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Chloride leaching of silver and lead from a solid residue after atmospheric leaching of flotation copper concentrates

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Abstract: Recovery of silver and lead by means of chloride leaching of solid residue after atmospheric leaching of the copper concentrate from Lubin Concentrator (KGHM) was investigated. The effect of leaching temperature, chloride concentration, Fe(III) and oxygen presence, solid-to-liquid ratio and feed preleaching with NaOH on the silver and lead recovery was analyzed. Chloride leaching appeared to be very effective for recovery of lead, whereas satisfactory recovery of silver was observed after chemical pretreatment of the leaching feed with alkali solution of NaOH in order to liberate Ag entrapped in the jarosite structure. It was found that to achieve the satisfactory recovery of Ag and Pb leaching had to be performed in acidified 4 M chloride concentration at temperature of 90 °C. The presence of oxidants, that is O₂ and iron(III) ions, was beneficial in the initial stage of the process. The maximum recovery of Ag and Pb was found for the solid-to-liquid ratio of 1:10 after 10 hours leaching.

Keywords: *copper concentrate, atmospheric leaching, chloride leaching, silver, lead*

Introduction

Silver is a soft, white, lustrous metal, which possess high electrical and thermal conductivity. Silver occurs in ores in its native form as an alloy with gold (electrum) and other metals, and in minerals such as argentite and chlorargyrite. Most of silver is produced from by-products of copper, gold, lead and zinc refining. World silver mine production in 2015 was 27.3 Gg, while production of lead was 4.71 Tg (USGS, 2016).

About 50% of World Pb production takes place in China. International Lead and Zinc Study Group forecasts global refined lead production to be 10.8 Tg, a slight decrease from that in 2014, primarily driven by decreases in China and Peru. ILZSG projected global lead consumption to be 10.8 Tg in 2015, a slight decline from that in

2014, partially owing to a decrease in China's consumption. In 2015, global refined lead production was expected to be essentially the same as consumption. A 59% of refined lead metal produced in 2015 was from recycled material.

Both lead and silver are present in the polymetallic stratiform Kupfeshiefer ore partially located in the SW Poland. The ore contains more than 110 minerals. The most important minerals are copper, lead and zinc sulfides such as chalcocite (Cu_2S), bornite (Cu_5FeS), chalcopyrite (CuFeS_2), covellite (CuS), galena (PbS) and sphalerite (ZnS). The ore contains also numerous other elements such as Ag, Pb, Zn, Cd, Ni, Co, Fe, Au, Pt, Pd, Hg, V, Mo and Re. Accompanying metals either create their own mineral phases or are present in the form of admixtures of other minerals. They rarely exist as individual minerals. Recovery of accompanying metals from copper ores or concentrates is usually difficult because of very fine dissemination of valuable minerals in copper sulfides.

Silver is the second, after copper, metal which is produced from the polymetallic stratiform Kupfeshiefer ore by KGHM Polsk Miedz SA company and is recognized as the most important accompanying metal present in the copper ore. The content of this metal changes from 47.6 in carbonate, 79.9 in sandstone to 134 g/Mg in shale fractions of the ore (Piestrzynski, 2007). The common forms of silver are Cu-Ag-S sulfides. Another ones are isomorphic silver admixtures. The most important carriers of silver admixtures are either copper, zinc or lead sulfides. The content of silver depends on the size of mineral grains in the ore (Table 1).

Table 1. Average content of silver in sulfide minerals in the Kupfershiefer ore (in %) (Piestrzynski, 2007)

Mineral	chalcocite	digenite	bornite	chalcopyrite -Ag	chalcopyrite	pyrite	galena	tennantite
micro grain	0.150	0.16	5.06	3.69	<0.030	0.240	0.270	0.790
macro grain	0.227	-	0.07	-	0.030	0.015	0.008	0.035

Due to assumed mining directions, the lead concentration in the Polish copper ores has been increasing. It is observed particularly at the Lubin mining site. The mean content of Cu in the ore is about 0.14%. The lead content in the ore is usually connected with the presence of galena and minerals in which this metal is disseminated. The mineralogical data indicate that the concentration of Pb is much higher in bornite-chalcopyrite than in chalcocite. The observed content of lead in the Lubin flotation concentrate is currently above 5%. On the other hand, the concentration of silver decreases and currently is up to 455 g/Mg. The mean content of Ag in PbS is 0.27% (Piestrzynski, 2007).

Starting from 1990s there is an intensive development of hydrometallurgical methods for processing of copper ores and concentrates due to decreasing content of Cu and increasing complexity of the ore mined by KGHM Polska Miedz SA. Also there are numerous publications about recovery of lead (Correia and Carvalho, 1992; Raghavan et al., 1998, 2000; Godočíková et al. 2002; Zang et al., 2004; Geidarov et

al., 2009) and silver (Almedia et al., 1995; Puvvada and Murthy, 2000) from various materials using for instance chloride leaching solutions. The new processes are focused on processing of polymetallic raw materials containing precious metals that are not suitable for flash smelting. The concentrates and flotation middlings produced at KGHM have been investigated as a feed for hydrometallurgical treatment (d'Hugues et al. 2007, 2008).

