

Received April 1, 2011; reviewed; accepted May 4, 2011

Atmospheric leaching of copper flotation concentrate with oxygenated sulphuric acid solutions

**Tomasz CHMIELEWSKI, Kamil BOROWSKI, Krzysztof GIBAS,
Katarzyna OCHROMOWICZ, Barbara WOZNIAK**

Wroclaw University of Technology, Faculty of Chemistry, Division of Chemical Metallurgy, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, tomasz.chmielewski@pwr.wroc.pl

Abstract. Results of atmospheric leaching of copper sulphide concentrate from Lubin Concentrator (ZWR Lubin) with oxygenated aqueous H_2SO_4 and in the presence of Fe(III) have been presented. It was found that oxidative atmospheric leaching performed in acidified and oxygenated iron(III) solutions has to be preceded by a controlled, non-oxidative decomposition of acid-consuming carbonate components in order to further liberate finely disseminated metal-bearing minerals. Atmospheric leaching appeared to be a very efficient process for recovering Cu, Zn, Co and Ni from the Lubin concentrate due to favorable mineralogical composition and fine size of leached particles. A maximum recovery of Cu (95%), Zn (90%), Ni (40%) and Co (50%) was observed after 5-7 hours of leaching at 90°C in the oxygenated solutions containing 20-30 g/dm³ of Fe(III). The solid residue after atmospheric leaching will be further processed by flotation or chloride leaching to recover Ag, Pb and precious metals.

keywords: leaching, copper, sulphuric acid, industrial concentrate, galvanic interactions

1. Introduction

The application of modern hydrometallurgy, well known and already approved in the world for copper recovering, becomes an urgent necessity in Polish copper industry to reverse unfavorable trends in flotation results (decreasing concentrate grade and metals recovery), particularly at Lubin Concentrator (Grotowski, 2007). The application of atmospheric leaching can be considered as a complimentary process for processing of copper flotation concentrate in order to elevate the recovery of copper and to recover metals, which are being lost in the current technologies (Zn, Co, Mo, V).

The standard treatment of copper flotation sulphide concentrates by smelting, converting and electrorefining has dominated the World copper industry.

Pyrometallurgy is undoubtedly more feasible for high capacity processing and became not acceptable for small scale operations for economical reason. Research and development for hydrometallurgical alternatives to traditional pyrometallurgical processes has remarkably intensified in the recent years. A wide range of chemical and biological processes for copper recovery from concentrates have emerged (Dreisinger 2006, Gupta 1990, Habashi 1999, 2005, 2007, Jansen and Taylor 2000, Marsden 2007a, b, c, d, e, Peacey et al. 2003, Ramahadran et al. 2007, Letowski 1975). These processes are all successful in leaching of copper and accompanying metals from polymineral and chalcopyrite concentrates, purifying the leach solutions (PLS) using modern separation processes, mainly solvent extraction (SX), and recovering a high value, high purity copper metal product.

It is well known that the Polish copper deposits (LGOM - Lubin-Glogow Copper Basin, SW Poland) exhibit unique, sedimentary nature (Rydzewski 1996, Konstantynowicz 1990). They consist of three lithological fractions: dolomitic, sandstone, and shale. From those three ore fractions the shale fraction reveals two exceptional and opposite properties. It contains the highest concentrations of copper and accompanying metals (Ag, Ni, Co, Zn, Pb, V, Mo and others) and simultaneously is the most troublesome in the flotation circuits (Tomaszewski 1995, Konieczny and Kasińska 2009). In the case of the shale fraction, dissemination of fine metal sulfides in the carbonate matter and black shale-clay rocks that form the majority of the gangue is observed. Such fine dissemination of copper sulfides in the carbonate-organic matrix considerably reduces the susceptibility of the ore to both effective liberation and flotation. A relative increase of quantity of the shale-clay and carbonate fractions in flotation feeds, which are known as mostly hard-to-treat in flotation circuits, is currently observed. According to the latest data (Kubacz and Skorupska 2007) content of the shale fraction in the Lubin deposit can even occasionally exceed 25% and is expected to be at high levels in coming years.

A complex and unique mineralogical structure as well as chemical composition of the Polish copper ores mined from sedimentary deposits is the principal reasons for copper, silver and other metals losses to flotation tailings (Łuszczkiewicz 2000, 2004). The presence of shale creates additional technical, economical and ecological issues. Selective liberation of the fine metals-bearing sulphide particles from the carbonate host matrix would be the only way to enhance metals recovery. However, it appears to be ineffective in the existing milling circuits. Consequently, the hydrophilic gangue-sulphide intergrowths seriously reduce both the flotation selectivity and the metal grade in the concentrate (Łuszczkiewicz et al. 2006). Therefore, it can be concluded that the existing beneficiation technologies currently applied to Polish copper ores have reached the limit of their technological efficiency (Chmielewski and Charewicz 2006, Łuszczkiewicz and Chmielewski 2008, Chmielewski et al. 2007a).

