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Cementation of rhodium from waste chloride solutions using copper powder

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ABSTRACT

This work investigated the cementation of rhodium from waste chloride solutions using metallic copper powder. The effects on the rhodium precipitation (%) caused by the quantity of copper, reaction temperature and reaction time were explored in detail. In addition, the cementation kinetics of rhodium were studied, and the activation energy was determined to be 64.48 kJ/mol, which indicates that the reaction is chemically controlled. It was demonstrated that less than 40% of the rhodium could be precipitated using excessive quantities of copper powder (e.g., stoichiometric ratio of Cu/Rh = 40.3) at room temperature for 1 h, which resulted in a cementation reaction that was too slow. Increasing the reaction temperature to 55 °C resulted in almost 99% cementation after 1 h, even using stoichiometric ratio of Cu/Rh = 16.1. After a detailed observation of the dissolution behavior of the copper powder during the cementation process, it was demonstrated that most of the copper is preferentially consumed by free acid, a finding corroborated by pH measurements.

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1. Introduction

Rhodium is a member of the platinum group of metals (PGMs) and is hard, highly reflective and very stable to oxidation (Pletcher and Urbina, 1997).

Presently, rhodium is extensively used as a catalyst in automobiles, in plating baths, for chemistry research, in the electrical industry and in the glass industry. Unsurprisingly, there has been a significant market for rhodium coatings. For years, rhodium has been the precious metal most commonly electroplated, usually employing plating baths with sulfuric or phosphoric acid electrolytes. Many commonly used metals and alloys may readily be directly plated with rhodium (Pletcher and Urbina, 1997; Aktas, 2011; Benham, 1961).

Rhodium is the metal refined with the least efficiency compared to other PGMs, with a significant percentage of the metal value lost due to the inefficiency of the extraction technique (Benguerel et al., 1996). Due to the rapid growth of rhodium applicability, recovery of this metal from wastewater is becoming increasingly worthwhile.

The purification and recovery of rhodium have always been difficult because of its complex aqueous chemistry in chloride solutions. There are some studies in the literature that focused on the recovery and elective separation of rhodium. The methods capable of removing metal ions from wastewater solutions include solvent extraction (Benguerel et al., 1995, 1996), bacterial reduction (Ngwenya and Whiteley, 2006), cementation and ion replacement reactions (Aktas, 2011; Jaskula, 2009).

Solvent extraction methods cannot be directly applied to the recovery of rhodium from $RhCl_3$ solutions. Tin (II) chloride is required to reduce Rh(III) to Rh(I). The process includes additional steps such as extraction, re-extraction, use of various extracting solvents and ion exchange columns. Due to the multistep extraction process, recovery of rhodium from the solvent mixture is not cost effective and is difficult to implement.

The suitability of the bacterial reduction techniques for a particular metal recovery process depends on the pH, metal concentration and level of impurities. As a result of these parameters, the process needs to be improved.

The solvent extraction and bacterial reduction techniques result in medium efficiencies and generally do not ensure a complete recovery, so further treatment is required.

The cementation technique has been extensively used in industry for much longer than the solvent extraction and bacterial methods. The advantages of the cementation process include relative simplicity, ease of control and the ability to recover valuable metals (Doyle, 2005 and Habashi, 2005). However, the consumption and the redox potentials of sacrificial metals limit the application of this process (Aktas et al., 2010; Aktas, 2010; Aktas and Morcali, 2011). In the applied cementation process for this study, the more-active metal (in the present case, metallic copper powder) is oxidized through the acquisition of chloride from rhodium, which is more noble than copper. This process results in the production of rhodium black powder and an aqueous solution of copper(II) chloride (Pletcher and Urbina, 1997).

The standard reduction potentials, E values, (Lide, 2004) of Rh and Cu are provided below:

$$Rh^{3+} + 3e^- \rightarrow Rh^\circ \qquad E = +0.758\ V \tag{1}$$

$$Cu^{2+} + 2e^- \rightarrow Cu^\circ \qquad E = +0.337\ V. \tag{2}$$

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The overall reaction is expressed in Eq. (3):

$$2Rh^{3+}_{(aq)} + 3Cu^{\circ}_{(s)} \rightarrow 2Rh^{\circ}_{(s)} + 3Cu^{2+}_{(aq)}. \quad (3)$$

The potential difference between rhodium and copper is calculated to be 0.4184 V; therefore, the reaction is spontaneous and constructs a half pile because the reaction proceeds in the same tube (Aktas, 2008). Fig. 1 shows the theoretically calculated E values of the half pile reaction between rhodium and copper based on their concentrations present in the solution.

