

SEPARATION OF PALLADIUM AS A BY-PRODUCT IN OBTAIN HIGHT PURITY RHODIUM BY SOLVENT EXTRACTION

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ABSTRACT

This paper deals with the laboratory investigations of winning of palladium as a by-product during rhodium acid solution purification by solvent extraction. Tri-n-butyl phosphate (TBP), diluted in petroleum ether (ratio 1:3), was used as extraction agent. Change of the palladium concentration, depending on the extraction degree at different ratios between aqueous and organic phases, was observed. The results showed that the palladium extraction efficiency in experiments were: 86.54%, at the ratio of organic and aqueous phase 1:0,8, 83.87%, at the ratio of organic and aqueous phase 1:1,6 and 89.16%, at the ratio of organic and aqueous phase 1:0,4.

Keywords: Palladium, thre-n-butyl phosphate, solvent extraction.

1. INTRODUCTION

The recovery of palladium from industrial materials is of great interest because applications of palladium have been expanding in advanced technologies such as, catalysts, electric conductor, and corrosion resistant materials.

The palladium market was forecast to be in a very small annual surplus of 45,000 oz in 2010. Gross demand for palladium was set to rise by 15 per cent to 8.94 million oz in 2010 on the back of strong automotive and industrial demand. Demand for palladium in autocatalysis was forecast to increase by 27 per cent to 5.15 million oz in 2010. European gasoline catalysts now contain, on average, a ratio of 97:3 per cent palladium : platinum, while diesel formulations typically have a ratio of around 25:75 per cent palladium : platinum. Together with higher vehicle sales, this helped to lift gross automotive demand for palladium. Recovery of palladium from spent autocatalysis was forecast to increase by 37 per cent to 1.32 million oz as a higher palladium price and car scrap page schemes stimulated recycling [1].

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 melt with metal collectors (usually cupellation with copper), anodes are discharged, then electrolysis is done so that obtained anode slime is treated chemically to get platinum metals. The second procedure is related directly to the dissolution of 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.

The physical and chemical properties of these metals are very similar and thus it is difficult to separate the metals in metallurgy.

Various reagents have been studied on the solvent extraction of Pd(II), for example, trialkyl amines [2, 3], 1-phenyl-3-methyl-4-benzoylpyrazolone-5-one (HPMBP) [4].

In our previous work [5] we were present purification of a rhodium acid from traces of Pt using TBP as a extractant.

The aim of these investigations was the selective recovery of palladium for a mixed solution of platinum, palladium and rhodium from rhodium acid solution. Three-butyl phosphate, dissolved in petroleum ether was used as extractant in ratio of 1:3. Change in the concentration of platinum, ie, the extraction efficiency depending on the degree of extraction was investigating. It was worked with three solutions of a different Pt, Pd and Rh content. We compared various relations of water and organic phases For the regeneration of extractant, the used organic phase was contacted with equal volume of destiled water for 5 min. All experiments were conducted at room temperature.

2. EXPERIMENTAL

2.1. Apparatus

All experiments were conducted in a closed glass separating funnel using a electro shaker. Metal concentrations in the rhodium acid solution were measures on atomic emission spectrometry with inductively coupled plasma (ICP-AES). Detection limit of ICP-AES was $<0.001 \text{ g Pd/dm}^3$.

2.2. Preparation of solution

Laboratory studies were performed with the three from rhodium acid solution same concentration (6M free HCl), and different content of metals Pt, Pd and Rh. Initial concentration of all three solutions are shown in Table 1.

