Deposits of coal slurry as secondary resources of hard coal

Wiesław Blaschke¹, Ireneusz Baic², Wojciech Sobko³ and Beata Witkowska-Kita⁴

The article describes comprehensively, on the basis of inventoried sites, issues related to the suitability of coal slurry deposits for the energetic and economical application. The effect of inventory was the localisation of 62 coal-slurry deposits in which almost 16,5 mln Mg of coal slurry was stored. Due to the fact that part of the sites, on which coal slurry was stored, were subject to anthropogenic transformation a mathematical formula was developed that allows determining with the assumed accuracy the amounts of coal slurry produced and environmentally stored. The conducted estimated analysis, using this formula, showed that since 1945, there have been nearly 120 mln Mg of coal slurry stored in the environment that is eight times more than it was inventoried and what is currently recognised in official statistics. In order to develop the most cost-effective beneficiation technology of inventoried coal slurry deposits, detailed qualitative studies were conducted afterwards. They were carried out on the basis of an authorial research methodology which defines the scope of necessary physical and chemical parameters that must be determined for the particular samples of coal slurry. The obtained results show significant diversification in the quality of coal slurries stored in the particular settling ponds. The reason for this is the diversification of types of technological coal that come from the particular coal mines that used these settling ponds, as well as the efficiency of the technological solutions in terms of preparation processes applied by the particular coal mines. For this reason, there was an individual approach necessary to develop technologies of their preparation in order to obtain a full value fuel that meets the requirements set by the power sector. In the paper, the results of the analysis of the energetic potential of identified coal slurry deposits before and after the preparation process are also presented. Estimation of energetic potential was made using the authorial double-option algorithm. The presented results of coal slurry preparation studies and the analysis of their energetic potential have shown that as a result of preparation a significant amount of this potential is lost. This is the effect of movement of the finest grain of coal grains to refuse. The most favourable results, meaning the smallest losses of energetic potential according to the preparation results, were obtained using flotation technology. The conducted tests enable one to conclude that there is a possibility of preparation of coal slurry stored in the deposits. However, considerable losses of the energetic potential of these materials should be expected.

Keywords: coal slurry deposits, coal waste, settling ponds, waste treatment technology, preparation of coal

Introduction

Run-of-mine coal is a mixture of coal and waste rock particles which is of virtually no usable value on the market. In order to obtain a commercial product, run-of-mine coal is subjected to preparation processes in coal preparation plants. In industrial conditions, this process is based on methods of gravity preparation in a water medium or dense (magnetite) media. Methods for production of commercial coal that have been established and modified for years generate a considerable amount of by-products in the form of coal slurry.

Issues of processing and preparation of coal slurry deposits were the subject of many tests and analysis in Poland (Białas et al., 2001; Gawlik, 2005; Lorenz and Ozga-Blaschke, 2005) and other countries (Hlavata and Cablik, 2012; Rotunajanu and Lazar, 2014). However, they concerned only certain aspects like chemical properties, physical characteristics and economic application (Aghazadeh, Gharabaghi and Azadmehr, 2016; Galos and Szlugaj, 2014; Grudziński, 2005). Also carried out research on the content of heavy metals in sludge and their impact on the environment (Białecka, Grabowski and Bajerski, 2016; Yilmaz, 2011).

In 2009–2012, the Centre for Waste Management and Environmental Management, a Branch of the Institute of Mechanised Construction and Rock Mining, together with the Department of Mineral Processing and Waste Utilisation of The Silesian University of Technology implemented research and development project no. N R09 0006 06/2009 entitled "Identification of coal slurry deposits in Poland's fuel balance and technological development strategy for their utilisation" (Development Project No. N R09 006, 2009).

The main objective of the project was to determine the possibility of integrating the existing deposits of coal slurry, directly or through appropriate preparation processes, into Poland's fuel balance.

The first thing done as part of the project mentioned above was an inventory of the existing slurry deposits and their quantitative and qualitative assessment. Then, a mathematical model was developed to calculate the energy potential of each of the deposits, which will make it possible in the future to identify potential customers

¹ Wieslaw Blaschke, Institute of Mechanised Construction and Rock Mining, Branch in Katowice, Al. W Korfantego 193A 40-157 Katowice, Poland wsblaschke@gmail.com

² Ireneusz Baic, Institute of Mechanised Construction and Rock Mining, Branch in Katowice, Al. W Korfantego 193A 40-157 Katowice, Poland i.baic@imbigs.pl

³ Wojciech Sobko, Institute of Mechanised Construction and Rock Mining, Branch in Katowice, Al. W Korfantego 193A 40-157 Katowice, Poland w.sobko@imbigs.pl

⁴ Beata Witkowska-Kita, Institute of Mechanised Construction and Rock Mining, Branch in Katowice, Al. W Korfantego 193A 40-157 Katowice, Poland b.witkowska@imbigs.pl

and the quantities of possible supplies. On the basis of the assessment of the impact of the listed coal slurry deposits on various components of the environment and considering the score evaluation system developed, a ranking list of the deposits with potentially the greatest threat to the environment was compiled: the list takes into account the current status of the deposit, the phase of its possible exploitation and the status after completion of the exploitation. Also determined were future trends, scope and design guidelines for prospective reclamation of land left after exploitation of coal slurry deposits (Brenek, Santarius and Hudecek; 2014). For the coal slurry deposits that were inventoried and characterised qualitatively and quantitatively, technologies were developed to prepare them up to fully usable fuel for utility power plants. These technologies take into account the diverse physical structure and chemical properties of these slurries. Areas of potential utilisation of waste produced during preparation of coal slurry deposits were identified.

The final stage of the project comprised proposals of technical, organisational and legal solutions – along with the strategy of technological development – aimed at using in domestic power industry the coal slurries inventoried quantitatively and qualitatively (Baic, 2015; Blaschke and Baic, 2012; Development Project No. N R09 006, 2009). This article presents the results of quantitative and qualitative analysis of the chemical, physical and energy properties of the coal slurry deposits inventoried in the Silesian Province.

