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THE INFLUENCE OF ASH FROM FLUIDIZED-BED COMBUSTION OF LIGNITE ON RHEOLOGICAL PROPERTIES OF CEMENT SLURRIES**

1. INTRODUCTION

Cementing jobs is a very important element of drilling technology considering the completion of a given field. The selection of an appropriate recipe for sealing slurry is vital as this substance should meet a number of technological and rheological requirements. The selection of suitable additives and admixtures and their concentration in the slurry depends on individual geologic conditions as well as technical-technological conditions in the wellbore, where the cementing job is to be performed [1, 4, 7].

Rheological properties of sealing slurries are important at the stage of designing and also during sealing and reinforcing ground and rock mass with the use of drilling technologies. The high efficiency of sealing deep wellbores and rock mass with hole injection methods, attention should be paid to the selection of rheological parameters of slurries, which should depend on [2, 6]:

- reservoir conditions of sealed ground and rocks,
- geometry of wellbore and circulation system,
- interrelations between the volume of injected slurry and flow resistance in the course of pumping, especially in the sealed medium.

These conditions can be met if the selection criteria and then parameters of the rheological model have been properly chosen. The flow resistance can be calculated for specific cases on the basis of well determined rheological parameters of slurry, and from [5, 6]:

- technological parameters of slurry,
- character of flow (laminar, turbulent or piston).

Although numerous laboratory and experimental analyses have been performed in scientific and research centers for the last twenty years, no complex studies of slurries have been fully performed in the aspect of their rheological classification over the last twenty years. This is due to the complexity of the rheology of sealing slurries and plenty of physicochemical factors.

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2. CHARACTERISTIC OF FLY ASHES FROM FLUIDIZED COMBUSTION OF LIGNITE

Fly ashes are by-products of combustion of fossil fuels in industrial power plants. This is a group of substances which may considerably differ from raw minerals (anthracite, hard coal, lignite) and may also have different burning technologies (conventional furnaces, fluidized-bed furnaces).

These differences are important from the point of view of fly ashes as components of cements, or more generally, binders used in drilling technology. For this reason it is important to know the composition and build of fly ashes. The ash composition and so its properties can vary in a wide range. The chemical composition and the thermal history of ash particles determines their phase composition and build, which in turn, decides about the usability of particular types of fly ashes in various branches of industry, e.g. in cement-based technologies.

The first division with the chemical composition as a criterion, was made on the basis of standard BN-79/6722-09: *Popioły lotne i żużle z kotłów opalanych węglem kamiennym i brunatnym* (*Fly ashes and slags from hard coal and lignite – combusted boilers*). Three categories of fly ashes were distinguished: silica (K), aluminum (G), and calcium (W). The criteria of this classification are presented in Table 1.

Table 1

Classification of fly ashes from combustion of coals, after BN-79/6722-09

Ash	Symbol	SiO_2 [%]	Al_2O_3 [%]	CaO [%]	SO_3 [%]
Silica	K	>40	<30	<10	<4
Aluminum	G	>40	>30	<10	<3
Calcium	W	>30	<30	>10	>3

The ash composition primarily depends on the chemical composition of coal used in the furnace. Another important factor is the combustion technology, especially the temperature of burning, waste gases sweetening and also co-firing of biomass. Combustion of hard coals most frequently brings about ashes classified as K. Lignites from the Adamów, Konin and Bełchatów area usually produce ash W, which is enriched with calcium oxide. Fly ash from the Turoszów Coal Basin coals frequently belongs to category G because of the highest clayey minerals content in coal.

In the technologies based on common-use cements (standard PN-EN 197-1) and concrete (standard PN-EN 450-1) only ashes coming from the combustion of hard coals in conventional ash burners are admitted to use [3, 6].

