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INFLUENCE OF FLUIDAL ASHES FROM LIGNITE ON TECHNOLOGICAL PROPERTIES OF SLURRIES BASED ON G-CLASS DRILLING CEMENTS**

1. INTRODUCTION

Presently both organic and inorganic hydraulic binders of Polish and foreign production are available on the drilling and geoengineering market. These binders have a broad spectrum of physicochemical properties and vary in their prices [1, 4, 6, 7, 8].

Nonetheless, there is not a single binder, which could be used for making a universal sealing slurry meeting all technological requirements of insulation, stabilization, reinforcement and sealing ground and rock mass when drilling technology is involved. This is mainly caused by other objectives and aims of performed works.

Frequently, the sealing slurries based on Portland cement are not good as they reveal a number of disadvantages [2, 3, 9, 11, 12]:

- long time of bonding,
- inappropriate rheological properties,
- high permeability,
- weak adhesiveness to clayey-shaly strata,
- lower resistivity to corrosion in highly mineralized groundwater environment.

Unfavourable properties of cement slurries can be significantly improved by introducing properly selected mineral additives. Accordingly, over the last years there have been conducted intense investigations aimed at developing new generation binders known as geopolymers. Geopolymeric slurries are exclusively based on inorganic components.

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They are obtained by modifying the composition of slurries based on G-class drilling cement or common use cement, with puzzolana additives. Among the artificial puzzolana are dehydrated clayey minerals and fly ashes from coal combustion.

New generation fly ashes are a product of coal combustion in fluidized bed units with concurrent sulphur removal from gases. This process takes place at a temperature of about 850°C. The produced ashes fundamentally differ from traditional silica ashes in their physicochemical properties.

Fluidal ashes, produced in during lignite combustion, contain active puzzolana in the form of dehydrated clayey minerals and active components enhancing hydration of such ashes as CaO, anhydrite II and $CaCO_3$ [4, 5, 7].

2. CHARACTERISTIC OF FLY ASHES FROM FLUIDAL COMBUSTION OF LIGNITE

Fly ashes are by-products of fossil fuels combustion in power plants. This is a group of substances which may considerably differ mainly with respect to the raw mineral (anthracite, hard coal, lignite) and also technology of burning (traditional boilers, fluidized bed units).

Firstly, the ash composition depends on the chemical composition of coal used for burning. Other important factors are the combustion technology, mainly the temperature of combustion, methods used for sulphur removal from waste gases and possible integrated combustion of biomass. Combustion of hard coal results in the production of *K*-type ashes. Lignite from the Adamów, Konin and Bełchatów area usually brings about *W*-type CaO-rich ash. Fly ash from coal coming from the Turoszów Coal District usually is of *G-class* as the coal was high in clayey minerals.

Fly ashes from fluidal combustion of lignite considerably differ from ashes of *V*- and *W*-types used in the traditional cement technology. The differences mainly stem from the technology of coal combustion.

The temperature of combustion in fluidized bed units can be lowered to about 850^{o}C. This is important both for the combustion process itself and also properties of the produced fly ash. One of the consequences is lowering the amount of generated nitrogen oxides which is very advantageous as far as environmental issues go. Combustion in a fluidized bed unit allows for limiting nitrogen oxides emission to about 100–150 ppm without any additional systems installed.

Owing to the intense mixing in the reservoir and its stationary character the sulphur can be removed from waste gases directly in the reservoir. For the reason of doing this the sulphur oxide sorbent, which in a majority of cases is limestone, is introduced to the reservoir. It reacts with sulphur oxide forming anhydrite. From this point of view it is very important to know that for a temperature range of 800–900^{o}C optimum bonding is observed for calcium carbonate and SO_2. Due to the specific character of sulphur removal and the presence of sorbent in the reservoir, type II anhydrite is present in the fly ash generated during fluidal combustion, and this is crucial for hydration of binders.

