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INVESTIGATION OF COPPER CEMENTATION KINETICS BY ROTATING ALUMINUM DISC FROM THE LEACH SOLUTIONS CONTAINING COPPER IONS

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Abstract. Recovery of metallic copper from the leach solution containing copper (II) ions by cementation process using aluminum disc has been examined. Solutions obtained from the leaching of malachite in aqueous acetic acid solutions were used in the study. It was determined that the cementation rate increased with increasing solution concentration, temperature and rotating speed, and decreasing solution pH. The reaction rate fits to the first order pseudo homogeneous reaction model and is controlled by diffusion. The activation energy of this process was calculated to be 32.6 kJ/mol.

keywords: copper cementation, leaching, malachite, activation energy

1. Introduction

Most of metals are found in nature as complex mixtures of their sulfides, oxides, carbonates, silicates etc. Metals are generally produced after being extracted from an ore or its concentrates. The extraction of metals from the metal sources is carried out either by pyrometallurgy or hydrometallurgy (Venkatachalam, 1998; Gupta and Murkherjee, 1990). Hydrometallurgical methods in processing ores, concentrates, and secondary metal sources (various industrial wastes) have gained recently increasing importance in the extraction of nonferrous metals from ores.

Hydrometallurgy is essentially concerned with methods whereby metals, metal salts, or other metal compounds are produced by means of chemical reactions involving aqueous and organic solutions (Gupta and Murkherjee, 1990). It covers a large variety of processes ranging from the leaching of metal values in an aqueous solvent through the purification of the solutions to the recovery of the metals or their compounds by chemical or electrochemical precipitation (Venkatachalam, 1998; Rosenqvist, 2004).

Leaching is the first step of any hydrometallurgical process. Leaching is the term applied to the process of recovering a metal from the metal source by a solvent or lixiviant. The metallic value in a metal source passes into the solution by dissolving in

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the leaching step. During this step, in addition to the desired metal, other metals present in the ore matrix may also pass into the solution. Therefore, before the final recovery of the desired metal, purification processes are applied to remove the impurities from the leach liquor. There are many ways to achieve this goal (Venkatachalam, 1998; Gupta and Murkherjee, 1990; Han, 2002). Metal value can be directly obtained from the leach liquor without purification in some cases.

The final part of a hydrometallurgical flow sheet concerns the recovery process. The acquired product is either the elemental metal or its suitable compound. The various techniques available for the recovery of a metal from the leach liquors with or without purification are crystallization, ionic precipitation, reduction with a gas, electrochemical reduction (cementation), and electrolytic reduction (Gupta and Murkherjee, 1990).

Among the metal gaining processes, cementation, which is basically an electrochemical reduction process, is one of the most effective and economic methods applied successfully for obtaining of valuable metals from industrial solutions. The advantages of this technique are its relative simplicity, ease of control, and low energy consumption (Venkatachalam, 1998; Gupta and Murkherjee, 1990; Naubactep, 2010; Kuntyi et al., 2011). That process involves the chemical reduction of metal ions by galvanic interaction between noble metal ions and a more active metal in an aqueous solution medium. (Venkatachalam, 1998; Gupta and Murkherjee, 1990**)**. For any cementation reaction the overall reaction equation can be written as follows

$$N^{n+} + M^0 \longrightarrow N^0 + M^{m+} \tag{1}$$

where, N is the noble or precipitating metal, M is the reductant metal.

Copper is among the most intensively applied and valuable metals used by industry. It is used mostly in the electrical and electronics industries because of its high electrical conductivity. In addition, copper and its alloys are utilized in the engine, communication, and aviation industries, for electricity production and distribution, in measuring devices, in chemical industry etc. (Dib and Makhloufi, 2004; Arzutug et al., 2004).

Copper generally is found in nature in the form of sulfide and oxide minerals, such as azurite, malachite, tenorite, chrysocolla, bornite, brochantite, enargite, chalcopyrite, chalcocite, covellite (Akçıl, 2002; Arzutug et al., 2004; Bingöl et al., 2005). Metallic copper is produced from these ores by pyrometallurgical and hydrometallurgical methods. In production of copper from low-grade oxidized copper ores, hydrometallurgical methods are commonly preferred because pyrometallurgy is not feasible for these type ores.

