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Industrial Scale Testing and Evaluation of Silver Recovery Process

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Abstract: In this paper an industrial scale testing and evaluation of a silver recovery process for treating silver-containing materials is presented. The process that is based on the thiourea leaching, followed by silver cementation allows for recovery of the majority of silver as a metallic product. The thiourea leaching was developed specifically for the zinc cake residue, produced from the conventional zinc roast-leaching process at the KCM 2000 AD (Bulgaria), which contains up to 200 g/t silver. The material has a complex zinc ferrite dominated mineralogy with minor zinc hydrosulfate, gypsum, anglesite and plumbojarosite. The feed zinc cake residue is washed with water to remove water soluble zinc by pulping it into 25-30% solids slurry. The washing is carried out in 60 minutes and the resulted slurry is sent to the solid/liquid separation section for filtration. The resulted solids are sent to thiourea leaching and the zinc-containing solution is sent for further zinc recovery. The washed (water-soluble zinc free) solids is pulped into 20% solids slurry. Using thiourea as lixiviant, ferric iron as oxidant, sodium metabisulfite as a reductant and sulfuric acid for pH control, the leaching is performed for 35 minutes at 35^{o}C. Within the leaching process the operating conditions are controlled to allow high silver extraction, while reducing the detrimental effects of thiourea degradation. Silver is recovered from the pregnant leach solution by cementation that results in the formation of a high-grade silver cement product. Iron powder is used as a cementation agent to recover over 94% silver at ambient temperature for 90 minutes. Details of the development work and key process steps are described. The operational data and outcomes of the industrial scale testing are presented along with process performance evaluation.

Keywords: Silver, thiourea, leaching, cementation

Introduction

Process Description

Silver recovery process is a hydrometallurgical process for treating silver-containing materials that combines thiourea leaching and silver cementation to produce high quality silver cement. The key process steps involved are outlined in more details below.

Feed Pretreatment for Water-Soluble Zinc Removal

The majority of zinc in the feed zinc cake residue exists primarily as franklinite ($ZnFe_2O_4$) with lesser amounts of water-soluble gunningite (Zn, Mn^{2+})SO_4H_2O). Prior to the leaching, it is necessary to remove the water-soluble zinc which otherwise interfere with the process. This zinc if not removed reports largely to pregnant leach solution that is undesirable as it has the potential of consuming excessive thiourea amounts (Hiskey, 1984). Removal of water-soluble zinc is achieved by water leaching of the material in mechanically agitated reactors, followed by solid/liquid separation to produce washed solids and zinc-containing solution.

Thiourea Leaching

- Selection and peer-review under responsibility of the Organizing Committee of the Conference

The chemistry of the thiourea leaching is complex. However, by maintaining suitable pH and by controlling the concentrations of reagents, its addition, temperature and leach time, high silver extraction with low reagent consumption can be achieved.

The leaching of silver and silver sulfide by thiourea, using ferric iron as an oxidant can be represented by the following reactions (Bruckard et al., 1993):

$$Ag + 3CS(NH_2)_2 + Fe^{3+} = Ag[CS(NH_2)_2]_3^+ + Fe^{2+} \quad (1)$$

$$Ag_2S + 6CS(NH_2)_2 + 2Fe^{3+} = 2Ag[CS(NH_2)_2]_3^+ + 2Fe^{2+} + S \quad (2)$$

The washed (water-soluble zinc free) material from the previous process step is slurried to 20% solids with sulfuric acid solution at about pH 1.7 in mechanically agitated leach reactors. Thiourea, iron (III) and sodium metabisulfite are added to the leach slurry to achieve following concentrations: 6 g/l $CS(NH_2)_2$, 1 g/l Fe (III) and 0,3 g/l $Na_2S_2O_5$. Sodium metabisulfite is used in the process to control the leach potential at a value where adequate silver leaching rate is achieved and thiourea degradation is minimized. Leaching is maintained at an optimum temperature of 35°C with the addition of steam. The leaching time is limited to 20 minutes and then the leach slurry is pumped to a solid-liquid separation stage, where the leach residue is separated from the silver-containing pregnant leach solution by filtration.

