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VARIOUS
TECHNOLOGIC PROCESSES

# Extraction and Concentration of Palladium(II) from Simulated Refining Process Solutions Using 1*H*-1,2,4-Triazole Derivatives

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**Abstract**—A procedure was developed for recovery and concentration of residual palladium(II) from a “lean” refining solution by extraction with 1*H*-1,2,4-triazole derivatives. Palladium(II) is extracted quantitatively from 1 M hydrochloric acid solutions and under optimum conditions is selectively separated from platinum(IV) and rhodium(III).

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Processing of mineral resources at enterprises of ferrous and nonferrous metallurgy and of oil refining and petrochemical industry involves formation of wastes that are an important secondary source of platinum group metals (PGMs). The hydrometallurgical reprocessing of industrial wastes, including spent catalysts, broken electronics components, and other resources involves formation of large volumes of difficultly processable aqueous solutions with low PGM concentration. One of the most important problems in refining is complete recovery of noble metals from multicomponent process solutions and prevention of their loss. On the other hand, in accordance with the modern environmental requirements, the concentration of palladium and other PGMs in wastewaters should not exceed 1 mg $L^{-1}$. Therefore, lean process and waste solutions are additionally treated to recover the residual PGMs, because their compounds are toxic, cause tumor diseases, and pose significant hazard to human health.

Palladium owing to its unique physicochemical properties is one of the most demanded strategic metals and is in high demand on the world market. It is known [1] that, in the classical precipitation method used in refining, palladium is separated from the other metals in the form of diammine dichloride. However, this method does not ensure sufficiently complete palladium recovery. In the final step of hydrometallurgical processing, the process solutions after the recovery of palladium concentrates contain up to 100–400 mg $L^{-1}$ palladium, which corresponds to the solubility of the salt being precipitated [2]. They also contain platinum, rhodium, and traces of some nonferrous, ferrous, and heavy metals. The methods presently used for recovering palladium from wastewaters, such as electroless deposition, sorption, filtration through membranes, electrodialysis, photocatalysis, etc., have a number of significant drawbacks [3]. The recovery of residual palladium from large volumes of lean process solutions with moderate levels of acidity and salt content can be successfully performed using extraction, including liquid membrane extraction [4, 5].

Particular attention has been given recently to the palladium(II) recovery from lean solutions and wastewaters. For example, Othman et al. [6] studied the extraction of palladium(II) (10 mg $L^{-1}$) with Cyanex 302 (0.0001 M, kerosene diluent) from a solution simulating industrial wastewater (pH 1). Palladium is extracted to 100% at the 1 : 1 ratio of the aqueous and organic phases (A : O) and contact time of 18 h. Najafi et al. [7] suggest quantitative extraction of palladium(II) from chloride solutions (pH 2) containing 50–300 mg $L^{-1}$ metal using Alamine 300 hydrochloride (0.004 M, toluene, 20 min, Composition of solutions simulating solutions from the refining process after separation of the palladium concentrate

| Solution no. | Metal and its concentration, mg $L^{-1}$ | | | $c_{HCl}$, M | $c_{NaCl}$, g $L^{-1}$ |
|---|---|---|---|---|---|
| | Pt | Pd | Rh | | |
| 1 | 212.0 | 344.0 | 8.2 | 0.5 | 10.0 |
| 2 | | | | 1.0 | |
| 3 | | | | 3.0 | |

A : O = 1:1). Analysis of the literature shows that the extraction studies were mainly performed using model solutions with preset salt background, containing PGMs only.

The other topical problem, along with the recovery of residual palladium(II), is its selective separation from platinum(IV) and rhodium(III) [8–13]. The known commercial extractants do not always ensure the selective separation of platinum(IV) and palladium(II). For example, Alamine 336 (0.03 M, toluene, 30 min, A : O = 1 : 1) recovers palladium(II) and platinum(IV) from a solution containing 776 mg $L^{-1}$ Pd and 897 mg $L^{-1}$ Pt (pH 1) to only 66.8 and 79.6%, respectively [14]. Furthermore, when developing a procedure for extraction recovery of metals from wastewaters, the toxicity of the reagents and diluents and their solubility in water should be taken into account [15].

