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THE RELATIONSHIPS BETWEEN DETERMINISTIC AND STOCHASTIC MODELS OF FLOTATION

ZWIĄZKI POMIĘDZY DETERMINISTYCZNYMI I STOCHASTYCZNYMI MODELAMI FLOTACJI

The paper presents a short review of selected models of flotation kinetics the aim of which was a synthesis of the results obtained in different types of models. The authors compared the stochastic and determinist models of both the cyclic and continuous flotation in the multi-chamber machine. The determinist model of cyclic and continuous flotation and the stochastic model of cyclic flotation, based on the birth and death process were discussed very thoroughly.

The synthesis of these models generates expressions by means of which, after removing the flotation kinetics curve, it is possible to investigate quantitatively the process of adhesion of mineral particles to air bubbles as well as detachment of particles from bubbles, and the value of equilibrium recovery.

Key words: flotation kinetics, flotation rate constant, adhesion, stochastic model, birth and death model, probability

Flotacja — jak każdy proces technologiczny, w którym o wynikach decyduje wiele czynników o charakterze losowym — jest procesem zachodzącym w czasie. Matematycznie przebieg procesu flotacji w czasie ujmują równania kinetyki flotacji. Występująca w tych równaniach stała prędkości flotacji jest wielkością makroskopową, która powinna zawierać informacje o czynnikach wpływających na proces. Na przestrzeni ostatnich kilkudziesięciu lat powstało wiele modeli kinetyki flotacji, począwszy od modeli deterministycznych po modele stochastyczne odnoszące się zarówno do flotacji cyklicznej, jak i ciągłej w maszynie wielokomorowej. Każdy z tych modeli wnosi pewne informacje o procesie, przy czym efekty końcowe uzyskiwane z różnych typów modeli powinny być zbieżne, a informacje powinny się uzupełniać.

W artykule przedstawiono analizę deterministycznych oraz stochastycznych modeli kinetyki flotacji cyklicznej I rzędu, a także flotacji ciągłej w maszynie wielokomorowej. Analiza i porównanie tych modeli pozwoliły na uzyskanie wyrażeń na stałe prędkości adhezji, prędkości odrywania, prędkości flotacji oraz wartości równowagowej uzysku flotowanego minerału w produkcie pianowym.

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W modelach deterministycznych (Schuhmanna, Beloglazova, Melkicha, Yoona, Mao i Luttrella) uzyskuje się wyrażenia na zależność uzysku flotowanego minerału od czasu flotacji (wzory 1, 5 i 6), a stała prędkości flotacji powiązana jest z prawdopodobieństwem zderzenia ziarna z pęcherzykiem P_c, adhezji ziarna do pęcherzyka P_a oraz trwałością piany F (wzór 2) lub ilością pęcherzyków gazu N przechodzących przez zawiesinę w jednostce czasu (wzór 7) bądź całkowitą powierzchnią pęcherzyków gazu przepływającego przez jednostkę powierzchni przekroju poprzecznego komory flotacyjnej w jednostce czasu (wzór 8). Na trwałość połączenia ziarna z pęcherzykiem zwrócił uwagę Sutherland uwzględniając w wyrażeniu na prawdopodobieństwo mineralizacji pęcherzyka, prawdopodobieństwo oderwania ziarna od pęcherzyka P_d (wzór 38). Yoon, Mao i Luttrell wychodząc z zasad pierwszych wyprowadzili wzory na prawdopodobieństwa zderzenia, adhezji i oderwania ziarna od pęcherzyka (wzory 40, 41, 46, 47 i 48).

Ze wzoru (48) wynika, że istnieje określone prawdopodobieństwo oderwania ziarna od pęcherzyka. Uwzględniając ten fakt Stachurski przedstawił model kinetyki flotacji oparty na stochastycznym procesie narodzin i ginięcia, w którym ilość ziaren wynoszonych przez pęcherzyki do warstwy piany $N(t)$ jest zmienną losową. Rozwiązując układ równań Kołmogorowa-Fellera (wzory 16 i 18) otrzymał wyrażenie na uzysk ziaren wyniesionych do warstwy piany (wzór 22). Ze wzoru (22) oraz porównania tego modelu z modelem deterministycznym można wyznaczyć stałą prędkości flotacji k (wzór 54), prędkości adhezji λ_0 (wzór 24), prędkości odrywania μ_0 (wzór 23), uzysk równowagowy ε_∞ (wzór 23) oraz powiązać te wielkości z prawdopodobieństwami zderzenia, adhezji i oderwania (wzory 55 i 56).

