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Effect of Hemihydrate gypsum on the basic properties of oil-well cement

ABSTRACT

The purpose of the study was to determine the influence of gypsum in different phase states (dihydrate or hemihydrate), an active additive of granulated blast furnace slag, and the total SO3 content on free water separation, the spread of well cement slurry, and the flexural and compressive strength of cement mortar. Laboratory and production cement mills were used to compare the results. The conducted research cycle enabled the quantitative determination of these parameters. Gypsum was preheated in a furnace at 200 °C for 60 minutes. It was found that the presence of hemihydrate gypsum in the cement does not significantly affect free water separation but has some impact on the spread of the well cement slurry. Additionally, the study revealed the influence of hemihydrate gypsum on compressive strength at 28 days and flexural strength at 1 day. The research also discovered that the presence of hemihydrate gypsum in the cement reduces the thickening time by 60 minutes. The presence of granulated blast furnace slag in the cement reduced free water separation in the well cement slurry. The research conducted at the production cement mill confirmed that the presence of hemihydrate gypsum in the cement reduced the spread by 25 mm and free water separation by 1 ml. The results from the production cement mill and laboratory mill are comparable and representative.

Keywords. *oil-well cement, free water separation, spreading of the well cement slurry*

1. INTRODUCTION

The properties of the well cement slurries intended for cementing oil and gas wells are produced both by the composition of determined mixtures and by the composition of cement, as well as by the finesses of grinding [1]. The requirements for the composition of well cements are regulated by an international standards ISO-10426-1 and API Specification 10A which establish requirements for the chemical, mineralogical and material composition of cement [2, 3]. An important component of the cement is dihydrate gypsum. The main task of gypsum is to regulate the setting time due to formation on the C_3A surface - the most rapidly hardening cement phase of hydrosulfoaluminate protective shells [4,5].

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Recent studies have shown that the mechanism of gypsum influence is also associated with a change in the concentration of active centers on cement particles and, accordingly, the speed of the coagulation process [5]. Gypsum also effects on the most other properties of cement [6]. Optimizing the addition of gypsum leads to a certain increase in early strength, a decrease in shrinkage deformation, and an increasing in the plasticity of cement mortars [6]. Gypsum content in well cements, in terms of total SO_3, normalized within 1,5-3,5%, for cements with high sulfate resistance – up to 3%, taking into account the low C_3A content.

One of the important properties of well cement slurries is a high water-holding capacity, which can be ensured both by adding various additives and by the composition of well cement, including hemihydrate gypsum [7,8]. During grinding cement, the temperature can reach to 150°C and more, which leads to dehydration of gypsum and the formation of hemihydrate $CaSO_4{\cdot}0,5H_2O$. At a high content of hemihydrate, so-called "false set" is possible, which causes to the rapid loss of plasticity of the mortar mixture, the need for a significant increase in water consumption and, as a result, the deterioration of the main properties of mortar [1]. However, when the hemihydrate gypsum content is below the critical level, his effect on the properties of well mortars is ambiguous. There is no simple rule to determine the optimal SO_3 content, as it depends on a range of different parameters including particle size [6].

It was established [9] that with presence of hemuihydrate gypsum in the cement, associated with a lack of SO_3 ions in the initial period of cement hydration, ettringite is not formed on the C_3A surface, but formed in the intergranular space. This increases the degree of hydration and increases the strength of the cement in the early stages [9].

Experimental results [9] showed that cements containing hemihydrate gypsum have reduced free water separation due to the difference in the mechanism of formation of hydrated phases [9]. However, in this research were studied Ordinary Portland Cements (OPC) and a technique was used to determine free water separation in percentage and with W/C=1,0 [10], while at this article attention is focused specifically on the well cements with a different method of determining free water separation, which is measured in milliliters with W/C=0,5 [11].

The available experimental data will not allow to quantitatively assess the influence of the ratio of dihydrate and hemihydrate gypsum on the main properties of oil-well mortars, considering the content of active mineral additives in the cement. The influence of this ratio allows to select the appropriate mode of cement grinding to ensure the necessary parameters of its properties. Solving this task is the goal of the research, the results are given in this article.

