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RECOVERY OF COBALT AND NICKEL BY ATMOSPHERIC LEACHING OF FLOTATION SULFIDE CONCENTRATE FROM LUBIN CONCENTRATOR

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Abstract. An experimental study on leaching of cobalt and nickel from a Lubin (Poland) sulfide flotation copper concentrate with oxygenated sulphuric acid solution in the presence of iron(III) sulfate is presented. The effect of temperature, iron(III) concentration, initial sulphuric acid concentration, oxygen flow rate and chloride ions addition on cobalt and nickel leaching were examined. The obtained results show, that enhancing investigated leaching parameters increases both the rate and leaching recovery of nickel and cobalt. The effect of iron(III) ions concentration is particularly significant. Additionally, a significant correlation between copper and nickel/cobalt leaching recovery was observed. Due to the fine dissemination of nickel and cobalt, they were leached remarkably faster when copper leaching recovery exceeded 90%.

Keywords: *atmospheric leaching, cobalt, nickel, sulphuric acid, Lubin copper concentrate.*

Introduction

The traditional treatment of copper flotation sulphide concentrates by smelting, converting and electrorefining is becoming dominant in the world copper industry for technical and economic reasons. Research and development of hydrometallurgical alternatives to traditional pyrometallurgical processes has remarkably been intensified in the recent years. A wide range of chemical and biological processes for copper recovery from concentrates have been developed (Gupta and Mukherjee, 1990; Habashi, 1999; 2005; 2007; Jansen and Taylor, 2000; Peacey et al., 2003; Dreisinger, 2006; Marsden and Wilmot, 2007; Ramahadran et al., 2007). These processes are all successful in leaching of copper from polymineral and chalcopyrite concentrates, purifying pregnant leach solutions (PLS) using modern separation processes, mainly solvent extraction, and recovering a high value and purity copper metal product.

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A complex and unique mineralogical structure as well as polymetallic chemical composition of Polish Kupferschiefer copper ores mined from sedimentary deposits is the principal reason for copper, silver and other metals losses to flotation tailings (Luszczkiewicz, 2000). The presence of clay-carbonate shale and increasing content of organic carbon in ores and concentrates creates additional technical and ecological issues, particularly in flash smelting. Therefore, it can be concluded that the existing beneficiation technologies combined with smelting and refining have already reached the limit of their technological efficiency for processing of Polish copper ores (Chmielewski and Charewicz, 2006; Chmielewski et al., 2007).

The quality of the Polish copper ores, which exhibit a decreasing copper content and growing amount of shale fraction as well as increasing concentration of impurities (Pb, As) have been deteriorating for many years (Chmielewski and Charewicz, 1984; Bachowski et al., 2003; Grotowski, 2007; Konieczny et al., 2009; Chmielewski, 2012). It essentially affects the decreasing copper content and recovery in the flotation concentrates (KGHM data, Konieczny et al., 2009) and is the main reason of high costs of copper production. An analysis of flotation indices at all KGHM Polska Miedz S.A. concentrators reveals a descending trend for both recovery and concentrate grade. It is particularly apparent at Lubin Concentrator (ZWR Lubin), where copper recovery is currently below 87% and the metal content in concentrate is about 14% (Fig. 1).

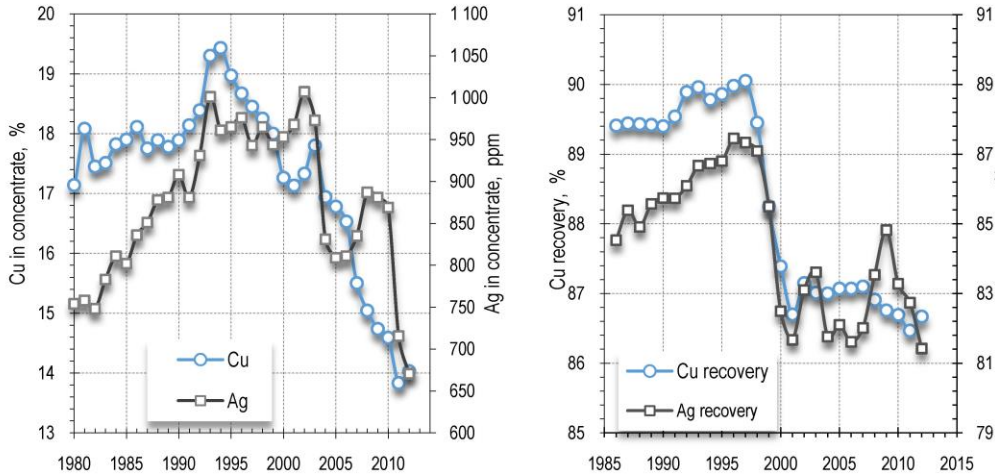

Fig. 1. Lubin flotation copper concentrate quality and Cu and Ag recovery within the period from 1980 to 2012 (based on Kukuc and Bazan, 2013)

A similar unfavorable trend is also observed for silver. Moreover, even when the content of other accompanying metals is relatively high (Pb, Zn, Ni, Co, Mo, V) some of them are either recovered only partially or not at all. Currently used technologies at

ZWR Lubin have already reached limit of their efficiency and they are the major reason of increasing metals losses and production costs.

