ANTAL KERPELY DOCTORAL SCHOOL OF MATERIALS SCIENCE & TECHNOLOGY

The Behavior of Noble Metals and Rare Earth Elements During Biomass Combustion

Thesis Booklet

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1. INTRODUCTION

In the context of industrialization and urbanization, the world is facing a series of issues such as environmental pollution, climate change, and the depletion of natural sources comprising fossil fuels and metal resources. These ongoing problems promote the utilization of biomass for thermal and electric energy production, as well as enforce the world to recover metals from secondary minerals. Phytomining has opened a new era in reclaiming metals including noble metals (NMs) and rare earth elements (REEs) from brownfields where traditional mining techniques are not competitive. Phytomining is another possibility to produce NMs and REEs offering high value with environmentally friendly methods and economic feasibility. The concept of phytomining depicted in *Figure 1* is a combination of three scientific areas: i) Phytoextraction is the first stage in accumulating metals from polluted soils to plants; ii) Following that, the metals are concentrated in solid residuals called bio-ores via the enrichment process; iii) Eventually, extraction of metals from the bio-ores is the last step in the overall picture of phytomining.

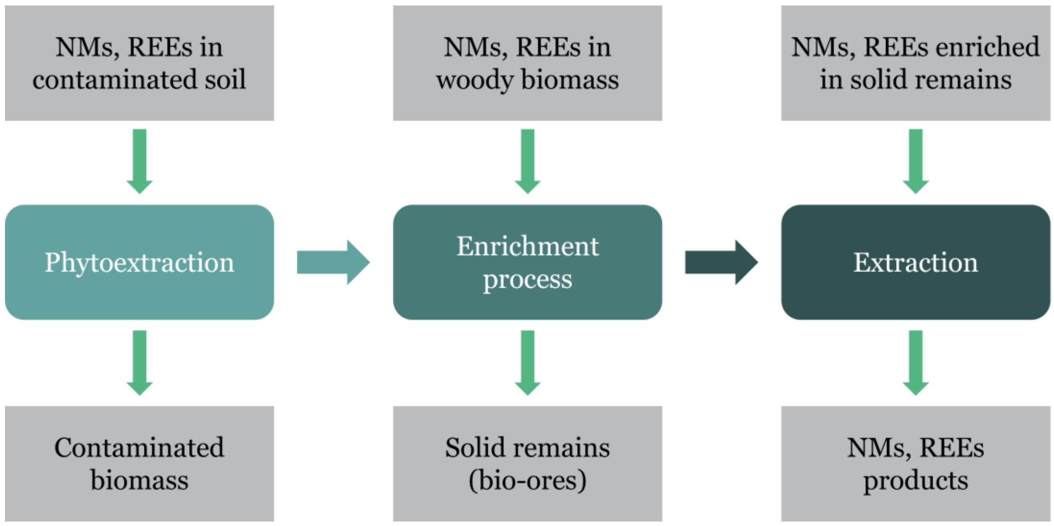

Figure 1. The overall phytomining concept of NMs and REEs.

Phytoextraction refers to using plants to accumulate NMs and REEs from contaminated lands and transport them in roots and other plant parts. Hyperaccumulators actively transfer NMs and REEs from roots to shoots, and storage of the metals in root parts is generally limited. The distribution of NMs and REEs within the major components of plants varies substantially, depending on the plant species and metals. *Brassica juncea* (Indian mustard) and *Berkheya coddii* (Asteraceae) are commonly used in the phytomining of NMs. Meanwhile, REE phytomining employs *Phytolacca americana* (pokeweed) and fern species.

During the phytoextraction process, plants accumulate NMs and REEs from contaminated soils and then translocate and store these metals in their roots and shoots. NMs and REEs accumulated in woody biomass can be recovered by applying extraction techniques. Prior to extracting NMs and REEs, the bulky contaminated plants should be lessened to a manageable amount and volume; the metal grade is then elevated in the solid residues called bio-ores. Enrichment of NMs and REEs is crucial in the entire pathway of phytomining; it not only lowers the transportation costs but also minimizes the size of the downstream processing apparatus. Several enrichment approaches including thermal conversion (ashing, pyrolysis, gasification, combustion), composting, or compaction have been introduced. Of these methods, combustion is considered the most promising manner because of its superior volume reduction and efficient metal enrichment.

