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A COMPARISON OF THE KINETIC AND ADSORPTION MODEL OF METAL PRECIPITATE FLOTATION IN THE ABSENCE OF COLLECTOR

A kinetic model of dissolved air flotation of $\text{Cu}(\text{OH})_2$ in the absence of collector and frother was proposed and compared to an adsorption model.

The results of experimental studies on the effect of some parameters on the flotation kinetics were described either by "normal" (N-kinetic model) or "S" saturation curves (S-kinetic model). Both the calculated and experimentally determined values of the kinetic constants corresponding to different conditions of pressure, temperature, initial concentration of $\text{Cu}(\text{OH})_2$, and different salt concentrations give a sufficiently realistic description of the equilibrium state of the system.

The mathematical analysis performed is in agreement with the physico-chemical nature of the investigated process. A significant correlation between the present kinetic model and the one previously reported, i.e., adsorption model of metal precipitate flotation, was found. General characteristics of these models is their formal similarity to the Langmuir equation for adsorption equilibria.

DENOTATIONS

b – empirical constant,

C – correction,

$C_{\text{Cu}(\text{OH})_2}$ – initial concentration of $\text{Cu}(\text{OH})_2$,

C_S – total salt (CaCl_2) concentration,

D – bubble diameter,

F, f – functions,

$M_{\text{Cu}(\text{OH})_2}^E$ – equilibrium amount of $\text{Cu}(\text{OH})_2$ moles recovered in the foam,

$M_{\text{Cu}(\text{OH})_2-c}^E$ – calculated value of the equilibrium kinetic constant for different physico-chemical parameters,

$M_{\text{Cu}(\text{OH})_2-e}^{E(p;C_{\text{Cu}(\text{OH})_2};C_{\text{CaCl}_2};T)}$ – experimental values of the equilibrium kinetic constant determined under different conditions of pressure, initial concentration of $\text{Cu}(\text{OH})_2$, concentration of CaCl_2 and temperature,

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- $M_{\text{Cu(OH)}_2}^t$ — amount of Cu(OH)_2 moles recovered during time t ,
 p — pressure,
 Q — air flow rate,
 r^2 — coefficient of determination,
 T — temperature,
 t^E — equilibrium time of flotation,
 $\Gamma_{\text{Cu(OH)}_2}^E$ — surface equilibrium concentration of Cu(OH)_2 .

1. INTRODUCTION

Precipitate flotation encompasses all the processes in which a ionic species is concentrated from an aqueous solution by formation of a precipitate, which is then separated by flotation [1], [2].

It has been shown earlier that with the use of surfactants as collectors, metal hydroxides can be separated from water suspensions by precipitate flotation, i.e., colloid flotation [1]–[13]. The applicability of dissolved air precipitate flotation (DAF) in the absence of collector and frother has been also demonstrated [14]. Besides, mainly theoretical aspects of these methods have been dealt with [13], [15]–[17].

The primary objective of this study is to set up an empirical model of dissolved air flotation of Cu(OH)_2 in the absence of collector and frother, based on kinetic investigations of the process. For this purpose, the effects of various factors, such as the initial concentration of Cu(OH)_2 , pressure, temperature, concentration of the salt, etc., have been studied in detail. A mathematical analysis of the derived relations is carried out, and the model compared with the adsorption model, described earlier.

2. EXPERIMENTAL

Batch precipitate flotation of Cu(OH)_2 with dissolved air was carried out by means of a conventional laboratory set-up for microflotation, adopting the procedure described earlier [14]. The air flow rate corresponding to the saturation pressures (100, 200 and 300 kPa) was dependent on the duration time of the process and ranged from 0.150 to 0.026 cm^3/s .

Suspensions of different Cu(OH)_2 concentrations were prepared and analysed as described earlier [14], [17].

The statistical data treatment was performed on a Hewlett–Packard, HP-25C, calculator.

3. ANALYSIS

The system under investigation was described first in terms of the advanced adsorption model, proposed earlier [17]. The surface equilibrium concentration of $\text{Cu}(\text{OH})_2$ per unit surface area of the air bubble was defined as:

$$\Gamma_{\text{Cu}(\text{OH})_2}^E = \frac{M_{\text{Cu}(\text{OH})_2}^E \cdot D}{6Q \cdot t^E} \quad (1)$$

where $M_{\text{Cu}(\text{OH})_2}^E$ is the equilibrium number of moles of $\text{Cu}(\text{OH})_2$ separated in the foam, D the bubble diameter, Q the air flow rate, and t^E the equilibrium time (the time needed for the equilibrium in the system to be established).

