

## EVALUATING THE POSSIBILITIES OF OBTAINING INITIAL CONCENTRATES OF RARE EARTH ELEMENTS (REEs) FROM FLY ASHES

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The article presents the results of initial laboratory research into the possibilities of obtaining REE from fly ash from one of Polish powerhouses. In the work the authors have presented the results of investigations into the obtaining of initial REEs concentrations from fly ashes by physicochemical and hydrometallurgical methods. These investigations provide a basis for developing a technology of RRE recovery from fly ashes produced in the process of hard coals combustion.

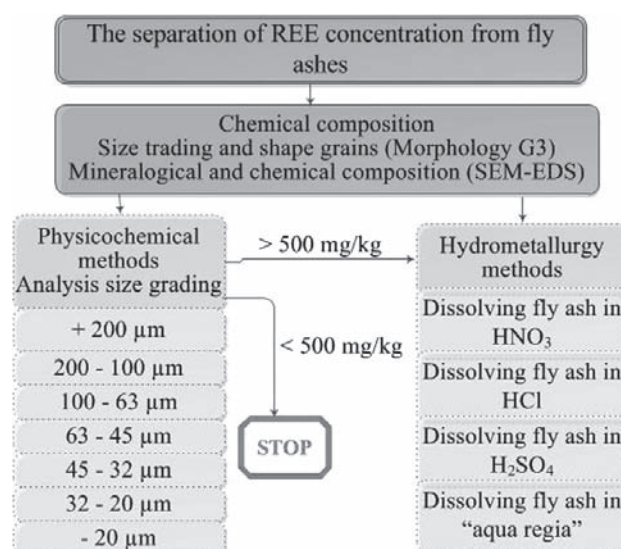
*Key words:* rare earth elements, fly ashes, physicochemical methods, hydrometallurgy, recovery

### INTRODUCTION

Rare earth elements (REEs) are a group of 17 elements, including 15 lanthanides as well as scandium and yttrium. REEs are fairly common in nature. Their estimated concentration in the crust ranges from 150 to 220 mg/kg [1]. REEs are materials of strategic importance for economic development. Due to their low concentration, the process of obtaining rare earth elements concentrates is complex; it depends on the ore chemical composition and involves a number of combined processing methods, which has a negative impact on the environment: flotation, hydrochloric acid leaching, gravity methods using jigs, spirals, conical concentrators and concentrating tables, magnetic and electrostatic separation methods are also applied as well as dissolving in hot solutions of acids and extractions by means of concentrated NaOH [2]. Ashes from the process of hard coal combustion contain a considerable amount of precious metals. Investigations into fly ashes from hard coal combustion processes aimed at determining their content of lanthanides were conducted by Smółka-Danielowska [3] and Całus Moszko, Białecka [4]. The average clarke for hard coal combustion ashes is 388,3 mg/kg [5]. In all the examined waste from the hard coal combustion process the content of cerium (39 - 186 mg/kg, clarke=140 mg/kg) and lanthanum (16 - 86 mg/kg, clarke=76 mg/kg) was high. The previously developed methods of separating elements from fly ashes involve the extraction of ashes with acids characterized by low pH at appropriately selected temperatures and leaching times [6]. The article presents the results of laboratory research on the possibilities of obtaining REEs from fly ashes.

### EXPERIMENTAL WORK

The aim of the conducted investigations was to evaluate the possibility of applying physico-chemical (processing) as well as hydrometallurgical (digestion with acids) methods to obtain initial concentrates of rare earth elements from fly ashes produced in the process of hard coal combustion. Fig. 1 presents a diagram of the conducted experimental research. The separation of grain classes have been applied as physic-chemical method. The hydrometallurgical methods involved digesting the ash with nitric acid, aqua regia and hydrofluoric acid. The research material was a sample of fly ash from hard coal combustion in a pulverized-fuel boiler in one of Polish coal-fired powerhouses. The fly ash samples were subjected to grain composition analysis (granulometric) by means of an optical analyser,



**Figure 1** Diagram of research into obtaining REE concentrates from fly ashes

morphological analysis using SEM-EDS and chemical composition analysis. The contents of main elements as well as the contents of rare earth elements were defined by wavelength dispersive X-ray fluorescence spectrometry. Calibration was performed on the basis of reference materials.

The chemical composition (main elements) and results of rare earth elements' contents of the original sample of fly ash has been presented in Table 1 and Table 2 respectively.