The methodology of identification of coal slurry deposits in the Upper Silesian coal basin

In order to identify existing coal slurry deposits, information from the following databases and documents was analysed: Register of Mining Areas (ROG), the MIDAS Database, and Regional Geographical Information System for the province of Silesia (RSIP) and other planning documents, such as reports on implementation of waste management plans, environmental protection programs, environmental surveys and others. It has been found from the scope of this information that it is too general and can only provide an indication as to the information about the owner and the location of a given deposit of coal slurry. Also, it has been found that the information about the amount of coal slurry deposited is not regularly updated, which in the current market situation (change of ownership, exploitation, and land reclamation) prevents their utilisation (Baic, Blaschke and Sobko, 2011; Baic, Sobko and Łukowska, 2012; Lutyński, A., Suponik and Lutyński, M., 2013).

Therefore a questionnaire was carried out among selected business entities currently producing coal slurry, which control lands on which deposits of coal slurry are located, and among the institutions which may store archival documents. As a result of the questionnaire and numerous site visits, 62 settling ponds were located, where nearly 16.5 million Mg of coal slurry is deposited. A summary of the coal slurry deposits inventoried (without information about their location or the users, due to confidentiality clauses with the owners of these facilities), is shown in Table 1 (Baic, Blaschke and Sobko, 2011; Baic, Sobko and Łukowska, 2012).

Tab. 1. A list of coal slurry deposits inventoried.

No.	Deposit No.	Number of ponds	Mass of coal slurry deposited [Mg]
1.	K18	1	200000
2.	K4/1-19	19	1102000
3.	K11/1-3	3	1521000
4.	K12/1-5	5	65000
5.	K1/1-2	2	228000
6.	K17	1	130000
7.	K2/1-2	2	460000
8.	K3/1-2	2	1293000
9.	K6	1	163000
10.	K7	1	644000
11.	K5/1-4	4	620000
12.	K9/1-2	2	560000
13.	K10	1	100000
14.	K8	1	150000
15.	K13	1	670000
16.	K14	1	221000
17.	K15	1	42250
18.	K16	1	25000
19.	K19/1-3	3	580000
20.	K20	1	800000
21.	K21	1	40000
22.	K22/1-2	2	1261600
23.	K23	1	1365000
24.	K24/1-2	2	100000
25.	W1/1	1	1629000
26.	W2/2-3	2	2498000
	TOTAL	62	16467850

Due to the fact that some of the areas in which coal slurry was deposited in the 1990s have been anthropogenically transformed into recreational areas, industrial sites, water reservoirs, etc., a mathematical formula was developed which makes it possible to estimate the amount of coal slurry produced between 1945 and 1989. An estimate analysis conducted using the mathematical formula showed that almost 120 million Mg of coal slurry had been deposited in the environment since 1945, which is eight times more than inventoried and is now reported in the official statistics.

Chemical properties of coal slurry deposits

In order to develop the most cost-effective preparation technology, chemical properties of coal slurry samples from the inventoried deposits were studied. For this purpose, a research algorithm was developed and the scope of necessary properties defined. First of all, the chemical composition of coal slurry samples was analysed for the content of SiO₂, Al₂O₃, TiO₂, Fe₂O₃, CaO, MgO, K₂O, Na₂O, S_c, C, P₂O₅ in order to characterise them qualitatively (Baic, 2013; Baic, 2015; Baic et al., 2012; Blaschke W. and Blaschke Z., 2005). Limiting the results of the chemical composition analysis of coal slurry from all the deposits studied are shown in Table 2. This table also gives the research method used to investigate the chemical composition of the coal slurry samples.

Tab. 2. Results of the chemical composition of coal slurry samples.

No.	Component	Limiting content [%]	The method according to Polish Standard
1.	SiO ₂	27.81–63.96	PN-G-04528/03:1977
2.	Al_2O_3	4.83-10.26	PN-G-04528/04:1977
3.	TiO ₂	0.01-0.30	PN-G-04528/08:1978
4.	Fe ₂ O ₃	0.46–1.78	PN-G-04528/04:1977
5.	CaO	0.01-0.14	PN-G-04528/06:1977
6.	MgO	0.35-1.20	PN-G-04528/07:1977
7.	K ₂ O	1.19–2.98	PN-G-04528/10:1998
8.	Na ₂ O	0.32-1.33	PN-G-04328/10:1998
9.	Sc	0.57–2.98	PN-90/G04514/16
10.	C	11.15–31.80	PN-B-04481:1988
11.	P_2O_5	0.001-0.015	PN-G-04528/11:1979

Based on these studies, it was found that the main constituents of coal slurry samples are silica (27.81-63.96 %) and carbon (11.15-31.80 %). Such a composition is typical of a fine-grained waste of this type. The values that deviate from the data reported in the literature are very low Al_2O_3 and TiO_2 contents.

Direct analysis of slurry samples covered tests for the presence of such metals as arsenic, barium, chromium, tin, zinc, aluminium, cadmium, cobalt, magnesium, manganese, copper, molybdenum, nickel, lead, mercury, vanadium and calcium. The contents of these metals were determined by atomic emission spectrometry with inductively coupled plasma (ICP-AES) using a JY 2000 spectrometer. Table 3 shows the results for barium, zinc, cobalt and nickel, the content of which exceeded the maximum permissible concentrations in soils, according to the regulation by the Minister of Environment of 1 September 2016 (Dz. U. 2016, item. 1395).

Tab. 3. Results of the determination of selected metals in coal slurry samples.

D '4		Metals									
Deposit	Barium	Zinc	Cobalt	Nickel							
No.		[mg/kg c	dry weight]								
MPC ¹⁾	200.00	300.00	20.00	100.00							
K18	417.92	499.69	92.67	178.98							
K11	877.98	601.27	184.03	102.10							
K3	1123.4	405.96	144.23	156.08							
K4	n.e.	n.e.	85.67	n.e.							
K6	534.67	n.e.	n.e.	n.e.							
K2	333.24	n.e.	55.68	n.e.							
K17	777.27	n.e.	49.35	n.e.							
K1	422.37	n.e.	38.55	n.e.							
K5/1	423.91	n.e.	55.22	n.e.							
K5/4	599.06	n.e.	20.33	n.e.							

MPC ¹⁾— maximum permissible concentrations of heavy metals in the soil - land II-1 (Dz.U. 2016, item. 1395) n.e. - not exceeded

It was found that the cases of exceeded permissible concentrations of the metals mentioned above are not only due to their presence in the exploited deposit but also to anthropogenic pollutants and their presence in the land surrounding the area of the deposits studied. The results for the other metals did not exceed the permissible values of concentrations in soil (land II-1) in accordance with this Regulation.

