

# Potential of Metal Recovery from Coal Combustion Products. Part II. Leaching of Selected Elements

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## Summary

*The paper presents leaching results of coal combustion products: fly ashes from the three stages of dust collecting system, slag and slurry from wet flue gas desulphurization. The static leaching method was used at room temperature, at a pH value of 1, 4, 7, 10 and 13 for 10 days. H<sub>2</sub>SO<sub>4</sub> and NaOH were added as extraction media and L/S ratio was set to the value of 10. The highest recovery ratio was attained during leaching at a pH value of 1 for fly ash from the third stage of dust collecting system and slurry.*

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

## Introduction

In the year 2011 in Poland 116 million tonnes of industrial wastes were generated, out of which a significant amount was assigned to coal fly ashes (3.8%), fly ashes-slag mixtures from wet combustion waste disposal system (2.1%), mixtures of fly ashes and solid wastes from calcium methods of flue gases desulphurization (1.5%), and finally slag (1.1%) [1]. All of them, due to their considerable potential of economic utilization, are commonly named as coal combustion products (CCPs). The CCPs management in Poland is mostly connected with building materials industry, road construction and filling mine's excavations. Recently the CCPs, especially fly ashes, have been subjected to the series of research in order to evaluate the environmental impact with regard to heavy metals content. For this purpose the two most important methods were used: leaching with one agent [2-7] and sequential extraction using various extraction agents [8-12]. What is more, a comparison of different leaching methods with respect to fly ashes was made [13]. In addition, the research on heavy metals leaching from CCPs was conducted in order to assess the potential of valuable metals recovery [2, 14].

In the existing national papers there are limited number of examinations concerning metal recovery (i.a. [15-17]), but all of them indicate a great potential with regard to rare earth elements included in fly ashes. On the other hand there is no

data including complex investigations of various CCPs types regarding heavy metals and rare earth elements contents with evaluation of their leaching potential under different chemical conditions, which was the primary objective of the present paper.

## Materials and Methods

Coal combustion products were derived from EDF Rybnik Inc Power Plant, which is based on steam boiler OP-650 fed with bituminous coal co-incinerated with 10% biomass. Three types of CCPs were investigated: fly ashes from the electrostatic dust collecting system (from the first (FA<sub>I</sub>), the second (FA<sub>II</sub>) and the third (FA<sub>III</sub>) stage), slag (S) and slurry from wet flue gas desulphurization (S-wFGD). The slag and S-wFGD samples were subjected to initial drying and grinding operations to obtain a powdered material for an analysis and leaching tests, whereas fly ashes were in their primary form.

On the basis of the granulometric analysis results, fly ashes and slag samples were divided into two fractions using 63 µm sieve as a borderline. On the other hand, S-wFGD, because of its different grain-size distribution, was divided according to 250 µm sieve. The aim of the classification was to compare leaching effectiveness of two fractions of the examined materials. Mass fractions and designations of individual fractions were tabulated (Tab. 2).

The leaching experiment was conducted in 50 PP containers, in which distilled water was added to 10.0 g of the examined samples in such an amount as to obtain a constant liquid/solid ratio of 10:1. Afterwards, the samples were set up to five different pH values (1, 4, 7, 10, 13) using specific volumes of 9M H<sub>2</sub>SO<sub>4</sub> or 6M NaOH. The final L/S ratios were in the range of 9.9 to 10.4. The process of extraction was performed at room temperature for 10 days and the samples were subjected to mechanical shaking for 1 hour every day. Liquid phase samples (4 ml) were collected from the extraction system on the first, the fifth and the tenth days for ICP-MS elemental analysis as well as changes of pH values in the solutions were measured. In order to determine the concentrations of elements in the extract, four elements from three groups were chosen: primary elements (Al, Fe, Ti, Mn), trace elements (Zn, Ni, Ga, As) and rare earth elements (Nd, Eu, Tb, Y). Table 1 shows the total concentration of selected elements in the initial material without fractional classification.

