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The leaching kinetics of gold from gold scraps in Cl_2-saturated HCl solutions

Cl_2 gazı ile doyurulmuş HCI çözeltilerinde altın hurdalarından altının liçing kinetiği

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Abstract

In order to explain the model of kinetics control on the leaching of gold in gold-bearing scraps, the effects of the reaction temperature, solid/ liquid ratio, particle size and stirring speed and acid concentration are investigated. In the examination of the leaching kinetics of gold in Cl_2-saturated HCI solutions, Cl atoms occurring in the medium react more rapidly than Cl_2 molecules with gold scraps. This reaction takes place simultaneously with the reaction of dissolution and in situ-generated chlorine is called. Also, the method doesn't have some disadvantages such as the storage of generated chlorine. It is determined that the leaching rate decreases with increasing particle size and solid to liquid ratio while it increases with increasing reaction temperature, acid concentration and stirring speed. For fluid/solid systems, shrinking core models are analysed by using of experimental results. It is observed that the leaching of gold from gold-bearing scraps is chemically controlled. Also, the leaching rate controlled by the chemical reaction is supported by the relationship between the particle diameter and rate constant. The activation energy of leaching process by using Statistica Package Program is determined as 34.40 kJ/mol.

Keywords: Gold-bearing scraps, Chlorine, Leaching kinetics

Öz

Altın içeren hurdalardan altının liçingi üzerine kinetiği ortaya koyan modeli açıklamak için, reaksiyon sıcaklığı, asit konsantrasyonu, katı-sıvı oranı, karıştırma hızı ve partikül boyutunun etkileri araştırılmıştır. Cl_2 ile doyurulmuş HCI çözeltilerindeki altın liç kinetiğinin incelenmesinde, ortamda meydana gelen Cl atomları, altın hurdaları ile Cl_2 moleküllerine göre daha hızlı reaksiyon vermektedir. Bu reaksiyon, çözünme reaksiyonu ile eşzamanlı olarak gerçekleşir ve yerinde oluşturulan klor olarak isim alır. Yöntemin, üretilen klorun depolanması gibi bazı dezavantajları da yoktur. Liçing hızının, artan reaksiyon sıcaklığı, karıştırma hızı ve asit konsantrasyonunu ile artarken; katı-sıvı oranı ve partikül boyutunun artmasıyla azaldığı belirlenmiştir. Katı-sıvı sistemleri için büzülen nüve modellerini kullanan deneysel veriler analiz edilerek, altın içeren hurdalardaki altının liçinginin kimyasal kontrollü olduğu gözlenmiştir. Keza; çözünmenin kimyasal reaksiyon ile kontrol edilen liçing hızı, hız sabiti ve partikül boyutu arasındaki ilişki ile de desteklenmiştir. Liçing prosesinin aktivasyon enerjisi Statistica Paket Programı kullanılarak 34.40 kJ/mol olarak tespit edilmiştir.

Anahtar Kelimeler: Altın içeren hurdalar, Klor gazı, Liçing kinetiği

1 Introduction

Over the last 20 years or so, many processes have been improved for the recovery of gold from primary sources such as sulphide, telluride, oxide ores or elemental state and from secondary sources such as gold-bearing scrap. Gold recovery from its sources may require two major recycling techniques, such as pyrometallurgical, hydrometallurgical processes, and both combined with mechanical pre-treatment [1]-[3]. Pyrometallurgy, as traditional method to recover precious and non-ferrous metals from secondary sources, includes high temperature processes where chemical reactions achieve among solids and molten materials. Pyrometallurgical processes such as calcining, roasting, and melting etc. are expensive for requiring high temperature and pressure and corrosion resistant materials [4]-[6]. Therefore, a lot of researchers for recovery of precious metals from gold-bearing scraps have aimed on hydrometallurgical techniques which are more exact, predictable, well controlled and environment-friendly in recent years [7]-[9].

Traditionally, hydrometallurgy process consists of two stage such as leaching and recovery. Modern hydrometallurgy of gold is focused on the selective and fast leaching of the precious metal by using chemicals such as aqua regia and cyanide. But, there are a number of disadvantages such as slow leaching rate, long-term dissolution, limited treatment of complex or refractory minerals, safety and health risks for researchers and great threat for the environment.

