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NEW-GENERATION SEALING SLURRIES FOR BOREHOLE INJECTION PURPOSES

ZACZYNY USZCZELNIAJĄCE NOWEJ GENERACJI DO INIEKCJI OTWOROWEJ

The development of techniques and technologies thanks to which parameters of the ground medium can be modified makes specialists look for new recipes of geopolymers – binders for the reinforcing and sealing of unstable and permeable grounds. The sealing slurries are expected to meet a number of strict requirements, therefore it is important to find new admixtures and additives which could modify the fresh and hardened slurry. Special attention has been recently paid to the fluid ash – a by-product of the combustion of hard coals. However, the use of this additive is associated with the application of appropriate superplastifier.

Laboratory analyses of rheological parameters of fresh sealing slurries and the ways of improving their liquidity by a properly selected third-generation superplastifier are presented in the paper. The slurries were based on Portland cement CEM I, milled granulated large-furnace slag and fly ash from fluidized-bed combustion of hard coal.

Keywords: Cement slurry, Fluid ash, Geopolymers

Rozwój technik i technologii modyfikacji parametrów ośrodka gruntowego wymusza ciągłe poszukiwanie nowych receptur geopolimerów używanych jako spoiwa do wzmacniania i uszczelniania gruntów niestabilnych i przepuszczalnych. Wychodząc naprzeciw oczekiwaniom spełnienia przez zaczyn uszczelniający szereg rygorystycznych wymagań należy poszukiwać nowych domieszek i dodatków modyfikujących jego parametry w stanie świeżym i stwardniałym. Szczególne znaczenie w ostatnich czasach nabiera wzbogacenie receptur o dodatek popiołów fluidalnych ze spalania węgli kamiennych. Aplikacja tego dodatku wymaga jednak uplastycznienia zaczynu uszczelniającego właściwym superplastyfikatorem.

W artykule przedstawiono badania laboratoryjne parametrów reologicznych świeżych zaczynów uszczelniających, w aspekcie poprawy ich płynności przez doświadczalne dobranie superplastyfikatora trzeciej generacji. Zaczyny sporządzono w oparciu o cement portlandzki CEM I, mielony granulowany żużel wielkopiecowy oraz popiół lotny z fluidalnego spalania węgla kamiennego.

Słowa kluczowe: zaczyn uszczelniający, popiół fluidalny, geopolimery

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1. Introduction

Geotechnical problems are frequently encountered while conducting mining, hydrotechnical and engineering work. A solution to this is the reinforcement and sealing of both ground and the rock mass medium. The basic activities thanks to which the assumed goal can be achieved are usually realized with geoengineering methods and properly selected sealing slurries. Portland cement-based slurries frequently turn out to have a number of disadvantageous features:

- long time of bonding,
- poor rheological properties,
- high permeability,
- poor adhesiveness to clay-shale layers,
- low resistance to corrosiveness of strongly mineralized reservoir waters.

These unfavorable properties of sealing slurries can be significantly improved by introducing properly selected mineral additives and organic admixtures. Accordingly, the new recipes of slurries have been intensely investigated for the last years to obtain a new generation high-durability specialist binders, i.e. geopolymers (Bensted., 2008; Brylicki et al., 1994; Bujok et al., 2013; Galos & Eliasz-Bocheńczyk, 2005; Giergiczny, 2006; Pinka et al., 2006).

Geopolymer-based slurries are made exclusively of inorganic components. They are obtained by modifying the composition of properly selected and prepared slurries based on multi-component common-use cements or milled granulated large-furnace slags with additives having puzzolana properties (Czarnecki & Łukowski; Deja, 2004; Kucharska, 2000; Stryczek et al., 2006, 2014).

2. Geopolymer slurries for injection purposes

The use of chemical additives and admixtures frequently is a prerequisite of sealing slurries with good technological parameters. The classification, *modus operandi* and changes of properties of fresh and hardened slurry under the influence of various admixtures have been discussed in many papers.