Afterwards, the DAF system was considered as a kinetic process in which the concentration of flotated species, $\text{Cu}(\text{OH})_2$, changes in time. The amount of $\text{Cu}(\text{OH})_2$ (in moles) separated in the foam during time t , $M_{\text{Cu}(\text{OH})_2}^t$, is a general function of the following physico-chemical parameters:

$$M_{\text{Cu}(\text{OH})_2}^t = F | f(\text{pH}(t)); f(p(t)); f(C_{\text{Cu}(\text{OH})_2}(t)); f(C_S(t)); f(T(t)) \quad (2)$$

where p is the pressure in DAF, $C_{\text{Cu}(\text{OH})_2}$ the initial concentration of $\text{Cu}(\text{OH})_2$, C_S the total salt concentration, and T the temperature. On the basis of experimental results, the dependence of $M_{\text{Cu}(\text{OH})_2}^t$ on different parameters during time could be expressed by a local empirical equation:

$$M_{\text{Cu}(\text{OH})_2}^t = at^b \quad (3)$$

where a and b are the empirical constants for particular parameters.

The mathematical and physico-chemical correlation between $M_{\text{Cu}(\text{OH})_2}^E$ from equation (1) and the term $M_{\text{Cu}(\text{OH})_2}^t$ in equations (2) and (3) is not possible. If we assume $t \rightarrow \infty$, then $M_{\text{Cu}(\text{OH})_2}^t$ in equation (3) would also increase to infinity:

$$\lim_{t \rightarrow \infty} M_{\text{Cu}(\text{OH})_2}^t = \infty \quad (4)$$

which does not correspond to the physico-chemical nature of the process. Namely, in a real system the term $M_{\text{Cu}(\text{OH})_2}^t$ can only amount to its equilibrium value $M_{\text{Cu}(\text{OH})_2}^E$. Therefore, other empirical equations were defined assuming the condition:

$$M_{\text{Cu}(\text{OH})_2}^t = M_{\text{Cu}(\text{OH})_2}^E \quad (5)$$

For normal saturation curves, describing the dependence of $M_{\text{Cu}(\text{OH})_2}^t$ on different parameters in time, the following kinetic model was examined (N model):

$$M_{\text{Cu}(\text{OH})_2}^t = \frac{M_{\text{Cu}(\text{OH})_2}^E \cdot t}{t + b} \quad (6)$$

where b is the empirical constant. Further, the "S"-form saturation curves were described using the expression (S model):

$$M_{\text{Cu(OH)}_2}^t = M_{\text{Cu(OH)}_2}^E + \frac{t^2}{b} \quad (7)$$

After linearization of the proposed expressions, it was possible to calculate the $M_{\text{Cu(OH)}_2}^E$ values by least squares method. For the given physico-chemical parameters, this quantity can be conditionally termed "equilibrium kinetic constant".

The correction method for fitting the experimental results to kinetic curves was based on the following general function:

$$M_{\text{Cu(OH)}_2}^t = F(t) + C\varphi(t), \quad (8)$$

where $C\varphi(t)$ denotes the correction.

Taking for $M_{\text{Cu(OH)}_2}^t$ one of the above kinetic models, for $F(t)$ one of the functions describing the dependence of flotation kinetics on the particular physico-chemical parameter (equation 2), and for $\varphi(t)$ we obtain

$$\varphi(t) = \frac{t^2}{t^2 + 1} \quad (9)$$

The correction can be expressed by the following total equation:

$$C = \frac{\sum F_i \varphi_i(t_i)}{\sum (\varphi_i(t_i))^2} \quad (10)$$

4. RESULTS AND DISCUSSION

Tables 1–4 contain the values of the kinetic constants of equilibrium both calculated and determined experimentally by variation of all the above physico-chemical parameters influencing kinetics of flotation in the absence of collector and frother. The calculations were carried out by using both the equation (6) (N-model) and (7) (S-model).