Silver Cementation

Silver cementation involves precipitation of silver by addition of fine iron powder to the silver-containing solution. The process is based on the fundamental principle, according to which “more electropositive” metals are recovered from the solution in metallic form through addition of ‘’more electronegative’’ metal.

The mechanism for silver cementation on to iron metal from the thiourea leach solution (Lee et al., 1997) can be expressed as:

At the cathode:

$$Ag[CS(NH_2)_2]_3^+ + e = Ag + 3CS(NH_2)_2,\ E^0 = -\ 0.025\ V \quad (3)$$

At the anode:

$$Fe = Fe^{2+} + 2e,\ E^0 = -\ 0.440\ V \quad (4)$$

The overall cementation reaction can be expressed as:

$$2Ag[CS(NH_2)_2]_3^+ + Fe = 2Ag + 6CS(NH_2)_2 + Fe^{2+} \quad (5)$$

Reaction (5) indicates that one mole of iron can cement two moles of silver.

Silver is recovered from the silver-containing pregnant leach solution, generated in the thiourea leaching process step by cementation for 90 minutes in mechanically agitated reactor using an excess then the stoichiometric amount of iron powder. The produced silver cement is filtered out from the solution after cementation and the thiourea solution is sent to the effluent treatment.

Simplified Block Process Diagram

As can be seen in the block process diagram shown in Figure 1, the process contains the following steps: feed material pretreatment to remove water-soluble zinc and solid/liquid separation of the resulted slurry, thiourea leaching of silver and solid/liquid separation of the leach slurry, silver cementation and solid/liquid separation to recover silver cement product.

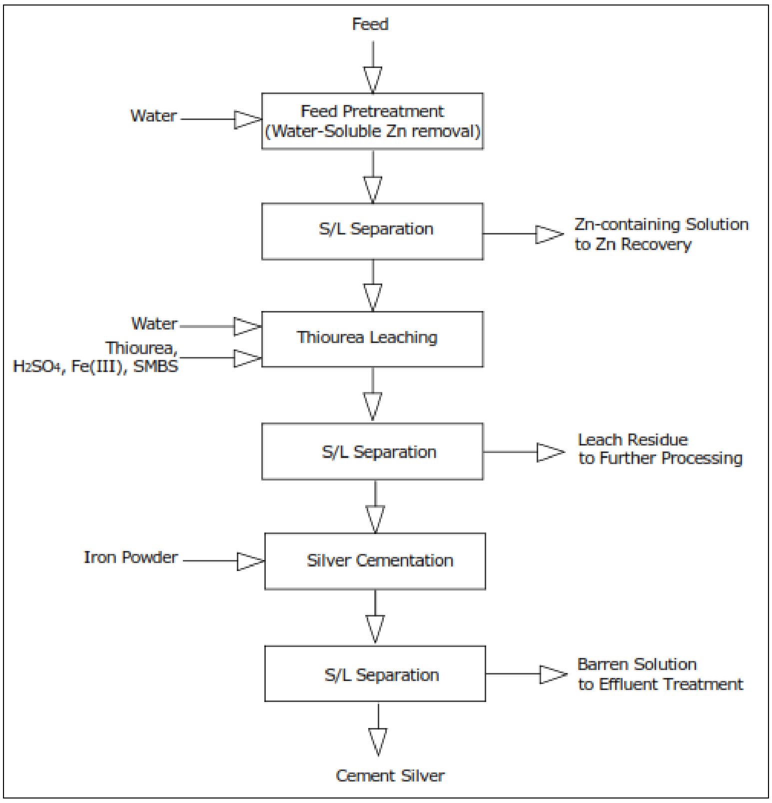

Figure 1. Simplified silver recovery process block diagram

Method

Background

Central Laboratory of Raw Materials Processing and Waste Management at the University of Mining and Geology "St. Ivan Rilski" (UMG) performed extensive metallurgical laboratory testing of the zinc cake residue, produced after two stage of leaching of a zinc calcine from KCM 2000 AD, Plovdiv, Bulgaria. The test sample contained 150 g/t silver, 18.7 % zinc, 1.03 % copper and 5.0 % lead. The purpose of the testwork was to examine a variety of leach systems and cementation agents and to indentify the optimum operating conditions for silver recovery from the material (Angelov et al., 2016a; Angelov et al., 2016b). Because of environmental concerns only non-cyanide lixiviants - thiourea and thiosulfate - were considered. The overall results of the testwork indicated that:

- Of the two leach systems trialed the thiourea was found to be more feasible for the recovery of silver from the zinc cake residue;
- Silver extraction over 94% was achieved using 10 g/l $CS(NH_2)_2$; 4 g/l Fe(III) as $Fe_2(SO_4)_3.9H_2O$; 0,5 g/l $Na_2S_2O_5$; pH=1; 40% solids, at 30°C in 20 minutes;
- Iron was selected as cementation agent due to its high-performance efficiency and relatively low cost;
- More than 90% of the silver was recovered from thiourea pregnant leach solution with iron powder at ambient temperature in 60 minutes.

Industrial Scale Testing Design

Following the successful laboratory testing that demonstrated viable process options for silver recovery from zinc cake residue, further laboratory testwork was carried out to provide essential data for the industrial testing design. The work, undertaken again at UMG's Central Laboratory of Raw Materials Processing and Waste Management was aimed at:

- Assessing the influence of pH on leaching behavior of copper and iron, which are detrimental to both silver leaching and cementation;

- Defining the optimum operating conditions to allow high silver extraction, while suppressing the dissolution of copper and iron.

Two series of leach tests were conducted. The first explored the effect of pH, Eh and iron (III) on copper and iron dissolution and the second series was carried out to establish the reagent concentrations and its addition. First test series: A series of 4 tests were undertaken to assess the effect of pH on copper and iron dissolution. The parameters studied were pH and addition of iron (III). The test conditions are summarized in Table 1 and the test results in Table 2.

Table 1. First series test conditions

Parameter	Test 1	Test 2	Test 3	Test 4
Slurry density, %	20	20	20	20
pH	1.5	1.5	1.0	1.0
Fe (III), g/l	-	4	-	4
Temperature, °C	22	22	22	22
Time, min	45	45	45	45

Table 2. First series test results

Test №	pH	Eh, mV	Cu, g/l	Fe (III), g/l	Fe (II), g/l
1	1.45	248	0.051	0.28	-
2	1.42	251	0.057	4.31	-
3	1.10	270	0.060	0.30	-
4	1.10	278	0.063	4.33	-

The results indicate that lowering the pH (with or without the addition of iron (III)) leads to: 1) an increase of Eh; 2) a slight increase of copper concentration in the solution and 3) essentially no iron dissolution. Second test series: In order to clarify the conditions under which maximum silver extraction could be achieved, a further series of 6 tests were conducted. The tests were carried to optimize parameters such as leach time, the reagent concentrations and its addition. The thiourea remaining in the solution was determined at the end of each test to indicate its consumption. A summary of the test conditions is shown in Table 3, while metallurgical results are shown in Table 4 and in Figure 2.

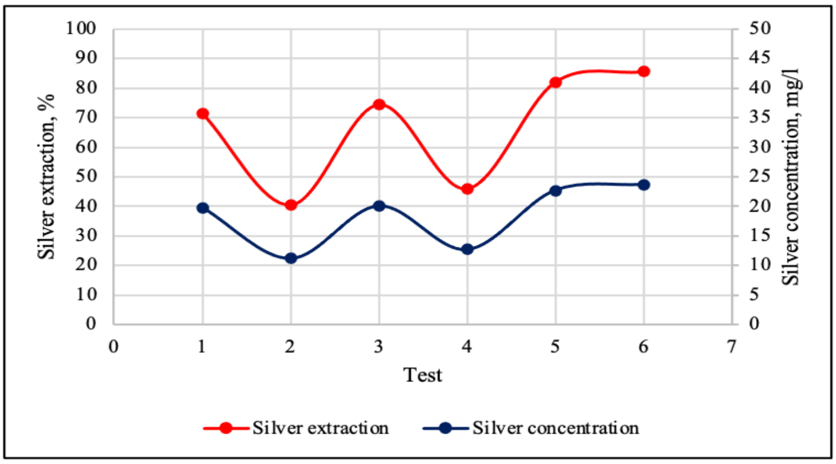

Figure 2. Second test series: silver extraction (%) and silver concentration (mg/l)