Analogiczne skojarzenie deterministycznego modelu flotacji ciągłej w maszynie wielokomorowej z modelem stochastycznym umożliwia powiązanie współczynnika intensywności wyflotowania ziaren λ oraz współczynnika intensywności przejścia z komory do komory μ ze stałą prędkości flotacji k oraz średnim czasem przebywania zawiesiny w komorze flotacyjnej τ (wzory 35 i 37).

Wyprowadzenie równań kinetyki flotacji na podstawie zasad pierwszych umożliwia powiązanie flotacji cyklicznej z flotacją ciągłą w maszynie wielokomorowej poprzez stałą prędkości flotacji k (wzory 5 i 35).

Powiązanie modeli deterministycznych z modelami stochastycznymi flotacji stanowi istotne dopełnienie informacji dotyczących wielkości charakteryzujących ten proces.

Słowa kluczowe: kinetyka flotacji, stała prędkości flotacji, adhezja, prawdopodobieństwo, model stochastyczny, proces narodzin i ginięcia

1. Introduction

Flotation, as every technological process in which the results are determined by numerous random factors, is the process occuring in time. One of this factors is constituted by the quantity of potential interactions of a electromagnetic type between a mineral particle and an air bubble, determining, among others, a stable connection of the particle with the bubble. The random character of interactions results from the fact that their quantities are determined by the particle surface properties which change not only from one particle to another but can also be changed within the confines of the surface of the same particle.

In order to obtain a stable connection between the particle and the air bubble, first of all a collision between them must occur and the kinetic energy of the particle must be included in a certain range of values, on one hand large enough to overcome the barrier of the potential of interaction between the particle and the bubble and, on the other hand, little enough to prevent the particle to break from the bubble. Both the collision between

the particle and the bubble as well as the value of kinetic energy of the particle are of random character.

As it can be observed, a set of random events, whose probabilities influence the velocity of the process course, determine the stable connection between the particle and the bubble. The higher the probability, the faster flotation process.

Therefore there is an analogy between the mechanism of the origin of the chemical reaction and the mineralization of the air bubble in the flotation process. Consequently, the flotation kinetics is described by equations which are analogical to the equations of kinetics of the chemical reaction. The flotation rate constant, occuring in these equations, is a macroscope value which should contain the information about the factors affecting the process. This information is recorded by means of the models of the flotation rate constant which determines the process kinetics.

In the last decades many models of flotation kinetics appeared, starting from deterministic ones to stochastic, concerning both the cyclic flotation and the continuous one in the multi — chamber machine. Each model delivers certain information about the process but the final effects obtained from respective models should be convergent. On the other hand, however, the models, which are most correct metodologically and which bring the largest amount of information, are those which are derived from the first principles, i.e. the basic laws of physics according to which the process between particle — bubble occurs. These laws are the same, both in the multi — chamber machine and the cyclic — operation machine of the same type. Therefore the relations obtained for cyclic flotation, after some modifications connected with different conditions of the process course, can be transferred to the continuous process.

The next chapters will present deterministic and stochastic models of kinetics of cyclic flotation as well as deterministic and stochastic models of continuous flotation in the multi — chamber machine. The analysis of these models contributes to presenting the expressions for rate constants of adhesion, detachment and flotation, as well as equilibrium recovery of mineral under flotation in the foam product.

2. Deterministic models of kinetics of cyclic flotation

Zuniga assumed a model analogical to the equation of kinetics of the first order chemical reactions for the description of the process of flotation kinetics (Zuniga 1935):

$$\varepsilon = 1 - e^{-kt} \tag{1}$$

where:

ε — recovery of the given mineral in the foam product after the flotation time,
t, k — flotation rate constant.

Schuhmann observed that from the mathematical point of view the flotation process is similar to the kinetics of the first order chemical reaction and the kinetics of coagulation. He connected the flotation rate constant with the probability of collision

between the particle and air bubble P_c, the probability of adhesion of the particle to bubble P_a and foam stability F (Schuhmann 1942):

$$k = P_c P_a F \tag{2}$$

Beloglazov assumed that in the process of mineralization of air bubbles the mass of particles dm attached to the bubbles in the time dt is proportional to the concentration of particles $m(t)$ in the flotation chamber in the moment t, the number of air bubbles N passing through the suspension in the unit time and the coefficient P, determining the probability of collision and permanent connection of the particle and bubble (Beloglazov 1947). Consequently, the mass of particles which left the flotation chamber in the time dt is equal:

$$dm = -c_1 mNPdt \tag{3}$$

where:

c_1 — coefficient of proportionality.