Table 1

Dependence of experimental $M_{\text{Cu(OH)}_2}^{Ep}$ and calculated $M_{\text{Cu(OH)}_2}^{Ep}$ (N-model), $M_{\text{Cu(OH)}_2}^{Es}$ (S-model) values of the equilibrium concentrations on pressure

P kPa	$M_{\text{Cu(OH)}_2}^{Ep}$	$M_{\text{Cu(OH)}_2}^{Es}$	$*r^2$	$M_{\text{Cu(OH)}_2}^{Ep}$	$*r^2$
100	0.66×10^{-3}	2.83×10^{-3}	0.97	0.66×10^{-3}	0.99
200	2.71×10^{-3}	4.46×10^{-3}	0.83	1.91×10^{-3}	0.69
300	2.96×10^{-3}	5.46×10^{-3}	0.96	3.15×10^{-3}	0.99

$C_{\text{Cu(OH)}_2} = 4.1 \times 10^{-3}$ (M/dm³); pH = 8; T = 20.0°C.

* r^2 - determination coefficient.

Table 2

Dependence of experimental $M_{\text{Cu(OH)}_2-e}^{\text{ECu(OH)}_2}$ and calculated $M_{\text{Cu(OH)}_2-e\text{N}}^{\text{ECu(OH)}_2}$ (N-model), $M_{\text{Cu(OH)}_2-c\text{S}}^{\text{ECu(OH)}_2}$ (S-model) values of the equilibrium concentrations on initial concentrations of Cu(OH)_2

$C_{\text{Cu(OH)}_2}$ M/dm ³	$M_{\text{Cu(OH)}_2-e}^{\text{ECu(OH)}_2}$	$M_{\text{Cu(OH)}_2-e\text{N}}^{\text{ECu(OH)}_2}$	r^2	$M_{\text{Cu(OH)}_2-c\text{S}}^{\text{ECu(OH)}_2}$	r^2
1.025×10^{-3}	0.64×10^{-3}	1.71×10^{-3}	0.94	0.85×10^{-3}	1.00
2.05×10^{-3}	1.78×10^{-3}	2.22×10^{-3}	0.90	1.91×10^{-3}	0.97
4.10×10^{-3}	2.96×10^{-3}	5.46×10^{-3}	0.96	3.15×10^{-3}	0.99
8.20×10^{-3}	7.21×10^{-3}	10.48×10^{-3}	1.00	12.42×10^{-3}	0.93

pH = 8; $T = 20.0^\circ\text{C}$; $p = 300$ kPa.

Table 3

Dependence of experimental $M_{\text{Cu(OH)}_2-e}^{\text{ECaCl}_2}$ and calculated $M_{\text{Cu(OH)}_2-c\text{S}}^{\text{ECaCl}_2}$ (S-model) values of the equilibrium concentrations on concentration of CaCl_2 (C_S)

C_{CaCl_2} g/dm ³	$M_{\text{Cu(OH)}_2-e}^{\text{ECaCl}_2}$	$M_{\text{Cu(OH)}_2-c\text{S}}^{\text{ECaCl}_2}$	r^2
0.62	3.61×10^{-3}	3.82×10^{-3}	0.94
1.25	3.35×10^{-3}	3.66×10^{-3}	0.96
2.5	3.30×10^{-3}	3.76×10^{-3}	1.00
5.0	3.11×10^{-3}	4.75×10^{-3}	1.00

$C_{\text{Cu(OH)}_2} = 4.1 \times 10^{-3}$ (M/dm³); $p = 300$ kPa; pH = 8, $T = 16.5^\circ\text{C}$.

Table 4

Dependence of experimental $M_{\text{Cu(OH)}_2-e}^{\text{ET}}$ and calculated $M_{\text{Cu(OH)}_2-e\text{N}}^{\text{ET}}$ (N-model), $M_{\text{Cu(OH)}_2-c\text{S}}^{\text{ET}}$ (S-model) values of the equilibrium concentrations on temperature

T $^\circ\text{C}$	$M_{\text{Cu(OH)}_2-e}^{\text{ET}}$	$M_{\text{Cu(OH)}_2-e\text{N}}^{\text{ET}}$	r^2	$M_{\text{Cu(OH)}_2-c\text{S}}^{\text{ET}}$	r^2
20	0.64×10^{-3}	1.71×10^{-3}	0.99	0.85×10^{-3}	1.00
30	0.74×10^{-3}	1.04×10^{-3}	1.00	0.67×10^{-3}	0.97
40	0.89×10^{-3}	1.03×10^{-3}	0.98	0.82×10^{-3}	0.93

$C_{\text{Cu(OH)}_2} = 1.025 \times 10^{-3}$ (M/dm³); $p = 300$ kPa; pH = 8.

