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#### Abstract

The basic principles of foam separation techniques are discussed. A review of the research concerning bubble-particle interaction and its role in the kinetics of the flotation process is given. Most of the research in this area deals with the use of theoretical models to aredict the effects of bubble and particle sizes, of liquid flow, and of various forces on the capture and retention of particles by bubbles. A discussion of fluid mechanical aspects of particle flotation is given.


## INTRODUCTION

Foam flotation is a separation method that has been applied to a wide variety of substances and has been utilized for many years in the field of mineral processing. Recently, many new variations of these techniques have been developed in which removals of species such as organic compounds and colloidal substances have been achieved.

In order to maximize the efficiency of foam flotation techniques, the attachment of particles to bubbles must be made more likely. An understanding of the factors involved in particle-bubble encounters and interactions is essential. Another factor that must be investigated is the effect of viscous drag forces on a particle attached to a bubble.

## gENERAL DESCRIPTION OF FOAM FLOTATION TECHNIQUES

Foam flotation is a subdivision of adsorptive bubble separation techniques, a group of separation techniques based on differences in surface activity. Material of various types and composition is selectively adsorbed at the surfaces of bubbles rising through a liquid and is thereby concentrated or separated. A substance which is not itself surface active can often be made effectively surface active through interaction with a surface active species. A classification scheme for adsorptive bubble separation techniques is shown in Figure 1 [1].

In practice, foam separation involves the passage of a gas through the solution containing the species to be removed and a surfactant. The adsorbed components are separated by removal of the foam. Figure 2 shows two modes of foam column operation. In the batch system, shown in Figure 2(a), gas bubbles are generated in the liquid and the foam is collected. This method is impracticle for large-scale processes, so the continuous mode of operation, shown in Figure 2(b), is used. The bulk solution may be fed into the column continuously and the bulk residue collected continuously. Part of the foamate may be fed back to the top of the column to increase the separation factor. The column may be operated in the stripping mode by introducing the feed into the foam so that separation takes place while it is descending through the foam.

## THEORETICAL ASPECTS OF PARTICLE FLOTATION

Two models have been used to investigate adsorption of particles at an air-water interface. In the Coulombic model [2], the binding force between particle and the air-water interface is due to coulombic attraction between the charged interface and the oppositely charged particles. The charge at the interface is due to the adsorption of ionic surfactant.

In the second model, the non-Coulombic model [3], adsorption of surfactant molecules to the surface of the solid particles, results in a hydrophobic surface. Nonzero contact angles then allow bubble attachment and flotation. The binding energy of the particle to the air-water interface may be estimated as follows: Assume the floc particles are spherical and that the radius of the air bubble is much larger than that of the floc particle. The free energy change during attachment is given by

$$
\begin{equation*}
\Delta G=-\gamma_{A W} \pi r^{2}(1-\cos \theta)^{2} \tag{1}
\end{equation*}
$$

where $\gamma_{A w}$ is the interfacial free energy at the air-water interface, $r$ is the particle radius, and $\theta$ is the contact angle as shown in Figure 3.

In Table 1 [4], the magnitude of the floc particle-air bubble


Figure 1. Classification of Adsorptive Bubble Separation Techniques


Figure 2. Modes of Foam Column Operation

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## Figure 3. Model of Floc-Bubble Attachment [4]

| $\cos \theta$ | $-\Delta G($ erg $)$ |
| :--- | :---: |
| 1.0 | $0.0 \times 10^{-10}$ |
| 0.9 | 1.257 |
| 0.8 | 5.027 |
| 0.6 | 20.11 |
| 0.4 | 45.24 |
| 0.2 | 80.42 |
| 0 | 12566 |
| -10 | 502.64 |
| $-14 \times 10^{-14}$ erg at 298 K. |  |

Table 1. Floc-Bubble Binding Energy as a Function of Contact Angle
interaction energy is given as a function of $\theta$. For these calculations, 40 dyne/cm was chosen for $r$ and a value of 0.1 mm was used for $r$. It is apparent that even for small particles, the floc-bubble binding energy is several orders of magnitude larger than kT unless the contact angle is almost zero.

