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THE INFLUENCE OF SELECTED LIQUEFIERS ON THE RHEOLOGICAL PARAMETERS OF CEMENT SLURRIES**

1. INTRODUCTION

The growing depth of wellbores, as well as differing geological, hydrogeological conditions and physicochemical and mechanical properties of the rock mass, pose more challenging tasks to engineers who design the process of rock mass sealing.

The efficiency of sealing and reinforcing rocks depends on providing the appropriate parameters of sealing slurries, and also using the proper technology for making and injecting to the rock mass or annular space between the wellbore wall and the casing column.

Providing efficient sealing of the casing in a wellbore greatly depends on the degree to which the drilling mud is displaced in the annular space by sealing slurry in the course of sealing [1, 4, 8].

Apart from the character of flow, the efficiency of displacement of drilling mud with the sealing slurry depends on the following factors [2, 10, 11, 13]:
– rheological properties of technological fluids, drilling mud, sealing slurry, displacement fluid),
– specific weight of drilling mud and sealing slurry,
– use of buffer fluids between sealing slurry and drilling mud,
– coaxiality of the casing column in a wellbore,
– moving casing in the course of sealing,
– use of scrapers.

The aim of the work described in this paper was a comparison of the operation of I, II and III generation liquefiers.

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The realization of this goal required:
- defining appropriate concentrations of liquefier in the slurry in a function of technological parameters,
- performing laboratory tests on the technological parameters of fresh slurries,
- establishing relations between liquefier concentration and obtained technological parameters of fresh slurries used in drilling technology and geoengineering tasks.

2. THE INFLUENCE OF RHEOLOGICAL PARAMETERS OF SEALING SLURRIES

The type of admixture added to the sealing slurry is usually defined in view of its effect on technological parameters of the slurry. In the case of plastifiers (plastifiers [PL] I generation liquefiers) as well as traditional and new generation liquefiers (II generation liquefiers) their basic impact lies in the modification of rheological properties of fresh sealing slurries [3, 5, 6, 9].

One of the basic conditions of the rational and optimum use of liquefiers is the full knowledge about the results of their impact on the sealing slurry. The state of the art analyses reveal that the only reliable method of providing efficient operation of liquefiers is rheometric measurements performed with the use of, e.g. rotary viscometers.

The role of admixtures improving the properties of slurries lies in:
- lowering of the amount of working fluid,
- increasing slurry liquidity.

The admixtures usually reduce the quantity of water in the slurry by 5% to 10%, and sometimes even up to 15%.

Water reducing admixtures are added to the cement slurry to lower the water/cement ratio, maintaining required viscosity, or alternatively, to improve viscosity and rheological parameters at a given value of the cement/water ratio.

The water reducing admixtures assumed in standard PN-EN934-2 are divided into two groups: plastifiers (A) and liquefiers (B) [3, 4, 8].

The plastifiers (PL) were already used in the 1930s and covered such substances as:
- salts of lignosulphonate acids (calcium lignosulphonate, potassium lignosulphonate, sodium lignosulphonate),
- hydroxycarboxylic acid (Ca, Na, triethanolamine), e.g. glicolic acid,
- hydroxyl polymers (e.g. from starch),
- carmanide compound,
- nonylphenol ethoxylates.

Their efficiency is evaluated on the basis of water reduction on the level of 5–15%.

Among liquefiers (SP) we have:
- sulfonated melamine-formaldehyde condensates,
- sulfonated naphtalene-formaldehyde condensates,
- modified calcium lignosulphonates or sodium lignosulphonates,
- esters of sulphuric acid and hydrocarbons.

Their efficiency is evaluated on the basis of water reduction level 10–25%.

In the 1990s very effective III generation admixtures (KAE) were introduced. They were based on [7, 14]:

- polyarboxylates (acrylates),
- carboxylic ether.

The efficiency of superplastifiers in water reduction is on the level of 20–40%.

The effect of liquefiers on cement slurries is complex and involves numerous functions. Generally, rheological properties of cement slurries are considered to be improved both by the operation of plastifiers and superplastifiers in the course of:

- lubrication – inner friction between particular slurry components is lowered;
- influence of single-sign electrically charged particles of the slurry; increasing of mobility of slurry particles due to the repulsion through the electrostatic forces;
- lowering of surface tension of water; water particles can more easily wet the solids in the slurry, as a result of which the forces between the particles are decreased.

The concentrations of applied plastifying admixtures usually change from 0.2% to 0.5% with respect to the mass of cement. An admixture below 0.2% does not bring about the liquefaction effect; higher concentrations than 0.5% do not increase the liquefaction. Obviously, these limits may vary for different liquefiers.

The liquefaction mechanism of cement slurries with superplastifiers significantly differs from traditional liquefaction methods. New generation superplastifiers liquefy slurries through the steric effect. In this case the basic role is played by their spatial structure connected with the presence of polymer branches, thanks to which the cement particles can approach one another. In this mechanism the admixtures do not break the existing cement agglomerates, but prevent their formation (Fig. 1).

