# Article

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### Heat-Resistant Backfill Materials, Expanding During Hardening

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#### Abstract

The article analyzes the problem of improving the quality of demarcation of rocks, oil as well as gas horizons. The results of theoretical and experimental researches of the backfill materials expanding at hardening on the basis of ash mixes are stated. Clinker heat-resistant autoclave hardening backfill materials that expand during hardening, with high performance properties on the basis of man-made by-products of industry have been developed and studied. The selection of optimal formulations of new heat-resistant backfill materials of autoclave hardening, which expand during hardening, is carried out. The results of the work have practical application in the cementation of oil and gas wells in complex mining and geological conditions in exploration areas and industrial fields of oil and natural gas as well as gas condensate.

**Keywords**: Backfill material, Cement stone expansion, Heat resistance, Density, Cements stone strength, Gas permeability.

#### 1. Introduction

The occurrence of overflow in the process of development and operation of oil and gas wells, due to poor cementing of production casings, is one of the most acute problems, it causes significant losses of hydrocarbons, subsoil pollution, environmental degradation and fire risk. The increase in the number of wells with borehole flows <sup>[1]</sup> is the evidence of insufficient efficiency of their fastening technologies (imperfection of technical means and recipes of backfill materials), which do not prevent the occurrence of channels in the cement stone and its contact with the casing and rock, destruction of the cement ring by various loads.

The statistical analysis of the quality of fastening of oil and gas wells for the previous and last years by standard cementitious materials testifies to insufficient quality of coupling of a cement stone with a casing <sup>[2]</sup> (Table 1). Interstratal flows at oil and gas fields in Ukraine over the past twenty years have been observed in almost 30% of wells <sup>[3]</sup>.

Table 1. Statistical analysis of the quality of fastening of oil and gas wells by geological enterprises SE Poltavanaftegazgeologiya and SE Chernihivnaftogazgeologiya

Enterprise	Backfill material	The quality of con	tact of cement stone w cording to the AKC, %	ith the casing, ac-
		Dense contact	Weakened contact	Weak contact
SE Poltavnafte-	PSCHT-120	19.6	12.4	68.0
gazgeologiya	CZkC	44.2	48.6	7.2
SE Chernihiv oil	PSCHT-120	20.1	13.7	66.2
and gas geology	CZIC	36.4	53.3	10.3

Based on the research of a number of authors <sup>[2, 4]</sup> it is established that when cementing oil and gas wells with ordinary cements, high-quality contact of cement stone with casing and well walls is formed in the intervals of permeable rocks, where it is possible to filter excess water mixing into the reservoir and access water from the outside. In the intervals of impermeable rocks, which are the roof of productive horizons or separating redistribution between permeable layers, as well as in the intervals of intercolumn space, a stone with shrinkage deformation and high gas permeability is formed, where the contact of cement stone with casing and rock is poor. As a rule, this phenomenon is the main reason for poor cementing and formation of interlayer flow channels.

Studies <sup>[2]</sup> found that under normal conditions of hardening of Portland cement concretes deformation of their shrinkage due to water evaporation and carbonation of cement, the linear value of which is 0,05 – 0,1%. In the work <sup>[5]</sup> it is also noted that shrinkage deformation is observed not only in standard Portland cements, but also in slag and cement-ash backfill materials.

A promising way to solve the problem of obtaining a stable tight and durable contact of cement stone with the casing and well walls and a sufficient degree of compaction of the filtration crust on porous rocks to prevent the occurrence of columnar interstratal flows, is the creation of non-shrink backfill materials <sup>[6]</sup>.

Solving the problem of creating a non-shrinking (expanding) composition in conditions of high pressures and temperatures is a difficult task. Therefore, we will dwell in more detail on the general laws of the process of expansion of binders used in the construction of various structures. Today there are three main ways to expand the cement stone:

- 1. The composition of cement includes substances that in a chemical reaction form gaseous
- products. Gas bubbles increase in volume and cause the cement composition to expand.
- 2. Formation of complex salts such as calcium hydrosulfoaluminate of trisulfate form (etringite) 3CaO·Al<sub>2</sub>O<sub>3</sub>·3CaSO<sub>4</sub>·31H<sub>2</sub>O.
- 3. Hydration of free oxides of calcium <sup>[7-8]</sup> or magnesium <sup>[9]</sup> to obtain Ca(OH)<sub>2</sub> or Mg(OH)<sub>2</sub>, which are about 2 times larger in volume than the initial oxides <sup>[10-11]</sup>.

