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Gümüşköy Gümüş Cevherinin Siyanürleme Kinetiği

Sermin GÖKSU[1*], Ahmet Hakan AKTAŞ[1], Emin Cafer ÇİLEK[2]
[1] *Süleyman Demirel Üniversitesi, Fen-Edebiyat Fakültesi Kimya Bölümü / ISPARTA*
[2] *Süleyman Demirel Üniversitesi, Mühendislik-Mimarlık Fakültesi, Maden Mühendislhiği Bölümü / ISPARTA*
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Özet: Bu çalışmada, Gümüşköy/Kütahya'dan alınan gümüş cevherlerinin siyanür liçinde, en önemli değişkenlerinden olan ortam pH'sı ve siyanür konsantrasyonunun siyanürleme kinetiği üzerine etkisi araştırılmıştır. Öncelikle, metalik gümüş, arjantit ve bunların yapay karışımının siyanürleme performansları belirlenmiş ve kinetik olarak değerlendirilmiştir. Gümüş ve/veya gümüş minerallerinin siyanürleme kinetiğinin belirlenmesi için optimum siyanürleme şartları belirenmiş ve daha sonra bu şartlarda Gümüşköy cevheri üzerinde deneylere geçilmiştir. Cevher içindeki gümüşün çözünme hızının ortam pH'sı ve siyanür konsantrasyonu ile doğrudan ilişkili olduğu bulunmuştur. Ayrıca, yapay cevherdeki gümüşün çözünme hızı ile cevherdeki gümüşün çözünme hızının birbirine çok yakın olduğu gözlenmiştir. Diğer taraftan, metalik gümüşün çözünme hızı ve çözünme hız sabiti cevherdeki gümüşten oldukça farklı gerçekleştiği belirlenmiştir.

Anahtar Kelimeler: Siyanür, Siyanür Liçi, Çözünme Kinetiği, Gümüş Cevheri.

The Kinetics of Cyanidation of the Gümüşköy Silver Ore

Abstract: In this study, the effects of pulp pH and cyanide concentration on silver dissolution rate in a silver ore sample taken from Gümüşköy/Kütahya were examined. The leaching performances of the some native silver, argentite and their mixtures (as an artificial ore) were determined and evaluated kinetically. In order to investigate the cyanidation kinetics of silver and/or silver minerals, firstly the optimum leaching conditions were determined from the cyanidation tests using the artificial ore and, the cyanidation tests on the ore sample were performed under the conditions determined. It was determined that the dissolution rate of silver in the ore was proportional to the cyanide concentration with high pulp pH values. In addition, the dissolution rate of silver in the artificial ore is akin to the ore sample used. On the other hand, it was observed that the dissolution rate of the native silver was quite different from that of silver minerals.

Keywords: Cyanide, Cyanide Leaching, Dissolution kinetics, Silver Ore.

Introduction

Cyanidation, as a hydrometallurgical process, is only method industrially employed to extract gold and silver from ores and concentrates since over 100 years ago. Silver mineral processing is usually based on the cyanidation, which is performed using alkaline cyanide solutions that produce lixiviates containing mixtures of metal cyanide complexes such as $\mathrm{Ag(CN)}_2^-$ (Zhang et al., 1997; Çelik et al., 1998; Habashi, 1999; Senanayeke, 2006). In the leaching of silver using cyanide, base metals and/or their minerals present difficulties due to the lack of selectivity of cyanide for silver over base metals. In other words, cyanide also forms complexes with a number of other metals, including iron, which forms $\mathrm{Fe(CN)}_6^{4-}$, nickel and zinc, forming $\mathrm{Ni(CN)}_4^{2}$ and $\mathrm{Zn(CN)}_4^{2-}$ The result of the formation of these complexes is a decrease in the level of free cyanide present in the pulp to drive the leaching of silver. Since the sulphide minerals are to some extent soluble in cyanide solutions, there will always be some sulphur species present in the leaching solution. It is generally believed that the presence of such species results in high consumption of cyanide and oxygen. The dissolution of silver sulphide in cyanide solution is governed by the following sequential reactions,

$$\mathrm{Ag_2S(s)} \rightarrow 2\mathrm{Ag}^+ + \mathrm{S}^{2-} \qquad (1)$$

$$2\mathrm{Ag}^+ + 2\,n\mathrm{CN}^- \rightarrow 2\,\mathrm{Ag(CN)}_n^{(n-1)-} \qquad (2)$$

while n = 1; 2; 3; 4

In the case of high cyanide concentration, $\mathrm{Ag(CN)}_3^{2-}$ and $\mathrm{Ag(CN)}_4^{3-}$ would form and in low cyanide concentration insoluble AgCN will precipitate. Pyrite ($\mathrm{FeS_2}$) and pyrrhotite can also be found in many silver ores. The dissolution of these sulphide minerals in cyanide solution can be expressed as follows (Habashi, 1987; Hiskey and Sanchez, 1990; Smith and Mudder, 1991; Haque, 1992; Habashi, 1999; Mudder et al., 2001 Senanayeke, 2006).