## REVIEW OF RESEARCH ON BUBBLE-PARTICLE ATTACHMENT

Gaudin [5] analyzed collision between an air bubble and a mineral particle with the assumptions that water is non-viscous and incompressible, the mineral particles are large compared with the mean free path of the water molecules, bubble and particle are rigid spheres, bubble and particle are the only factors that affect flow of liquid, and there is streamline flow around the spheres. From his analysis, he determined that collision between bubble and particle was impossible unless the center of the particle was located on the central line of motion of the bubble. Sutherland [6] points out that Gaudin's analysis was based on an erroneous assumption that two bodies move independently in a fluid. He also defines the "collision radius" of a bubble, D, which is given by

$$
\begin{equation*}
D=\sqrt{3 r R} \tag{2}
\end{equation*}
$$

where $r$ is the particle radius and $R$ is the bubble radius. Particles lying within this distance from the line of motion of the bubble will collide with it.

Trajectories for particles in the path of a spherical bubble rising in an infinite pool of liquid were calculated by Flint and Howarth [7]. They defined a collision efficiency, which is the ratio of the number of particles that actually collide with the bubble to the number that would collide if the fluid streamlines were not diverted by the bubble. Whether or not a particle collides with the bubble depends on the balance of viscous, inertial, and gravitational forces acting on it, and the form of the streamlines around the bubble. Their theoretical analysis predicted two regions of particle-bubble behavior. For larger particles, collision efficiency depends most strongly upon inertial forces. In this coarse particle region, collision efficiency is increased by increasing the bubble size. For smaller particles, inertial effects of the particle may be neglected and collision efficiency is independent of whether Stokes or potential flow is assumed. They also showed that the collision efficiency of particles with bubbles in a swarm can be several times as large as those calculated from a single sphere model.

The concept of two types of bubble-particle interaction is also given by Reay and Ratcliff [8]. They define a collision regime which applies to particles larger than about 3 microns diameter. In this regime, particles will come into contact with the bubble only if their hydrodynamically-determined trajectories come within one particle radius, $r$, of the bubble surface. The collection efficiency should increase with increasing $r$ since larger particles have a better chance
of intercepting the bubble. For this regime, they assume that the flow pattern around the front of the bubble is given by the Stokes equation for creeping flow around a rigid sphere, that electrical interactions between particle and bubble have a negligible effect on the particle trajectory, that the motion of the bubble is not affected by the presence of the particle, and that the fluid velocity used in computing the drag on a particle is the velocity which would exist at the point occupied by the center of the particle if the particle were absent. In the diffusion regime, submicron particles reach the bubble mainly by Brownian diffusion. In this regime, the collection efficiency should decrease with increasing $r$ since larger particles diffuse more slowly.

The analysis of Reay and Ratcliff gave the following results: In the collision regime, gravity is the only factor causing the particle's trajectory to deviate from the fluid streamlines. (2) In the collision regime, the number of particles picked up by a bubble is independent of bubble size and proportional to bubble frequency. (3) In the collision regime, flotation rate should increase with the square of the particle diameter. (4) In the diffusion regime, the flotation rate should be inversely proportional to particle diameter. Experimental results were in general agreement with theory.

Schulze and Gottschalk [9] performed experiments on hydrodynamic interaction between a single immobile air bubble streamlined by a flow of liquid and solid particles. The trajectories of individual particles were recorded stroboscopically. They found that the experimental particle trajectories followed the streamline given by potential flow around the bubble. The particle radius in their experiments was 0.080 mm and the bubble had a radius of 1.53 mm .

The coordinate system of particle-bubble attachment used by Schulze and Gottschalk is shown in Figure 4. Kinetic energy of particles flowing near the symmetry axis of the bubble is used for the elastic deformation of the bubble surface. These particles are repelled from the bubble once or several times. The time of contact on collision is less than 4 ms and the energy loss on the first collision is more than $70 \%$. If $\phi<30^{n}$, there are no collisions - the particles slide over the bubble. The attachment appears to occur mainly in the transition region between colliding and sliding. The fraction of particles that attach to the bubble varies from 0.2 to 0.5 .