Among the most commonly applied mineral additives applied to cement are:

- fly ash from the combustion of hard coal,
- fly ash from the fluidized-bed combustion of hard coal,
- milled granulated large-furnace slags.

Fly ash is an additive having puzzolana properties, whereas milled granulated large-furnace slag exhibits puzzolana-hydraulic activity.

Inorganic hydraulic binders with fly ash and/or milled granulated large-furnace slag have a number of more favorable properties than the classic sealing slurries based on Portland cements CEM I.

The composition of fly ash primarily depends on the chemical composition of coal used in the furnace. Other important factors are the combustion technology, mainly temperature of burning, waste gases sweetening method and sometimes biomass co-firing.

In the technology of common-use cements (standard PN-EN 197-1) and concrete (standard PN-EN 450-1) only ashes coming from the combustion of hard coal ashes in conventional dust furnaces are admitted to use.

Fly ash from fluidized-bed combustion of coal differs from ashes type V and W which are used in the traditional cement technology. These differences mainly stem from the technology of coal burning. Accordingly, the respective standards do not admit the ashes from the combustion of coal in fluidized-bed furnaces as a component of common-use cements nor as component of concrete. It has only a technical approval. Recently such ashes have been investigated in view of their application in sealing slurries for geoengineering works. The results obtained so far (Grzeszczyk & Lipowski, 2002; Kon & Jóźwiak, 2000; Kurdrowski, 2010; Małolepszy, 1989; Neville, 2012; Nocuń-Wczelik et al., 2009) show to their positive influence on the usability of slurries and the role they play in modifying cements; they can be also used as an additive lowering the density of slurries or rheology modifier.

The large-furnace slag is a by-product of the iron production in a large furnace. Apart from the chemical composition, the chemical activity of the large-furnace slag is influenced by the amount and build of the glassy phase. This, in turn, mainly depends on the way in which the slag has been cooled, less on its chemical composition.

The slags added to cements based on Portland klinker improve some of its properties which may be advantageous when sealing the rock mass with borehole injection methods.

Milled granulated large-furnace slag has hydraulic properties, i.e. in the presence of water or an activator (e.g. calcium hydroxide, sodium carbonate, alkali, calcium sulfate) binds creating C-S-H phase as the main product. The bonding may also take place without the activator, which slows down the process very much. Thanks to the bonding abilities, the large furnace slag plays the role of an active hydraulic binder. The C-S-H phase formed at the stage of hydration of large-furnace slags has a lower CaO/SiO_2 ratio as compared to Portland cement. The lover C/S ratio is favorable as far as the chemical durability is concerned.

Cement admixtures are classified according to their basic function they play in the slurry, though may also have other effect on the technological parameters of the slurry.

Plastifiers and superplastifiers (according to the standards – admixtures which reduce and considerably reduce water content) occupy a special position among admixtures. Thanks to these admixtures the time in which the slurry maintains its plasticity at a low water/cement ratio (binding, mixing) can be controlled.

In practice this means that the pumpability (workability) of the sealing slurry can be improved and maintained for at least 90 minutes. By significant lowering of the w/c (w/b) ratio, the activity of this type of admixtures favorably changes the most significant usability properties of fresh and hardened sealing slurry.

Plastifiers and superplastifiers influence the processes taking place between the hydrating binder and the admixed water solution (especially at the initial stage of hydration) in the slurry. After applying water to cement we have to do with adsorption of water particles on the surface of binder grains, preceding the hydrolysis and hydration of klinker phases. A cement gel layer (primary hydrate) is formed on the surface of grains within a few minutes after the cement has been mixed with water. Disadvantageously for the superplastifiers, the conditions of their good cooperation (compatibility) with cement have not been fully recognized yet.

