

Silver Extraction from Argentite by Thiosulphate Leaching

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Tiyosülfat liçiyile Arjantitten Gümüş Özütleme

Özet

Bu çalışmada, gümüş sülfür cevherinden (Ag_2S) tiyosülfat yöntemiyle gümüş özütlenmesi gerçekleştirilmiştir. Yöntemde, kükürt dioksit (SO_2) ve hidrojen sülfür (H_2S) arasındaki redoks reaksiyonu ve kompleksleştirici olarak tiyosülfat kullanılmıştır. Reaktif sarfiyat ı, zaman ve sıcaklık gibi liç parametreleri araştırılmıştır. pH 4.0 de 0.010 M tiyosülfat ($S_2O_3^{2-}$), 0.010 M sülfite (SO_3^{2-}), 0.0010 M tetratiyonat ($S_4O_6^{2-}$) ve 0.0010 M sülfat (SO_4^{2-}) içeren çözeltiyle cevherin liçi 55-65 °C ve 6-8 saat de % 98 oranında gerçekleştirilmiştir.

Abstract

In this study thiosulphate leaching for silver extraction from silver sulphide ore (Ag_2S) has been developed. The method utilises thiosulphate as complexing agent and the redox reaction between sulphur dioxide (SO_2) and hydrogen sulphur (H_2S). The method was investigated in terms of reagent consumption and leach parameters such as time and temperature.

Leaching the ore with a solution containing 0.01 M thiosulphate ($S_2O_3^{2-}$), 0.010 M sulphite (SO_3^{2-}), 0.0010 M tetrathionate ($S_4O_6^{2-}$) and 0.0010 M sulphate (SO_4^{2-}) resulted in over 98% silver extraction in 6-8 hours at 55 °C -65 °C and pH 4.0.

Keywords: Thiosulphate leaching, silver extraction, silver sulphide, argentite

1. Introduction

Gold and silver have been recovered from their ores by different leaching methods. Only a limited number of ligands form complexes of sufficient stability for use in gold and silver extraction processes. Cyanide, the oldest one, has been recognized for a long time as a powerful complexing agent for gold and silver, forming very stable cyano complexes with both metals [1-3]. Although the process is so simple, efficient and inexpensive, cyanide solutions are toxic and must be handled carefully to avoid damaging the environment [4].

Because of these limitations and increasingly stringent pollution control regulations, use of complexing agent other than cyanide for recovery of silver and gold has received considerable attention during the past two decades [5- 7].

However, they also possess some drawbacks and none of them are widely applicable.

In recent years, there has been renewed interest in the use of thiosulphate as a substitute for cyanide in gold and silver leaching because the thiosulphate is a non-toxic reagent with a low cost. Thiosulphate solution allows the solubilization of gold and silver as stable anionic complexes. Leaching by thiosulphate decreases interferences from foreign cations and results in a lower environmental impact.

The recovery of precious metals using thiosulphate was first proposed early in the 1900's. In a process known as Von Patera, gold and silver ores were first subjected to a chloridising roast and then leached with thiosulphate [8]. Ter-Arekelyan et al. demonstrated that copper ions could speed up the dissolution of gold and silver in thiosulphate leaching [9].

Berezowsky and Sefton studied thiosulphate leaching by developing an atmospheric ammoniacal thiosulphate leach process to recover gold and silver from residues of the

ammonia oxidation leaching of sulphide copper concentrates [10]. More recent work has concentrated on understanding and improving the atmospheric ammoniacal thiosulphate leach process [11- 13].

Thermodynamically, thiosulphate oxidizes to tetrathionate between pH ranges of 4.0 to 6.0. The oxidative degradation of tetrathionate is promoted by cupric ion [11]. Higher gold and silver dissolution rates have been reported at temperatures in the range of 40°C – 60°C [10, 11].

Unlike the cyanidation process, the thiosulphate leaching process has not been studied in great detail, and work has been limited to laboratory evaluations.

In a previous publication, we have reported preliminary results on the development of a new leaching method for silver extraction from silver sulphide ore [14]. The leaching process is based on the reaction between sulphur dioxide and hydrogen sulphide, with thiosulphate as the complexing reagent. This process provides an environmentally safe method for silver extraction but according to preliminary results, it was not economically feasible because of high reagent consumptions ($[S_2O_3^{2-}] = 0.80 \text{ M}$ etc.) and energy input.

