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SOLVENT EXTRACTION IN HYDROMETALLURGICAL PROCESSING OF POLISH COPPER CONCENTRATES

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Recently, very unfavorable trends of decreasing copper content and increasing complexity of the Polish copper ores as well as lowering quality of final concentrates and metals recovery from concentration plants have been observed. This is also a major problem for the Polish copper smelters, which capabilities are not adapted to the complex and declining deposit conditions. The solution of this problem should be sought in hydrometallurgical methods (Leach-SX-EW). This paper focuses on the role of solvent extraction (SX) in recovering valuable metals from pregnant leach solutions. The problems related to the separation of undesirable and toxic metals are also discussed.

keywords: copper sulphides, copper ores, leaching, solvent extraction

1. INTRODUCTION

The most important operation in hydrometallurgy is leaching of properly prepared raw material by means of a specific chemical compound – leaching agent. Usually leaching agents and process conditions are selected depending on the material type and mineralization, in order to selectively and effectively extract the valuable elements to the solution and to avoid emission of dangerous or toxic gases to the atmosphere. The purification of solutions after leaching and subsequent recovery of useful elements requires application of appropriate separation processes. Among many separation processes used in hydrometallurgy, solvent extraction (SX) deserves special attention and is widely used on an industrial scale.
Solvent extraction is an important operation in many hydrometallurgical technologies, because it enables extraction of valuable metals from pregnant leach solutions (PLS) and acquisition of concentrated and purified solutions directed afterwards to appropriate unit operations (electrowinning, crystallization or precipitation of hard-soluble compounds). One of SX merits is the possibility of sulphuric acid waste management and isolation of sulphur as elementary sulphur (Apostoluk and Walkowiak, 2009).

SX is a process of transfer of soluble metal compounds occurring between aqueous and organic phase, in the liquid multicomponent two-phase system. Extraction is a chemical reaction between extracted metal ion existing in the aqueous phase and extractant from the organic phase. Here, the pregnant leach solution (PLS) constitutes the aqueous phase. Its composition has an enormous impact on the SX performance. The presence of valuable metals is as important as the presence of undesirable constituents. Therefore, the metals recovery will largely depend also on the mineralogical composition of the starting copper ore.

All over the world, leaching followed by SX/EW has been a rapidly developing technology in recent years. The role of SX in copper production is irrefutable. International Copper Study Group estimates that solvent extraction – electrowinning (SX-EW) production of copper is expected to increase by 4.4% annually to reach 5.2 Tg (megatones) in 2013 (ICSG Press Release, 2010). It is around 25% of the total copper production in the world.

Hydrometallurgical methods may be applied when high copper content standards are not fulfilled. This is also currently an issue in the Polish copper smelters which capabilities are not adapted to the complexity of ores and declining deposit qualities, including observed decrease in the copper content.

This paper brings some data on the unique nature of the Polish copper deposits. It also discusses several factors that must be considered in operating a copper SX-EW plant.

2. DESIGN FACTORS

In operation of a copper SX-EW plant many important factors have to be considered. The most crucial are the nature and metals content in the pregnant leach solution which depend on specifics and composition of the processed material, leaching medium, its type and concentration and other leaching parameters. The composition of PLS is diversified and differ in pH, Cu(II) and other valuable metals (Zn, Ni, Co, Fe etc.) concentration, as well as unwanted contaminants, like Fe(III), arsenic compounds, colloidal silica etc. Typically leach solutions contain from 20 to 80 g/dm³ Cu, 0 to 30 g/dm³ Fe, a host of other metals (Co, Ni, Zn, As) and a pH from < 1 to > 2 at relatively elevated temperatures (Kordosky, 2002).
The Polish copper ores exhibit very favourable mineralogical composition in terms of leachability. Chalcocite (Cu₂S) and bornite (Cu₅FeS₄), easily leachable minerals predominate in the Polish ores, while content of chalcopyrite (CuFeS₂) and covellite (CuS) is significantly lower (Chmielewski, 2007, Chmielewski, 2009). Mineralogical analyses of concentrate samples indicated, that the content of chalcopyrite was within 17-20%, while only the traces of chalcopyrite were detected in the shale by-product (middlings). In this material copper practically exists as chalcocite and bornite.

Copper containing sulphide materials (ores and concentrates) have different mineralogical and metallic compositions. Zinc, nickel, cobalt, silver, gold and platinum group metals, as valuable metals, are economically important components of polymetallic sulphide materials. Iron and arsenic are the most unwanted contaminants of the sulphide copper ores and concentrates. The hydrometallurgical processing of such materials consists of copper (main component) extraction, recovery of accompanying valuable metals (Ni, Co, Zn), and effective removal of arsenic and iron, as undesired and difficult to process elements.