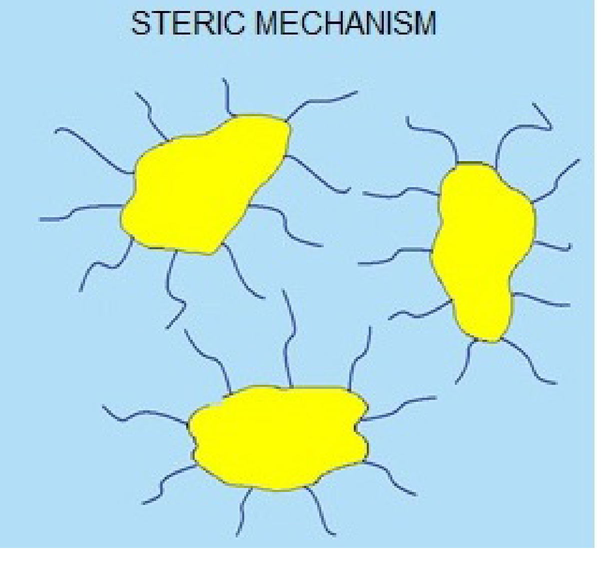

Fig. 1. Steric mechanism of sealing slurries liquefaction [10]

The effect of superplastifiers depends on a number of factors, e.g.:
- type of cement (some superplastifiers cannot be used along with metallurgic cements),
- granulation of mineral additives (especially participation of dusty fraction),
- type of gypsum introduced to cement as bonding time regulator,
- consistency of slurry,
- concentration of liquefying admixture,
- type and chemical composition of admixture,
- water/binder ratio,
- way and time in which the admixture is introduced to the slurry.

The efficiency of interaction of superplastifiers should be analyzed in two aspects:technical and economic.

Technical efficiency is expressed as a proportion of required basic effect, i.e. change of rheological properties of slurry, and minimum dose of superplastifier needed to evoke such an effect.

Economic efficiency is defined as a cost of a basic unit effect of modification performed in this way. In practice, the economic efficiency should decide about the choice of the liquefier. Meeting the economic efficiency condition means obtaining required effect of admixing at the lowest possible cost.

The rheological parameters of slurries can be modified with superplastifiers in the desired way if we have a well balanced recipe and technology of performing slurries, and also if we know:
- the mechanism of interaction of particular components of the slurry,
- dependence between the basic effect of the superplastifier and the output and modification factors,
- kind of cooperation of particular output factors and modification of sealing slurry.

The research problematics connected with the methods of determining the effect of superplastifiers on rheological properties of cement slurries has raised considerable interest (a number of scientific and technical publications on this subject have been written), however, attention should be paid to the fact that these problems are far from being definitely and unambiguously solved. The use of the rheometric test in the cognitive analyses as the only ones representing the physical mechanism of plastifiers' and superplastifiers' operation should be beyond any discussion. It should be also taken into consideration that the time of efficient (in the rheological sense) operation of superplastifiers in the sealing slurry is limited. With time, the slurry changes its rheological properties. This effect should be accounted for while designing sealing casing columns in deep wellbores.

3. LABORATORY TESTS

The laboratory tests were oriented to comparing the I, II and III generation plastifiers and determining their proper concentrations. The tests were done for [5, 7, 9, 10]:
- I generation liquefier – Argonite S – alkalized lignite – powdered sodium lignite of density ca. 1.5 kg/dm^3, in 80% water soluble. Offered by companies: CAUSTILIG, MESUCO CL, CC-16, LIGCON.

– II generation liquefier – PSP 042 applied by Polish Drilling Mud Services – being a mixture of specially modified mixture of polynaphtalene sulphonates. It is water soluble, density of 0.5–0.7 kg/dm^3.
– III generation liquefier – SKY 596 by BASF Polska Sp. z o.o. (The Chemical Company) – Concrete Admixtures Department – admixture based on polycarboxyl ethers, the chains of which are adsorbed on the binder grains forming a steric or electrostatic barrier. It is a yellowish fluid of density 1.05 kg/dm^3.

Sealing slurries to be used for analyses of technological parameters after using an admixture of liquefiers was based on cement class G, where w/c = 0.4. The slurries were admixed I to III generation liquefiers in the concentration 0.2%; 0.4%; 0.6% and 0.8% BWOC (with respect to the mass of cement). For the sake of obtaining the basic recipe, the parameters of sealing slurries based on the same cement for w/c = 0.4; 0.5 and 0.6 were analyzed. The temperature of sealing slurries analyzed for rheological equaled to 20°C (±2°C) [293 K]. Network water, devoid of any mechanical contaminations, was used as a working fluid.

Laboratory experiments on rheological parameters of sealing slurries were based on the standard PN – EN ISO 10426 – 2. *Oil and gas industry. Cements and materials for cementing wellbores. Part 2: Analysis of drilling cements*. 2006.

The laboratory tests covered:
– spillability test (spillability table and trunkated cone AzNII),
– relative viscosity test (Ford cup no. 4),
– settlement test (cyllinder),
– measurement of time of bonding (Vicata by Tonitech),
– density measurement (Baroid weight),
– determining rheological parameters (plastic viscosity, apparent viscosity, yield point) – with rotary viscometer of coaxial cylinders Ofite 900, with twelve rotational speeds (600, 300, 200, 100, 60, 30, 20, 10, 6, 3, 2, 1 r.p.m., which corresponds to the shear rates: 1022.04; 511.02; 340.7; 170.4; 102.2; 51.1; 34.08; 17.04; 10.22; 5.11; 3.41 and 1.70 s^{-1});
– defining the rheological model – the optimum selection of rheological model of sealing slurries lied in determining a rheological curve, thanks to which the measurement results could be better described in the coordinates system: tangent stress (τ) – shear rate (γ). Rheological parameters were determined for particular models with the regression analysis. Then the statistical tests were performed and optimum rheological models were selected for particular recipes of sealing slurries. For the sake of facilitating calculations, the computer program "Rheo Solution" was used. It belongs to the Faculty of Drilling, oil and Gas AGH-UST and is used in scientific-research works [11, 12].

