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RESEARCH OF LIME-ASH PLUGGING MIXTURES

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Abstract. Lime-ash plugging mixtures (LAPM) with a density of 1450–1780 kg/m^3 have been developed and studied as new and competitive plugging compositions. LAPM consisting of lime and acid fly ash were found to be expanded during setting. The composition of the products formed during LAPM hydration was determined by means of X-ray phase analysis. Kinetic curves of plugging material expansion have been obtained at the temperatures of 348–413 K. Rational temperature regimes of LAPM setting according to the criteria of strength and gas permeability of cement stone have been determined.

Keywords: well cementing, plugging material, cement hydration, lime, acid fly ash, water-mixture ratio, cement stone.

1. Introduction

Currently, Portland cement, Portland slag cement and cement-ash mixtures are mainly used for cementing of wells at drilling enterprises of Ukraine. Taking into account the growing cost of cement and its scarcity, the saving of energy-intensive cement is a relevant task.

The research is aimed at creating new plugging mixtures based on multi-tonnage by-products of Ukrainian industry. The use of such materials will ensure high quality cementing of wells with a significant reduction in the cost of plugging operations.

A prerequisite for sustainable development of society is the minimization of industrial impact on the environment. The introduction of technologies for the gas emissions treatment,[1,2] monitoring of the hydrosphere[3,4] and the widespread introduction of technologies for wastewater treatment[5,6] should be noted, but the introduction of technologies for solid industrial and household waste should be of particular importance, in particular their involvement as raw materials in energy,[7] industrial,[8] agricultural[9,10] technologies and in the building materials industry.[11,12] Therefore, at the end of the last century the cement-ash mixtures (CAM) have begun to be widely introduced at the drilling plants of Ukraine. Acid fly ash, which is obtained after coal combustion at Kurakhiv, Ladyzhyn, Burshtyn and Dobrotvorsk state district power plants (SDPP), serves as an active aluminosilicate additive to Portland cement.[13] This allows to achieve the required physico-chemical characteristics of drilling rigs and utilize the industrial waste. Detailed studies on technological properties of cement-ash mixtures were carried out by the researches of the Ukrainian State Geological Exploration Institute (Poltava branch), the results of which are presented in the relevant normative documents.[13,14]

CAM have a number of advantages:

– thermocorrosion resistance of a stone increases;

– the density of plugging solutions decreases to 1500 kg/m^3;

– the pumping time of the plugging solution in the well increases at high temperatures;

– the cost of plugging material decreases.

Ash is formed during the combustion of coal of the Donetsk and Lviv-Volyn coal basins and belongs to the so-called “acid ashes”. This is determined by the low content of calcium oxide (up to 6 %).

The experience has been gained with the application of “high-calcium ash”. Studies on the technological properties of mixtures consisting of Portland cement and high-calcium ash of Estonian oil shale were conducted by Krykh and co-workers.[15] Such mixtures were characterized by high operational properties, in particular expansion during setting, but the thermal range of their application was limited to a range of 363–373 K.

Some foreign researchers used various calcium additives, in particular nano-$CaCO_3$ obtained from eggshell waste[16] to improve the mechanical properties of cement stone. Significant improvement in the mechanical properties of cement stone has been reported by Khaliq and Khan,[17] who used calcium aluminate additives (calcium aluminate $CaO·Al_2O_3$). Adjei *et al.*[18] considered geopolymer as an alternative to Portland cement. Geopolymer is synthesized *via* the reaction of aluminosilicate materials and alkaline solution; it is resistant to

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acidic and saline environments, has high compatibility with drilling fluid.[18] Geopolymer based on fly ash of grade C was found to be the prospect material for cementing of wells.[19]

At the end of the twentieth century in the Laboratory of Well Cementing of the Ukrainian State Geological Exploration Institute (Poltava branch) the cementing materials with different component ratios were developed based on high-calcium ash of Estonian oil shale and acid fly ash from Kurakhiv and Ladyzhyn SDPP.[15] However, the supply of high-calcium ash from Estonia was disrupted and the implementation of the developed technology was stopped.

Dolomite-ash mixtures (DAM) were widely used for column cementing in oil and gas wells. In these compositions a binder was powdered by-product produced by the Mykytiv dolomite plant.[15] The main advantage of DAM was their low cost but the temperature range of application was limited by 373 K. The use of DAM was eliminated due to the stoppage of dolomite supply.

Cement-chalk plugging solutions were also used at different enterprises of State Committee of Ukraine for Geology and Subsoil Use.

The aim of this work is to study the physico-chemical characteristics of plugging materials hydration that expand during setting and the regularities of their setting, as well as the kinetics of expansion during setting. To achieve this aim, it was necessary:

– to study the composition of hydration products of lime-ash plugging materials that expand during setting – mixtures that set for a long time at high temperatures;

– to investigate the kinetics of expansion of plugging material during setting, to analyze the expansion curves in terms of the effect of physico-chemical factors on the rate of setting;

– to examine the dependence of technological properties of cement stone based on lime-ash plugging materials expanded during setting on physico-chemical factors, in particular, the composition of the plugging mixture, temperature, pressure and setting time.

2. Experimental

2.1. Materials

The investigated cement stone was obtained from lime-ash mixture, consisting of the following components: fine powdered lime, which is a by-product of lime production (BPLP), acid fly ash from Kurakhiv or Ladyzhyn SDPP and technical (tap) water.

