Course Distribution

Particulate solid handling and their properties

- **Particle characterization** (defining a particle/distribution) ✓
  - Particle size and shape ✓
  - Particle size investigation ✓
    - **Size measurement of fine particles** ✓
      - Defining a fine particles
      - Measurement
    - Sieving ✓
  - Industrial screening equipment ✓

- **Size Reduction** ✓
  - Primary/Coarse size reduction ✓
  - Intermediate size reduction ✓
    - Energy requirement and efficiency calculation ✓
  - Fine size reduction ✓
  - Classification ✓

- **Separation**
  - Solid-Liquid separation ✓
    - **Dynamics of particle in liquid medium** ✓
      - Sedimentation ✓
      - Flotation
  - **Solid-Gas separation**
    - **Dynamics of particle in gas medium**
      - Miscellaneous methods
      - Fluidization

- **Storage, Handling and Transport of Solids**
  - Storage of solids
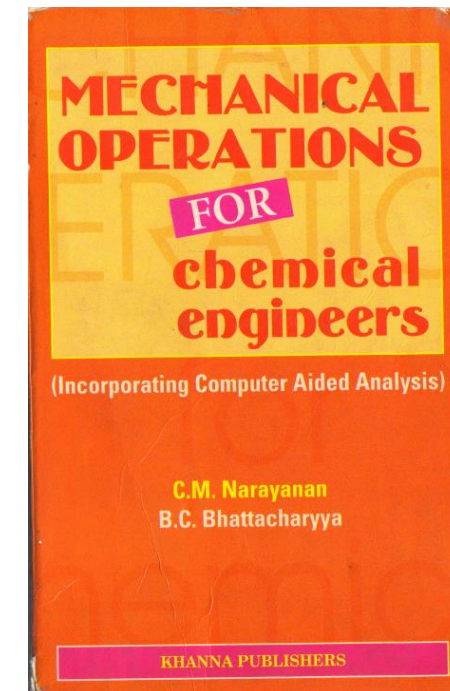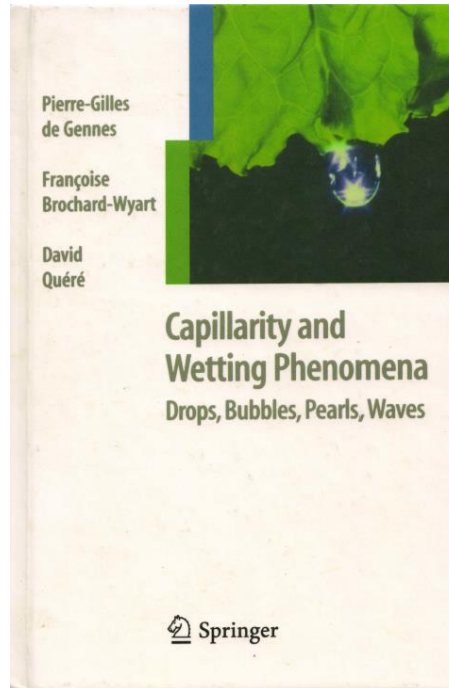 - Transport of solids

FLOTATION

# Resource

- **Books**
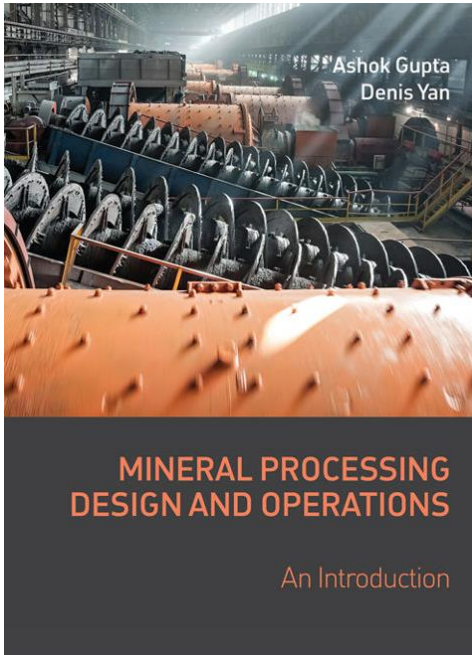
Chapter 18

- **Relevant journal papers mentioned in the individual topics**

➢ Flotation is a process of ***separation and concentration based on differences in the physicochemical properties of interfaces.***

➢ The flotation process has also been used extensively in mineral processing, paper recycling and mining industries since a long period of time.

➢ The essence of the flotation process is the concentration of finely divided minerals on the basis of variation in their ability to keep themselves on a phase interface.

➢ Under these conditions, the particles to be separated float out or are removed in some way, together with the phase to which they attach themselves. Flotation is carried out in aqueous medium (the first phase), the other phase being air or some other gas or much more rarely used, oil.

Flotation can take place either at a liquid–gas, a liquid–liquid, a liquid–solid or a solid–gas interface. Depending upon the type of interface involved, the flotation process can be further subdivided into

1. **Froth Flotation** in which the flotation takes place on a gas–liquid interface.
2. **Film Flotation** in which the flotation takes place on a free water surface.
3. **Oil Flotation** in which the flotation takes place on the interface between oil and water.

Detachment
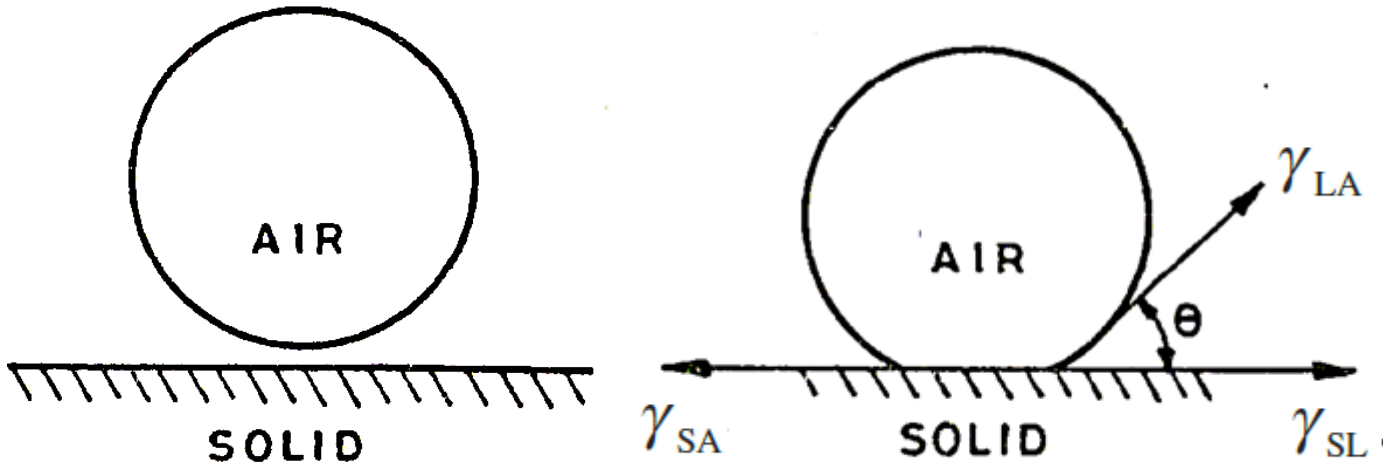
At equilibrium, the balance of the surface forces is given by the Young equation

