MICROWAVE ASSISTED LEACHING APPROACHES TO RECOVER PLATINUM GROUP METALS FROM WASTE AND INTERMEDIATE STREAMS

J. Spooren[1,*], T. Abo Atia[1,2], F. Kukurugya[1]

[1]*Waste Recycling Technologies, Flemish Institute for Technological Research, VITO N.V., Boeretang 200, B-2400 Mol, Belgium*
[2]*KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. box 2404, B-3001 Leuven, Belgium*
jeroen.spooren@vito.be

Keywords: *Microwave, Chemical applications, Process intensification, Optimization, Residue/Side-stream, Chemistry, Waste.*

Abstract
Microwave (MW) assisted chloride leaching was studied to extract platinum group metals (PGMs) from waste and intermediate materials. Recently, we have shown that MW assisted leaching of spent ceramic car catalysts in 6 M HCl at 150 °C extracted PGMs without the need to add an oxidation agent at very fast leaching times (3-25 min). We present a similar approach to recover PGMs from three other materials: spent metallic foil car catalysts, capacitors from waste printed circuit board assemblies (PCBAs) and an industrial intermediate anode slime. These three materials contained elevated concentrations of metallic impurities, which dissolved during MW leaching in 6 M HCl at 150 °C. This caused consumption of the acid and a decrease in oxidation potential, which lowered the PGM leachability. Thus, for each material a two-step (MW) leaching process was developed. In the first leaching step, metal impurities were removed, and the reducing potential of the material was decreased. Whereas, in the second MW leaching step in 6 M HCl and 10 vol% H_2O_2 (30% (w/v)), the PGMs leached efficiently (>90% Pd, >97% Pt, >73% Rh). This approach increased the overall PGM extraction and their concentration in the final leachates, which is advantageous for downstream processing.

Introduction
Recent studies have shown the feasibility to apply microwave (MW) assisted processes to improve the extraction of platinum group metals (PGMs) from spent ceramic automotive catalysts. By applying a MW assisted leaching process in 6 M HCl at 150 °C a high PGM leachability (i.e. 94% Pd, 98% Pt and 71% Rh) could be reached for milled spent ceramic catalysts in short leaching times (15 min ramp to + 10 min dwell at set temperature) and without the need to add an oxidation agent [1]. Furthermore, by exploiting the possibility to heat ionic solutions, such as 6 M HCl, very fast by microwaves, the PGM extraction for non-milled catalysts could be further improved to reach a leachability of 99% Pt and 95% Rh in just 3 min (i.e. heating + dwelling time) at 220 °C [2].
Aside from ceramic catalytic converters, 5-10% of the automotive catalyst market is represented by metal carrier catalytic converters. These catalysts contain higher PGM loads than ceramic catalysts and are used in race and luxury cars due to their better performance [3]. However, in hydrometallurgical processes the metallic support dissolves preferentially, leading to inefficient PGM dissolution in most mineral acids in a single leaching stage [4]. Even the use of concentrated HCl solutions, whereby PGMs dissolve as chloro-complexes, achieved unsatisfactory PGM leaching efficiencies, unless a strong oxidant was used [5].
Monolithic ceramic capacitors, present on printed circuit board assemblies (PCBAs), are known to contain palladium. Earlier studies claimed that Pd leaching from monolithic ceramic capacitors require extremely harsh conditions, whereby Pd leached quantitatively

after 24 h in a pure aqua regia solution as no Pd leaching was observed in fuming (12 M) HCl solution [6]. Under these leaching conditions, large quantities of Ba (142 mM), Ni (141 mM) and other base metals co-dissolved along with Pd (1 mM). Such large quantities of impurities made subsequent Pd recovery (83%) and refining (98.8% purity) difficult [6].
Another secondary source of PGMs, as well as Ag and Au, are anode slimes [7]. In the case of copper anode slimes, the presence of metalloids, such as Te, Sb, Se and As, strongly influence the recovery of the noble metals. Therefore, several hydrometallurgical pre-treatment methods, ranging from acid to alkaline leaching, have been tested to remove such base metals prior to the extraction of the noble metals. Furthermore, it is generally assumed that in the case of HCl leaching the presence of an oxidation agent, such as NaClO, $NaClO_3$, H_2O_2, HNO_3 or Cl_2, is necessary to dissolve Au and PGMs from anode slimes. For PGMs, H_2O_2 is the preferred oxidation agent [7].
As shown above, spent metallic carrier catalysts, monolithic ceramic capacitors and copper anode slime are all potential secondary PGM sources, but have challenging compositions to obtain PGM extraction in simple HCl lixiviants. This study proposes to extract PGMs from these three materials by means of two-step leaching processes, whereby in a first step base metals are removed and the second PGM extraction step occurs through microwave-assisted HCl leaching.

