

Recovery of Ruthenium Via Zinc in the Presence of Accelerator

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Abstract In this study, the recovery of ruthenium from spent bath solutions via cementation reaction with zinc powder was investigated. Studied parameters included the quantity of zinc, reaction temperature, reaction time and sodium chloride additions to understand their effects on the reaction. Tests were performed in a temperature controlled water-bath with temperatures between 20 and 70 °C at atmospheric pressure. Furthermore, in order to determine activation energy of cementation reaction, several mathematical kinetic models were used and the activation energy, which was calculated from best fit, was found to be 12.48 kJ/mol. Addition of sodium chloride to the solution greatly accelerated the cementation reaction, in that, more the addition of sodium chloride, the better was the precipitation efficiency. In the absence of sodium chloride at 25 °C a percentage of ruthenium recovery was below 75% whereas 1000 mg sodium chloride addition at 65 °C ensured a percentage of ruthenium recovery more than 95%. This corresponded to more than about 28% increase.

Keywords Ruthenium · Zinc · Cementation · Recovery · Spent bath solutions

1 Introduction

The importance of the Platinum group metals (PGMs) in our present day civilization is a result of a growing dependence upon catalysis electronic and plating in industry. There are many application fields for PGMs, such as their use for inert tools in laboratories and the glass industry, for dental applications, in the electronics industry, for special alloys and some specific compounds etc.

Ruthenium (Ru) is one of the most important metal in PGM's and it is inexpensive compared with others but more expensive than silver and base metals (i.e. Cu, Zn, Pb etc.) due to the fact that it is very rare in nature and normally found in combination with nickel or platinum. The extraction and recovery of Ru from industrial scrap and effluent solution is of increasing importance as world demand grows. Up to now, most of the Ru manufactured is used for wear-resistant electrical contacts and the production of thick-film resistors. And other application of Ru is its use in some platinum alloys, and as a catalyst [1, 2].

Nowadays, many companies prefer Ru coatings rather than Rh since the former gives better black plating and also as a consequence of its lower cost and similar properties compared to Rh [3]. Sulfuric acid bath of Ru has been frequently used for a long time [4] and it is usually used for plating common metals and alloys for industrial applications [1, 3, 4]. The refining process of PGMs from ores involves more complex step compared to other base metals and in these steps, significant amount of PGMs are lost owing to the inadequacy of the production method [5–7]. Due to increasing use of Ru in plating industry, treatment of wastewater is one of the most important topics for recovery of Ru process. However, there are not much studies in the literature that investigates the recovery of Ru. Some studies have been related with removing Ru ions

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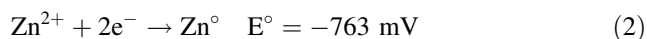
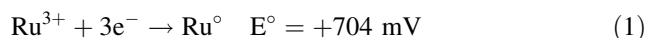
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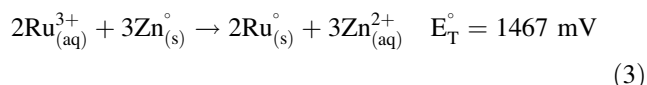
from solutions by solvent extraction [1, 8, 9], adsorption [1, 10–13] and cementation [1, 14–16]. Because of some advantages of the cementation method such as its reaction path, cost, time and ease of applicability than other processes, it is employed to recuperate Ru. Cementation processes are heterogeneous systems in which a noble metal in solution is reduced by a less noble (sacrificial) metal that dissolves as the reaction proceeds.

Zinc is a cementing agent historically used for recovering all precious metals (e.g. Platinum, Rhodium, Gold, Silver, Copper etc.) Zinc (Zn) has been chosen as cementator metal in this study because of its low cost [1, 7, 17, 18].

The possible form of the cementation reaction appears below:



The general reaction is shown in Eq. (3):



where Ru is noble metal being reduced and Zn is the reductant metal.

This work examines the influence of sodium chloride (NaCl) the rate of cementation of Ru^{3+} with zinc powder by temperature-controlled shaking bath in order to correlate the thermodynamic parameters of activation.