On the basis of a comparison of the calculated and experimentally determined kinetic constants of equilibrium it can be concluded that both models can be, in principle, used for description of the kinetic process under study. If the N-model is employed to calculate the equilibrium concentrations of Cu(OH)_2 , then the values obtained are in all cases higher than both the equilibrium concentrations determined

by experiment and initial concentrations of $\text{Cu}(\text{OH})_2$. The only exception is the value of $M_{\text{Cu}(\text{OH})_2-\text{cN}}^{Ep}$ at $p = 100$ kPa (tab. 1). On the other hand, if the S-model is used to calculate the equilibrium concentrations, they are closer to the experimental and initial concentrations of $\text{Cu}(\text{OH})_2$.

After taking into account all the above, it is possible to propose the following complex function (which satisfies the condition of equation (5)) to describe kinetics of the process studied:

$$\begin{aligned} M_{\text{Cu}(\text{OH})_2}^t &= F f(p(t)); f(C_{\text{Cu}(\text{OH})_2}(t)); f(C_S(t)); f(T(t)) \\ &= M_{\text{Cu}(\text{OH})_2}^{E(p; C_{\text{Cu}(\text{OH})_2}; C_S; T)} + \frac{t^2}{b}. \end{aligned} \quad (11)$$

The dependence of $M_{\text{Cu}(\text{OH})_2}^t$ on pH was described earlier by a local empirical equation of linear and power law type [14].

A consistent (strict) application of equation (10) to calculate the corrections of the experimental values for kinetic curves can lead to meaningless results. This is especially true if the relatively large experimental errors and a rather poor reproducibility of the experimental data are taken into account.

Following the proposed mathematical analysis, it can be concluded that both the calculated and the experimental values of kinetic equilibrium concentrations presented here and the maximal amounts of species separable by flotation, calculated in [17] (adsorption model), have essentially the same physico-chemical meaning. They are, namely, the correlative quantities.

5. CONCLUSIONS

The values of equilibrium concentrations $M_{\text{Cu}(\text{OH})_2}^E$, determined by experiment and calculated by employing the N- and S-models for variations of different physico-chemical parameters give a sufficiently realistic description of the equilibrium state of the flotation system.

A common feature of the models described here, as well as of the adsorption model, is a formal similarity to the Langmuir equation for adsorption equilibria.

REFERENCES

- [1] BAARSON R. S., RAY C. L., *Precipitate flotation, a new metal extraction and concentration technique*, American Institute of Mining, Metallurgical and Petroleum Engineers Symposium, Dallas 1963.
- [2] SEBBA F., *Ion flotation*, Elsevier, Amsterdam 1962.
- [3] MACNEV A. I., *Ochistka stochnikh vod flotaciej*, Budivel'nik, Kiev 1976.
- [4] WILSON D. J., THACKSTON E. L., *Foam flotation treatment of industrial wastewaters: Laboratory and pilot scale*, EPA-600/2-80-138, June 1980.