Leaching experiments (Chmielewski, 2009) showed that the shale by-products (middlings) from the Lubin Concentrator (ZWR Lubin) can be effectively processed using hydrometallurgical methods (non-oxidative and atmospheric leaching) in order to recover copper and accompanying metals. Non-oxidative leaching is a fast, selective and easy controllable process. Atmospheric leaching with sulphuric acid was found to be surprisingly efficient for copper, zinc and cobalt recovery from the by-product (middlings) – tailings from the 1st cleaning flotation of the 1st technological circuit at ZWR Lubin. For nickel removal it is necessary to grind coarse grains to obtain granulation below 40 μm. Moreover, the introduction of Fe(III) ions to the leaching solution causes a significant and beneficial change in the leaching kinetics. An increase of the leaching rate of Cu(II), Co(II), Ni(II) was observed.

Atmospheric leaching extracts also arsenic to the solution. Its concentration at 90°C reaches 45 mg/dm³ in single-step leaching. Therefore, this element has to be separated from the leaching solutions and isolated in an environmentally safe form. The PLS, after atmospheric leaching of the Lubin concentrate, usually contains: Cu 15-23 g/dm³, Zn 0.7-1.1 g/dm³, Ni 4-21 mg/dm³, Co 16-76 mg/dm³, Fe 10-30 g/dm³ and its pH is around 1.

3. EXTRACTION OF VALUABLE METALS

The most important part of a solvent extraction circuit is a proper selection, and preparation of organic solution containing extractant. The choice of organic diluent will also influence process and operational variables such as pH and temperature. Depending on application, extractants have different chemical nature: acidic, basic and organic salts, chelating, solvating etc.

Beside extractant, an important component of the organic phase is organic diluent. Practical importance (in extraction used in hydrometallurgical technologies) has only
hydrocarbonaceous diluents. Kerosene containing heavier aliphatic hydrocarbons can be used as a diluent, for example the C_{12}-C_{14} fraction, which does not show solvating extractant features. Aromatic hydrocarbons show relatively weak solvating ability. Usually, hydrocarbonaceous diluents are mixtures of different types of hydrocarbons. High boiling and flash-points are desired features for good diluents because they allow lowering their losses due to evaporating and minimize fire hazard.

Aromatic hydroxyoximes (HA) extract metal cations (M^{n+}), forming hydrogen ions according to the chemical reaction:

\[ M^{n+}_{(a)} + nHA_{(o)} = MA_{n(o)} + nH^+_{(a)} \]

where subscripts (a) and (o) are related to aqueous and organic phase, respectively. According to Eq. 1, extraction of different metal cations with HA extractant depends on acidity of aqueous phase, measured by the pH value. The pH of the aqueous phase corresponding to extraction of given metal with efficiency of 50% is defined as half extraction (pH_{50}) (Szymanowski, 1990). Metal cations extracted with different extractants under similar experimental conditions can be ranked according to their increasing pH_{50} value. This, the so-called selectivity series of metal’s extraction, allows estimating the possibility of metal ions separation. It is assumed that a pair of chosen metals can be effectively separated when their pH_{50} values differ at least by one unit.

![Fig. 1. The effect of pH on metals extraction with LIX 84 (Szymanowski, 2003)](image-url)
From Fig. 1 the following series can be seen: Cu(II) > Fe(III) > Ni(II) > Co(II) > Zn(II). For extractants belonging to other chemical group of compounds, Fe(III) usually precedes Cu(II), while Zn(II) precedes Ni(II) and Co(II). In some cases Co(II) precedes Ni(II), where differences between the pH50 values are usually small, which means that effective separation is difficult or impossible. An example of an extraction sequence of metals with carboxylic acids is given below:

\[
\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}, \text{Co}^{2+} > \text{Mn}^{2+} > \text{Fe}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ , \text{K}^+
\]

The complexing ability of copper ions by hydroxyoxime group from acidic sulphate solutions decreases in the following series of substituent Y: H > CH$_3$ > C$_6$H$_5$ (Szymanowski, 2003). Therefore, complexation of copper ions with increasing acidity of aqueous phase is more effective.