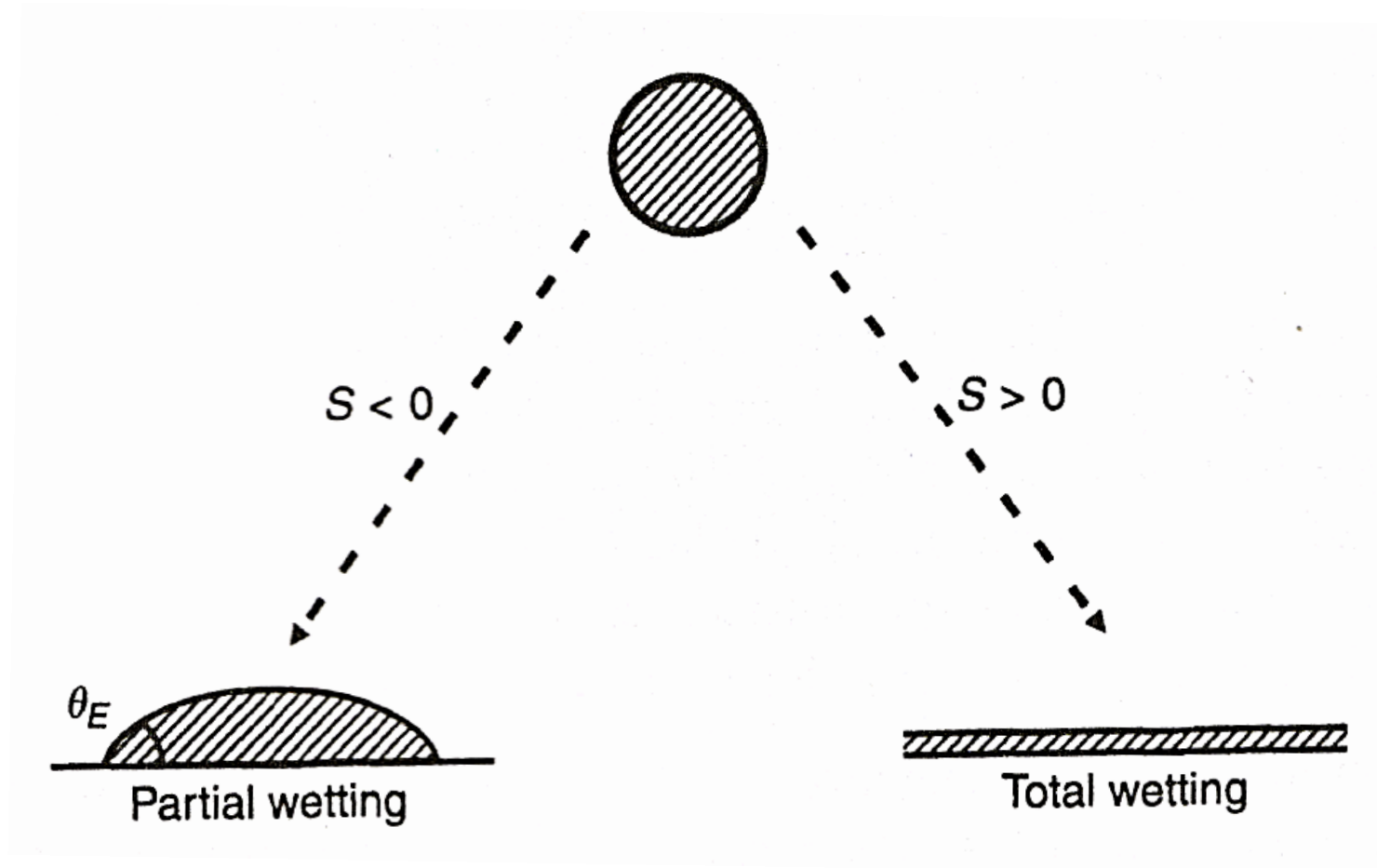$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos\theta \qquad \text{.......(1)}$$

➢ The detachment of a particle and bubble occurs when the force exerted by the surface tension is exceeded by shear forces and gravitational forces.

➢ These forces are complex and vary within the cell. High shear will be experienced close to the impeller of a mechanical flotation cell and mostly gravitational force in the collection and cleaning zone of a flotation column.

➢ Froth flotation depends on the selective adhesion of air bubbles to mineral surfaces in a mineral/water slurry. The air bubbles will attach to more hydrophobic particles. The attachment of the bubbles to the surface is determined by the interfacial energies between the solid, liquid, and gas phases.

The Spreading Parameter, S

➢ The parameter that distinguishes the spreading of liquid on a solid surface is called spreading parameter (S)

➢ It measures as the difference between the surface energy (per unit area) of the substrate when dry and wet

$$S = [E_{Substrate}]_{dry} - [E_{Substrate}]_{wet}$$

$$S = \gamma_{SA} - (\gamma_{SL} + \gamma_{LA}) \qquad \ldots\ldots(2)$$

S>0 : (Total Wetting)

If the parameter S is positive, the liquid spreads completely in order to lower the surface energy. The final outcome would be a film of nanoscopic thickness resulting from the competition between the molecular and capillary force.

S<0 : (Partial Wetting)

The liquid does not spread but, instead, forms at equilibrium a spherical cap like sahape resting on the substrate with a contact angle θ_E .

Law of Young–Dupre

$$ S = \gamma_{LA} (\cos \theta_E - 1) $$

It is evident that θ_E can be defined only if the spreading parameter is negative. θ_E increases (and S decreases) when the liquid is non-wetting.

