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DEVELOPMENT OF A HYDROMETALLURGICAL TECHNOLOGY FOR PRODUCTION OF METALS FROM KGHM POLSKA MIEDZ S.A. CONCENTRATES

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Abstract: Rapidly declining quality of copper concentrates produced by Lubin Concentrator of KGHM Polska Miedz SA, having very low content of Cu, high content of Pb, As and organic carbon as well as significant contents of Ag, Co, Ni, Zn, Re, V and Mo, makes the concentrates difficult-to-process by flash smelting. Currently hydrometallurgy, using sulfuric acid in the presence of iron(III) and oxygen as a leaching medium for base metals and chloride leaching for silver and lead, seems to be an alternative for pyrometallurgy. The goal of the work is to discuss main aspects of the necessity of application a new hydrometallurgical technology, based on different unit operations, including non-oxidative atmospheric, chloride and pressure leaching, recovery of Pb and Ag, separation of Cu and accompanying metals from PLS and arsenic neutralization. The unique lithological, mineralogical and chemical properties of the process feed were discussed in details. The results of laboratory investigations performed at the Wroclaw University of Technology and assumptions of the process scale-up for acquisition of data for full scale technology were summarized. Planned investigations on the pilot plant scale will provide technical and economic data for a pre-feasibility study of the future hydrometallurgical plant.

Keywords: *hydrometallurgy, copper concentrates, leaching*

Introduction

The declining quality of Polish copper ores reflects general unfavorable trends observed in the World copper metallurgy. These negative trends are perceived in particular at the Lubin plant of KGHM, where the most complex and hardest-to-treat ores are mined and beneficiated. There, for years, deteriorating properties include a decreasing copper and silver content in the feed (Figs 1 and 2) and growing amount of shale fraction (Table 1) as well as increasing impurities such as Pb, As and organic carbon. These properties essentially affect the decreasing copper and silver content in flotation concentrates (Fig. 3), considerably reducing recovery of the produced metals

(Fig. 3) and become the main reason for growing technological concerns both in flotation and flash smelting, creating high costs of copper production.

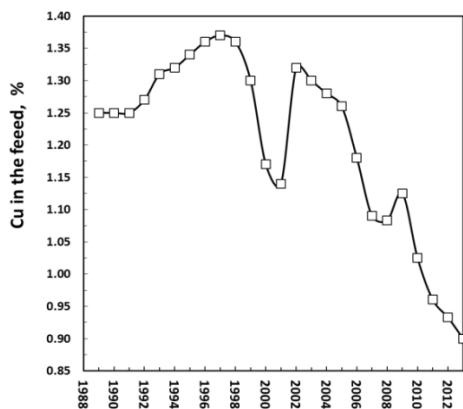


Fig. 1. Decreasing content of Cu in the feed of Lubin Concentrator (after Kukuc and Bazan, 2013)

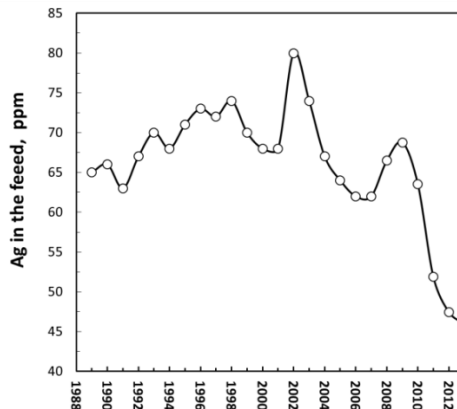


Fig. 2. Decreasing content of Ag in the feed of Lubin Concentrator (after Kukuc and Bazan, 2013)

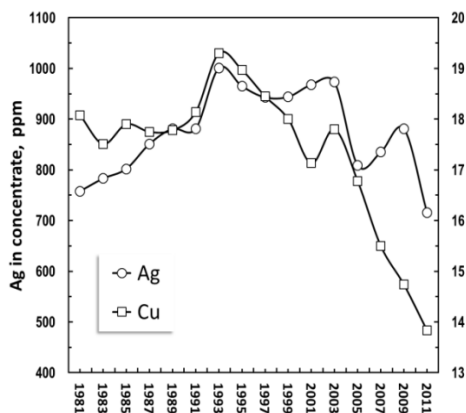


Fig. 3. Lubin concentrate grade from 1981 to 2012 (after Kukuc and Bazan, 2013)

