

INFLUENCE OF AGITATION AND TEMPERATURE UPON EXTRACTION OF GOLD TO THIOUREA SOLUTION

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VPLYV MIEŠANIA A TEPLoty NA VÝŤAŽNOSŤ ZLATA DO ROZTOKU TIOMOČOVINY

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Abstrakt

Bola skúmaná závislosť výťažnosti zlata do roztoku tiomočoviny od rýchlosti miešania a teploty. Bola použitá metóda rotačnej diskovej elektródy. Plocha elektródy z elektrolytického zlata bola $0,385 \text{ cm}^2$. Bolo zistené, že kritické otáčky sú 300 min^{-1} . Teplota je dôležitým faktorom rýchlosti rozpúšťania zlata. Aktivačná energia je 99 kJmol^{-1} pre teplotný interval $25\text{-}35^\circ\text{C}$.

Pri vyšších teplotách dochádza k rozkladu tiomočoviny a pasivácii povrchu zlata ortorombickou sírou.

Abstract

Influence of agitation and temperature upon extraction of gold to thiourea solution was studied. Rotating disc electrode technique was used for this purpose. The area of the rotating disc electrode was 0.385 cm^2 . Critical value of rotations per minute was found to be 300 min^{-1} . Temperature showed to be another important factor effecting the rate of gold dissolution. Activation energy was found to be 99 kJmol^{-1} for temperature interval from 25°C to 35°C . Decomposition of thiourea and passivation of gold surface by orthorhombic sulphur occurred at higher temperatures.

1. Introduction

Lodejščíkov et al. [1] studied the kinetics of precious metals dissolution in acidic thiourea solutions. They found that maximum rate of silver extraction was obtained at thiourea to its sulphide ratio equal to 4:1. According to their results $\text{Fe}_2(\text{SO}_4)_3$ does not oxidise thiourea and hence it represents a suitable oxidant for oxidation of materials to be dissolved.

Schulze [2] studied kinetics of gold and silver dissolution in thiourea. He studied influence of Fe^{3+} ions, temperature and addition of SO_2 upon dissolution rate of gold and silver. Golden plates with surface of 0.25 cm^2 and silver granules of 0.2 mm to 0.7 mm in diameter were used for his experiments.

The dissolution rate of gold depended on concentrations of both complexing and oxidising agents. From the two oxidants - ferric ions and formamidine disulphide - the latter was considered being more effective. As it can be seen from equations (1-3), the simplified kinetic equation comprised only the initial concentration of thiourea and a conversion factor x , which represented that portion of thiourea which had been oxidised to formamidine disulphide. In the last step the maximum rate was derived corresponding to conversion factor equal to $x=1/2$ at addition of SO_2 .

(1)

(2)

(3)

where

- C_{Au} - concentration of Au,
- c_{TU} - concentration of thiourea,
- c_{ox} - concentration of oxidant,
- $c_{\text{Fe}^{3+}}$ - concentration of Fe^{3+} ions,
- t - time,
- k_1^0, k - constants

This simple function is the key to high leaching rates and low consumption of reagents. Experimental results of work [2] showed that the increasing concentration of Fe^{3+} ions caused an increase of dissolution rates of Au and Ag, however, only in a certain range.

Chen et al. [3] investigated kinetics of dissolution of Au and Ag. They used a concentrate for their leaching experiments and they found that the dissolution rate in thiourea solution was ten times higher than that in 0.5% solution of NaCN.

Comparison of dissolution of gold in thiourea with its dissolution in cyanide solution can be found in works of Hiskey [4] and Deventer et al. [5]. The dissolution rate of gold in thiourea was higher than that in cyanide solution in all cases.

2. Experimental

2.1. Materials for experiments

Gold of electrolytical purity (PLATAURUM) was used for rotating disc experiments.

All other chemicals used in experiments were commercially available p.a. purity:

thiourea $\text{CS}(\text{NH}_2)_2$, Lachema Brno

sulphuric acid H_2SO_4 , 95%

ferric tri-sulphate $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, Lachema Brno

2.2. Experimental techniques

The overall gold content was determined by atomic absorption spectrometry using VARIAN spectrometer.

Measurements of thiourea content were performed on samples taken in regular intervals using potentiometric titration by KIO_3 with an ion selective iodide electrode. The range of this technique covers 10^{-1} to 10^{-6} per cent content.