Conclusions of Schulze and Gottschalk are: (1) Particle attachment takes place within a time interval longer than that of collision shorter than that of sliding. Collision times range from 1 to 4 ms and sliding times range from 30 to 50 ms . (2) The time of contact has a maximum at angles of about $\emptyset=30^{\circ}$ and there is an optimum distance for attachment.

Anfruns and Kitchener [10] measured the rate of capture of quartz particles of 0.012 to 0.040 mm diameter by single rising bubbles of 0.5 to 1.1 mm diameter. They described a model of particle capture in which the particle must first make a hydrodynamic collision with the bubble.

```
\mp@subsup{V}{B}{\prime}
    Est - kinetic energy on collision of particles and the bubble,
~st - time of contact on collision,
|Gr - polar angle representing a transition from collision to
        sliding.
\tau
    |
        intercepted by the bubble
    E - hydrodynamic efficiency of collision.
```



Figure 4. Coordinate System of Particle-Bubble Interaction [9]

During the collision period of a few milliseconds, the thin liquid film between particle and bubble ruptures. The contact meniscus then expands rapidly over the particle.

Derjaguin, Dukhin, and Rulyov [11] analyzed the kinetic theory of flotation of small particles. For comparison purposes, their analysis included some aspects of the theory of flotation of large particles. They divided the flotation act into two stages. The first is the approach of the particle to the bubble and the second is the fixation of the particle to the bubble. In agreement with Reay and Ratcliff [8], they postulate different mechanisms for small and large particle flotation. In the case of large particles, formation of a three-phase wetting perimeter is able to resist detachment forces. They refer to this phenomenon as contact flotation. For small particles a three-phase wetting perimeter is not formed but the detachment forces are several orders of magnitude smaller than for large particles and can be overcome by London-van der Waals attractions. This is called contactless flotation. In most cases the particle and the bubble have like charges and overlapping of the double layers results in repulsion. In the case of large particles, this repulsion can be overcome by an inertial impact on the bubble surface. Small particles do not undergo such an impact but hydrodynamic forces may press the particle into the bubble surface.

## FLUID MECHANICAL ASPECTS OF PARTICLE FLOTATION

It has been shown that the binding energies of particles to the air-water interface are much greater than the thermal energies of the particles [2]. It is possible that viscous drag forces could detach adsorbed particles from bubbles rising through a liquid. An analysis of these drag forces is helpful in the determination of the efficiency of bubble-particle attachment and in the efficiency of foam flotation techniques.

Several models that vary in sophistication have been used to estimate the viscous drag force on a floc particle attached to a rising bubble [12]. The viscous force seems to be several orders of magnitude smaller than the force that binds the particle to the bubble. The results of calculations based on these models show that if the bubble size is small, the viscous forces are much too small to detach particles from the bubbles and as bubble size increases, viscous drag forces also increase. It should, be noted that these models are approximate and qualitative because of the use of presuppositions and simplifying assumptions.

A much more rigorous analysis of the fluid mechanical aspects of particle-bubble attachment has been made by French and Wilson [13]. The floc particle is subject to three forces; the binding force $\mathrm{F}_{B}$, a drag force $F_{D}$, and a lift force $F_{L}$. Each of the three forces was calculated by numerical methods and it was found that the sign of the lift force was negative, indicating that the lift force pressed the particle into the bubble.

Also, the nature of the binding force is such that the particle is free to move about on the bubble surface. The effect of $\mathrm{F}_{\mathrm{B}}, \mathrm{F}_{\mathrm{D}}$, and $\mathrm{F}_{\mathrm{L}}$ is to roll the floc particle toward $\theta^{\prime}=0^{\circ}$. As shown in Figure 5, an axisymmetric cap of particles would be formed on the bubble about $\theta^{\circ}=0^{\circ}$.