Hereby, for gold recovery, the alternative reagents such as tiyocyanete, thiourea, halides, thiosulfates, ammonia were used. In especially, halides are widely used under acidic solutions and in the using of a strong oxidant for the dissolution of precious metals [10]-[13]. Different mixtures of oxidants (such as hypochlorite, hydrogen peroxide) can be used together with the halides (iodide, bromide and chloride) to obtain the optimum leaching conditions. An important alternative is a chloride solution with an proper oxidizing agent. Some of the appropriate oxidizing agents for this process are hypocloride, ozone and chlorine gas [14]-[16].

In a study performed by Kozin et al. [17], it was worked the effect of the leaching rate on the medium pH, the temperature and concentration of sodium hypochlorite. For the gold leaching at temperatures range of 277 to 304 K, the rate constants and other parameters are determined. It was observed that the activation energy for system is about 53.43 kJ/mol.

Furthermore, Vinals et al. [18] performed the dissolution of palladium and gold by ozone in aqueous media in chloride

solutions. The recovery of palladium and gold for metallic scraps can be performed out by ozone-leaching at environment temperature and low Cl^- and H^+ concentrations. It is observed that mass transfer to the solid/liquid interface of O_3 was first order according to $[O_3]_{aq}$.

In a study by Baghalha [19], the leaching kinetics of two types of gold ores (carbonaceous and oxide) with iodide/iodine solutions is published. The effect of factors such as ore type, iodide/iodine concentration, and combination the of oxygen in solution on gold leaching was studied. It is obtained that the gold extraction for carbonaceous ore is 20 %, but the gold recovery for the ore bearing oxide is 77% in 6 h and 89% in 24 h. From experimental study, to model the gold recovery kinetics in iodide/iodine mixtures, a power law rate equation is exercised. According to tri-iodide concentration, it is found that the reaction rate is to fit first order.

The chlorination processes to conventional cyanidation might be taken into account as a non-toxic alternative method [20]-[22].

The goal of the work is to test the leaching of gold in the gold-bearing scraps in hydrochloric acid solutions saturated by chlorine gas in situ-generated.

2 Experimental

The gold scraps provided from jewellers are first sieved at 187.5 µm average particle size to use in the experiments. Then, for determining chemical composition, the powder is analyzed and the results obtained are presented in Table 1. To prepare the leaching solutions, all the reagents used are analytical grade chemicals, except sodium hypochlorite, which is commercial level. The concentration of NaOCl solution used in the experiments is 1.53 M.

Table 1: Chemical analysis of gold scraps.

Component	wt (%)
Au	89.50
Cu	6.36
Zn	3.02
Ag	1.12

The leaching tests are made in a glass reactor furnished with a constant temperature circulator and a stirrer. Reactor contents are adjusted automatically to the wanted temperature after joining 50 mL of hydrochloric acid solution. A known amount of the solid is put in to acid solution and the leaching experience is begun by adding NaOCl solution with proper flow rate from a sensitive burette assembled on the glass reactor to product Cl_2 in the reaction medium and the stirring. In each experiment, totally 10 mL of NaOCl solution is used. During leaching, a known amount of slurry is taken from reaction medium. Afterwards, the gold content of the filtrate is analyzed by atomic-absorption method. The parameters and their values affecting the dissolution of gold in gold-bearing scraps are given in Table 2.

Table 2: Parameter values used for experiments.

Parameter	The parameter Values			
Solid/liquid ratio (g/mL)	0.004	0.010	0.020	0.040
Medium temperature (°C)	18	20	25	30
tirring speed (rpm)	0	400	650	850
	960	1000	1125	1250
Acid concentration (M)	0.5	2.0	3.5	5.0
Particle size (mm)	0.231	0.196	0.165	0.138

3 Results and discussion

3.1 Temperature effect

The reaction temperature effect on the leaching process (converted fraction of gold) was examined in interval of 18-30 ^{0}C. Solid/liquid ratio, HCl concentration, stirring speed, particle diameter and chlorine concentration (continuously saturated) were taken as 0.004 g mL^{-1}, $8.99x10^{-2}$-$6.22x10^{-2}$ mol L^{-1}, 960 rpm, 187.5 µm and 5 M, respectively. The results obtained were shown in Figure 1.

