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Copper separation from nitrate/nitric acid media using Acorga M5640 extractant

Part I: solvent extraction study

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Abstract

The extraction of copper(II) from nitrate/nitric acid aqueous solutions using Acorga M5640 has been studied. The metal extraction rate has been examined and also the effect of the aqueous pH, and metal and extractant concentrations. The increase of temperature increases copper extraction ($\Delta H^0 = 16.4\,\text{kJ}\,\text{mol}^{-1}$). Numerical treatment of the data indicated that the extracted species can be represented by the general stoichiometry CuR_2 (R being the active substance of the extractant) with $\log K_{\text{ext}} = 2.11 \pm 0.09$. The copper loading isotherms were obtained at 0.1 and 0.5 M nitric acid concentrations and 20 °C, whereas the stripping isotherm was obtained at 45 °C and using a solution of $180\,\text{g}\,\text{l}^{-1}$ sulphuric acid as strippant for copper. The oxime becomes degraded under prolonged contact time with nitric acid solution, but not with sulphuric acid. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nitrate acid; Copper(II); Acorga M5640; Solvent extraction

1. Introduction

Since the availability of the first hydroxyoxime extractants (LIX 63 and LIX 64) in 1964, there have been a continuous development of reagents which match the realities of the copper hydrometallurgical industry along these years.

In 1986, ICI presented new extractants of the Acorga type, being Acorga M5640 the newest and the lattest reagent of the series. However, and despiting the fact of its appearance 14 years ago, there are few data available in the literature concerning the application of Acorga M5640 in copper and/or metal extraction [1–6].

On the other hand, the characteristics and applications of hydroxyoxime extractants have been discussed in numerous literature; most of the applications had been reported in sulphate/sulphuric acid media, with few data reporting copper extraction from nitrate/nitric acid media [7–9]. The main reason should be that the latter is considered to degrade oximes.

Copper is also presented in a number of effluents or waste waters of various nature, being also its elimination a primary target from an environmental point of view, with solvent extraction and membrane technologies gaining an important role in this approach.

This first part of the two-part investigation reports on the use of conventional solvent extraction in the separation of copper from nitrate/nitric acid media using Acorga M5640 and under various experimental conditions: aqueous pH, metal and extractant concentrations, etc. the performance of the extractant (i.e. against degradation) under this aggresive medium is also investigated.

2. Experimental

Acorga M5640 (AVECIA [10]) was used as received by diluting it to the desired concentration in Iberfluid diluent. The active substance of the reagent is the 5-nonylsalicylaldoxime which also contained a fatty ester as modifier. According to its composition, the reagent, a salicyl aldehyde alkyl derivative, belongs to the fourth group of hydroxyoxime extractants, which form the second generation of hydroxyoxime reagents [5]. The presence of a modifier of this novel type improve the extraction properties of the basic oxime substance, including the selectivity for copper over iron, increases its resistance to hydrolisis and decrease formation of a fine dispersion that impedes phase disesangement in the settler [5,11]. Iberfluid (CS, Spain) is a kerosene type diluent which has the following specifications: density (20 °C), $785\,\text{kg}\,\text{m}^{-3}$; boiling range, 210–284 °C; flash point,

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96 °C; aromatic contents, <2%. Copper stock solution was prepared by dissolving electrolytic (grade A) copper in nitric acid and diluting the solution to the desired volume with distilled water. All other chemicals were of AR grade.

Extraction and stripping experiments were carried out in separatory funnels thermostatted at 20 °C and mechanically shaken (700 min^{-1}). A phase ratio O/A of 1 was used unless otherwised stated. The pH of the aqueous solutions was adjusted with nitric acid solution. Copper was analysed by AAS spectrometry (Perkin-Elmer 1100B spectrophotometer).

Extractant long term stability test was done in a reflux provided stirred beaker thermostatted also at 20 ± 1 °C. For the estimation of the copper loading, the organic phase was washed, prior to extraction, with water until it was acid free (pH of the raffinate 5.5–6).

3. Results and discussion

3.1. Rate of extraction

The data on rate of extraction are important in the design of equipment since it should be a critical factor which affects to the overall throughput and, therefore, the equipment dimensions and capital costs. Fig. 1 shows the rate of copper extraction from aqueous solutions which contained 1 g l^{-1} copper and different nitric acid concentrations by 10% (v/v) Acorga M5640 in Iberfluid.