The hydrometallurgical processes can be divided into predominantly sulphate, mixed sulphate/chloride, and chloride types (Ramahadran et al. 2007). Within the sulphate grouping, processes can be sub-grouped as either atmospheric or super-

atmospheric in pressure, and chemical or biological in the leaching process. There are fewer chloride processes but advances in chemistry, equipment, and process development have vaulted the chloride systems back into the competition. The sulphate atmospheric leaching has been previously investigated as an alternative for processing of flotation middlings (shale enriched feed) from the technological circuit at Lubin Concentrator (Chmielewski 2007).

This paper presents the results of initial investigations on atmospheric leaching of the Lubin flotation concentrate in oxygenated aqueous sulphuric acid in the presence of iron(III) ions.

2. Material and experimental procedure

A commercial flotation concentrate from flotation circuit at Lubin Concentrator (ZWR Lubin) was used as leaching feed. The output of the concentrate at the Lubin plant is almost 0.5 Tg (teragrams)/year and corresponds to the copper production of 65 Gg/year. The feed for leaching had been collected in the form of water slurry for about two weeks to provide a representative leaching feed. The slurry of the industrial sample was then vigorously stirred and split on 1-2 dm³ laboratory samples, which were kept in sealed containers isolated from the effect of air.

The feed material applied for the laboratory experiments of non-oxidative leaching followed by atmospheric leaching in oxygenated sulphuric acid was subjected to various analyses including chemical assay, granulometric composition, demand for sulphuric acid for total decomposition of carbonates ($Z_{\text{H}_2\text{SO}_4}^{\text{max}}$), mineralogical composition, organic and total carbon as well as total sulphur content. The results of analyses are given in Tables 1 and 2 and in Fig.1. The content of organic carbon was observed to be very high (about 8.1 %) and is not acceptable for flash smelting.

Table 1. Chemical compositions of copper flotation concentrate from Lubin Concentrator

Cu, %	Ag, g/Mg	Pb, %	Ni, g/Mg	Co, g/Mg	Zn, %	As, %	Mo, g/Mg	V, g/Mg	C _{org} , %
15.4%	870	2.67	475	1 160	0.95	0.29	290	650	8.1

The content of carbonates in two concentrate samples corresponds to the utilization of 220-260 g H₂SO₄/kg of dry solid for total decomposition of carbonates. Therefore, the application of atmospheric leaching, taking place in acidic conditions, required previous non-oxidative leaching with acid in order to decompose totally the acid consuming components, mainly calcium and magnesium carbonates (Luszczkiewicz and Chmielewski 2006) Chmielewski et al. 2007a, b).

Non-oxidative leaching was always performed before each atmospheric leaching experiment. The particle size composition of the leaching feed was in reported examinations the same as in flotation ($D_{80} = 110-120 \mu\text{m}$, Fig.1). The feed was not subjected to additional particle size reduction.

The flotation concentrate from Lubin Concentrator (Table 1) exhibits considerably lower content of copper (15.5% Cu) with regard to Rudna and Polkowice, but the content of silver (870 g/Mg) and other base metals, particularly zinc (0.95%) and cobalt (1 160 g/Mg), which are present as sulphides, was remarkably higher with regard to other concentrates produced at KGHM. Unfortunately, the high value of accompanying metals is currently underestimated, taking into account their market value. The content of molybdenum (290 g/Mg) and vanadium (650 g/Mg) is also evidently elevated. Zinc, cobalt, vanadium and molybdenum are not recovered in currently applied technologies. Moreover, extremely high content of organic carbon (Table 1) makes the Lubin concentrate not suitable for flash smelter.

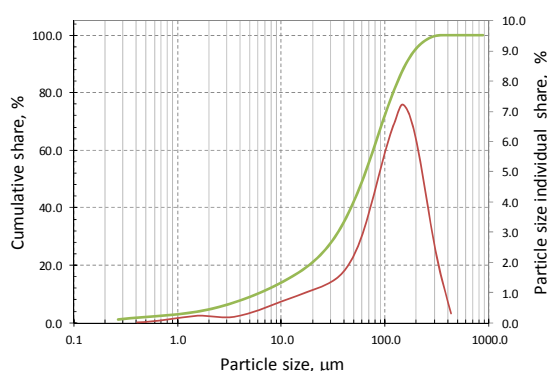


Fig. 1. Granulometric analysis of copper concentrate from Lubin Concentrator

Table 2. Maximum demand for sulphuric acid, organic and total carbon content and total sulphur content in two samples of Lubin flotation concentrate

