15th International Research/Expert Conference
"Trends in the Development of Machinery and Associated Technology"
TMT 2011, Prague, Czech Republic, 12-18 September 2011

OBTAINING THE REQUIRED QUALITY OF PALLADIUM FOR Pd TRAP MAKING

Dana Stanković
Ljiljana Mladenović
Biserka Trumić
Draško Stanković
Vesna Krstić
Mining and Metallurgy Institute Bor
35 Zeleni bulevar,19210 Bor
Serbia
E-mail: radojka.jonovic@irmbor.co.rs

ABSTRACT

This paper describes the process of obtaining the high purity palladium, 99.99% Pd, from anode slime, formed in the electrolytic refining of copper anodes, obtained by copper melting from raw materials based on precious metals. Physical and chemical characterization of anode slime was carried out.

The aim of research is to determine the optimum conditions for obtaining the pure palladium, 99.99% Pd, which is the basic raw material for production $PdNi_5$ alloy in making the trap for Pt and Rh particles from platinum catalyst in the production of nitric acid.

Palladium obtaining and refining, up to the quality of 99.99% Pd, consists of three technological stages:

- *dissolution of anode slime as the main raw material,*
- *separation of palladium from base metals and associated metals of platinum group,*
- *palladium refining to the quality of 99.99% Pd.*

By experimental testing in dissolution of anode slime, the most optimum solvent and technological parameters of work are defined.

The best results were obtained during dissolution in HCl 1: 1 in the presence of gaseous chlorine as an oxidant.

Palladium was selectively separated from Pt and Rh and refined to the high purity products.

Key words: anode slime, dissolution, palladium quality

1. INTRODUCTION

Precious metals are a group of metals that have very important and the most diverse use in the industry [1,2,3,4]. Palladium is the basic metal for manufacturing the palladium traps and it belongs to the precious metals group in addition to Pt, Ir, Rh, Ru and Os. Platinum metals are rarely found in the earth crust, they are scattered in various rocks and rarely form the significant sites [5]. Platinum and palladium, like other metals of platinum group, occur in the copper nickel sulfide deposits. In these deposits, the platinum metals are often concentrated, so these sites are the most important sources for their production.

In the copper mines in Bor, the platinum metals follow the sulfide ores of copper and nickel. In processing of these ores, palladium together with other platinum metals is concentrated into anode copper and transforms into anode slime in the electrolytic refining of anode copper [5].

Anode slime is the basic raw material for obtaining the palladium and other platinum group metals. Palladium is less precious compared to platinum but it is chemically active so it easily forms the chemical compounds.
The subject of this paper is obtaining the palladium of commercial quality, i.e. 99.99% Pd from anode slime in order to prepare Pd – traps.

2. PART EXPERIMENTAL

For experimental investigation, non-decopperized anode slime was used with the given chemical content in Table 1.

Table 1. Chemical composition of anode slime

Ord.No.	1	2	3	4	5	6	7	8	9	10
Chemical element	Pt	Pd	Rh	Ag	Au	Cu	Sb	Sn	Pb	Zn
Content in %	2.29	4.17	14.78	0.038	Ø	72.50	0.0082	0.026	0.048	0.010

Chemical analysis of anode slime was carried out using the methods: ICP- AES – atomic emission spectrometry with inductive coupled plasma, SF – spectrophotometry, XRFA – X-ray fluorescent analysis.