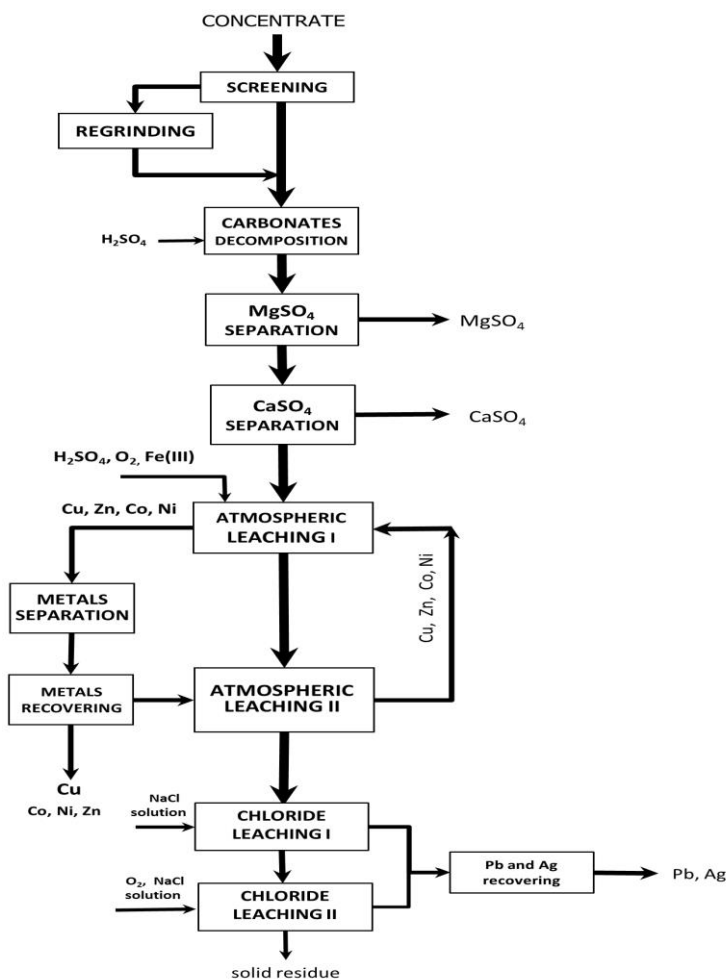


Fig. 1. Hydrometallurgical treatment of flotation copper concentrates from Lubin Concentrator of KGHM Polska Miedz S.A. Flowsheet according to the HYDRO process (Chmielewski, 2015)

A new HYDRO process was worked out (Fig. 1) which is based on non-oxidative (Kowalczyk and Chmielewski, 2010) and next either atmospheric or pressure leaching of concentrate in oxygenated sulfuric acid solutions in the presence of Fe(III) (Chmielewski et al., 2011; Chmielewski et al., 2013; Chmielewski 2015). During

atmospheric leaching with oxygenated sulfuric acid solutions containing Fe(III), such metal as Cu, Zn, Fe, Ni and Co are leached out to the solution, forming soluble sulfates. Solvent extraction (SX) is intended to be used for separation of Cu and other metals. The solid residue after atmospheric leaching contains silver and lead, which are not leached in the sulfate environment. The recovery of these metals could be accomplished by chloride leaching. An attempt of the application of chloride leaching is described in this paper. The results of chloride leaching of silver and lead from solid residue after non-oxidative leaching followed by atmospheric leaching of the Lubin flotation copper concentrates in oxygenated sulfuric acid and in the presence of Fe(III) are presented. The paper evaluates the effect of major parameters: temperature, chloride and iron(III) ions concentration, oxygen flow rate as well as the solid-to-liquid ratio on the leaching rate and metals recovery.

Experimental

Materials

The sample used in chloride leaching was a solid residue obtained by non-oxidative leaching with sulfuric acid to remove carbonates followed by atmospheric leaching in oxygenated aqueous sulfuric acid solutions in the presence of iron(III) ions of the copper ore and concentrate manufactured by the KGHM Polska Miedz SA at the Lubin Concentrator (Fig. 1) (Chmielewski 2012, 2015).

The chemical compositions of the copper concentrate and two solid residue samples after non-oxidative sulfuric acid treatment and atmospheric leaching with oxygenated sulfuric acid and in the presence of Fe(III) are given in Table 2. It can be seen that silver, lead and organic carbon content in the leached samples increased as a result of non-oxidative and atmospheric leaching in sulfuric acid due to sample mass reduction.