By-products of lime production are available at most metallurgical plants of Ukraine. We examined BPLP from Mariupol metallurgical plant "Azovstal", Yenakiyevo and Kryvyi Rih metallurgical plants. BPLP is a fine powder accumulated in cyclones and electrostatic precipitators during the production (burning) of lime. The burning temperature is very important for the properties of BPLP-based plugging materials. It was found that cement materials with a lime burned within 1123–1473 K form an expanding stone during setting, and the degree of expansion increases with increasing temperature. If lime was burnt at the temperatures of 1573–1673 K, the stone is destroyed due to irregular changes occurred in a volume.[20] Since the burning temperature of lime produced at "Azovstal" was 1573–1673 K, and that of lime produced at Yenakiyevo and Kryvyi Rih metallurgical plants was 1373–1573 K, we selected BPLP from Kryvyi Rih for detailed study. It is a fine grayish-white powder with a density of 2850–2950 kg/m^3 and a specific surface area of 700–750 m^2/kg.

Particle size distribution of fractions: 0.25 % (2.00–1.00 mm); 0.65 % (1.00–0.63 mm); 1.30 % (0.63–0.10 mm); 0.70 % (0.10–0.07 mm) and 97.1 % (less than 0.07 mm).

Chemical composition regarding the oxides: CaO 68.8 %; MgO 10.0–11.0 %; SiO_2 1.4 %; Al_2O_3 0.7 %; Fe_2O_3 0.4 %; weight loss during calcination (w.l.c.) 14.2 % ($CaCO_3$, CO_2, H_2O).

Consumers are supplied with a BPLP mixture from cyclones and electrostatic precipitators.

The most suitable silica additive to the cement mixtures is an acid fly ash from power plants. In this work we used acid ashes from Kurakhiv (AA_K) and Ladyzhyn (AA_L) SDPP.

AA_K is a powder of dark gray color, with the density of 1950–2050 kg/m^3, bulk density of 1100–1150 kg/m^3 and specific surface area of 350–400 m^2/kg.

Chemical composition regarding the oxides: SiO_2 52.0–54.0 %; Al_2O_3 15.0–24.0 %; Fe_2O_3 17.0–23.0 %; CaO 2.2–2.8 %; MgO 2.0–3.0 %; K_2O+ Na_2O 1.7–3.4 %; w.l.c. 3.4–3.7 %.

AA_L is a greenish-gray powder, with the density of 2300–2500 kg/m^3, bulk density of 1500–1600 kg/m^3 and specific surface area of 230–250 m^2/kg.

Chemical composition regarding the oxides: SiO_2 55.0–59 %; Al_2O_3 21.0–24.0 %; Fe_2O_3 10.0–12.0 %; CaO 2.0–2.2 %; MgO 1.9–2.1 %; K_2O+ Na_2O 1.8–2.3 %; w.l.c. 5.1–5.4 %.

2.2. Methods and Instruments

2.2.1. Investigation of physical properties of powdered materials

The density of the original powdered materials was determined by the pycnometric method, and their specific surface – by the method of air permeability using the PSH-2 device.[21]

The bulk density of powders in the loose and compacted state was determined according to the standard procedure.[22]

The fractional composition of the starting materials was determined by sieving them through sieves, after which the percentage of fractions was calculated.[21]

2.2.2. Investigation of the plugging solution properties

The main properties such as mobility, sedimentation stability and density were determined according to the standard methods (DSTU BV.2.7-86-99).

Water loss was investigated using the device VM-6. The rate of plugging solutions setting was determined using the Vicat apparatus, the pumping time – by KC-3 consistometer.[15,23] Pumping of plugging solution is the solution mobility under the conditions of well (temperature, pressure)/ It is the ability to be pumped when cementing the well.

2.2.3. Investigation of physical and mechanical properties of cement stone

The samples were formed as cylinders with a height and diameter of 3 cm and preserved under the conditions simulating the well conditions (temperature, pressure, chemical composition of the medium) in an autoclave AU-1-71-IE (designed by the specialists of Ukrainian State Geological Exploration Institute (Poltava branch)). The temperature was maintained with the deviation of ±5 K.

The mechanical strength of the cement stone was measured using a PSU-10 press (measurement accuracy is ± 0.25 MPa).

Expansion of cement compositions during setting was studied using a special attachment to the consistometer[15] (Fig. 1). This attachment allows to study the kinetics of volume changes in time.

The adhesion of the cement stone with the metal was measured using the attachment to the PSU-2 press (Fig. 2). The samples set in autoclaves in the special forms, which are coaxial cylinders,[15] simulating a cased well regarding the ratio of diameters. The attachment was installed on the movable plate of the PSU-10 hydraulic press and the force (adhesion) at which the metal rod shifts from the cement stone *5* was determined.

The study of gas permeability of cement stone was performed using GK-5 device.[15,23]

Corrosion resistance of plugging mixtures was determined by the following method. Solutions of 5 % magnesium sulfate, magnesium chloride, bischofite and 0.8 % hydrochloric acid were prepared taking into account the different nature of formation waters. The samples of cement stone were formed within 2 days in autoclaves at a temperature of 373 K. After determining the strength, the samples were placed in a corresponding medium. We observed the properties of cement stone for 2 years.