Another important consequence of lower temperature as compared to traditional burning places is a different build of ash grains. In the case of traditional burners these are usually spherical grains formed by the waste material enclosed in coal and vitrified at a temperature of 1200–1300^{o}C, whereas in fluidized bed units the temperature is too low for the liquid phase to form, therefore ash grains have irregular shapes. Clayey minerals in the waste rock are dehydroxylated, and their structure is partly restructured. As a result amorphous forms of aluminosilicates with disturbed laminar structure are generated. Such products have high puzzolana activity. The presence of thermally activated clayey minerals decides about good pozzolana properties of such ashes. Another component of the discussed fly ashes is anhydrite, which is also active. Anhydrite itself has some bonding properties, and besides constitutes a source of sulfate ions. Fluidal ashes are also composed of unreacted $CaCO_3$ sorbent and free CaO. Depending on the efficiency of the combustion process, some amounts of non-burnt coal may be present in the ashes [10, 11].

Unlike ashes from traditional units, the fluidal ash grains are of irregular, frequently sharp-edged in shape. The surface of such grains is not smooth as in the case of vitrified balls, but coarse and irregular. As a consequence of this shape of grains and water sorption ability of clayey minerals the water demand of fluidal ashes is high. Apart from the free calcium and anhydrite content, this is one of the most important factors which considerably limit the usability of such ashes for common-use cement production, in compliance with standard PN-EN 197-1.

Specific properties of ash and its increasing amounts in power plants are a source of problem with storing and utilization of ashes from fluidal combustion of lignite. They can be used on a large scale as sealing slurry additives in drilling and geoengineering works. In the case of drilling slurries, the problem of high water demand and anhydrite content can be coped with. Such ash can be used as an additive lowering the density of the slurry. From this point of view the high water demand of the binder is advantageous. Fluidal ashes may be a component of binders used for drilling slurries. The presence of calcium sulfate and calcium oxide may be potentially used for obtaining the controlled expansion slurries, needed in some situations to provide suitable adhesiveness to the ground and rock mass media.

3. LABORATORY EXPERIMENTS

The objective of laboratory experiments was to determine the influence of concentration of ashes from fluidal combustion of lignite on technological properties of fresh and set sealing slurries based on drilling cements.

Laboratory experiments related with the measurement of rheological properties of fresh sealing slurries followed the standards below:

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

The laboratory analyses of sealing slurries lied in determining the following parameters, e.g.:

– rheological parameters (plastic viscosity, apparent viscosity, yield point) – with the use of rotary viscosimeter with coaxial cylinders of type 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, 1 rot/min, which corresponds 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 optimal rheological model of sealing slurries lied in determining rheological curve to best describe the results of measurements in the coordinates system: tangent stress (τ) – shear rate (γ).
– fluidity with a truncated cone (AzNII);
– relative viscosity with the Ford cup No. 4,
– mechanical bending and compressive strengths,
– density of sealing slurry,
– water loss of sealing slurry,
– filtration with filtration press (API),
– initial and end time of bonding with Vicat apparatus.

The regression analysis method was used for determining rheological parameters of particular models. Then followed the statistical tests, during which the optimal rheological model was determined for a given recipe of sealing slurry [13, 14, 15].

For the reason of facilitating calculations aimed at optimizing rheological models of analyzed sealing slurries, the 'Rheo Solution' software was used. This computer program is owned by the Department of Drilling and Geoengineering, Faculty of Drilling, Oil and Gas AGH-UST [14].

The sealing slurries were made of the following materials:

– G-class drilling cement, HSR – produced by the cement plant REJOWIEC S.A., Grupa Ożarów S.A.,
– G-class drilling cement, HSR – imported from Germany by Cementing Service of Naftgaz Wołomin – PNiG Jasło,
– ash from fluidal combustion of lignite (sample D – averaged fly ash being the by-product of dust removal from waste gases),
– network water.

Table 1 gives mineral compositions of analyzed G-class cements. Chemical composition of the studied ash was analyzed with the «wet» method, in line with standard PN-EN 196-2; the results are presented in Table 2.

The density of ash determined with the pyknometer method with the use of oil was 2660 kg/m^3, whereas the surface was defined on the basis of the BET isotherm and was equal to 74200 cm^2/g.