The first method is not suitable for the creation of backfill materials used in high pressures that counteract the expansion of gas bubbles.

The second way is the effect of expansion with the formation of etringitis and it can be observed in two systems:

- 1. In the interaction of dissolved gypsum with crystals of calcium hydroaluminates. In this case, large crystals of calcium sulfoaluminate do not fit in the volume occupied by calcium hydroaluminates and cause the stone to expand.
- 2. In the formation of calcium sulfoaluminate by crystallization from solution, but in such a period of hardening of the cement stone, when the crystallization framework has sufficient rigidity.

If the growth rate of calcium sulfoaluminate crystals reaches a maximum in the period when the structure of the cement stone has sufficient rigidity, the expansion will be significant. If the crystals of calcium sulfoaluminate complete the growth in a still weakly structured solution, they only compress the gel-like mass and the expansion of the system practically does not occur. Changing the rate and nature of crystallization of etringite is achieved by adjusting the degree of supersaturation of the aqueous solution in the hardening stone CaO,  $SO_4^{2-}$ ,  $Al_2O_3$ .

It is very difficult to regulate the reaction of synthesis of etringitis because there is a danger of late expansion, and as a consequence, the destruction of the stone. In addition, cements with a high content of ettringite usually harden quickly and are heat-resistant. Such cements include alumina cement with gypsum admixtures, a mixture of Portland cement, high alumina slag, gypsum and active mineral impurity <sup>[12]</sup>, a binder based on belite-sulfoaluminate clinker.

A number of researchers have confirmed the effectiveness of the use at low temperatures  $(-5\div20^{\circ}C)$  of compositions that expand during hardening due to the formation of calcium hydrosulfoaluminate.

For a wide range of backfill materials are more suitable impurities based on free oxides of calcium and magnesium, which expand during hardening. The rate of hydration of CaO and MgO depends on the firing temperature of the raw material (carbonates, dolomites, etc.), as well as the fineness of grinding of the finished product. Cement compositions fired at 858 ÷

1200°C, which contain free lime, with a relatively large amount of expansion form a stone that does not collapse, and compositions with lime fired at 1400°C due to uneven expansion, which occurs after the formation of a "rigid structure", are prone to cracking and loss of strength.

Expandable cement is obtained by introducing impurities of ground quicklime, the content of which can vary from 5 to 20% depending on the specific tasks.

Increasing the temperature to 80 °C and above accelerates the hydration process. Thus transition of CaO to calcium hydroxide passes to formation of structure and expansion practically does not occur. Therefore, in order to obtain an expansion of the cement structure, it is promising to use as an expanding impurity materials in which the grains of free lime are externally protected by a shell. This can be observed in some types of slag and fuel ash.

To increase the heat resistance while maintaining the effect of expansion, you can create a complex composition, which includes slag cement, shale ash, nitrilotrimethylphosphonic acid, ferrochrome lignosulfonate, bentonite clay powder and iron sulphate.

The use of chromate sludge, waste from the production of chromium salts has been used to create backfill materials that expand during hardening, as they contain a significant amount of free calcium oxide. Portland cement, slag cements, etc. were used as binders in such materials.

In wells with bottomhole temperatures higher than 120°C, magnesium oxide, which is less active than CaO, can be used as an expansion impurity. Calcined at 1200-1300°C magnesium oxide can be used as an expanding impurity for cement, which hardens at temperatures of 120-160°C. At temperatures above 160°C, MgO calcined at a higher temperature can be used as an expansion impurity. Calcined periclase can be used as an expansion impurity for temperatures of 180°C.

Mentioned wastes of chromium salt production and chromate sludge in addition to free calcium oxide contain 36% periclase. This waste is used to create expandable cement, the expansion and self-stress. They are significant and allow to obtain a uniform contact in the system well-cement-stone-casing.

However, there have not been studied enough the peculiarities of the kinetics of expanding heat-resistant cementing materials of autoclave hardening (for example, ash mixtures), as well as their technological properties.