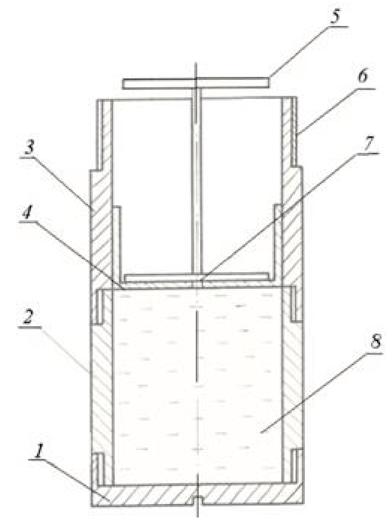

Fig. 1. Consistometer attachment to determine the expansion of plugging materials: 1 – removable bottom of the glass; 2, 3 – elements of the glass body; 4 – separating piston; 5 – coil; 6 – connecting thread; 7 – hole; 8 – plugging solution

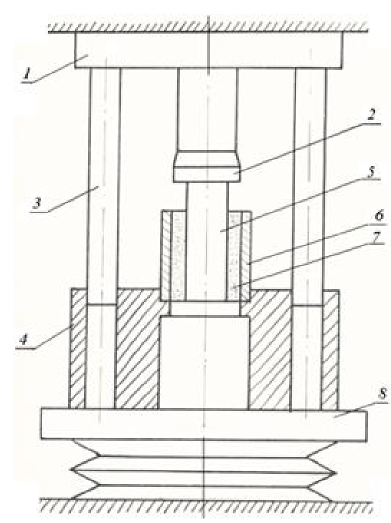

Fig. 2. PSU press attachment to determine the adhesion of cement stone with metal: 1 – pressure plate; 2 – cylinder; 3 – the rod-clamp; 4 – housing; 5 – metal rod; 6 – cylindrical shape; 7 – cement stone; 8 – movable plate of the hydraulic press PSU-10

The main criterion of corrosion resistance was the coefficient of resistance *k*, which reflects the strength ratio of the samples stored in aggressive environment and similar samples stored in tap water.

X-ray phase analysis of the cement stone was performed using DRON-2 installation equipped with a copper cathode with a monochromator. The test material was stuffed into a cuvette (diameter 0.0275 m, depth 0.005 m), which was rotated around the axis at a constant speed of 20 min^{-1}.[15]

3. Results and Discussion

3.1. Investigation of the Phase Composition of Cement Stone Setting Products

Several researchers[24-32] show that the main factors influencing the phase composition of plugging materials, which set under conditions of wells, are temperature, pressure and time, but the effect of pressure is negligible.

There are various explanations for the negative impact of temperature on the technological properties of cement stone. The most common theory explains the decrease in strength at the temperatures of 373 K and higher due to the formation of highly basic calcium hydrosilicates of $C_2SH(A)$ type, prone to recrystallization, which leads to the destruction of the formed structure. To minimize the negative effect of high temperatures on cement stone the active mineral additives containing silica are added. This reduces the concentration of calcium oxide in the cement mortar resulting in the formation of low-basic hydrosilicates of CSH(B) type; the formed stone has high values of strength.

Hydration of compositions based on by-products of lime production has its own peculiarities. It is similar to the hydration of lime-sand mixtures, but with some differences, because ash contains a number of other minerals in addition to SiO_2. Therefore, the phase composition of hydration products is more diverse.

Fig. 3 shows the X-ray pattern of dry (non-hydrated) BPLP. It clearly shows the lines corresponding to calcium oxide (d = (1.88; 2.41; 2.78)·10^{-10} m), calcium carbonate (d = (2.29; 2.49; 3.87)·10^{-10} m), calcium hydroxide (d = (1.92; 2.64; 4.98)·10^{-10} m) and dolomite.[33] Other minerals are in small quantities. A significant amount of calcium carbonate is due to its presence in the material as a result of incomplete burning and calcium oxide carbonization during transportation and storage.

The hydration of lime-ash mixtures at the temperatures of 373 and 413 K is of considerable interest because the processes are accelerated under such conditions and the formed products have a stable phase composition even at the early stages of setting.[34]

Figs. 4-6 show the X-ray patterns for different BPLP:ash ratios.

For BPLP:AA_L mixtures, which set at 413 K, after 2 days of storage we identified (see Fig. 4) low-base calcium hydrosilicates of C_2S_2H type (d = (2.53; 2.76; 3.68)·10^{-10} m), tobermorite-like mineral $C_4S_5H_5$ (d = = (1.82; 2.98; 11.40)·10^{-10} m) and gyrolite $C_2S_3H_2$ (d = = (2.09; 2.49; 3.36)·10^{-10} m). We also observed the traces of silica (d = (2.28; 3.36; 4.27)·10^{-10} m) and calcite (d = = (1.88; 2.28; 3.05)·10^{-10} m). The composition is also characterized by the formation of C_3ASH_4 hydrogarnets, which exhibit high thermal and corrosion resistance.

For BPLP:AA_L mixtures, which set at 373 K, after 14 days of storage the composition of hydration products is very close to that of mixtures, which were stored for 2 days (Fig. 5).

The patterns show that that a basicity of calcium hydrosilicates increases; mainly C_2SH_2 is formed (d = (1.63; 2.10; 2.74)·10^{-10} m); tobermorite-like calcium hydrosilicates and hydrogarnets are not formed.

Fig. 6 shows X-ray patterns for BPLP:AA_K mixtures. In comparison with the mixtures containing ash from Ladyzhyn SDPP (AA_L), the mixtures with AA_K (ash from Kurakhiv SDPP) have a higher crystallization degree of the formed products, as evidenced by clearly defined peaks on the patterns. If we compare the intensity of SiO_2, $CaCO_3$ peaks and peaks of other unreacted minerals (Figs. 4 and 6), we observe some retardation of the hydration process. The formula of the formed hydrogarnets is somewhat different: $C_3ASH_{2.8}$ (d = (1.60; 2.13; 2.21; 2.71)·10^{-10} m) instead of C_3ASH_4.