Extraction is the eventual step in the phytoextraction-enrichment-extraction chain to recover NMs and REEs from brownfields. Basically, conventional and newly developed methods can be used to recover metals from urban mines. Conventional techniques of recycling metals comprise pyro-metallurgical, hydro-metallurgical, and bio-metallurgical approaches. Meanwhile, emerging approaches consist of the ionic liquid method, mechanochemical technique, supercritical fluid pathway, and electrochemical technology applied to recycle valuable metals from waste materials. It is worth noting that applying only one single approach could not completely separate and purify metals. Thus, a collaboration of two or more approaches is commonly used to carry out metal recycling.

Phytomining has been widely applied to reclaim nickel from contaminated soils. Meanwhile, studies focusing on NM and REE accumulation in plants and extraction from plants are limited. When compared with NMs and REEs, the phytomining of nickel has been intensively investigated and is much closer to practical applicability. The common application of nickel phytomining can lay a foundation for the evolution of this technology in terms of NMs and REEs. The enrichment process is a vital stage in the overall concept of phytomining to recover high-value metals such as NMs and REEs, however, the available information about the method is sparse and scanty. This research investigates the combustion process of biomass containing valuable metals, and the behavior of metals as well as the influence factor on the metal flows, focusing on NMs and REEs. Generally, the PhD topic titled “The Behavior of Noble Metals and Rare Earth Elements During Biomass Combustion” contributes to addressing global concerns, its impacts extend to various industries comprising waste management, energy production, and metal recovery.

2. MATERIALS AND METHODS

Biomass utilized in this research is harvested from contaminated land located in Gyöngyösoroszi, Hungary (*Figure 2*), where industrial mining operated until 1986. Populus tremula a species of poplar native to the area was collected. The harvested plant parts including the trunk, branches, and leaf were left in a laboratory under natural conditions for a few weeks for air drying. The different parts of the biomass were individually shredded and then mixed in the proportion of 75% trunk, 16% branches, and 9% leaf which corresponds to the weight distribution of a real tree. The biomass blend was pelletized to the required dimensions for the boiler operation. The pellet was 10–30 mm long and 6 mm in diameter; its general properties are presented in *Table 1*. The thermal analysis result of the pellet is depicted in *Figure 3*. The thermal measurement is conducted in a thermogravimetric analyzer branded MOM Derivatograph C/PC. The operating temperature is heated up to 1000 °C with a heating rate of 10 °C min^{-1} under an air atmosphere.

Figure 2. Location for contaminated biomass sampling.

Table 1. Ultimate, proximate, HHV, and density analysis of the biomass pellet used for combustion.

Ultimate, % by weight	N_{db}	0.40
	C_{db}	46.75
	H_{db}	6.05
	S_{db}	0.01
	O^*_{db}	33.43
Proximate, % by weight	Fixed carbon	34.10
	$Volatile_{db}$	52.53
	$Moisture_{db}$	11.07
	Ash	2.30
HHV_{db}, MJ/kg		18.2
Density, kg m^{-3}		422

HHV: Higher heating value, db: dry basis, *: by difference.