In this study we have studied optimisation of leach time, temperature and particle size using both theoretical calculations and experiments. As a result, optimum concentration of thiosulphate has been considerably reduced and the process now appears much more economically feasible.

2. Preliminary Theoretical Considerations

As could be seen in Figure 1 calculation of targeted solubility is attempted at first. This calculation is necessary to reach the desired solubility in leaching. The silver extraction from the ore should be 99% for it to be economically feasible.

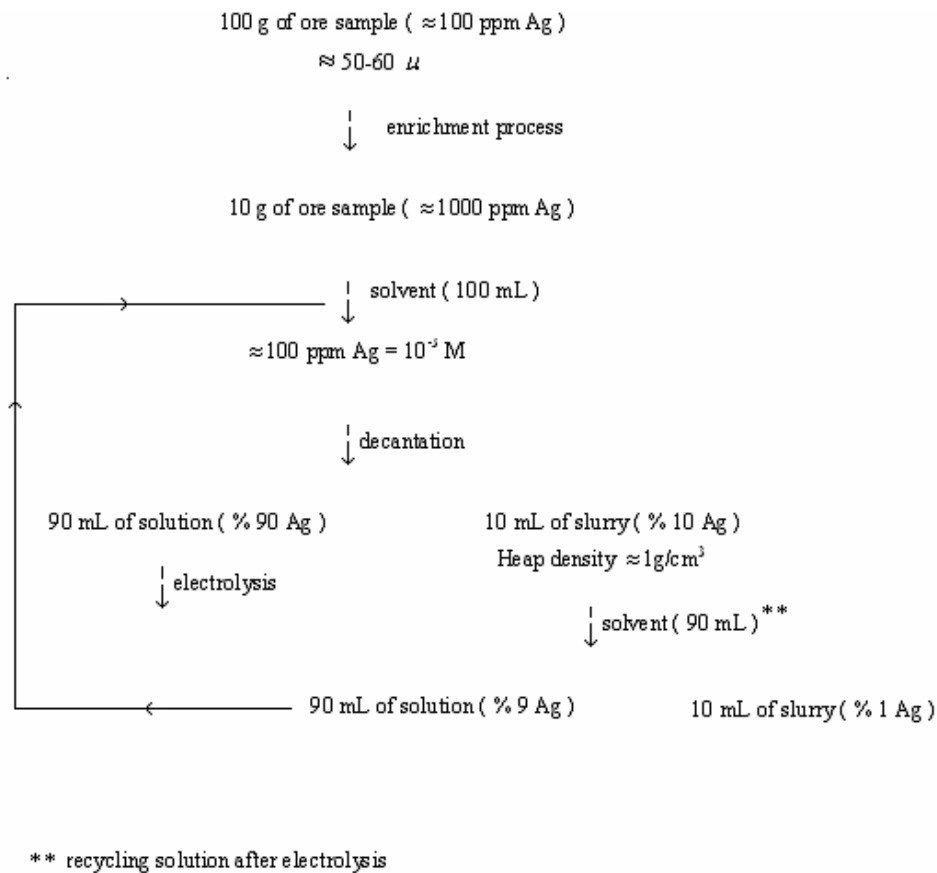
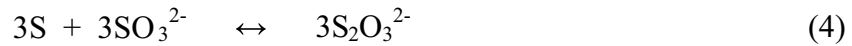
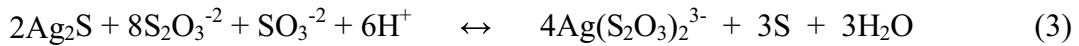


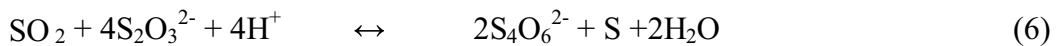
Figure 1. The flow diagram of the worthwhile solubility process.

It is thought that SO_2 is an appropriate oxidising agent for the purpose. Its acidic nature would provide considerable amount of protons required at leaching process. Also the oxidising agent should be powerful enough to be able to oxidise any metallic silver-found in the ore during process- to silver cations.

SO₂ should be used in a quantity to prevent the formation of sulphate which may cause formation of metallic silver by interacting with silver cation. The following reactions show the dissolution of the ore.



