Abstract: Flotation separation is mainly used for removing particulates from aqueous dispersions. It is widely used for ore beneficiation and recovering valuable materials. This paper reviews the hydrodynamics of flotation separations and comments on selected recent publications. Units are distinguished as cells of ideal and non-ideal flow. A brief introduction to hydrodynamics is included to explain an original study of the hybrid flotation-microfiltration cell, effective for heavy metal ion removal.

Keywords: fine particles, flotation, flow pattern, hydrodynamics, metal ions removal, water, wastewater, minerals, recovery

1 Introduction

1.1 The process and materials recovery

Flotation separation originated with mineral processing (froth flotation). Its importance to the global economy is enormous. Without it many familiar metals and inorganic raw materials would be exceedingly scarce and costly. It has also found wide application to metal recovery from a wide variety of heavy metal bearing waste streams [1,2].

There are two broad categories, depending on the method of bubble generation [3]:

i) Dispersed-air flotation, including electroflotation (electrolytic flotation), where air is introduced by propellers or pumped through diffusers. Bubble size is relatively large (100–1000 μm). High shear and high bubble rise rate limit this to processes such as ore beneficiation, and

ii) Dissolved-air flotation (DAF), clarifies wastewaters by removal of suspended oil or solids. Air is dissolved in the wastewater under pressure and released in a flotation tank. The resulting tiny bubbles adhere to the suspended matter and float to the surface where it is removed by skimming. DAF is widely used in treating effluents from refineries, petrochemical and chemical plants, natural gas processing plants, paper mills, similar industrial facilities, and general water treatment.

The design and efficient operation of flotation cells requires knowledge of processes inside the cell: how much time is allowed for the particles to mix with the air bubbles; whether there are dead spaces where matter gets trapped, or bypassing, with either air or pulp leaving the cell too soon. All these malfunctions – termed non-ideal flow – lead to poor performance. The hydrodynamics governing the aeration, collection and separation steps of the flotation process have also been investigated by the equipment suppliers to develop new technologies.

The internal flow pattern is important in chemical unit design. The liquid characteristics, the unit scale, the baffles, and the impeller are among the factors that influence the flow pattern. Units are distinguished as cells of ideal and non-ideal flow [4]. In ideal cells the transport and mixing processes can be described mathematically, in contrast to real ones where the transport processes are only approximately known and must be modelled.

A flotation tank can be thought of as consisting of two basic regions: a ‘noisy’ reaction zone and a ‘quiet’ flotation zone. In the reaction zone bubbles are brought in contact with incoming contaminated water and particles and bubbles attach. In the flotation zone, bubble/particle aggregates rise achieving separation. In a properly operating flotation tank no settling particles occur in both zones [5].
Bubble size plays an important role in fine particle flotation [2]; electroflotation bubbles (both hydrogen and oxygen) have a mean diameter near 50 μm under normal operating conditions with horizontal stainless steel sheet electrodes [7]. Although much attention has been paid to particle size, the role of bubble size has been comparatively disregarded and deserves more attention [1b]. However, unconventional bubble generation methods utilize fine bubbles, as in electroflotation.

A large amount of valuable minerals has been discarded as fines and ultrafines because of inadequate technology to process them economically. On the other hand, fine particles often constitute a problem in chemical industry, and raw materials processing, often as by-products [3].

Research in hydrodynamic cavitation for natural resource recovery has been reviewed [8]. Interactions between tiny bubbles and fine particles in an aqueous slurry were analyzed based on particle surface properties and types of gas nuclei. Tiny bubbles generated by cavitation increased the contact angle of solids and attachment force, bridged fine particles to form aggregates, minimized slime coating, removed surface oxidation layers, and reduced reagent consumption.

A complex model has been used to describe liquid-phase mixing in a typical flotation column (for mineral beneficiation), involving a fully-mixed zones-in-series model which allowed both forward and backward flow between the zones [9,10]. The model involved two parameters: the number of zones and the ratio of backward to net forward flow. The degree of mixing in the gas-liquid flotation column, important for performance, was affected by the relative magnitude of the gas and liquid flows.

A computational fluid dynamic model incorporating flotation kinetic expressions has been developed by Kostoglou et al. to simulate the performance of flotation tanks [5]. The simulations revealed key dissolved-air flotation characteristics in determining local flotation rates. This study focuses on tanks that operate without external flow mixing (impeller, etc.), such as DAF tanks where bubble buoyancy, particle settling and turbulence contribute comparably to local flotation rates; their relative contributions were examined. In Denver type dispersed-air flotation tanks turbulence is dominant due to the intense mixing imposed by an impeller, so gravitational/buoyant effects can be ignored.