In this paper the results of recovering of nickel and cobalt observed during atmospheric leaching of the Lubin concentrate in oxygenated sulphuric acid and in the presence of Fe(III) are presented. The paper discusses the effect of major parameters on leaching rate and metals recovery during the investigated process.

Experimental

Material and experimental procedure

The subject of the study is a commercial flotation sulfide concentrate produced at Lubin Concentrator (KGHM Polska Miedź S.A.). The concentrate consists of copper and other metals, such as Zn, Co, Ni, Ag, V, Mo, that significantly increase the value of this material. The decreasing concentrate copper grade, high content of organic carbon, presence of lead and arsenic, make the concentrate a potential and suitable feed for a hydrometallurgical treatment (Chmielewski, 2012).

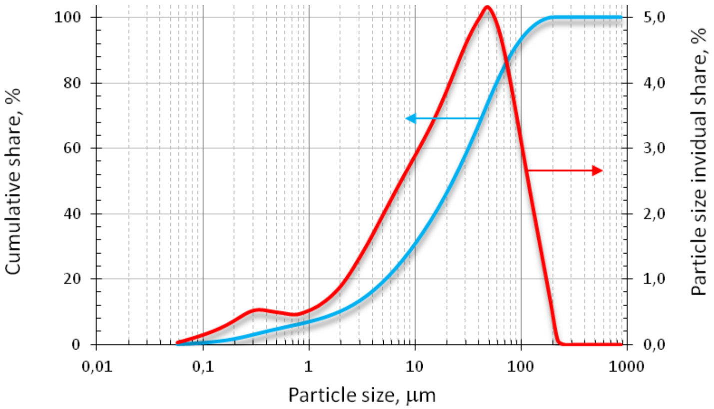

Fig. 2. Granulometric analysis of copper concentrates from Lubin Concentrator

The Lubin concentrate is a polymetallic and polymineral material. The valuable metals are present in the sulfide form, while the majority of barren contents are magnesium and calcium carbonates. A chemical composition of the concentrate is presented in Table 1. The possibility of cobalt and nickel recovery by hydrometallurgical methods becomes more attractive when considered is the stable content of nickel and increasing concentration of cobalt, which currently is totally lost, and the efficiency of nickel extraction is rather low (Chmielewski, 2012).

The content of carbonates and particle size distribution of the concentrate were determined during concentrate characterization. The carbonates content is described by the $Z_{H_2SO_4}^{\max}$ parameter, which is the mass of sulfuric acid consumed during total chemical decomposition of carbonates contained in 1 kg of dry concentrate. For the studied material the $Z_{H_2SO_4}^{\max}$ values were between 200 and 250 g of sulphuric acid per 1 kg of concentrate. The particle size distribution is given in Fig. 2.

Three commercial flotation copper concentrate samples were examined (KLA, KLB and KLC). Table 1 shows that the samples have similar chemical composition.

Table 1. The chemical composition of "Lubin" flotation concentrate

Concentrate symbol,	$Z_{H_2SO_4}^{\max}$ g/kg	Cu, %	Zn, %	Ni, g/Mg	Co, g/Mg	Fe, %	Pb, %	Ag, g/Mg	As, %	V, g/Mg	Mo, g/Mg	S, %	C_{org}, %
KLA	228	15.85	0.95	415	1040	7.05	3.63	881	0.29	762	344	12.41	8.10
KLB	255	15.26	0.93	488	1206	6.71	3.95	938	0.34	569	265	12.40	8.10
KLC	248	14.56	0.57	483	1250	7.55	3.91	755	0.26	672	221	13.54	7.23

Leaching procedure

A series of atmospheric leaching experiments were conducted. The effect of following process parameters on the cobalt and nickel leaching efficiency was examined: temperature, iron(III) concentration, sulfuric acid concentration, solid/liquid ratio (s/l), oxygen flow rate and chloride ions addition. The leaching experiments were conducted in a stirred glass reactor immersed in a water bath. The agitation rate of 500 min^{-1} was kept the same for all experiments. A leaching slurry was continuously oxygenated using a glass tube. The oxygen flow rate was controlled by a rotameter. The leaching reactor was equipped with a condenser, to avoid rapid vaporization of the leaching solution at higher process temperatures. The density of the leaching slurry was described as a solid to liquid phase ratio (g/cm^3).