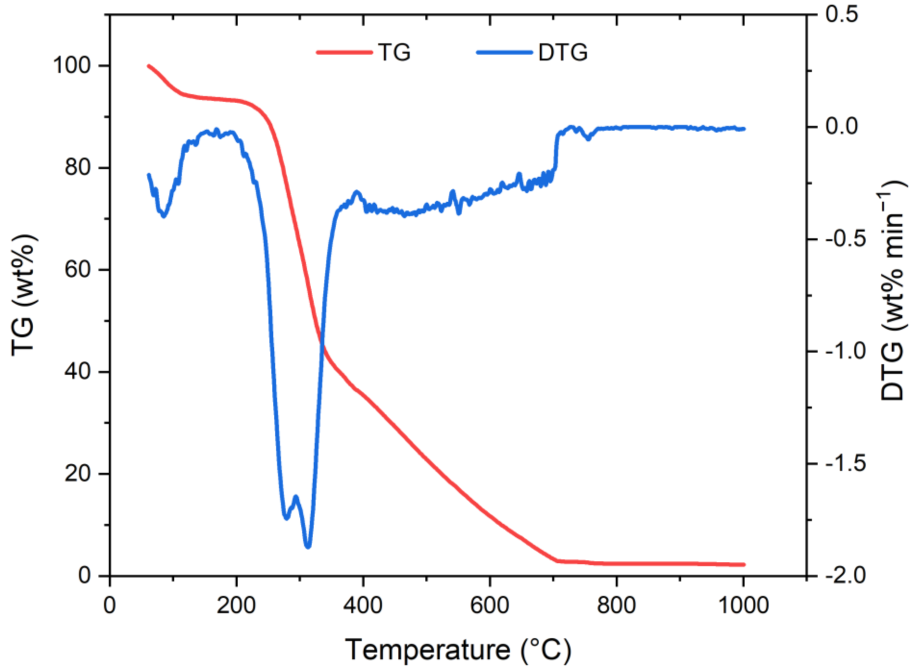

Figure 3. Thermogravimetric analysis of the pelletized biomass.

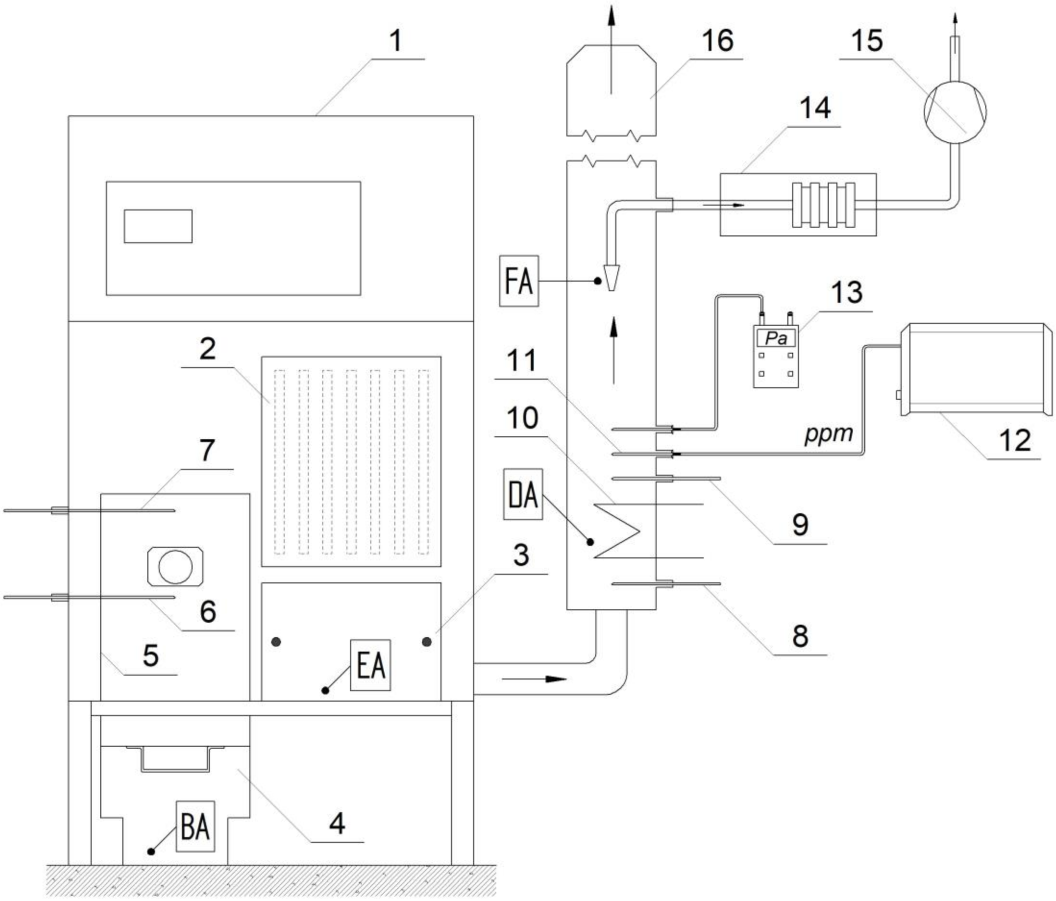

Figure 4. Schematic illustration of the measurement setup: (1) boiler body, (2) water heat exchanger, (3) chamber after the water heat exchanger, (4) ashtray, (5) combustion chamber door, (6, 7, 8, and 9) thermocouples, (10) air heat exchanger, (11) gas sampling probe, (12) portable flue gas analyzer, (13) manometer, (14) impactor, (15) pump, and (16) VFD controlled flue gas fan. Ash samples: BA – bottom ash, EA – after heat exchanger ash, DA – deposited ash, FA – fly ash.