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*sermin_goksu@hotmail.com

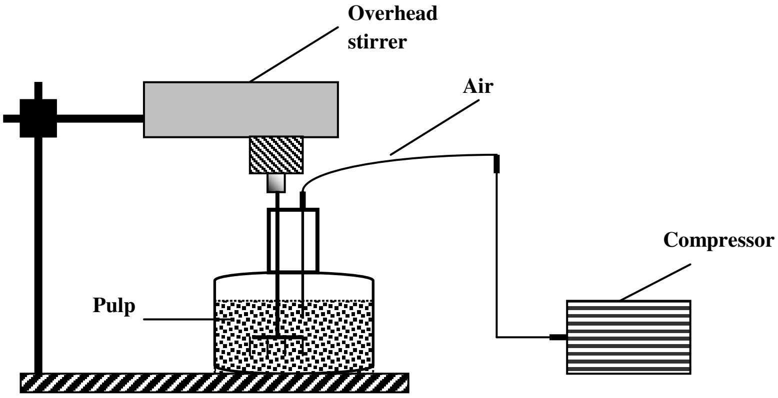


***Figure 1**. Experimental set-up used in the leaching tests*

$$FeS_2(s) + 6CN^- \rightarrow Fe(CN)_6^{4-} + S_2^{2-} \qquad (3)$$

Pyrrhotite accompanying silver in some ores decomposes in alkaline medium forming ferrous oxide/hydroxide and sulphide ion:

$$FeS\,(s) + 2OH^- \rightarrow Fe(OH)_2(s) + S^{2-} \qquad (4)$$

In presence of oxygen, ferrous hydroxide is easily oxidized to ferric hydroxide:

$$2Fe(OH)_2\,(s) + {}^1/_2O_2\,(g) + H_2O \rightarrow 2Fe(OH)_3\,(s) \qquad (5)$$

while sulphide ion is partly oxidized to thiosulphate and polysulphide:

$$S^{2-} + H_2O \rightarrow HS^- + OH^- \qquad (6)$$

$$2\,HS^- + {}^1/_2O_2\,(g) \rightarrow S_2^{2-} + H_2O \qquad (7)$$

$$S^{2-} + CN^- + {}^1\!/_2\,O_2\,(g) + H_2O \rightarrow CNS^- + 2\,OH^- \qquad (8)$$

The main objective of this study is to determine the effect of the pulp pH and concentration of cyanide on the dissolution of the Gümüşköy silver ore. Kinetics and mechanism of the dissolution of silver minerals mixed other minerals in the ore can be different from native silver and pure silver minerals like argentite. Understanding and interpreting of these differences are very important from a retarding effect of cyanicides point of view. Prior to leaching tests with the ore sample, several tests were conducted to determine the cyanidation rate of native silver and argentite, which present in the ore sample as a major silver component. The results obtained from these tests were also evaluated kinetically to develop a kinetic model of the cyanidation of the ore.

Material and Method

Material

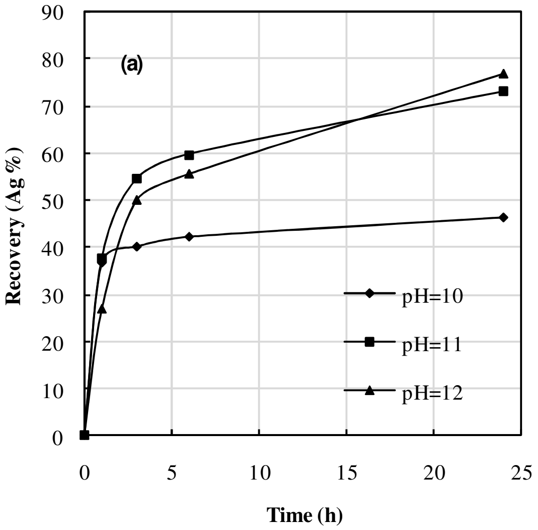
A representative ore sample was taken from the fine ore bin of the Gümüşköy silver plant. The sample contained an average 240 g/t Ag, 2.62 % Fe and $5.55x10^{-3}$ % Cu. The sample was ground to d_{80}=0.075 mm and divided into samples of 200 g as needed. NaOH, HNO_3, $AgNO_3$, KI, NH_3 and NaCN from Merck, HCl and Ag_2S from Riedel-de Haen were used in the experiments. Solutions and pulp (or suspension) were prepared with water deionized with a Milli-Q system (Millipore).

