

## Recovery of Palladium from a Mixture of Pt, Pd and Rh by Solvent Extraction

Kimberly S. Svalstad\*, Nam-Soo Kim\*\* and Kenneth N. Han\*

\*Department of Materials & Metallurgical Engineering  
South Dakota School of Mines and Technology

\*\* PGM Recovery Ltd.

Platinum group metals (pgm) are useful to many industries such as chemical, dental and medical, petroleum, refining, electrical and electronic, and automotive. Researchers at the South Dakota School of Mines and Technology and PGM Recovery Ltd. have developed jointly an environmentally sound and metallurgically efficient process for extracting these metals from secondary sources. Once these metals have been dissolved in the leach liquor, the individual metals mainly platinum, palladium, and rhodium, should be separated in order to recover the individual metals with high purity.

During this investigation, solvent extraction has been chosen as the method used to achieve the separation and extraction of platinum, palladium, and rhodium from the leach liquor. There were three solutions used throughout this procedure: 1) Synthetic solution (200 ppm Pt, 80 ppm Pd, 20 ppm Rh; 300 ppm Pt, 180 ppm Pd, 50 ppm Rh), and 2) Auto catalysts leach liquors (100 ppm Pt, 30 ppm Pd, 20 ppm Rh). The solvents investigated included Lix 84(2-hydroxy-5-nonylacetonphenone oxime in a mixture with 5-dodecylsalicyloxime), Lix 84-I, ACORGA CLX-50 (diester of pyridine 3,5 dicarboxylic acid), and di-hexyl sulfide.

The extraction values achieved using ACORGA CLX-50, Lix 84, and Lix 84-I were respectively Pt (25%, 0%, 0%), Pd (100%, 99.8%, 95.3%), and Rh (99.1%, 35.5%, 4.25%). The stripping processes for the Lix 84, and Lix 84-I were proven to be more involved than others. The solutions were required to be simultaneously heated and stirred. The percentages acquired through these processes yielded unsatisfactory results. The stripping procedure for the ACORGA CLX-50 was easier to execute, yet the percentage recovered from this process was also unsatisfactory.

Overall the di-hexyl sulfide has proved to be the most successful organic for this procedure. The average percent extracted for palladium was excellent with 99.9% - 100% with very little platinum and rhodium extracted. The ability of stripping palladium in ammonia solution was also found to be excellent.

### Introduction

The elite assembly of platinum group metals consists of platinum (Pt), osmium (Os), iridium (Ir), palladium (Pd), ruthenium (Ru), and rhodium (Rh). In this investigation however, platinum group metals (pgm) refers to only Pt, Pd and Rh, since extraction of these three metals will be discussed in this study. Pgm are often used in such industries as automotive (38%), electric and electronic (29%), dental and medical (9%), chemical (4%), and petroleum refining (5%).<sup>1</sup>

Every year about 45 million cars are retired to various junkyards worldwide.<sup>2</sup> About 15 million of which are attributed to the United States. If a process to recover the pgm from these automobiles could be utilized, significant resources could be recovered.

Currently, pgm are available from two types of sources, namely primary and secondary sources. There are three different primary sources available for pgm. These include gold ores, nonferrous metal sulfide ores (ex. Cu-Ni sulfide ores), and pgm sulfide deposits. Platinum group metals can also be extracted from secondary sources. This is provided most frequently through the discarding of used products such as printed circuit boards, auto-exhaust catalysts, computers, etc. Another secondary source would be the waste generated by

The availability of pgm is fairly limited but the demand is high, hence the need to recover them from both primary and secondary sources. Presently the metals are usually imported to the US in large quantities from sometimes economically and politically unstable countries.

A significant change in importation and use of pgm is not expected to occur any time in the near future. However, some companies have decided to incorporate small substitutions in their products. Some automotive companies have begun substituting Pd for Pt in their catalytic converters.<sup>1</sup> Such substitution of Pt by Pd has caused a sharp increase in the price of Pd in recent years. Pt is more resistant to sulfur and lead poisoning than Pd, however Pd is known to be useful for controlling emissions from diesel-powered vehicles.

