Platinum Group Elements Recovery from Used Catalytic Converters by Acidic Fusion and Leaching

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Abstract: The recovery of platinum group elements (PGE (platinum group element coating); Pd, Pt, and Rh) from used catalytic converters, using low energy and fewer chemicals, was developed using potassium bisulfate fusion pretreatment, and subsequently leached using hydrochloric acid. In the fusion pre-treatment, potassium bisulfate alone (without the addition of an oxidant) proved to be an effective and selective fusing agent. It altered PGE into a more soluble species and did not react with the cordierite support, based on X-Ray Diffraction (XRD) and metallographic characterization results. The fusion efficacy was due to the transformation of bisulfate into pyrosulfate, which is capable of oxidizing PGE. However, the introduction of potassium through the fusing agent proved to be detrimental, in general, since potassium formed insoluble potassium PGE chloro-complexes during leaching (decreasing the recovery) and required higher HCl concentration and a higher leaching temperature to restore the solubility. Optimization on the fusion and leaching parameter resulted in $106\% \pm 1.7\%$, $93.3\% \pm 0.6\%$, and $94.3\% \pm 3.9\%$ recovery for Pd, Pt, and Rh, respectively. These results were achieved at fusion conditions: temperature 550 °C, potassium bisulfate/raw material mass ratio 2.5, and fusion time within 30 min. The leaching conditions were: HCl concentration 5 M, temperature 80 °C, and time within 20 min.

Keywords: platinum group elements; catalytic converters; acidic fusion; acidic leaching; sulfation

1. Introduction

Platinum group elements (PGE) have found their use in numerous applications including catalysts, electronic components, jewelry, chemicals, and drugs [1]. Due to their essential role in future modern and green technology, and the fact that the natural resources of these elements exist only in a handful of locations (e.g., South Africa, Russia, and Canada [2]), these elements are categorized as critical elements [3]. These reasons further encourage the effort to explore new research (i.e., secondary resources through recycling processes). Aside from maintaining a steady supply, the processing of secondary resources would reduce the pressure to the environment.

One potential secondary resource for further development is catalytic converters. The majority of PGE (i.e., Pd, Pt, and Rh) would be used as catalysts in vehicles to convert hazardous gases, formed as a result of combustion, into less toxic gases, such as carbon monoxide into carbon dioxide. The content of PGE in catalytic converters varies [4] and could reach 0.5% [5], while the rest would be support, consisting of silicate (e.g., cordierite) and oxide (e.g., alumina, titanium dioxide, and silica).

Several processes had been proposed in order to extract PGE in catalytic converters, which could be grouped into a high temperature process (pyrometallurgy), a low temperature process by leaching

(hydrometallurgy), or a combination of the two processes. In pyrometallurgical approaches, the most notable one is metal smelting collection and volatilization [6–11]. In the smelting method, the raw materials containing PGE would be mixed with fluxes, a reductor, and a collector and further heated until reaching the melting point. In this process, PGE would be reduced into metals and incorporated into the collector phase (e.g., Pb, Cu, and Fe). The PGE could be further separated from the collector using an electrochemistry method, while the flux would bind to the gangue phase, such as silicate. The advantages of the smelting method are the simple process of separating PGE from the gangue phase and the high recovery of PGE, with somewhat lower Rh recovery [5]. The other pyrometallurgical approach is volatilization, which transforms the PGE into chloride compounds at a high temperature and recovers as vapor/volatile compounds [12]. In general, the pyrometallurgy approach requires a considerably large energy input and may involve toxic and corrosive gases and compounds (especially chlorine and lead oxide).

In the hydrometallurgy approach, PGE were recovered by a dissolution process using a strong acid (e.g., hydrochloric acid, nitric acid, and sulfuric acid) or a combination of two or more of these acids (e.g., aqua regia), or by the addition of oxidants into these acids (e.g., iodine, bromine, chlorine, and hydrogen peroxide) [13–17], or using a complexant (e.g., cyanide) [18,19]. Aside from the direct leaching of PGE, another approach in hydrometallurgy includes upgrading the PGE in raw materials by leaching out the supporting materials. Mishra (1987) [20] successfully removed the alumina support by exploiting the amphoteric nature of alumina, which could be leached using sulfuric acid. Although hydrometallurgy could effectively deal with low grade raw materials, the consumption of hazardous and highly corrosive chemicals is substantial, due to the relatively stable nature of PGE.

Apart from the pyrometallurgical approach and the hydrometallurgical approach, there is another approach: the fusion method. This basic approach is to transform the insoluble phase into a soluble phase through reaction with an additive (fusing agent) during moderate heat treatment (in general, less than 800 °C), meaning a lower energy input in comparison to pyrometallurgy. The soluble phase produced could be leached in relatively mild conditions (less hazardous chemicals used compared to hydrometallurgy). Generally, the fusion method was applied for PGE upgrading (i.e., matrix decomposition) using alkalies (e.g., sodium hydroxide) [21] or an acidic fusing agent (e.g., potassium bisulfate). Subsequent leaching would remove the matrix and leave the PGE as insoluble residue for further processing stages.

