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Research of Expanding Tamponing Compositions for Cementing of Oil and Gas Wells

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Abstract

In the article the problem of improving the quality of demarcation of rocks and oil and gas-bearing horizons is analysed. The results of theoretical and experimental studies of expanding tamponing compositions based on mixtures of dolomite powder for mine construction (PDM) and tamponing Portland cement PCTI-100 are presented. New expanding tamponing compositions (ETC) based on mixtures of dolomite powder for mine construction of PDM and tamponing Portland cement PCTI-100 with density of 1710-1800 kg/m^3 have been developed and researched. Components: dolomite powder for mine construction (PDM), tamponing Portland cement PCTI-100. The technological properties of tamping solutions based on ETC, the technological temperature modes of ETC hardening according to the criteria of strength, adhesion, gas permeability and expansion of cement stone, and corrosion resistance in aggressive environments were determined. The selection of optimal recipes of ETC was carried out.

Keywords: *Expanding tamponing mixture; Technological properties of tamponing mixtures; Expansion of tamponing stone; Water mixture ratio; Tamponing stone; Corrosion resistance of tamponing stone.*

1. Introduction

One of the problems of tamponing oil and gas wells is improvement of quality of insulation of the borehole annulus and demarcation of layers of mine workings. Tamponing materials used in Ukraine for cementing deep oil and gas wells are prone to contraction (reduction of the volume of the system due to swelling of the substance in the solvent as a result of interaction (solvation) of the substance with the solvent) and shrinkage while hardening, which negatively affects the quality of their fastening. Taking it into account, as well as the high cost of energy-consuming tamponing cement and the scarcity of its special modifications, the task of developing new modified tamponing materials that expand during hardening is urgent. The solution to this problem is the use of man-made mineral products that contain calcium and magnesium oxides.

The purpose of the conducted researches is to create new expanding tamponing compositions with high operational properties. The use of man-made mineral materials will also ensure a reduction in the cost of tamponing compositions and, accordingly, tamponing works in wells.

In Ukraine, special expanding tamponing materials are not produced by the industry, so research and development of new tamponing materials were carried out in this direction. The Poltava branch of the Ukrainian State Geological Survey Institute (UkrDSGSI) has developed tamponing materials expanding during compression.

Among the developments are clinker-free ash mixtures (AM) based on high-calcium ash from burning of Baltic oil shales at TPPs and acidic fly ashes from burning of hard coal at thermal power plants (TPPs). Such tamponing mixtures expand while hardening [1-2]. Their main advantages are expansion of tamponing stone, increased thermal corrosion resistance of stone, as well as low cost of the tamponing material.

A group of researchers of the UkrDSGSI headed by Krykha developed and researched tamponing materials based on mixtures of Portland cement and high-calcium ash of Baltic oil shales [1]. Such tamponing materials have high operational properties, in particular, they expand when pressed, the tamponage stone can withstand temperatures of 90-100°C.

At the end of the 20th century, the Poltava branch of UkrDSGSI developed dolomite-ash tamponing mixtures (DATM) with density of 1565-1815 kg/m^3, which expand while hardening [3].

Another development in the field of expanding tamponing materials was lime-ash tamponing mixtures (LATM), which include lime and acid ash removed from TPPs. They expand while hardening at temperatures of 75–140°C and have density of 1450–1780 kg/m^3 [4].

All the mentioned tamponing materials are currently not used in Ukraine due to technical, economic and logistical reasons. The goal of this work is to create expanding tamponing compositions (ETC) with high operational properties. To achieve this goal, the following research tasks are set:

– study of the technological properties of the tamponing solution of compositions based on mixtures of dolomite PDM powder and PCTI-100 tamponing Portland cement mixed with technical water;
– study of the dependence of the technological properties of tamponing stone compositions based on mixtures of dolomite PDM powder and tamponing Portland cement PCTI-100, mixed with technical water, on physicochemical factors, in particular, the composition of the tamponing mixture, temperature and pressure;
- study of the technological properties of tamponing stone based on mixtures of dolomite PDM powder and tamponing Portland cement PCTI-100 mixed with salt solutions.

