Recovery of rhodium from secondary raw materials for usage in electronic devices

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This paper presents the method of rhodium purification and separation from other platinum and non-precious metals. Separation of non-precious metals from rhodium acid solution was carried out using ion exchange. Process of solvent extraction was carried out to separate Pt (IV) and Pd(II) from rhodium by using TBP dissolved in petroleum ether. Platinum and palladium stripping was carried out with distilled water. Flow sheet of the process of pure rhodium winning of the 98.97% purity is presented in this paper. Obtained rhodium is convenient for usage among other purposes in electronic devices.

1. Introduction

The high cost of platinum and its extensive use in catalysis, electronic and electric devices, jewelry, medical instruments, dental equipment and space materials has made the recovery of this metal from spent sources a viable and cost effective alternative. Platinum demand in 2003/2004 was higher than the world supply [1]. Although the demand decreased 2.3% in 2008, platinum supply decreased 4.2% [2]. Gross platinum demand was forecast to rise by 11 % to 7.56 million oz in 2010. Recycling of platinum in the autocatalyst, jewellery and electrical sectors was expected to increase by 31 % to 1.84 million oz. Gross demand for palladium was set to rise by 15 % to 8.94 million oz in 2010 on the back of strong automotive and industrial demand. Recovery of palladium from spent autocatalysts was forecast to increase by 37 % to 1.32 million oz as a higher palladium price and car scrappage schemes stimulated recycling.[3] The rhodium market was forecast to be in a modest surplus of 79,000 oz, with gross demand climbing by 22 % to 876,000 oz as recovery in autocatalyst and industrial demand took place [4].

The active components of automotive catalytic converters, which have been widely used since 1975 platinum-group metals (PGMs) [5] and especially platinum, palladium, and rhodium.

The total content of PGMs in spent catalysts, in automotive catalytic converters is in the range of 0.5 to 2.0 grams per pound of catalyst, and from 4-9 grams per catalyst depending on the size of cars. Platinum metals, because of its catalytic properties and resistance to high temperatures, are used in automotive catalytic converters all over the world and demand for them keeps growing. In 2001, 37% of world demand for Pt, 72% for Pd and 85% for Rh, was for their usage in automotive catalytic converters. Due to the high cost and scarcity of platinum

metals, their recovery eg. extracting from spent automotive catalysts has enormous significance.

Recycling of platinum metals from automotive catalysts has steadily increased over the past two decades and it is considered that this trend will continue in the future.

The physical and chemical properties of these metals are very similar so, it is difficult to separate these metals in metallurgy [6, 7, 8].

In the early nineties, developed countries have begun seriously engaging in problem of PGMs extracting from exhausted catalysts. Upon first procedure, initial raw materials are directly melted with metal collectors (usually cupellation with copper), anodes are casted, then electrolysis is done and than obtained anode slime is treated chemically to get platinum metals. The other procedure to get PGMs is to dissolve raw material in strong acids, usually aqua regia. Various separation techniques such as solvent extraction, ion exchange, cementation, etc.., are used for the separation and purification.

Extraction of metals with extractants dissolved in organic solvents has been gainin importance since the 1990s. It has been reported that extraction (and separation) of PGMs by liquid–liquid extraction (LLE) is a very difficult task because their chemistry is very similar [9].

Literature survey revealed that the extraction of PGMs, in particular of Pd and Pt, have been reported extensively by many researchers from chloride media, mostly from synthetic solutions at low metal concentrations employing extractants such as Amines[10-16], Cyanex 921[17, 18], Aniline [19], 2-hydroxy-4-sec-octanoyl diphenyl-ketoxime [20], dibutyl sulfoxide [21], N,N dimethyldithiocarbamoylethoxy [22], TBP [23,24,25], Nonylthiourea [26], Oximes [27].

In commercial processes, PGMs are dissolved using concentrated chloride media. Rhodium forms octahedral

aqua chloride complexes of the general formula $[RhCl_x(H_2O)_{6-x}]$ ($X \geq 5$) in those solutions, which are nearly impossible to extract [28, 29].

The present investigation examines the possibility of separating platinum, palladium and rhodium from rhodium acid solution by tributyl phosphate as an extractant. In order to define optimal conditions of the whole process, it is necessary to remove the impurities, to investigate different aqueous organic phase ratios and different contact times of organic and aqueous phase. Work examines include the use of distilled water as stripping agent of metal from organic phase.