Among the oxidized copper ores, malachite is the most popular. The leaching and kinetics of malachite has been investigated by various researchers (Oudenne and Olson, 1983; Künkül et al., 1994; Yartaşı and Çopur, 1996; Ekmekyapar et al., 2003; Bingöl and Canbazoğlu, 2004; Arzutuğ, 2004; Bingöl et al. 2005; Lui et al., 2010). Malachite ore can be used to produce metallic copper and copper compounds by hydrometallurgical techniques. After leaching of malachite with a convenient lixiviant, copper in the purified leach solution can be precipitated by cementation, deposited by direct electrowinning or solvent extraction-electrowinning methods. In cementation and direct electrowinning methods copper is obtained in metallic state, while in solvent extraction-electrowinning method, copper is first selectively recovered from the solution by chelating Cu^{2+} and dissolving in an organic solvent, and then the solvent is stripped off from the chelat by a strong acid to give a solution to be amenable to electrowinning process (Ekmekyapar et al., 2003; Elamari et al., 2006).

In the recovery of copper from the leach solution by cementation process, when aluminum is used as reductant metal, copper ions are easily reduced to its metallic state due to the difference between the electrode potentials of these two metals. The standard reduction potentials of copper and aluminum are 0.34 and -1.67 V, respectively. During the cementation process, the half-cell reactions occurring are:

$$Cu^{2+} + 2e^{-} \leftrightarrows Cu^{o} \quad \text{(reduction reaction)} \quad E^{o} = 0.34\ \text{V} \tag{2}$$

$$Al^{o} \leftrightarrows Al^{3+} + 3e^{-} \quad \text{(oxidation reaction)} \quad E^{o} = -1.67\ \text{V} \tag{3}$$

Thus, the whole cementation reaction of copper ions onto aluminum disc may be expressed by the following reaction equation:

$$3Cu^{2+} + 2Al^{o} \longrightarrow 3Cu^{o} + 2Al^{3+} \quad \Delta E^{o} = 2.01\ \text{V} \tag{4}$$

As can be seen from Equation (4), the potential of this cementation reaction is positive, and the standard free energy, ΔG^{o}, is negative ($\Delta G^{o} = -nF\Delta E^{o}$). The negative value of the standard free energy indicates that this process is favorable thermodynamically, and thus a spontaneous heterogeneous reaction takes place in the galvanic cell.

Recovery of copper from various solutions containing copper (II) ions by cementation reaction has been studied by many researchers. In these studies related to copper cementation iron has been generally used as sacrificial metal because of its cheapness. However, zinc and aluminum have been also used as precipitant or reductant metals (MacKinnon and Ingraham, 1970; MacKinnon and Ingraham, 1971; MacKinnon et al., 1971; Annamalai et al., 1978; Annamalai and Murr, 1978; Chen and Lee, 1994; Wei et al., 1994; Masse and Piron, 1994; Djokic, 1996; Stefanowicz et al., 1997; Dönmez et al., 1999; Kanungo et al., 2001; Stankoviç et al., 2004; Dib and Makhloufi, 2004; Kanungo et al., 2003; Karavasteva, 2005; Fouad and Abdel Basir, 2005; Hung et al., 2005; Demirkıran et al., 2007; Amin and El-Ashtoukhy, 2011).

In most of works in the literature copper cementation with a reductant metal has been mostly carried out using synthetic pure solutions containing copper ions. In the present study, metallic copper was recovered by using the actual solution which is derived from after the leaching of malachite ore in acetic acid solution. For the recovery of copper a rotating aluminum disc was used as the reductant metal. In the experiments the influence of copper ion concentration, reaction temperature, solution pH, and disc rotation speed on copper cementation were investigated. The kinetics of the cementation reaction was evaluated by measuring the rate of decrease of copper concentration in the solution.