Elemental sulphur and sulphite produce thiosulphate by combining as seen in the above reactions, which raises solubility. However, concentration of SO₂ is crucial due to the risk of oxidation of thiosulphate to tetrathionate. The redox equilibrium between the sulphur dioxide- thiosulphate is represented by the reaction (6) [15]:



The data are ; $E^\circ_{\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}} = 0.17 \text{ V}$, $E^\circ_{\text{SO}_2/\text{S}} = 0.46 \text{ V}$,

$[\text{S}_2\text{O}_3^{2-}] = 0.01 \text{ M}$, $[\text{H}^+] = 10^{-4} \text{ M}$; and if $[\text{S}_4\text{O}_6^{2-}]$ is buffered to 0.0010 M, oxidation tendency of thiosulphate will be prevented; in addition, this level of tetrathionate will not raise the density of the solution. From these data, equilibrium concentration of SO₂ can be found as

$$[\text{SO}_2] = 10^{-3.3} \text{ M}. \quad (7)$$

It is clear that at acidic pH levels SO₂ will be found in HSO₃⁻ form [16].

$$[\text{H}^+][\text{HSO}_3^-] / [\text{SO}_2] = K_1 \quad (8)$$

The data are: $[\text{H}^+] = 10^{-4} \text{ M}$, $[\text{SO}_2] = 10^{-3.3} \text{ M}$ and first acidity constant for SO₂ $K_1 = 10^{-1.7}$ at 55 – 65 °C. From these data and eq.(8), equilibrium concentration of HSO₃⁻ can be found as

$$[\text{HSO}_3^-] = 0.1 \text{ M}. \quad (9)$$

As mentioned before, metallic silver found in the medium for different reasons could be converted into silver cations depending on the concentration of SO₂ used providing that its solubility reaches the level of 10⁻³ M. The following calculations show sulphur dioxide concentration would be [15, 16]:

$$[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] / [\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]^2 = \beta \quad (10)$$

The data are: Complex stability constant (β) = 10¹², solubility = $[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] = 10^{-3}$ M and $[\text{S}_2\text{O}_3^{2-}] = 0,1$ M at 55 – 65 °C.

From these data, $[\text{Ag}^+] = 10^{-13}$ M; depends on this value, $[\text{SO}_2]$ is calculated from the redox equilibria between metallic silver- silver ion and sulphur dioxide- elemental sulphur couples. The data are: $E^{\circ}_{\text{Ag}^+/\text{Ag}} = 0.8$ V, $E^{\circ}_{\text{SO}_2/\text{S}} = 0.46$ V.

From these data, equilibrium concentration of SO₂ can be found as

$$[\text{SO}_2] = 10^{-13.3} \text{ M.} \quad (11)$$

Even this level of $[\text{SO}_2]$ will easily oxidize metallic silver to the silver cation. Furthermore, as it has been mentioned in an earlier equation (7), the level of $[\text{SO}_2]$ is much higher than this level.

There can be another risk; $[\text{SO}_2]$ might be oxidized to the sulphate ion meanwhile the silver cations might be reduced to metallic silver. However, the reaction was experimentally observed to be kinetically controlled at selected temperature.

In solubilization of Ag₂S, the acidity, and the concentrations of complexing agent and oxidizing agent should be optimized against possible risks.

At $[\text{SO}_2] = 10^{-13.3}$ M, thiosulphate is not oxidized and also that level of sulphur dioxide easily oxidizes the metallic silver.

The data are: $E^0_{(S/H_2S)} = 0.14$ V, $E^0_{SO_2/S} = 0.46$ V, $[SO_2] = 10^{-13.3}$ M and $[H^+] = 10^{-4}$ M

[7]. From these data, equilibrium concentration of H_2S can be found as:

$$[H_2S] = 10^{-9} \text{ M.} \quad (12)$$

Using the above concentration of H_2S and from the acid dissociation constants $K_1K_2 = 10^{-19}$ for H_2S at $55 - 65$ °C [16]:

$$[S^{2-}] = 10^{-20} \text{ M.} \quad (13)$$

The data are: $[S^{2-}] = 10^{-20}$ M, $K_{sp} = 10^{-44}$ for Ag_2S [14]:

From these data, equilibrium concentration of Ag^+ can be found as

$$[Ag^+] = 10^{-12} \text{ M.} \quad (14)$$

And finally, the data are: Solubility(S) = $[Ag(S_2O_3)_2^{3-}]$, $[S_2O_3^{2-}] = 0.01$ M, $\beta = 10^{12}$ and using eq.(10) ;

$$\text{From these data, solubility (S) = } 10^{-2} \text{ M} \quad (15)$$

can be found.

