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Ligia Stoica<sup>a</sup>; Gabriela Carmen Oproiu<sup>a</sup>; Roxana Cosmeleata<sup>a</sup>; Magda Dinculescu<sup>a</sup>

<sup>a</sup> Department of Inorganic Chemistry, "Politehnica" University Bucharest, Bucharest, Romania

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## Kinetics of $\text{Cu}^{2+}$ Separation by Flotation

**Ligia Stoica,\* Gabriela Carmen Oproiu,  
Roxana Cosmeleata, and Magda Dinculescu**

Department of Inorganic Chemistry, “Politehnica” University  
Bucharest, Bucharest, Romania

### ABSTRACT

Precipitate flotation is one of the most efficient and economic separation methods that has been widely applied in the last few years for ion-molecular and colloidal species, both representing pollutant and useful substances.

The separation of  $\text{Cu}_{\text{aq}}^{2+}$  species from diluted aqueous systems is often studied for environment protection and for the recovery of copper. A systematical study of the whole process has to consider the dynamics of the process in order to optimize it.

This paper represents a study concerning the kinetics of  $\text{Cu}_{\text{aq}}^{2+}$  ions separation by precipitate flotation using alkylamine type (laurylamine) and alkylammonium salt (lauryltrimethylammonium chloride) as cationic collectors and alkylsulphate and alkylcarboxilic type (sodium laurylsulphate and sodium oleate) as anionic collectors. The experimental data

\*Correspondence: Ligia Stoica, Department of Inorganic Chemistry, “Politehnica” University Bucharest, Splaiul Independentei 313, Sector 6, Bucharest, Romania; E-mail: l.stoica@oxy.pub.ro.



have been used in order to verify the classical first order model and three other first-order models, respectively, adjusted to the classical model. The experimental data have been analyzed with the PEAKFIT program.

The results of the study sustain—by interpretation of the fitting parameters (the correlation coefficient,  $r$ , and the curve fit standard error,  $e$ )—a first-order kinetics for the separation process of Cu(II) hydroxide species by precipitate-flotation method.

Among the studied kinetic models, the classical first-order model and the first-order reversible model is well fitting the experimental data, and the fully mixed reactor model describes, with acceptable errors, the  $\text{Cu}_{\text{aq}}^{2+}$  ions separation process by flotation.

*Key Words:* Copper; Separation; Recovery; Precipitate flotation; Kinetic model.

## INTRODUCTION

The impurities of metallic ion-type are dangerous pollutants that may represent a real source of useful substances as well. For the improvement of environmental quality and for simultaneous recovery of the useful compounds, several separations—recovery methods have been developed in the last years that are generally unconventional procedures based on interface mass transfer. The group of separation methods, using adsorptive bubbles, which also includes ion-molecular and colloidal-particle flotation (Dissolved Air Flotation, DAF variant) represents an alternative to the classical methods.<sup>[1]</sup>

Ion and precipitate flotation was developed as a consequence of the progresses registered in the ores-flotation field, where the separated particles are of micrometer/millimeter size. The principles of macroparticles flotation can be also applied in the flotation of the ion-molecular and colloidal species.

In the ores-flotation process, the separation is achieved by natural hydrophobicity of solid particles or by artificially created (adding small quantities of collector) hydrophobicity.

In ion-flotation process, the hydrophobicity is achieved by a stoichiometric reaction of hydrophilic species with a tensioactive agent (TSA) as collector. The product formed by the collector—metallic ion (colligand) interaction, named sublate, becomes surface-active and it is concentrated into the foam through the mobile phase (gas bubbles).

In precipitate-flotation process, the aqueous hydrophilic ion species become hydrophobic species by the precipitation with another reagent than the tensioactive agent. The precipitate hydrophobicity can be increased when it is treated with a tensioactive agent in lower quantities than the stoichiometrical ones.<sup>[2]</sup>

Thus, the main condition for achieving the flotation process is the hydrophobicity of the species that are to be separated. At low pH values, in aqueous systems, the metal cations are present as hydrophile aqueous complex  $[M(OH_2)_x]^{n+}$  type. By increasing of pH, the  $[M(OH_2)_x]^{n+}$  species are involved in a successive deprotonation reaction leading to polymeric-hydroxide species and, finally, to the formation of hydroxide precipitate  $[M_p(OH)_y(OH_2)_x]^{np-y}$  type. This process is known as the olation and oxolation process.<sup>[3]</sup>