➤ It must be remembered that this is a thermodynamic function expressing the maximum possible increase in free energy of the system resulting from the bubble-particle detachment, which is realized only when there are no other energy-consuming effects such as deformation of the bubble surface, and where all gravitation effects are absent and the system is at equilibrium.

Flotation Reagents

➤ A different component/chemical is introduced into the system it will adsorb or concentrate at an interface to reduce the surface energy of the interface.

1. Collectors: organic chemicals which make the surface hydrophobic and hence the mineral is capable of being collected in the process.

2. Frothers: organic chemicals which reduce the surface tension of the water to stabilize the bubbles into a froth layer at the top of the flotation cell to make concentrate removal easier.

3. Modifiers: organic or inorganic chemicals used to modify the slurry conditions to enhance the difference in surface chemistry between the valuable and gangue minerals.

Collectors

➢ The collectors used in flotation contain a non-polar hydrocarbon chain with a polar group on the chain

➢ The polar group is also modified to be specifically attracted to certain minerals.

➢ Collectors may be non-ionic (hydrocarbon oils) or ionized.

➢ The ionised collectors are either cationic, (amines) or anionic (fatty acids or sulphydril compounds such as xanthates or dithiophosphates).
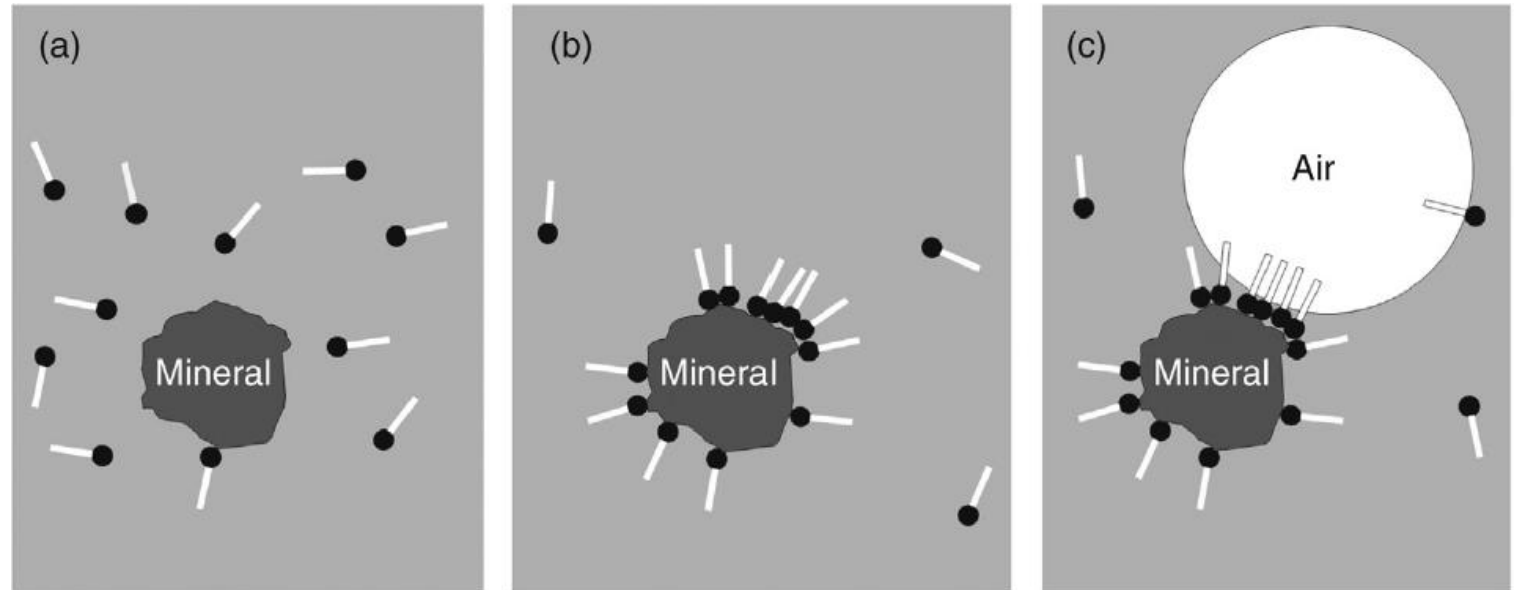
(a) Collector Dissolved in the Aqueous Phase. (b) Adsorption onto a Mineral Surface. (c) Attachment of an Air Bubble onto the Hydrophobic Surface.

Frothers

➢ Frothers are surfactants, usually organic heteropolar compounds such as alcohols or polyglycol ethers.

➢ Due to the heteropolar nature, the frother adsorbs at the air/water interface and as a result, lowers the water surface tension.

➢ This has the effect of producing smaller bubbles and more importantly it stabilises the froth when it reaches the top of the slurry.

➢ Frothers commonly used include natural chemicals such as pine oil, cresylic acid and synthetic reagents such as methyl isobutyl carbinol (MIBC) and polyglycol ethers.

Modifiers

➢ This class of reagents covers all chemicals whose principal function is neither collecting nor frothing.

➢ These may be further divided into depressants, activators and *pH* regulators.

➢ The main use of these modifying agents is in the successive removal of two or more valuable minerals from each other by flotation.

➢ For example, the separation of each copper, lead, zinc and iron sulphides from a single ore is selective flotation whereas the flotation of the combined sulphides from the gangue is referred to as bulk flotation.