2. Materials and Methods

Before recovery of metallic copper from the leach solution by cementation reaction, malachite ore was leached in aqueous acetic acid solution. The aim of the leaching experiment is to produce the liquor required for cementation tests.

Malachite ore sample, an oxidized copper ore, used in the leaching process was supplied from Palu region Elazığ, Turkey. The ore sample was crushed, ground, and then sieved using ASTM sieves to obtain the desired particle size fractions. The fraction of 164 µm was utilized for the leaching tests in our experiment. The mineralogical analysis of the malachite ore sample was performed by means of a Rigaku RadB-DMAX II X-ray diffractometer. The results of X-ray analysis are given in Fig. 1. The chemical composition of the sample is shown in Table 1.

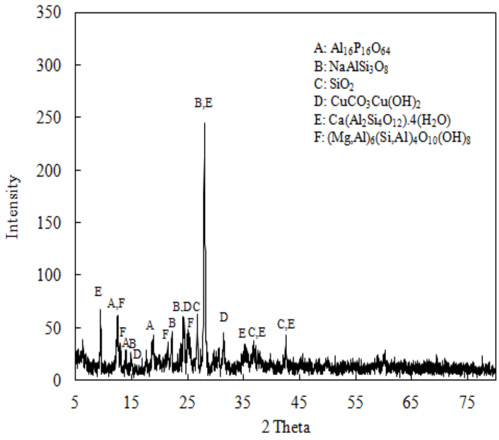

Fig. 1. X-ray diffractogram of malachite ore used in the study

Table 1. Chemical analysis of malachite ore used in the study

Component	SiO_2	Al_2O_3	MgO	Fe_2O_3	CuO	CaO	Na_2O	TiO_2	Ignition loss	Other oxides
Value, %	46.40	17.00	7.30	6.87	5.20	3.30	2.30	1.30	8.00	2.33

The leaching experiment was carried out in a glass reactor of 1 dm^3 volume equipped with a mechanical stirrer having a digital controller, a thermostat and a back-cooler. The optimum conditions of leaching determined by preliminary tests were temperature 40ºC, solution concentration 1 mol/ dm^3, stirring speed of 400 rpm, solution volume 500 cm^3, particle size of 164 µm, ore amount 2 g, leaching time 120 min.

After pouring 500 cm^3 of acetic acid solution (1 mol/dm^3) into the reactor and bringing it to the desired reaction temperature (40ºC), a given amount of malachite ore

(2 g) was added to the solution, and the stirring speed was set to 400 rpm. The leaching process was carried out for 120 min of reaction time. At the end of this operation the content of the reactor was immediately filtered. The amount of copper (II) ion in the filtrate was determined by complexometric titration using EDTA as a titrant and murexide as an indicator. The amount of extracted copper from the ore after 120 min of leaching time was calculated as 1.58 g/dm^3. The solution attained in the leaching step was considered as the mother liquid and it was diluted by adding distilled water to reach the desired concentration of copper(II) ion for utilization in the cementation stage. Process variables chosen for cementation process are given in Table 2. Cementation studies were performed in a 1 dm^3 glass reactor equipped with a mechanical stirrer, a reaction temperature control unit, and a cooler to avoid loss of solution by evaporation. The leach solution containing copper(II) ion of 500 cm^3 volume was added into the reaction vessel. The pH of the solution was adjusted to the desired value by diluted sulfuric acid solution. When the reactor content reached the desired reaction temperature, aluminum disc (height of 0.005 m, diameter of 0.05 m, working surface area $1.73 \cdot 10^{-2}$ m^2) was immersed in the solution. The disc was screwed onto the end of a thin stainless steel rod which was attached to the mechanical stirrer. The disc was rotated at controlled speeds in the solution. The progress of the cementation reaction was followed by measuring the concentration of copper ions in the solution. Aliquots of 5 cm^3 each were withdrawn at regular intervals during the reaction and immediately filtered using filter paper. The filtered samples were analyzed for copper ion content by titrating with EDTA in the presence of murexide indicator. The amount of deposited copper was calculated according to difference between the initial and final copper concentrations of the solution. The fraction of cemented copper was calculated as follows:

x = initial copper concentration/copper concentration at time t.