We have discovered previously that some 1H-1,2,4-triazole derivatives efficiently extract palladium(II), platinum(IV), rhodium(III), gold(III), copper(II), and some rare metals from hydrochloric and nitric acid solutions. Copper(II), nickel(II), iron(III), and cobalt(II) are extracted with these compounds at the aqueous phase acidity higher than 3 M HCl. The use of the novel effective extractants should favor improvement of the classical refining flowsheet and solution of complex problems concerning separation of noble metals and prevention of their loss with wastewaters.

The typical composition of industrial waters from hydrometallurgical processing after precipitation of palladium in the form of diammine dichloride is as follows (mg $L^{-1}$): palladium, 350; platinum, 200; rhodium 10; ruthenium, gold, silver, copper, iron, lead, tin, and nickel, less than 1; selenium and tellurium, less than 10; salt background, 1 to 20 g $L^{-1}$NaCl; acidity, up to 0.1 M HCl.

This study deals with the recovery of residual palladium(II) and its separation from platinum(IV) and rhodium(III) from hydrochloric acid solutions simulating wastewater after palladium separation.

## EXPERIMENTAL

To examine the possibility of the extraction recovery of residual palladium and its separation from the concomitant platinum and rhodium, we prepared model solutions simulating the process solutions formed after separation of the palladium concentrate (see table). These model solutions corresponded to the average composition of the real solutions in the PGM content and salt background but did not contain other metals present in negligible concentrations.

The model solutions were prepared by dissolving weighed portions of hexachloroplatinic acid $H_2PtCl_6 \cdot 6H_2O$ (pure grade), palladium chloride $PdCl_2$ (pure grade), rhodium chloride $RhCl_3 \cdot 4H_2O$ (pure grade), and sodium chloride (chemically pure grade) in hydrochloric acid (chemically pure grade) solutions of preset concentration.

As extractants we used 1-{[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]-methyl}-1*H*-1,2,4-triazole (propiconazole, $L^1$), (*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)pentan-3-ol (tebuconazole, $L^2$), and (*RS*)-1-[2-(2,4-dichlorophenyl) pentyl]-1*H*-1,2,4-triazole (penconazole, $L^3$), taken as 0.25 M solutions. These chemicals are produced on the commercial scale (Bayer Crop Science AG, Janssen Pharmaceutical, and Ciba-Geigy) and are widely used as fungicides in agriculture. As shown by preliminary experiments, the 0.25 M concentration of the extractants is optimum for quantitative recovery of palladium(II). Chloroform used as a diluent meets all the requirements to diluents for commercial extractants [16].

The extraction was performed in separating funnels at an A : O ratio of 10 : 1 (20°C); no third phase formed. After the extraction completion, the raffinates were separated and analyzed for the metal content. For palladium(II) stripping, we prepared a 4 M aqueous solution of ammonia (chemically pure grade) and a 1 M solution of thiourea (chemically pure grade) in 0.5 M HCl. The PGM concentration in the initial model solutions and raffinates was determined with a SensAA atomic absorption spectrometer (GBC) in acetylene–oxygen flame (lamps with a hollow cathode made of the metals being analyzed; analytical wavelength in determination of palladium, platinum, and rhodium 247.6, 265.9, and 343.5 nm, respectively), and that in the organic phases was determined from the material balance (difference between the concentrations in the initial solution and raffinates). The determination error did not exceed 5 rel %.

## RESULTS AND DISCUSSION

Taking into account the fact that the reagents meet the requirements to industrial extractants, we performed experiments aimed at examining the possibility of recovering and concentrating residual palladium(II) from solutions simulating the solutions after separating palladium concentrate. To choose the optimum acidity of the aqueous phase, the PGM extraction with the chosen reagents was performed from model solutions containing 0.5, 1, and 3 M HCl.