The **purpose** of this work is to study the kinetics of expansion of backfill material in the process of hardening, as well as to study the technological properties of heat-resistant grouting materials that expand during hardening, and the patterns of the process of hardening. To achieve this goal, the following **research objectives** are:

- to study of the kinetics of expansion of backfill material in the process of hardening, analysis of expansion curves in terms of influencing the rate of hardening of physicochemical factors;
- to study of technological properties of heat-resistant backfill materials mixtures that have hardened for a long time at high temperatures;
- to establish the dependence of the technological properties of the stone on the basis of heat-resistant grouting materials that expand during hardening, from physicochemical factors, in particular, the composition of the grouting mixture, temperature, pressure and duration of hardening.

## 2. Experimental

Preparation (kneading) of grouting solutions in the laboratory was carried out in the standard way with kneading in tap water using a paddle mixer at a shaft speed of  $1500 \pm 100 \text{ min}^{-1}$ . The amount of water was taken in accordance with a certain water mixture ratio (W/C).

The water-mixture ratio was determined based on the flowability of the grouting solutions using a flow cone, which should be in the range of 0,18 - 0,22 m of flow in a circle.

The properties of grouting solutions were evaluated by sedimentation resistance and water separation rate, which were determined by standard methods. The density of grouting solutions was determined using a calibrated pycnometer with a capacity of  $100 \text{ cm}^3$  with a predetermined (pure and dry) mass  $m_1$  in grams. Water separation was determined by standard

methods. According to the requirements of the standards, for Portland cements, the amount of water separation should not exceed 7.5  $\div$  10 mL. The pumping time of the grout was investigated on a CC-3 consistometer.

Determination of the volumetric deformation of the expansion of the grouting material during hardening was performed using a prefix to the consistometer CC-3, which makes it possible to obtain the expansion curve of the grouting material at high temperatures and pressures <sup>[2]</sup>.

Storage of samples of cement stone was carried out in the autoclave installation AI-1-71-IE (an autoclave installation of the Poltava branch of UkrDGRI), which consists of autoclaves, electrical and hydraulic strapping, measuring and recording devices for temperature and pressure control in autoclaves. The installation is designed for temperatures up to 523K and pressures up to 100 MPa, and control over these parameters is carried out automatically <sup>[2]</sup>.

The samples were made in the form of cylinders with a diameter of 0.03 m and a height of 0.03 m and beams with a size of  $0.04 \times 0.04 \times 0.16$  m. The forms with samples of cement were collected in a battery, according to the working volume of autoclaves, and placed in a preheated environment. The determination of mechanical strength in bending and compression was carried out according to standard methods.

Despite the fact that the mechanical strength of the stone formed in the laboratory cannot fully reproduce all the technological properties of grouting materials, today it is one of its main evaluation characteristics. Determination of the strength limits of cement stone was carried out according to typical methods: when bending on the device for testing specimens of beams for tensile bending, when compressing - on the press PS-10<sup>[2]</sup>. Determination of gas permeability of samples of cement stone was carried out on the installation of GP-5 according to the method described in the work <sup>[2]</sup>.

## 3. Result and discussion

To provide the geological industry of Ukraine with high-quality heat-resistant backfill cements, which expand during hardening, and to cover the deficit in these materials, a group of researchers on the laboratory base of the Poltava branch of the Ukrainian State Geological Survey (UkrDGRI) developed the formulations of clinker-free materials.

The basis for the creation of expansion heat-resistant grouting materials was high-calcium ash-removal (AR), formed during the combustion of oil shale at the Baltic TPP, which contains active calcium hydroxide. High-calcium ash of the Baltic (Estonian) shales is a light yellow powder with a density of 2800-950 kg/m<sup>3</sup>. There are two types of ash: cyclone and electrostatic precipitator. The specific surface area of the cyclone is 80-110 m<sup>2</sup>/kg, electrostatic precipitator is about four times larger. The chemical composition of cyclone ash is CaO-30-33 % (among them free CaO-6,5-,0%); SiO<sub>2</sub>-30-32%; Al<sub>2</sub>O<sub>3</sub>-7-8%; Fe<sub>2</sub>O<sub>3</sub>-4,0-4,5%; MgO-4-4,5%.

The chemical composition of electrostatic precipitator ash is CaO-30-33% (of which free CaO-6.5-7.0%); SiO<sub>2</sub>-30-32%; Al<sub>2</sub>O<sub>3</sub>-7-8%; Fe<sub>2</sub>O<sub>3</sub>-4.0-4.5%; MgO-4-4.5%. As a rule, a mixture of cyclone and electrostatic precipitator ash is supplied, so some fluctuations in its properties are possible.