Also analysed water extracts of coal slurry samples, which were prepared in accordance with PN - EN 12457-4:2006 standard. The scope of the study included the following basic properties: conductivity, pH, TDS, COD_{Cr} , phenols, ammonium nitrogen, nitrates(V), nitrates(III), cyanides, chlorides, sulphates(VI), sulphides, chromium(VI). Determination of metal content (the list of metals similar as in the case of direct analysis) of the waters extracts was performed by atomic emission spectrometry with inductively coupled plasma (ICP-AES) using a JY 2000 spectrometer.

Table 4 shows the results of the analysis of aqueous extracts of the slurry deposit samples for metals whose maximum permissible values were exceeded (barium, zinc, cobalt and nickel).

T 1 1 D 1	C.1 1 .	c	C 1 1	1 . 1
1 ab. 4. Results	ot the analysis o	f water extracts o	ot coal slurry (aeposit samples.

	Metals								
Deposit No.	Barium	Zinc	Cobalt	Nickel					
		[mg	:/1]						
MPV ¹⁾	2.000	2.000	1.000	0.500					
K18	0.880	0.055	0.088	0.440					
K11	0.068	0.108	0.183	0.440					
K3	0.633	1.220	0.177	1.020					
K4	0.055	0.102	0.067	0.009					
K6	1.550	0.089	0.011	0.010					
K2	0.777	0.022	0.022	0.011					
K17	1.120	0.011	0.980	0.055					
K1	0.858	0.009	0.013	0.009					
K5/1	0.023	0.089	0.022	0.098					
K5/4	0.010	0.033	0.032	0.011					

MPV¹⁾ - maximum permissible value, (Dz.U. 2014, item. 1800)

Analysis of water extracts of coal slurry samples for all basic properties and all analysed metals showed no exceeded maximum permissible values of substances harmful to the water environment in accordance with the Regulation of the Minister of Environment of 18 November 2014 (Dz.U. 2014, item. 1800). Consequently, it was concluded that the metals whose concentrations were found by direct analysis to be exceeded occur in bound forms, thus posing no threat to the environment.

Physical characteristics of coal slurry deposits

Coal slurry from the identified sedimentary ponds was studied in accordance with the methodology adopted. Basic scope of qualitative analysis was performed to determine (Baic, 2013; Baic, 2015; Baic, Blaschke and Grudziński, 2011; Lutyński and Szpyrka, 2012):

- surface moisture content W_{ex} and hygroscopic moisture content W_h (PN-80/G-04511, PN-80/G-04511, PN-G-04560:1998, PN-80/G-04511),
- ash content of the slurry on an air-dried basis A^a, on an "as-received" basis A^r and a dry basis A^d, (PN-G-04560:1998, PN-80/G-04512),
- sulphur content of the slurry on an air-dried basis S_t^a , on an "as-received" basis S_t^r and on a dry basis S_t^d (PN-90/G-04514/16),
- volatile matter content of the slurry on an air-dried basis V^a, on an "as-received" basis V^r and on a dry basis V^d (PN-G-04516:1998, PN-G-04560:1998, PN-ISO 562:2000)
- net calorific value of the slurry on an air-dried basis Q^a, on an "as-received" basis Q^r and on a dry basis Q^d (PN-81/G-04513).

Next, grain size analysis and densimetric analysis were performed on averaged samples. For each grain size fraction and density fraction, the following quantities were determined:

- yield,
- hygroscopic moisture W_h,
- ash content of the slurry on an air-dried basis A^a and a dry basis A^d,
- sulphur content of the slurry on an air-dried basis S_t^a and on a dry basis S_t^d ,
- volatile matter content of the slurry on an air-dried basis V^a on a dry basis V^d,
- the calorific value of the slurry on an air-dried basis Q^a and on a dry basis Q^d.

The samples were prepared for the analysis in accordance with PN-90/G-04502. The results of the analysis of physical properties carried out on coal slurry samples of the slurry are shown in Tables 5 and 6. Table 5 presents a summary of the results of the physical properties of coal slurry on an air-dried basis as statistical averages and the standard deviation of these averages for each deposit. Table 6 presents the results of the

physical properties of the coal slurry on an air-dried basis and dry basis in the grain size fraction <0.1 mm, as this grain fraction has the greatest share in the coal slurries analysed.

Tab. 5. Summary of the results of the physical properties of coal slurry on an air-dried basis.

Deposit No.	Ash content [%]	Standard deviation of the ash content [%]	Total sulphur content [%]	Standard deviation of the total sulphur content [%]	Volatile matter content [%]	Standard deviation of the volatile matter content [%]	Net calorific value [MJ/Mg]	Standard deviation of the net calorific value [MJ/Mg]
K13	27.47	2.99	1.90	0.84	28.50	4.32	15096	1509
K14	32.98	2.58	0.72	0.03	23.85	0.41	15646	829
K12	41.36	1.41	0.86	0.10	21.31	1.25	14813	581
K18/1	63.96	9.06	0.57	0.16	14.38	2.55	9325	2052
K18/2	63.04	17.76	0.64	0.25	14.39	5.47	10073	2746
K11/1	49.48	5.39	0.88	0.34	18.50	1.76	13297	2413
K3/1	60.43	10.56	0.70	0.20	16.41	3.13	9265	3498
K3/2	45.90	12.59	2.98	1.27	18.01	2.23	14877	5976
K2	58.34	8.24	2.26	0.67	14.29	1.17	12304	2803
K17	28.41	4.23	0.95	0.11	23.47	1.33	22807	1538
K1	26.98	3.46	0.95	0.15	23.77	0.75	23293	1444
K4/1	27.89	0.32	0.97	0.13	23.79	0.71	22941	590
K4/2	47.22	2.55	0.59	0.11	18.89	0.29	15813	937
K4/3	31.84	4.51	0.79	0.13	23.85	1.25	20828	2065
K5/1	53.79	5.17	1.21	0.19	16.99	1.52	12051	1504
K5/2	42.86	13.10	1.09	0.38	16.89	2.30	17802	5351
K5/3	37,59	1.44	0.94	0.08	20.64	0.87	19402	646
K5/4	35.22	1.28	0.97	0.02	21.54	0.40	20351	844
K11/2	37.33	1.29	0.92	0.06	20.72	0.54	19672	767
K6	38.83	5.88	0.94	0.15	20.16	2.12	18887	1834
Average	42.55	-	1.09	-	20.02	-	16427	-
Standard deviation	12.28	-	0.60	-	3.85	-	4520	-

Tab. 6. Summary of the results of the physical properties of coal slurry grain fraction <0.1 mm on an air-dried basis and on a dry basis.