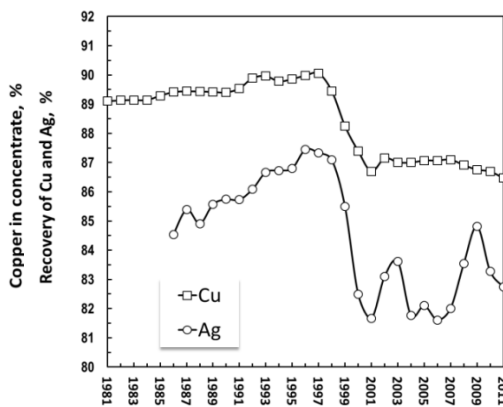


Fig. 4. Decrease of Cu and Ag recovery in Lubin concentrate from 1981 to 2012 (after Kukuc and Bazan, 2013)

The application of modern either hydro- or biometallurgy, well recognized and already approved in the world for copper recovering, becomes an urgent necessity for the Polish copper industry in order to reverse the mentioned unfavorable trends. The application of atmospheric and pressure leaching methods for copper concentrate processing have been recently investigated at the Wroclaw University of Technology as a complimentary process for treating copper concentrates and by-products from ZWR Lubin, which are difficult-to-beneficiate using the existing technologies. The

idea of application of hydrometallurgy at KGHM was previously considered by different authors and extensively investigated within the period from 2004 to 2007 in the BIOSHALE project financed by the European Commission in the VI Framework Project. The BIOSHALE project was carried out by 16 European universities and leading research institutions, including the Wroclaw University of Technology and KGHM Cuprum. The concept of application of either hydro- or biometallurgy for Lubin shale middlings was based on separation of the troublesome shale-enriched material (middlings) from the flotation circuits for a separate hydrometallurgical processing.

The role of hydrometallurgy as an alternative for production of copper and other accompanying metals has been growing for years. Nearly 25% of the world copper production is due to hydrometallurgy using sulphate, sulphate/chloride and chloride solutions. Significant progress have been recently made in advancing the use of hydrometallurgy for copper ore and concentrate treatment. Currently, at least five separate sulphate-based commercial plants have started or are under construction for copper recovery. These include the Mt. Gordon Copper Process (Richmont 2004, Richmont and Dreisinger 2002, Dreisinger et al. 2002), Phelps Dodge Total Pressure Oxidation (King et al., 1993, King and Dresinger 1995), Alliance Copper BIOCOP Process (Batty and Rorke 2005), the Oxiana Sepon Copper Process (Baxter et al., 2003) and InMet Las Cruces Copper Process (Smalley and Davis 2000). The Activox (Evans 1999), CESL (Jones 1999, CESL web page 2011), Dynatec (Barta 1999) and Xtrata Albion processes have been known for some time and are well represented in the literature.

The hydrometallurgical methods based on sulphate or mixed sulphate/chloride solutions and stirred tank leaching are currently at different development stage (Table 1). The optimum for parameters of leaching depends on feed mineralogy, metals dissemination, and concentration of accompanying metals. There is no versatile hydrometallurgical technology for copper concentrates, which can be applied for each leaching feed. It requires comprehensive investigations on laboratory and pilot scales combined with supplementing analyses and advanced measurements for products characterization. This article will focus on more recent sulphate process developed for very specific Polish sedimentary copper ores and concentrates which contain carbonate gangue.

Even though numerous hydrometallurgical processes are currently at different stages of development (Table 1), none of them can be considered as directly applicable for the KGHM flotation sulphide concentrates having a unique mineralogical and chemical composition. A high content of the carbonate gangue, very complex multimineral and multimetallic composition, dissemination of metals in sulphide and carbonate matter, high content of lead and silver, elevated organic carbon concentration and the presence of arsenic require a very specific and individual approach. An important criterion for selection of leaching environment for the KGHM

concentrates is an easy access to sulphuric acid, selected as the leaching medium, which is being produced in the KGHM-owned smelters (~ 650 gigagrams per year).