After intergrating equation (3), assuming that $m(0) = m_o$, we obtain:

$$m(t) = m_o e^{-kt} \tag{4}$$

where:

$k = c_1 NP$.

The recovery of particles under flotation in the foam product after the time t, according to equation (4) will be equal:

$$\varepsilon(t) = \frac{m_o - m}{m_o} = 1 - e^{-kt} \tag{5}$$

Thus the expression analogical to equation (1) is obtained.

The more general form above model can be written as follows:

$$\varepsilon(t) = \varepsilon_\infty (1 - e^{-kt}) \tag{6}$$

where ε_∞ is an equilibrium value of recovery depending, among others, on surface properties of the particles under flotation and on hydrodynamic conditions in the flotation chamber.

Melkich obtained the analogical result as Beloglazov, treating the process of bubble mineralization as a convolution of two events occuring with a certain probability, namely the collision between the particle and bubble and the permanent connection (adhesion) of the particle and bubble (Melkich 1963). He obtained a formula for flotating probability of particle (recovery) after the time t which is identical to formula (5) while the flotation rate constant is equal to:

$$k = NP_c P_a \tag{7}$$

where:

$P_c = \frac{v}{V}$, v — bubble volume,

V — volume of flotation chamber.

Yoon and Mao considered the movement of air bubbles in the column machine on the path of which the process of collisions with mineral particles took place and the permanent coagulation of particles with bubbles occurred with the determined probability P (Yoon and Mao 1996). They obtained the expression, analogical as the one above, describing the kinetics of flotation in which the flotation rate constant is expressed by the formula:

$$k = \frac{3V_g}{4R_b} P = \frac{1}{4} S_b P \tag{8}$$

where:

R_b — air bubble radius,

V_g — volume intensity of gas flow divided by the cross-section area of the flotation chamber,

S_b — total area of bubbles flowing through the area unit of the cross-section of the flotation machine in the time unit.

Expressing in formula (7) the number of bubbles N by the area S_b, as in formula (8), the following expression for the flotation rate constant is obtained:

$$k = \frac{S_b P}{4\pi R_b^2} \tag{9}$$

It results from formulas (8) and (9) that the larger the rate of dispergation of air bubbles, the higher the value of flotation rate constant.

3. Stochastic model of cyclic flotation

Due to the fact that both the collisions between the particle and air bubble as well as adhesion of the particle to air bubble are of a random character, the process of flotation can be considered as the stochastic process. Such a model was presented by Bodziony in 1965 (Bodziony 1965).

The number of particles under flotation which remain free in the chamber (not coagulated with air bubbles) to the time t is a random variable. Let $N(t)$ represent a random variable denoting the number of particles which were not subjected to adhesion to the time t. The following value:

$$P_{n+1}(t) = P[N(t) = n + 1] \tag{10}$$

is the probability of the fact that the random variable in the time moment t assumes the value $n+1$. Such a state of the process is marked as $E_{n+1}(t)$. From the physical point of view this is equivalent to the situation that till the time t, $n+1$ free particles remained in the flotation chamber. After the time $t + \Delta t$ the random variable assumes the value n. This state of the process is marked as $E_n(t + \Delta t)$. One particle was subject to adhesion to the air bubble after a moment of time Δt. Therefore it can be said that free particles disappear from the flotation chamber and such a stochastic process is called as the death process.

The probability of transfering from the state $E_{n+1}(t)$ to the state $E_n(t + \Delta t)$ is equal to:

$$P[E_{n+1}(t) \rightarrow E_n(t + \Delta t)] = \lambda(n+1)\Delta t + o(\Delta t) \tag{11}$$

where $\lambda(n)$ is the function of intensity of transfer from one state to another, or the function adhesion intensity. Expression (11) means that the probability of decreasing by one the number of free particles in the time Δt is proportional to this time with the accuracy to the infinitely small value of the higher order than $o(\Delta t)$. In other words, the probability of an event consisting in the fact that in the time Δt more than one particle is subject to adhesion to the air bubble decreases faster to zero than the time Δt.

