GAS NUCLEATION AND CAVITATION IN FLOTATION

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To the memory of

my father
If you can conquer yourself, you can conquer the whole world.

--- anonymous

To my family -

my mother,

my wife and

my children.

To myself -

my past,

my present and

my future.

To my friends -

known,

unknown and

going to be known.
ABSTRACT

The role of gas nucleation and cavitation in flotation has been systematically studied. It was shown theoretically that about a 10 m high recovery zone is required to ensure at least one collision between a particle less than 10 μm and a bubble, under conventional column flotation conditions, indicating that the collision is the rate limiting step for fine particle flotation. Direct formation of small bubbles on hydrophobic particle surfaces and in slurry by gas nucleation and cavitation has, therefore, been exploited as a way to accelerate the fine particle collection rate.

Experimentally, the existence of gas nuclei in water was demonstrated from coagulation, sedimentation and filtration tests of fine coal (d₅₀ ≈ 5 μm) and silica (d₅₀ ≈ 3.5 μm) particles. Small bubbles are generated from the expansion of the pre-existing gas nuclei by hydrodynamic cavitation induced by flow of liquid through a nozzle at a velocity of 8 - 15 m/s, depending on nozzle diameter and length. This velocity of bubble initiation is reduced to 5 - 7 m/s when the liquid is gas-supersaturated. Surfactants do not affect the on-set of bubble formation by cavitation, but increase the amount of bubbles formed. The addition of a small amount of hydrophobic particles in gas-supersaturated systems increases the quantity of bubbles generated, while the presence of hydrophilic particles reduces bubble formation.

Dissolved air (or carbon dioxide) flotation of fine silica (d₅₀ ≈ 1.6 μm) has shown that recovery increases with the slurry flow velocity, regardless of the saturation pressures applied (102 - 310 kPa). Releasing the gas-supersaturated slurry into a solution gives a higher recovery than releasing the gas-supersaturated solution into a slurry. These observations suggest that bubble nucleation is a better mechanism for enhancing particle collection compared with the direct particle-bubble contact.
Flotation results using a newly designed flotation reactor indicate that adding a cavitation tube and a small amount of air in the feed stream increases recovery significantly, and that bubbles formed by hydrodynamic cavitation play a role in improving flotation kinetics, even in the absence of added gas in the stream.
RÉSUMÉ

Une étude systématique du rôle de la nucléation des gaz et de la cavitation dans la flotaison a été effectuée. Il a été montré théoriquement que dans des conditions conventionnelles d'utilisation de la colonne de flotaison, une zone de recouvrement d'approximativement 10 m est requise afin d'entre assurer d'au moins une collision entre une particule de moins de 10 μm et une bulle. Ce résultat indique que la collision est l'étape déterminante pour la flotaison des fines particules. La formation directe de bulles à la surface de particules hydrophobiques ainsi que dans la solution, par nucléation des gaz et cavitation, a été utilisée afin d'accélérer le recouvrement des particules fines.

L'existence de nuclei gazeux dans l'eau a été démontrée expérimentalement par des tests de coagulation, de sédimentation, et de filtration pour des fines particules de charbon (d50 ≈ 5 μm) et de silica (d50 ≈ 3.5 μm). Les petites bulles sont générées par l'expansion de nuclei gazeux pré-existant, par un mécanisme de cavitation hydrodynamique induite par le passage d'un liquide à travers une canule, à une vitesse de 8 à 15 m/s dépendant du diamètre et de la longueur de la canule. Cette vitesse de formation des bulles est réduite à 5 - 7 m/s quand le liquide est supersaturé en gaz. L'utilisation de surfactants ne modifie pas les conditions de formation des bulles par cavitation, mais augmente le nombre de bulles formées. L'addition d'une petite quantité de particules hydrophobiques dans un système supersaturé en gaz augmente la quantité de bulles générées, alors que la présence de particules hydrophiles réduit la quantité de bulles formées.

La flotaison de fines particules de silica (d50 ≈ 1.6 μm) par une mixture saturée en air (ou en dioxyde de carbone) a démontré que le recouvrement augmente lorsque que la vitesse d'écoulement de la mixture augmente, et ce indépendamment de la pression de supersaturation utilisée (102 - 310 kPa). Il a aussi été montré que l'introduction d'une mixture supersaturée en gaz dans une solution réussie en un meilleur recouvrement que
l'introduction d'une solution supersaturée en gases dans une mixture. Ces observations indiquent que pour augmenter le recouvrement des particules, la nucléation des bulles est un mécanisme préférable à la méthode directe de contact bulle-particule.

Les résultats obtenus dans ce réacteur de flotaison nouvellement conçu indiquent que l'addition d'un tube de cavitation ainsi qu'une faible quantité d'air dans le flot d'alimentation améliorent le recouvrement de façon notable. Ces résultats montrent aussi que les bulles formées par cavitation hydrodynamique jouent un rôle dans l'amélioration de la cinétique de flotaison, même en l'absence de gases ajoutés dans le flot d'alimentation.
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LIST OF SYMBOLS

A  bubble surface area.
A_r  the filtration area (m²)
\( a_{11} \)  coefficient (Eq. 3-15)
\( a_{21} \)  coefficient (Eq. 3-16)
b  the half lateral length of liquid envelope enclosing a gas bubble (Eq. 3-3)
c  constant (Eq. 2-1)
C  percent solids in the supernatant (Eq. 6-1)
\( C_b \)  coefficient related to the blade factor and the effect of the acceleration of liquid over the surface of the blade (Eq. 2-3)
\( C_c \)  coefficient related to the contraction of flow (Eq. 4-4)
\( C_o \)  percent solids in the initial slurry (Eq. 6-1)
\( c_o \)  equilibrium concentration of the gas in liquid at \( P_o \) (Eq. 5-1)
\( c_s \)  the saturation concentration of the gas in liquid at \( P_s \)
d  diameter of the nozzle
D  diameter of the main stream tube
d_s  volumetric mean diameter of an aggregate
d_g  diameter of gas nuclei
\( D_L \)  gas diffusion coefficient in the absence of adsorbed films at the gas/liquid interface
\( D_{Lr} \)  gas diffusion coefficient in the presence of adsorbed films at the gas/liquid interface
d_p  diameter of a particle
\( E_c \)  the settling efficiency (Eq. 6-1)
h  the depth of a blade immersed in water (Eq. 2-3)
H  Henry's constant
H, agitation zone height  
H, froth zone height  
H, energy loss due to contraction of the flow  
H, recovery zone height (cm)  
H, min minimum recovery zone height (cm)  
l, photoelectric current  
l, background photoelectric current  
J, superficial gas velocity (cm/s)  
J, superficial liquid velocity (cm/s)  
k floatation rate constant  
K, bubble interaction coefficient  
K, cavitation number  
K, incipient cavitation number  
K, gas cav gaseous cavitation number  
K, vap cav vaporous cavitation number  
L length of the nozzle  
L, the distance between the neighboring two layers of bubbles (Eq. 3-3) (cm)  
L, thickness of the cake at time t (m)  
l length of the tip  
N the total number of layers of bubbles in a column  
n b the total number of bubbles in each layer  
N b the number of bubbles  
n, the number of molecules of species i within a bubble  
N, the rotational speed of the impeller  
P pressure  
P b bubble internal pressure  
P(C, the probability of a particle dropping from the (i-1)th layer and colliding with a bubble in the ith layer  
P(C, the probability of a particle escaping from the bubbles in the ith layer when dropping from the (i-1)th layer
**LIST OF SYMBOLS**

- $P_{i,i}$: the overall probability of a particle dropping from the first layer and colliding with bubbles in the $i$th layer.
- $P_{i,i}^c$: the overall probability of a particle dropping from the first layer and not colliding with bubbles in the $i$th layer.
- $P_g$: the collision probability due to the gravitational effect
- $P_{ic}$: the collision probability due to the interceptional effect
- $P_i$: static pressure of liquid at point $i$
- $P_{vac}$: the local static pressure in a liquid stream (Eq. 2-4)
- $P_{sa}$: the sum of the collision probability (Eq. 3-6)
- $P_{rs}$: the supersaturation pressure
- $P_{st}$: the supersaturation pressure
- $P_{r}$: pressure difference across the cake and the medium (Pa)
- $P_{tc}$: the overall particle-bubble collision probability in a column
- $P_{vap}$: vapor pressure of liquid
- $r^*$: the inverse of the permeability coefficient for the modified Darcy expression (1/m$^2$)
- $R$: the support medium resistance (1/m$^2$) (Eq. 6-5)
- $R_b$: bubble radius (cm)
- $R_{bc}$: the critical radius of a bubble (Eq. 5-1)
- $R_{bi}$: the radius of bubbles at the $i$th layer from the top (cm)
- $R_c$: recovery
- $r_p$: particle radius (cm)
- $r_s$: the specific resistance (m/kg)
- $R_t$: bubble radius after time $t$ (Eq. 5-2)
- $Re_b$: bubble Reynolds number
- $Re_{bs}$: bubble Reynolds number in a bubble swarm system ($= 2R_bV_s\rho_f/\mu_f$)
- $t$: time
- $U$: voltage applied (v)
- $V_s$: settling velocity of an aggregate
LIST OF SYMBOLS

$V_b$ the bubble volume
$V_{ba}$ average bubble rise velocity in a bubble swarm (cm/s)
$V_i$ liquid flow velocity at point i
$V_{loc}$ local liquid flow velocity
$V_\alpha$ the filtrate volume at time t (m$^3$)
$V_p$ particle settling velocity in slurry bubble column (cm/s)
$V_{sl}$ slip velocity between bubbles and liquid [$= U_{ba} + J/(1 - c_{en})$] (cm/s)
$V_t$ the volume of liquid (slurry) remaining in a receiving vessel (Eq. 5-1)
$W_c$ the wight of concentrate
$W_t$ the weight of tailings