A negative feature of hydroxyoxime extractant solutions in hydrocarbonaceous diluents used for copper(II) extraction is their low extraction capacity (maximum copper concentration to obtain in loaded organic phase), which reaches from 6 to 8 g Cu(II)/dm$^3$ (Szymanowski, 1990). According to Eq. 1, the extraction reaction of metal cations is reversible towards hydrogen ions. Equilibrium state of the reaction (Eq. 1) is shifted towards products, when hydrogen ions concentration in aqueous phase is low, while high H$^+$ concentration in aqueous phase favours reextraction, shifting equilibrium towards substrates. However, in solutions, such as concentrate pressure oxidation liquors, where copper concentrations can be in excess of 40 g/dm$^3$, Eq. 1 adds a significant amount of acid to the PLS. This in turn can shift the equilibrium towards stripping. The simplest and most expensive solution to this problem is a direct neutralization of acid in the mixers:

\[
\text{H}_2\text{SO}_4 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{SO}_4 + \text{CO}_2 + \text{H}_2\text{O}. \tag{2}
\]

This requires no additional equipment or flowsheet changes, but reagent costs can be prohibitive. Another solution is to adsorb acid with ion exchange resins. However, this yields a relatively useless dilute acid (Grinbaum, 2007). In the case of Polish copper ores, by-products or concentrates, the excess of acid, which is formed during extraction, can be utilized in non-oxidative decomposition of carbonates, which are the major component of barren rocks.

Reextraction has two basic goals: getting cleaned and concentrated aqueous
solution of valuable metal salt and regeneration of extractant solution in organic diluent. Loaded organics contain usually a series of impurities, mainly as fine suspended mineral substances, dust and dispersed aqueous phase. Therefore, loaded organics should be first rinsed with water and then subjected to reextraction. For stripping of copper(II) from organic phase, sulphuric acid solutions are used. Usually, they are spent electrolytes retreated from electrolysis.

Preliminary extraction studies of valuable metals from PLS after leaching of middlings from the Lubin Concentrator exhibited promising results (Rotuska and Chmielewski, 2007). PLS contained 4300 ppm of copper, 4.7 ppm of nickel, 8.7 ppm of cobalt, 2060 ppm of iron, 115 ppm of zinc and 13.5 ppm of arsenic. Aromatic hydroxyoximes: LIX 84, 612 and 984 were investigated as copper(II) extractants. D2EHPA was used for zinc(II) and Cyanex 272 for nickel(II) and cobalt(II) extraction.

It was demonstrated that application of aromatic hydroxyoximes for copper(II) extraction can give satisfying results. The best extraction power exhibited LIX 984 with yield of extraction E = 99.4% at A/O 1:1. Under the same conditions LIX 84 appeared to be less effective (E = 85%). In each case the increase of extractant concentration in the organic phase increases yield of copper(II) extraction. When A/O ratio was equal to 2:1 the yield of extraction was lower for LIX 84 (around 57%) but still high for LIX 612 and LIX 984, respectively. However, none of these extractants were selective enough and other metal ion species present in leach solutions were also transferred to the organic phase.

Copper(II) reextraction from loaded organic with 1M H₂SO₄ was not satisfactory. Moreover, the stronger Cu(II) extractant used in extraction stage the lower efficiency obtained in reextraction stage. Probably, reextraction of copper(II) could be facilitated by higher concentration of H₂SO₄ in a strip solution or by addition to the organic phase of an appropriate quantity modifier, e.g. tridecanol or nonylphenol.

Recovery of the remaining metal was very low. Cyanex272 was used as Co(II) and Ni(II) extractant and was able to extract only 16.5% and 14% of cobalt(II) and nickel(II), respectively. Probably, the use of another extractant or its combination with some modifier could increase those metals recovery. Separation selectivity of such ion pair like Ni(II) and Co(II) extracted with carboxylic acid can be improved by modification of organic phase composition. Introduction of additional compound, called synergetic agent, causes a significant increase of extraction of one metal, even at low pH conditions, and does not have significant impact on extraction of the other metal.

In extraction systems of Ni(II) and Co(II) with carboxylic acids, aldehyde oxime or aliphatic ketone can be used as the synergetic agent. It is illustrated by extraction curves of these metals with naphtenic acids mixture and the same mixture in presence of iso-tridecane aldehyde oxime (Fig. 2).

Concentration of metal in the organic phase is a function of its concentration in
aqueous phase, acid concentration in aqueous phase and extractant concentration in organic phase and also type and structure of extractant, organic diluent and different additives existing in both phases (modifiers in organic phase and electrolytes in aqueous phase). Therefore, additional experiments are necessary to establish the optimal conditions of Cu(II), Co(II), Ni(II), Zn(II) extraction and reextraction processes.

