

*Received March 16, 2012; reviewed; accepted July 9, 2012*

## CONTAMINANTS OF POST-LEACHING COPPER SOLUTIONS AND THEIR BEHAVIOR DURING EXTRACTION WITH INDUSTRIAL EXTRACTANTS

Leszek GOTFRYD, Grzegorz PIETEK

Institute of Non-Ferrous Metals, Sowińskiego 5; 44-100 Gliwice, Poland, leszekg@imn.gliwice.pl

**Abstract:** Several copper extractants have been examined in laboratory glassware with a special attention paid to their behavior towards cations others than copper(II). In the studies 25 vol. percent of hydrocarbon (Exxsol D80 AZ) solutions of six industrial copper extractants have been used. They were mainly reagents of hydrooxime type (LIX 860N-IC, LIX 984, LIX 984N, LIX 84-I, Acorga M5640) and diketone type LIX 54-100. Individual isotherms of independent extraction of copper(II) and selected cations ( $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mg}^{2+}$ ) versus equilibrium pH have been compared. Investigations have been conducted with synthetic 0.1 mol/L solutions of their sulfates. The values of  $\text{pH}_{50\%}$  – parameter defined as an equilibrium pH at the moment of half-and-half extraction of the investigated cationic species have been presented. Also  $\Delta\text{pH}_{50\%}$ , that is differences between values of  $\text{pH}_{50\%}$  for specific cation Me(II) and copper(II):  $\Delta\text{pH}_{50\%} = \text{pH}_{50\%}(\text{Me}) - \text{pH}_{50\%}(\text{Cu})$ , have been given. In addition to that 25% LIX 984 has been used in counter-current pilot trials for copper(II) extraction from naturally contaminated solutions produced by bioleaching of industrial sulfide copper concentrate to observe behavior of investigated contaminants such as correlations between their real co-extraction with copper(II) and the position of their extraction on the pH scale. Copper electrolyte/strip solution, working alternately within close loop of coupled stripping - electrowinning system, has been analyzed during consecutive cycles to observe building up of the contaminants concentrations in the course of test.

**Keywords:** *industrial copper extractants, copper contaminants, copper extraction isotherms*

### Introduction

Dominant amounts of worldwide copper production come from copper ores which, after mining, crushing, grinding and enrichment by flotation to 20-30 % Cu, are processed pyrometallurgically into metallic copper. Also most of copper scrap is recovered by melting and pyrometallurgical refining. Crude blister copper is finally refined using hydrometallurgical electrolytic means to produce copper cathodes. A simpler, fully hydrometallurgical method to obtain electrolytic copper is based on the ion exchange solvent extraction technique. About 20% of the world copper production is

processed this way. Mostly poor and oxidized raw materials, unsuitable for flotation, are processed by means of extraction even though quite effective methods of bioleaching are available, which guarantee dissolution of rich sulfide copper concentrates by bioleaching (bacterial and/or fungal) and transforming them into copper(II) sulfate(VI) solutions and elemental sulfur. Generally, hydrometallurgical technology of copper production consists of raw material leaching (often using heaps or piles) with sulfuric acid solutions in the form of post-extraction raffinate or depleted copper electrolyte, solid/liquid separation (sedimentation and filtration) and final extractive treatment of the solution. The extracted copper is recovered as a stripped liquor being a moderately acidic copper sulfate solution and containing, for example, 55 g/dm<sup>3</sup> Cu(II) and 130 g/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>). Next, it is subjected to electrolysis to obtain copper cathodes as the final product, with a simultaneous acid regeneration in amounts equimolar to deposited copper (e.g. 30 g/dm<sup>3</sup> Cu(II) and 179 g/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>). Regenerated electrolyte is used again in cycles as a stripping factor.

### Reagents for copper extraction

Currently there are two basic types of reagents capable to extract copper(II) from concentrated and/or acidic solutions which show high selectivity towards iron(III). They are of (hydroxy)oxime character – derivatives of aromatic ketones or aldehydes with elongated linear alkyl substituent attached – i.e. alkylaromatic ketoximes or aldoximes.