Fusion using bisulfate has attracted attention from several research groups [22–25]. Batista and Afonso [22] intended to upgrade the PGE from a used catalyst by matrix (alumina) decomposition, believing that Pt would not react with bisulfate during fusion and would be accumulated in the residue. The other researchers mentioned, with the same confidence, that bisulfate alone would be ineffective to transform Pt into the soluble phase, so they combined the bisulfate with a strong oxidant (e.g., perchlorates) during fusion to make the transformation applicable. However, none of the studies cited above clearly defined the interaction between fusing agents and PGE or the interaction between fusing agents (i.e., bisulfate and chlorate).

This belief was probably rooted in the fact that PGE (especially Pt) are some of the most inert metals, and Pt is extensively used as a material of apparatus in highly corrosive conditions. For example, the standard procedure of titanium oxide decomposition using potassium pyrosulfate is carried out in a platinum crucible [26]. However, several researchers have documented that Pt could be attacked by a sulfoxide compound at an elevated temperature to form Pt sulfate salt. For example, $Pt_2(HSO_4)_2(SO_4)_2$ was produced by reacting Pt metal and sulfuric acid at 350 °C [27], and $[Pt(S_2O_7)_3]^{2-}$ was produced by reacting Pt metal with oleum (65% SO_3) at 160 °C [28]. In the case of Rh, researchers have successfully produced $Rh_2(SO_4)_3 \cdot 2H_2O$ by reacting Rh metal with sulfuric acid at 465 °C [29].

Our preliminary observation showed that potassium bisulfate alone would effectively alter Pt, Pd, and Rh (Figure 1). Based on observation on the color of the compound produced, the compounds formed were assumed to be PGE-sulfates, which were amenable for further leaching using dilute hydrochloric acid. The hydrochloric acid was chosen in order to stabilize the PGE in an aqueous

solution as a chloro-complex. In our studies, the hypotheses we proposed were the transformation of potassium bisulfate into potassium pyrosulfate ($K_2S_2O_7$) during thermal decomposition and, further, the pyrosulfate as a strong oxidant would react to PGE to form PGE-sulfate, according to this reaction:
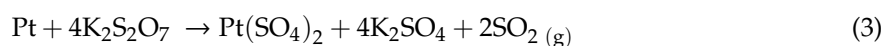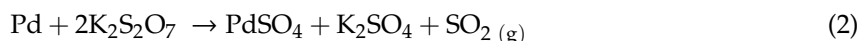
$$2KHSO_4 \rightarrow K_2S_2O_7 + H_2O \tag{1}$$

$$Pd + 2K_2S_2O_7 \rightarrow PdSO_4 + K_2SO_4 + SO_{2\,(g)} \tag{2}$$

$$Pt + 4K_2S_2O_7 \rightarrow Pt(SO_4)_2 + 4K_2SO_4 + 2SO_{2\,(g)} \tag{3}$$

$$2Rh + 6K_2S_2O_7 \rightarrow Rh_2(SO_4)_3 + 6K_2SO_4 + 3SO_{2\,(g)} \tag{4}$$

Figure 1. PGE salts from left (Pd, Pt, and Rh) produced by reacting PGE metal powder with potassium bisulfate in a muffle furnace at 550 °C for 3 h.

Based on the above hypotheses, the feasibility of recovering PGE from catalytic converters, using potassium bisulfate as the sole fusing agent, followed by hydrochloric acid leaching, would be tested. The parameters investigated included: fusion temperature, mass ratio between raw materials and fusing agents, fusion duration, and leaching parameters (pulp density, HCl concentration, leaching time, and temperature). The characterizations would also be carried out to confirm the fusion and leaching efficacy using X-Ray Diffraction and metallographic observation.

2. Method, Material, and Instrumentation

2.1. Material and Instrumentation

A used catalytic converter sample was obtained from a local scrapyard in Sapporo, Japan. The honeycomb-structured converter was then ball milled and sized with a 270 mesh (53 μm) screen that was used in fusion and leaching studies. Potassium bisulfate, hydrochloric acid, nitric acid, sulfuric acid, and sodium hydroxide were obtained from Merck, Darmstadt, Germany all in analytical grade. Deionized water (MilliQ) was used throughout the experiment.