In a properly operating flotation tank no settling particles occur in both zones. Ill-functioning may occur if a tank is operated using bubbles larger than it was designed for [11]. The interrelationships among parameters acting at different length scales make the applied models exceedingly complicated, and new multiscale generalizations have been developed [12]. Despite the significance of turbulence in enhancing flotation there has been no unified approach to modeling flotation in turbulent flow.

Literature examining sustainable mineral and mining mostly concerns global and national scales [13]. New economic activities are surprisingly dependent on traditional raw materials. All electronic appliances use copper and require electrical power which may be generated by coal and transmitted by aluminum and copper wire. A home PC typically contains around thirty mineral ingredients [14]. Hence, recycling is important.

Recent flotation research is leading towards green chemistry [15]. Sustainability in chemical and process industry is essential, as the need for fresh drinking water sources is becoming urgent worldwide. Environmentally friendly biosurfactant flotation agents (produced by yeast or bacteria from sugars, oils, alkanes and wastes) could replace chemosynthetic surfactants [16]. Biosurfactants can potentially be as effective as synthetic surfactants with some distinct advantages including high specificity, biodegradability and biocompatibility.

Heavy metal wastewaters usually derive from electroplating, plastic manufacturing, fertilizer, pigment, mining and metallurgical processes. They are usually toxic and metals accumulation through the food chain poses a serious health hazard [17]. Thus, gradually stricter regulations press for innovative removal treatments.

The perceived gap between dispersed-air (froth) flotation and dissolved-air flotation was a conference sub-theme [18]. The gap perhaps originates from the separate traditions and the infrequent interaction among the separate applications. The different foci (selective separation or not), the difference in particle concentrations, and the use of chemical reagents may explain the gap. Mineral processing may be lucrative; however, effluent treatment imposes costs.

### 1.2 Hydrodynamic background

“Flotation cells seem never to have been seriously researched; admittedly, there are many ingenious inventions in the patent literature; but they were not the fruits of a deep knowledge of the hydrodynamics” [19]. The following is intended mainly for those not close to chemical engineering, although a flotation cell is not a typical chemical reactor. There is no reaction but separation and no density change.
Real equipment always deviates from ideal flow patterns. Deviation from the two ideal patterns can be caused by channeling, recycling, or by stagnant regions [20].

The simplest type is the plug flow reactor. The flow velocity is constant everywhere. This is a fair approximation in a simple channel or pipe. Plug flow allows definition of an unambiguous residence time (τ) that is the same for every streamline, since velocity is constant and the channel length the same for all streamlines.

\[ \tau = \frac{V}{Q} \]  

(1)

\( V \) is the reactor volume and \( Q \) the flow rate.

Ideal mixed flow reactors occur when the components enter the reactor separately. Their exit is gradual and some remain for smaller or longer intervals; there is no residence time, rather a residence time distribution [20a]. Recycle tanks and the tanks in which air is fed represent ideal mixed flow reactors.

The simplest way to find the RTD uses a physical or non-reactive tracer; for special purposes, a reactive tracer is used. For a non-reactive tracer, the methods include pulse, step, periodic and random inputs. The pulse and step inputs are most common and the effect of an electrolyte pulse on cell conductivity can be monitored. The responses to a pulse input for plug flow, completely mixed flow, and non-ideal flow are given in Levenspiel’s handbook [20a]. The residence time distribution from a pulse input is characterized as an E distribution.

Real reactors show a combination of the two ideal flow types, attributed to dead volumes, recycling, bypassing and channelling. The approach to non-ideal flow is by empirical and theoretical mathematical models. One or many parameters combine the two ideal types in various percentages. One-parameter empirical models are more common.

Axial dispersion model – The axial dispersion model postulates that mixing is due to departures from ideal plug flow caused by disturbances in the flow front [20a]. Similar to the Fick diffusion equation for concentration,

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} \]  

(2)

\( D \) is the axial dispersion coefficient, \( x \) the linear dimension and \( u \) the liquid velocity.

It is usually written in dimensionless form,

\[ \frac{\partial C}{\partial \theta} = N_d \frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z} \]  

(3)

\( N_d \) is the dimensionless dispersion number (\( N_d = D/ul \)), \( L \) the vessel length, \( z \) the dimensionless linear dimension and \( \theta \) the dimensionless time.