Method

Direct cyanidation tests were conducted with a 500 mL solution in an overhead stirred reactor at room temperature. A schematic illustration of the experimental set-up is shown in Fig. 1. The agitation speed was kept constant at 400 rpm. During the tests, pH and cyanide concentration of the pulp were controlled. Air was injected to maintain aeration of the pulp. A 10-mL pulp sample was taken at 1, 3, 6, and 24 h. The solids portion of each sample taken was returned to the reactor after filtering. The pregnant solutions (undiluted) were titrated for free cyanide with silver nitrate and, assayed for silver by atomic absorption spectrophotometry.

Results and Discussion

Mineralogical investigations showed that the main silver mineral is argentite in the Gümüşköy ore. On the other hand, native silver and other silver minerals are also present in the ore (Göksu, 2008). Dissolution rates of pure argentite and the ore sample could be different. These differences can be used to elucidate the retarding effects of the minerals within the ore, and the optimum cyanidation conditions can be determined to improve the leaching performance of the ore. For these reasons, in order to determine the effects of the pulp pH and concentration of cyanide on the silver extraction from pure argentite, several cyanidation tests were conducted and the results obtained are illustrated in Fig. 2.



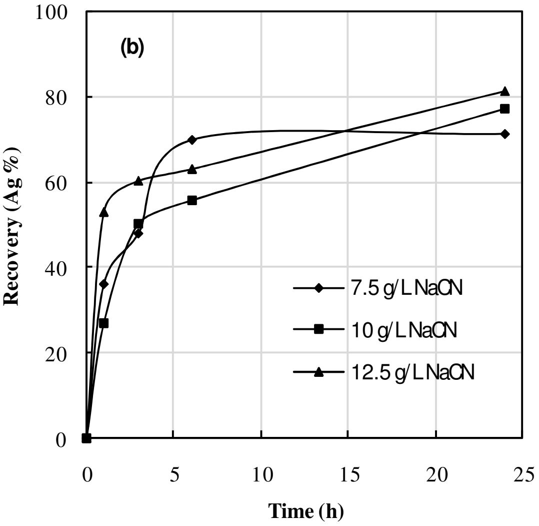


***Figure 2**. Dissolution rate of silver from argentite as a function of the pulp pH (a) and concentration of cyanide (b)*

As can be followed from Fig. 2, a maximum leaching performance was obtained at pH 12. As expected, an increase in the concentration of cyanide increased the silver dissolution recovery. Similar results were obtained from the tests conducted by using the ore samples at 10 g/L cyanide. It must be noted that even if a high extraction value is obtained in high concentration of cyanide, it cannot be used in industrial application of cyanidation due to excessive cyanide consumption. As mentioned previously, base metals (i.e., copper, iron etc.) present difficulties due to the lack of selectivity of cyanide for silver over other metals. Therefore, 1.5-2 g/L of cyanide is commonly used in its industrial applications, and there is no advantage at high cyanide addition rates.

As seen from Fig. 3, 64 % silver was extracted from the ore at the end of the test conducted with 1.67 g/L cyanide at 24 h. This result is equivalent to that of the Gümüşköy plant at 48 h. It must be noted that the leaching time is very important from a leaching performance and profitability point of view.

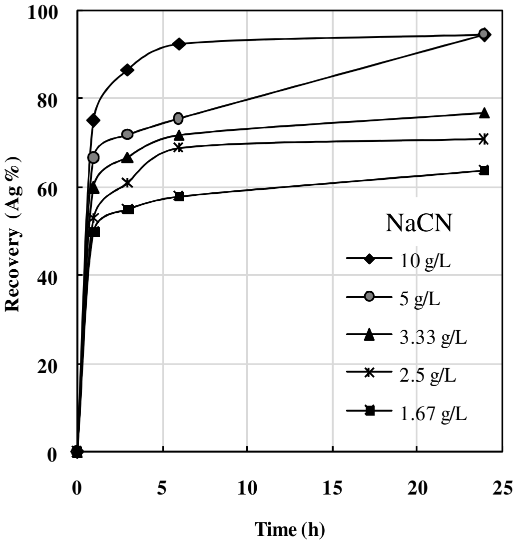


***Figure 3**.The silver extraction from the ore as a function of the cyanide concentration*

Kinetic modelling

In order to investigate the kinetics of dissolutions of native silver, pure argentite and the ore sample, the cyanide leaching tests on these materials were performed under the predetermined leaching conditions. The data obtained from these tests were used to build a statistical model. The experimental data is illustrated in Fig. 4.