All mixtures with 10 % BPLP have less quantity of formed products to compare with those containing 20 % of BPLP, due to insufficient reactivity of calcium oxide.

Low-basic calcium hydrosilicates and hydrogarnets, characterized by high thermal and corrosion resistance, are formed in the process of setting. This is confirmed by the results obtained in the study of cement stone technological properties (Table 1).

The main parameters that characterize the technological properties of plugging solutions are density, solution yield from 1 ton of dry material, water-holding capacity (sedimentation stability) and setting time under different thermodynamic conditions.

According to the existing classification, the plugging materials are divided into three main groups relative to the density: lightweight (1400–1650 kg/m^3), normal (1650–1950 kg/m^3) and weighted (1950–2300 kg/m^3).[26]

The mixtures with BPLP as a binder are characterized by a wide range of densities: from 1450 to 1780 kg/m^3.

Water gain during cementing of wells is mainly observed, when the plugging solutions after pushing into the annulus do not set for a long time. In this case the sedimentation of solid phase particles takes place under the action of gravity. Also, water gain is observed in the presence of permeable layers in the cementation intervals.

These phenomena are not desirable, as they may adversely affect the quality of cementation.

The introduction of fine materials into the plugging mixture reduces water gain and improves sedimentation stability.[26] BPLP of Kryvyi Rih Metallurgical Plant is characterized by a high specific surface area of 700–750 m^2/kg (this is their advantage over other BPLP) and therefore it adsorbs a significant amount of mixing water on its surface, thereby significantly increases the stability of plugging solution (Table 1).

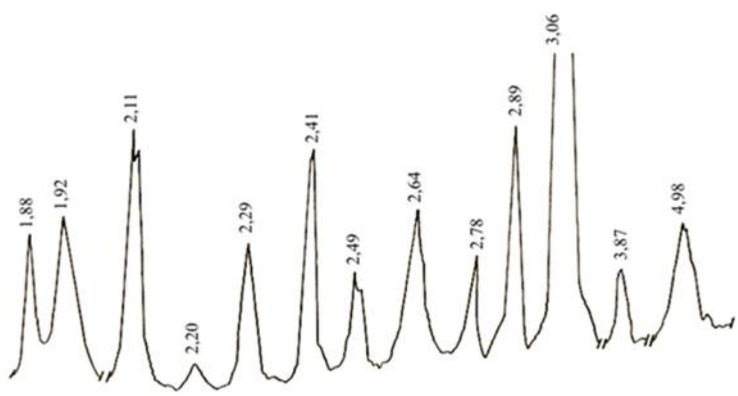

Fig. 3. X-ray pattern of non-hydrated BPLP

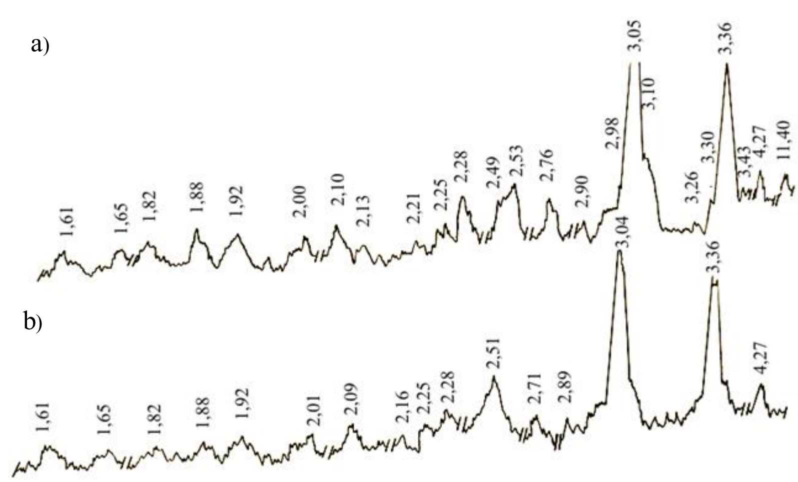

Fig. 4. X-ray patterns of hydrated BPLP:AA_L mixtures with different ratios (w/w): 20:80 (a) and 10:90 (b). Setting conditions: 2 days, 413 K, 60 MPa

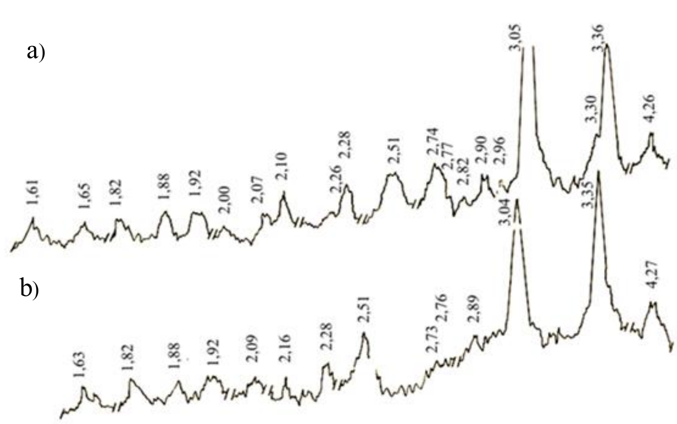

Fig. 5. X-ray patterns of hydrated BPLP:AA_L mixtures with different ratios (w/w): 20:80 (a) and 10:90 (b). Setting conditions: 14 days, 373 K K, 40 MPa

