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A comparison of the predictability of batch flotation kinetic models

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ABSTRACT

Batch flotation test data of a mixture of pyrite and calcite were used to compare regression parameters of four kinetic model structures. The work included the use of unoxidized or a mixture of partially oxidized pyrite (by microwave irradiation). The objective of floating oxidized pyrite was to have mineral particles with different floatability, closer to a real situation. The models considered include: single rate constant, distributed rate constants (*i.e.* rectangular and gamma distributions), and a recently introduced approach based on fractional calculus. Such models were selected due to their good tradeoff between simplicity and accuracy. The regressions were performed (1) taking all the data points and comparing the mean square error (*MSE*) and adjusted correlation factor $\left(R^2_{Adj}\right)$ as indicators of the goodness of fit; and (2) taking the first data points while neglecting the last ones (from 1 to 3) and observing the variability of the model parameters and the prediction of maximum recovery (R_∞). For the latter regression scheme, besides *MSE* and R^2_{Adj}, a predictive factor, *E*, was defined by subtracting the final measured recovery from the calculation obtained by the model. This allowed to measure the ability of each model to extrapolate the omitted points on the recovery vs. time curve.

Results from this study showed that the single constant model had a satisfactory performance with the advantage of having the least parameters compared to the other structures. The gamma model was effective and robust. The rectangular model gave an acceptable goodness of fit but overestimated the maximum and final recovery. Finally, the fractional calculus approach gave the best goodness of fit, overall, but failed in predicting the maximum recovery, which occurred when the derivative order was greater than 1.

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1. Introduction

Flotation is an important mineral concentration process, which involves the attachment of particles suspended in an aqueous medium to bubbles. The bubble-particle aggregates rise to the froth phase, from which they are recovered as concentrate. Whether or not the particle-bubble aggregate forms and reports to concentrate depends on numerous parameters. Such parameters affect the response (*e.g.* the kinetics) associated with the process (Xu, 2000). This helps to define the flotation machine sizing for a given capacity, flowsheet configuration and target recovery/grade.

Flotation parameters can be classified into machine, chemical or physical ones (Nguyen, 2007). Examples of machine parameters include the bubble generation system, turbulence and gas flow rate. Physical parameters include particle shape and size, bubble size, and hydrodynamics of the system. Chemical parameters refer to the interfacial tensions between the three phases (*i.e.* air-water, air-solid and solid-liquid), interactions between the species in solution (*e.g.* bulk precipitation, species hydrolysis, *etc.*), and adsorptions at solid-liquid interface (*i.e.* physical or chemical adsorption of species). Some factors are not independent, but interact with one another. For example, bubble size depends on frother addition and the bubble generation system.

Unlike factors such as gas flow rate or reagent addition, some cannot be completely controlled (Lynch, 1981). Some examples include mineral dissolution, changes in the surface properties of minerals (*e.g.* as result of sulphide oxidation), reagents degradation, and changes in the feed mineralogy (Arbiter et al., 1985). Although simple in principle, the combination of factors makes the flotation process very complex.

Design and control of flotation plants relies on the prediction of the species transferred from the pulp to the concentrate, in terms of flotation parameters. As a consequence, extensive research has been conducted on developing models of flotation kinetics. The prediction of flotation metallurgical performance by understanding the

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kinetics has been a goal pursued by numerous researchers. Flotation kinetics can be defined as the study of concentrate as a function of time, the qualitative determination of all rate control factors and the mechanisms by which such factors affect the recovery and grade.

Formal flotation kinetic studies can be traced back more than 50 years, with models having different starting points. For example, Schumann's seminal work (1942) was perhaps the first in expressing flotation kinetics as the probability of three consecutive events occurring: particle-bubble collision; attachment; and disengagement. Since this theoretical approach was introduced, a large number of improvements and a degree of sophistication has been added. For example, the work by Yoon and Luttrell (1989), proposed expressions to calculate such probabilities in terms of flotation parameters. Although significant effort has been made in obtaining flotation micro-scale models/analyses, up until the present day this has not been satisfactorily achieved, largely due to the complexity of the process. Even if this can be achieved, there is a strong chance that such a model would become overly complicated and thus impractical.

Kinetic models that consider the flotation process as a reaction between particles and bubbles are popular, due to their simplicity and capacity to simulate reasonably well batch flotation (Ofori et al., 2014; Polat and Chander, 2000; Klimpel, 1980; Woodburn and Loveday, 1965; García-Zúñiga, 1935). These models are formulated in terms of the rate of flotation and can be quantified in terms of the physical, chemical and hydrodynamic parameters of the flotation system. Batch flotation reported in literature supports this type of models reasonably well. To conduct a more precise validation, the data should be contrasted with the model predictability and its diagnosis capabilities.

2. Theory

For an analogy with chemical reactions, the batch flotation kinetics for the collection zone can be defined as the derivative of concentration of the valuable mineral with respect to time, provided the delivery of bubbles remains constant (*i.e.* size distribution, number of bubbles per unit time) (Eq. (1)).

$$\frac{dC}{dt} = -k \cdot C^n \tag{1}$$

where C (*e.g.* mass/volume) is the concentration of valuable mineral; n, the kinetic order; and k (*e.g.* [volume/mass]$^{n-1}$ t), the flotation rate constant.

