Comparing the Precipitation Techniques
on Rhodium Recovery from Waste Solutions

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Experimental study performed in this research aimed at precipitating various rhodium compounds from the spent solutions of rhodium plating. Optimum conditions for the rhodium hydroxide precipitation, corresponding to a final Rh^{3+} concentration of 50 ppm, were found to be pH=7.5, $50^{o}C$ temperature, and 6 hours of reaction period, when NaOH is used as a neutralizer. Characterization studies were also carried out to inspect the suitability of precipitated rhodium compounds for the manufacturing of pure metallic rhodium and rhodium salts. Optimum conditions for rhodium precipitation are 180 g/l sodium formate concentration, $100\,^{\circ}C$ temperature and over 6 hours time. Sodium formate precipitation of rhodium has been carried out with an efficiency of higher than 75%.

1. Introduction

Rhodium is manufactured and refined during the last step of the production line of platinum group of metals (PGM), due to its having the most difficult metallurgical production technique among the PGM and noble metals. It is almost impossible to find literature, related to the process parameters of rhodium production and thus, rhodium metallurgy differ from the conventional hydrometallurgical techniques. Used plating solutions (containing about 100-400 ppm Rh^{3+}) are taken out of the baths and treated by the hydroxide precipitation and "selective dissolution & selective complex precipitation" methods[1,2], although the details are not disclosed in the literature.

Rhodium plating is widely used in Turkish jewelry sector for decorative plating purposes. Typical rhodium plating baths used in jewelry industry are sulfate based and contains 2 g/l Rh^{3+}, where working temperature is 40-50 $^{\circ}$C and current density is 1-1.5 A/dm^2 and the plating thickness is approximately 2-4μm. Decorative rhodium plating surfaces have important advantages such as brightness and resistance to tarnishing [3,4]. Approximately 3000 liters of initial plating solution is used per annum with 20 g/l concentration. This initial solution is first diluted to 2000 ppm and utilized in plating baths until its content decreased to 100–400 ppm. Additions to this plating solution can be made a few times but it must be replenished when the acidity increases and when discoloration starts on the plated surfaces.

Rhodium recovery from waste solutions with hydrometallurgical techniques is strongly dependent on the process parameters such as, pH of the solution, temperature, types and concentrations of reagent, types of reducing agents and solvents, etc. There are not much of literatures about the recovery of rhodium. A laboratory experiment was carried out for the recovery of platinum group metals from waste solutions with sodium formate reduction as an alternative to zinc cementation [5]. Sodium formate efficiency was over 80% for platinum, palladium, and rhodium. Authors determined the optimized parameters as, starting pH value of 1.5, temperature of 100 $^{\circ}$C and sodium formate concentration of 30 g/dm^3, and claimed that this technique was 37% cost effective as compared to zinc cementation. The conventional rhodium production/recovery flow chart is given in Figure 1. The first two steps are hydroxide precipitation and dissolution of precipitate in HCl. Theoretical background of these two steps can be explained by the help of two diagrams as seen in Figures 2 and 3.

Rhodium hydroxide precipitation is possible above pH 1.5 according to Pourbaix diagram.

However, this is a theoretical diagram and in fact, as seen at Figure 3, there are 7 different chloro complex of rhodium and for almost all conditions there are at least two different species in the solution. The number of Cl^- at the ligand can be changed according to chloride activity of solution and $[RhCl_6]^{3-}$ that is an important complex anion for the production of rhodium compounds or metallic rhodium. This complex anion is stable only at 6M or higher HCl concentrations. Therefore, hydroxide precipitation and dissolution after the filtration step is the most critical step for the recovery of rhodium. If the process parameters are not controlled and adjusted strictly, further process steps become impossible.
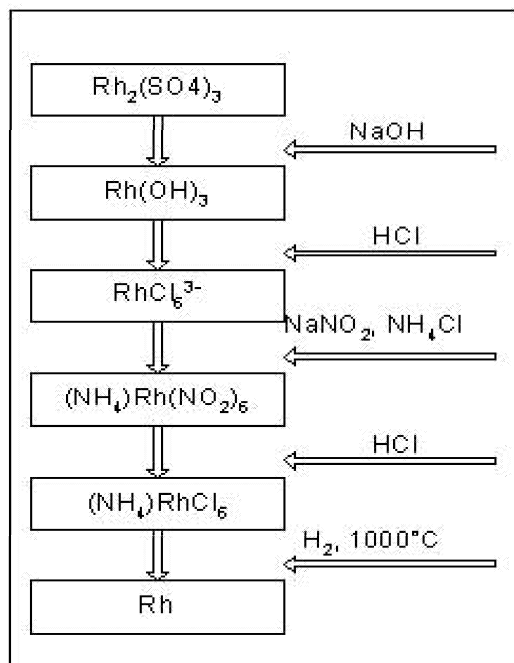

Figure 2. Pourbaix diagram of Rh-H_2O system [6].

ml HWS glass reactor was used for the experiments. Electrolyte temperature was thermostatically controlled by a Haake D8 heater ($\pm 0.1\,^\circ$C). A Nel brand pH meter and an INGOLD brand pH electrode were used for measuring the pH values of solutions. Chemical analysis performed with a Perkin Elmer 3030 Atomic Absorption Spectrophotometer. All chemicals used in the experiments were analytical grade.