Ashes from the fluidized-bed combustion of coal are obtained in the process of fluidization, which was discovered by Fritz Winkler in 1921. In this process solids are disposed in a deposit, through which air is passed from the top downward at a definite rate. Such a behavior of the deposit (resembling that of boiling fluid) enables the efficient mixing of solid phase and gives a large solid/gas interface. Owing to the fast circulation of grains, the temperature in the system remains almost the same, even though the heat is produced and absorbed very irregularly. Thanks to this the fluidization process creates very advantageous conditions for chemical reactions with large chemical effects.

Moreover, some properties of the fluidized system are similar to those of fluids, thanks to which solids can be quickly removed from the system.

The fluidized-bed combustion technology involves high temperatures (ca. 850 to 950°C), thanks to which the synthesis of nitrogen oxides in air can be minimized [6].

Unlike ash from a conventional furnace, the fluidized-bed ash grains have an irregular, frequently sharp-edged shape. The surface of such grains is not smooth as in the case of glassed balls, but rough and irregular. As a consequence of this and the water sorption ability of clayey minerals, the ash from the fluidized-bed combustion requires much water. Apart from the free calcium and anhydrite content, this is the most important feature limiting the applicability of this type of ash for the production of common-use cements in line with standards PN-EN 197-1.

3. METHODICS OF LABORATORY TESTS

Laboratory analyses of rheological parameters of cement slurries are based on the following standards:

- PN-EN 197-1:2002. *Cement – Część 1: Skład, wymagania i kryteria zgodności dotyczące cementów powszechnego użytku* (*Cement. Part 1. Composition, requirements and criteria for common use cements*),
- PN-EN ISO 10426-1. *Przemysł naftowy i gazowniczy. Cementy i materiały do cementowania otworów. Część 1: Specyfikacja* (*Oil and gas industry. Cements and materials for cementing boreholes. Part 1. Specification*),
- PN-EN ISO 10426-2. *Przemysł naftowy i gazowniczy: Cementy i materiały do cementowania otworów wiertniczych. Część 2: Badania cementów wiertniczych* (*Oil and gas industry. Cements and materials for cementing boreholes. Part 2: Analyses of drilling cements*).

The laboratory experiments were aimed at establishing the influence of ash from the fluidized-bed combustion of Turoszów lignite on rheological properties of fresh sealing cement slurries based on drilling cement class G (after API). Among the analyzed variables were:

- water/cement ratio,
- ash concentration (wt% in relation to the dry mass of cement).

Preparing cement sealing slurries for laboratory tests

The water/cement ratio for the analyzed sealing slurries equaled to 0.6 and 0.7. The ash concentration from fluidized-bed combustion of lignite was 30, 40, 50, 60 and 70 wt% (with respect to cement dry mass). Cement and ash were weighed on an electronic device (accuracy of ± 0.1%). The slurry was made with the use of a mixer of 1 liter (1 quart) capacity driven at the bottom and equipped with mixer blades.

The temperature of working fluid (network water) and dry cement was similar to that of the mixer and the blades, i.e. 23°C ± 1°C (73°F ± 2°F).

Cement designed for making slurries (after ISO 25911-1 and ISO 3310-1) was sifted through three wire screens 1.0; 0.20 and 0.08 mm of square mesh. Only sieved cement was used for making slurries. Cement used for the production of slurry was so comminuted that the leftovers did not exceed 2% on the sieve 0.20 mm of mesh, and were less than 20% on the sieve of 0.08 mm mesh.

The working fluid was established on the basis of the assumed w/c ratio and then poured into the mixer cup. The measured amounts of cement and ash were added within 15 seconds and the formed slurry was constantly mixed at a rotational speed of 4000 rpm ± 200 rpm. The mixing was continued at a rate of 12 000 rpm ± 500 rpm for 35 s ± 1 s. Thus, the prepared slurry was analyzed in the shortest possible time after it has been prepared.