Table 1 The amount of main elements in terms of oxides in the initial ash sample / wt. %

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O
51,58	25,82	8,72	2,10	4,50	1,49
K <sub>2</sub> O	SO <sub>3</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	
2,87	0,72	1,17	0,27	2,87	

Table 2 The content of rare earth elements in the initial sample of fly ash

Metals	/ mg/kg	Metals	/ mg/kg
Scandium	30,4	Gadolinium	5,4
Yttrium	34,0	Terbium	1,5
Lanthanum	50,7	Dysprosium	8,2
Cerium	130,3	Holmium	0,4
Praseodymium	13,5	Erbium	3,2
Neodymium	45,7	Thulium	0,5
Samarium	7,4	Ytterbium	2,7
Europium	1,2	Lutetium	0,4
Σ LREE	254,2		
Σ HREE	50,9		
Σ REE	335,5		

Light rare earth elements LREE (mainly: Ce, La, Nd, Pr) have the highest contents – 76 %. Grain composition was determined using an analyser of the size, shape and number of particles – Morphologi G3S-ID (Table 3).

Table 3 Systematic parameters of the initial ash sample grain size analysis

Parameter [mg/kg]	Fly ash	
CE Diameter d / μm	d <sup>10</sup>	0,22
	d <sup>50</sup>	0,29
	d <sup>90</sup>	4,26
CE Diameter Mean / μm	1,55	
CE Diameter Max / μm	201	

Explanations: d<sup>10</sup>, d<sup>50</sup>, d<sup>90</sup> - characteristic grain diameters below which: 10 %, 50 %, 90 % of the analysed material is found respectively

In the ash sample it is silicon, aluminium and oxygen that dominate. Iron, calcium, sodium and potassium are found in much smaller amounts. The initial ash contained slight amounts of: magnesium, sodium, titanium, sulphur and phosphorus. The conducted SEM investigations indicate that the main component of the initial ash sample is aluminosilicate glaze.

## RESULTS

### Application of physicochemical methods for obtaining initial REE concentrates from ashes

To determine the technological characteristics of ash in terms of REE contents, 7 grain classes were separated. Grain classes were separated by the method of wet sieve analysis, using sieves with the following meshes: 200, 100, 63, 45, 32, 20 μm, in accordance with the standard: PN-ISO1953:1999 Hard coal – Grain analysis by sieving. In the separated grain classes the contents of REEs were determined and enrichment factor was calculated according to the formula (1). The results of determinations and calculations have been presented in Table 4. The enrichment factor *EF* of the concentrates obtained from ashes was calculated according to the following formula:

$$EF = \frac{A_k}{A_p}, \quad (1)$$

$A_k$  – ΣREE content in the concentrate / mg/kg,  
 $A_p$  – ΣREE clarke value 388,3 mg/kg [5].

Table 4 Contents of REEs in fly ash grain classes

Sample	J1	J2	J3	J4	J5	J6	J7
Size grade / μm	+ 200	200 -100	100 -63	63 -45	45 -32	32 -20	- 20
Yield / %	1,98	13,20	11,93	7,00	6,64	8,32	50,93
REE	c / mg/kg						
Sc	24,9	17,0	29,4	26,3	33,5	33,1	33,6
Y	29,4	29,4	31,4	35,1	38,0	40,5	37,1
La	59,3	55,9	56,0	50,8	48,8	71,5	61,9
Ce	133,5	135,1	131,2	146,4	163,4	154,8	140,6
Pr	10,2	9,9	9,9	13,9	11,4	12,2	14,2
Nd	44,3	43,2	38,4	42,2	38,8	48,2	49,4
Sm	6,6	7,4	6,4	6,9	8,9	6,3	8,0
Eu	1,7	1,4	1,2	1,2	0,8	1,4	0,9
Gd	5,5	6,0	5,4	7,1	7,4	8,0	6,4
Tb	1,1	1,1	1,2	1,4	1,3	1,5	1,3
Dy	8,7	7,3	8,5	9,1	9,1	10,0	8,4
Ho	1,1	1,3	1,1	2,9	1,5	1,1	1,1
Er	4,6	4,5	4,3	4,1	4,0	3,6	3,2
Tm	0,6	0,3	0,4	0,4	0,5	0,4	0,4
Yb	3,4	3,7	3,4	2,7	2,7	2,7	2,3
Lu	0,8	0,9	0,6	0,6	0,6	0,5	0,3
ΣREE [ppm]	335,7	324,4	328,8	351,1	370,7	395,8	369,1
EF	0,86	0,84	0,85	0,90	0,95	1,02	0,95

The share of the finest grain class reaches 50,9 % and the share of grains bigger than 200 μm does not exceed 2 %. The total content of REEs in the whole initial sample is 335,5 mg/kg and in particular grain classes ranges from 329 to 396 mg/kg. The calculated value of enrichment factor oscillates slightly within the range of 0,86 - 1,02, the total contents of REEs in grain class-

es below 45  $\mu\text{m}$  being slightly higher than in grain classes above 45  $\mu\text{m}$ .

