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# Investigation of Dolomite-Ash Grouting Mixtures for Cementing Oil and Gas Wells

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**Abstract**

The article analyses the issue of improving the quality of separation of rocks and oil and gas horizons. The results of theoretical and experimental studies of grouting compositions based on dolomite-ash grouting mixtures have been presented. New competitive grouting compositions, viz. dolomite-ash grouting mixtures (DAGM) with a density of 1.565-1.815 kg/m$^3$, have been developed and researched. Components: dolomite-firing by-product (DFBP), PZT-1-100 grouting Portland cement, acid fly ashes from thermal power plants. X-ray phase analysis of grouting stone has clarified the composition of new formations in the process of DAGM hydratation. Rational temperature regimes of DAGM hardening according to the criteria of strength and gas permeability of cement stone have been determined. The selection of optimal formulations of dolomite-ash grouting mixtures has been carried out.

***Keywords**: Grouting Portland cement; Grouting mixture; Dolomite; Acid fly ash; Water-mixture ratio; Cement stone.*

## 1. Introduction

One of the main problems of cementing wells is to improve the quality of insulation of the annulus while reducing the cost of cementing operations. Given the growing cost of cement and its scarcity, the task of saving energy-intensive grouting cement is also becoming urgent. The solution to this complex problem lies in the application of mineral by-products and industrial waste.

The purpose of the research done is to create new grouting materials using mineral by-products of industry. The use of mineral materials from by-products would reduce the cost of grouting operations with high quality of well fastening.

In the 1980s, drilling enterprises in Ukraine used cement-ash mixtures (CAM), in which acid fly ashes from burning coal at power plants were used as an admixture to grouting Portland cements [1]. The use of acid fly ashes is due to their pozzolanic activity, which has a positive effect on the heat resistance and corrosion resistance of cements [2]. Studies of operational properties of cement-ash mixtures were conducted by the Poltava Branch of the Ukrainian State Institute of Geological Exploration (PB UkrSIGE) [1-3]. The advantages of those mixtures are the heightened thermal corrosion resistance of the stone, lowered density of grouting solutions, increased pumping time of a solution at high temperatures, as well as reduced cost of grouting material.

Acid ashes are formed during the combustion of coal. They have a low content of calcium oxide (up to 6%). BV. Krych conducted studies of grouting binding materials based on mixtures of Portland cement and high-calcium ash of Estonian oil shales [2]. Such grouting mixtures showed high performance properties, in particular the expansion of grouting stone, but the temperature of their application was 90-100°C.

In the 1990s, grouting mixtures were developed using high-calcium ash from Baltic oil shales and acid fly ash from coal burning [2, 4]. However, their implementation was terminated for technical reasons.

**The goal** of this research is to study the physicochemical characteristics of hydratation of dolomite-ash grouting materials and the patterns of their hardening process. In order to achieve this goal, the following research objectives have been set:

– study of the composition of hydratation products of dolomite-ash grouting mixtures that harden for a long time at high temperatures;
– study of the dependence of operational properties of stone based on dolomite-ash cement mixtures on physicochemical factors, in particular, the composition of the grouting mixture, temperature, pressure and duration of hardening.

## 2. Experimental

### 2.1. Methods and materials

The density of the powders was determined using a pycnometer. Knowledge of the volume (bulk) mass of powdered materials is necessary to calculate the amount of material when dosing in bulk, for example, in the hopper of a cement mixer. This parameter was determined in a loose and compacted state [2, 5]. The specific surface area of powders was determined using the PSH device (Khodakov devices, http://khodakov.ru/priboryi-psh/) by the method of air permeability [2, 5]. The grain size composition of the source bulk materials was determined by sieving them, and then the percentage of grain size fractions was calculated [5].

Preparation (mixing) of grouting solutions was carried out in a standard way using a paddle mixer with a paddle device speed of (1,500 ± 100) min.$^{-1}$, according to the State Standard of Ukraine BV.2.7-86-99, using water from the water mains, whose amount was added in accordance with a certain water-mixture ratio (W/M) [6].

The water-mixture ratio was determined based on the flowability of solutions of dolomite-ash grouting mixtures using the KR-1 cone (2, 7). According to the State Standard of Ukraine BV.2.7-86-99, the flowability of grouting solutions must be within 0.18-0.22 m of their spreading range in a circle.

The properties of the solutions were evaluated by sedimentation resistance and water transfer rate that were determined by standard methods [2, 7]. The density of grouting solutions was determined using a calibrated pycnometer with a capacity of 100 cm$^3$.

Water separation was determined by the standard methods [2, 7]. According to the State Standard of Ukraine BV.2.7-86-99, the water separation value must not exceed 7.5 ÷ 10 ml for grouting Portland cements.

The thickening time of grouting solutions was determined using the KZ-3 consistometer in Bearden units of consistency (Bc), in accordance with the metrological system of the State Standard of Ukraine BV.2.7-88-99, that are dimensionless and are not directly related to viscosity. According to the State Standard of Ukraine BV.2.7-86-99, the thickening time of cement paste is the time from the beginning of mixing cement with water until the moment when the cement paste reaches a consistency of 30 Bc [2, 5].