It can be seen that equilibrium is generally reached within 10 min of contact and beyond this no further improvement is achieved. The increase of the initial nitric acid concentration, although does not affect to the copper rate of extraction, decreases the extent of copper loaded into the organic solution (0.99, 0.57 and 0.24 g l^{-1} copper at 10 min of contact and 0.1, 0.5 and 1.0 M nitric acid, respectively).

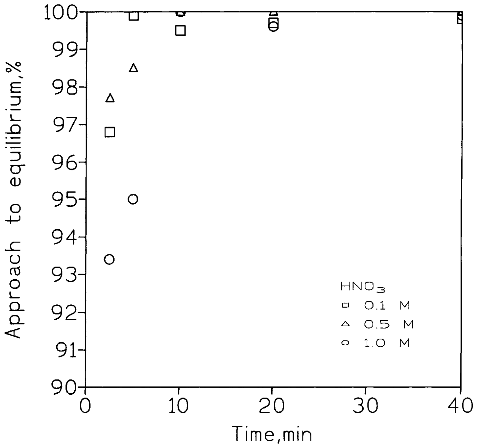


Fig. 1. Influence of equilibration time on copper extraction. Temperature: 20 °C.

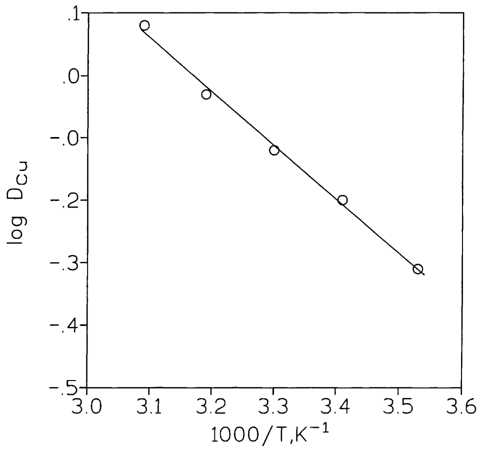


Fig. 2. Arrhenius plot for copper extraction. Aqueous phase: 3.5 g l^{-1} Cu and 0.1 M HNO$_3$. Organic phase: 5% (v/v) Acorga M5640 in Iberfluid. Equilibration time: 10 min.

3.2. Influence of temperature

The effect of this variable on copper extraction was also studied. The results, shown in Fig. 2, indicate that an increase in temperature brings about an increase in copper extraction. As stated in literature [12,13], the linear relationship of $\log D$ versus $1/T$ plot for complex formation should be an indication that only a single species is involved. This indirectly supports the assumption (see further) that only CuR$_2$ species is formed in the organic solution. Fig. 2 shows $\Delta H^0 = 16.4\,\mathrm{kJ\,mol^{-1}}$ indicating the sligthly endothermic reaction of extraction.

3.3. Influence of pH and extractant concentration

Being copper extraction by Acorga M5640 dependent on the initial acidity of the aqueous solution, further studies were carried out in order to discern the influence of the aqueous pH on copper extraction. In this study, aqueous solutions of 0.1 g l^{-1} copper (in nitrate media and pH-adjusted with nitric acid) and different phases of Acorga M5640 (0.5, 1 and 2.5% (v/v)) in Iberfluid were used. Equlibration time was of 10 min.

The results obtained were shown in Fig. 3, plotting the percentage of copper extraction versus equilibrium pH. It is evident that the pH of the aqueous solution affects copper extraction by Acorga M5640, although even using a relatively low extractant concentration as 2.5% (v/v) almost complete copper extraction can be performed at an aqueous pH of 1.

From data represented in this figure it also can be seen that the curves are shifted to the left as the extractant concentration is increase, this should be due to the shift to the right of the corresponding mass-equilibrium:

$$\mathrm{Cu^{2+}_{aq}} + n\mathrm{HR_{org}} \rightleftarrows \mathrm{CuR_2(HR)_{(\mathit{n}-2)_{org}}} + \mathrm{2H^{+}_{aq}} \qquad (1)$$

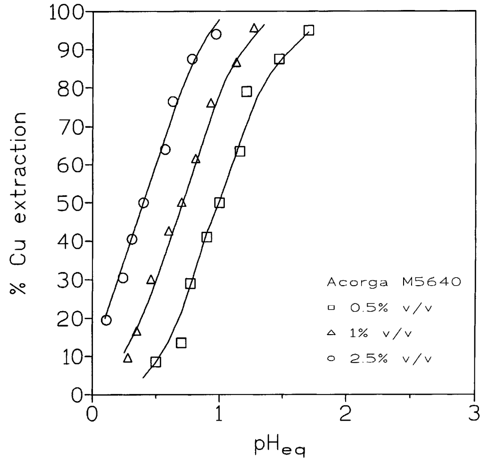


Fig. 3. Influence of pH and Acorga M5640 concentration on copper extraction. Temperature: 20 °C.