Table 2. Chemical compositions of flotation copper concentrate from Lubin (1) and the solid residue after the concentrate atmospheric leaching with oxygenated sulphuric acid and in the presence of Fe(III) (2 A and B)

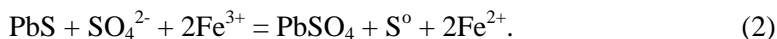
Material type	Cu, %	Ag, g/Mg	Pb, %	Ni, g/Mg	Co, g/Mg	Zn, %	Fe, %	C _{org} , %	
1	14.56	755	4.32	483	1250	0.57	7.55	7.23	
2	A	1.74	838	5.12	565	1450	0.20	5.02	8.63
	B	1.73	900	5.15	568	1407	0.21	5.35	9.12

The mineralogical analysis (Table 3) indicated that chalcopyrite, bornite, chalcocite-digenite, and covellite were present in the copper concentrate, which was used for non-oxidative and atmospheric leaching. Copper was almost totally leached out from chalcocite, almost completely from bornite and only partially from chalcopyrite and covellite (Table 3).

Table 3. Mineralogical composition of flotation copper concentrate and feed for chloride leaching

Material	unit	Chalcocite		Chalco-	Pyrite		Sphalerite	Tennantite	Galena
		Bornite	Digenite	pyrite	Markasite	Covellite			
		Cu ₅ FeS ₄	Cu ₂ S/Cu _{1.8} S	CuFeS ₂	FeS ₂	CuS	ZnS	Cu ₁₂ As ₄ S ₁₃	PbS
Copper concentrate	% mass	10.99	5.96	12.05	5.03	0.61	1.48	0.81	3.06
Feed for chloride leaching	% vol.	0.49	0.00	3.41	3.32	0.31	0.33	0.09	0.80

During atmospheric leaching under oxidative conditions galena (PbS) is chemically converted to anglesite (PbSO₄) (Figs. 2-4) according to reactions 1 and 2:



Initially, anglesite is formed as a growing layer on the surface of galena (Fig. 3). After that galena is further converted to PbSO₄ (Fig. 4) and the content of PbS remarkably decreases in the leached solid (Table 3).

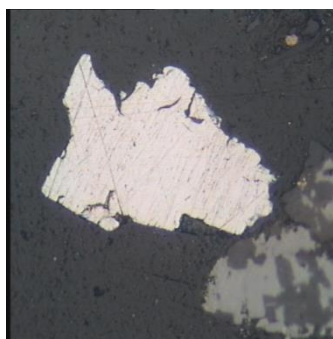


Fig. 2. Galena grain before leaching

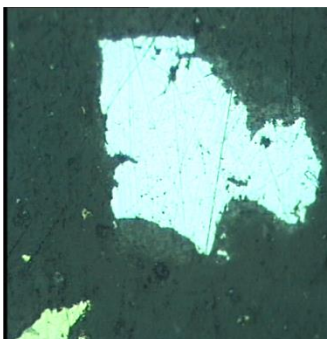


Fig. 3. Galena grain leached partially



Fig. 4. Galena grain after atmospheric leaching

The dominating copper mineral identified in the feed for chloride leaching was chalcopyrite with a small admixture of bornite and covellite. Pyrite and marcasite were also identified in the feed. Lead was predominantly present in the feed as anglesite (PbSO₄), which contained small amount of non-converted galena. Silver was found in the feed as silver sulfide and was also present as an admixture in the crystallographic lattice of other minerals such as pyrite, chalcopyrite, sphalerite (Puvvada and Murthy, 2000). The content of silver in copper and iron sulfides may be in the range from 0.7 to 2.7% by volume.

All the reagents used for the leaching experiments such as H_2SO_4 and NaCl were of analytical grade. The chemical analysis of metals in leached solutions was carried out using atomic absorption spectroscopy (AAS).

Leaching procedure

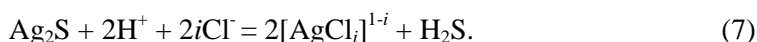
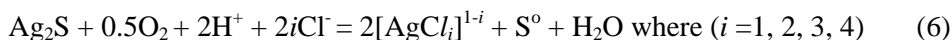
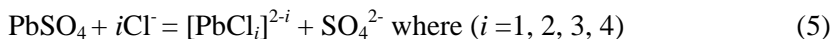
Non-oxidative leaching with sulfuric acid was performed by controlled carbonate decomposition to remove carbonates. Atmospheric leaching of the copper concentrate was carried out at 90°C for 6 hours at the solid-to-liquid phase ratio equal to 1:6. The composition of the atmospheric leaching solution was as follows: 50 g/dm^3 H_2SO_4 , 30 g/dm^3 Fe(III) and 3 g/dm^3 chloride ions. The oxygen flow rate was $60\text{ dm}^3/\text{h}$.

Chloride leaching of the solid residue after atmospheric leaching of copper concentrate was performed in a 2.5 dm^3 glass reactor with controlled stirring rate, gas flow rate and temperature. The leached material was introduced to the reactor in the form of a water slurry of a known solid content. The solid-to-liquid phase ratio during leaching was $s:l = 1:10$ (200 g of dry solid/ 2000 cm^3 of solution). The concentration of NaCl in the leaching solution was 4 M and 0.05 M sulfuric acid was also added to acidify the solution. Leaching was carried out at a constant oxygen flow rate of $30\text{ dm}^3/\text{h}$. Leaching process parameters are given in Table 4.

