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INFLUENCE OF POLYCARBOXYLATE SUPERPLASTICIZERS ON RHEOLOGICAL PROPERTIES OF CEMENT SLURRIES USED IN DRILLING TECHNOLOGIES

WPŁYW SUPERPLASTYFIKATORÓW Z GRUPY POLIKARBOKSYLANÓW NA WŁAŚCIWOŚCI REOLOGICZNE ZACZYNÓW CEMENTOWYCH STOSOWANYCH W TECHNOLOGIACH WIERTNICZYCH

Sealing slurries, mainly the cement-based ones, are concentrated dispersive systems, containing solid particles of considerably developed specific surface. Rheologically, such systems are very complex. This also stems from the fact that the rheological properties have a significant effect on:

- additives and admixtures modifying technological properties of fresh and set slurries,
- chemically complex mechanism of hydration in a slurry in a function of time.

Special attention should paid to plasticizing (plasticizers PL) and liquefying (traditional and new-generation superplasticizers SP) admixtures affecting the modification and optimization of rheological properties of fresh cement slurries as far as providing efficiency of sealing of casing pipes is concerned.

Laboratory analyses were focused on proving the following thesis: properly selected type of superplasticizer [by BASF Polska Sp.z o.o. (The Chemical Company) – Admixtures for Concrete Division] advantageously affects the rheological parameters of sealing slurry based on metallurgical cement CEM III /A 32,5.

The following variables were used in the analyses:

- type of superplasticizer,
- type of batch fluid.

The laboratory experiments were made on superplasticizers produced by BASF:

- SKY 501,
- SKY 503,
- SKY 591,
- ACE 430,
- Glenium 115.

The superplasticizer concentration in the slurry was 0.5 wt% (as compared with mass of dry cement). Water to cement ratio for the analyzed sealing slurries was equal to 0.5.

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The sealing slurries were made of metallurgical cement CEM III/A 32,5 N-LH/HSR/N Lafarge Cement S.A. in Małogoszcz.

Keywords: sealing slurries, rheological properties, rheological models, superplastifiers, sealing of ground and rock medium, cement slurries, metallurgical cement

Zaczyny uszczelniające, a zwłaszcza typu cementowego, są skoncentrowanymi układami dyspersyjnymi, zawierającymi cząstki stałe o znacznie rozwiniętej powierzchni właściwej. Układy takie pod względem reologicznym należą do niezwykle złożonych. Wynika to między innymi z faktu, że na właściwości reologiczne w sposób istotny wpływają:

- dodatki i domieszki modyfikujące właściwości technologiczne świeżych i stwardniałych zaczynów,
- złożony chemicznie mechanizm reakcje hydratacji zachodzące w zaczynie w funkcji czasu.

Na szczególną uwagę ze względu na zapewnienie skuteczność uszczelniania kolumn rur okładzinowych w otworach wiertniczych zasługują domieszki uplastyczniające (plastyfikatory PL) i upłynniające (superplastyfikatory SP typu tradycyjnego oraz nowej generacji) wpływające na modyfikację oraz optymalizację cech reologicznych świeżych zaczynów uszczelniających.

Przeprowadzone badania laboratoryjne miały na celu udowodnianie następującej tezy: odpowiednio dobrany rodzaj superplastyfikatorów [firmy BASF Polska Sp.z o.o. (The Chemical Company) – Dział Domieszek do Betonu], wpływa korzystnie na parametry reologiczne zaczynu uszczelniającego sporządzanego na osnowie cementu hutniczego CEM III /A 32,5.

W przeprowadzanych badaniach zmiennymi były:

- rodzaj superplastyfikatora,
- rodzaj cieczy zarobowej.

W badaniach laboratoryjnych zastosowano następujące superplastyfikatory firmy BASF:

- SKY 501,
- SKY 503,
- SKY 591,
- ACE 430,
- Glenium 115.

Koncentracja superplastyfikatora w zaczynie wynosiła: 0,5% wagowo (w stosunku do masy suchego cementu).

Współczynnik wodno-cementowy dla badanych zaczynów uszczelniających wynosił: 0,5.

Do sporządzania zaczynów uszczelniających stosowano cement hutniczy klasy CEM III/A 32,5 N-LH/HSR/NA – Cementownia Małogoszcz, Grupa Lafarge Cement S.A. w Małogoszczy.