The biomass pellet was incinerated in a fixed-grate pilot-scale boiler to investigate the fate of NMs and REEs as well as the influence of the firing rate on the metal flow. The incineration experiments were conducted under different firing rate levels of 10 kW (combustion temperature T_c = 693 °C, flue gas temperature T_f = 83 °C, and fuel feeding rate f = 4.6 kg h^{-1}), 20 kW (T_c = 840 °C, T_f = 106 °C, and f = 6.8 kg h^{-1}), and 30 kW (T_c = 924 °C, T_f = 149 °C, and f = 10 kg h^{-1}).

Combustion solid remains were captured from different positions in the burning system, illustrated in *Figure 4*, along with the measurement setup. Bottom ash was taken from the ashtray located below the combustion chamber, meanwhile, after heat exchanger ash was sampled from the chamber after the water heat exchanger. The deposited ash was collected from the surface of the air heat exchanger. The fly ash collection was implemented by an isokinetic fly ash sampling system utilizing Dekati® PM10 three-stage cascades impactor. The concentrations of fly ash in the flue gas were 191 mg Nm^{-3}, 383 mg Nm^{-3}, and 511 mg Nm^{-3} for the combustion experiments of 10 kW, 20 kW, and 30 kW, respectively. The sampling process was commenced after the boiler reached steady-state operational conditions, and the capturing method met the regulations of the ISO23210 standard. A Horiba PG350 flue gas analyzer analyzed the composition of flue gas. The thermal input was regulated by the rotation speed of the fuel screw conveyor, while the combustion air was regulated based on the oxygen content of dry flue gas. A variable frequency drive connected to the stack fan controlled the flue gas pressure. A typical experiment lasted eight hours of operation (after the initial heat-up period).