Generally, pgm are extracted by concentrated HCl with Cl<sub>2</sub>, direct smelting of the concentrate in order to produce a pgm containing matte, or aqua regia, HCl/HNO<sub>3</sub>.<sup>3-5</sup> Extraction can be fairly expensive due to the inertness of this group of metals.<sup>6,7</sup> When these processes are used, some problems such as severe acid corrosion and a rather high acid consumption may also be encountered. In order to account for some of these problems, researchers at the U.S. Bureau of Mines

removing pgm from catalytic converters.<sup>8-10</sup> Their process uses cyanide in an autoclave at high temperatures and pressures. Some disadvantages of this process are a high consumption of the reagent, low percent recovery of rhodium, and the use of cyanide in order to carry out this process. New processes have been developed and patented by researchers at the South Dakota School of Mines and Technology (SDSM&T).<sup>11-14</sup> One process uses halogen salts, in an autoclave at high pressures and temperatures, to recover these metals from spent catalysts. This process is both environmentally sound and metallurgically efficient.

Three grades of catalytic converters can be recovered through this process.<sup>2</sup> Grade 1 consists of 2200 ppm of Pt, 200 ppm of Pd, and 300 ppm of Rh, Grade 2 consists of 1000 ppm of Pt, 200 ppm of Pd, and 100 ppm of Rh. Lastly, Grade 3 consists of 875 ppm of Pt, 250 ppm of Pd, and 30 ppm of Rh. The SDSM&T process consists of two phases. Phase 1 involved determining that the process would actually work. The process was indeed metallurgically efficient and environmentally sound.

In this investigation, attempts have been made to recover pgm from the leach liquor resulting from the SDSMT leaching technology. A special emphasis has been made to recover pure palladium from the leach liquor containing all three metals namely platinum, palladium and rhodium using solvent extraction.

## Literature Review

Researchers at SDSM&T have developed and patented a process for the removal of platinum group metals from spent catalysts. The original process developed by SDSM&T researchers utilizes halogen salts in an autoclave at high temperatures and pressures in order to leach the desired metals from spent auto-catalytic converters.<sup>11,14</sup> Excellent extraction recoveries of all three metals were obtained in such dissolution investigations. A simplified process flowchart of the SDSM&T extraction technology is shown in Fig. 1.

When all three pt-group metals are extracted in solution, there are many different ways to remove these metals from the leach liquor. These methods may include chemical precipitation using such chemicals as ammonium sulfide (Fig. 2) or any reducing agents, solvent extraction and electrowinning. When these metals are removed from the leach liquor, the mixture of

these metals are then subjected to metal separation to produce better than 99.95% pure individual metals. Traditionally, this is done by leaching the mixture of these metals in aqua regia and then subsequently precipitated chemically the individual metals.

Chemical precipitation occurs when an insoluble compound is formed through the addition of a chemical reactant to a liquid solution.<sup>15</sup> As shown in Fig. 2, silver (Ag) and gold (Au) are usually taken out of the system first, since the system favors to remove Ag as silver chloride (AgCl) and Au as elemental Au precipitated by reduction. This is possible because Au is the most noble metal of all of the metals present in the solution. At this stage, platinum is in four valence state and palladium in divalent state. Platinum is then extracted by the addition of ammonium chloride, with the final product being  $\text{Pt}(\text{NH}_4)_2\text{Cl}_6$ . Next palladium can be removed through the addition of sodium chlorate or other oxidants. Lastly, after Pt and Pd have been removed, Rh can be extracted. This is accomplished by adding zinc dust in order to produce cementation of the metal.

