TECHNICAL NOTE

Method for Evaluating Flotation Kinetics Parameters

by P. Somasundaran and I. J. Lin

There are several methods described in the literature' for the determination of the order and the rate constant for the flotation of minerals. These often involve some type of computational or graphical procedures. A relatively simpler method developed on the basis of a technique used by Chang^{8,3} in chemical kinetics is described in this paper. Chang's technique, like most others in chemical kinetics,⁵⁴ is based on the law of mass action which states that the rate of a chemical reaction is proportional to the active masses of the reacting substances at any given time. Application of this law to the flotation of minerals would involve the adaptation of the terms "flotation" for "chemical reaction" and "floatable amount of the minerals" for "the active masses of the chemical reactants." There are indeed a large number of physical processes controlling the actual flotation rate. The most inefficient one of these could be considered equivalent to the slowest reaction in a series of chemical reactions. If variables such as aeration rate and agitation are kept at constant levels, the rate of flotation under free flotation conditions (i.e., conditions under which the suspension is dilute) will be given by the following equation:

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

where C is the concentration of the floatable minerals in the pulp at any given time t, K is the rate constant, and n is the order of the reaction. If we represent the floated fraction of the floatable mineral at time t as m ($0 \le m \le 1$) and C at t = 0 as C_{*}, integration of Eq. 1 yields

$$\ln \frac{1}{1 m} = Kt_m \quad \text{for } n = 1 \tag{2}$$

and

P. SOMASUNDARAN, Member SME, is Associate Professor, and I. J. LIN, on leave from Technion, Israel, is Visiting Professor, Henry Krumb School of Mines, Columbia University, New York, N.Y. TN 718207. Manuscript, Mar. 8, 1971.

$$\frac{1}{n-1} \left[(1-m)^{1-n} - 1 \right] = Kt_m \cdot C_*^{n-1} \quad \text{for} \quad n \neq 1.$$
 (3)

These equations can now be used in the manner described below to evaluate the order and the rate constant for flotation.

Evaluation of the Order: For time $t_{m'}$, when the floated fraction of the floatable minerals is m', Eqs. 2 and 3 become, respectively,

$$\ln \frac{1}{\mathbf{k} - \mathbf{m}'} = K t_{\mathbf{m}'} \quad \text{for} \quad n = 1 \tag{4}$$

and

$$\frac{1}{n-1} \left[(1-m')^{1-n} - 1 \right] = Kt_{m'} C_{\bullet}^{n-1} \quad \text{for} \quad n \neq 1.$$
 (5)

Division of Eq. 2 by Eq. 4 and Eq. 3 by Eq. 5 yields the following equations

$$\frac{\ln \frac{1}{1-m}}{\ln \frac{1}{1-m'}} \frac{t_{m}}{t_{m'}} \quad \text{for } n = 1$$
 (6)

and

$$\frac{(1-m)^{1-n}-1}{(1-m')^{1-n}-1} = \frac{t_m}{t_{m'}} \quad \text{for } n \neq 1.$$
 (7)

Values of $t_m/t_{m'}$ evaluated after Chang for various values of *n* are plotted in Fig. 1.

In the case of the flotation of minerals, m, the fraction of the floatable mineral at any given time, is equivalent to R/R_{\bullet} where R is the weight fraction recovery of the floated minerals at any given time t_{\pm} and R_{\bullet} is the maximum possible recovery at infinite time under the conditions used. To determine the order of a particular flotation operation, we plot the values for flotation recovery as a function of time and from the smoothed curve obtained, time t_{\pm} for various values of m are read on the assumption that the recovery at the end of flotation is equal to R_{\bullet} . Various t_{\pm}/t_{\pm} are then calculated and the order of flotation under consideration is read from Fig. 1.

Evaluation of the Rate Constant: $Kt_mC_o^{n-1}$ (or $Kt_{R/R_o}R_o^{n-1}$) is only a function of m at constant n, since according to Eqs. 2 and 3

for n = 1

(8)

 $Kt_{B/B_0} = \ln \frac{1}{1 - P(P)}$



Fig. 1—A plot of the order of reaction vs. t_m/t_m' for various combinations of m and m'.



Fig. 2—A plot of the order or reaction vs. $Kt_mC_{\bullet}^{\kappa-1}$ for various values of m.

$$Kt_{R/R_{\infty}}R_{\infty}^{n-1} = \frac{1}{n-1} \left[(1 - R/R_{\infty} - 1) \text{ for } n \neq 1 \right]$$

Values obtained for $Kt_{E/R_n}R_n^{n-1}$ with the help of Chang's method for various values of *n* are given in Fig. 2. Fig. 2 can now be used in the following manner for the easy determination of the rate constant of any particular flotation operation after its order has been determined. Values of $Kt_{E/R_n}R_n^{n-1}$ are first read from Fig. 2 for various R/R_n values for the particular order that had already been determined for the flotation under consideration. These values are now divided by the experimental values of $t_{E/R_n}R_n^{n-1}$ to obtain the rate constant K. Some examples are given below to illustrate the use of this technique.

Recently Harris and Chakravarti' have discussed in detail methods for interpreting semi-batch flotation data in terms of a first-order kinetics model and a distribution of species. They have succeeded in attributing the discrepancies between previous theories and experimental data to the existence of a rate constant distribution. While this treatment using a species distribution has the danger of making an actual non-first order flotation appear as a first order process, it has the merit of taking into account the highly possible presence of the distribution. Our present technique is suitable for only cases with nondistributing species and as a result the order obtained might be considered as an apparent order. We do not however think that an order other than one is completely unlikely.

