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Technical note

Batch flotation kinetics: Fractional calculus approach

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ABSTRACT

As in many separation processes, design of flotation systems is governed by kinetics, which is a function of chemical, physical and machine parameters. Several kinetic models have been presented in literature, those based on a homogeneous chemical reactions being the most widespread. In this technical note an alternative approach based on the use of fractional calculus to describe batch kinetic characterization is presented.

Batch flotation test data for porphyry ores of copper and molybdenum were used to compare the fractional calculus approach with first-order models. Comparisons include single rate constants as well as distributed rate constants (i.e., rectangular and Gamma distributions). Results showed a derivative order lower than 1, ranging from 0.60 to 0.95, which is related to a retarded flotation response at the beginning of the process. The fractional calculus approach was in all cases superior to the rectangular distributed kinetic constant, but comparable to the Gamma distribution approach. The proposed approach gives acceptable results for slow flotation processes, which is in good agreement with Gamma distributions with high fraction of slow rate constants.

1. Introduction

Flotation is a major technique for mineral concentration since it allows valuable minerals to be economically processed from complex, low grade ores. Flotation exploits differences in surface properties: interfacial tension and surface charge. The former yields differences in wettability (or hydrophobicity), whereas the latter may determine particle-chemical species and particle–particle interactions. The principle consists of particles suspended in an aqueous solution which are introduced to tanks (e.g., flotation cells) where gas is introduced to form bubbles. Hydrophobic particles will tend to attach to bubbles, forming particle–bubble aggregates. These aggregates will rise in the flotation machine forming the froth zone and the floatable minerals are removed as a concentrate stream. At present, flotation is being successfully applied in other fields including the chemical industry and for environmental engineering (Rao and Leja, 2004).

Flotation variables can be divided into machine (e.g., bubble generation system, gas flow rate and turbulence), chemical (e.g., mineral dissolution, type and dosage of reagents, and surface chemistry of minerals) and physical factors (e.g., particle size, particle–bubble interactions and froth drainage). These variables determine the dynamic response or the kinetics associated with the process, which define the size of the flotation machines (Xu, 2000).

Significant efforts have been made to develop a kinetic model based on fundamental principles and empirical correlations. For instance, Duan et al. (2003) proposed a methodology to estimate the flotation rate constant as a function of particle size, contact angle, bubble size and velocity, and level of turbulence inside a flotation cell; Gorain et al. (1997) reported a linear correlation between the flotation rate and the bubble surface area flux when considering four different impellers in a 2.8 m^3 flotation cell; Ahmed and Jameson (1985) showed that the flotation rate of fine particles is significantly affected by the bubble size, impeller speed and particle density; Yoon and Luttrell (1989) defined the kinetic response as the probability of three consecutive events: (1) collision of a particle and a bubble, (2) attachment (i.e., the thin film that separates the particle and the bubble must be ruptured), and (3) non-disruption of the particle–bubble aggregate. However, the flotation process includes a series of heterogeneous sub-processes, such as mixing, fluid dynamics, bubble formation, particle–particle and bubble–particle interactions. Thus, efforts to conduct a first principle model for flotation kinetics are limited or only applicable to specific operational conditions.

In this technical note, a new approach to describe the flotation rate based on fractional calculus is presented. The proposed model

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was applied to several batch flotation tests of copper porphyry ores and compared with classical kinetic first-order models (with single and distributed rate constants, namely, rectangular and Gamma distribution). The fractional calculus is proposed as an alternative methodology to represent the flotation rates, where the overall process is characterized by a derivative order along with a rate constant.

2. Flotation rate modeling for batch tests

Kinetic models consider the collection process in flotation machines as a reaction between bubbles in excess and particles. Those models have been widely used based on the analogy with homogeneous chemical kinetics, in which the concentration in a batch reactor is modeled by a first-order differential equation:

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

with C the concentration of valuable mineral; n, the kinetic order; and k, 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:

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

where R_∞ is the maximum recovery ($t \to \infty$) and k is the first-order rate constant.

The classical first-order model of Eq. (2) does not account for the wide range of conditions present in any flotation system (e.g., particle and bubble size distribution, differences in particle shapes and surface properties, among others). Thus, models with distributed rate constants are typically used. If the kinetic constant distribution can be expressed as a continuous function, $F(k)$, the concentration at any time is obtained by Eq. (3) (Polat and Chander, 2000),

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

Table 1 summarizes the flotation rate distributions most extensively employed to describe first-order batch processes, which include: unique rate constant (Eq. (2)), rectangular model (Klimpel, 1980) and the Gamma distribution (Yianatos et al., 2010; Woodburn and Loveday, 1965). These model structures have shown acceptable performance while keeping a low number of parameters.