As shown in Fig. 1, the reaction is spontaneous at room temperature and indicates that all rhodium ions can be replaced by copper powder, which should result in approximately 100% cementation.

The objectives of this work were the following: 1) to remove rhodium out of a waste chloride solution via cementation with copper powder, 2) to study the dissolution behavior of copper powder and 3) to observe the effects of temperature and pH variation during the cementation process.

2. Materials and methods

A seasoned rhodium sulfate plating solution, procured from a rhodium-plating workshop (Savaş Ltd., Istanbul, Turkey), was employed as the rhodium source in this work. Rhodium failed to precipitate from sulfate solution by the addition of copper powder, so rhodium sulfate was first precipitated as rhodium hydroxide ($Rh(OH)_3$) and then converted to rhodium chloride in HCl solution.

All of the chemicals used in this study were analytical grade. The following cementation parameters were optimized: time, temperature, quantity of copper powder (particle size < 150 μm, Aldrich), and pH. The rhodium content (C_o) and copper content of the waste solution was determined to be 535.8 ppm and 7.54 ppm, respectively, using a Perkin Elmer AAnalyst 800 Atomic Absorption Spectrophotometer. The chlorine concentration of the waste solution was measured to be around 12.8 g/L. The pH of the solution was determined to be 0.46 using a WTW pH 315i pH meter. For each cementation experiment, 5 mL of rhodium-containing waste solution was employed. The experiments were conducted inside a 15 mL-falcon tube that was placed in a temperature-controlled shaking bath to ensure uniform heat convection at the surface of the falcon tube. The copper content of the treated solution was measured using a Titroline Easy Titrator by means of 0.01 M EDTA titration solution.

A solid/liquid separation was performed following each cementation experiment. For the analyses, 5 mL of the filtered solution was introduced into the instrument (AAS) at an appropriate dilution when necessary. The cementation (%) of rhodium during the cementation process was calculated using the following equation:

$$\text{Cementation } (\%) = [(C_o - C_t)/C_o]x100 \quad (4)$$

where C_o is the initial rhodium concentration (535.8 ppm), and C_t is the rhodium concentration in solution at the end of the experiment.

To investigate the rhodium cementation behavior from the waste solution, a kinetic study was performed. After the cementation reactions, all of the rhodium black powders were combined, and the excess copper was digested in 0.05 M HNO_3 (pH = ~1.3) to clean the product thoroughly.

3. Results and discussion

The process outlined in this paper could be used to precipitate almost all of the rhodium present in the waste solution. In the following section, we examine the process parameters in detail.

3.1. Cementation of rhodium using copper powder

Fig. 2 shows that the rhodium cementation (%) increased with increasing stoichiometric ratio of Cu/Rh, which is in agreement with previous studies that investigated the cementation percentage with regard to the quantity of the cementator (Aktas, 2008; Aktas et al., 2010; Aktas, 2011). However, in contrast to other metal cementation reactions, the rhodium cementation did not go to completion even though excess copper powder (100 mg i.e. 40.3 stoichiometric ratio) was used. Normally, as the amount of the cementator (copper powder) increases, the total surface area of copper powder per rhodium ion increases. Therefore, the likelihood of interaction between metallic copper atoms with rhodium ions present in the solution increases, which should result in a higher cementation (%) (Farahmand et al., 2009). Similar observations were also made in a study by Aktas (Aktas, 2010), where silver cementation (%) increased with increasing quantities of copper.

Fig. 2. The variation in rhodium cementation (%) with the stoichiometric ratio of Cu/Rh (25 °C, 100 rpm, 1 h and 5 mL of 535.8 ppm Rh^{3+}).