2. MATERIALS AND METHODS

The clinker used for research of oil-well cement class I-G had the following chemical and mineralogical composition: SiO_2 – 22,1%, Al_2O_3 – 4,06%, Fe_2O_3 – 5,31%, CaO – 64,63%, MgO – 0,61%, SO_3 – 0,71%, K_2O – 0,53%, Na_2O -–0,14%, CaO_{Free} – 0,65%, LSF – 0,914; C_3S – 57,75%; C_2S – 21,59%; C_3A – 1,57%; C_4AF – 15,81%. Gypsum stone, which was added to the cement, had a $CaSO_4{\cdot}2H_2O$ content - 93,1%. The blast granulated slag had the following chemical and mineralogical composition: SiO_2 – 36,44%, Al_2O_3 – 5,87%, CaO – 43,48%, MgO – 4,63%, Cao+MgO+SiO_2 – 84,55%, Glass – 97,89%, Merwinite – 1,41%, Melilite – 0,38%, Hedenbergite – 0,32%.

For the purpose to generate experimental-statistical models and establishing the relationship between the presence of hemihydrate gypsum and blast granulated slag (as the active additive in quantity of 15%) in cement and total SO_3 content, was applied full factors experiment for the three factors [12]: clinker content (x_1), hemihydrate gypsum content (x_2) and total SO_3 content of cement (x_3). The terms for planning experiments are given in table 1. The interval of the amount of gypsum hemihydrate from 1 to 3 % was chosen from the state of limited content in oil-well cement class I-G. The researches were conducted using the mathematical planning of experiments [12]. The phase state of gypsum (dihydrate and hemihydrate) was determined by X-ray Difraction (XRD diffractometer) (Fig. 1, a), total SO_3 content by analyzer LECO CS744 (Fig. 1, b), free water separation and spreading were determined according to the methods by Ukrainian standard “DSTU B V.2.7-86-99” for oil-well cements, testing methods (Ukraine) [11]. This techniques are similar to the requirement of international standards [2, 3,11].

a)

b)

Figure 1. Common view of the XRD diffractometer (a) and LECO CS744 analyzer (b)

Table 1. Terms for planning experiments

Factors		The levels of variation	
Natural view	Coded names	-1	+1
Clinker content at the cement, %	x_1	80	95
Hemihydrate gypsum content at the cement, %	x_2	1	3
SO_3 content, %	x_3	1,8	3,5

3. RESULTS AND DISCUSSION

Research was conducted in laboratory conditions on a laboratory mill with mixed (balls and cilpebs) loading. To study the influence of hemihydrate gypsum, which used in a laboratory mill, gypsum was preheated to a temperature of 200°C in a muffle furnace for 60 minutes. After heat treatment, the XRD diffractometer confirmed the complete transition of dihydrate gypsum to hemihydrate gypsum. At the same time, the received cements were also checked for compliance with other requirements according to Ukrainian standard “DSTU B V.2.7-86-99 Portland oil-well cements. Technical terms” (Ukraine) [5], that is: flexural strength in 1 day (should be not less than 3,5 MPa) and thickening time to the consistency 30 Bc (not less than 90 min).

The XRD diffractograms of cements are presented in Fig. 2 and 3. The experimental results, that were obtained during the implementation of the experiments, are given in the table. 2.