![Figure 2](image.png)

**Fig. 2.** Co(II) and Ni(II) extraction with 0.5 M solution of naphtenic acids in xylene (dashed lines) and mixture of 0.5 M naphtenic acids with 0.1M iso-tridecane aldehyde oxime (solid lines)

## 4. EXTRACTION OF UNDESIRABLE AND TOXIC METALS FROM PLS

### 4.1. IRON

Iron, which is a major component of pregnant leach solution is particularly inconvenient in solvent extraction circuits. It affects the design and operation of a solvent extraction plant in several ways. Very often, iron concentration in solutions reaches a much higher level than those of useful compounds, which seriously complicates the process of selective extraction of these metals. Moreover, its presence in electrolyte introduced to electrolysis is highly unwanted, because it negatively affects current efficiency (Szymanowski, 1990). Unfortunately, PLS will contain iron and its concentration will be increasing as a result of leaching of minerals such as CuFeS₂, Cu₅Fe₄S₁₄ and FeS₂. Therefore, it has to be reduced from the circuits and separated from the remaining metals.

In copper extraction from acidic solutions (pH between 1 and 2), selectivity of copper extraction over iron is very important. Currently, the application of ester modified reagents offers the best copper/iron selectivity (Szymanowski, 1990). Good effects can be achieved also by using carboxylic acids, for example a mixture of naphtenic acids, H₂A₂, which are effective and selective towards iron, extracting iron at much lower pH than other useful metals (Fig. 3).
Iron(III) can also be removed from solutions after atmospheric or pressure leaching with sulphuric acid by means of mixed extractants based on amines and solvating diluents and also organophosphorous acids, tributyl phosphate and phosphine oxides. Besides extraction, the most frequently used and the cheapest method of iron(III) removal from acidic solutions is precipitation of hardly soluble iron hydroxide - Fe(OH)₃, goethite - FeO(OH), hematite - Fe₂O₃ or jarosite - MFe₃(SO₄)₂(OH)₆, where M = H, Na, K, NH₄, 1/2Pb, precipitated from sulphatic solutions. In each case, partial neutralization is necessary, for example with milk of lime, in order to obtain optimal pH value:

\[
2\text{Fe}^{3+} + 3 \text{Ca(OH)}_2 \rightarrow 2\text{Fe(OH)}_3 + 3\text{Ca}^{2+} \quad (3)
\]

\[
2\text{Fe}^{3+} + 3\text{Ca(OH)}_2 \rightarrow 2\text{FeO(OH)} + 3\text{Ca}^{2+} + 2\text{H}_2\text{O}. \quad (4)
\]

Another solution is the use of ion exchange resins to treat a bleed from the electrolyte and selectively remove iron. This is the Fenix Iron Control Process and it was effective at controlling iron in the Mount Gordon copper plant (Shaw et al., 2006).

Fig. 3 The effect of pH on selectivity of metals extraction with naphtenic acids
4.2. ARSENIC

In hydrometallurgy, close attention is paid to soluble arsenic compounds, which are very toxic and dangerous. Arsenic is an element which is almost always present in copper ores and its separation from technological circuits or stabilization in ecologically acceptable form became the key concern in copper industry. In solutions after leaching of ores, concentrates, dusts and slag, and also in spent electrolytes, liquors and wastes, different amounts of As(III) and As(V) occur. Significant amounts of arsenic sulphides occur in copper sulphide concentrates containing enargite (Cu₃AsS₄) and tennantite (Cu₁₂As₄S₁₃). Selective leaching of this concentrates with sodium sulphide leads to chalcocite concentrates with small content of arsenic, directed then to smelter (Apostoluk, 2005). In the Lubin Concentrator the content of arsenic reaches 3.3 kg/Mg of concentrate and is currently not acceptable for technical and environmental reasons.

It is worth mentioning that in the case of hydrometallurgical processing of copper-arsenic sulphide concentrates, there is no known solution with application of solvent extraction of arsenic. From solutions after leaching, containing excess of acids and contaminated with Fe(III) and As(V), compounds with optimal ratio of Fe/As can be precipitated in the form of scorodite (FeAsO₄·2H₂O) after appropriate correction of pH with milk of lime. Elevated temperature and pressure are recommended for precipitation of crystalline scorodite, which exhibits the lowest solubility among arsenic compounds.

In practice, only extractive removal of As(V) from spent electrolytes is used. In spite of a vast number of extractants effective in extraction of As(V), tributhyl phosphate is used worldwide to remove arsenic from the spent electrolytes. Its drawback is relatively high solubility in raffinates. Hydrophobic oxides of trialkylphosphines, like TOPO, Cyanex 921, mixtures of these oxides (Cyanex 923 and 925) and di(2,4,4-trimethylpentyl) ditiophosphinic acid are free of this drawback and are efficient for removal of As(III) and As(V) from solutions in sulphuric acid (Iberhan and Wiśniewski, 2002).