Kiefer and Wilson [14] investigated a "squeeze-out" mechanism in which drag forces on the cap of floc particles cause development of a surface pressure which, if large enough, will "pop" a floc particle from the cap. Their model is shown in Figure 6. The assumption is made that the viscous drag force on the floc particle is independent of its position on the bubble surface. It is shown that the fraction of the area of the bubble that is covered by particles is a function of bubble size. As the radius of the bubble increases, the fraction of its surface that is covered decreases. There is a critical bubble radius, $r$, which represents the maximum radius of a bubble that can be completely covered. The critical bubble radius is given by

$$
\begin{equation*}
r_{c}=\left(\frac{3 \Delta G}{\pi \alpha \rho g}\right)^{1 / 2} \tag{3}
\end{equation*}
$$

where $\Delta G$ is the energy of attachment, $\alpha=\pi a^{2}$ ( $a$ is the particle radius), $\rho$ is the density of the solution, and $g$ is the gravitational constant. If a is chosen as $0.1 \mu \mathrm{~m}$ and $G \cong 2 \times 10^{-9} \mathrm{erg}$, the value of $\mathrm{r}_{c}$ is approximately 0.080 cm , meaning that bubbles of this radius and smaller may be completely covered. If the radius of the bubble increases to 0.112 cm , its coverage drops to $50 \%$. It should be noted that these calculations are quite rough.

This "squeeze-out" model was reexamined [15] by an approach that took into account the variation of the surface pressure with position and the separation of the boundary layer, and was also applicable to larger bubble sizes. Figure 7(a) shows the geometry that was used in the development of the model. In this diagram, represents the top of the particle cap and represents the point at which boundary layer separation occurs. In Figure 7(b) a plot is given of the void (uncovered) fraction of bubble surface vs. bubble radius. Figure 7 (c) gives a plot of total surface/volume and loaded surface/volume vs. bubble radius. It can be seen that in agreement with the simpler model, if bubbles are of radius $>0.080 \mathrm{~cm}$, the fraction of covered surface and, therefore, the efficiency of flotation will decrease.

$$
c-4
$$



Figure 5. Effect of Various Forces on Particle Attachment [13]


Figure 6. Model of a Spherical Cap of Floc Particles on the Bottom of a Rising Bubble [14]

(a) Boundary Layer Separation Around a Rising Bubble

(b) Void Fraction of Bubble Surface as a Function of Bubble Radius
(c) Total Surface/Volume and Loaded Surface/Volume as Functions of Bubble Radius

Figure 7

The interaction of bubbles and particles is a complex process which has been investigated by many researchers from different approaches. It is evident that there is general agreement on several important points, and disagreement on others.

The attachment of particles to bubbles depends upon the degree of hydrophobicity of the particle surface and in most cases viscous drag forces are far too small to detach a single particle from the bubble surface. There are two different mechanisms for bubble-particle attachment, depending on the particle size. There is disagreement as to the role of various forces for the attachment of large and small particles. Particles may slide to the back of the bubble after attachment, creating a cap in which excess pressure may cause detachment.

It would be helpful to investigate some of the aspects of particlebubble attachment that are not understood clearly. Experimental work in this area could be carried out by means of a captive bubble technique which would allow better control of conditions by eliminating problems associated with uncontrollable bubble rise. A flow of liquid past a captive bubble can be used to simulate the rise of a bubble in a liquid. Some suggested experiments are:

1. In the absence of bubble rise, determine the extent of particle capture as a function of particle size, bubble size, and flow rate.
2. Investigate the extent of particle capture as a function of particle hydrophobicity. This could give insight into the mechanism of particle capture. The particle hydrophobicity can be varied by addition of surfactant.
3. Determine the effect of added electrolytes on particle capture.
4. Determine bubble coverage as a function of bubble size and flow rate.
5. There is disagreement concerning the role of gravity in particlebubble attachment. A possible experiment for low gravity conditions is to observe what effect the absence of gravity has on particlebubble interaction.
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