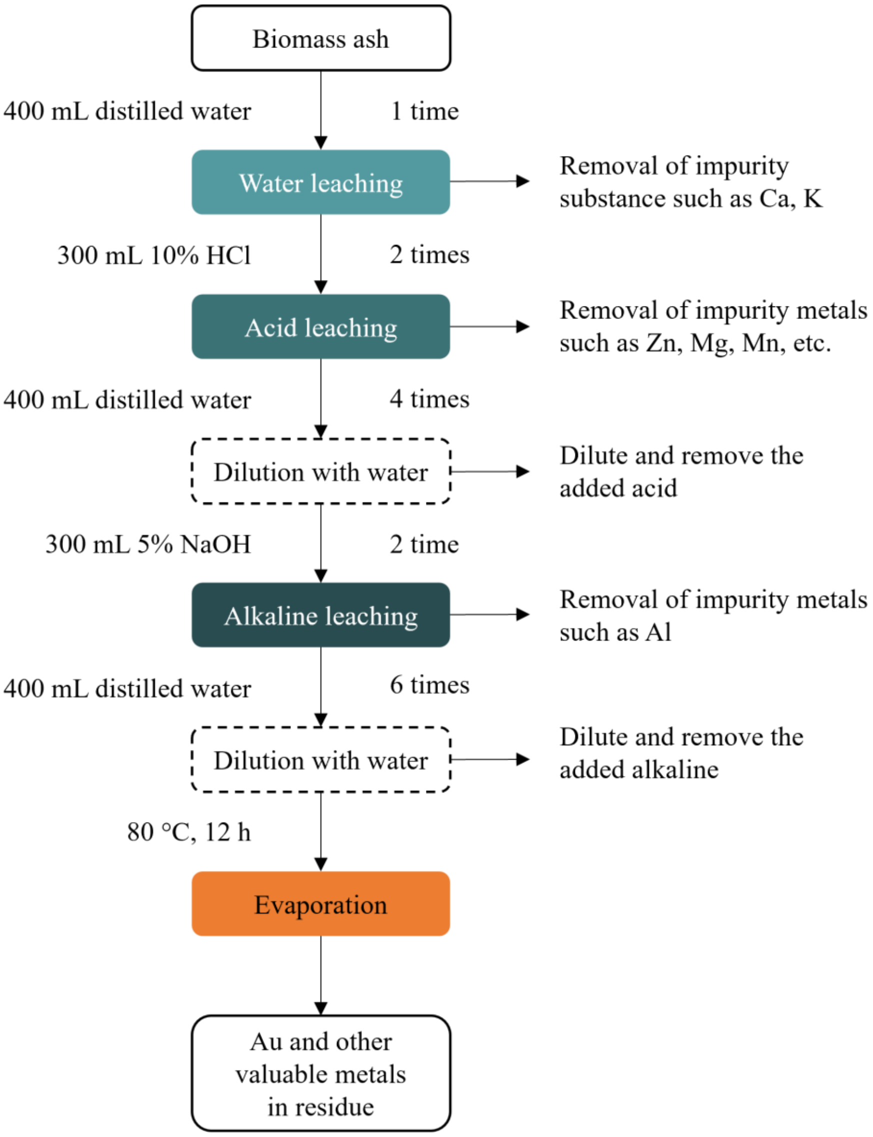

Figure 5. Flow chart of leaching procedure for biomass ash samples.

Following the combustion process, leaching experiments were conducted as the first step to predominately reclaim gold alongside other high-value metals from biomass-derived ashes. The leaching process aims to remove impurity substances and primarily recover gold along with other valuable metals in the leaching residues. The flow chart of the leaching procedure is depicted in *Figure 5*, including three major stages: water leaching, acid leaching (10% HCl), and alkaline leaching (5% NaOH).

The woody biomass, the biomass combustion solid remains, and the leaching residues derived from the leaching of combustion ashes were taken for the elemental analysis to investigate the behavior of metals in the burning system and the efficiency of the leaching process. The chemical composition of the solid samples was identified by ICP (Inductively Coupled Plasma) spectrometry. Perkin Elmer Avio 200 inductively coupled plasma-optical emission spectrometer (ICP-OES) and ICP mass spectrometry (ICP-MS) were utilized. The samples were prepared based on the Hungarian standard MSZ EN 13346:2000. Noble metals and rare earth elements are major interests of the ICP measurements.

Biomass combustion solid remains and leaching residues were characterized using SEM (scanning electron microscopy) and EDS (energy dispersive spectroscopy). SEM analyses aim to investigate the formation of valuable metals in the ashes as well as to find evidence for the ICP measurement results. The SEM examination was performed by employing a ZEISS EVO MA10 scanning electron microscope that is equipped with backscattered and secondary electron detectors combined with EDS. This scanning electron microscope employs high-energy electron beams scanning on a sample surface area of 3 µm, going below 1 µm depth of the surface. In preparation for the SEM-EDS examination, representative sections of the solid samples were suspended onto aluminum plates. Noble metals and rare earth elements are major interests of the scanning.

3. NEW SCIENTIFIC RESULTS

1st Claim

The highest concentration of silver in the solid remains gathered from the combustion of pelletized woody biomass (including logs, branches, and leaves) in a fixed-grate pilot-scale boiler within the firing range of 10–30 kW_{th} is presented in the fly ash sampled from the stack at 83–149 °C. This follows the solid residue sampled after the water heat exchanger of the boiler, while the lowest concentration can be detected in the bottom ash. On the other side, the concentration of rare earth elements follows a different tendency, meaning that bottom ash gives the highest concentration, followed by the ash gathered after the heat exchanger.