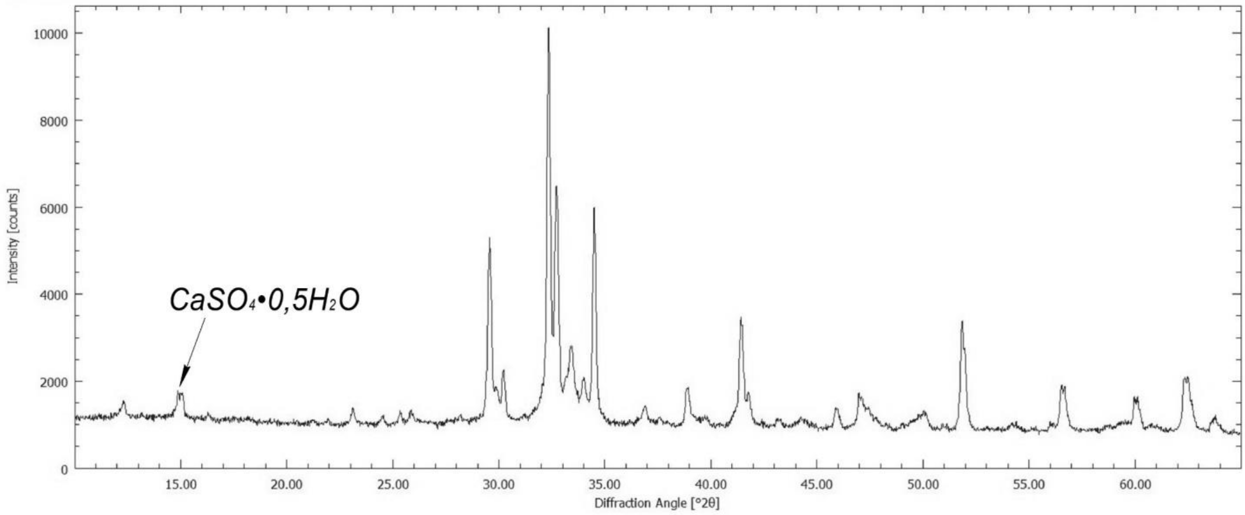


Figure 2. XRD diffractogram of cement with hemihydrate gypsum in the amount of 3%

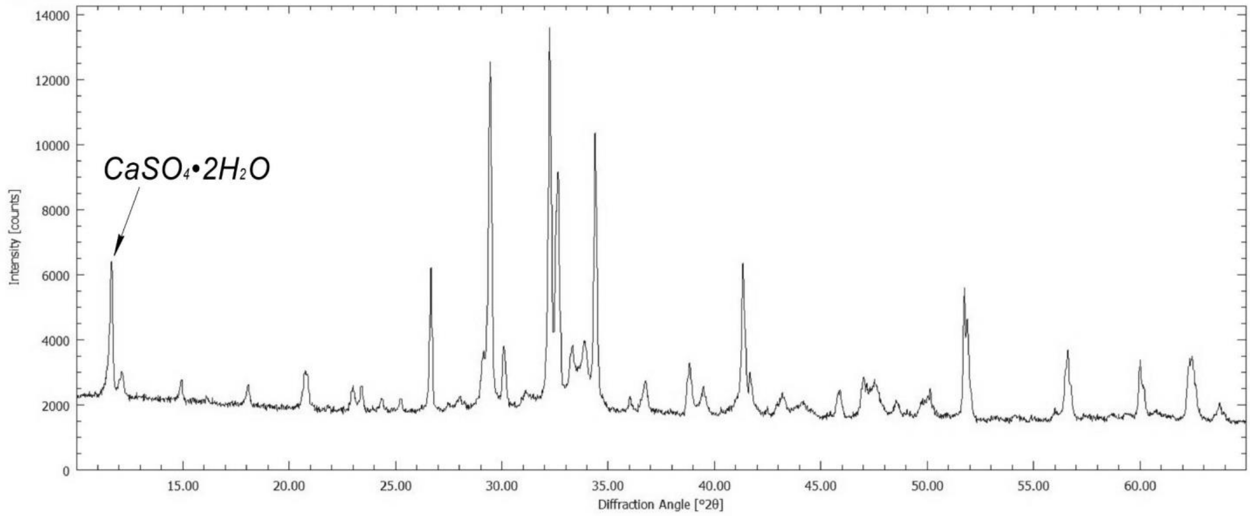


Figure 3. XRD diffractogram of cement with dihydrate gypsum in the amount of 5%

Statistical processing of the results made it possible to obtain experimental-statistical models of free water separation (Eq. 1), spreading (Eq. 2), flexural strength at the age of 1 day (Eq. 3) and thickening time to a consistency of 30 Bc (Eq. 4):

$$y_1=4{,}56+1{,}0625x_1-0{,}1875x_2-0{,}3125x_3-0{,}4372x_1x_2-0{,}0625x_1x_3+0{,}1875x_2x_3 \quad (1)$$

$$y_2=240{,}63+15{,}625x_1-9{,}375x_2-6{,}875x_3-9{,}375x_1x_2-1{,}875x_1x_3-1{,}875x_2x_3 \quad (2)$$

$$y_3=6{,}09+0{,}085x_1-0{,}1975x_2-0{,}0225x_3-0{,}6275x_1x_2+0{,}0975x_1x_3-0{,}135x_2x_3 \quad (3)$$

$$y_4=150{,}13+5{,}875x_1-9{,}625x_2+2{,}875x_3+22{,}125x_1x_2+4{,}625x_1x_3+7{,}625x_2x_3 \quad (4)$$