Table 3. Second series test conditions

Parameter	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
Slurry density, %	20	20	20	20	20	20
pH	1.7	1.7	1.7	1.7	1.7	1.7
$CS(NH_2)_2$, g/l	10	5	6	6	6	6
Fe (III), g/l	4	4	2	-	2	1
$Na_2S_2O_5$, g/l	0.5	0.5	0.3	-	0.3	0.3
Temperature, °C	22	22	22	22	22	22
Time, min	45	45	45	45	30	30

Table 4. Second series test results

Test №	pH	Eh, mV	Cu, g/l	Fe (III), g/l	Fe (II), g/l	$CS(NH_2)_2$ (res.), g/l
1	1.71	239.2	0.080	0.65	3.49	4.4
2	1.74	237.6	0.077	2.34	2.05	0.2
3	1.73	228.2	0.083	0.48	1.90	3.3
4	1.70	241.8	0.063	0.06	0.22	3.7
5	1.72	240.1	0.072	0.23	2.06	2.7
6	1.70	236.4	0.067	0.11	1.17	3.0

The conclusions obtained from the results of the second test series are:

- The highest silver recovery of 85.6% was achieved at thiourea and iron (III) concentrations of 6 g/l and 1 g/l respectively, in the presence of $Na_2S_2O_5$ and with a leach time of 30 minutes as shown in Tables 3 and 4;
- Higher iron (III) concentration increases thiourea consumption significantly;
- The ratio of thiourea and iron (III) must be closely controlled;
- Shorter leach time is beneficial for silver extraction.

Based on the metallurgical results from testwork conducted, the following operating parameters were selected for the industrial scale testing:

- Leach slurry density - 20%
- pH – 1.7
- Thiourea concentration in the leach solution - 6-8 g/l
- Iron (III) concentration in the leach solution - 1 g/l
- Sodium metabisulfite concentration in the leach solution – 0.3 g/l
- Temperature - 35°C
- Leach time – 20, 25 and 35 min.

Industrial Scale Testing

Further to the laboratory testwork, an industrial testing was performed to address the following:

- Demonstrate the silver recovery process on a big scale;
- Confirm thiourea leaching process parameters and silver extraction;
- Confirm that the silver can be recovered as a metallic product by cementation.

Figure 3. Industrial testing facility, KCM 2000, Plovdiv, Bulgaria

The testing was conducted in the Installation for water/alkaline washing at the KCM 2000 production site in Plovdiv, Bulgaria. The test schedule included testing of the thiourea leaching process, followed by separate testing of silver cementation, both under a preferred set of conditions. The operating conditions are summarized in Table 5 and the specifications of the key equipment are listed in Table 6.

Table 5. Industrial testing operating conditions

Parameter	Тест 1.I	Тест 2.I	Тест 3.I
Thiourea Leaching			
Slurry density, %	20	20	20
pH	1.7	1.7	1.7
$CS(NH_2)_2$, g/l	6	8	6
Fe (III), g/l	1	1	1
$Na_2S_2O_5$, g/l	0.3	0.3	0.3
Temperature, °C	35	35	35
Leach time, min	20	35	25
Cementation			
Iron powder dosage, % excess stoichiometric requirement	110	110	110
Cementation time, min	90	90	90

Table 6. Industrial testing equipment specifications

Item	Characteristics	Number
Leach Reactor	Mechanically agitated; Capacity - 20 m^3	1
Cementation Reactor	Mechanically agitated; Capacity - 20 m^3	1
Filter press	Plate and frame type; Number of filter plates - 72; Filter plate size - 800 x 800 mm;	1
Filter press	Plate and frame type; Number of filter plates - 25; Filter plate size - 800 x 800 mm	1

For the industrial testing 3 separate bulk samples of prewashed zinc cake residue were prepared. Analyses of the prepared samples are presented in Table 7.