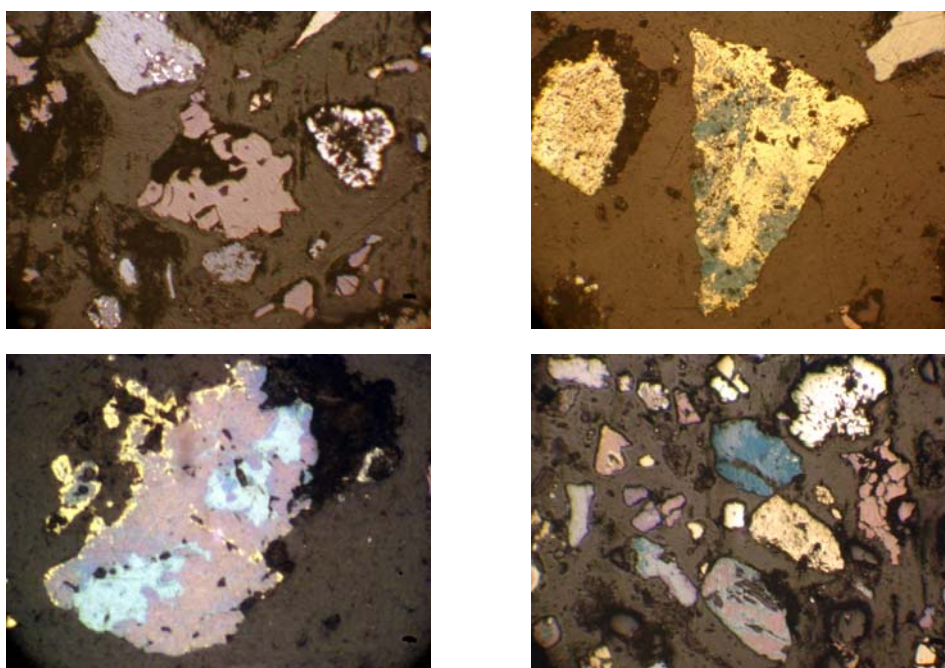
	Concentrate sample	Maksimum demand for H ₂ SO ₄ , $\zeta_{\text{H}_2\text{SO}_4}^{\text{max}}$	Organic carbon	Total carbon	Total sulphur	Particle size, D_{80}
		g H ₂ SO ₄ /kg				
1.	KLA	220	8.1	10.20	12.41	110-120
2.	KLB	260	8.1	10.19	12.40	110-120

Effective leaching of copper and accompanying metals from their sulphidic minerals is only possible when an oxidation agent is present in the leaching system. Gaseous oxygen and iron(III) ions were selected for this purpose, taking into account technical, economical and ecological aspects. Laboratory tests were performed at various temperatures (50, 70, and 90°C), various iron(III) concentration (0, 10, 20, 30 g/dm³) and constant concentration of sulphuric acid (50 g/dm³). The concentration – leaching time relationship for Cu, Zn, Fe, Ni, Co, and As, concentration of sulphuric acid and redox potential of the slurry during leaching was examined. The solid residue was examined for metals content and mineralogical SEM

observation were conducted to assess liberation of the remaining metals (mainly Ag and Pb) for further recovery.

Table 3. Mineralogical composition of copper ores - feed for flotation at KGHM „Polska Miedź” SA Concentrators (Luszczkiewicz and Drzymala, 2009)

Mean data 2007-2008	Bornite Cu_5FeS_4	Chalcocite digenite $\text{Cu}_2\text{S}/\text{Cu}_{1.8}\text{S}$	Chalko- pyrite CuFeS_2	Pyrite Markasite FeS_2	Covellite CuS	Sphalerite ZnS	Tennantite $\text{Cu}_{12}\text{As}_4\text{S}_{13}$	Galena PbS
Lubin	33.1	14.5	26.1	17.4	3.5	1.8	2.0	1.9
Polkowice	13.6	55.5	12.0	10.9	3.7	1.2	1.5	1.6
Rudna	24.8	40.4	7.2	15.0	5.8	3.1	1.5	2.3



Multimineral intergrowths of sulphide minerals in flotation concentrate from Lubin. Reflected light, original magnification about 120x

The Polish copper ores mined from the Lubin, Polkowice-Sieroszowice and Rudna deposits, in contrast to majority of world copper chalcopyrite (primary deposits), are of sedimentary origin and exhibit very favorable mineralogical composition with regard to hydrometallurgical processing. Chalcocite (Cu_2S) and bornite (Cu_5FeS_4) are the dominating, while chalcopyrite (CuFeS_2) and covellite (CuS) minor copper minerals (Table 3). Moreover, the presence of pyrite and marcasite, particularly in the Lubin ore, is expected to be beneficial for oxidative leaching, due to

the presence of galvanic contacts between copper mineral and pyrite – marcasite grains (Chmielewski and Kaleta 2010).

Detailed mineralogical analysis of the flotation feed for Lubin, Polkowice and Rudna Concentrators are given in Table 3. Photographs on page 201 exhibits examples of galvanic intergrowths existing in the examined concentrate. Consequently, one can expect rather high leaching recovery of copper and other base metals from by-products or concentrates even under mild conditions of atmospheric leaching. The presence of finely dispersed grains of copper sulphide in the shale-dolomitic gangue and sulphide-sulphide intergrowths is an additional beneficial factor, particularly after their chemical liberation by non-oxidative leaching.

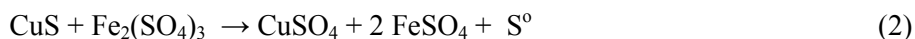
Separation of the Lubin concentrate exhibiting a very high content of organic carbon (Table 1 and 2) for alternative processing has an additional beneficial effect leading to reduction of organic carbon in the flash smelter feed, what is particularly significant for the Glogow II metallurgical plant. Presently, the observed elevated content of organic carbon in the concentrates already exceeds 8 % and is the main reason for undesirable, significant decrease in the smelter throughput (Kubacz and Skorupska 2007).

