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## THIOSULFATE LEACHING OF SILVER FROM A SOLID RESIDUE AFTER PRESSURE LEACHING OF INDUSTRIAL COPPER SULFIDES FLOTATION CONCENTRATES

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**Abstract:** Hydrometallurgical recovery of silver from a solid residue after pressure leaching of a flotation copper concentrate from the Lubin Concentrator (KGHM Polska Miedz S.A.) was investigated. Thiosulphate leaching was examined with regard to the highest possible leaching efficiency and optimization process parameters. The effect of thiosulfate ions concentration within the range from 0.25 to 1.00 mol/dm<sup>3</sup> at a constant ammonia concentration, and ammonia concentration within the range from 0.40 to 1.00 mol/dm<sup>3</sup> at a constant thiosulfate concentration on leaching recovery of selected metals were examined. Moreover, the effect of copper(II) ions addition on silver leaching was studied. It was shown that the leaching recovery of silver increased with increasing thiosulfate and ammonia concentration. At the highest thiosulfate ions concentration, the observed silver leaching recovery was 60%. The best results were obtained at an ammonia concentration of 0.80 mol/dm<sup>3</sup>, where the leaching recovery of Ag reached 75%. It was established that addition of Cu(II) did not affect silver leaching. Nearly 100% efficiency of thiosulohate silver leaching was achieved by pretreatment of the solid residue after pressure leaching with NaOH solutions.

**Keywords:** *atmospheric leaching, silver, sodium thiosulfate, ammonia, Lubin copper concentrate*

### Introduction

Noble metals such as silver, platinum group metals (PGM) and gold are recovered from primary and secondary resources by means of leaching. The richest sources of these metals, being a feed for leaching, are noble metals ores, by-products of nonferrous metals processing, anodic slimes from copper electroraffination and solid residues from hydrometallurgical circuits. The basic sources of silver are concentrates, scraps, anodic slimes, photographic films, ashes after thermal treatment, jewelry, coins

and metal alloys. The growing silver demand has resulted in an intense development of research for improving existing hydrometallurgical methods of noble metals production (Fleming, 1992; Orab et al., 2014).

Either significant or dominating role of hydrometallurgical unit operations both in production of numerous non-ferrous (Al, Ni, Co, Cu, Zn) and precious metals (Ag, Au, PGE) is an evidence of the essential position and important meaning of chemical methods of metals manufacturing in modern extractive metallurgy (Gupta and Mukherjee, 1990; Habashi, 1999; Chmielewski, 2012; Agacayak, 2014).

The most important operation in hydrometallurgy is leaching of properly prepared raw material by means of a specific chemical compound – leaching agent. Usually the leaching agents and process conditions are selected depending on the type of material and mineralization, in order to selectively and effectively extract the valuable elements to a solution and to avoid emission of dangerous and toxic gases to the atmosphere. Ores and concentrates have different mineralogical and metallic compositions. Zinc, copper, cobalt, nickel, silver, gold and platinum group metals, as valuable metals, are economically important components of polymetallic sulphide materials (Marsden et al., 2003; Ochromowicz and Chmielewski, 2011). The leaching experiments (Everett and Moyes, 1992; Chmielewski, 2009) showed that a shale by-products from the Lubin Concentrator (ZWR Lubin) can be effectively processed using hydrometallurgical methods (thiosulfate atmospheric leaching) in order to recover silver and other accompanying metals.

Leaching of noble metals using oxygenated sodium cyanide solutions was patented in 1887. The major benefit of this method is high selectivity of silver versus gold extraction and very high stability of noble metal-cyanide complexes (Sayiner 2014; Aromaa, 2015). Despite many benefits of cyanide leaching, there is a continuous quest for an alternative method of noble metals recovery, which is characterized by high recovery, selectivity and non-toxicity (Fleming, 2007). Thiosulfate leaching is one of the promising alternative to the cyanide leaching method, with regard to its low toxicity and high efficiency of ores and concentrates leaching. Another benefit of this method is relatively low price of chemical agents used as the leaching medium in the process (Briones and Lapidus, 1998; Mahmoud 2015).