Furthermore, the results of element concentrations analysis during the process of extraction were converted into the percentage of recovery ratio for an individual element ‘%R’ (1). Then, the recovery ratios with respect to the whole initial material without grain-size fractional classification for optimal leaching conditions (time, pH value) for particular elements were calculated. Additionally, the

percentage of fraction enrichment ‘%E’ was computed (2), which presents by how many percent the recovery ratio can be increased if only a given fraction is used as a raw material for extraction, in comparison to the whole initial material. The following expressions were used:

$$\%R_i = \frac{10 \cdot c_{E,i} \cdot \%frac}{c_p} \quad (1)$$

$$\%E_i = \left( \frac{c_{E,i}}{c_p} \cdot \frac{1000}{\%R_1 + \%R_2} - 1 \right) \cdot 100, \quad (2)$$

where:  $c_{E,i}$  – an element concentration in the extract, [mg/l];  $c_p$  – an element concentration in the material, [mg/kg]; where  $i=1$  for ‘S N/1’ samples;  $i=2$  for ‘S N/2’ samples;  $1 \leq N \leq 5$ .

## Results and Discussion

pH values measurements during the process of extraction (Tab. 1) indicate that for extreme initial pH values (pH 1 and pH 13), the pH values did not vary significantly during the leaching experiments. An exception was the sample S 3/2, whose pH value was 2.3 after 10 days. The reason for this phenomenon is probably a longer time of equilibrium stabilization at a pH value of 1 at the beginning of the experiment for the finest fraction of all materials. For the starting pH values of 4, 7 and 10, the pH values measured during the leaching tests varied approaching an equilibrium value,

Tab. 1. Concentrations of selected elements in the examined CCPs.

Tab. 1. Stężenia wybranych pierwiastków w badanych produktach spalania węgla

Element	Element conc. in the solid material [µg/g]				
	Slag	FA <sub>I</sub>	FA <sub>II</sub>	FA <sub>III</sub>	S-wFGD
Al	32097	40731	41312	59878	35270
Fe	26656	32282	25898	29663	19450
Ti	265	432	444	556	275
Mn	347	530	419	509	226
Zn	37.4	124.8	229.2	483.3	367.3
Ni	39.0	55.7	81.9	113.4	31.5
Ga	33.2	55.2	76.9	117.9	50.2
As	4.96	22.0	39.8	68.8	33.2
Nd	8.72	15.17	17.68	31.12	21.95
Eu	0.43	0.93	0.97	1.29	0.91
Tb	0.31	0.63	0.67	0.83	0.91
Y	9.28	17.00	20.34	23.70	50.64

which is characteristic of an individual solid material and connected with their reaction.

The highest element concentrations in the extract were obtained for samples at a pH value of 1. For a basic condition most of the determined element concentrations were below the limit of detection (LOD). The exceptions are amphoteric elements i.e. Al, As and Ga, for which only few measured concentrations were below LOD (Fig. 1). Moreover, the maximum recovery for As at a pH value of 13 was as high as 58% (S 3/2).

The maximal recovery ratios for primary and trace elements were achieved on the tenth day and for rare earth elements on the fifth day, due to the fact that on the tenth day of the extraction the measured concentrations for REE were lower than at the beginning. The cause of such a behaviour can be the presence of a slow process associated with the transfer of REE from a solution to precipitate. However, in the slag sample rare earth elements concentrations grow proportionally to leaching time. Fly ash FA<sub>III</sub> (S 3/2), whose non-standard pH values were discussed earlier, exhibited different behaviour as well because of its maximal elements concentrations in the extract, which was on the fifth day for Fe and on the first day for

As, Ti and Ga. Additionally, for slag samples the fifth day was assumed as optimal extraction conditions for Zn, due to a considerable difference between two fractions in the results from the tenth day. The reason for the presence of the recovery ratio value above 100% in some samples is most likely the fact that the examined materials are not ideally homogeneous. Hence, the measured element concentrations related to a small amount of a sample may be insignificantly different from an individual element concentration in the material subjected to leaching. Since the method of element determination using the process of mineralization is destructive for a sample, the same material cannot be analysed and further leached.

In the case of fly ashes and slag, the percentage of fine fractions enrichment was greater than for coarse fractions, therefore the fine fraction was assumed as more efficient as opposed to S-wFGD, the fine fraction of which turned out to be slightly less efficient. However, obtained values of average fraction enrichment for more efficient fraction (for all of the elements) were as low as: 5.8% for slag, 19.6% for FA<sub>I</sub>, 10.0% for FA<sub>II</sub>, 0.7% for FA<sub>III</sub> and 0.9% for S-wFGD.

