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SOLVENT EXTRACTION OF COPPER(II) FROM CONCENTRATED LEACH LIQUORS

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Abstract: Hydrometallurgical treatment of complex copper sulfidic ores, by-products and concentrates requires aggressive, oxidative leaching methods and application of Fe(III) ions and oxygen or bacteria assisted environment. Leach liquors generated in the process are usually copper and iron-rich solutions of high acidity. Such conditions require the application of suitably strong and selective reagent to extract copper in SX operations. This paper discusses the copper extraction behavior of commercial copper reagents: LIX 984N, LIX 612N-LV and Acorga M5640. Aqueous feed solutions used in SX studies were PLS' generated in atmospheric leaching of commercial flotation concentrate, produced at Lubin Concentrator (KGHM). McCabe-Thiele diagrams were generated and copper net transfer values were compared and discussed. It was shown that stronger modified aldoxime reagents (Acorga, LIX 612) are superior over non-modified salicylaldoxime/ketoxime mixture (LIX 984N). Particularly, the ester modified Acorga M5640 showed advantages in recovery and copper net transfer values.

Keywords: *copper ore, hydrometallurgy, separation, Acorga, LIX*

Introduction

Solvent extraction (SX) has been recognized as a one of the most important separation techniques for metals in solutions.The technology is increasingly being used in hydrometallurgy to separate, purify and concentrate metals such as nickel, cobalt, copper, zinc, uranium and rare earths. In the meantime a considerable amount of work has been carried out and reported (Szymanowski, 1993; Habashi, 1999; Ritcey, 2006; Flett, 2005; Apostoluk et al., 2009).A number of plants have been designed and operated to extract copper from leach solutions of various composition. Until recently typical pregnant leach solutions (PLS) contained from 0.5 to 4 g/dm^3 Cu. Such leach liquors are usually generated in heap and dump leaching of copper oxide ores or by-products, which are readily leached under ambient conditions.

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In recent years, there has been a considerable development of hydrometallurgical processes for copper extraction applying SX combined with electrowinning (EW) for the production of high-grade electrolytic copper. As a result, more than 20% of world copper production is currently produced from heap leaching–SX operations of oxide copper ores. The low capital and operating costs of SX plants together with the easy operation and the production of top quality electrolytic metals close to the mine site make the economics of the SX processes very attractive, being suitable and feasible in the range of small to medium capacities, where conventional smelting process is not applicable.

Copper flotation sulfide concentrates are mainly processed by means of smelting, converting and electrorefining, the unit operations that have dominated the World copper industry for technical and economic reasons. 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 has been developed (Dreisinger, 2006; Gupta, 1990; Habashi, 1999; 2005; 2007; Jansen and Taylor, 2000; Marsden, 2007; Peacey et al., 2003; Ramahadran et al., 2007). These processes appeared to be successful in leaching of copper from polymineral and chalcopyrite concentrates, purifying the leach solutions (PLS) using modern separation processes, mainly solvent extraction, and recovering a high value, high purity copper metal product. Chmielewski (2012) discussed the possible role of hydrometallurgy in more effective processing of polymetallic concentrates or by-products from Polish copper industry.

In the past ten years, a great deal of attention has been paid to development of hydrometallurgical treatment of complex copper sulfidic ores, by-products and concentrates (Hyvärinen and Hämäläinen, 2005; Dreisinger, 2006). This type of material requires more aggressive, oxidative leaching methodsand application of Fe(III) ions and oxygen or bacteria assisted environment. Higher grades of solids are employed in the leaching operations resulting in more concentrated leach liquors with higher metal content than those produced in heap leaching. Usually leaching of sulfide concentrates is realized with the use of iron(III) salts and sulfuric acid as a leaching medium. Leach liquors generated in the process can contain from 20 to 80 g Cu/dm^3, from 0 to30 g Fe/dm^3 and other metal values which have to be sequentially recovered (Kordosky, 2002). Moreover, the acidity of leach liquors changes in the pH range from below 1 to around 2.