Słowa kluczowe: zaczyny uszelniające, właściwosci reologiczne, modele reologiczne, superplastyfikatory, uszczelnianie ośrodka gruntowego i masywu skalnego, zaczyny cementowe, cement hutniczy

1. Introduction

Rheological properties of sealing slurries play a very important role in designing and performing works related to sealing and reinforcing rock mass media. To provide highly efficient sealing of casing pipes in deep boreholes and ground sealing with hole injection methods, the rheological parameters should be selected in view of the following factors (Gonet & Stryczek, 2001; Pinka et al., 2006; Stryczek et al., 2012):

- Reservoir conditions of ground and rocks to be sealed,
- Geometry of the borehole and the circulation system,

- Mutual relations between the flux of the injected sealing agent and resultant flow resistance, especially in the sealed medium.

Meeting these criteria is connected with proper selection of rheological models, followed by determining rheological parameters for the assumed model.

Rheological properties of fresh cement slurries raise interest because they are also connected with:

- slurry bonding process,
- consistency,
- stability,
- selected injection technology,
- slurry flow resistance in the circulation system.

Although numerous laboratory and experimental investigations have been realized at various scientific-research units (Gonet & Stryczek, Kurdowski, 1991; Wiśniowski & Skrzypaszek, 2006; Wiśniowski et al., 2007) over the last 20 years, we are still missing a complete and complex evaluation of sealing slurries in view of their rheology. This is mainly caused by the fact that rheology of sealing slurries is complex and depends on many physicochemical factors (Giergieczny et al., 2002; Kurdowski, 1991; Stryczek et al., 2012).

Sealing slurries, mainly the cement-based ones, are concentrated dispersive systems, containing solid particles of considerably developed specific surface. Rheologically, such systems are very complex. This also stems from the fact that the rheological properties have a significant effect on:

- additives and admixtures modifying technological properties of fresh and set slurries (Jasiczak & Mikołajczak, 2003; Kon & Jóźwiak, 2000; Kucharska, 2000),
- chemically complex mechanism of hydration in a slurry in a function of time (Kurdowski, 1991).

2. Admixtures regulating rheological properties of sealing slurry

Special attention should paid to plasticizing (plasticizers PL) and liquefying (traditional and new-generation superplasticizers SP) admixtures affecting the modification and optimization of rheological properties of fresh cement slurries as far as providing efficiency of sealing of casing pipes is concerned.

According to the standard PN-EN934-2, admixtures reducing water quantity have been divided into plasticizing (A) and liquefying (B) agents (Stryczek et al., 2012).

The plasticizers (PL) were already used in the 1930's and covered such admixtures as:

- Salts of lignosulfone acids,
- Hydroxycarboxyl acid (Ca, Na),
- Hydroxyl polymers,
- Carbamino compounds,
- Ethoxy nonyl phenol.

Their efficiency can be evaluated on the basis of water reduction level of 5÷15%.

Among the liquefiers (SP) are such admixtures as:

- Sulfonated melamine formaldehyde (SMF),
- Sulfonated naphthalene-formaldehyde (SNF) condensates,
- Melamine-naphthalene sulfonate mixtures,
- Modified calcium or sodium lignosulfonates,
- Sulfonic acid and hydrocarbon esters,
- other products – polymers having mostly unknown properties, the characteristic of which is given only by the producer, e.g. copolymers of formic acid and naphthalene-sulfonic acid or methylnaphthalene-sulfonic acid, copolymers of methacrylic acid with sodium salt or polyethylene glycol, polycyclic sulfonates, acids, sulfonated polystyrenes, and other.

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

In the 1990's very effective III generation admixtures (KAE) were introduced. They were based on:

- polycarboxylates (acrylates),
- carboxyl ester.

The efficiency of water reduction level in the liquefier (super superplasticizer) group is of 20÷40%.

The concentration of dosed plasticizer admixtures varies within 0.2 to 0.5% with respect to the mass of cement.

3. Laboratory analyses

Laboratory analyses were focused on proving the following thesis: properly selected type of superplasticizer [by BASF Polska Sp.z o.o. (The Chemical Company) – Admixtures for Concrete Division] advantageously affects the rheological parameters of sealing slurry based on metallurgical cement CEM III/A 32,5.

The following variables were used in the analyses:

- type of superplasticizer,
- type of batch fluid.

