

A Novel Technique for Silver Extraction from Silver Sulphide Ore

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A novel technique for silver extraction from Ag_2S is described. The method utilizes thiosulphate as complexing reagent and the redox reaction between SO_2 added as Na_2SO_3 powder and H_2S gas evolved.

The parameters of the reaction such as pH, the reaction temperature, the complex equilibrium of Ag^+ ion with thiosulphate and the solubility of Ag_2S were investigated. Silver ions, obtained by this means are collected in high purity (99%) by applying appropriate electrolysis conditions. The interference from other metallic impurities, namely copper, gold, iron and zinc, is eliminated by choosing an appropriate electrolysis potential.

Key Words: Silver recovery, silver extraction, thiosulphate leaching

Introduction

Precious metals such as gold and silver have traditionally been recovered from ores by leaching with alkaline cyanide solution¹⁻³. By reaction with oxygen and cyanide ions, silver is converted into a stable cyanide complex ion which is recovered from the leaching solution by different methods. However, the high toxicity of cyanide results in severe environmental consequences⁴. Therefore, cyanide causing irreversible destruction of nature should not be used in any quantities. On the other hand, the reaction with gold ores is slow and requires longer contact times such as 24 - 72 h. Thiourea has been used as an alternative lixiviant for the dissolution of silver from ores⁵⁻⁶. Although it is effective, high reagent consumption and uncertain extent of gold and silver recovery hinder large scale application.

Other processes have been developed for the use of halogens in the extraction and recovery of precious metals from ores. The methods based on chlorine and iodine use cannot be applied to mass production, since their stocks are limited. Furthermore, these processes introduce toxic wastes into the environment⁷.

Adaptation of the bacteria to specific sulphide minerals before the bioleaching process enhances the rate and extent of sulfide oxidation significantly⁸⁻⁹. The nature of the substrate used for bacterial adaptation plays an important role in its subsequent selectivity towards different materials. However, these bacteria are poisoned by copper, even in minute quantities found in silver ore. Therefore, alternative methods for silver recovery from ores excluding the use of cyanide are necessary.

In this study, a novel method for silver extraction from silver sulphide ore is described. The leaching process is based on the reaction between SO₂ and H₂S, with thiosulphate as the complexing reagent.

Experimental

Materials and reagents

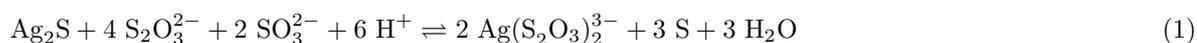
The technical grade Na₂S₂O₄, Na₂SO₃, Na₂S₂O₃, NaH₂PO₄, H₃PO₄ and NH₃, and analytical grade concentrated HNO₃ were used. The leaching process was carried out in a 1L beaker placed on a hot plate with a magnetic stirrer. In electrolysis studies the Junke & Kunkel electrolysis system with a grid and spiral platinum electrodes was used. A GBC 904 Atomic Absorption Spectrometer was used for silver analysis. The pH was measured with a Jenway 3040 Ion Analyzer. Raw material argentite was supplied from Gumuskoy-Kutahya. Qualitative analysis showed that its chemical composition was mainly silver, zinc, copper, gold, ferrum sulphides and silicon dioxide. The ore sample was homogenized and ground into a particle size of 100 μ before use.

Procedure

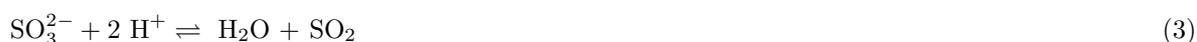
The silver content of the ore sample was analyzed by an AAS. 1.00g of ore sample of less than 100 μ was subjected to leaching with conc. HNO₃. Following the complete dissolution, nitric oxides were removed and the solution was heated until dryness. This procedure was repeated several times with distilled water until neutral pH was obtained. The silver ions were converted into complexes by addition of excess NH₃ (1:1). The silver content was determined to be 79.86+11.55 ppm. For the recovery studies, 10.00g of ore sample was placed in a 1L beaker and mixed with 0.1 M Na₂SO₃ and 0.1 M NaH₂PO₄. The pH of the solution was made 4.0 by the addition H₃PO₄ solution, Na₂S₂O₃ powder was added to the beaker to be 0.8 M in the solution and then the stirrer was switched on. The temperature of the solution increased to 50 - 60°C. The leaching process is complete in 4 - 6 hours and then the solution was transferred into the electrolysis cell. The potential was made gradually more negative until dark electrolytic deposition of silver is observed at the platinum grid electrode.

Theoretical Calculations

The process was based on the reaction between silver sulphide thiosulphate and sulphite ions according to the following equation:



In order to reveal the reaction mechanism, it is necessary to consider all the reactions that took place in the reaction vessel as given below.