Table 1. Sulphate-based copper hydrometallurgical processes (stirred tank leaching) for sulphide ores and concentrates at different status of development

Process	Status	Temp. °C	Pressure atm	Regrind d_{80} , μm	Special conditions
AA-UBS Process	Pilot plant	150	10–12	10-15	Reground chalcopyrite pressure leaching with addition of surfactant
CESL Copper Process	Demo plant	140–150	10–12	37	Chloride assisted pressure sulphate leaching of chalcopyrite
Dynatec Process	Pilot plant	150	10–12	37	Pressure leaching of chalcopyrite using low grade coal as additive
Mt. Gordon Process	Commercial	90	8	100	Pressure leaching of chalcocite/pyrite ore in Fe(III) solution
Platsol Process	Pilot plant	220–230	30–40	15	Total pressure oxidation in the presence of 10–20 g/dm ³ NaCl. Precious metals leached in one step
Sepon Copper Process	Commercial	80 °C – Cu 230 °C – FeS ₂	1 at 30-40	100 50	Atmospheric leach for copper from Cu ₂ S. Pressure leaching of FeS ₂ to produce H ₂ SO ₄ and Fe ³⁺ for copper leaching
Total Pressure Oxidation Process	Commercial	200-230	30–40	37	Extreme conditions of <i>T</i> and <i>p</i> designed to rapidly destroy chalcopyrite and other sulphides
Las Cruces Copper Process	Commercial	90	1	100	Atmospheric leach of copper from sulphide ore using oxygenated and acidified Fe(III)

Current state of copper production at KGHM

An analysis of flotation indices at all KGHM concentrators reveals a descending trend for both metals recovery and concentrate grade. This tendency is particularly visible at the Lubin Concentrator (ZWR Lubin), where copper recovery currently only slightly exceeds 86% and the copper content in the concentrate is only about 14%. This concentrate is now almost not acceptable for processing by flash smelting, and has to be subjected to more effective and alternative processing methods. A similarly unfavorable trend has been also observed for silver in the form of decreasing grade

(about 700 g/Mg) and recovery (83 %) (Kukuc and Bazan, 2013). Despite an appreciable content of other accompanying metals (Pb, Zn, Ni, Co, Re, Mo, V), some of them are either recovered only partially (Pb, Ni) or not at all (Zn, Co, V, Mo). Currently, the used technology at ZWR Lubin reached a limit of its efficiency and it is a major reason of growing metals losses and increasing production costs.

Unique properties of Polish copper ores and concentrates

Polish LGOM copper deposits exhibit unique, sedimentary and complex nature. It results in the presence of three lithological ore fractions: dolomitic, sandstone, and shale (Table 2). Among the three ore fractions, the shale component reveals two exceptional and contradictory properties. Although the shale exhibits the highest concentrations of copper and accompanying metals (Ag, Ni, Co, Zn, Pb, Re, V, Mo) it is simultaneously the most troublesome in terms of flotation upgradeability. Fine dissemination of metal sulfides in the carbonate matter and black shale - clay rocks, that form the majority of the gangue, is observed. Such a fine dissemination of copper sulfides in the carbonate-organic matrix considerably reduces the susceptibility of the ore to both effective sulphides liberation and to froth flotation.

Table 2. Composition of lithological ore layers and content of copper, silver, and organic carbon in feed of KGHM copper concentrators in nineties (Luszczkiewicz, 2000) and in 2004 (Luszczkiewicz, 2004)

Ore component	Rudna		Polkowice –Sierszowice		Lubin	
	'90s	2004	'90s	2004	'90s	2004
Carbonate ore %	51.0	33.0	84.0	75.0	38.0	25.0
Shale ore, %	5.0	11.0	6.0	17.0	8.0	15.0
Sandstone ore, %	44.0	56.0	10.0	8.0	54.0	60.0
Cu content, %	2.05	2.23	1.81	2.0	1.36	1.28
Ag content, g/Mg	47.0	53.0	34.0	40.0	68.0	67.0
C _{org} content, %	0.64	1.49	1.14	1.66	1.76	1.62

A relative increase of concentration of shale-clay and carbonate fractions in the flotation feeds, which are known as hard-to-treat in flotation circuits, is currently observed. According to the latest data, the content of the shale fraction in the Lubin deposit is about 15% and occasionally can reach 25% (Kubacz and Skorupska, 2007). It was found that separation of the shale middlings from the Lubin flotation circuit for alternative, either by bio- or hydrometallurgical treatment (Fig. 5), could be considered as one of the ideas of intensification of metals recovery at KGHM (Chmielewski and Charewicz, 2006; Chmielewski et al., 2007). The results of comprehensive laboratory investigations indicated, that the main reason for the observed metal losses in flotation was fine dissemination of sulphides in the shale-carbonate fraction (Fig. 4 and Table 2).