Berezowsky and Sefton (1979) investigated silver recoveries from oxidation leach residues of copper sulfide concentrates in different leaching systems, including cyanide, thiourea, chloride and thiosulfate solutions. The results of thiosulfate leaching showed that the presence of copper in the solution enhanced silver extraction and the chemical behavior of copper ions in this system is very complex (Kerley, 1981). Li et al. (1995) found that thiosulfate ions stabilized silver in the soluble form in the solution, while ammonia and copper accelerated the leaching reaction. The oxidation state of copper in the thiosulfate leaching solutions are of the critical importance for the silver leaching process. Moreover, it is necessary to keep the proper molar ratio of ammonia to thiosulfate to enhance the leaching. To the contrary, the copper might be stabilized in Cu(I) and Cu(II) oxidation states, reducing its ability to

catalyze the silver leaching reaction. Research priorities should be focused on the detailed description of reactions involved and should determine the role of different copper complexes in establishing the optimum molar ratio between ammonia, thiosulfate and copper complexes (Flett et al., 1983; Wassink, 2011; Deutsch and Dreisinger, 2013).

The objective of this study was to examine the thiosulfate leaching recovery of silver from a solid residue after pressure leaching of the copper flotation concentrate from Lubin Concentrator (KGHM Polska Miedz S.A.). Effect of the dose of ammonia, copper and thiosulfate ions on silver recovery was investigated.

## Experimental

The leaching feed in the study was a commercial flotation copper sulfide concentrate produced at the Lubin Concentrator (KGHM Polska Miedz S.A.). The concentrate contained copper and other metals, such as Zn, Co, Ni, Ag, V, and Mo, which significantly increase the value of this material. A continuously decreasing copper concentrate grade, high content of organic carbon, presence of lead and arsenic, make the concentrate a potential and suitable feed for hydrometallurgical treatment. The Lubin concentrate is a polymetallic and polymineral material (Grotowski, 2007; Chmielewski, 2012). The chemical composition of Lubin flotation concentrate (KLE) is presented in Table 1. The concentrate has a unique mineralogy. Copper is mainly present in two easy-to-leach sulfides, that is bornite and chalcocite. Furthermore, a significant amount of pyrite additionally enhances the copper leaching rate by galvanic effects (Chmielewski, 2012).

A series of thiosulphate leaching experiments was conducted. The effect of thiosulfate ammonia copper ions concentration on silver leaching efficiency was examined. In addition, the effect of solid residue modification in NaOH solutions was investigated. The leaching experiments were conducted in a stirred glass reactor immersed in a water bath with controlled temperature. The agitation rate of  $400 \text{ min}^{-1}$  was kept in all experiments. All experiments were carried out at room temperature. The leaching reactor was equipped with a condenser, to avoid rapid vaporization of the leaching agent. The density of the leaching slurry was expressed as a solid-to-liquid phase ratio ( $\text{g/cm}^3$ ).

During each leaching experiment, samples of the slurry were taken from the reactor and filtered for analysis of metals concentration, using the Atomic Absorption Spectroscopy (AAS) technique. The leaching efficiency was evaluated by determining metals recoveries according to the formula:

$$R_{\%} = \frac{c \cdot V}{m \cdot \alpha} \cdot 100\% , \quad (1)$$

where:

$R_{\%}$	metal leaching recovery, %
$C$	metal concentration in the solution, g/dm <sup>3</sup> (mg/dm <sup>3</sup> )
$V$	leaching solution volume, dm <sup>3</sup>
$M$	mass of the concentrate, g
$A$	metal content in the concentrate, % (g/Mg).