During each leaching experiment, the slurry samples were taken from the reactor and filtered for analysis of metals concentration, using an atomic absorption spectroscopy technique (AAS). The redox potential of the leaching slurry was also measured using a Pt-Ag/AgCl combined electrode and a mV/pH-meter. Because of carbonates presence in the concentrate, each leaching experiment was preceded by the controlled, selective carbonates decomposition process with sulfuric acid under non-oxidative conditions (in the absence of oxygen iron(III) ions). After non-oxidative carbonates decomposition, the leaching slurry was heated and when it reached a given temperature, oxygen and iron(III) ions were introduced into the reactor. The leaching efficiencies were evaluated by determining metals leaching recoveries, according to equation:

$$R_{\%} = \frac{cV}{m\alpha} \cdot 100\% \qquad (1)$$

where:

$R_{\%}$ metal leaching recovery, %
c metal concentration in the solution, g/dm^3 (mg/dm^3)
V leaching solution volume, dm^3
m mass of the concentrate, g
α metal content in the concentrate, % (g/Mg).

Results and discussion

Correlation between Co, Ni and Cu leaching recoveries

The analysis of metals leaching exhibited a very strong relationship between nickel, cobalt and copper recovery. It was found, that both the Ni and Co leaching rate and leaching recovery depend on copper leaching recovery value. Cobalt and nickel start to leach very rapidly when about 90 – 95% of copper is leached out. This suggests, that Co and Ni sulfides are disseminated in the matrix of copper minerals and leaching solution has a very limited access to them at the beginning of the process. It is expected, that enhancing the copper leaching rate will have a positive effect on the leaching recoveries of cobalt and nickel as the Co and Ni bearing minerals will be faster exposed to the leaching solution. Figure 3 presents the relationship between Co and Ni recovery vs. Cu recovery for one of the leaching processes, as an example. A similar dependency was observed in all experiments.

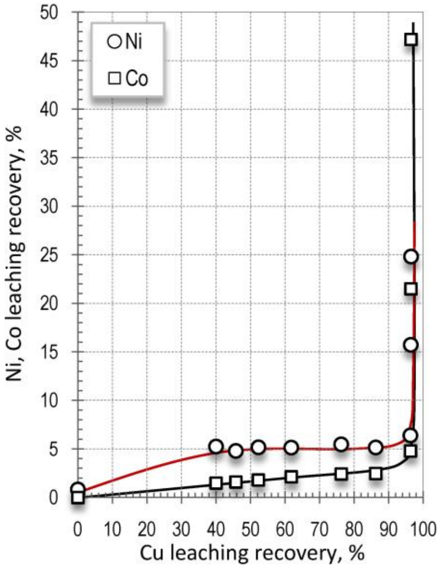

Fig. 3. Ni and Co recovery vs. Cu recovery in atmospheric leaching; s/l = 1:6, initial H_2SO_4 concentration 100 g/dm^3, temperature 90 ^{o}C, O_2 flow rate 60 dm^3/h, iron(III) ions concentration 30 g/dm^3

Effect of temperature

A series of atmospheric leaching experiments were conducted using a KLA sample of the Lubin concentrate (Table 1). Three different temperatures were examined (50, 70 and 90 ^{o}C). Other process parameters were constant (s/l = 1:8, initial H_2SO_4 concentration = 50 g/dm^3, no iron(III) ions addition, oxygen flow rate = 30 dm^3/h, leaching time = 5 h).

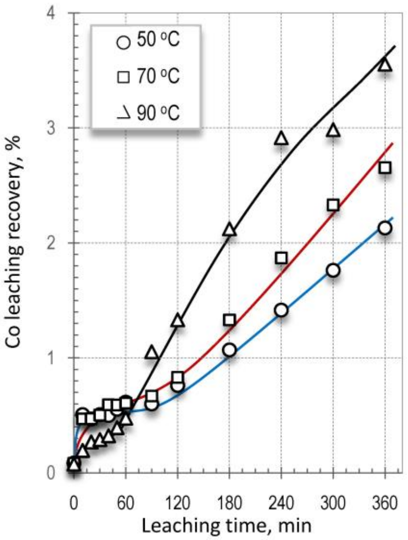

Fig. 4. Effect of temperature on Co leaching recovery; s/l = 1:8, initial H_2SO_4 concentration 50 g/dm^3, O_2 flow rate 30 dm^3/h

