.0769	5.8080	15.6180	31.9790	1.8997	4.6380	4.2584	4.3869	2.7504
	Coefficient of consistency, Pa·s ⁿ	9.5936	12.2924	9.1489	19.6989	31.2099	1.9809	0.8940	1.0721	1.3721	3.1114
	Exponent, -	0.4196	0.3541	0.3880	0.3104	0.2791	0.5313	0.4381	0.6284	0.5903	0.5207
	Correlation coefficient, -	0.9989	0.9986	0.9967	0.9971	0.9950	0.9988	0.9958	0.9971	0.9955	0.9972

The P6 base slurry has a 1.9 Pa Herschel–Bulkley flow limit. The presence of Hblock results in an HB flow limit in the range of 2.75 Pa (sample P10) to 4.64 Pa (sample P7). The HB consistency coefficient ranges from 0.89 Pa·sⁿ (sample P7 with 1% Hblock content) to 3.11 Pa·sⁿ (sample P10 with 20% Hblock content). Casson viscosity of slurries prepared on the basis of CEM I 42.5R Portland cement ranges from 0.08 Pa·s (sample P3 with the addition of 6% Hblock) to 0.12 Pa·s (sample P5 with the addition of 20% Hblock) (Figure 16). In turn, the exponent *n* decreases with the increase in the Hblock addition (Figure 16). In the case of slurries prepared on the basis of drilling cement G, the Casson viscosity values are lower than in the previous group of slurries and range from 0.05 Pa·s to 0.07 Pa·s (sample P10 with 20% Hblock) (Figure 17). The exponent *n* has an irregular course and does not show a satisfactory correlation with the concentration of the Hblock measure (Figure 17).

For a thorough analysis of the rheological parameters and determination of the effect of the addition of fine-grained Hblock on the rheology of the cement slurry, diagrams of the flow curves of the tested slurries were prepared. The decrease in the dynamic viscosity of the slurry with the increase in the Hblock agent in the range from 1% to 6% (samples P2, P3, P4) in the slurries prepared on the basis of CEM I 42.5R Portland cement is visible from the slope of the curves (Figure 18), i.e., the decreasing tangent of the angle that forms with the line of abscissa. This is confirmed in previous studies of rheological parameters, where the Casson viscosity values and the plastic viscosity described by the Bingham model decrease due to the increasing amount of Hblock in the slurry. Only in the case of the slurry with the highest amount of Hblock (20% bwoc) (sample P5) is the flow curve above the base slurry curve (P1—red line) visible. This proves the increase in the dynamic viscosity of the cement slurry with a significant (20%) concentration of the Hblock agent.



Figure 16. Summary of selected test results for rheological parameters of cement slurries (cement class CEM I 42.5R).

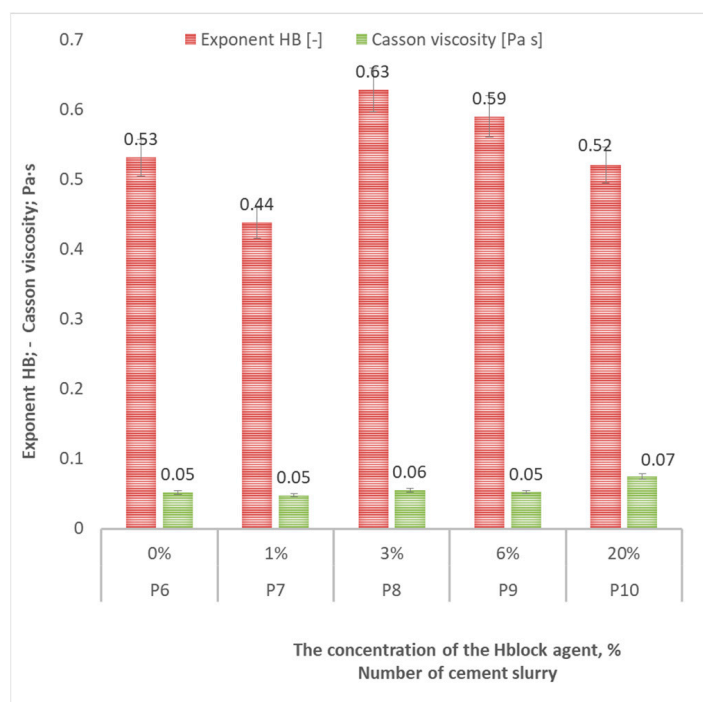


Figure 17. Summary of selected test results for rheological parameters of cement slurries (cement class CEM G).

