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INFLUENCE OF POLYCARBOXYLATES ON RHEOLOGICAL PROPERTIES OF SEALING SLURRIES

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Abstract:

Sealing slurries should have proper technological properties to well perform in the borehole. Slurries should have definite time of bonding and strictly defined pumpability over the entire cementation time. Set cement slurry cannot corrode. It must be impermeable and adhesive to the drilled rocks and casing pipes. Its strength parameters should remain unchanged over the time of exploitation of a given borehole.

The results of laboratory experiments and analyses of new generation superplastifiers based on plycarboxylate ethers Glenium® by BASF on rheological properties of sealing slurries based on metallurgical cement CEM III/A 32.5R; Portland cement CEM I 42.5 R and multicomponent Portland cement CEM II/B- M (S-V) are presented in the paper.

Determined rheological parameters for a specific model can create bases for detailed calculations of flow resistivity of sealing slurry in the process of cementing the casing pipes.

1. Introduction

Providing effective sealing of the casing in boreholes greatly depends on the degree in which the drilling mud is expelled from the anular space by the sealing slurry in the process of sealing.

Apart from the character of flow, the high effectiveness of substitution of the drilling mud with sealing slurry is also influenced by the factors:

- Rheological properties of slurries used in the cementing procedure (drilling mud, sealing slurry, buffer liquid, tamping),
- Specific gravity of drilling mud and sealing slurry,
- Use of buffering fluid between sealing slurry and drilling mud,
- Coaxiality of the casing in the borehole,
- Moving the casing in the course of sealing operations,
- Use of borehole wall scrapers.

The paper is a result of laboratory analyses focused on the analysis of influence of various types of superplastifiers by BASF Polska Sp. z o.o. [The Chemical Company – Concrete Admixtures Section] on rheological parameters of fresh sealing slurries.

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The authors attempted to experimentally prove that the type and concentration of a new generation superplastifier can be so selected for the cement slurry that its proper action on rheological parameters is guaranteed. Accordingly, there exist real possibilities of increasing the effectiveness of cementing the casing in boreholes.

2. Fluidizing mixtures (FM)

Fluidizing mixtures (superplastifiers) change the force of friction enhancing the cement slurry dispersion. Thanks to this the quantity of make-up water can be reduced even by 35 % without changing the consistency of the slurry.

Superplastifiers are polymers with particles having a developed linear structure, without side offshots, thanks to which they can well surround the cement grains, and act on them so more effectively. They can be introduced to the slurry in bigger quantities than plastifiers (BV). Superplastifiers can be classified according to the following groups [2, 4]:

- Sulfonated melamine-formaldehyde (SMF) resins,
- Sulfonated naphtalene-formaldehyde (SNF) resins,
- Melamine-naphtalene sulfonate mixtures,
- Modified calcium or sodium (MLS) lignosulfontes,
- Formic acid and methyl naphthalene-sulfoniate acid or naphtalene methyl-sulfonate acid co-polymers,
- Modified salts of lignosulfonate (MLG) acids,
- Polycarboxylates (PC),
- Aromatic sulfonate (AS) amines,
- Acrylic acid and acrylates (CAE) co-polymers,
- Cross-linked acrylic resins (CLAP) – a new generation superplastifiers.

New generation superplastifiers are compounds, e.g. polycarboxylates, acrylic acid and acrylic esther co-polymers, cross-linked acrylic resins or polycarboxylate ethers. The mechanism of plastifying cement slurries with the use of superplastifiers significantly differs from traditional such methods. In the case of traditional superplastifiers the process is based on the so-called electrostatic process in which the SO_3^- ions are electrostatically pushed away. On the other hand, the new generation superplastifiers base on the steric effect. The principal role here is played by their spatial structure connected with the presence of side-chains, because of which they cannot get closer to the cement grains.

The mechanism of superplastifiers operation is complex. Depending on the type of applied plastifying admixtures they may have influence on [1, 2, 6]:

- formation of new cement grains and microfillers in the "lubricant" layer, lowering the inner friction in the slurry,
- surrounding of cement grains with negatively charged ions, causing their pushing away, lowering the surface tension of water with respect to cement and microfillers,
- steric effect – long chains of polymers make it impossible for the cement grains to get closer to one another. This mechanism causes that new generation admixtures act „as a prevention"; instead of destroying the existing agglomerates of cement grains, they do not let the new ones get formed.