The laboratory experiment aimed at determining rheological parameters of fresh sealing slurries concentrated on establishing:

- rheological parameters (plastic viscosity, apparent viscosity, yield point) with the use of a rotational viscometer with two coaxial cylinders Chan – 35 API Viscometer – Tulsa, Oklahoma USA EG.G Chandler Engineering, having twelve rotational speeds (600, 300, 200, 100, 60, 30, 20, 10, 6, 3, 2, 1 rpm, corresponding to the shearing 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});
- rheological model – selection of an optimum rheological model of sealing slurries lied in defining a rheological plot which would best describe the results of measurements of measurement results in a coordinates system: tangential stress (τ) – shearing rate (γ).

The rheological parameters were established for particular models with the regression analysis method. Then followed statistical tests in the course of which the optimum rheological model was selected for a given recipe of sealing slurry.

The following rheological models were analyzed [8, 9, 11]:

– 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
$$\sqrt{\tau} = \sqrt{\tau_y} + \sqrt{\eta} \cdot \sqrt{\left(-\frac{dv}{dr}\right)},$$

– 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 in Newton model; plastic viscosity in Bingham model, plastic viscosity in Casson model [$Pa \cdot s$],
$\frac{dv}{dr}$ – gradient of velocity of shearing – γ – [s^{-1}].

A computer program “Rheo Solution” worked out by the authors of this paper and owned by the Department of Drilling and Geoengineering, Faculty of Drilling, Oil and Gas AGH UST [8, 10] was used to simplify the calculation of the optimum rheological models for the analyzed slurries. Cement class G, HSR (after API) imported from Germany was used for making the slurry. The mineral composition of the analyzed cements class G are listed in Tables 2 and 3.

Table 2

Mineral composition of drilling cement class G used for laboratory tests

Component	Drilling cement G (API) content [%]
C_3A	1.20
C_4AF	15.50
C_3S	51.00
C_2S	19.30
$C_4AF + 2 \cdot C_3A$	19.60

Table 3

Exemplary composition of ash from lignite combustion (Turoszów Coal Basin) in fluidized-bed furnace [6]

Component	Content [%]
Combustion loss 1000° C/1 h	2.83
SiO_2	31.20
Al_2O_3	20.00
Fe_2O_3	5.80
CaO	26.40
MgO	1.00
SO_3	7.80
K_2O	1.76
Na_2O	1.78
free CaO	9.87
Total:	99.84

The composition of analyzed recipes of sealing slurries are presented in Table 4.

Table 4

Recipes of sealing slurries used for laboratory tests

No.	w/c [–]	Ash concentration [%]
1	0.6	30
2	0.6	40
3	0.6	50
4	0.6	60
5	0.6	70
6	0.7	30
7	0.7	40
8	0.7	50
9	0.7	60
10	0.7	70

4. RESULTS OF LABORATORY TESTS

The results of laboratory tests are shown in Table 5 and Figure 1.

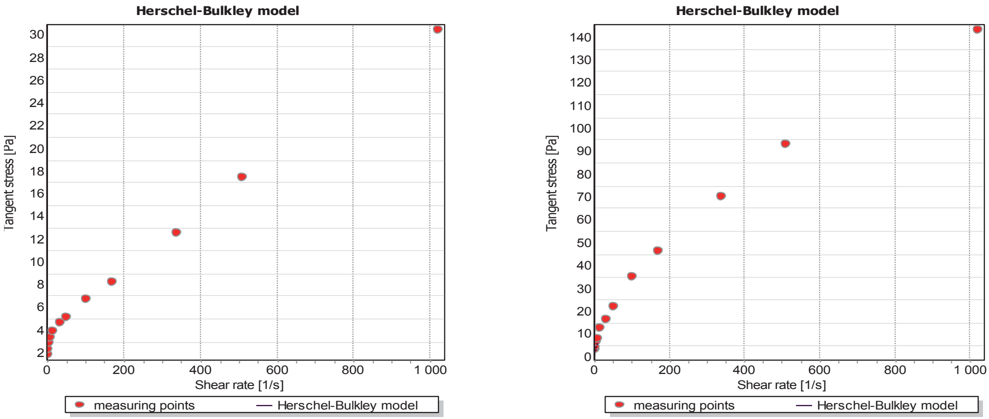
Table 5

Rheological parameters of mathematical models of cement slurries of water/cement ratio 0.6 and 0.7 with additional fluidal ash (30% to 50%); model with the highest correlation coefficient for particular slurries has been marked