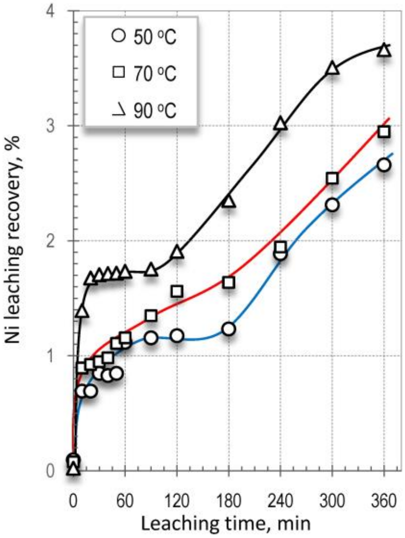

Fig. 5. Effect of temperature on Ni leaching recovery; s/l = 1:8, initial H_2SO_4 concentration 50 g/dm^3, O_2 flow rate 30 dm^3/h

The leaching results (Figs. 4 and 5) showed that temperature has a significant effect on the Co and Ni leaching rate and efficiency. However, in the examined range of parameters the leaching recovery of these metals was relatively low even at the highest tested temperature (90 °C). It was a result of using only oxygen as an oxidizing agent (iron(III) ions were not added). For the further leaching experiments the temperature of 90 ^{o}C was chosen.

Effect of iron(III) ions concentration

To investigate the iron(III) ions effect on Co and Ni leaching, a KLA concentrate sample was used. The initial concentration of iron(III) ions varied from 10 to 30 g/dm^3. Other leaching parameters were as follows: temperature = 90^{o}C, s/l = 1:8, initial H_2SO_4 concentration = 50 g/dm^3, oxygen flow rate = 30 dm^3/h, leaching time = 5 h. The sample "zero" was taken after carbonates decomposition. It was found that even the lowest iron(III) ions addition would have a significant effect on the Co and Ni leaching rate and efficiency (Figs. 6 and 7).

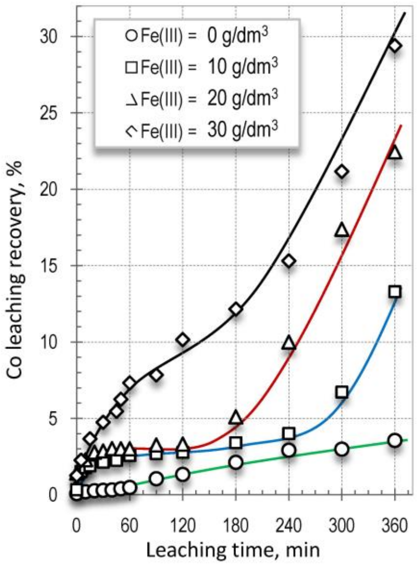

Fig. 6. Effect of iron(III) ions concentration on Co leaching recovery; s/l = 1:8, initial H_2SO_4 concentration 50 g/dm^3, temperature 90 ^oC, O_2 flow rate 30 dm^3/h

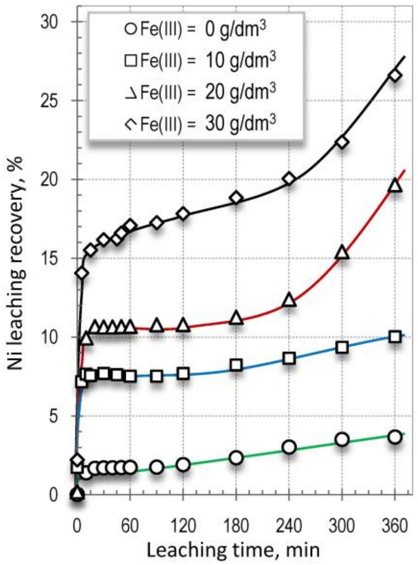

Fig. 7. Effect of iron(III) ions concentration on Ni leaching recovery: s/l = 1:8, initial H_2SO_4 concentration 50 g/dm^3, temperature 90 ^oC, O_2 flow rate 30 dm^3/h

With increasing iron(III) ions addition, the cobalt and nickel leaching recovery increase remarkably, compared to the process without iron(III) ions (Figs. 6 and 7). Although the standard reduction potential of oxygen (+1.23 V) is much higher than the one for Fe^{3+}/Fe^{2+} (+0.77 V), leaching of Co and Ni with oxygen as the only oxidant is ineffective. This can be explained by low oxygen dissolution in the leaching solution and low reduction rate on the sulphides surface.