Materials and Methods
In this work three PGM containing materials were tested as input material for microwave assisted leaching, namely (i) a representative milled sample of spent metallic foil catalysts, provided by Monolithos ltd. (Greece), (ii) milled monolith ceramic capacitors from end-of-life printed circuit board assemblies, (iii) a copper refinery intermediate from which Se and Te were removed, provided by an industrial operator. During the experiments, following chemicals were used: HCl (Merck, 37%, for analysis), H_2O_2 (Merck, 30% (w/v), for analysis), H_2SO_4 (Merck, 95-97%, for analysis), KOH (pellets, AnalR NORMAPUR, purity >85 wt%), NaOH (pellets, Merck, technical grade). During all the experiments Milli-Q water was used.
Explorative MW leaching experiments were carried out in a *Milestone FlexiWave* digestor equipped with a spinning carousel, holding 15 pressure-sealed Teflon® lined reactors (p_{max}=100 bar, T_{max}= 250 °C, V_{max} = 100 mL). The reactor vessels were typically loaded with 3-5 g of solid sample and 30-50 mL of lixiviant to obtain a liquid to solid ratio (L/S) of 10. The cavity is irradiated in multimode by a dual magnetron system (950 W each) working at 2.45 GHz. The heating program used during all MW assisted leaching experiments was 15 min. ramp to the selected temperature (100 or 150 °C) and 10 min. dwelling at the set temperature. After cooling down to room temperature, the slurry was vacuum filtrated and the solid residue was washed with a predetermined amount of Milli-Q water. Larger scale MW leaching experiments were performed using a 1 liter single reaction chamber microwave reactor (hybrid *SynthWave-UltraWave* configuration with monomode microwave irradiation at 2.45 GHz, *Milestone*) that enables to control the leaching atmosphere (e.g. N_2 flushing) and is equipped with a mechanical stirring system. This reactor was typically loaded with 50 g of solid sample and 500 mL of lixiviant. The applied heating program also consisted of 15 min heating ramp and 10 min dwell time at 150 °C. In the case of copper anode slide intermediate a first step leaching was performed in an alkaline solution of either NaOH or KOH at an L/S = 20. A weighted amount of sample was brought in a plastic beaker and the correct volume of leaching solution was added. The beaker was placed in a shaking water bath at 25 °C and shaken at 250 rpm for a set time. All experiments were performed in duplicate.
After the leaching reaction, the reacted slurries were vacuum filtrated and the solid residue was washed over the filter with a known volume of Milli-Q water, which was also collected

for analysis. Subsequently the solid residue was dried at 40 °C. The leachates and solid residues were analyzed by ICP-OES. The elemental composition of the as-obtained solid samples was essayed by an optimized microwave digestion (100 mg, 3 mL H_2O_2, 4 mL HNO_3, 5 mL HCl, 3 mL HBF_4) followed by ICP-OES analyses (Perkin Elmer, Optima 3000 DV, Avio 500). Leachates were also analyzed by ICP-OES. Energy dispersive XRF (X-LAB 2000, Spectro) was employed for determination of Ce and Si in the solids.

Results and Discussion

The PGM and main elemental composition of the three studied materials is given in Table 1. The metallic carrier catalyst was rich in Al, Fe and Cr from the carrier material and Ce, Al and Zr from the wash coating. The monolithic ceramic capacitor material was very rich in Ba, Ti and Ni and contained also elevated concentrations of Cu, Fe, Pb, Sn and Zr. Whereas the copper anode slide was particularly rich in As, Ba, Cu, Ni, Pb, Sb and Sn. For all materials the PGM concentrations were relatively low in comparison to those of other base metals, hence it can be expected that many of these metals will dissolve in an acid leaching system. Furthermore, metallic base metals will react with oxidation agents before more noble metals. Therefore, it can be expected that in the case of metallic carrier catalyst the oxidizing power of any lixiviant will be neutralized by metallic base metals before reaction with PGMs is possible.

Table 1. Elemental composition of the three tested secondary PGM sources.