Autoclaving of samples was performed using the AU-1-71-IE autoclave installation developed by the Poltava Branch of the Ukrainian State Institute of Geological Exploration, which is designed for a maximum operating pressure of 100 MPa and a maximum temperature of 523 K. Deviation from the temperature set constituted ± 5°C. The samples were shaped to take the form of cylinders with a height and diameter of 3 cm [2].

Determining the stone strength range was carried out according to the standard compression methods using the PSU-10 press [2, 7]. Determining the gas permeability of stone samples was carried out using the GK-5 installation according to the methods described in [2, 5, 7].

The strength of the contact of the stone samples with the retaining metal surface was evaluated by the adhesion of the hardened stone to the metal rod, and it was taken to mean the tangential shear stress, at which the cement-metal contact is broken during the extraction of the rod. In order to study the adhesion of stone samples to metal, the PSU-10 laboratory press with a hydraulic drive and a special attachment for studying adhesion was used (Fig. 1).

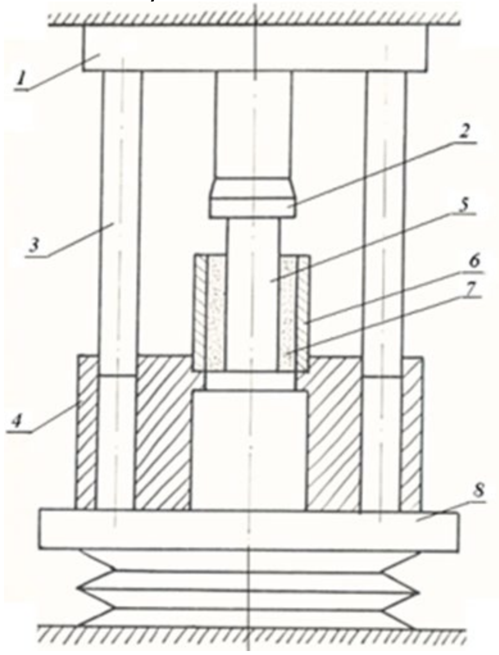


Figure 1. Attachment to the PSU-2 press for determining the adhesion of cement stone to metal; 1 – pressure plate; 2 – cylinder; 3 – retainer bar; 4 – housing; 5 – metal rod; 6 – cylindrical form; 7 – cement stone; 8 – movable plate of the PSU-10 hydraulic press

The X-ray phase analysis was performed using the DRON-2 instrument with a copper cathode and a monochromator installed along the reflected beam of radiation. Radiographs were taken under the following conditions. The size of the slits limiting the X-ray beam was 0.002 x 0.004 m, the size of the slits in front of the meter was 0.0025 x 0.008 m; the test material was loaded into a cuvette with a diameter of 0.0275 m and a depth of 0.005 m; when taking radiographs, the cuvette was rotating in a horizontal plane at a constant speed of 20 $min^{-1}$. The rotation speed of the meter was 2 degrees per minute. The voltage at the cathode was 29 kV, the current was 19 μA, the speed of the film reached 0.72 m/h [2-3, 5, 8-9].

## 3. Results and discussion

In order to provide drilling companies of the oil and gas industry of Ukraine with high-quality heat-resistant grouting materials, reduce their cost and cover the shortage in these materials, researchers at the laboratory facilities of the Poltava Branch of the Ukrainian State Institute of Geological Exploration (PB UkrSIGE) developed formulations of heat-resistant dolomite-ash grouting mixtures (DAGM) with high operational properties.

The grouting solution was obtained from a dolomite-ash mixture that included the following components: by-product of dolomite firing, viz. semi-fired dolomite powder (SFDP) (fine-grained pulverized dolomite), fly acid ash of the Ladyzhyn or Kurakhove TPP, process (tap) water. Some formulations additionally contained PZT-1-100 grouting Portland cement.

SFDP is formed during the firing of dolomite in rotary kilns. The separation of SFDP from the final product, i.e. metallurgical dolomite, is carried out by the countercurrent method. That means that the dolomite raw material is burned and moved to the one end, while SFDP is directed by the air flow to the other end of the kiln. SFDP therefore contains a significant percentage (63-36%) of unburned dolomite [2]. SFDP is produced in accordance with TU 14-14-147-85, is a powder grey-green to brown in colour, has a density of 2,700-2,850 $kg/m^3$ and a specific surface area of 260-290 $m^2/kg$. The grain size distribution by the sieve analysis is as follows: 1 mm – 0.50 %; 0.5 mm – 0.50 %; 0.25 mm – 3.9 %; 0.1 mm – 87,5 %.

Chemical composition by oxides: CaO – 36 ÷ 40 %; MgO – 19 ÷ 22 %; $Fe_2O_3$ – 1.5 ÷ 2.5 %; $Al_2O_3$ – 0.5 ÷ 1.0 %; $SO_3$ – up to 0.5 %; $SiO_2$ – up to 2 %; mass loss during calcination – 30 ÷ 36 %.

From the rotating kilns, the SFDP enters the sedimentation chambers where the largest fractions are collected. Fine fractions of the SFDP (dolomite dust) enter battery cyclone separators through the waste heat recovery boiler, and then farther to the electric filters. From the cyclone separators, the SFDP is pumped through a shipping hopper to railway cars. A mixture of cyclone separator (up to 10-15%) and electric filter (85-90%) SFDPs is delivered to consumers.