The leaching experiment was carried out in the Research Unit for Mineral Technology of Indonesian Institute of Sciences, Lampung Selatan, Indonesia. Converter sample total decomposition was carried out using alkali fusion and subsequent HCl-HNO$_3$-H$_2$SO$_4$ digestion, followed by measurement using ICP-OES (Analytik Jena, Plasma Quant 9000 Elite, Jena, Germany) to determine Pd, Pt, and Rh content in the sample after the decomposition (Table 1) or in the liquid phase after the leaching test was completed, in order to calculate the recovery (*R*, %) according to Equation (5). Characterization on materials both before and after treatment was conducted using XRD (Panalytical, Expert3 Powder, Malvern, UK) in Research Unit for Mineral Technology, Indonesian Institute of Sciences. Metallographic microscopy (Reichert MEF 4M microscope equipped with AxioCam MRc5 camera from Carl-Zeiss,

Oberkochen, Germany) was conducted in Dept. of Metallurgical and Materials Engineering, Colorado School of Mines.

$$R = \frac{C_E \times V}{C_o \times m} \times 100\% \tag{5}$$

where:

C_E PGE concentration in liquid phase after fusion and leaching (µg/mL)

C_o PGE content in catalytic converters (µg/g)

m mass of catalytic converters used in leaching (g)

V leaching agent volume (mL)

Table 1. Chemical composition of PGE in used catalytic converters.

Elements	Pd	Pt	Rh
Content (µg/g)	112.0 ± 1.7	1299.4 ± 3.5	316.0 ± 6.6

2.2. Method

Acidic fusion-leaching studies were carried out by a batch method. Typically, 0.5 g of catalytic converter powder was mixed with potassium bisulfate with certain mass ratio in a 30 mL porcelain crucible. The mixture was then introduced into a muffle furnace with a temperature higher than 350 °C. After the fusion was completed, the solid product was put into a conical flask, hydrochloric acid was added, and the mixture was homogenized using an orbital shaker (speed 200 rpm). After leaching was concluded, the supernatant solution was separated by centrifugation and filtration, and the PGE content was determined using ICP-OES. All fusion and leaching data was obtained in duplicates.

3. Results and Discussion

3.1. Characterization Results

Characterizations were conducted on materials before and after treatment, and they were carried out using XRD combined with a metallographic analysis, in order to confirm the efficacy of the fusion and leaching process. The XRD results (Figure 2) on powdered raw materials before and after fusion (fusion temperature 550 °C, $KHSO_4$/raw material mass ratio 2, and fusion time 3 h) show that the cordierite matrix of catalytic converters was partially affected by the fusion process to form potassium alum ($KAl(SO_4)_2 \cdot 12H_2O$). However, based on the metallographic observation of catalytic converters, both before and after fusion, and subsequent leaching using hydrochloric acid 5 M, the cordierite matrix was unaffected, while the PGE coating was clearly washed out (Figure 3). This confirms the efficacy of potassium bisulfate as a fusing agent and its capability as the sole oxidant in transforming PGE into soluble species.

