

Potential of Metal Recovery from Coal Combustion Products. Part I. Physicochemical Characterization

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Summary

The paper presents physicochemical characteristic of coal combustion products: fly ashes from three stages of electrostatic dust collecting system (FA_I , FA_{II} , FA_{III}), slag (S) and slurry from wet flue gas desulphurization (S-wFGD). Fly ashes are classified as 'siliceous' or 'sialic-high acid'. The concentrations of selected heavy metals indicate that their values increase in accordance with consecutive stages of dust collecting system. Fly ash FA_{III} and slurry from wet FGD have the largest heavy metals content. The results show the increment of lanthanides and itrium (REY) contents in CCPs from slag, through FA_{II} and FA_I to S-wFGD and FA_{III} .

Keywords: coal combustion products, rare earth elements, heavy metals, fly ash, slag, slurry from wet flue gas desulphurization

Introduction

Coal combustion products (CCPs) refer to all types of wastes, generated in the process of thermal and electric energy production, which can be reused. These are, among others, fly ashes, slags, ash-slag mixtures and slurry from flue gas desulphurization. All of them are a part of the subgroup '10.01' in the Polish Waste Catalogue and their total amount generated in Poland in the year 2011 was around 22.9 million t. Fly ashes represent about 20% of that amount, slags 8% and fly ash-slag mixtures 35%. The remaining wastes include mixtures of ashes and flue gas desulphurization products (18%) as well as synthetic gypsum (10%). In the year 2011 a total degree of CCPs economical utilization was 60% whereas for fly ashes it was 94%, 73% for slags and 82% for gypsum [1]. In spite of the significant amount of utilized CCPs, it still remains a serious environmental issue and further research in the field of multi-component utilization, including carbon, cenospheres or metal recovery [2], seems to be intended. Therefore, complete recognition of CCPs physicochemical properties is necessary in order to conceive novel, more economically and ecologically accepted methods of its utilization.

In the literature there are numerous results of fly ash examination [3-5], however there are limited numbers of physicochemical study of all types of coal combustion products as well as fly ashes di-

vided into different fractions from dust collecting system. Furthermore, there is no detailed data in the subject of Polish CCPs including rare earth elements and heavy metals content. In this paper an attempt to determine selected physicochemical properties of various coal combustion products was made.

Materials and Methods

Coal combustion products derived from EDF Rybnik Inc Power Plant, which is based on steam boiler OP-650 fed with bituminous coal co-incinerated with 10% biomass, were investigated. Three types of CCPs were examined: fly ashes from the electrostatic dust collecting system (from the first (FA_I), the second (FA_{II}) and the third (FA_{III}) stage), slag (S) and slurry from wet flue gas desulphurization (S-wFGD). In order to conduct a physicochemical analysis, slag and slurry from FGD were subjected to initial drying and grinding operations to obtain a powdered material whereas fly ashes were used in their primary form. The humidity content and loss on ignition were determined according to Polish Standards [6-7]. Microscopic research was performed on scanning electron microscope (SEM) Hitachi model TM3000. In order to perform a grain-size analysis of fly ashes, a 200 mm sieve assembly with mesh size of 63, 125, 250 and 500 μm was used. The results are an average of two measurements, varying not more than 5% of fraction share

for a given fraction. Phase analysis was carried out using X-ray powder diffraction (XRD) Philips PW1830 device with Cu lamp in the range of 5-80 (2 θ). Afterwards the studied solid materials were put into microwave mineralization to perform an elemental analysis. For the determination of elements ICP-OES Plasm 40 and ICP-MS ELAN 6100 Perkin Elmer spectrophotometer were used. The silica content was established by the gravimetric method. Furthermore, the calculation of elements with the highest amount into their oxides was made.

Data referring to rare earth metals – lanthanides and yttrium, named in short as REY (rare earth & yttrium), were analyzed in accordance with the criteria and classification, which were published [8]. The proposed model assumes that the basic usability criterion of a given fly ash as REY resource is REY oxides (REO) content in the material, which should be at least 1000 ppm (0.1%) and the second condition is a substantial amount of especially valuable metals. According to the predictions about

REY demand, it was evaluated that Nd, Eu, Tb, Dy, Er and Y will be considered as important and crucial for industry in the near future. From that ‘outlook coefficient’, ‘C_{outl}’:

$$C_{outl} = \frac{Nd + Eu + Tb + Dy + Er + Y}{Ce + Ho + Tm + Yb + Lu}$$

was defined, in which the names of elements refer to their concentrations in the material.