Table 2. Parameters and their ranges used in the experiments

Parameter	Value
Concentration, mol/dm^3	0.0025, 0.005, 0.010, 0.020
Temperature, ºC	20, 30, 40, 50, 60
Rotating speed, rpm	200, 300, 400, 500
pH	1.0, 1.5, 2.0, 2.5, 3.26

3. Results and Discussion

In order to observe the effect of rotation speed of Al disc on the cementation rate of copper the experiments were carried out at different rotation speeds in the range of 200 to 500 rpm. The results obtained from these tests showed that the cemented copper fraction increased with increasing the disc rotation speed. This result indicates that the copper cementation rate is probably the diffusion controlled under these experimental conditions. During cementation reaction, a solid layer of metallic copper is formed onto the surface of aluminum disc. This solid layer prevents the contact of copper ions with aluminum disc surface. If the rotation speed of the disc is strong enough, the deposit formed onto the disc can peel off from aluminum surface. This fact can facilitate the diffusion of ions towards the metal disc surface, and thus the cemented fraction of copper increases as the rotation speed of the disc increases. Furthermore, the diffusion layer thickness decreases as the rotation speed of the disc increases, which facilitates the diffusion of copper ions towards disc surface.

The effect of the initial pH of the leach solution on the copper cementation was investigated using different initial pH values in the range of 1.00-3.26. The experimental findings exhibited that the solution pH had a considerable effect on the copper cementation rate. During the experiments, it was observed that the fraction of cemented copper increased with decreasing the initial pH of leach solution. The recovery of metallic copper from the leach solution involves two main processes: adsorption of copper ions on the surface of metallic aluminum disc and the cementation of copper ions on the disc. The presence of a passive oxide layer on aluminum surface inhibits the cementation reaction rate generating a resistance to diffusion of copper ions towards the metal disc surface. This oxide film formed on the disc surface can be destroyed by the acidity of solution. Hence, the oxide film dissolves more readily at low pH values, and it may cause an increase in the cementation rate with increasing acidity (decreasing pH) of the leach solution (MacKinnon et al., 1971).

The effect of initial copper(II) ion concentration on the cementation rate was studied at the concentrations of 0.0025, 0.0050, 0.0100, and 0.0200 mol/dm^3. According to the results of the experiments the cementation rate increased with increasing copper concentration in the leach solution. During the cementation reaction the deposited copper accumulates onto the surface of the aluminum disc and a product layer (metallic copper) appears on the disc surface. This surface deposit shows a resistance to the diffusion of copper ions. Depending on the nature of the surface deposit its presence can enhance or diminish the cementation rate. If the metallic layer formed on the reductant metal is a coherent deposit the cementation rate decreases with increasing deposit mass. This case was observes at low initial copper ion concentration conditions. If the surface deposit formed on the reductant metal is a porous metallic layer the cementation rate may increase when the deposit layer thickness increases. When the initial copper ion concentration is high a coarse and porous precipitate on the metal disc surface appears. Under such conditions the diffusion of copper ions from the bulk of the solution to the disc surface occurs through the porous layer easily and the cementation rate can increase with the increase of the layer thickness. Besides, the coarse or dense precipitate formed onto the disc can be peeled off the disc surface by rotating the aluminum disc (Miller, 1973; Puvvada and Tran, 1995; Amin et al., 2007).

In order to investigate the effect of the reaction temperature on the copper cementation from the actual leach solutions some experiments were performed in the temperature range of 20 - 60ºC. The results showed that the deposited copper fraction increased with increasing the reaction temperature. At low temperatures the deposit on the disc surface was coherent. It was observed that the deposit formed on aluminum disc was thick and relatively coarse as the reaction temperature increased. This type of deposit is generally porous and it does not hinder the diffusion of copper ions to the disc surface. Furthermore, high temperatures help to strip the oxide layer off the disc surface, and therefore the cementation reaction proceeds at a faster rate (Kanungo et al., 2003; Lamya and Lorenze, 2005; Farahmand et al., 2009).