According to Eq. (1)

$$M^{n+}_{(a)} + nHA_{(o} \leftrightarrows MA_{n(o)} + nH^{+}_{(a)} \tag{1}$$

the extraction reaction of metal cations M^{n+} by extractant HA is reversible towards hydrogen ions. It means that for each mole of copper extracted, the raffinate acidity is increased by one mole. In solutions where copper concentrations can be in excess of 40 g/dm^3 a significant amount of acid is generated to the raffinate. This in turn can shift the equilibrium towards stripping reaction. A solution is to use a stronger copper extractant, which will be able to extract copper at higher acidity, but which in turn requires more acid to be stripped. One can also increase the concentration of extractant in order to extract more copper. This can in turn result in more viscous organic phases, particularly the loaded organic, leading to poorer phase separation performance with increased entrainment losses, and increased impurity transfer to the strip side. One can also operate at a higher organic to aqueous phase ratio (O/A). The choice of parameters depends on how high the copper concentration is and what else is in the ore or in the feed (Molnar and Verbaan, 2003).

Presented paper discusses the copper extraction behavior of commercial copper reagents with copper sulfide concentrate leach solutions. The performance of LIX 984N, LIX 612N-LV and Acorga M5640 in Escaid 100 diluent were investigated. McCabe–Thiele diagrams were generated, copper net transfer values were compared and discussed.

Experimental

Reagents and solutions

Aqueous feed solutions used in SX studies were PLS' generated in atmospheric leaching of commercial flotation concentrate, produced at Lubin Concentrator (KGHM). Leaching with sulfuric acid solution resulted in a leach liquors (PLS) containing 25–27 g/dm^3 Cu, ~30 g/dm^3 total Fe, 1.4–1.9 g/dm^3 Zn, 0.06–0.1g/dm^3 Co and 0.02–0.03 g/dm^3 Ni. The solution was highly acidic, H_2SO_4 concentration varied between 20 and 30 g/dm^3.

LIX®984N and LIX®612N-LV, applied in SX laboratory tests, were manufactured by Cognis and supplied by Cognis Ireland Ltd., Acorga M5640 were manufactured by Cytec Canada Inc. and supplied by Cytec Netherdlands. LIX®984N was a mixture of oximes: 5-nonylsalicylaldloxime and 2-hydroxy-5-nonylacetophenone oxime. LIX®612N-LV was a proprietary mixture of 2-hydroxy-5-nonylbenzaldehide oxime and a high flash point hydrocarbon diluents with low viscosity. The active substance of Acorga M5640 reagent is 5-nonylsalicylaldoxime and a fatty ester 2,4,4-trimethyl-1,3-pentanediol diisobutyrate (modifier).

Escaid®100, used as a diluent, was supplied by Exxon Mobil Chemical. This is kerosene type diluent containing 19% of aromatic compounds. In copper extraction systems alky-aromatic diluents, containing below 20% of aromatics are preferred because of better solubility of formed complexes. Moreover, in some cases when such diluents are used the modifier content may be reduced or even eliminated.

Analytical methods

The aqueous solutions were analyzed for metals concentration by AAS using a Varian SpectrAA 20Plus.The free acid content in the leaching solution was determined by the titration method with pH control. The concentration of copper in organic phase was calculated from a difference between its initial concentration in PLS and its concentration in raffinate at fixed O/A phase ratios. Measurements of the pH were carried out with Elmetron CX-731 pH-meter using a Hydromet glass electrode.

Results and discussion

Aqueous phase pretreatment

Leaching of sulfide flotation concentrates from Lubin Concentrator with oxygenated ferric sulfate solutions acidified with sulfuric acid results in highly acidic pregnant leach solutions. Therefore, neutralization of the acid before copper extraction is required, considering lowering extraction efficiency with increase in acidity of the aqueous PLS phase. It is preferable to neutralize feed solution and start extraction at pH 1.5–2, depending on the applied extractant.