Flotation Kinetics

Batch Flotation

➢ The concentrate obtained from a batch flotation cell changes in character with time as the particles floating change in size, grade and quantity.
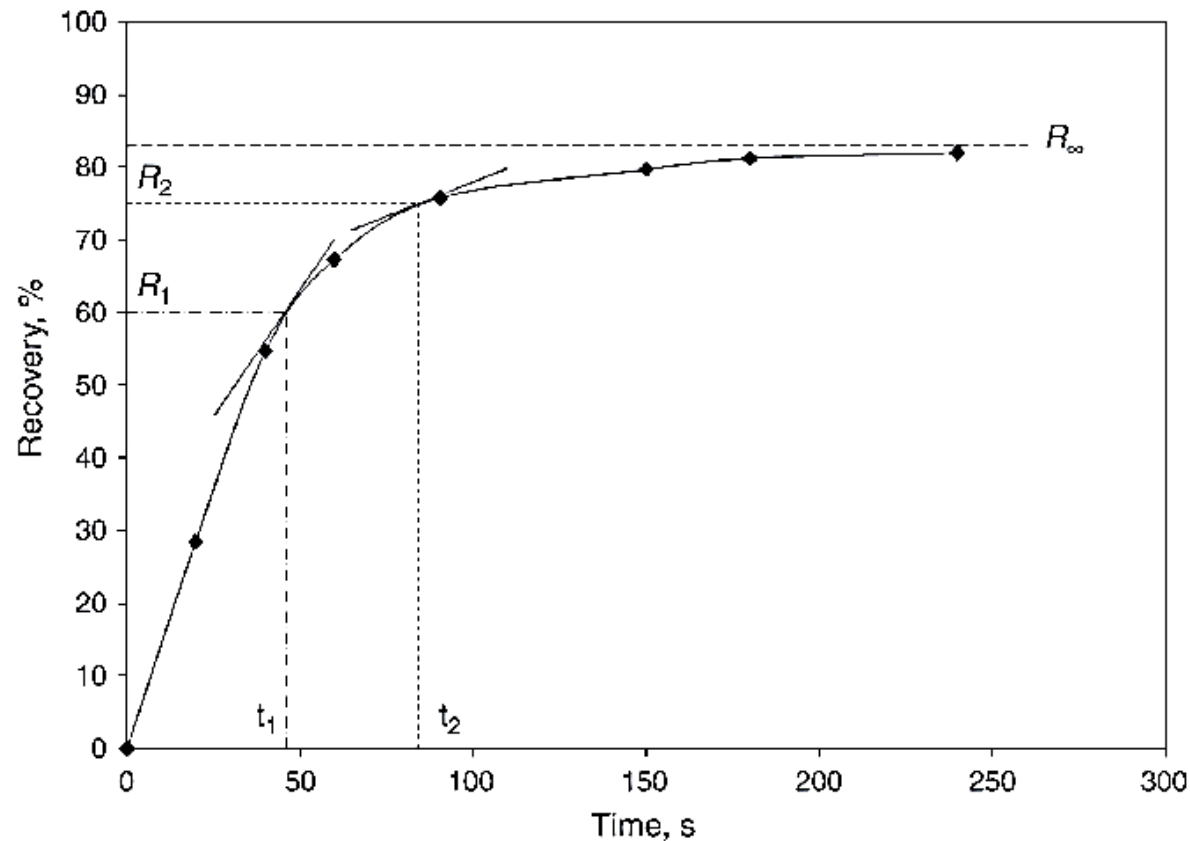
$$R = \frac{C_0 - C}{C_0}$$

C concentration of concentrate (floating material)

Time–Recovery Plot From Batch Flotation Test

➢ There is a direct relationship between the rate of flotation and the amount of floatable material remaining in the cell

$$\frac{\text{Slope at } t_1}{(R_\infty - R_1)} = \frac{\text{Slope at } t_2}{(R_\infty - R_2)} = k$$

R= rate of change of concentration (C) at any time, t

Flotation rate = $k \times$ (concentration in the cell)^n

➢ The flotation rate is equal to the rate of change of concentration of floatable material in the cell

$$-\frac{dC}{dt} = kC^n \qquad \text{.......(3)}$$

First-Order Rate Equation

$$-\frac{dC}{dt} = kC \qquad \text{gives} \qquad C = C_0 e^{-kt}$$

Where,

C_O = the concentration of valuable material in the cell at zero time, and

C = the concentration of valuable material remaining in the cell at time t.

As the 100% recovery rare, if the concentration of valuable material remaining unfloated in the cell after infinite flotation time is C_∞

$$\ln\left(\frac{C_0 - C_\infty}{C - C_\infty}\right) = kt$$

In terms of recovery, *R*,

$$R = R_\infty (1 - e^{-kt})$$

Where *R* is defined as,

$$R = \frac{C_0 - C}{C_0} \quad ....(4)$$

It has been assumed that the only independent variable has been the ***concentration of floatable material***, and that everything else has remained constant such as
- the bubble concentration,
- size and size distribution,
- reagent concentrations,
- Cell operation *etc.*

When other variables are not held constant, the rate equation may be written in general form

$$-\frac{dC}{dt} = k \prod C_i^{ni} \qquad ....(5)$$

C_i = the concentration of any species which might affect the rate of flotation of the particular species in question and
n_i = the order of the equation with respect to C

k is a complex function involving reagent concentrations, particle and bubble sizes, induction times, flotation cell design, rate of froth removal, power input and previous treatments and will only be constant as long as these conditions remain constant.

Second-Order Rate Equation

$$-\frac{dC}{dt} = kC^2 \qquad \text{gives} \qquad \frac{C_0}{C} = 1 + C_0 kt$$

It is important to always work in terms of floatable material rather than total material. That is, always take into account the value of C_∞ or R_∞ For graphical plotting, the above equation becomes

$$\frac{C_0 - C_\infty}{C - C_\infty} = 1 + (C_0 - C_\infty)kt \qquad \text{.......(6)}$$

Therefore a plot of $(C_O - C_\infty)/(C - C_\infty)$ vs. t will yield a straight line if the flotation rate is second order ($n = 2$)

In terms of recovery, R

$$\frac{dR}{dt} = k(R_\infty - R)^2 \qquad \text{gives} \qquad \frac{1}{t} = \frac{kR_\infty^2}{R} - kR_\infty \qquad ....(7)$$

is the form for graphical representation. Data for very short periods of flotation are required to be able to distinguish second-order kinetics by this graphical method.

Non-Integral Order

The rate equation can be considered, in general, to be somewhere between first order and second order, approaching first order for flotation of single minerals or in very dilute pulps, and approaching second order for low-grade ores or more concentrated pulps.

$$k^i t = \frac{\dfrac{R^i}{R^i_\infty}}{1 - \left(\dfrac{R^i}{R^i_\infty}\right)}\left[1 - \frac{R^i_\infty}{R_\infty}\right] - \left(\frac{R^i_\infty}{R_\infty}\right)\ln\left[1 - \frac{R^i}{R^i_\infty}\right] \qquad ....(8)$$

where R_∞ is the total mineral present of all species 'i'.

➢ When only one mineral is involved or if the solid-to-liquid ratio is very low ($R^i_\infty = R_\infty$) then this equation simplifies to the first-order equation and if $R_i << R$, equation reduces to a form of the second-order equation.

➢ Thus, equation 8 is the general equation describing the flotation process, based on the kinetic model of flotation.