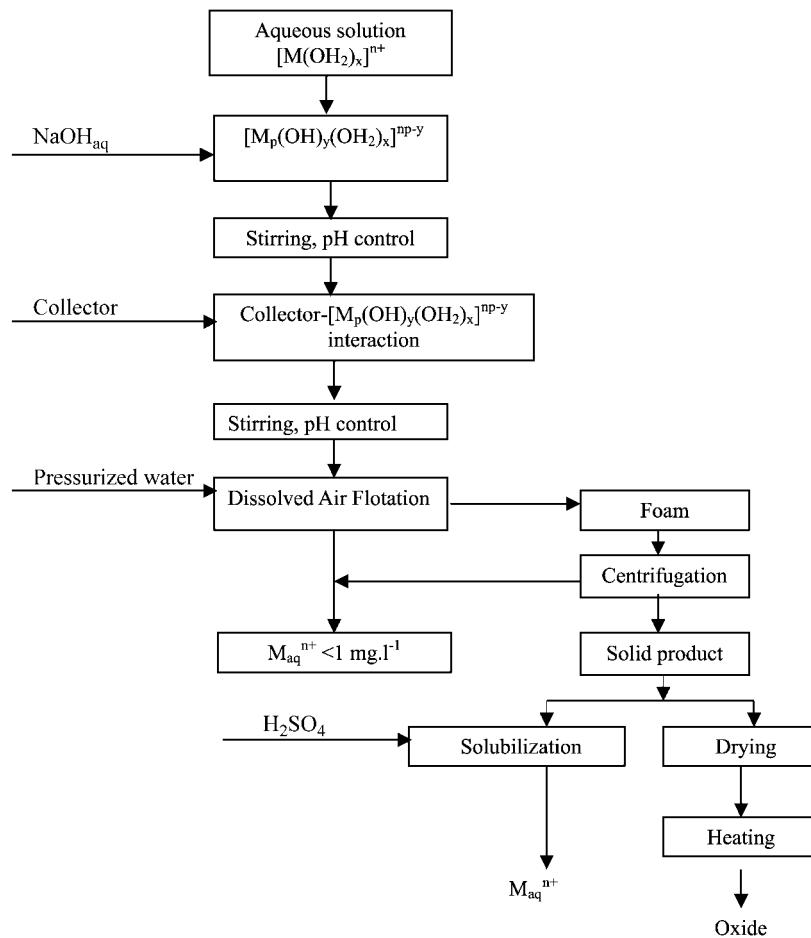


Figure 1. Separation scheme of flotation processes (DAF).



In Fig. 1, a schematical presentation of the flotation process, including the processing of the separated foam, is given.

Flotation as a complex separation process depends on chemical factors (pH, molar ratio collector:colligand  $C_C:C_M^{n+}$  and,  $M^{n+}$  concentration) and hydrodynamic and mass-transfer factors, too. The study of the acid-base complex equilibrium, correlated with the species structure and with the possibility of recovery of the metallic ions from the foam, allows the inclusion of flotation within the group of purification methods.<sup>[4]</sup>

Ion flotation and its variant, precipitate flotation, are considered separation methods with wide application possibilities (Fig. 2), especially for the small concentrations range of noxious components having high ecological and economical performances. The theoretical approach of the precipitate flotation process has to consider the dynamics of the process, and therefore, the kinetic aspects.<sup>[5]</sup> However, there are many difficulties in establishing the kinetic equations because the flotation is a complex process determined by many factors, some of them depending on the component nature and structure<sup>[6]</sup> and others on the design characteristics of the separator apparatus.<sup>[7]</sup>

Therefore, the complexity of the flotation process is determined by:

- the number of elementary microprocesses which are simultaneously and successively developed in space and time, each of them with a definite probability [adhesion, collision, and the bubble-particle complex formation<sup>[6]</sup>];
- the structural and dimensional diversity of organic or inorganic compounds in real aqueous systems (ions, molecules, colloids, precipitates, etc.);
- the special properties of interfaces, and physical-chemical and hydrodynamic factors.

Theoretical equations of flotation kinetics presented in literature are generally deduced for ore flotation<sup>[8]</sup> by analogy with chemical kinetics, without taking into account the particularities of this process and the specific interactions between hydrophobic particles and gas bubbles. The first paper concerning the ores flotation kinetics was published by Garcia-Zuniga<sup>[9]</sup> who noticed that the extraction efficiency is an exponential function of time.

An important contribution to the theoretical fundament of flotation kinetics is that of Huber-Panu,<sup>[10]</sup> who studied the factors influencing the process and proposed a general model equation that could be accommodated with some peculiar cases already described in literature.

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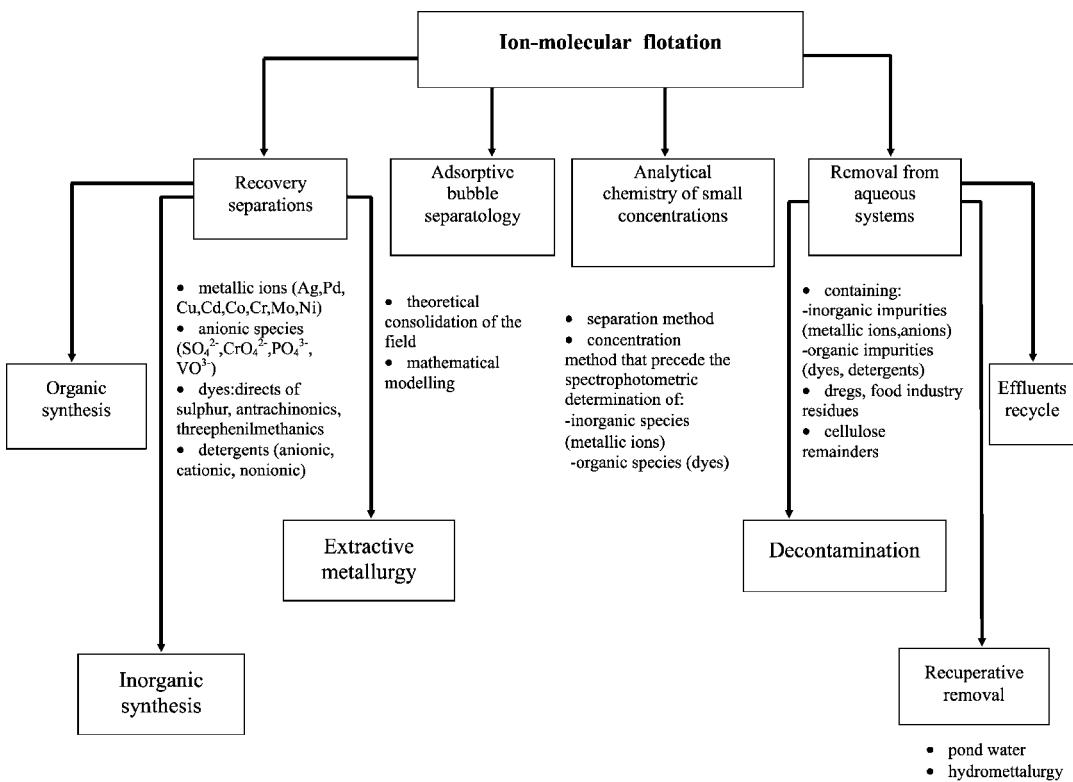


Figure 2. Applications of ion-molecular flotation.