2. Experimental work

2.1. Apparatus and reagents

All analytical measurements of platinum (IV), palladium and rhodium (III) in the aqueous phases were obtained using inductively coupled plasma atomic emission spectrometer (ICP-AES). Detection limit for ICP-AES is $<0,0001 g$ Pt/dm^3.

Concentration of free hydrochloric acid in rhodium acid solution was 6M [16]. Concentration of PGMs in rhodium acid solution was: Rh - 0,292; Pt- 0,0017 and Pd- 0,009 mg/dm^3.

The organic solution was prepared by dissolving tributyl phosphate TBP ($(CH_3CH_2\ CH_2\ CH_2O)\ PO$) in petroleum ether in ratio 1: 3 (25% solution of TBP). Due to the high viscosity, which value is closed to water viscosity, TBP ($0,79 \cdot 10^3$ kg/m^3) was applied diluted with an inert organic solvent (kerosene, hexane, petroleum ether). Undiluted, it would be in a form of emulsion and it would be difficult to separate it.The loaded organic phases were stripped with distilled water.

2.2. Preparation of solution for solvent extraction

Automotive catalysts contain a low percentage of platinum metals (Pt, Pd and Rh), so they have to be processed in several stages:
 - Preparation of materials

 - Smelting process to accomplish cupellation of platinum metals in copper and casting of anodes with increased content of platinum metals
 - Electrolysis of anodic copper with increased content of platinum metals
 - Anode slime processing to separate and refine platinum metals (PGMs)

After platinum metals concentrating in anodic slime, refining process follows to separate platinum, rhodium and palladium to win pure metals of commercial quality.

Platinum and palladium are got by chemical methods but some quantity of those metals always remains in rhodium acid solution. It is very difficult to remove them by chemical methods and rhodium utilization is under 50%.
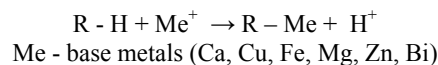
Rhodium acid solution except platinum metals includes a low percentage of base metals.

Chemical composition of rhodium acid solution including impurities-base metals (Ca, Cu, Fe, Mg, Zn, Bi) was obtained using inductively coupled plasma atomic emission spectrometer and the results are shown in Table 1.

PGMs separation from base metals (Ca, Cu, Fe, Mg, Zn, Bi) was done by cation exchange from chloride solutions. The most effective separation of platinum metal from base metals ions was achieved by absorption on a strong acidic cation exchange resins.

In this experiment, cation exchange resin Ambrelite IR 120 was used. The pH value in the solution was 2.

Absorption mechanism of base metals at very acidic ion exchangers is carried out according to the following mechanism:

$$R - H + Me^+ \rightarrow R - Me + H^+$$
Me - base metals (Ca, Cu, Fe, Mg, Zn, Bi)

Contact time of solution and cation exchange resins was 30 minutes. Chemically analysis of the ion exchange solution confirmed that the base metal ions had been absorbed by the resin. Platinum metals remained in solution.

Table 1. Chemical composition of rhodium acid solution before ion exchange.

Elements	Rh	Pt	Pd	Ag	Ca	Cu	Fe	Mg	Zn	Bi
g/dm³	0,44	0,0029	0,018	0,003	0,019	0,021	0,007	0,01	0,0019	0,0012

2.3. Solvent extraction procedure

Suitable volumes of aqueous (100 ml) and organic phases were contaced for 5 min (initial experiments showed that equilibrium was reached in 1 min) in glass separating funnels (max. volume 200 ml). All the experiments were conducted at room temperature ($25\pm1°C$). The concentration of the metal in the organic phase was calculated from the mass balance. These results were further used to estimate the extraction efficiency of metal.

Extraction percentage of Pd(II) or Pt (IV) was calculated according to Eq.:

$$\%E\ (extraction) = \frac{[M]_{(o)}}{[M]_{(a,total)}} \times 100$$

where $[M]_{(o)}$ is metal ion concentration of organic phase, $[M]_{(a,total)}$ is the metal concentration of stock solution before extraction.