3.2. Acidic Fusion Using $KHSO_4$

To study the effect of fusion on PGE recovery, the leaching parameters were set constant i.e., hydrochloric concentration 5 M, pulp density 20 mL/g, leaching time 6 h, and leaching temperature 30 °C.
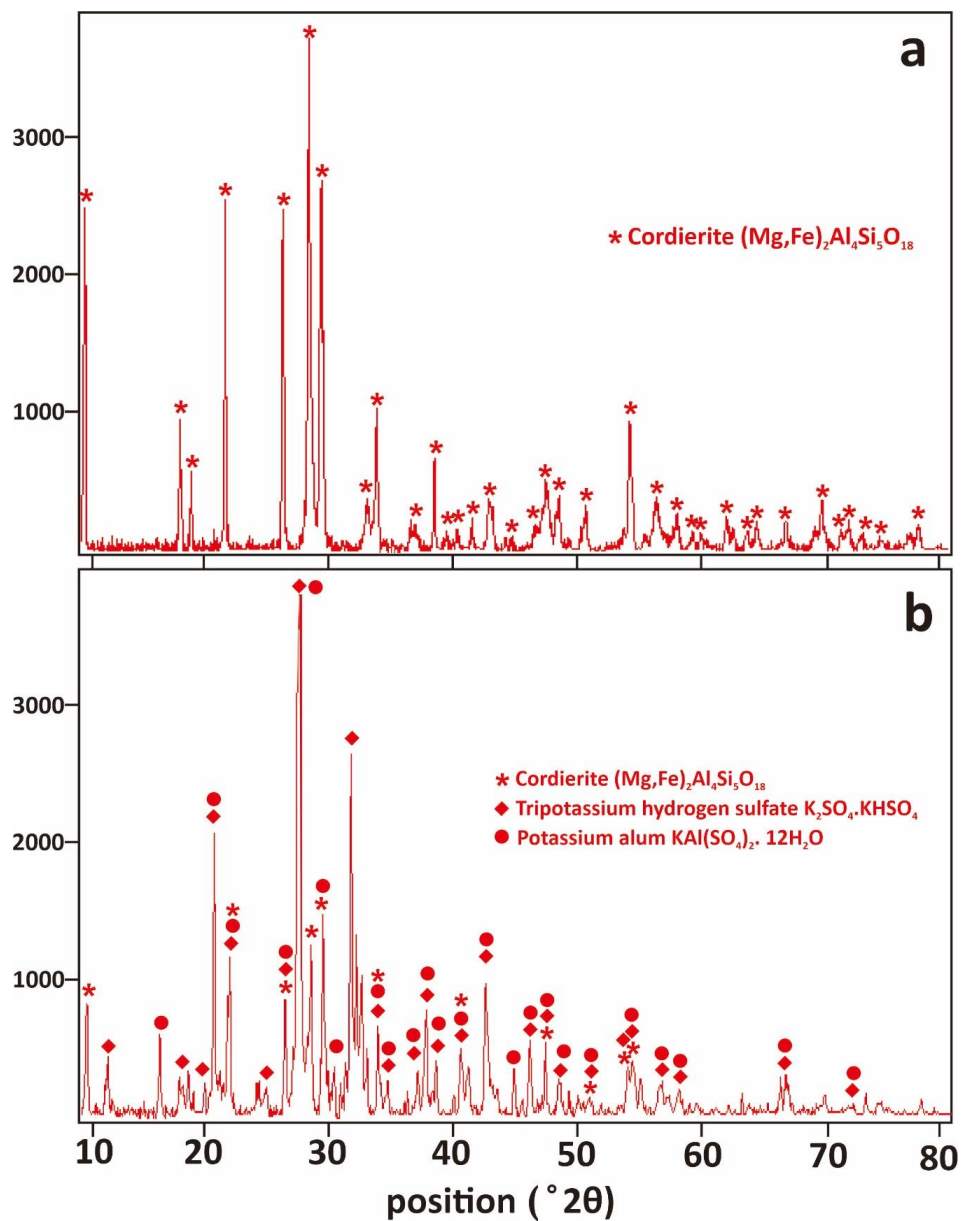
Figure 2. X-Ray powder diffraction of raw materials (**a**) before and (**b**) after fusion with potassium bisulfate.
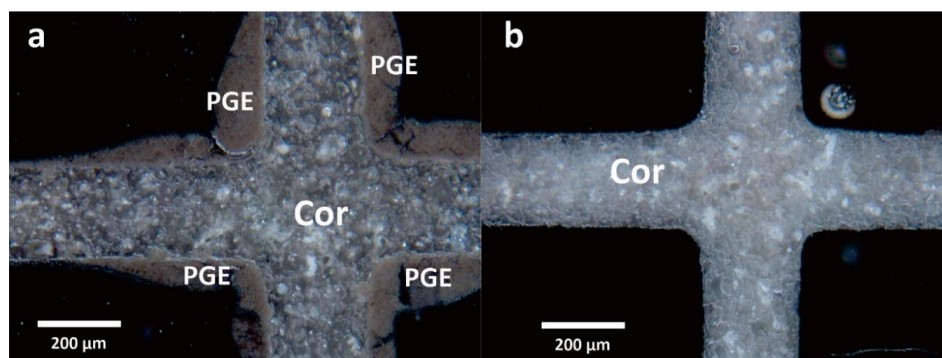

Figure 3. Metallographic observation on catalytic converters mounted on resin (**a**) before and (**b**) after fusion using potassium bisulfate, followed by leaching using hydrochloric acid 5 M. (Cor: cordierite matrix; PGE: platinum group element coating).

3.2.1. Effect of Fusion Temperature

The effect of fusion temperature was studied between 350 and 750 °C, with a constant fusion variable: mass ratio ($KHSO_4$/catalytic converters powder) 2 and fusion duration 3 h. The results were depicted in Figure 4, which showed that the recovery of PGE increased as temperature increased, until it reached the optimum fusion temperature at 550 °C (recovery Pd 92%, Pt 50%, and Rh 78%), and, then, decreased (Pd and Rh) or became relatively constant (Pt). The increasing recovery up to 550 °C, then decreasing recovery, indicates the advantage of thermal decomposition of $KHSO_4$ into $K_2S_2O_7$, which oxidized the PGE present in the raw material. A higher fusion temperature caused further decomposition of potassium pyrosulfate into potassium sulfate (T > 600 °C) [30], which has less oxidative power than pyrosulfate. The XRD data confirmed the transformation of potassium bisulfate into potassium pyrosulfate during fusion up to 650 °C and partial transformation into potassium sulfate at higher temperatures, (Supplementary Materials).
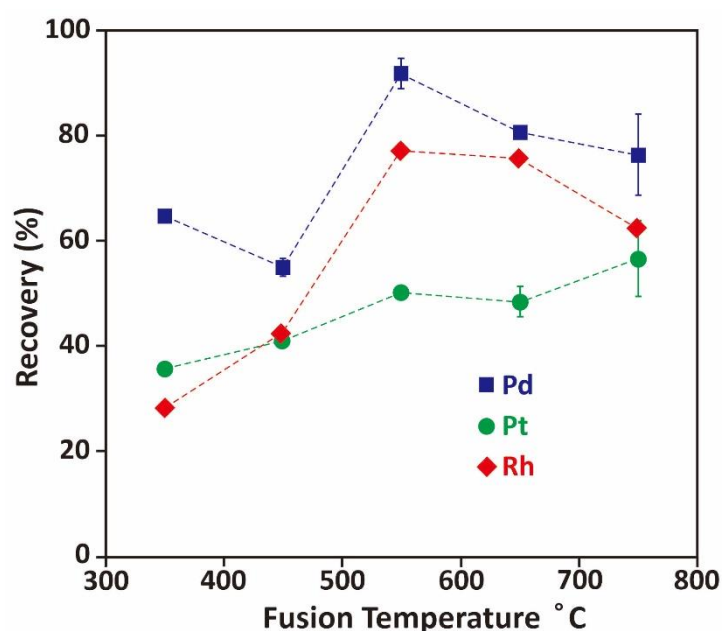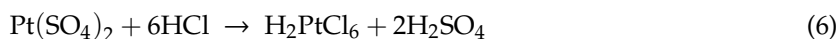

