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Recovery of silver from zinc cakes

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The present experimental study investigates the feasibility of thiosulfate recovery of silver from zinc cakes produced in the process of wet recovery of zinc cakes at the KCM Ltd in Bulgaria. The impact of various factors on the rate of silver recovery through thiosulfate leaching is studied. It is found that the rate of silver recovery is 70-74 % within the temperature range of 30-50ºC at 20% pulp density and leaching time of 30 min, irrespective of the solution pH. The behavior of copper, lead, zinc and iron during thiosulfate extraction is also observed. The thiosulfate solution pH is maintained to 7-8 in order to reduce by hydrolization the concentration of the metals that have been transferred to the solution except silver. After subsequent precipitation of the silver by means of Na_2S, silver concentrate is produced. The possibility of regeneration of the thiosulfate solution is discussed. The solid residue from thiosulfate leaching contains 10-40 g/t silver and can be processed by a Waelz process.

Keywords: *zinc cake, silver, thiosulfate leaching.*

1. INTRODUCTION

The wet recovery of zinc by the technology adopted at KCM Ltd in Bulgaria takes place at relatively low acidity of the solution without bringing the impurities contained in the zinc concentrates into the solution. Thereupon, the metals are concentrated in the zinc cake which subsequently is subjected to Waelz-processing. After Waelz-processing the precious metals completely pass into the clinker and, due to the lack of a proper technology for their recovery they are irretrievably lost.

To prevent the loss of precious metals, attempts for their recovery from the zinc cakes are made at some plants with similar technology.

All known methods for zinc cakes processing in the world-wide practice can be divided into three groups [1]:

1. Waelz-process; reductive flash roasting; smelting in gas-generator, shaft, reverberatory, cyclone, and electric furnaces.
2. Roasting of the cakes in a mix with zinc or pyrite concentrates; treatment with SO_2 or sulfation with sulfuric acid.
3. Direct dissolution of the cakes in sulfuric acid at increased acidity and temperature.

Usually the hydrometallurgical methods of zinc cakes processing based on the reactions of ferrite decomposition using sulfuric acid at atmospheric or higher pressure have achieved greater development.

The complex composition and a large amount of very small size classes in the zinc cake make it a difficult object for leaching and flotation.

In recent years, there has been renewed interest in the use of thiosulfate as a substitute for cyanide in gold and silver leaching [2]. Many attempts have been taken for leaching silver sulfide with thiosulfate, each utilizing different additional reagents and conditions [3,4]. The cupric-ammonia catalyzed system has been the most commonly studied system because of its ability to leach gold, silver and silver sulfide.

The developed and patented hydrometallurgical method of zinc cake processing [5] is of certain interest. It is based on silver recovery by means of sodium thiosulfate in the presence of ammonium sulfate as an activator at a temperature of 30-60ºC and pH=4-6. In this process, the silver passes into the solution wherefrom it is recovered by cementation with zinc powder. The solid residue is re-pulped by the same thiosulfate solution and is subjected to floatation. The drawbacks of that method are the low rate of silver recovery in the cement precipitate, its circulation in turnover with the flotation concentrate, considerable losses (over 10 %) with the clinker, as well as considerable loss of zinc in the thiosulfate solutions.

The purpose of this experimental work is to determine the behavior of silver and other metals contained in the zinc cakes at thiosulfate leaching and to investigate the feasibility of solution regeneration after precipitation of the silver by Na_2S.

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2. EXPERIMENTAL

2.1. Materials

The subject of the investigation is a zinc cake – a waste product from the wet recovery of zinc cakes at KCM Ltd. The chemical composition of the cake was determined through atomic absorption analysis as presented in Table 1.

The phase analysis of zinc cake obtained at similar plant applying the same technology for zinc cakes processing [6] shows that:

1. The zinc exists in the form of sulfate, oxide, silicate, sulfide and ferrite.
2. The lead in the cake exists in the form of anglesite ($PbSO_4$), cerusite ($PbCO_3$), galenite (PbS), plumbojarosite $PbFe(SO_4)_3(OH)_{12}$.
3. The copper is a very thin (up to 3 microns) edging of sulfide Cu_2S on zinc silicate and zinc oxide grains and as isomorphic admixture in sphalerite and zinc ferrite.
4. The silver in the zinc cake is mainly contained in the crystal lattice of the secondary covelline, while part of it is adsorbed by the iron hydroxides [7]. According to the authors, in the process of recovery of the zinc cakes, the copper and silver pass into the solution, and after that their ions interact with the zinc sulfide by the reaction:

$$(Cu,Ag)SO_4+ZnS = (Cu,Ag)S+ZnSO_4 \quad (1)$$

Cake, for the most part, consists of particle aggregates with size 10-15 microns. The latter contain particles to submicron size. More than 90% of the silver is concentrated in size classes less than 40 microns [6].