TPP acid fly ashes were used as a siliceous admixture in the grouting mixtures. Compositions using acid ash of Kurakhove TPP (AAk) and Ladyzhyn TPP (AAl) [2-4] were investigated in the grouting mixtures developed. Acid fly ash of the Kurakhove TPP is a dark-grey powder with a density of 1,950-2,050 kg/m$^3$ and a specific surface area of 350-400 m$^2$/kg, its bulk weight is 1,100-1,150 kg/m$^3$.

Chemical composition by 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 %; mass loss during calcination – 3.4 ÷ 3.7 %.

Acid fly ash of the Ladyzhyn TPP is a greenish-grey powder with a density of 2,300-2,500 kg/m$^3$ and a specific surface area of 230-250 m$^2$/kg, its bulk weight is 1,500-1,600 kg/m$^3$.

Chemical composition by oxides: $SiO_2$ – 55.0 ÷ 59.0 %; $Al_2O_3$ – 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 %; mass loss during calcination – 5.1 ÷ 5.4 %.

The main factors influencing the phase composition of grouting materials that hardened under the conditions of deep wells are temperature, pressure and time, the effect of the pressure being insignificant [3, 10-17].

It is known that grouting Portland cements for "moderate" temperatures, such as PZT-1-100 grouting Portland cement, are undesirable to use at temperatures above 90°C due to their low heat resistance [2, 5].

Among scientists, there are various explanations as to the negative effects of temperature on the heat resistance of cement stone. The most common theory is that the decrease in strength at temperatures of 100°C and higher occurs because high-basicity calcium hydrosilicates of the $C_2SN(a)$ type are formed that are prone to recrystallization [2, 5]. This leads to the disintegration of the formed structure of the cement stone. The negative impact of high temperatures on cement stone can be avoided by introducing an active mineral (pozzolanic) admixture containing silica into the composition of the Portland cement. In this case, the concentration of calcium oxide in the cement solution decreases, as a result of which low-basicity hydrosilicates of the CSH(B) type are identified in the process of crystallization hardening among new formations; such a stone has high strength indicators.

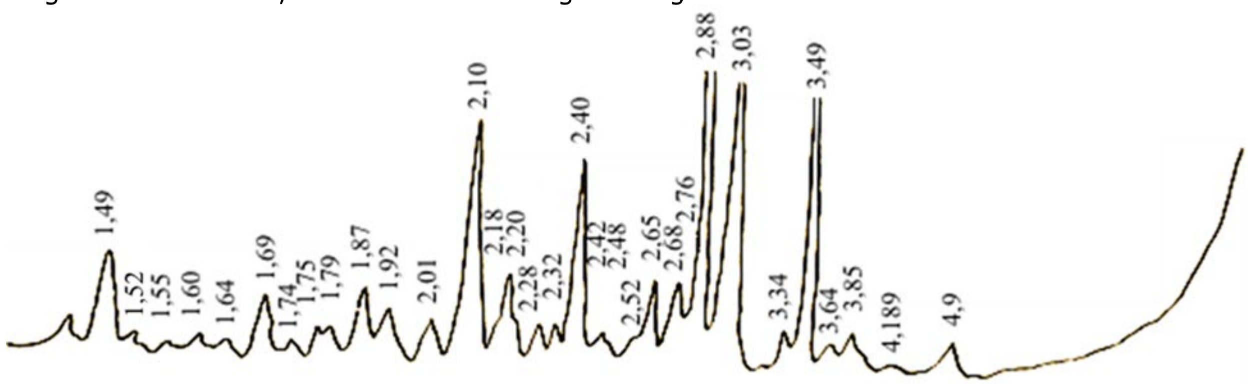


Figure 2. Radiograph of the unhydrated SFDP

Figure 2 shows a radiograph of unhydrated SFDP. It shows clearly the main responses that correspond to calcite – d = (1.60; 1.92; 3.03; 3.85…) × $10^{-10}$ m, dolomite – d = (2.01; 2.18; 2.88) × $10^{-10}$ m, anhydrous gypsum (anhydrite) – d = (1.74; 1.87; 2.32; 3.49) × $10^{-10}$ m, calcium oxide – d = (1.69; 2.40; 2.76) × $10^{-10}$ m, magnesium oxide – d = (1.49; 2.10; 2.42...)

× 10$^{-10}$ m, calcium hydroxide – d = (1.79; 2.65; 4.90) × 10$^{-10}$ m, which was formed due to the interaction of CaO with air moisture.