It is assumed for the adhesion function that:

$$\lambda(n) = n\lambda_o \tag{12}$$

where λ_0 is the constant characterizing the process. In other words, the intensity of the adhesion process is proportional to the number of free particles.

Solving the appropriate system of Kolmogorov — Feller's differential equations for this process we obtain an expression for the recovery of particles which underwent adhesion, identical to expression (1) while the λ_o is the flotation rate constant.

In the above model the particles which underwent adhesion to air bubbles cannot return to the free state. This so-called pure death process. Yet it is known from the previous experiments that as a result of turbulence of the medium in the flotation chamber a process opposite to the adhesion occurs, namely the detachment of particles from air bubbles. Therefore the description of the flotation process by a pure death process is not sufficient. The model based on the birth and death process (Bailey 1964) is a more complete and depicts the character of phenomena occuring in the flotation chamber. Such a model was presented by Stachurski for the process of foamless ionic flotation where the mechanism of detachment is slightly different than in case of flotation of minerals (Stachurski 1970).

Two mechanisms occur in the volume of the flotation chamber: adhesion and detachment of the already attached particles from the air bubbles as a result of turbulence of the medium in the flotation chamber.

The random variable $N(t)$ is constituted by the amount of particles lifted by the air bubbles up to the foam layer till the time t. The function of transfer probability is defined as follows:

$$P_{jl}(t, t + \Delta t) = P[N(t + \Delta t) = l \mid N(t) = j] \qquad 0 \le t \le t + \Delta t \tag{13}$$

This is a conditional probability of the fact that in the moment $(t + \Delta t)$ there are k particles attached to the air bubbles if in the moment t their number was j. Assuming that the process is time-homogeneous, i.e.:

$$P_{jl}(t+\Delta t) = P_{jl}(\Delta t) \tag{14}$$

the following postulates are formulated for the transfer probability:

$$P_{jl}(\Delta t) = \begin{cases} \lambda(j)\Delta t + o(\Delta t) & \text{for } l = j+1 \quad (15a) \\ \mu(j)\Delta t + o(\Delta t) & \text{for } l = j-1 \quad (15b) \\ 1-[\lambda(j)+\mu(j)]\Delta t + o(\Delta t) & \text{for } l = j \quad (15c) \\ o(\Delta t) & \text{for } l \neq j-1, j, j+1 \quad (15d) \end{cases}$$

where $\lambda(j)$ denotes the intensity function of adhesion process while $\mu(j)$ the intensity function of detachment process of the particles from the air bubbles.

Equation (15a) means that the probability of increasing by one the number of attached particles is proportional to the time Δt with accuracy to an infinitesimal value of the higher order. Analogically, (15b) means that increasing by one the number of detached particles is proportional to the time Δt. In the state of equilibrium the process is characterized by the sum of effects of adhesion and detachment. Respectively, expression (15c) means that during the time Δt no change of the amount of particles in the chamber occurred. Expression (15d), on the other hand, means that the probability that in the time Δt more than one particle was subject to adhesion or detachment from the bubble is an infinitesimal value.

It is obvious that $N(0) = 0$. The probability of transfer $P_{ol}(t) = P_l(t)$ is fulfilled by Kolmogorov-Feller's system of differential equations:

$$\frac{dP_l(t)}{dt} = -[\lambda(l)+\mu(l)]P_l(t) + \lambda(l-1)P_{l-1}(t) + \mu(l+1)P_{l+1}(t) \tag{16}$$

The above system of equations expresses the principle of probability conservation.

The intensity functions of adhesion and detachment processes, by analogy with equation (12) are expressed by the following formulas:

$$\lambda(l) = \lambda_o(n_o - l) \tag{17a}$$

$$\mu(l) = \mu_o l \tag{17b}$$

Therefore the intensity of adhession process is proportional to the number of free particles $(n_0 - l)$ whereas the intensity of detachment process is proportional to the number of particles attached to bubbles (l). After taking into consideration formulas (17), equations (16) assume the form:

$$\frac{dP_l(t)}{dt} = -[\lambda_o(n_o - l) + \mu_o l]P_l(t) + \lambda_o(n_o - l + 1)P_{l-1}(t) + \mu_o(l+1)P_{l+1}(t) \tag{18}$$