Table 2. Experimental results

Points of the plan	Factors			Experimental results					
	X_1	X_2	X_3	Free water separa-tion, ml	Spre-ading, mm	Flexu-ral stre-ngth, 1 day, MPa	Thicke-ning time to the consis-tency 30 Bc, min	Compres-sive strength 2 days, MPa	Compres-sive strength 28 days, MPa
1	95	3	3,5	5	225	5,4	192	20,95	44,04
2	95	3	1,8	5	250	5,3	145	19,17	41,6
3	95	1	3,5	5,5	270	7,1	135	17,5	42,6
4	95	1	1,8	7	280	6,9	152	19,71	41,79
5	80	3	3,5	3,5	220	6,07	110	17,89	43,43
6	80	3	1,8	4	230	6,8	115	19,54	41,12
7	80	1	3,5	3	220	5,7	175	11,83	38,96
8	80	1	1,8	3,5	230	5,45	177	15,93	41,03

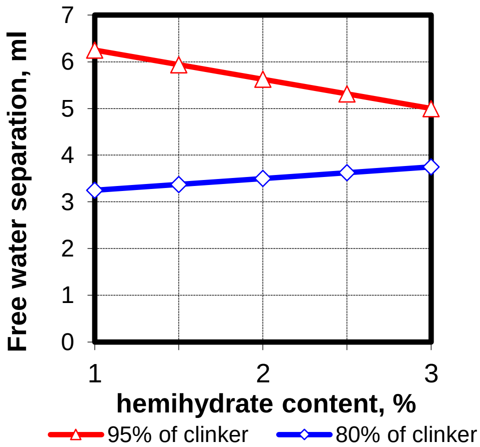
Analyzing the mathematical model of free water separation (Eq. 1), can see that an increase of the clinker content (absence of slag), during grinding cement, significantly increases the indicator of free water separation, and the combination of factors of slag content and the presence of dihydrate gypsum - reduces free water separation. The presence of hemihydrate gypsum slightly affects to the indicator of free water separation (Fig. 4, a).

During analyzing the mathematical model of spreading (Eq. 2), it can be stated that the content of blast granulated slag in cement significantly reduces the indicator of spreading, the presence of hemihydrate in cement, and combination of slag content and dihydrate gypsum also reduces spreading. The presence of hemihydrate gypsum in cement reduces spreading by 15-20 mm compared to dihydrate gypsum (Fig. 4, b).

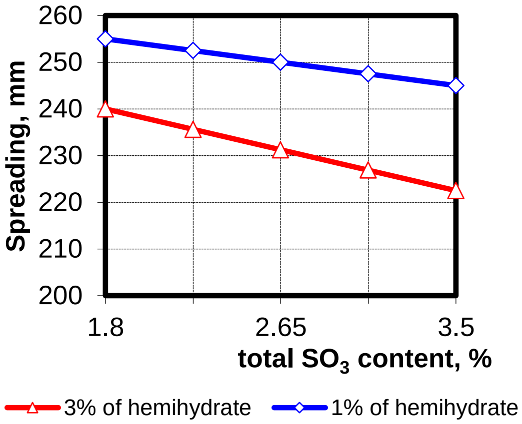
Analysis of the mathematical model of flexural strength at the age of 1 day (Eq. 3) shows that the combination of factors of slag content and the presence of dihydrate gypsum reduces the strength index.

A mathematical model of the thickening time to a consistency of 30 Bc (Eq. 4) shows that the combination of the factors of slag content and the presence of dihydrate gypsum adds 22 minutes to the thickening time, while the presence of hemihydrate gypsum - reduces the thickening time.

According to the results of the experiments and the processing of that results, was found that in the presence of hemihydrate gypsum in additive-free cement, the free water separation decreases by 1 ml, compared to the presence of dihydrate gypsum, which can be seen in fig. 4, a. In percentage terms, this figure will be 0.24%, which is not a significant decrease.



a)



b)

Figure 4. Dependencies of free water separation from hemihydrate gypsum content and % of additive (slag) in cement (a), and spreading from hemihydrate gypsum content and % of total SO_3 content in the cement (b)

Analyzing the results, it can be seen that the flexural strength (3) decreases in the presence of hemihydrate and without the blast granulated slag content (Fig. 5, a), as well as with the simultaneous presence of hemihydrate in the cement and the total SO_3 content of 3,5%.