Approximately 2.481 mg of copper (stoichiometric ratio of Cu/Rh = 1) would be stoichiometrically adequate to cement all the rhodium from a 5 mL solution containing 2.679 mg of rhodium. Interestingly, 40 times excess copper over the stoichiometric amount was insufficient for complete rhodium cementation; however, the Nernst equation

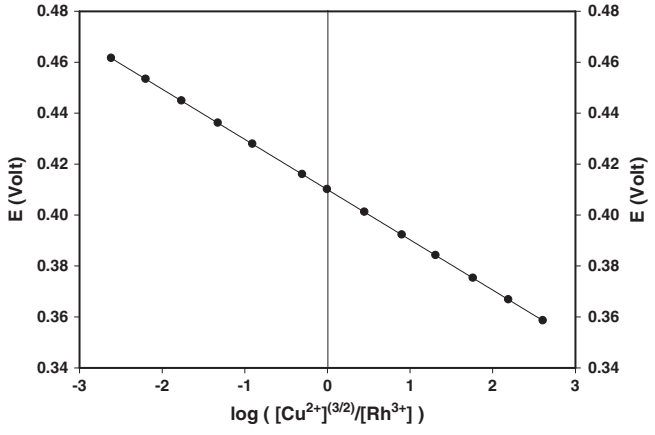

Fig. 1. Theoretical E values with respect to log function of molar ratio.

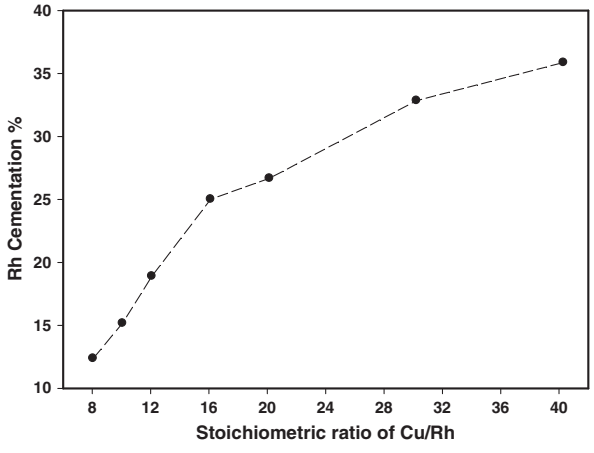

Fig. 2. The variation in rhodium cementation (%) with the stoichiometric ratio of Cu/Rh (25 °C, 100 rpm, 1 h and 5 mL of 535.8 ppm Rh^{3+}).

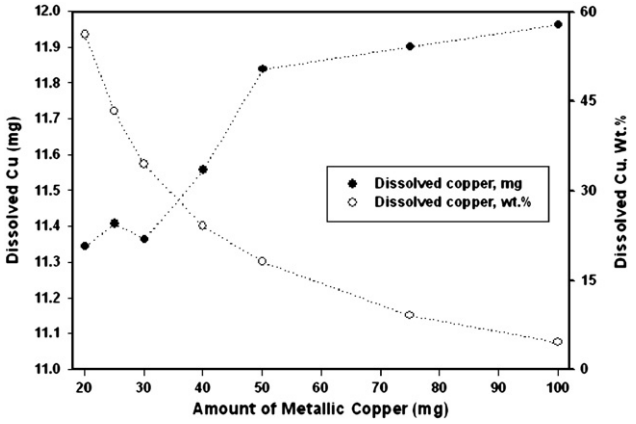

Fig. 3. The levels of dissolved copper (mg) with different quantities of copper (25 °C, 100 rpm, 1 h, 5 mL of 535.8 ppm Rh^{3+}).

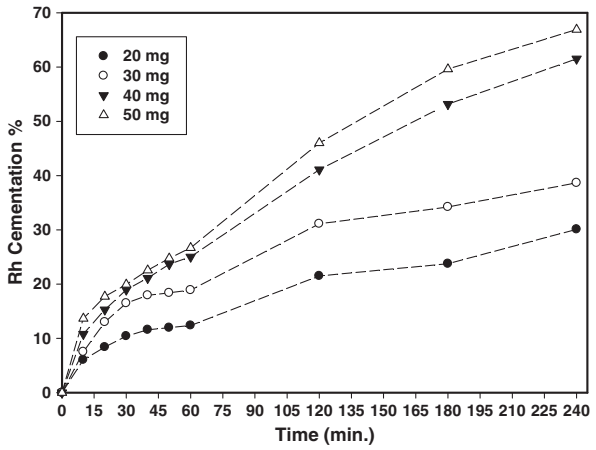

Fig. 4. Variation in solution rhodium cementation (%) over time (25 °C, 100 rpm, 5 mL of 535.8 ppm Rh^{3+}).