Considering the initial conditions:

$$P_l(0) = 1 \qquad \text{for } l = 0 \tag{19a}$$

$$P_l(0) = 0 \qquad \text{for } l = 1, 2, ..., n_o \tag{19b}$$

system (18) results in the following solution:

$$P_l(t) = \binom{n_o}{l} \frac{l}{(\lambda_o + \mu_o)^{n_o}} [(\mu_o + \lambda_o)e^{-(\lambda_o+\mu_o)t}]^{n_o - l}[1 - e^{-(\lambda_o+\mu_o)t}]^l \tag{20}$$

The average value of random variable $N(t)$ is:

$$E[N(t)] = \sum_{l=0}^{n_o} lP_l(t) = \frac{n_o\lambda_o}{\lambda_o + \mu_o}[1 - e^{-(\lambda_o+\mu_o)t}] \tag{21}$$

Thus, the recovery of particles lifted up to the foam layer is expressed by the formula:

$$\varepsilon(t) = \frac{E[N(t)]}{n_o} = \frac{\lambda_o}{\lambda_o + \mu_o}[1 - e^{-(\lambda_o+\mu_o)t}] \tag{22}$$

The form of this formula is analogical to formula (6) whereas $\varepsilon_\infty = \frac{\lambda_o}{\lambda_o + \mu_o}$ and $k = \lambda_o + \mu_o$. It can be said that constants λ_o and μ_o are the rate constants of adhesion and detachment processes respectively. These constants can be calculated from formula (22) because:

$$\lim_{t\to\infty} \varepsilon(t) = \frac{\lambda_o}{\lambda_o + \mu_o} \tag{23}$$

$$\left.\frac{\partial\varepsilon(t)}{\partial t}\right|_{t\to 0} = \lambda_o \tag{24}$$

Fitting the empirical dependence to the model one it is possible to evaluate the largeness of the process of adhesion and detachment in given physicochemical and hydrodynamic conditions in the flotation chamber.

4. Model of kinetics of the continuous process of flotation in the multi-chamber machine

In the continuous process, as opposed to the cyclic flotation, the feed is continuously delivered into the flotation machine as well as the products of flotation are continuously

taken away. In general, the volume of tailings is much larger than the volume of concentrate leaving the machine in a unit of time. Without a larger mistake the flotation productivity can be determined by the volume of tailings leaving the flotation machine. Let Q denotes the volume productivity of the machine, measured by the volume of suspension included in tailings whereas let a be a fraction of the volume of the flotation chamber occupied by air. Then the product $(1 - a)V$ will denote the volume of suspension in the chamber of the flotation machine which volume is equal V.

The probability of the fact that a particle in the time interval Δt will find its way to tailings will be expressed by the following formula (Mełkich 1963):

$$\Delta P_w = \frac{Q\Delta t}{(1-a)V} \tag{25}$$

Since the possibility of the particle to be in the concentrate in the interval Δt is equal to:

$$\Delta P_k = k\Delta t \tag{26}$$

hence the probability that the particle will remain in the flotation chamber in the time Δt is as follows:

$$\Delta P_o = 1 - \Delta P_k - \Delta P_w = 1 - \Delta t\left[k + \frac{Q}{(1-a)V}\right] \tag{27}$$

Let the flotation time be $t = m\Delta t$ where m is the number of intervals Δt into which the flotation time was divided. The probability of remaining of the particle in the chamber after the time t, i.e. after all m time intervals Δt wil be:

$$P_{om} = \left\{1 - \Delta t\left[k + \frac{Q}{(1-a)V}\right]\right\}^m = \left\{1 - \frac{t}{m}\left[k + \frac{Q}{(1-a)V}\right]\right\}^m \tag{28}$$

The above function sequence has a limit:

$$\lim_{m\to\infty} P_{om} = P_o = \exp\left\{-\left[k + \frac{Q}{(1-a)V}\right]t\right\} \tag{29}$$

Therefore the probability of leaving the flotation chamber by the particle is expressed by the formula:

$$P_k + P_w = 1 - \exp\left\{-\left[k + \frac{Q}{(1-a)V}\right]t\right\} \tag{30}$$

The probabilities P_w and P_k of particle's finding its way to tailings and concentrate can be calculated from formulas (25), (26) and (30):

$$P_w = \frac{Q}{Q + k(1-a)V}\left\{1 - \exp\left[-\left(k + \frac{Q}{(1-a)V}\right)t\right]\right\} \tag{31}$$

$$P_k = \frac{k(1-a)V}{Q + k(1-a)V}\left\{1 - \exp\left[-\left(k + \frac{Q}{(1-a)V}\right)t\right]\right\} \tag{32}$$