Various first-order model forms were tested on recovery of silver against the time, concentration of cyanide and pulp pH by using the non-linear estimation method. The coefficients and exponents of the silver recovery model were determined by a numerical method, called Quasi-Newton. In each statistical calculation, a new model expression was proposed and then the estimated and observed values of the silver recovery were linearly correlated. The coefficient of determination, R^2 which is a measure of the goodness of it, was used to judge the adequacy of the silver recovery model. The leaching process follows kinetic model $R = 1 - a_0 \exp(-kt)$. Schematic plotting of the dissolution rate of the Gümüşköy ore is given in Fig. 5. It was evident that the rate constant was proportional to the cyanide concentration with high pulp pH values.

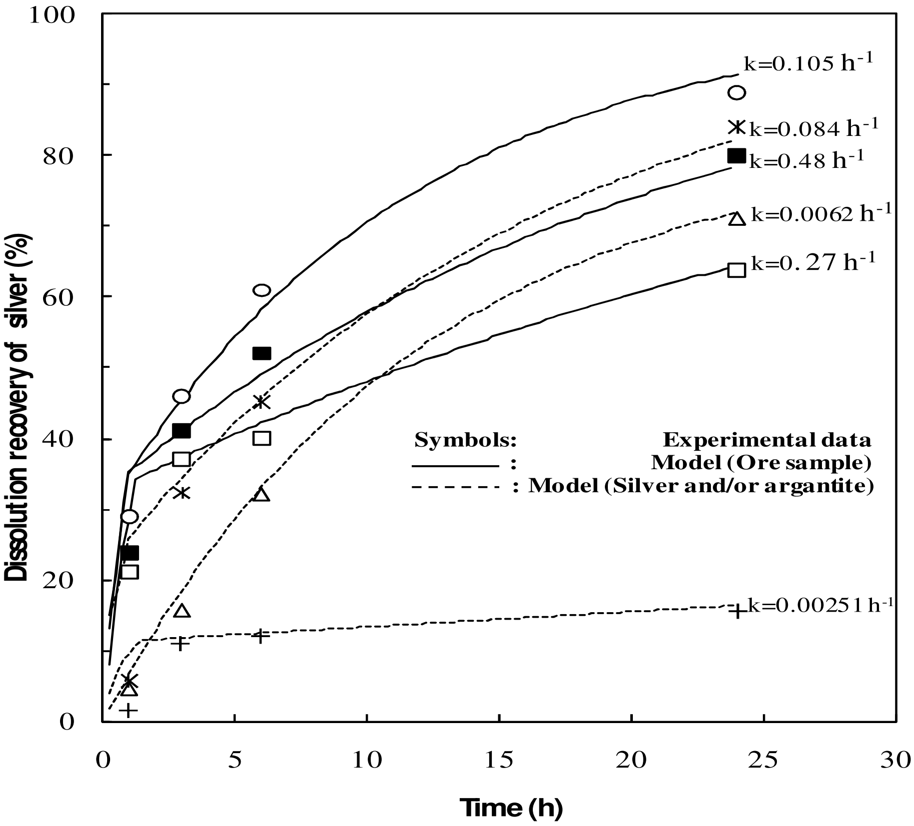


***Figure 4**. Comparison of experimental results and estimated results from the model for the ore sample, native silver and/or argentite*