Upon recovery of the zinc cake with water for 1 hour at a temperature of 70ºC, 3.97 % of the copper and 16.19 % of the zinc pass into the solution. The total content of water-soluble compounds in the zinc cake is 18.75 %.

For recovery of silver from the cake a sodium thiosulfate pentahydrate solution was used. Water solution of sodium sulfide was used as precipitator of the silver.

2.2. Methods

The leaching experiments for silver recovery from the cake were carried out in a thermostat in order to maintain the defined temperature. The stirring of the pulp was realized by means of a mechanical stirrer. The defined level of solution pH was reached and maintained by means of lime milk.

The silver precipitation experiments were carried out using a magnetic stirrer at room temperature. Atomic absorption analysis was used to determine the concentration of Ag, Cu, Fe, Pb, Zn in the thiosulfate solution, the solid residue, and the sulfide concentrate.

RESULTS AND DISSCUSION

3.1. Thiosulfate recovery of silver from zinc cake

The factors influencing the rate of silver recovery by thiosulfate leaching of zinc cake are: sodium thiosulfate concentration, type and quantity of the additions which stabilize the solution, temperature, pulp density, leaching time and pH of the medium.

Thiosulfate ion is a metastable anion with a tendency to chemical decomposition in water solutions. The oxidation of thiosulfate is fast in neutral and acidic solutions.

For the purpose of reducing thiosulfate consumption, various researchers propose addition of sulfites and sulfates that would transform the free sulfide ion into thiosulfate during the recovery process or would retard the decomposition process by increasing the concentration of decomposition products.

Ammonium sulfate was used in the subsequent experiments as activator of the process of thiosulfate recovery of silver from the zinc cake and as inhibitor of the thiosulfate ion decomposition, in analogy to [5].

The following conclusions can be drawn from the experiments performed to determine the factors influencing the rate of recovery, the results of which are presented in Figures 1-5:

- With the increase of sodium thiosulfate concentration up to 25 g/l the rate of silver leached increases. The increase of thiosulfate concentration above 25 g/l does not result in a higher rate of silver recovery (Figure 1).
- The joint action of sodium thiosulfate and ammonium sulfate increases the rate of silver recovery. As illustrated by Figure 2, an increase of the $Na_2S_2O_3$:$(NH_4)_2SO_4$ ratio above 1 does not lead to further increase of the rate of silver recovery. For this reason the experiments were carried out at a ratio $Na_2S_2O_3$:$(NH_4)_2SO_4$=1.
- The decomposition rate of the thiosulfate leachant is directly proportional to sodium thiosulfate concentration in the solution. Upon rising of the temperature to 40 - 80ºC, the thiosulfate decomposition increases four times. There are two temperature zones of thiosulfate decomposition, from 40 to 60ºC and from 60 to 80ºC, which are related to different decomposition mechanisms. The maximum

rate of decomposition of the thiosulfate ions is observed at 80ºC and sodium thiosulfate concentration 80g/l. The experiments carried out in the temperature range up to 50ºC showed that the increase of temperature above 30ºC does not result in any significant increase of silver recovery from the zinc cake (Figure 3).

- The lowest rate of silver recovery is achieved at solid:liquid ratio = 1:3 (Figure 4). This is most probably due to the depletion of thiosulfate, because other metals also simultaneously pass into the solution with the silver.
- The results of the experiments showed (Figure 5) that pH of the solution does not influence the rate of silver recovery.
- In all experiments, the highest reached silver recovery degree is 74 %.

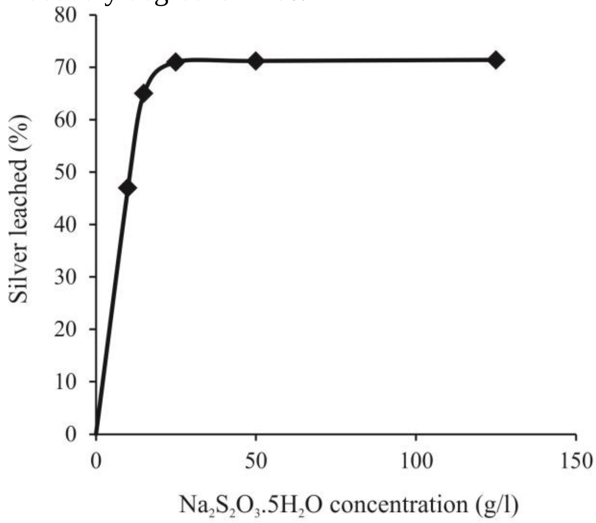

Fig. 1. Effect of thiosulfate concentration on silver leaching (T=50ºC, τ=60 min, S:L=1:10, pH=6).