- [5] LEMLICH R., *Adsorptive bubble separation techniques*, Academic Press, New York 1972.
- [6] PINFOLD T. A., *Separation Science*, 5 (1970), 379–384.
- [7] BHATTACHARYA D., CARLTON J. A., GRIEVES R. B., *A. I. Ch. E. Journal*, 17 (1971), 419–424.
- [8] GRIEVES R. B., SCHWARZ S. M., *J. Appl. Chem.*, 16 (1966), 14–17.
- [9] KALMAN K. S., RATCLIFF G. A., *Canad. J. Chem. Eng.*, 49 (1971), 626–632.
- [10] DOBRESCU L., DOBRESCU V., *Epurarea apelor uzate prin flotatie*, Ministerul agriculturii, industriei alimentare, silviculturii si apelar, Bucuresti 1971.
- [11] MIŠKOVIĆ D., *The recovery of metal precipitates and surfactants by flotation*, Ph. D. Thesis, Faculty of Sciences of Novi Sad, Yugoslavia, Novi Sad 1977.
- [12] KARLOVIĆ E., *The recovery of heavy metal hydroxides from metal finishing industries wastewaters by flotation with surfactants*, M. Sc. Thesis, Faculty of Sciences of Novi Sad, Yugoslavia, Novi Sad 1977.
- [13] CLARKE A. N., WILSON D. J., *Foam flotation: Theory and applications*, Marcel Dekker, New York 1983.
- [14] MIŠKOVIĆ D., KARLOVIĆ E., DALMACIJA B., *The investigation of application of dissolved air precipitate flotation in the absence of collector and frother for the purification of wastewater containing metal ions*, [in:] *Studies in Environmental Science* 23, Elsevier, 1984, pp. 245–252.
- [15] KLASSEN V. I., *An introduction to the theory of flotation*, Butterworth, London 1963, pp. 89–138.
- [16] SCHMIDT I. L., HAJNMAN J. A., PROSKURJAKOV A. V., *Zh. Prikl. Khim.*, 43 (1970), 2553–2558.
- [17] MIŠKOVIĆ D., KARLOVIĆ E., DALMACIJA B., *Study on adsorption equilibria in the flotation system of metal precipitate and collector*, [in:] *Studies in Environmental Science*, Elsevier, 1986, pp. 311–323.

PORÓWNANIE KINETYCZNEGO I ADSORPCYJNEGO MODELU WYTRĄCANIA METALI W PROCESIE FLOTACJI BEZ CZYNNIKA AGREGUJĄCEGO

Zaproponowano kinetyczny model flotacji $\text{Cu}(\text{OH})_2$ bez stosowania środka agregującego i pianotwórczego oraz porównano go z modelem adsorpcyjnym.

Wyniki badań doświadczalnych, obejmujące wpływ wybranych parametrów na kinetykę flotacji, opisano za pomocą modelu konwencjonalnego (model kinetyczny N) oraz za pomocą modelu krzywych nasycenia (model kinetyczny S). Stwierdzono, że zarówno obliczone, jak i doświadczalnie wyznaczone wartości stałych kinetycznych odpowiadające różnym warunkom fizyczno-chemicznym (ciśnienie, temperatura, początkowe stężenie $\text{Cu}(\text{OH})_2$, stężenie soli) dają wystarczająco realistyczny opis stanu równowagi systemu.

Analiza matematyczna zgadza się z fizyczno-chemicznym charakterem badanego procesu. Stwierdzono dobrą korelację między modelem kinetycznym a modelem adsorpcyjnym (wcześniej przedstawionym) wytrącania metali w procesie flotacji. Cechą charakterystyczną tych modeli jest ich podobieństwo do równania równowagi adsorpcyjnej Langmuira.

СРАВНЕНИЕ КИНЕТИЧЕСКОЙ И АДСОРБЦИОННОЙ МОДЕЛИ ОСАЖДЕНИЯ МЕТАЛЛОВ В ПРОЦЕССЕ ФЛОТАЦИИ БЕЗ АГРЕГИРУЮЩЕГО РЕАГЕНТА

В настоящей работе предложили кинетическую модель флотации $\text{Cu}(\text{OH})_2$ без применения агрегирующего и пеногенного средств, а также сравнили ее с адсорбционной моделью.

Результаты экспериментальных исследований, охватывающие влияние избранных параметров на кинетику флотации, описали при помощи конвенциональной модели (кинетическая модель N), а также при помощи модели кривых насыщения (кинетическая модель S). Установили, что как рассчитанные, так и определенные экспериментально значения

кинетических постоянных, отвечающие разным физико-химическим условиям (давление, температура, начальная концентрация $\text{Cu}(\text{OH})_2$, концентрация солей), дают достаточно реалистическое описание состояния равновесия системы.

Проведенный математический анализ согласен с физико-химическим характером исследуемого процесса. Была установлена хорошая корреляция между кинетической и адсорбционной (представленной раньше) моделями осаждения металлов в процессе флотации. Характерной чертой этих моделей является их сходство с уравнением адсорбционного равновесия Лангмуара.