(displayed in Eq. (5)) indicates that copper should displace almost all the rhodium.

$$E_{total} = E_{Rh} - E_{Cu}$$

$$E_{Cu} = 0.337 + 0.0296 \log\left[Cu^{2+}\right]; \qquad E_{Rh} = 0.758 + 0.0197 \log\left[Rh^{3+}\right]$$

$[Cu^{2+}] = 1$ M was assumed to simplify the calculations. At equilibrium, $E_{total} = 0$, so $E_{Cu} = E_{Rh}$,

$$0.337 = 0.758 + 0.0197 \log\left[Rh^{3+}\right] \tag{5}$$

$$\log\left[Rh^{3+}\right] = -21.37, \text{thus} \left[Rh^{3+}\right] = 10^{-21.37}.$$

This calculation suggests that almost all rhodium ions present in the solution could be cemented out by copper powder.

It is also worth mentioning that the cementation reaction was relatively slow at room temperature, which resulted in lower cementation percentages. The contact time should be increased to ensure complete precipitation at room temperature or the reaction temperature should be increased. The effects of time and temperature on cementation percentage are discussed in the following sections.

Fig. 3 shows the changes in the amount of dissolved copper in the solution with regard to the amount of copper powder initially added to the solution. Table 1 shows the copper balance of the cementation reaction.

As shown in Fig. 3 and Table 1, most of the copper dissolved in the chloride media instead of causing the cementation of rhodium to occur. Approximately 11 mg of copper was consumed by the free acid in each reaction. However, the use of an excessive amount of copper (e.g., 100 mg, stoichiometric ratio of Cu/Rh = 40.3) promoted the interaction between metallic copper and the rhodium ions, which resulted in higher Rh precipitation percentages.

Table 1
Copper balance in the cementation reaction.

Copper balance*				
Added quantity (mg)	Used for Rh cementation (mg)	Consumed by acid (mg)	Unreacted copper (mg)	Solution pH
20	0.32	11.02	8.66	0.51
25	0.39	11.02	13.59	0.51
30	0.48	10.88	18.64	0.51
40	0.64	10.92	28.44	0.51
50	0.68	11.06	38.26	0.52
75	0.84	11.06	63.10	0.52
100	0.92	11.05	88.03	0.52

* Conditions: 25 °C, 100 rpm, 1 h, initial pH = 0.46.

To observe the effect of time on rhodium cementation, experiments were performed at various time intervals. Fig. 4, Fig. 5 and Fig. 6 show Rh cementation (%), pH variation and dissolved copper (mg) measurements over time.

As shown in Fig. 4, time has an important role in the cementation percentage of rhodium, which increased with increasing reaction time. To achieve almost 100% cementation, the reaction required more than 2 days or 1000 times the stoichiometric amount of copper needed to be employed to increase the collision ratio between metallic copper and rhodium ions. However, we preferred to use a third route: controlling the reaction temperature to attain a higher cementation percentage of rhodium.

These three figures show that copper preferentially reacts with free acid, which results in an incremental increase in pH. The free acid reacts preferentially over rhodium cementation at room temperature. Consequently, copper was partially dissolved into the acidic solution, and then the remaining copper was subjected to the replacement reaction with Rh ions.

After the effects of time were observed, we investigated the effects of temperature on the cementation of rhodium. Some authors have suggested that temperature is the most influential parameter on cementation (Aktas, 2011). The effects of temperature on the cementation of rhodium are displayed in Fig. 7.

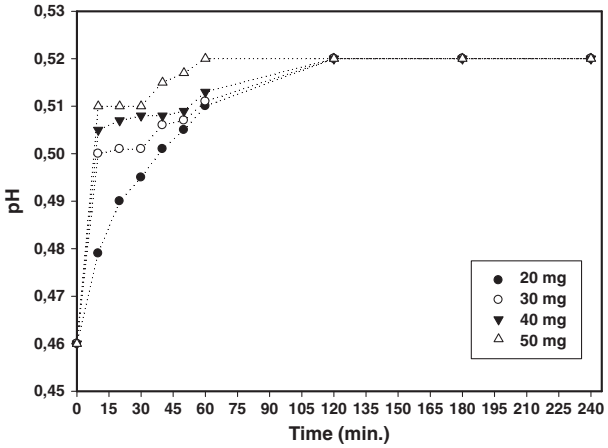

Fig. 5. Variation of solution pH over time (25 °C, 100 rpm, initial pH: 0.46, 5 mL of 535.8 ppm Rh^{3+}).