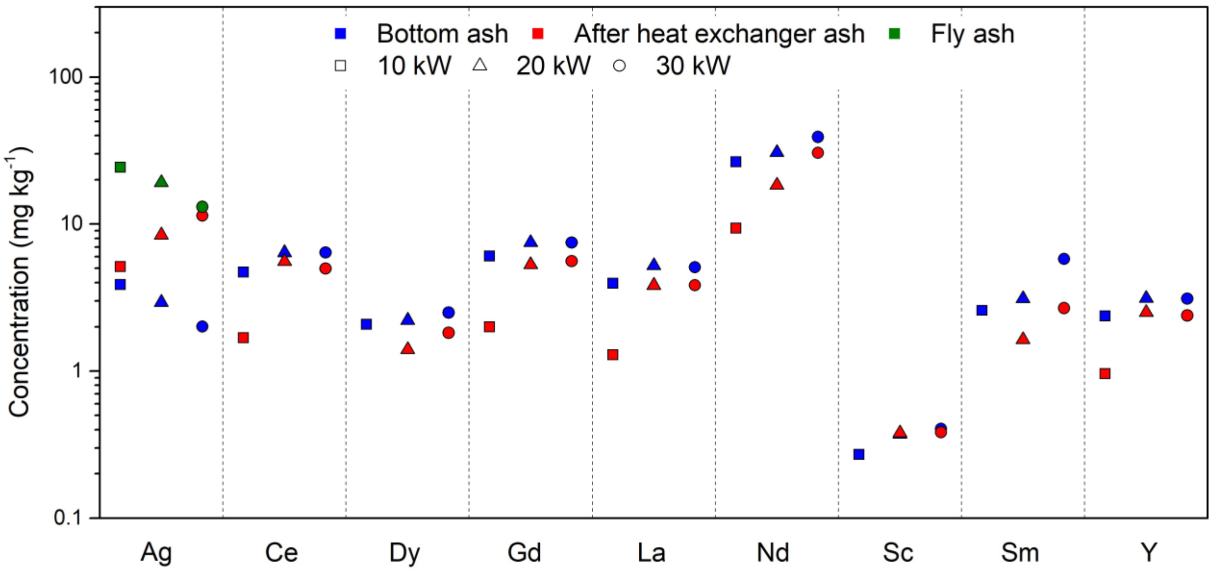

Figure 6. Concentrations of silver and rare earth elements in solid remains derived from contaminated biomass combustion experiments.

2nd Claim

The boiler performance has a significant impact on the metal concentration of the bottom ash derived from the combustion of pelletized woody biomass (including logs, branches, and leaves) in a fixed-grate pilot-scale boiler within the firing range of 10–30 kW_{th}. The concentration of silver in the bottom ash tends to decrease by 48% when the thermal power of the boiler is increased from 10 kW to 30 kW, while the concentration of rare earth elements including Ce, Dy, Gd, La, Nd, Sc, Sm and Y increases with the boiler performance by 44% on an average. Higher boiler performance or combustion temperature has a benefit for the enrichment of rare earth elements from biomass into bottom ash.

3rd Claim

The gold appears in pure form in all solid burning residues obtained from the combustion of pelletized woody biomass (including logs, branches, and leaves) in a fixed-grate pilot-scale boiler within the firing range of 10–30 kW_{th}. The formation associated with gold depends on the location of sampling. The gold particles are presented in neat form in the bottom ash with purity of higher than 95%, which particles are originated from the plant source used as fuel. Additionally, the size of a gold particle is significantly higher in bottom ash compared to other solid residues, which is elucidated by the fact that the relatively heavy gold particles cannot be transported out of the combustion chamber by the flue gas flow. Pure gold particles in the size of 1–2 µm are presented in the ash collected in the chamber after the heat exchanger, meanwhile, gold and silver in fly ash appear as a coating on a particle containing potassium, sodium, sulfur, and oxygen.

4th Claim

Noble metals and rare earth elements present in the initial woody biomass fuel can be enriched during biomass combustion. The enrichment factor (EF) is defined as the quotient of metal concentration in solid residues to that in woody biomass, which is used to describe the efficiency of the enrichment process. In the case of metals below detection limits in woody biomass, the enrichment factors are computed using the detection limits, which represent the worst-case scenarios or the lowest possible values. During the combustion of pelletized woody biomass (including logs, branches, and leaves) in a fixed-grate pilot-scale boiler with a firing range of 20 kW_{th}, the minimum enrichment factors of noble metals are relatively high in terms of deposited ash gathered from the stack surface (EF = 31 and 61 for Ag and Au, respectively) and fly ash (EF = 38 and 70 for Ag and Au, respectively). However, the most outstanding enrichment factor results are observed in the case of Gd (EF = 288, 204, and 60 for bottom ash, the ash gathered after heat exchanger and deposited ash gathered from the stack surface, respectively) and Sm (EF = 120 and 63 for bottom ash and the ash gathered after heat exchanger, respectively).

LIST OF PUBLICATIONS

Journal Papers

J.1. Truong Dinh, Zsolt Dobo, Helga Kovacs, “Phytomining of noble metals – A review”, *Chemosphere 286*, paper 131805, 2022, doi: https://doi.org/10.1016/j.chemosphere.2021.131805, **IF = 8.943 (D1)**

J.2. Truong Dinh, Zsolt Dobo, Helga Kovacs, “Phytomining of rare earth elements – A review”, *Chemosphere 297*, paper 134259, 2022, doi: https://doi.org/10.1016/j.chemosphere.2022.134259, **IF = 8.943 (D1)**

