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KINETICS OF FLOTATION. ORDER OF PROCESS, RATE CONSTANT DISTRIBUTION AND ULTIMATE RECOVERY

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Abstract: Kinetic models can be used to characterize the flotation process. In this paper, three primary parameters, namely, distribution of flotation rate constant $f(K)$, order of flotation process n and ultimate recovery R_∞ are presented to perform analysis of flotation kinetics. The flotation rate constant $f(K)$ is a function of both the size and hydrophobicity of particles. Though the more commonly used distributions are Delta function as well as Rectangular, Kelsall and Gamma models, there is no agreement in the literature as to which distribution function better characterize the floatability distribution. The first-order models can be used to describe most mineral flotation processes, while there is also evidence that the non-integral-order equation is capable of representing the kinetic characteristics of the batch flotation process. The order is lower than 1 in the initial moments of the flotation process. The solution of ultimate recovery calculated by the least squares method is greater than 100% (R_∞ >100%). An empirical model was proposed to avoid the improper phenomenon in the solution of ultimate recovery, which can improve the availability and validity of kinetic models. Finally, more attention should be paid to the overfitting resulting from the increase in the number of parameters in the statistical analysis of kinetic models.

Keywords: *kinetic mode, kinetic order, rate constant distribution, ultimate recovery, overfitting*

Introduction

Froth flotation is a process of separation and concentration based on differences in the physicochemical properties of interfaces (Allan and Woodcock, 2001). The technology has been used industrially in treatment of wastewater, bacteria, coal, clays, corn, resins, proteins, fats, rubber, dyes, glass, plastics, fruit juices, cane sugar, etc. (Matis and Zouboulis, 1995). Froth flotation is a selective separation process, which is affected by many factors related to the floated mineral such as grade, degree of liberation, surface properties and many operating variables etc. (Cilek, 2004).

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Flotation is a complex process which involves the interactions of three phases (gas, liquid and solid). Hence, the construction of mathematical models of flotation is proved to be very difficult. A flotation compartment can be defined as the pulp and froth. The transfer of any valuable or gangue components between pulp and froth zones is shown in Fig. 1. Irrespective of the transportation mechanism for reaching the froth region, particles can return to the pulp region or eventually leave the froth region into the concentrate launder if levels of manipulated variables allow froth removal.

Traditionally, evaluation of batch flotation tests is based largely on a rougher recovery value achieved at a defined time. Since the cumulative recovery of a component in the concentrate is proportional to flotation time, the flotation process can be considered as a time-rate recovery process. Therefore, a mathematical flotation model that incorporates both the recovery and rate function can completely describe flotation time-recovery profiles.

Subsequently, a large number of models have been proposed for a better understanding of the flotation process. Dowling et al. (1985) reviewed 13 different models of flotation process and attempted to differentiate among them based on several sets of data on time-recovery profiles of a porphyry copper ore. Lynch et al. (1981) defined three categories for these models (empirical models, probability models, and kinetic models). Empirical models are too specific to their environment and usually involve a trial and error feedback approach to optimization. More importantly, the model parameters obtained by statistical techniques do not have any physical significance and do not provide any insight into flotation process. The empirical models offer little predictive capacity beyond the conditions used in their evaluation (Nguyen and Schulze, 2004). The probability models basically consider the probabilities of particle-bubble collision, adhesion, froth stability, etc. The simple form of the probability approach is similar to the simplest form of kinetic models (Yuan et al., 1996; Sripriya et al., 2003). Consequently, this paper will consider only kinetic models.

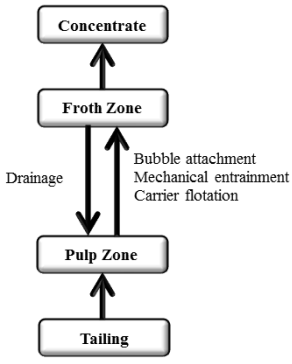


Fig. 1. Transfer of materials between pulp and froth zones (based on Lynch et al., 1981)

Kinetic models are established on the basis of the analogy between a chemical reaction (collision of molecules) and an important flotation mechanism, i.e., the collision between either hydrophilic or hydrophobic particles and air bubbles in the pulp volume. It is generally agreed that the first paper with flotation kinetics was published by Zuniga (1935) in Chile. He had applied the differential equation of chemical reaction kinetics to portray the flotation process and observed that the flotation recovery is an exponential function of flotation time. The differential equation of Zuniga (1935) can be written as:

$$\frac{dC}{dt} = -KC \tag{1}$$

where $C(t)$ is the concentration of floating particles remaining in the flotation chamber up to the flotation time t, K is the flotation rate constant.

In fact, Arbiter (1951) proposed a second-order equation to represent the results of Zuniga (1935), Beloglazov (1939) and Sutherland (1948), as well as his own results obtained in laboratory batch tests and other data produced by industrial cells. The original equation proposed by Arbiter (1951) is:

$$\frac{dC}{dt} = -KC^2 . \tag{2}$$

Equations 1 and 2 can be generalized as:

$$\frac{dC}{dt} = -KC^n \tag{3}$$

in which parameter n characterizes the order of the process (order of flotation kinetics).