Table 1. Composition of PLS and SX feed solutions after neutralization with dry/wet flotation concentrate

Feed composition	Cu g/dm^3	Fe g/dm^3	Zn g/dm^3	Co mg/dm^3	Ni mg/dm^3	pH	volume cm^3
PLS	26.9	30.7	1.81	98.0	21.9	0.3	1000
PLS I neutr (dry)	35.2	28.4	1.67	95.0	21.9	2.4	750
PLS	24.8	24.2	1.43	31.5	28.5	0.6	1000
PLS II neutr (wet)	26.0	23.8	2.04	29.0	26.3	2.2	1030

Flotation concentrates (dry or wet) of known moisture and carbonates (Ca, Mg) content were used for initial aqueous phase neutralization. In the first case, material was dried in laboratory dryer at 105°C for 24 h. Then, the small portions of dried solids were added to the pregnant leach solution and pH was measured. After stabilization of pH next portion was added until pH 2 was reached. Similarly, the neutralization of PLS with wet concentrate was realized. The content of aqueous phases before and after neutralization with dry/wet concentrate is given in Table 1.

After neutralization with dry concentrate one can observe increase in copper concentration. This is partially due to Cu leaching taking place during this step and partially because of solution losses in the filtration step. One can also notice the increase of copper and zinc concentrations in PLS after neutralization with wet concentrate, which was probably due to leaching of the material. The pre-neutralized leach solutions were used as feed solutions in solvent extraction step.

Extraction

All extraction agents were used as received by diluting them to the desired concentration with Escaid100 diluent. The extraction data were obtained by vigorously contacting barren organic and aqueous at various A/O phase ratio in laboratory shaker for 5 min at 25°C. After the phases separated, the copper(II) concentration in the aqueous phase was determined by AAS using standard methods.

The effect of extractant type on Cu-SX

Significant copper(II) concentrations in SX aqueous feed solutions enforce the application of organic phases containing high extractant concentrations. For this reason 30%(v/v) extractant solutions in Escaid 100 were used as an organic phase in all SX experiments. In the first place, extraction isotherms were generated for Cognis reagents. Based on the obtained results McCabe-Thiele diagrams were constructed and are presented in Fig. 1. Data on copper net transfer in organic are plotted as a function of overall O/A ratio in Fig. 2 for PLS I. The net transfer per unit of extractant is the g/L of solute removed from the aqueous feed per % extractant.

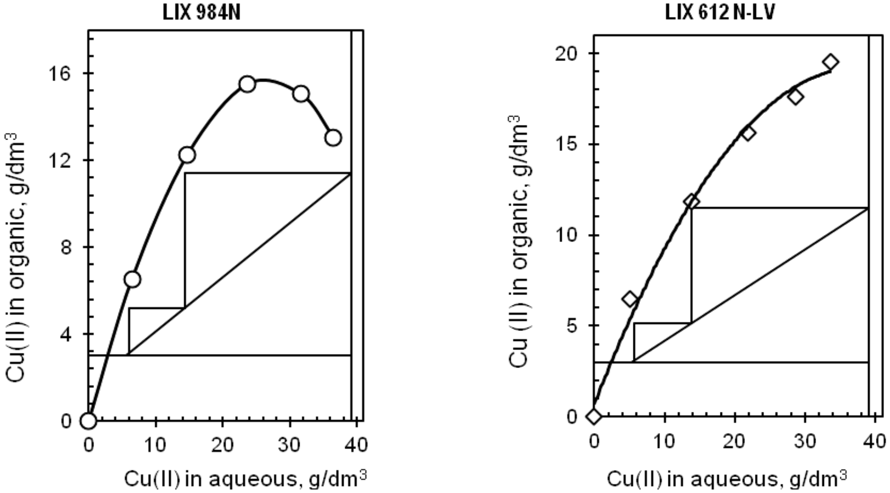

Fig. 1. The McCabe-Thiele diagram for 30 vol% of LIX 984 N and LIX 612 N-LV
in Escaid 100, feed: PLS I, pH 2.2, O/A 4.0