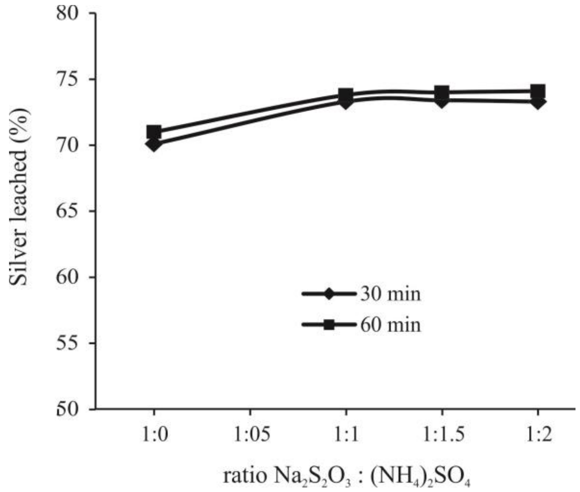

Fig. 2. Effect of ratio $Na_2S_2O_3$:$(NH_4)_2SO_4$ on silver leaching (25 g/l $Na_2S_2O_3.5H_2O$, T=50ºC, S:L=1:10, pH=6).

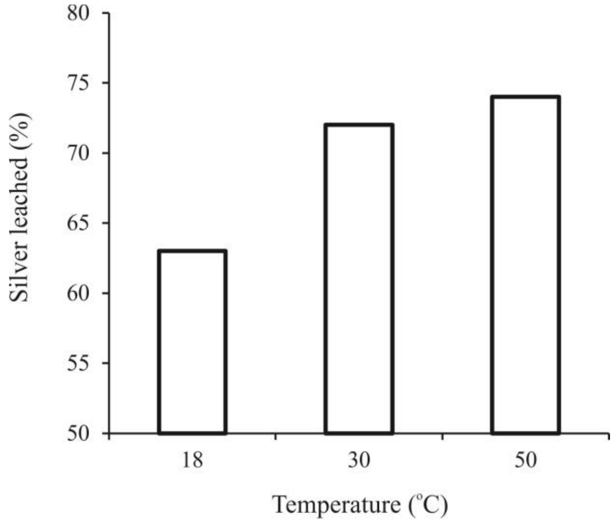

Fig. 3. Effect of temperature on silver leaching (25 g/l $Na_2S_2O_3.5H_2O$, 15 g/l $(NH_4)_2SO_4$, t =60 min, S:L=1:10, pH=6)

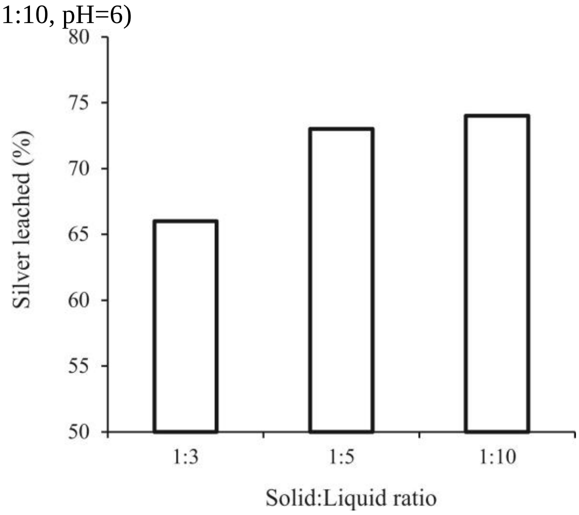

Fig. 4. Effect of solid:liquid ratio on silver leaching (25 g/l $Na_2S_2O_3.5H_2O$, 15 g/l $(NH_4)_2SO_4$, T=50ºC, τ =60 min, pH=6)