The laboratory experiments were made on superplasticizers produced by BASF (http://www.basf-admixtures.pl...):

- SKY 501,
- SKY 503,
- SKY 591,
- ACE 430,
- Glenium 115.

The superplasticizer concentration in the slurry was 0.5 wt% (as compared with mass of dry cement).

Water to cement ratio for the analyzed sealing slurries was equal to 0.5.

The sealing slurries were made of metallurgical cement CEM III/A 32,5 N-LH/HSR/NA – Lafarge Cement S.A. in Małogoszcz. The mineral composition of metallurgical cements used for the experiments is presented in Table 1.

TABLE 1

Mineral composition of metallurgical cements used for laboratory experiments

Metallurgical cement composition [%]		
Limestone	3.7	
Slag	60.8	
Klinker	35.5	
	Mineral composition of klinker [%]	
	C_3A	9.9
	C_4AF	9.7
	C_3S	62.9
	C_2S	10.7

The parameters of sealing slurries underwent rheological analyses at a temperature of 20°C (±2°C) [293 K].

Cements used for sealing slurries production were sifted in sieves 0.20 mm and 0.08 mm of square mesh.

Fresh water, devoid of any mechanical contaminations, and NaCl (fully) saturated brine (from Wieliczka Salt Mine) were used as the batch fluid.

The laboratory analyses of rheological parameters of fresh sealing slurries concentrated on the following measurements (Wiśniowski & Skrzypaszek, 2001, 2006; Wiśniowski et al., 2007):

- Rheological parameters (plastic viscosity, apparent viscosity, yield point) – with a rotary viscosimeter with coaxial cylinders Chan – 35 API Viscometer – Tulusa, Oklahoma USA EG.G Chandler Engineering, and twelve rotational speeds (600, 300, 200, 100, 60, 30, 20, 10, 6, 3, 2, 1 rot/min, 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; 1.70 s^{-1});
- Determining rheological model – the optimal rheological model of sealing slurries could be properly selected after determining the rheological curve, on the basis of which the measurement results could be best described in a coordinates systems: tangential stress (τ) – shear rate (γ).

The rheological parameters were determined for particular models with the regression analysis method. Then the optimal rheological model was specified for a given sealing slurry recipe with statistical tests.

The following rheological models were analyzed:

- Newton model $$\tau = \eta \cdot \left(-\frac{dv}{dr}\right)$$
- Bingham model $$\tau = \tau_y + \eta \cdot \left(-\frac{dv}{dr}\right)$$
- Ostwald de Waele model $$\tau = k \cdot \left(-\frac{dv}{dr}\right)^n$$
- Casson model $$\tau = \sqrt{\tau_y} + \sqrt{\eta} \cdot \sqrt{\left(-\frac{dv}{dr}\right)}$$

- Herschel-Bulkley model $\tau = \tau_y + k \cdot \left(-\frac{dv}{dr} \right)^n$

where:

n — exponent,

k — consistency coefficient $Pa \cdot s^n$,

τ_y — yield point, Pa,

η — dynamic coefficient of viscosity for Newton model; plastic viscosity for Bingham model, plastic viscosity for Casson model $Pa \cdot s$,

$\frac{dv}{dr}$ — shear rate gradient – γ – s^{-1}.

For the reason of facilitating calculations related with establishing optimal rheological models for the analyzed slurries, the computer program „Rheo Solution", owned by the Faculty of Drilling, Oil and Gas AGH-UST, was used (Wiśniowski & Skrzypaszek, 2001).

Table 2 gives a list of calculated rheological parameters of analyzed cement slurry models with w/c = 0.5 and 0.5% concentration of various fresh water-based superplasticizers. The flow curves for selected models are presented in figures 1 and 2.

