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ELECTROLITYCAL PURIFICATION OF Rh FROM $Rh_2(SO_4)_3$ SOLUTION

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ABSTRACT

The aim of this work was to obtain a high purity rhodium, the quality of min 99.95% Rh, from different raw materials which containing PGMs. Different chemical methods was used to remove traces of other base metals and precious metals from acid solutions of rhodium. Purified acid solution of rhodium (H_3RhCl_6) was treated in two ways:

1. *Reduction of rhodium-hydrazine hydrate was performed in the basic conditions*
2. *Rhodium from rhodium acids was translated into rhodium hydroxide, and this in rhodium sulfate. Elemental rhodium, the rhodium sulfate, was obtained by electrolytic deposition on a titanium cathode, using two previously activated titanium anodes.*

This paper presents a technological scheme of obtaining high purity rhodium from rhodium acid solution, containing impurities of non-precious and precious metals (Pt and Pd). Also, the paper describes the preparation of titanium anodes for electrolysis. Based on the experimental work optimal parameters of the process of electrolytic deposition of high purity rhodium, were determined.

Keywords: high-purity rhodium, solvent extraction, electrodeposition of rhodium

1. INTRODUCTION

Technologies for obtain rhodium purity of 99% Rh are known. These are chemical methods of refining and reduction of rhodium. Rhodium of high purity min 99,95% cannot be obtained only by chemical processes, but in a combination of chemical and electrochemical processes.

Figure 1 shows the technological scheme of processing solution of rhodium acid with content of non-precious metals and traces of platinum and palladium, as well as rhodium of high purity.

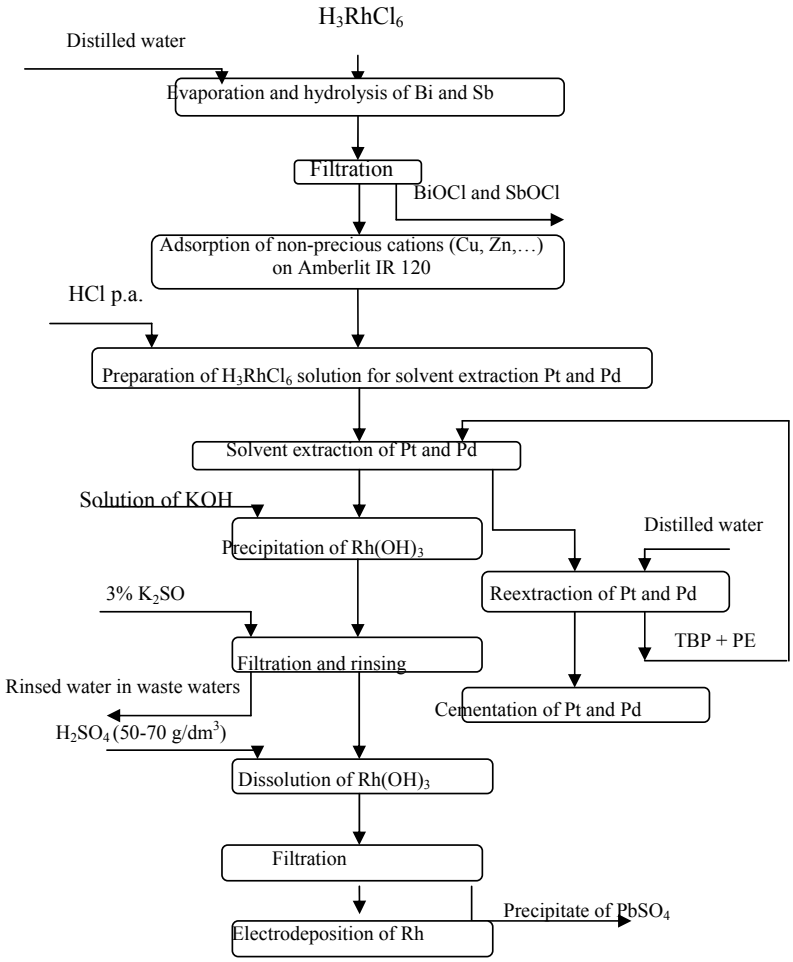

Figure 1. Technological scheme of processing of rhodium acid solution of non-precious metals and platinum metals to high purity rhodium

Acid solution of rhodium is obtained by dissolving the cement residue, after separation of platinum and palladium[1]. Dissolution is carried out in hydrohloric acid, with the addition of oxidative agents (introduction of chlorine gas in the reaction mixture), according to the following reaction (1):

$$Rh + 3HCl + \frac{3}{2}Cl_2 \rightarrow H_3RhCl_6 \quad (1)$$

Besides to rhodium, non-precious metals and residual platinum and palladium has been dissolved from cement sludge, according to the following reactions:

$$Me^{2+} + Cl_2 \rightarrow MeCl_2 \quad (2)$$

$$Pt + 2HCl + 2Cl_2 \rightarrow H_2PtCl_6 \quad (3)$$

$$Pd + 2HCl + Cl_2 \rightarrow H_2PdCl_4 \quad (4)$$

Non-precious metals which are present in cement sludge are, ussualy, the following: zinc, copper, lead, bizmunt and antimony[2].