Effect of initial sulfuric acid concentration

A sample of KLB Lubin concentrate was used as the feed for investigation of initial H_2SO_4 concentration effect on Co and Ni leaching. Two initial acid concentrations were compared: 50 and 100 g/dm^3. Other leaching parameters were as follows: temperature 90 ^oC, s/l 1:6, iron(III) ions concentration 30 g/dm^3, oxygen flow rate 60 dm^3/h, leaching time 10 h. Results are given in Figs. 8 and 9.

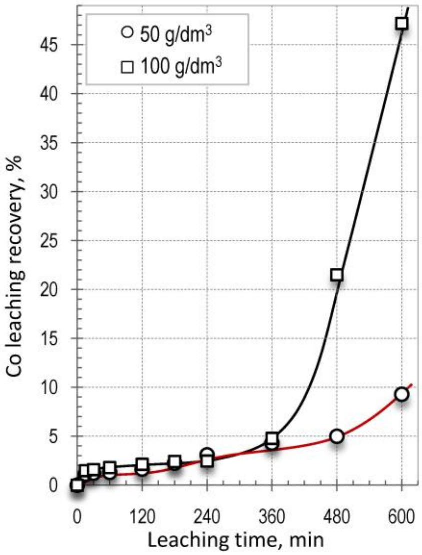

Fig. 8. Effect of initial sulphuric acid concentration on Co leaching recovery; s/l 1:6, iron(III) ions concentration 30 g/dm^3, temperature 90 ^{o}C, O_2 flow rate 60 dm^3/h

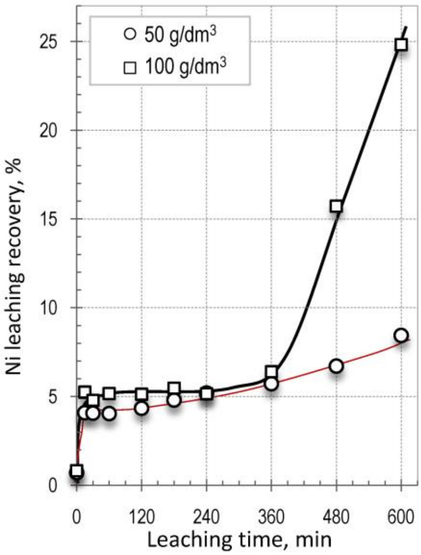

Fig. 9. Effect of initial sulphuric acid concentration on Ni leaching recovery; s/l 1:6, iron(III) ions concentration 30 g/dm^3, temperature 90 ^{o}C, O_2 flow rate 60 dm^3/h

The cobalt and nickel leaching recovery was much higher in experiments with higher initial acid concentration. After 10 hours of leaching for 100 g/dm^3 of initial acid concentration the recovery of cobalt and nickel was found as 48 and 25%, respectively (compared to 10 and 8% for 50 g/dm^3 of acid). It can be seen that the cobalt and nickel recovery curves are almost flat from the beginning of leaching and tend to raise in later leaching stages. The time needed for Co and Ni to begin their effective leaching is much shorter and the leaching rate of these metals is much higher in the experiments with higher initial acid concentration. This fact can be explained by a strong correlation between recoveries of Co, Ni and Cu (Fig. 3).

Effect of oxygen flow rate

A sample of KLA Lubin concentrate was used for evaluation of the oxygen flow rate on Co and Ni leaching. Three O_2 flow rates were compared: 30, 60 and 90 dm^3/h. Other process parameters remained constant for all experiments (temperature 90 ^{o}C, s/l 1:8, initial H_2SO_4 concentration 50 g/dm^3, iron(III) ions concentration 30 g/dm^3, leaching time 5 h).

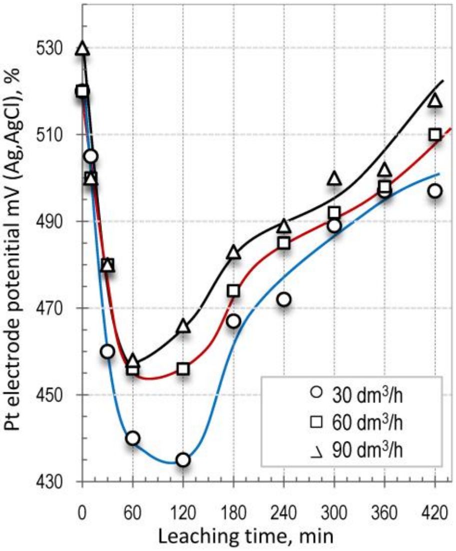

Fig. 10. Effect of oxygen flow rate. Potential of Pt electrode – leaching time during atmospheric leaching: initial H_2SO_4 concentration 50 g/dm^3, s/l 1:8, iron(III) ions concentration 30 g/dm^3, temperature 90 ^{o}C