The effectiveness of operation of a superplastifier depends on a number of factors, e.g.:

- type of cement (some superplastifiers cannot be used with the metallurgical cements),
- granulation of mineral additives (especially the dust fraction),
- type of gypsum introduced to the cement as a bonding time regulator,
- consistency of the slurry,
- concentration of fluidizing mixture,
- type and chemical composition of admixture,
- water-to-binder ratio,
- way and time of admixing the slurry.

3. Laboratory analyses

Laboratory analyses of rheological parameters of sealing slurries were based on the following standards:

1. PN – EN 197 – 1: 2002, Cement. Part 1. Composition, requirements and congruence criteria of common-use cements.
2. PN – EN ISO 10426 – 2. Oil and gas industry. Cements and materials for cementing boreholes. Part 2: Analysis of drilling cements. 2003.

The following variables were investigated:

a) water-to-cement ratio;
b) concentration of superplastifiers;
c) type of superplastifier,
d) type of cement.

The water-to-cement ratio for the analyzed sealing slurries equalled to: 0.35; 0.4.

The new generation superplastifiers used in the laboratory experiments were polycarboxylate ether-based admixtures, called Elenium 430,591 and 503 by BASF [5].

The concentration of the analyzed superplastifiers in the slurry was: 0.25; 0.5; 0.8; 1.2 wt.% with respect to the cement dry mass.

The sealing slurries were based on the following cements:

- Portland CEM I 42.5R,
- multicomponent Portland CEM II/B-M (S-V) 32.5 R,
- metallurgical CEM III/ A 32.5 R.

Laboratory experiments on determining rheological parameters of fresh sealing slurries cover the following measurements:

- Rheological properties (plastic viscosity, apparent viscosity, yield point) with the use of rotary viscosimeter with coaxial cylinders Chan – 35 API Viscometer – Tulusa, Oklahoma USA EG.G Chandler Engineering, having twelve rotary speeds (600, 300, 200, 100, 60, 30, 20, 10, 6, 3, 2, rot/min, which corresponds to the shear rate: 1022.04; 511.02; 340.7; 170.4; 102.2; 51.1; 34.08; 17.04; 10.22; 5.11; 3.41; 1.70 s^{-1});
- Determining rheological model – selection of optimum rheological model of sealing slurries lied in determining 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 specific models with the regression analysis method. Then the optimum rheological model for a given recipe of sealing slurry was established via statistical tests.

The calculations aimed at establishing optimum rheological models for the analyzed slurries could be facilitated by computer software „Rheo Solution”. This software is owned by the Faculty of Drilling, Oil and Gas AGH UST and is used in scientific and research works [7, 8, 9].

4 Discussion of laboratory analyses

Rheological parameters of cement slurries having water-to-cement ratio w/c=0.35 and w/c=0.4 are listed in Tables 1 to 3 and Tables 4 to 6, respectively.

The analysis of data in Tables 1 to 6 reveals that in a small amount of superplastifier (0.25 %) introduced to the sealing slurry, the rheological properties of the slurry change. With the increased superplastifier concentration the rheological parameters of the slurry also gradually get lower. The optimum concentration of analyzed new generation superplastifiers in sealing slurry based on various types of cement ranges between 0.5 and 0.8 % as compared to the cement dry mass.

The most accurate rheological model describing rheological parameters of the analyzed slurries is the Herschel–Bulkley model with the highest correlation coefficients as compared to the remaining analyzed models.