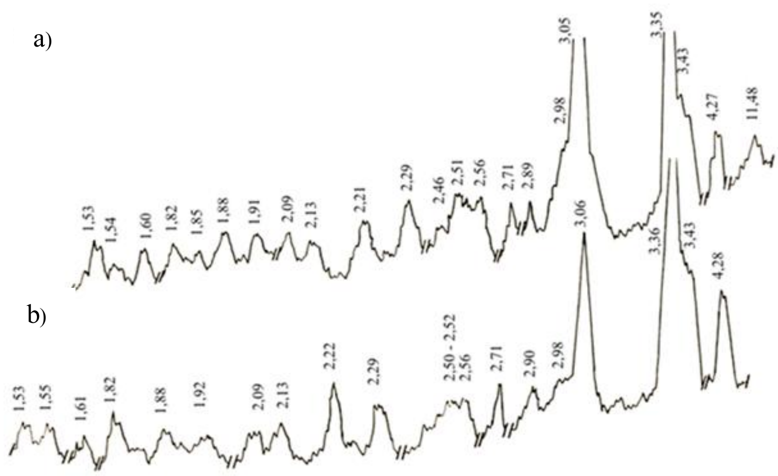

Fig. 6. X-ray patterns of hydrated BPLP:AA_K mixtures with different ratios (w/w): 20:80 (a) and 10:90 (b). Setting conditions: 2 days, 413 K, 60 MPa

Table 1. Technological properties of BPLP-based plugging solutions

Components, wt %				W/M**	Density, kg/m^3	Mobility, m	Water gain, mL	Pumpability, hours-min.	
BPLP	AA_L	AA_K	KLST-ME* (retarder)					T = 348 K, P = 30 MPa	T = 373 K, P = 40 MPa
10	90			0.45	1780	0.18	0	4–20	
10	90		1.0	0.53	1730	0.20	3.75		3–50
20	80			0.60	1690	0.24	5.0		
10		90		0.67	1500	0.17	8.75	4–00	
10		90	1.0	0.75	1450	0.21	12.5		4–10
20		80		0.85	1450	0.23	8.75		

Notes: * condensed lignosulfonate; ** water/mixture ratio

Table 2. Technological properties of BPLP-based stone

Components, wt %			Compressive strength, MPa						Gas permeability after 2 days, μm^2·10^{-3}					
BPLP	AA_L	AA_K	T = 348 K, P = 30 MPa		T = 373 K, P = 40 MPa		T = 413 K, P = 60 MPa		T = 348 K, P = 30 MPa		T = 373 K, P = 40 MPa		T = 413 K, P = 60 MPa	
			2 days	28 days	2 days	28 days	2 days	28 days	2 days	28 days	2 days	28 days	2 days	28 days
10	90		2.0	10.8	9.2	19.8	13.5	17.0	1.9	0.8	1.4	0.9	1.6	1.1
20	80		1.7	11.5	6.9	17.5	9.5	16.8	2.4	1.2	1.8	0.7	1.4	1.0
10		90	1.0	6.1	4.0	7.2	7.0	13.0	2.1	0.8	1.8	0.9	1.5	1.2
20		80	0.7	3.5	3.8	8.5	4.5	8.9	2.4	1.4	1.9	1.1	1.8	1.4

The pumpability of plugging solutions (thickening time) determines the suitability of the mixture for the well cementing under certain thermodynamic conditions (temperature and pressure at the bottom).

Table 1 shows the data on the pumpability of plugging solutions. The obtained results indicate that most mixtures (except for those with low water/mixture ratio) have sufficient pumpability at the temperature of 348 K without the addition of retarder. With the increase in temperature, the thickening time is reduced and at 373 K it is necessary to use the retarder, for example NTFK.[35]

Strength is one of the main quality indicators of cement stone. Some authors believe that the requirements for strength are often inflated and the main function of the stone in the well is insulating. Increasing the strength, as a rule, reduces the deformation of the formed cement stone. The minimum allowable compressive strength of cement stone is 0.91– 3.50 MPa.[15]

Table 2 shows physico-mechanical properties and gas permeability of the plugging mixtures, which set under different thermodynamic conditions.

The analysis of the obtained data shows that with increasing setting time the strength of the cement stone increases, and its gas permeability decreases for all compositions. The data of Table 2 also confirm the high heat resistance of the stone. This allows to use the raw materials at high temperatures of the cementing medium. Low gas permeability allows to use the mixtures for cementing columns of gas wells.

For high-quality separation of layers, it is necessary to ensure a reliable contact of the cement ring with the well walls and casing.

Standard Portland cement-based grout is prone to shrinkage. Therefore, under hydrothermal conditions during cementation it is necessary to use non-shrinking materials.[36] The effective expansion is provided by the presence of calcium or magnesium free oxides in the setting system.[37] Such binders are most suitable for oilwell cement, because the high burning temperature provides low chemical activity at elevated temperatures in deep wells. This allows to adjust the setting time within the required limits.

The use of expandable (non-shrinking) cements based on calcium and magnesium oxides has a number of advantages. $Ca(OH)_2$ and $Mg(OH)_2$ are stable compounds, which virtually have not phase transformations leading to the destruction of the formed stone structure.[15]

Due to the insufficient amount of calcium oxide and the high burning temperature of BPLP, a significant expansion of cement stone does not occur. Fig. 7 shows the kinetics of expansion of BPLP-based plugging mixtures. The expansion is completed after the first 2 h of hydration, when the mixture is in a state of dispersion or gel no crystallization contacts occur. After the stone formation, there is almost no increase in volume and thus, there is no danger of structure destruction.