Depending on the chemical composition of superplastifiers, they may evoke the following effects in the cement slurry (Gołaszewski, 2008; Gonet & Stryczek, 2001; *Materiały informacyjne...*):

- formation and introduction of a "lubricating" layer on the cement grains and introduced mineral additives, which lowers the internal friction in the cement slurry,

- adsorption on cement grains; surfaces of these grains acquire the same electrical charge, which causes their repelling (Coulomb forces); simultaneously, their electrokinetic potential increases,
- lowering of surface tension of water; these are surfactant admixtures,
- spherical effect related with the presence of side chains in the plastifier particles, hindering the approaching of cement particles; these are mainly polycarboxylate (PC) admixtures, copolymers of acrylic acid with acrylates (CAE) and cross-linked acrylic resins(CLAP).

The analyses revealed that superplastifiers slowed down the emission of heat of hardening, and so the hydration of cement: the higher was its participation in the cement, the slower was the hydration rate. This impact is strongest in cements with mineral admixtures, e.g. CEM II and CEM III.

The efficiency of superplastifiers depends on a number of factors, e.g. (*Materiały informacyjne...*; Śliwa et al., 2012; Wiśniowski & Skrzypaszek, 2001, 2006):

- type of cement (some superplastifiers can be used with metallurgical cements),
- granulation of mineral additives (especially dusty fractions),
- type of gypsum introduced to cement as a regulator of the time of bonding,
- consistency of slurry,
- concentration of liquefying admixture,
- type and chemical composition of admixture,
- water/binder ratio,
- manner and time in which admixture is introduced to the slurry.

3. Laboratory tests

During laboratory tests attempts were made to prove the thesis that properly selected inorganic additives and superplastifier admixtures introduced to the slurry based on Portland cement CEM I 42,5 positively affect the technological parameters of fresh and hardened cement slurry which are used for reinforcing and sealing the ground and rock mass media with the drilling technology methods.

The water/cement ratio of the analyzed sealing slurries equaled to 0.5 and 0.7. The concentration of the superplastifier produced by BASF Polska Sp. z o.o. (The Chemical Company – Dept. of Concrete Admixtures) in the slurry was: 0.25; 0.5 and 0.75wt% (in relation to the cement dry mass).

The following superplastifiers were used for the tests:

- Glenium SKY 591
- Glenium SKY 592
- Glenium SKY 686

Laboratory analyses of technological parameters of sealing slurries are performed on the basis of the following standards:

1. PN – EN 197 – 1: 2002, Cement. Part 1. Composition, requirements and congruence criteria for common-use cements.
2. PN – EN ISO 10426 – 1. Oil and gas industry. Cements and materials for cementing boreholes. Part 1. Specification. 2006

3. PN – EN ISO 10426 – 2. Oil and gas industry. Cements and materials for cementing boreholes. Part 2: Analysis of drilling cements. 2006.

The recipes of the analyzed sealing slurries (w/c = 0.5, w/c = 0.7), and with superplastifiers (w/c = 0.5; w/c = 0.7) are presented in tables 1 and 3. The parameters of rheological models of sealing slurries with various superplastifiers are given in tables 2, 4 and 5. The values of technological parameters of analyzed recipes of sealing slurries with superplastifiers added are listed in table 6. The obtained models were compared on the example of the Herschel-Bulkley curve, which was visualized in figs. 1÷3.

TABLE 1

Recipes of sealing slurries with various superplastifiers added (w/c = 0.5)

No. of recipe	w/m ratio	% share in recipe			
		Portland cement CEM I strength class 42,5 R	Milled granulated large-furnace slag	Fluid ash from combustion of hard coal	Super-plastifier
1	0.5	60	30	10	no
1a	0.5	60	30	10	SKY 591
1b	0.5	60	30	10	SKY 592
1c	0.5	60	30	10	SKY 686

TABLE 2

Parameters of rheological models for sealing slurries with various superplastifiers added (w/c = 0.5)