Distribution coefficient (D) of metal ion in organic and aqueous phase was calculated to Eq.:

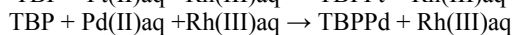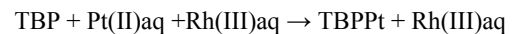$$D = \frac{[M]_{(o)}}{[M]_{(a)}} = \frac{E}{1-E}$$

where $[M]_{(a)}$ is residual metal concentration of aqueous phase after extraction , $[M]_{(o)}$ is metal ion concentration of organic phase.

Separation factor β $_{Pt/Pd}$ of Pt and Pd was expressed as:

$$\beta_{Pt/Pd} = \frac{D_{Pt}}{D_{Pd}} = \frac{E_{Pt}\ (1-E_{Pd})}{E_{Pd}(1-E_{Pt})}$$

Pt(II) and the Pd(IV), are extracted into organic phase, while Rh(III) remains in the aqueous phase. Rhodium does not extract, but remains in solution.

So, the mechanism of extraction with TBP can be represented by the following equations:

TBP + Pt(II)aq +Rh(III)aq → TBPPt + Rh(III)aq
TBP + Pd(II)aq +Rh(III)aq → TBPPd + Rh(III)aq

Used organic phase was contacted with eqal volume of distillated water for 5 min in order to regenerate extractant.

3. Results and discussion

3.1. Influence of contact time on extraction of platinum and palladium

Changes of concentration in solution were observed after different duration of contact between the organic and aqueous phases: 1, 3, 5, 10 and 15 minutes. It can be concluded that the extraction equilibrium of Pd, Pt and Rh can be established within 1 min because the extraction percentage of Pd, Pt, Rh was constant for the contact time of 1,3,5,10 or 15 min [17,21]. We determined that the optimal extraction time in all experiments was 5min.

3.2. Influence of phase ratio on extraction of platinum (IV) and palladium (II)

The same volume (100ml), the same initial composition of solution Rh – 0,292; Pt- 0,0017 and Pd-0,009 mg/dm^3 and the same HCl concentration, were applied in experimental work to determine the optimal ratio of organic and aqueous phase for separation of platinum and palladium from the rhodium acid solution. Only the volume of the organic phase has been changed.

This way six different ratios of aqueous and organic phases were applied in experiments: A/O=1:05; A/O=1:0,56; A/O=1:0,75; A/O=1:1; A/O=1:1,25; A/O=1:1,5. The duration of each extraction was 5 minutes. The results are shown in Fig. 1. The Fig. 1 shows that the increase of aqueous and organic volume degree causes the increase of platinum and palladium extraction percentage. As it can be seen in the Fig. 1, platinum extraction percentage reaches a maximum value of 94.11%, while the palladium extraction percentage significantly increases but reaches much lower maximum value of 50%.
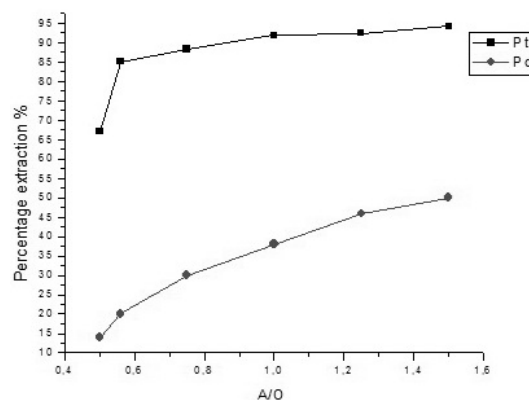

Fig. 1. Effect of phase ratio on the extraction of Pt and Pd.

3.3. Extraction isotherm

Feed solution and 25% TBP were in contact at different A:O phase ratios: 1:05; 1:0,56; 1:0,75;1:1; 1:1,25; and 1:1,5. Platinum concentrations in organic and aqueous phase were observed during all these experiments and used to obtain the extraction isotherm. This isotherm was used to find out theoretical number of stages and possibility of enriching Pt concentration in the loaded organic phase during extraction stage [30].