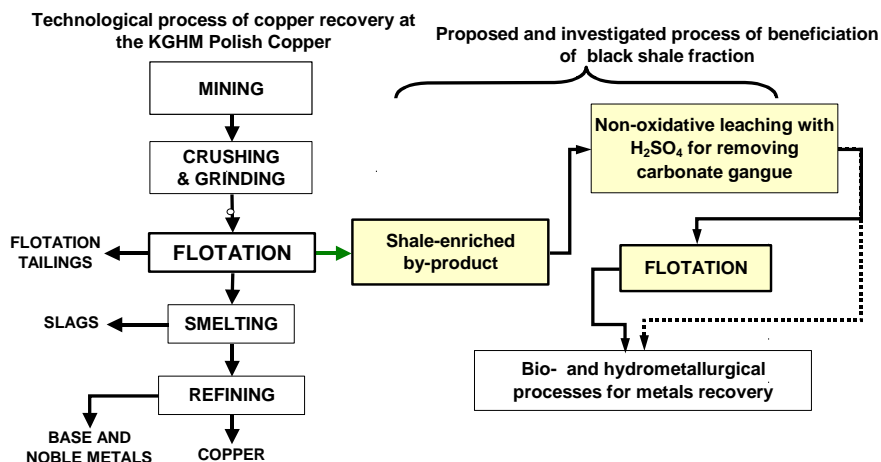


Fig. 5. General BIOSHALE concept of separate processing of black shale ore fraction from Polish copper deposits

The application of non-oxidative leaching for carbonate decomposition (Luszczkiewicz and Chmielewski, 2008; Chmielewski, 2007; Chmielewski et al., 2008; Chmielewski et al., 2007; Konopacka et al., 2007), followed by either atmospheric or pressure leaching and metals separation from PLS using solvent extraction (Chmielewski and Charewicz, 2006; Chmielewski, 2007; Wodka et al., 2007; Chmielewski and Wodka, 2010; Rotuska and Chmielewski, 2007), were considered as a complimentary way for processing of shale flotation by-product at ZWR Lubin, which is exceptionally difficult to beneficiate using existing techniques. This approach, presented by the author within the research program of BIOSHALE (Chmielewski and Charewicz, 2006; d'Hugues et al., 2007; d'Hugues et al., 2008) primarily involved the separation of the most troublesome ore fraction (shale containing middlings) from the flotation circuit and introduction of hydrometallurgical methods for their alternative, effective processing. All development concepts for processing of the Lubin-Glogow complex sedimentary copper ores were summarised by Chmielewski et al. (2014).

Table 3. Mineralogy of flotation feeds at KGHM Lubin Concentrators (2007-2008) (Luszczkiewicz, 2009)

Bornite %	Chalcocite digenite %	Chalcopyrite %	Pyrite marcasite %	Covellite %	Sphalerite %	Tennantite %	Galena %
33.1	14.5	26.1	17.4	3.5	1.8	2.0	1.9