Rheological parameters	No. of recipe	1	1a	1b	1c
Newton model	Newton dynamic viscosity [Pa · s]	0.0871	0.0418	0.0518	0.0646
	Correlation coefficient [-]	0.8913	0.6948	0.9677	0.9052
Bingham model	Plastic viscosity [Pa · s]	0.0708	0.0367	0.0459	0.0532
	Yield point [Pa]	10.4978	3.3538	3.8483	7.3826
	Correlation coefficient [-]	0.9843	0.9997	0.9969	0.9864
Ostwald de Waele model	Consistency coefficient [Pa · s^n]	3.5286	1.6189	1.4706	2.5761
	Exponent [-]	0.4181	0.3901	0.4490	0.4157
	Correlation coefficient [-]	0.9771	0.8838	0.9286	0.9699
Casson model	Casson viscosity [Pa · s]	0.0439	0.0222	0.0308	0.0333
	Yield point [Pa]	5.5278	1.8997	1.8450	3.8461
	Correlation coefficient [-]	0.9969	0.9953	0.9996	0.9980
Herschel-Bulkley model	Yield point [Pa]	5.5271	3.1627	2.6885	3.9434
	Consistency coefficient [Pa · s^n]	0.7268	0.0478	0.1376	0.4832
	Exponent [-]	0.6633	0.9614	0.8403	0.6808
	Correlation coefficient [-]	0.9985	0.9998	0.9999	0.9994
Apparent viscosity for 1022.04 [s^{-1}] [Pa · s]		0.0770	0.0400	0.0480	0.0570

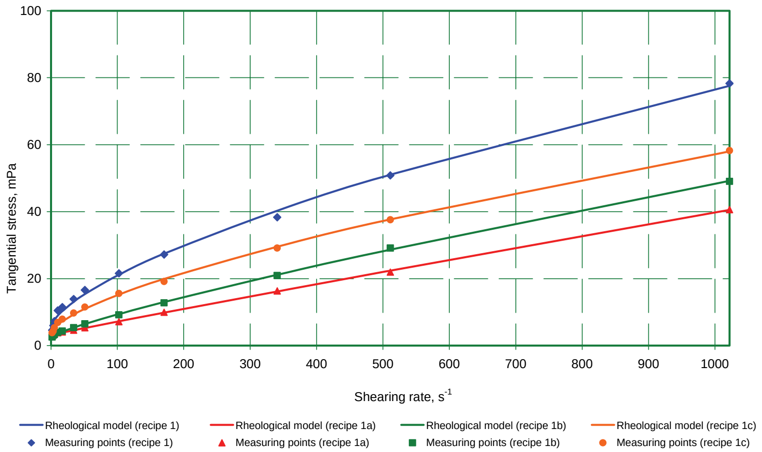

Fig. 1. Comparison of obtained models on the example of Herschel-Bulkley curve for sealing slurries with various superplastifiers added (w/c = 0.5)

TABLE 3

Recipes of sealing slurries with superplastifier Glenium SKY 591 (w/c = 0.5 and 0.7)

No. of recipe	**w/m ratio**	**% share in recipe**			
		Portland cement CEM I strength class 42,5 R	**Milled granulated large-furnace slag**	**Fluid ash from the combustion of hard coal**	**Superplastifier Glrnium SKY 591 (added in proportion to working fluid),**
1	0.5	60	30	10	no
1.1.a	0.5	60	30	10	0.25
1.1.b	0.5	60	30	10	0.5
1.1.c	0.5	60	30	10	0.75
2	0.7	60	30	10	no
2.1.a	0.7	60	30	10	0.25
2.1.b	0.7	60	30	10	0.5

TABLE 4

Parameters of rheological models for sealing slurries with superplastifier Glenium SKY 591 (w/c = 0.5)