From the results presented in Fig. 1 it is seen that in both cases about 86% of copper was extracted after two extraction steps at O/A ratio exceeding 4. Under virtually identical conditions raffinates with copper concentration of 5.5 and 5.2 g/dm^3 can be obtained for LIX 984N and LIX 612N-LV, respectively. However, the equilibrium curve obtained for LIX 984 N is not as smooth as that generated for LIX 612. This is probably due to impurity (Fe) that is co-extracted with copper resulting in decreasing loading of Cu. Moreover, the organic phase containing LIX 612N-LV can be loaded up to 20 g Cu/dm^3, whereas the other phase can only reach level of 16 g Cu/dm^3. Thus, LIX 612 have greater extraction capacity what is an advantage over LIX 984N. Only very slight difference in copper net transfer values can be observed between investigated extractants (Fig. 2).The presented comparison of copper net transfer for LIX 612 and LIX 984 N shows decreasing copper loading capacity with increasing O/A ratios.

Better performance of LIX 612 can be explained by the fact that this reagent is modified with additives ensuring low viscosity of organic phase, thus guaranteeing better extraction and stripping efficiency comparing to regular extractants. For this reason, LIX 612N-LV was selected for further comparison with Cytec reagent – Acorga M5640.

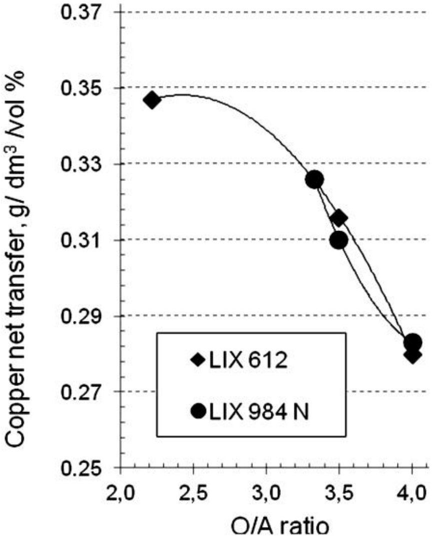

Fig. 2. Copper net transfer in organic phase at 30 vol % of reagent as a function of overall extractionO/A ratio, PLS I

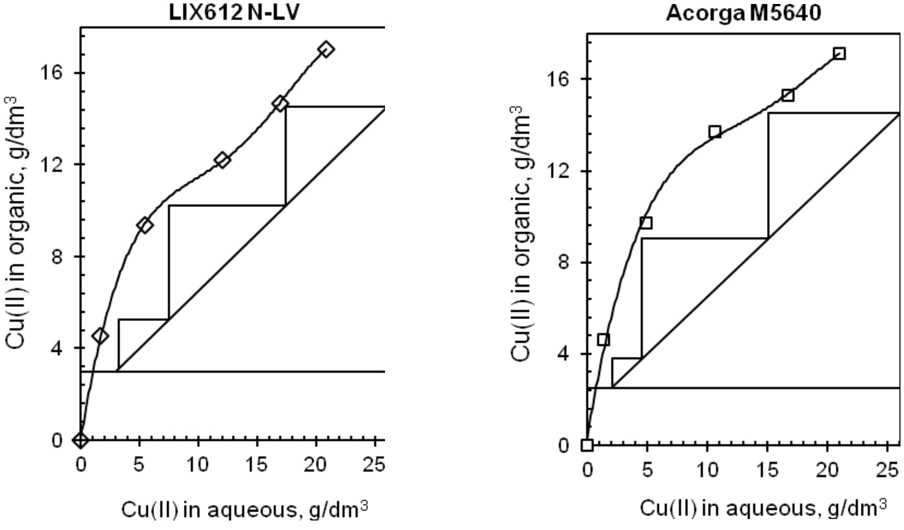

Fig. 3. The McCabe–Thiele diagram for 30 vol% of LIX 612 N-LV and Acorga M5640 in Escaid 100, feed: PLS II, pH 2.0, O/A 2.0