As it is clear from the above calculation the desired solubility can be easily reached even beyond the sufficient value.

The only parameter that could not be deduced from theoretical calculations is the temperature, which is determined experimentally.

3. Experimental

3.1. Chemicals and Equipments

In this study sodium thiosulphate ($Na_2S_2O_3$), sodium sulphite (Na_2SO_3), phosphoric acid

(H_3PO_4), sodium dihydrogen phosphate (NaH_2PO_4), sodium tetrathionate ($\text{Na}_2\text{S}_4\text{O}_6$) and sodium sulphate (Na_2SO_4), nitric acid (HNO_3) were used in analytical grade. In all cases, chemicals of the best available quality were used. Water was de-mineralised.

The leaching process was carried out in a 100mL glass vessel equipped with a thermostatic water jacket. Junke & Kunkel electrolysis system with grid and spiral platinum electrodes was used for electrolysis. The pH was measured with a Jenway 3040 Ion Analyser. The dissolved metals were analysed by using a GBC 904 Atomic Absorption Spectrometer.

3.2. Procedures

3.2.1. Sampling

Raw material argentite is supplied from Gumuskoy – Kutahya. Qualitative analysis showed that its chemical composition was mainly silver, zinc, copper, gold, iron sulphides and silicon dioxide. Half of the ore sample was homogenized and ground into different particle sizes. The ground sample was screened and each fraction was subjected to chemical analysis. The results of size distribution and silver content are reported.

The remaining half of the sample was ground into the particle size of $-1.00 + 0.800$ mm. A small fraction from the heap was left and remaining part was ground into the particle size of $-0.80 - +0.5$ mm. The same procedure was repeated until -0.063 mm particle size was obtained.

1.00 g ore sample of each fraction was subjected to leaching with concentrated HNO_3 . Following the complete dissolution, nitric oxides were removed and the solution was heated until dryness. This procedure was repeated several times with demineralized

water until neutral pH is obtained. The silver content of 35 representative ore samples (five samples from each fraction) were analysed by AAS.

3.2.2. Leaching

All parameters which affect the leaching process were tested to find optimum leach conditions. For the recovery studies the – 0.212 mm fraction was used. For leaching solution, 0.010 mole of Na_2SO_3 , 0.0010 mole of $\text{Na}_2\text{S}_4\text{O}_6$ and 0.0010 mole of Na_2SO_4 were mixed in a 1 L glass vessel by the addition of demineralized water. The pH of the solution was made 4.0 by dropwise addition of concentrated H_3PO_4 and 0.010 M NaH_2PO_4 .

$\text{Na}_2\text{S}_2\text{O}_3$ powder was added into the vessel to make the solution 0.01 M in $\text{S}_2\text{O}_3^{2-}$.

5.00 g of ore sample were placed in a 100 ml beaker and 100 ml leaching solution were added and then the contents were stirred at a selected temperature. The effect of temperature and effect of leach time were determined at different temperatures and time intervals (from 30 °C to 70°C). During the leaching process, H_3PO_4 was added in order to keep pH constant at 4.0. The silver content of extracted solution was determined by AAS. At the end of these tests the slurry was filtered. The slurry was subjected to the same procedure which was applied for sampling. In this solution, leach residues were analysed for silver (n = 5) using AAS.

3.2.3. Electrolysis

After the leaching process was completed the leach liquor was transferred into the electrolysis cell. The potential was made gradually negative and distance between the electrodes was adjusted without considering resistance of solution as the current density would be 1.5 – 2.0 A/dm^2 until dark electrolytic deposition of silver was observed on

the platinum grid electrode. Cathode must not get black due to the silver sulphide deposition and oxygen gas formation must be minimal at anode; otherwise, hydrogen ion concentration increases in the vicinity of anode and this causes turbidity due to the degradation of thiosulphate. 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 metallic impurities of the deposited silver on the grid platinum electrode were determined by AAS .