The subject of this study was a solid residue after pressure leaching of the commercial flotation sulfide concentrate produced at the Lubin Concentrator (KGHM Polska Miedz S.A.). To obtain the solid residue, the KLE sample of the concentrate was initially leached with sulfuric acid under hydrothermal oxygenated conditions. The parameters of pressure leaching process were: time 2 hours, O<sub>2</sub> partial pressure 0.75 MPa, solid-to-liquid ratio (s/l) 1:10, temperature 140 °C, agitation rate 400 min<sup>-1</sup>, and H<sub>2</sub>SO<sub>4</sub> initial concentration of 120 g/dm<sup>3</sup>. Table 2 presents the chemical composition of the solid residue after pressure leaching.

In the final step of thiosulfate leaching experiments, the recovery of silver and accompanying metals were evaluated for leaching of solid residue previously pretreated with NaOH solution. The pretreatment process parameters were: temperature 95 °C, time 3 hours, NaOH concentration of 100 g/dm<sup>3</sup>, solid-to-liquid ratio 1:6. The chemical composition of solid residue was presented in Table 3.

Table 1. Chemical composition of a commercial Lubin flotation concentrate (KLE)

Cu %	Zn %	Ni g/Mg	Co g/Mg	Fe %	Pb %	Ag g/Mg	As %	V g/Mg	Mo g/Mg	S %	C <sub>org</sub> %
12.9	0.74	49	148	7.6	5.42	455	0.165	657	272	13.34	9.44

Table 2. Chemical composition of solid residue after pressure leaching of Lubin concentrate KLE

Cu %	Zn %	Ni g/Mg	Co g/Mg	Fe %	Pb %	Ag g/Mg
1.44	0.092	178	345	0.92	8.00	380

Table 3. Chemical composition of solid residue after pressure leaching of Lubin concentrate followed by pretreatment with NaOH

Cu %	Zn %	Ni g/Mg	Co g/Mg	Fe %	Pb %	Ag g/Mg
2.2 2	0.14	5.31	274	1.43	12.30	585

## Results and discussion

The effect of thiosulfate ions concentration on Ag and Cu leaching was investigated for four different thiosulfate concentrations (0.25, 0.50, 0.75 and 1.00 mol/dm<sup>3</sup>). The leaching experiments were conducted at 25 °C and the leaching time was 6 hours. Figures 1 and 2 show the changes in Ag and Cu leaching recovery during the leaching process at various thiosulphate concentrations.

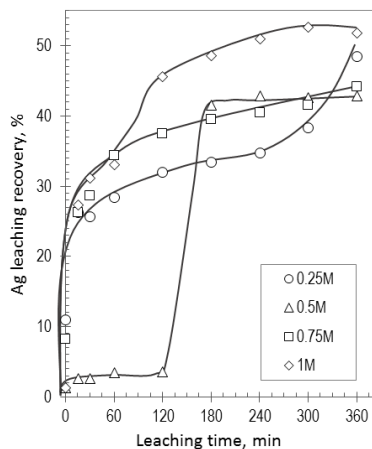


Fig. 1. Effect of thiosulfate ions concentration on Ag recovery;  $s/l = 1:10$ , initial  $\text{NH}_3$  concentration 0.6 mol/dm<sup>3</sup>, temperature 25 °C

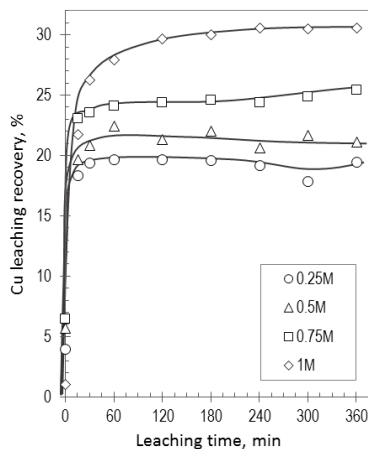


Fig. 2. Effect of thiosulfate ions concentration on Cu recovery;  $s/l = 1:10$ , initial  $\text{NH}_3$  concentration 0.6 mol/dm<sup>3</sup>, temperature 25 °C