In subsequent experiments the extraction behavior of LIX 612 N-LV was compared with Acorga M5640 reagent. Pregnant leach solution pre-neutralized with wet flotation concentrate was contacted with 30% (v/v) solutions of extractants at various phase ratios. The obtained extraction isotherms are presented in Fig. 3. Data on copper net transfer in organic is plotted as a function of overall O/A ratio for PLS II (Fig. 4).

The obtained results show that it is possible to remove about 88% and about 92% of Cu(II) from PLS with the use of LIX 612 and Acorga M5640, respectively. In both cases three extraction stages at an excess of organic phase of 2 are required. However, in the case of Cytec extractant lower raffinate can be obtained (2 g/dm^3) comparing to LIX reagent (3 g/dm^3). Both of investigated phases have similar capacity and can be loaded up to ~17 g/dm^3 Cu.

A comparison of the net transfer values (Fig. 4) shows a slight advantage of Acorga M5640 over LIX 612 N-LV. As before, a decrease in copper net transfer with increasing O/A ratio can be observed.

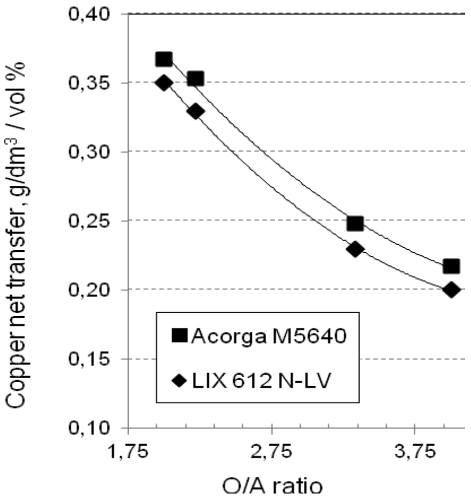

Fig. 4. Copper net transfer in organic at 30 vol % of reagent
as a function of overall extractionO/A ratio, PLS II

Both extractants were further compared in terms of their extraction behavior with less concentrated and more acidified solutions. Mixed raffinate solutions after single extraction with copper concentration level of 10 g/dm^3 and pH ~0.75 were used as SX feed (marked as Raffinate I). Organic and aqueous phases were contacted at various A/O ratios. Extraction isotherms and generated McCabe-Thiele diagrams for Cognis and Cytec extractants are presented in Fig. 5. Additional comparison of SX circuit recovery vs. pH and copper net transfer values are plotted in Figs 6 and 7.

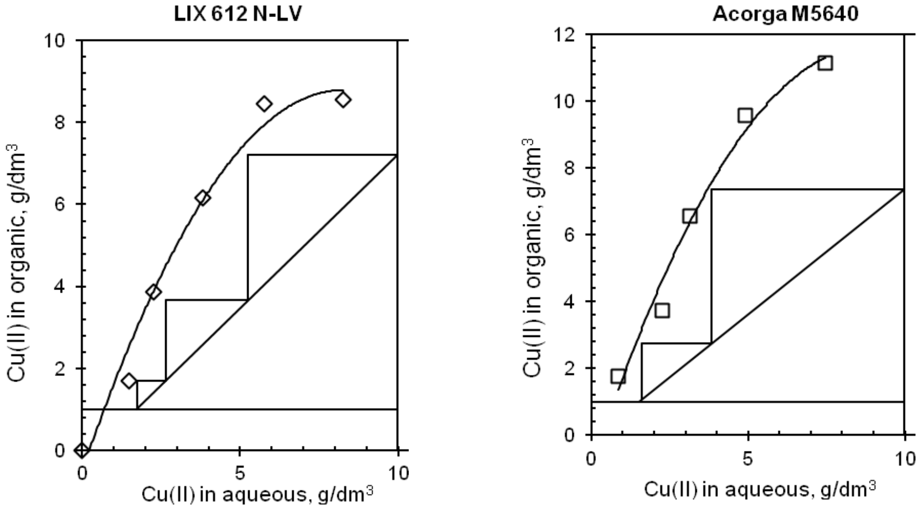

Fig. 5. The McCabe-Thiele diagram for 30vol% of LIX 612 N-LV and Acorga M5640 in Escaid 100, feed: raffinate I, pH 0.75, O/A 1.33