Continuous Flotation

If we consider a continuous, single-cell operation under steady-state conditions, then dC/dt = 0 and the batch rate equation breaks down.
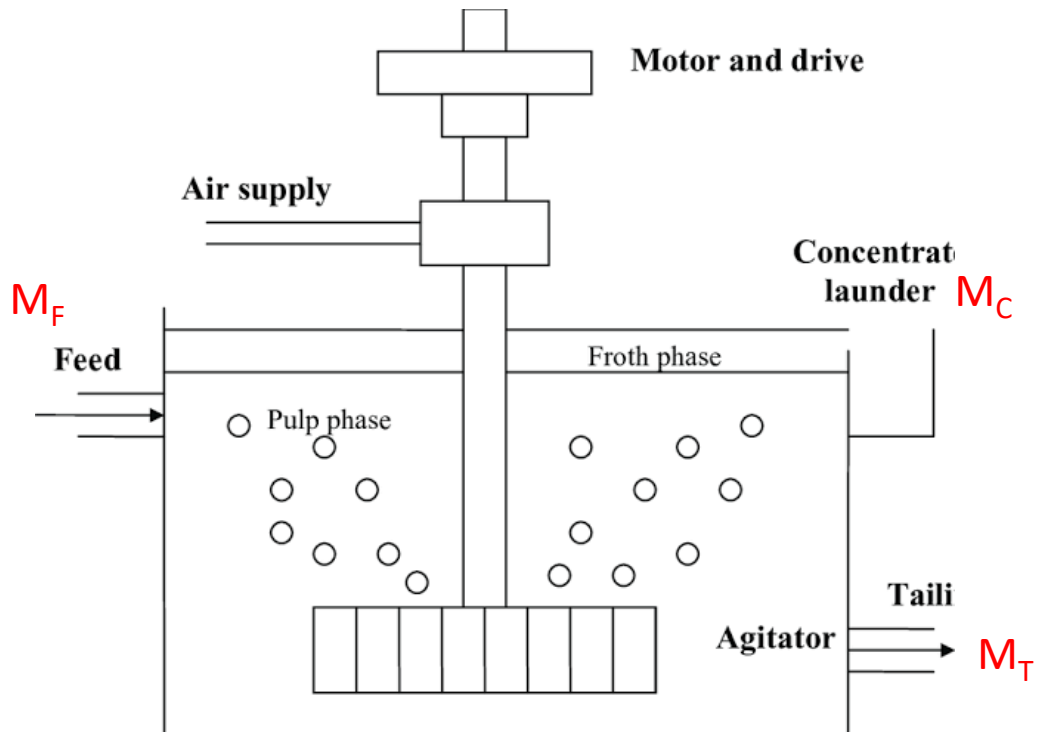
For continuous flotation the rate constant (or specific flotation rate) is defined as,

$$k = \frac{\text{flotation rate (mass/time)}}{\text{mass of flotable material remaining in the cell}}$$

$$= \frac{M_C / t}{M_T} \qquad \text{.......(9)}$$

Where M_C is the mass of solid concentrate, and M_T is the mass of solid tailing.

Assumptions

1. The cells in the bank are identical in all physical respects. That is, no change in physical environment occurs which might have an effect on the values of the rate constants.

2. The effective chemical environment of the particles remains constant throughout its flow through the bank. That is, no chemical change takes place which would affect the various values of the rate constant.

3. the cells are all ideal mixers and are baffled so that no pulp from any cell may flow into the preceding cell.

4. From a feed of constant quantity and quality the cell produces a concentrate and a tailing whose characteristics also do not change with time.

In terms of the fractional recovery in the single cell, assuming all of the mineral is floatable, (i.e., $R_\infty = 1$)

$$k\lambda = \frac{M_C}{M_T} \qquad \text{.......(10)}$$

where
λ = the nominal residence time of the pulp in the cell (cell volume/volume flow rate of tailings)
M_C = mass of solid in the concentrate and
M_T = mass of solid in the tailing

then $\qquad 1 + k\lambda = 1 + \dfrac{M_C}{M_T} = \dfrac{M_T + M_C}{M_T} = \dfrac{M_F}{M_T} \qquad \text{.......(11)}$

The fractional recovery in the cell, R' (the recovery from the feed to that cell), is given by

$$R' = \frac{M_C}{M_F} = \frac{M_C}{M_T}\frac{M_T}{M_F} = \frac{k\lambda}{1 + k\lambda} \qquad \text{.......(12)}$$

➤ For *N* such cells in series, where the volume of concentrate recovered from each cell is small compared with the total flow

    ➤ The fractional recovery in the first cell, from the feed to the first cell, will be

$$R_1' = R_1 = \frac{M_{C1}}{M_F} = \frac{k\lambda}{1+k\lambda} \qquad ....(13)$$

The recovery from the cell 2 in terms of the original feed to cell 1 (i.e., from the tailings of cell 1) will be

$$R_2 = \frac{M_{C2}}{M_F} = \frac{M_{C2}}{M_{T1}}\frac{M_{T1}}{M_F} = \frac{k\lambda}{1+k\lambda}(1-R_1) = R_1(1-R_1) \quad ....(14)$$

and the total recovery from *N* cells will be

$$R = R_1 + R_1(1-R_1) + R_1(1-R_1)^2 + ...+ R_1(1-R_1)^{N-1} = 1-(1-R_1)^N$$

$$R = 1-(1+k\lambda)^{-N} \quad ....(15)$$

Equation 15 is also obtained by substituting $t = Nt_R$ into Equation 4 where t_R is the effective residence time, given by

$$t_R = \frac{\ln(1 + k\lambda)}{k} \qquad ....(16)$$

This shows that under semi-batch conditions, the residence time for the same recovery as in a bank of N cells is Nt_R.

For a single continuous cell where $N = 1$

$$\frac{R}{(1 - R)} = k\lambda \qquad ....(17)$$

So that if the residence time is varied and the recovery measured, a plot of $R/(1 - R)$ vs. time will give a straight line of slope k.

Practical Considerations and suggested modifications

1. **Physical differences from cell to cell**

➢ Most of the other operating variables will differ to some degree from cell to cell, in particular cell impeller speeds, due to belt slippage, *etc.*, impeller-stator clearances (in some types of cells), due to wear, and air flow rates, due to partial blockage of air passages.

➢ For an ideally mixed cell, the pulp flowing out of the cell will contain air bubbles at a concentration equal to that in the cell. The concentration of air bubbles must be expected to rise from cell to cell.