J.3. Truong Dinh, Helga Kovacs, Zsolt Dobo, “The fate of noble metals and rare earth elements during pelletized biomass combustion”, *Heliyon*, 2023 doi: https://doi.org/10.1016/j.heliyon.2023.e23546, **IF = 4.0 (Q1)**

J.4. Zsolt Dobo, Truong Dinh, Tibor Kulcsár, “A Review on Recycling of Spent Lithium-Ion Batteries”, *Energy Reports*, vol. 9, 2023, doi: https://doi.org/10.1016/j.egyr.2023.05.264, **IF = 5.2 (Q1)**

J.5. Truong Phi Dinh, Helga Kovács, Zsolt Dobó, “Behavior and treatment of metals in burning system during biomass combustion - literature review”, *Materials Science and Engineering: A Publication of The University of Miskolc*, vol. 45, no. 1, pp. 63–76, 2020, doi: 10.32974.mse.2020.006

J.6. Truong Phi Dinh, Helga Kovács, Zsolt Dobó, “Distribution of metals within different plant parts of biomass gathered from a brownfield land located in Gyöngyösoroszi, Hungary”, *Materials Science and Engineering: A Publication of The University of Miskolc*, vol. 46, no. 1, pp. 14–22, 2021, doi: 10.32974/mse.2021.002

J.7. Truong Dinh, Zsolt Dobó, Helga Kovács, “Enrichment of rare earth elements from contaminated biomass prior to extraction”, *Analecta Technica Szegedinensia*, vol. 16, no. 1, pp. 77–82, 2022, doi: https://doi.org/10.14232/analecta.2022.1.77-82

J.8. T Dinh, Z Dobó, H Kovács, “The Overall Concept of Phytomining of Noble Metals”, *PhD Students Almanach*: A publication of the University of Miskolc, Faculty of Materials and Chemical Engineering, vol. 1, pp. 224–230, 2022

J.9. Truong Dinh, Zsolt Dobó, Helga Kovács, “Elemental Analysis of Contaminated Biomass Ashes for Phytomining of Rare Earth Elements”, *Analecta Technica Szegedinensia*, vol. 17, no. 3, pp. 26–32, 2023, doi: https://doi.org/10.14232/analecta.2023.3.26-32

J.10. T Dinh, Z Dobó, H Kovács, "Experimental system for combustion of contaminated biomass", *PhD Students Almanach*: A publication of the University of Miskolc, Faculty of Materials and Chemical Engineering, vol. 1, pp. 220–226, 2023

Publications in Conference Proceedings

P.1. T Dinh, Z Dobó, H Kovács, "The overall concept of phytomining of rare earth elements", *ME TKP2020-NKA conference*, pp. 113–120, 2022

P.2. HELGA KOVACS, TRUONG PHI DINH, ZSOLT DOBÓ, "Enrichment of Noble Metals and Rare Earth Elements from Contaminated Biomass before Extraction", *IASTEM* international conference, pp. 13–16, 2022

P.3. T. Dinh, Z. Dobo, H. Kovacs, "Enrichment of valuable metals from contaminated biomass into combustion solid remains", *11th EUROPEAN COMBUSTION MEETING 2023*, pp. 1–5, 2023

Oral and Poster Presentations

O.1. Truong Phi Dinh, "Theoretical Background of NM and REE Extraction from Biomass Ashes, Miskolc, Hungary", *Raw materials university day*, Miskolc, Hungary, 20/10/2020, poster presentation

O.2. Truong Phi Dinh, "Chemical Analysis of Biomass Ashes for Phytomining of REEs", *Raw materials university day*, Miskolc, Hungary, 20/10/2020, poster presentation

O.3. Phi Truong Dinh, Zsolt Dobó, Helga Kovács, "Elemental Analysis of Contaminated Biomass Ashes for Phytomining of Rare Earth Elements", *Science Cannot Wait: New Horizons*, Košice, Slovakia, 29/11/2021, oral presentation

O.4. Phi Truong Dinh, Zsolt Dobó, Helga Kovács, "Enrichment of Rare Earth Elements from Contaminated Biomass Prior to Extraction", *ICOSTEE 2022 - International Conference on Science, Technology, Engineering and Economy*, Szeged, Hungary, 2022/03/24, poster presentation

O.5. T. Dinh, Z. Dobo, H. Kovacs, "Enrichment of valuable metals from contaminated biomass into combustion solid remains", *ECM 2023 – 11th European Combustion Meeting 2023*, Rouen, France, April 26–28 2023, poster presentation