The recovery of particles in the froth product (R) after flotation time (t) is defined as:

$$R(t) = \frac{C_0 - C(t)}{C_0} = 1 - \frac{C(t)}{C_0} \tag{4}$$

where C_0 is the concentration of floating particles remaining in the flotation chamber with the initial condition (t = 0). Generally, it is considered that the value of C_0 is equal to 1. In other words, there is no froth product at the initial flotation time (t = 0).

All particles will undergo flotation, i.e., the recovery can be 100% because theoretically always more particles float that falls back when the flotation process is infinite under ideal conditions. Therefore, some larger and more difficult-to-float particles may still remain unfloated in the general case because, despite the adhesion

process to bubble, a reverse process occurs, i.e. detachment of the particles from the surface of bubbles into the pulp (Morris, 1952; Mika and Fuerstenau, 1968; Stachurski, 1970; Woodburn et al., 1971; Schulze, 1977; Schulze, 1992). According to Eq. 4, under the condition ($t\to\infty$) the ultimate recovery R_∞ can be expressed as:

$$R_\infty = 1 - C_\infty \tag{5}$$

Inserting Eqs. 4 and 5 into Eq. 3, gives:

$$\frac{dR}{dt} = K\left(R_\infty - R\right)^n. \tag{6}$$

It is clear that both the bubble surface area flux and collection efficiency are strongly dependent on the particle and bubble sizes so that unless–size ranges of bubbles and particles are extremely narrow, the rate constant K will be some sort of effective constant, which is appropriate only to the particular size distribution under the test with given conditions (Nguyen and Schulze, 2004; Polat and Chander, 2000). The distribution of the rate constant, $f(K)$, was introduced to represent the distribution function of K for different particles in the flotation cell, and thus Eq. 6 can be equal to:

$$\frac{dR}{dt} = f\left(K\right)\left(R_\infty - R\right)^n. \tag{7}$$

The ultimate recovery R_∞, distribution of flotation rate constant $f(K)$ and order of flotation kinetics n in Eqs. 6 and 7 can be determined from the experimental data of R versus t.

In the present article, it is sought to review kinetic models based on these three parameters, for instance, $f(K)$ n and R_∞, with a focus on the description of the flotation process and the reliable kinetic analysis procedure.

Distribution of *K*

The conception of distribution of the rate constant is introduced to extend the validity and applicability of kinetic models for the heterogeneity of particles. Various distributions have been proposed by different investigators to account for the variability of the rate constant. These distributions can be divided into three groups: discrete, continuous mean distributions of rate constants.

Discrete rate constants

There are several kinetic models involved with the discrete rate constant. The differences between them are the number of fractions assumed (Morris, 1952; Kelsall, 1961; Imaizumi, 1963; Kelsall and Stewart, 1971; Jowett, 1974; Cutrris, 1977).

A single phase discretely distributed species models is supposed to follow the well-known classical first-order and second-order kinetic model. The classical first-order flotation model is most widely used to optimize the design of flotation circuits (Agar, 1980; Xu, 1998). This is the standard classical first-order model and it was proposed by many investigators (Dowling et al., 1985; Wills, 1988; Vanangamudi et al., 1989; Radoev et al., 1990; Mazumdar, 1994; Gülsoy and Ersayin, 1996; Sripriya et al., 2003). The equation of the classical first-order models can be obtained by the integration of Eq. 6 when $n = 1$:

$$R = R_{\infty}(1 - e^{-K_B t}) \tag{8}$$

where K_B is the average flotation rate constant. Equation 8 is the simplest model with one average flotation rate constant for all particles and under the whole flotation conditions.

In fact, the classical first-order equation is also named as the first-order with Dirac delta function (Lynch et al., 1981). The K_B can be predicted using the fundamental model which takes into account superficial gas velocity, bubble size, collision efficiency and attachment efficiency (Jameson et al., 1977; Ralston, 1992):

$$K_B = \frac{3}{2}\frac{G_{fr}h}{d_b V_{cell}} E_c E_a \tag{9}$$

where h is the height of the flotation cell, G_{fr} is the gas flow rate, d_b is the diameter of the bubble, V_{cell} is the volume of the flotation cell. E_c and E_a are the efficiencies of the bubble-particle collision, attachment, and stability in the pulp zone. The efficiencies are affected by particle density, pulp viscosity, induction time, particle size, shape, and composition, gas hold-up, bubble size, turbulence, bubble viscosity, particle velocity, etc. (Danoucaras et al., 2013).

In addition to the classical first-order model, the single phase discretely distributed species model is also applied to the second-order flotation kinetics by Arbiter (1951).

The two-fraction incorporates two rate terms instead of the rate constant (Kelsall, 1961). The mathematical form of this model can be given as:

$$R = (1 - \phi)\left(1 - e^{-K_f t}\right) + \phi\left(1 - e^{-K_s t}\right) \tag{10}$$

where ϕ is the fraction of flotation components with the slow rate constant, K_f and K_s are the rate constants for fast and slow components, respectively. This model does not include an ultimate recovery parameter but rather the ultimate recovery is assumed to be 100%. As $K_s \rightarrow 0$, the term $(1 - e^{-K_s t})$ in Eq. 10 approaches 0. Thus, the slow-floating component cannot be recovered from the pulp and the term $(1 - \phi)$ becomes analogous to ultimate recovery.