The ultimate goals of this work are the following:

1. to recover Ru from a spent bath solution through cementation with the help of zinc powder,
2. to investigate the consumption of zinc powder during this process and
3. to examine pH changes during the cementation process as well as the effects of temperature on the cementation process.

2 Materials and Methods

A spent ruthenium sulfate bath solution, supplied from a decorative ruthenium plating workshop, was used as the Ru source in this work. The zinc powder used, obtained from Alfa Aesar, was 99.5% pure and with particle size less than 150 μm . Sodium chloride (NaCl) used as an inorganic salt, supplied from Aldrich, was 99.5% pure.

The effects of time, temperature, amount of Zn powder and addition of NaCl were studied. Also, the pH of solution was recorded for each sample regularly. Each solution sample was analyzed for Ru content by Atomic Absorption Spectrometer (Analytik Jena ContrAA AAS 300,

Germany). A pH meter was used for the determination of solution pH. 10 mL Ru-containing spent solution was used in all experiments.

Immediately after taking sample in the shaking bath, the solution was filtrated and the cementing agent was filtered out, thereby, ending the reaction. The Ru recovery percentage (%) was calculated by the formula given below:

$$\text{Ru Recovery (\%)} = [(C_i - C_f)/C_i] \times 100 \quad (4)$$

where C_i is the initial Ru concentration (547 ppm), and C_f is the final Ru concentration in solution at the end of the experiment.

3 Results and Discussion

Even though zinc powder is certainly one of the most inexpensive and effective reagent used in the Ru cementation process, reducing its quantity and finding its minimum required amount to meet the desired removal of Ru is at the core of optimization studies done on the process due to environmental concerns and diminishing access to resource.

Figure 1 shows that the Ru recovery (%) rises with the increased amount of Zn powder, which is in accordance with our previous works that studied the cementation percentage with regard to the amount of the sacrificial metal [17–21].

A linear relationship exists between amount of Zn and Ru precipitation percentage but only up to 30 mg/10 mL (3 g/L). The superficial explanation is that, increasing the amount of zinc increases the available surface area and, therefore, increases the rate of Ru removal. This result is supported by a study of Rh cementation via Zn by Aktas [18]. However, as the addition is increased up to levels

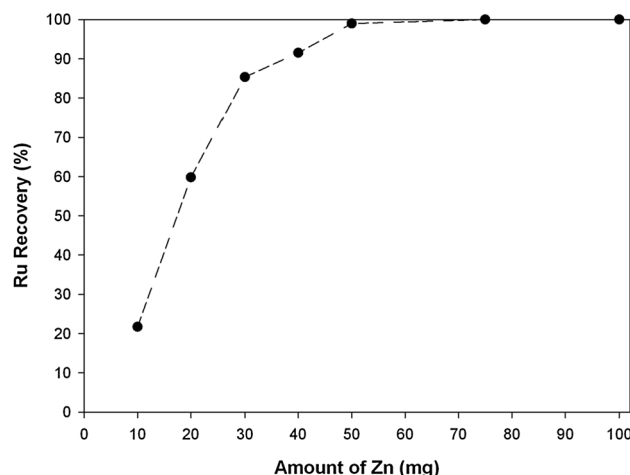


Fig. 1 The variation in ruthenium recovery (%) with the amount of zinc powder (25 °C, 200 rpm, 60 min., 10 mL sol.)

greater than 3 g/L, the relationship began to deviate from linearity.

Theoretically, 5.31 mg of zinc will be sufficient to precipitate all the Ru ions in 10 mL solution. Nevertheless 10 times excess zinc over the theoretical amount corresponding to 50 mg Zn is found to be adequate for reduction of Ru ions in the solution; however, the Nernst equation (see Eq. 5) shows that all Ru ions should be precipitated under standard conditions.

$$E_{\text{total}} = E_{\text{Ru}} - E_{\text{Zn}}$$

$$E_{\text{Zn}} = -0.768 + 0.0296 \log [\text{Zn}^{2+}];$$

$$E_{\text{Ru}} = 0.704 + 0.0197 \log [\text{Ru}^{3+}]$$

$[\text{Zn}^{2+}] = 1 \text{ M}$ has been selected to simplify the calculations. At equilibrium, $E_{\text{total}} = 0$, so $E_{\text{Zn}} = E_{\text{Ru}}$,

$$-0.768 = 0.704 + 0.0197 \log [\text{Ru}^{3+}] \quad (5)$$

$$\log [\text{Ru}^{3+}] = -74.72, \text{ thus } [\text{Ru}^{3+}] = 10^{-74.72}$$

This theoretically calculated result shows that nearly all Ru ions in the solution can be cemented out by Zn powder under standard conditions. However, this is not a standard condition. It is therefore concluded that much of Zn has been consumed by free sulfuric acid present in the bath solution. This is the reason why pH measurements have been undertaken to prove this unexpected zinc consumption.