Table 1. The chemical composition of solution before ion exchange

g/dm^3	I	II	III
Rh	0.77	0.30	0.29
Pt	0.007	0.026	0.41
Pd	0.039	0.31	0.24
Sn	0.011	<0.001	<0.001
Zn	0.036	0.006	0.006
Fe	>0.35	>0.034	>0.02
Si	>0.05	0.0047	>0.006
Ag	0.006	<0.001	>0.0034
Cu	>0.603	>0.061	>0.038
Mg	>0.492	>0.059	>0.006
Al	>1.67	>0.011	>0.036
Ca	>0.17	>0.02	>0.045

Before solvent extraction is necessary to remove all base metals, which would further disturb the purification process. The most effective method for separation of base metals (Ag, Ca, Cu, Fe, Mg, Zn, Bi) of PGMs metal ions is achieved by absorption on a very strong acidic cation exchange resins.

In this experiment the cation exchange was carried out on ion exchange resin type Ambrelit IR 120. After ion exchange atomic emission spectrometer with inductively coupled plasma (ICP-AES) has been determined that all the base metals ions absorbed on the resin, and in solution where only platinum metals.

Table 2. The content of platinum metals Rh, Pd and Pt (g/dm^3) in solutions before solvent extraction after acidification of the solution set of 6M HCl free (ie added to the acid solution compared to 1:1)

	Rh(g/dm^3)	Pd (g/dm^3)	Pt(g/dm^3)
I	0.385	0.039	0.0035
II	0.15	0.31	0.013
III	0.145	0.24	0.205

3. RESULTS AND DISCUSSION

Solvent extraction was performed the same volume of solvent TBP (2500 ml) for all three solutions, so that the ratios between organic and aqueous phases were: experiment I - O:A=1:0.8; experiment II -O:A =1:0.6, experiment III - O: A=1:0.4. Suitable volumes of aqueous and organic phases were contacted for 5 min in separating funnel.

After each extraction, the concentration of metal ions in aqueous solution was determined by atomic emission spectrometer with inductively coupled plasma (ICP-AES). The concentration of palladium in the organic phase was estimated by mass balance.

During the work is accompanied by changes in concentrations of Pd, depending of on extraction efficiency and the different ratios of aqueous and organic phase.

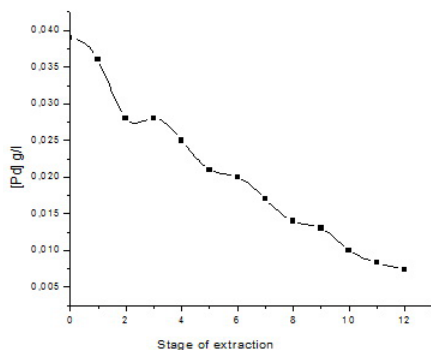


Figure1. Changes of palladium concentrations in aqueous phase with the increase extraction stages for experiment I

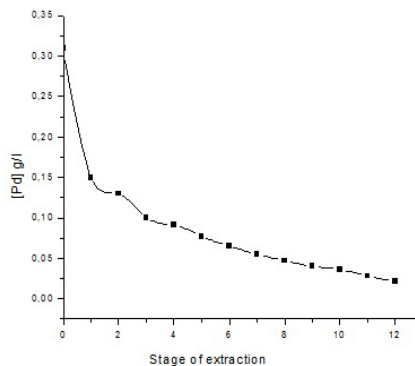


Figure2. Changes of palladium concentrations in aqueous phase with the increase extraction stages for experiment II

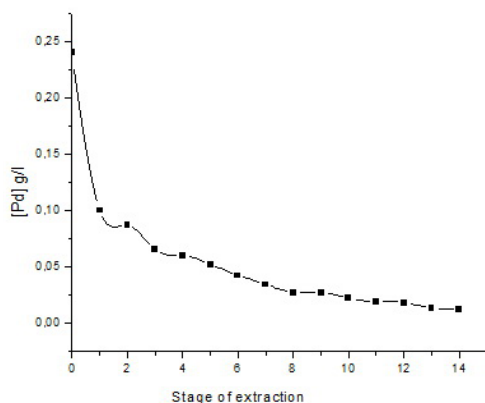


Figure3. Changes of palladium concentrations in aqueous phase with the increase extraction stages for experiment III