4. DISCUSSION OF THE RESULTS OF LABORATORY TESTS

The recipes and compositions of analyzed slurries are presented in Table 1. The obtained technological parameters are listed in Table 2. The parameters of rheological models of particular slurries are presented in the respective tables: for slurries with no liquefiers added – Table 3, for recipes containing I generation liquefier – Table 4, for recipes containing II generation liquefier – Table 5, for recipes containing III generation liquefier – Table 6.

Table 1

Recipes of analyzed sealing slurries

Recipe	Cement [%]	Water w/c	I generation Argolite S [%] BWOC	II generation PSP 042 [%] BWOC	III generation SKY 596 [%] BWOC
R1	100	0.4	–	–	–
R2	100	0.5	–	–	–
R3	100	0.6	–	–	–
R4	100	0.4	0.2	–	–
R5	100	0.4	0.4	–	–
R6	100	0.4	0.6	–	–
R7	100	0.4	0.8	–	–
R8	100	0.4	–	0.2	–
R9	100	0.4	–	0.4	–
R10	100	0.4	–	0.6	–
R11	100	0.4	–	0.8	–
R12	100	0.4	–	–	0.2
R13	100	0.4	–	–	0.4
R14	100	0.4	–	–	0.6
R15	100	0.4	–	–	0.8

Table 2

Technological parameters of analyzed sealing slurries

Recipe	Spillability [mm]	Density [kg/m^3]	Settling [%]	Relative viscosity [s]
R1	200	1.91	1	48
R2	>280	1.85	4	34
R3	>280	1.77	8	14
R4	210	1.91	0	48
R5	230	1.91	1	47
R6	250	1.91	1	45
R7	>280	1.91	2	34
R8	200	1.91	4	23
R9	250	1.090	8	19
R10	>280	1.91	12	15
R11	>280	1.91	25	14
R12	200	1.91	0	30
R13	220	1.91	1	24
R14	>280	1.090	2	20
R15	>280	1.91	4	18

Table 3

Parameters of rheological models for recipes R1 to R3 (without liquefiers); measurement at temperature 20°C

Models	Rheological parameters	Recipe		
		R1	R2	R3
Newton model	Newtonian dynamic viscosity [Pa · s]	0.1435	0.1049	0.0614
	Correlation coefficient [–]	0.8711	0.912	0.9071
Bingham model	Plastic viscosity [Pa · s]	0.1173	0.0878	0.0508
	Yield point [Pa]	16.9092	11.0378	6.8816
	Correlation coefficient [–]	0.9563	0.9774	0.9842
Ostwald–de Waele model	Consistency coefficient [Pa · s^n]	3.8814	2.7632	2.2176
	Exponent [–]	0.4961	0.4939	0.4349
	Correlation coefficient [–]	0.9987	0.9945	0.9783
Casson model	Casson viscosity [Pa · s]	0.0855	0.062	0.0328
	Yield point [Pa]	6.9794	4.7636	3.4391
	Correlation coefficient [–]	0.9753	0.991	0.9967
Herschel–Bulkley model	Yield point [Pa]	–1.1386	2.7257	3.2273
	Consistency coefficient [Pa · s^n]	4.1921	1.4272	0.5397
	Exponent [–]	0.4894	0.5982	0.6584
	Correlation coefficient [–]	0.9992	0.9993	0.9994

Table 4

Parameters of rheological models for recipes R4 to R7 (with I generation liquifiers); measurement at temperature 20°C

Models	Rheological parameters	Recipe			
		R4	R5	R6	R7
Newton model	Newtonian dynamic viscosity [Pa · s]	0.0977	0.0807	0.0748	0.0746
	Correlation coefficient [–]	0.9909	0.9972	0.9977	0.9979
Bingham model	Plastic viscosity [Pa · s]	0.0931	0.0792	0.0731	0.073
	Yield point [Pa]	3.0112	0.9481	1.0846	1.0562
	Correlation coefficient [–]	0.9951	0.9978	0.9986	0.9988
Ostwald–de Waele model	Consistency coefficient [Pa · s^n]	0.3754	0.3318	0.341	0.3415
	Exponent [–]	0.7948	0.7497	0.7353	0.7345
	Correlation coefficient [–]	0.9988	0.9589	0.9613	0.9606
Casson model	Casson viscosity [Pa · s]	0.086	0.0716	0.0653	0.0651
	Yield point [Pa]	0.4244	0.1613	0.2003	0.2002
	Correlation coefficient [–]	0.9965	0.9979	0.9989	0.9989
Herschel–Bulkley model	Yield point [Pa]	0.2264	0.2169	0.3829	0.4257
	Consistency coefficient [Pa · s^n]	0.3278	0.1246	0.1169	0.1118
	Exponent [–]	0.817	0.934	0.9316	0.938
	Correlation coefficient [–]	0.999	0.9983	0.9991	0.9992

Table 5

Parameters of rheological models for recipes R8 to R11 (with II generation liquifiers); measurement at temperature 20°C

Models	Rheological parameters	Recipe			
		R8	R9	R10	R11
Newton model	Newtonian dynamic viscosity [Pa · s]	0.0977	0.0807	0.0748	0.0746
	Correlation coefficient [–]	0.9909	0.9972	0.9977	0.9979
Bingham model	Plastic viscosity [Pa · s]	0.0931	0.0792	0.0731	0.073
	Yield point [Pa]	3.0112	0.9481	1.0846	1.0562
	Correlation coefficient [–]	0.9951	0.9978	0.9986	0.9988
Ostwald–de Waele model	Consistency coefficient [Pa · s^n]	0.3754	0.3318	0.341	0.3415
	Exponent [–]	0.7948	0.7497	0.7353	0.7345
	Correlation coefficient [–]	0.9988	0.9589	0.9613	0.9606
Casson model	Casson viscosity [Pa · s]	0.086	0.0716	0.0653	0.0651
	Yield point [Pa]	0.4244	0.1613	0.2003	0.2002
	Correlation coefficient [–]	0.9965	0.9979	0.9989	0.9989
Herschel–Bulkley model	Yield point [Pa]	0.2264	0.2169	0.3829	0.4257
	Consistency coefficient [Pa · s^n]	0.3278	0.1246	0.1169	0.1118
	Exponent [–]	0.817	0.934	0.9316	0.938
	Correlation coefficient [–]	0.999	0.9983	0.9991	0.9992