Solvent extraction is one of the widely used technologies in separating the individual metals from a mixture of many metals from solution. This technology has been used in separation of pgm in the past with success.<sup>16-22</sup> A number of investigations to separate palladium from platinum using solvent extraction have been carried out.<sup>23-26</sup>

In this study, it is intended to extract palladium preferentially by solvent extraction from the solution containing all three pt-group metals namely Pt, Pd and Rh. Solvent extraction is carried out by mass transfer between immiscible phases in which at least one phase is an organic liquid. Furthermore a solvent is the organic phase which dissolves the desired metal that is present in an aqueous solution. Since this process.

provided an easily executable procedure, it was decided that solvent extraction would be the most efficient way of separating Pt, Pd, and Rh. Furthermore, since Pd exhibits characteristics similar to Cu, organics that have been proven successful with Cu extraction were investigated.

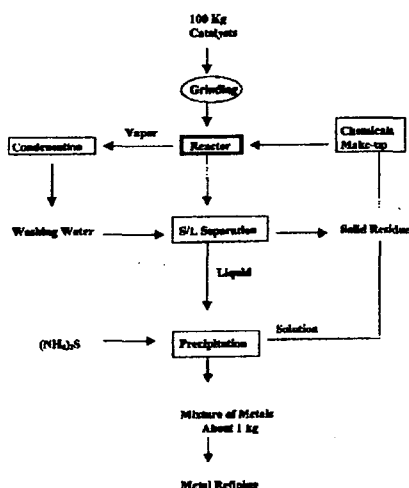


Figure 1. SDSM&T pgm extraction process flowchart.

### Experimental Procedure

Stock solutions were prepared by mixing known amounts of Pt, Pd, and Rh. One hundred ml of this solution, along with 60 ml of organic was poured into a 400 ml beaker. First solvent used to separate Pd from other metals was ACORGA CLX-50 (diester of pyridine 3,5 dicarboxylic acid). The organic used for this procedure was kerosene in which 3 cc of ACORGA CLX-50 was dissolved.<sup>7</sup>

Most of experiments for solvent extraction were carried out using a stock solution containing 200 ppm of Pt, 80 ppm of Pd and 20 ppm of Rh. However, a stock solution containing 300 ppm Pt, 180 ppm Pd and 50 ppm Rh was also used for various tests. All of these stock solutions were prepared by dissolving pure pt-group metals in aqua regia and diluted to the pH of the combined solution of about 1.

In addition, a number of leach liquors containing these three metals were also used to see the effect halogen salts on the solvent extraction performance. It should be noted that exact amounts of these metals in the stock solution are not critical. Exact values will be determined at the time of solvent extraction and the percentage of recovery will be determined more accurately at that stage.

There are two stages to this process: extraction and washing often known as stripping. The beaker containing 160 ml of solution was stirred vigorously via a magnetic stirrer. Periodically a solution sample of 10 ml of solution was drawn in order to determine the concentration of each metal in solution with respect to time. Also 2 ml of each 10 ml sample were diluted 10

times with distilled water. Chemical analysis was done using an AA (Atomic absorption spectrophotometer.) After the final sample had been taken, the remaining solution was poured into a separating funnel. This ensured a clean separation of aqueous and organic solutions.

The second stage of this process is washing. Washing allows for the stripping of Pd from the remaining organic. The remaining organic solution was taken and combined with 20%  $\text{NH}_4\text{OH}$  (20 ml of as received  $\text{NH}_4\text{OH}$  and 80 ml of distilled water). It should be noted that as received reagent grade  $\text{NH}_4\text{OH}$  solution contains 30%  $\text{NH}_4\text{OH}$  and 70%  $\text{H}_2\text{O}$ . The solution was stirred vigorously with a magnetic stirrer. Periodically, 10 ml samples were taken in order to establish a relationship between the concentration of the metal and time. Each sample was diluted as described above.

The next procedure is only a slight variation from the previously described procedure. The extraction process was identical to the first procedure (100 ml of synthetic Pt, Pd, Rh solution, 60 ml of organic), except that 5% Lix 84 (3 ml of Lix 84, 57 ml of kerosene) was used instead of the ACORGA CIX-50. Lix 84 is a 2-hydroxy-5-nonylacetonphenone oxime in a mixture with 5-dodecylsalicyl oxime. The 160 ml (Pt, Pd, Rh/ 5% Lix 84) solution was stirred vigorously and samples were periodically drawn. The remaining solution was poured into a separating funnel.

