Evaluation of the Possibility of the Hard Coal Sludge Enrichment by Flotation

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Abstract

Coal sludges are the smallest fraction of post-mining waste. Their grain size is less than 1 mm, and most grains have size below 60 µm. These wastes are mainly separated from the water-sludge circulations of the mines. Coal sludges are generally characterized by worse quality parameters in relation to the coal grades produced by mines. The fight against smog and the more stringent provisions in this area make it possible to monitor and control the quality of solid fuels, with particular emphasis on fuels directed for use in households and combustion plants with a rated thermal output of less than 1 MW which eliminated from the municipal and living market the coal sludges and post-flotation wastes containing less than 85% of hard coal, which are nuisance materials in the development process and their separation from the water-sludge circulation and dewatering requires many technological operations. The publication presents results of laboratory tests on the determination of conditions and possibilities of coal recovery from thermal coal sludges with an ash content of about 64%, using the froth flotation method. The experiments were conducted using a single operation method (fractional flotation) and a multiple operation method (main flotation, cleaning flotation). The tests were carried out using three types of the flotation reagents: standard (reference): ON MBIC (mixture consisting of diesel oil ON and 2-ethylhexanol OKT), specialized: Centroflot and proprietary: Klim III (non-ionic surfactants, auxiliary agents in a form of block copolymer of propylene and ethylene oxide and wetting additives, 2-ethylhexanol and a mixture of dioxane alcohols) to obtain the optimal concentrate.

Keywords: hard coal sludges flotation, reagent, mineral processing

1. Introduction

The most important source of air pollution, especially in the area of big cities, is the so-called low emission resulting from the combustion of low quality coal and other solid fuels in domestic furnaces. The European Union is pushing Member States to jointly limit the emission of greenhouse gases, increasing the share of renewable energy sources, improving energy efficiency and implementing new technologies of clean combustion of coal. The announcement on 30 November 2016 by the European Commission of the Winter Package - Clean energy for all Europeans is a natural consequence of pursuing a climate and energy policy from before almost 10 years (i.e. the principle 3×20). The current Directive of the European Parliament and of the Council 2010/75 / EU of 24 November 2010, on industrial emissions - IED and the records the conclusions of the BAT (Best Available Technology) concern the emission limit values, mainly CO2, NOx, SOx and dust, and are also one of the most important EU legal acts in the field of the environmental protection. At the same time, the Regulation of the Minister of Energy on quality requirements for solid fuels of 27 September 2018 constitutes the performance of statutory authorization contained in the Act of 25 August 2006 on the monitoring system and controlling the quality of fuels (Journal of Laws of 2018, item 427, 650, 1654 and 1669). These requirements make it necessary to strictly comply with quality standards, both for the fuel directed to the professional power industry and to the municipal and living market. The amendment introduces provisions enabling monitoring and controlling the quality of solid fuels, with particular emphasis on these intended for use in households and combustion plants with a nominal thermal power of less than 1 MW. At the same time, this legal act eliminated from the municipal and living market the coal sludges and flotation concentrates containing less than 85% of the hard coal.

Also due to the fight against smog and more stringent provisions, the Ordinance of the Minister of Development and Finance of 1 August 2017 on the requirements for solid fuel boilers entered into force on 1 October 2017. According to it, there are no longer permitted boilers, with an emission purity class lower than 5, to be placed on the market. The requirements are specified in the PN-EN 303-5:2012 standard. In addition, the voivodship parliaments (e.g. Lesser Poland in 2016, Silesia, Opole, Łódź in 2017) adopt anti-smog resolutions to counter the problem of low emissions.

Coal sludges are the smallest fraction of post-mining wastes. Their grain size is less than 1 mm, and most grains have size below 60 µm. These wastes are mainly separated from the water-sludge circulations of the mines. Coal sludges are generally characterized by worse quality parameters in relation to coal grades produced by mines. This applies in particular to the ash content (24–50%), moisture content (31-46%) and calorific value (8–11 MJ/kg). In the case of sulphur content (0.6-1.8%), the values may be higher or close to the sulphur content in the coal of the other assortments (Jelonek et al., 2010, 2016, Grudziński, 2005, Szpyrka and Lutyński, 2010). Post-flotation wastes from flotation processes have much higher quality parameters: ash content (4-18%), sulphur content (0.21-0.8%) and calorific value (18-25 MJ/kg) (Jelonek et al 2016).