Commercially available are 2-hydroxy-5-nonylacetofoxime /LIX 84-I/, 5-dodecylsalicylaldoxime /LIX 860/ and 5-nonylsalicylaldoxime /LIX 860N or Acorga P-50/ (MTC Redbook, 2011, Cytec Industries technical brochures, 2011, Kordosky et al., 1983, 2003; Merigold, 1996, Agers, 1972). They contain basic ingredients which are used to compose extractants applied in industry by blending them with organic solvents (hydrocarbon) as well as with some supplementary additives (modifiers), e.g. phenoles (p-nonylphenol), higher alcohols (tridecanol), esters and similar. Those extra components have some influence on extraction characteristics (mitigating, decreasing extraction power causing softening of the stripping conditions), as well as on physical and chemical properties such as diminishing viscosity and increasing surface tension (Merigold, 1996).

Presently there are three companies manufacturing industrial amounts of reagents of the discussed types. Cognis Corporation (MTC Redbook, 2011) mainly produces LIX 84-I and LIX 860N-I, whereas Cytec Industries Inc. (Cytec Industries technical brochures, 2011) supplies a reagent called (Acorga) P50 while AllCo Chemicals provides aldoxime type reagent MOC 45. Due to these reagents numerous commercial products are available including LIX 984, 984N, 973N (blends of LIX 84-I and LIX 860), LIX 622N and 664N (LIX 860 with tridecanol or ester added); Acorga M 5640, PT 5050, P5100 (modified P-50); MOC 55TD. Evaluation of both types of extractants shows an advantage of the ketoxime type reagents. They are more resistant to hydrolysis under stripping conditions at elevated temperature than aldoximes. One of the rea-

sons is that they do not need to be blended with modifiers. They can be stripped with a typical copper electrolyte (Kordosky, 2003; Merigold, 1996).

To extract copper other chemical compounds can be used, e.g.  $\beta$ -diketones, having structure of  $R^1COCH_2COR^2$ , where  $R^1 = -(CH_2)_6CH_3$ ,  $R^2 = -C_6H_4-R$  and R is an alkyl substituent /LIX 54-100 = 1-phenyldecane-1,3-dion/. Their power of copper extraction is slightly lower. Additionally, they are not selective against iron(III), which presents an important disadvantage, limiting in practice their application to cuprammonium solutions (Kordosky, 2003; Agers, 1972; Jenkins et al., 1999).

Copper(II) can be extracted with many other reagents, including organic derivatives of acidic compounds of phosphorus /DEHPA = bis(2-ethylhexyl)phosphoric acid, PC88A = (2-ethylhexyl)2-ethylhexylphosphoric acid, Cyanex 272 = bis(2,4,4-trimetyptenyl)phosphinic acid/, carboxylic /naphthenic, versatic/ and sulphonic acids, and hydroxyquinolines. Quite often they present disadvantage of poor selectivity against many cations and/or very strong co-extraction of Fe(III), which in practice leads to a permanent poisoning of the extractant.

## **Contaminants of the post-leaching solution and selectivity of copper extraction**

Leaching of copper-bearing materials with sulfuric acid solutions is not selective. Together with the main ingredient also its contaminants (Fe, Zn, Mg, Ni, Co, As) permeate to the solutions. Copper(II) extraction from such solutions, however, leads to production of relatively pure copper(II) sulfate(VI) solutions, which can be seen as a definite advantage of those extractants used for copper recovery. Requirements with respect to the contents of contaminants in copper electrolyte are not especially high (in comparison, for instance to zinc or manganese sulfate solutions prepared for electrolysis). Therefore, no special attention is paid to their level when they are present within relatively broad and acceptable limits. It is especially related to such ingredients as nickel, cobalt, arsenic, antimony, and to some lower degree also to iron. Some of them (Co) might be even desirable in the electrolyte, to prevent corrosion of insoluble lead anodes by causing their advantageous polarization. These facts, to a considerable degree, justify why there is scarcity of information in technical literature concerning levels of contaminants transferred to the electrolyte, except for iron, which is typically used to determine selectivity of copper extraction. It is suggested that selectivity of copper over iron defined as Cu/Fe in the stripped solutions (copper electrolytes) is from 2000 to  $\geq 2500$  (MTC Redbook, 2011; Cytec Industries technical brochures, 2011).