The obtained solution of the rhodium acid is evaporated, to remove free chlorine and hydrochloric acid, and carried out by the hydrolysis of bismuth and antimony, to the following reactions:

$$BiCl_3 + H_2O \rightarrow BiOCl\downarrow + 2HCl \quad (5)$$
$$SbCl_3 + H_2O \rightarrow SbOCl\downarrow + 2HCl \quad (6)$$

Hydrolysis of bismuth and antimony is performed due to cleaning of rhodium acid solution from the bismuth and antimony, and later they are separated by filtering.
Adsorption of other non-precious metals, except lead, is performed by cation exchanger [3] (Amberlit IR 120), according to the following reaction:

$$2R - H + Me^{2+} \rightarrow R_2Me + 2H^+ \quad (7)$$

After adsorption of non-precious metals from acid solutions of rhodium, the next stage of purification process was to remove residual amounts of platinum and palladium by solvent extraction. Solvent extraction of platinum and palladium is performed by the organic solvent (TBP:PE=1:3) [4,5], according to the following reactions:

$$TBP + Pt(IV)_{aq} + Rh(III)_{aq} \rightarrow TBPPt + Rh(III)_{aq} \quad (8)$$
$$TBP + Pd(II)_{aq} + Rh(III)_{aq} \rightarrow TBPPd + Rh(III)_{aq} \quad (9)$$

In solution of rhodium acid, after solvent extraction of platinum and palladium, as impurities, remains Pb, which is removed during the preparation of rhodium sulfate solution for electrodeposition. Namely, rhodium, from the rhodium acid, is deposited in the form of rhodium hydroxide, according to the following reaction:

$$H_3RhCl_6 + 6KOH \rightarrow Rh(OH)_3\downarrow + 6KCl + 3H_2O \quad (10)$$

After filtering and washing, rhodium hydroxide deposit dissolves in sulfuric acid according to reaction (11), in order to prepare an electrolyte:

$$2Rh(OH)_3 + 3H_2SO_4 \rightarrow Rh_2(SO4)_3 + 6H_2O \quad (11)$$

At the same time, lead which is residual at all stages of purification, its precipitated with sulfuric acid and hard resolve compound of lead sulfate was obtained and later removed from the solution of rhodium sulfate, according to the following reaction:

$$Pb(OH)_2 + H_2SO_4 \rightarrow PbSO_4\downarrow + H_2O \quad (12)$$

Deposited lead –sulfate is separated by filtration, and obtain filtrate – solution of rhodium - sulfate, certain concentration of rhodium and free sulfuric acid, was prepared for electrodeposition of rhodium. Electrodeposition of rhodium is performed on the titanium cathode, using previously prepared titanium insoluble anodes [6].

2. EXPERIMENTAL

Laboratory experimental research of all phases of the process of the refining solution of rhodium acid, preparation of rhodium sulfate solution and the conditions of electrolytic deposition of rhodium was carried out.Rhodium acid solution was purified by solvent extraction from traces of platinum and palladium to a concentration < 0,001 g Pt/l and <0,001 g Pd/l (limit of detection apparatus ICP-AAS). Namely, according to the literature data[7], voltages of the electrolytic deposition of platinum and rhodium are very close (for $Pt^{4+}E^0 = 0,74V$, and for Rh^{3+} $E^0 = 0,70V$), so the simultaneous deposition of rhodium and platinum is possible, and thus obtain rhodium deposits with high content of platinum (allowed content of platinum by ISTM standard in rhodium quality of 99,95% Rh is 200 ppm).

3. RESULTS AND DISCUSSION

Parameters of purification rhodium acid solution from non-precious metals and platinum traces are defined in the work.

In this paper was defined the conditions of electrolytic deposition of rhodium, at which you get high-purity rhodium.

Concentration Rh……2-5 g/l
Concentration H_2SO_4……50-100 g/l
The current density……$10A/dm^2$
Voltage……1 V
Cathode……Titanium plate
Anode……Titanium plate previously activated in a solution of oxalic acid (100 g/l)

4. CONCLUSION

By described process, a combination of chemical procedures, such as: ion exchange, solvent extraction and electrolytic deposition of rhodium, rhodium of high-purity (99,95%) was obtained. Efficiency degree of obtained rhodium from acid solutions of rhodium by the described procedure is min 98%.

5. ACKNOWLEDGEMENTS

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