The Kelsall model has been used to model the flotation kinetics by many researchers (Harris and Khandrika, 1985; Mehrotra and Padmanabhan, 1990; Apling and Ersayin, 1986; Albijanic et al., 2015).

The modified version of the Kelsall model adds the influence of ultimate recovery to the Kelsall model and brings the number of parameters to four (Jowett, 1974):

$$R = R_{\infty}\left[(1-\phi)\left(1-e^{-K_f t}\right)+\phi\left(1-e^{-K_s t}\right)\right]. \tag{11}$$

The modified Kelsall model which includes six parameters also provided the best fit to the flotation kinetic of iron ore (Saleh, 2010), galena of Rosh Pinah ore (Coetzer et al., 2003), waste coal (Sokolovic et al., 2012) and copper slag (Stanojlovic and Sokolovic, 2014).

The three-fraction kinetic model discretizes the floating material into fast, medium and slow floating components (Jowett, 1974; Apling and Ersayin, 1986).The model with the ultimate recovery is:

$$R = R_{\infty}\left[\phi_f\left(1-e^{-K_f t}\right)+\phi_m\left(1-e^{-K_m t}\right)+\phi_s\left(1-e^{-K_s t}\right)\right] \tag{12}$$

$$\phi_f+\phi_m+\phi_s=1 \tag{13}$$

where K_m is the flotation rate of medium floating fraction and ϕ_f, ϕ_m and ϕ_s are the fractions of flotation components with a fast, medium and slow rate constant, respectively.

Then, the first-order kinetic model gives by dividing the particle mixture into more floatability fractions (Huber-Panu et al., 1976):

$$R = R_{\infty}\sum_{i=1}^{m}\gamma_i\left(1-e^{-K_i t}\right) \tag{14}$$

$$\sum_{i=1}^{m}\gamma_i=1 \tag{15}$$

where subscript *i* describes the floatability fraction for each respective rate constant, *m* is the number of classified fractions and γ_i represents the proportion of fraction *i*.

Furthermore, flotation models with multi-distributed rate constant, where each mineral is not only broken up into different size fractions but these size fractions are also broken into floatability components, are either arbitrary as above or based on liberation or surface reagent coverage (King, 1976; Niemi et al., 1997).

It can be concluded that the multi-fraction models such as two-fraction and three fraction models show a better correlation than those models having two parameters. A relatively unsophisticated account for that is probably because the two models have

more parameters, while the other models only have two or three parameters (Albijanic et al., 2015). However, this interpretation cannot illustrate that those models based on the classical first-order model with two parameters also show a good fit to the experimental data (Agar, 1980; Agar et al., 1998; Xu, 1998; Ahmed, 2004; Mazumdar, 1994; Ucurum, 2009). Hence, there is a need for more investigations to portray the effect of increase parameters in the model and to determine their upper to provide an adequate model (Apling and Ersayin, 1986).

Besides, the population balance models are a special type of discrete kinetic models, where the principles based on the probability of certain flotation subprocesses occurrence are often used (Herbst and Harris, 2007; Jovanovic and Miljanovic, 2015). The population balance approach in the flotation process macro-scale modeling was also applied by Bloom and Heindel (1997), Sosa-Blanco et al. (1999); Casali et al. (2002) and Sbarbaro et al. (2008).

Continuous rate constant distribution

Imaizumi and Inoue (1963) introduced a new idea on flotation kinetics, stating that the first-order equation, generally written as Eq. 8 should be:

$$R = R_{\infty}\left[1-\int_{0}^{K} f(K)e^{-Kt}dK\right] \tag{16}$$

where K is the upper limit of the rate constant and $f(K)$ is the continuous distribution of the rate constant or K spectrum, which is normalized similarly to Eq. 17:

$$\int_{0}^{K} f(K)dK = 1. \tag{17}$$

From the combined early work, various continuous distribution functions were proposed to account for the variability in the K's, including gamma (Imaizumi and Inoue, 1963; Loveday, 1966), bimodal-gamma (Harris and Chakravarti, 1970), triangular (Harris and Chakravarti, 1970), rectangular (Huber-Panu et al., 1976; Klimpel, 1980), sinusoidal (Diao et al., 1992), exponential (Imaizumi and Inoue, 1963) and normal (Chander and Polat, 1994). Some first-order models and their continuous distribution functions are summarized in Table 1. Besides, the rectangular distribution was also used in second-order flotation kinetics by Klimpel (1980).

In fact, there is disagreement in the literature as to which continuous distribution function is better suited to characterize, especially for a wide range of flotation conditions, as no single model is sufficient to represent the flotation rate data and the best model may be different under various flotation conditions (Jowett, 1974; Harris and Cuadros-Paz, 1978; Fuerstenau et al., 1988; Vanangamudi and Rao, 1986; Dowling et al., 1985; Polat and Chander, 2000; Yianatos et al., 2010. Jovanovic and Miljanovic, 2015).

Mean rate flotation model

The mean rate flotation model, namely, Chen's model is generally based on the assumption that the rate of reduction in the flotation mean rate is proportional to flotation mean rate (Chen and Wu, 1978; Chen and Mular, 1982):

$$\frac{dK}{dt} = -gK\,. \tag{18}$$

The mathematical expression of Chen's model is:

$$\frac{dC}{dt} = -\overline{K(t)}C \tag{19}$$

$$\overline{K(t)} = K_Q e^{-gt} \tag{20}$$

where K_Q is the mean rate value at the beginning of flotation and g is a parameter. This alternative approach in fitting experimental data was also proved by Xu (1984) and Yi (1986).

