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ENRICHMENT OF RARE EARTH ELEMENTS FROM CONTAMINATED BIOMASS PRIOR TO EXTRACTION

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ABSTRACT

Under the context of reserve depletion, recovering rare earth elements (REEs) from secondary resources is essential which assists to strengthen the circular economy. Contaminated biomass growing from brownfield lands is a potential material for REE recovery. However, prior to the extraction stage, polluted plants need to be lessened to a manageable volume. In this study, contaminated biomass gathered from an abandoned mining area was combusted in a pilot-scale boiler, while solid residuals from different positions in the burning system were collected and analyzed. Higher REE concentration in the ash samples compared to that in the woody biomass indicates the efficiency of the combustion process from the metal enrichment point of view. The significant metal concentration in the solid remains is an advantage for the following step of extraction to reclaim REEs. It was concluded that the concentration of REEs in bottom ash is greater than in the other solid residuals. That indicates that the volatility of rare earth minerals is limited during biomass incineration.

Keywords: rare earth metals, contaminated biomass, combustion, recovery

1. INTRODUCTION

Rare earth elements (REEs) are a group of 17 chemically similar metallic elements comprising Y (yttrium), Sc (scandium), and 15 "lanthanides" elements [1]. The term “rare” refers to they are not commonly found in commercially viable concentrations. REEs are vital in green modern technologies such as wind turbines, batteries, electric cars, hybrid cars, etc [2]. These valuable elements are deemed as critical strategic materials due to their importance and vulnerable supply [3], [4]. The demand for rare earths has surged noticeably which could lead to reserve depletion. While recycling rate of REEs from end-products reportedly is only 1% [2]. Therefore, reclaiming rare earth minerals from secondary resources is essential to strengthening the circular economy.

Phytomining is an innovative approach for recovering REEs in brownfield lands where conventional mining techniques are neither effective nor profitable [5]. In the initial stage of the entire phytomining pathway, plants accumulate REEs from soils and store them into their roots and shoots referred to as the phytoextraction process [6]. Following that, rare earth minerals accumulated in plants could be reclaimed via extraction technologies [7]–[9]. However, before the extraction process, contaminated biomass needs to be reduced, and REEs would be enriched in solid residuals called bio-ores [10]. Several enrichment manners including composting, compaction, thermal conversion (ashing, pyrolysis, gasification, combustion) have been mentioned [11], [12]. To date, only a few studies about heightening REEs from biomass have been conducted so far. C. Liu et al. incinerated *Dicranopteris linearis* fern at 500 °C to remove organic matter and elevate rare earths in ash [13]. It was observed that 2032 mg kg^{-1} REEs in the plant was enhanced to 15956 mg kg^{-1} in the solid remain; and 93% of rare earth metal input from the biomass was converted into the ash sample. Likewise, incineration of the collected fern *Dicranopteris linearis* at 550 °C resulted in 92.3% mass reduction [10]. The concentration of REEs in the ash (30000 mg kg^{-1}) is over eleven times greater than in the plant (2700 mg kg^{-1}). In another study, an ecologically friendly pathway of vacuum-pyrolysis-condensation was proposed for elevating rare earth minerals [14]. The results unveiled that the pyrolytic product derived from harvested fern *Dicranopteris linearis* contenting 1948.67 mg kg^{-1} rare earths could reach a level of 6160 mg kg^{-1} REEs.

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Enrichment is a crucial stage in the whole concept of phytomining to recover rare earth metals. The available information pertained to that is scanty and sparse. This research investigates the heightening of REEs from contaminated biomass via the combustion process and the behavior of these metals in the burning system.

2. MATERIALS AND METHODS

The resource of biomass utilized in this research is a brownfield land located in Gyöngyösoroszi, Hungary. In fact, it is an abandoned mining area where industrial lead and zinc production was operating until 1986. The common ligneous plant species living there are oak, pine, wattle, walnut, birch, poplar, bushes, etc. From the contaminated land, bulk biomass collection was done including the necessary sample preparation steps such as drying, grinding, and pelletizing to the required dimensions for the boiler operation. The polluted woody pellet is a mixture of 75:16:9 % of trunk, branches, leaf respectively, corresponding to the mass ratio of a real tree. The general properties of the contaminated biomass are given in Table 1.