Greek Symbols

$\Sigma F$ the energy consumed for bubble formation in the tip
$\Sigma H_i$ the energy losses due to flow contraction, expansion and/or friction
$\Sigma W$ the total energy consumed in the flow
$\varepsilon_s$ gas holdup
$\varepsilon_{si}$ gas holdup at the point i from the top
$\rho_a$ apparent density of an aggregate
$\rho_l$ liquid density (g/cm$^3$)
$\rho_p$ particle (oil droplet) density (g/cm$^3$)
$\mu$ viscosity of slurry (N/s.m$^2$)
$\mu_l$ liquid viscosity
$\mu_{bi}$ gas molecular chemical potential of species i within a bubble
$\mu_{li}$ gas molecular chemical potential of species i in the bulk liquid
$\theta_c$ grazing angle
$\sigma$ liquid/air surface tension
$\sigma_{lg}$ liquid/air surface tension
$\delta$ the thickness of the adsorbed film.
$\omega$ mass of cake deposited per unit volume of filtrate (kg/m$^3$)
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CHAPTER 1

INTRODUCTION

Jameson [1984] predicted, in his review article on bubbles, that further studies on the interactions between bubbles and particles could lead to results of practical importance in the design of flotation cells. This has been borne out by the dramatic worldwide commercial utilization of flotation columns in the last decade, partly due to the pioneering fundamental and experimental work conducted by the mineral processing group at McGill University [Finch and Dobby, 1990, 1991; Dobby and Finch, 1991; Finch, et al., 1995]. The challenge of fine particle flotation and the example of the successful application of column flotation have brought a burst of new flotation cell designs to the mineral industry (e.g., Jameson cells [1988], pneumatic cells [Bahr, 1985], microbubble flotation cells [Yoon, et al., 1988; Adel, et al., 1991], bubble-injected hydrocyclone flotation cells [Miller et al., 1988; Jordan and Susko, 1992], Ken-float cells [Parekh and Groppo, 1990], contact cells [Amelunxen, 1993], centrifloat cells [Finch, 1995], etc.). However, the exact mechanisms for the fast flotation kinetics claimed by some of these new cells are still unclear. It is an urgent task for researchers to provide sound interpretations, both theoretical and experimental, to enable industry to confidently approach the new technology.

In general, flotation can be macroscopically divided into two processes: selective collection of hydrophobic particles by bubbles, and separation of hydrophobic particle-bubble aggregates from hydrophilic particles. A flotation machine should be designed to provide an optimal environment for capturing and transporting hydrophobic particles away
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1.1 DEVELOPMENTS IN FLOTATION CELL DESIGNS

1.1.1 Mechanical Cells

Since the commercial application of flotation at the early part of this century, mechanical subaeration flotation machines have dominated in mineral processing. The important features of the cells are shown in Fig. 1.1. In the agitation zone, solids are suspended by mechanical agitation, which also serves to generate bubbles by shearing and dispersing the air stream introduced at the base of the cell. Particles and bubbles interact in the recovery (or mixing) zone, with hydrophobic particles attaching to bubbles which rise to the froth zone. Vigorous agitation is normally required to prevent sanding at the base of the cell and to generate bubbles with suitable sizes for flotation (0.5 - 3 mm). Different designs of impeller, such as the Denver, Agitair, Wemco, Outokumpu, etc., have been developed to provide a suitable environment for flotation.

From the particle collection point of view, while it is necessary to agitate to increase the probability of particle-bubble contact, vigorous agitation may disrupt the particle-bubble
Figure 1.1 Schematic of a mechanical subaeration flotation cell
aggregates, i.e., increase the probability of particle detachment from the bubble. In addition, even if established conditions are well suited to collection, it is not clear whether it may be suited to product transport.

In this regard, another inherent limitation with mechanical cells is the recovery of fine hydrophilic particles by mechanical entrainment, which is a function of water recovery. In this case, particles are recovered with the water reporting to the froth product, due to their entrainment within the bubble wake and liquid film. The conventional method of minimizing entrainment is to create a 5 - 30 cm deep froth on the slurry surface [Dobby, 1984], which permits the gangue to drain back to the pulp. It is, however, impossible to eliminate the entrainment in a single cell because water is an essential component of the froth zone. The relationship between the recovery of hydrophilic particles with different sizes and water recovery has been reported [Trahar, 1981], which showed that recovery of - 5 μm quartz was 72% of the water recovery. To eliminate entrained particles, froth products are re-pulped and re-floated in cleaning stages. As a result, capital and operating costs increase compared to a single (roughing) stage.

The third disadvantage of mechanical subaeration cells is the amount of air induced by mechanical agitation is limited, and gas holdup in the cells is normally < 10% [Amelunxen, 1993], which indicates the air/liquid interfacial area is not large. Since flotation is a process of transporting hydrophobic particles on the air bubble surface, the limited interfacial area may affect the particle collection rates.

1.1.2. Flotation Columns

Flotation columns were patented in 1960's, and the first commercial flotation column in the Western World was installed at Les Mines Gaspé (Québec, Canada) in 1981 [Finch and Dobby, 1990]. Flotation columns are now commonly used in flotation circuits, especially in the cleaning stages.
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wash water
(0.05 - 0.3 cm/s)

feed
(1 cm/s)

sparger

concentrate

interface

bubbles
(dia. 0.5 - 3 mm)

gas
(0.5 < Jg < 3 cm/s)

tails (1 cm/s)

Figure 1.2 Schematic of Canadian or conventional flotation column
Three distinguishing features of flotation columns (Fig. 1.2) are the use of a sparger to generate bubbles near the base, a counter-current slurry/bubble flow in the collection zone, and a deep froth zone (0.5 - 2 m) coupled with the use of wash water to induce a "cleaning action." [Finch et al., 1995]

Rapid development of bubble generators for use in flotation columns has occurred over the last decade. From the initial porous spargers (cloth, rubber or stainless steel), installed near the bottom of the column to generate bubbles by injecting compressed air, to jetting techniques (U.S. Bureau of Mines, Cominco and Minnovex [Dobby and Finch, 1991], Flotaire [Rubinstein, 1995]) and external spargers (microcell [Yoon, et al., 1988]), the effort has been to avoid plugging and maintenance problems, and to some extent to control bubble size. The more recent external spargers use in-line static mixers [Yoon, et al. 1988; Jordan and Susko, 1992] to generate bubbles by shearing the air stream in a slurry stream, drawn either from the feed [Jordan and Susko, 1992; Xu, et al., 1994], or from column contents [Yoon, et al., 1988]. This promotes intimate contact between particles and bubbles in the stream. By adjusting the slurry flow and air rates, some control over bubble size is obtained.

Compared with mechanical cells, a major advantage of column cells is that they are cheap in capital and installation cost per unit residence time. Another reason for the acceptance and successful application of flotation columns in the mineral industry is the use of wash water added to the froth zone. This feature, in particular, distinguishes flotation columns from the pneumatic cells developed in the early days of flotation [Gahl, 1916], and the cells in China [Hu, et al., 1980; Liu and Hu, 1988] and Russia [Rubinstein, 1993, 1995]. Wash water serves to stabilize the froth, suppress feed water reporting to the froth product, and drive the entrapped gangue particles back to the pulp, thus permitting high upgrading in a single stage.

While the use of wash water and the counter current transport process contribute to enhanced separation efficiency, flotation columns offer no more improved mechanisms
over mechanical cells as far as the particle collection process is concerned, except perhaps to reduce detachment resulting from the quiescent conditions. However, it has been claimed that a column can achieve grades and recoveries superior to those from banks of mechanical cells, and that the superiority of the column increases as the particle size decreases [Flint, 1973]. It seems that the high recoveries arise from reduced detachment probability achieved in the flotation column. Another reason may be that high upgrading by wash water pushes the grade/recovery curve to a new, higher location portion, compared with that without wash water.

Although the quiescent, counter-current flow used in flotation columns may be ideal for theoretical analysis of particle-bubble interaction, it imposes limitations in practical situations for fine particle flotation, where fine bubbles and energy intensive conditions are required [Spears and Stanley, 1990]. If very fine bubbles (which have very low rise velocities in a bubble swarm) are used in a flotation column, the superficial slurry flow velocity in the column (the slurry flow rate per unit sectional area of the column) has to be reduced to avoid "flooding", i.e., the transition of uniform counter-current flow to regions of co-current downward flow. Some fine bubbles (alone or with loaded particles) may be drawn downwards, thus reporting as part of the non-floatable product [Luttrell et al., 1987]. This suggests that counter-current flow may be a disadvantage for fine particle flotation using fine bubbles.

The quiescent flow conditions in the column are not conducive to high flotation kinetics since the collision frequency between particles and bubbles is a function of shear rates, or turbulence. Although flotation columns are suggested as an alternative for fine particle flotation [Fuerstenau, 1980; Sivamohan, 1990], there is no fundamental basis nor practical evidence which indicates that flotation columns alone, under conventional flotation conditions, can be used to recover ultrafine particles, say, less than 10 μm, at an acceptable rate.
1.1.3. Reactor-separator design

The two sub-functions of a flotation machine, i.e., particle collection by bubbles and transport of particle products, are recognized in mechanical cell designs. The trend in mechanical cell development is the increase in the cell volume partly to provide a quiescent area above the impellers [Flint, 1973], and partly to reduce unit cost and maintenance cost - single train flotation plants are easier to control. However, it is difficult to optimize conditions to satisfy both particle collection and transport functions simultaneously in one cell, and the current design of flotation machines is a compromise between these two. Such a compromise may limit the overall performance [Finch, 1995].

The reactor-separator concept has been proposed [Li and Bahr, 1992; Finch, 1995], therefore, to insolate the two functions (Fig. 1.3). These two functions can be optimized independently and an overall improvement in machine performance may result. In the conceptual designs, the reactor provides vigorous particle-bubble interaction by high energy dissipation and high shear rates, while the separator provides quiescent conditions for particle-bubble aggregate/slurry disengagement with wash water added to limit mechanical entrainment.

The reactor-separator concept has been incorporated in some new flotation cells, such as the Jameson cell, the Bahr pneumatic cell, contact cell, etc. [Finch, 1995]. High collection kinetics has been achieved. The increased flotation kinetics in these cells may be attributed to the high energy dissipation and high shear rate developed in the reactor, which increase both the particle-bubble contact frequency and the kinetic energy to overcome the energy barrier between particles and bubbles [Jordan and Spears, 1990].