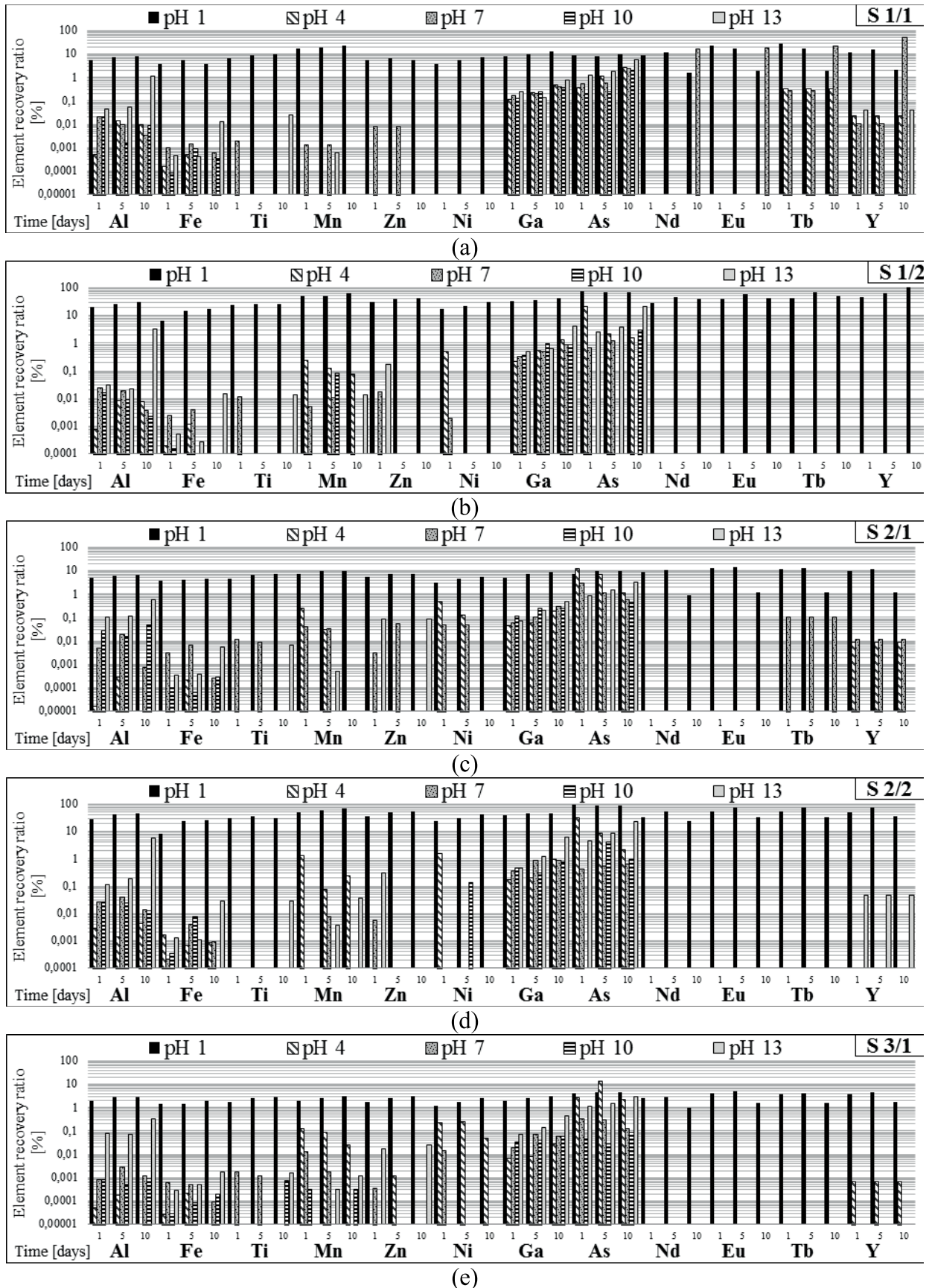
Tab. 2. The summary of designations, types and the share of fractions in the materials and changes of a pH value during the leaching process.

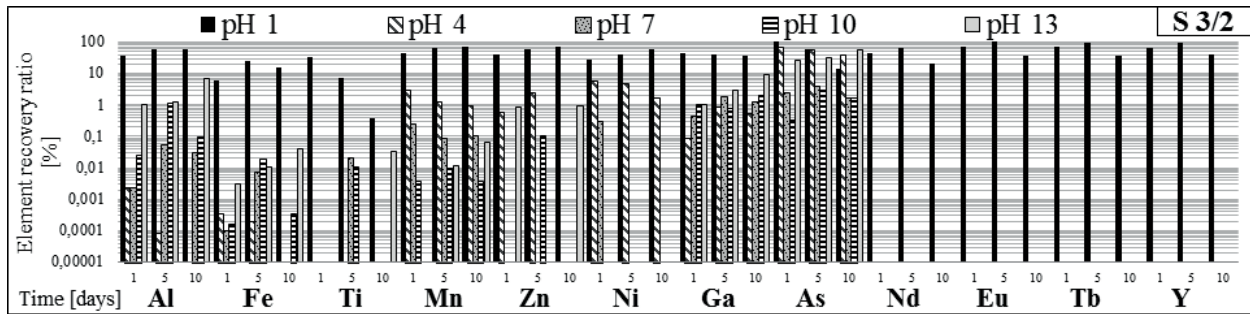
Tab. 2. Sumaryczny opis, typy i udział frakcji w materiale oraz zmiany wartości pH podczas procesu ługowania