Tab. 1 *Rheological parameters of sealing slurries based on Portland cement CEM I 42.5R having the water-to-cement ratio w/c=0.35.*

Recipe of the slurry / **Rheological parameters**		w/c=0.35	w/c=0.35 GLENIUM ACE 430 0.25 %	w/c=0.35 GLENIUM ACE 430 0.5 %	w/c=0.35 GLENIUM ACE 430 0.8 %	w/c=0.35 GLENIUM ACE 430 1.2 %
Newtonian Model	Newtonian dynamic viscosity [Pa*s]	0.9471	0.8556	0.5624	0.3555	0.2979
	Correlation coefficient [-]	0.7517	0.9038	0.9908	0.9995	0.9977
Bingham Model	Plastic viscosity [Pa*s]	0.6738	0.6806	0.5197	0.3494	0.3076
	Yield point [Pa]	30.1991	19.3412	4.7177	1.3175	-2.0936
	Correlation coefficient [-]	0.9819	0.9900	0.9993	0.9999	0.9990
Ostwald de Waele Model	Consistency coefficient [Pa*s^n]	16.0545	9.3138	2.4099	0.7837	0.1432
	Exponent [-]	0.3960	0.4869	0.6745	0.8370	1.1319
	Correlation coefficient [-]	0.9879	0.9876	0.9813	0.9877	0.9999
Casson Model	Casson's viscosity [Pa*s]	0.3571	0.4277	0.4130	0.3210	0.3241
	Yield point [Pa]	17.1769	9.0541	1.3332	0.1786	0.1911
	Correlation coefficient [-]	0.9963	0.9983	0.9997	0.9997	0.9632
Herschel-Bulkley Model	Yield point [Pa]	14.3536	8.6857	3.2670	1.3419	-0.2513
	Consistency coefficient [Pa*s^n]	5.7288	3.5770	0.7857	0.3468	0.1625
	Exponent [-]	0.5964	0.6844	0.9202	1.0013	1.1093
	Correlation coefficient [-]	0.9992	0.9998	0.9998	0.9999	0.9999

__Tab. 2__ Rheological parameters of sealing slurries based on metallurgical cement CEM I 42.5R having the water-to-cement ratio w/c=0.4.

Recipe of slurry / Rheological parameters		w/c=0.4	w/c=0.4 GLENIUM ACE 430 0.25 %	w/c=0.4 GLENIUM ACE 430 0.5 %	w/c=0.4 GLENIUM ACE 430 0.8 %	w/c=0.4 GLENIUM ACE 430 1.2 %
Newtonian Model	Newtonian dynamic viscosity [Pa*s]	0.4983	0.4590	0.2828	0.2290	0.1389
	Correlation coefficient [-]	0.6628	0.9666	0.9992	0.9993	0.9999
Bingham Model	Plastic viscosity [Pa*s]	0.3499	0.4038	0.2772	0.2256	0.1395
	Yield point [Pa]	32.1966	11.9819	1.8865	1.1378	-0.4040
	Correlation coefficient [-]	0.9667	0.9944	0.9998	0.9996	0.9999
Ostwald de Waele Model	Consistency coefficient [Pa*s^n]	15.2785	4.5466	0.7731	0.5037	0.0933
	Exponent [-]	0.3614	0.5578	0.8097	0.8482	1.0672
	Correlation coefficient [-]	0.9887	0.9766	0.9858	0.9890	0.9971
Casson Model	Casson's viscosity [Pa*s]	0.1845	0.2955	0.2537	0.2129	0.1438
	Yield point [Pa]	19.0418	4.4677	0.2692	0.1069	0.0243
	Correlation coefficient [-]	0.9905	0.9991	0.9999	0.9998	0.9963
Herschel-Bulkley Model	Yield point [Pa]	12.1340	5.5134	1.1178	0.2005	-0.6796
	Consistency coefficient [Pa*s^n]	6.3560	1.4713	0.3474	0.3142	0.1514
	Exponent [-]	0.5154	0.7795	0.9636	0.9467	0.9881
	Correlation coefficient [-]	0.9989	0.9997	0.9999	0.9998	0.9999

Tab. 3 *Rheological parameters of sealing slurries based on multicomponent Portland cement CEM II/B-M (S-V) 32.5 R having the water-to-cement ratio w/c=0.35 determined for various rheological models of fluids at temperature 20 °C.*