Table 6

Parameters of rheological models for recipes R12 to R15 (with III generation liquefier); measurement at temperature 20°C

Models	Rheological parameters	Recipe			
		R12	R13	R14	R15
Newton model	Newtonian dynamic viscosity [Pa · s]	0.1152	0.0907	0.0786	0.0783
	Correlation coefficient [–]	0.9947	0.9973	0.9988	0.9987
Bingham model	Plastic viscosity [Pa · s]	0.1102	0.0883	0.077	0.0766
	Yield point [Pa]	3.1718	1.5332	1.0728	1.1079
	Correlation coefficient [–]	0.9981	0.9985	0.9996	0.9996
Ostwald–de Waele model	Consistency coefficient [Pa · s^n]	0.965	0.3363	0.352	0.3523
	Exponent [–]	0.6333	0.7801	0.7426	0.7422
	Correlation coefficient [–]	0.9406	0.9836	0.352	0.9679
Casson model	Casson viscosity [Pa · s]	0.0932	0.081	0.0678	0.0675
	Yield point [Pa]	0.8034	0.2146	0.2346	0.2383
	Correlation coefficient [–]	0.9993	0.9993	0.9992	0.9992
Herschel–Bulkley model	Yield point [Pa]	1.2833	0.2752	0.9115	0.8822
	Consistency coefficient [Pa · s^n]	0.2429	0.1728	0.0859	0.0892
	Exponent [–]	0.8851	0.9022	0.9841	0.9778
	Correlation coefficient [–]	0.9996	0.9996	0.9997	0.9996

The comparison of curves representing rheological models of slurries with no liquefiers (w/c = 0.4 and w/c = 0.6) and slurries with all liquefiers at the same concentration are given in Figures 2–5 (Bingham model) and Figures 6–9 (Herschel–Bulkley model). Figures 10–13 illustrate the apparent viscosity values for analyzed recipes in a function of shear rate. The time of bonding for particular recipes are presented in Figure 14.

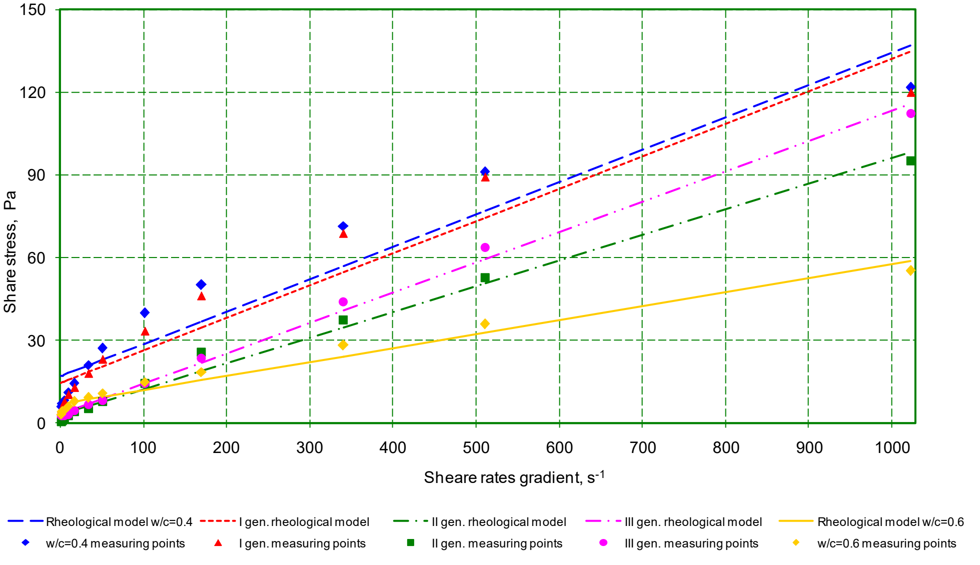

Fig. 2. Bingham rheological model for slurries with 0.2% admixture of I, II and III generation liquefiers

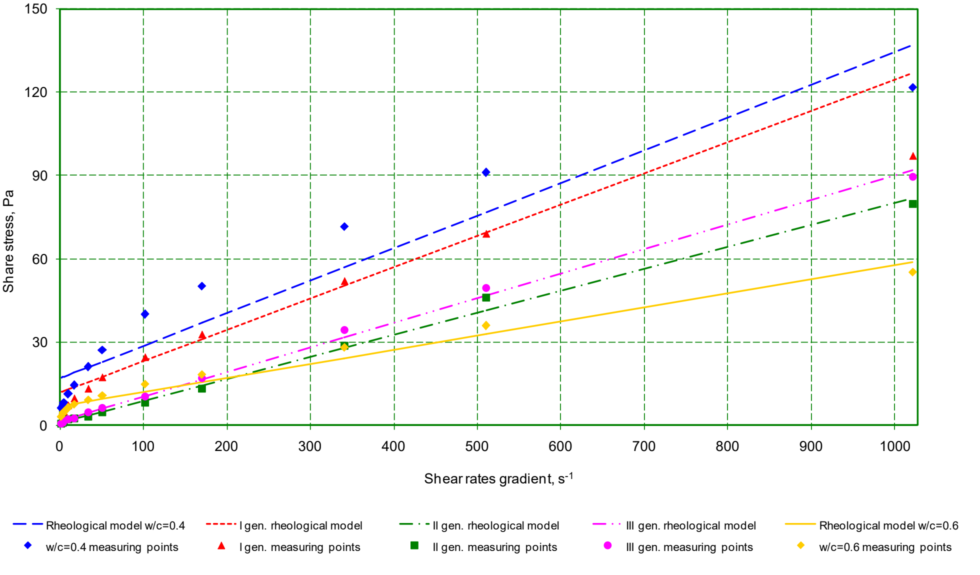

Fig. 3. Bingham rheological model for slurries with 0.4% admixture of I, II and III generation liquefiers

