



CHEMICAL REFINING PROCESS FOR Pb, Au AND Ag RECOVERY BY TREATMENT OF A BIOLEACH SOLID RESIDUE FROM SEDEX TYPE ORE: PART 2

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The mineralogical and physico-chemical characteristics of a polymetallic sample from a mine of West Serbia suggest that it can be classified as a SEDEX type of ore. Those ores contain multiple value components, being inter-dispersed as fine grained aggregates. This prevents concentration by gravity or flotation concentration processes. Mineralogically the valuable metals (Cu; Zn; Pb; Au and Ag) occur as pyrite, sphalerite, galena, tetrahedrite, chalcopyrite, covellite, arsenopyrite, and non-metallic minerals (barite, and waste minerals). Novel technologies are under development within this project for the recovery of all valuable metals from this very complex material.

The work comprises the further treatment of solid residue obtained after Cu and Zn extraction by bioleaching, for the subsequent recovery of Pb and the precious metals Ag and Au.

The residue is first treated with a saturated sodium chloride solution, whereupon a chloride solution of lead (NaPbCI3) is

The electrolytic deposit on the steel cathode is treated with 30-40% sulfuric acid. Gold and silver are obtained from the remaining acid-insoluble deposit by known chemical methods. 2 - Summary of Conditions

The Experimental conditions can be summarized as follow

I - Leaching of lead-sulfate: S:L ratio = 1:20; NaCl concentration: 250 g/l; temperature: 80°C leaching time

- Leaching of gold and silver: S:L ratio = 1:5; $S_2O_3^2$ concentration: 50 g/l; activator concentration: 0.5 g/l; catalyst concentration: 2.0 g/l; lixiviant concentration: 0.5 ml/l; temperature: 50°C; leaching time: 48 h. III - Electrolytic lead refining: Electrolyte composition: MSA 100 g/l, Pb 100 g/l; Organic additives: (Polyethylene glycol) 0.25g/l; temperature = 20-30°C; Current density:1.5-3.0 A/dm². IV - Electrolytic deposition of metals (Au, Ag and Cu) from thiosulphate solution: Electrolyte = thiosulphate solution of Au, Ag and Cu; pH=8-10; temperature = ambient; Current density: 3-3.5 A/dm²; Cathodes and anodes -high alloyed steel.

obtained. From the chloride solution, lead was deposited in the form of lead carbonate, followed by reductive melting, whereupon lead anode was obtained. Electrolytic refining of the lead anode, using a solution of PbCO3 in methane sulphonic acid (MSA-Methanesulfonic acid, min 99.5% CH₄O₃S, density 1.48 kg/dm³, Manufacturer: Carl Roth) as an electrolyte, yielded refined lead cathode. It should be noted that, after precipitation and separation of lead carbonate, the sodium chloride solution is restored to its original composition by the addition of make-up reagents and returned for another lead-sulfate leaching cycle.

The solid residue obtained after leaching lead-sulphate, is leached in thiosulphate solution, with the addition of an activator, a catalyst and lixiviant for gold, to yield a thiosulphate solution of gold and silver. Since the content of gold and silver in solution is low (below 1 mg/dm3), they are first electrolytically concentrated on steel cathode and then refined to pure metals using well-known chemical methods.

Note that, after the electrolytic separation of gold and silver, thiosulphate solution is recycled to the leaching step. Keywords

Sedex ore, complex structure, leaching residue, electrolytic refining

INTRODUCTION

In the MMI Bor, laboratory-scale bioleaching testwork was carried out on the polymetallic "SEDEX"-type of polymetallic material, bearing more than 10% of valuable non-ferrous and precious metals [1]. In addition to copper zinc and iron, which are extracted biologically was, it also contains other useful components which remain in the solid biological residue (namely lead, gold and silver).

MATERIALS AND METHODS

The biological residue was processed in two phases:

1 – Chloride leaching of lead-sulfate

A solution of sodium-lead-chloride (NaPbCl₃) was obtained by the chloride leaching of the bioleach residue [2]. After filtration, lead carbonate was precipitated from the resulting sodium-lead-chloride solution using saturated sodium carbonate solution, while gold and silver remained in the solid residue [3-6].

After separation of the lead carbonate sludge, the pH of the filtrate was adjusted to its original value and recycled to the lead sulfate leaching step. The lead carbonate sludge was melted with the addition of flux and reducing agent, whereupon elementary lead was obtained which was poured into anodes. During the chloride leaching of lead sulfate, small amounts of other residual metals from bioleaching (Cu, Zn, Fe and others) are also leached, and a fraction of it follows the lead during precipitation and melting to end up in the lead carbonate.