Figure 4. The recovery of PGE related to fusion temperature.

3.2.2. Effect of Mass Ratio

To assess the effect of the amount of fusion agent ($KHSO_4$) added relative to raw materials on the PGE recovery, the fusion was carried out with varied $KHSO_4$/catalytic converters mass ratios from 0.5 to 3. The constant fusion variables were temperature (550 °C) and fusion duration (3 h). The results are depicted in Figure 5. The figure shows the recovery increased as mass ratio increased until an optimum value of 2–2.5 (Pd 93%, Pt 76.5%, and Rh 77.6%), then the recovery decreased as mass ratio increased further. The decreasing recovery at higher mass ratio was probably caused by precipitation of PGE in the form of potassium salt of chloro-complexes (e.g., K_2PtCl_6 [31]) during leaching, due to an excess of potassium ion introduced during the fusion at higher mass ratios (reactions 6–7).

$$Pt(SO_4)_2 + 6HCl \rightarrow H_2PtCl_6 + 2H_2SO_4 \tag{6}$$

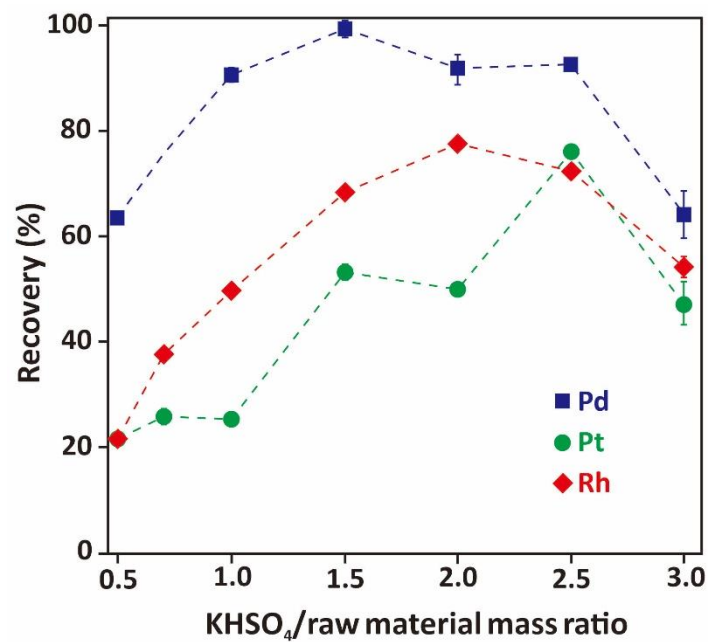$$K_2SO_4 + Pt(SO_4)_2 + 6HCl \rightarrow K_2PtCl_6 \downarrow + 3H_2SO_4 \tag{7}$$

Figure 5. The effect of fusion agent/catalytic converters mass ratios to PGE recovery.

3.2.3. Effect of Fusion Time

To evaluate the effect of fusion time to the PGE recovery, the fusion was conducted at a constant variable KHSO$_4$/raw material mass ratio 2.5 and a fusion temperature of 550 °C, while the fusion time varied between 5 and 240 min. The results shown in Figure 6 demonstrated that the saturation value of PGE recovery could be attained within 30 min of fusion (Pd 98.9%, Pt 63.2%, and Rh 71.3%). Longer fusion time did not significantly increase the recovery.
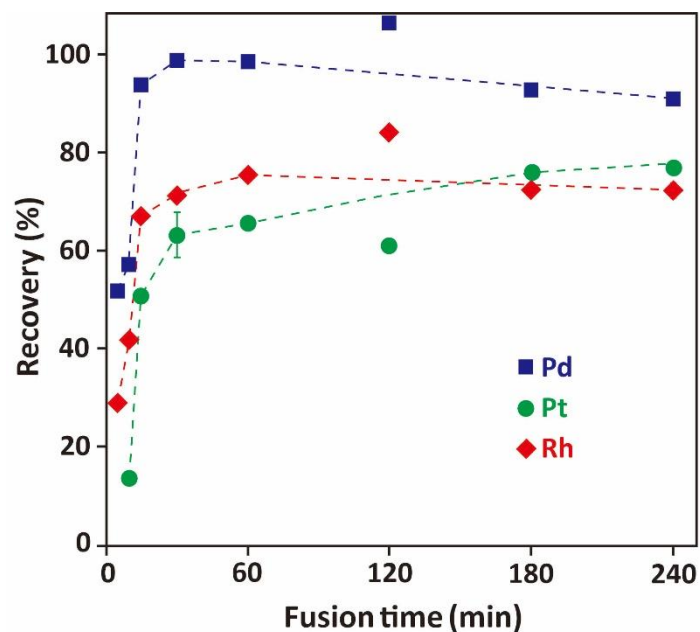
Figure 6. The effect of fusion time on PGE recovery.