Table 4. Chloride leaching parameters

Temperature, $^\circ\text{C}$	Concentration of NaCl mol/ dm^3	Concentration of H_2SO_4 , g/ dm^3	Concentration of Fe(III) , mol/ dm^3	Flow rate of O_2 , dm^3/h
90	4	5	0.18	30
90	4	5	-	30
50	4	5	-	30
90	2	5	-	30
25	4	5	-	30
25	4	5	-	-

During acidic chloride leaching, the examined solid residue obtained after atmospheric leaching contained lead and silver in the form of insoluble compounds such as PbSO_4 and Ag_2S . The following reactions most likely occurred under either the oxygenated or oxygen-free conditions:



Silver and lead can be leached out from the feed as chloride complex ions of Ag(I) and Pb(II) (reactions 5-7). It is known that the stability of complexes depends on many factors such as concentrations of ligands, ionic strengths, temperature and pH. The

effect of temperature and ionic strength on formation of lead chloride complexes was described in details by Luo and Millero (2007). The concentration of AgCl_i^{1-i} (or PbCl_i^{2-i}) complex ions depends on the equilibrium concentration of chloride ions in the solution. The correlation of all complex ions of Ag(I) and Pb(II) with equilibrium concentration of chloride ion is given by Wei-feng et al. (2010) and discussed by Nriagu and Anderson (1971).

Results and discussion

Effect of temperature

The temperature has an essential effect on chloride leaching of Ag, Pb and Co, Ni, Fe, Cu and Zn, present in either sulfide or sulfate forms in the examined feed material. The leaching process was conducted at the constant oxygen flow rate ($30 \text{ dm}^3/\text{h}$) using 4 M NaCl and 0.05 M H_2SO_4 as a leaching medium. The recovery of silver and lead vs. time of leaching was examined at 25, 50 and 90 °C (Figs. 5 and 6). The leaching rate and recovery of silver increased with the increase of temperature and after 10 hours of leaching reached 59, 69 and 82% at 25, 50 and 90 °C, respectively (Fig. 5). Leaching of lead was observed to be more effective than leaching of silver and Pb recovery was the highest at 90 °C (98% Ag recovery after about 2 h) (Fig. 6).

Comparing the chloride leaching results for other residual metals (Table 5) indicated that temperature had a considerable effect on extraction of Co, Ni, Cu, Zn and Fe present in the feed. At 25 °C the leaching recovery of these metals was rather low and did not exceed a few percent. It increased remarkably with the increase of temperature.

Table 5. Effect of temperature on leaching recovery of residual metals after 10 hours of chloride leaching (4 M NaCl), $5 \text{ g}/\text{dm}^3 \cdot \text{H}_2\text{SO}_4$, $30 \text{ dm}^3/\text{h O}_2$, s:l = 1:10

Metal	Leaching recovery of metals, %		
	25 °C	50 °C	90 °C
Cu	0.10	9.00	47.9
Co	3.70	9.02	61.5
Ni	3.85	5.08	30.9
Zn	1.50	5.88	44.8
Fe	1.03	2.61	22.0

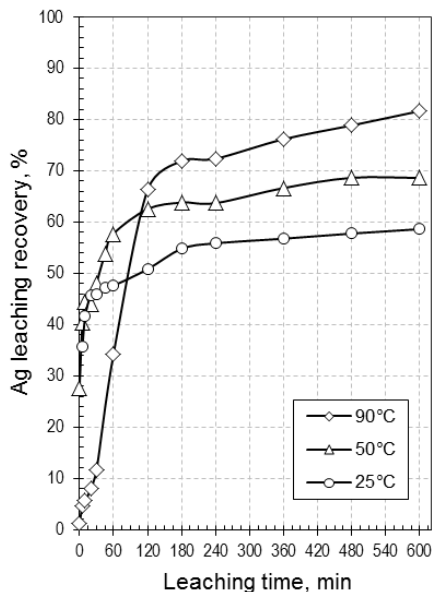


Fig. 5. Effect of temperature on Ag leaching rate and recovery in 4 M NaCl solution ($5 \text{ g/dm}^3 \text{ H}_2\text{SO}_4$, $30 \text{ dm}^3/\text{h O}_2$, stirring 500 rpm, solid/liquid ratio 1:10)