To obtain pure lead from the cast lead anodes, a lead cathode of commercial quality was obtained by electrolytic refining. The electrolytic refining of lead anodes was carried out in a methane sulphonic acid

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Figure 1 – Technological scheme of bioleach solid residue treatment

RESULTS AND DISCUSSION

3 – Flow diagram

Preliminary results of bioleach solid residue treatment are as follows First phase: Lead chatode, quality 99.95% Pb. Second phase: -Copper-sulphate, quality 98% CuSO₄x5H₂O, -Gold powder, quality 99.9% Au. -Silver powder, quality 99.8% Ag.

- (MSA) electrolyte (a solution of lead carbonate in methane sulfonic acid) [7,8].
- 2 Thiosulphate leaching of gold and silver from solid residue

The solid residue (obtained after chloride leaching of lead sulphate) was leached in thiosulphate solution, with the addition of catalyst, activator and lixiviant. After completion of leaching, the resulting solution was filtered off, and the electrolytic deposition of gold, silver and copper on a steel cathode was performed. The remaining thiosulphate solution, after electrolytic deposition of metal from solution and after adjustment of its composition by make-up reagents, was recycled to gold and silver leaching [9].

The cathode was dissolved in 30% sulfuric acid and the insoluble remnant contained a mixture of gold, silver and residual non-acid-soluble impurities. From this, silver was firstly dissolved and refined to commercial quality by known chemical methods, followed by the similar extraction and refining of the gold content.

BACKGROUND OF Pb, Au and Ag RECOVERY AND REFINING

1 – Process Chemistry

Lead occurs in the solid bioleach residue as lead sulphate (occurring in the ore as lead sulphide prior to t oxidative bioleaching process). Sodium-lead-chloride solution [2] is obtained by chloride leaching bioleach residue, according to the following reaction:

 $PbSO_4 + 3NaCI \rightarrow NaPbCI_3 + Na_2SO_4$ Lead from the sodium-lead-chloride solution (NaPbCL) can be valorized as several products such as lead carbonate, lead oxide [10] or cathodic lead, according to the following reactions:

 $NaPbCl_3 + Na_2CO_3 \rightarrow PbCO_3 + 3NaCl_3$ $PbCO_3 \rightarrow PbO + CO_2$ $2PbO + C \rightarrow Pb + CO_2\uparrow$

Cathode lead is obtained by the electrolysis of crude lead (which is obtained by the reductive melting of lead oxide), according to the following reactions [10]:

Cathode: Pb(CH₃SO₃)₂+2e⁻ \rightarrow PbO + 2CH₃SO³⁻

Anode: $H_2O \rightarrow \frac{1}{2}O_2 + 2H + 2e$

Electrolyte for electrolytic refining of lead is obtained by dissolving lead oxide or lead carbonate in methane sulfonic acid, according to the following reactions [7]: $PbO + 2CH_3SO_3H \rightarrow Pb(CH_3SO_3)_2 + H_2O$

During thiosulphate leaching, recovery of gold and silver was over 90% and 80%, respectively. **Reagents consumptions:**

1. For Cu regeneration from cathodic-deposits is consumed 0.5 cm³ 96% H₂SO₄ per g CuSO₄x5H₂O,

- 2. For Au regeneration from cathodic-deposits is consumed:
 - -HCI (36%) 6.0 cm³ per g Au,
 - -HNO₃ (65%) 2.0 cm³ per g Au,
 - $-C_6H_8O_6$ (pa > 99.5%), ascorbic acid, 1.1g per g Au.

3. For Ag regeneration from cathodic-deposits is consumed:

- -HNO₃ (65%) 1.0cm³ per g Ag,
- -NaCl (99%) 0.7g per g Ag,
- $-C_6H_{12}O_6$ (99.0%), dextrose, 1.0 g per g Ag.



Based on the results from this work, we suggest the Scheme of bioleaching solid residue treatment for obtaining high grade Pb, Au and Ag which is presented in Fig 1.

CONCLUSION

- Lead was recovered from the residue of a polymetallic ore, after the extraction of copper and zinc from it by bioleaching. At least 90% lead extraction could be achieved using chloride solution. 2. Following the precipitation of lead carbonate from the solution, it was restored with make-up reagents and recycled to the lead sulphate leaching step.
- From the solid residue, after lead-sulphate removal, a minimum of 90% of gold and 80% of silver were extracted by thiosulphate leaching.
- 4. After electrolytic deposition of metals (Au, Ag and Cu) from the thiosulphate solution, the thio-sulphate solution was recycled for gold and silver leaching after the addition of make-up reagents.
- 5. Copper sulphate, which is added as an activator in the process of gold and silver leaching, can beregenerated and recycled to the thiosulphate leaching of gold and silver.
- The results of this work offer one possible route for the treatment leaching residue from SEDEX type ore. This article addresses the extraction of three major valuable metals (by the extraction and refining of Pb and Ag, and Au by chemical methods). High extents of recovery are achieved by using environmentally and human friendly technologies.