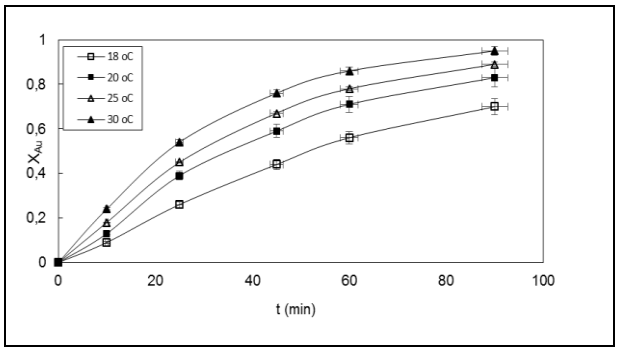

Figure 1: Reaction temperature effect on the gold leaching.

According to the figure, the leaching rate increases with increase of medium temperature. In most cases, it is known that the solubility of a material increases as the temperature raises.

3.2 HCl concentration effect

In the experiments, the acid concentration was determined in the ranges of 0.5-5 M. Solid-liquid ratio, stirring speed, particle diameter, reaction temperature and chlorine concentration (continuously saturated) were taken as 0.004 g mL^{-1}, 960 rpm, 187.5 µm, 30 °C and $3.96x10^{-2}$-$6.22x10^{-2}$ mol L^{-1}, respectively. Figure 2 shows the results obtained.

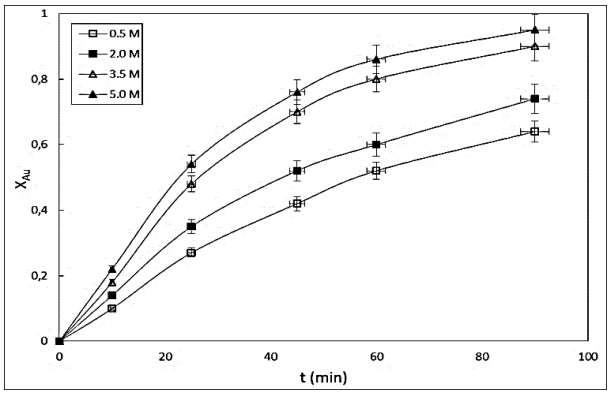

Figure 2: Acid concentration effect on the gold leaching.

At worked interval, it is observed that the increasing of acid concentration increases leaching rate.

3.3 Solid/liquid ratio effect

On leaching rate, solid/liquid ratio effect was examined in interval of 0.004-0.04 g mL^{-1}. In the experiments, it was fixed as HCl concentration 5 M, stirring speed 960 rpm, reaction temperature 30 °C, chlorine concentration (continuously saturated) $6.22x10^{-2}$ mol L^{-1} and particle size 187.5 µm. The results obtained from experiments were plotted in Figure 3.

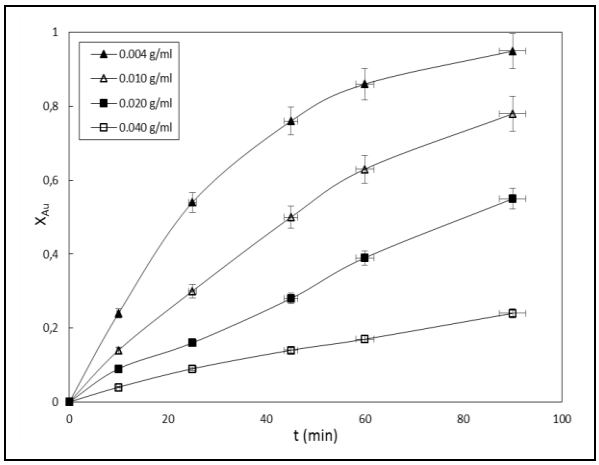

Figure 3: Solid/liquid ratio effect on the gold leaching.

3.4 Effect of stirring speed

Stirring speed effect was studied in range of 0-1250 rpm. The work conditions were determined as follows: HCl concentration 5 M, solid/liquid ratio 0.004 g/mL, reaction temperature 30 °C, chlorine concentration (continuously saturated) 6.22 x 10^{-2} mol L^{-1} and particle size 187.5 µm. The experimental results were given in Figure 4.

From Figure 3, the leaching rate declines with the increase of solid/liquid ratio. This situation can be explain with the decrease in the fluid reactant per unit weight in solid.