Coal sludges are wastes of 010412 code - the wastes generated during the flushing and cleaning of minerals according to the Regulation of the Minister of Environment from 2014. In the past, the majority of sludges was sent as waste to settling ponds, and only a small part of them was included into the coal mixes (Grudziński, 2005; Szpyrka and Lutyński, 2010; Lutyński at al. 2013; Lutyński and Lutyński 2014). At present, the sludges coming from current production of mines and partly from exploitation of settlers, are in some part used by professional power industry as low-energy fuel through addition to energy fines or combusted directly in fluidized-bed boilers (Jelonek at al., 2010; Jelonek and Mirkowski, 2015). In special installations, from the sludges there are produced sludge granules with addition of calcium oxide, which causes a significant reduction of moisture and improves transport conditions. Such installations are held by Haldex SA company and also by mining plants of the Tauron Wydobycie Group.

The quantity and type of the occurred sludges depend on the nature of the excavated rock accompanying the coal seams, method of coal mining and transport, as well as on the technology of the coal enrichment process. The procedure for handling sludge wastes depends on the content of the carbonaceous substance, the mineralogical composition and the depth of structural changes in the inorganic substance. The increase in the amount of coal sludges subjected to the enrichment processes due to the higher quality requirements of coal grades, affects the growth of the amount of material with a grain size below 0.5 mm. It should be borne in mind that coal sludge is a nuisance material in the development process and its separation from the water-sludge circulation and dewatering requires many technological operations. The waste sludges can be divided into:

- sludges from enrichment processes of + 20 mm and + 0.5 mm classes;
- post-flotation wastes;
- sludges from the enrichment of small classes in the classification hydro cyclones;
- sludges from sedimentation in the underground water settling tanks.

The publication presents results of laboratory tests on the determination of the conditions and possibilities of the coal recovery from thermal coal sludges with an ash content of about 64%, using the flotation method.

2. Material and methods

The subject of the research were samples of the coal sludge from ZG Janina mine belonging to TAURON Wydobycie SA. The place of sampling was determined by both parties after the analysis of the coal enrichment technological scheme. The samples were collected by hand and using a shovel, from two filter press stations, directly from the presses in several places, directly to the bags. In total, two bags of about 50 kg each were taken. As part of the research, samples were prepared for petrographic, grain composition and chemical composition of the raw material testing, as well as testing of processing procedures (development of technology). Technical analysis was carried out in accordance with the applicable Polish standards and included: calorific value in working condition Qr, ash in working condition Ar, total sulphur content in working condition Sr. In addition, the tests of the sludge samples included determination of the water content by gravimetric method, according to PN-EN 15934: 2012, determination of content of the roasting loss by gravimetric method, according to the internal test procedure, determination of total carbon C and total sulphur S content by high temperature combustion with IR detection, determination of total nitrogen N content by high temperature combustion with IR detection according to PN-G-04571: 1998, determination of mercury Hg content by atomic absorption spectrometry with cold vapor generation (CVAAS), determination of basic chemical composition: SiO2, Al2O3, Fe2O3, CaO, MgO, Na2O, K2O, SO3, TiO2, P2O5 by the fluorescence X-ray spectrometry with the wave dispersion according to PN-EN 15309: 2010, determination of trace elements content: Ag, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, V, Zn by the fluorescence X-ray spectrometry with the wave dispersion, leaching tests. The P_2O_5 content, determined in the ash, was converted to the content in the starting sample as P.

2.1 Characteristics of properties of the coal sludge

Samples of sludge with a grain size of less than 0.5 mm in the form of a slurry were used for the tests. The characteristics of sludges are presented in Tables 1-4.

Table 1. Grain composition of coal sludge from ZG Janina mine

Grain size [mm]	Yield [%]
0-0,045	82,49
0,045-0,063	1,02
0,063-0,08	1,28
0,08-0,1	4,72
0,1-0,2	3,86
0,2-0,3	4,72
0,3-0,5	1,15
0,5-1,0	0,76

Table 2. Chemical composition of coal sludge from ZG Janina

Element	Content [% wag. (% m/m)]
H_2O	2,27
C	18,62
S	0,42
N	0,26
P	0,015
	[ppm (mg/kg)]
Hg	< 0,01

Table 3. Oxides composition of coal sludge from ZG Janina

Oxide	Under condition of ash determination (air, 815ºC)	Content in the input sample [% wt. (% m / m)]
SiO_2	58,70	40,94
Al_2O_3	29,30	20,44
Fe_2O_3	3,57	2,49
CaO	0,25	0,17
MgO	1,34	0,93
Na_2O	1,02	0,71
K_2O	3,60	2,51
SO_3	0,35	0,24
TiO_2	1,19	0,83
P_2O_5	0,05	0,03
LOI	-	30,25
Content of ash		65,67