3.4. Copper loading and copper equilibrium isotherms

The loading of copper in Acorga M5640 solutions was study by two procedures. In the first procedure, a 10% (v/v) Acorga M5640 solution in Iberfluid was contacted for 10 min at various A/O ratios with an aqueous phase of 1 g l^{-1} copper at an initial pH of 1.0. Results obtained indicated that almost complete copper loading (3.7 g l^{-1}) of the organic solution is reached using an A/O ratio of 6. The second procedure uses an organic phase of Acorga M5640 5% (v/v) in Iberfluid which was repeatedly contacted with fresh aqueous solutions of 1.0 g l^{-1} copper at an initial pH of 2.2. Equilibrium time was of 10 min. In this case, a maximum loading of 2.8 g l^{-1} copper was reached after four extraction cycles.

The copper equilibrium isotherms were obtained from an organic solution of 10% (v/v) Acorga M5640 in Iberfluid and aqueous solutions of 1 g l^{-1} Cu and two levels of nitric acid concentrations (0.1 and 0.5 M) using the continuous O/A volume phase variation procedure. Equilibrium time was in all the cases of 10 min. Fig. 4 plotted the results obtained, it is shown that the concentration of acid in the aqueous feed clearly influences the shape of the isotherm and the copper loading in the organic phase. From data presented in this work it, thus, recommended that an organic phase of 10% (v/v) should be used for the treatment of aqueous phases which contained 0.1 M nitric acid, the increase of the aqueous acidity will lead to the use of more concentrated Acorga M5640 solutions in order to obtain better copper loadings in the organic phase.

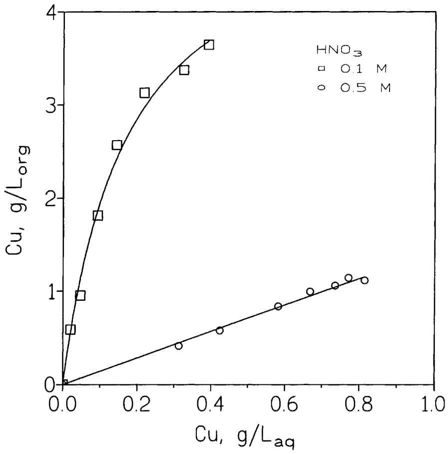


Fig. 4. Copper equilibrium loading isotherms. Temperature: 20 °C.

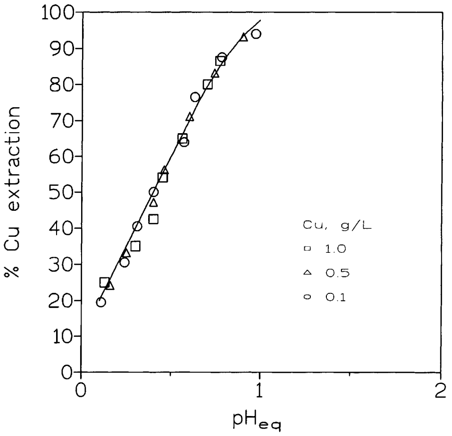


Fig. 5. Influence of initial metal concentration on copper extraction. Temperature: 20 °C.

3.5. Influence of metal concentration

This influence was studied using organic phases of 2.5% (v/v) Acorga M5640 in Iberfluid and aqueous phases of different copper concentrations. Equilibrium time was of 10 min. Results obtained were plotted in Fig. 5, it is shown that under the experimental conditions, the variation of the initial metal concentration does not affect the extraction of copper by Acorga M5640. This results should be indicative of the no-formation of polynuclear complexes in the organic solution.

3.6. Influence of ionic strength

The effect of varying the ionic strength was studied using aqueous solutions which contained various lithium nitrate concentrations, being the rest of the experimental conditions as described above. Results obtained from this set of experiments were presented in Table 1. It is shown that the

Table 1
pH_{50} values for copper extraction from lithium nitrate solutions[a]

$LiNO_3$ (M)	pH_{50}
–	0.40
0.1	0.38
0.25	0.41
0.5	0.40

[a] Aqueous phase: 0.1 g l^{-1} copper.