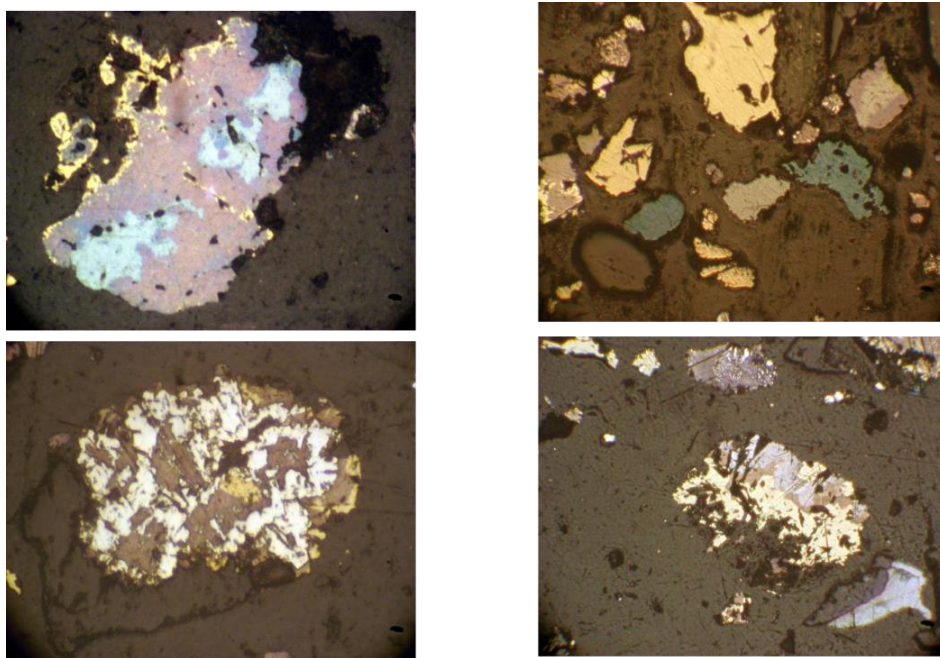


Fig. 6. Mineralogical images of polymineral Lubin concentrate (fraction $> 71 \mu\text{m}$) indicating possible and beneficial, for hydrometallurgy, galvanic interactions between minerals during leaching

The unique properties of Polish copper ores and concentrates make them very suitable for hydrometallurgy. Sedimentary copper ores from all three LGOM deposits (Polkowice, Rudna, Lubin) exhibit specific polymetallic and polymineral composition (Table 3). Bornite and chalcocite are generally dominating copper-bearing sulphides, with chalcopyrite and covellite as minor components. This is a very advantageous element for hydrometallurgical treatment, since chalcocite and bornite are the easiest leachable copper sulphides, in contrary to chalcopyrite, being the most refractory in leaching. Additionally, the Polish copper ores contain pyrite and marcasite, minerals which are well known as galvanic activators in leaching of sulphides.

Electrochemical nature of sulfides flotation (Chanturija and Vigdergauz, 2009) and leaching along with electrocatalytic properties of pyrite has already been described (Majima and Peters, 1968; Nowak et al., 1984; Holmes and Crundwell, 1995) and used for leaching of copper sulphidic concentrates in the Galvanox Process (Dixon and Mayne, 2007), where finely ground FeS_2 is added to the leaching slurry to intensify the process in a galvanic manner, by facilitating the charge transfer from the oxidant to dissolved sulfide. The presence of numerous sulphidic copper, iron, zinc and lead minerals in the feed to leaching coming from the Lubin Concentrator (Fig. 6) can advantageously result in mutual electrochemical interactions caused by different potentials attained by sulfides in leaching conditions. These interactions have already been examined for conditions of non-oxidative leaching of the Lubin shale middlings

(Kowalczyk and Chmielewski, 2010) and for atmospheric leaching conditions (Chmielewski and Kaleta, 2011) and are expected to create significant acceleration of copper leaching by forming a vast number of intergrowths and inter-mineral galvanic cells, which remarkably elevate the leaching rate.

Recently, hydrometallurgy has been investigated at the Wrocław University of Technology for improving Cu and accompanying metals recovery from Lubin flotation concentrates (Project HYDRO supported by NCBiR – National Centre for Research and Development, Poland). Advantageous for hydrometallurgy composition of these concentrates (Table 3, Figs 6 and 7) and rapidly declining Cu and Ag grade within the years of 2009-2013 (Table 4) indicate a necessity of essential technological changes and applications of hydrometallurgy for concentrate alternative treatment.

Table 4. Metals content in Lubin flotation concentrate within the years of 2009-2013

Year	Cu %	Zn %	Ni g/Mg	Co g/Mg	Ag g/Mg	Pb %	As %	V g/Mg	Mo g/Mg
2009	15.85	0.947	415	1040	na	2.67	0.290	-	-
2010	15.26	0.928	488	1206	938	na	0.343	569	265
2011	14.56	0.570	483	1250	755	na	0.258	672	221
2012	13.98	0.712	461	1325	736	4.48	0.313	670	257
2013	12.87	0.740	494	1482	455	5.42	0.266	657	272

Table 5. Metals content and quantity of metals in Lubin “high-in-recovery” flotation concentrate

Metal content in concentrate										
Cu, %	Zn, %	Ni, g/t	Co, g/t	Fe, %	Pb, %	Ag, g/t	As, %	V, g/t	Mo, g/t	Z _{max} ^{H2SO4} (kg/t)
7,42	0,436	498	1251	5,09	4,94	429	0,161	942	292	235
Metal quantity in concentrate, Mg/year										
66 800	3 930	449	1129	45 810	44 593	387	1 450	850	263	-

As a result of comprehensive laboratory studies and detailed analysis of possible leaching feed, both the final concentrate and the Lubin “high-in-recovery” concentrate, with lower Cu content (about 7%) and significantly elevated metal recovery (from 88 to 95%), were selected as the leaching feed (Tables 4 and 5). However, the suitability of the “high-in-recovery” concentrate was not confirmed by economical evaluation of the project, and the final concentrate currently produced at the Lubin Plant was indicated as more encouraging as a feed for hydrometallurgy, on the basis of laboratory investigations.