3.3. *Acidic Leaching using Hydrochloric Acid after KHSO$_4$ Fusion*

The effect of leaching parameters was studied at constant/optimum fusion parameters (temperature 550 °C, fusion agent/raw material mass ratio 2.5, and fusion time 30 min). Leaching parameters studied included pulp density, HCl concentration, temperature, and time.

3.3.1. Effect of Leaching Pulp Density

The effect of pulp density in the leaching stage was studied in the range of 5 to 25 mL/g. The pulp density (volume/mass) in this case was the ratio of lixiviant added to the mass of solid phase/fusion product. The constant leaching variables were HCl concentration 5 M, temperature 30 °C, and duration 6 h. The results in Figure 7 show the optimum recovery was attained at pulp density 15–20 mL/g.
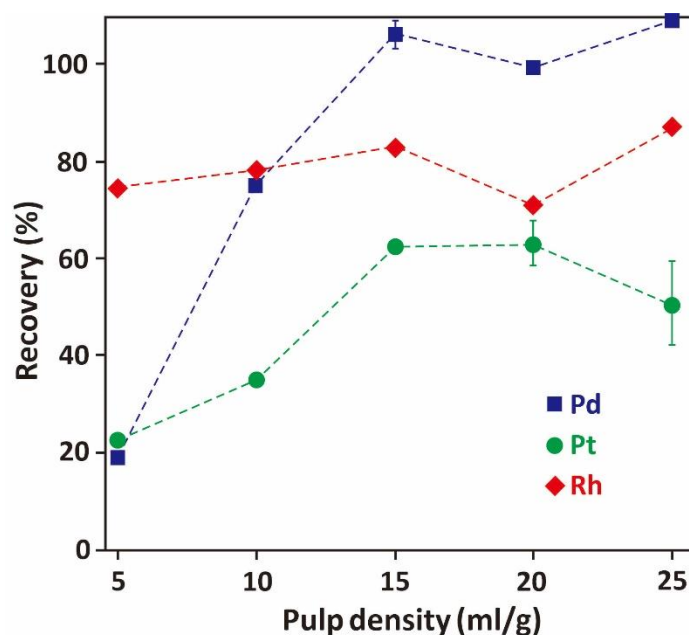

Figure 7. The effect of leaching parameter pulp density on PGE recovery.

3.3.2. Effect of Hydrochloric Acid Concentration

To study the effect of hydrochloric acid as a lixiviant, the leaching temperature, leaching time, and pulp density were fixed constant at 30 °C, 6 h, and 20 mL/g, respectively. Hydrochloric acid concentration as an independent variable was set from 0 to 5 M. The results depicted in Figure 8 show the recovery of Pd and Rh at control conditions (HCl concentration 0/leaching with deionized water) were quite significant (Pd 56.4% and Rh 73.6%), while Pt recovery was only 12%. These results also confirmed the efficacy of potassium bisulfate as the sole fusing agent to transform PGE into a soluble PGE compound. In general, excluding Rh, the PGE recovery increased as the hydrochloric acid concentration increased; this was caused by the stabilization of PGE as chloride complexes in pregnant leach solution. The Rh recovery showed a different trend; the recovery decreased as the hydrochloric acid concentration increased. This was possibly due to the formation of a less soluble Rh chloride complex (K$_2$RhCl$_5$) in a higher chloride concentration compared to Rh sulfate [32], Reaction (8). In the case of Pd, the increasing recovery at the higher hydrochloric acid concentration was due to the stabilization of Pd as a chloride complex.
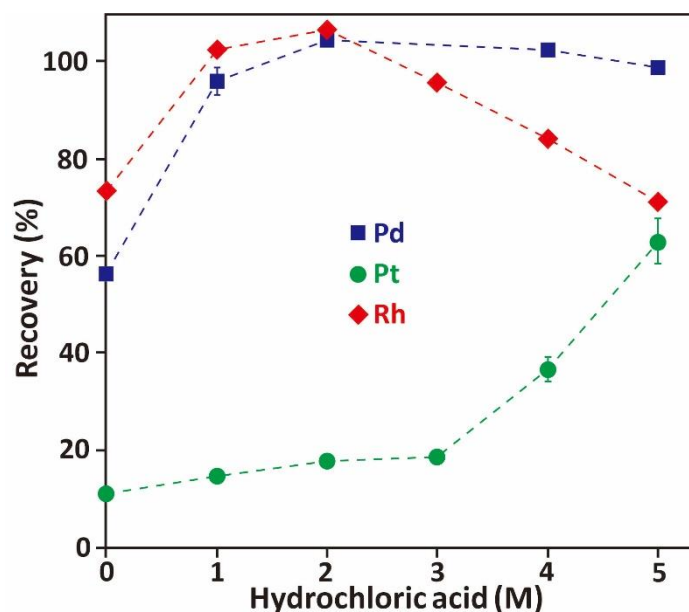
$$Rh_2(SO_4)_3 + 2K_2SO_4 + 10HCl \rightarrow 2K_2RhCl_5 + 5H_2SO_4 \tag{8}$$
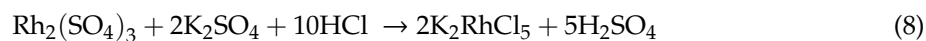
Figure 8. The effect of hydrochloric acid concentration as a lixiviant on the PGE recovery.