Table 1. Properties of the contaminated biomass

Pellet's diameter mm	Pellet's height mm	Element (m/m %)				Moisture content m/m %	Ash content m/m %
		N	C	H	S		
6	10–30	0.395	46.747	6.050	0.0143	5.62	2.30

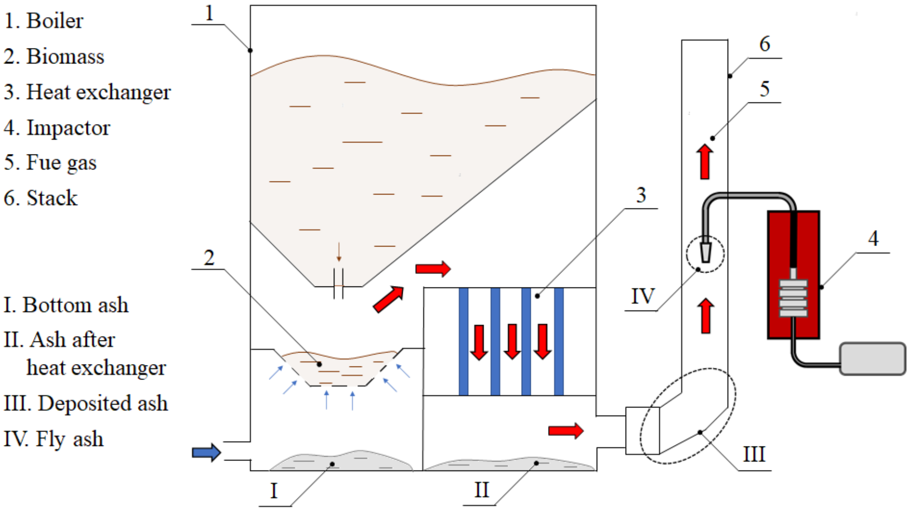

Figure 1. Positions of solid remain collection

To achieve the major purposes of the study, a series of four combustion experiments utilizing contaminated pellets was conducted in a pilot-scale boiler. The experiments were carried out under the same operational circumstances as follows firing rate: Q = 27.6–31.4 kW, fuel feed rate: f = 8.3 kg h^{-1}, typical combustion chamber temperature: T = 882–956 °C. Solid combustion residuals were captured from preselected points as seen in Figure 1. After experiments, bottom ash and after heat exchanger ash were respectively collected from the ashtray and at the position after the heat exchanger. The deposited ash sample was taken from the inside wall of the stack at the end of the combustion process. The capture of fly ash was implemented by an isokinetic fly ash sampling system using a three-stage cascades impactor labeled Dekati® PM10. The collection started after the boiler reached steady-state operational conditions, and the sampling method meets the regulations of the ISO23210 standard. The typical flue gas temperature at the point of fly ash sampling is in the range of 155-158 °C.

The woody biomass (WB) sample used for all the incineration experiments together with combustion ashes are taken for chemical analysis. The combustion ashes include four types of solid remains namely bottom ash (BA), after heat exchanger ash (EA), deposited ash (DA), and fly ash (FA) collected from four combustion experiments. The chemical analysis of the solid samples determined by ICP (Inductively Coupled Plasma) spectrometry was performed by an individual company in Hungary. Perkin Elmer Avio 200 inductively coupled plasma-optical emission spectrometer (ICP-OES) and ICP mass spectrometry (ICP-MS) are employed for the analysis. For the calibration of the measurement, an ICP-OES inner standard solution (Lutecium) was used. The samples were prepared based on the Hungarian standard MSZ EN 13346:2000. The analytical scale was used for taking 5 g samples for analysis. The preparation was carried out by microwave digestion with a Berghof Speedwave4 laboratory equipment, using nitric acid (2 ml, 67% concentrated) and hydrochloric acid (6 ml, 36% concentrated) solvents. The digestion and dissolution time were 30 minutes at 180 °C. The solution was filled up to 50 ml with 5% concentrated nitric acid after the filtration process using MN616 filters. The chemical measurement analyzes the concentrations of most REEs (15 elements namely Ce, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sc, Sm, Tb, Tm, Y, Yb) in the solid samples.