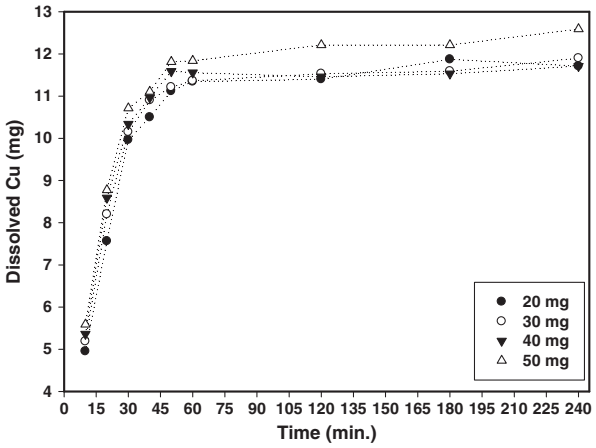

Fig. 6. Variation of dissolved copper over time (25 °C, 100 rpm, 5 mL of 535.8 ppm Rh^{3+}).

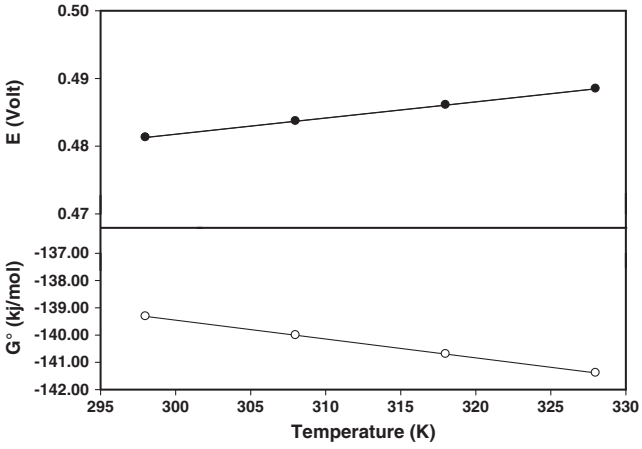

Fig. 9. E and ΔG values against temperature (K) before the reaction.

As shown in Fig. 8, temperature had an important role in the cementation of rhodium using copper powder. Temperature promoted the reaction between copper and rhodium ions. It is also worth mentioning that the plating process is generally conducted at approximately 60 °C because high temperatures facilitate the plating process. For instance, cementation of 20% of the rhodium was observed after 60 min using 40 mg of copper powder at room temperature. However, cementation of 93% of the rhodium was achieved at 65 °C with all the other conditions the same, which proves that the process is under chemical control (Nelson, 1998). The increased cementation (%) may be attributed to the increased temperature at which the deposited structure penetrates and destroys the oxide film of the copper, thus increasing the cementation rate (Farahmand et al., 2009; Aktas and Morcali, 2011).

Consideration of the thermodynamics suggests that increasing the temperature promotes the cementation reaction by increasing the reaction potential and decreasing Gibb's free energy (ΔG), as shown in Fig. 9.

The graph in Fig. 9 is depicted using the Nernst Equation based on the initial concentrations of Rh^{3+} (535.8 ppm) and Cu^{2+} (7.54 ppm). As the thermodynamic calculations suggested, the maximum driving force was obtained at 327 K, which resulted in the maximum rhodium cementation percentage.

Fig. 10 displays the E values versus temperature (K) before and after the reaction.

As can be seen from Fig. 10, as E values are proportional with temperature, they increased with increasing temperature at t = 0, but after 60 min E values are decreased since copper concentration increased while that of rhodium decreased, which ensures a higher cementation percentage. For example, at 298 K, the E value was 0.41 V after 60 min, which indicated that many rhodium ions were available to be reduced by the copper, so a longer reaction time would be required for a higher degree of cementation to occur. At

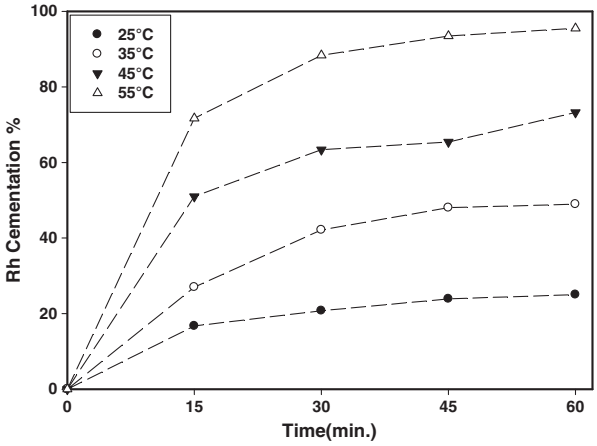

Fig. 7. The variation in rhodium cementation (%) over time at various temperatures. (40 mg copper, 100 rpm, 5 mL of 535.8 ppm Rh^{3+}).