The mineralogical composition of the “high-in-recovery” Lubin concentrate (Fig. 7) is very beneficial for hydrometallurgy. Copper is in the form of two dominating minerals: bornite and chalcocite/digenite. Moreover, the content of

accompanying metals (Pb, Zn, Co, Ni, Re, V, Mo) in the concentrate is also very high and comparable with final flotation concentrate (Table 4). Zn, Co, Mo and V are still underestimated components and are not recovered by the current technologies.

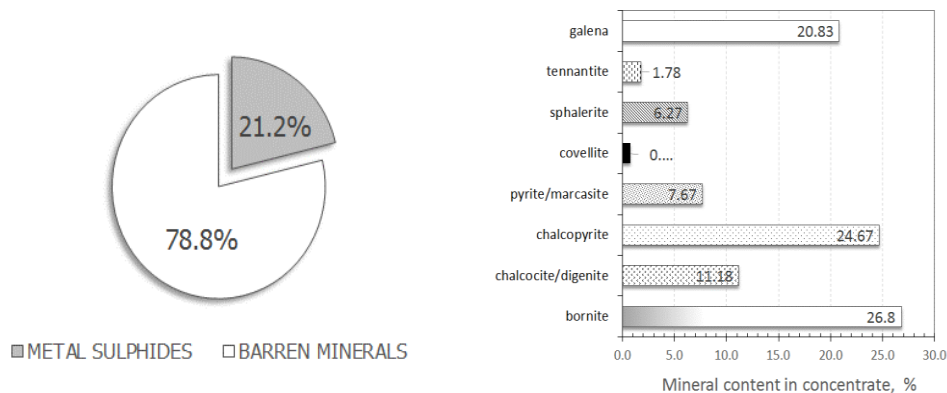


Fig. 7. Mineralogy of “high-in-recovery” Lubin concentrate used for hydrometallurgical investigations

A systematic control of mineralogical parameters of the feed, by-product and solid residues is a principal issue for every unit operation and at every stage of the process. Optical microscopy analyses, SEM examinations as well as MLA analysis are necessary for mineralogical assessment. The content of carbonate matter and acid-consuming components should be determined as a so-called Z_{\max} parameter, which is the amount (mass in kg) of H_2SO_4 required for total decomposition of these compounds per one megagram of concentrate. The procedures for such determinations were elaborated in our laboratory.

Hydrometallurgical processing

A commercial final flotation concentrate, containing about 14% of Cu, from the Lubin Concentrator and a “high-in-recovery” concentrate, being a low grade material (about 7.5% of Cu), were used for the hydrometallurgical processing to get general information about copper ores beneficiation properties. Basing on the obtained data a flowsheet was created (Fig.8). According to the flowsheet the non-oxidative leaching, a controlled decomposition of acid-consuming compounds (mainly Ca and Mg carbonates) with sulphuric acid, will be the initial chemical unit operation followed by separation of precipitated gypsum by flotation and separation of magnesium in soluble form of $MgSO_4$. The magnesium sulphate solutions will be a possible source of magnesium for manufacturing of MgO for either refractory ceramic or magnesium metal production by silicothermal reduction. The first step of Mg recovery includes purification of the solution by hydrolytic precipitation and/or cementation, followed by $MgSO_4$ crystallization. Finally, thermal conversion of $MgSO_4$ to MgO will be carried out.

The principal leaching operation to dissolve Cu, Zn, Co, Ni, Re, V and Mo will be conducted in sulphuric acid solutions containing iron(III) sulphate as necessary oxidant and gaseous oxygen for regeneration of Fe(II) to Fe(III) during leaching (Chmielewski et al., 2011; Gibas et al., 2014). The leaching process will be performed in stirred tanks under atmospheric conditions at temperature 90-95 °C, selected solid/liquid ratios (from 1:10 to 1:4), and controlled stirring and oxygen flow rates. The polymineral composition of examined concentrate and presence of pyrite appeared to be beneficial for leaching due to the formation of galvanic contacts facilitating both leaching rate and metals recovery.