An active mineral impurity with a high content of silica, such as acid ash, formed during the combustion of coal from the Donetsk or Volyn basins, must be added to the Baltic ash to obtain heat-resistant cement compositions with adjustable density. Acid ash-removal of thermal power plants is used as an active mineral (pozzolanic) impurity.

In this work, the mixtures of Estonian shale ash with the ash of Ladyzhyn and Kurakhiv TPPs were investigated. Both of these acid ashes have a high content of  $SiO_2$  (more than 50%), the proportion of other oxides in them is also approximately the same. The main difference between the ash of Kurakhivska TPP and the ash of Ladyzhynska TPP is in density and specific surface area. The ash of Kurakhivska TPP has a lower density and a larger specific surface area. Therefore, it is recommended to use to create lightweight grout mixtures.

The acid ash of Kurakhovskaya TPP is a dark gray powder with a density of 1980-2000 kg/m<sup>3</sup>, a specific outer surface of 350-420 m<sup>2</sup>/kg. Its bulk density is 1100-1150 kg/m<sup>3</sup>. The chemical composition of ash is SiO<sub>2</sub>-52-54 %; Al<sub>2</sub>O<sub>3</sub>-15-24 %; Fe<sub>2</sub>O<sub>3</sub>-17-22 %; CaO- 2,2-6,0 %.

The acid ash of Ladyzhyn TPP is a greenish-gray powder with a density of 2400-2500 kg/m<sup>3</sup>, a specific outer surface of 210-220 m<sup>2</sup>/kg. Its bulk density is 1500-1600 kg/m<sup>3</sup>. The chemical composition of ash is SiO<sub>2</sub>-57 %; Al<sub>2</sub>O<sub>3</sub>-23 %; Fe<sub>2</sub>O<sub>3</sub>-11 %; CaO-2,0 %; MgO- 2,0 %. The ratio of high-calcium and acid ashes in the mixtures varied in the range from 30:70 to 70:30% It was found that solutions from such formulations of ash mixtures have optimal technological properties (Table 2). The density of grout varies widely. It is possible to obtain compositions with normal density by introducing Ladyzhynskaya TPP ash into the mixture and facilitated by using Kurakhivska TPP ash.

Cementing mixtures with Estonian shale ash do not have high stability, especially for mixtures of the high-calcium ash namely the acid ash of Ladyzhynskaya TPP. This can be explained as follows. Estonian shale ash is a product that contains both electrostatic precipitator and cyclone ash, and cyclone ash has a very small specific surface area (3-4 times lower than that of Portland cement), which has a negative effect on stability. In the mixtures with ash acid, due to its high dispersion, it is possible to slightly increase the sedimentation resistance. As a stabilizer, if necessary, we can recommend standard reagents of oxyethylcellulose; in an amount of up to 0.15 % by weight of dry substance.

The compos	sition of the mixture,	wt. shares%				
High-cal- cium ash	Sour Acid ash at Ku- rakhiv TPP	<sup>·</sup> ash Acid ash of La- dyzhyn TPP	Water- mixture ratio	Mobility, m	Density, kg/m³	Water sepa- ration, mL
30	-	70	0.40	0.19	1790	10.0
50	-	50	0.50	0.21	1720	15.0
70	-	30	0.45	0.19	1740	10.0
30	70	-	0.55	0.19	1540	6.0
50	50	-	0.55	0.22	1570	12.0
70	30	-	0.55	0.20	1620	10.5

Table 2. Technological properties of cement mixtures from ash mixtures

Table	3.	Pumping	of	ash	mixtures
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Compositio	n of the mixtu	re,			Pur	nping, minu	ites	
				Tempera	ture, ⁰C; pres	sure, MPa;	impurity, nit	trilotrime-
High col	Acid ash of	Acid ash at	water-		thylph	osphonic ad	cid, %	
riyn-cal-	Ladyzhyn	Kurakhiv	mixture	t=75	T=75	T=100	T=100	T=100
cium asir	TPP	TPP	ratio	P=30	P=30	P=40	P=40	P=40
				c=0	c=0.05	c=0	c=0.05	c=0.10
50	50	-	0,50	2-40	4-10	1-00	3-00	3-30
70	30	-	0,45	1-50	2-30	0-30	1-40	2-30
30	70	-	0,40	3-20	4-30	1-20	3-30	4-30
50	-	50	0,55	3-30	4-00	1-10	3-30	4-10
70	-	30	0,55	2-30	2-50	1-00	2-40	3-20
30	-	70	0,55	4-00	4-40	1-20	3-50	4-30