Deposit No.	Yield of size fraction < 0.1 mm [%]	Hygr. moisture [%]	-	Ash content [%]		Total sulphur content [%]		Volatile matter content [%]		Net calorific value [MJ/Mg]	
	γ	$\mathbf{W_h}$	$\mathbf{A}^{\mathbf{a}}$	$\mathbf{A}^{\mathbf{d}}$	Sta	S_t^d	V^a	V^d	Q ^a	Q^d	
K13	27.90	4.30	53.00	55.38	1.21	1.26	17.21	17.98	12753	13326	
K14	60.79	3.97	55.64	57.94	0.66	0.69	12.66	13.19	10185	10606	
K12	70.16	4.61	53.02	55.58	0.86	0.90	15.20	15.94	11224	11766	
K18/1	69.33	2.99	73.49	75.75	0.44	0.45	10.60	10.93	1684	1736	
K18/2	54.75	2.13	77.23	78.91	0.47	0.48	7.92	8.09	6195	6330	
K11/1	67.87	4.07	58.94	61.44	0.74	0.77	16.25	16.94	10680	11133	
K3/1	28.43	1.51	57.73	58.62	4.15	4.21	15.62	15.86	8914	9051	
K3/2	48.36	1.38	67.20	68.14	2.49	2.52	13.56	13.75	6791	6886	
K2	57.23	2.56	52.49	53.87	0.67	0.69	16.21	16.63	12386	12712	
K17	77.58	2.87	64.43	66.33	1.29	1.33	14.37	14.80	8540	8792	
K1	65.75	1.57	49.91	50.71	1.36	1.38	16.15	16.40	15272	15515	
K4/1	67.76	2.07	37.03	37.81	0.21	0.21	22.27	22.74	18704	19099	
K4/2	54.80	1.92	41.19	42.00	0.38	0.39	20.02	20.41	16406	16727	
K4/3	57.57	1.83	39.75	40.49	1.36	1.39	19.91	20.29	17271	17593	
K5/1	75.76	1.64	45.53	46.29	0.96	0.98	17.83	18.13	15682	15943	
K5/2	72.87	2.03	44.20	45.12	1.00	1.02	18.00	18.37	15464	15784	
K5/3	68.53	1.24	42.58	43.11	1.05	1.06	17.98	18.21	16055	16257	
K5/4	68.12	2.08	43.01	43.92	1.04	1.06	18.42	18.81	18118	18503	
K11/2	78.93	2.57	63.13	64.80	0.69	0.71	14.30	14.68	7388	7583	
K6	72.97	1.33	57.24	58.01	0.61	0.62	16.36	16.58	11855	12015	
Average	62.27	2.43	53.84	55.21	1.09	1.11	16.04	16.44	12078	12368	
Standard deviation	14.26	1.05	11.31	11.71	0,88	0,89	3,30	3,34	4580	4658	

Based on the analysis of the results of the qualitative studies it can be stated that:

- the average net calorific value of the coal slurries (on an air-dry basis) deposited in individual settling ponds ranges from 9265 to 23293 MJ/Mg, and the standard deviation of this parameter is in the range from 581 to 5976 MJ/Mg
- the average ash content of the coal slurries (on an air-dried basis) deposited in individual settling ponds ranges from 26.98 to 63.96 % and the standard deviation of this parameter is in the range from 1.28 to 17.76 %,

- the average total sulphur content (on an air-dried basis) of the coal slurries deposited in individual settling ponds ranges from 0.57 to 2.98 % and the standard deviation of this parameter is in the range from 0.03 to 1.27 %,
- the average surface moisture content of the coal slurries deposited in individual settling ponds ranges from 11.69 to 34.48 % and the standard deviation of this parameter is in the range from 1.07 to 4.89 %,
- the average hygroscopic moisture content of the coal slurries deposited in individual settling ponds ranges from 1.04 to 7.92 % and the standard deviation of this parameter is in the range from 0.07 to 2.40 %,
- the average volatile matter content of the coal slurries deposited in individual settling ponds ranges from 14.29 to 28.50 % and the standard deviation of this parameter is in the range from 0.40 to 5.47 %,
- the grain size analysis of the coal slurry has shown that most particles are in the grain-size fraction below 0.1 mm. The average share of grains sized below 0.1 mm in all settling ponds amounts to 62.27 % and ranges for individual ponds ranges from 27.90 % to 78.93 % with a standard deviation of 14.26 % and only three settling ponds contained less than 50 % of this grain size fraction,
- the average net calorific value of the coal slurry (on an air-dried basis) in the grain size fraction below 0.1
 mm deposited in individual settling ponds is in the range from 6184 to 18704 MJ/Mg with a standard
 deviation of 4580 MJ/Mg,
- the grain-size fraction below 0.1 mm, has higher ash and sulphur contents.

The energy potential of coal slurry deposits

The quantitative and qualitative analysis of coal slurry deposits made it possible to estimate the energy potential of these slurries. For this purpose, an algorithm was developed for estimating the energy potential of the deposits inventoried. Two ways of estimating the energy potential were proposed (Baic, 2015; Baic, Lutyński A. and Lutyński M., 2012; Lutyński A. and Lutyński M., 2014). The first of these options is a rough estimate of the energy potential of a deposit, which is based on:

- the estimated mass of coal slurries in the deposit,
- the average net calorific value determined in a qualitative analysis of individual samples collected from the deposit.

This method is used to estimate the average approximate value of the energy potential of the deposit, which is most commonly used and reported in relevant studies. Although this is undoubtedly important information, to make this preliminary information more complete it is also important to specify the limits between which the energy potential of the coal slurry may fluctuate. For this purpose, in addition to the average value of the energy potential, also its limiting values are given, the lower and upper ones, based on the estimated standard deviation of the net calorific value determined for each sample. It is known from the theory of probability that 68 % of the individual estimates obtained from individual samples lie between these limiting values.

