ENRICHMENT OF NOBLE METALS AND RARE EARTH ELEMENTS FROM CONTAMINATED BIOMASS BEFORE EXTRACTION

[1]HELGA KOVACS, [2]TRUONG PHI DINH, [3]ZSOLT DOBÓ

Institute of Energy and Quality, University of Miskolc, 3515 Miskolc, Hungary
E-mail: [1]helga.kovacs@uni-miskolc.hu

Abstract - In this era of industrialization and metal reserve depletion, recovering noble metals (NMs) and 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 metal recovery. However, before the extraction process, the bulky contaminated biomass needs to be lessened to a manageable volume and amount. This study investigates the combustion process of biomass containing NMs, REEs, and the behavior of these metals in the burning system. 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 concentrations of NMs and REEs in the ash samples compared to that in the woody biomass indicate the efficiency of the combustion process from the metal enrichment perspective. The significant metal concentration in the ashes is an advantage for the following step of extraction to reclaim NMs and REEs. The results also show the low volatility of REEs, while NMs are highly volatilized during biomass incineration.

Keywords - Polluted Biomass, Biomass Combustion, Precious Metals, Rare Earth Metals

I. INTRODUCTION

Noble metals (NMs) comprise silver (Ag), gold (Au), and platinum sub-group metals including iridium (Ir), osmium (Os), palladium (Pd), platinum (Pt), rhodium (Rh), and ruthenium (Ru). Rare earth elements (REEs) are a group of 17 chemically similar metallic elements encompassing yttrium (Y), scandium (Sc), and 15 "lanthanides" elements [1]. NMs and REEs generally refer to mineral resources that are widely scattered, rare, and difficult to extract, in the natural environment [2]. These elements have a variety of applications in areas such as machinery, metallurgy, catalysts, and modern high-technology industries [3] due to their excellent physical and chemical properties [4]. NMs and REEs are considered critical strategic resources [5], [6] according to supply risk, economic importance, and cruciality to the progress of science and technology [7]. The demand for these valuable metals has been dramatically increased, while their natural ores are limited and unevenly distributed. Therefore, recovery NMs and REEs from urban mines such as tailings, waste catalysts, electronic wastes, slag, ashes, etc is crucial, it assists to secure resources for sustainable development.

Phytomining is an innovative approach for recovering NMs, and REEs in brownfield lands where conventional mining techniques are neither effective nor profitable[8]. In the initial stage of the entire phytomining pathway, plants accumulate NMs, and REEs from soils and store them in their roots and shoots referred to as the phytoextraction process[9]. Following that, NMs and REEs accumulated in plants could be reclaimed via extraction technologies[10]. However, before the extraction process, contaminated biomass needs to be reduced, and NMs, REEs would be enriched in solid residuals called bio-ores. Several enrichment manners including composting, compaction, and thermal conversion (ashing, pyrolysis, gasification, combustion) have been mentioned [11], [12].The enrichment process is a vital stage in the overall concept of phytomining to recover NMs and REEs. The available information about that is sparse and scanty.To date, only a few studies about heightening NMs, and REEs from biomass have been conducted so far[13]–[15].This research investigates the combustion process of biomass containing NMs, REEs,and the behavior of these elements in the burning system.

II. 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, and leaf respectively, corresponding to the mass ratio of a real tree. The general properties of the contaminated biomass are given in Table 1.

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

Table 1. Properties of the contaminated biomass

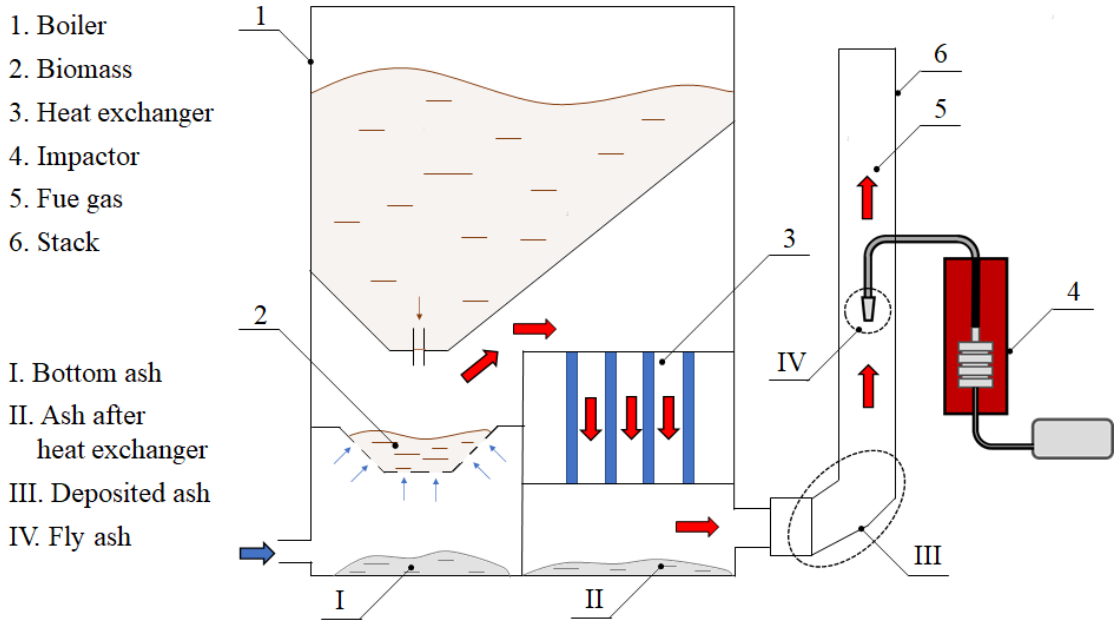


Figure 1. Positions of solid remain collection

To achieve the major purposes of the study, contaminated pellets werecombusted in a pilot-scale boiler. The experiment was carried out under the operational circumstances as follows firing rate: Q = 27.6 kW, fuel feed rate: f = 8.3 kg h^{-1}, typical combustion chamber temperature: T = 882 °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 around 155 °C.