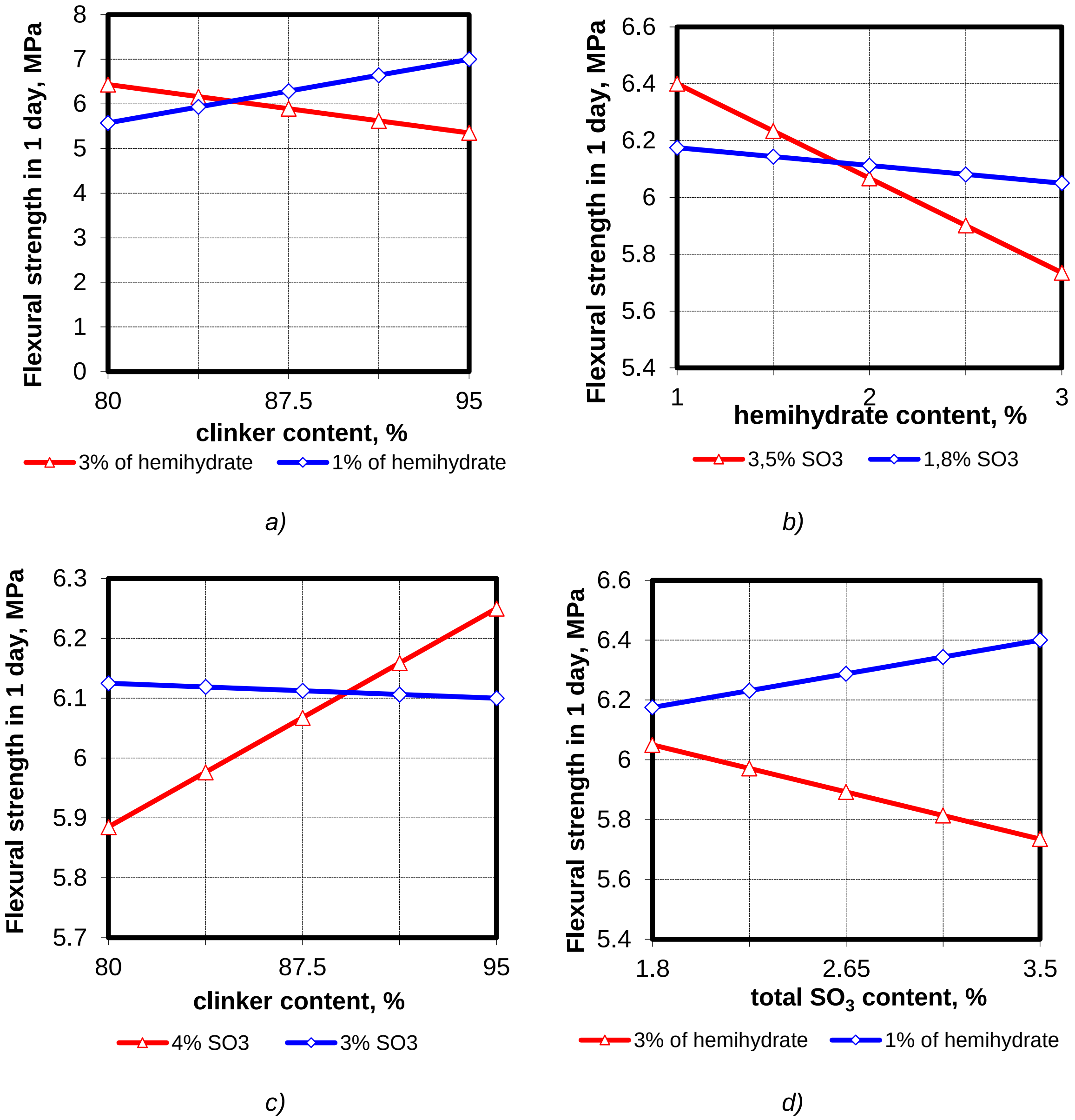
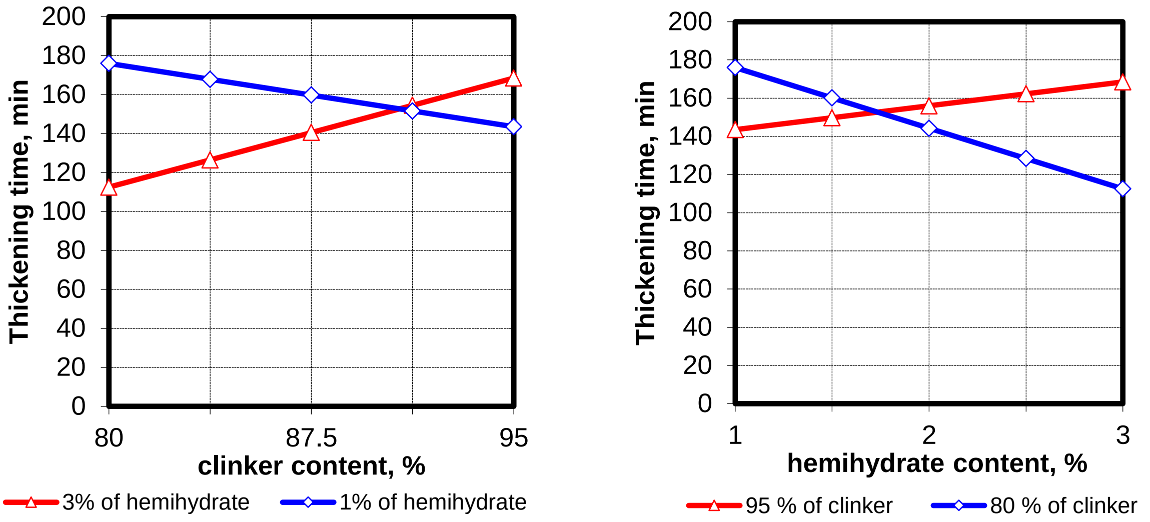