2.3. Experimental procedure

Rotating disc experiments (RDE) were performed in 500 ml volume of the leaching solution, which contained $10 \text{ g} \cdot \text{dm}^{-3}$ thiourea, $5 \text{ g} \cdot \text{dm}^{-3}$ Fe^{3+} ions, 1 % H_2SO_4 . The concentrations used in experiments were successfully experienced earlier [6]. The disc electrode made of electrolytic gold was immersed to the solution. The area of the golden plate was 0.385 cm^2 . Samples were taken in regular intervals in volume of 8 ml and were analysed for gold content. pH value of the leaching solution was measured by a Radelkis OP 205/1 pH-meter with glass electrode and an RCE 101 reference electrode. The system's redox potential was monitored by a Pt electrode against an RCE 101 reference electrode. The intensity of agitation was measured by a non-contact PU-420 rpm reader.

2.4. Influence of rpm upon dissolution rate of gold

The overall rate of a heterogeneous reaction of dissolution depends on several processes. The time dependence of gold extraction at various rpm levels is shown on Fig.1.

Fig.1 The concentration of Au ($\text{g} \cdot \text{dm}^{-3}$) vs. time (min) and intensity of agitation

Any increase of rpm reduces the thickness of the diffusion layer to such extent that the diffusion of the reagents becomes faster than the rate of the chemical reaction or than the inner diffusion. The boundary where the outer diffusion ceases to dominate is called "critical rpm".

Critical rpm can be determined by plotting a graphic dependence of dissolution rate as function of the second root of angular speed of disc rotation. Results obtained by such evaluation are presented in Fig.2.

As it is shown on Fig. 2, critical rpm are 300 min^{-1} . We can say that while up to this rpm value extraction of gold depends on rotation speed of the disc electrode, higher rotations, in our case being 800 min^{-1} , eliminate the influence of the intensity of agitation upon the gold extraction to leaching solution.

Fig.2 The dependence of gold dissolution rate on rpm

2.5. Influence of temperature

According to Pyper and Hendrix [7] thiourea gets decomposed at temperatures over 40°C . According to Deschenes and Ghali [8] thiourea is capable of leaching even at temperatures about 60°C and what is more, the extraction of gold at this temperature is higher than at lower temperatures. In regard of contradiction of these two statements, we investigated experimentally the possibilities for gold extraction at temperatures 25°C , 30°C , 33°C , 35°C , 48°C and 58°C .

Results of this investigation are presented in Fig.3 and 4.

As one can see, higher extraction of gold is reached at 35°C than at temperature of 25°C .

Fig.3 The concentration of Au (gdm^{-3}) vs. time (min) and temperature

At temperatures of 48°C and 58°C , though the essential part of gold is extracted within the first 30 minutes, however, the surface of the rotating disc gets passivated by a layer formed due to decomposition of thiourea. Formation of the passivating layer can be observed visually as a yellow coating on gold surface.

Fig.4 The concentration of Au (gdm^{-3}) vs. time (min) and temperature

3. Discussion

Experiments investigating dependence of gold extraction on rpm of a rotating disc electrode were made. It was found that critical rpm were 300 min^{-1} . Hence, rpm of 800 min^{-1} were used for further measurements.

Based on experiments carried out at various leaching temperatures a value of activation energy $99 \text{ kJ}\cdot\text{mol}^{-1}$ was found for temperature interval from 25 to 35°C . Based on the found value of activation energy we were able to make assumptions on course of kinetic processes. In our case, the Arrhenius equation for the dependence of the rate constant on temperature can be written as:

(4)

where $k(T)$ is rate constant, A is pre-exponential factor, E represents activation energy, R is molar gas constant and T is thermodynamic temperature.

In regard that kinetic time dependences for a rotating disc represent straight lines crossing the zero point of the co-ordinate systems, combination of the two above facts allows us to draw an equation for the amount of extracted gold as function of the elapsed time and thermodynamic temperature, as follows:

(5)

where m_{Au} is the amount of extracted gold and t represents the elapsed leaching time.

Graphic representation of the equation (5) is presented in Fig.5., where vertical lines represent experimental values. The agreement between the experimental and the calculated values is sufficient.

Fig.5 The graphic representation of equation (5)

At the temperatures of 48°C and 58°C the essential portion of gold is extracted within the first few minutes of leaching. Any further prolongation of the leaching time causes passivation of the rotating disc surface by formation of an elementary sulphur layer, which prohibits diffusion of reagents to the interphase boundary. XRD analysis proved that the layer consisted of orthorhombic sulphur. Its morphology is documented on photographs taken by electron raster microscope (Fig.6).

Fig.6 The morphology of precipitated sulphur

The precipitated sulphur proves presence of irreversible decomposition of thiourea and its complexes.

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