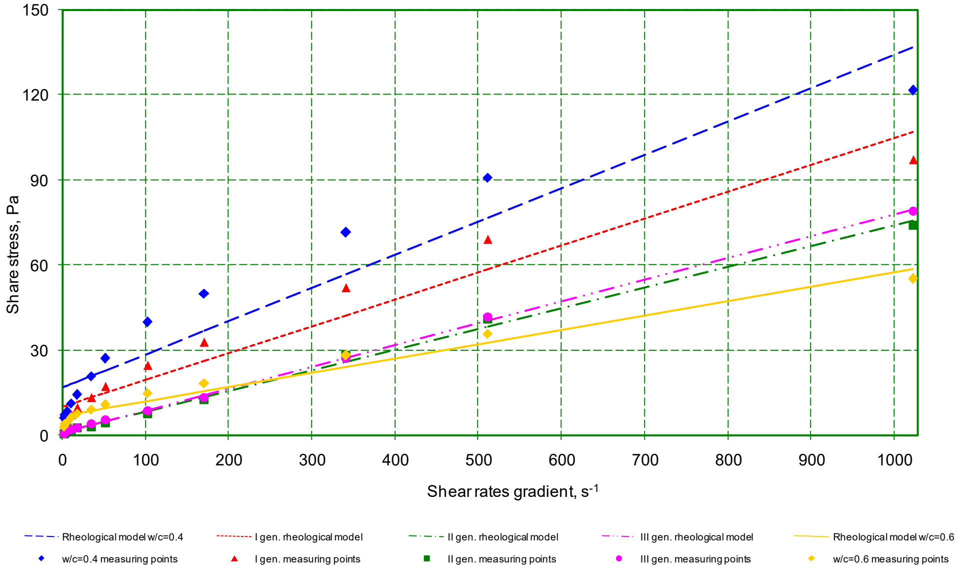

Fig. 4. Bingham rheological model for slurries with 0.6% admixture of I, II and III generation liquefiers

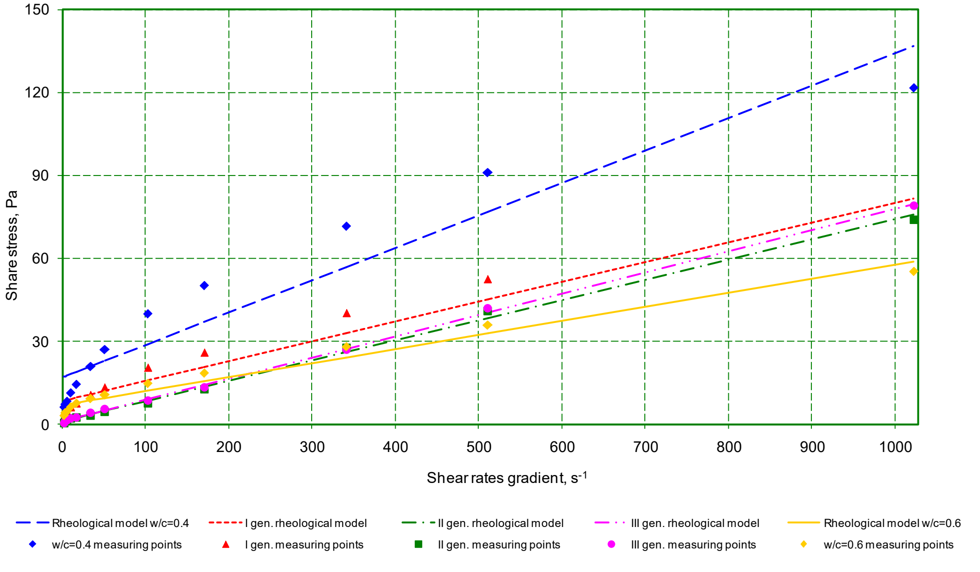

Fig. 5. Bingham rheological model for slurries with 0.8% admixture of I, II and III generation liquefiers