➢ The concentration of air in the Nth cell of a bank is given by

$$C_{AN} = C_{A1} \frac{r^{N-1}}{(1-r)} \qquad \text{where} \qquad r = \frac{k_A^{'}}{k_A + k_A^{'}}$$

k_A = rate constant for air removal via froth (dependent on interfacial area/volume ratio)

$k_A^{'}$ = rate constant for air removal via tailings (dependent on pulp flow rate)

2. Chemical differences from cell to cell

➢ As the pulp flows down the bank of cells, surface-active agents, particularly the frother, will be removed preferentially in the concentrate.

➢ This would be expected to reduce the values of the rate constant of all the particle types, although not necessarily by the same amount.

➢ It is probable, therefore, that the only important change in chemical environment would be that of frother concentration, except in those cases when chemical reactions are incomplete when the pulp enters the first cell.

3. Variation in residence time

➢ In most cases of flotation the volume flow rates of concentrate, at least from the first few cells in a bank of roughers, cleaners are not negligible and the residence time of the remaining pulp must increase from cell to cell.

➢ If the residence times in the various cells are t_1, t_2, ..., t_N, then
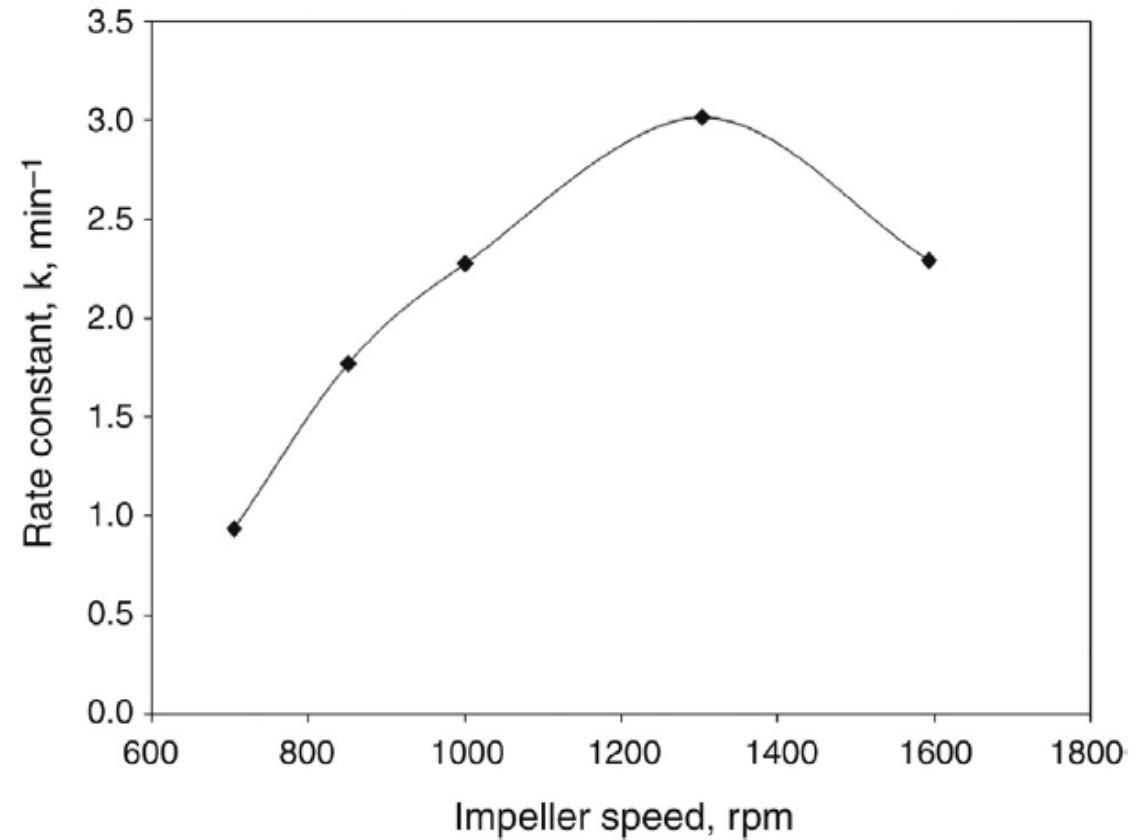
$$R_1 = \frac{k\lambda_1}{1+k\lambda_1}$$

$$R_2 = \frac{k\lambda_2}{1+k\lambda_2}(1-R_1)$$

$$R_N = \frac{k\lambda_N}{1+k\lambda_N}\left(1-\sum_{i=1}^{N-1} R_i\right)$$

The total recovery from the bank of N cells $= \sum_{i=1}^{N} R_i$

There is no algebraic simplification in this case and the expression must be solved numerically.