This study represents both an attempt to verify those data on iron(III) cation and also an effort to fill up the gap in information on the behavior of other elements. Therefore, it represents also an attempt to show potential differences between extractants, present on the market and in industry, considering their copper(II) extraction selectivity against iron(III) as well as against other ingredients of treated solutions.

## How to compare particular extractants? Methodology of the research

In this respect the indicative quantitative information is defined by pH of half extraction of the examined cation denoted as  $\text{pH}_{50\%}$ , indicating pH at which, at thermodynamic equilibrium, half of the amount of the cation in the feed solution subjected to extraction was extracted to the organic phase of the extractant. The value of  $\text{pH}_{50\%}$  depends on extractant concentration in the organic phase and cation concentration in the aqueous one. It depends on a volumetric ratio of reacting phases, temperature, and other factors. Generally, under established conditions, this parameter characterizes the pair of extractant and cation. Relative position on the pH scale of graphs presenting percent of extraction vs. equilibrium pH curves, and the  $\text{pH}_{50\%}$  values in particular, for various extracted cations, that is an order of their extraction, is a characteristic feature of a particular extractant. It describes its behavior versus the ingredients of treated solution. The range and the slope of the essential part of the particular curve is also of some importance.

To create extractant/cation characteristics for comparison, very diluted salt solutions of investigated cations  $\text{Me}^{2+}$  ( $0.001\text{--}0.01\text{ mol/dm}^3$ ) and from 2.5 to 3.0-fold concentrated organic solutions of extractants are tested. For more practical applications the extractants are prepared in a form and concentration used by industry and the cations in a form of their independent and still comparatively diluted ( $0.05\text{--}0.1\text{ mol/dm}^3$ ) salt solutions. The second method has been applied in the presented study.

## Experimental

### Extractants and chemicals

The following solvent extraction reagents were used (main ingredients in parenthesis):

- LIX 860N-I (5-nonylsalicylaldoxime),
- Acorga M5640 (5-nonylsalicylaldoxime modified with TXIB /2,2,4-trimethyl-1,3-pentanediol di-isobutyrate/),
- LIX 84-I (2-hydroxy-5-nonyl-acetophenone oxime),
- LIX 54-100 (1-phenyldecane-1,3-dione),
- LIX 984N (blend of LIX 860N and LIX 84-I),
- LIX 984 (blend of LIX 860 /= 5-dodecylsalicylaldoxime/ and LIX 84-I).

Composition and typical properties of the reagents were available from Blue Line Technical Bulletins (Tech. Bull. 1996-2000) and/or their Safety Data Sheets, routinely provided by producers with the samples. They were used as received after dilution to 25 vol% with Exxsol D80 AZ dissolvent (Exxon Chemicals). Salts, bases, acids were delivered by POCH Gliwice, and were of AR grade.

### Pregnant leaching solutions (PLS) – feed for copper extraction

The composition of the solutions from microbiological leaching of copper concentrate is shown in Table 1. They were used in extractive continuous and counter-current experiments.

