Recovery of Cobalt Powder and Tungsten Carbide from Cemented Carbide Scrap - Part I: Kinetics of Cobalt Acid Leaching

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ABSTRACT

The aim of this study is to investigate the effectivity of nitric acid leaching and the leaching kinetics of cobalt from cemented carbide scrap. The studied variables were reaction temperature, time, nitric acid concentration and stirring speed. The best leaching conditions were found to be 25°C, 2 h, 0.5 M HNO_3, stirring speed of 900 rpm (corresponds to Reynolds-number of 25000) and 1/10 solid/liquid ratio. A cobalt leaching efficiency of 91.5 % was reached under these conditions. An positive effect of higher temperatures is not apparent and cobalt can be extracted at room temperature. At higher temperature, the rate of cobalt leaching decreases. The leaching rate is also decreasing with increasing HNO_3 concentration. It is found that the stirring speed has the most important influence on the leaching rate. The leaching process follows the kinetic models $1-2/3x-(1-x)^{2/3} = k\,t$ and the apparent activation energy is determined to be 13.77 kJ/mol at 25-70°C. It is concluded that the leaching process of cobalt from cemented carbide scrap in nitric acid solution is controlled by diffusion.

Keywords: Acidic Leaching, Kinetics, Hydrometallurgy, Cobalt, Cemented Carbide (Hard-Metal) Scrap.

Rückgewinnung von Kobalt Pulver und Wolframkarbid aus Hartmetallschrotten – Teil I: Kinetik der Sauren Kobaltlaugung

ZUSAMMENFASSUNG

In der vorliegenden Arbeit wurde die Laugung von Kobalt aus Hartmetallschrott-Pulver mit Salpetersäure sowie die entsprechende Kinetik untersucht. Eine Laugungstemperatur von 25°C, eine Laugungsdauer von 2 Stunden, eine anfängliche HNO_3-Konzentration von 0,5 M, eine Rührgeschwindigkeit von 900 U/min (Reynoldszahl: 25000) und eine Trübedichte von 1/10 erwiesen sich als optimale Laugungsbedingungen. Die erzielte Kobaltausbeute betrug 91,5%. Die Laugungstemperatur hat keine ausschlaggebende Wirkung auf das Kobaltausbringen. Es wurde festgestellt, dass die Rührgeschwindigkeit der entscheidende Parameter für das Kobaltausbringen ist. Für die Laugung von Kobalt bei 25 – 70°C gilt die kinetischen Gleichung 1-2/3x-(1-x)2/3 = kt, die Aktivierungs-Energie wurde zu 13,77 kJ/mol berechnet. Daraus ergibt sich die Schlussfolgerung, dass die Diffusionsgeschwindigkeit den Laugungsprozess von Kobalt aus Hartmetall-Schrott in Salpetersäure bestimmt.

Schlüsselwörter: Säurelaugung, Kinetik, Hydrometallurgie, Kobalt und Hartmetallschrott

Récupération de cobalt poudre et carbure de tungstène à partir de chute de carbure cémenté Partie I: Cinétique de la lixiviation acide du cobalt

Recuperación de cobalto y carburo de tungsteno a partir de chatarra de carburos cementados. Parte I :Cinética de lixiviación ácida de cobalto