Dowling, Klimpel, and Aplan<sup>[11]</sup> have experimentally tested 14 kinetic models presented in literature in order to establish their validity. These models correspond to first- or second-order kinetic with different adjustments for a better fit for the experimental data. In the present paper, the following kinetic models are verified.

The classical first-order model<sup>[10]</sup> describes the hydrophobic particles flotation having a constant floatability [Eq. (1)]. For the case of a monodisperse feed, where all particles have the same floatability, the equation is expressed by:

$$R = R^* [1 - \exp^{*}(-kt)] \quad (1)$$

where  $R$  is the recovery at time  $t$ ,  $R^*$  is the ultimate recovery for an infinite time, and  $k$  is the rate constant.

The first-order reversible model<sup>[12]</sup> describes the transfer of a component from the liquid phase to the foam and the subsequent drainage of a portion of this component from the foam. The mathematical form of this model is:

$$R = R^* k_+ / (k_+ + k_-) [1 - \exp^{*}(-(k_+ + k_-))] \quad (2)$$

where  $k_+$  is the rate constant of the transfer process of the component from the solution to the foam and  $k_-$  is the rate constant of the transfer process of the component from the foam to the solution.

The fully mixed reactor model<sup>[12]</sup> is a first-order kinetic model where floatability has an exponential distribution; this feature adds flexibility over the classical first-order model. The kinetic equation has the expression:

$$R = R^* [1 - 1/(1 + t/k)] \quad (3)$$

where  $R$  is the recovery at time  $t$ ,  $R^*$  is the ultimate recovery for an infinite time, and  $k$  is the rate constant.

The first-order model with zero-time adjustment<sup>[12]</sup> has the first-order kinetic equation according to the first presented model [Eq. (1)] modified by including a zero-time factor:

$$R = R^* [1 - \exp(-k(t + t^*))] \quad (4)$$

where  $t^*$  is the time correction factor, introduced because of the difficulty in physically assigning time zero.

In ore flotation, the most hydrophobic solids may have some air bubbles attached, which makes them float faster than they normally would; this can cause a positive time correction. Literature provides few experimental data concerning the kinetics of precipitate flotation so that some study about this



aspect is necessary in order to optimize the parameters and to increase the separation efficiency.

The present paper continues a series of previous works referring to Cu<sup>2+</sup> ions separation with cationic tensioactive agents (laurylamine-LA, C<sub>12</sub>H<sub>25</sub>-NH<sub>2</sub>, and lauryltrimethylammonium chloride—LTMACl, [C<sub>15</sub>H<sub>25</sub> N(CH<sub>3</sub>)<sub>3</sub>]Cl) and anionic tensioactive agents (sodium laurylsulphate—NaLS, C<sub>12</sub>H<sub>25</sub>OSO<sub>3</sub>Na, and oleic acid—HOL-NaOL, C<sub>18</sub>H<sub>33</sub>O<sub>2</sub>Na). These works are based on the correlation between metallic ions species structure in aqueous systems and the metallic ions affinity for different atoms and electron-donor groups, potential ligands, in their interaction with TSA and then offer a study on:

- influencing factors, allowing to decide upon the optimum separation parameters;
- verification of the established parameters on real aqueous systems (wastewaters from copper plating or mines);
- TSA-Cu interaction with respect to the optimum separation parameters in order to elucidate the separation mechanism.

The results obtained for the systems selected for the kinetic studies are presented in Table 1. In Table 1, the structure of the species isolated at optimum pH and different collector:colligand molar ratios is also presented. Chemical elementary analysis, thermal analysis, IR and electronic reflection spectrometry, RES, and electrical conductivity measurements were used to investigate the structure of the isolated species.

In order to do a kinetic study of the flotation process, four Cu-TSA systems are studied at optimum separation parameters and the applicability of first kinetic model in precipitate flotation is investigated.

## EXPERIMENTAL

### Reagents

- CuSO<sub>4</sub>.5 H<sub>2</sub>O p.a., Merck (Germany) (stock “model,” solution of 2 g l<sup>-1</sup>) in distilled water, has been used to prepare working solution according to Cu<sup>2+</sup> concentration in real systems (100 mg l<sup>-1</sup>).
- Cationic collectors: laurylamine (LA) Fluka (Hungary) p.a., 0.2% solution and lauryl- trimethylammonium chloride LTMACl Fluka p.a, 0.2% solution.