As an alternative to atmospheric leaching, pressure leaching in sulphuric acid solutions, under elevated oxygen pressure (from 2 to 20 atm) and temperature (from 120 to 180° C), will be recommended as a method of process intensification. This intensive pressure leaching, performed in stirred pressure reactors (autoclaves), was found to be very effective during laboratory examinations in terms of high metals recovery and short leaching time. Neither Ag nor Pb will be leached in sulphate environment and will require an additional unit operation for recovering.

The suspension after leaching operations will be subjected to CCD decantation and filtration for phase separation. The PLS will be subsequently subjected for purification and metals separation by means of SX (Solvent Extraction) and IX (Ion Exchange), whereas a solid residue will be a feed for further leaching of Ag and Pb in chloride solutions (concentrated NaCl). The solution after stripping will be used in the EW process to produce metallic cathodic copper of high quality.

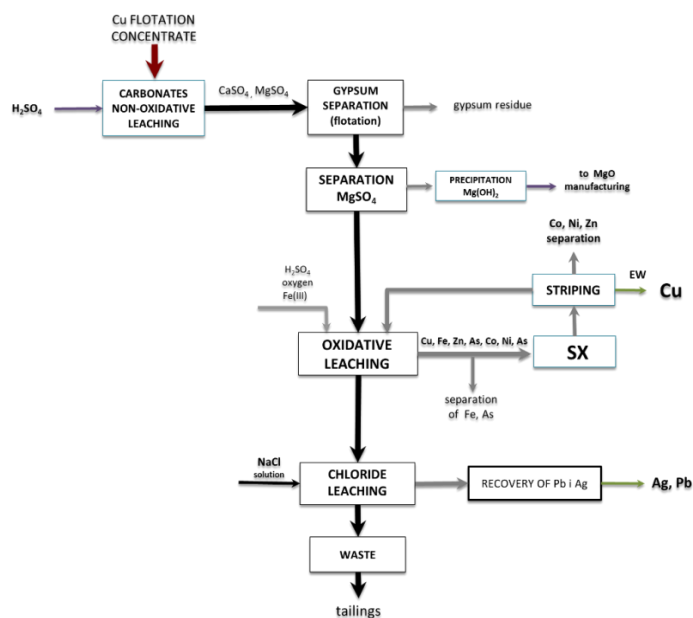


Fig. 8. General flowsheet of hydrometallurgical processing of Lubin flotation concentrate

Solvent extraction (SX) is a separation process typically used to isolate the solutes from solutions, as well as their separation and concentration. During the HYDRO research project, different flotation concentrates were leached (Chmielewski et al., 2011, Gibas et al., 2014), resulting in solutions of varying composition, particularly with regard to copper(II). Initially, the metal concentration in PLS reached 30 g/dm^3 , while in the final stage low-grade material was selected for leaching, which resulted in solutions containing up to 10 g/dm^3 of Cu. In the initial stages of the HYDRO project, three commercial hydroxyoxime reagents were tested as copper(II) extractants: LIX 984N, LIX 612 and N-LV Acorga M5640. The effect of diluent on extraction efficiency was also considered. In this case two commercial reagents differing in the content of aromatic compounds were compared: Escaid 100 (20%) and Escaid 110 (<0.5%) (Ochromowicz and Chmielewski, 2013). Due to the high acidity of PLS, neutralization of the excess acid was suggested using raw concentrate (containing carbonate), or alkali, such as CaCO_3 , in order to increase Cu(II) extraction efficiency.

The obtained results exhibited that the best extraction system was 30% (v/v) + Acorga M5640 Escaid 110. The preliminary flowsheet concept developed assumes the need of partial copper extraction from 30 g Cu/dm^3 to 10 g Cu/dm^3 and recycling the raffinate to the leaching operation. We have also assumed that it will be feasible to produce electrolyte containing at least 40 g Cu/dm^3 in the stripping section, which will be used in the copper electrolysis. In the later stages of the research the Cu/Fe extraction selectivity was also investigated. It was shown that transfer of iron between ongoing operations can be effectively controlled and thus washing operation between extraction and stripping operations was suggested. Few simulations of countercurrent extraction process were performed in order to compare two models: with wash stage (2-1-2) and without washing (2-0-2). Significant reduction in the concentration of iron in strip solutions in 2-1-2 model was noticed when compared to the 2-0-2 model.