The absolute value of the expansion depends on the BPLP amount. The higher the CaO content, the greater the expansion value. With the increase in temperature, the expansion slightly decreases due to the rapid formation of $Ca(OH)_2$, when the system does not have coagulation contacts and therefore the increase in volume is minimal.

It is known that one of the main causes of well watering is insufficient contact of cement stone with casings and rocks that make up the walls of wells.

The adhesion of the cement stone to the boundary surface depends on many factors, the main of which are the composition of the contact surfaces, namely the plugging mixture, and the ambient temperature. Rock pressure has almost no effect on the adhesion of cement stone to metal,[22] because it is mainly due to the Van der Waals forces of adhesive–substrate. Adhesion of cement stone to rocks may also include H-bonds and individual chemical bonds between the components of the plugging solution (and further between stone components) and the wall of the rock, which had previously undergone mechano-chemical destruction during drilling.[38,39]

Table 3 shows the results of studies on the adhesion of cement stone to metal under different thermodynamic conditions.

The cement stone, which expands at setting, has high adhesion. The increase in expansion value increases the the adhesion to contact surfaces.

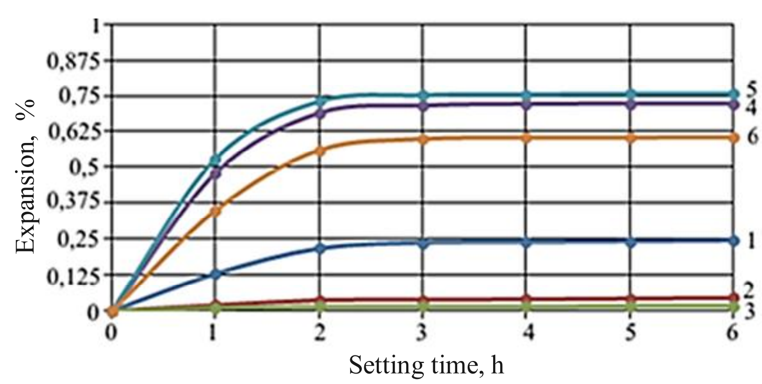

Fig. 7. Kinetics of expansion for BPLP:AA_L mixtures with different ratios (w/w): 10:90 (1, 2, 3) and 20:80 (4, 5, 6). Setting conditions: $T = 348$ K, $P = 30$ MPa (1, 4); $T = 378$ K, $P = 40$ MPa (2, 5); $T = 413$ K, $P = 60$ MPa (3, 6)

Table 3. Adhesion of BPLP-based stone to metal

Components, wt %			Adhesion to metal, MPa					
BPLP	AA_L	AA_K	$T = 348$ K, $P = 30$ MPa		$T = 373$ K, $P = 40$ MPa		$T = 413$ K, $P = 60$ MPa	
			2 days	28 days	2 days	28 days	2 days	28 days
10	90		1.8	6.8	2.5	5.6	5.2	7.4
20	80		1.9	7.3	3.3	4.7	7.3	7.3
10		90	0.5	2.2	1.0	2.5	2.6	5.8
20		80	1.0	4.1	1.8	3.1	3.1	4.2

4. Conclusions

The composition of hydration products of lime-ash cement mixtures, which set for a long period of time at high temperatures, was specified by the X-ray phase analysis of cement stone. The formed products were found to have a number of low-basic calcium hydrosilicates of C_2S_2H type ($2CaO{\cdot}2SiO_2{\cdot}H_2O$), tobermorite, hydolite and hydrogarnets. This allows to predict the high heat resistance and strength of the cement stone. At the same time, the absence of calcium hydroxide indicates the stability of the compositions in aqueous medium, as well as in the environment with high concentrations of $MgCl_2$ and $MgSO_4$.

Kinetic expansion curves of the plugging materials show that the expansion process is practically completed within the first 2 h; and the expansion value is maximum at higher lime content (20 % *vs.* 10 %).

The peculiarities of technological properties of BPLP-based stone are the following:

– the stone strength of after 28 days of setting is twice higher than that after 2 days;

– the highest strength is observed for cement mixtures containing AA_L, which set at 373 K and mixtures containing AA_K, set at 413 K;

– the gas permeability of the BPLP-based stone is in the range of $(0.8–2.4){\cdot}10^{-3}$ μm^2, which is sufficient for high-quality insulation of wells.

Thus, non-shrinking lime-ash plugging mixtures (LAPM) with a density of 1450–1780 kg/m^3 were developed on the basis of lime production by-product and acid fly ash from thermal power plants. According to their operational parameters, the obtained LAPM are characterized by high heat resistance, high strength, low permeability, absence of shrinkage in the setting process and wide range of density.

The introduction of new cement mixtures will ensure high-quality reinforcement of wells.

References

[1] Belokon, K.; Manidina, Y.; Fedchenok, A.; Banakh, A.; Mosiyevych L. The Physical and Mechanical Properties of Intermetallic Catalysts for the Neutralization of Carbon-Containing Components of Emission Gases. *Procedia Environ. Sci. Eng. Manag.* **2021**, *8(1)*, 95-102.