Results and Discussion

Slag and S-wFGD exhibited considerable humidity contents, 33% and 40%, respectively, whereas fly ashes contained less than 1% of hygroscopic water. Microscopic images of the latter were shown in Fig. 1. In the pictures zoomed 500 times, an increment of a smaller fraction share, in accordance with the consecutive stages of dust collection system, can be observed. The grain shape of fly ashes, which are made of siliceous glaze is spherical, which is characteristic of crumbled coal incinerated at elevated temperature in conventional boilers. However, the

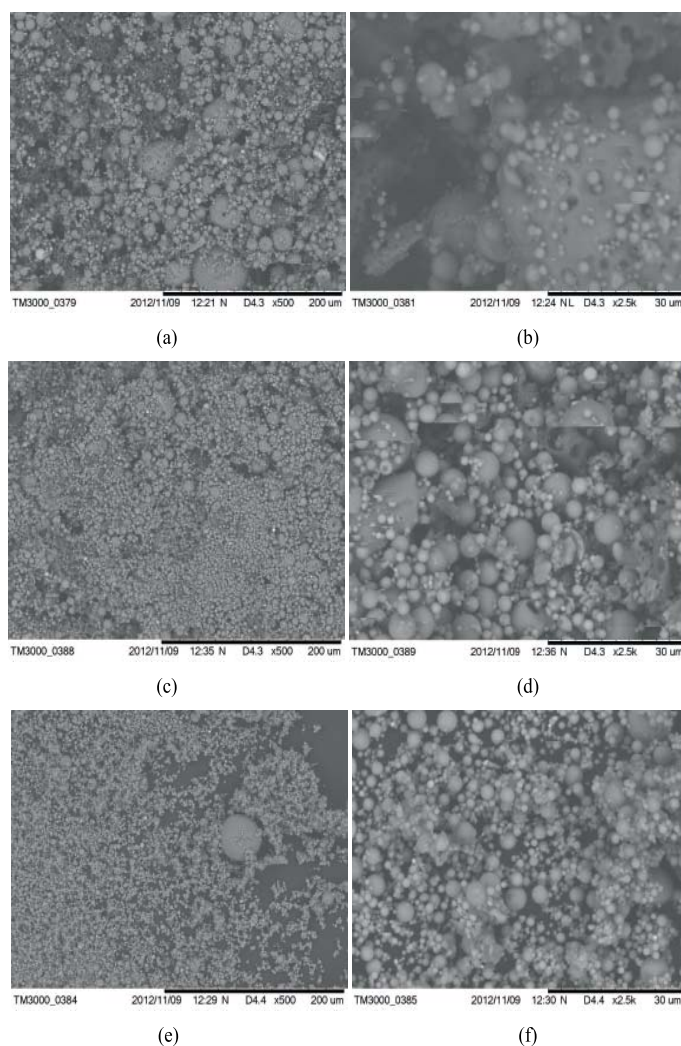


Fig. 1. Images of fly ashes: a, b) FA_I; c, d) FA_{II}; e, f) FA_{III} zoomed 500x and 2500x.

Rys. 1. Widok popiołów lotnych: a, b) FA_I; c, d) FA_{II}; e, f) FA_{III} powiększony 500x oraz 2500x

particle size varies considerably and is included in the range of 1-400 μm . Spherical aluminosilicate microspheres in majority have a smooth, uniform external surface, whereas some of their walls have been damaged (Fig. 1).

The granulometric analysis results (Fig. 2) show that fly ashes exhibit the greatest share of fraction below 63 μm (-63 μm), the value of which increases in accordance with the consecutive stages of dust collecting system. According to fly ashes classifications BN-79/6722-09 [9], fly ash FA_I, which has got over 30% of residue on 63 μm sieve, is considered as ‘average fly ash’, whereas fly ashes FA_{II} and FA_{III} - as ‘fine fly ash’.