**Table 1.** Preliminary data required for kinetical studies.

| Studied system | $C_{i\text{Cu}^{2+}}$<br>/mg l <sup>-1</sup> | Separation parameters |                                   |      | $C_{\text{f}\text{Cu}^{2+}}$<br>/mg l <sup>-1</sup> | Cu-TSA interaction   |  | Compounds to be obtained   |
|----------------|--|-----------------------|-----------------------------------|------|---|----------------------|--|----------------------------|
|                |  | pH                    | $C_{\text{C}}:C_{\text{Cu}}^{2+}$ | %R   |   | Interactions         | Isolated species   |                            |
| Cu-LA          | 10–1000                                      | 9.5                   | $10^{-1}$                         | 99   | 0.75  | Coordination type    | Hydroxo and Hydroammine species mixed  | CuO                        |
|                |  |                       | 1                                 | 99.2 | 0.93  | Coordination type    | Hydroxoammine species of $[\text{Cu}_2(\text{OH})_4(\text{LA})(\text{H}_2\text{O})]$ type  |                            |
| Cu-LTMACl      | 10–1000                                      | 7                     | $10^{-2}$                         | 98.3 | 1.27  | Electrostatical type | Possible ion-pair complex  | CuO                        |
| Cu-NaLS        | 10–1000                                      | 9                     | $10^{-1}$                         | 99.6 | 0.30  | Electrostatical type | Possible ion-pair complex  | $\text{CuSO}_{4\text{aq}}$ |
| Cu-NaOL        | 10–100                                       | 7                     | $10^{-1}$                         | 99.2 | 0.57  | Coordination type    | Hydroxosulphate and Hydroxooleate sulphate species mixed   | CuO                        |
|                |  |                       | 1                                 | 98.1 | 1.41  | Coordination type    | Hydroxooleatosulphate species of $[\text{Cu}_3\text{L}_6(\text{OH})_4\text{SO}_4]$<br>$\text{Na}_6\cdot 2\text{H}_2\text{OL} \rightarrow \text{CH}_3\text{-(CH}_2\text{)}_7\text{CH=CH-(CH}_2\text{)}_7\text{COO}^-$ |                            |

- Anionic collectors: sodium laurylsulphate (NaLS) Fluka p.a., 0.2% solution, and oleic acid (NaOL) Fluka p.a., 0.2% solution.
- NaOH p.a., 6 M and 2 M solutions as precipitation reagent.

### Apparatus

- Flotation equipment adapted for kinetic studies having thermostat system and sampling possibility<sup>[13]</sup> (Fig. 3).
- pH-meter ORION 290 A.
- Atomic absorption spectrophotometer PYE UNICAM SP 9.

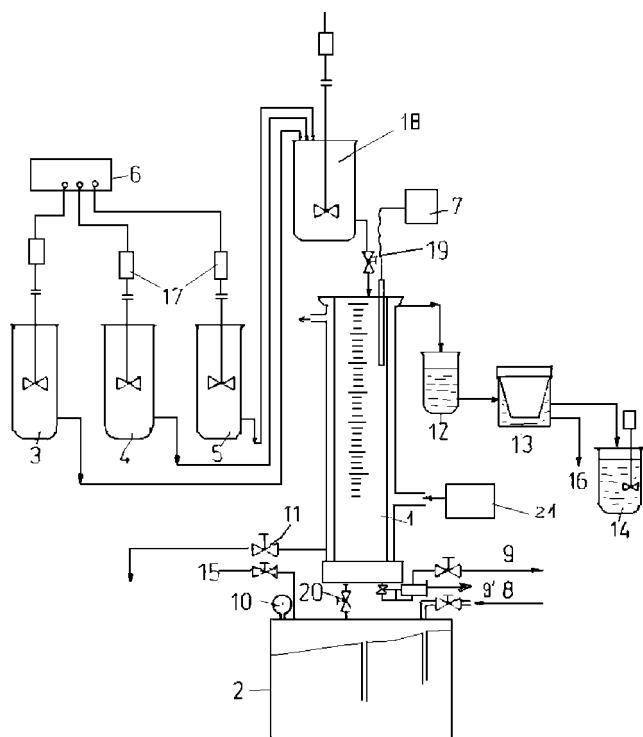


Figure 3. Flotation equipment adapted for kinetic studies.



### Methods

Kinetic studies were carried out using  $\text{CuSO}_4\text{aq}$  samples ( $100 \text{ mg l}^{-1}$ ,  $V = 0.31 \text{ l}$ ).  $\text{NaOH}$  6 M and 2 M, was used in order to obtain  $\text{Cu(II)}$  hydroxide species at optimum pH separation values for each studied system. The samples containing  $\text{Cu(II)}$  hydroxide species were treated with collector reagent under continuous stirring and then were introduced into the flotation cell where the separation process by air bubbles was achieved. For air-bubbles generation, pressurized water ( $p = 4 \cdot 10^5 \text{ N m}^{-2}$ ,  $V_{\text{sample}} : V_{\text{water}} = 3 : 1$ ) was used. Every 10 sec, 2 ml of the dispersion was sampled and the concentration of  $\text{Cu}^{2+}$  was determined. For determination of  $\text{Cu}^{2+}$  as soluble species, the samples were treated with 0.05 ml concentrated  $\text{H}_2\text{SO}_4$ . We made the volume correction corresponding to:

- the dilution generated by the pressurized water used for separation;
- the reagents used for correction pH and precipitate solubilization;
- the diminution of the volume by each sampling.

The recovery  $R$ , is expressed as:

$$R = (1 - C_t/C_o) * 100 \quad (5)$$

The initial concentration of  $\text{Cu}^{2+}$ ,  $C_o$ , and the concentration at the time  $t$ ,  $C_t$ , expressed in  $\text{mg l}^{-1}$ , were determined by atomic absorption spectrophotometry.