From the extraction isotherm, it can be seen that the Pt extraction efficiency of 94.11% is achievable in the fourth stage at A/O phase ratio of 1:1,5. From the results, shown in Table 2, it can be concluded that the optimal volume ratio of organic to aqueous phase is A:O=1:1, because the efficiency of aqueous phase is A:O=1:1, because the efficiency of extraction process is higher when the values of aqueous and organic phases ratios are smaller. Comparing with phase ratio A:O=1:1.25 and A:O= 1:1.5, there is no significant increase in extraction efficiency but, extractant consumption is much higher. To reduce the volume of organic phase used in the extraction process, due to define the extraction parameters for further experimental research, the experiments were carried out with the phase ratio A:O=1:1. TBP shows complete selective separation of Pt from Rh. Along with the extraction of platinum, the extraction of palladium is carried out too, but not completely. So, TBP can be used

as extractant for palladium, but under different conditions of extraction, which in this work are not investigated. The extraction efficiency of palladium increases with increasing of water and organic phase ratio. Maximum of the 50% of palladium was extracted with a volume ratio of aqueous and organic phases A: O = 1:1.5.

Table 2. The dependance between extraction efficiency and aqueous and organic phase ratio.

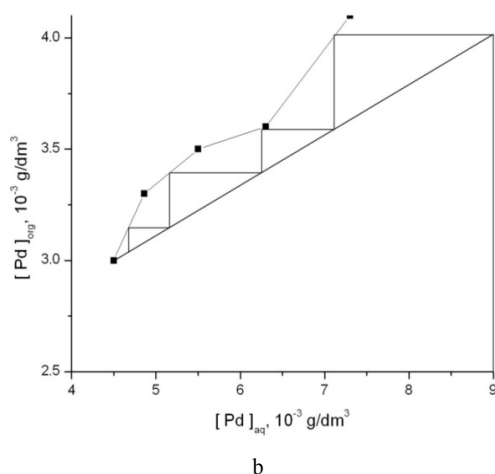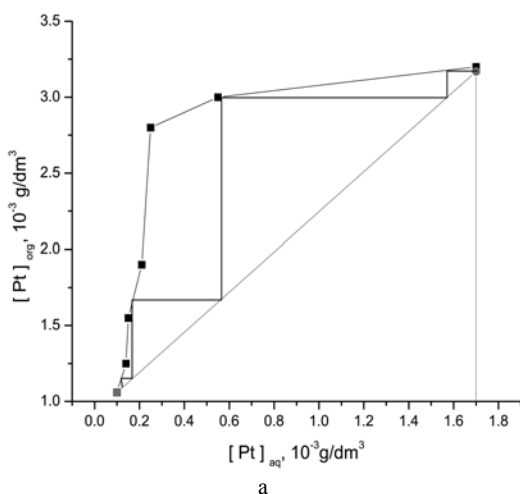| Extractant	Volume ratio A:O	Extraction efficiency (%)	
		Pt	Pd
25% TBP+ petrolether	1:0.5	67	10
	1:0.56	85	20
	1:0.75	88.23	30
	1:1	91.76	38
	1:1.25	92.35	46
	1:1.5	94.11	50

a

b

Fig. 2. Extraction isotherm for Pt(a) and Pd(b).

Fig. 2 shows that the maximum extraction efficiency of the 50% of palladium is achieved after the fourth stage of extraction. However, it is much lower value compared with accomplished extraction efficiency of platinum, which is 94.11%, after the fourth stage of extraction.

The separation factor between platinum and palladium was calculated using the relation of Pt and Pd distribution ratios It is a measure of the system ability to separate two metals. The results are shown in Table 3.

Table 3. Separation factor for Pt and Pd.

A:O	D_{Pt}	D_{Pd}	$\beta_{Pt/Pd}$
1:0,5	6,8	1,13	6,01
1: 0,56	7,6	1,22	6,22
1: 0,75	8,5	1,42	5,98
1: 1	11,3	1,55	7,29
1:1,25	13,07	1,87	6,89
1: 1,5	17	2,5	12,31

It can be observed from the data that, when the volume ratio of aqueous and organic phase increases, the distribution coefficien increases too. The difference is that the values of separation coefficients for palladium have lower values than platinum separation coefficients.

The data in Table 3 shows that the value of the separation factor of platinum and palladium increases with the increase of aqueous and organic phase ratio. The greatest separation factor for platinum and palladium is 12, ie. the best separation of platinum and palladium from rhodium acid solution is when the volume of organic phase is 1.5 times higher than the volume of water phase. Despite above mentioned facts, when the ratio of aqueous and organic phase is 1:1, the separation factor $\beta_{Pt/Pd}$ has a high value of 7.29, so we can conclude that the optimal ratio of organic and aqueous phases was A:O = 1:1 for platinum and palladium separation from rhodium acid solutions at a concentration of 6M HCl.