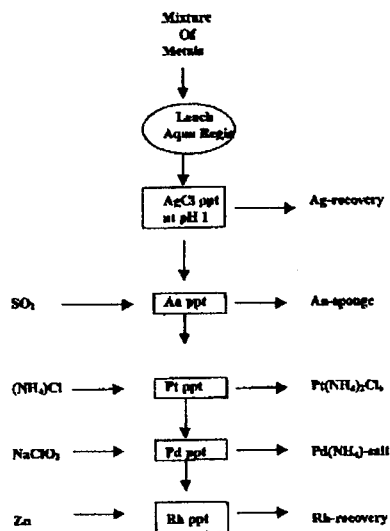


Figure 2. Typical flowchart for metal precipitation of pt-group metals.

The washing stage for the second procedure was also similar to the first procedure. Various trials of this stage were executed.

a.) The first trial was exactly the same as the previous washing stage. The remaining organic solution was taken and combined with 20%  $\text{NH}_4\text{OH}$  (20 ml of  $\text{NH}_4\text{OH}$ , 80 ml of distilled water). The solution was stirred vigorously.

b.) The remaining organic solution was taken and combined with 10%  $\text{NH}_4\text{OH}$  (10 ml of  $\text{NH}_4\text{OH}$ , 90 ml of distilled water). The solution was stirred vigorously. Periodically, 10 ml samples were taken and each sample was diluted for accuracy.

c.) The remaining organic solution was taken and combined with 100 ml of leaching solution. The solution was heated for 10 minutes or until the temperature reached  $90^\circ\text{C}$ , and stirred for 20 minutes. Heating was necessary because it was extremely difficult to wash ppm from the organic phase when the Lix group solvents were used.

The third procedure was also similar to the others, except that a different organic was used. The organic used for this procedure was Lix 84-I (100 ml of kerosene, 3 ml of Lix 84-I). There were two stages, extraction and washing, to this trial as well. Two hundred ml of solution was poured into a 400ml beaker (100 ml of the real Pt, Pd, and Rh solution, 100 ml of organic). The solutions were stirred vigorously via a magnetic stirrer, and samples were periodically drawn. The remaining solution was poured into a separating funnel.

The washing stage was also similar. The remaining organic solution was taken and combined with 60 ml of HCl and 40 ml of distilled water. The solution was stirred vigorously, while simultaneously the solution was heated at a temperature of  $50^\circ\text{C}$ . Periodically, 10 ml samples were taken and each sample was diluted for accuracy. After the final sample had been drawn, the solution was transferred to a separating funnel. An AA analysis was performed on the samples collected throughout this procedure.

The organic di-hexyl sulfide was used throughout the fourth procedure. The two stages, extraction and washing, were also present with this procedure. Many trials were performed using this organic. The extraction stage was similar for each trial; the only difference being the concentration of organic used. The first two trials used 3 ml of di-hexyl sulfide/97 ml of kerosene, and the remaining trials with this organic used 5 ml of di-hexyl sulfide/95 ml of kerosene.

The washing stage was also similar to the previous stages. The remaining organic solution was taken and combined with a strong ammonia solution. Depending on which trial was in progress, different conditions were

used. Typically 20%  $\text{NH}_4\text{OH}$  solution was used to wash the organic phase. Periodically, 10 ml samples were taken and each sample was diluted for accuracy. After the final sample had been drawn, the solution was transferred to a separating funnel. An AA analysis was performed on the samples collected throughout this procedure.

## Results and Discussion

Figures 3-8 show typical graphical representations of the actual values that were obtained during the AA analysis for Pt, Pd, and Rh. Various organics were investigated including ACORGA CLX-50, Lix 84, Lix 84-I, and di-hexyl sulfide. Results for both the extraction and stripping stages with respect to each metal are contained in this investigation.