Rheological parameters \ **Number of recipe**		**1**	**1.1.a**	**1.1.b**	**1.1.c**
1	**2**	**3**	**4**	**5**	**6**
Newton model	Newton dynamic viscosity [Pa · s]	0.0871	0.0779	0.0571	0.0395
	Correlation coefficient [-]	0.8913	0.5846	0.8509	0.9679
Bingham model	Plastic viscosity [Pa · s]	0.0708	0.0548	0.0446	0.0348
	Yield point [Pa]	10.4978	14.9584	8.0180	3.0529
	Correlation coefficient [-]	0.9843	0.9369	0.9920	0.9999
Ostwald de Waele model	Consistency coefficient [Pa · s^n]	3.5286	5.1848	3.6510	1.6239
	Exponent [-]	0.4181	0.3599	0.3352	0.3728
	Correlation coefficient [-]	0.9771	0.9971	0.9387	0.8558

1	2	3	4	5	6
Casson model	Casson viscosity [Pa · s]	0.0439	0.0303	0.0235	0.0206
	Yield point [Pa]	5.5278	8.8742	5.0202	1.7937
	Correlation coefficient [-]	0.9969	0.9715	0.9985	0.9922
Herschel-Bulkley model	Yield point [Pa]	5.5271	1.1691	6.2187	3.0703
	Consistency coefficient [Pa · s^n]	0.7268	4.5545	0.2187	0.0339
	Exponent [-]	0.6633	0.3759	0.7694	1.0039
	Correlation coefficient [-]	0.9985	0.9973	0.9980	0.9999
Apparent viscosity at 1022.04 [s^{-1}] [Pa · s]		0.0770	0.0650	0.0510	0.0380

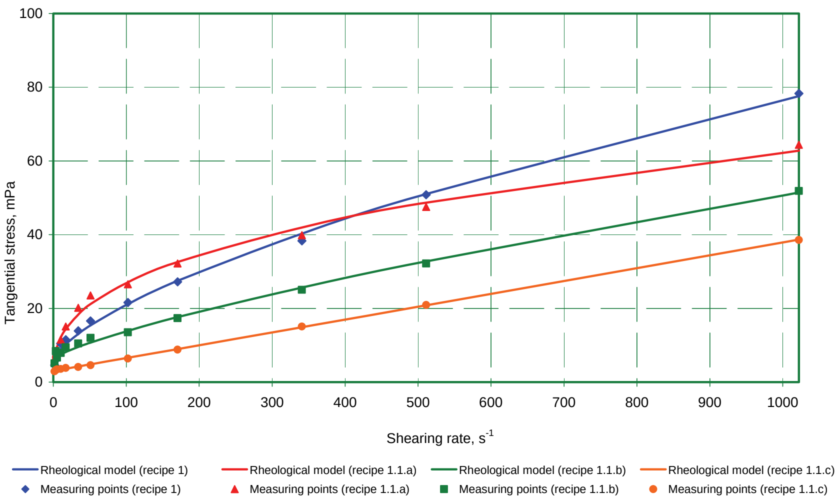

Fig. 2. Comparison of obtained models on the example of Herschel-Bulkley curve for sealing slurries with superplastifier Glenium SKY 591 (w/c = 0.5)

TABLE 5

Parameters of rheological models for sealing slurries with superplastifier Glenium SKY 591 (w/c = 0.7)

Rheological parameters / **Number of recipe**		**2**	**2.1.a**	**2.1.b**
1	**2**	**3**	**4**	**5**
Newton model	Newton dynamic viscosity [Pa · s]	0.0228	0.0191	0.0138
	Correlation coefficient [-]	0.7718	0.8866	0.9415
Bingham model	Plastic viscosity [Pa · s]	0.0214	0.0153	0.0117
	Yield point [Pa]	4.7452	2.4107	1.3584
	Correlation coefficient [-]	0.9983	0.9926	0.9978
Model Ostwald de Waele model	Consistency coefficient [Pa · s^n]	2.8061	1.0521	0.6083
	Exponent [-]	0.2577	0.3564	0.3819
	Correlation coefficient [-]	0.8740	0.9378	0.9117
Casson model	Casson viscosity [Pa · s]	0.0093	0.0085	0.0068
	Yield point [Pa]	3.4127	1.4426	0.7891
	Correlation coefficient [-]	0.9906	0.9984	0.9962