Element	Spent metallic carrier catalyst	Monolithic ceramic capacitors	Copper anode slime intermediate
	PGMs (mg/kg)		
Pd	6145 ±21	1947 ±23	2730 ±40
Pt	1265 ±7	<20	953 ±110
Rh	626 ±4	<20	50 ±33
Ru	<20	<20	114 ±76
	Main elements (mg/kg)		
Al	139000 ±18000	1140 ±270	1660 ±170
As	<10	<10	46300 ±300
Ba	17000 ±141	404000 ±6100	53100 ±13000
Ca	12700 ±70	3160 ±75	192 ±2
Ce	49700	140 ±8	<10
Cr	41300 ±1130	620 ±34	20 ±3
Cu	698 ±2	27000 ±3400	46300 ±600
Fe	178000 ±4950	10600 ±490	3010 ±160
Ni	6040 ±64	130000 ±5500	13400 ±1300
Pb	627 ±4	16000 ±870	97200 ±700
Sb	<20	<20	24700 ±9200
Si	25300	-	15400
Sn	<20	37300 ±1700	13800 ±600
Ti	2680 ±92	151000 ±6500	42 ±2
Zn	12000 ±71	3600 ±140	934 ±28
Zr	60600 ±140	20600 ±305	<20

For the spent metallic carrier catalyst it is important to remove the base metals Al, Fe and Cr before the PGM extraction. On the one hand it is important to remove such metals as they are present in their metallic state and reduce the oxidative power of the lixiviant and on the other hand particularly Fe is a difficult to remove impurity in subsequent split anion

solvent extraction refining steps [8]. Therefore, MW-assisted leaching in 2 M HCl solution was tested as a pre-treatment step to remove base metals. Two leaching temperatures, 100 and 150 °C, were tested in the *FlexiWave* MW digestor. After filtration, the solid residues on the filter were washed with Milli-Q water to remove the retained leachate. At 150 °C MW-assisted leaching for 10 min in 2 M HCl more base metals were removed then at 100 °C (Fig. 1). At both temperatures no PGMs were dissolved. Therefore, 150 °C was selected as the most suitable reaction temperature for the first leaching step.

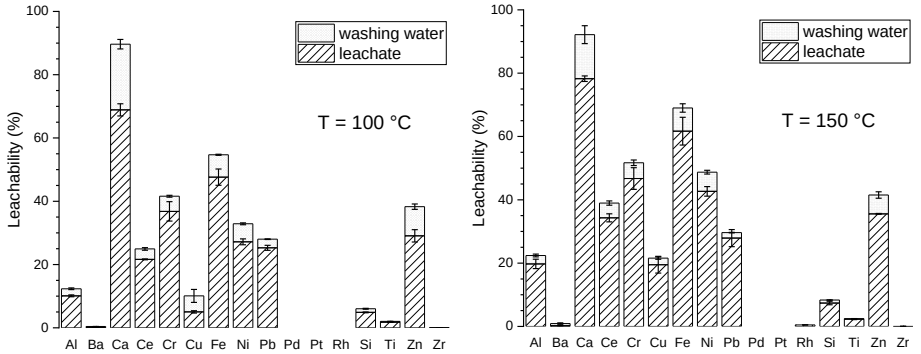

Fig. 1. Leachability of elements from spent metallic carrier catalyst in a first MW-assisted leaching step in 2 M HCl for 15 min ramp and 10 min dwell at 100 °C (left) and 150 °C (right).

The selected first leaching step process was repeated in the *SynthWave* MW reactor on a larger amount of spent metallic carrier catalyst sample. Due to better stirring in the *SynthWave* system with respect to the *FlexiWave* (i.e. mechanical vs. magnetic, respectively) the dissolution of base metals in the first leaching step was even better than previously tested (Fig. 2). The first leaching step removed about 49 wt% of the matrix material, leading to a concentration of PGMs in the leaching residue (i.e. to 11500 mg/kg Pd, 2480 mg/kg Pt and 1010 mg/kg Rh from 6145 mg/kg Pd, 1265 mg/kg Pt and 626 mg/kg Rh in the original sample). It needs to be noted that during the first leaching step about 13% of Pt was leached.

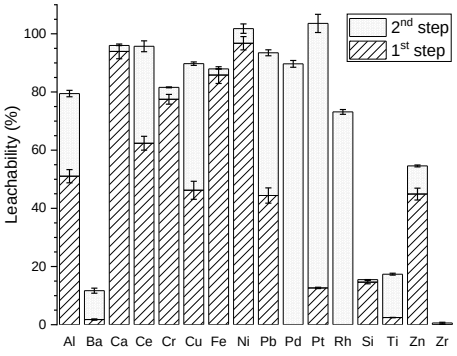

Fig. 2. Leachability of elements from spent metallic carrier catalyst in a first leaching step in 2 M HCl and a second leaching step in 6 M HCl, 10 vol% H_2O_2. Both leaching steps were executed in a MW system for 15 min ramp and 10 min dwell at 150 °C.