Experimental data were analyzed using the PEAKFIT program, obtaining the dependence  $C_{\text{Cu}}^{2+} = f(t)$ , expressed as  $R = f(t)$  for each of the four studied models in the range  $0 \div 120 \text{ sec}$  for 13 experimental points (it was considered that after 120 sec the equilibrium status was attained) at constant temperature ( $20^\circ\text{C}$ ). This program offers information about the fit quality and about the manner in which experimental data verify the theoretical models. The parameter that expresses the fit quality is the correlation coefficient,  $r$ , which represents a measure of the correlation between the theoretical kinetic model and the experimental data:

$$r = \frac{\text{cov}(x, y)}{\varepsilon_x * \varepsilon_y} \quad 0 < |r| < 1 \quad (6)$$

$$\text{cov}(x, y) = \frac{1}{N} * \sum (x_i - \bar{x}) * (y_i - \bar{y}) \quad (7)$$

where  $N$  is the number of points on the flotation curve, and  $\bar{x}$  and  $\bar{y}$  are



the medium values of x and y. Standard errors are expressed as:

$$\begin{aligned}\varepsilon_x &= \sqrt{\frac{\sum(x_i - \bar{x})^2}{N}} \\ \varepsilon_y &= \sqrt{\frac{\sum(y_i - \bar{y})^2}{N}}\end{aligned}\quad (8)$$

## RESULTS AND DISCUSSION

The classical first-order model is the most representative model among the models proposed for the ore-flotation kinetics and is appropriate for being applied to the precipitate-flotation process.

The first-order reversible model, the fully mixed reactor model, and the first-order model with zero-time adjustment were obtained from the classical first-order model after some adjustments were made<sup>[12]</sup> considering, the dimensional homogeneity of the compounds, the distribution of the floatability, the foam dispersion, and the characteristics of the flotation cell.

### The Classical First-Order Model

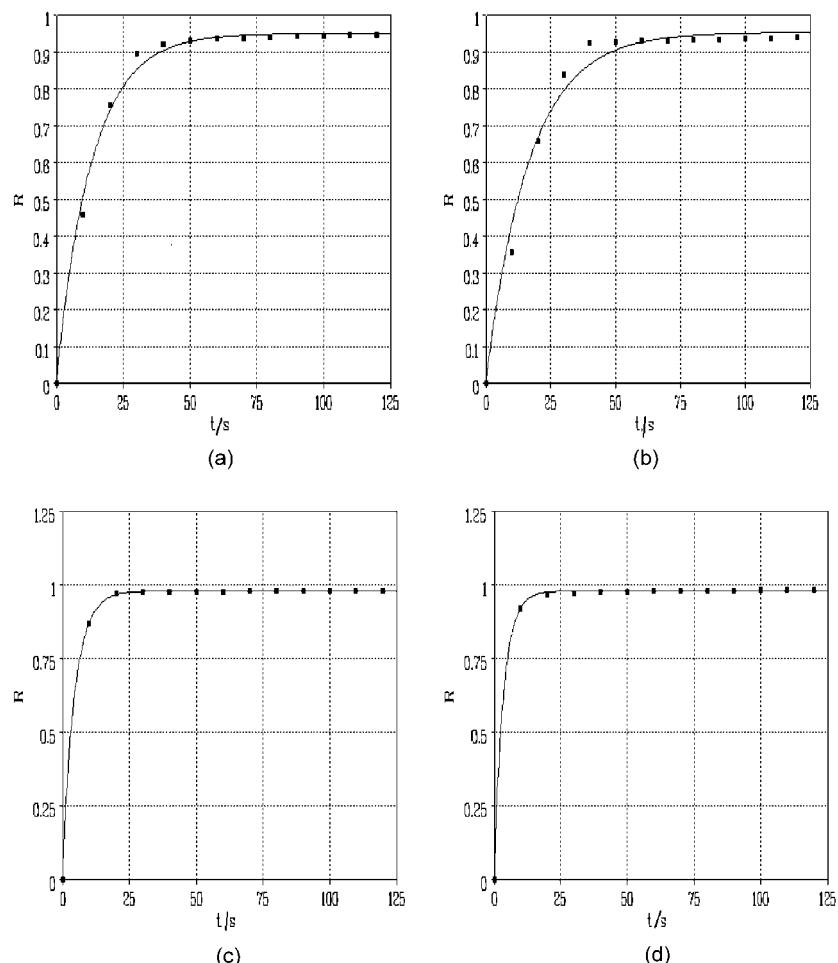
For each system studied, it was obtained the dependence  $C_{Cu}^{2+} = f(t)$ , expressed as  $R = f(t)$  in the range 0 ÷ 120 sec, was considered to be the time corresponding to equilibrium status at the constant temperature (20°C). The

**Table 2.** Rate constant and statistical fitting parameters for the classical first-order model.

| Studied system | pH  | $C_C : C_{Cu}^{2+}$ | R*    | $k/s^{-1}$ | $\varepsilon_k$ | r     | e      |
|----------------|-----|---------------------|-------|------------|-----------------|-------|--------|
| Cu-LA          | 9.5 | $10^{-1}$           | 0.951 | 0.067      | 0.0041          | 0.999 | 0.0288 |
| Cu-LTMACl      | 7   | $10^{-2}$           | 0.950 | 0.059      | 0.004           | 0.994 | 0.033  |
| Cu-NaLS        | 9   | $10^{-1}$           | 0.977 | 0.281      | 0.0082          | 0.999 | 0.0046 |
| Cu-NaOL        | 7   | $10^{-1}$           | 0.977 | 0.22       | 0.0024          | 0.999 | 0.0026 |

$C_C : C_{Cu}^{2+}$ —molar ratio collector:Cu<sup>2+</sup> concentration, R\*—the ultimate recovery, k—the rate constant,  $\varepsilon_k$ —the standard errors for the kinetic rates, r—the correlation coefficients, e—curve-fit standard error.

theoretical kinetic Eq. (1) was verified at optimum parameters determined for all the systems. The theoretical curves were compared with the experimental ones,  $R = f(t)$ , and the statistical fitting parameters were obtained. The results obtained after analyzing experimental data are given in Table 2.