3. Results and Discussion

3.1. Hydroxide Precipitation

The pH value was investigated as the first parameter since the precipitation behavior of a metal hydroxide depends on pH value of solutions. Experiments performed at room temperature, and 250 ml of solution was used. Figure 5 displays the rhodium concentration of solution after the pH value was set. According to the Pourbaix diagram of Rhodium-Water system, it is simple to precipitate $Rh(OH)_3$ above pH = 1. However, as shown in Figure 5, there was not adequate precipitation through pH=4. Precipitation was not observed until pH=2 and it started just above 2. But it was determined by the experiments that, $Rh(OH)_3$ which precipitated at low pH values, was not soluble in acids. After pH

Figure 1. Flow chart of rhodium production [1,2].

2. Experimental

In the experimental work, waste solutions of rhodium plating were used, provided by some jewelry companies of Türkiye, containing 0,4 g/l Rh^{3+}. Figure 4 displays the precipitation reactor. pH of solutions was less than 1. A 250
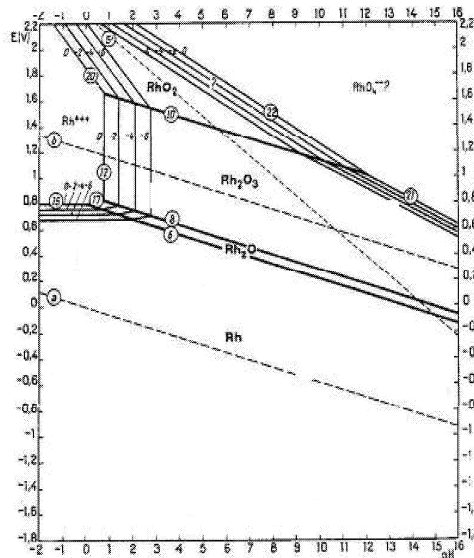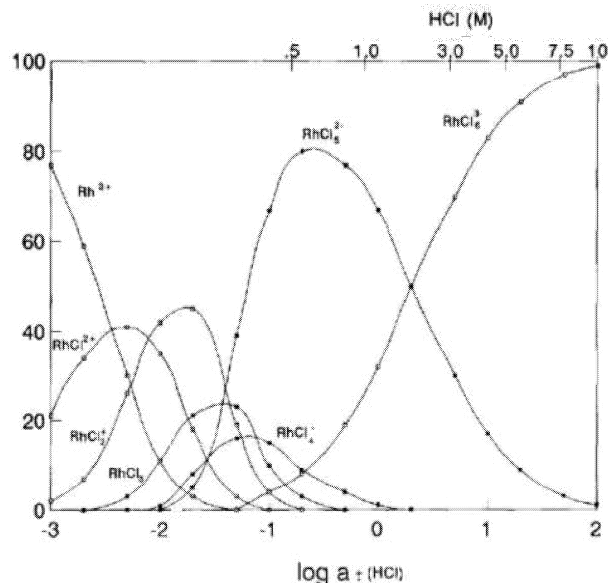
Figure 3. Speciation diagram for chloride solutions [2].

1. Glass Reactor
2. pH meter and pH Electrode
3. Thermostat
4. Magnetic Stirer
5. Thermometer
6. Condenser

Figure 4. Closed System Precipitation Reactor

value of solution was set over 4, a rapid precipitation was observed and analyzed. After pH=6 there was a decrease on the precipitation and it lasted until pH=7. $Rh(OH)_3$ precipitated at this pH value had a different modifications and these were not also dissolved in acids easily. This parameter was investigated by the repeated trials. The optimum pH value of solution is 7.5 and $Rh(OH)_3$ which precipitated at this pH value can easily be dissolved in HCl.

Temperature of solution is important for precipitation processes. Increasing temperature increases the kinetic energy of particles and thus it increases the precipitation efficiency. Figure 6 displays the results.

Rh^{3+} concentration of solutions decreases with increasing temperature, a fact similar to the literature [7,8]. On the other hand, above 50 °C there was a rapid increase in the Rh^{3+} concentration of solutions a trend which lasted up to 65 °C and become normal afterwards.