The second leaching step was performed on the obtained residue in 6 M HCl at L/S = 10 and 10 vol% H_2O_2 addition, giving an overall L/S = 1. MW-assisted leaching was performed for 15 min ramp and 10 min dwell at 150 °C. In the second leaching step 90 ±1% Pd, 91 ±3% Pt and 73.2 ±0.8% Rh leached.

In case of monolithic ceramic capacitors, a similar two-step leaching approach was investigated as for metallic foil catalyst sample, with the aim to remove base metals, such as Cu, Fe, Ni, Pb, Sn and Zn (see Table 1) prior to leaching PGMs. During the first MW-assisted leaching step in 2 M HCl the base metals Fe, Ni, Pb, Sn and Zn were largely removed (Fig. 3 left). Whereas, also the mostly abundant $BaTiO_3$ phase dissolved for about 35-40% (based on the Ba and Ti leachabilities). A total mass loss of 49.2 ±0.7 wt% was achieved after the first leaching step, leading to an up-concentration of Pd from 1947 mg/kg in the original material to 4070 mg/kg in the leaching residue. During the subsequent MW-assisted leaching step in 6 M HCl and 10 vol% H_2O_2 89.3 ±0.7% of Pd was recovered in the pregnant leach solution and a further 6.3 ±0.4% of Pd was recovered by washing the residue over the filter with Milli-Q water. With respect to the pregnant leaching solution in the first leaching step, the concentrations of Ba, Fe, Ni, Pb, Sn and Zn were strongly reduced in the pregnant leaching solution of the second leaching step. However, with respect to the Pd concentration in the leachate of the second step, the Ba, Cu, Ni, Ti and Zr concentrations are still high and will need to be removed in a subsequent refining step.

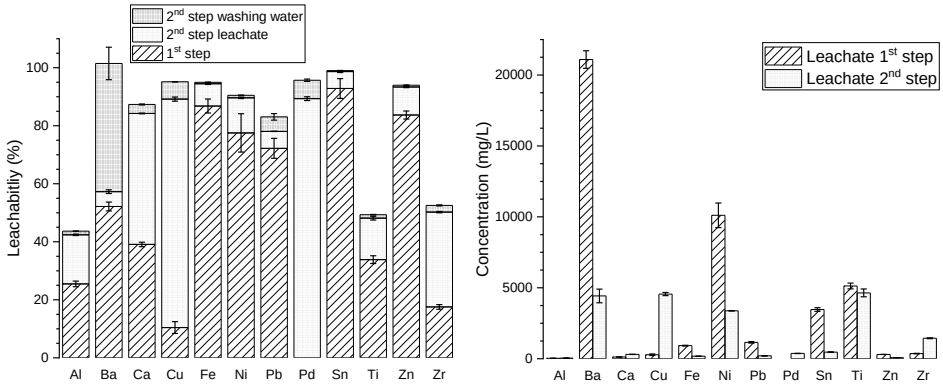

Fig. 3. Leachability (left) and concentrations in the leachates (right) of elements from monolithic ceramic capacitors in a first leaching step in 2 M HCl and a second leaching step in 6 M HCl, 10 vol% H_2O_2. Both leaching steps were executed in a MW system for 15 min ramp and 10 min dwell at 150 °C.

In case of the intermediate copper anode slime, also a two-step leaching approach was investigated. The anode slime sample contains high As content (4.6%) which might present a risk of formation highly toxic arsine gas during acidic treatment. Furthermore, the presence of base metals, such as As and Sb, are known to negatively influence PGM extraction [7]. Therefore, in order to reduce the content of base metals, in particular As, in the material, alkaline leaching at atmospheric conditions was applied as a first leaching step. First, the influence of alkaline source was tested by leaching the copper anode slime in 4 M NaOH or KOH at an L/S = 20 for 4 h at 25 °C. Leaching results showed that the most prominent base metals As, Cu, Pb and Pb leached better in NaOH (Fig. 4 left). Therefore, NaOH was chosen as an alkaline source and the influence of the NaOH concentration on the base metal leachability was further investigated at L/S = 20 for 4 h at 25 °C. Results showed that an optimal removal of base metals at 25 °C required a high