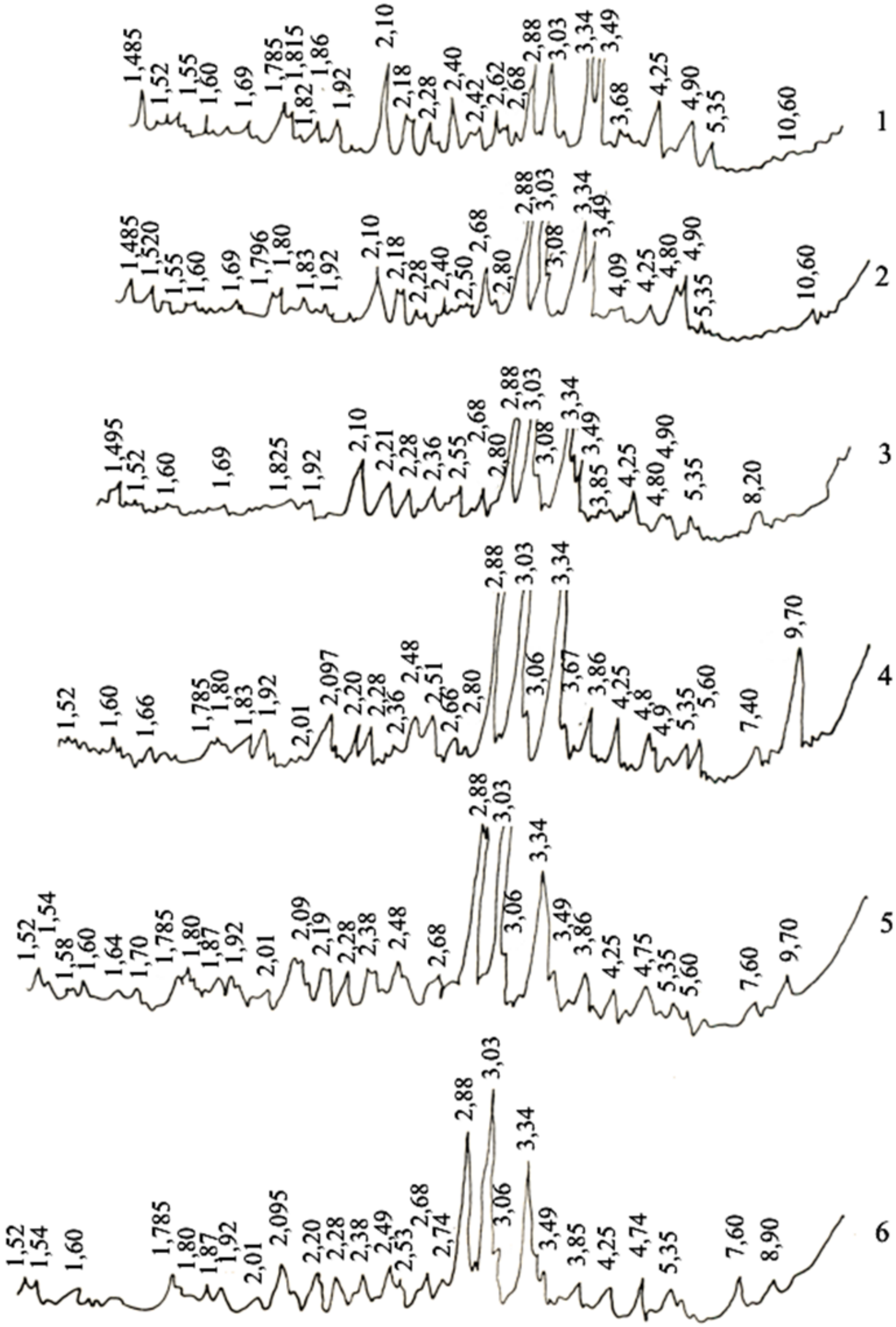


Figure 3. Radiographs of hydratated dolomite-ash grouting mixtures (DAGMs)
Binding material – SFDP: AAk – 50 : 50; W/M = 0.55; hardening conditions: $t$ = 75 $^0$C; $P$ = 30 MPa; hardening time: 1. – 1 hour; 2. – 8 hours, 3. – 1 day; 4. – 2 days; 5. – 28 days; 6. – 180 days