Efficient leaching of Pt was only attained at a high concentration of hydrochloric acid. The concentration of potassium seemed to play a major role in the stabilization of the Pt complex in the liquid phase. At lower HCl concentrations, Pt would tend to exist as the potassium complex K_2PtCl_6 (9), which has a very low solubility. As the HCl concentration increased, the Pt complex would be transformed into the highly soluble species H_2PtCl_6 (10), since potassium concentration in the liquid phase would decrease, due to the formation of $KHSO_4$ (11), which has a very low solubility.

$$Pt(SO_4)_2 + K_2SO_4 + 6HCl \rightarrow K_2PtCl_6 \downarrow + 3H_2SO_4 \tag{9}$$

$$K_2PtCl_6 + 2HCl \rightarrow H_2PtCl_6 + 2KCl \tag{10}$$

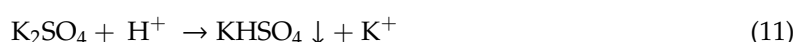$$K_2SO_4 + H^+ \rightarrow KHSO_4 \downarrow + K^+ \tag{11}$$

Figure 9 represents the recovery of PGE based on two leaching variables: HCl molarity (1, 2 and 5 M) and leaching temperature (30, 50 and 80 °C), with constant variable pulp density and leaching time (20 mL/g and 1 h, respectively). The temperature clearly increased the recovery of PGE, which was due to increasing solubility of PGE complex in liquid phase during acidic leaching. This was pronounced in the case of Pt.

3.3.3. Effect of Leaching Time

The effect of leaching time (0–60 min) was studied at various temperatures (30, 50, and 80 °C) while hydrochloric acid concentrations and pulp density were set constant at 5 M and 20 mL/g, respectively (Figure 10). It is demonstrated that the leaching reaction occurred fast, and the maximum recovery was attained within 20 min.

Figure 10 also shows that the saturation value of recovery increased, as a result of increasing the leaching temperature. In the case of Pt, the leaching efficiency reached 99.9% ± 2.8% within 5 min at 80 °C, while, for Rh, the recovery increased from 87.2% ± 1.4% (50 °C) to 101.4% ± 6.8% (80 °C). For Pd, the effect of increasing temperature was less significant than it was for Pt and Rh.