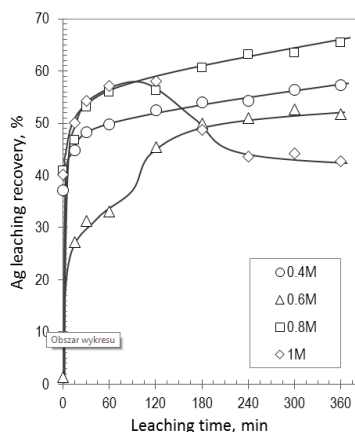


Fig. 3. Effect of ammonia ions concentration on Ag recovery;  $s/l = 1:10$ , initial  $\text{S}_2\text{O}_3^{2-}$  concentration 1.0 mol/dm<sup>3</sup>, temperature 25 °C

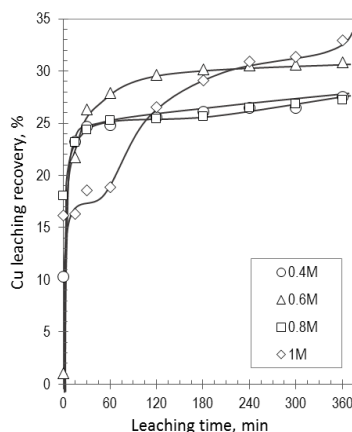


Fig. 4. Effect of ammonia ions concentration on Cu recovery;  $s/l = 1:10$ , initial  $\text{S}_2\text{O}_3^{2-}$  concentration 1.0 mol/dm<sup>3</sup>, temperature 25 °C

The observed leaching results show that with increasing thiosulfate ions concentration the leaching efficiency increases for both Ag and Cu. At the highest thiosulfate ions concentration the leaching recoveries of Ag and Cu were 60 and 35%, respectively. It confirms the possibility of thiosulfate leaching application for silver extraction.

The effect of Cu(II) ions addition on silver leaching from solid residue after pressure leaching was investigated at thiosulfate and ammonia concentrations of 0.5 and 0.6 mol/dm<sup>3</sup>, respectively. The concentration of Cu(II) was 0.1 mol/dm<sup>3</sup>. The leaching was conducted at 25°C for 6 hours. The results are presented in Figs. 5-7. The aim of the experiment was to investigate the possibility of enhancing the leaching efficiency of silver by copper(II) ions addition to the leaching solution.

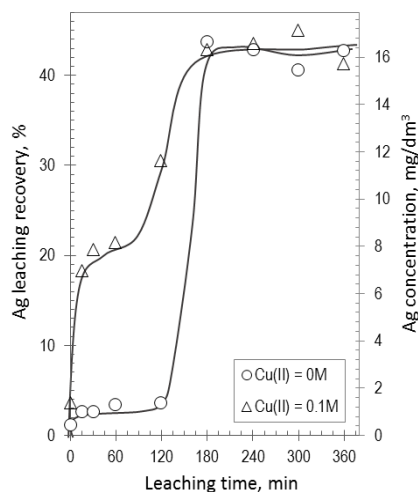
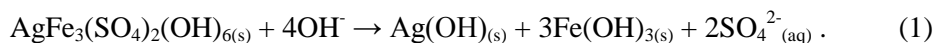


Fig. 5. Effect of addition of Cu(II) on Ag recovery;  $s/l = 1:10$ , initial  $\text{NH}_3$  concentration 0.6 mol/dm<sup>3</sup>, initial  $\text{S}_2\text{O}_3^{2-}$  concentration 0.5 mol/dm<sup>3</sup>, temperature 25 °C

The obtained results show that the addition of Cu(II) did not affect the final silver concentration and recovery. However it had a significant effect on the initial silver leaching rate. It can be concluded that Cu(II) is not needed in the process.