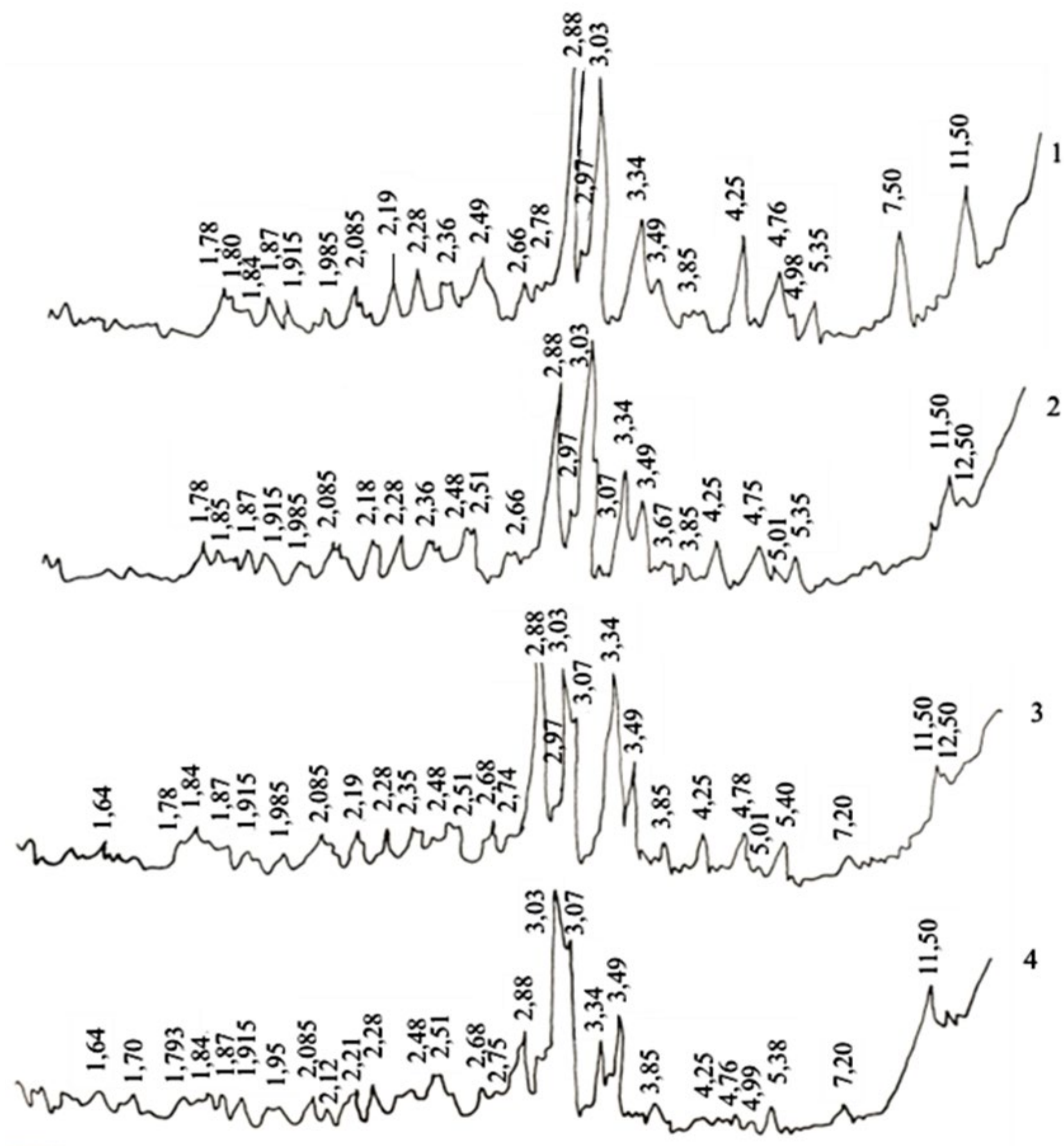


Figure 4. Radiographs of hydratated dolomite-ash grouting mixtures (DAGMs)
Binding material – SFDP: AAk – 50: 50; W/M = 0.55; hardening conditions: $t$ = 100 °C; $P$ = 40 MPa; hardening time: 1. – 2 days; 2. – 7 days; 4. – 28 days; 5. – 180 days

Figures 3 and 4 show radiographs of SFDP mixtures with Kurakhove TPP ash that hardened over different periods of time at 75 °C and 100 °C, respectively. At the initial phase of hydratation, significant changes in the phase composition are not observed (Fig. 3). The intensity of CaO and MgO peaks decreases slightly, the intensity of $Ca(OH)_2$ peaks increases accordingly, responses corresponding to silica change slightly – d = (2.28; 3.34; 4.25) × $10^{-10}$ m, weak peaks of calcium hydrosilicates of the $C_2SH_2$ type – d = (1.83; 2.80; 3.08) × $10^{-10}$ m, as well as calcium hydroaluminate $C_4AH_{12}$ – d = (2.50; 2.88; 4.09; 10.60) × $10^{-10}$ m are observed.

During the first 8 hours of hydratation, the processes described above mostly continue. After one day, significant changes in the composition of hydratation products occur accompanied by the formation of the crystallization structure of the samples of the grouting composition. During this period, calcium hydrosulfoaluminates are formed – d = (3.86; 5.60; 9.70) × $10^{-10}$ m, the transition of four-calcium hydroaluminate $C_4AH_{19}$ into $C_4AH_{13}$ – d = (2.48; 3.9;

8.2) × $10^{-10}$ m takes place, as well as that of high-basicity hydrosilicate calcium $C_2SH_2$ into CSH(B) – d = (1.66; 1.825; 2.80; 3.03) × $10^{-10}$ m.

During prolonged hydrothermal action, the change in the phase composition of new formations is significantly affected by recrystallization that occurs over time. After 28 days of hardening in the autoclave, along with hydrosulfoaluminates, hydroaluminates of calcium and magnesium, hydrogarnets are formed – d = (1.64; 1.985; 2.84; 5.0) × $10^{-10}$ m and dihydric gypsum transitions into anhydrite – d = (1.87; 2.20; 3.49) × $10^{-10}$ m. SFDP : AAk – 50 : 50; W/M = 0.55; hardening conditions: $t$ = 75 $^0$C; $P$ = 30 MPa; time: 1. – 1 hour; 2. – 8 hours, 3. – 1 day; 4. – 2 days; 5. – 28 days; 6. – 180 days.

After 180 days, ettringite (hard-to-dissolve calcium hydrosulfoaluminate) completely decomposes, and calcium monosulfoaluminate lines remain on the radiograph. There are almost no other phase changes. Hydratation products are represented by low basicity calcium hydrosilicate of the CSH(B) type, serpentine, $C_3ASH_4$, anhydride.

