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STUDY OF PLATINUM TRACES BEHAVIOR DURING HIGH PURITY RHODIUM WINNING BY SOLVENT EXTRACTION

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ABSTRACT
Research, showed in this paper is continuance of the previous investigations of PGMs (Pt, Pd, Rh), winning from spent automotive and catalyst from chemical industry. Platinum was obtained as a by-product in the process of high purity rhodium winning from rhodium acid solution by solvent extraction. TBP (tri-n-butyl phosphate), diluted in petroleum ether, was used as extraction agent. Different aqueous /organic phase ratios were used in experiments: 0,8:1; 1,6:1; and 0,4:1. All parameters of solvent extraction were determined based on experimental work. Changes in platinum concentrations in aqueous and organic phases were observed during experimental work. The best Pt extraction percentage, 99,51% was at A/O ratio 0,4:1.
Keywords: Platinum, solvent extraction, extraction percentage

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. This metal is also a very rare element in Earth's crust; the worldwide reserves are concentrated in only two regions, Siberia and South Africa.
Worldwide efforts are being made to recover and refine palladium (Pd) and platinum (Pt) from various spent materials.
Recovery of PGMs are reported by classical precipitation methods [1,2] with a relatively poor selectivity, numerous unit operations, recycle streams and refining steps. On the other hand, hydrometallurgical leaching followed by solvent extraction separation of metals offers a number of advantages over the classical precipitation methods due to their higher selectivity, scrubbing step to achieve high metal purity, and complete removal of metals by multi-stage extraction steps [3].
Extraction of metals with extractants dissolved in organic solvents has been gainin importance since the 1990s. 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 TBP, amines, oximes, thio-phosphoric acid, phosphonic acid, etc. There is no report on separation and recovery of Pd and Pt from hydrochloric acid leach solutions of spent automobile catalysts
The extraction study of platinum metals with organophosphorus extractants has been reported by different authors [1-4].
This paper presents the separation of platinum as a by-product during purification of rhodium acid solutions of Pt and Pd traces using solvent extraction in order to obtain rhodium of commercial quality.

2. EXPERIMENTAL

All experiments were carried out in a closed type reactor with electrostirrer. Measurements of elements concentrations in the rhodium acid solutions were done on atomic emission spectrometry with inductively coupled plasma (ICP-AES). ICP-AESC detection limit was < 0,001 g Pt/dm^3. All experiments were conducted at room temperature.

TBP ($CH_3CH_2\,CH_2\,CH_2O$)PO in petrol ether rated 1: 3 (25% solution TBP), was used as extractant. Due to high viscosity, TBP (0,79·103 kg/m^3), is commonly applied diluted with some of organic dissolvent (kerosene, hexane). Stripping was done with aqua bidestilata

Process of ion exchange was done before the solvent extraction in order to remove all base metals which would disturb further purification process. Cationic exchange was carried out by using ion exchanger Ambrelite IR 120. Using atomic emission spectrometry with inductively coupled plasma (ICP-AES), it was confirmed that all non-precious metals had been adsorbed on this resin after ion exchange. Only PGMs metals were left in the solution.

Solutions which contain 6 mols of HCl were used for experimental laboratory work of Pt solvent extraction from the rhodium acid solutions. Optimal time of extraction duration was 5 min. Extraction was carried out. Research has been carried out with tree stock solutions of a different platinum content RI – 0.0035 g/dm^3 Pt; RII – 0.013 g/dm^3 Pt; RIII – 0.205 g/dm^3 Pt.

The rates of aqueous and organic phase were different in experiments RI- A/O was 0,8: 1; RII- A/O was 1,6:1; RIII- A/O was 0,4: 1

3. RESULTS AND DISCUSSION

Mechanism of the platinum extraction with already mentioned extractant (TBP+PE), from rhodium acid solution was done in our previous work [8].

Optimal time of extraction duration, ie. optimal time of contact between the aqueous and the organic phase was 5 minutes. After 5 minutes, the influence of time is not of any importance, because the reaction is instantaneous and ends after only 1 minute [5, 6]. .

According to the literature, the optimal concentration of free hydrochloric acid for the process of platinum solvent extraction, is in the range of 4-6 M [7]. Dependence between changes in Pt concentrations and the stage of extraction and different rates of aqueous and organic phase were observed during experimental work. Results are shown in the Figures 1, 2 and 3.