The results of the study of pumping, conducted on the consistometer CC-3 (Table 3), can be recommended as a thickening agent nitrilotrimethylphosphonic acid. At temperatures of 75°C and below, almost all compositions have a pumping rate of more than two hours, and formulations containing 50–70 % acid ash, that is more than three hours, ie there is a possibility of using ash mixtures without a moderator for cementing shallow wells.

The expansion of the ash mixtures occurs due to the transition of free oxides of CaO and MgO into the corresponding hydroxides <sup>[2]</sup>. Ethereitis may also contribute to the increase in volume. It is important that the expansion process occurs before the formation of a rigid crystallization structure, ie in the period when the system is capable of plastic deformation without destruction.

Ash mixtures expand after injection and punching of the grouting material for 2-5 hours (Figures 1, 2). At elevated temperatures (more than  $75^{\circ}$ C) almost ends the formation of Ca(OH)<sub>2</sub> and etringitis and the expansion process is preferably completed. Thus, the possibility

of destruction of the grouting stone in the late stages of hardening is excluded. The relative magnitude of the expansion varies from 0,4 to 3%, and in mixtures of the high-calcium ash. These figures of the acid ash at Kurakhiv TPP are much higher than in mixtures of the high-calcium ash (the acid ash at Ladyzhyn TPP).



Figure 1. Dependence of the amount of expansion on the ratio of components in the mixture Hardening conditions: temperature 348K, pressure 30 MPa;1, 2, 3 - the high-calcium ash: the acid ash at Kurakhiv TPP accordingly 70:30, 50:50, 30:70, B/C-,55



Figure 2. Dependence of the magnitude of expansion on pressure and temperature Hardening conditions: 1 - temperature 323 K, pressure 20 MPa; 2 – temperature 373 K, pressure 40 MPa; 3 - temperature 433 K, pressure 60 MPa, 1, 2, 3 – the high-calcium ash: the acid ash at Kurakhiv TPP – 50:50, B/C–0,55

There are different opinions as to the relationship between the strength of the cement stone and the quality of insulation of the annulus of the well. Some experts believe that the existing requirements for the strength of the stone are inflated. In the work <sup>[2]</sup>, the minimum allowable value of compressive strength, which is 0.9 - 3.5 MPa, is substantiated. The data in Table 4 indicates high physical and mechanical properties of the ash mixtures.

The ash mixtures have high heat resistance. Strength increases over time at high temperatures in formulations that contain 30-50 % of high-calcium ash. At temperatures up to  $100^{\circ}$ C, optimal results are obtained for mixtures where the proportion of high-calcium ash is 50-70%. Comparative analysis shows that the strength of the studied mixtures is much higher than that of standard lightweight cements such as lightweight cementing cements. Up to 28 days, this excess reaches 2-3 times.

The	composit	ion of			Bendir	ig / compres	sion strengt	h, MPa		
high-	acid ash	acid ash		t=75ºC, F	P=30 MPa			t=120°C,	P=50 MPa	
cal- cium ash	of La- dyzhy n TPP	at Ku- rakhi v TPP	2 days	7 days	28 days	6 months	2 days	7 days	28 days	6 months
30	70	-	5.2/11.0	7.2/12.1	7.6/15.8	8.5/18.0	3.9/12.5	4.7/12.9	6.2/14.4	6.5/14.0
50	50	-	6.2/13.1	7.2/16.2	8.0/16.8	9.0/18.8	4.1/12.8	4.9/14.8	5.5/15.2	5.8/14.2
70	30	-	6.8/16.5	7.0/16.0	7.1/19.6	8.0/19.8	5.9/18.5	6.7/20.5	7.7/20.9	6.0/13.8
30	-	70	3.9/10.1	4.2/11.1	5.1/13.2	7.1/16.6	3.4/6.8	3.8/9.1	5.1/13.9	5.5/13.5
50	-	50	5.1/10.5	5.5/10.9	8.5/11.5	9.5/17.5	3.9/12.2	5.4 13.5	6.3/15.3	6.6/15.6
70	-	30	6.5/13.9	7.1/15.1	9.1/16.8	8.9/18.5	6.2/13.7	7.4/18.7	7.9/21.0	6.3/15.5