TABLE 2

Rheological parameters of cement slurries based on metallurgical cement CEM III/A 32,5 and fresh water for w/c = 0.5, admixed with selected superplasticizers defined at a temperature of 20°C for various rheological models

Rheological parameters \ **Superplasticizer**		**No super-plasticizer**	**SKY 591**	**ACE 430**	**SKY 501**	**Glemium 115**	**SKY 503**
Newton model	Newtonian dynamic viscosity [Pa·s]	0,090	0,078	0,060	0,072	0,069	0,054
	Correlation coefficient [-]	0,857	0,998	0,994	0,977	0,999	0,998
Bingham model	Plastic viscosity [Pa·s]	0,071	0,076	0,057	0,065	0,068	0,053
	Yield point [Pa]	12,211	1,278	2,012	4,621	0,763	0,972
	Correlation coefficient [-]	0,984	0,999	0,999	0,998	0,999	0,999
Ostwald de Waele model	Consistency coefficient [Pa·s^n]	4,459	0,486	0,573	1,573	0,179	0,322
	Exponent [-]	0,388	0,683	0,625	0,495	0,833	0,696
	Correlation coefficient [-]	0,972	0,945	0,956	0,942	0,984	0,957
Casson model	Casson's viscosity [Pa·s]	0,041	0,065	0,046	0,046	0,065	0,045
	Yield point [Pa]	6,971	0,364	0,620	2,053	0,060	0,272
	Correlation coefficient [-]	0,996	0,998	0,999	0,999	0,999	0,998
Herschel-Bulkley model	Yield point[Pa]	7,554	1,567	1,482	3,443	0	1,186
	Consistency coefficient [Pa·s^n]	0,662	0,062	0,090	0,149	0,120	0,042
	Exponent [-]	0,677	1,030	0,934	0,879	0,916	1,033
	Correlation coefficient [-]	0,996	0,999	0,999	0,999	0,999	0,999
Apparent viscosity at 1022.04 [s^{-1}] [Pa·s]		0,080	0,078	0,059	0,068	0,067	0,054

The analysis of data presented in Table 2 and in Figures 1 and 2 reveals that:

- The highest Newtonian dynamic viscosity is observed for a slurry with admixed SKY501 – practically twice as high as the slurry admixed with Glenium 115;

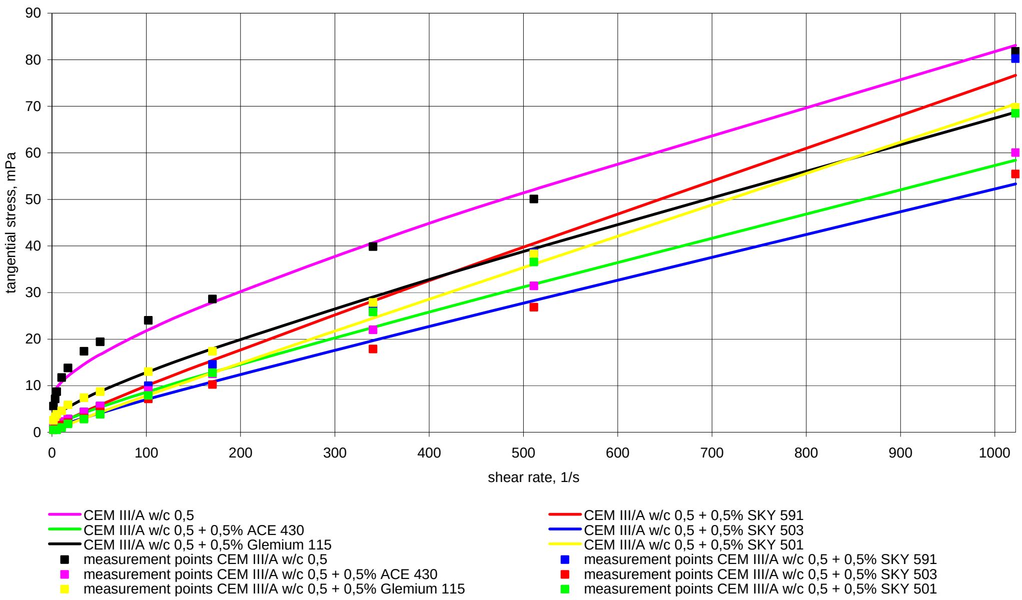

Fig. 1. Flow curves for sealing slurries based on metallurgical cement CEM III/A 32,5 and fresh water with superplasticizers (polycarboxylates) in the Casson model