NaOH concentration of 4 M (Fig. 4 right). Finally, by increasing the leaching time from 4 h to 24 h, the As and Sn leachability further increased to 91 ±2% and 63 ±2%, respectively, whereas the leachabilities of Cu (42 ±5%) and Pb (49 ±5%) did not further increase with respect to 4 h leaching. A mass loss of 38 ±5 wt% was obtained and a slight up-concentration of noble metals in the residue with respect to the original material took place (Fig. 5)

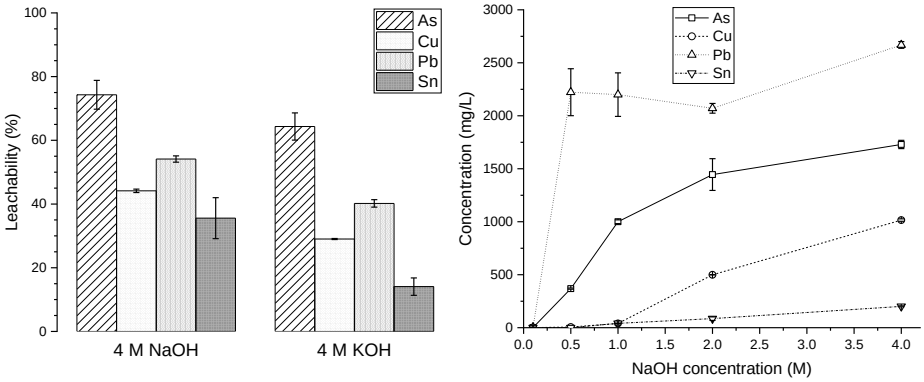

Fig. 4. Leachability of elements from the anode slime intermediate material in a first leaching step in 4 M NaOH and KOH (left) and concentrations of the same elements in the pregnant leach solutions after leaching in different NaOH concentrations. All leaching reactions were performed for 4 h at 25 °C in L/S = 20.

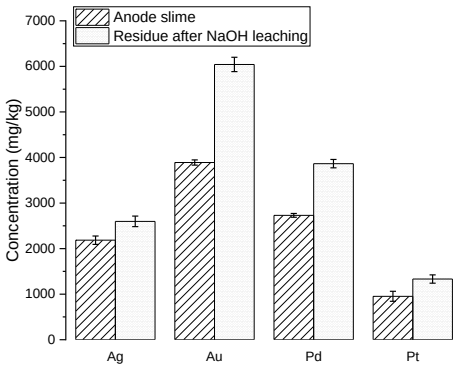

Fig. 5. Concentration of noble metals in the anode slime and the solid residue after leaching in 4 M NaOH at L/S = 20 for 24 h at 25 °C.

Subsequently, the anode slime treated by the first alkaline leaching step was subjected to MW-assisted leaching at 150 °C in 6 M HCl in the presence and absence of 10 vol% H_2O_2 addition in the *FlexiWave* MW digestor. Remarkably, the PGM leachability did not improve significantly upon H_2O_2 addition, as the concentration of most noble metals in the leachates was similar (Table 2).

Table 2. Average concentrations of noble metals in the pregnant leaching solutions after the second step MW-assisted leaching of anode slime in 6 M HCl and 6 M HCl + 10 vol% H_2O_2.

Element	6 M HCl	6 M HCl + 10 vol% H_2O_2
Ag (µg/L)	21000 ±790	19000 ±5700
Au (µg/L)	481000 ±4800	495000 ±101000
Ru (µg/L)	2270 ±14	2170 ±300
Pd (µg/L)	305000 ±2800	302000 ±42000
Ir (µg/L)	868 ±8	854 ±140
Pt (µg/L)	91500 ±2400	80600 ±14000
Rh (µg/L)	1340 ±42	1200 ±130

Based on the above results a final two-step leaching process for copper anode slime intermediate was tested whereby initially the sample was leached in 4 M NaOH at L/S = 20 for 24 h at 25 °C and subsequently the obtained residue was leached in the *SynthWave* reactor system in 6 M HCl, L/S = 10 for 15 min heating and 10 min dwell at 150 °C. Fig. 6 gives and overview of the overall extraction of base metals and noble metals from the starting material. It can be noted that a considerable amount of As (94%) was extracted in the first alkaline leaching step, as well as 42% Cu, 50% Pb and 65% Sn. In the second MW-assisted leaching step in the presence of solely 6 M HCl 51% Au, 84% Pd, 73% Pt and 19% Ru were extracted.