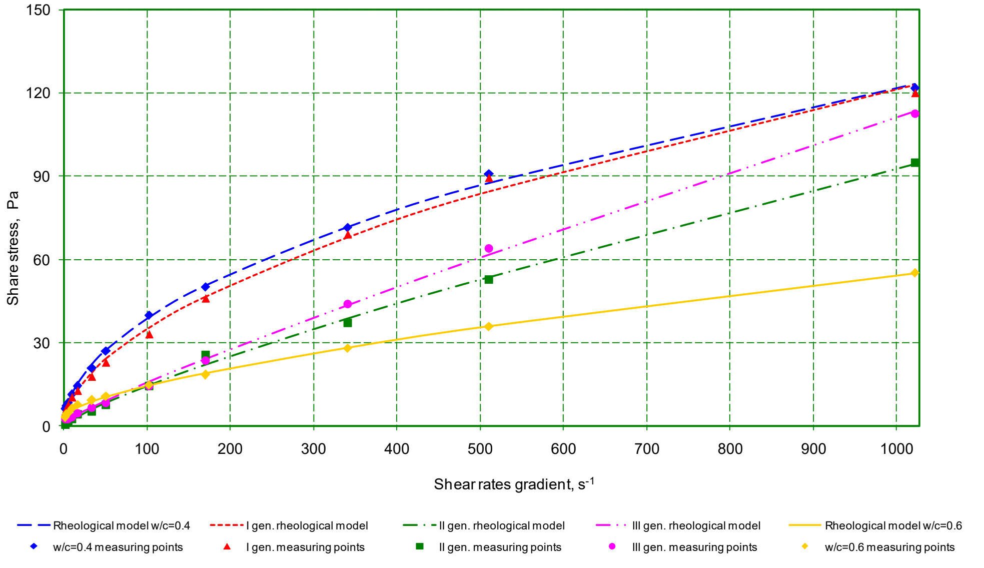

Fig. 6. Herschel–Bulkley rheological model for slurries with 0.2% admixture of I, II and III generation liquefiers

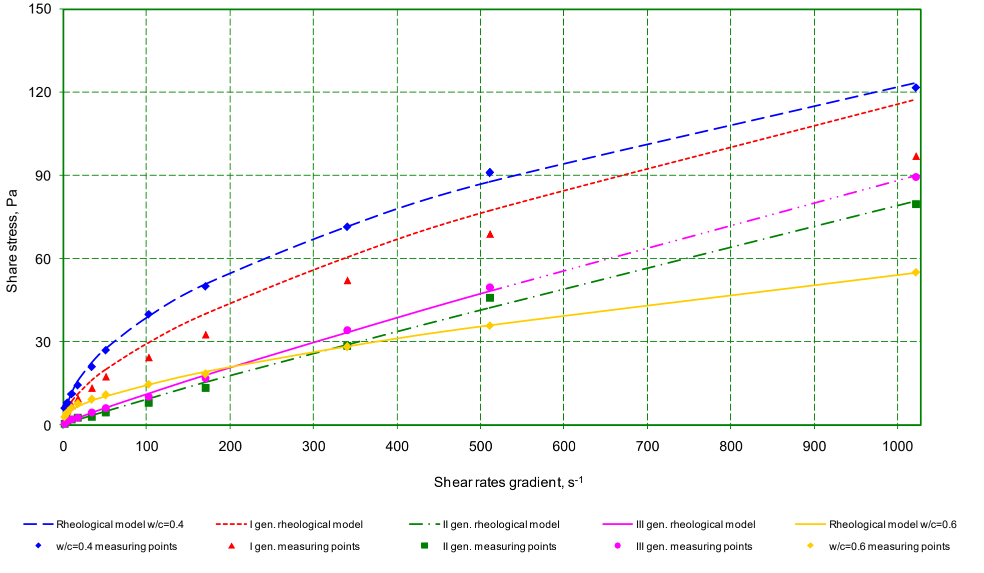

Fig. 7. Herschel–Bulkley rheological model for slurries with 0.4% admixture of I, II and III generation liquefiers

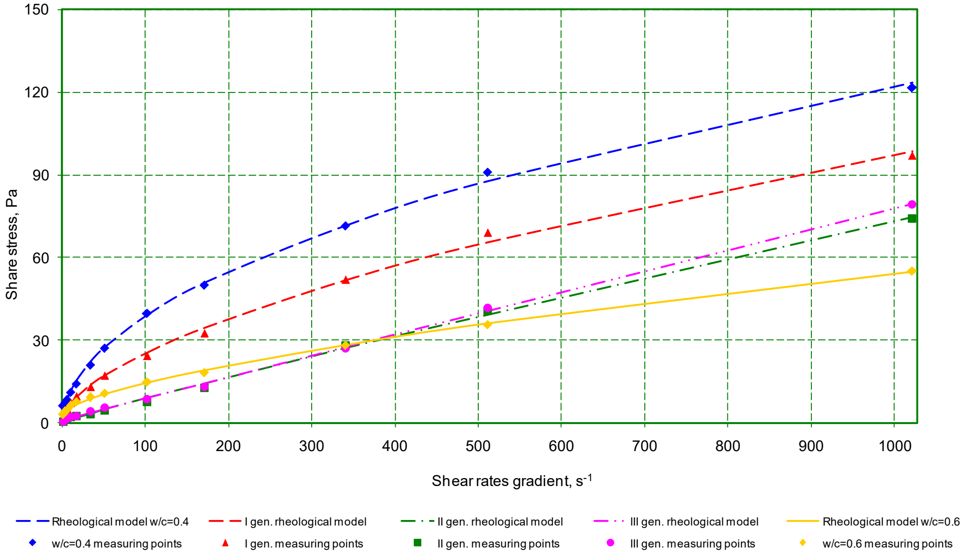

Fig. 8. Herschel–Bulkley rheological model for slurries with 0.6% admixture of I, II and III generation liquefiers