The temperature of 100 °C is characterized by some differences (Fig. 3). After two days of hardening, the radiographs show dihydric gypsum – d = (2.87; 4.29; 7.6) × $10^{-10}$ m, magnesium hydroxide – d = (1.80; 2.36; 4.16) × $10^{-10}$ m, hydrogarnets – d = (1.985; 2.74; 4.98) × $10^{-10}$ m, tobermorite – d = (1.84; 2.97; 11.5) × $10^{-10}$ m, serpentine – d = (2.09; 2.49; 2.51) × $10^{-10}$ m, as well as anhydride, quartz, dolomite, and calcite. After 7 days, this composition mostly remains the same and practically does not change for 180 days, only the amount of minerals changes; the content of quartzite, dolomite and calcite decreases while, accordingly, the amount of hydratated materials increases.

The stone from dolomite-ash mixtures has therefore high performance properties, i.e. high strength and low permeability in the temperature range of 50-140$^o$C. In addition, grouting solutions based on dolomite-ash mixtures require a long duration of pumping (more than 3 hours at 75 $^0$C) that can be easily regulated at higher temperatures using standard retardants (Table 1) [18]. This gives grounds for a reasonable conclusion about the suitability of dolomite-ash mixtures for cementing productive horizons under various mining and geological conditions [19].

Table 1. Operational properties of DAGM-based grouting solutions

| Ser. no. | Mass fraction of components, wt. % | | | | | | W/M | Density, kg/m$^3$ | Fluidity, m | Water separation, mL | Pumpability, hours-minutes | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | SFDP | PZT-1-100 | AAl | AAk | KLST-ME | NTPA | | | | | t = 75 $^0$C, P = 30 MPa | t = 100 $^0$C, P = 40 MPa |
| 1 | 20 | 10 | 70 | | | | 0.50 | 1700 | 0.20 | 2.5 | | |
| 2 | 20 | 10 | 70 | | 1.0 | | 0.50 | 1700 | 0.20 | 2.5 | 3-40 | 3-00 |
| 3 | 30 | | 70 | | | | 0.45 | 1720 | 0.22 | 1.25 | 3-20 | |
| 4 | 30 | | 70 | | 1.0 | | 0.45 | 1720 | 0.22 | 1.25 | | 3-45 |
| 5 | 50 | | 50 | | 1.0 | | 0.43 | 1820 | 0.18 | 0 | 3-50 | 3-10 |
| 6 | 70 | | 30 | | | | 0.50 | 1750 | 0.18 | 0 | | |
| 7 | 20 | 10 | | 70 | | | 0.58 | 1565 | 0.18 | 5.0 | 4-05 | |
| 8 | 20 | 10 | | 70 | | 0.03 | 0.58 | 1565 | 0.18 | 5.0 | | 3-30 |
| 9 | 30 | | | 70 | | | 0.58 | 1560 | 0.18 | 5.0 | | |
| 10 | 40 | 10 | | 50 | | | 0.55 | 1640 | 0.18 | 6.25 | | |
| 11 | 50 | | | 50 | | | 0.56 | 1600 | 0.18 | 10.0 | 5-00 | |
| 12 | 50 | | | 50 | | 0.03 | 0.56 | 1600 | 0.18 | 10.0 | | 4-15 |
| 13 | 70 | | | 30 | | | 0.52 | 1660 | 0.19 | 11.25 | | |

The density of grouting solutions in the formulations under investigation varies from 1.565 to 1.829 kg/m³. When the ash of the Kurakhove TPP is introduced into the mixture, the formulations have a lighter density, while when the ash of the Ladyzhyn TPP is introduced, they have a normal density.

Pumpability studies conducted using the KZ-3 consistometer (Table 1) suggest that condensed lignosulfonate (KLST-ME) should be recommended for wells with a reservoir temperature of 75°C and a nitrilotrimethylphosphonic acid (NTPA) for those with a reservoir temperature of 100°C.

At temperatures of 75°C and below, all formulations have a pumping duration of more than three hours, so it is possible to use DAGMs without a retardant for cementing shallow wells.

One of the main indicators of the quality of cement stone is its strength. Some researchers believe that the strength requirements are often overstated, while the main function of the stone in the well is an insulating one. Increasing the strength reduces, as a rule, the deformation of the cement stone formed. Based on the data from [2], the minimum allowable compressive strength of grouting stone is 0.91 ÷ 3.50 MPa.

Table 2. Strength of DAGM-based grouting stone

| Ser. no. | Mass fraction of components, wt. % | | | | Compressive strength, MPa | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | SFDP | PZT-1-100 | AAl | AAk | t = 50 $^0$C, P = 20 MPa | | t = 75 $^0$C, P = 30 MPa | | t = 100 $^0$C, P = 40 MPa | | t = 140 $^0$C, P = 60 MPa | |
| | | | | | 2 days | 28 days | 2 days | 28 days | 2 days | 28 days | 2 days | 28 days |
| 1 | 20 | 10 | 70 | | 1.3 | 5.5 | 2.2 | 10.2 | 3.5 | 12.8 | 7.1 | 12.0 |
| 2 | 30 | | 70 | | 1.0 | 4.6 | 4.0 | 5.2 | 4.0 | 11.3 | 6.4 | 12.2 |
| 3 | 40 | 10 | 50 | | 2.0 | 7.5 | 3.0 | 8.2 | 4.7 | 15.0 | 8.8 | 11.1 |
| 4 | 50 | | 50 | | 1.7 | 5.5 | 2.1 | 8.4 | 3.6 | 11.2 | 6.8 | 11.0 |
| 5 | 20 | 10 | | 70 | 0.4 | 2.5 | 2.9 | 6.8 | 6.6 | 15.7 | 13.1 | 16.1 |
| 6 | 40 | 10 | | 50 | 0.6 | 2.5 | 3.5 | 7,1 | 6.5 | 15.1 | 14.0 | 13.1 |
| 7 | 50 | | | 50 | – | 2.2 | 1.2 | 3.2 | 2.6 | 4.1 | 4.0 | 4.4 |