Another method for arsenic separation from spent electrolytes is adsorption. The ability for effective adsorption of arsenic compounds from diluted solutions is possible by activated carbon, pyrite and metal’s oxides or hydroxides like dioxide of manganese, tin, titanium, magnetite, iron(III) and magnesium(II) oxides.

4.3. SILICA

Silica can also be present in the copper leach solution as a result of presence of sandstone in the copper ore or in the host rock. The presence of silica in the copper leach solution can be problematic in the solvent extraction circuit. Main difficulties are related to poor phase disengagement, high levels of entrainment and poor organic
recovery in the flotation columns. These issues were recognized in Girilambone copper SX-EW plant (Miller et al., 1997). It was found that running the operation in aqueous continuous mode caused crud formation throughout the organic phase. Significant build up of crud was occurring in the strip stage. There were a gelatinous film and solids observed. To solve those problems the operation was conducted in organic continuous regime. The reduction of aqueous entrainment in the organic and decreased silica levels were observed.

4.4. LEACHING ADDITIVES

Occasionally, leaching requires addition of different agents which are able to elevate recovery or kinetics of this stage. Usually, leaching additives are surfactants, which can improve the penetration of the leach solution into the pores of ground minerals by reducing the surface tension of the leach solution (Kordosky and Virnig, 2007).

Unfortunately, these chemicals are still present in the PLS when entering the SX-EW segment of the circuit. Therefore, they can significantly affect further performance. A low surface tension of the aqueous phase can help in stabilization of dispersions, increasing the time for settling and phase separation. In the organic phase surfactants may cause formation of reverse micelles, which will carry impurities from the leach solution to the electrolyte (Kordosky and Virnig, 2007). Therefore, it is important to consider the possible negative effects of leaching aids on the SX-EW process and how to best mitigate them.

4.5. CALCIUM AND MAGNESIUM

This case can be expected in leaching and extraction of metals from the Polish copper ores and concentrates containing elevated amounts of Ca and Mg carbonates as a gangue.

In sulphate solutions containing Co(II) and Ni(II), small amounts of Ca(II) and Mg(II) can also be present. During Co(II) and Ni(II) extraction with Cyanex 272, Mg(II) and Ca(II) are co-extracted to organic phase. Cobalt(II) and nickel(II) reextraction with spent electrolytes causes precipitation of relatively sparingly soluble calcium sulphate and contamination of these electrolytes with calcium and magnesium.

To prevent this situation, 2-methyl-2-ethylheptane acid (Versatic 10) with the addition of tributhylphosphate (TBP) was suggested for Ni(II) and Co(II) extraction from almost neutral (pH=6.5) sulphatic solutions containing calcium and magnesium (Apostoluk, 2005).
5. CONCLUSION

Solvent extraction is permanently related with hydrometallurgical technologies of copper polymetallic sulphide concentrates processing. The main fields of application of this operation are cleaning of pregnant leach solutions from unwanted additives and recovery, separation and concentration of valuable metals.

The effectiveness of selective recovery of ions is determined by many factors starting from deposit and feed characteristics, leaching method and leach solution properties, the properties of used chemical compounds, which enables efficient, selective and fast recovery of appropriate metal ions.

Having in mind unfavourable trend of lowering quality of concentrates and metals output at Lubin Concentrator, the solution of this problem should be sought in hydrometallurgical methods. The preliminary studies indicate that application of Leach SX-EW technology will help to overcome this negative trend.

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Od kilkunastu lat obserwuje się bardzo niekorzystny trend obniżania zawartości miedzi i wzrostu zawartości metali towarzyszcych i węgla organicznego w polskich złożach miedzi LGOM oraz zmniejszania jakości koncentratów z zakładów wzbogacania. Stanowi to ogromny problem dla polskich hut miedzi, których zdolności nie są dostosowane do trudnych i pogarszających się warunków złóżowych. Rozwiązaniem tych problemów może być wprowadzenie nowoczesnych metod hydrometalurgicznych (ługowanie – ekstrakcja rozpuszczalnikowa – elektroliza). W pracy omówiono rolę ekstrakcji rozpuszczalnikowej w odzyskiwaniu cennych metali z roztworów po ługowaniu. Omówiono także problemy związane z separacją metali toksycznych lub niepożądanym z tych roztworów

słowa kluczowe: siarczki miedzi, ruda miedzi, ługowanie, ekstrakcja rozpuszczalnikowa