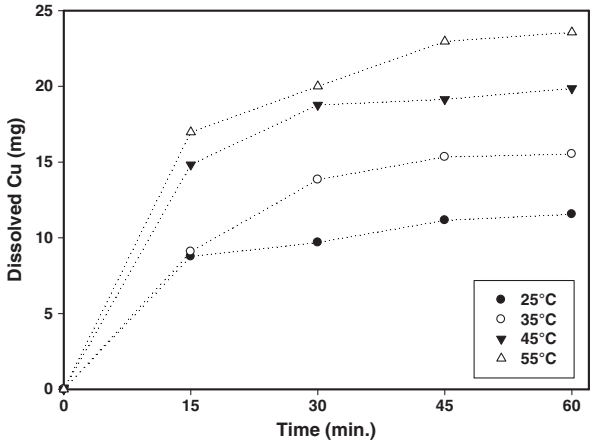

Fig. 8. The variation of dissolved copper over time at various temperatures. (25 °C, 40 mg copper, 100 rpm, 5 mL of 535.8 ppm Rh^{3+}).

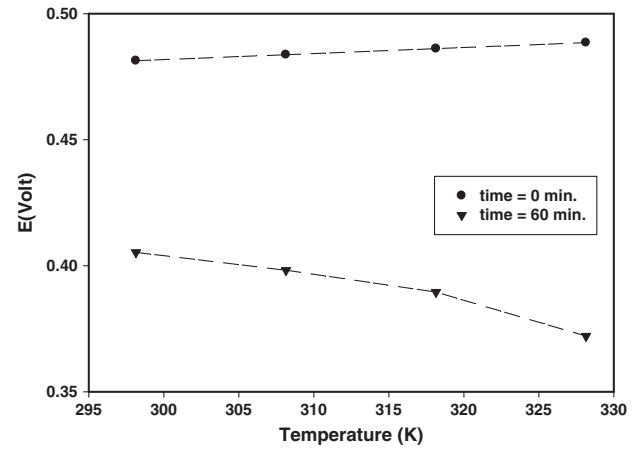

Fig. 10. E values against temperature (K) before and after the reaction.

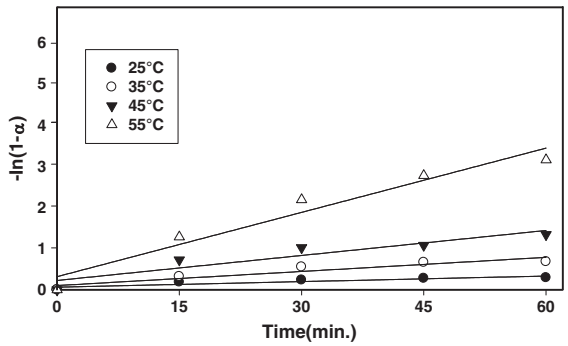

Fig. 11. The plot of − ln (1-α) versus time.

328 K, the E value was 0.39 V after 60 min, which indicated that the rhodium concentration dropped considerably, so a low concentration of rhodium ions was available to be reduced by the copper powder.

After demonstrating the importance of temperature on the cementation reaction, which was also observed in previous studies (Aktas, 2010, 2011), the rate constant (k) of rhodium cementation within the temperature range of 298–328 K was determined.

For this purpose, − ln (1-α) was plotted over time (Havlik, 2008), as shown in Fig. 11. α denotes the cementation (%).

The activation energy (E_a) was calculated using the Arrhenius equation according to the following formula:

$$k = Ae^{-Ea/RT} \quad \text{or} \quad \ln k = \ln A - Ea/RT$$

where k is the rate constant, E_a is the activation energy, R is the gas constant and T is the temperature (K). Fig. 12 shows the Arrhenius plot of ln k vs. $10^3/T$ for rhodium cementation. At a temperature range between 25 and 55 °C, the activation energy for rhodium cementation was calculated to be 64.48 kJ/mol, which indicates that the cementation process is mainly governed by a chemically controlled process (Habashi, 1976).