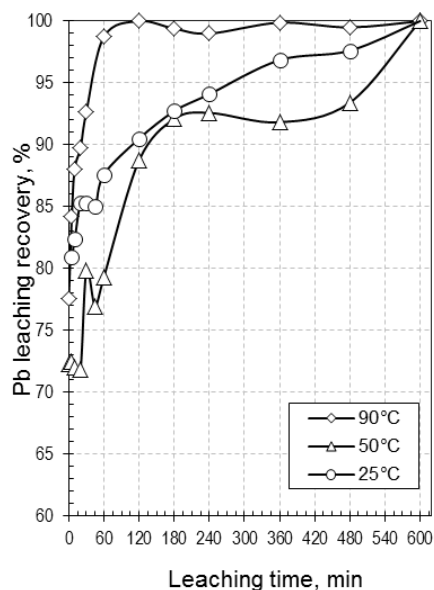


Fig. 6. Effect of temperature on Pb leaching rate and recovery in 4 M NaCl solution ($5 \text{ g/dm}^3 \text{ H}_2\text{SO}_4$, $30 \text{ dm}^3/\text{h O}_2$, stirring 500 rpm, solid/liquid ratio 1:10)

Effect of chloride ions concentration

As shown in Table 1, the content of lead in the feed material was above 5%. Insoluble lead sulfate can be leached out as soluble lead chloride complexes of general formula of $[\text{PbCl}_i]^{2-i}$ where i is 1, 2, 3 and 4, using acidic, concentrated solution of Cl^- ions (reaction 5). It was important to evaluate the concentration of chloride ions in the leaching solution for the maximum recovery of lead. The leaching tests were conducted at a constant flow rate of oxygen ($30 \text{ dm}^3/\text{h}$) at 90°C using either 2 or 4 M NaCl solution of and $0.05 \text{ M H}_2\text{SO}_4$. The concentration of chloride ions was 75 (2 M) and 150 g/dm^3 (4 M).

According to the results presented in Figs. 7 and 8, the concentration of chloride ions in the leaching solution was an essential parameter influencing silver and lead leaching rate and recovery. Increase of chloride ions concentration from 75 to 150 g/dm^3 resulted in the increase in silver extraction from 57 to 82% after 10 hours of leaching (Fig. 7). Simultaneously, the effect of chlorides concentration was observed to be more pronounced for lead leaching than for silver. The observed increase of lead recovery was from 37 to 99.5% for the same chloride concentration changes (Fig. 8) after less than 2 hours of leaching. It was additionally observed that PbCl_2 precipitated after cooling the leach solution to the room temperature when the leaching process

was conducted with the 2 M sodium chloride solution. Therefore, 4 M NaCl was selected for leaching.

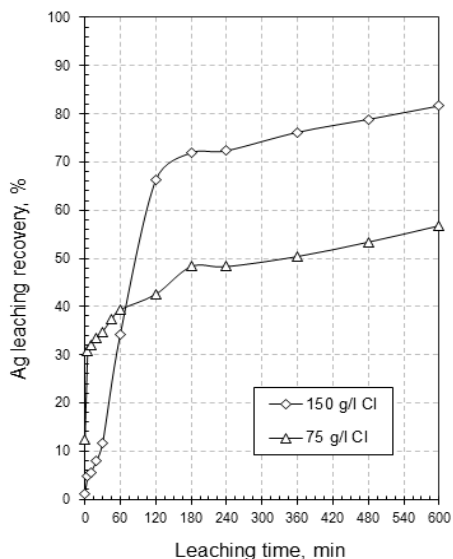


Fig. 7. Effect of chlorides concentration on Ag leaching rate and recovery in NaCl solution (4 M) and $5 \text{ g/dm}^3 \text{ H}_2\text{SO}_4$ at 90°C , solid/liquid ratio 1:10, oxygen flow rate $30 \text{ dm}^3/\text{h}$

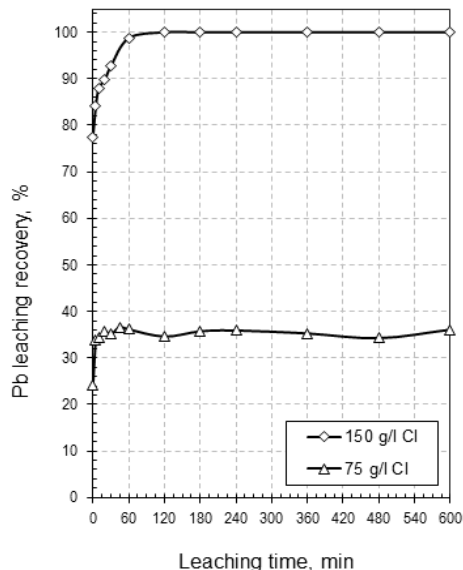


Fig. 8. Effect of chlorides concentration on Pb leaching rate and recovery in NaCl solution (4 M) and $5 \text{ g/dm}^3 \text{ H}_2\text{SO}_4$ at 90°C , solid/liquid ratio 1:10, oxygen flow rate $30 \text{ dm}^3/\text{h}$

Effect of Fe (III)

Fe(III) ions belong to the most effective oxidation agents in leaching of sulfide minerals and secondary raw minerals containing silver in either native or sulfide form. To determine the effect of the of main parameters on leaching of Ag, Pb, Co, Ni, Cu, Zn i Fe, experiments were carried out under standard conditions (90°C , $30 \text{ dm}^3/\text{h O}_2$) using 4 M NaCl, 0.05 M H_2SO_4 with or without Fe(III) ions (10 g/dm^3). In the case of silver and lead extraction there was an evident effect of Fe(III) ions on leaching only in the first stage of the process. The effect of Fe(III) on Ag and Pb recovery was negligible (Figs. 9 and 10). The maximum recovery of silver only slightly exceeded 80%, whereas the recovery of lead was about 98%. The beneficial effect of Fe(III) can be attributed to the presence of silver and lead in the sulfidic forms.