High shear rates also provide other potentially important functions. Slime coating may be minimized by removing fines attached on coarse particles due to attrition under high shear [Valderrama, et al., 1995]. Surface oxidization products may be removed [Smart, 1991]. In addition, high shear rates may also induce particle aggregation by hydrophobic flocculation (or shear-flocculation) [Warren, 1975a, b; Bilge, et al., 1994; Raju, et al..]
Figure 1.3  The general concept of the reactor/separator design of flotation machine
1991: Jordan and Stanley, 1994: Bulatovic, et al., 1995], and generate tiny bubbles instantaneously on hydrophobic particle surfaces and in the slurry by cavitation, which also enhance particle collection. Which mechanism dominates the collection is yet to be determined. It is reasonable to expect that understanding particle collection mechanisms may give rise to the next generation of flotation cells, especially for fine particle separation.

1.2. OBJECTIVES AND ORGANIZATION OF THESIS

1.2.1. Objectives

The first objective of the present work is to review and evaluate the potential application of new flotation technologies by systematically analyzing and exploring the role of gas nucleation and cavitation in flotation and flotation cell designs. Particle-bubble collision in bubble swarms will be explored to illustrate the combined effect of bubble size, gas holdup and bubble-bubble interaction on the requirement of minimum particle recovery zone height, and the importance of employing shearing flow conditions in the cell to increase the contact frequency of particles with bubbles.

As most new cells are employing relatively high pressures and velocities in the feed stream, the second objective is to explore experimentally the generation of small bubbles by hydrodynamic cavitation and by gas-supersaturation, and to evaluate the role of such bubbles in promoting particle collection under these conditions.

Since gas nucleation on particle surfaces eliminates the collision stage, it may provide an exploitable mechanism. Hence, the third objective is to demonstrate experimentally the existence of gas nuclei in water and explore their effect on particle/particle, particle/bubble interactions, which provides a fundamental basis for applying cavitation principles in flotation cell design.
CHAPTER 1 INTRODUCTION

Based on the aforementioned, the fourth objective is to design and test a new reactor for fine particle flotation, and experimentally demonstrate the possible application of cavitation and gas nucleation in accelerating fine particle collection during flotation processes.

1.2.2. Organization of Thesis

The thesis is a summary and condensation of some results from the following 10 papers either published, submitted, in preparation, or presented at conferences during the Ph.D. program:


CHAPTER 1 INTRODUCTION

In chapter one, a brief introduction to the objectives and organization of the thesis is given. Chapter two is a review of cavitation in flotation. An attempt is made to identify the mechanisms for the accelerated particle collection rates in some of the new flotation cells. The role of gas nuclei and tiny bubbles in flotation in these cells is emphasized, and a two-stage attachment model is used as a possible explanation for the observed high flotation rates.

Chapter three discusses particle-bubble collision in bubble swarm systems. A model is developed to predict the minimum recovery zone height in flotation columns. The collision stage is analyzed as a limiting factor for fine particle flotation. Using fine bubbles and high shear rates is therefore recognized as an approach to enhance fine particle flotation.

Chapters four and five concern small bubble generation by hydrodynamic cavitation and gas-supersaturation. Different physical and chemical factors are examined, and the role of pre-existing gas nuclei, surfactants, and dissolved gas on bubble formation is identified.

Chapter six discusses the interaction between gas nuclei and fine particles. The existence of gas nuclei in water and their effect on particle-particle, particle-bubble interaction are
demonstrated by coagulation, sedimentation and filtration tests of fine coal and silica.

Chapter seven discusses fine particle flotation and the design of a new flotation reactor based on cavitation principles. Preliminary tests of the reactor on flotation of fine silica are described, and the role of bubble nucleation and the applicability of a two-stage attachment model are demonstrated.

The general conclusions for the thesis are given in Chapter eight.
CHAPTER 2

CAVITATION IN FLOTATION:
A BRIEF REVIEW*

2.1. INTRODUCTION

Cavitation means the creation and growth of a "hole" in a liquid (i.e., gas and/or vapor filled void) [Westwater, 1964; Robertson, 1969; Young, 1989], with the first stage of cavitation, i.e., the creation or birth of cavities being defined as nucleation [Westwater, 1964]. In other words, nucleation/cavitation is a process whereby the liquid structure is ruptured to form a hole by external forces. It is evident that any rupture must have started at a "weak" location where the intermolecular forces momentarily approached zero [Pease and Blinks, 1947]. Such weak points exist in flotation systems because of the presence of hydrophobic particles. If particle-bubble attachment occurs by the nucleation of a bubble on a particle surface, there will be no need for the collision stage which is often a rate limiting step in conventional flotation. Therefore, nucleation/cavitation may provide an exploitable mechanism for particle collection in flotation.

* A revised version of this chapter, co-authored by Z. A. Zhou, Zhenghe Xu, and J. A. Finch, has been published in *Minerals Engineering*, 7(9), 1073-1084 (1994)
The theoretical basis of flotation by gas precipitation was proposed by Klassen and coworkers more than three decades ago [Klassen, 1960; Klassen and Mokrousov, 1963; Glembotskii et al., 1963]. They showed that, for strongly hydrophobic particles, the energy required to generate a new bubble on a solid surface is considerably lower than the energy expended to form a bubble in the bulk water and then attach it to a mineral particle. Therefore, they postulated that collection of mineral particles will occur preferably through micro-bubble formation on the mineral ("nascent bubble flotation" [Crozier, 1992]) rather than by attachment of existing bubbles to a suspended particle. They used vacuum and dissolved air flotation tests to support their hypothesis. However, this theory was mainly established on thermodynamic reasoning and failed to consider whether it is physically possible for bubbles to form on particle surfaces by precipitation of gas under the typical pressures encountered in dissolved air flotation (3-5 atm). Furthermore, questions related to the interaction of dissolved gas with liquid and solids were not addressed. This chapter reviews and discusses the process, the role and the application of cavitation and gas nucleation in flotation.

2.2. BUBBLE FORMATION

For gas-supersaturated systems such as in dissolved air flotation or vacuum flotation, the formation of bubbles occurs as a result of various interactions between the liquid, the solid particles and dissolved gas. Bubble formation events are triggered by energy and density fluctuations at the molecular level not readily predictable from the continuum macroscopic equilibrium properties of the liquid-gas system [Hemmingsen, 1978]. It is generally accepted that water undergoes very rapid fluctuations in molecular density and structural configurations due to the random motion of the water molecules individually or in clusters, leading to a continuous formation and collapse of molecular voids [Hemmingsen, 1978]. It is likely that such voids serve as the foci, or nuclei, for the initial cavities. On the other hand, gas molecules dissolved in water may occupy some of
these structural voids [Schroder, 1969]. Successful bubble nucleation depends on the availability of a large number of adjacent gas molecules, which must simultaneously obtain sufficient kinetic energy to overcome the forces of attraction between them to enter into and be retained in the void to prevent its immediate collapse [Dean, 1944]. This requires that the gas have a higher tendency to transfer from the water to the "gas phase" by diffusion than in the reverse direction. However, such voids rarely have radii greater than 10-20 Å, and their lifetimes are in the order of $10^{-12}$ second or less [Walstra, 1989; Yount, 1989]. If such voids could survive, they would have to withstand a pressure of about 1440 atm [Yount and Kunkle, 1975; Walstra, 1989]. Therefore, spontaneous homogeneous nucleation of gas bubbles in a supersaturated liquid should not occur under practical conditions [Walstra, 1989].

However, samples of sea water, tap water, or even distilled water form visible bubbles when subjected to tensile, ultrasonic, or supersaturation pressures as small as 1 atm [Yount, 1979]. In dissolved air flotation, usually 3-5 atm pressures are used to generate a sufficient amount of tiny bubbles (< 100 μm) to float aggregates and fine minerals [Zabel et al., 1980; Gochin and Solari, 1983; Zabel, 1992]. This level of pressure is two orders of magnitude lower than the supersaturation required for spontaneous nucleation of bubbles in bulk water [Hemmingsen, 1975, 1977; Gerth and Hemmingsen, 1976; Finkelstein and Tamir, 1985], and it implies that cavitation must be initiated by processes other than modest changes in pressure and the random motion of water and gas molecules [Yount, 1979].

### 2.2.1. Cavitation by Supersaturation

The fact that the actual gas-supersaturation pressure used to initiate bubble formation is much smaller than the theoretical tensile strength of pure water has suggested alternative mechanisms of bubble formation in gas supersaturated water. In such systems inhomogeneities must have been present in the liquids [Flynn, 1964]. This includes pre-
existing gas nuclei, gases trapped in crevices of solid particles and cracks in the container walls.

2.2.1.1. Heterogeneous nucleation model

Plesset [1969] attributed the much lower than predicted cavitation thresholds to the existence of tiny solid particles in water, based on the fact that real liquids are always contaminated with more or less impurities, even in the highly denucleated water used in obtaining such limits on de novo formation of bubbles [Apfel, 1970; Holl, 1970]. He thus proposed a physical model to describe the heterogeneous nucleation process, which consisted of a solid sphere of radius \( r_o \), surrounded by a concentric vapor phase that extended to the larger radius \( r \). This system was modelled by the canonical distribution of statistical mechanics to estimate the probability of bubble formation due to the changes in the free energy of the system. This model was further modified by Yount and Kunkle [1975], who imposed the condition that the thickness of the vapor shell around the solid sphere must be larger than the average distance between molecules in water (i.e., \(-3\,\text{Å}\)). They concluded that smooth spheres of any size, whether hydrophobic or not, can only reduce the tensile strength of water by at most 30%. Such particles are not effective in generating a vapor phase when the sphere radii are greater than about 10 Å. This indicates that theoretically a supersaturation pressure of about 1000 atm is still needed to generate cavities. Recent investigations by Ryan and Hemmingsen [1993] and Ryan [1991], using particles with a diameter of 1 to 2.5 \( \mu \text{m} \), demonstrated that smooth surfaces, no matter whether hydrophilic or hydrophobic in nature, do not facilitate gas bubble formation by dissolved gas in water at pressures up to 50-120 atm \( \text{N}_2 \). Therefore, the presence of solids can not account for the fact that experimental tensile strengths for water are far below the predictions from homogeneous nucleation theory. This also indicates that the gas precipitation mechanism for bubble-particle attachment in dissolved air flotation proposed by Klassen and coworkers, as discussed earlier, may not be adequate, because a sudden release of pressure from 5 atm to ambient pressure would not be sufficient to generate bubbles by precipitating gas on particle surfaces, or to tear the
2.2.1.2. The crevice model

Despite the above arguments, there are ample examples [Dean, 1944; Hemmingsen et al., 1990; Ryan and Hemmingsen, 1993] which show that particles can promote bubble formation, even at gas supersaturation of 5 atm or less: the requirements appear to be a hydrophobic and rough surface. When crystals with hydrophobic surfaces were precipitated from salt solutions, bubbles formed at gas supersaturation of a few atmospheres [Yount and Kunkle, 1975; Gerth and Hemmingsen, 1980]. But if outgassed by heating and quenching in water, even graphite was unable to promote bubble formation [Dean, 1944]. Therefore, it was suggested that the solids promoted bubble formation due to air trapped in capillary spaces on the rough surfaces. This was extended to include capillary spaces and cracks both in the wall of the container and in dust particles always present in the liquid [Dean, 1944; Harvey et al., 1944; Ryan, 1991], and this process has been modelled by numerous researchers [Flynn, 1964; Apfel, 1970; Winterson, 1977; Wilt, 1986; Trevena, 1987].