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$PbCO_3 + 2CH_3SO_3H \rightarrow Pb(CH_3SO_3)_2 + H_2O + CO_2 \uparrow$

After the chloride leaching of lead sulphate, the concentration of gold and silver in the solid residue increases, and the grains are opened (after the bioleaching of copper, zinc and iron and chloride leaching of lead sulphate), so that it is possible to achieve a high extent of leaching of the gold and silver. After bioleaching of the ore and chloride leaching of the lead sulphate, the thiosulphate leaching of gold and silver from the remaining residue was carried out (with the addition of catalyst, activator and lixiviant). The thiosulphate leaching of gold and silver takes place according to the following reactions:

$4Au^{0} + 8S_{2}O_{3}^{2} + O_{2} + H_{2}O \rightarrow 4[Au(S_{2}O_{3})_{2}]^{3} + 4OH^{2}$ $4Ag^{0} + 8S_{2}O_{3}^{2^{-}} + O_{2} + H_{2}O \rightarrow 4[Ag(S_{2}O_{3})_{2}]^{3^{-}} + 4OH^{-}$

Since the content of leached gold in solution is lower than 0.2 mg/l and that of silver about 10mg/l, it is not possible to recover them from the solution by conventional chemical methods. Therefore, they are firstly concentrated electrolytically on a steel cathode, at current density of 30-3.5A/dm² [9], according to the following reactions:

Cathode: $[Au(S_2O_3)_2]^{3-} + e^- \rightarrow Au^0 + 2 S_2O_3^{2-}$ $[Ag(S_2O_3)_2]^{3-} + e^- \rightarrow Ag^0 + 2S_2O_3^{2-}$ $Cu^{2+} + 2e^- \rightarrow Cu^0$

Anode: $4OH^2 - 4e^2 \rightarrow O_2 + H_2O$

The thiosulphate solution, after electrolytic extraction of metal from solution and after adjustment of its composition by the addition of make-up reagents, is recycled to gold and silver leaching. Copper-sulphate is used as an activator in the process of leaching Au and Ag. The electro-deposition of Au and Ag on the steel cathodes also leads to the electro-deposition of Cu. By treatment of the cathodic deposit, Cu is transformed to copper-sulphate again and is returned for a new cycle of thiosulphate leaching (9).

REFERENCES

(8)

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(10)

(11)

(12)

1. V. Conić, M. Rajčić Vujasinović, V. Trujić, V. Cvetkovski, Copper, Zinc, and Iron Bioleaching from Polymetallic Sulphide Concentrate, Transactions of Nonferrous Metals Society of China, 24 (2014) 3688-3695. 2. V. Conic, B. Pesovski, V. Cvetkovski, Z. Stanojević-Šimšić, S. Dragulović, D. Simonović, S. Dimitrijević, Određivanje optimalnih uslova luženja olovo-sulfata rastvorom natrijum-hlorida, Hemijska industrija 67(3)485-494(2013). (In Serbian) 3. Patent U.S. 7985277, Process for extracting gold from gold-bearing ore, https://www.google.com.ar/patents/US7985277

4. Patent 2014/0212346 A1, Process of leaching precious metals, https://www.google.ch/patents/US20140212346

5. Patent WO 2013023297 A1, Process of leaching precious metals, https://www.google.com/patents/WO2013023297A1?cl-en

6. Manfred Jordan, Modern Electroplating, Electrodeposition of lead and lead alloys, Fifth Edition, 2010. John Wiley & Sins. Inc.

7. Patent US 2014/0131219 A1, Recovering lead from a mixed exidized material, www.google.com.bz/patents/US20140131219?cl=en

8. Ratent WO2012141607 A1, Gold and silver extraction technology, www.google.nl/patents/WO2012141607A1?hl=nl&cl=un

9. S. Dragulović, D. Simonović, B. Anđelić, N. Petrović, B. Pešovski, V. Conić, Mogućnost proizvodnje olovo II oksida za potrebe kupelacije iz olovo sulfata dobijenog bioluženjem polimetaličnih sulfidnih koncentrata, Bakar, 38(2013)1 pp.11-16. (In Serbian)

10. V. Conić, S. Dragulović, D. Milanović, S. Magdalinović, V. Trujić, M. Bugarin, Recycling of precious metals from secondary raw materials by ecological processing, XI International Symposium on Recycling Technologies and Sustainable Development, Hotel Albo, Bor, 02-04 November 2016., p.159-164.