Table 1. Composition of pregnant leach solutions from biological leaching of copper concentrate

Feed	pH	H <sub>2</sub> SO <sub>4</sub>	Cu	Fe(II)	Fe(III)	Mg	Zn	Ni	Co	Ag	As	Cl	SO <sub>4</sub>
PLS/1	1.78	15.1	44.91	0.27	5.50	6.00	2.99	0.22	0.42	< 0.0002	0.24	0.46	116.4
PLS/2	1.68	17.4	28.6	0.29	6.25	4.30	2.09	0.17	0.32	< 0.0002	0.20	0.39	89.5

g/dm<sup>3</sup>

### Experimental methods

The characteristics of the extractants have been examined with reference to copper(II) and six other cations of non-ferrous metals, i.e. Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup>, Mg<sup>2+</sup>, and also to both Fe<sup>3+</sup> and Fe<sup>2+</sup> cations. During these trials individual synthetic solutions of metal sulfates of 0.1 mol/dm<sup>3</sup> concentrations have been used, except for iron, which was used in a form of equimolar (0.1 + 0.1 mol/dm<sup>3</sup>) Fe(III) and Fe(II) solutions.

Determination of pH<sub>50%</sub> for extractant/cation couples was performed by reading their values from the graphs relating extraction vs. equilibrium pH. The preparation of the curves was based on point-by-point collection of data on concentration of extracted cation in aqueous and organic solutions and corresponding equilibrium pH. The experiments consisted of mixing of reacting phases, i.e. the aqueous (A) solution of metal salt and the organic (O) solution of the extractant at their volumetric ratio A:O = 1:1, for the period of 10 minutes. Then, the phases were separated and sampled to analyze concentrations of the extracted cation. Gradual increase of pH of the reaction environment, and thereby progress of the reaction, was forced by a regular addition of a 5.0 mol/dm<sup>3</sup> NaOH solution in small portions.

### More advanced tests

Beside the described procedures for creation of pH<sub>50%</sub>, to be used in a quasi-quantitative assessment of a particular extractant behavior versus copper(II) and cations of accompanying metals, in one case (LIX 984) a more advanced tests was performed during the pilot trials of copper extraction from the real feed solution. This test was conducted with a slightly excessive set of eight extractors of mixer-settler type, each of 0.5/1.5 dm<sup>3</sup> in capacity, combined into 4/4 (extraction/stripping) counter-current system and fed by three membrane pumps. At the first stage the extractant (25% LIX 984/Exxsol D80) was saturated with copper(II) during the contact with the feed solution (PLS/1 or PLS/2) and at the second stage it released copper in favor of the sulfuric acid solution of 2.2 mol/dm<sup>3</sup> initial concentration (in the first cycle) or in favor of depleted electrolyte from copper electrolysis. Operating media were provided by pumps and were flowing between particular extractors due to gravity, with some

support of sucking operation of the rotors of the mixer. The obtained strip solutions were collected and directed to electrolysis, after remaining organic phase removal with active carbon. The electrolytes depleted by electrolysis were used again as stripping agents. Samples of stripped solutions, taken from particular cycles, were analyzed for content of all impurities.

The extraction system was of 0-4-0-4 type, i.e. no extractant pretreatment, 4 steps of counter-current extraction, no scrubbing stage and 4 steps of counter-current stripping. Experiments were conducted at room temperature. Other conditions applied are listed in Table 2.

Table 2. Conditions of continuous counter-current copper(II) solvent extraction / stripping process

Process	Counter-current steps	Medium	Composition	Flow [dm <sup>3</sup> /h]	O:A ratio [vol./vol.]	Cycles
–	–	Organics	25 % vol. LIX 984 / Exxsol D80	4.12	–	–
Extraction	4	Feed 1	PLS/1 (table 1)	1.20	3.45	1
		Feed 2	PLS/2 (table 1)	1.88	2.20	2,3,4
		Strip 1	2.2 M H <sub>2</sub> SO <sub>4</sub>	0.92	4.50	1
Stripping	4	Strip 2	Copper electrolyte 35 g/dm <sup>3</sup> Cu	3.10	1.35	2,3,4

The strip solution obtained in cycle 1 was gathered and directed to copper electrolysis, after removal of the remaining organic phase with active carbon. The depleted by electrolysis (to the level of 35 g/dm<sup>3</sup> Cu) electrolyte was used again as a stripping agent in the second cycle. Four campaigns of such extraction – stripping – electrolysis cycles were performed. The circulating extractant performed a role of a copper carrier from the feed (PLS) to the strip solutions. A portion of about 70 dm<sup>3</sup> of electrolyte/stripping solution was circulating as copper carrier from saturated organic extractant to the metal cathode. Samples of stripped solutions, taken from particular campaigns, were analyzed for content of acid, copper and all impurities.