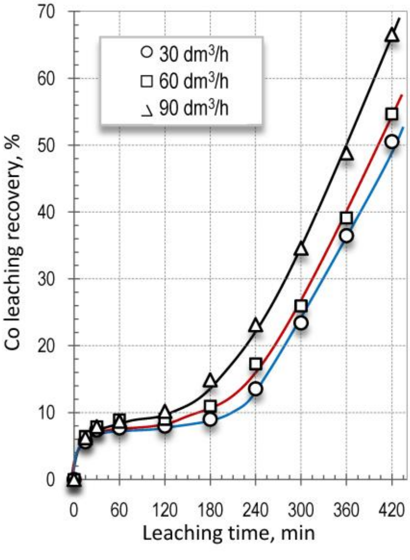

Fig. 11. Effect of oxygen flow rate on Co leaching recovery: initial H_2SO_4 concentration 50 g/dm^3, s/l 1:8, iron(III) ions concentration 30 g/dm^3, temperature 90 ^{o}C

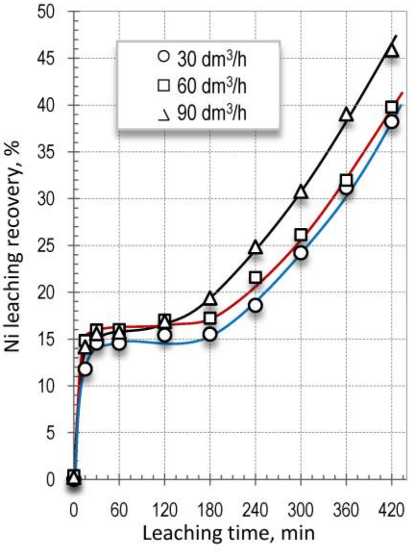

Fig. 12. Effect of oxygen flow rate on Ni leaching recovery: initial H_2SO_4 concentration 50 g/dm^3, s/l 1:8, iron(III) ions concentration 30 g/dm^3, temperature 90 ^{o}C

The oxygen flow rates had an expected effect on the redox potential of the slurry (Fig. 12). The main role of oxygen in the presence of iron(III) ions is to regenerate them by oxidizing Fe^{2+} to Fe^{3+}. With increasing O_2 flow rate, the redox potential values were slightly higher, as the iron(III) ions regeneration reaction was more efficient. This had also an effect on Co and Ni leaching recoveries (Figs. 10 and 11).

In the atmospheric leaching processes there are two simultaneous reactions: anodic dissolution of sulfide minerals, where sulfur is oxidized from its sulfide to elemental form by iron(III) ions, which are reduced to iron(II) and reaction of iron(II) to iron(III) ions regeneration with oxygen. For all leaching experiments the initial redox potential was about 530 mV (Ag, AgCl). In the first phase of atmospheric leaching a rapid decrease in the potential is observed. This is due to the dissolution rate of easy-to-leach copper minerals (bornite and chalcocite), which is much higher than the rate of iron(III) ions regeneration reaction. It shows, that the atmospheric leaching process needs to be optimized in terms of oxygen distribution and hydrodynamic conditions (more efficient way of introducing oxygen, use of baffles, etc.) in order to enhance the copper leaching rate in the first phase of the process by limiting the redox potential drop. The highest decrease of redox potential was observed in the experiment with 30 dm^3/h of O_2 flow rate (Fig. 12). Higher oxygen flow rates cause a higher potential of the slurry. Furthermore, with higher oxygen flow rates it takes less time for iron(III) ions regeneration rate to dominate over the sulfide minerals leaching rate.

Effect of chloride ions addition

Mining plants at KGHM Polska Miedz S.A. (Lubin, Polkowice-Sieroszowice and Rudna) generate together 75 000 m^3 of mine water per day (KGHM data, 2013). The 95% of the mine water contains 3–5 g/dm^3 of chloride ions. In the case of application of the hydrometallurgical technology for concentrates, mine water would be used for the atmospheric leaching process. Therefore, it is necessary to evaluate the effect of chloride ions on the leaching rate and efficiency.

In this experiment the commercial flotation concentrate KLC sample was selected. Two atmospheric leaching experiments were conducted: the first one without chloride ions addition, and the second one with 3 g/dm^3 addition of chlorides. The experiments showed (Figs. 13 and 14) that even a small addition of chloride ions causes significant increase in the leaching recovery. The Co recovery after 7 hours of leaching with chlorides addition was 28%, whereas the Ni recovery was 23%. The chloride ions concentration of 3 g/dm^3 is low enough to prevent silver and lead leaching into the solution (less than 0.1% of lead and silver was leached out). Only leaching process at elevated concentration of chloride ions gives the possibility for effective recovery of Pb and Ag. Therefore, the presented research confirms possible application of mine water in the atmospheric leaching processes.