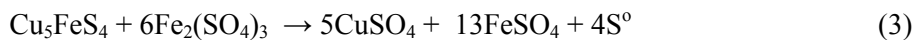
The leaching experiment were performed in a thermostatic, stirred 1 dm³ glass reactor with an oxygen sparger. The effect of temperature, Fe(III) concentration, and s/l ratio on the recovery of Cu, Zn, Ni and Co was examined. The samples of leaching slurry were taken during leaching, filtered and subjected to chemical analyses. Additionally, a potential of Pt electrode was monitored to evaluate leaching conditions.

3. Results and discussion

The leaching experiments of the Lubin concentrate under atmospheric conditions evidently showed that two parameters are most essential for the process kinetics and copper leaching efficiency: temperature (Fig. 2) and iron(III) concentration (Fig. 3). The results of experiments confirmed earlier expectations that due to the beneficial mineralogical composition of the concentrate (Table 3), copper can be relatively easily subjected to leaching. It is seen, that even in the solution without addition of iron(III) (Figs. 2 and 3) the process is quite fast and leads to the final concentration of Cu in the solution about 20 g/dm³.

The presence of iron(III) ions remarkably improves leaching conditions and process rates. The leaching process becomes much faster and the maximum concentration of copper can reach 25 g/dm³. According to experimental data shown in Fig.3, the initial concentration of 20 g/dm³ of Fe(III) in leaching solution is high enough for effective leaching of copper. The following chemical reactions can be attributed to the leaching of copper sulphides from Lubin concentrate:





Elemental sulphur is a dominating product of oxidation of sulphidic sulphur. To maintain the effective leaching conditions iron(II) sulphate has to be continuously regenerated to iron(III) sulphate by gaseous oxygen in the following reaction:

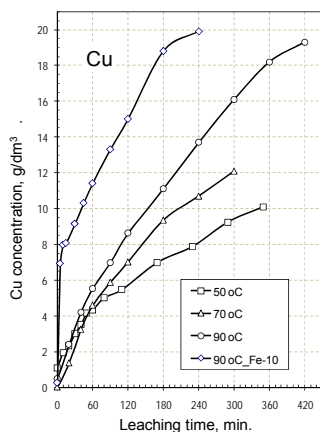
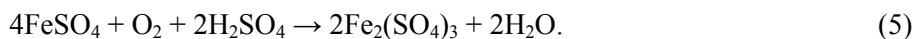


Fig. 2. Effect of temperature (50, 70 and 90°C) and presence of Fe(III) ions (10 g/dm³) on the Cu leaching rate from Lubin concentrate in oxygenated sulphuric acid (50 g/dm³). Solid/liquid = 1:8. Initial H₂SO₄ concentration – 50 g/dm³, oxygen flow rate – 30 dm³/h

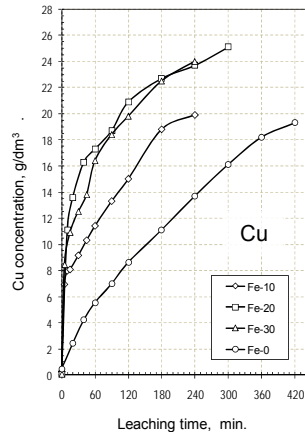


Fig. 3. Effect of concentration of Fe(III) ions on the Cu leaching rate from Lubin concentrate in oxygenated sulphuric acid (50 g/dm³) at 90°C. Solid/liquid = 1:8. Fe(III) conc. – 0, 10, 20 and 30 g/dm³. Initial H₂SO₄ concentration – 50 g/dm³, oxygen flow rate – 30 dm³/h

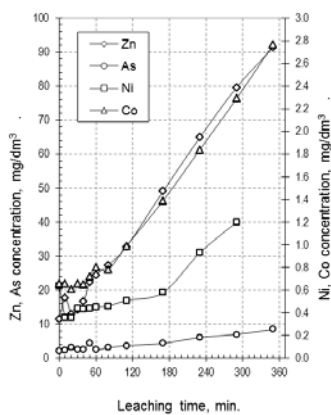


Fig. 4. Concentration – leaching time plots for Zn, As, Ni and Co during copper concentrate leaching in oxygenated sulphuric acid (50 g/dm³) at 90°C. Initial H₂SO₄ concentration – 50 g/dm³, s/l = 1:8, no Fe(III) added, oxygen flow rate – 30 dm³/h

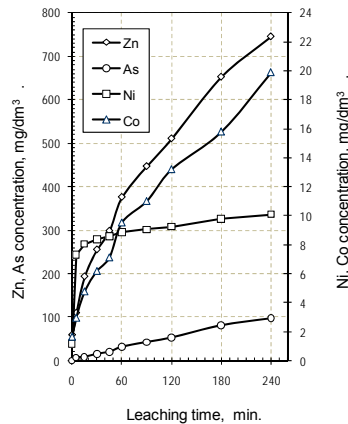


Fig. 5. Concentration – leaching time plots for Zn, As, Ni and Co during copper concentrate leaching in oxygenated sulphuric acid (50 g/dm³) at 90°C and presence of Fe(III) ions (30 g/dm³). Initial H₂SO₄ concentration – 50 g/dm³, s/l = 1:8, oxygen flow rate – 30 dm³/h