In the leaching experiments conducted with thiosulfate ions, the course of the process was investigated under the most optimum conditions, determined from the previous investigation of solid phase pretreated with NaOH. The parameters of modification process were as follows: NaOH concentration of 2.5 mol/dm<sup>3</sup>, temperature 95°C, time 3 hours,  $s/l$  ratio 1:6. The purpose of this process was to liberate the silver-bearing grains by dissolution of argentojarosites (Patino et al., 2010). The process occurs according to the following reaction:



It was expected, that silver liberation from argentojarosites would allow to maximize the leaching recovery of metal in thiosulfate leaching. The mass decrease of a solid after chemical modification with NaOH was about 35%.

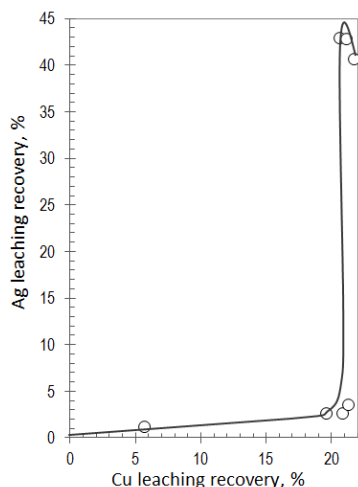


Fig. 6. Ag recovery vs. Cu recovery in thiosulfate leaching without addition of Cu(II) ions;  $s/l = 1:10$ , initial  $\text{NH}_3$  concentration  $0.6 \text{ mol/dm}^3$ , initial  $\text{S}_2\text{O}_3^{2-}$  concentration  $0.5 \text{ mol/dm}^3$ , temperature  $25^\circ\text{C}$

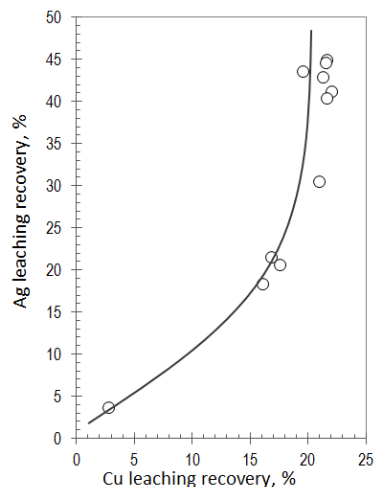


Fig. 7. Ag recovery vs. Cu recovery in thiosulfate leaching with addition of  $0.1 \text{ mol/dm}^3$  Cu(II) ions;  $s/l = 1:10$ , initial  $\text{NH}_3$  concentration  $0.6 \text{ mol/dm}^3$ , initial  $\text{S}_2\text{O}_3^{2-}$  concentration  $0.5 \text{ mol/dm}^3$ , temperature  $25^\circ\text{C}$

In the closing stage of the experiments regarding thiosulfate leaching, the leaching recovery of silver and copper from pretreated solid residue were determined. The leaching experiments were conducted at the optimum parameters, which were: thiosulfate ions concentration  $1.0 \text{ mol/dm}^3$ , ammonia concentration  $0.8 \text{ mol/dm}^3$ , temperature  $25^\circ\text{C}$ , time 6 hours. Figures 6 and 7 present the results.

From Figures 8-10 it is clearly seen that solid residue modification with NaOH allowed to extract almost 100% of silver in thiosulfate leaching after 4 hours. It proves the hypothesis that silver is locked inside the jarosites structure in the solid residue after pressure leaching. The leaching recovery of copper reached 20 % after 6 hours, while other accompanying metals such as Ni and Co did not leach into the solution. The leaching curves of Ni and Co are not given in the paper, as the efficiency was close to 0%. The chemical composition of solid residue after thiosulfate leaching was presented in Table 4.