Thus, the average approximate value of the energy potential of a deposit (on an as-received basis or an airdried basis) is estimated from the relationship:

$$E_{av} = M \bullet Q^{rva}_{av} \bullet 10^{-3}, [GJ] \tag{1}$$

where:

 E_{av} average value of the energy potential of the deposit, [GJ]

M is estimated mass of coal slurries in the deposit, [Mg]

 Q^{rva}_{av} average net calorific value (on an as-received basis or an air-dried basis) determined by qualitative analysis of individual samples collected from a deposit, which is estimated from the relationship:

$$Q^{rva}_{av} = \frac{1}{n} \sum_{i=1}^{n} Q^{r_i} [kJ/kg]$$
(2)

The limiting values of the energy potential of a deposit are estimated from the relationships:

$$E_{max} = M \bullet (Q^{rva}_{av} + S_Q) \bullet 10^{-3}, [GJ]$$
(3)

and

$$E_{min} = M \bullet (Q^{rva}_{av} - S_Q) \bullet 10^{-3}, [GJ]$$

$$\tag{4}$$

where:

 S_Q standard deviation of the net calorific value estimated from the relationship:

$$S_{Q} = \sqrt{\frac{1}{n-1}} \sum_{i=1}^{n} (Q^{ra}_{i} - Q^{ra}_{av})$$
 [GJ]

The results of the estimation are shown in Tables 7 and 8.

Tab. 7. The energy potential of coal slurry (on dry basis) deposited in settling ponds.

	Approx. weight	Average net	Standard deviation of the	Energy potential (as received basis)			
Deposit No.	of the deposit	calorific value	net calorific value	average	maximal	minimal	
	[Mg]	[MJ/Mg]	[MJ/Mg]	[GJ]	[GJ]	[GJ]	
K13	1000000	12380	674	12380000	13053891	11706109	
K14	300000	12552	607	3765600	3947736	3583463	
K12	1000.000	12179	568	12178667	12748949	11610385	
K18/1	100000	7737	1673	773747	941065	606428	
K18/2	100000	8587	2369	858675	1095554	621796	
K11/1	640000	11087	2324	7095825	8583052	5608598	
K3/1	1521000	6874	2270	10455354	13907739	7002969	
K3/2	176000	13115	4655	2308240	3127660	1488819	
K2	1117000	10213	1975	11408107	13614438	9201776	
K17	155000	18979	1732	2941794	3210402	2673187	
K1	153000	19352	1062	2284311	2409719	2158902	
K4/1	345600	19285	1290	6664939	7110828	6219049	
K4/2	163000	12038	724	1962221	2080363	1844078	
K4/3	460000	16155	1394	7431258	8072425	6790091	
K5/1	130000	8256	967	1073316	1199042	947589	
K5/2	228000	13648	3628	3111873	3938967	2284779	
K5/3	106000	14869	680	1576075	1648248	1503903	
K5/4	102000	15385	763	1569270	1647164	1491375	
K11/2	176000	15057	464	2650090	2731792	2568388	
K6	236000	14636	1268	3453624	3753031	3154214	

Tab. 8. The energy potential of coal slurry (on an air-dried basis) deposited in settling ponds.

	Approximate	Average net	Standard deviation of the		Energy potential (air-dried basis)	
Deposit No.	weight of the deposit	8		average	maximal	minimal
	[Mg]	[MJ/Mg]	[MJ/Mg]	[GJ]	[GJ]	[GJ]
K13	1000000	15096	1509	15095667	16604265	13587068
K14	300000	15646	830	4693800	4942657	4444943
K12	1000000	14813	581	14812667	15393327	14232006
K18/1	100000	9325	2052	932547	1137768	727326
K18/2	100000	10073	2747	1007325	1281976	732674
K11/1	640000	13297	2413	8509964	10054237	6965690
K3/1	1521000	9265	3498	14092825	19413371	8772280
K3/2	176000	14877	5976	2618308	3670019	1566597
K2	1117000	12304	2803	13743987	16874910	10613064
K17	155000	22807	1538	3535074	3773403	3296745
K1	153000	23293	1444	3563810	3784749	3342871
K4/1	345600	22941	590	7928525	8132297	7224753
K4/2	163000	15813	937	2577600	2730378	2424822
K4/3	460000	20829	2065	9581173	10530941	8631404
K5/1	130000	12051	1504	1566590	1762060	1371119
K5/2	228000	17802	5351	4058928	5279050	2838807
K5/3	106000	19402	646	2056612	2125131	1988132
K5/4	102000	20351	844	2075761	2161898	1989625
K11/2	176000	19672	767	3462345	3597362	3327329
K6	236000	18887	1834	4457435	4890353	4024518

The second variant of estimating the energy potential of the deposits is based on a deeper knowledge of the material accumulated in the deposit, including knowledge of the future utilisation of the slurry and method of its preparation. The energy potential is estimated based on:

- the defined mass of coal slurries in the deposit,
- the yield of the concentrate obtained using the selected preparation technology,
- the average net calorific value determined for the concentrates obtained from samples prepared by individual technologies.

Because of the need to compare the energy potentials of slurries prepared using different technologies, net calorific values on the air-dried basis were used in the estimation.

The average value of the energy potential of the deposit was estimated from the relationship:

$$E_{av} = M \cdot U \cdot Q^{a}_{av} \cdot 10^{-3} \quad [GJ]$$
 (6)

where:

 E_{av} average estimated value of the energy potential of the deposit [GJ]

M estimated mass of the coal slurries in the deposit, [Mg]

 Q^a_{av} average net calorific value (on an air-dried basis) determined by qualitative analysis of individual samples prepared using the preparation technology selected, [MJ/Mg]

U yield of the concentrate obtained using the selected preparation technology

The results of the estimation of the energy potential on an air-dried basis for four preparation methods along with the expected loss of this potential are shown in Tables 9, 10, 11 and 12 (Baic, 2015; Baic, Blaschke and Grudziński, 2011; Lutyński A. and Lutyński M., 2014).

Methods used in the study:

- preparation in hydrocyclone with a diameter 150 mm; feed density of 150 g/l,
- preparation in a centrifugal drainer, feed density of 150 g/l; preliminary de-sliming on sieve 0.1 mm,
- preparation in Reichert 5 -spiral of LD 4 type; feed density 400 g/l; preliminary de-sliming on sieve 0.1 mm,
- preparation in flotation machine; feed density 100 g/l; flotation reagent type MONTANOL 505, dose of flotation reagent 0.6 kg/l (Fećko et al., 2011; Szpyrka and Lutyński, 2012; Wang et al., 2014).