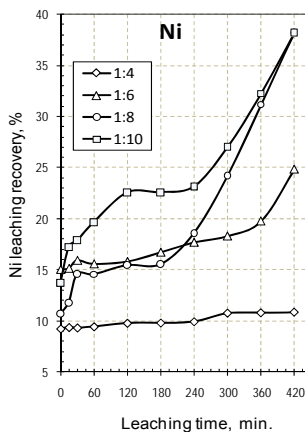


Fig. 6. Effect of solid/liquid ratio on the leaching recovery for nickel during copper concentrate leaching in oxygenated sulphuric acid (50 g/dm^3) at 90°C . Initial H_2SO_4 concentration – 50 g/dm^3 , temperature 90°C , Fe(III) conc - 30 g/dm^3 , oxygen flow rate – $30 \text{ dm}^3/\text{h}$

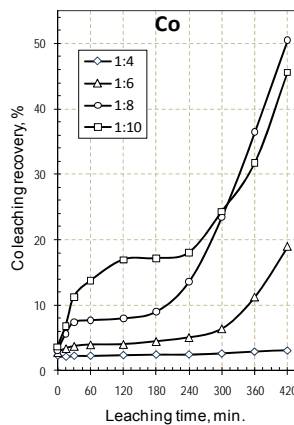


Fig. 7. Effect of solid/liquid ratio on the leaching recovery for cobalt during copper concentrate leaching in oxygenated sulphuric acid (50 g/dm^3) at 90°C . Initial H_2SO_4 concentration – 50 g/dm^3 , temperature 90°C , Fe(III) conc - 30 g/dm^3 , oxygen flow rate – $30 \text{ dm}^3/\text{h}$

According to leaching and regeneration reactions taking place during concentrate atmospheric leaching, one can evaluate that the need for oxygen and acid depends remarkably on the mineralogical composition of the leached feed and has to be determined by laboratory examinations.

Zinc, nickel, cobalt and arsenic were also leached from the copper concentrate. The effect of oxygen and Fe(III) on leaching rate of Zn, As, Ni and Co (Figs. 4 and 5) was similar to that observed for leaching of copper (Figs. 1 and 2). The leaching rate and concentration of metals remarkably increased in the presence of iron(III) ions (Fig. 5). From the shape of concentration–time plots for nickel and cobalt, we could preliminarily assume that both metals are entrapped or disseminated in particles of copper or iron sulphides. The leaching rate of Ni and Co increases with increasing recovery of copper.

The effect of solid/liquid ratio was examined on the recovery of nickel and cobalt during atmospheric leaching (Figs. 6 and 7). The results confirmed the previous assumption that the observed, after about 4 hours of leaching, acceleration of Ni and Co leaching can be attributed to dissemination of nickel and cobalt sulphides in the copper sulphide matrix. The observed recovery of nickel (about 40%) and recovery of cobalt (50%) are somewhat low and a further increase of this parameter will require a reduction of the particles size and further optimization of the leaching parameters. It can also be concluded that the s/l ratio is an essential leaching parameter and the process has to be conducted at s/l above 1:6. When the s/l ratio was 1:4, the observed recovery of Ni and Co was very low (Figs. 6 and 7).

Zinc, which according to the mineralogical examinations, was in the Lubin concentrate in the form of liberated particles of sphalerite, was found to be

surprisingly very easily leachable under atmospheric conditions (Figs. 8 and 9). It may suggest an important effect of a direct chemical reaction between sphalerite and sulphuric acid. Detailed examination of the effect of temperature and concentration of iron(III) on leaching of zinc exhibited that temperature of 90°C is recommended for zinc leaching. The optimum initial concentration of Fe(III) was found to in the range of 20–30 g/dm³.

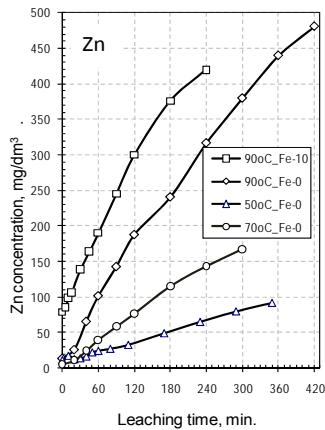


Fig. 8. Effect of temperature (50, 70 and 90°C) and presence of Fe(III) ions (10 g/dm³) on the Zn leaching rate from Lubin concentrate in oxygenated sulphuric acid (50 g/dm³). Solid/liquid = 1:8

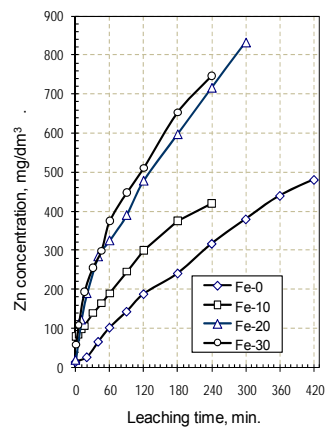


Fig. 9. Effect of concentration of Fe(III) ions on the Cu leaching rate from Lubin concentrate in oxygenated sulphuric acid (50 g/dm³) at 90°C. Solid/liquid = 1:8. Fe(III) conc. – 0, 10, 20 and 30 g/dm³)