In flotation, mineral particles are always irregular in shape with rough surfaces. The surfaces of mineral crystals contain minute microscopic cracks [Klassen and Mokrousov, 1963; Gregg and Sing, 1976]. These cracks, which are separated from each other by tens to hundreds of atoms, result from a shrinkage of the surface caused by the presence of non-equilibrated forces. Taking coal as an example, about 80 percent of the pores appearing on the surface have a diameter less than 10 μm [Klassen and Mokrousov, 1963].

The adsorption of gases on solids has long been associated with the presence of cracks or pores [Gregg and Sing, 1976]. If particles are not fully wetted, the crevice model proposed above may account for part of the bubble-particle attachment observed after releasing the pressure, because of the gas entrapped in surface crevices. This may explain...
why some particles can be floated under aspiration, as in the case of vacuum flotation. However, the crevice model may not be applicable to the particles originally hydrophilic in nature, but chemically rendered hydrophobic (e.g., in a conditioning tank), because initially gas would not be entrapped or retained in the crevices of such particles. A possible explanation for the attachment mechanism in this case may be as follows: gas nuclei existing in the slurry attach to the particle surface, and then after release of the pressure, these gas nuclei collect all of the gas molecules dissolved within their neighborhood [Yount and Strauss, 1976] and expand to become visible bubbles. An alternative explanation could be due to hydrodynamic cavitation when slurry passes through restriction regions where pressure is reduced (e.g., nozzles). This latter possibility will be entertained later.

2.2.1.3. Free gas nuclei and the Varying Permeability (VP) model

In practice, engineers approach the problem of low threshold bubble formation on the assumption that free gas nuclei are present in all "real" fluids [Ryan, 1991]. It has been directly observed [Johnson and Cooke, 1981; Yount et al., 1984; Yount, 1989] that bubbles less than 1 \( \mu \text{m} \) up to as large as 15 \( \mu \text{m} \) in diameter can be stabilized in seawater, distilled water and in blood. It is difficult to see how such a gas nucleus could survive and be stabilized in water. Due to the surface tension \( \sigma \), the internal pressure of a spherical gas bubble of radius \( R_b \) is higher than the pressure in the surrounding liquid by \( 2\sigma /R_b \).

According to Henry's law, the solubility of a gas in a liquid is proportional to the gas pressure. Therefore, for a small bubble, the enclosed gas should quickly dissolve or flow outward into the surrounding liquid until the radius diminishes to zero.

Basically, the rate of growth or collapse of a bubble in a liquid can be regulated at least by one of the following three mechanisms [Epstein and Plesset, 1950; Westwater, 1964]: mechanical force, heat and mass transfer, with in general, the latter being the dominant factor. Fox and Herzfeld [1954] postulated that the stabilization of tiny bubbles is caused by a "skin" or film of organic impurity surrounding a spherical gas bubble in the body.
of a liquid. Such a skin might give some structural integrity to the bubble and inhibit diffusion of gas out of the bubble into the liquid. This theory was further extended and improved by Yount [1979; 1982; 1989; Yount and Yeung, 1981], who proposed a varying permeability (VP) model, or surfactant model to explain the stability of gas nuclei. The essence of this model is that a cavitation nucleus consists of a spherical gas phase, covered by a film of surface-active molecules, that is small enough to remain in solution but strong enough to resist collapse, the mechanical compression strength being provided by the elasticity of the film of surface-active molecules. Ordinarily, VP films are gas permeable, but they can become effectively impermeable when the skin molecules are tightly packed under high compressions, typically exceeding 8 atm. However, recent communication with Hemmingsen [1993] indicated that the attempt to experimentally repeat and verify the VP model by them was unsuccessful: the bubble formation did not follow the pattern reported by Yount and the VP model.

Another difficulty in this area is how to predict the bubble size after the release of pressure. For gas supersaturated systems, thermodynamic analysis shows [Blander and Katz, 1975; Blander, 1979; Takahashi et al., 1979] that to every supersaturation pressure \( p_{\text{sat}} \) a corresponding critical radius \( R_{\text{cr}} \) exists such that any gas phase (or gas nucleus) in the liquid with characteristic radius larger than \( R_{\text{cr}} \) following decompression will grow into a macroscopic bubble, and those with a size less than \( R_{\text{cr}} \) would shrink to zero spontaneously. However, due to the film of adsorbed surfactants, which provide the mechanical strength to oppose any changes, the actual expansion and compression of gas nuclei may not be predictable from the thermodynamic analysis, depending on system variables. Yount and Strauss [1976] demonstrated that the procedure of gas supersaturation has a great effect on the stability of gas nuclei. Slow compression permits some diffusion of gas into nuclei, allowing the nuclear surfaces to remain near their equilibrium configurations and thereby resist shrinking. Gas nuclei can be crushed, and the subsequent number of bubbles greatly reduced by fast compression, due to the rapid increase in hydrostatic pressure. High and rapid rise in pressure may eliminate all the gas
nuclei in water, which has been used as a common method to obtain gas nuclei-free liquid samples [Hemmingsen, 1975, 1977; Ryan, 1991]. In order to prevent the crushing of gas nuclei in water, the supersaturation pressure should be increased slowly: a large amount of dissolved gas and a quick dispersion of gas in liquids would also help.

2.2.1.4. Ionic Skin Model

Since air bubbles themselves are usually negatively charged in pure water (because of preferential adsorption of OH\(^-\), owing to its lower hydration energy compared to H\(^+\) [Yoon and Yordan, 1986]), it is postulated that the repulsion of these like charges tends to prevent total collapse of the bubble and prevent complete dissolution of the gas in the bubble, thus stabilizing the nucleus [Mesler, 1985]. Recently, Vinogradova et al. [1995] suggested that cavitation by optical methods is associated with the submicrocavity structures of water (~10 nm). Electrostatic repulsion may lead to the dispersion of gas nuclei by avoiding collapse, while the charge on a gas nucleus can, in principle, provide possible diffusion stabilization (although the question of the diffusion stability of a submicrobubble remains unresolved).

However, the experimental work by Sirotyuk [Mesler, 1985], who investigated the stabilization of gas bubbles in highly purified water, failed to show any support for the ionic skin model.

2.2.2. Hydrodynamic Cavitation

Hydrodynamic cavitation normally occurs whenever the pressure at a point in a liquid is momentarily reduced below its vapor pressure [Hayward, 1970]. In a flowing system, the liquid is subject to local accelerations. At the points of highest velocity, low, or even negative, pressures may exist and minute air or vapor-filled bubbles open. This phenomenon was first observed by Reynolds about 100 years ago [Trevena, 1987], and can be explained by Bernoulli's equation:
in which $V$ is the water flow velocity at a point where the pressure is $P$ and $\rho$ is the density of water. The above equation can be rewritten as

$$V^2 + \frac{2P}{\rho} = \frac{2C}{\rho}$$  \hspace{1cm} (2-2)$$

It can be seen from Eq. (2-2) that if the water flow velocity $V$ exceeds $(2C/\rho)^{1/2}$ the pressure at that point in a water stream must be negative. In this situation the water tends to form cavities which expand and relieve the negative pressure [Young, 1989].

On the other hand, it is well known that propellers used in ships and other hydraulic machines which rotate at high speeds produce copious quantities of bubbles, even though no external gas is bubbled or drawn in. A practical conclusion from this observation is that bubbles can always be produced by active stirring or turbulent circulation of the liquid [Dean, 1944]. Hydrodynamic cavitation does not occur in rectilinear flow, i.e. in simple parallel non-shear flow without turbulence, since a change of direction or a convergence of streamlines is necessary [Daily and Johnson, 1956; Young, 1989]. At high turbulence, the liquid streamlines are separated or detached from an immersed obstacle, e.g., a blade or a wire, and a fixed cavity is formed which attaches to the obstacle [Young, 1989; Sato, 1992]. The relationship between the pressure $P$ on the surface of the blade immersed in water and the rotational speed of impeller $N$ was recently given by Evans et al. [1991] as:

$$P = \frac{1}{2} \rho V^2 \left( \frac{2C}{\rho} \right)^{1/2}$$
where $P_o$ is the local atmospheric pressure, $h$ is the depth of the blade immersed in water, $C_h$ is a coefficient related to the blade factor and the effect of the acceleration of liquid over the surface of the blade. This equation shows that at high impeller speeds, the pressure $P$ may approach water vapor pressure, or even become negative, thus generating cavities or vapor bubbles.

The presence of tiny pockets of undissolved gas in crevices on, say, dust or mineral particles, in the flowing stream would assist the cavitation, due to the expansion of these gas pockets under the low or negative pressures at that point. Furthermore, the existence and the shape of the particles or obstacles present in the water and the roughness of the inner wall of the water tunnel would also influence the occurrence of cavitation [Daily and Johnson, 1956; Holl, 1960a, b, 1969; Arndt and Ippen, 1968], resulting from the increased pressure fluctuations in the stream.