Fig. 3 shows the ppm up-take by solvent. As can be seen in this figure, the initial concentration of Pt was 200 ppm and about 40 -50 ppm of Pt was taken up by CLX-50 after 20-60 minute contacting time. This represents about 75% recovery of Pt by this solvent. However, the recovery of Pd was 100% after 20 min and that of Rh was nearly zero. Washing of Pd from the organic phase with ammonia solution was found to be quite efficient as shown in Fig. 4.

Since palladium is chemically very similar to copper and copper is effectively extracted using Lix group solvents, Lix 84 and Lix 84-I were tested to extract palladium from the stock solution. As can be seen in Fig. 5, the recovery of palladium was excellent, while those of platinum and rhodium were not as good. However, it was found that washing of the organic phase was extremely difficult. At room temperature, the washing of these metals was found to be almost impossible even after 2-3 hours of washing with ammonia solution as well as hydrochloric acid. Therefore, the organic phase was heated to  $80-90^\circ\text{C}$  to facilitate the washing process. As can be seen in Fig. 6, only less than 4 ppm of palladium was washed off from the organic phase after washing it at  $90^\circ\text{C}$  for one hour. When Lix 80-I was used, about 20 ppm of palladium was washed off with a solution containing 50% HCl.

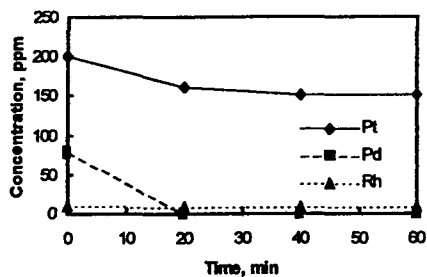


Figure 3. Concentration of Pt, Pd and Rh as a function of time when ARCOGA CLX-50 was used as an extractant.

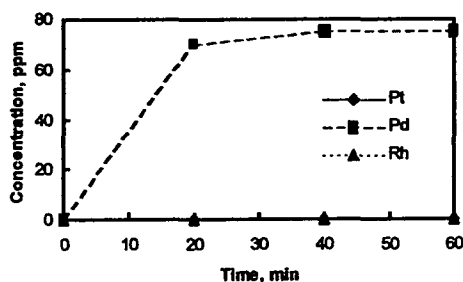


Figure 4. Concentration of Pt, Pd and Rh in the aqueous phase as a function of time when the organic phase was washed with 20% NH<sub>4</sub>OH.

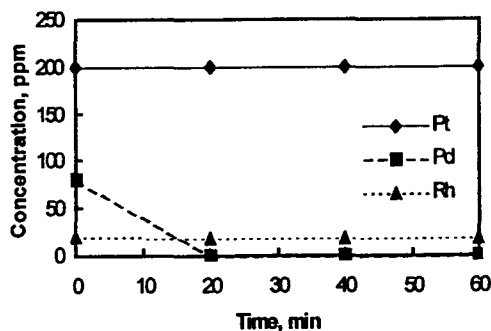


Figure 5. Concentration of Pt, Pd and Rh as a function of time when Lix 84 was used as an extractant.

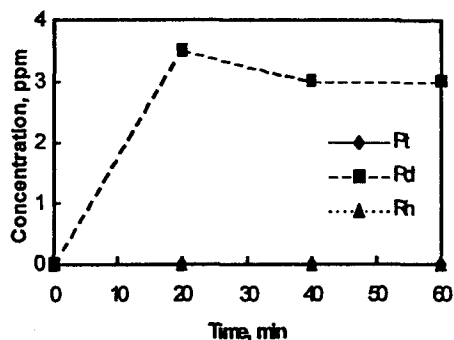


Figure 6. Concentration of Pt, Pd and Rh in the aqueous phase as a function of time when the organic phase was washed with 50% HCl solution at 80°C.