1 Introduction

‘‘Cemented carbides’’, often called “Hard Metals” are a range of very hard, refractory, wear-resistant materials made by powder metallurgical techniques (sintering). These materials have found wide usage in applications such as cutting tool inserts (about 50-60 %), dies, nozzles, valve components, etc., where severe wear and high temperature properties are required. The structure of cemented carbides consists of one or more carbide phases containing carbides of metals such as W, Ti, Ta, Nb, Mo and binder metals, usually cobalt or nickel. The majority of cemented carbides are based on WC and Co (classic type) [1-6]. When the tools and components are scrapped, they are collected with a view to recovering the tungsten and cobalt in the light of the strategic importance of these metals. A number of recycling processes have been developed which are classified into different categories. The first group involves chemical modification of the component metals into intermediate products which are then processed to obtain pure metals. The second group involves removal of the binder medium from the matrix, leaving behind a finely divided tungsten carbide which can be recycled in fabricating new tools. Many contaminated scraps -either soft or hard- are today treated in the chemical conversion process [oxidation (750-900 °C), pressure digestion (NaOH, 200 °C, 20 bar, filtration, purification, conventional W and WC powder manufacturing route) to gain back virgin powders of the hard metal constituents [5,7]. The “Zinc melt” and the “Cold-Stream” process are also popular methods to recycle cemented carbide. However selective leaching is a potential alternative in view of its lower energy consumption and environmental impact [2, 5-7]. Regarding the “Zinc melt” process, the bonding metal (cobalt) reacts with high purity zinc (99.995%) during the cemented carbide recovery operation. The energy consumption is therefore high, about 4000 to 6000 kWh is required for one ton of tungsten carbide scrap. The cycle time of the complete Zinc process is 24 hours. The “Cold-Stream” process is a mechanical method. The cemented carbide scrap is transported by a high velocity air-stream (>1000 km/h) to hit on a cemented tungsten carbide plate. Nitric acid is used to dissolve the binder medium (anodic dissolution of cobalt) at a current density of 2-10 A kg^{-1} of the scrap (an electrochemical process) [8, 9]. Further on several hydrometallurgical processes have been developed and used to extract cobalt from various sources [2]. In recent years, stringent environmental controls and resource conservation policies have led to renewed interest in developing cemented carbide recycling techniques that are not only economically viable but also ecologically acceptable. Thus, direct recycling techniques, i.e. transformation of the as-supplied scrap to a product of commercial value by physical or chemical means, are becoming increasingly important, compared to indirect recycling. Some of the processes designed to recover tungsten and cobalt result in impure metals in the first stage. Very complicated after-processes are required to recover the metals in a pure form. Cobalt leaching from cemented carbide scrap is a hydrometallurgy-method for cobalt recovery offers the potential of a environmental friendly management. There is no thorough investigation in the literature about the leaching kinetics of cobalt dissolution in nitric acid. This study contributes to this lack of information. Nitric acid selected because it is an acid leachant which cobalt will be in the leaching solution. Nitric acid was selected to be the leaching reagent in this study, since it dissolves cobalt more rapidly as compared to the sulfuric and hydrochloric acids.

2 Experimental

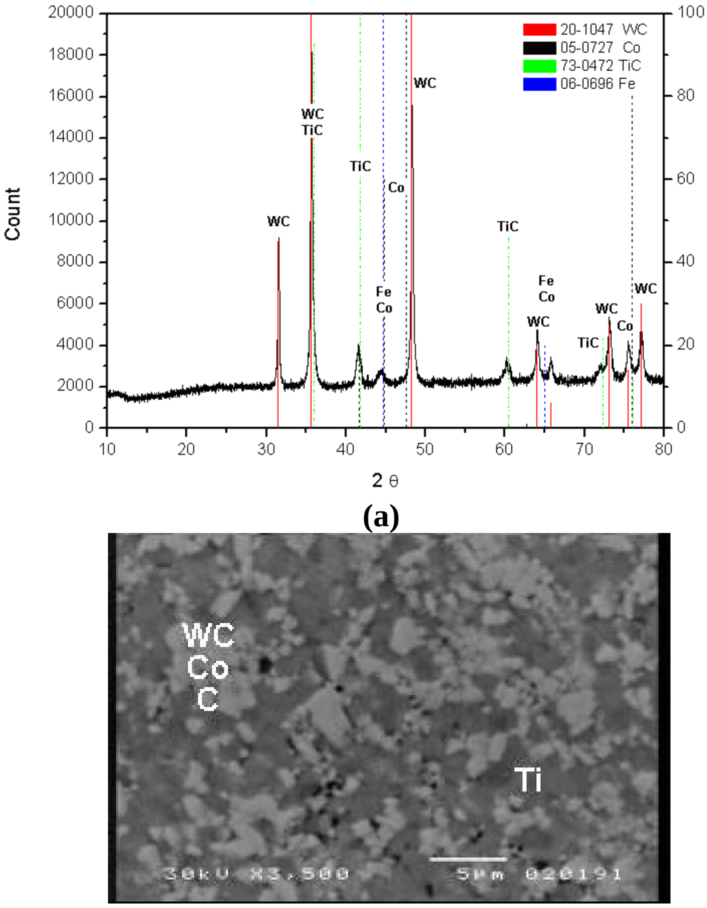
2.1 Investigated cemented carbide scrap

Experiments were carried out with powderized cemented carbide scrap, supplied by Sert Metal-Istanbul. The chemical composition of the cemented tungsten carbide scrap powder is given in Table 1.