In order to measure the resistance of the flow to cavitation, the cavitation number $K_c$ has been introduced as [Young, 1989]

$$K_c = \frac{P_{loc} - P_{vap}}{\frac{1}{2} \rho V_{loc}^2}$$

where $P_{loc}$ is local pressure, $V_{loc}$ is local flow velocity, and $P_{vap}$ is water vapor pressure.

Cavitation occurs when the local value of $K_c$ approaches, or falls below, the incipient or
threshold cavitation number $K_i$, which can be determined experimentally (typically, $K_i < 1$). Cavitation is more easily initiated the higher the value $K_i$. If cavitation is occurring, lowering the cavitation number $K_c$ by decreasing the static pressure or by increasing the flow speed will increase the extent of cavitation [Young, 1989].

According to variations in the amount of dissolved gas and the pressure (although there is no simple dimensionless number to describe the effect of dissolved gas content), three types of streaming cavitations in a circulating water tunnel have been distinguished [Knapp, et al., 1970; Hennessy, 1989]:

a). Vaporous cavitation - normal pressure, low dissolved gas content
   - $K_i$ is low, there is a time delay in first appearance of microbubbles after the cavitation threshold is reached.

b). Gaseous cavitation - normal pressure, high dissolved gas content
   - depends on dissolved gas content and resident population of gas nuclei. the time delay decreases with increasing dissolved and free gas content, more undissolved gas creates more gas nuclei
   - for high gas content $K_i$ increases and gaseous cavitation number $K_{i, \text{gas cav}} >$ vaporous cavitation number $K_{i, \text{vap cav}}$

c). Hyperbaric cavitation - high pressure, high dissolved gas content
   - the threshold for inception of gaseous cavitation will occur at a relatively low flow speed and small pressure drop, compared with vaporous and gaseous cavitation.

From this classification, it follows that cavitation is much easier under high pressure and high dissolved gas content, as in the case of dissolved air flotation. Holl [1960; 1969; 1970] investigated the effect of air content on the occurrence of cavitation in a water tunnel, and found that the cavitation was directly proportional to the dissolved air content.
CHAPTER 2  CAVITATION IN FLOTATION: A BRIEF REVIEW

It was photographically shown [Wu, 1969] that adding organics produced smaller and many more cavities, due to the stabilization of the cavity by the adsorption of an organic film on the bubble surface, which prevented collapse and coalescence. This point is important for flotation: adding frothers may have the same effect, i.e., to protect the cavities formed from immediate collapse.

2.3. THE ROLE OF GAS NUCLEI AND MINUTE BUBBLES

It is well known that the behavior of bubbles (e.g., local velocity and motion) is important in particle collection in flotation processes. It was found by Dziensiewicz and Pryor [1950] in dynamic contact experiments that smaller bubbles attached much more readily to a polished hydrophobic surface than large bubbles. This is because large bubbles have a higher rise and rebound velocity from the surface, due to their high buoyancy force and kinetic energy. Another possible reason is that tiny bubbles have a high specific surface free energy seeking satisfaction, which can be obtained by their rapid adherence to the mineral surface. The efficient attachment of particles to conventional-sized air bubbles was significantly improved if the mineral surface was first "frosted" with tiny bubbles. This observation led Dziensiewicz and Pryor to suggest a "two-stage" attachment model: first, a conditioning stage, with no special attempt to float, but with provision of minute air-bubbles permitting first-stage attachment, i.e., frosting of the mineral surface (such bubbles may be too small to be observed under practical experimental conditions); next the attachment of particles via their frosting of minute bubbles onto relatively large air-bubbles for transport to the froth. In this way, it was suggested that flotation rate can be improved. Similar observations were reported by Horesly and Bannerji [1950] and Shimiizaka and Matsuoka [1982].

The role of tiny bubbles in accelerating particle-bubble attachment and improving flotation was elucidated by Wrobel [1952]. He distinguished the existence of gas (air) in water in
two forms, i.e., nucleated gas (submicroscopic dimensions) and dissolved gas (molecular dispersion). He proposed that the adsorption of nucleated air on to the conditioned mineral was the key to the fast attachment of large bubbles produced in flotation machines. This hypothesis was supported by his ingenious experiments, which showed: a) the removal of gas nuclei in water by subjection to high hydrostatic pressure (650 to 700 atms) made the attachment of a bubble onto a polished mineral surface more difficult; and, b) both the flotation rate and recovery were proportional to the amount of gas nuclei present in the system. Table 1 shows the comparison of galena flotation with and without hydrostatic compression. It indicates that flotation in hydrostatically compressed water gives lower recovery than that in non-compressed water, which is attributed to the removal of gas nuclei. On this argument, the water most suitable for flotation should contain an abundance of gas nuclei, the latter partly acting as the basis for air-bubble formation in flotation machines and probably as a link in the attachment of gas nuclei-activated mineral particles to large air bubbles [Wrobel, 1952].

The importance of the combination of gas nuclei and bubbles for accelerating flotation is illustrated by the experiments of Klassen and coworkers [1960; Klassen and Mokrousov, 1963]. They showed that flotation by air supersaturation combined with bubbles generated mechanically gave a higher recovery than was the case for either gas nuclei or bubbles alone. Shimoiizaka and Matsuoka [1982] also found the same trend. This supports the two-stage attachment model [Dziensiewicz and Pryor, 1950] as the explanation of increased flotation rates.

The attachment of a bubble to a mineral particle by coalescence with a frosting of tiny bubbles on its surface was termed the "coalescent" attachment mechanism by Klassen and coworkers [1960; Klassen and Mokrousov, 1963]. The feature of this process is that tiny bubbles present on the particle surface facilitate the attachment of larger bubbles and activate flotation. There are a number of factors which favor this mechanism [Klassen and Mokrousov, 1963]. First, coalescent attachment involves a greater decrease in the free
CHAPTER 2  CAVITATION IN FLOTATION:  
A BRIEF REVIEW

Table 2.1  Flotation of galena (-60 mesh) with and without hydrostatic pressurization (675 atm) (from Wrobel, [1952])

<table>
<thead>
<tr>
<th></th>
<th>Time lag</th>
<th>% Recovery in the froth after</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(s)</td>
<td>2 min.</td>
</tr>
<tr>
<td>Pressurized sample</td>
<td>50</td>
<td>22</td>
</tr>
<tr>
<td>Non-pressurized, non-aerated</td>
<td>10</td>
<td>67</td>
</tr>
<tr>
<td>Non-pressurized, aerated</td>
<td>0</td>
<td>95</td>
</tr>
<tr>
<td>After 4 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressurized sample</td>
<td>70</td>
<td>20</td>
</tr>
<tr>
<td>Non-pressurized, non-aerated</td>
<td>10</td>
<td>59</td>
</tr>
<tr>
<td>Non-pressurized, aerated</td>
<td>0</td>
<td>92</td>
</tr>
<tr>
<td>After 16 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressurized sample</td>
<td>85</td>
<td>21</td>
</tr>
<tr>
<td>Non-pressurized, non-aerated</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>Non-pressurized, aerated</td>
<td>0</td>
<td>94</td>
</tr>
</tbody>
</table>

energy of the flotation system than direct attachment, with the result that spontaneous adherence is more favorable. Second, the surface of a bubble is in general less hydrated than the surface of mineral particles. The bubble/bubble coalescence is, therefore, more favored than bubble/solid attachment. Third, the greater the difference in bubble sizes, the more rapidly they coalesce, probably resulting from thinning of the intervening water layer being driven by the high internal bubble pressure [Klassen and Mokrousov, 1963;
Another factor which has not been mentioned by previous researchers is that if gas nuclei are frosted on a mineral particle, its apparent size is increased (particularly for particles less than 10 μm), thus increasing the collision probability of the particle with bubbles. Consequently, gas nuclei function to increase both the collision and attachment efficiencies, and finally increase the flotation rate. Therefore, from a practical point of view, producing a large quantity of gas nuclei in the slurry is beneficial to flotation.

2.4. APPLICATION OF CAVITATION PRINCIPLES TO FLOTATION

Both the occurrence and significance of cavitation in flotation have been the subject of speculation almost since flotation was introduced [Taggart, 1927]. Cavitation in mechanical cells may take place during separation of liquid from the impeller blade, and in any regions of high shear and turbulence in the liquid streams [Klassen and Mokrousov, 1963]. Since the region behind a rotating impeller blade is normally at a pressure below that of the surrounding fluid, air is sucked into this region and an air cavity forms. Even in the absence of added air, cavitation may occur if the relative velocity between impeller and fluid is sufficiently large, so that the local pressure becomes lower than a critical value, e.g., the vapor pressure of the fluid [Grainger-Allen, 1970]. In this case, some bubbles may redissolve when subsequently exposed to regions of increased pressure. However, in the presence of adsorbed surfactant which retards dissolution, a considerable portion of these bubbles could take an active part in flotation [Klassen and Mokrousov, 1963]. Deliberate exploitation of bubble formation by cavitation to intensify particle-bubble interaction may improve flotation performance, especially for fine particle recovery. This makes cavitation phenomena worth investigating.
et al., 1980a, b; Zabel et al., 1980; Zabel, 1992] that introducing the air on the suction side of the recycle pump gave saturation levels (i.e., the ratio of the released amount of air from the supersaturated water to the theoretical value) from 60 to 80%, which could be increased to 90% by fitting a turbine type mixer in the saturation vessel. From the earlier discussion on cavitation, it suggests: 1) injecting air and a high dissolved gas content in water facilitate cavitation; 2) mixers increase the turbulence in the stream, and disperse the air more effectively; and the combination produces more stable cavities, which increase the gas evolution rate or saturation level for a given time.

