Modelling of solvent extraction equilibrium of Cu(II) from sulphuric acid solution with MOC-55TD[(•)]

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Resumen The extraction of Cu(II) from acidic sulphate aqueous solutions using the commercial MOC-55TD extractant is studied. A predictive model, which consists in a set of non-linear mass action and mass balance equations is proposed. The model was solved using a tailor-made equation-solving program. The extraction of copper can be described by the formation of CuR_2 species (log K_{ext}= 0.717 ± 0.03) in the organic phase. The copper equilibrium isotherm was also obtained at 20 °C.

Palabras clave: **Solvent extraction. Modelling. Copper. MOC-55TD.**

Modelización del equilibrio de extracción con disolventes cobre-MOC-55TD en disoluciones de ácido sulfúrico

Abstract Se estudia la extracción de Cu(II) de disoluciones acuosas ácidas, en medio sulfato, mediante la oxima comercial MOC-55TD. Se propone un modelo para predecir la extracción del metal; este modelo consiste en una serie de ecuaciones no lineales de acción de masas y balance de masas. El modelo se resolvió empleando un programa de ordenador específicamente definido para este tipo de equilibrios. La extracción de cobre se describe por la formación de la especie CuR_2 (log K_{ext}= 0,717 ± 0,03) en la fase orgánica. Se ha obtenido la isoterma de extracción de cobre a 20 °C.

Keywords: **Extracción con disolventes. Modelización. Cobre. MOC-55TD.**

1. INTRODUCTION

Solvent extraction operation is becoming more and more attractive in the hydrometallurgical processing of raw and secondary materials because of potentially low energy costs and minimization of environmental impact. Tipically, selective extraction of metals from multi-elemental aqueous solutions is required in order to obtain high purity solutions suitable for final metal recovery techniques, e.g. electrowinning.

In the case of copper, recent changes in copper production processing have made it possible to achieve favourable operations with marginal ores. Probably the most important change is the increasingly widespread use of the solvent extraction-electrowinning circuit as a major copper production method (Table I) and in the most economical way (4).

The design of new solvent extraction-electrowinning plants or even the modification of existing ones, requires a series of experiments to develop reliable and efficient plant operating parameters. Here is where solvent extraction prediction modelling enters into scene. A good

TABLE I.– Worlwide production of refined copper (1-3)

TABLA I.– Producción mundial de cobre refinado (1-3)

	Total (ton. 103)	SX/EW (ton. 103)	% over total
1981	7350	700	9.5
1991	8863	950	10.7
2000[a]	11000	2310	21.0

[a] Estimated

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predictive model can take a number of chosen conditions and predict, with good accuracy, the equilibrium values, and, therefore, reducing the required experimentation.

A number of prediction models of various nature have been suggested (5-13); in the other hand, several new oximes extractants are being introduced into the industry and adopted by different plants (14).

This research presents the development of a chemical based model for describing and predicting the solvent extraction of copper from acid solutions by the new extractant MOC-55TD.

2. EXPERIMENTAL PROCEDURE

MOC-55TD was supplied by Allco Chem. (actually Inspec Mining Chemicals), its characteristics have been published elsewhere (15 and 16). The desired extractant concentration was prepared by diluting the as-received MOC-55TD with toluene (AR grade). The measure of the extractant concentrations was carried out by the ultimate loading (3), as this appears to be of most practical use in determining oxime concentrations.

Stock solutions of Cu(II) sulphate were prepared by dissolving $CuSO_4 \cdot 5H_2O$ (AR grade) with distilled water. The pH values were adjusted to the desired values using sulphuric acid (AR grade).

Extraction experiments were carried out by shaking equal volumes of the appropriate aqueous and organic solutions in separatory funnels provided with mechanical shaking (700 rpm) for 5 min and 20 ± 0.5 °C. Previous experiments shown that this contact time is sufficient to achieve metal extraction equilibrium.

The copper equilibrium isotherm was generated in the same conditions as described above but using the continuous A:O phase ratio variation method. In this case, Iberfluid (CS (Spain)), a kerosene type diluent, was used to dilute the reagent; the main characteristics of Iberfluid are: density (20 °C) 782 kg/m³, boiling range 210-284 °C, flash point 96 °C, aromatics content < 2 %.

Copper concentration in the aqueous phases and raffinates was analyzed by AAS spectrophotometry. The metal concentration of the corresponding organic phases was calculated by mass balance. The pH of the aqueous solutions was measured using a Crison 506 pH-meter.