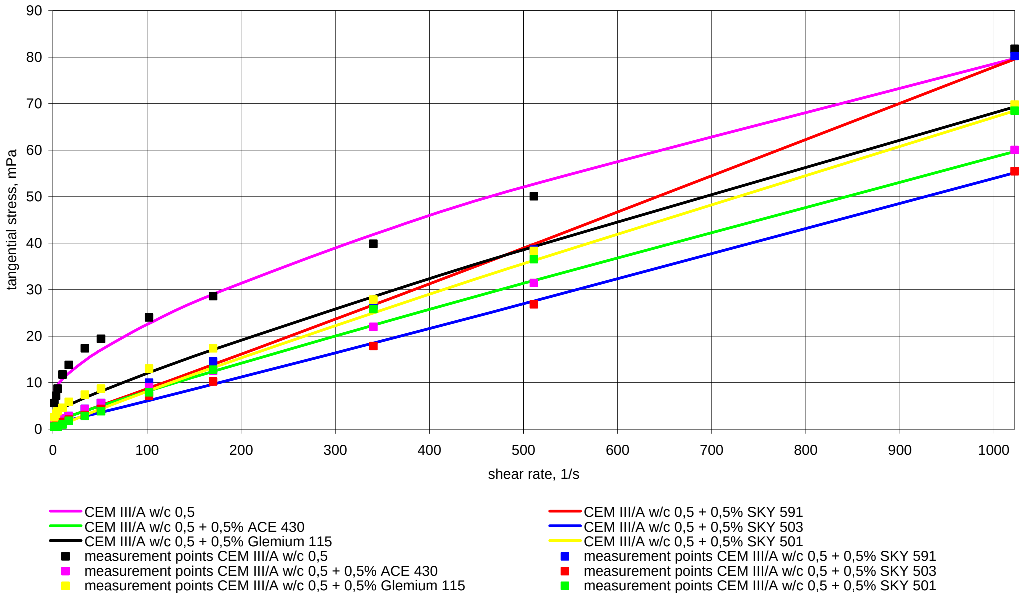

Fig. 2. Flow curves for sealing slurries based on metallurgical cement CEM III/A 32,5 and fresh water with superplasticizers (polycarboxylates) in the Herschel-Bulkley model

- The highest and the lowest plastic viscosity values (in Bingham model) are observed for slurries admixed with SKY503 and Glenium 115, respectively;
- The highest and the lowest Casson viscosity values are noted for the slurries admixed with SKY503 and SKY591, respectively;
- The highest yield point values are observed for a slurry admixed with SKY501; This exceeds over 20 times (Bingham model) and 10 times (Casson model) the slurry with the Glenium 430 admixture;
- The highest consistency value is noted for a slurry with SKY501 admixture, i.e. over 10 times higher than for the slurry admixed with Glenium 430, which has the highest exponent for the consistency coefficient.

Casson model best describes rheological parameters of slurries admixed with SKY591 and SKY503, whereas the Herschel-Bulkley model is more appropriate for describing slurries with SKY503, Glenium 430 and Glenium 115 admixtures. They have the highest correlation coefficients among all presented models.

Among the analyzed superplasticizers SKY 503 turns out to be most efficient. The admixed slurry is described with the Herschel-Bulkley model and the obtained correlation coefficient is equal to 0.999 (Table 2).

The rheological parameters for various models of brine-based slurries are presented in Table 3, whereas flow curves for the Casson and Herschel-Bulkley models in Figs. 3 and 4, respectively. Also in this case SKY 503 appeared to be the most efficient superplasticizer.

TABLE 3

Rheological parameters of cement slurries based on metallurgical cement CEM III/A 32,5 and NaCl saturated brine for $w/c = 0.5$, admixed with selected superplasticizers defined at a temperature of 20°C for various rheological models