Table 2
Species for copper extraction by Acorga M5640 in Iberfluid[a]

Species	$\log K_{ext}$	$\sigma(\log K_{ext})$	U	σ
CuR_2	2.11 ± 0.09	0.03	0.41	0.14

[a] Number of experimental points 45. The standard deviation is defined as $\sigma = (U/N - N_K)^{1/2}$, where N_K is the number of constants to be adjusted.

presence of the salt does not affect the pH_{50} value (equilibrium pH at which 50% metal extraction proceeds) for copper extraction.

3.7. Copper extraction mechanism by Acorga M5640 from nitrate/nitric acid medium

The experimental data obtained in the distribution equilibrium experiments were treated numerically using the program LETAGROP-DISTR [14] in order to define the stoichiometry of the extracted species and the value of the extraction constant. The program searches, for a given model, the best set of equilibrium constants that would minimize the expression:

$$U = \sum (\log D_{cal} - \log D_{exp})^2 \tag{2}$$

where D_{exp} is the distribution coefficient of copper determined experimentally and D_{cal} the value calculated by the program solving the mass balance equation for the different components of the reaction. Various models with species of different stoichiometries were tried in order to investigate the possibility of finding different species which could improve the fit to the experimental results. For the present system, the program fits the existence of one species in the copper-loaded organic phase, the corresponding stoichiometry is given in Table 2, which also shows the value of $\log K_{ext}$.

Accordingly, the extraction of copper can be represented by the equilibrium shown in Eq. (1) in which $n = 2$, the extraction is, therefore, a cationic exchange (chelating) reaction. From the value of $\log K_{ext}$ is obtained $\Delta G^0 = -11.8\,\mathrm{kJ\,mol^{-1}}$, and hence $\Delta S^0 = 96.2\,\mathrm{J\,mol^{-1}\,K}$. The negative value of ΔG^0 is an indication of the low pH values necessary to allow copper extraction to proceed, whereas the positive ΔS^0 indicates that copper is being transferred from a disordered state to one of a greater disorder.

3.8. The effect of nitric acid on Acorga M5640

Sulphuric acid degrades oximes, although the degradation is a slow reaction [15,16], nitric acid should be more aggresive against hydroxyoximes, thus, the reaction of Acorga M5640 with nitric acid was studied. The organic phase was of 5% (v/v) Acorga M5640 in Iberfluid, whereas the aqueous solution contain 2 M nitric acid. The degradation of the oxime was studied using its maximum copper loading and net transfer capacity after stripping with sulphuric acid (2 M) or nitric acid (2 M). Fig. 6 shows the copper loading versus time for these experiments, in Table 3, the net copper transfer capacity (T) is given. S-values remained almost constant through the experiment and indicates that near complete copper stripping is obtained, on the other hand, similar net copper transfer values were obtained using either sulphuric of nitric acid solutions.

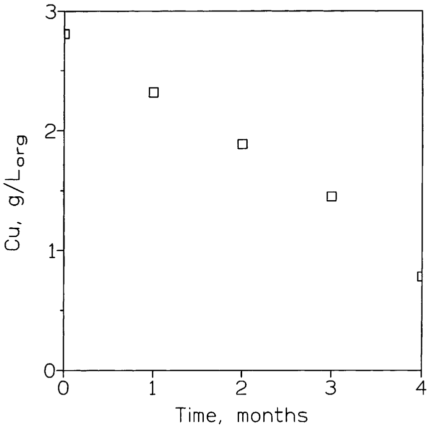


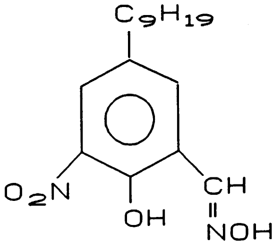
Fig. 6. Copper loading of 5% (v/v) Acorga M5640 in Iberfluid after continuous contact with 2 M nitric acid. Aqueous phase for extraction: $1\,\mathrm{g\,l^{-1}}$ copper at pH 2.2. Temperature: 20 °C; equilibration time: 10 min.