[2] Kruzhilko, O.; Polukarov, O.; Vambol, S.; Vambol, V.; Khan, N.A.; Maystrenko, V.; Kalinchyk, V.P.; Khan A.H. Control of the Workplace Environment by Physical Factors and SMART Monitoring. *Arch. Mater. Sci. Eng.* **2020**, *103(1)*, 18-29. https://doi.org/10.5604/01.3001.0014.1770.

[3] Odnorih, Z.; Manko, R.; Malovanyy, M.; Soloviy, K. Results of Surface Water Quality Monitoring of the Western Bug River Basin in Lviv Region. *J. Ecol. Eng.* **2020**, *21(3)*, 18-26. https://doi.org/ 10.12911/22998993/118303.

[4] Popovych, V.; Telak, J.; Telak, O.; Malovanyy, M.; Yakovchuk, R.; Popovych N. Migration of Hazardous Components of Municipal Landfill Leachates into the Environment. *J. Ecol. Eng.* **2020**, *21(1)*, 52-62. https://doi.org/ 10.12911/22998993/113246.

[5] Malovanyy, A.; Plaza, E.; Trela, J.; Malovanyy, M. Combination of Ion Exchange and Partial Nitritation/Anammox Process for Ammonium Removal from Mainstream Municipal Wastewater. *Water Sci. Technol.* **2014**, *70(1)*, 144-151. https://doi.org/10.2166/wst.2014.208

[6] Kostenko, E.; Melnyk, L.; Matko, S.; Malovanyy, M. The Use of Sulphophtalein Dyes Immobilized on Anionite Ab-17X8 to Determine the Contents of Pb(II), Cu(II), Hg(II) and Zn(II) in Liquid Medium. *Chem. Chem. Technol.* **2017**, *11(1)*, 117-124. https://doi.org/10.23939/chcht11.01.117.

[7] Voytovych, I.; Malovanyy, M.; Zhuk, V.; Mukha, O. Facilities and Problems of Processing Organic Wastes by Family-Type Biogas Plants in Ukraine. *J. Water Land Dev.* **2020**, *45 (IV–VI)*, 185-189. https://doi.org/10.24425/jwld.2020.133493.

[8] Malovanyy, M.; Lyashok, Y.; Podkopayev, S.; Povzun, O.; Kipko, O.; Kalynychenko V.; Virich, S.; Skyrda, A. Environmental technologies for use of coal mining and chemical industry wastes. Environmental Technologies for Use of Coal Mining and Chemical Industry Wastes. *J. Ecol. Eng.* **2020**, *21(2)*, 95-103. https://doi.org/10.12911/22998993/116339.

[9] Tymchuk, I.; Malovanyy, M.; Shkvirko, O.; Zhuk, V.; Masikevych, A.; Synelnikov, S. Innovative Creation Technologies for the Growth Substrate Based on the Man-Made Waste – Perspective Way for Ukraine to Ensure Biological Reclamation of Waste Dumps And Quarries. *Int. J. Foresight Innov. Policy* **2020**, *14(2/3/4)*, 248-263. https://doi.org/ 10.1504/IJFIP.2020.111239.

[10] Tymchuk, I.; Shkvirko, O.; Sakalova, H.; Malovanyy, M.; Dabizhuk, T.; Shevchuk, O.; Matviichuk, O.; Vasylinych, T. Wastewater a Source of Nutrients for Crops Growth and Development. *J. Ecol. Eng.* **2020**, *21(5)*, 88-96. https://doi.org/ 10.12911/22998993/122188.

[11] Sanytsky, M.; Sobol, K.; Shcturmay, M.; Khymko, O. Low Energy Consuming Modified Composite Cements and Their Properties. *Chem. Chem. Technol.* **2011**, *5(2)*, 227-230. https://doi.org/10.23939/chcht05.02.227.

[12] Marushchak, U.; Sanytsky, M.; Pozniak, O.; Mazurak O. Peculiarities of Nanomodified Portland Systems Structure Formation. *Chem. Chem. Technol.* **2019**, *13(4)*, 510-517. https://doi.org/10.23939/chcht13.04.510.

[13] Orlovskyi, V.M. Improving the Quality of Heat–Resistant Borehole Cements. *Geotechnologies* **2019**, *2*, 16-21.

[14] Orlovskyi, V.M.; Pokhylko, A.M.; Krytskyi, V.V. Modern Borehole Cements. *Geotechnologies* **2018**, *1*, 44-52.

[15] Orlovskyi, V.M. *Tamponazhni materialy, shcho rozshyriuiutsia pry tverdinni*; PoltNTU im. Yu. Kondratiuka: Poltava, 2015.

[16] Salman, A. D.; Tatjána, J.; Al-Mayyahi, M. A.; Ibrahim, R. I.; Abdullah, T. A.; Khader, E. H. Improvement of Mechanical Properties of Oil Well Cement by Incorporate Nano-$CaCO_3$ Prepared from Eggshell Waste. *IOP Conference Series: Materials Science and Engineering* **2020**, *765(1)*, 012006. https://doi.org/10.1088/1757-899X/765/1/012006

[17] Khaliq, W.; Khan, H.A. High Temperature Material Properties of Calcium Aluminate Cement Concrete. *Constr. Build. Mater.* **2015**, *94*, 475-487. https://doi.org/10.1016/j.conbuildmat.2015.07.023

[18] Adje, S.; Elkatatny, S.; Aggrey, W.N.; Abdelraouf, Y. Geopolymer as the Future Oil-Well Cement. *J. Pet. Sci. Eng.* **2022**, *208(B)*, 109485. https://doi.org/10.1016/j.petrol.2021.109485.