In selecting suitable rate distributions (discrete, continuous and mean), distributions with a minimum number of parameters, which also have physical significance, should be considered primarily. As the number of parameters in a model is increased to the maximum possible (dependent on the number of experimental points), a better fit of the model to the experimental data is expected (Lynch et al., 1981). However, it is expected that overfitting generally occurs when a model is excessively complex, such as having too many parameters relative to the number of observations. As the number of parameters increases, significant overfitting and increasingly poor generalization are evident (Lawrence et al., 1997.). A overfitted model will generally have poor predictive performance as it can exaggerate minor fluctuations in the data. Hence, it is necessary that more effort should be placed on the overfitting of the kinetic modelling in the flotation process.

Nevertheless, in spite of many attempts to determine the rate constant K as accurate as possible, and consequently to define the most appropriate flotation process model as possible, the widely accepted conclusion is that there is no single model that is suitable to describe the characteristics of flotation kinetics well enough under various flotation conditions.

Order of flotation kinetics

The actual order of flotation kinetics has been investigated by many researchers (Volkova, 1946; Arbiter, 1951; Bogdanov et al., 1954; Horst and Morris, 1956; Klassen and Mocrousov, 1963; Tomlinson and Fleming, 1965; Somasundaran and Lin, 1973; Hernainz and Calero, 1996, 2001; Brozek and Młynarczykowska, 2007;

Bakalarz and Drzymala, 2013; Gharai and Venugopal, 2016; Bu et al., 2016). The interpretations of the order of flotation kinetics can be divided into three categories including first-order, second-order and non-integral-order equations.

First-order flotation kinetics (n = 1)

The first-order flotation kinetics introduced by Zuniga (1935) and Schuhmann (1942) is the most widely accepted approach ((Imauzimi and Inoue, 1963; Tomlinson and Fleming, 1965; Harris and Chakravarti, 1970; Jameson et al., 1977; Dowling et al., 1985; Polat and Chander, 2000; Sripriya et al., 2003; Natarajan and Nirdosh, 2006; Oproiu et al., 2009; Yianatos et al., 2010; Li et al., 2013; Luo et al., 2015; Ni et al., 2016). Many models of first-order kinetics have been developed on the assumptions that the rate of the particle-bubble collision is first-order with respect to the number of particles and that the bubble concentration remains constant (Sutherland, 1948).

Model 1: classical first-order model

The classical first-order model was discussed and presented by Eq. 8. It describes flotation of a monodispersed feed containing particles with an average rate constant (K_B), i.e., floatabilities of particles are constant. There is an interesting phenomenon that the ultimate recovery calculated by this model is smaller than the maximum recovery obtained in the flotation test (Mazumdar, M., 1994; Bu et al., 2016).

Table 1. Summary of distribution functions of K

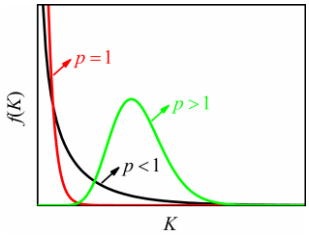
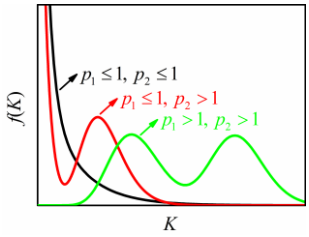
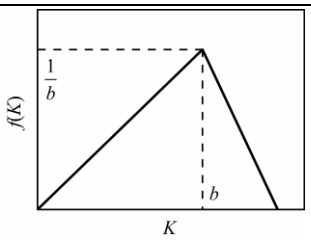
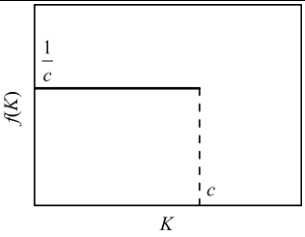
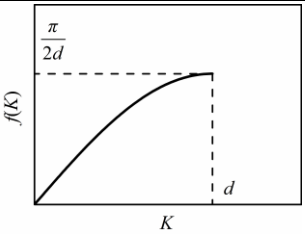
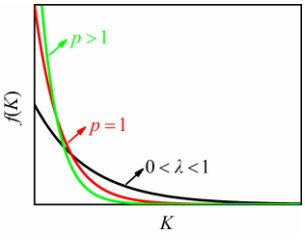
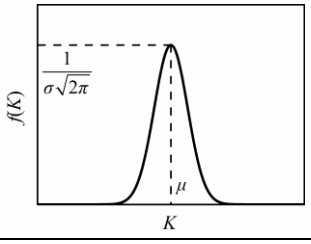
Name	Form of distribution	$f(K)$	$R(t)$ (first-order)
Gamma		$\frac{K^{p-1}}{\Gamma(p)}a^{-p}e^{-\frac{K}{a}}$	$R_\infty\left[1-\left(\frac{1}{1+at}\right)^{p}\right]$
Bimodal-Gamma		$\left[\begin{array}{l}\gamma_1\frac{K^{p_1-1}}{\Gamma(p_1)}a_1^{-p_1}e^{-\frac{K}{a_1}}\\ +\gamma_2\frac{K^{p_2-1}}{\Gamma(p_2)}a_2^{-p_2}e^{-\frac{K}{a_2}}\end{array}\right]$ $(\gamma_1+\gamma_2=1)$	$R_\infty\left\{\begin{array}{l}\gamma_1\left[1-\left(\frac{1}{1+a_1t}\right)^{p_1}\right]\\ +\gamma_2\left[1-\left(\frac{1}{1+a_2t}\right)^{p_2}\right]\end{array}\right\}$

Table 1 Summary of distribution functions of K (cont.)