First, decopperization of anode slime was carried out, that is dissolving and removal of present copper that is in this anode slime 72.5% Cu.
Such prepared anode slime is divided into 4 samples of same weight. In order to find the optimum solvent for dissolution, the different solvents were used for all four samples under the same conditions. The following solvents were used: aqua regia, diluted aqua regia, water after annealing mixture the mixture of samples in a stream of chlorine and diluted HCl with introduction of Cl_2 as an oxidant [2].
Platinum, palladium and rhodium exist in the resulting solution after dissolution of anode slime in the form of anions $[PtCl_6]^{2-}$, $[PdCl_4]^{2-}$, $[RhCl_6]^{3-}$, while the base metals are present in the form of cations (Ni^{2+}, Fe^{3+}, Cu^{2+}, etc.).
This solution is suitable for selective separation of precious from base metals using the ion-exchange. Passing the solutions through the ion exchange resin, the cations of base metals are absorbed on the resin, while the anions of precious metals remain in the solution [6,7].
From the purified solution after ion exchange, first platinum is separated by deposition in the form of ammonium hexachloroplatinate, and a part of rhodium and almost all palladium remain undeposited .
From solution after separation of Pt-salt, palladium is obtained. Based on tested and defined parameters to the aim of separation and refining of palladium, the solution is treated with excess of ammonia where the present rhodium is deposited in the form of complex salt $[Rh(NH_3)_5Cl]Cl_2$. The obtained complex rhodium salt is separated from solution by filtration and merged to rhodium, obtained as a byproduct in the refining of platinum and together with the waste solution, obtained after refining of palladium, is treated in order to obtain the pure rhodium.
After separation of Rh – complex, palladium is deposited, at precisely defined conditions, in the form of $Pd(NH_3)_2Cl_2$. This operation of palladium redeposition is repeated two or three times depending on the contamination of starting raw material [2]. The purified $Pd(NH_3)_2Cl_2$ is reduced to metal under strictly defined conditions (temperature, pH value of the solution, concentration of Pd, etc.). A series of reducer was experimentally tested a series (HCOOH, NaCOOH, $N_2H_4 \times H_2O$) and hydrazine hydrate was shown as the best raducer for all three metals. The obtained palladium powder by this procedure has the purity of 99.98% - 99.99% Pd and can be used to prepare the $PdNi_5$ alloy, used for manufacturing the palladium traps in the industry of nitric acid production.

3. RESULTS AND DISCUSSION

Based on the measurements of undisolved residue after dissolution of decopperized anode slime and considering the complexity of sample preparation for dissolution, it was concluded that the most effective solvent for decopperized anode slime is HCl with introduction of Cl_2 as an oxidant.

Table 2 gives the solvents used for dissolving the decopperized anode slime and quantities of the obtained undisolved residues.

Table 2. Solvents for decopperized anode slime and quantity of undisolved residue

Ord.No.of sample	Solvent	Undisolved residue (g)
Sample 1	Aqua regia	1.62
Sample 2	Diluted aqua regia 1:1	2.9
Sample 3	H_2O after sample annealing	ø
Sample 4	$HCl + Cl_2$	ø

Palladium of required purity with the quality according to the ASTM Standard was obtained by the given method of palladium separation and refining from anode slime.
Table 3 gives the chemical content of refined palladium with the quality according to the ASTM Standard

Table 3. Chemical content of the refined palladium

Ord.No.of element	1	2	3	4	5	6	7	8	9	10	11
Chemical element	Pt	Ag	Rh	Ir	Au	Sn	Pb	Zn	Fe	Cu	Si
Content of ppm	<5	4	<5	<5	21	<10	<10	18	25	15	10

Chemical analysis of refined palladium was carried out using the methods: ICP- AES – atomic emission spectrometry with induced coupled plasma.

4. CONCLUSIONS

Based on the experimental results, it can be concluded that the anode slime is very complex raw material and that obtaining and refining of palladium from anode slime is very complex and long process with lots of return material. Processing of anode slime results into obtaining palladium of commercial quality of purity 99.99% Pd, with the realized recovery of 98% for palladium from this raw material.
The most effective solvent for dissolving the decopperized anode slime is HCl 1:1 with addition of Cl_2 gas as an oxidant.

5. ACKNOWLEDGEMENT

The research results were made within the implementation of technological development of TR 034 029 and TR 034 004(from the 2011) for which the funds were provided by the Ministry of Science of the Republic of Serbia.

6. REFERENCES

[1] Z. M. Rdzawski, J. P. Stobrawa, J. Mater. Processing Tech. 153–154 (2004) 681–687
[2] F.J. Vidal-Iglesias, A. Al-Akl, D. Watson, G.A. Attard, J. Electroanalytical Chem. 611 (2007) 117–125
[3] F. Xiao, F. Zhao, D. Mei, Z. Mo, B. Zeng, Biosensors and Bioelec., 24 (2009) 3481–3486
[4] F.J. Vidal-Iglesias, J. Solla-Gullon, V. Montiel, J.M. Feliu, A. Aldaz, J. Power Sourc. 171(2007) 448– 456
[5] L. Jovanović, D. Mitrović, "Technological Process of Regeneration Pt Metal from PtRh PtRhPd Catalysts", Yu Patent N°4858 (in Serbian)
[6] L. Jovanović, G. Jovanović, D. Mitrović, "Regeneration and Refining of Platinum, Rhodium and Palladium from the Spent Catalytic Nets", Study1999, Copper Institute Bor (in Serbian)
[7] D.Stanković, B. Trumić, "Development and Winning of PtRhPd Metal Catalysts for the Production of Nitric Acid ", Study 1999, Copper Institute Bor (in Serbian)