**Figure 4.** Comparison of the theoretical predictions [solid lines—Eq. (1)] with the experimental data (points) for the dependence  $R = f(t)$  (classical first-order model): a) Cu-LA, pH = 9.5,  $C_C:C_{Cu}^{2+} = 10^{-1}$ ; b) Cu-LTMACl, pH = 7,  $C_C:C_{Cu}^{2+} = 10^{-2}$ ; c) Cu-NaLS, pH = 9,  $C_C:C_{Cu}^{2+} = 10^{-1}$ ; and d) Cu-NaOL, pH = 7,  $C_C:C_{Cu}^{2+} = 10^{-1}$ .



Because the correlation coefficient values ( $r$ ) are greater than 0.994, we assumed that a good agreement of the theoretical curve and the experimental one was obtained (see Fig. 4). The curve-fit standard errors ( $e$ ) are acceptable for all studied systems [0.0288 (LA), 0.033 (LTMACl), 0.0046 (NaLS), and 0.0023 (NaOL)] and the standard errors for the kinetic rates ( $e_k$ ) suggest that this kinetic model could describe the Cu(II) hydroxide species separation. The model is well fitting the experimental data, especially in the case of anionic collectors. The classical first-order model refers to the global order of the kinetic process, considering the elementary microprocesses components of the global process. Therefore, it was necessary to verify other first-order kinetic models which represent different variants of the classical first-order model, with adjustments, for a better fit with the experimental data.

### The First-Order Reversible Model

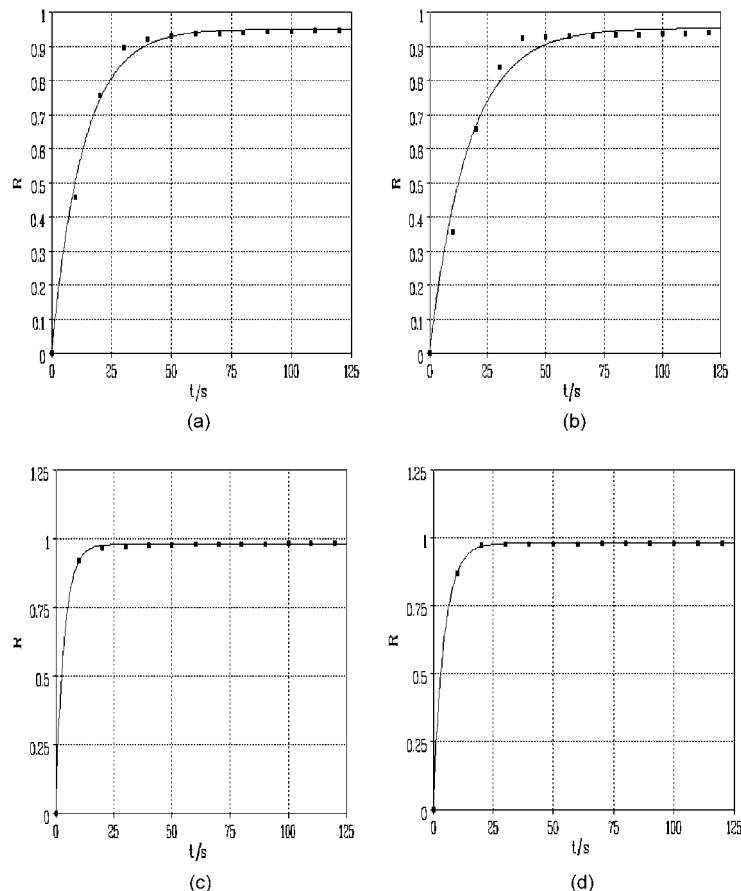
In order to apply this model to the precipitate-flotation process, the dependence  $C_{Cu}^{2+} = f(t)$  and  $R = f(t)$  were studied for four Cu-TSA systems. Experimental results were fit on the theoretical curves described by Eq. (2) (Fig. 5). The correlation coefficient values are very close to 1,  $0.994 < r < 0.999$ , (Table 3); therefore, the experimental curve is considerably closer to the theoretical one for all the studied systems. The standard curve-fit errors are very small ( $0.0048 < e < 0.03$ ), indicating also a good correlation of the two curves (experimental and theoretical).

The model is well fitting the experimental data, so we can assume that the drainage reverse process of a portion of the component from the foam to the liquid phase may also probably take place.

### The Fully Mixed Reactor Model

Using Eq. (3) of the theoretical curve, the dependence  $C_{Cu}^{2+} = f(t)$ , expressed as  $R = f(t)$ , was studied. The statistical fitting parameters for all the systems were determined from the correlation of the theoretical curves with the experimental curves in the range 0  $\div$  120 sec. The fitting data presented in Table 4 revealed that this model permits the greatest values for the correlation coefficients:  $0.995 < r < 0.999$ .

The values of curve-fit standard errors are low [0.029 (LA), 0.00742 (LTMACl), 0.0035 (NaLS), and 0.0013 (NaOL)], indicating that this model also describes the flotation kinetics of the insoluble species



**Figure 5.** Comparison of the theoretical predictions [solid lines—Eq. (2)] with the experimental data (points) for the dependence  $R = f(t)$ : a) Cu-LA,  $pH = 9.5$ ,  $C_C:C_{Cu}^{2+} = 10^{-1}$ ; b) Cu-LTMACl,  $pH = 7$ ,  $C_C:C_{Cu}^{2+} = 10^{-2}$ ; c) Cu-NaLS,  $pH = 9$ ,  $C_C:C_{Cu}^{2+} = 10^{-1}$ ; and d) Cu-NaOL  $pH = 7$ ,  $C_C:C_{Cu}^{2+} = 10^{-1}$  (the first-order reversible model).

of  $Cu^{2+}$  (Fig. 6). The maximum ultimate recovery values for this model are the highest in comparison to previous models ( $0.989 < R^* < 0.999$ ). We can assume that the flotation cell could function like a fully mixed reactor.