Table 4. Elemental composition of coal sludge from ZG Janina

Element	Under condition of ash determination (air, 815ºC)	Content in the input sample [% wt. (% m / m)]
Ag	< 2	< 2
As	< 2	< 2
Ba	337	235
Cd	< 2	< 2
Co	3	2
Cr	117	82
Cu	43	30
Mn	186	130
Mo	< 2	< 2
Ni	38	27
Pb	67	47
Rb	229	160

Sb	3	2
Sn	3	2
Sr	105	73
V	152	106
Zn	116	81

The sludge waste is a fine-grain material. Table 1 shows that over 80% are grains with a grain size below 45 μm. A small share of 100-45 μm grain classes is characteristic for this sludge. In terms of mineralogical composition, dominating in the sludges are kaolinite, with content of 32% by mass, and coal, with content of 31% by mass. The other ingredients are mainly: hydrargillite, gypsum, epsomite, allophane, ankerite, siderite, quartz (Girczys, 1996).

The presented description of the sludge wastes indicates the possibility of the sludge management, taking into account the presence of valuable components such as: coal and clay substances in them. For this purpose, the two components should be separated and flotation enrichment is one of the methods which can be applied.

2.2 Studies on the separation of the sludge components as a result of the flotation process

Flotation is an enrichment method in which the separation of grains of a mixture of different minerals takes place on the base of differences in the surface properties of these minerals, further increased by the use of flotation reagents The separation consists of elevating hydrophobic grains (not moistened by water) through air bubbles, to the surface of the suspension. Not floating grains (hydrophilic) remain in suspension or form a precipitate (Sablik, 1998). Flotation is a process used to separate small coal grains from water-sludge circulation for coking coals. The obtained results encourage the use of this method for separation of coal from the waste sludges of thermal coal. The aim of the research is to determine the possibility of conducting this process, to determine the type and amount of reagents that can be used. According to the literature data, the presence of oxygen groups on the surface determines flotation properties of coals (Furstenau et al., 1993).

As part of the work, laboratory tests were carried out to determine the conditions and possibilities of coal recovery from thermal coal sludges with an ash content of about 64% using the froth flotation method. The experiments were conducted according to two methodologies:

1. by a single operation method (fractional flotation),
2. by multiple operations (main flotation, cleaning).

Three series of experiments were carried out. The concentration of solids in the slurry subjected to flotation was about 300 g/dm^3. A total of 37 experiments was performed in those three series. The tests were carried out using three types of flotation reagents: standard (reference): ON + MBIC (mixture consisting of diesel oil ON and 2-ethylhexanol OKT), specialist: Centroflot and proprietary: Klim III (non-ionic surfactants, auxiliary agents in the form of a block copolymer of propylene and ethylene oxide and wetting additives, 2 -ethylhexanol and a mixture of dioxane alcohols) to obtain the optimum concentrate.

The laboratory tests were carried out on the stand for flotation tests at the Central Mining Institute using a flotation machine with a working chamber capacity of 1 dm^3 (Figure 1). The air was supplied under pressure in the amount of 2 dm^3/min. The feed was mixed in the machine for 60 seconds with the reagent (100% reagent), then, after supplying air, flotation was performed until the empty foam appeared. The concentrate and waste products from the flotation process were dewatered, dried and weighed to determine yields. On the base of the amount (yield) of the concentrate and the content of ash in it, as well as the ash content in the feed, the yield of the combustible substance in the concentrate ε [%] was calculated according to the formula:

$$\varepsilon = \gamma \frac{100 - \lambda}{100 - \alpha}$$

where:

α - content of ash in the feed, %,

γ - yield of the concentrate, %,

λ - content of ash in the concentrate, %

Fig. 1 Laboratory tests of flotation enrichment process of the coal sludge

3. Results and disscution

The obtained results for flotation enrichment of the coal sludge using individual reagents are presented in Tables 5,6 and 7.

Table 5. Results of the sludge flotation using the ON + MBIC reagent

	Reagent	Dose kg/Mg	Time min	Yield %	Content of Ash A^a %	Average Content of Ash A^a %	Yield of the combustible substance in the concentrate ε %
K	ON+10%MIBC	2	2,2	4,62	29,1	29,10	12,5
O				93,84	66,8	64,48	
		Total		100,00			
K	ON+10%MIBC	4	2,15	34,81	45,54	45,54	54,7
O				65,19	75,09	64,80	
		Total		100,00			
K	ON+10%MIBC	6	2,12	33,58	51,22	51,22	46,8
O				66,42	71,33	64,58	
		Total		100,00			
K	ON+10%MIBC	3,85	1,15	22,50	49,9	49,9	64,2
K		2,3	2,5	21,80	48,63	49,28	
O		6,15		55,70	76,72	64,56	
		Total		100,00			
K	ON+10%MIBC	3,85	1,2	23,34	48	48,00	66,3
K		3,85	2,45	21,30	44,92	46,53	
O		7,7		55,36	79,04	64,53	
		Total		100,00			