Name	Form of distribution	$f(K)$	$R(t)$ (first-order)
Triangular		$\begin{cases} \dfrac{K}{b^2} & \text{for } 0 \le K \le b \\ \dfrac{(2b-K)}{b^2} & \text{for } b < K \le 2b \\ 0 & \text{for } 2b < K \end{cases}$	$R_\infty\left[1-\dfrac{1+e^{-2bt}-e^{bt}}{(bt)^2}\right]$
Rectangular (continuous uniform)		$\begin{cases} \dfrac{1}{c} & \text{for } 0 \le K \le c \\ 0 & \text{for } c < K < \infty \end{cases}$	$R_\infty\left[1-\dfrac{1-e^{-ct}}{c\,t}\right]$
Sinusoidal		$\begin{cases} \dfrac{\pi}{2d}\sin\dfrac{\pi K}{2d} & \text{for } 0 \le K \le d \\ 0 & \text{for } d < K < \infty \end{cases}$	$R_\infty\left[1-\dfrac{1-2dt\dfrac{e^{-dt}}{\pi}}{\left(1+\dfrac{2dt}{\pi}\right)^2}\right]$
Exponential		$\lambda e^{-\lambda K}$	$R_\infty\left(1-\dfrac{1}{t/\lambda}\right)$
Normal (Gaussian)		$\begin{cases} \dfrac{1}{\sigma\sqrt{2\pi}}e^{-\frac{1}{2}\left(\frac{K-\mu}{\sigma}\right)^2} & \text{for } 0 \le K \le 2\mu \\ 0 & \text{for } 2\mu < K < \infty \end{cases}$	$R_\infty\left[1-\dfrac{\operatorname{erf}\left(\dfrac{\left(\sigma t+\frac{\mu}{\sigma}\right)}{\sqrt{2}}\right)-\operatorname{erf}\left(\dfrac{\left(\sigma t-\frac{\mu}{\sigma}\right)}{\sqrt{2}}\right)}{2e^{\mu t+\frac{(\sigma t)^2}{2}}}\right]$

Note: parameters a, b, c, d and λ are the kinetic constants of first-order models with gamma, bimodal-gamma, triangular, rectangular, sinusoidal and normal distributions, respectively; parameter p is the exponential number of the first-order model with gamma distribution; σ and μ represent the mean rate constant of the normal distribution and standard deviation or the width of the distribution, respectively; γ_1 and γ_2 are the fractions of the component with distribution of gamma 1 and 2, respectively.

Model 2: classical first-order model with time correction

This model is suggested first by Agar (1983) and used by Dowling et al. (1985) and Gulsoy and Ersayin (1996). Modified flotation rate constant and selectivity index were introduced based on this model by Xu (1998), which was applied to the optimization of flotation process by Sripriya et al. (2003), Ucurum and Bayat (2007) and Vapur et al. (2010). The mathematical form of this model can be given as:

$$R = R_{\infty}\left[1 - e^{-K_1(t+t_c)}\right] \tag{21}$$

where t_c is the time correction and K_1 is the rate constant of the classical first-order model with time correction.

Model 3: first-order model with rectangular distribution of floatability

This model is summarized in Table 1. The monodispersed feed with the rectangular distribution of floatabilities was introduced for a better description of the flotation process. In fact, it was proved that this model is a better form of the first-order one (Mazumdar, 1994; Yuan et al., 1996; Gulsoy and Ersayin, 1998; Ahmed, 2004; Bayat et al., 2004; Ni et al., 2016).

Model 4: first-order model with rectangular distribution of floatabilities including time correction

One of the problems of the flotation process is the definition of zero time. It was suggested that this might be partially solved by rejecting the concentrate collected after the first interval and defining the start of the second period as the zero time (Gulsoy and Ersayin, 1998). A mathematical form of this model, which was proposed by Agar (1983), is as follows:

$$R = R_{\infty}\left\{1 - \frac{1}{K_2\left(t+t_c\right)}\left[1\text{-}e^{-K_2\left(t+t_c\right)}\right]\right\} \tag{22}$$

where K_2 is the rate constant of the first-order model with a rectangular distribution of floatabilities including time correction.

Model 5: Kelsall model (first-order model with discretized distribution of floatability)

The Kelsall model is a discretized distribution that describes the fractions and rate constant of fast and slow-floating materials and ultimate recoveries are considered as 100%. The form of this model is shown in Eq. 10.

Model 6: modified Kelsall model (first-order model with discretized distribution of floatability)

The modified Kelsall model, which adds the ultimate recovery as a parameter, is given in Eq. 11.