4. Results and Discussion

The sample was ground and screened. Each fraction has been subjected to chemical analysis. The size distribution and silver content of the ground and screened samples are given in Table 1.

Table 1. Screen size analyses of the argentite.

Size mm	Sample		Ag Content		Ag, μg
	Weight, g	% of total	mg/kg	% of total	
+2.000	88.04	27.09	65	22	5723
-2.000 + 1.000	82.98	25.52	70	22	5809
-1.000 + 0.800	18.28	5.62	82	5.8	1499
-0.800 + 0.500	33.70	10.37	150	19.4	5055
-0.500 + 0.300	24.10	7.41	80	7.4	1928
-0.300 + 0.212	14.28	4.39	94	5.2	1342
-0.212 + 0.106	25.23	7.75	87	8.4	2195
-0.106 + 0.063	19.63	6.05	80	6.0	1570
-0.063	18.88	5.80	79	5.7	1492
Total	325.18	100.00	80	100	26014

Argentite (Ag_2S) ore has been ground into different particle sizes, and the optimum particle size for extraction was determined. The results of the analyses are reported in Table 2.

Table 2. The silver contents of each fraction of argentite.

Size mm \pm	Ag contents (ppm)
-1.000	25 ± 1
-0.800	60 ± 8
-0.500	72 ± 11
-0.300	72 ± 5
-0.212	84 ± 5
-0.106	85 ± 4
-0.063	68 ± 5

For leaching studies the particle size of 0.212 mm was chosen. Silver content of ore was found to be 84 ± 5 ppm at particle size of 0.212 mm.

In the light of theoretical calculations, extraction of silver from argentite which has very low solubility has been found possible only with using of oxidant, ligand, acidity and certain degree of heat. In experimental study sodium sulphite was chosen as SO_2 source, which is the most proper oxidant, sodium tiosulphate was chosen as the source of ligand and phosphoric acid as the proton source. The solution pH was kept at 4.0 with phosphate buffer. To prevent oxidation of thiosulphate to higher oxidation levels, sodium tetrathionate and metallic silver formation, sodium sulphate were used. The leach solution should be kept at pH 4.0 since thiosulphate decomposes.

Effect of temperature and leach time on silver extraction are the important parameters. For optimization the results were observed at different temperatures in relation with time. Dependence of extraction efficiency and silver on the temperature and leaching time can be seen in Figure 2.

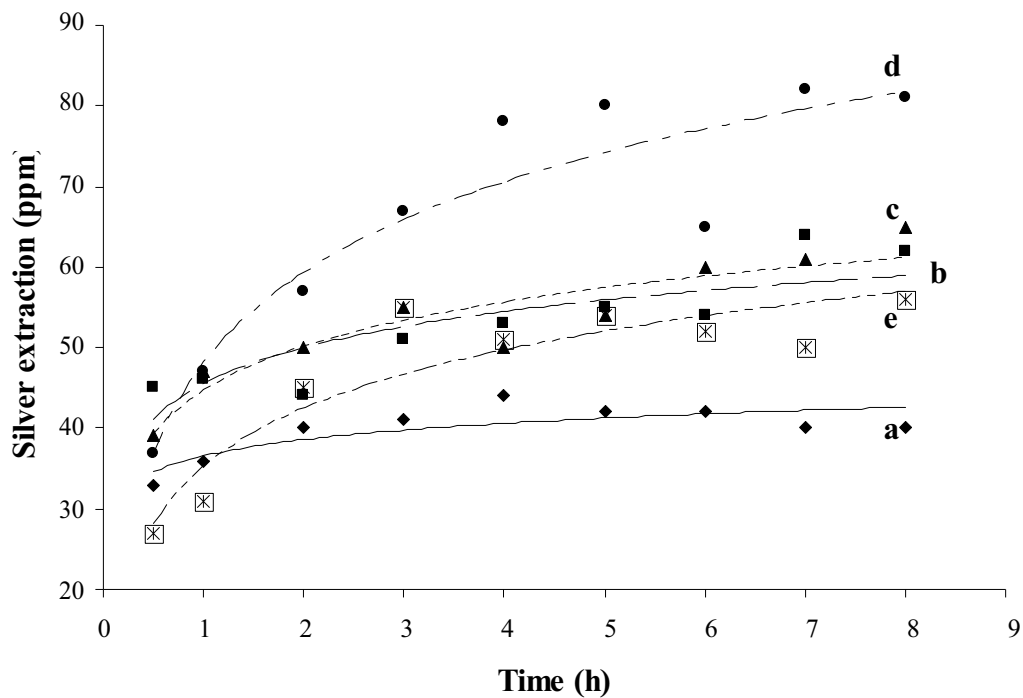


Figure 2. Effect of time on silver extraction by thiosulphate leaching at pH = 4.0.