Figure 2 displays the change in solution pH with different quantities of zinc.

In the course of an experiment, the pH rises due to consumption of hydronium ions $[\text{H}_3\text{O}^+]$ in the hydrogen evolution reaction. As can be seen in Fig. 2, the pH of the solution (initially $\text{pH} = 0.46$) increases as the amount of zinc powder increases, which indicates that zinc has

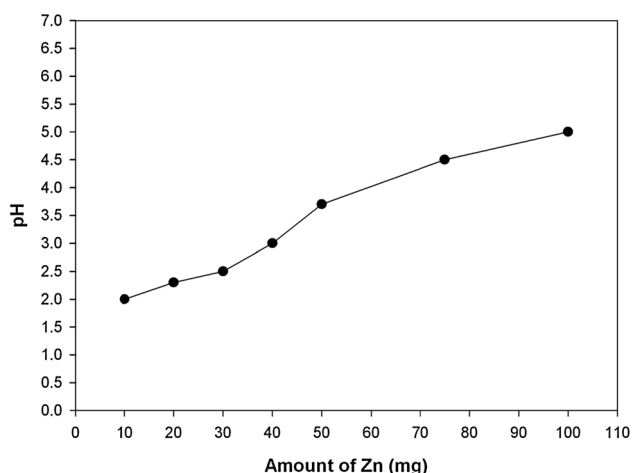


Fig. 2 The variation in solution pH with different quantities of zinc (25 °C, 200 rpm, 60 min., 10 mL sol.)

preferentially reacted with free sulfuric acid rather than causing the cementation of Ru to take place.

For cementator metal consumption, all the effects are significant. Not only do the two factors (replacement and acid) have significant main effects, but there are interactions between them all as well. In order to understand zinc powder consumption, a new experimental series have been carried out. Zinc powder consumption has been determined by calculating the weight of the dissolving zinc powder from the weight of the initial amount used in the experiment. Figure 3 and Table 1 present that most of cementator has been consumed by hydronium ions $[\text{H}_3\text{O}^+]$ instead of Ru when small amount of Zn is used.

At 60 min, almost 6 mg of Zn has been used by the free sulfuric acid (see Table 1). Nevertheless, when the quantity of Zn used is 50 mg or above, the reaction between Zn powder and Ru ions increases and as a result, higher Ru precipitation percentages are obtained. In scientific literature, the pH of the solution rises during cementation due to the consumption of hydrogen ions by the hydrogen evolution reaction. This increase in pH is more substantial near the surface of zinc powder, where the H_3O^+ ions get reduced.

It is well known that cementation reactions are slower at room temperature than at high temperature. So as to improve the recovery percentage, both reaction temperature and time should be selected according to the behavior of reaction conditions.

The role of reaction time in the Ru cementation process has been studied systematically. As can be seen in Fig. 4, reaction time is one of the important parameter and has a significant effect on Ru (%). Increasing reaction time (from 5 to 120 min with 50 mg Zn) enhances the recovery percentage of the Ru substantially. In this way, a Ru concentration of 0.1 mg/L (above 99%), can be obtained in