Table 3. Gas permeability of DAGM-based grouting stone

| Ser. no. | Mass fraction of components, wt. % | | | | Gas permeability, μm² ×10⁻³ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | SFDP | PZT-1-100 | AAl | AAk | t = 50 $^0$C, P = 20 MPa | | t = 75 $^0$C, P = 30 MPa | | t = 100 $^0$C, P = 40 MPa | | t = 140 $^0$C, P = 60 MPa | |
| | | | | | 2 days | 28 days | 2 days | 28 days | 2 days | 28 days | 2 days | 28 days |
| 1 | 20 | 10 | 70 | | 1.0 | 0.9 | 1.0 | 0.7 | 0.7 | 0.6 | 0.6 | 0.5 |
| 2 | 30 | | 70 | | 2.2 | 1.6 | 1.6 | 1.0 | 1.4 | 0.9 | 1.0 | 1.0 |
| 3 | 40 | 10 | 50 | | 2.5 | 1.6 | 1.9 | 1.5 | 1.8 | 1.5 | 1.0 | 0.9 |
| 4 | 50 | | 50 | | 2.0 | 1.1 | 1.3 | 0.5 | 0.7 | 0.4 | 0.6 | 0.4 |
| 5 | 20 | 10 | | 70 | 2.6 | 1.1 | 1.4 | 1.2 | 1.3 | 0.9 | 1.0 | 0.7 |
| 6 | 40 | 10 | | 50 | 2.0 | 0.9 | 1.4 | 1.1 | 1.3 | 0.8 | 1.1 | 0.8 |
| 7 | 50 | | | 50 | - | 1.0 | 1.6 | 1.1 | 1.6 | 0.9 | 1.0 | 0.9 |

Table 4. Adhesion of grouting stone to metal when using the DAGMs

| Mass fraction of components, wt. % | | | | Coupling force, MPa | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| SFDP | PZT-1-100 | AAl | AAk | t = 75 $^0$C, P = 30 MPa | | t = 100 $^0$C, P = 40 MPa | | t = 140 $^0$C, P = 60 MPa | |
| | | | | 2 days | 28 days | 2 days | 28 days | 2 days | 28 days |
| 30 | | 70 | | 0.8 | 1.2 | 0.6 | 3.3 | 3.2 | 4.6 |
| 50 | | | 50 | 0.4 | 0.9 | 0.3 | 1.8 | 2.5 | 3.3 |

Tables 2, 3, and 4 show the strength, gas permeability, and adhesion of stone to DAGM that hardened at different temperatures and pressures. It should be noted that the strength of the vast majority of the formulations under investigation meet the requirements for light-weight and normal grouting cements (Table 2).

With increasing hardening time, the strength increases, while the gas permeability decreases in all compositions without exception, which confirms their high heat resistance and allows them to be used at high temperatures. In order to increase the rate of the strength gain at temperatures below 75°C, Portland cement can be added to the formulations.

Low gas permeability makes it possible to recommend most formulations for cementing production columns of gas wells (Table 3). One of the main causes of well flooding is insufficient contact of cement stone with casing pipes and rocks that make up the well walls.

The adhesion of the grouting stone to the boundary surface depends on many factors, the main of which is the composition of the grouting material and temperature. Reservoir pressure has little effect on adhesion [2, 5].

Analysing the results obtained (Table 4), we can note the following. As a rule, adhesion is related to the strength of the stone, and the higher the strength, the higher the adhesion. This is especially evident as exemplified by Portland cement. At temperatures up to 100°C, standard grouting stone has high adhesion to metal. At 140°C, the strength of the grouting stone decreases sharply, since it is not sufficiently heat-resistant, and the adhesion decreases accordingly [2, 5].

## 4. Conclusions

The composition of hydratation products of dolomite-ash grouting mixtures that hardened long time at high temperatures has been specified by the method of X-ray phase analysis of grouting stone. It has been established that new formations of DAGM hardening contain type CSH(B) low basicity calcium hydrosilicate, tobermorite, serpentine, type $C_3ASH_4$ tricalcium hydrosulfoaluminate and hydrogarnets. This gives grounds for predicting high heat resistance and strength of the dolomite-ash grouting stone. The absence of calcium hydroxide makes it possible to predict the stability of grouting stone in an aqueous medium and in media with high concentrations of $MgCl_2$ and $MgSO_4$.

Studies of the dependence of operational properties of the DAGM-based grouting stone on physicochemical factors, in particular, the composition of the grouting mixture, temperature, pressure and duration of hardening give grounds to establish the following: 28-day old grouting stone has strength that is, on average, 2 times higher than that of 2-day old one; DAGMs with an admixture of PZT-1-100 that hardened at t = 100 °C and 140 °C feature the highest strength; the gas permeability of DAGM-based grouting stone is within $(0.4 \div 1.9) \times 10^{-3}$ μm$^2$, which is sufficient for high-quality well insulation.