(temperatures = a: 30 °C ; b: 40 °C ; c: 50 °C ; d: 60 °C ; e: 70 °C)

It is certain that increasing temperature raises the solubility of the ore by enhancing thiosulphate formation and increasing equilibrium constants. The high temperatures (70 – 100 °C) are undesirable due to the following two reasons:

- a) high energy requirement
- b) metallic silver formation reaction which depends on sulphate formation will become kinetically uncontrolled and this would decrease the solubility. Thus temperature was optimized between ranges of 55 - 65°C which makes solubility maximum.

Silver extraction as a function of the temperature for different durations is also given in Fig.3.

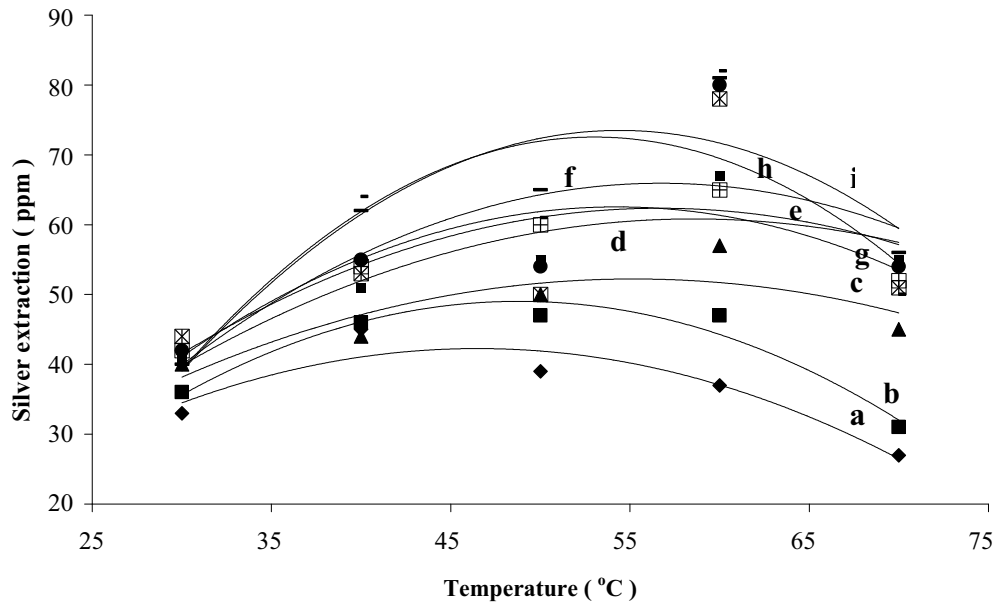
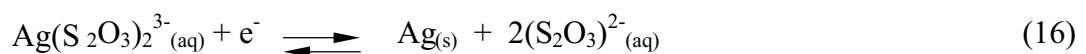


Figure 3. Silver extraction as a function of the temperature for different durations.

(durations = a: 30min.; b:1 hours; c: 2 hours; d: 3 hours; e: 4 hours; f: 5 hours; g: 6 hours; h: 7 hours; i: 8 hours)

Under the conditions described above, the ore sample was treated with leach liquor at pH 4,0 in the temperature range 55 - 65°C.

Indeed, the reaction proceeded in agreement with the theoretical assumptions and the ore sample was almost completely (98%) dissolved to give $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ complex in 6 – 8 hours . However, as the reaction proceed at higher concentrations of the complex the reaction rate was decreased. For this reason the electrolytic recovery of silver from the leach solution was considered. The silver content of the solution was deposited on the grid electrode according to the following reaction:



The silver recovered from the grid electrode was dissolved in concentrated HNO₃. The metallic impurities of the solution are given in Table 3.

Table 3. The metallic impurities deposited on the electrode.

