Application of kinetic, incentive, limits and arrheniusan curves for flotation characterization

J Drzymala
Wroclaw University of Science and Technology, Faculty of Geoengineering, Mining and Geology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

Abstract. Separation curves such as kinetic (recovery R versus process time t), limits (kinetic constant k versus maximum recovery $R_{\text{max}}$), incentive (R vs incentive parameter i), and arrheniusan (ln k vs 1/energy - for a regent concentration (i=c) being $kT\ln(c/c_0)$), were characterized and discussed. Their usefulness for flotation was described and relations between the curves were presented. All the separation curves provide valuable parameters. The arrheniusan curves are exceptionally useful because they deliver activation energy, expressed in the terms of energy, a parameter indicating how well a separation system responds to a change of an incentive parameter. The incentive parameter can be temperature, reagent concentration, pH, particles size and many others.

1. Introduction
Flotation is one of many separation processes capable to separate useful components of ores and raw materials from unwanted elements [1]. The process of flotation is very unique because, in addition to numerous parameters, both thermodynamics and kinetics play there an important role [2, 3, 4]. Therefore, a meaningful characterization of flotation requires taking onto account many parameters simultaneously. In such a case, graphical methods of flotation characterization become important because two or more parameters can be evaluated [5]. The goal of this work is to present a system of graphical representation of flotation results based on the so-called kinetic [1], limits [6, 7], arrheniusan [8] and incentive curves, that can be used for characterization of separation processes.

2. Kinetic curves
Flotation can be performed as a batch as well as a continuous process. In both cases the kinetics (process rate $dR/dt$ or kinetic constant k) and thermodynamics (ultimate recovery $R_{\text{max}}$) determine the outcome of the process (figure 1). For a given flotation process both parameters can be determine if the relationship between flotation recovery (one of two or many components) ($R=\varepsilon$) or yield (all components) ($R=\gamma$) and flotation time is available. This relation, known as the flotation kinetic curve, provides useful information about the process. The kinetic curves can be found in numerous papers.
Figure 1. The kinetic separation curve. Here separation process follows the first order kinetics with kinetic constant $k = k_1$. Other properties of the curve are given.

By an appropriate manipulation of flotation data available as the kinetic curve, both kinetics of the process in the form of either kinetic constant $k$ (or constants) or specific rate [6] and the thermodynamics of the process in the form of ultimate (maximum) yield $\gamma_{\text{max}}$ (for all components) or recovery $\varepsilon_{\text{max}}$ (for a selected component), or shortly $R$ for both yield and recovery, is obtained. The calculation of $k$ and $R_{\text{max}}$ is very easy when the process follows the first order kinetic law as is shown in figure 1.

3. Incentive curves

Frequently, flotation process is run by using different levels of the investigated parameters such as temperature, reagent concentration, pulp density, particle size distribution etc. In such a case the data from the kinetic curve (figure 1) are usually used for plotting another relation, that can be called the incentive curve. The incentive curve relates recovery $R$ (either recovery of all components called yield $\gamma$ or recovery of a selected component $\varepsilon$ for a given flotation time) and the numerical value of the incentive parameter used for modification of the separation processes. The incentive curve plot is presented in figure 2 using flotation data as an example.
The incentive curves are available in the literature in many papers dealing with separation processes.

4. Limits curves
The kinetic curves provide two essential process parameters, that is $k$ and $R_{\text{max}}$. Graphical relation of these parameters provides another type of curve, that is the limits curve. The available in literature limits curve indicates that in many separation processes there is a simple relation between kinetics ($k$) and thermodynamics ($R_{\text{max}}$) of the processes. Figure 3 presents a limits curve as a relation between $k$ and $R_{\text{max}}$ for flotation of shale.

Figure 2. The incentive separation curve. After Kowalczuk et al., 2014 [8].