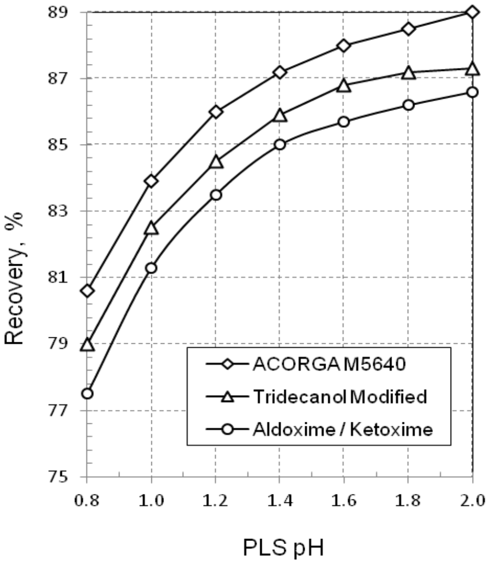

Fig. 6. SX circuit recovery comparison (30 vol % extractant, 25 g/dm^3 of copper in PLS) (Moore et al., 1999)

The obtained results show that the application of Acorga provides much better copper recovery than the use of LIX reagent. The following extraction efficiencies and organic phase capacities were found: 73% and 8.5 g/dm^3 for LIX, 83% and 11.1 g/dm^3

for Acorga. Both experiments were performed at a small excess of organic phase (O/A = 1.33) and high acidity of aqueous phase. Copper recovery at the indicated level with organic phase containing LIX reagent requires three stages of extraction ending up with 1.7 g/dm^3 Cu raffinate, whereas the other reagent is able to reach lower raffinate (1.5 g/dm^3 Cu) after two extraction steps.

It is clear that Acorga M5640 ensures better copper recovery under identical conditions. This is consistent with the results presented in Fig. 6 (Moore et al.1999). Authors demonstrated that across the whole pH range, the ester modified Acorga M5640 provided the highest copper recovery of all the reagents tested, compared at the same reagent strengths.

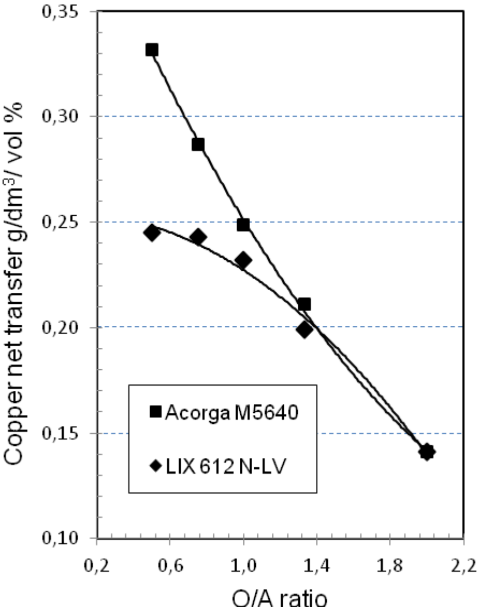

Fig. 7. Copper net transfer in organic phase at 30 vol % of reagent as a function of overall extraction O/A ratio, raffinate, pH 0.75

A graphical comparison of the copper net transfer values (Fig. 7) confirms previous observations and shows a decrease organic phase capacity with growing O/A ratio. Moreover, it reconfirms limited copper loading capacity of LIX 612 N-LV reagent.