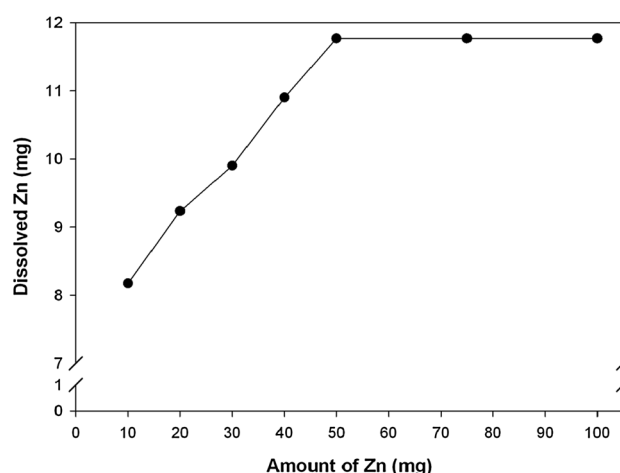
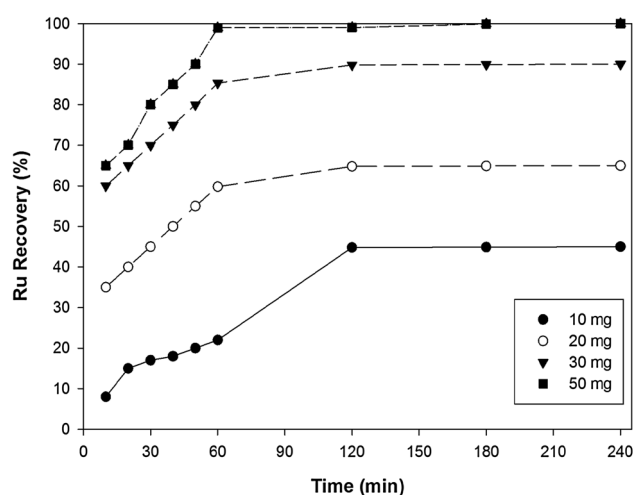


Fig. 3 The levels of dissolved zinc (mg) with different quantities of zinc (25 °C, 200 rpm, 60 min., 10 mL sol.)

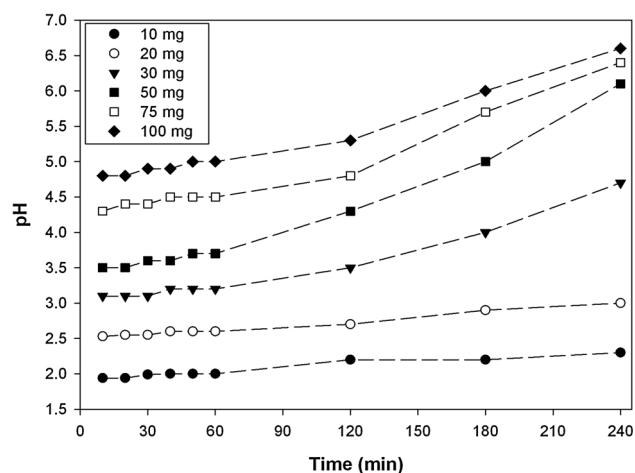
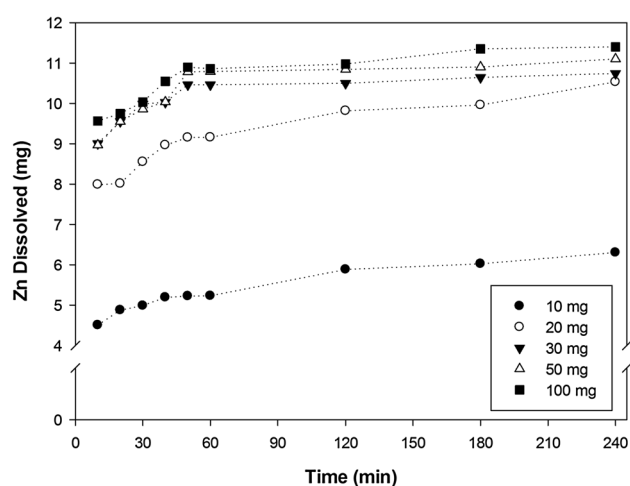
Table 1 Zinc consumption in the Ru recovery process (25 °C, 200 rpm, 60 min.)