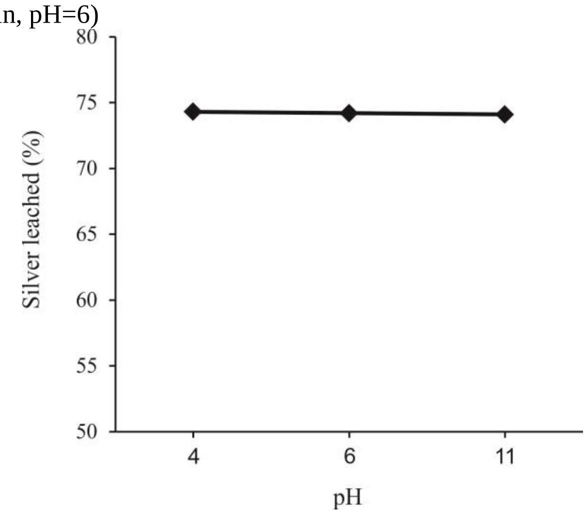

Fig. 5. Effect of pH on silver leaching (25 g/l $Na_2S_2O_3.5H_2O$, 15 g/l $(NH_4)_2SO_4$, T=50ºC, S:L=1:5, τ =60 min

As a result of thiosulfate leaching of the zinc cake at 25 g/l $Na_2S_2O_3.5H_2O$, 15 g/l $(NH_4)_2SO_4$, 20 % pulp density, 30 min process duration and pH=6, a solution with chemical composition as presented in Table 2 is obtained.

Table 1. Chemical composition of zinc cake, %

Cu	Pb	Fe	Zn	Ag, g/t
1.27	4.40	27.69	18.10	158

Table 2. Chemical composition of thiosulfate solutions, g/l

Cu	Pb	Fe	Zn	Ag
0.07	0.64	1.81	4.65	0.026

Table 3. Chemical composition of undissolved residue, %

Cu	Pb	Fe	Zn	Ag, g/t
1.14	4.85	31.95	17.00	30

As can be seen in Table 2, the thiosulfate solution contains predominantly zinc.

The chemical composition of the solid residue obtained after thiosulfate leaching of the zinc cake at these conditions is presented in Table 3.

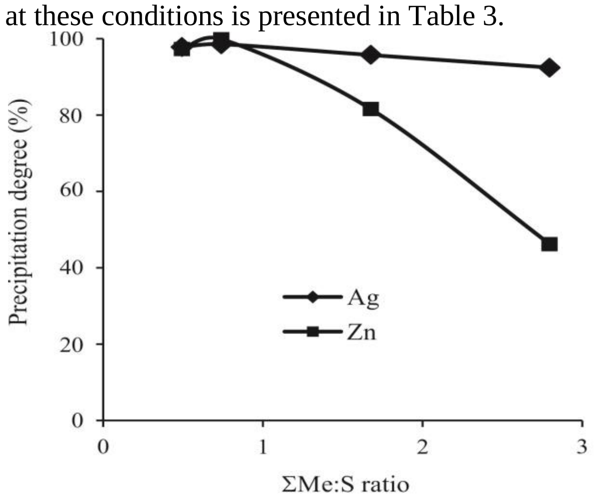

Fig. 6. Effect of ΣMe:S on precipitation degree.

Silver can be extracted from the thiosulfate solutions through cementation, electrolysis or precipitation of low-soluble compounds. The choice of a proper method will be determined by the regeneration capability of the solution. Probably the most suitable method of silver recovery is precipitation of silver sulfide by means of sodium sulfide.

3.2. Precipitation of silver from thiosulfate solutions

Of all reagents proposed for silver precipitation, sodium sulfide is the most affordable, inexpensive and reliable in terms of completeness and rate of the reaction which is described with the following equation:

$$2Na_5[Ag(S_2O_3)_3] + Na_2S \rightarrow Ag_2S + 6Na_2S_2O_3 \qquad (2)$$

Various quantities of 10 % Na_2S solution are used for metal precipitation from solution produced as a result of thiosulfate leaching of zinc cake. The dependency of the rate of silver and zinc precipitation on the ratio of the sum of metals (ΣMe) in the solution to the amount of sulphur introduced with Na_2S is presented in Figure 6.

Depending on the quantity of Na_2S, pH of the thiosulfate solution varies from 6 to 11, whereupon, to different degrees, the zinc is precipitated as a hydroxide. The chemical composition of the hydroxide-sulfide precipitate obtained at ΣMe:S = 0,74 is presented in Table 4.