The mineral composition of fly ashes and slag is primarily glassy phase made of siliceous glass in an amount of up to 100% [10]. This phenomenon can be seen on XRD spectra (Fig. 3a), in which among the dominating amorphous phase, typical of background elevation in the angular range of 15-35 (2θ), small quantities of crystalline quartz (Q) and mullite (M) are present. On the other hand, on S-wFGD XRD spectra (Fig. 3b), almost pure crystalline gypsum phase (G) and slight quartz (Q) and fluorite(F) content, can be observed.

The presence of essential oxides in the tested CCPs materials and their loss on ignition was tabulated (Tab. 1). The main components of slag and fly ashes are silica (75-80%) as well as aluminium and ferrous oxides, 6-11% and approx. 4%, respectively. The sum of the three aforementioned oxides ranges from 87 to 92%. The remaining oxides content is relatively low in comparison to fly ashes described in the literature both Polish (EC Wybrzeże FA) [5] and foreign (median for 23 UE FAs) [11] fly ashes. According to the fly ashes standard BN-79/6722-09, the investigated fly ashes can be classified as ‘siliceous’ ($\text{SiO}_2 > 40\%$; $\text{Al}_2\text{O}_3 < 30\%$; $\text{CaO} < 10\%$;

$\text{SO}_3 < 4\%$). The fly ashes FA_I and FA_{III} are C class in accordance with ASTM C-618 standard [12] ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 50\%$; $\text{SO}_3 < 5\%$; humidity content $< 3\%$; loss on ignition $< 6\%$). Moreover, fly ash FA_{III} is A class and FA_I is B class as per EN-PN 450-1 standard [13] ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$; $\text{SO}_3 < 3\%$; loss on ignition: 2-7%). In turn, a novel fly ashes classification [14] based on chemical composition, labels examined fly ashes as ‘sialic-high acid’ (S-HA) fly ashes ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{TiO}_2 + \text{P}_2\text{O}_5 > 89\%$; $\text{CaO} + \text{MgO} + \text{SO}_3 + \text{Na}_2\text{O} + \text{MnO} < 11.5\%$; $\text{Fe}_2\text{O}_3 < 11.5$). Fly ash FA_{II} shows a significant loss on ignition value (14.3%), which can be caused by specific concentration of unburned coal particles in this stage of dust collecting system.

The contents of heavy metals, boron and arsenic exhibit a characteristic tendency of content increase for all the elements from slag to fly ash FA_{III} (Tab. 2). Therefore, the growth of these elements concentrations occurs in accordance with consecutive stages of dust collecting system. Chromium is an exception, due to the highest content in fly ash FA_{II}. On the other hand, S-wFGD has got a smaller amount of trace elements than FA_{III}. According to national data, the studied fly ash FA_{III} is considerably more abundant in heavy metals (Zn, Ni, Cu) and has got a comparable amount of Cr. In comparison to foreign fly ashes, on the example of an average content of elements in 39 Massachusetts fly ashes [15], FA_{III} exhibits similar Zn, Ni and Cu concentrations, and lower Cr, As and Mo concentrations.

Moreover, the contents of heavy metals and rare earth elements (REY) in the tested CCPs were compared to their occurrence in the upper continental crust (UCC) [16]. According to the criteria of CCPs usability as the REY resource, the examined fly ashes and slag possess M-type distribution of rare earth

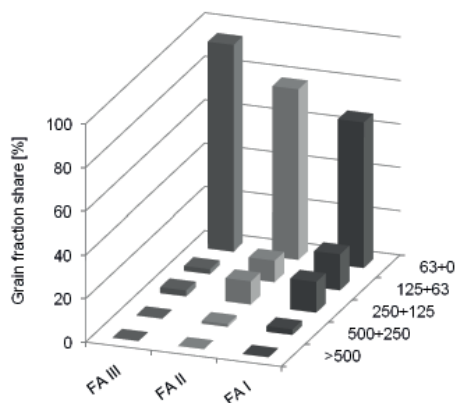


Fig. 2. The share of individual grain fractions for the examined fly ashes.