The above argument can also be justified from the measurements made by Klassen (1960). He observed that when a frother was used, the quantity of gas released from the air-supersaturated water under dynamic conditions, over a given time interval, was higher than when no frother was added, the amount of released gas increasing with the frother concentration. The addition of hydrophobic solids also promoted gas evolution, giving a high volume of gas released. These phenomena cannot be explained by the existing theories in flotation, either from a flotation chemistry or physics point of view. Although adding surfactants affects the water vapor pressure, it is to reduce, rather than to increase it [Shinoda, 1963; Anon, 1985], which suggests that the presence of surfactants would tend to reduce gas evolution rates. However, this phenomenon can be reasonably explained from nucleation principles. As discussed earlier, adding frothers protects the cavities or gas nuclei formed from immediate collapse. These gas nuclei could have been crushed and eliminated if there was no frother present. Therefore, there are relatively more gas molecules in the form of gas aggregates or gas nuclei in the liquid. Such gas nuclei would have a size much larger than the molecules, depending on the supersaturation pressures applied [Blander, 1979], typically in the range of about 1-10 μm [Flynn, 1964; Yount, 1989], and they would have higher rise velocities (or gas transfer rates) in the liquid, thus giving higher evolution rates.

In the micro-bubble flotation columns [Yoon et al., 1988; Adel et al., 1991] and the
bubble-injected hydrocyclone flotation cells [Miller and Ye. 1989; Jordan and Susko. 1992], both high feed injection speeds and static mixers are used. The frequent change of direction or a convergence of streamlines and the pressure fluctuations in the bulk liquid caused by the mixers are anticipated to promote cavitation and nucleation. Adding air further enhances this effect and makes the cavitation easier. While it may be argued that the high flotation rates obtained by using static mixers could be mainly caused by shearing to break the air stream into small bubbles, the contact cell [Amelunxen, 1993] and Ken-float cell [Parekh and Groppo, 1990] appear to be two examples of direct exploitation of cavitation and gas nucleation. Basically, these cells can be considered as a combination of dissolved air flotation with conventional column flotation, the only main difference being that the contact cell does not have air spargers in the column. Therefore, Ken-float cells may be considered as an example of the application of two-stage attachment model, with gas nuclei and tiny bubbles generated in the dissolved air flotation chamber, and flotation-sized bubbles provided in a flotation column.

In mineral flotation, pneumatic cells [Bahr, 1985] and Jameson cells [Jameson, 1988] are reported to give high flotation rates. A key feature of these cells is a high slurry velocity, ranging from 6 to 12 m/s generated through an injection nozzle. One of the reasons for the jet is to aspirate and disperse air into the receiving chamber (a similar mechanism to that used in venturi tubes [Jackson, 1964; Jackson and Collisions, 1964] or jet pumps [BHRA, 1968]). High slurry velocities with a high concentration of solid particles could initiate cavitation in the stream and gas nucleation on the particle surface. When the feed emerges from the feed nozzle, gas nuclei in the slurry and those attached to hydrophobic particles expand, due to the sudden reduction in pressure. (The same phenomenon is often observed when turning on a tap and the water stream turns milky as a result of tiny bubbles.) These gas-nucleated particles then contact with relatively large bubbles at high gas holdups (up to 50 - 60%), which ensures high collision and attachment probabilities resulting in high flotation rates. This may be another example of the two-stage attachment process [Dziensiewicz and Pryor, 1950] in action.
2.5. SUMMARY OF CHAPTER

Compared with other particle-bubble attachment mechanisms, cavitation/gas nucleation is a rapid process. Its possible application in accelerating flotation rates is therefore attractive. Generating a large quantity of gas nuclei in a slurry should be beneficial to flotation performance. Gas nuclei (cavities) and tiny bubbles can be generated, according to cavitation principles, by strong shear or turbulence and high fluid velocities which create the necessary pressure fluctuations in the bulk liquid so that at some locations the pressure drops below a critical value. A high dissolved gas content, the presence of solid particles in the liquid and the surface roughness of the container and particles facilitate the initiation of cavities. Whether the gas nuclei will stabilize, and grow or collapse is determined by the mechanical strength of any surface film of adsorbed surfactants and gas diffusion rates. High dissolved gas content in a liquid will accelerate the rate of gas diffusion into and retention by the cavities thus preventing their immediate collapse. The presence of surfactants on the bubble surface retards the gas flow into or out of the bubble, thus reducing bubble growth/shrinkage rates and increasing the life time of the bubble in the liquid. Increasing the adsorption rates of surfactants, either by adding salts [Shao and van de Ven, 1988] or increasing concentration, has a profound effect on reducing the gas diffusion rate, thus generating smaller bubbles. At the same time, the adsorbed surfactant film provides the mechanical strength to oppose shrinkage by changes in the hydrostatic pressure, making gas nuclei more stable.

It should be noted, however, that gas nuclei alone may not induce flotation, due to their small size and buoyancy. Hydrodynamic cavitation caused by fast flow of slurry (> 2 m/s) in the presence of surfactants may convert a limited number of tiny gas nuclei to bubbles large enough to levitate particles. A more convenient approach is to produce relatively large bubbles elsewhere and bring them into contact with these gas nuclei-frosted particles. These bubbles can be generated either by mechanical means, sparging
or by air aspiration. Therefore, both tiny gas nuclei and flotation-sized bubbles are available for improving flotation performance.
CHAPTER 3

PARTICLE-BUBBLE COLLISION IN BUBBLE SWARMS

3.1. INTRODUCTION

The flotation of fine particles poses a major challenge to mineral processing engineers. One of the key problems in flotation of fine particles is their low inertia, meaning they tend to follow and be carried by liquid streamlines around a bubble, resulting in low collision probabilities. Their low inertia also implies that fine particles may not have sufficient kinetic energy to rupture the liquid film between particles and bubbles to form three-phase contact [Derjaguin et al., 1984], resulting in low attachment probabilities.

One of the most significant developments in fine particle flotation recently is the application of column flotation, mainly due to its quiescent conditions which reduce particle-bubble detachment, and froth washing which rejects mechanically entrained gangue particles. Its application has now also been extended to treat a variety of coarse, fast floating materials such as coal [Reddy et al., 1988], talc [Kho and Sohn, 1989],

* A revised version of this chapter, co-authored by Z. A. Zhou, Zhenghe Xu and J. A. Finch, has been published in Trans. IMM., 104, C102-C106 (1995).
graphite [Narasimhan, 1972; Xu et al., 1994] and oil droplets [Pal and Masliyah, 1990]. To design and scale-up flotation columns, suitable models and criteria are necessary. Progress has been made in this regard, including the adaptation of first-order chemical reaction kinetics [Jameson et al., 1977; Finch and Dobby, 1990], axial-dispersion [Finch and Dobby, 1990], and interfacial mass transport models [Ityokumbul, 1992]. Since particle-bubble collision is a fundamental sub-process in (column) flotation, the interaction between particles and bubbles has to be considered to improve our understanding of how hydrophobic particles are transferred from the liquid phase to the surfaces of bubbles.

A current debate in the design of flotation columns concerns their height [Yianatos et al., 1988; Ounpuu and Tremblay, 1991; Ityokumbul, 1996]. In general, the required height is a complex function of system characteristics: bubble and particle sizes, particle hydrophobicity, gas rate and hold-up, and flow and mixing patterns, which determine the particle-bubble collision frequency and attachment efficiency. In terms of particle collision, the minimum recovery zone height required could be defined as that where the event of a particle colliding with a bubble has occurred at least once. This chapter discusses particle-bubble collision in flotation columns, and employs a particle-bubble collision model to explore the factors that determine the minimum recovery zone height on the basis of this definition.

3.2. MODEL DEVELOPMENT

Numerous models have been proposed to describe the probability of collision of a single particle with a single bubble under different flow regimes [Yoon and Luttrell, 1989; Finch and Dobby, 1990; Nguyen-Van and Kmet, 1992; Yoon, 1993]. However, the prediction of particle-bubble collision in a real system is complicated by the gas holdup effect, the interaction between neighboring bubbles, and the presence of multilayers of bubbles, all of which tend to straighten the liquid streamlines around a bubble, thus increasing the
overall probability of collision. Models incorporating the effect of gas holdup on the collision efficiency have been proposed by Rulev et al. [1977], Finch and Dobby [1990], and Nguyen-Van and Kmet [1994]. Modelling particle-bubble collision in column flotation is further complicated by the fact that gas holdup varies with column height [Finch et al., 1995], due to changes in hydrostatic head. To simplify the analysis, column height here is simulated by the effect of the number of layers of bubbles on overall collision probability, with the following assumptions:

3.2.1. Assumptions

1). Plug bubbly flow is maintained in the column; such a flow regime is characterized by an approximately linear relationship between superficial gas velocity and gas holdup, and by a homogeneous distribution of bubbles of fairly uniform size, which rise at a fairly uniform velocity [Finch and Dobby, 1990]. Under this condition, bubbles in the column can be regarded as arranged in layers, and as rising with relatively constant average velocity [Zhou and Egiebor, 1993; Finch et al., 1995]. The velocity of bubble rise, $V_{ba}$, is given by:

$$V_{ba} = \frac{J_g}{\varepsilon_g}$$  \hspace{1cm} (3-1)

where $J_g$ is the superficial gas velocity and $\varepsilon_g$ is the gas holdup.

2). Gas holdup at point $i$, $\varepsilon_{gi}$, is defined as the volumetric ratio of a spherical bubble with a radius, $R_{bi}$, to a cubic liquid envelope with a side length of $2b$ that encloses the bubble:
$\varepsilon_{gi} = \frac{4\pi R_{bi}^3}{(2b)^3} = 0.523 \left( \frac{R_{bi}}{b} \right)^3 \tag{3-2}$

The distance, $L_b$, between two neighboring layers of bubbles is then given by

$$L_b = 2b = 1.612 \frac{R_{bi}}{\varepsilon_{gi}^{1/3}} \tag{3-3}$$

If the height of recovery zone is $H_z$, then the total number of layers of bubbles, $N$, in the column can be estimated from

$$N = \frac{H_z}{L_b} = 0.62 \frac{H_z \varepsilon_{gi}^{1/3}}{R_{bi}} \tag{3-4}$$

3). When a bubble rises it expands, but in the presence of frothers bubble coalescence is minimized. Thus the number of bubbles can be assumed to be constant in each layer of bubbles along the column. Under these conditions the following relationship holds [Zhou and Egiebor, 1993]:

\[ \text{Equation} \]
3.2.2. Mathematical Derivation

The method employed here is similar in principle to that used to model deep bed filtration [Tien, 1989] or particle capture in a magnetised matrix [Svoboda and Ross, 1989]. By extending the collision model of Weber and Paddock [1983], and accounting for the effects of gas holdup, bubble interaction, and multilayers of bubbles, the probability of collision between a descending particle and rising bubbles along a column is then obtained by summation of the collision probability between the particle and bubbles at each layer.