Tab. 9. The energy potential of coal slurry in individual deposits as a result of preparation in hydrocyclone

		Raw deposit data			Hydro	cyclone	
Deposit No.	Weight	Net calorific value	Potential E _{av}	Recovery	Net calorific value	Potential Eav	Loss of potential
	[Mg]	[MJ/Mg]	[GJ]	[-]	[MJ/Mg]	[GJ]	[%]
K13	1000000	15096	15095667	0.47	18121	8516870	44
K14	300000	15646	4693800	0.56	20362	3420816	27
K12	1000000	14813	14812667	0.50	17281	8640500	42
K18/1	100000	9325	932547	0.50	9295	464750	50
K18/2	100000	10073	1007325	0.60	8576	514560	49
K11/1	640000	13297	8509964	0,51	15990	5219136	39
K3/1	1521000	9265	14092825	0.57	16277	12377730	12
K3/2	176000	14877	2618308	0.63	12027	1333553	49
K2	1117000	12304	13743987	0.58	14234	9221639	33
K17	155000	22807	3535074	0.44	13444	916880	74
K1	153000	23293	3563810	0.52	17972	1429852	60
K4/1	345600	22941	7928525	0.51	24363	4294124	49
K4/2	163000	15813	2577600	0.59	24557	2073136	20
K4/3	460000	20828	9581173	0.57	25501	6686362	30
K5/1	130000	12051	1566590	0.46	21415	1180617	25
K5/2	228000	17802	4058928	0.48	21085	2307542	43
K5/3	106000	19402	20566631	0.50	21161	1121533	45
K5/4	102000	20351	2075761	0.51	21844	1136324	45
K11/2	176000	19672	3462345	0.44	12008	92999	97
K6	236000	18887	4457435	0.47	18022	1999000	55
av.	-	16427	-	0.53	16950	-	44

Tab. 10. The energy potential of coal slurry in individual deposits as a result of preparation in a centrifugal drainer with preliminary de-sliming.

		Raw deposit data	1	Centrifugal drainer				
Deposit No.	Weight	Net calorific value	Potential Eav	Recovery	Net calorific value	Potential Eav	Loss of potential	
	[Mg]	[MJ/Mg]	[GJ]	[-]	[MJ/Mg]	[GJ]	[%]	
K13	1000000	15096	15095667	0.23	18916	4350680	71	
K14	300000	15646	4693800	0.36	20654	2230632	52	
K12	1000000	14813	14812667	0.10	22042	2204200	85	
K18/1	100000	9325	932547	-	-	-	-	
K18/2	100000	10073	1007325	-	-	-	1	
K11/1	640000	13297	8509964	0.04	21043	538700	94	
K3/1	1521000	9265	14092825	0.14	25840	5502369	61	
K3/2	176000	14877	2618308	-	-	-	-	
K2	1117000	12304	13743987	0.48	24104	11923600	13	
K17	155000	22807	3535074	0.03	18965	88187	97	

		Raw deposit data	1	Centrifugal drainer				
Deposit No.	Weight	Net calorific value	Potential E _{av}	Recovery	Net calorific value	Potential E _{av}	Loss of potential	
	[Mg]	[MJ/Mg]	[GJ]	[-]	[MJ/Mg]	[GJ]	[%]	
K1	153000	23293	3563810	0.08	25046	306000	91	
K4/1	345600	22941	7928525	0.28	24095	2331625	71	
K4/2	163000	15813	2577600	0.47	24164	1851204	28	
K4/3	460000	20828	9581173	0.52	24315	5816148	39	
K5/1	130000	12051	1566590	0.25	24430	793975	49	
K5/2	228000	17802	4058928	0.22	24043	1205997	70	
K5/3	106000	19402	20566631	0,26	23802	655983	68	
K5/4	102000	20351	2075761	0.22	24281	544865	74	
K11/2	176000	19672	3462345	0.02	18519	65187	98	
K6	236000	18887	4457435	0.08	24124	455461	90	
av.	-	16427	-	0.22	22846	-	68	

Tab. 11. The energy potential of coal slurry in individual deposits as a result of preparation in Reichert spiral with preliminary de-sliming.

	Raw deposit data			Reichert spiral				
Deposit No.	Weight	Net calorific value	Potential E _{av}	Recovery	Net calorific value	Potential E _{av}	Loss of potential	
	[Mg]	[MJ/Mg]	[GJ]	[-]	[MJ/Mg]	[GJ]	[%]	
K13	1000000	15096	15095667	0.29	18825	5459250	64	
K14	300000	15646	4693800	0.41	20271	2493333	47	
K12	1000000	14813	14812667	0.18	21523	3874140	74	
K18/1	100000	9325	932547	0.04	21042	92585	90	
K18/2	100000	10073	1007325	-	-		-	
K11/1	640000	13297	8509964	0.15	20760	1992960	77	
K3/1	1521000	9265	14092825	0.23	25843	9040657	36	
K3/2	176000	14877	2618308	0.06	24258	150564	94	
K2	1117000	12304	13743987	0.50	24335	12602267	9	
K17	155000	22807	3535074	0.09	19136	266947	92	
K1	153000	23293	3563810	0.14	24241	519000	85	
K4/1	345600	22941	7928525	0.30	24459	2535909	68	
K4/2	163000	15813	2577600	0.50	23763	1936684	25	
K4/3	460000	20828	9581173	0.52	24333	5820454	39	
K5/1	130000	12051	1566590	0.30	23352	910728	42	
K5/2	228000	17802	4058928	0.27	23666	1456879	64	
K5/3	106000	19402	20566631	0.30	24035	764313	63	
K5/4	102000	20351	2075761	0.27	24195	666330	68	
K11/2	176000	19672	3462345	0.07	18756	231074	93	
K6	236000	18887	4457435	0.14	24256	801000	82	
av.	-	16427	-	0.25	22687	-	64	

Tab. 12. The energy potential of coal slurry in individual deposits as a result of preparation in a flotation machine.