It is also important to note the net transfer changes for reagents under different conditions (Table 2).It can be seen that the copper net transfer can be quite high (case 3, 4) or satisfactory (case 1, 2) at higher O/A ratios and lower acidity of the feed solution. In such cases reagent can achieve quite good copper recovery. However, when a reagent needs to make a comparatively high copper recovery but at higher acidity of the feed solution, the work that reagent is doing is much poorer. It results in lower net transfer values, regardless of much beneficial O/A ratio (case 5,6).

Table 2. Summarized extraction data

	Feed g/dm^3 Cu	Reagent 30 vol%	Advance O/A	Recovery %	PLS pH	Copper net transfer g/dm^3/vol %
1.	39.1	LIX 984 N	4.0	86.0	2.2	0.280
2.	39.1	LIX 612 N-LV	4.0	86.7	2.2	0.283
3.	26.0	LIX 612 N-LV	2.0	88.5	2.0	0.383
4.	26.0	Acorga M5640	2.0	92.3	2.0	0.400
5.	9.97	LIX 612 N-LV	1.33	82.9	0.75	0.207
6.	9.97	Acorga M5640	1.33	84.9	0.75	0.212

Considering all the results presented in this paper the investigated reagents can be ranked regarding their suitability for copper extraction from concentrated solutions. Starting from the best the order is following: Acorga M5640, LIX 612 N-LV, LIX 984N.

Conclusions

The obtained results demonstrated that investigated copper solvent extraction reagents are suitable for application to concentrated feed solutions from atmospheric or pressure leaching of copper concentrate. Among the reagent properties examined in this paper, the stronger modified aldoxime reagents (Acorga, LIX 612) was shown to be superior overnon-modified salicylaldoxime/ketoxime mixture (LIX 984N). In particular, the ester modified Acorga M5640 showed advantages in recovery and copper net transfer values.

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References

APOSTOLUK W., WALKOWIAK W., DUDA L.L., 2009, *Rola procesów rozdzielczych we współczesnej hydrometalurgii*, XII Seminarium "Metody hydrometalurgiczne a rozwój produkcji w KGHM „Polska Miedź" S.A. Lubin, 77–100.

CHMIELEWSKI T., 2012, *Hydrometallurgy in KGHM Polska Miedz SA – Circumstances, Needs and Perspectives of Application*, Separ. Sci. Technol., 47, 1264–1277.

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

FLETT D.S., 2005, *Solvent extraction in hydrometallurgy: the role of organophosphorus extractants*, J. Organometallic Chem., 690, 2426–2438.

GUPTA C.K., MUKHERJEE T.K., 1990, *Hydrometallurgy in extraction processes*, Vol. I and II, CRC Press.

HABASHI F., 1999, *Textbook of Hydrometallurgy*, 2nd Ed. 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, 43–55.

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

HYVÄRINEN O., HÄMÄLÄINEN M., 2005, *HydroCopper^{TM} – a new technology producing copper directly from concentrate*, Hydrometallurgy, 77, 61–65.

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.,

KORDOSKY G.A., 2002, *Copper solvent extraction for concentrate leach solutions*, (Paper presented at ALTA Conference 2002), May 2002.

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

MOLNAR R.E., VERBAAN N., 2003, *Extraction of copper at elevated feed concentrations*, materials presented at Hydrometallurgy 2003 – Fifth International Conference, Vol. 2: Electrometallurgy and Environmental Hydrometallurgy.

MOORE T., TOWNSON B., MAES CH., TINKLER O., 1999, *Solvent Extraction of Copper from Concentrated Feed Solutions*, paper presented at ALTA Copper 1999.

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.), 205–222.

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

RITCEY G.M., 2006, *Solvent Extraction in Hydrometallurgy: Principles and Application to Process Metallurgy*, 2nd Ed. , Ottawa, Canada.

SZYMANOWSKI J., 1993, *Hydroxyoximes and Copper Hydrometallurgy*, CRC Press, Boca Raton, FL.