Another limitation of the present model to be noted is that it might not possibly be capable of taking into account all of the various physical processes that occur in flotation. Several such processes however could realistically be considered to play their role by affecting the forward or backward rate of the major process on which the model is based.

Examples: Case 1—Data obtained by Somasundaran⁵ for the flotation of quartz with various concentrations of dodecylammonium acetate in a modified hallimond cell is plotted in Fig. 3 as a function of flotation time in seconds. Values for various t_m/t_m are read from this figure for various collector concentrations and are presented in Table 1. The order of the flotation is now read directly from Fig. 1 and is presented as an average value in Table 1. Values of $Kt_{B/B_n}R_n^{n-1}$ corresponding to the order obtained, are now read from Fig. 2 for various R/R_n values. These values when divided by experimental $t_{B/B_n}R_n^{n-1}$ gave the values for K given in Table 1.

Table 1. Values Obtained for $t_m/t_{m'}$ and n With The Use of Fig. 1 and for K With The Use of Fig. 2 for Data Shown in Figs. 3-6*

Case	$i_{1/2}/t_{2/3}$	$t_{1/2}/t_{3/4}$	$t_{1/4}/t_{1/2}$	$t_{1/3}/t_{1/2}$	$t_{1/3}/t_{2/3}$	$t_{1/8}/t_{1/4}$	t _o , Sec.	R	\overline{n}	K, Sec-1	Flotation Rate Equation
1	0.500	0.360	0.337	0.500	0.250	0.440	2	1.00	2	0.12	$\frac{R}{1-R} = 0.12 t$
		0.384	0.333	0.500	0.258	0.430	4	0.80	2	0.10	$\frac{R}{0.8 - R} = 0.10 t$
2	0. 62 5	0.500	0.428	0.580	0.363	0.453		1.00	1	0.020	$\ln\left(\frac{1}{1-R}\right) = 0.020 \ t$
	0.507	0.330	0.336	0.500	0.252	0.435	0	0.90	2	0.023	$\frac{R}{0.9 - R} = 0.021 t$
• b.	0.500	0.336	0.333	0.507	0.253	0.434	0	0.88	2	0.020	$\frac{R}{0.88 - R} = 0.017 t$
4	0.500	0.354	0.340	0.499	0.249	0.431	5	0.92	2	0.014	$\frac{R}{0.92 - R} = 0.013 \ (t - t_o)$
- b.	0.610	0.444	0.407	0.582	0.354	0.480	ŧ	0.96	1	0.008	$\ln\left(\frac{0.96}{0.96-R}\right) = 0.008 \ (t - t_0)$

Fig. 3 (Case 1a: 10^{-4} mole per l; Case 1b: 5 × 10^{-5} mole per l dodecylammonium acetate); Fig. 4 (Case 2); Fig. 5 (Case 3a: -0.2) + 0.15 mm; Case 3b: -0.15 + 0.10 mm size fractions); Fig. 6 (Case 4a: apatite; Case 4b: hematite).

Case 2—Data obtained by Agar and coworkers⁶ for the flotation of quartz with dodecylammonium hydrochloride during four different experiments in a chambered flotation cell similar to that used by Tomlinson¹⁰ was treated in the same manner as described previously. Results obtained using the best least-square curve for flotation recovery as a function of time are given in Fig. 4 and Table 1. It might be noted at this stage that the value obtained for rate constant using the relatively



Fig. 4—Flotation of quartz in a chambered cell as a function of time during four tests with dodecylammonium hydrochloride (8x10⁻⁶ mole per I) as collector.

simple technique described here is identical to the value 0.020 obtained by Agar and coworkers using the conventional procedure.

Case 3—Data reported by Panu¹¹ for the flotation of -0.15/+0.10 mm and -0.20/+0.15 mm pyrite ore shown in Fig. 5 as a function of time is also treated in a similar manner and the results obtained are given in Table 1. Values for the order is found to be two in this case for both fractions, but the -0.15/+0.10 mm fraction is found to have a higher rate constant than the -0.20/+0.15 mm size fraction in line with the trend of Panu's calculated rate constants for various size fractions.

Case 4—Data obtained by Tomlinson and Fleming¹⁰ for the flotation of apatite and hematite in the chambered cell using 1.55×10^{-5} mole per 1 potassium oleate as collector at pH 8.0 ± 0.01 and temperature $25 \pm 1^{\circ}$ C is shown in Fig. 6, and the results obtained by applying the present method to the data are given in Table 1. Tomlinson and Fleming report the overall rate for apatite flotation to correspond to a second order equation and that for hematite flotation close to a first order. It can be seen that the results obtained for the order using the present method are in agreement with the foregoing values.

Summary and Conclusions

The method presented here using the general curves presented in Figs. 1 and 2 offers a relatively simple and fast way for the evaluation of the order and the rate



Fig. 5—Flotation of pyrite ore of -0.20 + 0.15 mm and -0.15 + 0.10 mm size fraction as a function of time (after Panu⁽¹¹⁾).



constant of a flotation operation. Results obtained using this technique are identical within experimental errors, to those obtained using conventional procedures. The technique developed here, using the analogy between chemical reactions and flotation processes, is of general application with no restrictions as to the type of ores processed or the type of flotation operations used.

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