It has been reported that cementation reactions follow the first order kinetic with respect to the noble metal, and the rate limiting step is to be the transfer of mass to the reaction surface (Puvvada and Tran, 1995; Nosier and Sallam, 2000; El Batouti, 2003; Younesi et al., 2006; Demirkıran et al., 2007). In the present study, the kinetic analysis was performed according to the first order kinetics. The equation describing the kinetics of the first order reaction is:

$$-\ln(1-x) = k\,t \qquad (5)$$

where x is the cemented copper fraction at time t. The influence of several parameters, such as solution concentration, reaction temperature, and stirring rate on the cementation rate should be considered because the cementation is a heterogeneous reactions. Hence, the effects of these parameters on the reaction rate were analyzed on the basis of the first order kinetic model.

The data on cemented copper fraction obtained from the experiments were used to perform $-\ln(1-x)$ versus time graphs. The constructed graphs can be seen in Figs. 2-5. As can be seen from the plots given in Figs. 2-5, the straight lines passing through the origin were obtained. The apparent rate constant values determined from the slopes of the lines in Figs. 2-5 and their correlation coefficients for each parameter are given in Table 3. The results in Figs. 2-5 and in Table 3 indicate that the kinetics of this process follows the first order kinetic model.

To deduce whether a cementation reaction is mass transfer limited (diffusion controlled), the relationship between the reaction rate and the disc rotation speed is usually determined. For this aim the Levich equation is usually used (Makhloufi et al., 1998; Makhloufi et al., 2000; Dib and Makhloufi, 2007):

$$k = 0.62\, D^{2/3}\, v^{-1/6}\, \omega^{1/2} \qquad (6)$$

where k is the reaction rate constant or the mass transfer coefficient (cm/s), D is the diffusion coefficient of reactant species (cm^2/s), v is the kinematic viscosity of solution (cm^2/s), and ω is the angular velocity of disc (rad/s).

If the mass transfer is the rate determining step, then the plot of k versus $\omega^{1/2}$ in Eq. (6) must be a straight line. Using the apparent rate constants obtained for various rotation speeds (Table 3) a graph of k versus $\omega^{1/2}$ was drawn in Fig. 6. As shown in

Fig. 6, a linear relationship between the apparent rate constants and the square root of the disc rotational speeds was obtained. The linear dependence of the cementation rate on the square root of the rotation speed supports the conclusion that the cementation is mass transfer limited or diffusion controlled. It is clear that the rate of copper cementation increase with increasing disc rotation speed. This may be attributed to the decrease in the diffusion layer thickness as the rotational speed of the disc increases, thus giving a higher rate of transfer of copper ions from the bulk of the solution to the aluminum surface.