3. RESULTS AND DISCUSSION

The analytical outcomes of the solid samples are divided into two metal groups. The first classification consists of Er (erbium), Eu (europium), Ho (holmium), Pr (praseodymium), Tb (terbium), Tm (thulium), Yb (ytterbium) which are below the detection limit (BDL) in all the solid samples. No further investigation nor discussion was made for these elements.

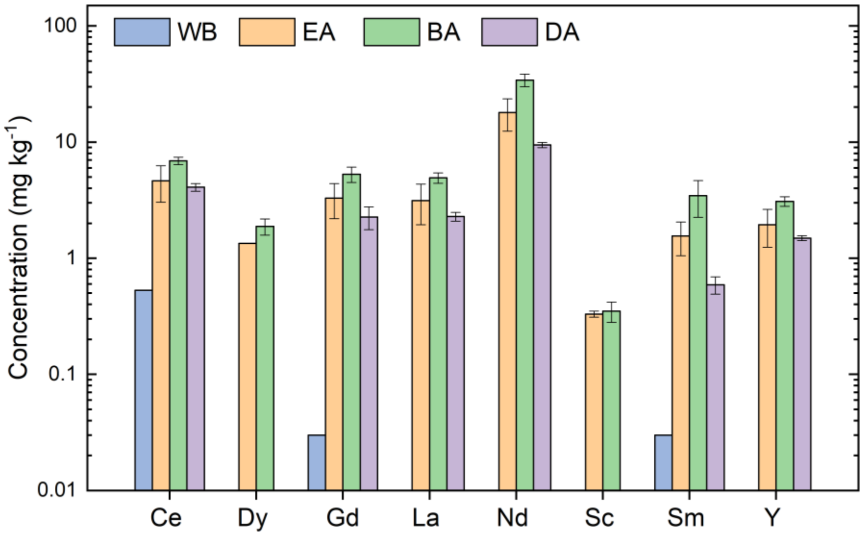

Figure 2. Average concentration of detectable REEs

The second metal group comprises Ce (cerium), Dy (dysprosium), Gd (gadolinium), La (lanthanum), Nd (neodymium), Sc (scandium), Sm (samarium), Y (yttrium) which are detectable in at least one sample. These elements depicted in Table 2 are used for further investigations and calculations. The concentration magnitudes were colorized in the increasing order of green-yellow-red. Intuitively, the elemental concentration results of different experiments in the combustion series largely perform the similarity. In

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order to deeply assess the reproducibility as well as for further discussion and evaluation, the mean value of the outcomes alongside its standard deviation are calculated and presented in Table 2. Based on the graph, the level of standard deviation is not so high versus its average concentration. It demonstrates that the combustion experiments and their upshots are reproducible.

Several REEs were identified in the solid samples at considerable levels. The most significant results were observed in the case of Nd, such as 34.2 mg kg^{-1} in bottom ash, 18 mg kg^{-1} in after heat exchanger ash, and 9.43 mg kg^{-1} in deposited ash. On the other hand, Sc was scarcely found in the solid remains. The concentration of REEs in fly ash is either below the detection limit or not available. REEs show a consistent trend in the burning system, their levels follow the decreasing order: bottom ash > after heat exchanger ash > deposited ash > woody biomass (Figure 2). The greater concentration in bottom ash versus other ash samples unveils the low volatility of rare earth metal compounds during incineration.

Table 2. Concentration of detectable REEs (mg kg^{-1})

Sample		Element							
		Ce	Dy	Gd	La	Nd	Sc	Sm	Y
Biomass	WB	0.526	<1*	0.026	<0.25*	<0.5*	<0.01*	0.026	<0.25*
Fly ash	FA-1	-	<7.5*	<3*	-	-	-	<3*	-
	FA-2	-	<7.5*	<0.2*	-	-	-	<0.2*	-
	FA-3	-	<10*	<4*	-	-	-	<4*	-
	FA-4	-	<7.5*	<0.2*	-	-	-	<0.2*	-
After heat exchanger ash	EA-1	6.29	<1*	4.03	4.04	18.8	0.344	1.64	2.39
	EA-2	5.71	1.34	4.35	4.16	23.9	0.309	2.18	2.64
	EA-3	3.77	<1*	2.91	2.53	19	<0.25*	1.22	1.60
	EA-4	2.80	<1*	1.87	1.81	10.4	<0.01*	1.15	1.11
Bottom ash	BA-1	6.59	1.50	6.26	4.72	37	0.290	3.49	2.93
	BA-2	7.22	2.16	5.30	5.25	35.8	0.416	5.04	3.35
	BA-3	6.35	1.66	4.30	4.25	27.9	0.304	2.30	2.79
	BA-4	7.44	2.18	5.27	5.47	36.2	0.402	2.97	3.30
Deposited ash	DA-1	4.21	<2*	<10*	2.61	8.73	<0.5*	<5*	1.57
	DA-2	3.81	<2*	2.43	2.20	9.30	<0.01*	0.667	1.45
	DA-3	4.37	<4*	2.62	2.06	9.94	<1*	<2*	1.51
	DA-4	3.91	<2*	1.73	2.26	9.73	<0.01*	0.51	1.41