Table 7. Prewashed zinc cake residue analysis

Parameter	Тест 1.I	Тест 2.I	Тест 3.I
Silver, g/t	161	163	157
Gold, g/t	0.35	<0.3	<0.3
Zinc, %	18.6	18.1	18.3
Copper, %	1.36	1.38	1.5
Iron, %	30.85	32.03	32.95

Results and Discussion

Thiourea Leaching

Key variables investigated were thiourea concentration, thiourea to oxidant ratio and leach time. A series of 3 batch tests were carried out in 20 m^3 mechanically agitated leach reactor at 20% slurry density. The required reagents were added as a 50/50% split prior to and after zinc cake addition.

Table 8. Leach Residue Composition

Parameter	Тест 1.I	Тест 2.I	Тест 3.I
Silver, g/t	27	28	26
Gold, g/t	< 0.3	< 0.3	< 0.3
Zinc, %	18.45	18.25	18.2
Copper, %	1.39	1.35	1.35
Iron, %	33.3	32.3	33.6

Silver extractions over 80%, accomplished at 35°C, 20 – 35 minutes and pH=1.7, 6 - 8 g/l $CS(NH_2)_2$); 1 g/l Fe (III), 0.3 g/l $Na_2S_2O_5$, indicated fast leach kinetics. No significant dissolution of copper and iron was observed. The composition of leach residue and silver extractions are presented in Table 8 and Table 9.

Table 9. Silver extraction

Test	Silver content in leach residue, g/t	Silver extraction, %
Тест 1.I	27	83.2
Тест 2.I	28	82.8
Тест 3.I	26	83.4

Silver Cementation

A series of 3 batch cementation tests were carried out for 90 minutes in 20 m^3 mechanically agitated cementation reactor using freshly produced silver-containing thiourea leach solution and iron powder. The amount of zinc powder used in each test was estimated based on the silver, copper and iron concentrations. The iron powder was added upfront with 110% excess than stoichiometric requirement. The silver cementation process efficiencies for Test 1.I, Test 2.I and Test 3.I were 93.4%, 94.6% and 94.8%, respectively. The data in Table 10 shows that cementation process generated a cement product containing up to 7.8% of silver. The cement silver normally contains unreacted iron and co-cemented gold, copper and zinc.

Table 10. Silver cement product composition

Parameter	Тест 1.I	Тест 2.I	Тест 3.I
Silver, %	4.085	7.82	4.95
Gold, g/t	34.8	NA	53.4
Zinc, %	2.04	4.4	7.95
Copper, %	12.35	25.45	27.8
Iron, %	3.13	12.25	14.3

Tests Results Evaluation

Key data and results from the industrial scale testing are discussed in detail below:

Thiourea Leaching

- Silver extractions obtained in Test 1.I, Test 2.I and Test 3.I were 83.2%, 82.8% and 83.4%, respectively. The repeatability of the results indicates that the operating conditions of the thiourea leaching are properly selected;
- Maximum silver extraction of 83.4% was achieved using 6 g/l $CS(NH_2)_2$, 1 g/l Fe (III), 0.3 g/l $Na_2S_2O_5$, pH=1.7, 20% solids at 35°C in 25 minutes;
- Silver extraction is consistent with the results from batch leach tests;
- Optimum operating conditions:

  - pH of 1.7: The rate of silver dissolution is strongly dependent on pH value. Maintaining this pH limits the oxidative degradation of thiourea and consequently the passivation of the silver surfaces with fine adhesive elemental sulfur, excessive copper dissolution and possible silver-thiourea complex formation (Pesic & Seal, 1990).
  - Thiourea concentration - 6 g/l: An increase in thiourea concentration decreased the efficiency of silver extraction and increased thiourea consumption.
  - Iron (III) concentration - 1 g/l: There is an optimum amount of oxidant that can be used depending mainly on the material being leached. Excess iron (III) although beneficial in slowing thiourea oxidation decreased the efficiency of silver extraction and increased both thiourea consumption and copper dissolution from the material (Pyper & Hendrix, 1981). In addition, higher iron (III) concentration negatively affects cementation process performance. During the process iron (III) is reduced to iron (II) that leads to (1) an increase in the iron powder consumption (Gupta & Mukherjee, 1990) and 2) possible re-dissolution of the cement product due to increased ferrous ions concentration.