Added Zn quantity (mg)	Used for cementation (mg)	Consumed by acid (mg)	Unreacted zinc (mg)	Final pH
10	1.154	5.016	3.830	2.01
20	3.178	5.052	11.770	2.32
30	4.536	5.364	20.100	2.50
40	4.866	6.034	29.100	3.07
50	5.261	6.309	38.430	3.76
75	5.316	6.454	63.230	4.53
100	5.316	6.614	88.070	5.05

**Fig. 4** Variation in solution ruthenium recovery (%) over time (25 °C, 200 rpm and 10 mL sol.)

just 60 min with 50 mg Zn, something that could not be obtained in similar time using 40 mg of Zn.

Additionally, the solution pH and dissolved Zn amount with regard to time are shown in Figs. 5 and 6,

**Fig. 5** Variation of solution pH over time (25 °C, 200 rpm, initial pH = 0.46 10 mL sol.)**Fig. 6** Variation of dissolved zinc over time (25 °C, 200 rpm, 10 mL sol.)

respectively. From the obtained results, it can be inferred that an increase of zinc powder amount from 10 to 100 mg expectedly lead to an increase in the level of pH. After dissolving zinc in free acid, the rest of zinc reacts with Ru ions to produce black Ru cement [15, 17]. Ru cementation has been studied in the temperature range of 25–65 °C. The results are summarized in Figs. 7 and 8.

As the results show, the lowest Ru concentrations in solution achieved after 240 min and the fastest Ru precipitation rates are experienced with 20 mg Zn at 55 °C, the highest temperature tested (see Fig. 7). However, same recovery percentage is obtained in 60 min with 50 mg Zn at same temperature.

Consequently, Ru removal experiments and the final Ru concentrations are both improved with increasing temperatures [17–19, 21]. In scientific literature, high temperature has been cited to be the most effective reaction parameter with regard to the increase of cementation yield performance [17].

Following section establish the effect of temperature on the cementation reaction. The rate constant (k) of Ru is

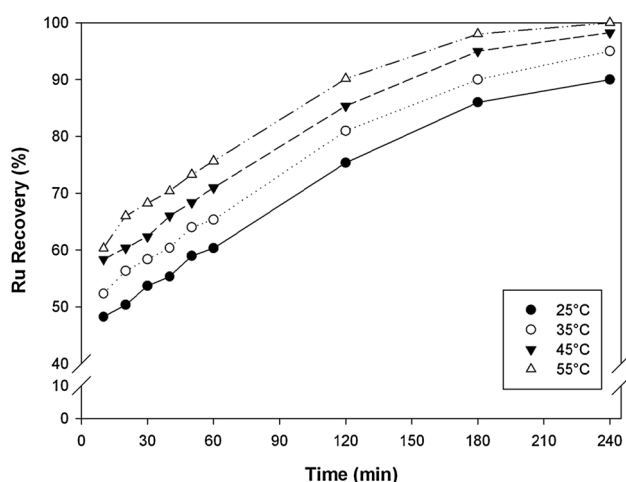


Fig. 7 The change in ruthenium recovery (%) over time at various temperatures (20 mg zinc, 200 rpm, 10 mL sol.)

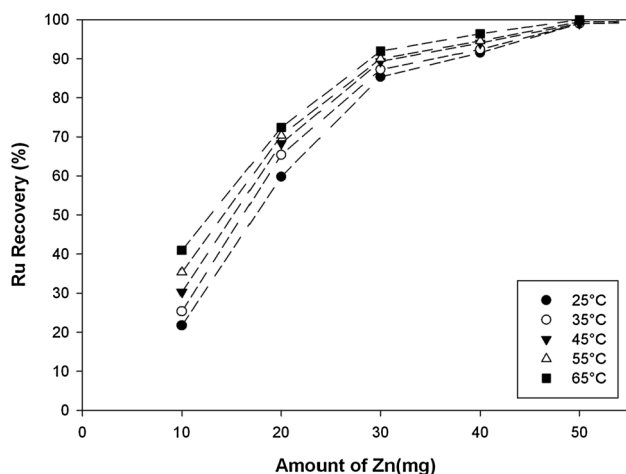


Fig. 8 The variation of dissolved zinc over time at various temperatures (200 rpm, 60 min., 10 mL sol.)

determined by taking the slope of the line within 313–343 K. For each calculated value of k , the corresponding correlation coefficient, R^2 , is greater than 0.99, indicating excellent agreement with the linear model describing first order kinetics $[-\ln(1 - \alpha)]$ [22–24]. The plot is given in Fig. 9.