Table 1

Mineral composition of drilling cements used for laboratory experiments

Component	% content in G-class drilling cement HSR (Rejowiec), [%]	% content in G-class drilling cement HSR (imported from German), [%]
C_3A	1.90	1.20
C_4AF	16.69	15.50
C_3S	56.11	51.00
C_2S	17.07	19.30
$C_4AF+2\cdot C_3A$	19.97	19.60

Table 2

Chemical composition in sample D

Ash component	Component content in ash D, [%]
Roasting losses 1000°C/1h	2.83
SiO_2	31.20
Fe_2O_3	5.80
Al_2O_3	20.00
TiO_2	1.27
CaO	26.40
MgO	1.00
SO_3	7.80
Na_2O	1.78
K_2O	1.76
total	99.84
free CaO	9.87

The analysis of the phase composition (with XRD method) of averaged ash D revealed the presence of anhydrite ($CaSO_4$), calcium oxide (CaO), quartz (SiO_2), calcite ($CaCO_3$) and hematite (Fe_2O_3).

The water-to-cement and water-to-mixture ratios for the analyzed sealing slurries were: 0.4; 0.5; 0.6 and 0.5; 0.6; 0.7, respectively.

The concentration of ash from fluidized bed combustion of lignite was 40 wt% (in relation to mass of dry components).

The temperature of sealing slurries used for analyzing rheological parameters was 20^{o}C (±2^{o}C) [293 K].

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

The working fluid was the network water free of any mechanical contaminations.

4. RESULTS OF LABORATORY EXPERIMENTS

The obtained results of technological parameters and their times of bonding of liquid sealing slurries based only on drilling cements are listed in Table 3. Technological parameters of sealing slurries based on mixtures of drilling cement and fluidal ashes are presented in Table 4. Parameters of mathematical equations describing particular rheological models of analyzed sealing slurries for pure cements are given in Table 5 and for cement and ash mixtures in Table 6. The mechanical strengths of set sealing slurries (bending and compressive strengths) performed after 1, 2, 14, 28 days for slurries based on pure cement are presented in Table 7, and for cement and ash mixtures in Table 8.

Table 3

Technological parameters and bonding times of fresh sealing slurries based on drilling cement (HSR, from cement plant REJOWIEC S.A.) and drilling cement G-class (API) imported from Germany for various water-to-cement ratios

Type of cement	Drilling cement HSR			Drilling cement G (API)		
Water-to-cement ratio	0.4	0.5	0.6	0.4	0.5	0.6
Density, [kg/m^3]	2.02	1.9	1.86	1.87	1.83	1.75
fluidity with a truncated cone AzNII, [mm]	140	220	over 300	230	over 300	over 300
Relative viscosity (Ford cup no. 4), [s]	no	23	12	28	14	11
Water loss, [%]	4	8	18	5	8	16
Specific filtration ΔP = 0.7MPa, [cm^3/s]	25/30	27/17	31/17	22/19	28/17	34/12
Plastic viscosity η_p, [Pa·s]	no	41.00	8.00	48.50	6.50	15.50
Yield point τ_y, [Pa]	no	17.72	9.58	23.70	16.76	4.07
Beginning of bonding time, [h]	5.5	7.66	7.75	7	8	15.25
End of bonding time, [h]	7.5	9.83	12.25	10.16	13.16	17.25

Table 4

Technological parameters and bonding times of fresh sealing slurries based on drilling cement (HSR, from cement plant REJOWIEC S.A.) and drilling cement class G (API) imported from Germany and fluidal ash for various water-to-mixture ratios