In every commercial extraction process, it is important to regenerate extractant and reuse for further extraction experiments.

Different solutions, as the combination of thiourea and HC [25] or thiosulphate [12], have been used for regeneration of the extractant TBP.

Stripping of Pt from organic phase was carried out with distilled water. Contact time between water and organic phase was 5 min. After the phase separation liquid phase was chemically analyzed by using inductively coupled plasma atomic emission spectrometer (ICP-AES). Compared to other stripping reagents, advantage of distilled water was the regeneration efficiency of organic solvents and it is more economic.

3. 5. Flow sheet of processes for the purification of the rhodium acid solution

The procedure of rhodium acid purification from the traces of platinum and palladium, in order to obtain pure

rhodium was successfully done by combining several separate procedures. Using a combination of cation exchange, where the complete absorption of non-precious metal ions (Ca, Fe, Mg, Zn, Bi), is carried out by the resin Amberlite IR120, and process of solvent extraction, when platinum and palladium are separated with TBP dissolved in petrol ether, is possible to obtain rhodium of the purity of 98.97%.

Table 5 gives the values of the obtained rhodium purity in percents   (degree of refinement) in dependence of aqueous and organic phase volume ratio (A / O = 1:0,5-1:1,5) during solvent extraction, while other process parameters were constant. The duration of the phases contact was 5 minutes, the concentration of Rh - 0.292 mg/dm^3, Pt- 0.0017 mg/dm^3 and Pd-0.009 mg/dm^3. The concentration of HCl was 6 M.
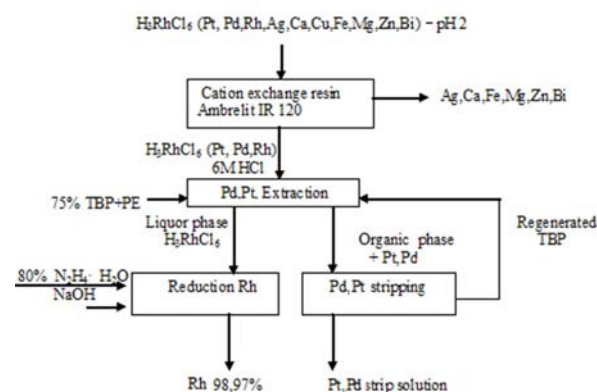

Fig. 3. Flow sheet of the process for the solvent extraction separation and recovery of Pd, Pt and Rh from rhodium acid solution.

The Table 4 shows that the most purified solution is when organic and aqueous phase ratio is (A / O): 1:1.5. The reached purity of rhodium is 98.97%. After purification of rhodium acid solution from non-precious and precious metals, follows the reduction of rhodium with 80% $N_2H_4\cdot H_2O$ in basic conditions with warm saline. Rhodium, obtained by this procedure, is of the maximum purity 98.97%.

Table 4. Values of the obtained purities of rhodium for different aqueous and organic phase ratios.

Phase ratio(A/O)	1:0,5	1:0,56	1:0,75	1:1	1:1,25	1:1,5
Rh %	97,37	97, 55	97,82	98,00	98,34	98,97

4. Conclusion

1. Removal of non-precious metals from rhodium acid solution (pH 2) is possible using ion exchange on strong acidic ion exchangers type Ambrelite 120 IR.
2. TBP shows complete selectivity for platinum and partly for palladium in
3. rhodium acid solution containing 6M free hydrochloric acid. Extraction efficiency of platinum reaches value of 94.11%. The extraction of palladium is carried out parallely with platinum extraction. The max. extraction efficiency of palladium was 50%.
4. The optimal contact time between the organic and aqueous phase was 5 minutes. The reaction is instantaneous and equilibrium is achieved after only 1 minute.
5. Optimal ratio of aqueous and organic phase of platinum and palladium extraction is 1:1, considering that the efficiency for this ratio was 91.76%.
6. This paper presents a high efficiency of stripping by distillated water. Platinum and palladium stripping was carried out at the same time. Stripping efficiency of the both of themis 98%.
7. Rhodium of the purity of 98.97% was obtained by applying the procedure presented in this paper.

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