Recipe of slurry / **Rheological parameters**		**w/c= 0.35**	**w/c = 0.35 SKY 591 (0.25 %)**	**w/c = 0.35 SKY 591 (0.50 %)**	**w/c = 0.35 SKY 591 (0.80 %)**	**w/c = 0.35 SKY 591 (1.20 %)**
Newtonian Model	Newtonian dynamic viscosity [Pa*s]	0.8158	0.9976	0.9489	0.4892	0.3423
	Correlation coefficient [-]	0.0000	0.4950	0.7418	0.9340	0.9872
Bingham Model	Plastic viscosity [Pa*s]	0.4739	0.6459	0.6708	0.4082	0.3142
	Yield point [Pa]	37.7859	38.8655	30.7294	17.5863	6.1099
	Correlation coefficient [-]	0.9334	0.9827	0.9847	0.9935	0.9991
Ostwald de Waele Model	Consistency coefficient [Pa*s^n]	21.3792	23.3067	16.8691	7.3639	2.6291
	Exponent [-]	0.3138	0.3256	0.3838	0.4821	0.5945
	Correlation coefficient [-]	0.9925	0.9798	0.9845	0.9739	0.9605
Casson Model	Casson's viscosity [Pa*s]	0.2064	0.2895	0.3467	0.2660	0.2388
	Yield point [Pa]	24.8167	25.1712	17.8899	8.1786	2.1031
	Correlation coefficient [-]	0.9715	0.9976	0.9978	0.9997	0.9997
Herschel-Bulkley Model	Yield point [Pa]	**2.6226**	**24.4058**	**16.6552**	**10.1781**	**4.2562**
	Consistency coefficient [Pa*s^n]	**18.8003**	**5.1634**	**4.9541**	**1.6891**	**0.5562**
	Exponent [-]	**0.3382**	**0.6075**	**0.6219**	**0.7580**	**0.9033**
	Correlation coefficient [-]	**0.9931**	**0.9991**	**0.9996**	**0.9998**	**1.0000**

Tab. 4 *Rheological parameters of sealing slurries based on multicomponent Portland cement CEM II/B-M (S-V) 32.5 R having the water-to-cement ratio w/c=0.40 determined for various rheological models of fluids at temperature 20 °C.*

Recipe of slurry / Rheological parameters		w/c = 0,40	w/c = 0,40 SKY 591 (0,25 %)	w/c =0,40 SKY 591 (0,50 %)	w/c = 0,40 SKY 591 (0,80 %)	w/c 0,40 SKY 591 (1,20 %)
Newtonian Model	Newtonian dynamic viscosity [Pa*s]	0,4524	0,2985	0,2376	0,2024	0,1336
	Correlation coefficient [-]	0,7407	0,8697	0,8998	0,9594	0,9934
Bingham Model	Plastic viscosity [Pa*s]	0,3294	0,2364	0,1912	0,1752	0,1272
	Yield point [Pa]	26,7087	20,9622	15,6766	9,1756	4,1379
	Correlation coefficient [-]	0,9656	0,9757	0,9911	0,9957	0,9978
Ostwald de Waele Model	Consistency coefficient [Pa*s^n]	11,7548	7,3231	6,4936	3,6038	0,9917
	Exponent [-]	0,3934	0,4495	0,4197	0,4848	0,6653
	Correlation coefficient [-]	0,9901	0,9949	0,9748	0,9651	0,9676
Casson Model	Casson's viscosity [Pa*s]	0,1862	0,1490	0,1133	0,1175	0,1092
	Yield point [Pa]	14,7901	10,3923	8,4700	4,2083	0,9614
	Correlation coefficient [-]	0,9880	0,9915	0,9992	0,9999	0,9996
Herschel-Bulkley Model	Yield point [Pa]	**7,9134**	**4,9772**	**9,4872**	**5,5704**	**1,4434**
	Consistency coefficient [Pa*s^n]	**5,9401**	**4,1077**	**1,1967**	**0,6568**	**0,3282**
	Exponent [-]	**0,5166**	**0,5493**	**0,7071**	**0,7882**	**0,8621**
	Correlation coefficient [-]	**0,9976**	**0,9997**	**0,9993**	**0,9999**	**1,0000**