The woody biomass (WB) sample together with combustion ashes including bottom ash (BA), after heat exchanger ash (EA), deposited ash (DA), and fly ash (FA) were taken for chemical analysis. The 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 NMs (Ag, Au, Ir, Os, Pd, Pt, Rh, Ru) and REEs(Ce, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sc, Sm, Tb, Tm, Y, Yb) in the solid samples.

III. RESULTS AND DISCUSSIONS

The analytical outcomes of the solid samples are divided into two metal groups. The first classification includesa couple of NMs (Ir, Os, Pd, Pt, Ru) and several REEs (Er, Eu, Ho, Pr, Tb, Tm, Yb)which are below the detection limit (BDL) in all the solid samples.No further investigation nor discussion was made for these elements.The second metal group comprisessome NMs (Ag, Au, Rh) and REEs (Ce, Dy, Gd, La, Nd, Sc, Sm, Y)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.

Element	Name	Concentration (mg/kg)				
		WB	BA	EA	DA	FA
Noble metals						
Ag	Silver	<0.5*	0.795	3.59	13.2	14.5
Au	Gold	<0.05*	<0.05*	1.15	2.94	1.98
Rh	Rhodium	<0.01*	<0.01*	<0.01*	<0.01*	0.207
Rare earth elements						
Ce	Cerium	0.526	7.44	2.80	3.91	-
Dy	Dysprosium	<1*	2.18	<1*	<2*	<7.5*
Gd	Gadolinium	0.026	5.27	1.87	1.73	<0.2*
La	Lanthanum	<0.25*	5.47	1.81	2.26	-
Nd	Neodymium	<0.5*	36.2	10.4	9.73	-
Sc	Scandium	<0.01*	0.402	<0.01*	<0.01*	-
Sm	Samarium	0.026	2.97	1.15	0.51	<0.2*
Y	Yttrium	<0.25*	3.30	1.11	1.41	-

Table 2. The concentration of detectable elements

***** 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

NMs such as Ag, Au, and Rh were not found in the woody biomass, however, their concentration became high enough to be identified in the combustion solid remains as a result of the enrichment process. Rh was solely detectable in the fly ash at the level of 0.207 mg kg^{-1}. It is a valuable finding from the scientific point of view since this element was barely reported before. Other noble metals including silver and gold were detected in each ash sample. The highest concentrations of Ag (14.5 mg kg^{-1}) and Au (2.94 mg kg^{-1}) were observed in the fly ash and the deposited ash, respectively. The higher concentration of the detectable NMs in FA, DA, and EA compared to BA indicates that these metals are relatively volatile.

Several REEs were identified in the solid samples at considerable levels. The most significant results were observed in the case of Nd, such as 36.2 mg kg^{-1} in BA, 10.4 mg kg^{-1} in EA, and 9.73 mg kg^{-1} in DA. On the other hand, Sc was scarcely found in the solid remain. The concentration of REEs in FA is either below the detection limit or not available. REEs show a consistent trend in the burning system, their levels follow the decreasing order: BA>other solid remains>WB. The greater concentration in BA versus other ash samples unveils the low volatility of rare earth metal compounds during incineration.

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 Ag, Au, Rh,Dy, La, Nd, Sc, and 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 2. In terms of detectable metals in plants including Ce, Gd, and Sm, the real values of the enrichment factors are calculated and visualized in the graph (Figure 2). 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 = 72) and Sm (EF-BA = 114, EF-EA = 44).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 NMs and REEs from solid residues.

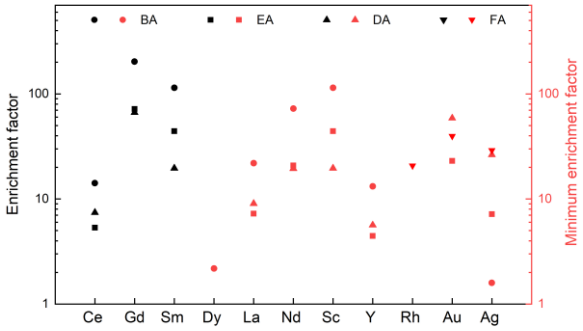


Figure 2. Enrichment Factor

IV. CONCLUSION

The woody biomass harvested from a contaminated location was combusted in a pilot-scale boiler, while solid remains from different positions in the burning system were collected and analyzed.NMs are relatively volatile as their concentrations in FA, DA, and EA are higher than in BA.Meanwhile, the greater concentration in BA versus other ash samples indicates the low volatility of REEs during biomass incineration. The enrichment factor is significant indicatingthe efficiency of the combustion process in elevating metal concentrations from biomass into solid remains.High levels of NMs and REEs in the

ash samples have benefits for the further step of extraction to reclaim these valuable elements.

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