Extraction of Cu, Co, Ni, Zn i Fe after 10 h processing under the same leaching conditions without Fe(III) ions addition was equal to 39.7, 76.9, 59.4, 65.9 and 39.7%, respectively. A comparing experiment results without and with addition of Fe(III) ions indicated that the presence of Fe(III) in the leaching solution increased extraction of Co, Ni, Zn i Fe and slightly decreased extraction of Cu (from 48 to 40%).

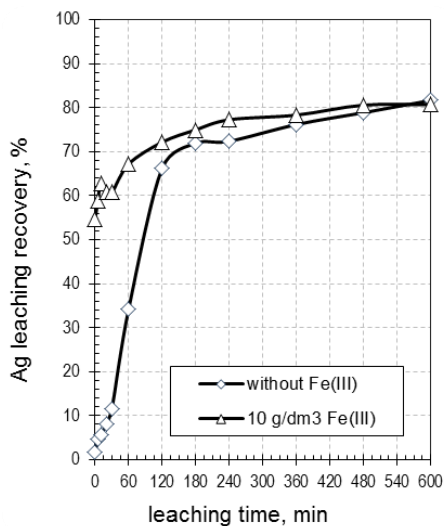


Fig. 9. Effect of Fe(III) ions on Ag leaching recovery in NaCl solution (4 M) and 5 g/dm³ H₂SO₄, solid/liquid ratio 1:10, temperature 90 °C, oxygen flow rate 30 dm³/h

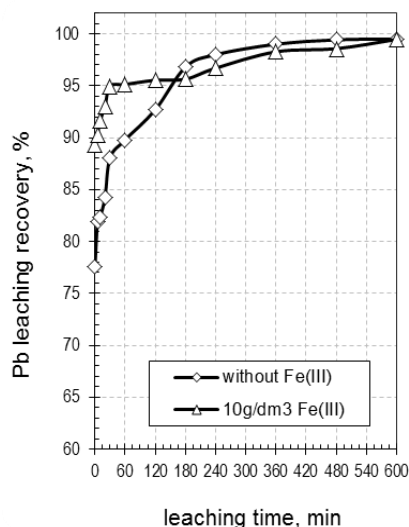


Fig. 10. Effect of Fe(III) ions on Pb leaching recovery in NaCl solution (4 M) and 5 g/dm³ H₂SO₄, solid/liquid 1:10, temperature 90 °C, oxygen flow rate - 30 dm³/h

Effect of oxygen

Besides Fe(III) ions, also oxygen is an oxidant frequently used in the leaching process. Additionally, oxygen can also act as a regenerating agent and oxidizes Fe(II) to Fe(III), that subsequently effectively oxidizes sulfide minerals and is responsible for leaching. To check whether addition of oxygen affects leaching of Ag, Pb, Co, Ni, Cu, Zn and Fe from sulfide minerals, experiments at standard temperature of 25 °C, using the solution containing 4 M NaCl, 0.05 M H₂SO₄ in either presence or absence of oxygen, were carried out. The results showed the effect of oxygen on silver and lead leaching from the examined material (Figs. 11 and 12). The leaching rate of Ag increased, particularly in the initial stage, in the presence of oxygen, but recovery of Ag did not accomplish 60%. The presence of oxygen resulted in a more essential increase of both rate and recovery of lead. The lead recovery exceed 95%. Under the oxygen-free conditions, the leaching recovery was close to zero. Comparing the values with the results presented in Table 5 (oxidized conditions), it was shown that oxygen played a crucial role in leaching. The mineralogical analysis of solid residue after chloride leaching (Table 5) also showed that leaching of sulfide minerals in the presence of oxygen was more effective (Table 6).

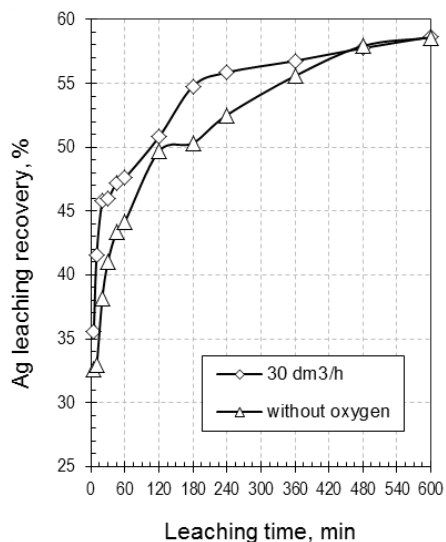


Fig. 11. Effect of oxygen on Ag leaching recovery in NaCl solution (4 M) and 5 g/dm³ H₂SO₄, solid/liquid ratio 1:10, temperature 90 °C