The figure shows how the extraction of palladium(II), palladium(IV), and rhodium(III) with the chosen reagents depends on the contact time and aqueous phase acidity.

We have found that the PGM recovery depends on the HCl concentration. From 0.5 M HCl solutions, platinum(IV) and rhodium(III) are not noticeably extracted with the chosen reagents, and the degree of recovery of palladium(II) depends on the phase contact time (20–60 min), which is caused by lability of the palladium(II) chloride complexes and by the metal recovery by the coordination extraction mechanism under these conditions. Extraction at low acidity of the aqueous phase can be accompanied by hydrolysis of salts of base metals and formation of the third phase.

The degree of recovery of palladium(II) from 1 M HCl solutions with reagents $L^2$ and $L^3$ at a phase contact time of 5 min is 100%, and that of platinum(IV) and rhodium(III) does not exceed 1% even at a phase contact time of 1 h (separation factor $\beta_{Pd/Pt,Rh} \sim 1 \times 10^4$). Reagent $L^1$ extracts palladium(II) considerably more slowly, and its complete recovery requires the phase contact time no shorter than 1 h.

From 3 M HCl solutions, palladium(II) is recovered in 5–15 min quantitatively but unselectively, with appreciable coextraction of platinum(IV) and rhodium(III). On the other hand, high acidity of the aqueous phase is unfavorable from the viewpoint of technology, as it can promote the equipment corrosion.

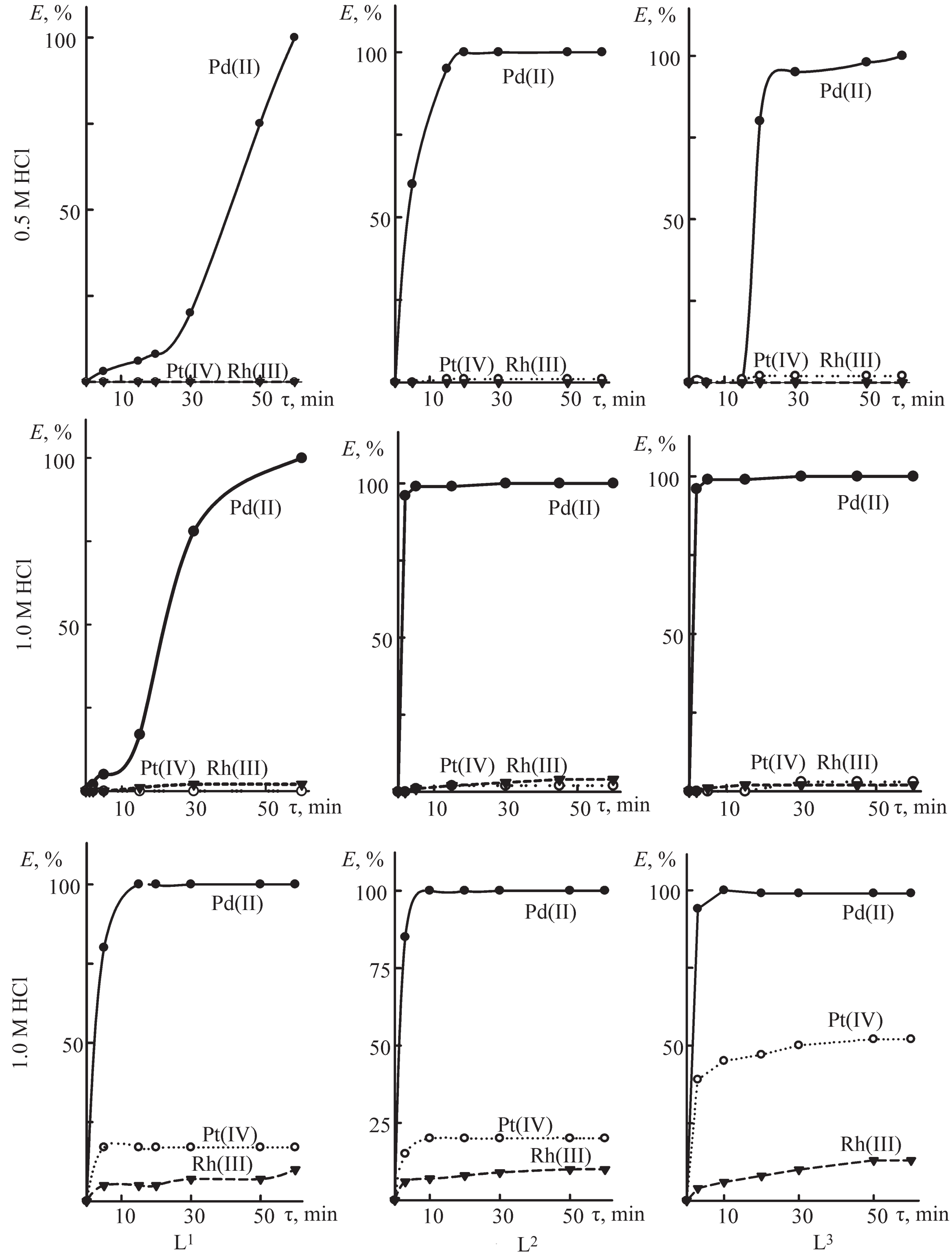
Because the ratio of the aqueous and organic phases is 10 : 1, palladium(II) is not only selectively recovered, but also concentrated by a factor of 10, which is advantageous from the viewpoint of technology.