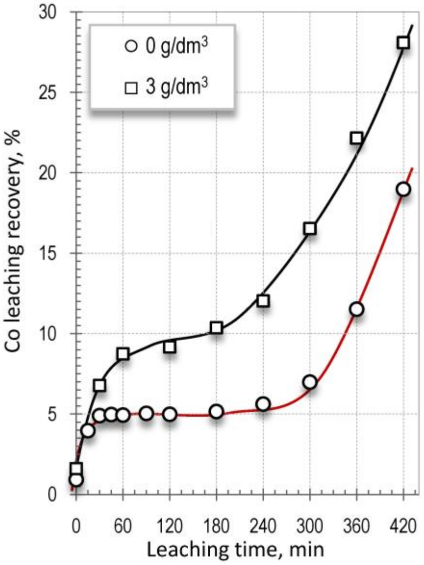

Fig. 13. Effect of chloride ions addition on the Co leaching: initial H_2SO_4 concentration 50 g/dm^3, s/l 1:6, iron(III) ions concentration 30 g/dm^3, temperature 90 ^{o}C, O_2 flow rate 60 dm^3/h

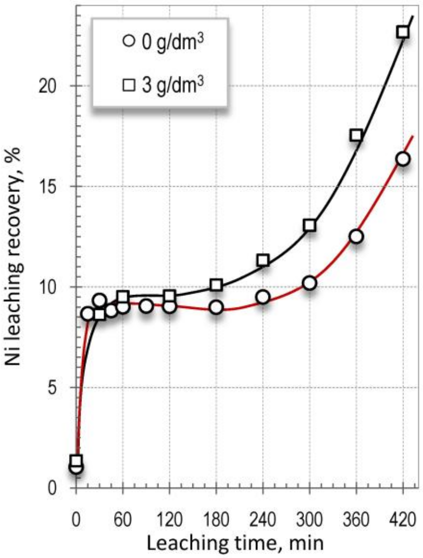

Fig. 14. Effect of chloride ions addition on the Ni leaching: initial H_2SO_4 concentration 50 g/dm^3, s/l 1:6, iron(III) ions concentration 30 g/dm^3, temperature 90 ^{o}C, O_2 flow rate 60 dm^3/h

Conclusions

In this paper atmospheric leaching of cobalt and nickel from the Lubin copper concentrate is presented. The effect of following parameters on the leaching efficiency was investigated: temperature, iron(III) ions, sulfuric acid and chloride ions concentration and oxygen flow rate. It was found that enhancing all the investigated parameters resulted in the higher rate of cobalt and nickel leaching. The most significant effect was observed for increased both, iron(III) ions and initial sulfuric acid concentrations. It was also observed, that cobalt and nickel leaching rates dramatically increased when the copper recovery was higher than 90%.

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References

BACHOWSKI C., STASZAK J., BYSZYNSKI L., BOCZAR W., TEODORSKI D., 2003, *Search for alternative methods of processing of copper ores in KGHM ,, Polska Miedz'' S.A. –*

hydrometallurgical technologies, VIII Seminar „Hydrometallurgy of Sulphide Copper Resources'', Lubin, June 26. 2003: 125, (In Polish).

CHMIELEWSKI T., 2012. *Hydrometallurgy in KGHM Polska Miedz SA – Circumstances, Needs and Perspectives of Application*, Separation Science and Technology 47, 9, 1264-1277.

CHMIELEWSKI T., CHAREWICZ W., 1984. *Pressure leaching of sulphide copper concentrate with simultaneous regeneration of the leaching agent*, Hydrometallurgy 13, 63-72.

CHMIELEWSKI T., CHAREWICZ W., 2006, *Hydrometallurgical processing of shale by-products from beneficiation circuits of Lubin Concentrator, In: Perspectives for applying bioleaching Technology to process shale-bearing copper ores*, BIOPROCOP'06, Lubin 2006, KGHM Cuprum, Wroclaw 2006, 125-145.

CHMIELEWSKI T., LUSZCZKIEWICZ A., KONOPACKA Z., *Acidic pretreatment of hard-to-tread copper ore flotation middlings to facilitate flotation efficiency*. Proceedings of XXIV International Mineral Processing Congress, Beijing 24-28 Sept. 2008, Vol. 3, Wang D.D., Sun C.Y., Wang F.L., Zhang L.C., Han L. (Eds), Science Press, 1189-1200

DREISINGER D., 2006. *Copper leaching from primary sulfides: Options for biological and chemical extraction of copper*, Hydrometallurgy 83, 10 – 20.