These adjusted rate constants have been employed to plot an Arrhenius graph in which the activation energy for the Ru recovery process, that is calculated from the slope of an Arrhenius plot in Fig. 10, is 12.8 kJ/mol, which proves the process to be of diffusion controlled nature. The first order rate constant including, the diffusion coefficient, determines the rate of cementation of Ru from spent plating solutions and total reaction performance [22].

It is well known that no displacement reaction occurs in sulfate media between rhodium and copper metal. [18]. And we thought that similar behavior can be observed in

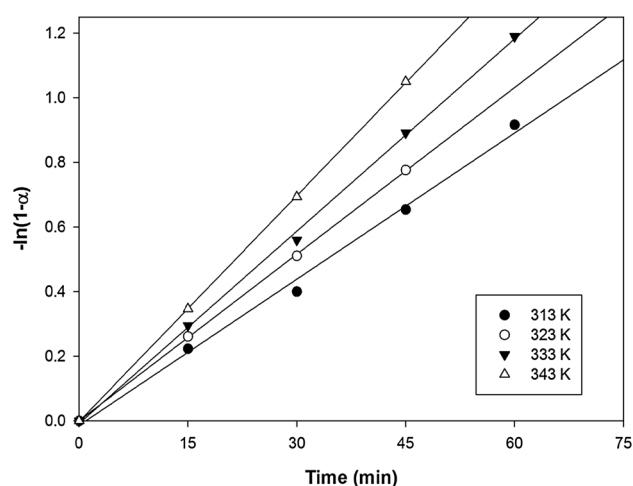


Fig. 9 The plot of $-\ln(1 - \alpha)$ versus time

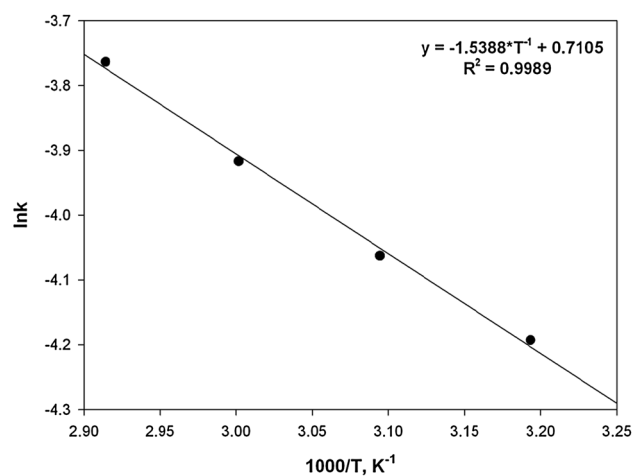


Fig. 10 The Arrhenius plot of $\ln k$ versus $1000/T$ for the cementation of ruthenium by zinc powder

ruthenium sulfate media. That's why sodium chloride has been used as a chloride source so as to increase displacement reaction between ruthenium and zinc in sulfate media instead of exposing the media to chlorine.

As can be seen from the Fig. 11, addition of NaCl greatly accelerates cementation reaction due to the presence of chloride ion. Addition of hydrochloric acid is not recommended since it will unnecessarily increase zinc consumption rate which has been already proved by pH measurements. On the other hand, as NaCl has a neutral nature it does not affect pH negatively. It is also worth mentioning that with the combination of temperature, addition of sodium chloride plays a significant role in the Ru recovery percentage in that in the absence of NaCl at 25 °C, a percentage of Ru recovery is below 75% whereas addition of 1000 mg NaCl at 65 °C ensures a percentage of Ru recovery more than 95%. This corresponds to a more than 28% increase for a reaction with duration of 2 h.