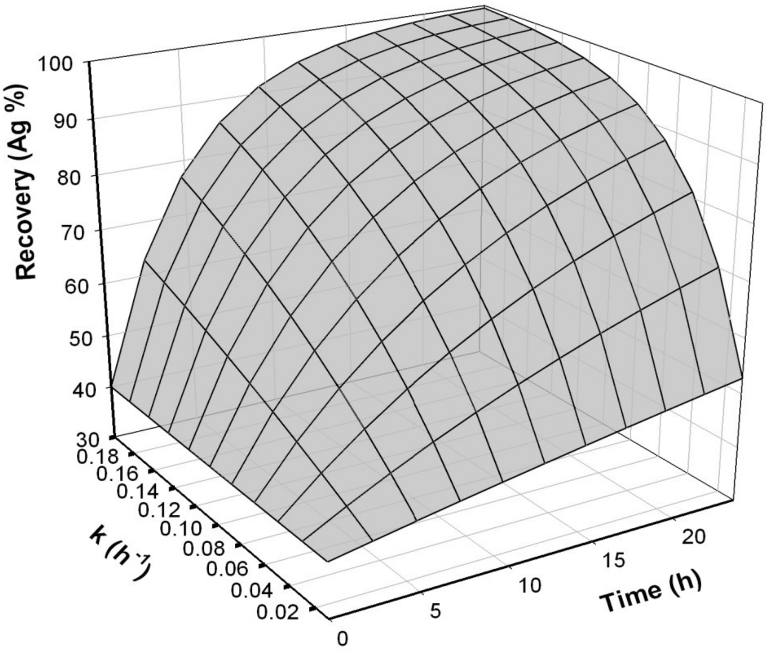


***Figure 5**. Schematic plotting of the dissolution rate of the Gümüşköy ore as a function of the rate constant and time*

In addition, the dissolution rate of silver in the artificial ore is akin to the ore sample used. On the other hand, it was observed that the dissolution rate of metallic silver is quite different from that of silver in argentite (Ag_2S). As can be followed from Figs. 4 and 5, for the Gümüşköy ore, silver dissolution can be sub-divided into two steps: the silver dissolution is fast in first three hours of the cyanidation. After this point, a very slow dissolution rate is observed. This indicates that the ore contains some important minerals/base metals which have retarding effect and, their effects are pronounced after the first three hours of the leaching.

The rate constant can also be used to determine the optimum cyanidation conditions of the ore. The effects of concentration of cyanide on the leaching performance of argentite and the ore sample can clearly be followed from Figure 6.

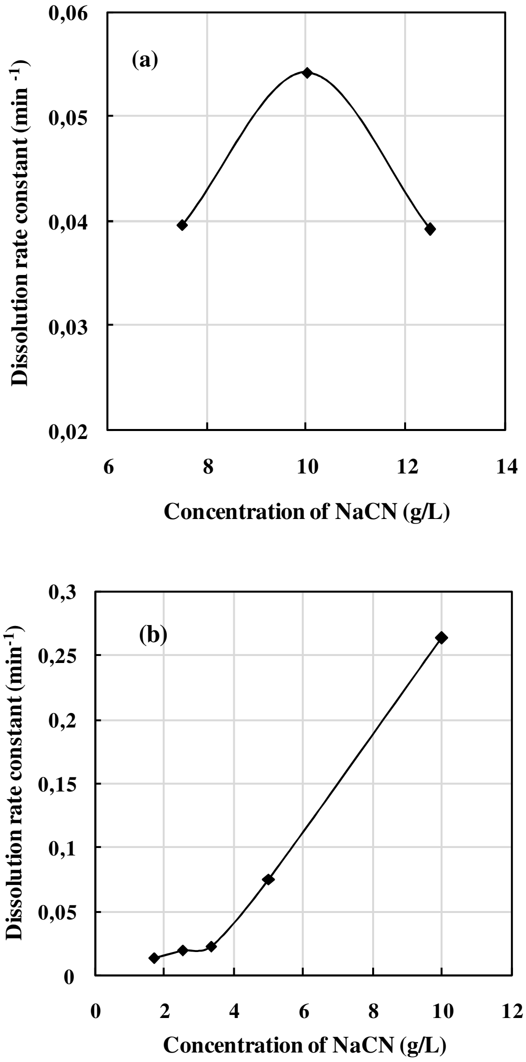


***Figure 6**. Effects of the cyanide concentration on the rate constant for argentite (a) and the ore (b)*

Conclusions

In order to investigate the kinetics of dissolutions of native silver, pure argentite and the Gümüşköy ore, the cyanide leaching tests on these materials were performed at various cyanide concentrations and pH. A maximum leaching performance was obtained at pH 12. As expected, an increase in the concentration of cyanide increased the silver dissolution recovery for all materials. In addition, 64 % silver was extracted from the ore at the end of the test conducted with 1.67 g/L cyanide at 24 h. This silver extraction is equivalent to that of the Gümüşköy plant at 48 h.

It was found that there was a significant difference between the leaching kinetics of the ore sample and the other materials. Silver dissolution can be sub-divided into two steps: the silver dissolution is fast in first three hours of the cyanidation of the Gümüşköy ore. After this point, a very slow dissolution rate is observed. This indicates that base metals and/or their minerals like iron and/or pyrite in the ore have retarding effect and, their effects are pronounced after the first three hours of the leaching.

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