Table 1: Chemical composition of the cemented tungsten carbide scrap powder used in the experiments.

Wt %	<90 µm	Wt %	>90 µm
W	75.86	**Co**	8.59
Co	8.14	**Fe**	2.90
C	6.07	**Ni**	0.06
Ti	4.18		
Nb	1.35		
Ni	1.00		
Fe	3.40		

X-ray analysis and SEM micrograph of the raw material are given in Fig. 1a und b respectively.



(a)

(b)

Fig.1: (a) X-ray analysis and (b) SEM micrograph of cemented carbide scrap powder (<90µm)

By the X-ray Diffractometer, it was found that the structure of cemented carbide scrap are WC, TiC and Co. Experimental work was conducted mostly with the portion of the cemented tungsten carbide scrap powder which has a particle size of <90 µm.

2.2 Experimental Procedure

Cemented tungsten carbide scrap was ground in a vibrating mill for 15 minutes. Screening of the ground material was conducted in a Retzsch brand sieve. Leaching experiments were carried out in a three-neck glass reactor with 0.5 l capacity, heated by a thermostatically controlled heater (Heraeus). The mixture was stirred from the top with a teflon-plated propeller which was hooked on to a mixer (IKA-WERK RW-20) with adjustable speed and stirring direction. A spiral condenser was also utilized to return water losses to the system. The ground cemented carbide scrap powder was added into the agitated nitric acid solution at the required temperature. Samples of the solution were taken in a thirty minutes interval. All the samples were filtered and analyzed by ICP (Spectroflame Modula EOP). Carbon content of cemented carbide scrap was determined by using LECO-CS 400 analyzer. An X-ray diffractometer (Siemens D 5000) and a scanning electron microscope (JEOL, JSM T330) were utilized for the characterization of the cemented tungsten carbide scrap powder. All the chemicals used in the experiments were analytical grade (Merck). The leaching tests were designed to examine the effects of temperature, time, HNO_3 concentration and stirring speed. Generally, the experiments were conducted under the following conditions: a solid/liquid ratio of 1:10 (g/ml), 20 g sample and <90μm particle size.

3 Results and Discussion

3.1 The Effect of Leaching Temperature

The temperature effect was examined in the range of 25-70°C under the standard conditions of <90μm particle size, 0.5 M HNO_3, 2h, 900 rpm, and 1/10 solid/liquid ratio. Figure 2 shows the effect of temperature on the dissolution of cobalt in the HNO_3 and H_2O system. As seen from Fig. 2, cobalt solubility decreases from 91.5 % to 78.2 % between the temperatures of 25 and 70°C.

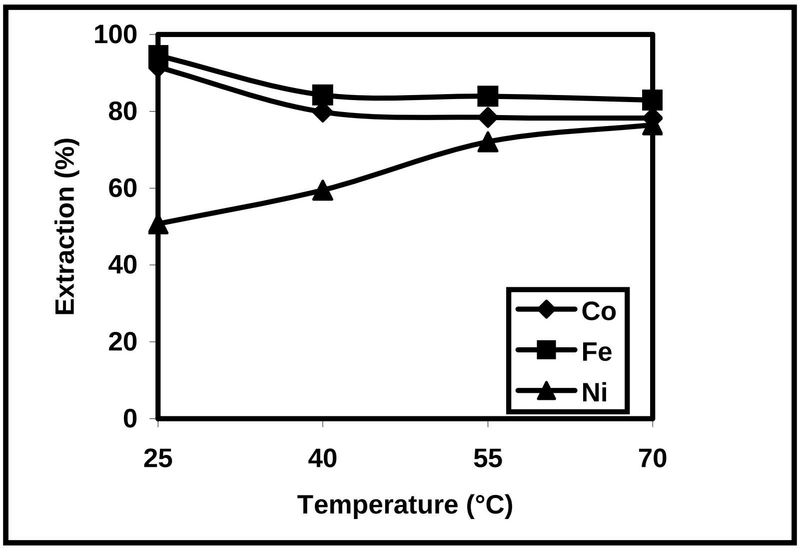


Figure 2: Effect of temperature on the dissolution of cobalt and associated elements [<90μm, 2h, 0.5 M HNO_3, 900 rpm, and S/L: 1/10]