Several additional model structures have been proposed 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 Savaassi, 2005), among others. These model structures require numerical integration of Eq. (3), a higher number of parameters or complex interpretation of $F(k)$, with negligible advantages regarding the Gamma model.

Table 1
Summary of flotation rate distribution and mineral recovery for batch tests.

Model	$F(k)^*$	$R(t)$
Single rate constant	$\delta_k(k)$	$R_\infty \cdot [1 - \exp(-k \cdot t)]$
Rectangular (Klimpel)	$\frac{1}{k_{MAX}} \cdot \left[\mu_0(k) - \mu_{K_{MAX}}(k)\right]$	$R_\infty \cdot \left[1 - \frac{(1-\exp(-k_{MAX} \cdot t))}{k_{MAX} \cdot t}\right]$
Gamma	$\frac{b^a}{\Gamma(a)} \cdot k^{a-1} \cdot \exp(-b \cdot k)$	$R_\infty \cdot \left[1 - \left(\frac{b}{b+t}\right)^a\right]$

* δ_x, μ_x and Γ denote the Dirac, Heaviside and Gamma function, respectively.

2.1. Fractional calculus approach

Fractional calculus was introduced as an important tool to deal with the analysis and modeling of processes in which memory and/or nonlocal effects are relevant (Vásquez, 2004; Hilfer, 2000). As stated before, flotation systems are complex, with several phenomena occurring simultaneously where memory effects might be relevant. Since fractional calculus takes into account such effects, it seems to be appropriate for modeling flotation kinetics.

Fractional calculus is an extension of traditional calculus considering a non-integer derivative order. The concentration evolution is represented via non-integer derivatives, which are defined as (Caputo, 1967):

$$\frac{d^\alpha f}{dx^\alpha} = \frac{1}{\Gamma(n-\alpha)} \int_0^x \frac{f^{(n)}(\xi)}{(x-\xi)^{1-(n-\alpha)}} d\xi \tag{4}$$

which corresponds to the Caputo definition of fractional derivatives, where n is the smallest integer greater than α.

Ideally an expression like Eq. (1) should be sufficient to describe most batch processes. However, this approach has been shown to be inadequate in several cases, leading to the development of models that consider additional parameters, justified from having different time scales for the kinetics and/or distributed rate constants. However, it is believed that anomalous kinetics can be caused by long waiting or trapping times for the particles, the role of turbulent dispersion and fast paths for particles. Anomalous kinetics can be described by fractional calculus as:

$$\frac{d^\alpha C}{dt^\alpha} = -k_\alpha \cdot C \tag{5}$$

where α corresponds to the derivative order and k_α to the fractional rate constant. Integer derivative order ($\alpha = 1, 2, 3$) are commonplace in engineering. However, non-integer derivative order (example, $\alpha = 0.5$) can be considered to represent anomalous processes. The solution of Eq. (5) is given by (Kazem, 2013):

$$C(t) = C_0 \cdot E_\alpha(-k_\alpha \cdot t^\alpha) \tag{6}$$

where E_α is the Mittag–Leffler function, which is defined as,

$$E_\alpha(z) = \sum_{i=0}^{\infty} \frac{z^i}{\Gamma(\alpha \cdot i + 1)} \tag{7}$$

Note that for $\alpha = 1$, the Mittag Leffler function becomes the exponential function, $E_1(z) = \exp(z)$, restoring the traditional first order kinetics.

From Eq. (6), it is possible to propose an alternative kinetic expression for the mineral recovery as follows:

$$R(t) = R_\infty \cdot [1 - E_\alpha(-k_\alpha \cdot t^\alpha)] \tag{8}$$

Eq. (8) requires three parameters to characterize a flotation process: maximum recovery (i.e., recovery at long time), R_∞, fractional kinetic order α, and a fractional rate constant k_α.

3. Materials and methods

Samples of copper porphyry ore sourced from different zones of a Chilean mineral deposit were used for this study. Each sample was blended, riffled and split to get an adequate amount for flotation tests. Thiocarbamate MX 7017 C (20 g/t) and diesel (20 g/t) were added before grinding at ca. 65% solids. Ore was milled to $P_{80} = 210$ μm.

Batch flotation tests were carried out in a 3 L Denver cell with forced air. Pulp was diluted to ca. 30% solids and sodium isopropyl xanthate Flomin C-3330 (10 g/t) and methyl isobutyl carbinol Aerofroth 70 (ca. 10 mg/L of solution) were added and mixed for a minute; pH was adjusted to 9 and pulp was then poured into the cell.