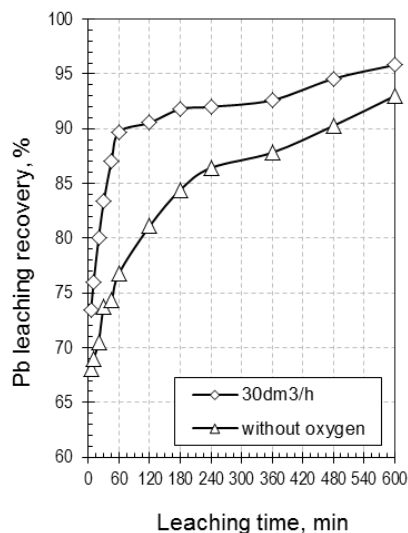


Fig. 12. Effect of oxygen on the Pb leaching recovery in NaCl solution (4 M) and 5 g/dm³ H₂SO₄, solid/liquid ratio 1:10, temperature 90 °C

Table 6. Mineralogical composition of solid residue after chloride leaching without oxygen and in the presence of oxygen. Leaching conditions: 4 M NaCl, 5 g/dm³ H₂SO₄, 25 °C, solid/liquid ratio 1:10, oxygen flow rate 30 dm³/h

Leaching conditions	Unit	Bornite Cu ₅ FeS ₄	Chalcopyrite CuFeS ₂	Pyrite Markasite FeS ₂	Covellite CuS	Sphalerite ZnS	Tennantite Cu ₁₂ As ₄ S ₁₃	Galena PbS
without O ₂	% vol.	0.29	2.96	2.91	0.10	0.20	0.08	0.10
with O ₂	% vol.	0.07	2.48	2.34	0.21	0.20	0.07	0.04

Effect of solid-to-liquid ratio

To verify whether a density of the pulp affects the efficiency of silver and lead leaching derived from tested material, the process was performed under conditions: 25 °C, 4 M NaCl, 0.05 M, for two solid-to-liquid ratios equal to 1:10 and 1:5. Based on the results shown in Figs. 13 and 14 it was found that the increase of the solid-to-liquid ratio from 1:10 to 1:5 caused a minor decrease in silver extraction from 59 to 53%. Also, a two-fold decrease of recovery of lead was observed.

To check the influence of temperature on the silver and lead recovery, the experiments were conducted at two different temperatures at the constant the solid-to-liquid ratio equal to 1:5 (Figs. 13 and 14). According to the leaching results, it can be concluded that the increase of temperature to 50 °C did not influence the lead recovery. At both temperatures, that is 25 and 50 °C, the leaching recovery of lead did

not exceed 50%. Therefore, it can be concluded that the key parameter which influenced lead extraction was the chloride ions concentration in the leaching solution. In the case of silver, a beneficial effect of temperature on the leaching recovery of Ag was observed. After 10 h at the temperature of 50 °C of leaching 74% of Ag was extracted to the solution in comparison to 53% at 25 °C.

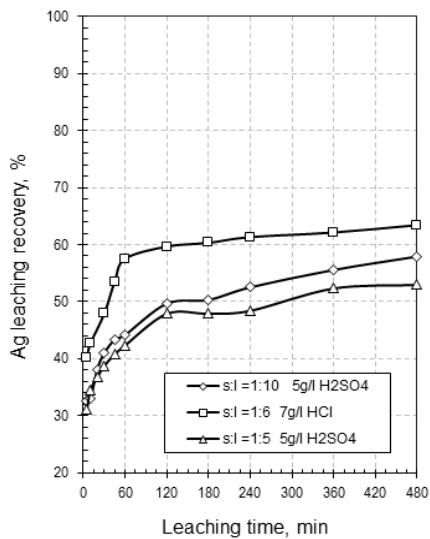


Fig. 13. Effect of solid-to-liquid ratio on leaching recovery of Ag in 4 M NaCl and 5 g/dm³ H₂SO₄ at 90°C

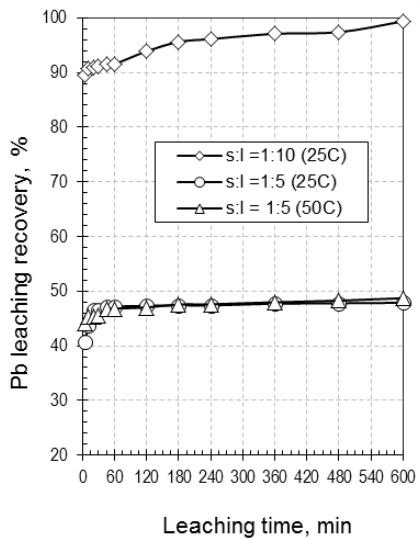


Fig.14. Effect of solid-to-liquid ratio on leaching recovery of Pb in 4 M NaCl solution and 5 g/dm³ H₂SO₄ at 25 and 50°C

The leaching process of residual metals (Co, Ni, Zn, Cu and Fe) was also examined in acidified chloride solutions (4 M NaCl, 0.05 M H₂SO₄) under non-oxidative conditions at 25 and 50 °C at the solid-to-liquid ratio 1:5 (Table 7). Comparing these results with the results shown in Table 4 it can be concluded that the higher the density of the pulp, the less effective is the leaching process of Co, Ni, Zn, Cu and Fe. The observed leaching recovery of metals from the tested material did not exceed a few percent.