If it is necessary to use the ash mixtures at temperatures below  $35^{\circ}$ C to accelerate their setting and strength in the early stages of hardening, you can add standard setting accelerators, such as CaCl<sub>2</sub> in the amount of 2 – 3 %. The main property of a cement stone, especially in terms of its suitability for cementing production columns, is permeability.

According to the research, the permeability of the Portland cement stone with V/C 0.5 is from 1.5 to  $5.0 \times 10^{-3} \,\mu\text{m}^2$  after 2 days of hardening in the temperature range 20 -  $130^{\circ}$ C. Despite the water content in the ash mixtures, the value of gas permeability of the stone on their basis is approximately an order of magnitude lower and is in the range of  $0.09 \div 0.90 \times 10^{-3} \,\mu\text{m}^2$  (Table 5).

Table 5. Gas permeability of a grouting stone	e 5. Gas permeability of a grouting	stone
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The comp	osition of the wt. %	e mixture,		Gas	permeability,	microns <sup>2</sup>	×10 <sup>-3</sup>	
hich col	acid ash	acid ash	t=7	75°C, P=30	MPa	t=1	20ºC, P=50	MPa
cium ash	dyzhyn TPP	rakhiv TPP	2 days	7 days	6 months	2 days	7 days	6 months
30	70	_	0,70	0,52	0,09	0,16	0,15	0,10
50	50	-	0,51	0,48	0,11	0,15	0,18	0,09
70	30	-	0,35	0,88	0,08	0,43	0,43	0,16
30	-	70	0,62	0,48	0,10	0,52	0,43	0,21
50	-	50	0,58	0,55	0,09	0,18	0,12	0,15
70	_	30	0,45	0,51	0,12	0,06	0,08	0,09

The low values of gas permeability are apparently due to the compaction of the stone structure based on the ash mixtures, which occur due to the filling of the pores with finegrained hydration products, in particular, low-basic calcium hydro silicates. Therefore, the stone of the ash mixtures has high performance properties: it has a high strength and low permeability in the temperature range 35-120°C. In addition, these mixtures have a high corrosion resistance in various aggressive environments. All this allows us to conclude about the naturalness of the ash mixtures for cementing productive horizons in difficult mining and geological conditions.

## 4. Conclusion

The analysis of the kinetic curves of expansion of the grouting material obtained in the process of hardening shows that, first, the expansion process is almost completed in 2-5hours; secondly, the magnitude of the expansion is maximum at high temperatures (373-433K) and lower at 323K; the third increase in the content of the high-calcium ash in the ash mixture significantly affects the amount of expansion.

The study of technological properties of heat-resistant grouting materials-mixtures that hardened for a long time at high temperatures allowed to establish the following characteristics:-6-month strength of grouting stone exceeds 2-day; - the highest strength have ash mixtures, hardened at t = 100°C; the gas permeability of the cement stone obtained on the basis of the ash mixtures is in the range (0.08–0.88) × 10<sup>-3</sup> µm<sup>2</sup>, which is sufficient for high-quality insulation of wells.

The study of the dependence of technological properties of the grouting stone on the basis of heat-resistant grouting materials that expand during hardening on physicochemical factors, in particular, the composition of the grouting mixture, temperature, pressure and duration of hardening allowed to establish the following characteristics: based on the ash mixtures, affects the duration of hardening, with increasing hardening time the strength increases; - the value of gas permeability of the cement stone obtained on the basis of the ash mixtures is affected by the duration of hardening, with increasing hardening time the gas permeability decreases.

In the process of the research of new heat-resistant grouting materials that expand during hardening, the selection of optimal formulations of the developed compositions was carried out; the kinetics of their expansion during hardening was studied. The dependence of strength characteristics, as well as the permeability of the stone on the ratio of components in the grout mixture has been investigated. This is the scientific value of the proposed development. The use of the new heat-resistant grouting materials that expand during hardening makes it possible to improve the quality of formation separation in oil and gas wells, it has a practical value.