GROTOWSKI A. 2007. *Possibilities and perspectives for implementation of hydrometallurgical methods in KGHM Polska Miedz S.A.*, Proc. VIII International Conference on Non-ferrous Ore Processing, Wojcieszyce (Poland), May 21–23, KGHM Cuprum Wroclaw 2007.

GUPTA C.K., MUKHERJEE T.K., 1990. *Hydrometallurgy in Extraction Processes*, Vol. I and II; CRC Press: Boca Raton, FL.

HABASHI F., 1999, *Textbook of hydrometallurgy*, Metall. Extract. Quebec.

HABASHI F., 2005, *Recent Advances in the Hydrometallurgy of Copper*, Proc. Int. Copper Hydrometallurgy Workshop "Hydrocopper 2005" (Menacho J.M., Casas de Prada J.M., Eds.), Santiago, Chile, pp. 43-55.

HABASHI F., 2007, *Abandoned but not forgotten – the recent history of copper hydrometallurgy*, The John Dutrizac Symposium on Copper Hydrometallurgy, Proceedings 6th International Copper-Cobre International Conference, August 3-20, 2007, Toronto, Canada, vol. IV, Met. Soc.

JANSEN M., TAYLOR A., 2000, *Key elements in the selection of sulphide leach processes for copper concentrate leaching*, Alta Cu 2000, August 2000, Int. Proj. Dev. Serv. Pty Ltd.,

KONIECZNY A., KASIŃSKA-PILUT E., PILUT R., 2009. *Technological and technical problems in mineral processing of Polish copper ores at Division of Concentrators KGHM ''Polska Miedz'' SA*, Proc. IX International Conference on Non-Ferrous Ore Processing, ICNOP Ladek Zdroj (in Polish), 18–20 May 2009: 11, in Polish.

KUKUC R., BAZAN B., *Improvement of technology indices of DoC Lubin Plant within the context of decreasing copper content in ore*, Proceedings of the Mineral Engineering Conference MEC2013, Kowalczuk P.B. (ed.), Swieradow-Zdroj, Poland, 16-19 September 2013, pp. 95-108

LUSZCZKIEWICZ A., 2000, *Utilisation of black copper shale ores from Lubin-Glogow region. in: Recent problems on copper ores processing in Poland*, November 16, 2000., Conference Proceedings, Mining Committee of Polish Academy of Sciences and KGHM "Polish Copper", 137-156 (in Polish).

LUSZCZKIEWICZ A., 2009, Physicochemical Problems of Minerals Processing Seminar, Niepolomice, Poland, 16-18 Sept, 2009, plenary lecture.

MARSDEN J.O., WILMOT J.C., 2007a, *Medium-temperature pressure leaching of copper concentrates* – Part I: Chemistry and initial process development, Min. Metall. Processing, 24(4) 193-204.

MARSDEN J.O., WILMOT J.C., 2007b, *Medium-temperature pressure leaching of copper concentrates* – Part II: Development of direct electrowinning and acid-autogenous process, Min. Metall. Processing, 24(4) 205-217.

MARSDEN J.O., WILMOT J.C., 2007c, *Medium-temperature pressure leaching of copper concentrates* – Part III: Commercial demonstration at Bagdad, Arizona, Min. Metall. Processing, 24(4) 218-225.

MARSDEN J.O., WILMOT J.C., 2007d, *Medium-temperature pressure leaching of copper concentrates* – Part IV: Application at Morenci, Arizona, Min. Metall. Processing, 24(4) 226-236.

MARSDEN J.O., 2007e, *Sulphate-based flowsheet options for hydrometallurgical treatment of copper sulphide concentrates*, The John Dutrizac Symposium on Copper Hydrometallurgy, Proceedings 6th International Copper-Cobre Conference, August 25-30, 2007, Toronto, Canada, vol. IV, Met. Soc., pp.77-100.

PEACEY J.I., GUO X.J., ROBLES E., 2003, *Copper Hydrometallurgy – Current Status, Preliminary economics, Future Direction and Positioning versus Smelting*, Copper 2003 - Cobre 2003, vol.VI, (Book 1) Santiago – Chile (Riveros P.A., Dixon D., Dreisinger D., Eds.), pp. 205-222.

RAMACHADRAN V., LAKSMANAN V.I., KONDOS P.D., 2007, *Hydrometallurgy of copper sulphide concentrate*, The John Dutrizac Symposium on Copper Hydrometallurgy, Proceedings 6th International Copper-Cobre Conference, August 25-30, 2007, Toronto, Canada, vol. IV, Met. Soc., pp.101-128.