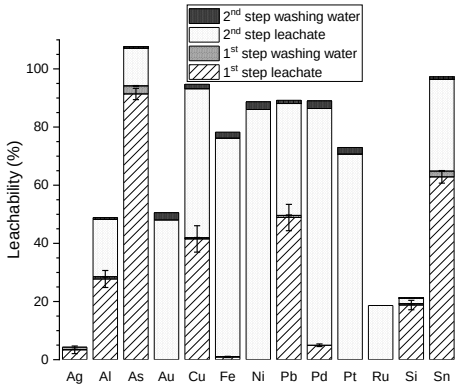

Fig. 5. Overall extraction of base and noble metals from copper anode slime intermediated according to a two-step leaching system.

Conclusions

In the current study MW-assisted hydrochloric acid leaching routes were explored to extract platinum group metals from three secondary raw materials, namely spent metallic carrier autocatalysts, monolithic ceramic capacitors and copper anode slime intermediate. All three materials contain base metals that are known to impede or hinder PGM extraction and refining. Therefore, dedicated two-step leaching systems were developed, whereby in a first leaching step undesired elements were removed, leading to an up-concentration of the valuable PGMs and a second MW-assisted leaching step in 6 M HCl at 150 °C in which PGMs were extracted. The spent metallic carrier catalyst and capacitor materials required the addition of an oxidation agent (H_2O_2) during the second leaching step to enhance PGM leachability, whereas for the anode slime no addition of oxidation agent for PGM extraction was required. MW-assisted leaching lead to high PGM extraction yields for the spent metallic carrier catalysts (90% Pd, 91% Pt and 73% Rh) and the monolithic ceramic

capacitors (96% Pd), whereas for the anode slime (84% Pd, 73% Pt and 19% Ru) the PGM extraction could be further improved by exploring harsher MW-assisted leaching conditions, such as the increase of leaching temperature, in future work.

Acknowledgements
The presented work was executed within the PLATIRUS project, which has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 730224.

References

[1] T. Abo Atia, W. Wouters, G. Monforte, and J. Spooren, "Microwave chloride leaching of valuable elements from spent automotive catalysts: Understanding the role of hydrogen peroxide," *Resources, Conservation and Recycling*, vol. 166, 2021, doi: 10.1016/j.resconrec.2020.105349.
[2] T. Abo Atia and J. Spooren, "Fast microwave leaching of platinum, rhodium and cerium from spent non-milled autocatalyst monolith," *Chemical Engineering and Processing - Process Intensification*, 2021, doi: 10.1016/j.cep.2021.108378.
[3] A. Fornalczyk and M. Saternus, "Removal of Platinum Group Metals from the Used Auto Catalytic Converter," (in English), *Metalurgija*, vol. 48, no. 2, pp. 133-136, Apr-Jun 2009. [Online]. Available: <Go to ISI>://WOS:000263346500016.
[4] A. Fornalczyk *et al.*, "Dissolution of Metal Supported Spent Auto Catalysts in Acids," *Archives of Metallurgy and Materials*, vol. 61, no. 1, pp. 233-236, 2016, doi: 10.1515/amm-2016-0043.
[5] J. Willner and A. Fornalczyk, "Dissolution of Ceramic Monolith of Spent Catalytic Converters by Using Hydrometallurgical Methods / Rozpuszczanie Monolitu Ceramicznego Zużytych Katalizatorów Na Drodze Hydrometalurgicznej," *Archives of Metallurgy and Materials*, vol. 60, no. 4, pp. 2945-2948, 2015, doi: 10.1515/amm-2015-0470.
[6] D. Fontana, M. Pietrantonio, S. Pucciarmati, G. N. Torelli, C. Bonomi, and F. Masi, "Palladium recovery from monolithic ceramic capacitors by leaching, solvent extraction and reduction," *Journal of Material Cycles and Waste Management*, vol. 20, no. 2, pp. 1199-1206, 2017, doi: 10.1007/s10163-017-0684-3.
[7] W. D. Xing, S. H. Sohn, and M. S. Lee, "A Review on the Recovery of Noble Metals from Anode Slimes," *Mineral Processing and Extractive Metallurgy Review*, vol. 41, no. 2, pp. 130-143, 2019, doi: 10.1080/08827508.2019.1575211.
[8] G. Nicol *et al.*, "Platinum Group Metals Recovery Using Secondary Raw Materials (PLATIRUS): Project Overview with a Focus on Processing Spent Autocatalyst," *Johnson Matthey Technology Review*, vol. 65, no. 1, pp. 127-147, 2021, doi: 10.1595/205651321x16057842276133.