In further stages of HYDRO project, the extraction of zinc(II) from solutions simulating CuSX raffinates, assuming complete elimination of Fe was studied. Two commercial organophosphorus acids: D2EHPA and Cyanex 272 were chosen as Zn(II) extractants. These studies have shown that Zn(II) extraction efficiency is significantly improved at elevated temperatures, and that much better results were obtained for D2EHPA system. It was also proved that it is possible to effectively strip loaded organic phase using H_2SO_4 solutions.

In the closing phase of the project, a final choice of material for leaching was made. Therefore the composition of pregnant leach solution has drastically changed, especially with respect to copper(II). Despite this change Acorga M5640 in Escaid 110 was still proposed as the best extraction system for Cu(II).

While maintaining the previously proposed extractant concentration in the organic phase Cu, extraction efficiency can reach from 72 to 96%, depending on whether the PLS is subjected to neutralization prior to the first extraction step. Solutions directed to electrolysis contain about 50 g/dm^3 of Cu.

Separation of Ag from chloride leach solution can be accomplished by cementation on metallic lead. Pb will be precipitated from chloride solutions in the form of lead carbonate (using soda or CO_2). Precipitate can be then used for production of Pb bullion in existing plant at the Glogow smelter.

The solid residue after the oxidative leaching contains considerable amount of elemental sulfur and organic carbon. It is necessary to develop a method of carbon and sulphur elimination from the sludge and management of the gaseous phase from the process. The proposed process will involve a roasting operation. It allows to reduce the flow of material streamed to the extraction of lead and silver with simultaneously enrichment in these components. The management of the gaseous phase allow to utilize SO_2 and simultaneous heat recuperation, which is produced during combustion of carbon and sulfur. It is expected that as the result of such process, the material with more favorable chemical properties will be obtained. It will increase the lead and silver extraction efficiency and make the final residue sustainable management possible.

Investigations of Zn, Ni, Co, Re, V and Mo recovery processes will be possible only after performing continuous operation using laboratory and pilot installations. It is necessary to achieve solutions with the appropriate concentration of these metals (recirculation). Combinations of different hydrometallurgical techniques like oxyhydrolysis, precipitation, cementation, SX, IX and crystallization will be used in the tests of the metals recovery in form of saleable chemical compounds like either $\text{ZnCO}_3/\text{ZnSO}_4$, NiSO_4 , CoSO_4 , NH_4ReO_4 , V_2O_5 , MoO_3 or metals concentrates.

In the process, it is necessary to control the iron concentration in the leach solutions by its precipitation as goethite, jarosite and hematite. The application of hydrothermal hydrolysis at elevated temperatures is also considered. The process can also control the concentration of As in the leaching – SX circuits by hydrothermal or atmospheric precipitation of scorodite: $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$, the safest form of arsenic for storage.

Unit operations of the new technology

The proposed hydrometallurgical processing of the Lubin copper concentrate is a sum of a great number of single unit operations. They include various mineral processing, hydrometallurgical and thermal techniques, comprising:

- non-oxidizing leaching of magnesium and calcium (controlled decomposition of barren rock dolomites with the solution of sulfuric acid),
- decantation and filtration of magnesium sulphate for further treatment and application,
- froth flotation: at the stage of feed preparation and initial treatment of the concentrate for testing and its purification after the non-oxidizing leaching operation (gypsum removal by flotation),
- oxidative leaching of the concentrate valuable and barren components, including acidic oxidizing leaching of the key sulfide valuable components (Cu, Zn, Ni, Co,

V, Re, Mo) with the oxygenated solution of sulfuric acid in the presence of Fe(III) at elevated temperatures (atmospheric and pressure processes),

- chloride leaching of silver and lead,
- various techniques of phase separation (sedimentation-decantation, pressure filtration),
- solvent extraction (SX) - for PLS purification and metals separation: copper, zinc, cobalt and nickel, in systems operating in counter-current mode,
- ion-exchange (IX) separation of metals from recirculation solution in leaching – SX circuit; ion-exchange columns for recovering associated metals (e.g. Re, V, Mo),
- electrodeposition of copper (EW) from strip solutions or directly from pressure leaching PLS,
- precipitation and cementation for recovery of silver and lead from brine solutions, as a method for production of concentrates of the metals,
- crystallization for recuperation of magnesium salt,
- thermal processes to valorise the final process wastes or the sludge between the acid and chloride leaching,
- technology for purification of the process effluents.

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