Rheological parameters		w/c + additional fluidal ash [%]					
		0.6 + + 30%	0.6 + + 40%	0.7 + + 30%	0.7 + + 40%	0.7 + + 50%	0.7 + + 60%
Newton model	Newton dynamic viscosity [Pa·s]	0.0320	0.1577	0.0338	0.0523	0.0831	0.1321
	Correlation coefficient [–]	0.9419	0.9519	0.9460	0.9454	0.9474	0.9473

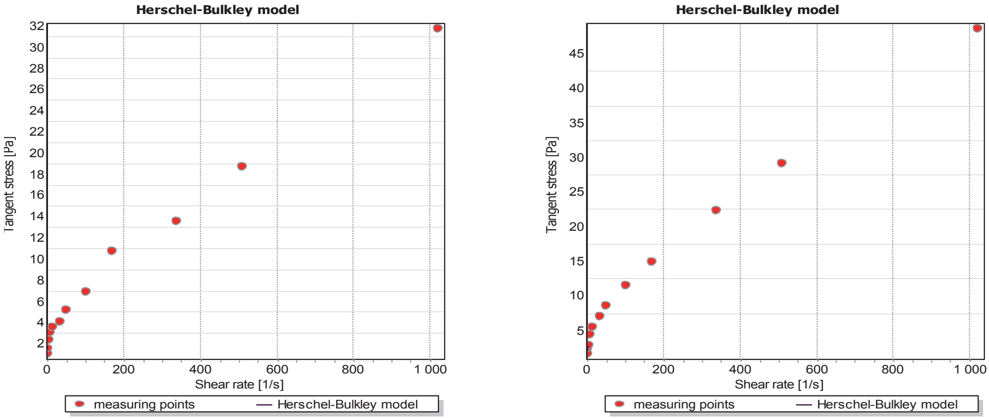
Table 5 (cont.)

Bingham model	Plastic viscosity [Pa·s]	0.0271	0.1393	0.0292	0.0451	0.0717	0.1156
	Yield point [Pa]	3.1069	11.9785	2.9990	4.6309	7.3524	10.6536
	Correlation coefficient [–]	0.9969	0.9816	0.9897	0.9890	0.9910	0.9820
Ostwald–de Waele model	Consistency coefficient [Pa·s^n]	1.2817	2.0782	0.8448	1.1985	2.1818	2.1754
	Exponent [–]	0.4012	0.6056	0.4921	0.5098	0.4813	0.5664
	Correlation coefficient [–]	0.9281	0.9992	0.9760	0.9853	0.9725	0.9962
Casson model	Casson viscosity [Pa·s]	0.0163	0.1127	0.0201	0.0318	0.0491	0.0900
	Yield point [Pa]	1.7398	3.6687	1.3498	1.9905	3.3496	3.6851
	Correlation coefficient [–]	0.9975	0.9898	0.9969	0.9973	0.9982	0.9914
Herschel–Bulkley model	Yield point [Pa]	2.6301	0.7458	1.6604	2.1874	4.0793	1.5512
	Consistency coefficient [Pa·s^n]	0.0609	1.7297	0.1671	0.3209	0.4077	1.4035
	Exponent [–]	0.8823	0.6364	0.7469	0.7157	0.7479	0.6396
	Correlation coefficient [–]	**0.9983**	**0.9999**	**0.9971**	**0.9986**	**0.9984**	**0.9999**
Apparent viscosity at 1022.04 [s^{-1}] [Pa·s]		0.030	0.030	0.031	0.047	0.076	0.117