### Analytical procedures

All samples and solutions were processed and analyzed by modern instrumental methods: ASA or AES-ICP (Horizon or Perkin-Elmer Optima 5300 V) for determination of complex mixed solutions, and by more traditional titration methods for determination of pure single components.

### Results and discussion

The studied extractants consisted of 25 vol% organic solutions of the following reagents: LIX 860N, LIX 984, LIX 984N, Acorga M5640, LIX 84-I and LIX 54-100 in Exxsol D80 AZ dissolvent. The results are presented in a graphical form as sets of

curves showing dependency of the degree of extraction and equilibrium pH curves (% of extraction – pH) for particular cations and each investigated extractant (Fig. 1 a–f), and also in a form of collected data in Table 3 with  $pH_{50\%}$  values, as well as in Table 4 with characteristic differences between those values for particular cation and Cu(II) values.

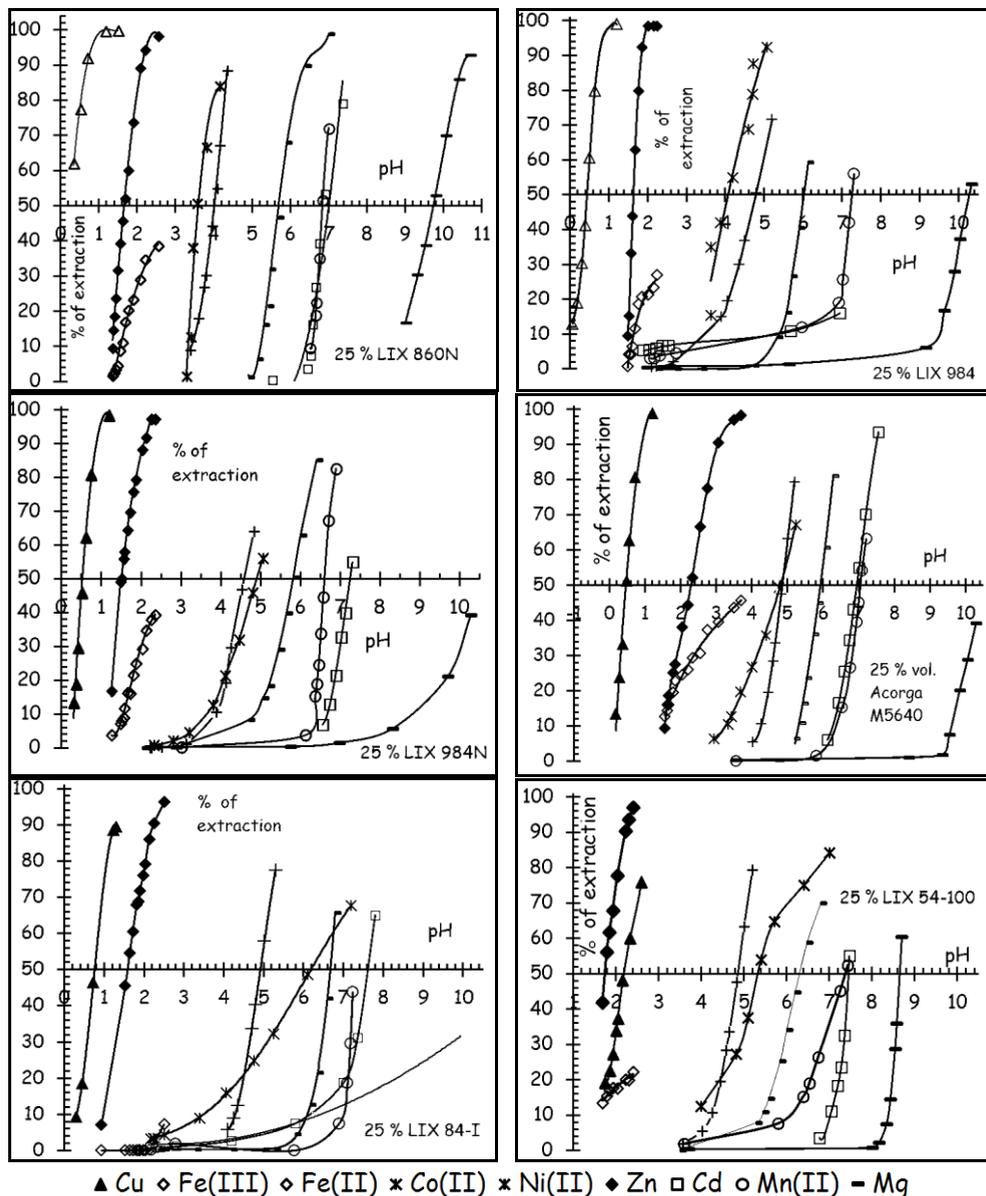


Fig. 1. Extraction of different cations with selected extractants intended for selective extraction of copper(II)

Table 3.  $pH_{50\%}$  values for cations extraction with 25 vol% organic solutions (Exxsol D80 AZ) of selected industrial copper(II) extractants obtained during extractant contact with  $0.1 \text{ mol/dm}^3$  aqueous solutions of metal sulfates