140.	12. The energy p	- V		Electrical machine			
	Raw deposit data			Flotation machine			
Deposit No.	Weight	Net calorific value	Potential \mathbf{E}_{av}	Recovery	Net calorific value	Potential E _{av}	Loss of potential
	[Mg]	[MJ/Mg]	[GJ]	[-]	[MJ/Mg]	[GJ]	[%]
K13	1000000	15096	15095667	-	-	-	-
K14	300000	15646	4693800	-	-	-	-
K12	1000000	14813	14812667	-	-	-	-
K18/1	100000	9325	932547	-	-	-	-
K18/2	100000	10073	1007325	-	-	-	-
K11/1	640000	13297	8509964	-	-	-	-
K3/1	1521000	9265	14092825	-	-	-	-
K3/2	176000	14877	2618308	0.45	24687	1955210	25
K2	1117000	12304	13743987	0.41	20670	9466240	31
K17	155000	22807	3535074	0.74	27620	3168014	10
K1	153000	23293	3563810	0.80	27120	3319488	7
K4/1	345600	22941	7928525	0.81	26880	7524680	5
K4/2	163000	15813	2577600	0.65	21525	2280574	11
K4/3	460000	20828	9581173	0.41	24520	4624472	51
K5/1	130000	12051	1566590	-	-		
K5/2	228000	17802	4058928	0.58	24670	3262361	20
K5/3	106000	19402	20566631	0.72	25875	1974780	4
K5/4	102000	20351	2075761	0.71	25810	1869160	10
K11/2	176000	19672	3462345	0.70	25845	3184104	8
K6	236000	18887	4457435	0.72	25465	4327013	3
av.	-	16427	-	0.64	25057	-	15

The results of coal slurry preparation by four methods are shown in Tables 9, 10, 11 and 12, and the analysis of their energy potential showed that a significant part of this potential is lost during the preparation process.

During the preparation process of coal slurry, the smallest losses of energy potential were obtained using flotation machine. In this case, the average loss of the energy potential was 15 %. However, for individual settling ponds, this losses ranged between 3 and 51 %. The average net calorific value of the flotation concentrates obtained by this preparation method was 25,057 MJ/Mg. It was the highest value of all analysed preparation methods. Unfortunately not all coal slurries were sensitive to preparation in flotation machine with the use of flotation reagent type MONTANOL 505 for this studies.

The preparation in a centrifugal drainer with preliminary de-sliming on sieve 0.1 mm turned out less preferred method. In this case, the average losses of the energy potential were 68 %. These losses ranged from 13 % up to 98 % for individual settling ponds. On the other hand, the net calorific value of the concentrates obtained by this preparation method was 22,864 MJ/Mg.

These results were similar to the results obtained by preparation in Reichert spirals with preliminary desliming of the feed on sieve 0.1 mm. In this case, the average losses of the energy potential were 64 %, and the average net calorific value of the concentrates was 22,678 MJ/Mg.

During the preparation process of coal slurry in hydrocyclone net calorific value of the concentrate (16,950 MJ/Mg) increased slightly in relation to the net calorific value of the raw slurry (16,427 MJ/Mg). In this case, the average losses of the energy potential were 44 %. For individual settling ponds, the losses of the energy ranged from 12 % up to 97 %. This method should not be used for preparing the coal slurries deposited in the settling ponds.

Based on these studies it can be concluded that it is possible to prepare coal slurry deposited in settling ponds. Most favourable results were obtained using the flotation method. Good quality concentrates one can obtained during the preparation in Reichert spirals and centrifugal drainer. However, in these methods, the average loss of the energy potential is much higher than for flotation.

Discussion of the results

Summing up:

- The inventory of coal slurry deposits has shown that more than 16.5 million Mg of coal slurry is deposited into the environment. When used directly, or after employing an appropriate preparation technology, these slurries can become a valuable fuel for the power industry.
- Estimation analysis employing a mathematical formula presented here showed that almost 120 million Mg of this feedstock had been deposited into the environment since 1945, which is eight times more than evidenced by physical inventory and currently reported in the official statistics.
- Most of the land into which coal slurry was deposited in the 20th century has undergone an anthropogenic transformation, thus preventing exploitation and utilisation of the coal slurry deposited. These areas have been reclaimed, in part or in whole, to become recreational areas or areas with industrial or service facilities.
- The main components of coal slurry samples are silica (27.81-63.96 %) and carbon (11.15-31.80 %). This composition is typical of a fine-grained waste of this type. The values that deviate from the data reported in the literature are very low Al₂O₃ and TiO₂ contents.
- Direct analysis of chemical properties of slurry samples from the inventoried settling ponds showed permissible concentrations of metals such as barium, zinc, cobalt and nickel were exceeded. This is not only due to their presence in the deposit, but also most likely to anthropogenic pollutants, and the presence of these metals in the land surrounding the settling ponds studied.
- Analysis of water extracts of coal slurry samples for basic properties and metals showed no exceeded
 maximum permissible value of substances harmful to the water environment. This means that the metals
 present in coal slurry, including those for which the permissible limiting values were found to be exceeded,
 occur in chemically bonded forms. Consequently, they neither pose a threat to the environment nor do they
 restrict possible areas of their utilisation.
- The results of physical properties of coal slurry samples studied show a considerable variation in the quality of slurry deposited in individual settling ponds, which is obvious due to the varied geological and mining conditions of individual mines which deposited coal slurry in these ponds.
- The qualitative and quantitative results of coal slurry deposits indicate a significant energy potential, which can be effectively used of appropriate preparation technologies.
- The results of coal slurry preparation by four methods and the analysis of their energy potential have shown that a large amount of this potential is lost as a result of preparation. It is the result of the smallest coal particles passing through to the tailings. Most favourable results were obtained using the flotation method.

• The analysis showed that industrial use of coal slurry would be effective if the method devoided of any additional preparation operations is applied, such as pelletizing (Borowski and Hycnar, 2013; Hycnar and Borowski, 2016; Hycnar and Bugajczyk, 2004).