The enrichment factors obtained by separating the grain classes did not allow obtaining a raw material with the assumed content of  $\Sigma\text{REEs}$  500 - 2 000 mg/kg, corresponding to the poorest natural resources of rare earth elements – apatite deposits from Chibin peninsula [7]. Therefore, there are no technological bases for applying mechanical processing methods as an initial stage of REEs separation from ashes. It is suggested that further investigations into the application of physico-chemical methods should be conducted as a subsequent stage after the initial separation of REEs by other methods.

### Application of hydrometallurgical methods for obtaining initial concentrates of REEs from ashes

A reduced sample of fly ash was ground and sieved < 200  $\mu\text{m}$ . Next the sample was subjected to digestion:

- in 10 % and 30 % nitric acid (V). The ash/acid mass ratio was 1:5.
- in „aqua regia” (a mixture of concentrated hydrochloric acid and nitric acid (V)). The ash to acid ratio was 1:2.
- in 40 % hydrofluoric acid. The ash to acid mass ratio was 1:5.
- in „aqua regia” in the ash to acid ratio of 1:2; next the sediment was treated with 40 % HF until gaseous products of the reaction mixture stopped releasing. The ash-to-acid mass ratio was 1:3.

Table 5 Contents of rare earth elements after digestion in acid/ mg/kg

	10N	30N	CN31	F5	CNF
REE	c / mg/kg				
Sc	16,4	16,6	17,1	66,4	70,9
Y	27,0	27,7	30,5	99,3	120,8
La	45,8	52,4	54,1	122,1	174,8
Ce	130,5	116,0	153,0	230,9	344,7
Pr	10,1	9,4	12,4	23,2	39,0
Nd	43,1	31,7	39,5	100,9	135,1
Sm	4,9	10,5	7,8	10,8	13,9
Eu	1,0	1,4	1,2	1,5	1,7
Gd	4,2	3,5	3,2	10,9	13,8
Tb	1,2	1,1	1,2	0,8	0,9
Dy	7,6	6,3	6,4	2,8	2,3
Ho	1,3	1,2	0,9	3,4	3,5
Er	3,4	17,5	5,1	3,2	6,8
Tm	0,5	0,4	0,5	1,0	1,2
Yb	3,1	3,5	3,1	2,0	2,4
Lu	0,4	5,3	1,1	0,5	1,8
$\Sigma\text{REE}$	300,5	304,5	337,1	679,7	933,6
<i>EF</i>	0,77	0,78	0,86	1,75	2,40

Explanations: 10 % nitric acid (10N), 30 % nitric acid (30N), aqua regia (CN31), hydrofluoric acid (F5), in aqua regia and next in hydrofluoric acid (CNF)

The contents of rare earth elements in the obtained sediments and the values of recovery effectiveness calculated from the formula presented in Table 5.

As a result of the conducted extractions of the initial fly ash sample aimed at obtaining an initial concentrate of rare earth elements, it was found that:

- REEs content in the sediment obtained after the initial ash digestion in nitric acid dropped by approximately 10 % - some of the rare earth elements migrated to the solution. The content of most REEs in the obtained sediment was lower than in the initial sample – the biggest loss was observed in the case of scandium, for the sample digested in both 10 % and 30 % nitric acid,
- the use of concentrated acids (aqua regia) for digestion does not improve the effectiveness of obtaining the concentrates,
- removal of silica matrix by means of concentrated HF allowed obtaining a high enrichment factor *EF* (2,40), and the concentration of rare earth elements in the mineral sediment was nearly three times higher in relation to their content in the initial ash sample.

### CONCLUSIONS

Application of physicochemical methods for obtaining initial concentrates of rare earth elements from fly ashes produced as a result of hard coal combustion does not allow obtaining products with a total content of rare earth elements corresponding to their content in the poorest natural resources of these metals (min. 500 mg/kg). The differentiation of rare earth elements' contents versus grain size is probably too small to provide a basis for their use in the processes of REEs concentration from ashes. Physicochemical methods can be used in further works on the recovery of REEs from ashes as a subsequent stage after initial digestion of ashes with acids.

Based on investigations conducted for the initial ash sample by the hydrometallurgical method, it was found that rare earth elements, except Tb, Dy and Yb, occur mainly in minerals which is sparingly soluble even in concentrated inorganic acids. Application of 10 % and 30 % nitric acid caused the leaching of approximately 10 % of metals in relation to the initial sample. Application of aqua regia did not influence the total content of rare earth elements in the ash sample. Application of aqua regia and hydrofluoric acid enabled obtaining an ash-based concentrate with a total content of rare earth elements corresponding to the content found in the poorest ores of these metals. It is therefore possible to use hydrometallurgical methods for obtaining initial concentrates of rare earth elements.

The dominant metals in the obtained concentrate include light rare earth elements, i.e. La, Ce, Pr, Nd, which are most commonly used in technologies related to electronics, renewable energy generation and defence industry.

The results of the above research are a basis for developing a technology of rare earth elements' recovery from ashes as a potential source of critical elements.

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