Material type		FA <sub>I</sub>		FA <sub>II</sub>		FA <sub>III</sub>		S		S-wFGD	
Sample name		S 1/1	S 1/2	S 2/1	S 2/2	S 3/1	S 3/2	S 4/1	S 4/2	S 5/1	S 5/2
Fractions [μm]		+63	-63	+63	-63	+63	-63	+63	-63	+250	-250
Share of the fractions [%]		33.3	66.7	21.8	78.2	5.1	94.9	47.5	52.5	55.0	45.0
pH	Time										
	0 days	10.0	10.1	6.3	6.4	5.1	5.2	9.5	9.9	6.6	6.7
pH 1	5 days	1.5	1.4	1.2	1.4	1.3	1.9	1.0	1.0	0.9	1.0
	10 days	1.5	1.5	1.3	1.4	1.3	2.3	1.0	1.1	0.9	1.1
pH 4	5 days	11.4	10.0	8.2	9.2	6.7	6.8	8.9	8.7	6.2	5.9
	10 days	11.4	10.3	9.0	9.5	6.9	7.2	9.3	8.8	6.3	6.1
pH 7	5 days	11.5	11.9	9.3	11.6	9.1	9.0	10.6	9.3	6.7	6.8
	10 days	11.5	12.0	9.5	11.5	9.0	9.1	11.0	9.6	6.8	6.8
pH 10	5 days	11.6	12.1	11.1	11.7	9.3	9.7	10.7	10.3	7.7	7.8
	10 days	11.6	12.0	10.9	11.7	9.2	9.5	10.8	9.9	7.6	7.5
pH 13	5 days	12.9	13.0	12.9	12.9	13.1	12.9	13.0	13.0	13.0	13.0
	10 days	13.0	13.2	13.0	13.1	13.0	13.1	13.1	13.1	13.1	13.1

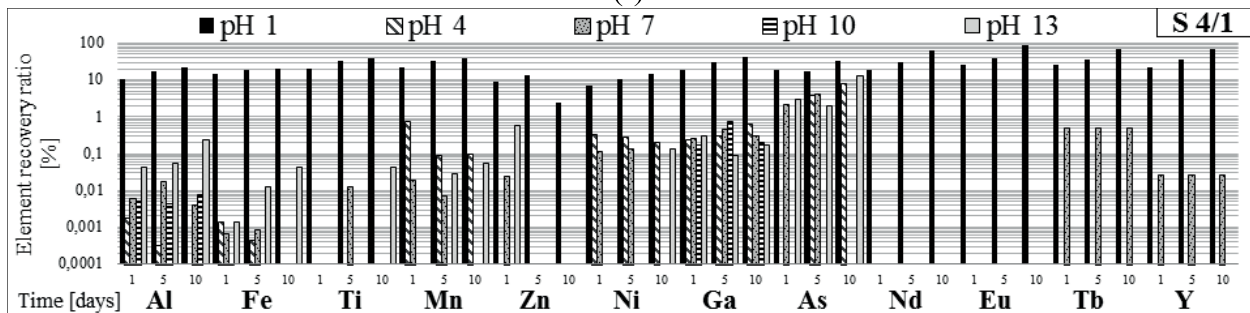
Fig. 1. The recovery ratio of selected elements for all samples:  
a) S 1/1; b) S 1/2; c) S 2/1; d) S 2/2; e) S 3/1; f) S 3/2; g) S 4/1; h) S 4/2; i) S 5/1; j) S 5/2.