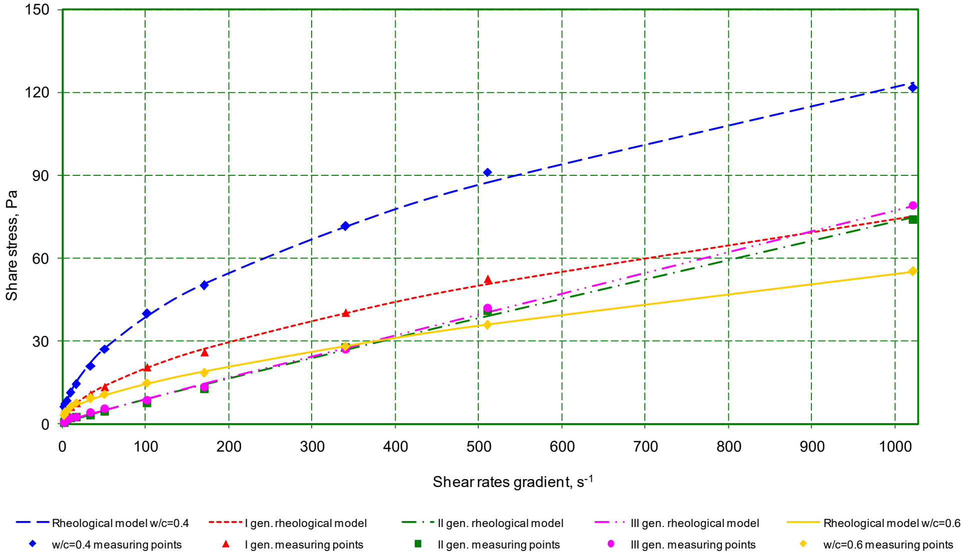

Fig. 9. Herschel–Bulkley rheological model for slurries with 0.8% admixture of I, II and III generation liquefiers

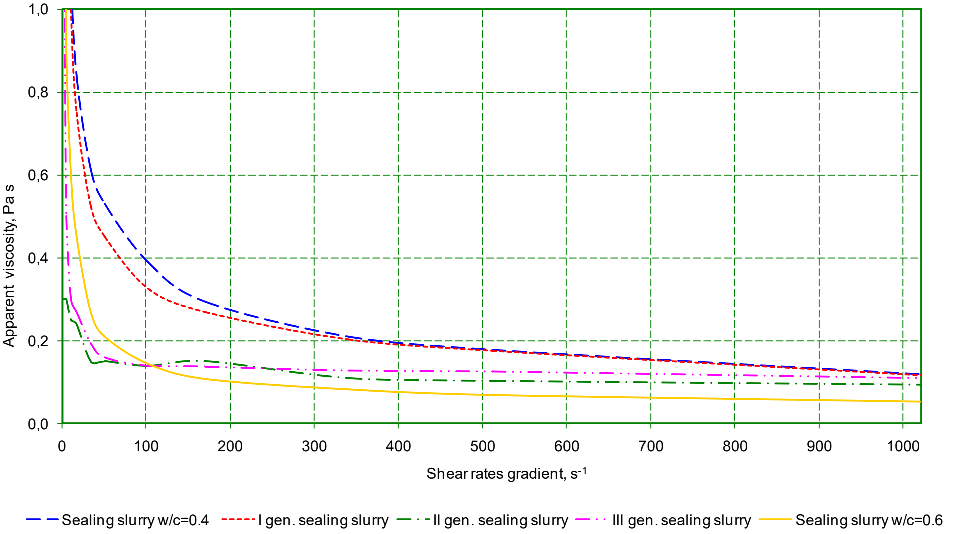

Fig. 10. Apparent viscosity for slurries with 0.2% admixture of I, II and III generation liquefiers

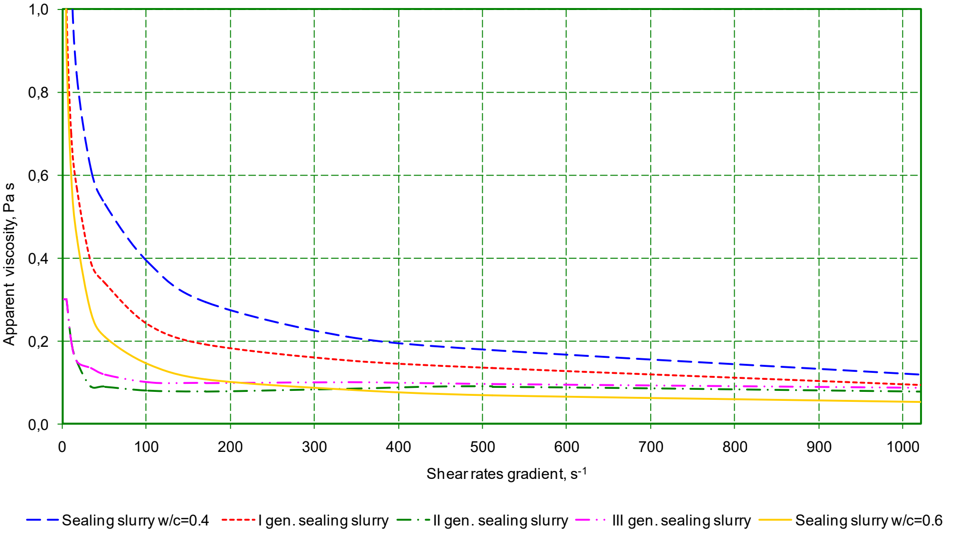

Fig. 11. Apparent viscosity for slurries with 0.4% admixture of I, II and III generation liquefiers