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**Table 3.** Rate constant and statistical fitting parameters for the first-order reversible model.

| Studied system | pH  | $C_C:C_{\text{Cu}}^{2+}$ | $R^*$ | $k_+/\text{s}^{-1}$ | $e_{k+}$ | $k_-/\text{s}^{-1}$ | $e_{k-}$ | $r$   | $e$    |
|----------------|-----|--------------------------|-------|---------------------|----------|---------------------|----------|-------|--------|
| Cu-LA          | 9.5 | $10^{-1}$                | 0.946 | 0.07                | 0.0093   | 0.0037              | 0.0007   | 0.998 | 0.03   |
| Cu-LTMACl      | 7   | $10^{-2}$                | 0.945 | 0.06                | 0.01     | 0.0065              | 0.00016  | 0.994 | 0.035  |
| Cu-NaLS        | 9   | $10^{-1}$                | 0.988 | 0.278               | —        | 0.0031              | —        | 0.999 | 0.0048 |
| Cu-NaOL        | 7   | $10^{-1}$                | 0.996 | 0.215               | —        | 0.004               | —        | 0.999 | 0.0027 |

$C_C:C_{\text{Cu}}^{2+}$ —molar ratio collector:  $\text{Cu}^{2+}$  concentration,  $R^*$ —the ultimate recovery,  $k_+$ —the rate constant of the transfer process of the component from the solution to the foam,  $k_-$ —the rate constant of the transfer process of the component from the foam to the solution,  $e_{k+}$ ,  $e_{k-}$ —the rate constants errors,  $r$ —the correlation coefficients,  $e$ —curve fit standard error.



**Table 4.** Rate constant and statistical fitting parameters for the fully mixed reactor model.

| Studied system | pH  | $C_C:C_{Cu}^{2+}$ | R*    | $K / s^{-1}$ | $e_k$ | r     | e      |
|----------------|-----|-------------------|-------|--------------|-------|-------|--------|
| Cu-LA          | 9.5 | $10^{-1}$         | 0.999 | 5.38         | 0.72  | 0.995 | 0.029  |
| Cu-LTMACl      | 7   | $10^{-2}$         | 0.999 | 8.175        | 2.425 | 0.997 | 0.0742 |
| Cu-NaLS        | 9   | $10^{-1}$         | 0.989 | 0.696        | 0.045 | 0.999 | 0.0035 |
| Cu-NaOL        | 7   | $10^{-1}$         | 0.996 | 1.199        | 0.189 | 0.999 | 0.0013 |

$C_C:C_{Cu}^{2+}$ —molar ratio collector: $Cu^{2+}$  concentration, R\* —the ultimate recovery,  $k$ —the rate constant,  $e_k$ —the standard errors for the kinetic rates, r—the correlation coefficients, e—curve fit standard error.

### The Fist-Order Model with Zero-Time Adjustment

By correlating the two curves as previously described, this model allows the determination of the rate constant, the time correction factor, and the fitting parameters. As can be observed from Table 5, the time correction factor has very low values ( $5.5 \cdot 10^{-10} < t^* < 0.00013$ ), and therefore, it can be neglected and the Eq. (4) is reduced to Eq. (1), [ $R^*$  values are almost identical with those from the Eq. (1)]. The first-order model with zero-time adjustment then becomes the first order classical model (Table 5). In the precipitate flotation process this adjustment is not necessary because the ionic species do not have air bubbles attached, and the bubble-particle interaction is produced after the creation of insoluble species.

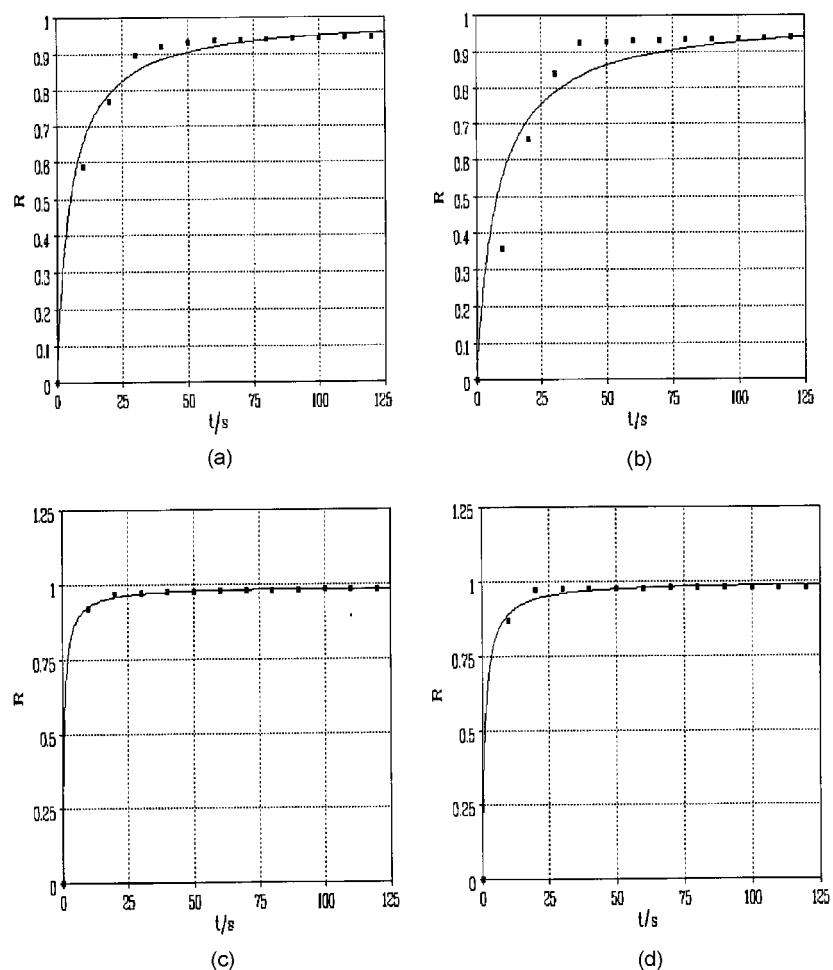
### The Temperature Influence on the Flotation Kinetics