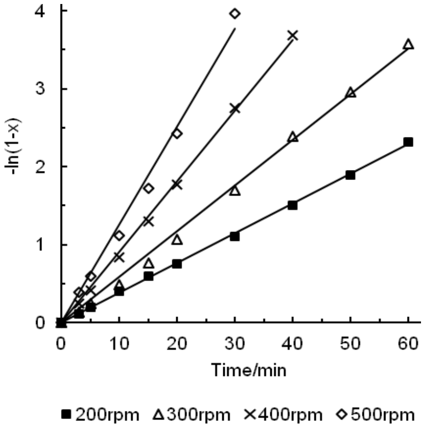

Fig. 2. Plot of –ln(1-*x*) versus *t* for different rotation speed

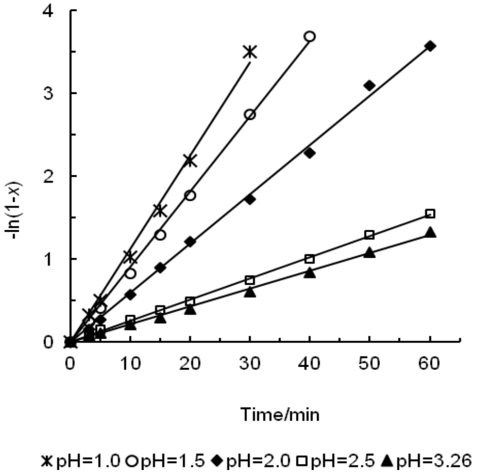

Fig. 3. Plot of –ln(1-*x*) versus *t* for different pH

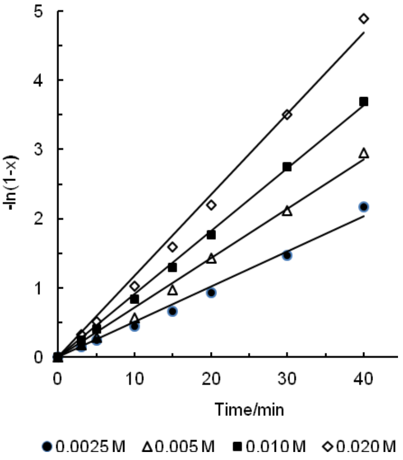

Fig. 4. Plot of –ln(1-*x*) versus *t* for different concentrations

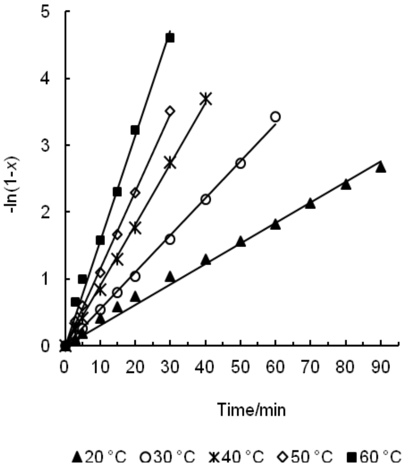

Fig. 5. Plot of –ln(1-*x*) versus *t* for different temperatures

Table 3. The apparent rate constants and their correlation coefficients

Parameter	First-order kinetic model	
	k*10^3, s^{-1}	R^2
Concentration, mol/dm^3		
0.0025	0.846	0.988
0.0050	1.188	0.993
0.0100	1.513	0.998
0.0200	1.956	0.994
Temperature, ºC		
20	0.513	0.993
30	0.920	0.998
40	1.513	0.998
50	1.938	0.998
60	2.612	0.994
Rotation speed, rpm		
200	0.635	0.999
300	0.975	0.997
400	1.513	0.998
500	2.097	0.992
pH		
1.0	1.883	0.995
1.5	1.513	0.998
2.0	0.993	0.998
2.5	0.427	0.998
3.26	0.358	0.997

To represent the influence of the cementation parameters on the rate constant of reaction, a mathematical model was proposed:

$$k=k_o\,(C)^{a}\,(RS)^{b}\,(pH)^{c}\,\exp(-E_a/RT) \qquad (7)$$

where k_o is the frequency or pre-exponential factor (1/s), C is the initial copper concentration, RS is the rotational speed of aluminum disc (rpm), pH is the initial pH of solution, E_a is the activation energy of reaction (J/mol), R is the universal gas constant (J/molK), T is the reaction temperature (K), and a, b and c are the reaction orders according to concentration, rotational speed, and pH, respectively. Combining Eqs. (5) and (7), the following equation is obtained:

$$-\ln(1-x)= k_o\,(C)^{a}\,(RS)^{b}\,(pH)^{c}\,\exp(-E_a/RT)\,t \qquad (8)$$

To calculate the values of constants a, b and c, the apparent rate constants given in Table 3 were used. Using the rate constant values for concentration a plot of ln k versus ln C was drawn in Fig. 7. The slope of straight line in Figure 7 is the reaction order with respect to solution concentration. The reaction order in respect to concentration is 0.40 with a correlation coefficient of 0.994. The orders of reaction with respect to rotation speed and pH were also calculated by means of data in Table 3. According to the obtained results the reaction order is 1.31 for rotation speed and -1.54 for pH. The correlation coefficients of these parameters are 0.99 and 0.91, respectively.