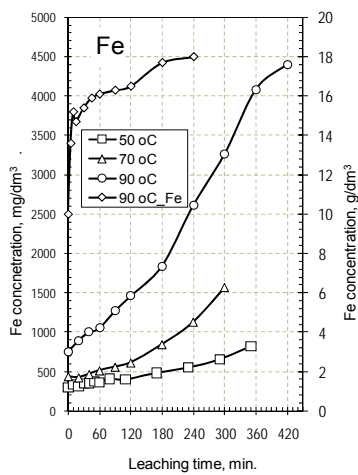


Fig. 10. Effect of temperature (50, 70 and 90°C) and presence of Fe(III) ions (10 g/dm³) on the Fe leaching rate from Lubin concentrate in oxygenated sulphuric acid (50 g/dm³). Solid/liquid = 1:8

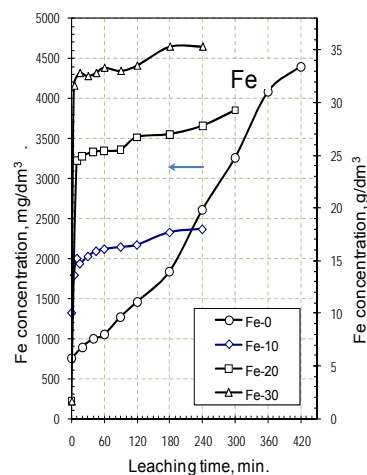


Fig. 11. Effect of concentration of Fe(III) ions on the Cu leaching rate from Lubin concentrate in oxygenated sulphuric acid (50 g/dm³) at 90°C. Solid/liquid = 1:8. Fe(III) conc. – 0, 10, 20 and 30 g/dm³)

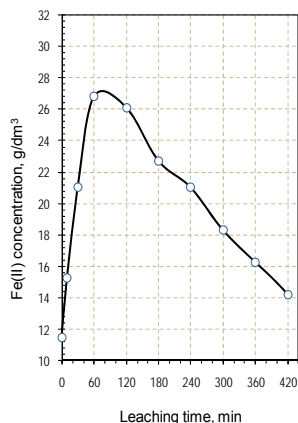


Fig. 12. Fe(II) concentration – leaching time during atmospheric leaching of Lubin concentrate in oxygenated sulphuric acid (50 g/dm^3). Solid/liquid = 1:8, Fe(III) conc. - 30 g/dm^3 , temperature 90°C , oxygen flow rate – $30 \text{ dm}^3/\text{h}$

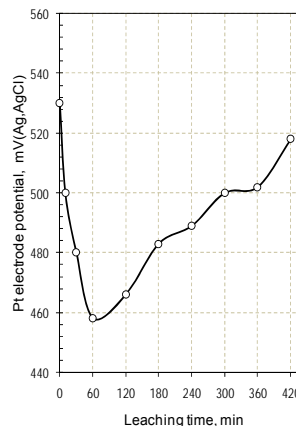


Fig. 13. Potential of Pt electrode – leaching time during atmospheric leaching of Lubin concentrate in oxygenated sulphuric acid (50 g/dm^3). Solid/liquid = 1:8, Fe(III) conc. - 30 g/dm^3 , temperature 90°C , oxygen flow rate – $30 \text{ dm}^3/\text{h}$

The presence of bornite, chalcopyrite and pyrite–marcasite results in leaching of iron to the solution. Even if iron(III) were initially not introduced to the solution, its concentration after 7 hours of atmospheric leaching at 90°C reached about 4.5 g/dm^3 (Fig. 10). When leaching process was performed in the iron(III) solution with initial concentration of 10 g/dm^3 the observed increase of Fe concentration was 8 g/dm^3 (Fig. 10). A similar increase of Fe(III) was observed during leaching at higher initial concentration of Fe(III) (Fig 11). The increase of concentration of iron(III) in leaching solution is undoubtedly beneficial for the copper leaching rate but the excess of Fe has to be reduced to an optimum level in downstream separation processes.

Two reactions take place during the examined process using iron(III) as a leaching medium. First is the leaching of copper or copper and iron with simultaneous formation of elemental sulphur and iron(II) ions (reactions 1–5). Second is the regeneration of Fe(II) to Fe(III) with gaseous oxygen (reaction 5). The rates of these processes are changing in the course of leaching and the momentary concentration of Fe(II) reflects their mutual relation (Fig. 12). In the first hour of the process leaching reaction rates are remarkably higher than regeneration of Fe(II) to Fe(III) and the concentration of Fe(II) increases rapidly. Subsequently, the leaching became slower than regeneration and Fe(II) concentration decreases with increasing concentration of Fe(III). Then, a favorable improvement of leaching conditions is observed.

The conditions of leaching can also be monitored by means of electrochemical measurements of potential of a Pt electrode immersed in the leaching slurry (Fig. 13). At the starting point of leaching the potential was 520 mV(Ag, AgCl) . In parallel to the increase of Fe(II) (Fig. 12) a decrease of Pt electrode potential was recorded down to nearly 430 mV . After about 1-2 hours, when regeneration rate was higher than leaching rate, the potential of Pt electrode was found to increase.