An increase in the degree of recovery of metal ions with increasing acidity of the aqueous phase can be attributed to the salting-out effect. The efficiency of the palladium(II) recovery with the chosen reagents increases in the order $L^1 < L^3 < L^2$, which correlates with their basicity.

The extraction of palladium(II) from the refining mother liquor with 1*H*-1,2,4-triazole derivatives allows virtually quantitative recovery of residual palladium with the subsequent concentration after the separation of the major fraction of palladium in the form of diamminepalladium dichloride. In so doing, palladium(II) is simultaneously separated from concomitant platinum(IV) and rhodium(III). This procedure is well compatible with the classical refining flowsheet.

After the palladium separation, platinum and rhodium remain in the raffinate. Platinum can be recovered by the classical procedure, extraction with tributyl phosphate, and rhodium solutions can be concentrated. Although the study was aimed at solving a relatively narrow, specific problem within the framework of PGM reprocessing, its results are useful for reprocessing industrial solutions of large volume but low useful component content, obtained from secondary resources, and allow improvement of the refining process.

The repeated use of extractants is economically advantageous. The chosen reagents can be used repeatedly if their loss in the cyclic extraction–stripping process is timely replenished. Palladium(II) can be stripped from the organic phase with a 4 M aqueous ammonia solution or a 1 M solution of thiourea in 0.5 M HCl. At A : O 1 : 1 and $\tau = 10$ min, the degree of palladium stripping with these compounds in one step is no less than 98%.



Degree of recovery $E$ of palladium(II), platinum(IV), and rhodium(III) with reagents $L^1$, $L^2$, and $L^3$ from solutions simulating solutions from the refining process after separation of the palladium concentrate as a function of the aqueous phase acidity and phase contact time τ (20°C, 10 g $L^{-1}$ NaCl, A : O = 10 : 1, $c_L$ = 0.25 M, chloroform diluent).

## CONCLUSIONS

1*H*-1,2,4-Triazole derivatives such as (*RS*)-1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)pentan-3-ol ($L^2$) and (*RS*)-1-[2-(2,4-dichlorophenyl)pentyl]-1*H*-1,2,4-triazole ($L^3$) can be recommended for the extraction and concentration of palladium(II) from 1 M hydrochloric acid process solutions with its simultaneous separation from platinum(IV) and rhodium(III). The suggested procedure for recovering residual palladium(II) allows improvement of the classical refining flowsheet.

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