Tanks-in-series model – Alternatively, the cell may be treated as either a single perfectly mixed region or as a series of perfectly mixed zones in series. The tanks-in-series model is simple, can be used with any kinetics, and can be extended to any arrangement of compartments, with or without recycle. The theoretical RTD profile for \( N \) cells in series is:

\[ E(\theta) = \frac{N(N\theta)^{N-1}}{(N-1)!} \exp(-N\theta) \]  

(4)

Once the mean \( \tau \) and variance \( \sigma^2 \) of an experimental residence time distribution are determined, the value of \( N \) is [20a]:

\[ N = \frac{\tau^2}{\sigma^2} \]  

(5)

Flotation unit efficiency is a function of the residence time distribution, and the mixing conditions influence the three internal phases, in particular the liquid [6]. The solid particle RTD appears to be shorter than that of the liquid and the two tend to equalize as the particle size decreases. The tracer introduction location, measurement technique, bubble diameter and pulp density determine the behavior [4].

The mean RTD is:

\[ \tau = \frac{\sum_{i=1}^{n} t_i C_i \Delta t_i}{\sum_{i} C_i \Delta t_i} \]  

(6)

\( t \) is time and \( C \) the conductivity. \( E_i \) is:

\[ E_i = \frac{C_i}{\sum_{i=1}^{n} C_i \Delta t_i} \]  

(7)
The dimensionless form is usual, so the time $t$ and function $E_t$ are:

$$E_\theta = \tau E_t$$  \hspace{1cm} (8)

and

$$\theta = \frac{t}{\tau}$$  \hspace{1cm} (9)

As the flow in a real system is a combination of the two ideal types, it is approximated and the model compared with experiment. If the results do not differ significantly, the model adequately describes the real system. If they differ another model is applied (Fig. 3a).

### 2 Survey of recent literature

#### 2.1 Flotation in minerals processing

The contact angle is a measure of the solid surface hydrophobicity and is important in froth flotation. The hydrophilic/hydrophobic balance at the mineral surface can be evaluated from the contact angles developed among the liquid, solid, and gas. The effects of surface roughness, heterogeneity, and particle shape and size on contact angle measurements are highly important. Contact angle measurement methods include sessile drop, drop shape on the solid surface, captive bubble, capillary rise, capillary pressure, air bubble detachment force from solid in liquid and many others. The contact angles in the gas/liquid/solid system are strongly influenced by forces acting inside and outside of the system. Therefore, different contact angles, called advancing, receding, intermediate, equilibrium, etc., can be distinguished [21].

In mining, valuable minerals are usually separated from gangue by froth flotation to maximize throughput and economic outcome. Collectors are added to selectively adsorb onto the target mineral and render its surface highly hydrophobic, which generally gives strong mineral-bubble attachment and high recovery. Understanding the interaction between mineral particles and bubbles is a key to understanding flotation.

Measurement of the interaction forces has only recently been made possible with the atomic force microscope (AFM). AFM uses a light lever to detect the deflection of a fine cantilever spring as it interacts with the bubble or other surface beneath it when moved by a piezoelectric transducer. A laser light is focused onto the back of the cantilever and the reflected light directed onto a split photodiode detector, which produces a signal proportional to the deflection. The approach speed and relative bubble–particle position are accurately controlled by a voltage across the piezoelectric crystal and varied over three orders of magnitude. In force measurements $x$ and $y$ motions are disabled and the crystal moves the surface in the $z$ direction while the cantilever deflection is continuously measured. The deflection can be converted to force using Hooke’s law and the known spring constant.

An AFM bubble probe technique was employed to directly measure the interaction forces between an air bubble and sphalerite mineral surfaces of different hydrophobicity under various conditions [22]. The critical role of hydrodynamic and surface forces in bubble–mineral interaction and attachment was demonstrated. These agree well with theoretical calculations based on Reynolds lubrication theory and the augmented Young-Laplace equation including the effect of disjoining pressure.

The overall flotation performance (grade and recovery) depends on the quality and quantity of solid collected from the pulp, transferred to the froth, and surviving as bubble-particle aggregates into the overflow. The role of solids on pulp hydrodynamics, froth bubble coalescence intensity and water overflow rate has been extensively studied by Wei and Frinch [23]. Solids influenced froth stability. Talc, a surface-active gangue, behaves differently from silica (also hydrophilic non-sulfide gangue).

Analysis of high-speed images by a new device developed in our laboratory gave trajectories and velocities of particles flowing around a stationary bubble in an aqueous surfactant [24]. Velocity profiles around the bubble indicated that the bubble surface was pretty mobile, not surprising based on the low surfactant concentration employed. Experimental trajectories and velocities were compared to those predicted by a model also developed. Under the experimental conditions interception was the dominant collision mechanism; other mechanisms had a small but non-negligible effect.