Type of mixture	Drilling cement HSR + 40% fluidal ash			Drilling cement G (API) + 40% fluidal ash		
Water-to-mixture ratio	0.5	0.6	0.7	0.5	0.6	0.7
Density, [kg/m^3]	1.83	1.73	1.68	1.83	1.73	1.67
Fluidity with a truncated cone AzNII, [mm]	100	190	230	100	180	240
Relative viscosity (Ford cup no 4), [s]	no	27	17	no	no	20
Water loss, [%]	2	4	10	1	4	7
Specific filtration ΔP = 0.7MPa, [cm^3/s]	15/24	25/9	30/10	10/16	16/10	27/19
Plastic viscosity η_p, [Pa·s]	no	54.00	34.50	no	21.50	36.00
Yield point τ_y, [Pa]	no	79.5	47.25	no	68.50	50.75
Beginning of bonding time, [h]	4.33	8.25	8.83	3.33	5.25	8
End of bonding time, [h]	6.33	11.25	12.25	5.25	12.25	12.83

Table 5

Parameters of rheological models of sealing slurries based on drilling cement (HSR, from cement plant REJOWIEC S.A.) and G-class drilling cement (API) imported from Germany for various water-to-cement ratios

Rheological parameters \ Slurry recipe, water-to-cement ratio		Drilling cement HSR			Drilling cement G (API)		
		0.4	0.5	0.6	0.4	0.5	0.6
Newtonian model	Newtonian dynamic viscosity [Pa·s]	0.265	0.069	0.022	0.085	0.032	0.022
	Correlation coefficient [–]	0.872	0.860	0.672	0.848	0.537	0.806
Bingham model	Plastic viscosity [Pa·s]	0.214	0.055	0.016	0.068	0.022	0.017
	Yield point [Pa]	16.981	8.955	3.993	11.389	6.212	3.436
	Correlation coefficient [–]	0.954	0.973	0.957	0.968	0.912	0.986
Ostwald–de Waele model	Consistency coefficient [Pa·s^n]	3.5780	2.532	1.567	3.120	2.034	1.495
	Exponent [–]	0.576	0.445	0.340	0.449	0.369	0.336
	Correlation coefficient [–]	0.988	0.993	0.989	0.996	0.995	0.957
Casson model	Casson viscosity [Pa·s]	0.161	0.035	0.009	0.044	0.013	0.009
	Yield point [Pa]	6.223	4.516	2.434	5.619	3.562	2.154
	Correlation coefficient [–]	0.969	0.990	0.986	0.987	0.954	0.997
Herschel–Bulkley model	Yield point [Pa]	–8.315	3.193	1.518	2.732	–0.754	2,422
	Consistency coefficient [Pa·s^n]	8.747	1.063	0.580	1.805	2.606	0,138
	Exponent [–]	0.423	0.573	0.488	0.529	0.333	0,697
	Correlation coefficient [–]	0.999	0.997	0.998	0.998	0.996	0,996
Apparent viscosity at 1022.04 [s^{-1}] [Pa·s]		no	0.059	0.018	0.073	0.024	0.020

Tabela 6

Parameters of rheological models of sealing slurries based on drilling cement (HSR, from cement plant REJOWIEC S.A.) and G-class drilling cement (API) imported from Germany and fluidal ash for various water-to-mixture ratios

Rheological parameters / Mixture recipe, water-to--mixture ratio		Drilling cement HSR + 40% fluidal ash			Drilling cement G (API) + 40% fluidal ash		
		0.5	0.6	0.7	0.5	0.6	0.7
Newtonian model	Newtonian dynamic viscosity [Pa·s]	0.392	0.108	0.056	0.256	0.091	0,053
	Correlation coefficient [–]	0.955	0.860	0.936	0.900	0.901	0,881
Bingham model	Plastic viscosity [Pa·s]	0.340	0.088	0.047	0.219	0.076	0,043
	Yield point [Pa]	11.326	12.901	5.560	15.176	9.727	6,712
	Correlation coefficient [–]	0.990	0.946	0.994	0.968	0.975	0,985
Ostwald–de Waele model	Consistency coefficient [$Pa \cdot s^n$]	3.685	2.521	2.092	4.350	2.296	2,360
	Exponent [–]	0.577	0.527	0.418	0.515	0.505	0,404
	Correlation coefficient [–]	0.992	0.997	0.946	0.996	0.997	0,973
Casson model	Casson viscosity [Pa·s]	0.254	0.067	0.029	0.150	0.055	0,026
	Yield point [Pa]	4.031	4.935	2.998	6.207	4.110	3,661
	Correlation coefficient [–]	0.997	0.965	0.998	0.983	0.989	0,997
Herschel–Bulkley model	Yield point [Pa]	3.121	–3.379	4.306	–0.698	1.892	3,846
	Consistency coefficient [$Pa \cdot s^n$]	1.930	4.265	0.148	4.278	1.413	0,410
	Exponent [–]	0.705	0.449	0.833	0.526	0.580	0,674
	Correlation coefficient [–]	0.999	0.999	0.997	0.998	0.999	0,997
Apparent viscosity at 1022.04 [s^{-1}] [Pa·s]		no	0.089	0.051	no	0.079	0.047