Rheological parameters	**Superplasticizer**	**No super-plasticizer**	**SKY 591**	**ACE 430**	**SKY 501**	**Glemium 115**	**SKY 503**
Newton model	Newtonian dynamic viscosity [Pa·s]	0,222	0,055	0,056	0,061	0,047	0,043
	Correlation coefficient [-]	0,970	0,951	0,984	0,989	0,970	0,933
Bingham model	Plastic viscosity [Pa·s]	0,197	0,050	0,053	0,057	0,044	0,037
	Yield point [Pa]	8,474	3,706	2,205	2,710	1,916	4,008
	Correlation coefficient [-]	0,995	0,974	0,991	0,998	0,978	0,981
Ostwald de Waele model	Consistency coefficient [Pa·s^n]	2,870	0,864	0,381	1,149	0,205	1,271
	Exponent [-]	0,545	0,555	0,694	0,500	0,774	0,457
	Correlation coefficient [-]	0,976	0,968	0,989	0,899	0,992	0,964
Casson model	Casson's viscosity [Pa·s]	0,142	0,040	0,046	0,041	0,041	0,026
	Yield point [Pa]	3,370	1,127	0,045	1,211	0,242	1,780
	Correlation coefficient [-]	0,998	0,983	0,995	0,996	0,980	0,993
Herschel-Bulkley model	Yield point [Pa]	4,598	0	0,043	2,423	0	1,396
	Consistency coefficient [Pa·s^n]	0,707	0,575	0,261	0,073	0,411	0,379
	Exponent [-]	0,795	0,646	0,768	0,963	0,676	0,664
	Correlation coefficient [-]	0,998	0,994	0,999	0,998	0,994	0,998
Apparent viscosity at 1022.04 [s^{-1}] [Pa·s]		-	0,047	0,051	0,058	0,041	0,037

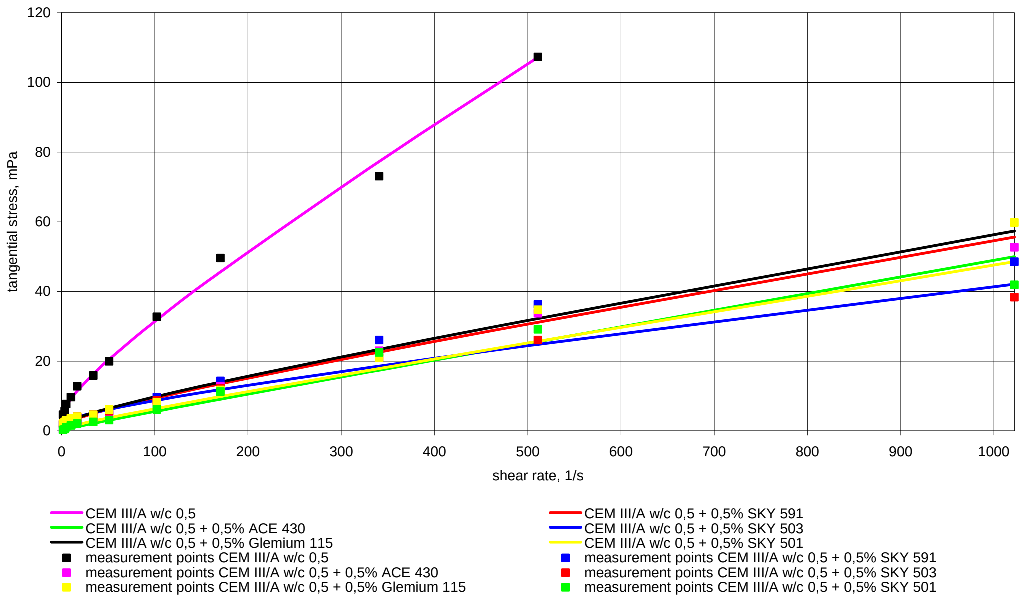

Fig. 3. Flow curves for sealing slurries based on metallurgical cement CEM III/A 32,5 and NaCl brine with superplasticizers (polycarboxylates) in the Casson model