2. Experimental (methods and materials)

The density of the powder was determined by the pycnometric method, and the external specific surface was determined by Tovarov's method on the PSKh-2 device [2-3, 5-6]. The fractional (granulometric) composition of PDM was determined by sieve analysis [3, 5-6]. Tamponing solutions were mixed in a standard way according to [1-2, 7] using water from the water supply network or salt solutions, which amount was taken according to the required water-to-mixture ratio (W/M)

The water mixture ratio was determined based on the regulated spreadability of tamponing solutions by the standard [7], using the KR-1 cone [1,5-6]. According to the standard, the spreading of tamponing solutions should be within 0.18 - 0.22 m on the spreading circle. The properties of tamponing solutions, in particular, fluidity, sedimentation resistance, density, pumpability were determined according to standard methods [2-3,6-7].

Samples were autoclaved according to the method described in [1-2,6]. Samples of tamponing stone were formed in the form of cylinders with a height and diameter of 3 cm. The mechanical strength of the tamponage stone was measured on the PSU-10 hydraulic press (error ±0.25 MPa) [2-3,6-7].

Adhesion of tamponing stone to metal was determined using a special device [3]. The expansion of tamponing mixtures during hardening was studied using an attachment to the KC-3 consistometer [4]. This technique allows measuring the increase in the volume of tamponing material in conditions simulating reservoir conditions of the well, at the corresponding pressure and temperature during the experiment. This is very important, based on the fact that an increase in pressure from normal to 20 MPa leads to the inhibition of expansion several times, and sometimes to its complete cessation.

The gas permeability of the tamponing stone was studied at the GK-5 installation according to the methodology [1-2,4,6]. The corrosion resistance of the tamponing material was studied in terms of sulphate and magnesium corrosion and leaching corrosion. A coefficient equal to the ratio of strength of samples stored in the aggressive environment to the strength of analogues that hardened in water for the corresponding periods was taken as the main criterion of stability [1,4].

3. Results and discussion

We will describe the materials and reagents used in the development of expanding tamponing compositions for cementing oil and gas wells. Dolomite powder for mine construction (PDM) is a finely dispersed powder, with a fractional composition close to tamponing Portland cement. PDM has a density in the range of 2900-3000 kg/m^3 and a specific surface from 270 to 370 m^2/kg. Granulometric composition according to the results of sieve analysis. The balance on the sieve, %: 1 mm – 0; 0.5 mm – 0; 0.25 mm – 0.5; 0.16 mm – 0.7; 0.05 mm – 16.5.

Chemical composition by oxides: CaO – from 38.3 to 45.8%; MgO – from 22.1 to 27.8%; SiO_2 – from 3.1 to 6.4%; R_2O_3 – from 2.6 to 4.1%; l.m.c. ($CaMgCO_3$, $CaCO_3$) – from 20.0 to 30.2%. PDM is issued in accordance with the technical specifications for this product.

Tamponing Portland cement for moderate temperatures PCTI-100 is produced according to DSTU B V.2.7-88-99 Tamponing Portland cements. Technical specifications [8]. NTPHA - nitrilotrimethylphosphonic acid - retarder of thickening and hardening of tamponing solutions. TTA - tartaric acid - retarder of thickening and hardening of tamponing solutions.

In the process of researching tamponing solutions based on new expanding tamponing compositions (ETC) based on mixtures of dolomite PDM powder and tamponing Portland cement PCTI-100, the following technological properties were obtained, Table 1.

Table 1. Technological properties of tamponing solutions based on ETC.

Composition of tamponing mixture of parts by mass к %		V/C	Density, kg/m^3	Mobility, m	Water separation, mL	Pumpability, hour-min	
PDM	PCTI-100					t=75°C P=30 MPa	t=75°C P=40 MPa
30	70	0.55	1800	0.19	3.75	3-30	4-00
40	60	0.55	1790	0.20	6.25	3-40	4-00
50	50	0.60	1750	0.22	11.25	4-00	4-00
60	40	0.60	1730	0.23	10.0	4-10	4-00
70	30	0.60	1710	0.24	8.75	4-35	4-00

The analysis of the obtained experimental studies of the technological properties of tamponing solutions based on ETC shows that they have satisfactory technological parameters of mobility and water separation, which correspond to DSTU B B.2.7-88-99.