For the one-chamber machine

$$\lim_{t\to\infty} P_w = \frac{Q}{Q + k(1-a)V} \tag{33}$$

This formula expresses the probability of particle's finding its way to the tailings for the established process of the continuous flotation. The probability of particle's finding its way to the tailings in the n-th chamber multi-chamber machine is:

$$P_{wn} = \left(\frac{Q}{Q + k(1-a)V}\right)^n \tag{34}$$

In relation with this, the probability of particle's finding its way to the concentrate of the n-th chamber machine and simultaneously the recovery of the mineral of the useful component will be expressed by the formula:

$$\varepsilon(n) = 1 - \left(\frac{Q}{Q + k(1-a)V}\right)^n = 1 - \frac{1}{(1+k\tau)^n} \tag{35}$$

while $\tau = \frac{(1-a)V}{Q}$ presents the average time of remaining of the suspension in the flotation chamber.

Applying formula (35) it is possible to calculate the recovery of the useful mineral in the i-th chamber of the flotation machine:

$$\varepsilon_i = \varepsilon(i) - \varepsilon(i-1) = \frac{k\tau}{(1+k\tau)^i} \tag{36}$$

The analogical expression for the recovery of the useful mineral in the multi-chamber flotation machine was obtained by Siwiec when treating flotation as Markov's process of the finite number of states (Siwiec 1981):

$$\varepsilon(n) = 1 - \frac{1}{\left(1 + \frac{\lambda}{\mu}\right)^n} \tag{37}$$

where λ presents the intensity of particles flotating while μ the intensity of transfer from one chamber to another. Substituting $k = \lambda$ and $\frac{Q}{(1-a)V} = \mu$ in equation (35), formula (37) will be obtained.

Formulae (35) and (36) enable to transfer from the model of cyclic flotation characterized by the flotation rate constant to the model of continuous flotation in the multi-chamber machine, additionally characterized by the average time of remaining in the flotation chamber.

5. The flotation rate constant

In the above approaches to the kinetics of flotation the probability of permanent coagulation of the particle with the bubble occurs in the expressions for the flotation rate constant. The specification of this value by various authors leads to a wide range of models of flotation kinetics. Many models were proposed which connect the flotation rate constant with the phenomena occuring in the flotation chamber (King 1982; Geidel 1985; Jiang 1991).

Yoon and Mao proposed recently a more transparent (from the methodological point of view) model of the flotation rate constant, derived from the first principles, taking into consideration both the hydrodynamic and surface interactions (Yoon and Mao 1996). The flotation rate constant in this model is expressed by formula (8).

Taking after Sutherland the expression for probability P (Sutherland 1948):

$$P = P_c P_a (1 - P_d) \tag{38}$$

the flotation rate constant is expressed by the following formula:

$$k = \frac{3V_g}{4R_b} P_c P_a (1 - P_d) = \frac{1}{4} S_b P_c P_a (1 - P_d) \tag{39}$$

Considering the motion of the particle in relation to the air bubble in the flotation chamber along the line of the liquid current which surrounds the air bubble, Yoon and Luttrell derived the formula for the probability of collision and adhesion (Yoon and Luttrell 1989):

$$P_c = \left(\frac{3}{2} + \frac{4\mathrm{Re}^{0.72}}{15} \right) \left(\frac{R_p}{R_b} \right)^2 \tag{40}$$

$$P_a = \sin^2 \left[2 \operatorname{arc\,tg} \exp \left(- \frac{45 + 8\mathrm{Re}^{0.72}}{15 R_b \left(\frac{R_p}{R_b} + 1 \right)} u_b t_i \right) \right] \tag{41}$$

where:

Re — Reynolds number for the bubble,
u_b — velocity of ascending motion of the bubble,
t_i — induction time,
R_p — particle diameter.

When deriving formula (41) the following criterion was assumed: in order to achieve a breaking of a thin film between the particle and the bubble (necessary for adhesion of the particle and the bubble), the time of slip (contact) must be larger than the induction time which can be controlled by the appropriate procedure of reagents in the flotation proces.

The problem of adhesion of particles on air bubbles can be also studied by means of considering the energy relations in the particle — bubble interactions.