Table 3
Degradation of Acorga M5640 under contact with nitric acid ($T = 25 \pm 2\,°C$)[a]

Time (months)	$Cu_{loading}$ $(\mathrm{g\,l^{-1}})$	$S_{H_2SO_4}$	S_{HNO_3}	$T_{H_2SO_4}$	T_{HNO_3}
0	2.81	0.05	0.22	2.76	2.59
1	2.32	0.06	0.07	2.26	2.25
2	1.88	0.06	0.09	1.82	1.79
3	1.46	0.04	0.06	1.42	1.40
4	0.78	0.05	0.08	0.73	0.70

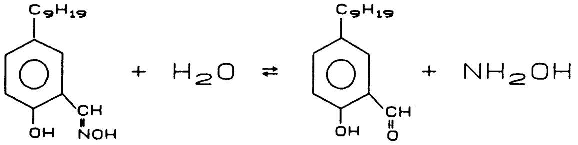
[a] $S_{H_2SO_4,HNO_3}$: copper remaining in the organic phase after stripping; $T_{H_2SO_4,HNO_3}$: net copper transfer capacity, defined as $Cu_{loading} - S_{H_2SO_4,HNO_3}$.

A small sludge formation in the organic phase occurred, this should be indicative of formation of less soluble reaction products. Taking into account the evidences obtained from this work, it can be deduced that in the reaction of Acorga M5640 with nitric acid, the formation of a product with general structure



as a consequence of an *ortho*-nitration of the extractant [7] should be discarded due to the very difficult strippability of a reagent of this type.

The degradation of the oxime should be due to the possible reaction [7,16]



which is acid catalysed. Comparative investigation using the same organic solution as described above and 180 g l^{-1} sulphuric acid showed that there is not appreciable oxime degradation over the contact period, between both phases, studied (4 months).

3.9. Copper stripping

Experimental data had shown that the contact of Acorga M5640 with nitric acid degrades the active substance of the extractant, on the other hand, sulphuric acid is not as oxidizing agent as nitric acid and is widely used as stripping reagent in copper solvent extraction plants. Having the same net transfer capacity than nitric acid (Table 3) sulphuric acid seems to be the best suitable stripping reagent for the present system. Acorga M5640 is a strong extractant for copper; the stripping of this element is best done with sulphuric acid concentrations in the 180 g l^{-1} range.

The stripping isotherm was obtained by contacting, at various O/A ratios, an organic phase of 40% (v/v) Acorga M5640 in Iberfluid (loaded with 22 g l^{-1} copper) with an aqueous solution of 180 g l^{-1} sulphuric acid for 10 min and 45 °C (typical of copper stripping operation). Previous experiments also showed that this contact time is sufficient to reach stripping equilibrium. The isotherm is represented in Fig. 7.

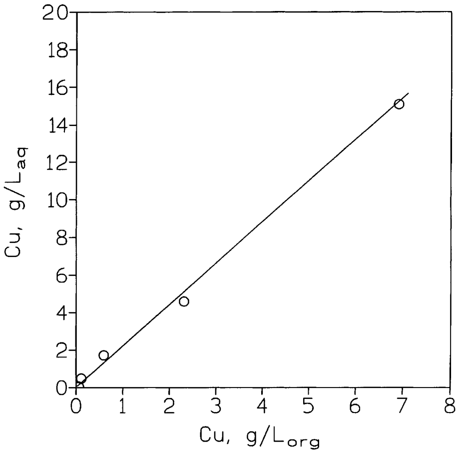


Fig. 7. Copper stripping isotherm.

4. Conclusions

The extraction of copper(II) with Acorga M5640 increases with pH value, reaching a maximum in the zone of pH 2 (0.5% (v/v) Acorga M5640 in Iberfluid). There is an increase of copper extraction with temperature (endothermic reaction). Numerical treatment of experimental data showed that copper extraction can be explained by the formation of CuR_2 species in the organic phase ($\log K_{\text{ext}} = 2.11 \pm 0.09$). Copper stripping from loaded organic solutions of Acorga M5640 can be readily achieved using sulphuric acid solutions typical of electrowinning operations (i.e. 180 g l^{-1}). Under contact with nitric acid the loading capacity of the oxime decreases with time. This can probably be explained by a hydrolisis of the active substance of the reagent. As the importance of this reaction decreases with the decreasing of nitric acid concentration in the feed solution, it is recommended that the extraction of copper from nitrate/nitric acid media is carried out at pH near 2–3, which also allows to obtain higher copper loadings in the organic phase with fewer stages.

Acknowledgements

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