Rys. 1. Stosunek odzysku wybranych pierwiastków we wszystkich próbkach:  
a) S 1/1; b) S 1/2; c) S 2/1; d) S 2/2; e) S 3/1; f) S 3/2; g) S 4/1; h) S 4/2; i) S 5/1; j) S 5/2

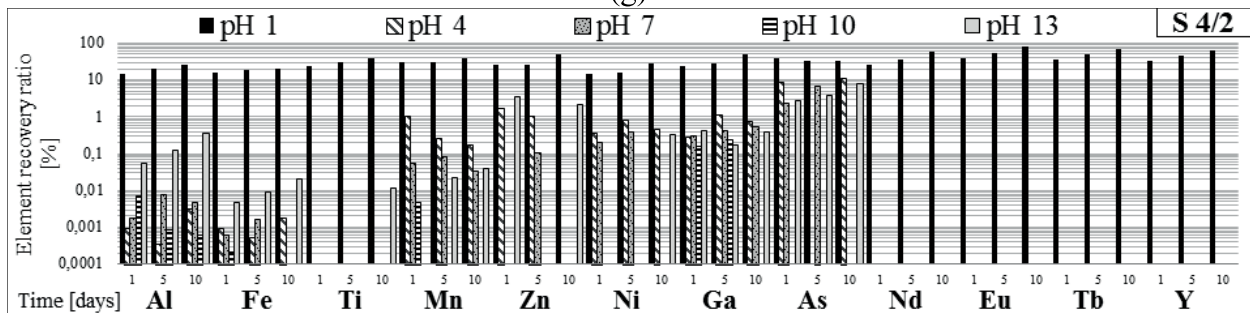




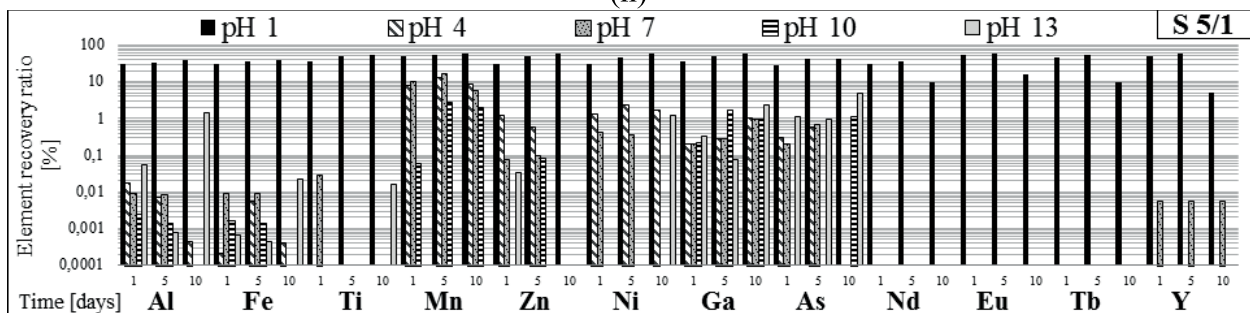
(f)



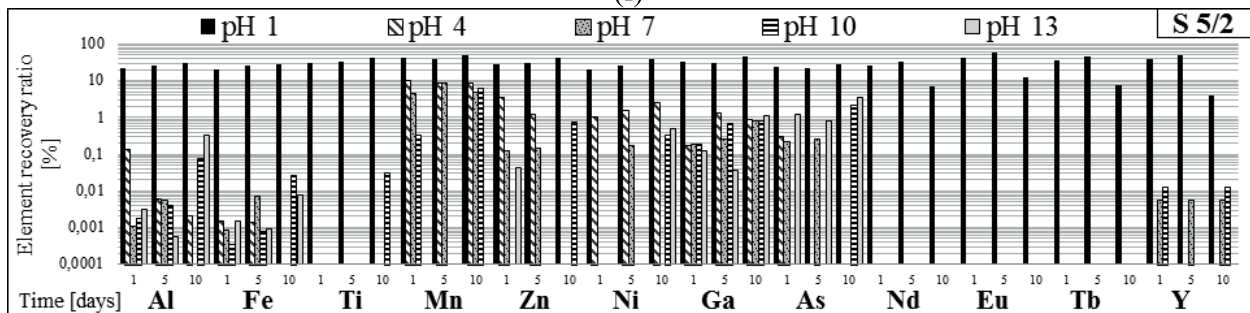
(g)



(h)



(i)



(j)



Tab. 3. Summary of maximum recovery ratio for a given element.

