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Research on Tartaric Acid as a Retardant of the Solidification Process of Well-Well Packing Solutions

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Abstract

This study explores the development of an effective retarding reagent for solidifying (thickening) well-packing solutions used in the cementing process of deep oil and gas wells. This research investigates the handling ability of packing cement with TA additives in environments that simulate reservoir conditions. The main aim is to identify and evaluate an effective retarding agent for solidifying (thickening) well-packing solutions. The retardant for solidifying (thickening) well-packing solutions under consideration should meet the following requirements: a broad operating temperature range, cost-effectiveness, and environmental friendliness.

Keywords: *Well-packing solution; Handling ability of well-packing solutions; Rheological properties; Solidification retardants.*

1. Introduction

It is essential to explore the potential use of specific chemical industry products as reagents for the oil and gas sector, given the limited range of reagents available for controlling the pumping time of well-packing solutions. Key properties of well-packing solutions that require controlling include pumping time (pumpability), flowability, and rheological characteristics (plastic viscosity, dynamic shear stress). The hardened stone formed during solidification of the well-packing solution must exhibit high stress-strain performance and low permeability.

The research [1] has identified and characterised various known solidification retardants that create protective films around cement particles in solidification solutions, preventing hydration hardening. The characteristics and grouping of certain retardants based on their chemical structure are also discussed in studies [2–8].

The main groups of solidification retarders for well-packing solutions include oxy-amino carboxylic acids and their salts; sugars; borates, phosphates; lignin derivatives; natural tannin products; humates; polysaccharide derivatives; vinyl and acrylic polymer-based products and others [1–8]. The first six groups also function as plasticising diluents for well-packing solutions.

According to literature sources [9], reagents containing hydroxylic and carboxylic groups, as well as sulpho-, amido- and amino- groups, belonging to mono- and dibasic carboxylic acids, sulfonic acids, amines, low-molecular amides, mono-, di- and triatomic aliphatic alcohols, have little effect on the solidification time of cement solutions.

Increasing the degree of polymerisation of organic compounds enhances their retarding effect on the solidification time of well-packing solutions [1].

Among chemical compounds, promising solidification retardants for well-packing solutions may include polyatomic polyphenols, dibasic aliphatic oxy acids with at least two COOH groups, mono- and dibasic cyclic oxy acids with at least three hydroxyl groups, cyclic oxysulfonic acids with a total of at least three sulfo- and hydroxyl groups per benzol, naphthalene, or other cyclic core [1].

More recent classifications of solidification retardants of well-packing solutions introduce an additional group: organic phosphonic complexing agents. This group includes, in particular, oxyethylidenediphosphonic acid (OEDP) and nitrilotrimethylphosphonic acid (NTP) [9-10].

Currently, there is no clear consensus on the effectiveness of certain additive reagents in well-packing solutions. To better understand how chemical compounds influence well-packing solutions and cement stone, we conducted a study on tartaric acid (TA), which controls the solidification (hardening) time.

The research goal is to explore the potential of tartaric acid (TA) as a retarding reagent for the solidification process of well-packing solutions used in oil and gas well cementing. To achieve this goal, the following research objectives were set:

– investigate the handling ability of well-packing solutions containing tartaric acid (TA), particularly the effect of TA on rheological properties of well-packing solutions (plastic viscosity and dynamic shear stress);
– assess the impact of TA on the handling ability of well-packing stone, specifically on its strength and stone-to-metal adhesion.

2. Methods and materials

The well-packing solutions were prepared under laboratory conditions using a standard method, mixing with faucet water in a paddle mixer at a shaft rotation speed of 1500 ± 100 min^{-1}. The amount of water was determined according to a water-to-cement ratio (W/C).

The flowability of well-packing solutions was determined using standard procedures (DSTU B V.2.7-86-99 Well-Packing Cement. Test Methods) [11]. The pumping time (pumpability), simulating the reservoir temperature and pressure conditions, was measured using a KTs-3 consistometer [1, 12]. The rheological properties of well-packing solutions were evaluated with a REOTECT-2 rotational viscosimeter [1, 13-14].