***Tab. 5** Rheological parameters of sealing slurries based on metallurgical cement CEM III 32.5R having the water-to-cement ratio w/c = 0.35 determined for various rheological models of fluids at temperature 20^{o}C.*

Recipe of slurry / Rheological parameters		**w/c= 0.35**	**w/c = 0.35 SKY 503 (0.25 %)**	**w/c = 0.35 SKY 503 (0.50 %)**	**w/c = 0.35 SKY 503 (0.80 %)**	**w/c = 0.35 SKY 503 (1.20 %)**
Newtonian Model	Newtonian dynamic viscosity [Pa*s]	2.2998	1.5081	0.4724	0.4286	0.3843
	Correlation coefficient [-]	0.7597	0.8449	0.9915	0.9901	0.9865
Bingham Model	Plastic viscosity [Pa*s]	1.5733	1.1214	0.4992	0.4545	0.4097
	Yield point [Pa]	24.9221	25.2072	-2.9544	-2.8683	-5.5185
	Correlation coefficient [-]	0.9954	0.9928	0.9951	0.9942	0.9922
Ostwald de Waele Model	Consistency coefficient [Pa*s^n]	18.0085	14.6778	0.2169	0.2193	0.1130
	Exponent [-]	0.4135	0.4509	1.1374	1.1057	1.1672
	Correlation coefficient [-]	0.9776	0.9838	0.9903	0.9807	0.9525
Casson Model	Casson's viscosity [Pa*s]	0.7857	0.6369	0.5281	0.4743	0.4341
	Yield point [Pa]	14.1696	13.0193	0.3439	0.3028	0.9068
	Correlation coefficient [-]	0.9969	0.9995	0.9161	0.9212	0.8797
Herschel-Bulkley Model	Yield point [Pa]	19.8834	15.4723	0.3748	0.3878	-0.2851
	Consistency coefficient [Pa*s^n]	3.4604	4.1435	0.1175	0.0922	0.0600
	Exponent [-]	0.8092	0.7264	1.2824	1.3116	1.3319
	Correlation coefficient [-]	0.9977	0.9997	1.0000	1.0000	0.9999

Tab. 6 *Rheological parameters of sealing slurries based on metallurgical cement CEM III 32.5R having the water-to-cement ratio w/c = 0.4 determined for various rheological models of fluids at temperature 20 °C.*

Receptura zaczynu / Parametry reologiczne		w/c = 0.40	w/c = 0.40 SKY 503 (0.25%)	w/c =0.40 SKY 503 (0.50%)	w/c = 0.40 SKY 503 (0.80%)	w/c 0.40 SKY 503 (1.20%)
Newtonian Model	Newtonian dynamic viscosity [Pa*s]	0.8964	0.7312	0.4484	0.3165	0.2555
	Correlation coefficient [-]	0.8625	0.9997	0.9945	0.9937	0.9969
Bingham Model	Plastic viscosity [Pa*s]	0.6893	0.7257	0.4695	0.3313	0.2638
	Yield point [Pa]	22.8749	0.6115	-2.3320	-3.2261	-2.8249
	Correlation coefficient [-]	0.9801	0.9998	0.9970	0.9967	0.9984
Ostwald de Waele Model	Consistency coefficient [Pa*s^n]	10.7160	1.2799	0.2479	0.1352	0.1252
	Exponent [-]	0.4717	0.8612	1.1023	1.1203	1.0882
	Correlation coefficient [-]	0.9927	0.9863	0.9926	0.9797	0.9785
Casson Model	Casson's viscosity [Pa*s]	0.4247	0.6716	0.4911	0.3486	0.2789
	Yield point [Pa]	10.9825	0.1036	0.2163	0.3918	0.3294
	Correlation coefficient [-]	0.9939	0.9992	0.9455	0.9369	0.9573
Herschel-Bulkley Model	Yield point [Pa]	6.4791	1.7162	0.1965	-0.3565	-0.9887
	Consistency coefficient [Pa*s^n]	5.9382	0.5582	0.1568	0.1047	0.1351
	Exponent [-]	0.5941	1.0509	1.2137	1.1987	1.1082
	Correlation coefficient [-]	0.9989	1.0000	1.0000	0.9998	0.9993

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