The pumpability of ETC is regulated using standard retarders [9]. In particular, from 0.05 to 0.20% of thickening and hardening retarder NTPHA was added to the researched formulations based on the mass of dry material, depending on the temperature conditions and the quantitative content of tamponing Portland cement PCTI-100.

The water separation of the main formulations of ETC approximately corresponds to the water separation of standard tamponing Portland cement PCTI-100 with V/C = 0.5.

The results of research of technological properties of tamponing stone based on ETC are given in Table 2. Compared to standard tamponing Portland cement PCTI-100, in similar conditions, the adhesion force of ETC increases by 1.2-1.6 times.

ETC-based stone has low gas permeability (from 0 to 0.3 μm^2 ×10^{-3}), and its value decreases with an increase in the hardening time of the tamponing stone. While hardening, ETC expands in the range from 0.7 to 2.2%. When studying the expansion process, the following regularities were revealed:

- expansion increases in the temperature range from 75 to 100°C;
- when the content of PDM in the mixture decreases from 70 to 50%, the expansion also increases;
- the amount of the retarder input does not significantly affect the absolute value of the expansion;
- the main percentage of ETC expansion occurs when the system is in a visco-plastic state and the crystallization structure just begins forming, which is very important, since the destruction of stone is excluded. Therefore, the absolute value of the volume increase is small (up to 2.2%) [1].

Table 2. Technological properties of tamponing stone based on ETC.

Composition of tamponing mixture of parts by mass %		V/C	Admixture of NTPHA, part by mass % from the mass of dry material	Strength for compression in 2 days, MPa		Adhesion through metal in 2 days, MPa		Expansion, %	
PDM	PCTI-100			t=75°C P=30 MPa	t=100°C P=40 MPa	t=75°C P=30 MPa	t=100°C P=40 MPa	t=75°C P=30 MPa	t=100°C P=40 MPa
50	50	0.6	0.02	9.8		3.9		1.0	
			0.10		9.3		4.5		2.2
60	40	0.6	0.02	10.1		4.3		0.9	
			0.10		10.5		5.0		1.7
70	30	0.6	0.02	13.0		4.8		0.7	
			0.10		9.4		5.3		1.1

The analysis of data shows that the tamponing stone based on ETC has satisfactory physical and mechanical properties and heat resistance at temperatures up to 100°C. This is confirmed by strength data. Adhesion to metal is in the range from 3.9 to 5.3 MPa, and its value increases when the content of the PDM component in the mixture increases.

The expansion mechanism is due to the transformation of free calcium and magnesium oxide into hydroxides with an increase in their volume. The results of research of the corrosion resistance of the stone based on ETC are shown in Table 3. They show that when stored in water for a year, the strength of the stone gradually increases, and the absolute indicators are higher in the formulations with the ratio of PDM: PCTI-100=50:50.

Table 3. Dependence of the resistance coefficient on the type of corrosion.

Composition of tamponing mixture		Strength for compression, MPa				Resistance coefficient (K)					
			in fresh water			in 5 % solution *MgCl₂*			in 5 % solution *MgSO₄*		
PDM	PCTI-100	initial	1 mon.	6 mon.	12 mon.	1 mon.	6 mon.	12 mon.	1 mon.	6 mon.	12 mon.
50	50	8.2	8.2	11.6	13.9	1.00	0.83	0.76	1.14	0.28	0.50
60	40	6.1	6.1	8.2	9.3	0.96	0.82	0.88	0.96	0.79	0.88
70	30	5.7	5.7	7.0	8.2	1.11	0.85	1.00	1.13	1.18	1.00

We will analyse the corrosion resistance of ETC-based stone in aggressive environments. Despite the stable strength indicators of the tamponing stone, which was in a 5% $MgCl_2$ solution, a decrease in the stability coefficient (K) is observed in the formulation of PDM:PCTI-100=50:50, and in the recipe with the ratio of PDM : PCTI-100=70:30 stability coefficient (K) is maximum.