The result of the work done is the creation of the DAGM with a density of 1,540-1,820 kg/m$^3$. The basis for this development is a by-product of dolomite firing and acid fly ashes from thermal power plants. According to their performance properties, when considered comprehensively, the DAGMs developed are characterized by heat resistance, high strength, low permeability, and a wide range of density change. Using dolomite-ash grouting mixtures would ensure high quality of well fastening.

### *Symbols*

| | |
|---|---|
| *PZT-1-100* | *grouting Portland cement for moderate temperatures;* |
| *TPP* | *thermal power plant;* |
| *CAM* | *cement-ash mixture;* |
| *DPP* | *district power plant;* |
| *PB UkrSIGE* | *Poltava Branch of the Ukrainian State Institute of Geological Exploration;* |
| *AU-1-71-IE* | *autoclave installation designed by the Poltava Branch of the Ukrainian State Institute of Geological Exploration;* |
| *W/M* | *water mixture ratio;* |
| *AAk* | *acid ash of the Kurakhove District Power Plant;* |
| *AAl* | *acid ash of the Ladyzhyn District Power Plant;* |

| | |
|---|---|
| *KLST-ME* | *condensed lignosulfonate;* |
| *NTPA* | *nitrilotrimethylphosphonic acid;* |

*Designations of chemical formulas of some minerals (used in the cement processing):*

| | |
|---|---|
| *C* | *$CaO$;* |
| *S* | *$SiO_2$;* |
| *A* | *$Al_2O_3$;* |
| *H* | *$H_2O$;* |
| *(A), (B)* | *modifications of calcium hydrosilicates;* |
| *$3CaO·Al_2O_3·3CaSO_4·31H_2O$* | *ettringite (trisulfate form of the calcium hydrosulfoaluminate);* |
| *$Ca(OH)_2$* | *calcium hydroxide;* |
| *$Mg(OH)_2$* | *magnesium hydroxide.* |

**References**

[1] Orlovskyi VM, Pokhylko AM. Lightweight grouting mixtures. Mineral resources of Ukraine. 2018; 3: 42-45.
[2] Orlovskyi VM. Grouting materials that expand during hardening: a monograph Poltava, 2015. 129 p.
[3] Orlovskyi V, Malovanyy M, Biletskyi V, Sokur M. Physics-Chemical Peculiarities of Weighted Thermostable Plugging Materials Hydration Chemistry & Chemical Technology, 2021; 15(4): 599–607. https://doi.org/10.23939/chcht15.04.599
[4] Orlovskyi VM, Biletskyi VS, Desna NA, Ponomarenko NV. Heat-Resistant Backfill Materials, Expanding During Hardening Petroleum and Coal, 2021; 63(1): 8-16.
[5] Gorskyi VF. Grouting materials and solutions. Chernivtsi, 2006. 524 p.
[6] Dvorkin LY, Skrypnyk IH. Physics-chemical and physical methods for the research of building materials Rivne: National University of Water Management and Management of Natural Resources, 2006. 220 p.
[7] Bulatov AI, Shamanov SA. Methods for testing grouting materials in 2 volumes. Krasnodar: Education-South Publishers, 2002. v. 1. 340 p.
[8] Pushcharovskiy DY. Radiography of minerals. Moscow. Geoinformmark LLC, 2000. – 288 p.
[9] Nizamutdinov EA. A study of the phase composition of high-temperature cement. Science, Education and Culture, 2017; 2(5): 5-8.
[10] Agzamov FA, Izmukhambetov BS, Tokunova EF. Chemistry of grouting and flushing solutions. St. Petersburg Moscow. Nedra, 2011. 268 p.
[11] Kurdowski W. Chemia cementu i betonu Warszawa: Polski cement, 2010. 728 s.
[12] Taimasov BT, Klassen VK. Chemical engineering of binding materials. Shymkent. Belgorod, 2017. 448 p.
[13] Andreyeva NA. Chemistry of cement and binding substances. St. Petersburg: St. Petersburg State University of Architecture and Civil Engineering. St. Petersburg, 2011. 67 p.
[14] Shmitko YI, Krylova AV, Shatalova VV. Chemistry of cement and binding substances. Voronezh. State University of Architecture and Civil Engineering, 2005. 164 p.
[15] Tayor HFW. Cement Chemistry. Publisher. Thomas Telford Publishin 2nd edition, 1997. 475 p.
[16] Brykov AS. Chemistry of silicate and silica-containing binding materials. St. Petersburg, 2011. 147 p.
[17] Kuzmenkov MI, Kunitskaya TS. Binding substances and production technology based on them. Minsk, 2003. 218 p.
[18] Izotov VS, Sokolova YA. Chemical additives for concrete modification. Moscow. Paleotip Publishers, 2006. 244 p.
[19] Ovchinnikov VP, Aksyonova NA, Ovchinnikov PV. Physics-chemical processes of hardening, behaviour in the well and corrosion of cement stone. Tyumen. Tyumen State University for Oil and Gas, 2011. 368 p.

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