In order to obtain further information about the separation kinetics, the variation of  $Cu^{2+}$  concentration with temperature for all the systems was studied.<sup>[14]</sup> Therefore,  $Cu^{2+}$  solutions  $100 \text{ mg l}^{-1}$  were floated with cationic-(LA, LTMACl) and anionic-(NaLS, NaOL) type collectors at different temperatures ( $20^\circ\text{C}$ ,  $30^\circ\text{C}$ ,  $40^\circ\text{C}$ , and  $50^\circ\text{C}$ ) and the activation energy was determined.

The low negative values of the activation energies obtained for all studied systems suggest an anti-Arrhenius behavior. Such behavior could be expected from a complex process in which the adsorption, molecular diffusion, and the bubble-particle complex diffusion to the foam are strongly depending on the temperature. The separation efficiency (%R) decreases

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**Figure 6.** Comparison of the theoretical predictions [solid lines—Eq. (4)] with the experimental data (points) for the dependence  $R = f(t)$ : a) Cu-LA, pH = 9.5,  $C_C : C_{\text{Cu}}^{2+} = 10^{-1}$ ; b) Cu-LTMACl, pH = 7,  $C_C : C_{\text{Cu}}^{2+} = 10^{-2}$ ; c) Cu-NaLS, pH = 9,  $C_C : C_{\text{Cu}}^{2+} = 10^{-1}$ ; and d) Cu-NaOL pH = 7,  $C_C : C_{\text{Cu}}^{2+} = 10^{-1}$  (the fully mixed reactor model).

**Table 5.** Rate constant and statistical fitting parameters for the fist-order model with zero-time adjustment.

| Studied system | pH  | $C_C:C_{Cu}^{2+}$ | R*    | k / s <sup>-1</sup> | $e_k$  | t*/s                  | $e_{t*}$ | r     | e      |
|----------------|-----|-------------------|-------|---------------------|--------|-----------------------|----------|-------|--------|
| Cu-LA          | 9.5 | $10^{-1}$         | 0.954 | 0.065               | 0.004  | $5.25 \cdot 10^{-10}$ | 0        | 0.999 | 0.03   |
| Cu-LTMACl      | 7   | $10^{-2}$         | 0.975 | 0.063               | 0.007  | 0                     | —        | 0.988 | 0.048  |
| Cu-NaLS        | 9   | $10^{-1}$         | 0.977 | 0.281               | 0.0087 | 0.00013               | 0.18     | 0.999 | 0.005  |
| Cu-NaOL        | 7   | $10^{-1}$         | 0.977 | 0.22                | 0.0026 | $4.3 \cdot 10^{-9}$   | 0.13     | 0.999 | 0.0027 |

$C_C:C_{Cu}^{2+}$ —molar ratio collector: $Cu^{2+}$  concentration, R\* —the ultimate recovery, k—the rate constant,  $e_k$ —the standard errors for the kinetic rates, t\* —is the time correction factor,  $e_{t*}$ —the standard errors for the time correction factor, r—the correlation coefficients, e—curve fit standard error.



with temperature increasing, probably involving an adsorption process as a slower step or an reversible initial process, which confirms the previous results.

## CONCLUSIONS

This paper presents a study regarding the kinetics of Cu(II) hydroxide species separation using flotation (DAF) with cationic (LA, LTMACl) and anionic (NaLS, NaOL) collectors. In order to compare the experimental data obtained for  $C_{Cu}^{2+} = f(t)$  with theoretical models, three first-order models, adjusted respectively to the classical model, were studied.

The adjustment has to take into account the following considerations:

The concentration trend of the metal ion in the froth is associated to the transfer tendency of some colligand in the pulp (the first-order reversible model).

The flotation cell behavior could be one of a fully mixed reactor (the fully mixed reactor model).

The zero-time adjustment (the first-order model with zero-time adjustment).

Using the mathematical models described by characteristic kinetic equations, it was proved that:

The first-order model with zero-time adjustment is identical with the classical first-order model.

The classical first-order model and the first-order reversible model is well fitting the experimental data.

The fully mixed reactor model describes with acceptable errors the Cu<sup>2+</sup> separation process by flotation.

The results obtained permit us to assume that the Cu(II) hydroxide species separation using precipitate flotation (DAF) with cationic (LA, LTMACl) and anionic (NaLS, NaOL) collectors follows an overall first-order kinetic.

Theoretical equations of flotation kinetics proposed for ore flotation could be applied with good results in precipitate flotation in the condition of performing the experiments according to the presented methodology.



Obtaining more points in the range 0–30 sec would allow a more exact interpretation of studied models.

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