Such a tendency is even more pronounced in case of sulphate corrosion. This can be explained by the significant presence in the stone with a high Portland cement content of $Ca(OH)_2$, $3CaO{\cdot}Al_2O_3$, which react with $MgCl_2$ and $MgSO_4$ according to the schemes [10-16]:

$$MgCl_2 + Ca(OH)_2 = CaCl_2 + Mg(OH)_2 \quad (1)$$

In this case, due to the very low solubility of *$MgOH_2$*, the reaction comes to an end:

$$\mathrm{MgSO_4 + Ca(OH)_2 + 2H_2O = Mg(OH)_2 + CaSO_4 \cdot 2H_2O} \quad (2)$$ and in future

$$3CaO \cdot Al_2O_3 + 3CaSO_4 + 32H_2O = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \quad (3)$$

and, as is known, the volume of the formed ettringite exceeds the initial volume of the binding material by more than 2 times, and therefore the destruction of the stone occurs [15-18].

One of the main reasons for the poor fastening of wells in intervals of salt deposits is related to dissolution of salts in the water of mixing the tamponing material during its hardening. As a result, a channel filled with liquid is formed between the wall of the well and the cement ring.

In order to partially avoid this negative phenomenon, it is necessary to use tamponing materials mixed with solutions of salts similar to the type of layer mineralization, and the salt concentration should be as high as possible under the given conditions.

Halite (*NaCl*), sylvine (*KCl*), bischofite ($MgCl_2{\cdot}6H_2O$) and others are among the most characteristic minerals of salt deposits [19-21]. With this in mind, the composition of the mixing liquid for ETC was selected during the research.

The research results, given in Table 4, show that to ensure the necessary mobility of tamponing solutions based on ETC, mixed with potassium chloride and bischofite solutions, it is necessary to introduce a plasticizer.

Table 4. Technological properties of expanding tamponing mixtures mixed with salt solutions.

Composition of tamponing mixture, parts by mass %		Mixing liquid (slat solution)	Retarder, % from mass of dry tamp. material.		Mobility, m	Hardening terms, h-min at t=75°C P=0.1 MPa		Pumpability, h-min t=100°C, P=40 MPa	Strength at compression, MPa , in 2 days	
PDM	PCTI-100		NTPHA	TTA		start	end		t=75°C P=30 MPa	t=100°C P=40 MPa
70	30	10 % solution *NaCl*	–	–	0.185	2–05	2–40	1–10	11.7	15.0
70	30	20 % solution *NaCl*	–	–	0.190	2–30	3–05	1–40	11.0	14.3
70	30	Saturated solution *NaCl*	–	–	0.200	3–15	4–15	1–55	9.8	13.0
50	50	10 % solution *NaCl*	–	–	0.190	1–45	2–20	1–00	14.5	16.6
50	50	20 % solution *NaCl*	–	–	0.200	2–10	3–05	1–25	13.9	14.9
50	50	Saturated solution *NaCl*	–	–	0.210	3–00	3–45	1–40	9.8	12.0
70	30	10 % solution *KCl*	0.02	–	0.195	4–00	5–50	–	12.1	–
70	30	10 % solution *KCl*	0.10	–	0.195	–	–	4–00	–	10.0
70	30	Saturated solution *KCl*	0.02	–	0.195	3–30	4–30	–	7.6	–
70	30	Saturated solution *KCl*	0.10	–	0.195	–	–	3–45	–	8.5
50	50	10 % solution *KCl*	0.02	–	0.205	3–40	4–20	–	12.1	–
50	50	10 % solution *KCl*	0.10	–	0.210	–	–	4–00	–	10.0
50	50	Saturated solution *KCl*	0.02	–	0.200	3–00	3–40	–	13.0	–
50	50	Saturated solution *KCl*	0.10	–	0.205	–	–	4–10	–	12.1
70	30	10 % bischofite solution	–	0.10	0.185	4–00	5–00	–	8.9	–
70	30	10 % bischofite solution	–	0.25	0.195	–	–	4–05	–	8.0
70	30	20 % bischofite solution	–	0.10	0.180	3–30	4–30	–	6.3	–
70	30	20 % bischofite solution	–	0.25	0.185	–	–	3–20	–	6.1
50	50	10 % bischofite solution	–	0.10	0.195	3–30	4–05	–	9.3	–
50	50	10 % bischofite solution	–	0.25	0.205	–	–	4–00	–	8.9
50	50	20 % bischofite solution	–	0.10	0.185	3–00	3–30	–	7.1	–
50	50	20 % bischofite solution	–	0.25	0.195	–	–	2–55	–	6.5

* *amount of mixing liquid in all recipes is 60% of the mass of dry material*

ETC mixed with sodium chloride solutions have satisfactory mobility. As plasticizers, reagents NTPHA (for recipes mixed with KCl) and TTA (for recipes mixed with bischofite solutions) were used [9]. At the same time, these reagents simultaneously perform the function of retarders of thickening and hardening for mineralized tamponing solutions.