References

- Aghazadeh S., Gharabaghi M., Azadmehr A. (2016). Increasing the useful heating value of coal using a physicochemical process. *International Journal of Coal Preparation and Utilization*, 36(4), s. 175–191.
- Baic I. (2013) Analiza parametrów chemicznych, fizycznych i energetycznych depozytów mułów węglowych zinwentaryzowanych na terenie województwa śląskiego; *Annual Set The Environment Protection, Vol. 15*, , *Part 2, pp. 1511-1524, Koszalin*
- Baic I. (2015) Analiza wielokierunkowego wykorzystania depozytów mułów węglowych wraz z ocena oddziaływania na środowisko; *Studia, Rozprawy, Monografie Nr 191, Wyd. IGSMiE PAN Kraków, s. 1-234, Krakow*
- Baic I., Blaschke W., Grudziński Z. (2011) Wstępne badania nad możliwością przewidywania parametrów jakościowych odpadów powstających w procesach wzbogacania węgli kamiennych; *Annual Set The Environment Protection, Vol. 13, Part 2, pp. 1373-1383, Koszalin*.
- Baic I., Blaschke W., Sobko W. (2011) Depozyty mułów węglowych inwentaryzacja i identyfikacja ilościowa; *Annual Set The Environment Protection, Vol. 13, Part 2, pp. 1405-1415, Koszalin*.
- Baic I., Lutyński A., Lutyński M. (2012) Potencjał energetycznych zdeponowanych mułów węglowych. *Polityka Energetyczna Vol. 15, issue 3, pp. 259–271, Krakow*
- Baic I., Sobko W., Łukowska M. (2012) Inwentaryzacja szacunkowa i in situ depozytów mułów węglowych. *Polityka Energetyczna Vol. 15, issue 3, pp. 221–229, Krakow 2012.*
- Baic I. Witkowska-Kita B., Lutyński A., Suponik T. (2012) Parametry chemiczne depozytów mułów węglowych. Baza danych DMW. Polityka Energetyczna Vol. 15, issue 3, pp. 231–245, Kraków 2012
- Białas M., Białas J., Lutyński A., Kasztan A., Narloch G. (2001). Wydzielanie ziaren węglowych z zawiesin odpadowych. *Gospodarka Surowcami Mineralnymi, 17, z spec*.
- Białecka B., Grabowski J., Bajerski A. (2016) Assessment of the mercury emission from burning mining waste dumps. *Acta Montanistica Slovaca Vol.21, issue 1, pp.29-36. Kosice 2016*
- Blaschke W., Baic I. (2012) Problematyka depozytów mułów węglowych w Polsce. *Polityka Energetyczna Vol.* 15, issue 3, pp. 211–219, Kraków.
- Blaschke W. Blaschke Z. (2005) Preparation of coal slurries deposited in ground settling ponds. *Acta Montanistica Slovaca Vol 10, special issue 1, pp. 17-21, Kosice 2005.*
- Borowski G., Hycnar J.J. (2013). Utilization of fine coal waste as a fuel briquettes. *International Journal of Coal Preparation and Utilization*, 33(4), s. 194–204.
- Brenek R., Santarius A., Hudecek V. (2014) Decontamination of waste dumpside of s.p. Diamo. *Acta Montanistica Slovaca Vol.19, issue 1, pp.6-14, Kosice*
- Development Project No. N R09 006 06/2009. "Identyfikacja potencjału energetycznego depozytów mułów węglowych w bilansie paliwowym kraju oraz strategia rozwoju technologicznego w zakresie ich wykorzystania. IMBiGS. Warsaw 2009.
- Fećko P., Hlavatá M., Podešvová M., Mucha N., Király A. (2011) New flotation agents on a slurry sample from Darkov Mine. *Journal of the Polish Mineral Engineering Society, No 1*(27), p. 27–38. *Kraków*
- Galos K., Szluga J. (2014). Management of hard coal mining and processing wastes in Poland. *Gospodarka Surowcami Mineralnymi Mineral Resources Management*, 30(4).
- Gawlik L. (2005) Prawne aspekty wykorzystania mułów węglowych zdeponowanych w osadnikach. Zeszyty Naukowe Politechniki Koszalińskiej. Zeszyt Nr 22, Seria: Inżynieria Środowiska. Issue 22, pp.377-386, Koszalin
- Grudziński Z. (2005) Analiza porównawcza jakości mułów węgla kamiennego pochodzących z bieżącej produkcji i zdeponowanych w osadnikach ziemnych. Zeszyty Naukowe Politechniki Koszalińskiej. Zeszyt Nr 22, Seria: Inżynieria Środowiska. Issue 22 (2005), pp.671-679, Koszalin
- Hlavata M., Cablik V. (2012) Application of Fine Tailings from Coal Preparation in the Ostrava Karvina District. Rocznik Ochrona Środowiska Annual Set the Environment Protection, Vol. 14, pp. 285-289, Koszalin
- Hycnar J.J., Borowski G. (2016) Metody podwyższenia kaloryczności drobnoziarnistych odpadów węglowych. Monografia, Politechnika Lubleska, s.156, Lublin
- Hycnar J.J., Bugajczyk M. (2004) Kierunki racjonalnego zagospodarowania drobnoziarnistych odpadów węglowych. Polityka Energetyczna Energy Policy Journal, Vol. 7 special issue, Kraków

- Lorenz U., Ozga-Blaschke U. (2005) Muły węgla kamiennego produkt czy odpad. Zeszyty Naukowe Politechniki Koszalińskiej. Zeszyt Nr 22, Seria: Inżynieria Środowiska. Issue 22, pp. 682-691, Koszalin 2005
- Lutyński A, Lutyński M. (2014) Assessment of coal slurry deposits energetic potential and possible utilization paths; *Physicochemical Problems of Mineral Processing*, Vol. 50,Issue 1, pp. 159-168, Wrocław.
- Lutyński A, Suponik T., Lutyński M. (2013) Investigation of coal slurry properties deposited at impoundments; *Physicochemical Problems of Mineral Processing, Vol. 49,Issue 1, pp. 22-35, Wrocław.*
- Lutyński A., Szpyrka J. (2012) Analiza własności fizykochemicznych depozytów mułów węglowych na Górnym Śląsku. *Polityka Energetyczna Vol. 15, issue 3, pp. 273–285, Krakow*
- Szpyrka J., Lutyński A. (2012) Badania wzbogacania depozytów mułów węglowych. *Polityka Energetyczna Energy Policy Journal, Vol. 15, issue 3, pp. 247-258, Kraków*
- Rotunajanu I., Lazar M. (2014) Hydrogeological classification and evaluation of coal deposits. *Mining Revue Vol.20, No 2/2014, pp. 7-14, University of Petrosani, Romania,*
- Wang Ch., Harbottle D., Liu Q., Xu Z. (2014). Current State of fine mineral tailings treatment: A critical review on theory and practice. *Minerals Engineering*, 58, s. 113–131.
- Yilmaz E. (2011). Advances in reducing large volumes of environmentally harmful mine waste rocks and tailings. *Gospodarka Surowcami Mineralnymi*, 27(2).