Factors Affecting the Rate of Flotation

➢ **Impeller Speed**

➢ Air Flowrate
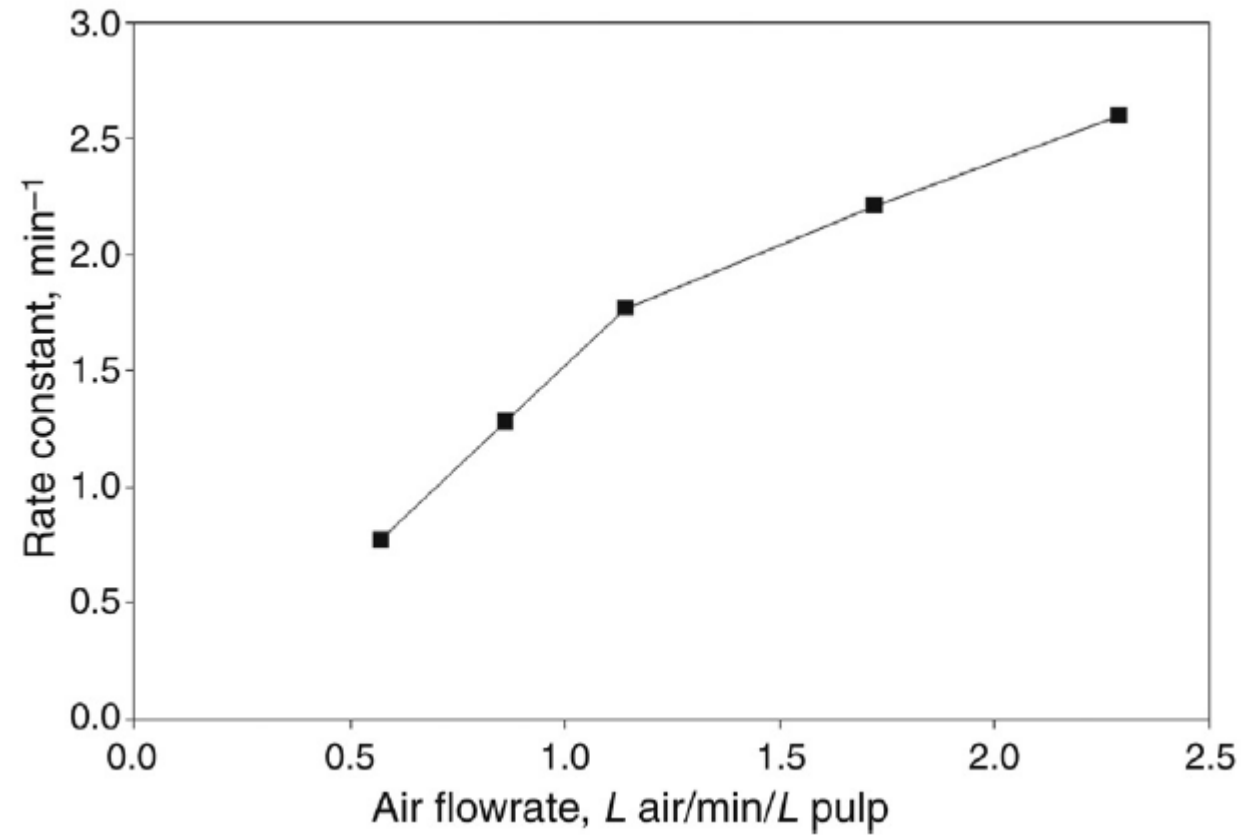
➢ **Particle Size**

The probability of collision and adhesion of a particle with a freely moving bubble must vary with the size of the particle because of

1. its projected area

2. its inertia which will govern whether or not a particle may cut across flow lines around the

bubbles

3. the possibility of its being thrown off the bubble even after adhesion has taken place due to

disruptive turbulence

4. the extent to which collision may distort the bubble and alter the time of contact and

5. the effect of particle size upon the induction time.