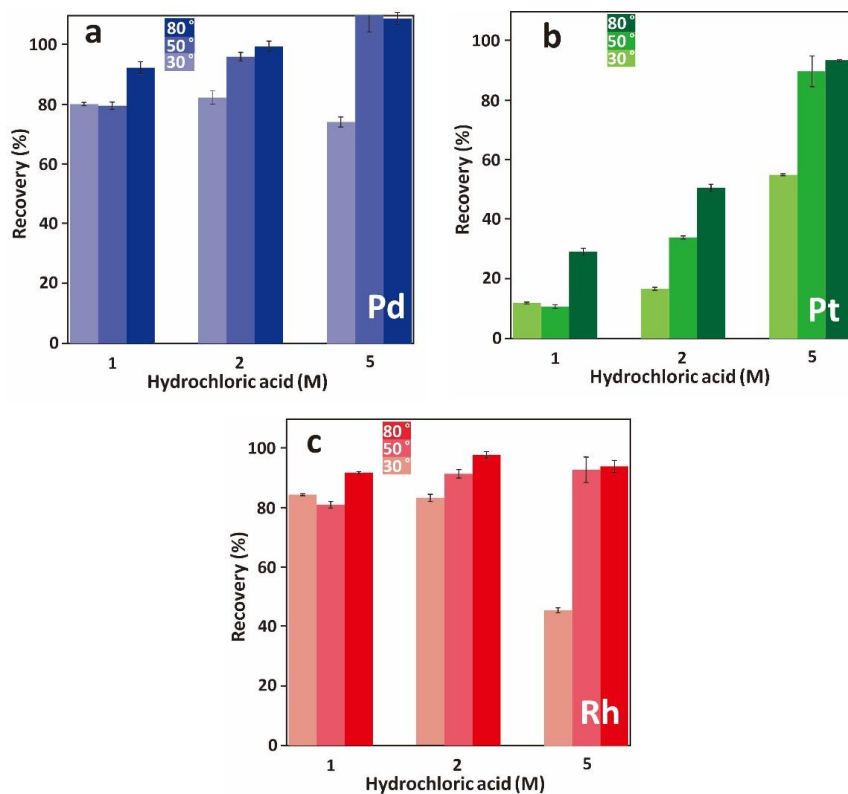**Figure 9.** PGE recovery as a function of different hydrochloric acid concentrations and leaching temperatures (**a**) Pd, (**b**) Pt, and (**c**) Rh.
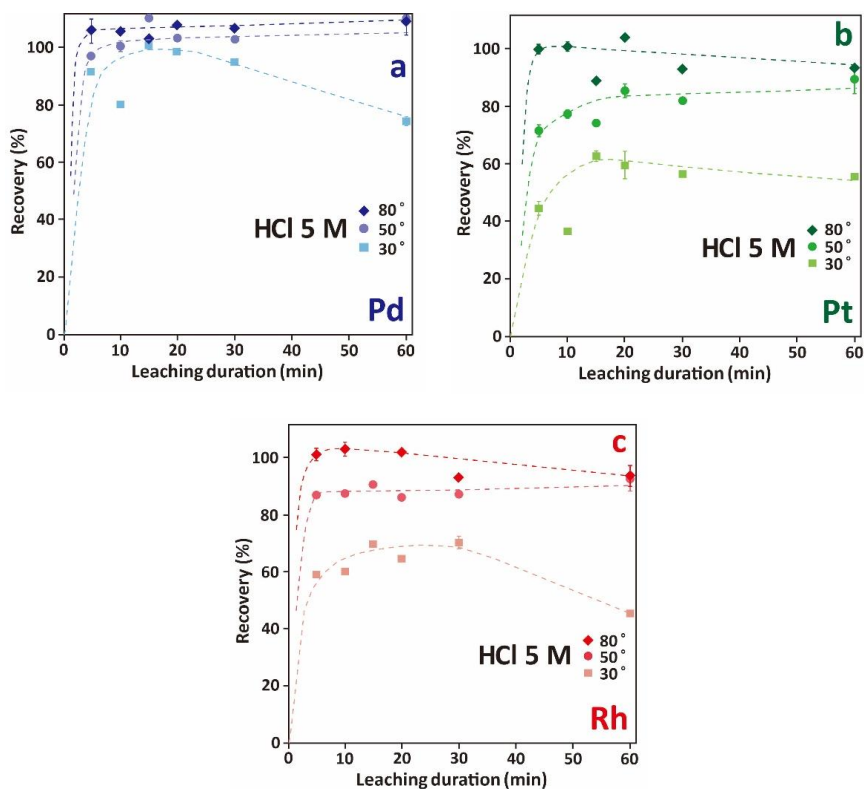

Figure 10. The effect of leaching duration and temperature on PGE recovery (**a**) Pd, (**b**) Pt, and (**c**) Rh at a constant hydrochloric acid concentration.

4. Conclusions

It was demonstrated that potassium bisulfate as the sole fusing agent effectively transformed PGE in catalytic converters into species which were amenable for mild condition leaching processes (HCl < 5 M, T < 80 °C). The advantages of using potassium bisulfate for PGE recovery were lower energy, lower chemical consumption, and selectivity, since potassium bisulfate only reacted with PGE (it did not react with cordierite). This was confirmed by XRD and metallography characterization results.

Generally, all three PGE showed the same trend according to all fusion parameters. The optimum recovery of PGE was achieved at a fusion temperature of 550 °C, a fusion agent-catalytic converters mass ratio of 2.5, and a fusion time within 30 min. In the case of leaching, Pd and Pt showed the same trend, which was that the increase of leaching temperature and HCl concentration would be beneficial. In this case, the recovery of Pd and Pt were 106% ± 1.7% and 93.3% ± 0.6%, respectively. On the other hand, Rh exhibited a different trend, which was that when leaching at room temperature, the increase of HCl concentration led to a recovery decline. However, at higher leaching temperatures, the trend followed the other PGE. At the optimum conditions (temperature 80 °C and HCl 5 M), the Rh recovery reached 94.3% ± 3.9%. A study on the effect of leaching time generally demonstrated that maximum recovery was attained within 20 min.

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