Model 7: first-order model with triangular distribution of floatability

This model is presented in Table 1. The triangular distribution is also known as a continuous uniform distribution. This model uses a triangular function to portray the distribution of rate constant instead of the rectangular distribution and it was proposed by Harris and Chakravarti (1970).

Model 8: first-order model with sinusoidal distribution of floatability

This model was proposed by Diao et al. (1992) and is shown in Table 1 (first-order model with sinusoidal distribution).

Model 9: gamma model (first-order model with gamma distribution of floatability

This model and the form of gamma distribution can be found in Table 1. Model parameter *p* influences the shape of the gamma distribution and parameter *a* is a scale parameter, representing the spread of the distribution function. It was found that this model showed a good fit to the experimental data (Apling and Ersayin, 1986; Saleh, 2010; Albijanic et al., 2015).

Model 10: bimodal-gamma model (first-order model with bimodal gamma distribution of floatability)

This model assumes that the distribution of floating particles is subordinated to bimodal-gamma distribution function (Harris and Chakravarti, 1970). The expression can be seen in Table 1.

Model 11: normal model (first-order model with normal distribution of floatability)

In fact, the normal distribution function, namely the gaussian distribution, can be transferred into the gamma distribution with the exponential decay (Yianatos et al., 2010).

Model 12: Rosin-Rammler's model

This model is based on the classical first-order equation (Eq. 8). The mathematical expression of this model is as follows (Tarjan, 1986):

$$R = R_{\infty}(1 - e^{-K_3 t^m}) \tag{23}$$

where *m* is the exponential parameter of flotation time and K_3 is the rate constant of Rosin-Rammler's model. This model was used to describe the flotation kinetics of Maghara coal (Ahmed, 1995).

Model 13: first-order two-stage kinetic model

Considering the flotation system composed of discrete pulp and froth volume, Meyer and Kelsall (1982) proposed a physical model incorporating rate terms describing the mass transfer of a component from the pulp to the froth and from the froth to the concentrate. This model, assuming that the rate of drainage from the froth is minimal, is derived as:

$$R = R_{\infty}\left[\frac{K_4(1-e^{-K_4 t})}{K_4 - K_4^*} - \frac{K_4^*(1-e^{-K_4^* t})}{K_4 - K_4^*}\right] \tag{24}$$

where K_4 and K_4^* are the rates of transfer from the pulp to the froth and from the froth to the concentrate, respectively. This three-parameter model describes a first-order two-stage process and is similar to the model derived by Harris and Rimmer (1966). As K_1 is always much greater than K_4^*, a transfer from the froth to the concentrate is the rate limiting step (Saleh, 2010). Furthermore, Eq. 24, when K_4 is large, can be written as Eq. 8 (Ek, 1992).

Model 14: first-order reversible model

The reversible model describes the transfer of a component from the pulp to the froth and the subsequent drainage of a portion of this component from the froth. The mathematical form of this model is written as (Ek, 1992):

$$R = R_{\infty}\frac{K_5}{K_5 + K_5^*}\left[1 - e^{-(K_5 + K_5^*)t}\right] \tag{25}$$

where K_5 and K_5^* are the rates of transfer of a component from the pulp to the froth and drainage of a portion of this component from the froth, respectively. It is observed that Eq. 25 can be reduced to Eq. 8 when K_5^* is negligible.

Model 15: fully mixed reactor model

Imaizumi and Inoue (1963) showed that the flotation results can be represented by an expression analogous to the equation describing the time concentration for a series of fully mixed reactors. This equation was reorganized into recovery terms and taking the number of reactors as one. This model equation can be obtained in Table 1 (first-order model with exponential distribution). This model, with the assumption of the exponential distribution of floatability, gives an added flexible over the classical first-order model and enables it to the experimental data very well (Dowling et al, 1985).

Model 16: gas/solid adsorption model

Meyer and Kelsall (1982) described a general gas/solid adsorption kinetic function as follows:

$$R = R_{\infty}\frac{K_6}{(1 + K_6 t)^l} \tag{26}$$

where l is the exponential parameter and K_6 is the rate constant of gas/solid adsorption model. The form of this model is very different from any of the previously described models. It does not include an ultimate recovery parameter. Furthermore, it can be shown that l is generally greater than 1, which results in R increasing to values greater than 1 for long times and decreasing thereafter (Ek, 1992).

Model 17: improved gas/solid adsorption model

Equation 26, when parameter l is equal to 1, has the same form as the Langmuir adsorption isotherm (Langmuir, 1918), which can be improved as the following equation:

$$R = R_{\infty} \frac{K_7}{1 + K_7 t} \tag{27}$$

where K_7 is the rate constant of Improved gas/solid adsorption model. This model can be derived from the fully mixed reactors model by substituting $1/K_7$ for λ.

Model 18: first-order model with discretized three fractions

In the three-fraction kinetic model (Eq. 12 and 13), one fraction with a medium flotation rate constant was assumed based on the modified Kelsall model (Jowett, 1974).

Second-order flotation kinetics (n = 2)

Model 19: second-order model

If Eq. 6 is integrated between the limits (t=0, R_0=0 and t= t, R= R), the second-first order equation is:

$$R = \frac{R_{\infty}^2 K_8 t}{1 + R_{\infty} K_8 t} \tag{28}$$

where K_8 is the rate constant of the second-order model.