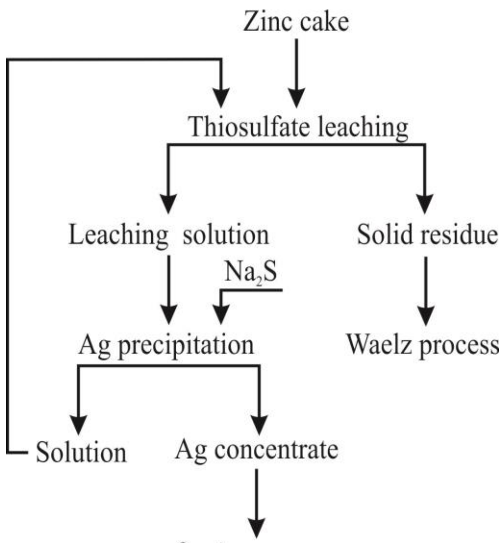

Fig. 7. Conceptual flow sheet for treatment of zinc cake.

Table 4. Chemical composition of sulfide concentrate, %

Cu	Pb	Fe	Zn	Ag	S
0.93	3.55	0.27	43.09	0.1616	10.74

Table 5. Metal precipitation degree, %

Cu	Pb	Fe	Zn	Ag
97.80	99.58	92.32	99.93	99.99

Table 6. Chemical composition of leaching solution (pH=7) and obtained concentrate

	Cu	Pb	Fe	Zn	Ag
Leaching solution, g/l	0.334	0.122	0.016	6.5	0.115
Concentrate, %	14.29	5.65	0.19	44.73	5.18

In that case, the degree of precipitation of the examined metals varies between 92 and 100% (Table 5).The technology of thiosulfate recovery of silver from zinc cake is attractive only if the solution is regenerated and reused, in which case the silver concentration is gradually increased to higher levels. Experiments for repeated use of the thiosulfate solution for dissolution of new batches of zinc cake were carried out and the precipitator consumption is being determined by the ratio ΣMe:S =1. It was found that upon dissolution of the second batch of cake the degree of silver recovery decreased from 74 % to 6 %, which was due to the presence of free S^{2-}, because of the high consumption of precipitator. Therefore, for successful regeneration of the thiosulfate solution the leaching process should be performed while maintaining pH=7-8, so as to secure hydrolization of the other metals except silver. Then, the consumption of precipitator will be considerably lower. For that purpose, experiments were carried out for quintuple use of the thiosulfate solution while maintaining pH=7 by means of lime milk. The consumption of sodium sulfide for silver precipitation is 1,1 g per 1 g of silver in the solution. After recovery of the fifth batch the thiosulfate solution has the chemical composition presented in Table 6. The chemical composition of the hydroxide-sulfide concentrate obtained after precipitation is also presented in the same table.

As a result of the quintuple use of the thiosulfate solution, the rate of silver recovery in the concentrate decreases from 74 to 70 %. It means that the thiosulfate solution should be adjusted at regular intervals. It can be assumed that if an even higher pH is maintained during the recovery, for example pH=8, whereby fuller hydrolization of the metals is secured, the silver content in the produced concentrate will increase significantly.

For treatment of the solid residue after thiosulfate leaching there are two possible ways – Waelz-process or floatation and Waelz-process.

The conceptual flow sheet for treatment of the zinc cake is presented in Fig. 7.

CONCLUSIONS

As demonstrated by the obtained experimental results, about 74% of the silver contained in the zinc cake can be recovered by thiosulfate technology and subsequent precipitation with Na_2S to produce silver concentrate. The proposed process diagram can be successfully applied in the end of the cycle of wet recovery of zinc cakes.

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ИЗВЛИЧАНЕ НА СРЕБРО ОТ ЦИНКОВИ КЕКОВЕ

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(Резюме)

В настоящата експериментална работа е изследвана възможността за тиосулфатно извличане на среброто от цинковите кекове, получени при мокрото извличане на цинкова угарка в КЦМ-Пловдив. Изследвано е влиянието на различни фактори върху степента на тиосулфатно извличане на среброто. Установено, е че степента на извличане на среброто е 70-74 % в температурния диапазон 30-50^{o}C при плътност на пулпа 20% и времетраене на извличането 30 min, независимо от pH на разтвора. Проследено е поведението на медта, оловото, цинка и желязото при тиосулфатното извличане. При поддържане на pH на тиосулфатния разтвор 7-8 с цел хидролизиране на металите, преминали в разтвора и следващо утаяване на среброто с Na_2S се получава сребърен концентрат. Разгледана е възможността за регенериране на тиосулфатния разтвор. Твърдият остатък от извличането съдържа 10-40 g/t и може да бъде преработван чрез Велц-процес.