The results shown in Fig. 2 indicate that the effect of a rising temperature on the leaching rate is not advantageous, and cobalt should be extracted at room temperature. Although, cobalt reacts rapidly with nitric acid at room temperature, a protective layer forms as a result of passivation at high temperatures, which stems from the chemical behaviors of cobalt and iron in nitric acid. This behaviour is less remarkable for nickel and is only visible above 50-55°C. Nitric acid breakdown and filtration problems may also arise in relation to the temperature increase.

3.2 The Effect of Reaction Time

The highest cobalt efficiency (% 91.5) was obtained after a leaching period of 2 h (Figure 3). Iron on the other hand, dissolves within the first hour of leaching with 90% efficiency and shows similar dissolution trend of cobalt for the rest of the leaching. This result shows that the reaction period and rate depending on the liberation rate of the particles in ground cemented carbide scrap. Opposite to the fact that cobalt gives a very fast dissolution reaction, nickel shows a slow reaction with HNO_3 and, acts as the rate-determining factor on total efficiency.

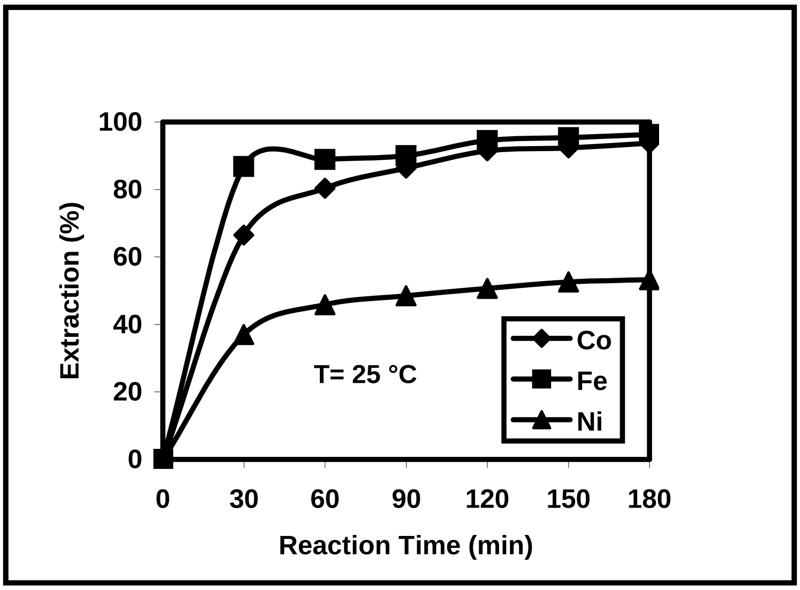


Figure 3: Effect of leaching time on the dissolution of cobalt and associated elements [<90µm, 25 °C, 0.5 M HNO_3, 900 rpm, and S/L:1/10]

In practice, 120 min of leaching time was found to be optimum. Extended leaching periods (over 120 min) seem to increase the efficiency for cobalt, iron, and nickel, only insignificantly.

3.3 The Effect of Initial Acid Concentration

Figure 4 displays the effect of acid concentration on the dissolution of cobalt at 25°C. Various experiments were carried out by changing the HNO_3 concentration from 0.5M to 1.5M. At 0.5 M HNO_3 concentration, 91.5 % cobalt extraction was obtained in 120 min, whereas at 1.0-1.5 M HNO_3 concentration the cobalt extraction of approximately between 90.5-89.9 % was reached within 120 min as shown in Fig. 4. Increasing the acid concentration from 0.5M to 1.5M caused the dissolution efficiency of iron to decrease from 94.5 % to 90.0 %. On the other hand the nickel extraction increased with increasing HNO_3 concentration.. The viscosity of the solution increased as a result of high acid concentration. This leads to a reduction of the diffusion rate of the ions. The reaction rate remained constant for higher acid concentrations, indicating stabilized iron dissolution. The main determining factor for the rate of leaching, as mentioned earlier, is the continuing reaction of cobalt particles that are entrapped in WC particles.