According to the broadened DLVO theory, the energy of particle — bubble interaction is the sum of three components:

$$V = V_d + V_e + V_h \tag{42}$$

where:

V_d, V_e, V_h denote, respectively, the potential of dispersive interaction (Van der Waals), the electric double layers and the potential of hydrophobic interaction and are expressed by the following formulae (Hogg et al. 1966):

$$V_d = -\frac{A_{132} D_p D_b}{12H(D_p + D_b)}\left(1 - \frac{1+2bl}{1+\frac{bc}{H}}\right) \tag{43}$$

$$V_e = \frac{\varepsilon D_p D_b (\psi_1^2 + \psi_2^2)}{8(D_p + D_b)}\left[\frac{2\psi_1\psi_2}{\psi_1^2 + \psi_2^2}\ln\left(\frac{1+e^{-\kappa H}}{1-e^{-\kappa H}}\right) + \ln(1-e^{-2\kappa H})\right] \tag{44}$$

$$V_h = -\frac{D_p D_b}{12(D_p + D_b)}\frac{K_{132}}{H} \tag{45}$$

where:

ε — dielectric constant of the medium,
A_{132} — Hamaker's constant in particle interaction (1) and bubble interaction (2) in the liquid (3),
H — distance between the surfaces of the bubble and particle,
b — parameter characterizing material (b is of the order 3×10^{-17} s for most materials),
$l = 3{,}3\times 10^{15}$ s — parameter characterizing the medium (water),
c — light velocity in the vacuum,
ψ_1, ψ_2 — surface potentials of the particle and bubble,

κ — Debye-Huckel's parameter,
K_{132} — constant of hydrophobic interaction.

Figure 1 presents the dependence *V(H)*. The particle kinetic energy must fulfill the condition $E_k \geq E_1$ (E_1 is the height of the energy barrier of the particle — bubble interaction) in order to achieve adhesion of the particle and bubble. In such a situation the probability of adhesion will be expressed by the formula:

$$P_a = \exp\left(-\frac{E_1}{E_k}\right) \tag{46}$$

The probability of detachment is expressed by the formula analogical to the equation for P_a since the detachment of particle from air bubble occurs when the particle kinetic energy is larger than the sum of adhesion energy W_a and E_1 (Laskowski et al. 1991):

$$P_d = \exp\left(-\frac{W_a + E_1}{E'_k}\right) \tag{47}$$

where E'_k is the kinetic energy necessary to detachment the particle from bubble. Expressing the adhesion energy by the angle of wetting θ and the surface tension on the liquid-air boundary γ_{lv}, we obtain the expression for detachment probability:

$$P_d = \exp\left(-\frac{\gamma_{lv}\pi R_p^2(1-\cos\theta)^2 + E_1}{E'_k}\right) \tag{48}$$

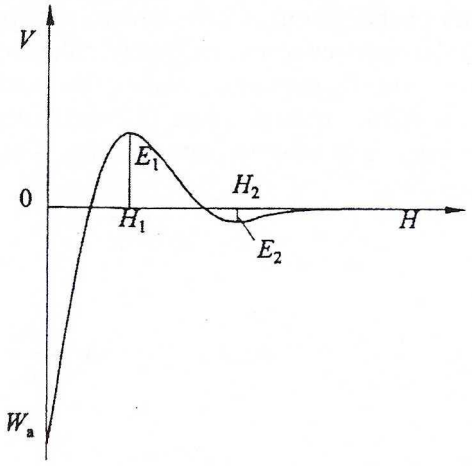

Fig. 1. A potential energy vs. distance diagram for bubble—particle interaction

Rys. 1. Zależność energii potencjalnej oddziaływania pęcherzyk—ziarno od odległości między nimi

Taking into consideration expressions (39), (40), (46) and (48) the flotation rate constant is expressed by the formula:

$$k = \frac{3V_g}{4R_b}\left(\frac{3}{2} + \frac{4\mathrm{Re}^{0.72}}{15}\right)\left(\frac{R_p}{R_b}\right)^2 \exp\left(-\frac{E_1}{E_k}\right)\left\{1 - \exp\left[-\frac{\gamma_{lv}\pi R_p^2(1-\cos\theta)^2 + E_1}{E'_k}\right]\right\} \tag{49}$$

Therefore the flotation rate constant is the function of factors characterizing the material under to be enriched (R_p), hydrodynamic conditions in the flotation chamber (R_b, Re, E_k, E'_k, V_g) and natural or modified (with appropriate reagents) surface properties of particle and bubble (E_1, θ, γ_{lv}).