1	2	3	4	5
Herschel-Bulkley model	Yield point [Pa]	4.5595	1.8353	1.2182
	Consistency coefficient [Pa · s^n]	0.0328	0.0690	0.0208
	Exponent [-]	0.9377	0.7817	0.9163
	Correlation coefficient [-]	0.9987	0.9978	0.9985
Apparent viscosity at 1022.04 [s^{-1}] [Pa · s]		0.0260	0.0170	0.0130

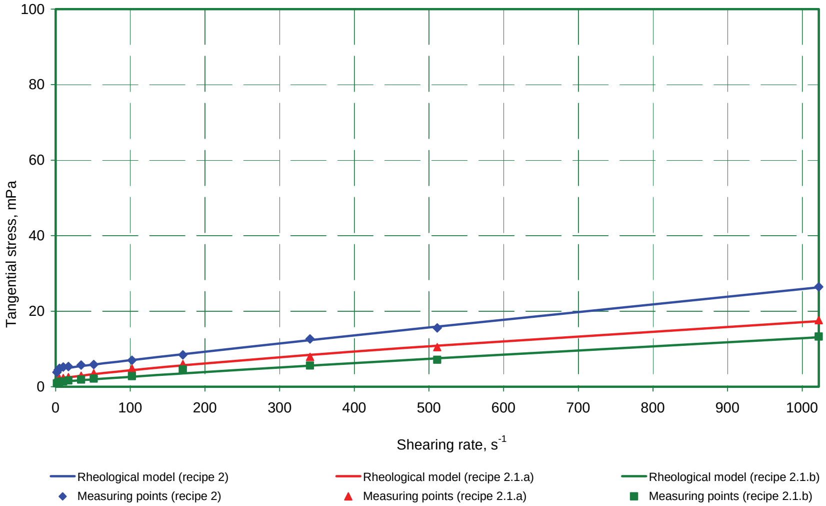

Fig. 3. Comparison of obtained models on the example of Herschel-Bulkley curve for sealing slurries with superplastifier Glenium SKY 591 (w/c = 0.7)

TABLE 6

Technological parameters of sealing slurries defined in laboratory conditions for temperature 20 (±2°C) [293 K]

Denotation of sealing slurry recipe [-]	Water/cement (water/mixture) ratio [-]	Density [kg/m^3]	Cone spillability (AzNII) [mm]	Relevant viscosity (Ford cup no. 4) [s]	Proper filtration ΔP = 0.7 MPa [cm^3/s]	Plastic viscosity η_p [mPa · s]	Apparent viscosity at 600 rpm η_a [mPa · s]	Yield point τ_y [mPa]
1	0.5	1810	215	25	61/17	58.00	77.75	18.84
1.1.a	0.5	1790	220	20	36/20	54.00	104.25	48.12
1.1.b	0.5	1790	260	16	40/20	36.50	39.75	3.11
1.1.c	0.5	1790	280	14	41/30	35.00	34.50	0.00
2	0.7	1650	270	16	83/15	23.50	27.00	3.35
2.1.a	0.7	1630	Above 280	12	52/18	19.00	17.25	0.00
2.1.b	0.7	1630	Above 280	11	50/17	12.75	13.75	0.48

4. Conclusions

- Addition of a small amount of .superplastifiers (0.25÷0.75 of the working fluid volume) results in considerable liquefaction of the prepared sealing slurries.
- Out of three analyzed superplastifiers, Glenium SKY 591 turned out to be the best for the prepared recipe.
- With the increasing concentration of Glenium SKY 591, the degree of liquefaction of the sealing slurry increases, too.
- By increasing w/v ratio from 0.5 to 0.7 at the same superplastifier concentration the apparent viscosity of the sealing slurry is expected to lower down four times.
- The Herschel-Bulkley curve is the best fitted curve which illustrates the rheological model.
- The addition of a superplastifier results in higher spillability, lower filtration and shorter time of outflow from the Ford cup.

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