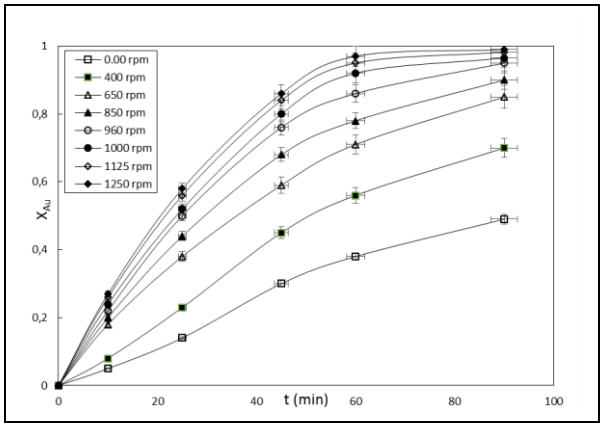

Figure 4: Stirring speed effect on the gold leaching.

Because of high specific gravity of gold scrap, supplying an exact suspension was rather difficult. After reaching complete suspension value (about 960 rpm), from the plots, it is observed that the effect of stirring speed isn't very important on the leaching.

3.5 Particle size effect

The particle size effect was investigated in interval of (-60+70)-(-100+120) mesh. The work conditions were determined as follows: HCl concentration 5 M, solid-liquid ratio 0.004 gmL^{-1}, reaction temperature 30 °C, stirring speed 960 rpm and chlorine concentration (continuously saturated) 6.22x10^{-2} mol L^{-1}. The experiment results are given in Figure 5.

According to the figure, with decreasing particle diameter of gold scraps, it is seen that the leaching rate rises. This situation may be imputed to the accrue of contact surface due to the reduction in the particle diameter.

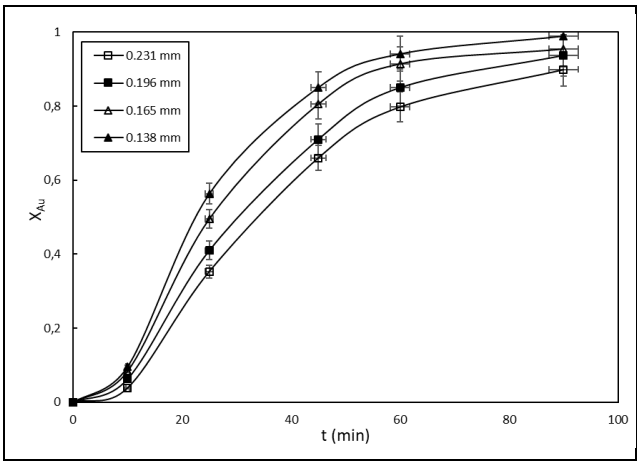

Figure 5: Particle diameter effect on the gold leaching.

4 Leaching kinetics

The leaching reactions of gold with chlorine gas in situ-generated can be given as follows:

$$NaOCl_{(aq)} + 2HCl_{(aq)} \rightarrow NaCl_{(aq)} + Cl_{2(aq)} + H_2O_{(aq)} \quad (1)$$

$$Cl_{2(g)} \leftrightarrow Cl_{2(aq)} \quad (2)$$

$$2Au_{(s)} + 2HCl_{(aq)} + 3Cl_{2(aq)} \rightarrow 2AuCl^-_{4(aq)} + 2H^+_{(aq)} \quad (3)$$

In addition, the Eq (3) may also be given by Eq (4) and (5):

$$2Au_{(s)} + 2HCl_{(aq)} + Cl_{2(aq)} \rightarrow 2AuCl^-_{2(aq)} + 2H^+_{(aq)} \quad (4)$$

$$2AuCl^-_{2(aq)} + 2Cl_{2(aq)} \rightarrow 2AuCl^-_{4(aq)} \quad (5)$$

The leaching rate for heterogeneous solid/fluid reactions may be explored by one of the following steps: diffusion of reactants through the fluid film surrounding the solid, the chemical reaction at the surface of the core of unreacted reagent and diffusion of reactants through the ash cover. If no ash (or solid product) layer covers the unreacted core as the reaction proceeds, there can be only two controlling steps, namely, diffusion through the fluid film or chemical reaction [23].

Then, the Eq (6) may be use If the process is checked by resistance of fluid layer:

$$t/\tau = 1 - (1 - X_B)^{2/3} \quad (6)$$

By resistance of chemical reaction, If process is controlled, the Eq (7) is used:

$$t/\tau = 1 - (1 - X_B)^{1/3} \quad (7)$$

The fit of all the experimental data into the integral rate is analyzed by using a computer program, and the multiple regression coefficients obtained for the integral rate expression are calculated. In the calculations, it is seen that the best value of regression coefficient correcting the rate expression is for surface reaction control. To confirm the results of these statistical analyses, the experimental data for each parameter are tested by graphical methods.

Also, the rate constant values can be linearly draw against the particle diameter (Figure 6).