w/c = 0.6 + additional 30% fluidal ash

w/c = 0.6 + additional 40% fluidal ash



w/c = 0.7 + additional 30% fluidal ash

w/c = 0.7 + additional 40% fluidal ash

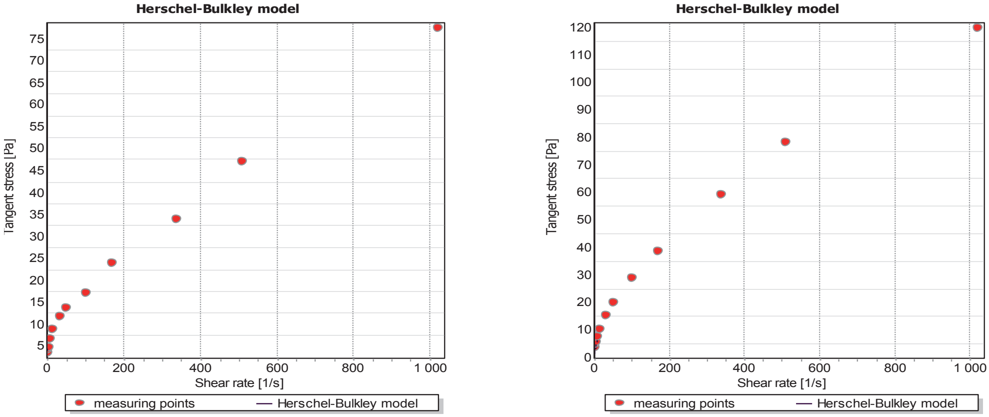


Fig. 1. Rheological models of highest (Herschel–Bulkley) correlation coefficient of analyzed sealing slurries

5. DISCUSSION OF RESULTS

The w/c ratio and concentration of ash from fluidized-bed combustion of lignite were selected experimentally. While working out new compositions of cement slurries the authors revealed that for low w/c ratios (0.4–0.5) measurement was impossible. A similar situation was encountered when the ash concentration was high and the w/c ratio was low and detailed measurements of changes of tangential stresses could not be precisely established in a function of shearing rate.

The analysis of data obtained during laboratory experiments reveals that the Herschel–Bulkley model is an optimum rheological model of cement slurries. It has typically high correlation coefficient being a measure of fitting of mathematical representation of tangential stresses in a function of shearing rates and the real dependences of slurries analyzed in laboratory conditions.

It can be concluded from the analysis of the tables that the consistency coefficient significantly increases with the increasing concentration of fluidal ashes in the discussed slurries which in practice may result in higher pumping resistance. Importantly, the yield point gradually increases with the growing concentration of fluidal ash, however, after exceeding a certain value of the yield point (e.g. by w/c = 0.7 for the slurry and 40% ash content) its value rapidly decreases. According to API standards, the Binngham pseudo-viscous fluid model and Ostwald–de Waele model are recommended for the analyses of rheological parameters of cement slurries; in this particular case the use of these models for the future determining of flow resistances would not be burdened with big error as the correlation coefficients of these models are high. However, the Herschel–Bulkley model has a nearly complete correlation and the use of such tools as the computer program RheoSolution will enable us to easily determine the parameters of this model, even in field conditions.

6. CONCLUSIONS

The addition of ashes from fluidized-bed combustion of lignite in cement slurries considerably influences the parameters of fresh sealing slurries:

- causes the increase of:
  - apparent viscosity,
  - plastic viscosity,
  - consistency;
- analyzed cement class G (API) HSR imported from Germany has good rheological parameters;
- increases both viscosity and yield point of slurries which in many cases necessitates the use of fluidization admixtures.

Working out of new hydraulic binders with admixtures of ash coming from fluidized-bed combustion of lignite is very important ecologically as it creates possibilities of broadening the range of ash recovery. In Poland we have over 1 mln tones of ash produced each year which is utilized only to a small degree.

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