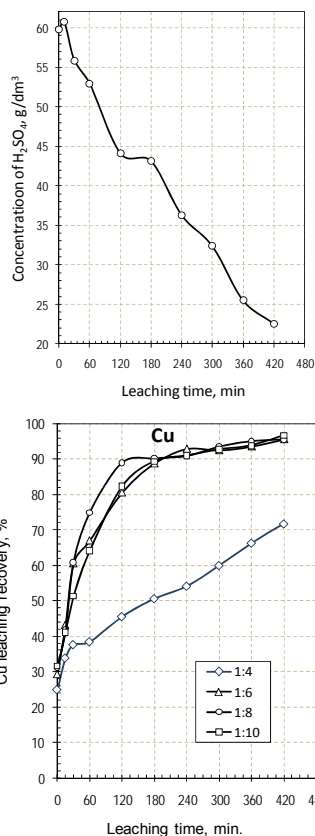


Fig. 14. Concentration of sulphuric acid during atmospheric leaching of copper concentrate at 90°C, initial concentration of Fe(III) – 30 g/dm³, oxygen flow rate – 30 dm³/h, and s/l - 1:4

Fig. 15. Effect of s/l ratio on the recovery of copper during atmospheric leaching of Lubin concentrate in oxygenated sulphuric acid (50 g/dm³), Fe(III) conc. - 30g/dm³, temperature 90 °C, oxygen flow rate – 30 dm³/h

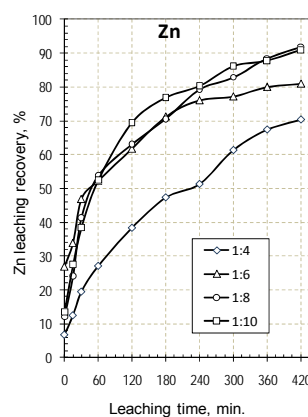


Fig. 16. Effect of s/l ratio on the recovery of zinc during atmospheric leaching of Lubin concentrate in oxygenated sulphuric acid (50 g/dm³), Fe(III) conc. - 30 g/dm³, temperature 90 °C, oxygen flow rate – 30 dm³/h

Sulphuric acid concentration is a parameter which has also to be monitored in atmospheric leaching. In numerous literature data the initial concentration of H₂SO₄ is recommended at the level of 50 g/dm³, as it was applied in this work. From the leaching reactions 1–4 we may assume that concentration of acid is expected to be constant. However, in the course of Fe(III) regeneration reaction (5), sulphuric acid is consumed. According to chemical analyses of acid concentration during leaching (Fig. 14), a decrease in the concentration by about 40 g/dm³ was observed. The magnitude of the decrease can vary with leaching parameters.

The results of atmospheric leaching were summarized for the best leachable metals - copper and zinc in the form of leaching recovery–time relationships (Figs. 15 and 16). It is well seen that copper recovery exceeds 90% after about 180 minutes of leaching at 90°C and at 30 g/dm³ of initial Fe(III). When the leaching time is 420

minutes the copper recovery reaches 95%. Zinc recovery was also surprisingly very high and reached 90% after 420 minutes of leaching. For both copper and zinc the s/l ratio from 1:6 to 1:10 is recommended. When s/l was 1:4 the efficiency of the process was too low to be acceptable.

4. Conclusions

Hydrometallurgy appears to be the only real chance for more rational utilization of the copper flotation concentrate of Lubin Concentrator. Hydrometallurgy, being more suitable for low grade feeds, can remarkably elevate copper recovery at ZWR Lubin and simultaneously produce metals, which are being lost for many years (Zn, Co, Mo, V). The advantageous chemical and mineralogical composition of the Lubin concentrate and easy access to sulphuric acid demonstrate the need for systematic and comprehensive research work on atmospheric and pressure leaching commenced at Wrocław University of Technology in HYDRO Project.

Leaching time, temperature, iron(III) concentration and solid/liquid ration are key parameters for atmospheric leaching of Cu, Zn, Ni and Co from the copper flotation concentrate from Lubin Concentrator. When the leaching process is conducted for about 7 hours at 90°C in oxygenated sulphuric acid acidic solution of Fe(III) at concentration of 20–30 g/dm³ and at s/l from 1:6 to 1:10 it is possible to recover above 95% of copper and 90% of zinc even without additional grinding of the feed.

The leaching recovery of Ni and Co from under the same conditions appeared to be much lower (from 40 to 50%) due to dissemination of nickel and cobalt sulphides in the copper sulphides matrix. Elevation of Ni and Co recovery is possible by additional grinding of the leaching feed and optimization of leaching parameters.

Atmospheric leaching conditions can be monitored by means of analysis of Fe(II) concentration as well as by measurement of the Pt electrode potential in leaching slurry.

Acknowledgements

This work was carried out in the frame of HYDRO project (Polish NCBiR project contract ZBP/56/66309/IT2/10). Authors acknowledge the financial support given to this project by the NCBiR (National Center for Research and Development) under the IniTech Enterprise. We also wish to thank our various partners of the project for their contributions to the work reported in this paper.

References

- Chmielewski T., Atmospheric leaching of shale by-product from Lubin concentrator, *Physicochemical Problems of Mineral Processing*, 41 (2007) 337-348.
- 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, Wrocław 2006, 125-145.