According to Weber and Paddock [1983], in a single particle-single bubble system with $R_b \gg r_p$, the collision probability, $P_{sc}$, is the sum of two probabilities: gravitational ($P_g$) and interceptional ($P_{ic}$), i.e.,

$$P_{sc} = P_g + P_{ic}$$  \hspace{1cm} (3-6)

It should be noted that the above equation is only valid when both $P_g$ and $P_{ic}$ are much less than unit, so that $P_g P_{ic} \ll P_g$ or $P_{ic}$, which is the case in fine particle flotation.

$P_g$ is given by [Reay and Ratcliff, 1973]

It should be noted that surface forces were not considered in Weber and Paddock's model.
where $V_p$ is particle settling velocity and $\theta_c$ is the grazing angle, which is given by [Dobby, 1984]:

\begin{align}
\theta_c &= 98.0 - 12.49 \log(10 \Re_b) \quad (1 < \Re_b < 20) \\
\theta_c &= 78.1 - 7.37 \log(\Re_b) \quad (20 < \Re_b < 400)
\end{align}

$P_c$, on the other hand, is given by [Weber and Paddock, 1983]

$$P_c = \frac{3}{2} \left(\frac{1}{1+V_p}\right) \left(\frac{x_p}{R_b}\right)^2 \left[1 + \frac{(3/16) \Re_p}{1+0.249 \Re_p^{0.56}}\right] \quad 0 < \Re_b < 300$$  

Consider a particle falling in a bubbly column with a square cross-section. If the particle does not collide with bubbles in the first layer, it may collide with bubbles in the second
or third layer, and so on. Therefore, the probability that a particle leaves the (i-1)th layer and collides with the ith layer of bubbles, \( P(C_i) \), will be the ratio of the total projected area of bubbles in the ith layer to the total sectional areas of the liquid cubes enclosing the bubbles, or the column cross sectional area, multiplied by \( K_b P_s c \), i.e.:

\[
P(C_i) = K_b P_s c \frac{n_b \pi R_{bi}^2}{n_b (2b)^2} = 0.25 \pi K_b P_s c \frac{R_{bi}^2}{D^2}
\]

(3-11)

where \( n_b \) is the total number of bubbles in a layer. The term \( K_b \) (\( \geq 1 \)) is a coefficient that is related to the changes in fluid streamlines caused by bubble interactions, mixing and liquid circulation. The interaction between bubbles is mainly due to the effects on the hydrodynamic field around a bubble caused by close neighbors. Thus, \( K_b \) is a function of bubble size and gas holdup. The greater the gas holdup and the closer the bubbles, the more distorted the liquid streamlines become, and thus, the larger the value of \( K_b \). If \( K_b = 1 \), the effect of neighboring bubbles can be ignored - a situation that corresponds to a very low gas holdup in the column - and Eq. (3-11) returns to expressing the collision probability of a single particle with single bubbles in a water column with a cross-section area of \( 4b^2 \). If \( K_b > 1 \), it indicates that interaction occurs and increases with \( K_b \).

Substituting Eq. (3-3) into Eq. (3-11) gives

\[
P(C_i) = 1.21 K_b P_s c \frac{R_{bi}^{2/3}}{R_{bi}^2} \epsilon_{i}^{1/3} = 1.21 K_b P_s c \epsilon_{i}^{2/3}
\]

(3-12)
The probability of the particle not colliding with the $i$th layer bubbles is

$$P(C_i^o) = 1 - 1.21K_bP_{oo}e_i^{2/3} \quad (3-13)$$

The overall probability of this particle colliding with bubbles in a column, $P_{TC}$, is therefore

$$P_{TC} = P_{C_1} + P_{C_2} + \cdots + P_{C_n} = 1 - P_{C_n}^o$$

$$= 1 - \prod P(C_i^o)$$

$$= 1 - \prod \left[1 - 1.21K_b(a_{1i} + a_{2i})x_p^2\left(\frac{e_i^{1/3}}{R_{di}}\right)^2\right] \quad (3-14)$$

where

$$a_{1i} = \frac{1.5}{1 + V_p} \left[1 + \frac{(3/16)Re_{bs}}{1 + 0.249Re_{bs}^{0.56}}\right] \quad (3-15)$$
The term $\text{Re}_{bl}$ in Eq. (3-15) is the Reynolds number of a bubble in a bubble swarm, which is defined as:

$$
\text{Re}_{bl} = \frac{2R_{bl} V_{sl} \rho_l}{\mu_l}
$$

(3-17)

where $V_{sl}$ is slip velocity between bubbles and liquid, and $\mu_l, \rho_l$ are the viscosity and density of the liquid, respectively. Because $R_{b1} \geq R_{b2} \geq \ldots \geq R_{bN}$, substituting Eq. (3-4) into Eq. (3-14) gives

$$
P_{TC} \geq 1 - [1 - 1.21 (a_{1N} + a_{2N}) K_b \left( \frac{\tau_{p} \nu_0^{2/3}}{R_{bl}^{3}} \right)^{1/3}]^N
$$
3.3. MODEL PREDICTIONS AND DISCUSSION

Figure 3.1 shows the effect of particle size on minimum recovery zone height (for conditions that approximately correspond to the flotation testwork of Ounpuu and Tremblay [1991]). The curves represent the predictions obtained from Eq. (3-18) for two different values of $K_b$. It can be seen that particle size has a significant effect on $H_{r,\text{min}}$. In the case of $K_b = 1$ (i.e., no bubble interaction), $H_{r,\text{min}}$ varies from about 30 m for $d_p = 10 \mu m$ to less than 20 cm for $d_p = 160 \mu m$. Increasing the degree of bubble-bubble interaction (i.e., $K_b = 7$) reduces $H_{r,\text{min}}$ to 500 cm for $d_p = 10 \mu m$, and to about 5 cm for $d_p = 160 \mu m$. Such short heights for coarse particles are because these particles fall approximately in a straight line, and thus have a high collision probability. In practice, recovery of particles larger than 150 $\mu m$ is generally lower than that for particles less than 10 $\mu m$ in a column [Fury and Moon, 1991]. The model indicates that flotation of coarse particles is not collision limited but may be related to the probabilities of attachment and detachment.

In flotation, bubble-bubble interaction is unavoidable. In Figure 3.2, the predicted collision probability, $P_{TC}$, reaches unity at $H_r \geq 4 - 5$ m when $K_b = 1$, but with $K_b = 7$, $P_{TC} = 1$ occurs at a height of only 50 - 60 cm, implying that bubble-bubble interaction is a significant factor in determining the minimum recovery zone height. Ounpuu and Tremblay [1991] examined the effect of recovery zone height on the recovery of sphalerite

\[
H_{r,\text{min}} = \left[ 1 - 1.21K_b(a_{1N} + a_{2N}) \left( \frac{2.5 \mu m}{R_{bW}} \right)^{1/3} \right] \frac{0.62H_{r,\text{min}}^{1/3}}{R_{bW}} \]  

(3-18)
Figure 3.1  Effect of particle size on minimum recovery zone height requirements

(Simulated conditions: $R_b = 0.1$ cm, $J_g = 1.6$ cm/s, $J_l = 1.14$ cm/s, $\varepsilon_g = 15\%$, $\rho_p = 4.0$ g/cm$^3$. Curves represent predictions obtained from Eq. 3-18)
Figure 3.2  Effect of bubble interaction on collision probability

(Simulated conditions: $d_p = 30 \, \mu m$; other condition as given for Fig. 3.1. Curves represent predictions obtained from Eq. 3-18; data points from Ounpuu and Tremblay [1991])
They changed the height of the recovery zone by relocating the spargers in the column to give three effective recovery zone heights of 490 cm, 180 cm and 50 cm (measured from the feed location to the spargers). They found that recovery was constant (at around 62%) regardless of height. This implies that unit collision probability had been achieved at a recovery zone height of 50 cm or less (and also that the bubbles had reached their maximum particle load).

Although it is difficult to predict the value of $K_h$, experimental data on recovery vs. height, such as those shown in Figure 3.2, can be used to back-calculate a value. With this approach a value of $K_h$ of ~7 (Fig. 3.2) gives unit probability at about 50 cm. Back calculation from a single point - attainment of maximum recovery in this case - is not recommended. Indeed, exactly what height is the correct experimental value to use is in question. (In Figure 3.2, the recovery zone is defined as extending from the spargers to the feed point, but it is possible to argue for adoption of the pulp/froth interface as the top of the recovery zone [Finch and Dobby, 1990], which would add about 260 cm to each height in this case.) However, using the present definition of $H_r$ has the advantage of giving a minimum recovery zone height on the conservative side. Taking $K_h = 7$ as an estimation of bubble-bubble interactions in industrial columns, it is concluded that the minimum recovery zone height ranges from several meters for $d_p < 10 \mu m$ to less than a meter for $d_p > 100 \mu m$.

The criterion for $H_{r,\text{min}}$, $P_{TC} = 1$, does not however translate directly to recovery. The probability of attachment (and detachment) must also be considered. Particles with low attachment probability (i.e., weakly hydrophobic ones) may require several collision events before attachment occurs, whereas particles with high hydrophobicity, such as coal, graphite, etc., may need only one or two collisions. Therefore, the actual recovery zone height will always be greater than $H_{r,\text{min}}$. Coal flotation appears to succeed with shorter columns than mineral flotation [Reid et al., 1988]; this may reflect the generally coarser size and higher hydrophobicity of coal, which favor both collision and attachment.
At the other end of the size spectrum, columns for fine kaolin clay processing have been built as high as about 16 m [Yoon, 1994; Yordan, 1994].

The effects of gas holdup and bubble size on the collision probability of fine \( (d_p = 5 \mu m) \) particles are shown in Figure 3.3. For a given recovery zone height, increasing gas holdup or decreasing bubble size increases the collision probability. Therefore, in general, small bubbles and relatively high gas holdup should be used to give large gas/liquid interfacial area. However, there are limitations to this combination in order to keep the system in the bubbly flow regime and to prevent "flooding" [Finch and Dobby, 1990]. It has been reported [Finch et al., 1995] that gas holdup doubles over a height of 10 m in a flotation column. This may become a factor in tall (>10 m) columns where it may be necessary to maintain a relatively low gas holdup at the bottom to keep the entire column in bubbly flow.