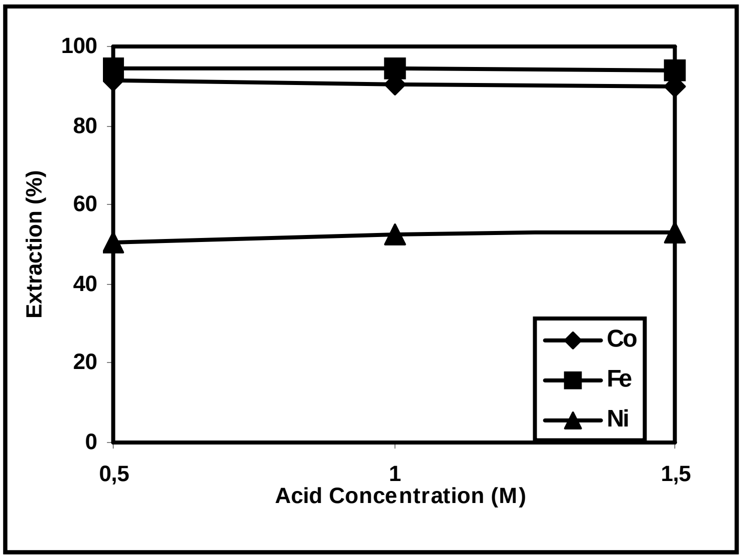


Figure 4: The effect of acid concentration on the dissolution of cobalt and associated elements [<90µm, 25 °C, 2h, 900 rpm. and S/L:1/10]

3.4 Effect of stirring speed

The effect of the stirring speed was studied under the conditions of <90µm particle size, 25°C, 0.5 M HNO_3, 2h, and 1/10 solid/liquid ratio. The results show that the leaching rate of the cobalt increases quickly when the stirring speed amplified from 700 to 900 rpm, which corresponds to a stirrer Reynolds number ($d_{St} \approx 6$ cm) of 19451-25000.
Dissolution ratios of Co, Fe and Ni in relation to the increasing stirring speed are given in Fig. 5. Up to now the highest extraction yield appeared to be at 900 rpm.

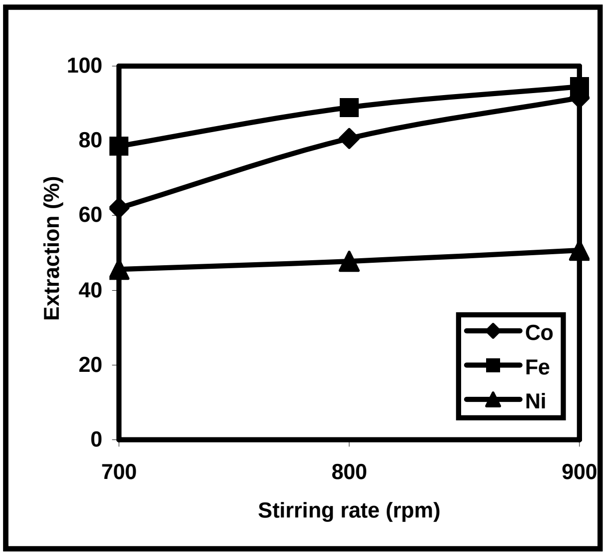


Figure 5: The effect of stirring speed on the dissolution of cobalt and associated elements [<90µm, 25 °C, 2h, 0.5 M HNO_3, and S/L:1/10]

It is known that higher stirring rates often result in an increased dissolution rate. In a diffusion – controlled process, the rate of dissolution can be expressed as a function of speed of stirring. In this case the process is diffusion controlled, the thickness of the boundary layer decreases with increased speed of stirring [10]. Stopic et al. [11] have been shown that the increased stirring speed can influence the increase of metal extraction during the leaching process.