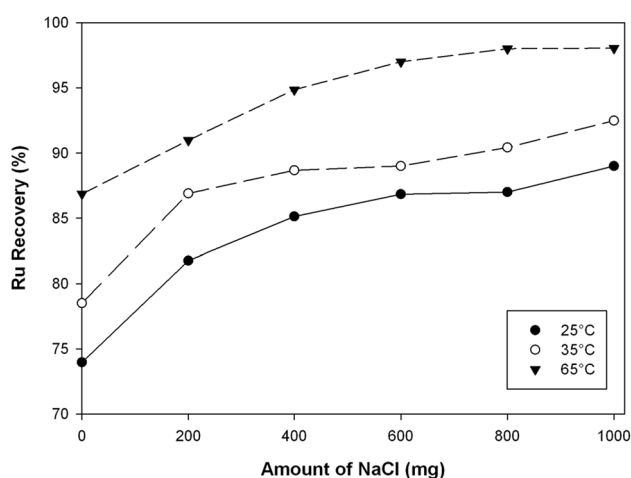


Fig. 11 The variation of Ru recovery (%) in the presence of NaCl at various temperatures (20 mg zinc, 200 rpm, 120 min., 10 mL sol.)

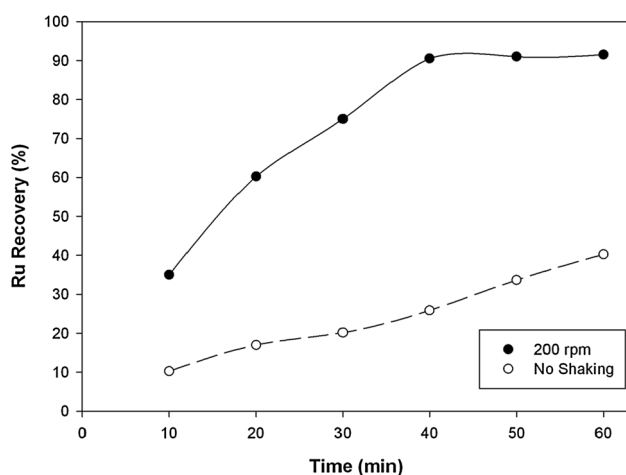


Fig. 12 The comparison of Ru recoveries between 200 rpm shaking and no shaking. (25 °C, 200 rpm, 40 mg zinc, 60 min., 1 g NaCl, 10 mL sol.)

Finally the effect of shaking has been investigated. Figure 12 displays that shaking plays an important role in this cementation reaction, which also proves that the reaction is a diffusion controlled reaction considering low activation energy [22, 23].

4 Conclusion

The goal of this study was to understand which parameters played major role on the cementation reaction of Ru ions contained in spent bath solutions, which were initially used for decorative purposes, by zinc powder. The variables tested were, amount of zinc, reaction temperature, reaction time, shaking and the addition of sodium chloride and their interactive effects. It was demonstrated that more than 99%

of the Ru would be recovered with much more theoretically calculated zinc powder (e.g., 75 mg per around 5.5 mg Ru^{3+}) at room temperature for 1 h. The reason for this was that zinc was favorably spent by free sulfuric acid, which was also verified by repeated measurements of zinc concentration and solution pH. A temperature increase to 65 °C resulted in nearly 100% cementation after 4 h, even though lower quantities of zinc powder (20 mg) was used. Both time and temperature were shown to be effective parameters. The activation energy of Ru recovery was found to be 12.8 kJ/mol, which indicated diffusion control reaction mechanism.

As the results showed, even in laboratory scale study, a large excess of zinc powder addition was required to reach the desired Ru recovery. The amount of zinc powder excess could be higher in the industrial plants due to the complexity of the industrial electrolytes. It might be interesting to track the added zinc powder to determine how and where it was transported.

- A large portion of the zinc powder was consumed (dissolved) with the hydrogen evolution reaction. Scientific literatures reported that $\text{H}_{2(\text{g})}$ evolution consumed over 100 times more zinc powder than the noble metal cementation.
- Besides the consumption of zinc powder with the hydrogen evolution reaction, passivation of the cementator with zinc salts was another parasitic phenomenon which made zinc powder inaccessible for the Ru cementation reaction.

In the absence of NaCl at 25 °C, a percentage of Ru recovery was below 75%, whereas 1000 mg NaCl addition at 65 °C ensured a percentage of Ru recovery more than 95%. This corresponded to more than about 28% increase for a duration of 2 h reaction. In the light of these results, if NaCl was to be dissolved in solution or added in solid form to obtain high recovery percentage, this should be done before addition of zinc powder to the solution.

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