

# Hydrometallurgical Process with Phosphonium-based Ionic Liquid for Selective Recovery of Platinum Group Metals from Automotive Catalyst

モチャマド, ルトフィ, ファマンサ

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氏 名 : モチャマド ルトフィ ファマンサ

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自動車触媒からの白金族金属の選択的回収のためのホスホニウム系イオン液体を用いた湿式製錬プロセス

### 論 文 内 容 の 要 旨

In the last several years, the demand-supply for PGMs is widening. Technical and operational cost makes mining PGMs much more difficult than before. In order to fulfill the supply, recovering PGMs from wastes is an attractive option. By doing this, the environmental burden due to mining could be lightened. Recovering PGMs from wastes also produces less byproduct that needs treatment prior to disposal. Not only beneficial in ecological aspect, recovering PGMs from wastes would also be beneficial in an economic aspect. PGMs content in waste is several times higher than that in their natural deposit. Solvent extraction is one of the good alternatives to the classical approach in metal processing. It consumes less energy, has better selectivity and lower environmental burden. The drawback of solvent extraction could be solved through the use of ionic liquids because it does not require additional solvent unlike conventional extractants. In the present thesis, based on the aim of developing effective hydrometallurgical separation systems for the separation and recovery of PGMs from a waste automotive catalytic converter, three subjects were investigated for their feasibility.

In chapter 2, the potential of undiluted phosphonium-based ionic liquid in the extraction of Pt(IV), Pd(II) and Rh(III) was explored. Trioctyl(dodecyl)phosphonium chloride ( $P_{8,8,8,12}Cl$ ) was firstly reported as an extractant in this chapter and its performance was compared to that of its commercial counterpart, trihexyl(dodecyl) phosphonium chloride ( $P_{6,6,6,14}Cl$ ). A slight modification in the structure of the cation moiety showed a notable difference in their physicochemical properties. A shorter asymmetrical alkyl chain and a longer symmetrical alkyl chain of  $P_{8,8,8,12}Cl$  contribute to its low viscosity and their high hydrophobicity than that in  $P_{6,6,6,14}Cl$ , respectively. Lower mass transport barrier due to its low viscosity allows faster extraction on  $P_{8,8,8,12}Cl$ . Pt and Pd extraction was quick and followed by Rh extraction. Rh extractability was improved as the chloride concentration decreased due to the change in dominant chlorocomplex species as evidenced by the spectroscopic study. The extraction of the metals was proceeded according to the anion exchange mechanism and their extractability was strongly influenced by the chloride concentration. The extraction performance with  $P_{8,8,8,12}Cl$  was also consistent after several cycles of regeneration unlike its counterpart which showed a

significant decrease after the several cycles. This could be caused by the loss of the phosphonium cation, which was higher in  $P_{6,6,6,14}Cl$  than in  $P_{8,8,8,12}Cl$ . Thus,  $P_{8,8,8,12}Cl$  shows the potential for the use as an extraction solvent for PGMs, and the present results demonstrate advantages related to the properties that can be readily tuned by changing the molecular structure of the ionic liquid.

Chapter 3 focused on the recovery of Pd(II) and Rh(III) from the chloride leachate of an unused automotive catalytic converter. Separation of Pd(II) and Rh(III) was successfully achieved by adjusting the chloride concentration in the feed in order to change the dominant chlorocomplex species in the feed solution. The recovery of Pd(II) and Rh(III) was achieved by using  $CS(NH_2)_2$  and HCl, after removing co-extracted Fe(III) with  $Na_2SO_3$ . A spectroscopic study shows that reduction of Fe(III) to Fe(II) plays an important role. The whole process resulted in a high purity PGMs product, which is 99 and 95% for Pd(II) and Rh(III), respectively. Simple treatment of contacting  $P_{8,8,8,12}Cl$  with the high concentration of HCl was enough to regenerate the  $P_{8,8,8,12}Cl$ .  $P_{8,8,8,12}Cl$  also shows remarkable stability after going through the whole process since there is almost no changes in the structure of the phosphonium part of  $P_{8,8,8,12}Cl$ .

The actual practicability of  $P_{8,8,8,12}Cl$  in recovering PGMs from the actual waste automotive catalyst was investigated in Chapter 4. The spent automotive catalyst was leached under the acidic conditions and mild temperature of 343K. It was found that the acid concentration, temperature and leaching time significantly influenced the leaching efficiency, with the optimal conditions for leaching are 5 mol L<sup>-1</sup> HCl at 343 K for 24 hours. Extraction of Pt and Pd was achieved efficiently and both metals were selectively recovered through the stripping process. The Pt recovery was done with nitric acid while selective Pd recovery was achieved with combination of thiourea and low acid concentration. However, it was also followed with extraction of Cu, Zn, and Fe. Removal of Cu and Zn was achieved through complexation with  $H_2SO_4$  which has stronger affinity towards Cu and Zn. Extraction of Rh(III) was successfully done by dropping the chloride concentration and recovered by using a high concentration hydrochloric acid. Through the whole process, high purity of PGMs was obtained, which was 99, 99, and 98% for Pt, Pd, and Rh. The results demonstrate the potential of well-designed ILs as extraction solvents for recycling valuable metals, such as PGMs, from waste products, which will contribute to solving environmental issues.