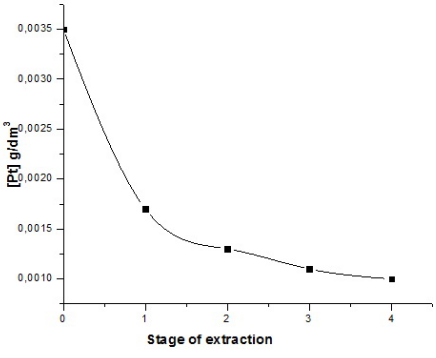

Figure1. Changes of the Pt concentration vs stage of the extraction (A/O = 0.8:1)

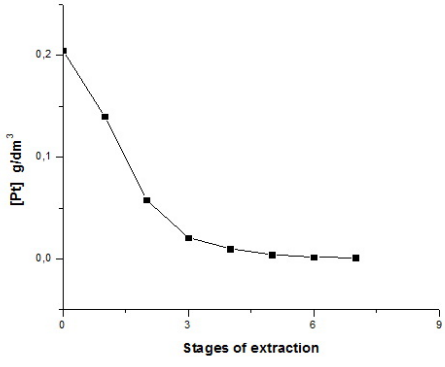

Figure 2. Changes of the Pt concentrations vs stage of the extraction (A/O=0.4 :1)

When the aqueous / organic phase rate was 0,8 : 1 (RI), solvent extraction was carried out in 4 stages. Curve shows (Fig1.), that the most intensive reaction of Pt extraction was in the first stage, and the concentration decreased from initial to the value of 0,0017 g/ dm^3 in aqueous phase.. Decrease of the Pt concentration in aqueous phase, in following extraction stages was carried out uniformly and slowly. After the fourth extraction stage, the concentration of platinum in the purified solution was 0.001 g/ dm^3 (apparature detection limit).. The concentration of platinum in the solution marked as RIII was significantly higher than in the other two solutions, 0.205 g/dm^3, and in accordance with that,

the extraction was carried out at seven stages. Curve in Figure 2 shows that the trend of Pt concentration decrease has gone uniformly.

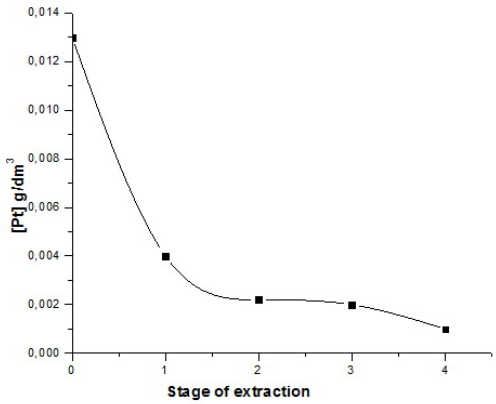

Figure 3. Changes of the Pt concentration vs stage of the extraction (A/O=1.6:1)

Table1. Obtained extraction percentage for different organic and aqueous phase

Stage	Extraction efficiency %		
	O/A	O/A	O/A
	1 : 0,4	1 : 0,8	1 : 1.6
1.	31,7	51,42	69,23
2.	71,70	62,85	83,00
3.	89,75	71,42	84,6
4.	95,12	**88,43**	**92,3**
5.	97,90		
6.	99,12		
7.	**99,51**		

Solvent extraction was carried out in four stages during work with stock solution marked as RII. The most intensive extraction was at the first stage, what can be seen in Figure 3, when initial concentration had decreased at value of 0,004g/dm^3 .

Analyzing the curves in the diagrams, it can be concluded that the decrease in Pt concentration proceeded in a similar way to cases where the ratio of aqueous and organic phases was 0.8:1 (RI) and 1.6:1 (RII). After a sharp drop of concentration in the aqueous phase during the first stage of extraction, watching the curves in the diagrams, it can be noticed no changes in concentrations during the second stage. In fact, the analysis shows that one leads to a slight fall of concentration, so it is almost unnoticeable on the diagrams (Fig.1 and Fig.3). In both cases the initial concentration of platinum in solution was significantly lower than the solution RIII, which was 0.205 g/dm^3.

The highest extraction efficiency of platinum has been achieved at aqueous organic phase ratio 0.4: 1 (RIII), when the realized extraction efficiency was 99.51%, which is consistent with the opinion that the higher aqueous organic phase ratio is better for a larger quantity of metal transition from water into organic phase. [3

At phase ratio A / O = 0.8 / 1 (RI) the total extraction efficiency was 88.43%, while at the phase ratio of A / O = 1.6 / 1 (RII), the extraction efficiency was 92.3%.

Analyzing the accomplished extraction efficiencies trough stages, it can be seen from table 1, that the highest extraction efficiency was achieved in solution with the A / O ratio of 1, 6 / 1 (RII), during the first stage. The same situation occurs in the second stage of extraction, where the extraction efficiency was 83% for the same stock solution. The highest extraction efficiencies were achieved for the case where the platinum initial concentration in the aqueous phase was highest 0.205 g/dm^3, and the ratio of A / O = 0.4: 1 (RIII), during third and fourth stage of extraction.

4. CONCLUSIONS

Platinum was obtained as a by-product in the process of high purity rhodium winning from rhodium acid solution by solvent extraction. TBP (tri-n-butyl phosphate), diluted in petroleum ether, was used as extraction agent. Stock solutions with different Pt initial concentrations and aqueous organic phase rfatios were used in experimental work. The highest extraction efficiency of platinum has been achieved at aqueous organic phase ratio 0.4: 1 (RIII), when the realized extraction efficiency was 99.51%.

5. ACKNOWLEDGEMENTS

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