Contents	Concentrations (ppm)
Au	10
Cu	28
Fe	22
Zn	14

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 electrolysis tank after the application. The precipitate was rinsed with demineralised water and dissolved in concentrated HNO₃. In this solution no silver in significant amounts was detected by AAS.

The leach solution can be reused after checking pH and sulphite concentration. This constitutes the practical aspect of the method.

There are a number of significant improvements between the optimum conditions found here and the preliminary conditions which were previously reported by Ayata and Yildiran [14]. These differences are summarised in Table 4.

Table 4. Conditions for the preliminary and optimised processes.

	Preliminary Process	Optimised Process
Leach Time	4 – 6 Hours	6- 8 Hours
Particle Size	~ 100 μ	~ 200 μ
Temperature	50 -60 °C	55 -65 °C
Thiosulphate Concentration(M)	~0.8	~0.01
Tetrathionate Concentration(M)	-	0.001
Sulphite Concentration(M)	0.1	0.01
Sulphate Concentration(M)	-	0.001

5. Conclusion

Optimisation of particle size, temperature and leaching time has been carried out and as a result a much smaller amount of reagents have proved necessary thereby making the process much more economically feasible. As seen in Table 2, the amount of silver which could be extracted from the ore increased with decreasing particle size. However, particles smaller than 63 μm have yield a lower content. This can be explained in a way that silver particles can not be sieved effectively and this can be utilized in enrichment of silver by simply choosing the proper size distribution of the ore sample. Dependence of extraction efficiencies on the temperature can be seen in Fig.3. The decrease in the extraction efficiency at temperatures higher than 60 $^{\circ}\text{C}$ indicates that silver ions are reduced at high temperatures probably by oxidising sulphite ion to sulphate ion in the mixture.

Sulphite and sulphide present in the medium generate thiosulphate which acts as a ligand towards silver ion. Thus the loss in thiosulphate in the medium can be partially compensated by these reagents.

This process has the advantage as the interference of the foreign cations is decreased. The recycled leach solution for re-use is another superiority of this technique.

Moreover, while the other thiosulphate methods are realised at alkaline pHs, this technique was at acidic pH.

This technique offers a low cost and enviromental friendly process in contrast to other leaching processes which use highly toxic chemicals such as cyanide.

The efficiency of the silver extraction is 98% and the purity of the final product is 99%.

6. References

- [1] Sanchez, L., Cruells, M., and Roca, A., *Hydrometallurgy* 42, 35-49, (1996)
- [2] McGrew, K.J. and Murphy, J.W., U. S. Patent 4,557,759 (1985)
- [3] Marshden, I.H., *The Chemistry of Gold Extraction*, Ellis Harwood, New York, (1992)
- [4] Abbruzzese, C., Fornari, P., Massidda, R., Veglio, F., Ubaldini, S., *Hydrometallurgy* 39, 265-276, (1995)
- [5] Murthy, D.S.R., Prasad, P.M., *Hydrometallurgy* 42, 27-33, (1996)
- [6] Qi, P.H., Hiskey, J.B., *Hydrometallurgy* 27, 47-62, (1991)
- [7] Lawrance, R.W. and Brynsten, A., *CIM Bulletin* 76, 107-110, (1983)
- [8] Alymore, M.G. and Muir, D.M., *Minerals Engineering* 14/2, 135-174, (2001)
- [9] Ter-Arekelyan, K.A. Bagdasaryan, K.A., Organyan, A.G., Mkrtychyan, R.T., and Babayan, G.G., *Izv.V.U.Z.Tsvetn. Metallurgy*, 72-76, (1984)
- [10] Berezowsky., R.M. et al, U. S. Patent 4,070,182, (1978)
- [11] Hemmati, M., Hendrix J.L., Nelson, J.H., Milosavljevic, E.B., *Extraction Metallurgy 89 Symposium, I.M.M.*, 665-678, (1989)
- [12] Perez, A.K. and Garaviz, H.D., U.S. Patent 4,654,078, (1987)
- [13] Kerley, B.J., U. S. Patent, 4,369,061, (1984)
- [14] Ayata, S., and Yildiran, H., *Turkish Journal of Chemistry* 25, 187-191, (2001)
- [15] W. W. Latimer, *Oxidation Potentials*, Prentice Hall, New York, (1952)
- [16] A.E. Martel and L. G. Sillen, *Stability Constants of Metal-Ion Complexes*, The Chemical Society, London, (1964)