3.5 Effect of particle size

The effect of particle size was studied using two ground size fractions of -90+0 μm and -250+90 μm at 25 °C , 2 h, 0.5 M HNO_3, 900 rpm and 1/10 solid/liquid ratio. It can be found that a smaller particle size results in a more effecient leaching extraction of cobalt.

Table 3: Effect of particle size on the dissolution of cobalt and associated elements [25 °C, 2 h, 0.5 M HNO_3, 900 rpm and S/L:1/10]

	Co %	Fe %	Ni %
<90 μm	91.5	94.5	50.7
>90 μm	68.5	49.1	54.1

As seen from the Table 3, leaching efficiencies are less than the ones obtained with particle size of <90 μm, which shows the effect of particle size.

4 Kinetics Model

In order to improve the leaching step, the leaching kinetics and mechanism were modelled. The experimental data in Fig. 6 were transformed and correlated to various kinetic models for solid-liquid reactions. The following diffusion-controlled (diffusionlayer, shrinking core model) kinetic equation (Eq. 1) was found to fit data best:

$$1- 2/3\, x - (1-x)^{2/3} = k\, t \qquad (1)$$

where k is the apparent reaction rate constant (min^{-1}), t is leaching time (min) and x is fraction reacted:

$$x = \%\ extraction\ /100 \qquad (2)$$

The effect of temperature and time on cobalt leaching from cemented carbide scrap is shown in Figure 6.

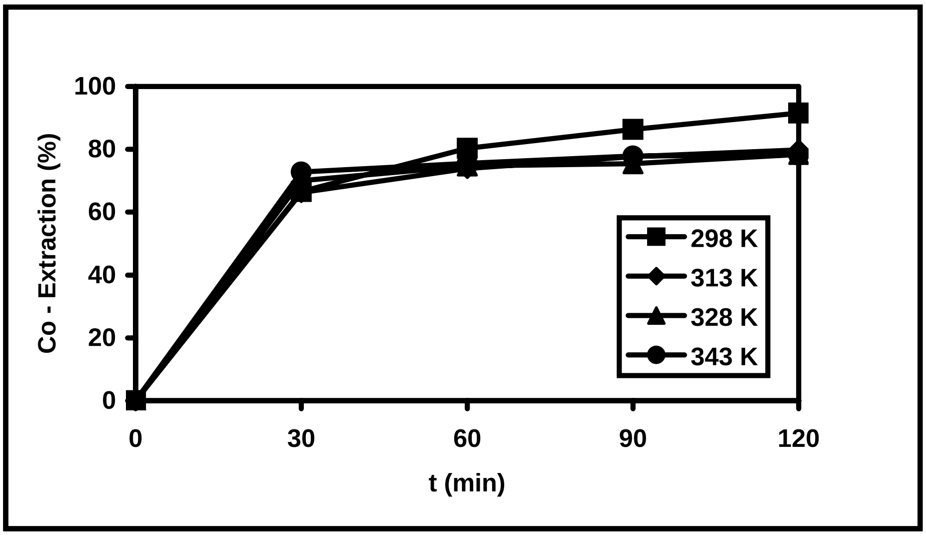


Fig. 6: Effect of temperature on cobalt leaching kinetics [<90 μm, 0.5 M HNO_3, 900 rpm and S/L: 1/10]

The yield of cobalt extraction increases with increasing leaching time. The maximal obtained value of cobalt extraction amounts 91.5 % at temperature of 298 K and a leaching time of 120 min. The data is plotted as 1- 2/3 x – $(1\text{-}x)^{2/3}$ values against *t* at various temperatures as can be seen in Fig. 7. The regression analysis shows that all *R* squares for the equations at the four temperatures are higher than 0.92.