The results of the work have a practical application in the attachment of deep wells in difficult mining and geological conditions in exploration areas and industrial deposits. New cementing materials that expand during hardening have been successfully implemented at the drilling plants of Ukrburgaz PJSC Ukrgazvydobuvannia PJSC during cementation of gas and gas condensate wells.

Symbols

CC-3	cement consistometer;
GH-5	gas permeability of the stone;
PS-10	press squeezer;
AI-1-71-IE	an autoclave installation of the Poltava branch of UkrDHRI;
ACC	acoustic cementometer\$
PSCHT-120	Portland slag cement for high temperatures;
OCG, OSHC	lightweight cementing cements;
CZkC	cement-ash mixture with the use of ash-removal of Kurakhiv TPP;
CZIC	cement-ash mixture with the use of ash-removal of Ladyzhenskaya
	TPP;
AC	high-calcium ash;
AA	acid ash (source of silica);
AAI	acid ash of Ladyzhyn TPP;
AAk	acid ash at Kurakhiv TPP;
W/M	water-mixture ratio;
W/C	water-cement ratio;
OXC	oxyethylcellulose;
NTPA	nitrilotrimethylphosphonic acid;
Ca(OH) <sub>2</sub>	calcium oxide;
Mg(OH)₂	magnesium oxide;
TPP	thermal power plant;
UkrBurGas	Ukrburgaz drilling department;
PV UkrDHRI	Poltava branch of the Ukrainian State Geological Exploration Insti-
	tute;
DSTU BV.2.7–86–99	State standard of Ukraine: Cement. Test methods;
3CaO·Al <sub>2</sub> O <sub>3</sub> ·3CaSO <sub>4</sub> ·31H <sub>2</sub> O	etringitis (calcium hydrosulfoaluminate trisulfate form);
JSC "Ukrgasvydobuvannya"	public joint-stock company Ukrgazvydobuvannya.

#### References

- [1] Trifonov SV, Chekanov SV, Skochelias A.B. et al. The introduction of expanding grouting material during FIXING of wells in difficult mining and neolonic conditions. Naftova i hazova promyslovist. 2003; 3: 30-32.
- [2] Orlovskyi VM. Cementing materials that expand during curing: Monohrafiia. Poltava, 2015; p. 129.
- [3] Bandur RV, Luzhanytsia OV, Mykhailenko SH et al. Analysis of the causes of poor delimitation of strata in the conditions of the Dnieper-Donetsk western. Rozvidka ta rozrobka naftovykh i hazovykh rodovyshch. 2003; 3: 127-130.
- [4] Hamzatov SY. Application of binders in oil and gas wells: Monohrafiia. Nedra: Moskow, 1985; p. 148.
- [5] Kertsman AZ. The clinker-free grouting material based on dolomite production: PhD. Thesis: 05.17.11. Poltava, 1984; p. 170.
- [6] Moncef LN, Anjuman S. Rheological properties of oil well cement slurries. Proceedings of the Institution of Civil Engineers Construction Materials, 2012; 165 (1): 25-44.
- [7] Liwu M, Min D, Mingshu T, Abir AT. MgO expansive cement and concrete in China: past, present and future. Cement and Concrete Research, 2014; 57: 1-12.
- [8] Parashchuk L, Kochubei V, Yakymechko Ya, Parashchuk L. The use of granulated modified lime for expansive cement with high-energy self-tension Chemistry and chemical technology, 2011; 3 (5): 341-345.
- [9] Jafariesfad N, Gong Y, Geiker M, Skalle P. Nano-Sized MgO with Engineered Expansive Property for Oil Well Cement Systems. SPE Bergen One Day Seminar, 2016. doi: 10.2118/180038-ms.
- [10] Orlovskyi VM. Stamping material for moderate and elevated temperatures, which expands during curing. Naftohazova inzheneriia, 2017; 2: 64-69.
- [11] Mazurok PS, Turhunov TSh, Sviderskyi VA, Tokarchuk VV. The influence of oxides of calcium and magnesium on the properties of expandable cements and grouting solutions / Eastern-European Journal of Enterprise Technologies, 2017; 4/6(88): 47-52.
- [12] Butt YuM, Sychov MM, Tymashev VV. Chemical technology of binders: Monohrafiia. Visshaia shkola: Moscow, 1980; p. 472.

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