Rys. 2. Udział pojedynczych frakcji ziaren dla badanych popiołów lotnych

Tab. 1. CCPs oxides composition in comparison with literature data ([%]).

Tab. 1. Produkty spalania węgla, utleniony skład w porównaniu z danymi z literatury ([%])

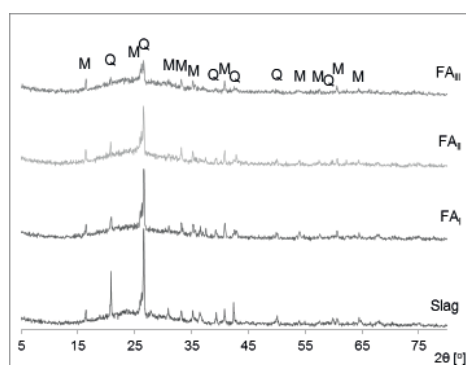
Component	S	FA _I	FA _{II}	FA _{III}	S-wFGD	Polish FA [9]	UE FAs [10]
SiO ₂	76.8	79.8	77.5	75.1	5.2	58.4	49.2
Al ₂ O ₃	6.1	7.7	7.8	11.3	6.7	18.5	26.1
Fe ₂ O ₃	3.8	4.6	3.7	4.2	2.8	3.3	7.5
CaO	2.1	3.7	3.4	3.1	30.4	7.2	4.0
MgO	1.4	2.2	2.1	1.7	0.8	1.4	1.6
K ₂ O	0.7	0.9	1.2	1.7	0.9	5.7	1.9
Na ₂ O	0.3	0.5	0.5	0.8	0.4	1.2	0.5
P ₂ O ₅	0.2	0.4	0.6	1.0	0.2	0.9	0.3
MnO	0.0	0.1	0.1	0.1	0.0	-	0.1
TiO ₂	0.0	0.1	0.1	0.1	0.0	3.4	1.0
SO ₃	0.0	0.0	0.2	0.9	14.5	-	0.6
Sum	91.4	99.9	97.1	100.0	62.0	100.0	92.8
LOI*	5.3	5.4	14.3	4.8	22.5	-	3.7

* loss on ignition at temperature of 850°C

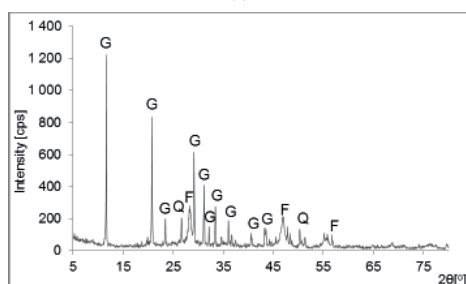
Tab. 2. CCPs element content in comparison with literature data ([μg/g]).

Tab. 2. Zawartość metalu w produkcie spalania węgla w porównaniu z danymi z literatury ([%])

Element	S	FA _I	FA _{II}	FA _{III}	S-wFGD	Polish FA [9]	USA FAs [14]	UE FAs [10]	UCC [15]
B	62.8	125.0	144.3	179.9	103.0			259.0	17.0
Zn	37.4	124.8	229.2	483.3	367.3	55.0	449.0	154.0	67.0
Cr	70.5	81.8	100.4	91.0	58.1	115.7	247.0	148.0	92.0
Ni	39.0	55.7	81.9	113.4	31.5	34.2	141.0	96.0	47.0
Ga	33.2	55.2	76.9	117.9	50.2				17.5
Cu	42.5	51.8	86.1	167.1	37.2	70.9	185.0	86.0	28.0
As	5.0	22.0	39.8	68.8	33.2		156.0	55.0	4.8
Mo	1.7	5.5	8.5	10.9	6.6		44.0	11.0	1.1
La	8.75	14.83	18.75	32.28	34.54				31.00
Ce	16.87	30.17	33.07	49.44	40.39				63.00
Pr	2.06	3.50	4.03	6.49	5.69				7.10
Nd	8.72	15.17	17.68	31.12	21.95				27.00
Sm	1.69	3.33	3.61	4.94	3.91				4.70
Eu	0.43	0.93	0.97	1.29	0.91				1.00
Gd	1.73	3.67	3.78	4.90	5.02				4.00
Tb	0.31	0.63	0.67	0.83	0.91				0.70
Dy	1.39	2.83	3.02	3.68	4.54				3.90
Y	9.28	17.00	20.34	23.70	50.64				21.00
Ho	0.25	0.55	0.57	0.67	0.92				0.83
Er	0.73	1.57	1.64	1.95	2.78				2.30
Tm	0.10	0.23	0.23	0.26	0.38				0.30
Yb	0.66	1.42	1.47	1.73	2.37				2.00
Lu	0.11	0.23	0.23	0.27	0.37				0.31