This model is a two-parameter expression describing the flotation of a mono-dispersed feed with particles having a constant floatability. The second-order model was applied to the discrimination of the optimal kinetic model for batch flotation (Arbiter, 1951). It can be noted that the fit calculated time-recovery profile and the optimal ultimate recovery values are found to be identical to that of fully mixed reactors and improved gas/solid adsorption model, but this form is not as good statistically as those determined by the first-order forms (Dowling et al., 1985; Yuan et al., 1996; Ek, 1992; Zhang et al., 2013; Ni et al., 2016). As seen from Table 2, the calculated values of R_{∞} of second-order model exceeded the appropriate range. The influence of the square of R∞ in Eq. 28 is too heavy when R∞ becomes large, which results in the exceeding phenomenon (R∞ >100%). The same phenomenon was also found by Luo et al. (2015).

Table 2. Calculated values of R_∞ from first-order and second-order models (Bu et al., 2016) %

Particle size (μm)	375	37
Classical first-order	88.39	89.70
First-order with rectangular	98.58	98.67
Second-order	105.98	105.37
Second-order with rectangular	116.07	114.69

Model 20: second-order model with rectangular distribution of floatability

Klimpel (1980) introduced rectangular distribution function into the second-order flotation kinetics. The mathematical form of this model is given as:

$$R = R_\infty \left\{1 - \left[\frac{1}{K_9 t}\ln\left(1+K_9 t\right)\right]\right\} \tag{29}$$

where K_9 is the rate constant of the second-order with rectangular distribution model.

The assumed two-order form introduces additional parameter dilution in the confidence intervals. As seen in Table 2, the fit to the observed data and the confidence intervals become increasingly worse as fractional recovery equal to 100% (Yuan et al., 1996).

Non-integral-order flotation kinetics

Although many researchers have argued either for first or second order rate equations, there is no necessary reason why the value of n in Eq. 6 must be integral (Arbiter and Harris, 1962). In fact, Volkova (1946) pointed out that the rate equation is in general between the first and second orders, and uses the first and second order for the flotation of simple minerals or in very dilute pulps, and low-grade minerals or more concentrated pulps, respectively. Volkova (1946) derived the differential equation which in the present terminology is given as:

$$\frac{dR_q}{dt} = K_{\mathrm{q}} \frac{\left(R_{q,\infty} - R_q\right)^2}{R_\infty - R_q} \frac{R_\infty}{R_{q,\infty}} \tag{30}$$

where R_∞ is the total mineral present of all species at infinite time and q represents the q' th mineral.

From an algebraic point of view, Eq. 30 is a first-order equation. When only one species is involved or the pulp is very dilute (R_∞=$R_{\mathrm{q},\infty}$), Eq. 30 can be integrated as:

$$R_q = R_\infty \left(1 - e^{-K_q t}\right). \tag{31}$$

It is observed that Eq. 30 is reduced to the classical first-order model (Eq. 8). Furthermore, if Rq <<R∞, the term R∞/(R∞ – Rq) is equal to 1 and Eq. 30 is then corrected to give:

$$\frac{dR_q}{dt} = \frac{K_q}{R_{q,\infty}}\left(R_{q,\infty} - R_q\right)^2 . \tag{32}$$

The solution of Eq. 32 is as follows:

$$R = \frac{R_{q,\infty} K_q t}{1 + K_q t} \ . \tag{33}$$

The relationship between Eq. 33 and second-order model (Eq. 28) is simply given as:

$$K_q = K_8 R_{q,\infty} \ . \tag{34}$$

After that, Horst and Morris (1956) described a 1.5-order equation:

$$\frac{dC}{dt} = -KC^{1.5} \tag{35}$$

and by integration:

$$R = R_\infty \left[1 - \frac{1}{\left(1 + 0.5 R_\infty^{0.5} K_{1.5} t\right)^2}\right] \tag{36}$$

where $K_{1.5}$ is the rate constant of the 1.5-order equation.

If the order of flotation kinetics is considered as a variable, the solution to Eq. 6 yields ($n \neq 1$):

$$R = R_\infty \left\{1 - \left[1 + \left(n-1\right) R_\infty^{n-1} K t\right]^{\frac{1}{1-n}}\right\} . \tag{37}$$

The integral-order and non-integral-order (except the first-order) flotation models can be derived from Eq. 37 by substituting the appropriate value for the parameter *n*.

Hernainz and Calero (1996, 2001) in testing the flotation process kinetics of the celestite and calcite concluded that the order of flotation kinetics is not an integer value. Bu et al (2016) observed that the non-integral-order equation gave a better fit to the test data of fine coal in average particle size 188 and 100 μm than that of first, second and third order models. The faster the flotation rate of particles is, the greater the values of *n* are. It suggests the order of flotation kinetics is non-integral for a

narrow range of particle size. In addition, the order of flotation kinetics can be lower than 1 in the initial moments of the process (Brozek and Mlynarczykowska, 2007; Vinnett et al., 2015).