It follows from the over all reaction that the process requires high acidity at room temperature. However, thiosulphate decomposes at $\text{pH} < 4.0$. This effect can be justified by studying at higher pHs and at elevated temperature. Therefore, theoretical assumptions are necessary. For a temperature range of 50 - 60°C, $K_{sp}(\text{Ag}_2\text{S}) \approx 10^{-40}$, the acidity constants for H_2S are $K_1K_2 \approx 10^{-20}$ and for SO_2 is $K_1 \approx 10^{-1.7}$ ^{10,11}.

From the electrode potential equations

$$0.14 + 0.03 \log[S][\text{H}^+]^2/[\text{H}_2\text{S}] = 0.45 + 0.015 \log[\text{SO}_2][\text{H}^+]^4/[S] \quad (5)$$

$$[\text{SO}_2][\text{H}_2\text{S}]^2 = 10^{-21} \quad (6)$$

can be obtained.

From the equilibrium of SO_2 dissolved in aqueous solution,

$$K_1 = [\text{HSO}_3^-][\text{H}^+]/[\text{SO}_2] \quad (7)$$

can be written. For pH 4.0 the HSO_3^- concentration can be assumed as C and therefore

$$[\text{SO}_2] = C[\text{H}^+]/[K_1] \quad (8)$$

can be written. At around this pH the equilibrium concentrations of HS^- and $\text{S}^{=}$ ions are negligible amounts. Therefore

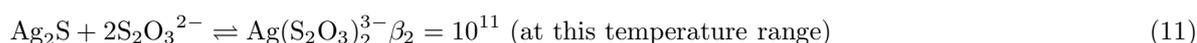
$$[\text{Ag}^+] = 2[\text{H}_2\text{S}] \quad (9)$$

can be assumed. It follows from the above equations,

$$[\text{SO}_2][\text{H}_2\text{S}]^2 = [C[\text{H}^+]/[K_1]][K_{sp}[\text{H}^+]^2/[K_1K_2]]^{1/3} = 10^{-21} \quad (10)$$

For 0.1 M HSO_3^- concentration, the optimum pH can be calculated as 4.0.

On the other hand, silver sulphide reacts with thiosulphate to give complexes:



assuming that 0.01 M of Ag_2S is converted into the complex where $[\text{SO}_3^{2-}] = 0.1$ M and $[\text{S}_2\text{O}_3^{2-}] = 0.8$ M.

The calculated concentrations of H_2S and SO_2 are 4.10^{-3} and 5.10^{-4} respectively. Therefore, the electrode potentials are calculated as given below;

$$0.14 + 0.03 \log[S][10^{-4}]^2/[4.10^{-3}] = 0.45 + 0.015 \log[5.10^{-5}]^4[10^{-4}]^4/[S] \quad (12)$$

$$-0.03\text{V} < 0.171\text{V} \quad (13)$$

The values obtained for electrode potentials show that this reaction occurs spontaneously as shown.

These calculations are the basis for the theoretical approach. It is plausible that the oxidation of thiosulphate to tetrathionate takes place rather than the oxidation of sulphide to elemental sulphur. However, this is not the case from the electrode potentials,

$$0.14 + 0.03 \log[S][\text{H}^+]^2/[\text{H}_2\text{S}] = 0.09 + \log[\text{S}_4\text{O}_6^{=}] / [\text{S}_2\text{O}_3^{2-}]^2 \quad (14)$$

$[\text{S}_4\text{O}_6^{=}] \approx 6.4.10^{-5}$ M is calculated.

Therefore, it can be concluded that the tetrathionate concentration is negligible.

Results and Discussion

Under the conditions described above, the ore sample was treated with thiosulphate and sulphite at pH 4.0 in the temperature range of 50 - 60°C. Indeed, the reaction proceeded in agreement with the theoretical assumptions and the ore sample was completely dissolved to give $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ complex in 4 - 6 hours. However, as the reaction proceeded, higher concentrations of this complex decreased the rate of the reaction. The silver content of the solution was deposited on the grid electrode according to the reaction below:



By this means, silver was recovered by using a current density in the range of 1.5 - 2.5 A/dm². It should be noted that the current density can be adjusted by careful observation of the electrodes in order that no gas evolution occurs. On the other hand, thiosulphate is not expected to decompose at this current density.

The metallic impurities namely copper and gold which may be present in the ore sample are eliminated by choosing an appropriate potential. The silver recovered from the ore sample was dissolved in concentrated HNO_3 . The metallic contents of the solution is given as ppm;

Au:10, Cu: 4, Fe:18, Zn:17.

As can be seen above, the silver content of the ore sample can be recovered in high purity (99%) by this technique.

The efficiency of the proposed method was tested by measuring the silver content of the precipitate left in the tank after the application. The precipitate was rinsed with distilled water and dissolved in conc. HNO_3 . In this solution no silver in significant amounts was detected by AAS. It can be concluded that this method is very efficient and proceeds well in agreement with the theory.

Consequently, the proposed method describes a simple and very effective leaching process for silver recovery from sulphide ores.

The reaction tank solution can be reused after checking the pH and sulphide concentration.

In addition, the temperature range used for recovery is also very suitable for the electrolysis.

This technique provides an economically feasible and environmentally safe method for silver recovery.

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