Increasing the concentration of *NaCl* from 10% to the saturated solution somewhat slows down the processes of structure formation. When KCl concentration in the solution increases, the mobility of the solution does not significantly decrease. The maximum possible concentration of bischofite in the mixing water of the tamponing material is 25%. Further increase in its concentration leads to unregulated structuring of the system and loss of pumpability after only 20-40 minutes.

Stone based on ETC mixed with salt solutions has satisfactory physical and mechanical properties. In particular, the strength of the KCl (NaCl) mounting stone increases by 1.1-1.3 times compared to similar formulations mixed in fresh water. There is also a slight drop in strength in ETC with a concentration of 10% bischofite in the mixing water. When the bischofite concentration increases up to 20%, the strength drops down to 30%.

It should be noted that the introduction of salts into the tamponing solution based on ETC leads to a decrease in the absolute value of the expansion during the hardening process compared to similar formulations mixed with fresh water. In particular, the volume reduction in ETC mixed with KCl and bischofite solutions is 0.5-1.0%, and with NaCl solutions – up to 0.5%.

4. Conclusions

Fulfilled researches of the technological properties of the tamponing solution based on mixtures of dolomite PDM powder and tamponing Portland cement PCTI-100 have shown that such solutions have satisfactory technological properties (mobility, water separation), and the terms of their thickening and hardening are regulated by standard retarders.

Study of the dependence of the technological properties of tamponing stone based on mixtures of dolomite PDM powder and tamponing Portland cement PCTI-100 on physicochemical factors, in particular, the composition of the tamponing mixture, temperature, pressure during compacting, provides grounds for establishing that the tamponing stone has satisfactory physical and mechanical properties, high adhesion to metal (1.2 - 2.0 times greater than that of PCTI-100 tamponing Portland cement) and low gas permeability.

The study of the amount of expansion of tamponing stone based on mixtures of dolomite PDM powder and tamponing Portland cement PCTI-100 found that the amount of expansion is in the range from 0.7 to 2.7%, and the expansion process ends before the formation of a rigid structure, which excludes the destruction of the stone from internal stresses.

The study of the corrosion resistance of the tamponing stone based on mixtures of dolomite PDM powder and tamponing Portland cement PCTI-100 established that the tamponing stone has corrosion resistance in aggressive environments.

The study of the technological properties of tamponing stone based on mixtures of dolomite PDM powder and tamponing Portland cement PCTI-100 mixed with salt solutions, which are intended for cementation in chemogenic sediments, showed that such tamponing materials have high technological properties of the strength of tamponing stone.

The implementation of this development will allow improving the quality of separation of layers in the well and reducing the costs of tamponing materials.

Symbols

PDM	*dolomite powder for mine construction;*
PCTI	*100 – tamponing Portland cement for moderate temperatures;*
ETC	*expanding tamponing composition;*
AM	*ash mixture;*
TPP	*thermal power plant;*
PV UkrDSGSI	*Poltava branch of the Ukrainian State Geological Exploration Institute;*
DSTU	*State Standard of Ukraine;*
DATM	*dolomite-ash tamponing mixtures;*
PSU-10	*hydraulic press;*
LATM	*lime-ash tamponing mixtures;*
W/M	*water mixture ratio;*
W/C	*water-cement ratio (analogy with water-mix ratio);*
l.m.c.	*loss of mass during calcination;*
R_2O_3	*simple metal oxides;*

NTPHA	*nitrilotrimethylphosphonic acid - retarder of thickening and hardening of tamponing solutions;*
TTA	*tartaric acid - retarder of thickening and thickening of tamponage solutions.*

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