Table 7

Mechanical strength to bending and compressive strength of set sealing slurries based on drilling cement (HSR, from cement plant REJOWIEC S.A.) and G-class drilling cement (API) imported from Germany for various water-to-cement ratios at temperature 20 (±2°C) [293 K]

Cement type		Drilling cement HSR			Drilling cement G (API)		
Water-to-cement ratio		0.4	0.5	0.6	0.4	0.5	0.6
Strength to bending, [MPa]	1 day	3.107	1.939	1.380	2.108	1.316	0.914
	2 days	6.716	2.542	1.955	3.160	2.945	2.653
	14 days	11.305	8.391	5.671	10.429	7.615	5.881
	28 days	11.504	8.756	7.142	10.836	9.860	6.970
Compressive strength, [MPa]	1 day	10.417	5.156	0.073	8.438	2.969	2.135
	2 days	18.854	9.792	6.354	20.156	11.094	7.552
	14 days	40.000	31.797	20.625	43.490	24.547	21.042
	28 days	53.073	34.219	26.250	54.219	32.656	21.875

Table 8

Mechanical strength to bending and compressive strength set sealing slurries based on drilling cement (HSR from cement plant REJOWIEC S.A.) and G-class drilling cement (API) imported from Germany and fluidal ash for various water-to-mixture ratios at temperature 20 (±2°C) [293 K]

Mixtutre type		Drilling cement HSR			Drilling cement G (API)		
Water-to-mixture ratio		0.5	0.6	0.7	0.5	0.6	0.7
Strength to bending, [MPa]	1 day	0.639	0.622	0.064	0.718	0.456	0.378
	2 days	3.335	1.856	1.181	2.856	1.302	1.140
	14 days	9.087	6.534	5.282	8.662	5.800	5.239
	28 days	13.572	10.029	7.168	12.919	9.587	8.906
Compressive strength, [MPa]	1 day	0.938	1.667	0.417	1.927	1.510	1.042
	2 days	10.573	5.833	2.969	8.438	3.125	3.073
	14 days	26.474	22.031	14.688	32.760	23.438	13.906
	28 days	35.521	24.896	18.281	36.563	26.042	18.802

5. CONCLUSIONS

- The addition of fluidal ashes to sealing slurries results in increased water demand and increased volume of working water to obtain a comparable fluidity of liquid sealing slurries.
- A sealing slurry based on a mixture of drilling cement and fluidal ash lowers the density of liquid sealing slurry.

– Addition of fluidal ashes significantly shortens the time of beginning and end of bonding of sealing slurries.
– The analysis of selected rheological models reveals that for obtaining similar values of mathematical parameters describing rheological models of sealing slurries based on pure cements and cements with fluidal ashes, the volume of working water has to be increased by about 20% in the latter case.
– Among rheological models used for describing dependences between tangent stresses and shearing rates, the highest correlation coefficient was obtained for the Herschel–Bulkley model.
– The addition of fluidal ash for the same water-to-mixture ratio values results in a higher strength of the set sealing slurries over a longer time.
– The addition of fluidal ash for the same water-to-mixture ratio values results in a drop of early strength of set sealing slurries.
– The use of fluidal ash as a component of sealing slurry for cementing drilling wells and for geoengineering works results in lower emissions of CO_2 produced during cement prosuction, and is a way of managing waste materials generated during combustion of lignite.

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