Table 6. Results of the sludge flotation using the Centroflot reagent

	Reagent	Dose kg/Mg	Time min	Yield %	Content of Ash A^a %	Average Content of Ash A^a %	Yield of the combustible substance in the concentrate ε %
K	centroflot	2	2,35	7,36	50,11	50,11	10,5
O				92,64	66,12	64,94	
		Total		100,00			
K	centroflot	4,0	2,,07	36,20	33,74	33,74	68,5
O				63,80	81,52	64,22	
		Total		100,00			
K	centroflot	2,67	2,30	13,42	23,73	23,73	67,2
K		2,33	3,00	19,94	32,02	38,69	
O		4,0		66,64	82,58	64,60	
		Total		100,00			
K	centroflot	3,33	1,60	14,80	39,12	39,12	60,2
K		2,0	3,2	19,79	36,11	37,40	
O		5,33		65,41	78,36	64,19	
		Total		100,00			
K	centroflot	3,33	1,5	14,03	32,47	32,47	89,7
K		3,33	1,5	32,42	45,60	41,63	
O		6,66		53,54	84,95	64,83	
		Total		100,00			

Table 7. Results of the sludge flotation using KLIM III reagent

	Reagent	Dose kg/Mg	Time min	Yield %	Content of Ash A^a %	Average Content of Ash A^a %	Yield of the combustible substance in the concentrate ε %
K	KLIM III	2	3,2	53,03	54,1	54,10	69,54
O				46,97	80,57	66,53	
		Total		100,00			
K	KLIM III	4	2,3	49,49	54,51	54,51	64,3
O				50,51	75,6	65,16	
		Total		100,00			
K	KLIM III	6	2,5	56,21	58,09	58,09	67,45
O				43,79	74,79	65,40	
		Total		100,00			
K	KLIM III	4	2,2	32,92	55,78	55,78	63,80
K		2	3,2	17,50	55,88	55,81	
O		6		49,59	72,28	63,98	
		Total		100,00			
K	KLIM III	4,5	2,2	49,20	58,82	58,82	84,16
K		2,7	3,4	22,33	65,55	60,92	
O		7,2		28,47	74,06	64,66	
		Total		100,00			

The analysis of the test results presented in the Tables showed that:
— the ash content in the concentrates, obtained from the flotation process using the standard flotation reagent, composed from diesel oil ON and 2-ethylhexanol OKT, amounts on average 50%, except for the experiment with a dose of 2kg/Mg, with ash content in the wastes over 75%.

— the ash content in the concentrates obtained from the flotation process using Centroflot flotation reagent was the best effect. The best results were obtained for the fractional two-stage flotation lasting 5,6 minutes with the use of the Centroflot reagent. The yield of the coal concentrate amounted over 67% with the ash content of about 28%. This result requires the use of about 4 kg of the reagent. At the same reagent dose, but for the one-stage flotation, the yield of the concentrate was similar and amounted to 68.5%, but the ash content was higher and amounted to 33%. The use of higher amounts of Centroflot resulted in the higher concentrate yield, almost 90%, however the ash content was also higher and amounted to 41.63%, but it did not affect the achievement of better quality concentrates. Attention is drawn to the high (over 80%) ash content in the wastes.

– the use of KLIM III's proprietary flotation reagent did not allow to separate selectively the concentrate from the waste despite high yields achieved.

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4. Conclusion

- Flotation of the coal sludge containing about 65% of ash allowed to achieve results which can be considered as technologically promising.
- Flotation of coal sludge lasting over 5 minutes, with the use of Centroflot flotation reagent gave a yield of about 67%, with ash content of 28%.
- Attention is drawn to the fairly high consumption of flotation reagent amounting to about 4 kg/Mg. Therefore, in case of implementing such solution it is essential to select appropriately and optimize the reagent which will allow to increase the yield and quality of the concentrate.
- The given results indicate the possibility of using flotation for coal recovery from the coal sludge. The obtained concentrate may be used as a fuel and directed to combustion in power plants, as well as added to the energy mixes.
- The flotation wastes have better properties as a raw material for ceramics due to the reduced carbon content.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article

Competing interests

"The authors declare that they have no competing interests"

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Authors' contributions

Joanna Całus Moszko - research concept, literature review, development of research results, editorial office

Agnieszka Klupa - conduct experiments, development of research results

Krzysztof Wierzchowski - conduct experiments, literature review, summary and correction.

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Figures

Figure 1

Laboratory tests of flotation enrichment process of the coal sludge

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