Extractant→	LIX	LIX	Acorga	LIX	LIX	LIX
Cation	860N-I	984	M5640	984N	84-I	54-100
<b>Cu(II)</b>	<b>0.30</b>	<b>0.43</b>	<b>0.47</b>	<b>0.55</b>	<b>0.76</b>	<b>2.20</b>
<b>Fe(III)</b>	<b>1.66</b>	<b>1.64</b>	<b>2.22</b>	<b>1.53</b>	<b>1.62</b>	<b>1.75</b>
Fe(II)	1.90	-	3.45	2.30	-	-
Co(II)	4.00	4.78	4.82	4.60	4.90	4.87
Ni(II)	3.60	4.10	4.74	4.80	4.00	5.35
Zn(II)	5.70	6.00	5.93	5.78	6.67	6.31
Mn(II)	6.84	7.24	7.05	6.60	7.21	7.34
Cd(II)	6.85	-	6.90	7.28	7.60	7.45
Mg(II)	9.72	10.27	10.50	10.5	-	8.65
$pH_{50\%}$ of cation extraction						

Table 4. Values of  $\Delta pH_{50\%} = pH_{50\%}(\text{Me}) - pH_{50\%}(\text{Cu})$  for cation extraction with 25 vol% organic solutions (Exxsol D80 AZ) of industrial copper(II) extractants, obtained during extractant contact with  $0.1 \text{ mol/dm}^3$  aqueous solutions of metal sulfates

Extractant→	LIX	LIX	Acorga	LIX	LIX	LIX
Cation	860N-I	984	M5640	984N	84-I	54-100
Cu(II)	0.00	0.00	0.00	0.00	0.00	0.00
Fe(III)	1.36	1.21	1.75	0.98	0.86	-0.45
Fe(II)	1.60	-	2.98	1.75	-	-
Co(II)	3.70	4.35	4.35	4.05	4.14	2.67
Ni(II)	3.30	3.67	4.27	4.25	3.24	3.15
Zn(II)	5.40	5.57	5.46	5.23	5.91	4.11
Mn(II)	6.54	6.81	6.58	6.05	6.45	5.14
Cd(II)	6.55	-	6.43	6.73	6.84	5.25
Mg(II)	9.42	9.97	10.03	9.95	-	6.45
$\Delta pH_{50\%} = pH_{50\%}(\text{Me}) - pH_{50\%}(\text{Cu})$						