A special case with first-order dependence, $n = 1$, transforms Eq. (1) to the following expression for the mineral recovery as a function of time (García-Zúñiga, 1935):

$$R(t) = R_\infty \cdot [1 - \exp(-k \cdot t)] \tag{2}$$

where R_∞ is the maximum recovery ($t \to \infty$) and k is the first-order rate constant. This equation introduces the possibility of isolating factors that affect k from those that affect R_∞.

To account for flotation classes (*e.g.* liberation degrees, "reagentized" ranges, particle size fractions, *etc.*), the models with distributed rate constants are typically used. If such a k distribution can be a continuous function $F(k)$, the recovery at any time can be obtained by Eq. (3).

$$R(t) = R_\infty \cdot \left[1 - \int_0^\infty \exp(-k \cdot t) \cdot F(k)\, dk\right] \tag{3}$$

A new approach for describing flotation kinetics that makes use of fractional calculus was recently introduced (Vinnett et al., 2015). In this model, the process is described by a derivative order parameter along with a fractional flotation rate (Eq. (4)). It has been stated that fractional calculus is appropriate for modelling systems in which memory and non-local effects are important, which might be relevant in slow kinetics flotation processes (Vinnett et al., 2015).

$$R(t) = R_\infty \cdot [1 - E_\alpha(-k_\alpha \cdot t^\alpha)] \tag{4}$$

In Eq. (4), α is the derivative order and E_α is the Mittag-Leffler function, which is defined as:

$$E_\alpha(z) = \sum_{i=0}^{\infty} \frac{z^i}{\Gamma(\alpha \cdot i + 1)} \tag{5}$$

In this study, a comparison of several kinetic models was performed. This was performed by two schemes: first, by using all data points of recovery vs. time curves; and second, neglecting the last data points (from 1 to 3). This attempted to show the capability of the models to predict the ultimate recovery. The chosen models include three of the most extensively used flotation rate distributions to describe first-order batch processes: unique rate constant (García-Zúñiga, 1935), the rectangular distribution (Klimpel, 1980); and the gamma distribution (Yianatos et al., 2010; Woodburn and Loveday, 1965). Other proposed schemes to represent $F(k)$ such as triangular, normal, sinusoidal (Polat and Chander, 2000), two rate constants (Kelsall, 1961), double normal (Ferreira and Loveday, 2000), Weibull (Dobby and Savassi, 2005) were not considered due to a higher number of parameters or complex interpretation of $F(k)$, with negligible advantages regarding the gamma model (Vinnett et al., 2015). Besides the three mentioned models, the fractional calculus approach was included. Table 1 summarizes the kinetic models compared in the present study.

These models were applied to kinetic data of flotation of pyrite from calcite using dodecylamine amine as collector and F150 as a frother. This system was chosen due to the relatively slow kinetic response (Bunkholt and Kleiv, 2015), which ensures more data points can be taken along the flotation and better accuracy in the recovery calculations.

The experiments included the use of "unoxidized" (virgin) or a mixture of oxidized (to a different degree) pyrite. In the first case, the system behaves in a more ideal way while the second approaches to a more realistic flotation, with minerals having different floatability classes.

3. Materials and methods

3.1. Sample preparation

Pyrite and calcite, purchased from VWR International (USA), were crushed and screened at 2630 μm. Pyrite (fraction +850/−2630 μm) was upgraded by hand sorting, with the high grade material being kept for the flotation tests. Calcite did not require upgrading due to the high quality of the sample. Minerals were ground separately and wet screened at 38 μm. Pyrite was rinsed with acetone to remove any residual water and air dried to avoid oxidation. The +38 μm fraction was dry screened using a

Table 1
Summary of compared kinetic models (adapted from Vinnett et al. (2015)).

Model	$F(k)$[a]	$R(t)$
Single rate constant	$\delta_{kGZ}(k)$	$R_\infty \cdot [1 - \exp(-k \cdot t)]$
Rectangular (Klimpel)	$\frac{1}{k_{MAX}} \cdot [\mu_0(k) - \mu_{K_{MAX}}(k)]$	$R_\infty \cdot \left[1 - \frac{(1-\exp(-k_{MAX} \cdot t))}{k_{MAX} \cdot t}\right]$
Gamma	$\frac{b^{a+1}}{\Gamma(a+1)} \cdot k^a \cdot \exp(-b \cdot k)$	$R_\infty \cdot \left[1 - \left(\frac{b}{b+t}\right)^{a+1}\right]$
Fractional calculus	$L^{-1}[E_\alpha(-k_\alpha \cdot s^\alpha)]_{t=k}$	$R_\infty \cdot [1 - E_\alpha(-k_\alpha \cdot t^\alpha)]$

[a] $\delta_x()$, $\mu_x()$ and $\Gamma()$ denote the Dirac, Heaviside and gamma function, respectively and L denotes Laplace Transform.

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