- Sodium metabisulfite concentration – 0.3 g/l: Addition of sodium metabisulfite to the leach slurry to control the redox potential decreased thiourea consumption.
- Leach time - 35 minutes: Leach times in excess of 35 min could lead to extraction and recovery problems that may be attributed to adsorption and reaction of silver with other mineral phases present in the material.
- Temperature - 35°C: An increase in leach temperature leads to an unmanageable decomposition of thiourea.
- Reagents addition - 50/50% split prior to and after zinc cake addition. This type of reagents addition increased the efficiency of silver extraction and decreased thiourea consumption and losses in silver during the leaching.

Silver Cementation

- Silver recovery from the acidic thiourea solution by cementation with iron powder is a high complexity process mainly due to (1) concentrated solution matrix, including thiourea, acid and various salt species, and (2) presence of some base metals co-leached with the silver.
- Efficiency of silver cementation process is in the range of 93.4-94.8%.
- Optimum operating conditions:

  - Cementation time - 90 minutes: Prolonged cementation time could possibly result in the re-dissolution of the cemented silver due to the increased concentration of ferrous ions, which are formed during the process.
  - Iron powder dosage - 110 % excess stoichiometric requirement. Theoretically, the silver cementation process requires one mole of iron for every two mols of silver in solution. However, due to side reactions as a result of acid and other species present in the solution, much more iron powder is required.

Silver Cement Product:

- Product composition: The average metal composition of the silver-bearing cement is approximately 4-8% Ag, 35-53 g/t Au, 12-28% Cu, up to 14% Fe and 8% Zn. The presence of more copper, zinc and iron in the product is due the use of excess than stoichiometric amounts of iron powder in the cementation process.
- Product further processing: The silver-bearing cement could be melted and cast into impure Dore bars and then refined and purified.

Process Performance

Silver recovery process performance at an industrial scale with silver extraction efficiency and reagents consumption is summarized in Table 11.

Table 11. Silver recovery process performance

Parameter	Unit	Value	Comment
Silver leaching extraction	%	83.1	Average of the three tests performed
Silver cementation efficiency	%	94.3	Average of the three tests performed
Overall silver recovery	%	78.4	Average of the three tests performed
Reagent consumption			
Thiourea	kg/t	23.5	To achieve thiourea concentration in the leach solution of 6 g/l
Ferric sulfate (as an Iron (III) source)	kg/t	25.3	To achieve iron (III) concentration in the leach solution of 1 g/l
Sulfuric acid	kg/t	14-26	To achieve and maintain pH of 1.7
Sodium metabisulfite	kg/t	1.2	
Iron powder	%	~110	The iron powder excess is needed for the silver cementation and side reactions

The table shows a silver extraction in thiourea leaching of 83.1% with silver cementation efficiency of 94.3%, yielding an overall process recovery of 78.4%. Further optimization of the process chemistry is required during larger scale testing to avoid excessive reagent consumption consistent with high silver extraction from the feed material.

Conclusion

In this work a silver recovery process was tested and evaluated at an industrial scale to demonstrate the optimal flowsheet and to generate the data needed to define process design criteria for construction of a commercial plant for treating silver-bearing zinc cake residue. The zinc cake residue responded favorably to thiourea leaching with silver extraction of over 80%. The optimal conditions in the leach stage were pH=1.7, 6 g/l $CS(NH_2)_2$); 1 g/l Fe (III) as $Fe_2(SO_4)_3.9H_2O$; 0.3 g/l $Na_2S_2O_5$, a temperature of 35°C and an approximately 35-minute leach time. The pregnant leach solution also proved to be amenable to the subsequent silver cementation using iron powder. Dissolved silver was successfully recovered to a cement product with acceptable purity in the batch cementation process. Greater than 94% of silver contained in the leach solution was cemented.

Although there is much left to do, this work demonstrated a technically feasible process for treatment of silver-bearing materials and provided essential data to be used for a further scale-up. The silver recovery process highlights can be summarized as follows:

- Direct recovery of silver from thiourea leach solution as a high quality, high value product.
- Simplified process flowsheet to save capital and operating cost.
- All reagents are commercially available and in reasonable price.
- The process can be readily coupled with zinc crystallization and electrowinning to obtain different zinc products.

Scientific Ethics Declaration

The author declares that he is solely responsible for the scientific, ethical, and legal aspects of the paper published in EPSTEM.

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