At > 50 °C, a different modification of rhodium hydroxide became the stable modification. However, back solubility experiments were performed for these different rhodium hydroxides. Rhodium hydroxides that obtained > 50 °C are not sol-

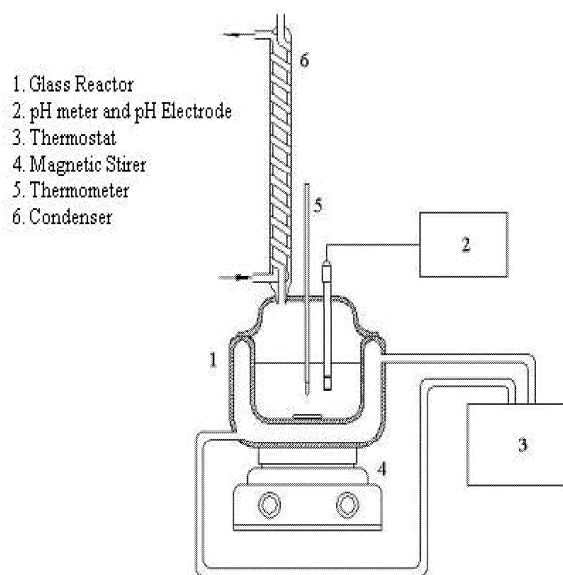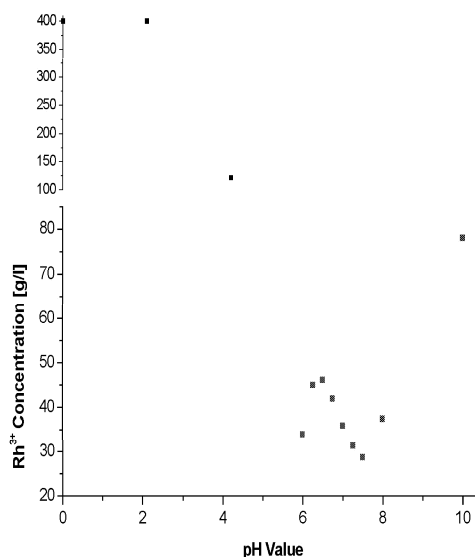Figure 5. Effect of pH value on $Rh(OH)_3$ precipitation.
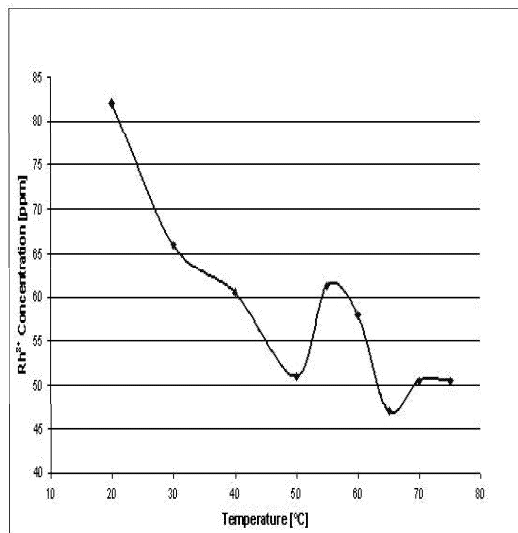
Figure 6. Effect of temperature on Rh(OH)$_3$ precipitation.

Figure 7. The effect of sodium formate concentration on the on therhodium precipitation (starting pH value 1.5, time 1 hour, 75 ° C)

uble in acids easily. Solubility of Rh(OH)$_3$that obtained from waste solutions is very important. Because next process step is to obtain [RhCl$_6$]$^{3-}$, an anion which is very important for metallic rhodium production or pure rhodium salts. This anion is obtained by the dissolutions of Rh(OH)$_3$ in HCl.

3.2. Metallic Rhodium Precipitation

Reduction of rhodium from waste solutions with sodium formate is a new technique and it is presented as an alternative to zinc cementation. In addition, this reagent is used for rhodium precipitation in the industrial plants of Turkey for rhodium recovery.

60-120 and 180 g/l sodium formate were used for rhodium precipitation in a one-hour time. Results are given in Figure 7. Sodium formate addition was carried out to the solutions in crystalline form. Figure 7 shows the Rh^{3+} concentration of solution after sodium formate addition. As shown, 180 g/l sodium formate addition gave the best results for rhodium precipitation. At the end of one hour, precipitation efficiency reached approximately 66% with 134 ppm Rh^{3+} concentration in the solution.
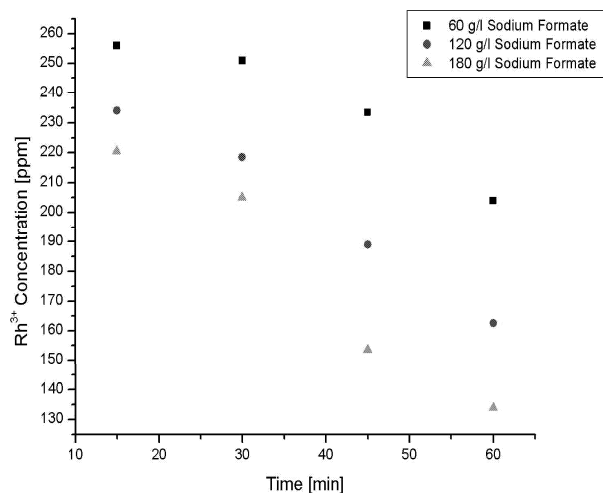
Time is important parameter for reduction of