6. Physical interpretation of the constants of birth and death model

It results from formula (1) for the recovery of the useful mineral in the foam product that after an appropriately long time (theoretically infinitely long) the entire bulk of the flotable mineral will transfer to the foam product. This is the result of the fact that in this model and in any other determinist model of the flotation kinetics the phenomenon of detachment of particles from the bubble — particle aggregates is not taken into consideration. The value of the equilibrium recovery $\varepsilon_\infty = 1$. All particles bound with air bubbles find their way to the foam product. It results from formula (1) that:

$$\frac{d\varepsilon}{dt}(t=0) = k \tag{50}$$

The comparison of this result with formula (24) leads to the conclusion that in case of the flotation without the phenomenon of detachment of particles the flotation rate constant is equivalent to the constant of non-returnable adhesion. All particles attached to air bubbles will transfer to the foam product. None of them will be detached from the flotation aggregate. As it results from formula (1), the flotation rate constant and, simultaneously, the non-returnable adhesion rate constant is equal to:

$$k = \frac{1}{1-\varepsilon}\frac{d\varepsilon}{dt} \cong \frac{1}{1-\varepsilon}\frac{\Delta\varepsilon}{\Delta t} \tag{51}$$

Since

$$\varepsilon = \frac{l}{n_o} \qquad \text{oraz} \qquad \Delta\varepsilon = \frac{\Delta l}{n_o} \tag{52}$$

consequently

$$k = \frac{\Delta l}{\Delta t(n_o - l)} = \frac{0.25 l_c S_b}{\Delta t(n_o - l)}\frac{\Delta l}{0.25 S_b l_c} = 0.25 S_b P_c P_a \tag{53}$$

where:

n_o — initial number of flotable particles in the flotation chamber,
l — number of particles attached to the bubbles till the time t,
Δl — number of particles attached to the bubbles in the time Δt,
l_c — number of particles colliding with the bubble in the unit time,
P_c and P_a — probabilities of collision and adhesion, respectively, equal:

$$P_c = \frac{l_c}{\Delta t(n_o - l)} \qquad P_a = \frac{\Delta l}{0.25 S_b l_c}$$

The condition for adhesion to occur is the previous particle — bubble collision. Therefore the non-returnable adhesion rate constant is the product of collision probability and adhesion probability on the surface of air bubbles passing the area unit of the cross-section of the flotation chamber in the time unit.

In case of the model flotation considering the process of particles detachment from the bubbles surfaces the following scheme of the process of adhesion meant as a balance of the number of particles:

non-returnable adhesion = adhesion with detachment + detachment

If we consider the fact that the flotation rate constant is equal to the non-returnable adhesion rate constant, the above scheme results from formula (22) in which the flotation rate constant is:

$$k = \lambda_o + \mu_o \tag{54}$$

Since the non-returnable rate constant is expressed by formula (53) while the adhesion rate constant with detachment by formula (39), consequently the detachment rate constant will be:

$$\mu_o = k - \lambda_o = \frac{1}{4} S_b [P_c P_a - P_c P_a (1 - P_d)] = \frac{1}{4} S_b P_c P_a P_d \tag{55}$$

Applying formulae (55) and (39), the value of equilibrium recovery can be calculated:

$$\varepsilon_\infty = \frac{\lambda_o}{\lambda_o + \mu_o} = \frac{0.25 S_b P_c P_a (1 - P_d)}{0.25 S_b P_c P_a} = 1 - P_d \tag{56}$$

Therefore P_d, λ_o and μ_o can be determined from the empirical dependence $\varepsilon(t)$. This fact creates an additional tool for investigating the basics of the process of mineralization of air bubbles.

7. Final remarks

The presented review of selected models of flotation kinetics is a short synthesis of determinist and stochastic models of both cyclic and continuous flotation in the

multi-chamber machine. Such a synthesis enables the results obtained in the determinist approach to be matched to the ones of the stochastic model which consequently, leads to mutual supplementing of the information obtained from respective model types. The obtained formulas will be applied to investigate the intensity of the course of flotation microprocesses, i.e. adhesion and detachment, and the value of equilibrium recovery, connected with them, in the function of physical and physicochemical parameters affecting flotation by means of the dependence of probabilities of collision, adhesion and detachment from these parameters.

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