Table3. Increase the extraction efficiency with increasing stage of extraction

stage	Extraction efficiency (%)		
	I experi- ment	II experi- ment	III experi- ment
1	29.09	3.2	16.6
2	34.54	16.6	27.5
3	49.09	35.4	45.83
4	54.54	41.29	50.0
5	61.881	50.32	56.6
6	63.63	58.06	65
7	69.09	64.51	71.66
8	74.54	69.67	77.50
9	76.54	72.90	80
10	81.81	74.19	81.66
11	81.91	76.77	84.16
12	84.91	81.93	85
13		83.22	88.36
14		83.87	89.16

In the experiment I, the concentration of palladium in stock solution was 0.039 g/dm^3 , volume ratio between organic and aqueous phases was 1:0.8. Extraction was done in 12 stages. Because after 12 stages it was impossible to extract palladium from rhodium acid solution. In the rhodium acid solution was left 0.074 g/dm^3 (Figure 1). Extraction efficiency of Pd was 86.54 %, using TBP as an extraction agent (Table 3).

Experiment II was carried out with the following conditions: concentration of palladium in stock solution was 0.31 g/dm^3 , volume ratio between organic and aqueous phases was 1:1.6. Extraction was done at 14 stages, and then the extraction efficiency of Pd was 83.87 % (Table 3). After fourteen stages of extraction in the solution was left 0.022 g/dm^3 Pd (Figure 2).

In the experiment III, the concentration of palladium in stock solution was 0.24 g/dm^3 , volume ratio between organic and aqueous phases was 1:0.4. Extraction was done in 14 stages. After fourteen extractions solution was left 0.012 g/dm^3 (Figure 3). Extraction efficiency of Pd was 89.16% (Table 3).

The table shows that the best extraction efficiency (89.16%) is achieved when the volume ratio between organic and aqueous phase was 1:0.4, compared with the experiments where organic volume ratio between organic and aqueous phase was 1:0.8 and 1:1.6.

In any commercial extraction process, it is important to back extract the metal from the loaded organic phase from the point of its regeneration possibility and reuse for further extraction experiments continuously. The loaded organic was stripped with distilled water at O:A phase ratios 1:1.

for the back extraction of the Pd.

Combination of ion exchange and solvent extraction process it is possible to refine rhodium acid solution of non-precious metals and PGMs (Pt and Pd), in order to obtain pure rhodium.

4. CONCLUSION

Separation of Pd from the rhodium acid solution is possible using three-butyl phosphate as an extractant dissolved in petroleum ether in ratio of 1:3. The best extraction efficiency is 89,16%, when is volume ratio between organic and aqueous phases 1:0.4. Regeneration of three-butyl phosphate is carried out using distilled water.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- [1] Platinum Metals Review, Johnson and Matthey Inc. 55 (2011) 41-42
- [2] Hasegawa, Y.; Kobayashi, I.; Yoshimoto, S. Extraction of palladium (II) and platinum(IV) as chlorocomplex acids into basic organic solvents. *Solvent Extr. Ion Exch.* 9 (1991) 759-768
- [3] Inoue, K.; Furusawa, T.; Nagamatsu, I.; Baba, Y.; Yoshizuka, K. Solvent extraction of palladium(II) with tri octyl methyl ammonium chloride. *Solvent Extr. Ion Exch.* 6 (1988) 755-769
- [4] Mirza, M.Y.; Bailey, R.T. Extraction of palladium (II) with 1-phenyl-3-methyl-4- benzoyl- pyrazole-5-one. *J. Inorg. Nucl. Chem.*, 41(1979) 772-773.
- [5] Dragulovic S; Trujic V ; Stanojevic Simsic Z; Cvetkovski V ; Ljubomirovic Z.; Dimitrijevic S.; Simonovic D; Platinum solvent extraction from rhodium-acid solution; 14th International Research/Expert Conference "Trends in the Development of Machinery and Associated Technology" TMT 2010, Mediterranean Cruise, 11-18 September 2010; 169-171