[19] Ahday, M.; Imqam, A. Fly Ash Class C Based Geopolymer for Oil Well Cementing. *J. Pet. Sci. Eng.* **2019**, *179*, 750-757. https://doi.org/10.1016/j.petrol.2019.04.106.
[20] Shtark, Y.; Viht, B. *Tsement i izvest*; Instytut budivelnykh materialiv im. Hrishmanova: Kyiv, 2008.
[21] Dvorkin, L.Y.; Skrypnyk I.H. *Fizyko-khimichni i fizychni metody doslidzhennia budivelnykh materialiv*; Natsionalnyi universytet vodnoho hospodarstva ta pryrodokorystuvannia: Rivne, 2006.
[22] Horskyi, V.F. *Tamponazhni materialy i rozchyny*; Chernivetskyi natsionalnyi universytet im. Yu. Fedkovycha: Chernivtsi, 2006.
[23] Bulatov, A.I.; Shamanov S.A. *Metody ispytaniya tamponazhnykh materialov*; Prosveschenie-Yug: Krasnodar, 2002.
[24] Agzamov, F.A.; Izmuhambetov, B.S.; Tokunova E.F. *Khimiya tamponazhnykh i promyvochnykh rastvorov*; Nedra: Saint Petersburg, 2011.
[25] Kurdowski, W. *Chemia cementu i betonu*; Polski cement: Kraków, 2010.
[26] Taymasov, B.T.; Klassen, V.K. *Khimicheskaya tekhnologiya vyazhushchikh materialov*; BGTU: Belgorod-Shymkent, 2017.
[27] Andreeva, N.A. *Khimiya tsementa i vyazhushchikh veshchestv*; SPbGASU: Saint Petersburg, 2011.
[28] Shmitko, E.I.; Krylova, A.V.; Shatalova, V.V. *Khimiya tsementa i vyazhushchikh veshchestv*; VGASU: Voronezh, 2005.
[29] Taylor, H.F.W. *Cement chemistry*; Thomas Telford Publishing: London, 1997.
[30] Brykov, A.S. *Khimiya silikatnykh i kremnezemsoderzhashchikh vyazhushchih materialov*; SPbGASU: Saint Petersburg, 2011.
[31] Kuzmenkov, M.I.; Kunitskaya, T.S. *Vyazhushchie veshchestva i tehnologiya proizvodstva izdeliy na ikh osnove*; BGTU: Minsk, 2003.
[32] Orlovskyi, V.; Malovanyy, M.; Biletskyi, V.; Sokur, M. Physico-Chemical Peculiarities of Weighted Thermostable Plugging Materials Hydration. *Chem. Chem. Technol.* **2021**, *15(4)*, 599-607. https://doi.org/10.23939/chcht15.04.599
[33] Pushcharovskiy, D.Yu. *Rentgenografiya mineralov*; Geoinformmark: Moscow, 2000.
[34] Nizamutdinov, E.A. Issledovanie Fazovogo Sostava Vysokotemperaturnogo Tsementa. *Nauka, obrazovanie i kultura* **2017**, *20 (Tom 2)*, 5-6.
[35] Izotov, V.S.; Sokolova, Yu.A. *Khimicheskie dobavki dlya modifikatsii betona*; Paleotip: Moscow, 2006.
[36] Agzamov, F.A.; Babkov, V.V.; Karimov, I.N. O Neobkhodimoy Velichine Rasshireniya Tamponazhnykh Materialov. *Territoriya neftegaz* **2011**, *8*, 14-15. https://neftegas.info/upload/iblock/4ed/4ed2387ae553085841245adae8c369e5.pdf
[37] Ovchinnikov, V.P.; Aksenova, N.A.; Ovchinnikov, P.V. *Fiziko-khimicheskie protsessy tverdeniya, rabota v skvazhine i korroziya tsementnogo kamnya*; TGNGU: Tyumen, 2011.
[38] Gorobets, L.; Verhorobina, I.; Biletskyi, V.; Krivenko, A.; Grishchenko, M.; Bulakh, O. Identification of Factors to Reduce the Energy Costs of Dispersing in Jets. *EasternEuropean J. Enterp. Technol.* **2020**, *6(1) (108)*, 55-62. https://doi.org/10.15587/1729-4061.2020.217253
[39] Biletskyi, V.; Horobets, L.; Fyk, M.; Al-Sultan, M. Theoretical Background of Rock Failure at Hydraulic Seam Fracture and after Effect Analysis. *Min. Miner. Depos.* **2018**, *12(3)*, 45-55. https://doi.org/10.15407/mining12.03.045

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ДОСЛІДЖЕННЯ ВАПНЯНО-ЗОЛЬНИХ ТАМПОНАЖНИХ СУМІШЕЙ

***Анотація**. Розроблено і досліджено нові конкурентоздатні тампонажні композиції – вапняно-зольні тампонажні суміші (ВЗТС), що розширюються при тужавінні, густиною 1450 – 1780 кг/м^3.Компоненти: вапно, кислі золи виносу ТЕС. Рентгенофазовим аналізом тампонажного каменю уточнено склад новоутворень у процесі гідратації ВЗТС. Отримано кінетичні криві розширення тампонажного матеріалу при температурах 348–413 К. Визначено раціональні температурні режими тужавіння ВЗТС за критеріями міцності і газопроникності цементного каменю.*

***Ключові слова**: цементування свердловин, тампонажний матеріал, гідратація цементу, вапно, кисла зола виносу, водосумішеве відношення, цементний камінь.*