Figure 5. Dependencies of flexural strength at the age of 1 day from hemihydrare gypsum content and clinker content (%) in cement (a), to the total SO_3 content in cement and hemihydrate gypsum content (b), to the total SO_3 content in cement and clinker content (c), to hemihydrate gypsum content and the total SO_3 content in the cement (d)

It should be especially noted that with an SO_3 content of 1,8%, the presence of hemihydrate gypsum in cement does not affect to the flexural strength at the age of 1 day, which can be seen in Fig. 5, c. In fig. 5, d shows that when the total SO_3 content in the cement is 3,5% and the presence of 3% hemihydrate gypsum - the strength decreases.

Considering the results of the thickening time to a consistency of 30 Bc, it can be concluded that the time decreases by 60 min with the presence of hemihydrate gypsum in the cement at the same time with slag, which can be seen in fig. 6, a. The thickening time increases to 170 min in the cement without additives and with the presence of hemi-hydrate gypsum, which can be seen in fig. 6, b.



a) *b)*

Figure 6. Dependencies of the thickening time to a consistency of 30 Bc from the hemihydrate gypsum content and clinker content (%) in cement (a), from the clinker content (%) in cement and the hemihydrate gypsum content (b)

In addition, during the experiments, was noted that the free water separation decreases with the slag content in the cement, which can be seen in fig. 1, a. Also spreading increases with additive-free cement compared to slag including cement, which can be seen in fig. 1, b. According that information we can conclude that the presence of an additive (in the form of slag) in cement has a positive effect on the indicator of free water separation and a negative effect on the indicator of spreading.

During laboratory tests, were performed also the compressive strength analyzes of the received cements at the age of 2 and 28 days, according to the methods for OPC [7]. The data are presented in table 2. Statistical processing of the results made it possible to obtain mathematical models of compressive strength at the age of 2 days (Eq. 5) and 28 days (Eq. 6).

$$y_5=17{,}82+1{,}5175x_1+1{,}5725x_2-0{,}7725x_3-0{,}845x_1x_2+0{,}665x_1x_3+0{,}805x_2x_3 \quad (5)$$

$$y_6=41{,}82+0{,}68625x_1+0{,}72625x_2+0{,}43625x_3-0{,}41375x_1x_2+0{,}37625x_1x_3+0{,}75125x_2x_3 \quad (6)$$

Analyzing the mathematical model of the compressive strength at the age of 2 days (Eq. 5), can see that cement without additives and presence of hemihydrate gypsum has increased early strength. The minimum level of total SO_3 content reduce the compressive strength at the age of 2 days. The combination of factors of additive content (slag) and hemihydrate gypsum also reduces compressive strength. The combination of factors of additive-free cement content together with the presence of hemihydrate gypsum - increases early compressive strength.