To sum up, the order of batch flotation kinetics is $1 \leq n < 2$. There is no doubt that the most widely accepted approach among the researchers is still the first-order kinetics, while the non-integral-order model is also suitable to characterize the flotation process of narrow size coal, celestite, and calcite. By contrast, the second-order and higher-order models are unfit to describe flotation time-recovery profiles.

Ultimate recovery

Some apparently floatable particles may still remain unfloated under the actual experimental conditions even the flotation time is prolonged. Experimentally, there also exists a maximum recovery (R_{max}) determined by a batch flotation process in which the flotation rate test is executed until negligible mineral floats in the last interval. A rate test is given where a number of concentrates is collected over various time periods in order to generate recovery-time, grade-time and mass-time curves. The data is used to estimate flotation kinetics. Thus, the value of R_∞ should range between R_{max} and 100%.

There are several methods which can be used for determination of the parameters in the kinetic model. These often involve some types of either graphical or computational procedures. The graphical representation of classical first-order model (Eq. 8) can be written as:

$$\ln\left(R_\infty - R\right) = \ln R_\infty - Kt \tag{38}$$

where the curve coordinates should also be a linear curve from which model parameters can be graphically determined.

The tangent of the slope angle is the kinetic constant, K_B, and the value of R_∞ is obtained by its ordinate at the origin. In more complex models, the distribution of floatability is multiply and the number of parameters is more than two. Accordingly, the graphical method of determining the model parameters is not accurate and can be used only to give some ideas of the process kinetics. To avoid this problem, the least squares method is widely used by most investigators for the solution of kinetic models (Somasundaran and Lin, 1973; Bulatovic, 2007).

The method of least squares is a standard approach in the regression analysis to approximate solution of over-determined systems, i.e., sets of equations in which there are more equations than unknowns. The best fit in the least-squares sense minimizes the sum of squared residuals (SSR), a residual being the difference between an observed value and the fitted value provided by a model (Nassif et al., 2015). The results of the least squares method are based on the SSR minimization without consideration in the rationality of calculated values, which leads to those improper

results, for instance, $R_{max} < R_\infty$ and $R_\infty \geq 100\%$. To avoid the problem, an empirical method for the solution of R_∞ has been developed. The estimate of R_∞ is based on the extrapolation from the tendency of the observed experimental data. The mathematical form of this model is (Ding, 1991; Luo et al., 2015):

$$R_\infty = R_m + \alpha \Delta_m \left(t_\infty - t_m \right) \tag{39}$$

$$\Delta_m = \frac{R_m - R_{m-1}}{t_m - t_{m-1}} \tag{40}$$

where t_∞ is the infinite flotation time, m is the number of the collection intervals of concentrates, α is the recovery coefficient and Δ_m represents the increment of the recovery in the m'th flotation time interval.

By the transform of formula, Eq. 39 can be written as:

$$\alpha = \frac{R_\infty - R_m}{\Delta_m \left(t_\infty - t_m \right)} . \tag{41}$$

As the process continues, the flotation rate decreases and the increase of recovery in the interval from t_m to t_∞ is smaller than Δ_m. Hence, it can be noted that the value of α is smaller than 1. If R_{m+1} and t_{m+1} are substituted for R_∞ and t_∞, respectively, α can be transferred as:

$$\alpha_m = \frac{\Delta_{m+1}}{\Delta_m} . \tag{42}$$

For a flotation rate test with five intervals, we let $\alpha = \alpha_5$. Then, the t_∞ can be written as:

$$t_\infty = t_m + \left(t_m - t_{m-1} \right). \tag{43}$$

In fact, t_∞ is considered as a definite time signifying the end of the flotation process in the developed method. Therefore, calculated t_∞ is approached by doubling the last interval. Luo et al. (2015) successfully applied this method to the fit of easy-to-float and difficult-to-float coal flotation kinetics. The empirical calculated R_∞ is shown in Table 3.

Table 3. Empirical calculated values of R_∞

Particle size (μm)	α	t_∞(min)	R_∞ (%)
37	0.39	8	95.13
375	0.25	8	93.67

As seen in Table 3, the empirical results range between R_∞ and 100%. This method solves the improper phenomenon of kinetic models on the basis of the extrapolation from the tendency of experimental data, which is helpful for the improvement of the availability of kinetic models.

Conclusions

Froth flotation is a highly versatile method for physical separation of particles based on differences in the ability of air bubbles to selectively adhere to the specific mineral surfaces in the pulp. The process involves the gas, liquid and solid phases and the interactions between physical and chemical factors. Flotation models can be generally divided into three categories: empirical, probability and kinetic models. Empirical models are related to a particulate plant and ore, and it is difficult to present a coherent body of common finding. Probability models are complex because of the consideration for the probability of different sub-processes within the flotation system. Kinetic models are reduced from probability models in certain constraints with three parameters such as $f(K)$ (distribution of flotation rate constant), n (order of flotation process) and R_∞ (ultimate recovery).

Despite various distribution functions of K are developed to describe the variety of floatabiliies of flotation feed, none of them is widely admitted. More attention has been paid to the first-order flotation kinetics, while the non-integral-order process cannot be negligible. An empirical model was developed to avoid the inappropriate phenomenon in the solution of ultimate recovery, which improved the availability and validity of kinetic models. Finally, more effort should be made to the overfitting phenomenon resulting from the increase in the number of parameters in the discrimination of kinetic models.

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