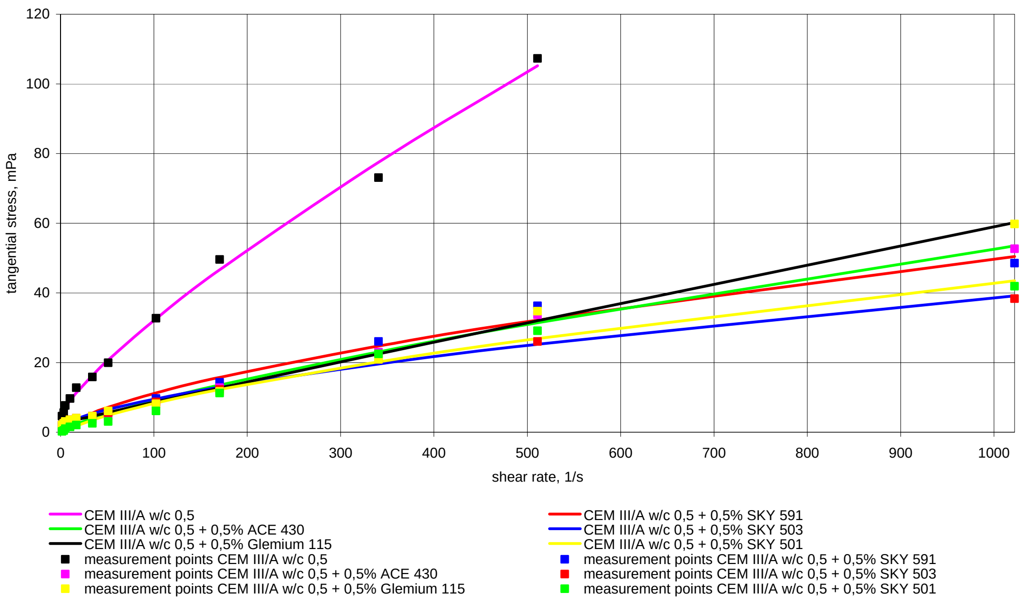

Fig. 4. Flow curves for sealing slurries based on metallurgical cement CEM III/A 32,5 and NaCl brine with superplasticizers (polycarboxylates) in the Herschel-Bulkley model

4. Conclusions

- Owing to their rheological parameters, all the analyzed sealing slurries can be best described by the Herschel-Bulkley rheological model.
- Newtonian and Bingham linear models of sealing slurries should not be used for calculating flow resistances which can take place in the process of sealing casing pipes in deep boreholes, and also during geoengineering works employing hole injection methods.
- When preparing sealing slurries based on metallurgical cement CEM III/A 32,5 N-LH/HSR/NA from Lafarge Cement S.A. in Małogoszcz one should account for the necessity to increase the w/c ratio to provide rheological parameters giving minimum flow resistances and proper injection time in the process of sealing casing pipes in boreholes.

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References

Giergieczny Z., Małolepszy J., Szwabowski J., Śliwiński J., 2002. *Cementy z dodatkami mineralnymi w technologii betonów nowej generacji*. Górażdże Cement Opole.

Gonet A., Stryczek S., 2001. *Reologia wybranych zaczynów uszczelniających wykonanych z cementów Górażdże Cement S.A.*, Sympozjum Naukowo-Techniczne „Cementy w budownictwie, robotach wiertniczych i inżynieryjnych oraz hydrotechnice", Piła.

Jasiczak J., Mikołajczak P., 2003. *Technologia betonu modyfikowanego domieszkami i dodatkami*. Alma Mater, Politechnika Poznańska.

Kon E., Jóźwiak H., 2000. *Klasyfikacje i wymagania dla domieszek do betonu, zaprawy i zaczynu.* Cement-Wapno-Beton, Nr. 1.

Kucharska L., 2000. *Tradycyjne i współczesne domieszki do betonu zmniejszające ilość wody zarobowej*. Cement-Wapno-Beton, Nr. 2.

Kurdowski W., 1991. *Chemia cementu.* PWN.

Małolepszy J., 1989. *Hydratacja i własności spoiwa żużlowo-alkalicznego*. Zeszyty Naukowe AGH nr 53, Wydawnictwa AGH Kraków.

Pinka J., Wittenberger G., Engel., 2006. *Dobyvanie ložisk vrtmi*. AMS F BERG, TU v Kosiciach, Kosice.

Stryczek S., Wiśniowski R., Gonet A., Złotkowski A., 2012. *Influence of specific surface of lignite fluidal ashes on rheological properties of sealing slurries*. Arch. Min. Sci., Vol 57, No. 2, p. 313-322.

Wiśniowski R., Skrzypaszek K., 2001. *Komputerowe wspomaganie wyznaczania modelu reologicznego cieczy – program Flow-Fluid Coef*. NTTB Nowoczesne Techniki i Technologie Bezwykopowe, nr 2-3.

Wiśniowski R., Skrzypaszek K., 2006. *Analiza modeli reologicznych stosowanych w technologiach inżynierskich*. Wiertnictwo, Nafta, Gaz, Tom 23, z. 1.

Wiśniowski R., Stryczek S., Skrzypaszek K., 2007. *Kierunki rozwoju badań nad reologią płynów wiertniczych*. Wiertnictwo, Nafta, Gaz, Tom 24, z. 1.

http://www.basf-admixtures.pl/PL/Pages/default.aspx z dnia 20.03. 2013 r.

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