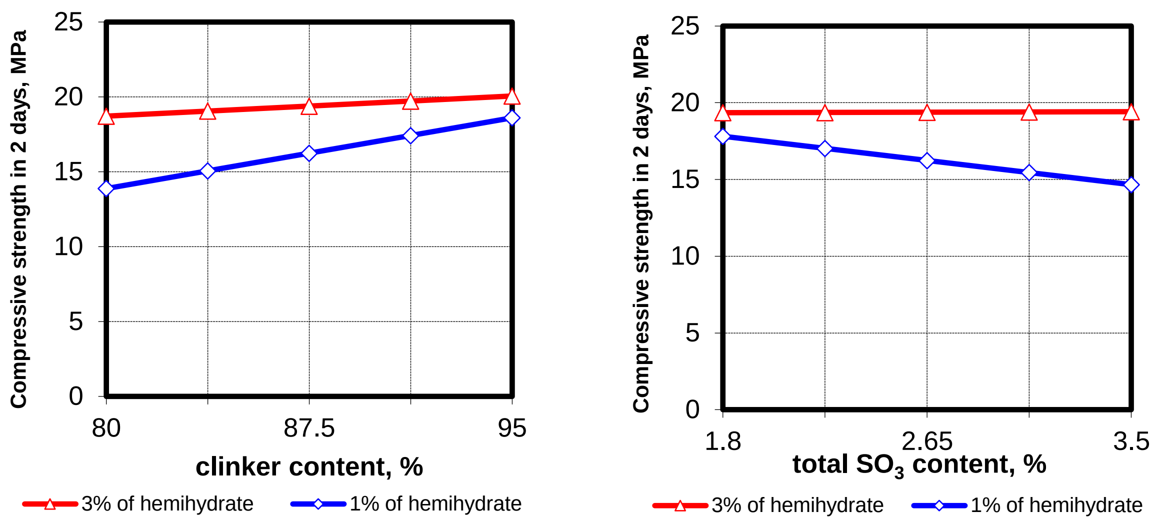
The mathematical model of compressive strength at the age of 28 days (Eq. 6) shows that the presence in additive-free cement hemihydrate gypsum and an increased total SO_3 content increased the compressive strength. The combination of factors of slag content cement with dihydrate gypsum reduces compressive strength. Combination factors of hemihydrate gypsum and the increased total SO_3 content has increased the compressive strength at the age of 28 days. Compressive strength (2 and 28 days) graphs are shown in fig. 7 and 8.

Along with this, was carried out a production test on a cement mill with two-chambers of standard size of 3.2x15 m with ball loading of the 1st and 2nd chambers. During the production process, the required contents of hemihydrate and dihydrate gypsum were achieved. The data are shown in table 3.

Analyzing the data obtained during the production experiment, it can confirm the results obtained during the laboratory study, namely: the presence of hemihydrate gypsum in the cement reduces free water separation and reduces spreading.

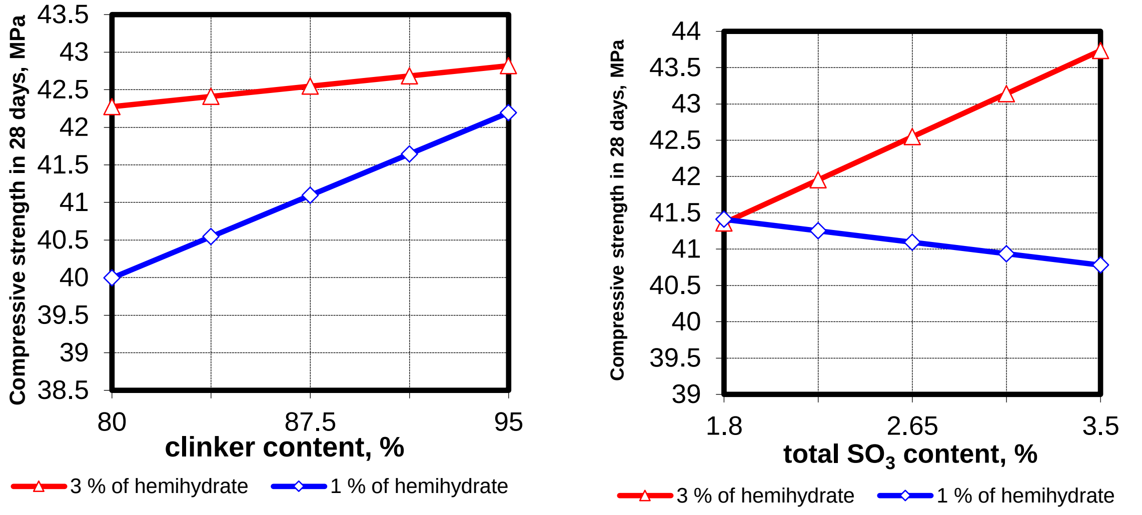
Table 3. Results of production experiments