Figure 3. The limits separation curve. After Nowak and Drzymala (2017) [9]. Here $k$ is the first order kinetic constant ($k = k_1$).
5. Arrheniusan curves
The arrheniusan curves can be created starting with the kinetic curve by replacing the process time $t$ with a specific parameter characterizing energy $E$ imposed to the separation system by the incentive parameter $i$ and for x axis replacing recovery $R$ with kinetic constant $k_n$, which combines process time $t$ with recovery $R$. In the case of incentive parameters being concentration $c$ of a reagent, the energy parameter is $kT\ln (c/c_o)$, where $k$ is the Boltzmann constant, $T$ absolute temperature, $c_o$ is a standard concentration. The incentive parameter can be temperature, particle size, regent concentration etc., and the energy $E$ imposed to the separation system by the incentive parameter can be found elsewhere [10]. When the experimental data points form a line, the slope of it is the activation energy $E_a$. The activation energy characterizes the impact of the incentive parameter on the process recovery being the most important parameter. Arrheniusan curves are shown in figure 4.

![Arrheniusan Curves](image)

**Figure 4.** The arrheniusan separation curve [10], [11]. Flotation of different types, arbitrarily denoted as P,S,L copper-bearing carbonaceous shales samples. Courtesy of the Physicochemical Problems of Mineral Processing journal.

6. Conclusion
Since flotation process is very complex, appropriate procedures for its delineation and characterization are necessary. For this purpose, it is useful to use different two-parameter relations called separation curves. In the case of flotation, very beneficial are kinetic, limits, incentive and arrheniusan 2D plots. Relations between curves are presented in figure 5.
Figure 5. Relation between kinetic, limits, incentive and arrheniusan separation curves.

The most unprocessed is the kinetic curve (figure 1). By replacement of certain parameters from the plot, for instance time $t$ with incentive parameter $i$, the incentive curve is created (figure 2), while mixing parameters of the kinetic curve ($t$ with $R$) produces the limits curve (figure 3). Both replacement and mixing provides additional curves. One of them is the arrheniusan plot (figure 4). This plot is especially useful because it provides a new parameter called the activation energy. This parameter is able to show the dynamics of the process, that is how strongly the incentive parameter influences the system. On the other hand, the limits curves are useful for showing a relation between kinetics and process thermodynamics.

Acknowledgements

This work was financed by the Polish Statutory Research Grant 0401/0129/17.

References

[1] Wills B A and Napier-Munn T J 2006 Wills’ Mineral Processing Technology (Elsevier: Amsterdam)
[2] Laskowski J S 1986 The relationship between floatability and hydrophobicity Advances in Mineral Processing (SME: Littleton) pp 189-208
[3] Laskowski J S 1989 Thermodynamic and Kinetic Flotation Criteria Mineral Processing and Extractive Metallurgy Review 5 pp 25-41
[4] Fuerstenau D W and Raghavan S 2007 Some aspects of flotation thermodynamics Froth flotation. A century of innovation (SME: Littleton)
[5] Drzymała J 2007 Mineral Processing (WUT: Wroclaw)
[6] Drzymała J, Ratajczak T and Kowalczyk P B 2017 Kinetic separation curves based on process rate considerations Physicochem. Probl. Miner. Process. 53 pp 983–95
[7] Drzymała J and Kowalczyk B P 2018 Classification of flotation frothers Minerals 8/53 pp 1-24
[8] Kowalczyk P B, Buluc B, Sahbaz O and Drzymala J 2014 In search of an efficient frother for preflotation of carbonaceous shale from the Kupferschiefer Stratiform copper ore Physicochem. Probl. Miner. Process. 50(2) 835-40
[9] Nowak J and Drzymala J 2017 Flotacja łupka miedzinośnogow w obecności spieniacza, zbieracza oraz depresora w postaci dekstryny Łupek miedzinośny III (PWr: Wroclaw) pp 118-28
[10] Drzymala J 2018 Arrheniusan activation energy of separation for different parameters regulating the process Physicochem. Probl. Miner. Process. 54(4) special issue dedicated to honor Professor Janusz Laskowski

[11] Kurkiewicz S and Ratajczak T 2017 Flotometryczna hydrofobowość łupków miedzianośnych w obecności NaCl Lupek miedzianośny III (PWr: Wroclaw) pp 118-28