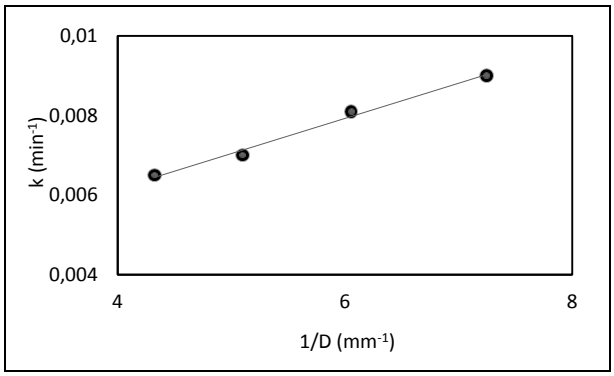

Figure 6: Plot of k versus 1/D.

According to the findings of the statistical data, it is obtained that the gold leaching in gold scraps in HCl solutions saturated with chlorine gas is chemically controlled. Eq (7) is written as follow:

$$kt = 1 - (1 - X_B)^{1/3} \quad (8)$$

According to Eq (8), for the reaction temperatures (18-30 ^{0}C), the 1-(1-X)$^{1/3}$ graph against time is given by Figure 7.

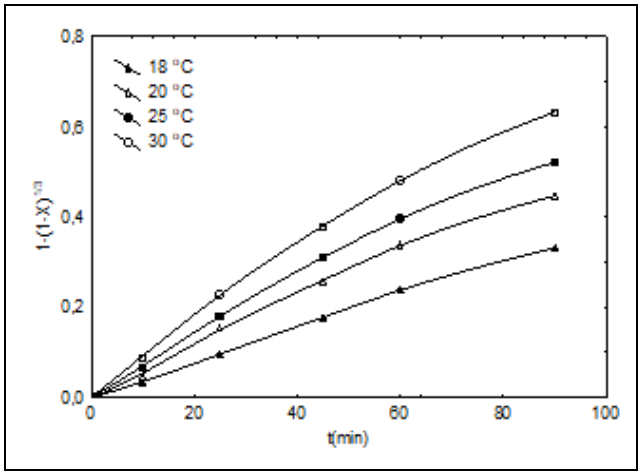

Figure 7: t/τ plots against time.

The rate constant values by plot slopes help are computed (see Table 3).

Table 3: Values of rate constants for various temperatures.

Temperature (^{o}C)	Rate constant, k (min^{-1})
18	0.0040
20	0.0046
25	0.0059
30	0.0071

lnk plot vs. 1/T was drawn (Figure 8), and the amount of activation energy was calculated as approximately 34.40 kJ.mol^{-1} from the slope of the curve.

The apparent rate constant in Eq (8) may be a function of acid concentration, particle diameter, solid to liquid ratio, reaction temperature and stirring speed. Therefore, the rate constant of the leaching process may be written by Eq (9).

$$k = k_o\ (S/L)^a\ (C)^b\ (W)^c\ (D)^d\ .e^{-E/RT} \quad (9)$$

Rearranging Eq (9) gives,

$$1 - (1 - X_B)^{1/3} = k_o\ (S/L)^a\ (C)^b\ (W)^c\ (D)^d\ e^{-E/RT}t \quad (10)$$

By the statistical calculations, results from multiple regression a=-2/3, b = 2/5, c = 3/4, d =- 3/4 and ko = 0.11 for the constants in Eq (10) are determined. Finally, the rate equation relating to dissolution of gold from gold-bearing scraps in HCl solutions saturated with Cl_2 gas has been given by Eq (11).

$$1 - (1 - X_B)^{1/3} = 0{,}11\ (S/L)^{-2/3}\ (C)^{2/5}\ (W)^{3/4}\ (D)^{-3/4}\ e^{-(4090/T)}t \quad (11)$$

To assay the agreement between the experimental conversion values and the values calculated from the semi-empirical equation (Eq 11), the graph of X_{theo} versus X_{exp} is plotted in Figure 9. It can be seen that the agreement between the experimental and calculated values is very good.