Well-packing stone samples were formed in cylindrical moulds with a diameter of 0.03 m and height of 0.03 m. These moulds were grouped according to the operating volume of the autoclaves, and placed in a pre-heated environment.

The solidification and curing of the stone samples was performed in conditions simulating reservoir temperature and pressure, using an autoclave system AU-1-71-IE developed by the Poltava Department of Ukrainian State Geological Survey Institute (USGSI). The system consists of autoclaves, electrical and hydraulic connections, and instruments to monitor and record temperature and pressure in the autoclaves. The system operates at temperatures up to 523 K and pressures up to 100 MPa (temperature fluctuation ± 5°C, pressure fluctuation ± 2 MPa). The temperature and pressure are automatically controlled [1, 15–17].

The mechanical strength of the well-packing stone was tested using a PSU-10 laboratory press (measurement accuracy ± 0.25 MPa) [1, 9, 12, 15, 17].

The adhesion of the well-packing stone to metal was tested using the PSU-10 laboratory press with an attachment for pushing a rod through the cement stone, formed under certain thermodynamic conditions (temperature, pressure) [12, 18].

The following binding materials and reagents were used in the study. Well-packing moderate heat Portland cement for moderate temperatures MHPC-100 and mixtures of MHPC-100 acidic ashes from Kurakhove and Ladyzhyn SDPPs. The MHPC well-packing moderate heat Portland cement is produced in Ukraine in accordance with the DSTU B V. 2.7-88-99 Well-Packing Portland cement. Technical Specifications [19].

Kurakhove SDPP ash is a fine dark-grey powder with a density of 1950–2050 kg/m^3 and a specific surface area of 350–400 m^2/kg. The chemical composition of Kurakhove ash 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; LoI – 3.4–3.7.

Ladyzhyn SDPP ash is a fine greenish-grey powder with a density of 2300–2500 kg/m^3 and a specific surface area of 230–250 m^2/kg. The chemical composition of Ladyzhyn ash by oxides, %: SiO_2 – 50.0–55.0; 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; LoI – 5.1–5.4.

Tartaric acid (TA) is an organic compound classified as a 2-basic carboxylic acid. Its salts and anions are known as tartrates (HOOC-CH(OH)-CH(OH)-COOH). The tartaric acid is produced from calcium tartrate and appears as white, crystalline, hydroscopic powder that is fully soluble in water. TA has a solubility of 150 g in 100 mL of distilled water at 25°C. Its molar mass is 150.1 g/mol, and TA density is 1760 kg/m^3 [20-21].

This study focused on handling ability of well-packing stone and solutions with TA retardant additives. The binding materials used included well-packing moderate heat Portland cement from Zdolbuniv Plant (MHPC-100) and mixtures of MHPC-100 acidic ashes from Kurakhove and Ladyzhyn SDPPs, respectively.

3. Results and discussion

The variables used in this study included: the composition of well-packing mixture (mass fractions of cement MHPC-100 and ashes AA_K, AA_L), the addition of tartaric acid, water-to-cement ratio (W/C). We monitored the following properties of the well-packing solution: flowability, plastic viscosity, dynamic shear stress. Table 1 shows the results of the study on how the TA reagent affects well-packing solutions.

Table 1. Handling characteristics of well-packing solutions containing the TA retardant.

Well-packing mixture composition (mass fraction, %)			TA (mass fraction % from the well-packing mixture mass)	W/C	Flowability of the well-packing solution, m	Plastic Viscosity of the well-packing solution, Pa·s	Dynamic shear stress of the well-packing solution, Pa
MHPC-100	AA_K	AA_L					
100	–	–	–	0.50	0.190	0.068	13.7
100	–	–	0.2	0.50	0.210	0.040	4.6
100	–	–	0.3	0.50	0.220	0.039	4.4
50	50	–	0.4	0.50	0.215	0.049	5.8
50	50	–	0.5	0.50	0.230	0.036	3.7
50	50	–	–	0.55	0.180	0.060	11.5
50	50	–	0.2	0.55	0.190	0.032	1.3
50	50	–	0.4	0.55	0.185	0.054	1.0
50	50	–	0.5	0.55	0.185	0.040	0.8
60	40	–	–	0.55	0.185	0.082	14.7
60	40	–	0.2	0.55	0.195	0.041	1.5
60	40	–	0.5	0.55	0.190	0.033	0.8
50	–	50	–	0.45	0.180	0.072	19.2
50	–	50	0.2	0.45	0.195	0.069	3.7
60	–	40	0.4	0.45	0.200	0.067	2.7
60	–	40	0.5	0.45	0.200	0.061	2.2
60	–	40	–	0.45	0.190	0.072	14.1
60	–	40	0.2	0.45	0.220	0.034	4.0
60	–	40	0.5	0.45	0.215	0.035	4.6
60	–	40	–	0.50	0.205	0.044	10.3
60	–	40	0.2	0.50	0.225	0.029	1.1