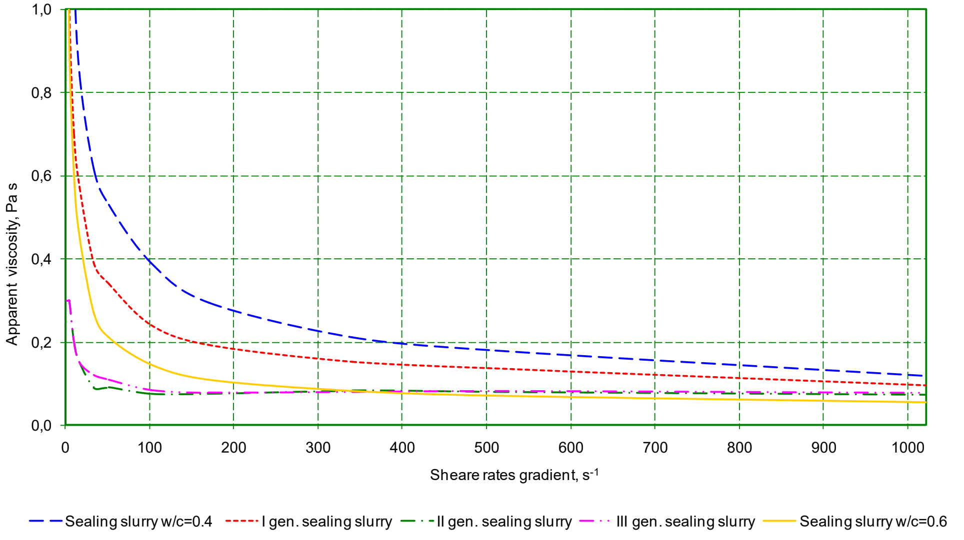

Fig. 12. Apparent viscosity for slurries with 0.6% admixture of I, II and III generation liquefiers

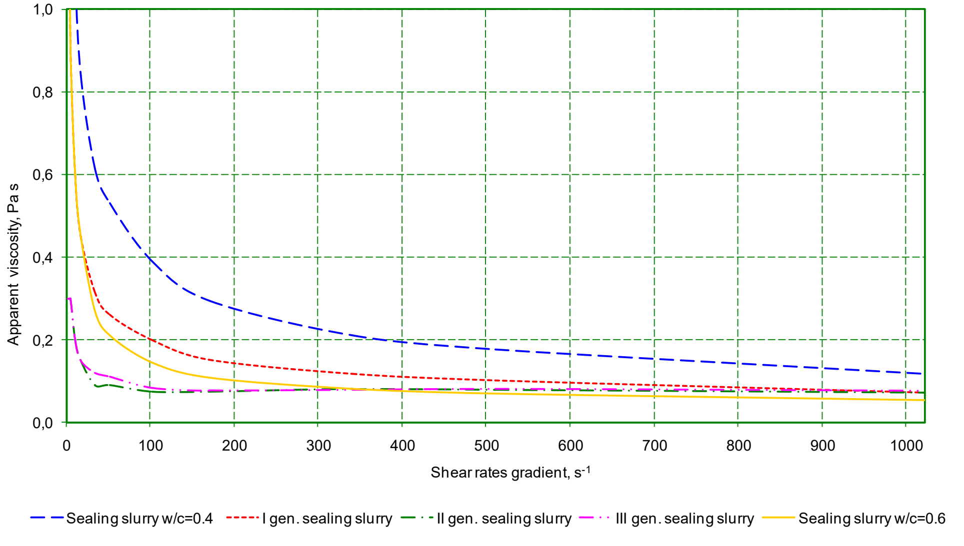

Fig. 13. Apparent viscosity for slurries with 0.8% admixture of I, II and III generation liquefiers

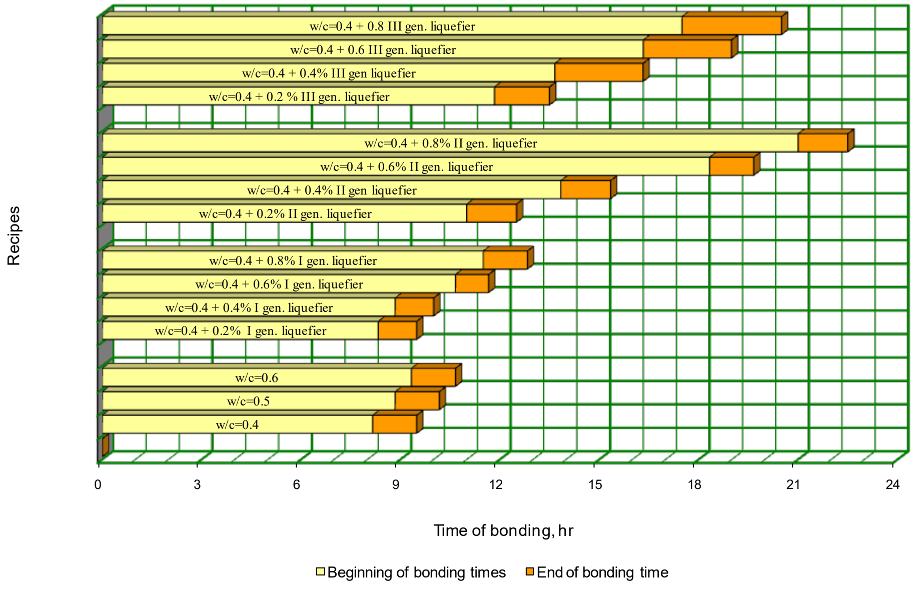

Fig. 14. Bonding time of analyzed sealing slurries

5. CONCLUSIONS

1. The analysis of selected concentrations of admixtures added to liquefiers with respect to cement mass) allowed for determining minimum and maximum values and their impact on the rheological properties of analyzed cement slurries.
2. The efficiency of II and III generation liquefiers manifests itself in lower concentrations, as compared to I generation liquefiers.
3. Considering rheology, the optimum concentrations for analyzed slurries are:
   – I generation liquefiers 0.4–0.8 wt.% (with respect to mass of dry cement),
   – II generation liquefiers 0.2–0.6 wt.%,
   – III generation liquefiers 0.2–0.6%.
4. I generation liquefier allowed for lowering the working water quantity by about 20%, whereas II and III generation liquefiers by about 30%.

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