* The concentration of the metal is BDL (below the detection limit), which is the limit that the concentration can be differentiated from the background noise.
"-" not available

Enrichment factor (EF) is defined as the quotient of metal concentration in solid remains to that in woody biomass. This index is employed to describe the efficiency of the enrichment process in heightening metal levels. Certain elements encompassing Dy, La, Nd, Sc, Y were below the detection limits in the woody biomass. Nonetheless, as a result of the combustion process, their concentrations became high enough to be identified in at least one ash sample. Their enrichment factors were calculated based on the detection limits, which are the minimum values or the worst-case scenario. The minimum enrichment factor of these elements highlighted in red is depicted in Figure 3. In terms of detectable metals in plants including Ce, Gd, Sm, the real values of the enrichment factors are calculated and visualized into the graph (Figure 3). Generally, the enrichment factors vary in a wide range from more than one to over 200. The outstanding results were observed in the case of Gd (EF-BA = 203, EF-EA = 127) and Sm (EF-BA = 133, EF-EA = 60). In similarity to metal concentration, EF of REEs performs the same trend as follows: bottom ash > after heat exchanger ash > deposited ash. The enrichment factor is significant indicating the effectiveness of the combustion process in elevating metal concentrations from biomass into ashes. That is an advantage for the further stage of extraction to reclaim REEs from solid residues.

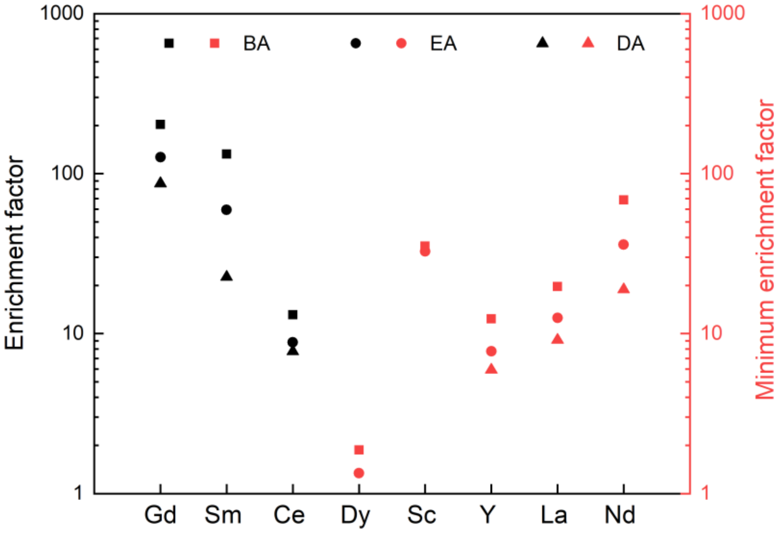

Figure 3. Enrichment factor

4. CONCLUSIONS

A series of combustion experiments utilizing contaminated pellets was conducted aiming to investigate the enrichment of REEs from biomass. Solid samples including woody biomass and solid residues were collected and dissected. The chemical analysis results are reproducible, which are the base of the following statements. The enrichment factor is significant indicating the efficiency of the combustion process in elevating metal concentrations from biomass into solid remains. High levels of REEs in the ash samples have benefits for the further step of extraction to reclaim these valuable elements. The greater concentration in bottom ash versus other ash samples indicates that the volatility of REEs is limited during biomass incineration. In the following study, major parameters having impacts on the distributions of REEs such as combustion temperature or flue gas temperature would be researched. Based on the results, further directions will be defined.

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