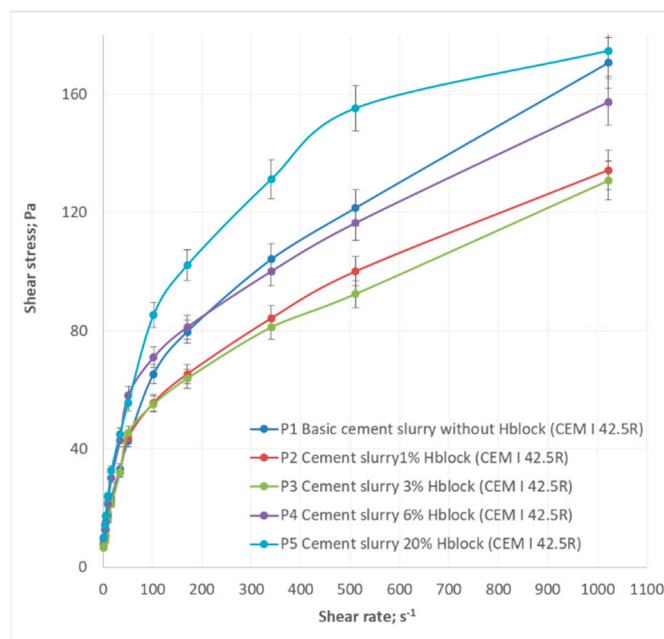


Figure 18. Flow curves for cement slurries with the addition of Hblock (cement class CEM I 42.5R).

A different course of the flow curves takes place during the interpretation of slurries with the addition of the Hblock agent prepared on the basis of drilling cement G (Figure 19). The curve for the base slurry (sample P6—red color) runs almost the lowest, and the recipe of this slurry has the lowest value of dynamic viscosity. A slightly lower course of the flow curve occurred only in the sample with the addition of 1% Hblock agent (sample P7), while successive increasing amounts of Hblock in the range from 3% to 6% caused an increase in viscosity manifested by a smaller slope of the curves. The greatest increase in viscosity is seen at the highest 20% concentration of Hblock (sample 10).

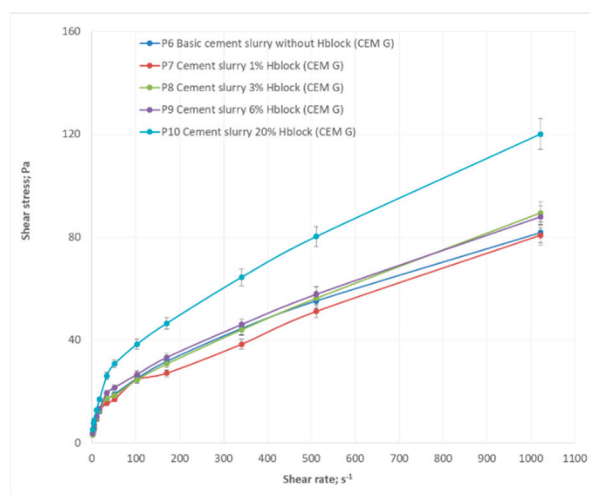


Figure 19. Flow curves for cement slurries with the addition of Hblock (cement class CEM G).

When analyzing the flow curves, a significant increase in shear stresses is visible at low shear rates in the group of slurries made on the basis of CEM I 42.5R Portland cement. This result confirms the thixotropic nature of cement slurries, which have high values of the yield point and structural strength (Table 9; Figure 18). In the case of slurries prepared on the basis of G drilling cement, comparable values of shear stresses in the low ranges of shear rates can be seen, which confirms the low values of rheological parameters in this group of slurries (Table 9; Figure 19).

The fine-grained material of Hblock significantly improves the parameters of both fresh and hardened cement slurry. The use of Hblock reduces the time of transition from the PW value to the KW value in all tested cement slurries (Table 2; Figures 9, 11 and 12). Compressive strength increases after 24 h of sample hydration with small (1% to 3%) amounts of Hblock (Table 2; Figure 13). The use of the tested Hblock agent results in the sealing of the cement matrix, which will result in a reduction in the gas permeability value (Table 2). The use of the Hblock fine-grained material is advantageous due to the fact that a compact and impermeable microstructure of the cement sheath is obtained, characterized by a higher value of compressive strength.

4. Conclusions

Based on the results of the work aimed at determining the effect of the fine-grained Hblock agent on selected parameters of the cement slurry, it is concluded that:

- The fine-grained material of Hblock causes an increase in the density of the slurry compared to the corresponding control samples without this additive.
- The use of Hblock in the formulation of the cement slurry based on CEM I 42.5R Portland cement shortens the setting time. On the other hand, when using G drilling cement, the presence of Hblock causes a slight increase in setting time.
- In all formulations, the presence of Hblock reduces the transit time from the initial time of the setting to the final time of the setting. This is very advantageous when designing cement slurries to seal columns of pipes in openings with an increased risk of gas migration.
- When analyzing the mechanical parameters of cement slurries with the addition of Hblock, a significant improvement in compressive strength is observed with the use of small amounts of Hblock (1% to 3% bwoc).
- The use of the Hblock agent in cement slurries tightens the structure of the hardened cement slurry, which is manifested by a reduction in the gas permeability of the tested samples.
- The Hblock fine-grained material causes a slight increase in the yield point according to the Herschel–Bulkley model, which may contribute to the improvement of the sedimentation stability of the cement slurry.

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Nomenclature

Symbol	Explanation
mD	Milidarcy (Gas permeability)
cm ² /g	Specific surface area
MPa	Megapascal (Compressive strength)
s ⁻¹	Shear rate
Pa	Shear stress
Pa·s	Apparent viscosity

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