The final organic that was tested was di-hexyl sulfide. The average percentages of metals extracted were found to be typically 95% of Pd, 1-2% of Pt and 10-20% of Rh. However, at the washing stage with ammonium hydroxide solution, nearly 100% of Pd was washed off, while nearly none of Pt and Rh was washed from the organic phase. These are shown in Figs 7 and 8 for extraction and washing, respectively.

In order to see the effect of halogen salts on the extraction behavior as well as washing, leach liquor was also used to test the effectiveness of di-hexyl sulfide. The results were almost identical to those found in Figs. 7 and 8.

After this determination had been made, equilibrium studies were performed on each of the metals (platinum, palladium, and rhodium). The purpose of performing these equilibrium studies were to calculate the distribution coefficients of these metals. The distribution coefficient,  $D$  is defined by:

$$D = \frac{(w - w_1)/V_o}{w_1/V_a}$$

where  $w$  represents original weight of the solute in the aqueous phase,  $w_1$  represents final weight of the solute in the aqueous phase, and  $V_o$  and  $V_a$  are respectively the volume of the organic phase and aqueous phase. The amount of rhodium extracted by di-hexyl sulfide was practically zero and therefore the distribution coefficient of rhodium was not able to determined.

The distribution coefficients were found to be 0.0245 and 470.3 respectively for Pt and Pd.

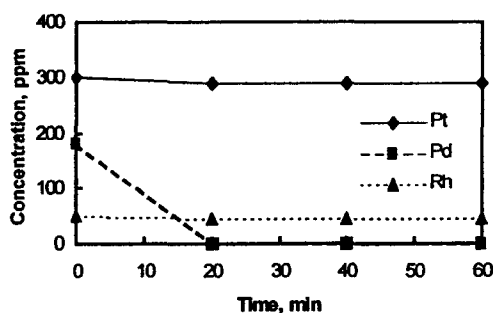


Figure 7. Concentration of Pt, Pd and Rh as a function of time when di-hexyl sulfide was used as an extractant.

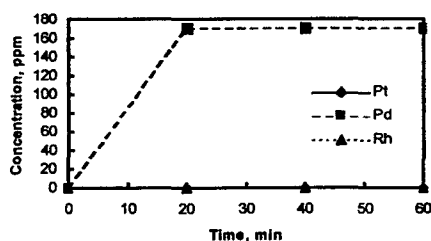


Figure 8. Concentration of Pt, Pd and Rh in the aqueous phase as a function of time when the organic phase was washed with 20%  $\text{NH}_4\text{OH}$  solution.

## Conclusions

There are several different methods of separation for metals from leach liquors. Three of these methods are chemical precipitation, electrowinning, and solvent extraction. Of these methods, chemical precipitation is often a more difficult procedure, yet a large portion of research is carried out using chemical precipitation. Electrowinning doesn't yield a pure separation for Pt-group metals, which was critical to this project. Like chemical precipitation, solvent extraction is also widely used throughout industry. Solvent extraction offers a relatively simple process to carry out that still produces a pure separation. For these reasons, solvent extraction was chosen as the method of separation for the current research.

Several organics were researched that could possibly be used to separate platinum, palladium, and rhodium from the leach liquor. The solvents investigated were ACORGA CLX-50 (diester of pyridine 3,5 dicarboxylic acid), Lix 84 (2-hydroxy-5-nonylacetonphenone oxime in a mixture with 5-dodecylsalicyloxime), Lix 84-I, and di-hexyl sulfide ( $\text{C}_6\text{H}_{13}\text{-S-C}_6\text{H}_{13}$ ). Each procedure

was carried out with a two-stage process. The first stage was extraction, followed by the washing or stripping stage. The extraction process was easily executed for each organic, however this was not the case for the washing. The process for the ACORGA CLX-50 and the di-hexyl sulfide was still simple, but the Lix 84 and Lix 84-I presented a more involved process.

Overall the only organic that produced satisfactory results for both stages of the process was di-hexyl sulfide. Excellent extraction and washing behavior were observed for palladium using di-hexyl sulfide resulting in the distribution coefficient value of 470 for palladium and 0.0245 for Pt and practically zero for Rh.

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