Tab. 3. Sumaryczny stosunek maksymalnego odzysku danego pierwiastka

Element	Maximum recovery ratio for a given fraction			Average maximum recovery ratio for all overall materials	
	Value [%]	Sample name	Time [days]	Value [%]	Samples above an average
Al	60.8	S 3/2	10	53.9	FA <sub>III</sub> , S-wFGD
Fe	37.6	S 5/1	10	37.2	S, S-wFGD
Ti	54.5	S 5/1	10	56.3	S, S-wFGD
Mn	71.4	S 3/2	10	84.8	FA <sub>I</sub> , S-wFGD
Zn	68.1	S 3/2	10	64.2	FA <sub>III</sub> , S-wFGD
Ni	59.5	S 5/1	10	57.1	FA <sub>III</sub> , S-wFGD
Ga	58.1	S 5/1	10	70.1	S, S-wFGD
As	107.3	S 3/2	1	84.3	FA <sub>II</sub> , FA <sub>III</sub>
Nd	65.9	S 4/1	10	64.5	FA <sub>II</sub> , FA <sub>III</sub> , S, S-wFGD
Eu	102.6	S 3/2	5	96.9	FA <sub>III</sub> , S-wFGD
Tb	92.7	S 3/2	5	91.1	FA <sub>III</sub> , S-wFGD
Y	122.0	S 1/2	10	89.1	FA <sub>III</sub> , S-wFGD

The calculated data indicate that the highest recovery ratios for Al, Mn, Zn, As, Eu and Tb were achieved in the fine fly ash FA<sub>III</sub> sample (S 3/2) (Tab. 3). However, Fe, Ti, Ni and Ga exhibited the best recovery ratios for the S-wFGD sample (S 5/1). What is more, the highest Nd yield was obtained for the slag sample (S 4/1), whereas the best efficiency of Y recovery for fly ash FA<sub>I</sub> (S 1/2). At last, recovery ratios for materials as a whole without grain-size classification were calculated and its average value for all the materials. As a results, for majority of elements the most effective materials were S-wFGD and fly ash FA<sub>III</sub>, what is more, for Fe, Ti, Ga and Nd slag was also distinguished.

### Conclusions

The results of the leaching experiment are compatible with those published in literature ([18]), which suggests that the mobility of elements presented in fly ashes is closely related to pH values. The highest recovery ratio for all the examined elements was achieved, when sulphuric acid at a pH value of 1 was used as an extraction agent. Furthermore, insignificant recovery ratios at pH values greater than 1 confirmed that the studied materials do not pose environmental risk connected with the processes of leaching metals into soil and infiltration into deep groundwater, because

obtained element concentrations were below limit of detection. Hence, heavy metals concentrations in mild acidic or basic water solutions do not depend on their initial contents in the solid material, but are only related to a pH value in the solutions. However, As, similarly to Cr, B, Mo, Sb, Se, V or W which are able to form oxygen anions, revealed a substantial recovery ratio. For that reason, environmental evaluation needs to be conducted for those elements in strongly basic conditions. Materials, for which the best recovery yields were achieved, were S-wFGD and fly ash FA<sub>III</sub>. The results shows that gain obtained due to the grain-size classification is relatively unimportant, the highest being for fly ash FA<sub>I</sub>. Therefore, an economic purpose of grain-size classification needs to be taken into consideration. In general, examined CCPs despite of possessing not significant amounts of valuable metals and rare earth elements, exhibited considerable values of its recovery ratios when acidic conditions were present. Thus, developed leaching method, which is typical of simplicity and requires usage of small quantities of leaching agent, can be successfully introduced to more abundant in precious element materials.

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*Potencjał odzysku metalu z produktów spalania węgla. Część II. Ługowanie wybranych pierwiastków*

Artykuł przedstawia wyniki produktów spalania węgla: popiołów lotnych z trzech etapów systemu gromadzenia pyłu (FA<sub>p</sub>, FA<sub>IP</sub>, FA<sub>III</sub>), żużlu oraz zawiesiny powstałej z odsiarczania mokrych spalin. Ługowanie statyczne zostało przeprowadzone w temperaturze pokojowej przez okres 10 dni, z wartościami pH wynoszącymi 1, 4, 7, 10 oraz 13. Dodano H<sub>2</sub>SO<sub>4</sub> i NaOH jako środek ługujący, stosunek L/S został ustawiony do wartości 10. Najwyższy poziom odzysku został uzyskany przy ługowaniu z pH o wartości 1 popiołu lotnego z trzeciego etapu systemu gromadzenia pyłu i zawiesiny.

Słowa kluczowe: produkty spalania węgla, kwasowe i zwykłe ługowanie, metale ziem rzadkich, metale ciężkie, popiół lotny, żużel, zawiesina powstała z odsiarczania mokrych spalin

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