№ of sample	Free water separation, ml	Spreading, mm	Flexural strength at 1 day, Mpa	Thickening time to the consistency 30 Bc, min	Total SO_3 content, %	Dihydrate gypsum ($CaSO_4$* $2H_2O$),%	Hemihydrate gypsum ($CaSO_4$* $0,5H_2O$), %	Anhydrite ($CaSO_4$), %
1	3,0	220	7,6	110	3,49	5,47	0,53	0,00
2	2,0	195	6	140	3,40	0,58	3,06	0,15



a) *b)*

Figure 7. Dependencies of compressive strength at the age of 2 days from the hemihydrates gypsum content and clinker content (%) in the cement (a), from the hemihydrate gypsum content and total SO_3 content (b)



a) *b)*

Figure 8. Dependencies of compressive strength at the age of 28 days from the hemihydrates gypsum content and clinker content (%) in the cement (a), from the hemihydrate gypsum content and SO_3 content (b)

Analyzing the intensity of influence researched factors on the studied properties (Eqs. 7-12) in the direction of reduction it can be ranked in the following sequence (the most significant coefficients are selected):

free water separation (y_1)

$$x1x2>x3>x2 \tag{7}$$

spreading (y_2)

$$x1>x2>x1x2>x3 \tag{8}$$

flexural strength at the age of 1 day (y_3)

$$x_1x_2> x_2> x_2x_3 \tag{9}$$

thickening time to a consistency of 30 Bc (y_4)

$$x1x2>x2>x2\ x3>x1>x1x3 \tag{10}$$

compressive strength at the age of 2 days (y_5)

$$x2>x1>x1x2>x2x3>x3 \tag{11}$$

compressive strength at the age of 28 days (y_6)

$$x2x3> x2>x1>x3 \tag{12}$$

4. CONCLUSION

The conducted cycle of research made it possible to obtain quantitative dependences of the influence of the additive content in cement (slag), the hemihydrate gypsum content and the total SO_3 content in cement.

The analysis of the obtained models allows that the presence of hemihydrate gypsum has an ambiguous effect on the properties of oil-well cement, reducing the spreading of the well cement slurry, but at the same time increasing the flexural strength at the age of 1 day.

The presence of hemihydrate in the cement in the amount of 3% - reduces free water separation and the thickening time to the consistency of 30 Bc. The presence of hemihydrate gypsum in the cement with a total SO_3 content of 1,8% practically does not affect the flexural strength. Also, in the presence of hemihydrate gypsum, the thickening time level is not less than the requred 90 minutes.

Numerical analysis of the coefficients of the models allows to rank the factors according to growth or decline and their influence on the corresponding initial parameters.

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IZVOD

UTICAJ HEMIHIDRATNOG GIPSA NA OSNOVNA SVOJSTVA ULJNOG CEMENTA

Tokom ovog istraživanja korišćeni su laboratorijski mlin i mlin za proizvodnju cementa za poređenje rezultata. Svrha istraživanja je bila da se utvrdi uticaj gipsa različitog faznog stanja (dihidrat ili hemihidrat), aktivnog aditiva granulisane šljake i ukupnog sadržaja SO_3 na separaciju slobodne vode, rasprostranjenost cementne suspenzije bunara i savijanje i pritisak. čvrstoća cementnog maltera. Sproveden ciklus istraživanja omogućio je dobijanje kvantitativne zavisnosti tih parametara. Za istraživanja je korišćen gips prethodno zagrejan u peći na 200°C u trajanju od 60 minuta. Tokom ovog istraživanja otkriveno je da prisustvo hemihidrata gipsa u cementu nema veliki uticaj na separaciju slobodne vode, ali ima izvestan uticaj na širenje cementne suspenzije bunara. Takođe, ovim istraživanjem je otkriven uticaj hemihidratnog gipsa na čvrstoću na pritisak u dobi od 28 dana i čvrstoću na savijanje u dobi od 1 dana. Tokom ovog istraživanja otkriveno je da prisustvo hemihidrata gipsa na cementu smanjuje vreme zgušnjavanja za 60 minuta. Prisustvo granulirane šljake na cementu smanjuje slobodnu separaciju vode u cementnoj suspenziji bunara. Tokom istraživanja u proizvodnom mlinu cementa obezbeđeno je da prisustvo hemihidrata gipsa na cementu smanji širenje za 25 mm i smanji slobodnu separaciju vode za 1 ml. Rezultati ispitivanja iz proizvodnog mlina za cement i laboratorijskog mlina su uporedivi i reprezentativni.
Ključne reči: *cement iz bunara, slobodna separacija vode, nanošenje bušotine cementne suspenzije.*

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