- Chmielewski T., Łuszczkiewicz A., Konieczny A., Kowalska M., Non-oxidative acidic treatment of copper sulfide concentrates in the flotation circuit, Proceedings of the 6th International Copper-Cobre Conference, Toronto, Canada 27-29 August 2007, Vol. II (del Villar R., Nasset J.E., Gomez C.O., and Stradling A.W. – Eds.), Can. Inst. Min. Metal. Petrol., 2007a, 53-62.
- Chmielewski T., Łuszczkiewicz A., Konopacka Ż., 2007b, Separation and concept of processing of black shale copper ore from Lubin Mine, 7th International Conference on Non-ferrous Ore Processing, May 21-23, Wojcieszycze, Poland, KGHM Cuprum, Wrocław 2007, 171-184.
- Chmielewski T., 2009, „Ługowanie atmosferyczne frakcji łupkowej jako alternatywa zmian technologicznych w ZWR Lubin”, Materiały XII Seminarium Lubin 17 Lutego 2009 (str. 37).
- Chmielewski T., Kaleta R., Galvanic interactions of sulphide minerals in leaching of flotation concentrate from Lubin Concentrator, Physicochemical Problems of Mineral Processing. 46 (2011) 21-34.
- Dreisinger D., 2006, Copper leaching from primary sulphides: 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 Miedź S.A., Proc. VIII International Conference on Non-ferrous Ore Processing, Wojcieszycze (Poland), May 21-23, KGHM Cuprum Wrocław 2007, 29-46.
- Gupta C.K., Mukherjee T.K., 1990, Hydrometallurgy in extraction processes, Vol. I and II, CRC Press.
- Habashi F., 1999, Textbook of hydrometallurgy, Metall. Extract. Quebec.
- Habashi F., 2005, Recent Advances in the Hydrometallurgy of Copper, Proc.Int. Copper Hydrometallurgy Workshop “Hydrocoper 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 Durtizac 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., Kasinska , 2009, Problemy Technologiczne I Techniczne Procesów Przeróbki Mechanicznej Rud Miedzi w Świetle Działalności i Roli Oddziału Zakładu Wzbogacania Rud KGHM, IX Międzynarodowa Konferencja Przeróbki Rud Metali Nieżelaznych, ICNOP Łądek Zdrój, 18 – 20 maj 2009.
- Konstantynowicz-Zielinska J. 1990, Petrology and genesis of the copper shale of the Foresudetic Monocline. Rudy i Metale Nieżelazne. Vol. 35, No. 5-6, 128-133 (in Polish).
- Kubacz N., Skorupska B. 2007. Estimation of influence of organic carbon on concentration and smelting processes. Conf. Proc. VIII International Conference On Non-ferrous Ore Processing, ICNOP’07, 21-23 May, Wojcieszycze, Poland, KGHM, IMN, 157-166 (in Polish).
- Łuszczkiewicz A. 2004, Evaluation of upgradeability of the ore with elevated content of black shale Report of Investigation, Archive of Laboratory of Mineral Processing, Wrocław University of Technology, Wrocław, (in Polish).

- 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., Chmielewski T., 2008, Acid treatment of copper sulfide middlings and rougher concentrates in the flotation circuit of carbonate ores, *Int.J.Min.Process* 88, 45-52.
- Luszczkiewicz A., Konopacka Z., Drzymala J., 2006, Flotation of black shale of Polish copper ore from Lubin. Proceedings: Perspectives for applying bioleaching technology to process shale-bearing copper ores, *BIOPROCOP '06*, Lubin, June 19, 2006, Publ. KGHM Cuprum Sp. z O.O., Wroclaw 2006, 29-47, in Polish.
- Luszczkiewicz A., Drzymala J., 2009. Possibility of reduction of lead, arsenic and organic carbon content in copper concentrates. *Physicochem. Prob. Min. Process.*, 44th Seminar, Niepolomice, Plenary Lecture (in Polish).
- Lętowski F., 1975, *Podstawy hydrometalurgii*, WNT, Warszawa.
- Marsden J.O., 2007e, Sulphate-based flowsheet options for hydrometallurgical treatment of copper sulphide concentrates, *The John Dutzic Symposium on Copper Hydrometallurgy, Proceedings 6th International Copper-Cobre Conference, August 25-30, 2007, Toronto, Canada, vol. IV, Met. Soc.*, pp.77-100.
- 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., Brewer, B. and Hazen, N., 2003, *Copper Concentrate Leaching Developments by Phelps Dodge Corporation, Hydro 2003, TMS Warrendale, 1429-1446.*
- 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 Dutzic Symposium on Copper Hydrometallurgy, Proceedings 6th International Copper-Cobre Conference, August 25-30, 2007, Toronto, Canada, vol. IV, Met. Soc.*, pp.101-128.
- Rydzewski A., 1996, Lithology of the deposit rocks. In: A. Piestrzynski (Ed.) *Monography of KGHM Polska Miedź S.A., CPBM Cuprum Sp. z o.o. Publisher, Lubin, 137-141 (in Polish).*
- Tomaszewski J., 1985, The problems of the efficient utilization of copper- polymetallic ores in the Foresudetic Monocline. *Physicochemical Problems of Mineral Processing, Vol. 17, 131-141 (in Polish)*