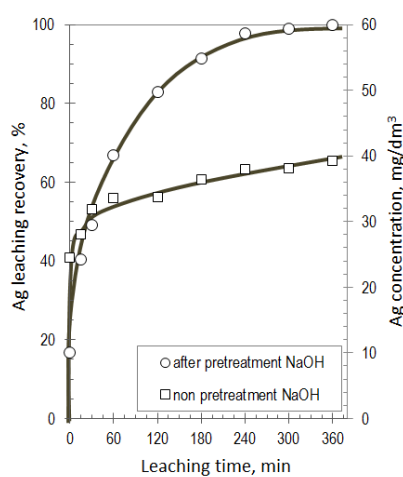


Fig. 8. Effect of NaOH modification on Ag recovery;  $s/l = 1:10$ ; initial  $\text{NH}_3$  concentration  $0.8 \text{ mol/dm}^3$ , initial  $\text{S}_2\text{O}_3^{2-}$  concentration  $1.0 \text{ mol/dm}^3$ , temperature  $25^\circ\text{C}$

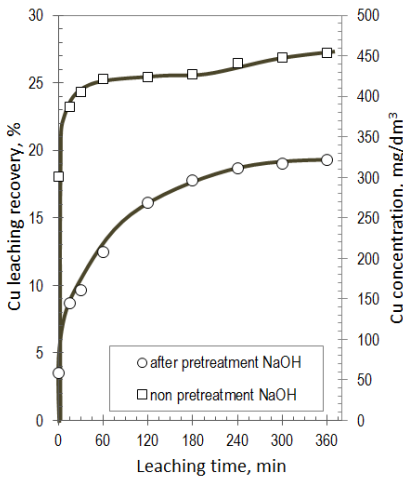


Fig. 9. Effect of NaOH modification on Cu recovery;  $s/l = 1:10$ ; initial  $\text{NH}_3$  concentration  $0.8 \text{ mol/dm}^3$ , initial  $\text{S}_2\text{O}_3^{2-}$  concentration  $1.0 \text{ mol/dm}^3$ , temperature  $25^\circ\text{C}$

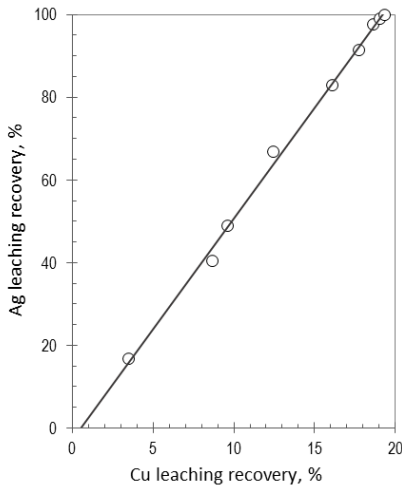


Fig. 10. Ag recovery vs. Cu recovery in thiosulfate leaching after modification with NaOH;  $s/l = 1:10$ , initial  $\text{NH}_3$  concentration  $0.8 \text{ mol/dm}^3$ , initial  $\text{S}_2\text{O}_3^{2-}$  concentration  $1.0 \text{ mol/dm}^3$ , temperature  $25^\circ\text{C}$

Table 4. Chemical composition of solid residue after thiosulfate leaching

Cu %	Zn %	Ni g/Mg	Co g/Mg	Fe %	Pb %	Ag g/Mg
1.96	0.12	4.65	233	1.25	6.34	5.15



## Conclusions

The results of silver and accompanying metals leaching from a solid residue after pressure leaching of the Lubin flotation concentrate (KGHM Polska Miedz S.A.), with concentrated thiosulfate solutions, indicate the possibility of effective silver extraction into the solution. The leaching efficiency of other metals (Cu, Ni, Co) in thiosulfate solutions is relatively low, resulting in poor leaching recoveries.

The results of leaching experiments of solid residue from pressure leaching pretreated with NaOH solutions show, that thiosulfate is very efficient in silver leaching from modified solid residues from pressure leaching with oxygenated sulfuric acid. The leaching recovery of silver reached nearly 100% after 4 hours of thiosulfate leaching at 25 °C. However, the pretreatment process with NaOH resulted in poor copper leaching efficiency and caused total inhibition of Ni and Co leaching.

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