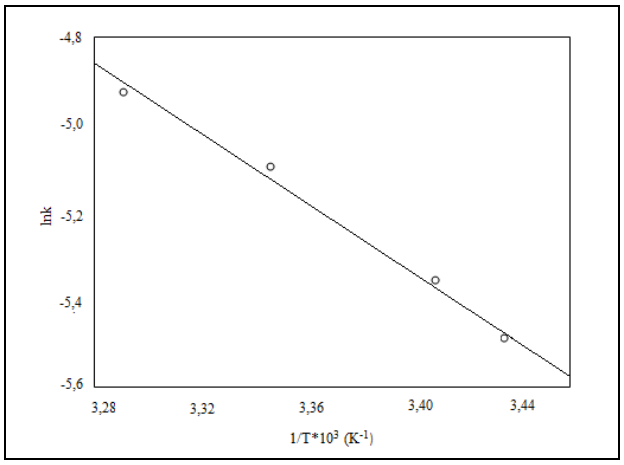

Figure 8: Arrhenius graph.

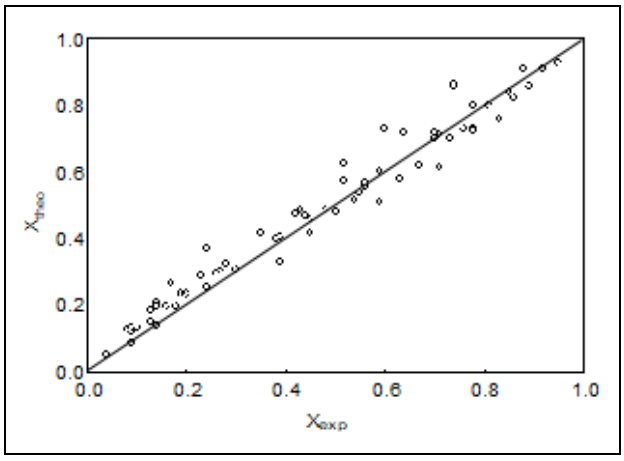

Figure 9: Corespondence between X_{exp} and X_{theo}.

5 Conclusions

To improve an environmentally friendly method, in the gold-bearing scraps, leaching kinetics of gold in Cl_2-saturated HCl solutions has been investigated. This work conclusions reveal the follows:

- It is observed that the leaching rate increases with increasing reactionmedium temperature and acid concentration, with the decreasing particle diameter and solid/liquid ratio,

- Cl atoms occurring in the medium can react more rapidly than Cl_2 molecules with gold scraps. This reaction takes place simultaneously with the reaction of dissolution and in situ-generated chlorine is called. The method doesn't have some disadvantages, such as the storage and handling of generated chlorine. Furthermore, due to highly reactive of chlorine in the reaction, according to cyanide, the leaching rate of gold is faster [14],
- In our studies, in terms of temperature, the maximum dissolution rate is achieved at 30 °C. For leaching process, the activation energy is found as 34.40 kJ/mol. The kinetic model controlling the leaching system fits the surface chemical reaction,
- Also, the stirring speed effect on gold leaching is worked. The results confirm the step controlling the process,
- To verify the kinetic modeling work, the experimental results versus the values found from the semi-empirical equation (Eq 11) are drawn (see Figure 9. It can be said that the relevance between the calculated and experimental results is very suitable [4],[18],
- According to literature, there are many works connected with either the dissolution of gold from ore with gold or the leaching of gold from gold-bearing scraps is performed by using some hazardous reagents such as aqua regia and cyanide. The reagents have serious disadvantages such as health, safety and environmental risks. In this research on dissolution of gold from gold-bearing scraps in HCl solutions saturated by chlorine gas is focused on a hydrometallurgical technique as non-toxic, eco-friendly, selective, easily controlled operation and low costs in contrast to the conventional cyanidation method [4],[17],
- Today, the efficient recovery of scraps and wastes in gold jewellery manufacture are a vital component of a profitable jewellery manufacturing business, irrespective of whether it is a large factory or small. The study is devoted to the preliminary evaluation of the dissolution of gold from gold-bearing scraps at a laboratory scale.

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Ek A: Nomenclature

X	:	Converted fraction of gold (leaching rate),
C	:	Concentration of HCl solution (M),
S/L	:	Solid-liquid ratio (g. mL^{-1}),

W : Stirring speed (rpm),
T : Reaction temperature (^{0}C),
D : Particle size (mm),
t : Reaction time (min),
k : Reaction rate constant (min^{-1}),
ko : Arrhenius constant,
a : A constant in Eq. 11,
b : A constant in Eq. 11,
c : A constant in Eq. 11,
d : A constant in Eq. 11,
E : Activation energy (kJ. mol^{-1}),
R : Universal gas constant ($J.K^{-1}mol^{-1}$).