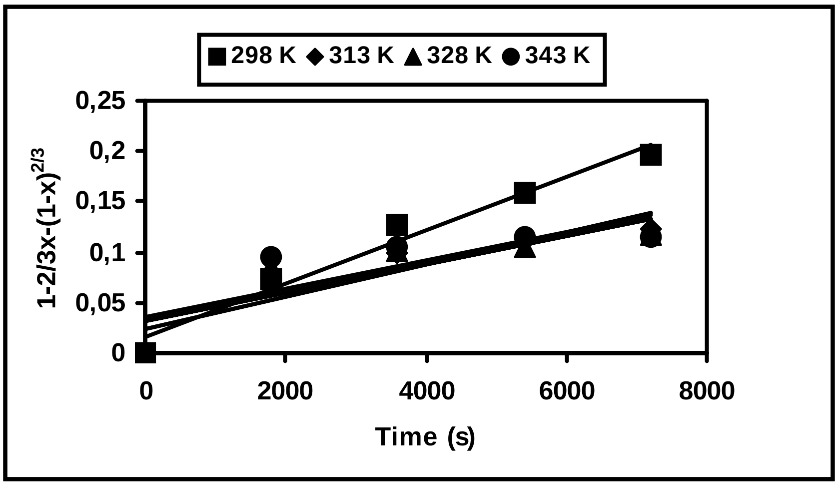


Figure 7: Relationship between 1-2/3 x - $(1\text{-}x)^{2/3}$ and leaching time for cobalt leaching at various temperatures (the conditions are the same as in Fig. 6).

Such results indicate that at 298 K the linear relationship between 1-2/3 x - $(1\text{-}x)^{2/3}$ and leaching time (*t*) is significant and suggest that the leaching rate of cobalt from cemented carbide scraps is controlled by diffusion.

The apparent activation energy was determined based on the Arrhenius equation:

$k = A \exp(-E_a / RT)$ (3)

$\ln k = \ln A - E_a / RT$ (4)

where *k* is a reaction rate constant, *A* is the frequency factor and E_a is the apparent activation energy. The ln*k* versus 1/*T* data were plotted for the four temperatures as shown in Fig. 8. The apparent activation energy (E_a) was, hence, determined to be 13.77 kJ/mol, which is typical value for diffusion controlled heterogeneous reaction [10, 12]. Fig. 7 shows that such a plot is linear. Thus the leaching of cobalt from cemented carbides is controlled by diffusion reaction under the presented experimental conditions.

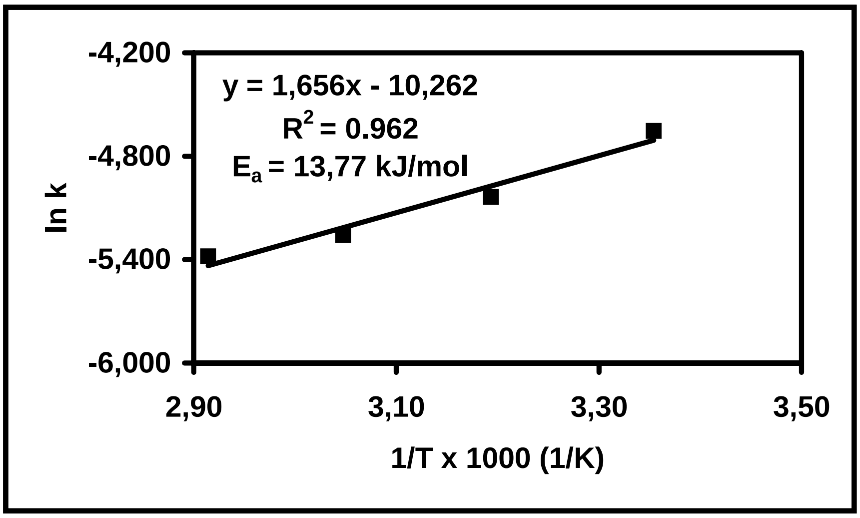


Figure 8: Arrhenius plot for the leaching of cobalt.

5 Conclusions

This paper has examined the leaching and the kinetic aspects of cobalt from cemented carbide scraps in nitric acid solution. Cobalt was dissolved by HNO_3 leaching of powderized cemented carbide scrap. The best results, in terms of cobalt recovery, were obtained under the following conditions; 25°C (298 K), 2 hours of leaching period, HNO_3 concentration of 0.5M, stirring speed of 900 rpm and S/L ratio of 1/10. The stirring speed had a significant effect on the leaching rate. The leaching process follows the kinetic model $1- 2/3\ x - (1-x)^{2/3} = k\ t$ with an apparent activation energy of 13.77 kJ/mol at 25-70 °C. The cobalt leaching is found to be diffusion – controlled.

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