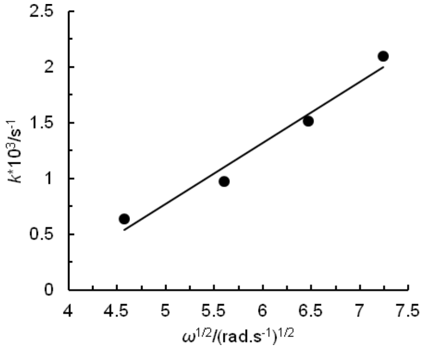

Fig. 6. Variations of apparent rate constant obtained for various rotation speeds with the square root of the disc rotation speed

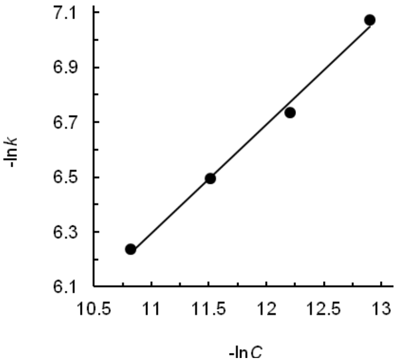

Fig. 7. Plot of ln k versus ln C

The activation energy of the cementation process was determined from the Arrhenius equation. The Arrhenius plot of the process is shown in Fig. 8. From the slope of the straight line in Fig. 8 the activation energy of reaction was calculated to be 32.6 kJ/mol. The intercept of the line was determined to be $2.7 \cdot 10^{-3}$. The value of the activation energy of process indicates that the copper cementation reaction by rotating aluminum disc is controlled by diffusion. The activation energy of diffusion controlled reactions is generally below 40 kJ/mol.

As a result, the mathematical model taking into account all parameters influencing the cementation reaction rate can be written as follows:

$$-\ln(1-x) = 2.7\text{x}10^{-3}\,(C)^{0.40}\,(RS)^{1.31}\,(\text{pH})^{-1.54}\,\exp(3924/T)\,t. \quad (9)$$

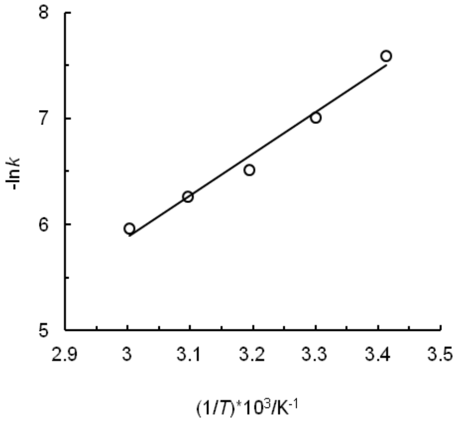

Fig. 8. Arrhenius plot for copper cementation reaction

4. Conclusions

In most of the papers published in the literature impurity-free copper solutions have been used for copper cementation. In the present paper, copper recovery has been carried out using the solutions containing some impurities after the leaching of malachite ore in aqueous acetic acid solution. The effect of the experimental parameters on the copper cementation reaction have been examined. It was observed that the rate of copper cementation increased with increasing concentration, temperature and rotation speed, and decreasing with pH. The results of the experiments conform to previously published reports in the literature. In this paper, unlike many other studies, in order to represent the cementation kinetics a mathematical model was proposed. It was found that the cementation rate was diffusion controlled. The activation energy of the cementation process was calculated to be 32.6 kJ/mol.

Cementation process seems to be appropriate for the recovery of copper from the leach solutions containing various impurities without any additional purification process. But the copper obtained in this process has rather low purity, especially due to its tendency to form oxide during drying at the air. The copper deposit obtained in this study was brown and contained 88 percent copper. However, the impure cemented copper can be purified to increase the copper content and marketed as a powder. As a result, it can be said that cementation process is a reproducible and low cost approach that does not require expensive and complicated equipments.

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