➢ In any given cell, considering the size of the bubbles produced and the disruptive forces present due to the turbulence of the pulp, there is a maximum size beyond which particles cannot be floated in mechanical cells.
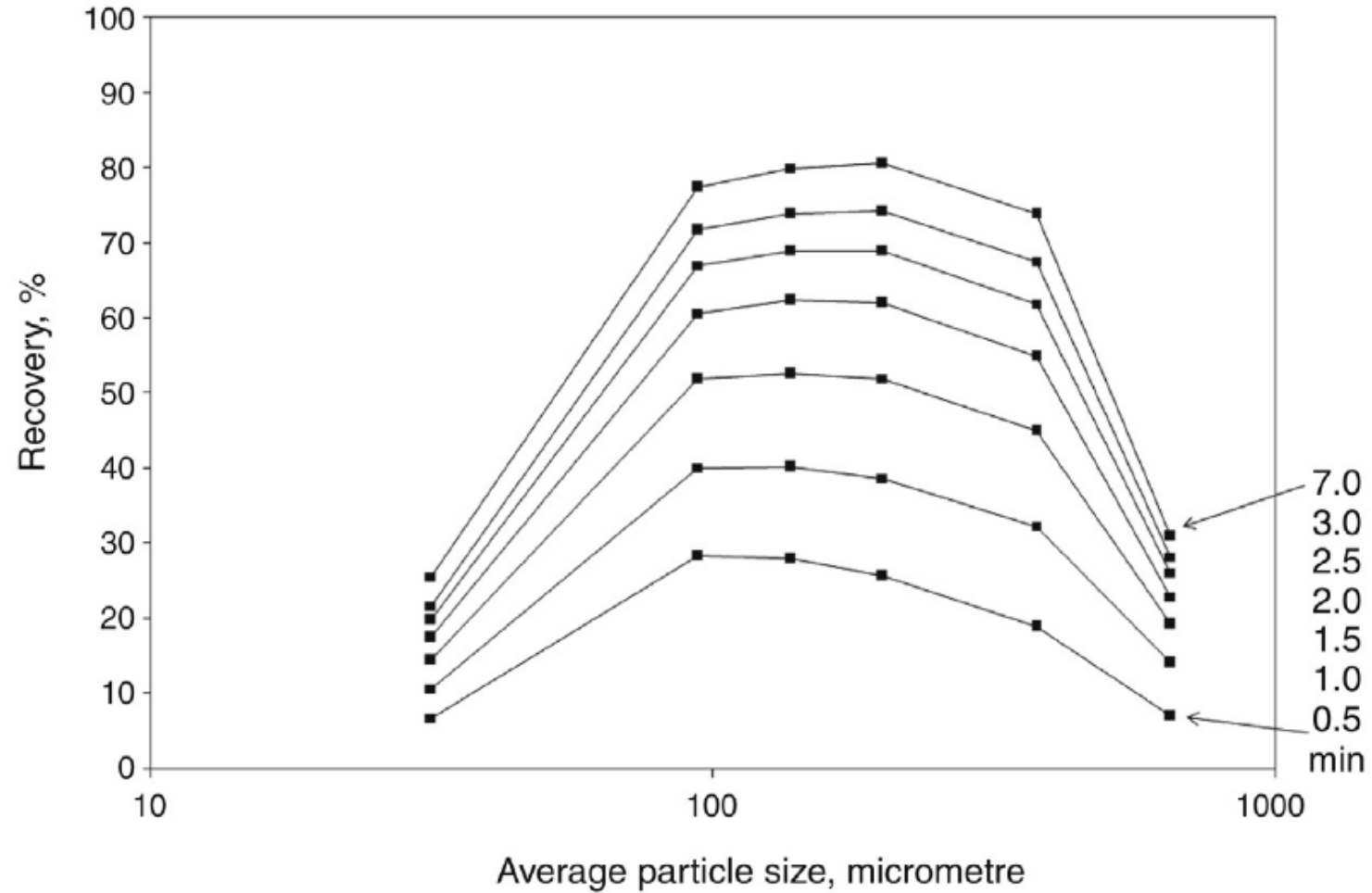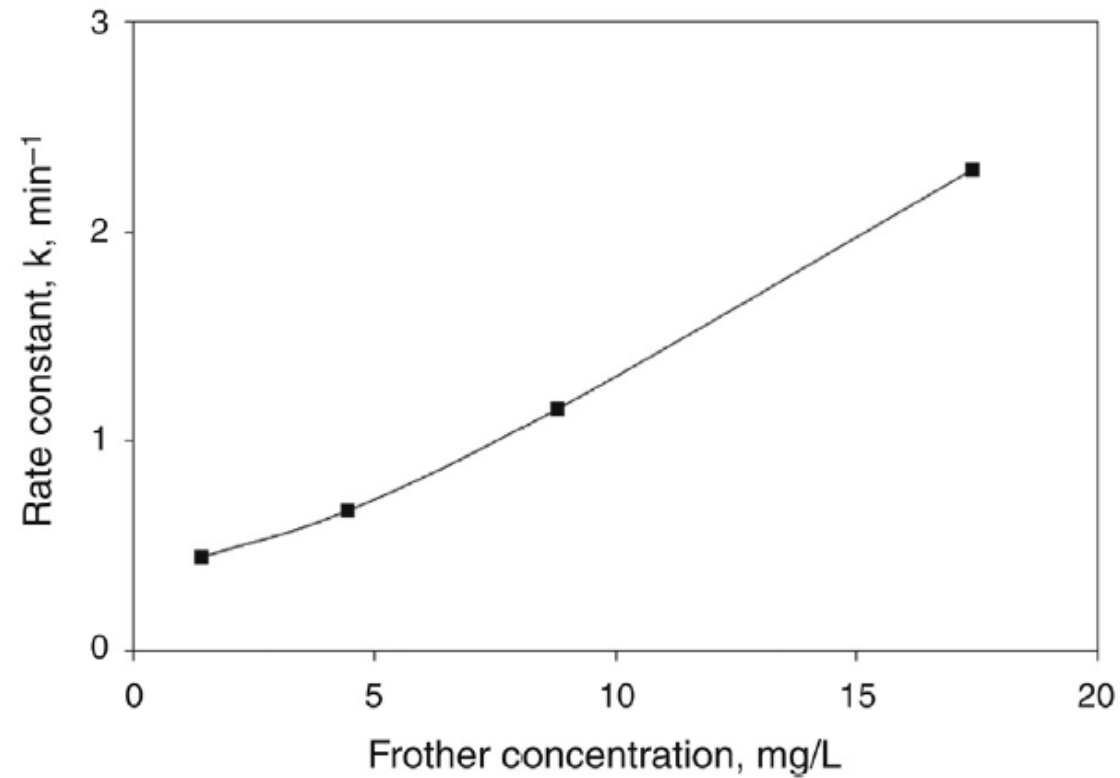
Relationship Between Recovery and Particle Size for Coal for Increasing Flotation Time
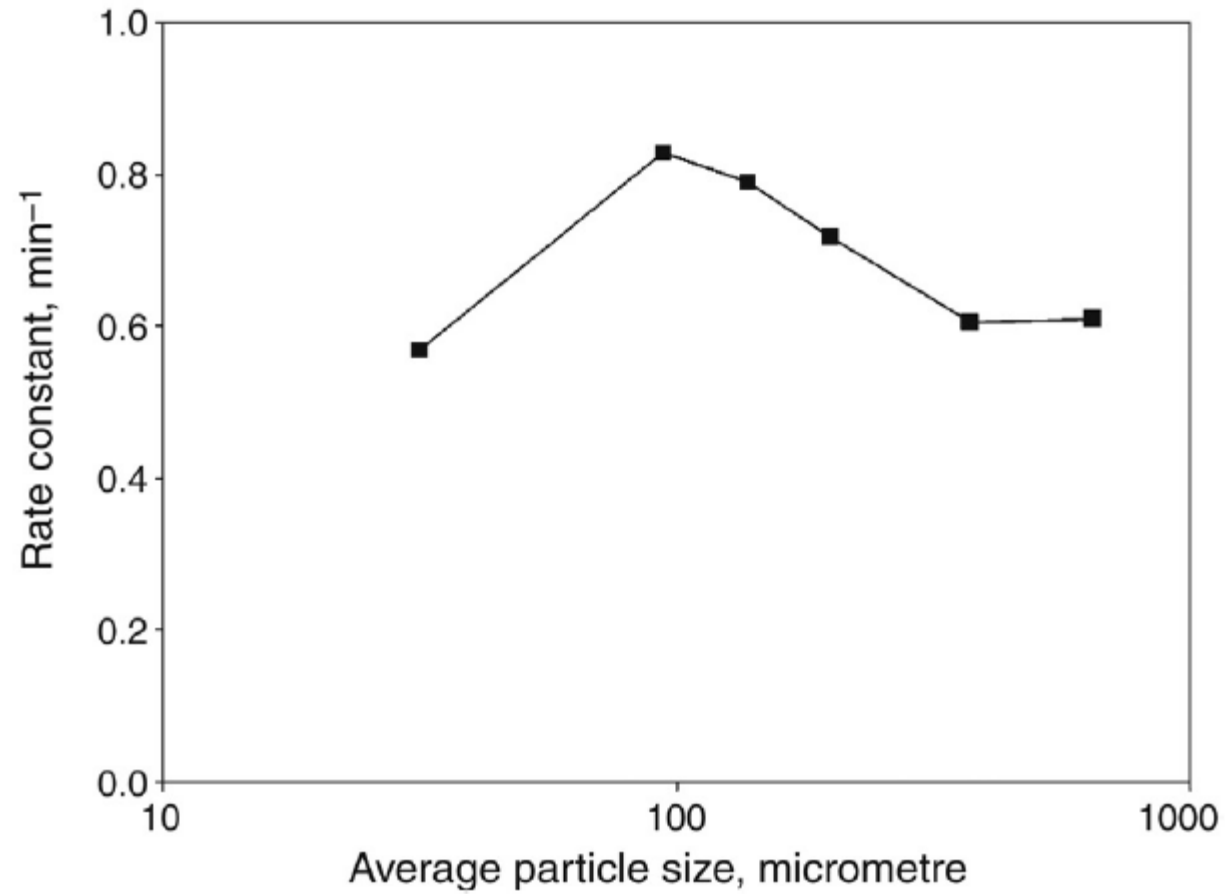
Relationship Between Flotation Rate Constant k and Particle Size for Coal

Reagents

➤ *Collectors*

➤ *Frothers*

Relationship Between Flotation Rate Constant k and Frother Concentration

Problem 1

Consider the treatment of a very simple ore that contains 5 t/h of pyrite and 95 t/h of mineral quartz, and that the ore is fed to a bank of 6 cells so that the retention time in each cell is 2 min. Calculate the grade of the concentrate.
If the recoveries in each cell are calculated as

R_{Pyrite} = 37.5% and
R_{quartz} = 3.8%