From Table 1, we can observe that the TA reagent has plasticising properties. It increases the flowability of well-packing solutions and reduces the rheological properties (plastic viscosity and dynamic shear stress). When the TA reagent is added, plastic viscosity (η) decreases by 1.5–2.12 times, and dynamic shear stress (τ) drops by 0.8–14.3 times. As the amount of the TA reagent increases in the well-packing solution, the rheological properties worsen.

Figure 1 and 2 show the graphs of rheological properties of well-packing solutions with TA additives. A significant reduction in dynamic shear stress lowers the point at which the well-packing solution changes from laminar flow to a turbulent one in the bore hole annulus, ensuring better replacement of the flushing fluid with the well-packing solution.

Pumpability is one of the key properties of well-packing solutions, as it indicates their suitability for well-packing under the pressure and temperature conditions of deep wells.

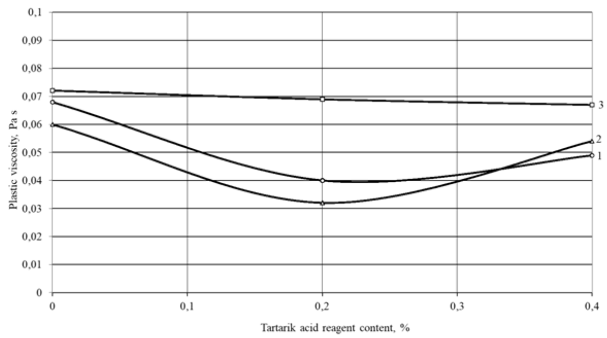

Figure 1. Plastic viscosity vs. TA reagent content in well-packing solutions. 1–MHPC-100, W/C=0.5; 2–MHPC-100: AA_K–50:50, W/C=0.55; 3– HPC-100: AA_L–50: 50, W/C= 0.45.

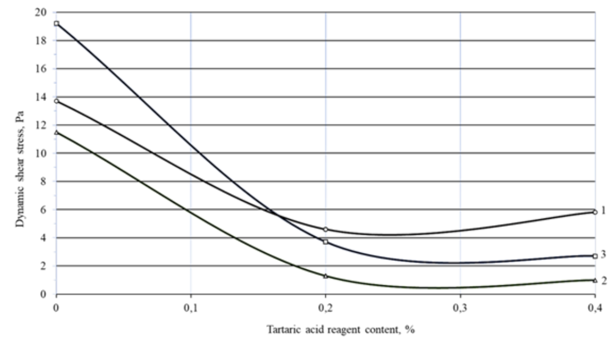

Figure 2. Dynamic shear stress vs. TA reagent content in well-packing solutions. 1–MHPC-100, W/C=0.5; 2–MHPC-100: AAK–50:50, W/C=0.55; 3–MHPC-100: AAL–50:50, W/C 0.45.

Table 2 shows the results of the study on the pumpability of well-packing solutions with TA additives at temperatures 75°C, 120°C, and 150°C.

Table 2. Pumping time (pumpability) of well-packing solutions with the TA retardant.