3. RESULTS AND DISCUSSION

Experimental conditions were chosen to simplify the model:

– the initial oxime concentration in the organic phase was less than 0.1 mol/L,
– an aromatic diluent was used to dilute the reagent; with these two conditions it is assumed that the oxime does not dimerize (4).

The assumed reaction in building the model is represented by the next equation:

$$Cu^{2+}_{aq} + 2HR_{org} \Leftrightarrow CuR_{2\,org} + 2H^+_{aq} \quad K_1 \quad [1]$$
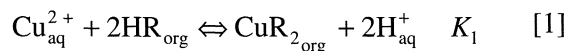
where HR represents the extractant, CuR_2 represents the copper-MOC-55TD complex and aq and org the aqueous and organic phases, respectively.

The mass-action equilibrium expression for the above reaction is:

$$[CuR_2]_{org} = K_1 \frac{[Cu^{2+}]_{aq}\,[HR]^2_{org}}{[H^+]^2_{aq}} \quad [2]$$

assuming also ideal behaviour in both organic and aqueous phases. In addition to the mass-action equation, the model also includes the following mass-balance equations:

$$[Cu]_{total} = [Cu^{2+}]_{aq} + V_{O/A}\,[CuR_2]_{org} \quad [3]$$

$$[HR]_{total} = [HR]_{org} + 2\,[CuR_2]_{org} \quad [4]$$

where $[Cu]_{total}$ is the total copper concentration in the system, $[HR]_{total}$ is the total extractant concentration in the system and $V_{O/A}$ is the organic to aqueous volume ratio.

The developed model consists of a set of mass-action equilibrium equation plus the appropriate mass-balance equations. The value of the equilibrium constant was calculated by treatment of experimental data by the program LETAGROP-DISTR (17). This program minimizes the sum of the squares defined as:

$$U = \Sigma\,(\log D_{cal} - \log D_{exp})^2 \quad [5]$$

where D_{cal} is the copper distribution ratio calculated by the program and D_{exp} is the value determined experimentally.

The results of the numerical calculation is given in table II. It can be concluded that the extraction of Cu(II) by MOC-55TD in toluene can be explained by the formation of CuR_2 species in the organic phase.

The equations describing the proposed model are a set of non-linear equations that can not be analytically simultaneously solved, thus a BASIC program has been developed to do the calculations.

TABLE II.– Results of the numerical treatment of experimental data in the extraction of Cu(II) by MOC-55TD

TABLA II.– Resultados del tratamiento numérico de los datos experimentales en la extracción de Cu(II) mediante MOC-55TD

Species	$\log K_{ext}$	$\sigma (\log K_{ext})$	U	σ
CuR_2	0.717 ± 0.03	0.01	0.095	0.055

Table III shows, in the form of rules used by the program, the complete set of equations for the model studied.

Finally, the mathematical model was developed using the experimentally measured equilibrium pH values in the raffinates, and from the total copper and oxime concentrations and the O:A volume ratio, all the equilibrium concentrations can be calculated.

The equilibrium data obtained in the present work at different equilibrium pH values on the system $Cu(II)-H_2SO_4-MOC-55TD$-toluene are given in table IV together with the predicted data. Figure 1 is a plot of $\log D_{Cu}$ calculated versus log
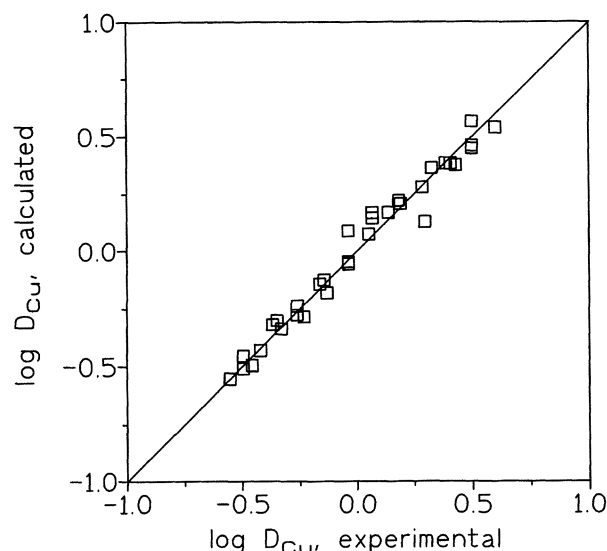

FIG. 1.— Comparison of $\log D_{Cu}$ predicted versus $\log D_{Cu}$ experimental.

FIG. 1.— Comparación de $\log D_{Cu}$ (teóricos) frente a $\log D_{Cu}$ (experimentales).