Flotation modeling has been used to understand the process per se as well as for process design, control and optimization. Hydrodynamic characteristics are paramount. The correlation of gas dispersion characteristics with flotation rate constant was analyzed [25]. Three main classes of bubble size histograms were distinguished with bubble interfacial area as hydrodynamic variable. The gas dispersion parameters in a fully controlled laboratory column flotation cell, (gas hold-up, superficial gas velocity and bubble size distribution) have been measured by image analyses and compared to those calculated using drift flux analysis [26]. The role of the
frother (Dowfroth 250) in energy dissipation in bubble generation and interfacial tensions were explored. The bubble / gas dispersion and hydrodynamic conditions clearly play an important role in flotation.

The influence of hydrodynamic parameters on fine particle collision probability has been investigated [27]; particle size is important and has been the focus of flotation research for decades. Collision probability was obtained using Stokes, intermediate I and intermediate II and potential equations. The effect of impeller speed on Sauter mean bubble diameter at different air flow rates was examined. Fine particles typically show slow recovery rates, owing to decreased particle–bubble collisions, and are prone to entrainment. Moreover, very small particles have large specific areas, which can lead to excessive reagent adsorption and other effects associated with chemically active particles. These factors can have a considerable impact on grades and recoveries [28].

Flotation modelers must consider processes ranging from bulk hydrodynamics to molecular chemistry. However, the micromechanics that bridge those processes is critical [29]. Direct observation of particle–bubble interaction through high-speed videography provides insight to allow prediction of attachment based on hydrodynamic and chemical factors.

Interactions between fine sub-bituminous coal particles and micron bubbles generated by hydrodynamic cavitation have been investigated [30] and pilot tests were conducted on the cavitation system at several Brazilian phosphate flotation plants. Increased fluid velocity increases the number of micron size bubbles. The method has been commercialized by Canadian Process Technologies, Inc.

### 2.2 Flotation in wastewater treatment

In a laboratory scale flotation column, high-speed photography has examined single bubble motion of and bubble swarm size distribution in the presence of surfactants [31]. Surfactant was distributed unevenly over a rising bubble surface inducing a Marangoni effect, which retards bubble deformation and increases drag.

The importance of horizontal flow patterns and aggregation to improve bubble removal during drinking water treatment were explored using CFD modeling [32]. Stratified flow (back and forth horizontal flow layers at the top of the separation zone) improved flotation efficiency. The models were evaluated at pilot scale DAF using measurements of residence time distribution, bubble layer position and bubble–particle contact efficiency [33].

A series of field tests and simulations was conducted to estimate collision-attachment efficiency using trajectory analysis to evaluate model sensitivity to size and zeta-potential in designing and operating dissolved air flotation for various wastewaters [34]. Bubble-particle collision attachment efficiency was described by stream hydrodynamics in Stokes’ flow and surface forces based on a classic DLVO theory (using Matlab software) and numerical analysis (5th Runge-Kutta method).

An electroflotation column has also been used to study bubble hydrodynamics in both batch and continuous régimes. Video recording and image treatment was adopted with model solutions [35]. Modified induced-air flotation treatment of oily wastewater containing anionic surfactant at the critical micelle concentration was examined [36]. The interfacial area, obtained from the bubble hydrodynamic parameters, and the velocity gradient were important for controlling efficiency and cost.

### 3 A case study

#### 3.1 Introducing the hybrid cell

The main limitation to combined and more compact membrane bioreactors is membrane fouling [37]; hydraulics can retard fouling and maintain stable operation. In the newly developed submerged membrane bioreactor cross-flow over the membrane surface produced by air bubbling induces moderate shear to remove sludge. It has energy saving as a further advantage.

Many techniques limit membrane fouling, such as liquid cross-flow, baffles, back flushing, trans-membrane pressure pulsing, and air sparging. The function of air can be:
- Gas back flush detaches and carries away deposited particles;
- Particle formation or concentration polarization may be prevented or limited; and
- A compound may be transferred by gas to the liquid phase.

A typical 90% preliminary flotation solids recovery can limit fouling. Studies of model systems and real mixtures of metal ions were applied to the hybrid cell. Microfiltration (MF) membranes “reacted” abnormally when removed from the steady state reached in the hybrid cell. Permeability and pore size or molecular weight cut-off were also important for efficiency and substance rejection [38].
Gas bubble enhancement of membrane performance was modeled; cross flow velocity was a function of air intensity. Intermittent membrane bioreactor air-jet mode was constrained by clogging and regular membrane cleaning to control biomass growth was necessary to prevent channeling. The reactor can operate under plug flow conditions. The gas/liquid two-phase flow was also studied with ceramic flat sheet ultrafiltration (UF) or microfiltration membranes installed either horizontally or vertically [39,40].