Well-packing mixture composition (mass fraction, %)			TA (mass fraction % from the well-packing mixture mass)	Pumpability of well-packing solutions, h.- min.		
MHPC-100	AA_K	AA_L		*t*=75 °C *P*=30 MPa	*t*=120 °C *P*=60 MPa	*t*=150 °C *P*=80 MPa
100	–	–	–	1-05	–	–
100	–	–	0.2	4-00	–	–
100	–	–	0.3	> 4-00	–	–
100	–	–	0.4	> 4-00	–	–
100	–	–	0.5	> 4-00	–	–
50	50	–	–	1-40	–	–
50	50	–	0.2	> 4-00	3-10	1-20
50	50	–	0.4	> 4-00	> 4-00	3-10
50	50	–	0.5	> 4-00	> 4-00	4-15
50	–	50	–	1-20	–	–
50	–	50	0.2	> 4-00	2-35	1-10
50	–	50	0.4	> 4-00	> 4-00	2-45
50	–	50	0.5	> 4-00	> 4-00	4-00
60	40	–	0.4	–	> 6-00	3-05
60	–	40	0.4	–	> 6-00	2-50

The study found that the optimal amount of the TA reagent is 0.2–0.5% (by mass) of the dry well-packing material. Increasing the amount of reagent additive beyond this unpractical.

The thermal limit for the TA reagent is 155°C when added at 0.6%.

When cementing casing columns between salt and inter-salt layers, to ensure quality isolation of the bore hole annulus, well-packing materials should be mixed with the corresponding salt solutions. The most common minerals found in salt deposits include halite (NaCl), sylvine (KCl), bischofite ($MgCl_2 \cdot 6H_2O$), among others.

Table 3 presents the results of the study on the effect of the TA reagent on the handling ability of well-packing solutions mixed with aqueous salt solutions.

Table 3. Handling ability of well-packing solutions mixed with aqueous salt solutions containing the TA retardant

Well-packing mixture composition (mass fraction, %)		TA (mass fraction % from the well-packing mixture mass)	Water mixing warehouse	W/C	Flowability of the well-packing solution, m	Pumpability of well-packing solutions, h.-min.	
MHPC-100	AA_K					t=80°C P=30 MPa	t=100°C P=40 MPa
50	50	–	fresh water	0.57	0.190	1-50	0-55
50	50	0.25	fresh water	0.57	0.210	>4-00	4-05
50	50	0.25	10% NaCl	0.57	0.210	4-00	3-10
50	50	0.25	20% NaCl	0.57	0.220	>4-00	4-00
50	50	0.25	saturated solution NaCl	0.57	0.220	>4-00	>4-00
50	50	0.25	10% KCl	0.57	0.225	>4-00	3-10
50	50	0.25	saturated solution KCl	0.57	0.225	4-00	2-45
50	50	0.40	saturated solution KCl	0.57	0.220	>4-00	4-00
50	50	0.25	10% bischofite	0.57	0.195	4-00	3-40
50	50	0.25	20% bischofite	0.57	0.180	1-10	–
50	50	0,25	10% KCl 10% bischofite	0.57	0.205	4-00	4-00
60	40	–	fresh water	0.57	0.200	1-30	0-45
60	40	0.25	saturated solution NaCl	0.57	0.230	>4-00	3-50
60	40	0.25	saturated solution KCl	0.57	0.230	>4-00	2-25
60	40	0.25	10% bischofite	0.57	0.185	4-00	3-05

The results demonstrate that in well-packing mixtures with low concentrations of NaCl (up to 10% in the mixing water), the pumping time slightly decreases. In this case, more retardant is needed. Increasing the NaCl concentration up to the saturation state increases the flowability of the well-packing solution and extends its pumping time. In well-packing mixtures with varying concentrations of KCl, the pumping time decreases. In this case, more retardant is required.

The most difficult well-packing mixtures to control are those based on bischofite solutions. Adding 10% bischofite reduces the flowability of the well-packing solution. Adding the TA reagent helps maintain normal flowability and sufficient pumping time at temperatures up to 100°C. When the bischofite concentration increases to 20%, achieving the required handling ability becomes impossible.

Similar results were found when studying the properties of well-packing solutions based on MHPC-100 with acidic ash from Ladyzhyn SDPP mixed with salt solutions. Table 4 provides the main technological properties of well-packing stone containing the TA reagent.