D_{Cu} experimental; good agreement between the experimental and calculated data is indicated by the r^2 value 0.975 between these two results and the

TABLE III.– The rules used by the BASIC program to model solvent extraction of copper by MOC-55TD[*]

TABLA III.– El programa BASIC para la modelización de la extracción con disolventes del cobre mediante MOC-55TD[*]

```
CLS : CLS 2: SCREEN 12
x$ = "[CuR2]"
y$ = "[Cu2+]"
z$ = "[HR]"
a$ = "[H+]"
m$ = "[Cu]tot"
v$ = "Voa"
e$ = "[HR]tot"
k$ = "k1"
LOCATE 1, 1: PRINT "data input"
LOCATE 2, 1: PRINT "_____ "
LOCATE 3, 1: PRINT a$: LOCATE 3, 10: INPUT a
LOCATE 4, 1: PRINT m$: LOCATE 4, 10: INPUT m
LOCATE 5, 1: PRINT v$: LOCATE 5, 10: INPUT v
LOCATE 6, 1: PRINT eS: LOCATE 6, 10: INPUT e
LOCATE 7, 1: PRINT k$: LOCATE 7, 10: INPUT k
LOCATE 8, 1: PRINT "_____ "
b= 2*m/v-e
c= a*a/k/v
d= -c+e
p= (3*c-b*b)/3
q= (27*d-9*b*c+2*b*b*b)/27
r= ((p/3)^3)+q*q/4
IF r<0 THEN 10
ha= SQR(r)-q/2: IF ha<0 THEN ma = -1 ELSE ma=1
aa= ABS(ha): aa=aa^(1/3): aa=aa*ma
hb= -SQR(r)-q/2: IF hb<0 THEN mb= -1 ELSE mb=1
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bb= ABS(hb): bb=bb^(1/3): bb=bb*mb
z1= aa+bb-b/3
x1= (e-z1)/2
y1= m-v*x1
LOCATE 10, 1: PRINT x$: LOCATE 10, 10: PRINT "="; x1
LOCATE 11, 1: PRINT y$: LOCATE 11, 10: PRINT "="; y1
LOCATE 12, 1: PRINT z$: LOCATE 12, 10: PRINT "="; z1
END
10 IF q<0 THEN mul = 1 ELSE mul = -1
ang= 27*q*q/4/((-p)^3): ang = SQR(ang)
phi= ATN(SQR(1-ang*ang)/ang)
phi= phi*180/3.1416
w = mul*2*SQR(-p/3)
FOR k = 1 TO 3
ang = (phi/3+120*(k-1))*3.1416/180
z(k) = w* cos(ang)-b/3
x(k) = (e-z(k))/2
y(k) = m-v*x(k)
NEXT k
LOCATE 10, 1: PRINT x$: LOCATE 10, 10: PRINT"=";
    x(1), x(2), x(3)
LOCATE 11, 1: PRINT y$: LOCATE 11, 11: PRINT"=";
    y(1), y(2), y(3)
LOCATE 12, 1: PRINT zS: LOCATE 12, 12: PRINT"=";
    z(1), z(2), z(3)
END
```

[*] On request, an electronic copy of the program may be obtained from the Editor (Prof. O.A. Ruano)