The main application of the combined process was the treatment of heavy metal wastewaters; these are treated before mixing with other of wastewater [41]. Separation depended primarily on the efficiency of the initial metals removal; “sorbent” particle size and distribution, concentration, and surface charge are important. Bubble size and air flow rate are also significant. Type and concentration of reagents used as collector(s), frother, etc. also affect flotation.

A technico-economic study applied SuperPro Designer (Intelligen, Inc.) [42]. A recent review focused on the removal of heavy metal ions from aqueous solution [43]. The processes were sorptive flotation, where metal bonding agents including biosorbents were added and the subsequent complexes separated by flotation, or ion flotation. Separation with brewery waste Saccharomyces yeast was successful. Removal of zinc from aqueous solution has been also investigated [44].

### 3.2 Experimental RTD study

An investigation of electroflotation hydrodynamics was undertaken, as efficiency was expected to be a function of the residence time distribution (RTD). The stimulus-response technique was used [6,7]. The tracer input was a step function electrolyte. A theoretical multiparameter model (Levenspiel) was applied consisting of interconnected dead water, back mix, plug flow, etc. regions, with by-pass, recycle, and cross flow through and around these regions.

The hybrid cell arrangement (Fig. 3b) was: a mixing tank connected by a peristaltic pump to the dispersed-air flotation column, having inside a membrane microfilter over the porous ceramic air diffuser; on the top a foam collection tank, and at the bottom a permeate collection tank. Control valves, thermometer, manometer, and air flowmeter were included [37]. Table 1 presents the experimental conditions and Figs. 1a and 2a show the conductivity versus operation time. Each experiment was repeated three times. \( \tau, E_{t}, \theta \) and were calculated for each experiment.

![Figure 1](image-url)
Figs. 1b and 2b compare the mean experimental data and theoretical curves for \( N = 1 \) in the tanks-in-series model, for small (\( h_L = 41.2 \) cm) and large columns (\( h_L = 84 \) cm). In both cases, the experimental data are well described by the theoretical curve; both systems behave as well-mixed vessels.

Some indicative RTD experiments have also been done in the small column, but without air bubbling (Fig. 4). The tanks-in-series model for \( N = 1 \) is not satisfactory and another model should be applied. Nevertheless, the hybrid flotation–membrane system always uses air, and in presence of air a well-mixed vessel can correctly describe it.

Under steady-state conditions a simple mass balance equation described the process based on first-order kinetics. The batch equation satisfactorily described the process, except the initial period. The flotation rate exhibited increasing solids removal up to approximately 80% recovery. The higher the current density the greater the recovery and the maximum electroflotation rate increased with higher feed concentrations. Tank scale up (~20X) was also successful. The most significant advantage of this technique was that the electric field gradient between electrodes aids flocculation and flotation, even without surfactant. The superiority of countercurrent contact flow was highlighted.
4 Conclusion

Mineral, metal values and by-products can be recovered by flotation separation. A promising new hybrid cell was described, focusing mainly on the hydrodynamics that affect its operation. Recalling what was argued during an Advanced Study Institute in Cambridge - though more than 30 years ago - “flotation cells are invented, not designed” [19]. However, this knowledge can place plant design and operation on a more concrete basis reduce reliance on costly trial and error.

These results were presented at the 13th Intl. Symp. Envrir. Pollution and its Impact on Life in the Mediterranean Region (MESAEP, 8-12 Oct. 2005, Thessaloniki).

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**Notation**

\( C \) conductivity [\( \mu \text{S cm}^{-1} \)]

\( D \) axial dispersion coefficient [-]

\( h_L \) column height [cm]

\( L \) vessel length [m]

\( N \) number of cells [-]

\( N_d \) dimensionless dispersion number [-]

\( V \) reactor volume [cm³]

\( Q_L \) liquid flow rate [cm³ min⁻¹]

\( Q_G \) air flow rate [cm³ min⁻¹]

\( t \) time [min]

\( U \) liquid superficial velocity [cm s⁻¹]

\( U_\circ \) air superficial velocity [cm s⁻¹]

\( x \) linear dimension [m]

\( z \) dimensionless linear dimension [-]

\( \theta \) dimensionless time [-]

\( \tau \) theoretical residence time distribution [min]

**Figure 4**: (a) Conductivity measurements and (b) RTD calculations in the hybrid cell without air; \((L/D = 4) Q_L = 15.82 \text{ cm}^3 \text{ min}^{-1}, Q_G = 0 \text{ cm}^3 \text{ min}^{-1}, h_L = 39.7 \text{ cm}, \tau_{\text{theoretical}} = 188 \text{ min}.\)
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