From Table 4, we can observe that well-packing materials with 0.2–0.4% TA of the dry material's mass (the amount of the additive reagent is determined by the required pumping time at temperatures of 100°C and 120°C, respectively) achieve high strength after 2 days of solidifying at 100°C. The strength development is somewhat slower at 75°C.

The addition of TA does not significantly reduce the adhesion of the well-packing stone to metal.

When using the TA reagent for well-packing casing columns longer than 1000 m (with the temperature difference greater than 30°C at cementing point), there is no need to prepare multiple batches of well-packing mixture with different amount of retardant.

Table 4. Technological properties of well-packing stone containing the TA retardant

Well-packing mixture composition (mass fraction, %)			TA (mass fraction % from the well-packing mixture mass)	W/C	Strength of well-packing stone under compression, MPa through				Adhesion of the well-packing stone to metal, MPa through		
					2 days	7 days	2 days		2 days		
MHPC-100	AA_K	AA_L			*t*=75 °C *P*=40 MPa		*t*=100°C *P*=60MPa	*t*=120°C *P*=80MPa	*t*=75°C *P*=40MPa	*t*=100°C *P*=60MPa	*t*=120°C *P*=80MPa
100	–	–	–	0.50	12.1	16.1	15.1	–	3.3	5.3	–
100	–	–	0.2	0.50	5.4	20.9	18.2	–	1.5	5.9	–
50	50	–	–	0.55	11.7	16.5	17.3	18.7	3.0	8.0	8.2
50	50	–	0.2	0.55	0.8	16.1	16.6	19.5	–	5.0	7.0
50	50	–	0.4	0.55	–	12.8	19.5	22.0	–	6.4	7.6
60	40	–	–	0.55	13.5	17.0	18.8	23.1	4.4	7.5	7.7
60	40	–	0.2	0.55	2.0	16.4	18.0	25.0	–	6.1	6.0
60	40	–	0.4	0.55	–	15.0	17.4	21.3	–	6.0	6.8
50	–	50	–	0.45	18.4	22.7	21.4	31.5	2.5	4.8	5.9
50	–	50	0.2	0.45	4.1	23.8	19.5	27.8	1.3	6.1	6.2
50	–	50	0.4	0.45	–	10.9	15.0	16.7	–	3.4	5.8
60	–	40	–	0.45	19.9	20.8	19.8	24.8	3.7	6.1	6.8
60	–	40	0.2	0.45	6.0	23.1	20.5	21.1	0.2	5.2	7.4
60	–	40	0.4	0.45	–	15.8	20.1	23.2	–	4.8	6.0

4. Conclusions

Research on the technological properties of well-packing solutions has shown that the TA reagent is an effective industrial retardant for well-packing solutions, slowing the solidification process at temperatures up to 150°C. The reagent also reduces the rheological properties of well-packing solutions (plastic viscosity and dynamic shear stress). Depending on the reservoir conditions, the optimal dosage of the TA additive ranges from 0.2 to 0.5% of the dry mass of the well-packing material.

The studies on the TA's impact on well-packing stone properties indicate that the TA reagent slows down cement hydration at the early-stages of solidification. The reagent does not hinder the development of the well-packing stone properties (strength, adhesion) during the 48-hour solidification period. Cement stone with the TA additives maintains high stress-strain performance.

The authors suggest that a promising direction for further research is exploring how the TA reagent influences the properties of well-packing solutions and cement stone in multi-component composite well-packing materials, creating a dense cement stone resistant to chemogenic deposits, which is particularly relevant for large deep wells (4–7 km), where oil and gas reserves have been identified in the Dnieper-Donets Rift (Ukraine).

Symbols

TA – tartaric acid;
DSTU – State Standard of Ukraine;
PD USGSI – Poltava Department of Ukrainian State Geological Survey Institute;
SDPP – state district power plant;
LoI – Loss on Ignition;
MHPC-100 – well-packing moderate heat Portland cement;
AA_K – acidic ash from Kurakhove SDPP;
AA_L – acidic ash from Ladyzhyn SDPP;
W/C – water-to-cement ration.

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