TABLE IV.– Equilibrium data for $CuSO_4$-H_2SO_4-MOC-55TD-toluene system

TABLA IV.– Datos de equilibrio para el sistema $CuSO_4$-H_2SO_4-MOC-55TD-tolueno

pH_{eq}	D_{Cu} experimental	$^a[Cu^{2+}]\cdot10^{-3}$ mol/L_{aq}	$^a[CuR_2]\cdot10^{-3}$ mol/L_{org}	$^a[HR]\cdot10^{-2}$ mol/L_{org}	D_{Cu} predicted
1.70	3.17	0.171	0.629	0.0167	3.68
1.48	1.17	0.334	0.466	0.0170	1.40
1.23	0.47	0.547	0.253	0.0175	0.46
1.72	4.00	0.358	1.24	0.0155	3.46
1.63	2.70	0.474	1.13	0.0158	2.38
1.54	1.56	0.610	0.990	0.016	1.62
1.40	0.92	0.842	0.758	0.0165	0.90
1.27	0.59	1.05	0.548	0.0169	0.52
1.15	0.32	1.22	0.380	0.0174	0.31
1.55	1.99	1.36	1.84	0.0143	1.35
1.36	0.74	1.93	1.27	0.0155	0.66
1.21	0.38	2.34	0.857	0.0163	0.37
1.20	2.57	0.234	0.566	0.0429	2.42
1.05	0.92	0.359	0.441	0.0431	1.23
0.77	0.32	0.594	0.206	0.0436	0.35
1.20	2.13	0.485	1.12	0.0418	2.31
1.10	1.17	0.646	0.954	0.0421	1.48
0.94	0.69	0.928	0.672	0.0427	0.72
0.85	0.43	1.08	0.523	0.0430	0.48
1.27	3.17	0.840	2.36	0.0393	2.81
1.15	1.53	1.20	2.00	0.0400	1.67
0.90	0.55	2.03	1.17	0.0417	0.58
0.84	1.94	0.275	0.524	0.0870	1.91
0.67	0.92	0.426	0.373	0.0873	0.88
0.45	0.35	0.606	0.194	0.0876	0.32
0.90	2.45	0.466	1.13	0.0857	2.42
0.79	1.38	0.645	0.955	0.0861	1.48
0.64	0.72	0.914	0.686	0.0866	0.75
0.55	0.45	1.06	0.533	0.0869	0.50
0.42	0.28	1.25	0.347	0.0873	0.28
0.95	3.17	0.823	2.38	0.0832	2.89
0.75	1.13	1.46	1.74	0.0845	1.19
0.57	0.55	2.09	1.11	0.0858	0.53

^{a} = Values calculated by the program

standard deviation 0.05 of residuals from the regression line.

Solvent extraction processing in a continuous counter-current basis requires knowledge on equilibrium loading isotherm. As copper acidic leaching solutions usually have a pH value in the 1.5-3.3 range (18), in the present work, an equilibrium isotherm was obtained at an initial pH value of 2.0. The copper concentration in the initial aqueous solution was 0.55 g/L.

The loading isotherm data for the present system obtained from the phase ratio variation method are given in table V. Figure 2 represents the loading isotherm for copper extraction with 1 % v/v MOC-55TD in Iberfluid. The isotherm curve can be mathematically represented by the equation:

$$[Cu^{2+}]_{org} = \frac{0.672[Cu^{2+}]_{aq}}{0.108 + [Cu^{2+}]_{aq}} \qquad [6]$$

where the concentrations represented the total metal equilibrium values in the respective phases.
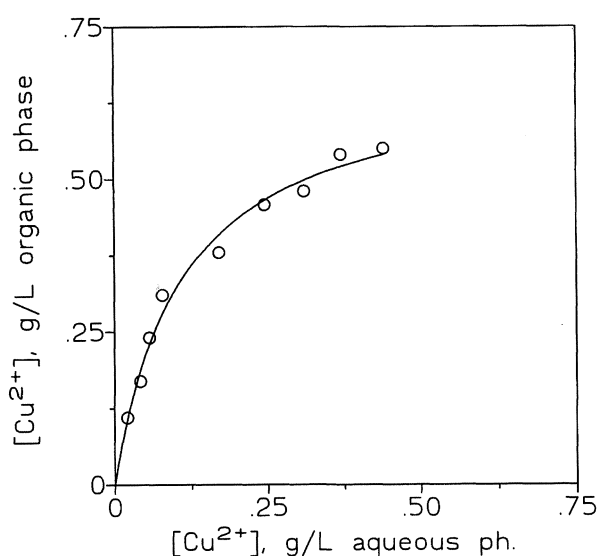
4. CONCLUSIONS

The solvent extraction of Cu(II) from acidic solutions using the commercial extractant MOC-55TD has been successfully predicted using the developed model. From experimentally obtained data it was demonstrated that the extracted species

TABLE V. – Loading isotherm data

TABLA V.– Datos de la isoterma de extracción

O/A ratio	$[Cu^{2+}]$, g/L aqueous phase	$[Cu^{2+}]$, g/L organic phase
5	0.02	0.11
3	0.04	0.17
2	0.06	0.24
1.5	0.08	0.31
1	0.17	0.38
0.67	0.25	0.46
0.50	0.31	0.48
0.33	0.37	0.54
0.20	0.44	0.55

FIG. 2.— Equilibrium loading isotherm for the system Cu_2SO_4-H_2SO_4-MOC-55TD-Iberfluid.

FIG. 2.— Isoterma de equilibrio de extracción para el sistema Cu₂SO₄-H₂SO₄-MOC-55TD- Iberfluid.

consists of one copper ion bound to two oxime molecules. Numerical treatment of the data indicated that log K_{ext} is 0.717 ± 0.03 using toluene as diluent of the organic phase. The equilibrium loading isotherm for the Cu(II)-H_2SO_4-MOC-55TD-Iberfluid system was obtained at 20 °C.

Acknowledgement

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