(a)



(b)

Fig. 3. XRD spectra of studied materials: a) slag and fly ashes, b) slurry from wet FGD.

Rys. 3. Widmo XRD badanych materiałów: a) żużel i popioły lotne, b) mokra zawiesina z OMS

elements ($La/Sm < 1$; $Gd/Lu > 1$), which indicates that they are rich in middle mass REY (MREY), i.e. Eu, Gd, Tb, Dy and Y. On the contrary, slurry from FGD shows H-type REY distribution ($La/Lu < 1$) and has got a dominance of heavy REY (HREY). It can be seen as well in the Figure 4, which presents rare earth elements concentrations with respect to its content in the UCC.

The content of rare earth elements oxides (REO) in the tested material amounts to 0.02% at maximum in fly ash FA_{III} . In comparison to the world average and the maximum values, 0.04% and 1.5% REO, respectively [8], the investigated CCPs can be considered as poor in rare earth elements. However, all of the materials possess the crucial REY share in the total REY content in the range of 30-50% (the most for S-wFGD, approx. 47%) and ‘outlook coefficient’ ranging from 0.7 to 1.9 (the most for S-wFGD, approx. 1.8). Hence, the studied materials can be included into a group of REY resources which are promising in terms of economic utilization.

Conclusions

The results of research on various types of coal combustion products, which are derived from the same power plant, allowed to make a comparison of physicochemical properties of wastes

generated during electricity production. Slag appeared to be a material with chemical and mineral compositions related to fly ashes and with the lowest metal elements content. Because of its significant humidity content and large, irregular particle shapes, slag is a problematic waste for utilization. The studied fly ashes can be classified as ‘siliceous’ or ‘sialic-high acid’. Hence, their potential applications are broad, e.g. as binders for the manufacture of building materials, raw materials for microspheres, aluminium, unburned coal or heavy metals recovery or for the synthesis of geopolymers and zeolites. What is more, the heavy metals content increases in accordance with the consecutive stages of dust collecting system. However, metals concentrations in the whole fly ash strongly depend on a fraction share of individual fly ashes: FA_I , FA_{II} and FA_{III} have got 90%, 9% and 1% share, respectively. Thus, fly ash FA_I shows the most important contribution to metals content in the whole fly ash. Moreover, the studied CCPs materials exhibit low share of REY oxides. In spite of that, CCPs possess lucrative REY distribution, especially slurry from wet FGD with the greatest percentage of crucial REY.

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Potencjał odzysku metalu z produktów spalania węgla. Część I: Opis właściwości fizykochemicznych

W artykule znajduje się opis właściwości fizykochemicznych produktów spalania węgla: popiołów lotnych z trzech etapów systemu gromadzenia pyłu (FA_I, FA_{II}, FA_{III}), żużlu oraz zawiesiny powstałej z odsiarczania mokrych spalin (Z z OMS). Popioły lotne dzielą się na krzemionkowe i kwaśne. Stężenia wybranych metali ciężkich wskazują na wzrost względem kolejnych etapów systemu gromadzenia pyłu. Popiół lotny FA_{III} oraz mokra zawiesina z OMS zawierają najwyższe poziomy zawartości metali ciężkich. Wyniki wykazują wzrost zawartości lantanowców i itrium (REY) w produktach spalania węgla z żużlu, przez FA_{II} i FA_I aż do Z z OMS i FA_{III}.

Słowa klucze: produkty spalania węgla, metale ziem rzadkich, ciężkie metale, popiół lotny, żużel, zawiesina powstała z odsiarczania mokrych spalin