Table 7. Recovery of metals after 10 hours of chloride leaching of solid residue after atmospheric leaching of copper concentrate in 4 M NaCl, 5 g/dm³ H₂SO₄, without O₂, s:l = 1:5

Metal	Leaching recovery of metals, %	
	25°C	50°C
Co	0.46	1.87
Ni	0.22	0.75
Zn	1.06	4.05
Cu	1.10	7.96
Fe	1.43	2.87

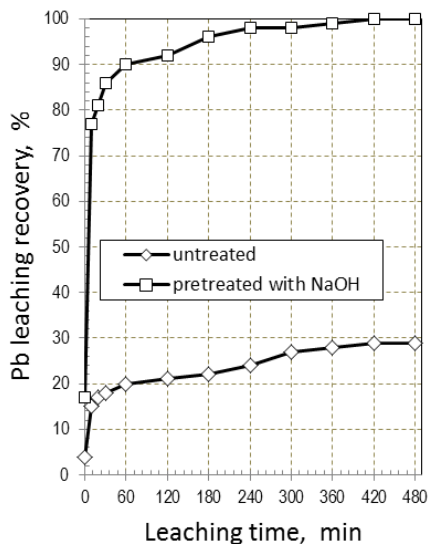


Fig. 15. Effect of preleaching with 0.25 M NaOH at 90 °C on Pb chloride leaching from solid residue after pressure leaching

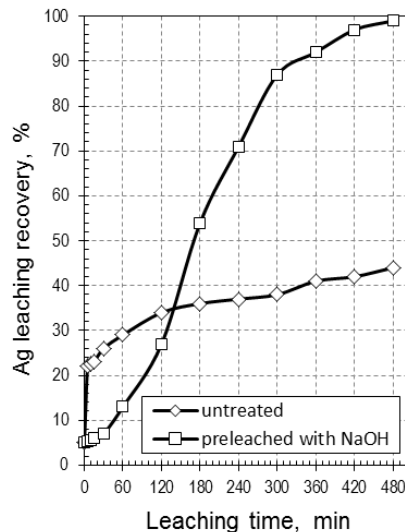


Fig. 16. Effect of pre-leaching with 0.25 M NaOH at 90 °C on Ag chloride leaching from solid residue after pressure leaching

Effect of preleaching with NaOH

The leaching disturbances predominantly observed as low efficiency of leaching of silver were attributed to formation of argento- and plumbojarosites in atmospheric leaching, which were well known compounds entrapping Ag and Pb in oxidative leaching using sulfate solutions. The undesirable role of jarosites was exclusively well noticeable in chloride leaching of Pb and Ag from the solid residue after pressure leaching of the copper concentrate in oxygenated sulfuric acid (Matuska and Chmielewski, 2016). The presence of these argento- and plumbojarosites in the solid after oxidative atmospheric leaching of copper concentrate was confirmed by the SEM and XRD analyses. Decomposition of jarosites and liberation of Pb and Ag for further effective chloride leaching was only possible by means of alkali pretreatment with the NaOH solution. It was found from experimental results that alkali preleaching of solid residue after pressure leaching with 0.25 M NaOH at 90 °C resulted in an apparent improvement of leaching rate and efficiency for both lead and silver (Figs. 15 and 16). The recovery of Pb was almost 100% (3 hour leaching) and Ag was almost entirely recovered after 8 hours leaching when alkali pretreatment of the feed for chloride leaching was applied.

Conclusions

Leaching of lead and silver from the solid residue after atmospheric leaching of the copper concentrate has to be performed in concentrated (4 M) chloride solutions. At low chloride concentration, the process was less effective, particularly for silver. Temperature was an essential parameter influencing the leaching rate and recovery and 90 °C appeared to be the most effective. The presence of oxidants, that is Fe(III) and oxygen, was favorable for Pb and Ag leaching due to the presence of sulfides of both metals in the feed. The solid concentration in the leaching slurry influenced the rate and recovery of Pb and Ag. Satisfactory results were observed when the solid-to-liquid ratio was equal to 1:10. It was found that chloride leaching of silver was significantly hindered in comparison to leaching of lead. This was attributed to entrapment of silver and lead in jarosite structures, which were formed in the atmospheric leaching. To enhance the chloride recovery of silver and lead to the satisfactory level it was necessary to apply the alkaline pretreatment of the feed using 0.25 M NaOH at temperature of 90 °C.

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