rhodium with sodium formate. Figure 8 shows effect of time on the rhodium concentration of solution after 4 hours.

As shown in Figure 8, after 4 hours, precipitation efficiency was 75%, and the rest of solution contained Rh^{+}, Rh^{2+}that can be determined by the green color of the solution. After one hour, precipitation rate decreased slightly. It is a disadvantage for using sodium formate to precipitate.

Temperature is one of the most important parameters for precipitation of rhodium with sodium formate. Reaction strictly depends on the temperature. Figure 10 displays the effect of the temperature on the precipitation.

As shown in Figure 9, at the low temperatures (< 50 ° C) no precipitation was observed. Precipitation started over 50 ° C. Nevertheless, acceptable rhodium reduction efficiency started over 75 ° C and the best results were obtained at 100 ° C.

4. Conclusions

The behavior of rhodium hydroxide precipitation, which was carried out with different reagents, has been investigated by the labora-
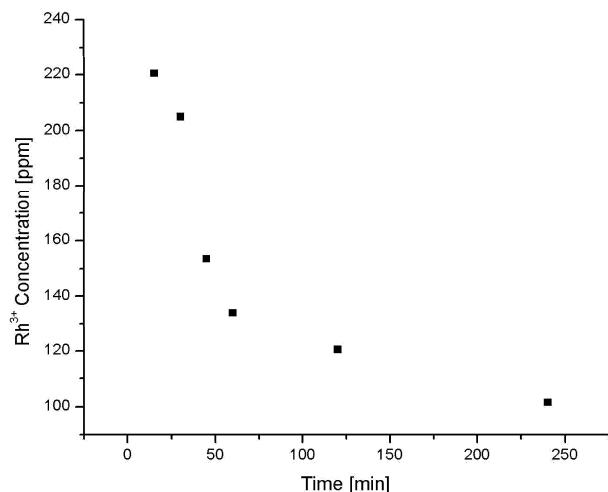
Figure 8. Effect of time on the rhodium precipitation (180g/l sodium formate, starting pH value 1.5, 75 ° C)
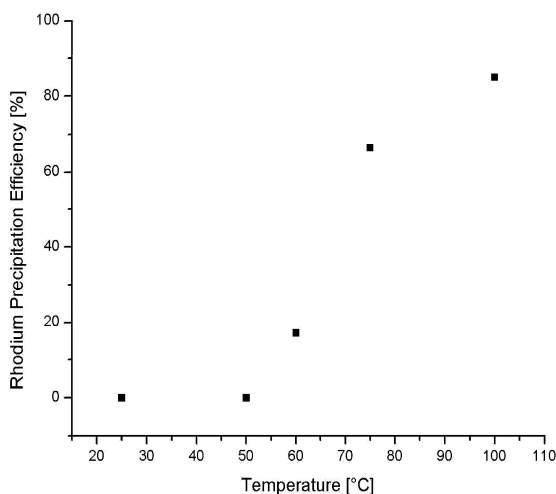

Figure 9. Effect of the temperature on the rhodium precipitation (180 g/l sodium formate, starting pH value 1.5, time 1 hour)

tory experiments. The optimum hydroxide precipitation conditions from sulfate based waste solutions were, pH value 7.5, working temperature of 50 ° C, 4-6 hours settling time, and NaOH as a neutralizer. After six hours, rhodium hydroxide efficiency reached over 90%. Following the precipitation and filtration under these conditions, precipitate can be easily dissolved in HCl.

The optimized rhodium precipitation conditions with sodium formate were, 180 g/l sodium formate, 100 ° C and more than 4 hours of time. After the precipitation, dissolution of rhodium in acids (H_2SO_4 and HCl) is simple. However, when this technique is used, other metals also precipitate. Therefore, this method is not suitable for all wastes that contain PGM.

Hydroxide precipitation method is more suitable than other precipitation techniques because, after the hydroxide precipitation step, rhodium selective precipitation step becomes so it is possible to obtain pure rhodium salts or metallic rhodium.

5. Acknowledgements

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