Table 5 shows composition of a few strip solution samples produced during pilot trials of copper extraction with 25 vol% LIX 984/Exxsol D80 and, for comparison, composition of a typical electrolyte from industrial copper electrorefining process. These data confirm the general effectiveness of ion-exchange solvent extraction technique in providing a barrier for iron(II/III) and the cations of non-ferrous metals other than copper(II) as well as prove the meaning of the data in Tables 3 and 4. Indirectly they demonstrate a sequence of minimal co-extractions of some elements – especially

Fe and Zn, which are present in the feed solutions in slightly bigger amounts, but also Ni, Co or Mn, and that sequence is similar to the that of extractions on the pH scale. These elements find their way to the strip solutions at relatively low level of several dozen (Fe – about 100, Zn – about 20–30) and in further cases (Ni, Co, Mn) of merely a few milligrams per liter and per cycle, while the other components of the feed solution (As, Sb, Se, Te, Bi, Pb and especially Sn, Cd, Cr, Ag) are practically absent in the strip solutions. Additionally, regardless of cationic ingredients, small amounts of chlorides, phosphates and silica are observed in the strip solutions.

Essential cationic (Fe, Zn, Ni, Co) as well as some anionic (chlorides, phosphates) components increase their concentrations during subsequent cycles of copper(II) extraction, gradually accumulating in strip solution which circulates between systems of stripping and electrolysis.

Table 5. Composition of copper strip solutions, obtained during pilot trials of copper extraction from post-leaching solutions with 25 % LIX 984/Exxsol D80 AZ

Component	> H <sub>2</sub> SO <sub>4</sub>	Cu	Ni	Co	Fe	As	Sb	Se	Cl	Zn
Electrolyte <sup>*)</sup>	172	43.2	7.56	0.10	0.13	4.0	0.37	0.095	0.046	0.029
Strip 1	135	55.5	<0.001	0.002	0.090	<0.001	<0.001	<0.001	0.020	0.030
Strip 2	140	50.2	0.0030	0.003	0.10	<0.001	<0.001	<0.001	0.035	0.020 g/dm <sup>3</sup>
Strip 3	148	53.7	0.0064	0.007	0.169	<0.001	<0.001	<0.001	0.028	0.082
Strip 4	145	57.6	0.0054	0.010	0.267	–	–	–	0.014	0.098
continued	Si	P	Sn	Cd	Cr	Te	Bi	Mn	Pb	Ag
Electrolyte <sup>*)</sup>	16	9	2.9	1	0.6	<0.5	<0.5	0.4	–	–
Strip 1	6	26	<0.1	<0.1	<0.1	<1	<1	3	<2.5	<0.1
Strip 2	3	30	<0.1	<0.1	<0.1	<1	<1	3	0.5	<0.1 mg/dm <sup>3</sup>
Strip 3	5.9	50	<0.1	<0.1	<0.1	<1	<1	5.9	2.6	<0.1
Strip 4	3.5	41	–	–	–	–	–	7.7	1.0	–

<sup>\*)</sup> composition of typical electrolyte of copper electrolytic refining; the other solutions are strip liquors, obtained during pilot plant trials from feed solution PLS/2 (Strip 1) or PLS/1 (Strip 2, 3 & 4)

## Conclusions

Six solvent extraction reagents – five of Cognis' LIX family: 860N-I, 84-I, 984N, 984 (hydroxyoximes), 54-100 (diketone) and Avecia's M5640 (modified salicylaldoxime of Acorga family), capable of selective extraction of copper(II), were characterized, with special attention paid to the selectivity of Cu(II) extraction against typical contaminants such as iron (Fe<sup>3+</sup>, Fe<sup>2+</sup>) and cations of other non-ferrous metals (Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup>, Mg<sup>2+</sup>). For the studies their 25 vol% solutions in hydrocarbon dis-

solvent Exxsol D80 AZ (ExxonMobil Chemical) were prepared. The most important our observations are:

- in most of the examined cases (except for LIX 54-100) copper(II) is the most strongly extracted cation ( $\text{pH}_{50\%}$  from 0.30 to 0.76),
- extractants, claimed as highly selective against iron, proved to be effective within a very narrow pH range of acidic solutions; extraction of Fe(III) begins at  $\text{pH} \geq 1.0$ –1.5, even with Acorga M5640, which was the best agent with  $\text{pH}_{50\%}^{\text{Fe(III)}} = 2.22$
- the distance between extraction of copper(II) and iron(III)  $\Delta\text{pH}_{50\%}^{\text{Fe(III)/Cu(II)}}$  is broad enough ( $\geq 1.0$ ) with the four reagents (M5640, 860N-I, 984N, 984); in that respect Acorga M 5640 (1.75) is definitely the best one; the rest (/LIX 84-I (0.86) and LIX 54-100 (-0.45)/ should rather be applied to extraction of copper(II) from ammonia solutions,
- iron(II) is the third to be extracted with respect to its position on pH scale, but in all cases the extraction is naturally strongly hampered and raises to merely 20–40% in the conditions under which other cations reach close to 100 % extraction,
- next, the pair of cobalt/nickel is extracted with a great distance to copper(II) at  $\text{pH}_{50\%}$  levels of 3.5-4.5 and 4.5-5.5 for Co(II) and Ni(II), respectively,
- cobalt(II) extraction is related to its partial oxidation and fractional permanent presence in organic phase (showing partial resistance to Co stripping), what was demonstrated by its permanent dark coloring; it seems that a similar situation takes place with all extractants,
- Mn(II) and Cd(II) form a similar ‘pair’ because they are extracted relatively close to each other and far from copper(II), at the level of 6.6-7.6 on the pH scale,
- zinc(II) extraction takes place earlier, between groups of Co(II)/Ni(II) and Mn(II)/Cd(II), at pH level about 5.5–6.0; slightly higher for LIX 54-100 and LIX 84-I.

Small co-extraction of some cations, in particular iron(III) and zinc(II), has a cumulative character. Therefore, when they are present in feed solutions in considerable amounts in the applied system of copper(II) extraction, a stage of organic phase scrubbing should be predicted.

## References

- AGERS D.W. et al, 1972, *The evaluation of new LIX reagents for the extraction of copper and suggestions for the design of commercial mixer-settler plants*; AIME Annual Meeting, San Francisco, Calif. TMS Paper Selection A72-87.
- Cytec Industries technical brochures; [www.cytec.com/specialty-chemicals](http://www.cytec.com/specialty-chemicals), (accessed Sept. 30, 2011), Acorga Extractants; Acorga OPT Series Solvent Extraction Reagents.
- JENKINS J. et al: *Electrolytic copper – leach, solvent extraction and electrowinning world operating data*, Proc. of Copper 99 – Cobre 99 International Conference; Vol. IV – *Hydrometallurgy of Copper*; Ed. by S.K. Young.
- KORDOSKY G.A., 2003, *Copper SX circuit design and operation - current advances and future possibilities*; Technical Proceedings ALTA 2003 SK/IX World Summit, Perth, Australia.

- KORDOSKY G.A. et al, 1983, *The LIX 860 series: Unmodified copper extraction reagents*, Proc. of the International Solvent Extraction Conf., Denver, Colorado,
- MERIGOLD C.R., 1996, *Copper extractants – modified and unmodified oximes, a comparison*, MID, CNNMIEC – Yunnan Company, BGRIMM Annual Technical Seminar, Kunming, Yunnan Province, PR of China,
- MTC Redbook technical brochure; *Solvent Extraction Reagents and Applications*. Mining Chemicals Technology Division, Cognis Corporation /Cognis Group/; (from [www.cognis.com](http://www.cognis.com), accessed Sept. 30, 2011);
- RITCEY G.M., 2006, *Solvent Extraction – Principles and applications to process metallurgy*, 2nd ed., Hong Kong,
- Tech. Bull. 1996-2000; LIX 860N-I, LIX 984, LIX 984N, LIX 84-I, LIX 54-100 particular Blue Line Technical Bulletins (accessed Sept. 30, 2011 at [www.cognis-us.com](http://www.cognis-us.com) )