3.2. Characterization of the obtained powders

Following the production of metallic rhodium powder, the powder was washed with fresh 0.05 M HNO_3 (pH = ~1.3), distilled water and then acetone. Subsequently, the powders were dried under a vacuum at 80 °C for 1 h.

To determine the purity of the produced powder, the powder was dissolved in fused sodium bisulfate ($NaHSO_4$) at approximately 600 °C to allow complete dissolution (Aktas, 2011). The sample was

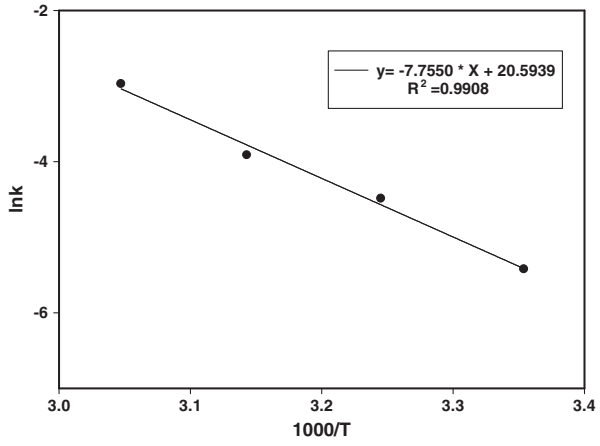

Fig. 12. The Arrhenius plot of ln (k) vs.1000/T for the cementation of rhodium by copper powder.

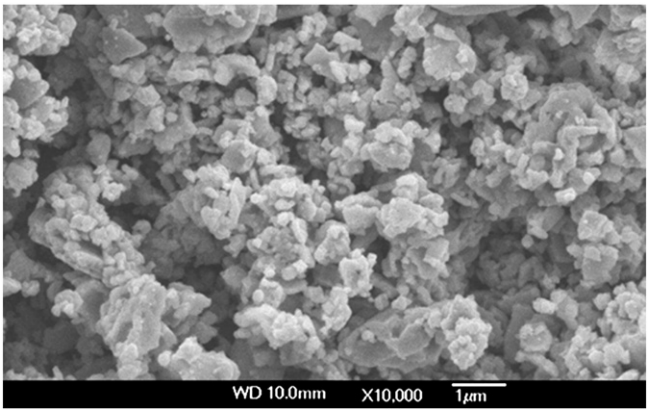

Fig. 13. SEM image of the rhodium powder obtained via cementation using copper powder (10,000×).

found to contain 98.65% rhodium. The copper content of the sample was determined to be 1220 ppm. According to the SEM images shown in Fig. 13, a porous powder was obtained containing nano-sized particles, and the powder had a structure that is typically obtained via cementation reactions.

4. Conclusion

In the present work, we attempted to precipitate rhodium from a rhodium-containing waste solution that was used in decorative rhodium plating. It was demonstrated that less than 40% of the rhodium metal in the waste solution could be recovered using excessive quantities of copper powder (e.g., 100 mg) at room temperature for 1 h. However, increasing the reaction time to 4 h using 50 mg of copper powder (stoichiometric ratio of Cu/Rh = 20.2) resulted in more than 60% cementation. Thus, it was concluded that the cementation reaction is too slow at room temperature. Increasing the reaction temperature to 55 °C resulted in almost 99% cementation even with 40 mg of copper powder (stoichiometric ratio of Cu/Rh = 16.1) after 1 h. Thus, temperature was shown to be an important parameter in the cementation reaction, which is in accordance with the literature. Most of the copper powder was consumed by the free acid in the medium before reacting with rhodium in the cementation process. The activation energy of rhodium cementation by copper was calculated to be 64.48 kJ/mol. The method used in this report resulted in a fine rhodium powder with a purity of 98.65%. The copper content of the powder were found to be 1220 ppm. The impure powder can be directly sold to any refinery but requires further purification prior to being used for the preparation of a rhodium sulfate plating solution. The proposed process avoids many environmental problems and allows for the non-hazardous hydrometallurgical treatment of valuable rhodium-containing waste solution.

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