To further demonstrate the validity of the model in diagnosing practical problems, recovery of oil from water emulsions in a flotation column described by Pal and Masliyah [1990] is used as an example. The column was 230 cm high and 10.4 cm in diameter. The recovery obtained was less than 60% for the following conditions: \( d_p = 24 \mu m \) (average), \( d_b = 0.28 \) cm, \( \rho_p = 0.78 \) g/cm\(^3\), \( \rho_i = 1.0 \) g/cm\(^3\), \( e_g = 10\% \), \( J_g = 1.5 \) cm/s, \( J_i = 1.0 \) cm/s and \( H_r = 150 \) cm. By using Eq. (3-18) and \( K_b = 7 \), the minimum recovery zone requirement and the collision probability in the column are listed in Table 3.1.

<table>
<thead>
<tr>
<th>( H_t ) (cm)</th>
<th>( H_{r, \text{min}} ) ((d_b = 0.28 \text{ cm}))</th>
<th>( P_{TC} ) ((d_b = 0.28 \text{ cm}))</th>
<th>( H_{r, \text{min}} ) ((d_b = 0.10 \text{ cm}))</th>
<th>( P_{TC} ) ((d_b = 0.10 \text{ cm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>940</td>
<td>0.57</td>
<td>85</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 3.1. Calculated \( H_{r, \text{min}} \) and Collision Probability, \( P_{TC} \).
Figure 3.3  Effect of gas holdup and bubble size on collision probability of fine particles ($d_p = 5 \mu m$)

Values of $\varepsilon_g$ and $R_b$ as shown in the figure; other conditions as given for Fig. 3.1. Curves represent predictions obtained from Eq. 3-18
It shows that the actual recovery zone height of 150 cm is much less than the calculated minimum recovery zone height \( H_{r, \text{min}} = 940 \text{ cm} \). Under this condition, the overall collision probability in the column is only 0.57, suggesting a poor recovery. One of the reasons is that the bubbles used were too large \( (d_b = 0.28 \text{ cm}) \). If the bubble diameter is reduced to 0.1 cm, the calculated \( H_{r, \text{min}} \) becomes only 85 cm, which is much shorter than the actual height used. Thus a particle can collide at least once with a bubble in the column, and improved performance might be expected. Therefore, for a fixed recovery zone height, changing the operating variables (e.g., by reducing bubble size or increasing gas holdups), to increase the total gas/liquid interfacial area in the column, can increase the collision probability of particles with bubbles.

Nguyen-Van and Kmet [1994] considered the effect of bubble-bubble interaction on the collision probability between particles and bubbles in bubble swarms, by correlating it to the gas holdup changes. However, estimation of the interaction between bubbles is complicated by the flow conditions in the column. Under plug flow conditions, bubbles rise smoothly. Bubble-bubble interaction is more or less similar to the “wall effect”, and should be a function of bubble size and gas holdup, as mentioned earlier. If flow deviates from plug flow, the trajectory of bubbles may change, due to back-mixing of liquid and turbulence, which may create an additional component to the hydrodynamic field of neighboring bubbles. In this case, considering bubble interaction as a function of bubble size and gas holdup alone may not be adequate to describe the real collision process. As shown in Figures 3.1 and 3.2, although gas holdups and bubble sizes are the same, a different collision probability was obtained with different values of \( K_b \). This strengthens that bubble-bubble interaction is also related to the flow and mixing conditions in the cell. In other words, there may exist a relationship between bubble-bubble interaction and liquid/gas axial dispersion coefficients.

The model has indicated that the minimum recovery zone height is a function of particle and bubble size, gas holdup, and bubble-bubble interaction. It has been shown that \( H_{r, \text{min}} \)
CHAPTER 3  PARTICLE-BUBBLE COLLISION IN  
BUBBLE SWARMS

increases as particle size decreases and exceeds about 10 m for $d_p < 10 \mu m$. This matches the initial impetus for the use of columns to treat slow-floating fines and the "conventional" design height was set around 10 m [Wheeler, 1988]. As applications move into coarser and more hydrophobic minerals, columns shorter than 10 m may be sufficient, as appears to be the case (e.g., Reddy et al., [1988]; Ounpuu and Tremblay [1991]; Ityokumbul [1992]).

As a final observation, since flotation is a rate process, the actual step of capturing particles by bubbles depends ultimately on the collision frequency, which can be increased by increasing the turbulence and shear rates in the cell [Jordan and Spears, 1990]. This may limit the ability of flotation columns to perform fine particle separation, as discussed earlier, it takes about 10 m for particles less than 10 $\mu m$ to collide with a bubble at least once. Bogdanov, et al., [1980] concluded, in their work with a column-like flotation cell, that moderate mixing compared to no mixing gives an increased rate of fine particle flotation by fine bubbles. This may be one of the reasons why recent developments in flotation cell design have started to exploit high energy dissipation and highly turbulent conditions, aiming at a high flotation kinetics of fine particles. However, flotation columns do provide ideal transport conditions for the separation of particle-bubble aggregates from gangue in the slurry. This suggests one approach is to accelerate the particle-bubble collection rate before the slurry is introduced to the columns.

3.4. SUMMARY OF CHAPTER

1. A model has been presented to predict the overall particle-bubble collision probability ($P_{TC}$) in flotation columns as a function of particle size ($d_p$), bubble size ($d_b$), gas holdup ($e_g$) and the magnitude of bubble-bubble interaction parameter, $K_b$. 

2. The criterion for minimum recovery zone height, $H_{r,\text{min}}$, is $P_{TC} = 1$.

3. Using a $K_b = 7$ in the model (to estimate bubble-bubble interactions in practice), $H_{r,\text{min}}$ is shown to decrease from $> 10$ m for $d_p < 10 \mu m$ to $< 1$ m for $d_p > 100 \mu m$. 
CHAPTER 4

GENERATION OF SMALL BUBBLES BY HYDRODYNAMIC CAVITATION*

4.1 INTRODUCTION

The size of bubbles plays an important role in particle collection during flotation [Flint and Howarth, 1971; Reay and Ratcliff, 1973; Dobby and Finch, 1986; Yoon and Luttrell, 1989]. Experimental results indicate that the flotation rate increases with the inverse of bubble size from the second to third power [Diaz-Penafiel and Dobby, 1994]. This is especially relevant for fine particle flotation. To improve fine particle flotation by accelerating flotation rates, three approaches to increase particle-bubble contact frequency are: increase apparent particle size (e.g., through selective flocculation or carrier flotation [Wang and Somasundaran, 1980; Attia and Yu, 1988]); use small bubbles [Yoon and Luttrell, 1989]; and increase energy dissipation [Jordan and Susko, 1992].

The last two decades have seen a burst of activity in flotation devices, partly in responding to the challenges of fine particle flotation, and partly reflecting the successful application of a new technology, column flotation. Nearly all these new designs are aimed at a flotation cell which gives high flotation rates and effective treatment of fine particles.

* A revised version of this chapter, co-authored by Z. A. Zhou, Zhenghe Xu and J. A. Finch, has been submitted to Inter. J. Miner. Process. for publication (1995)
CHAPTER 4  GENERATION OF SMALL BUBBLES BY HYDRODYNAMIC CAVITATION

Many of these cells employ high energy dissipation, in what may be called a bubble-particle "reactor" [Finch, 1994]. It is anticipated that this high energy dissipation may facilitate small bubble formation by cavitation.

The formation of small bubbles in some new flotation cell designs may be similar to the so-called colloidal gas aphrons (with bubble diameters of about 25 μm) developed by Sebba [1972; 1984; 1989]. While such small bubbles may not be suitable for mineral flotation on their own, it has been shown that in combination with relatively large bubbles, they increase flotation rates [Klassen, 1960]. This suggests a two-stage attachment process [Dziensiewicz and Pryor, 1950], as discussed in chapter 2. If cavitation takes place directly in the slurry, it may also be possible to take advantage of the fresh nature of the bubble surface created, which tends to have a greater de-wetting ability than "aged" surfaces [Klassen and Mokrousov, 1963; Finch and Smith, 1972; Crozier, 1992]. This chapter reports a systematic investigation into small bubble formation by hydrodynamic cavitation.

4.2. EXPERIMENTAL MATERIALS AND METHODS

The apparatus used to generate bubbles by cavitation is shown schematically in Fig. 4.1. A 10-L solution with a given dosage of chemicals was prepared and agitated in the container. The solution was forced through the cavitation tube by a peristaltic pump. The characteristics of the cavitation tubes tested are listed in Table 4.1.

The cavitation tube was placed either downstream of the pump (as shown), upstream or, in some tests, at both locations with the upstream one generating gas nuclei to feed to the downstream one. To examine the effect of added gas on cavitation, air was introduced in some experiments on the suction side of the pump, by aspiration at atmospheric conditions, and passed through a static mixer in the stream.
Figure 4.1 Schematic of the set-up for generating bubbles by cavitation
Table 4.1 Characteristics of cavitation tubes used in the study

<table>
<thead>
<tr>
<th>Series No.</th>
<th>Tube I.D., D (mm)</th>
<th>Tip I.D., d (mm)</th>
<th>Tip Length, l (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.5</td>
<td>1.30</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>8.5</td>
<td>1.65</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>8.5</td>
<td>1.92</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>8.5</td>
<td>2.35</td>
<td>0</td>
</tr>
</tbody>
</table>

* The size was measured by calipers and standard drills.

Bubble formation was detected by a light transmission method. A light source and detector (Fig. 4.1) were arranged across the cavitation tube which was installed in a light-tight (“black”) box to eliminate background light. When bubbles form, light is scattered, i.e., transmittance ($I/I_0$, ratio of photo-current in the presence and absence of bubbles) is reduced. A photodiode (Active, Montreal) was used as the detector, with a digital readout on a multimeter (Radio Shack, Montreal). Two light sources (Radio Shack, Montreal), $U = 2$ and $5$ volts, $250$ mA, were compared to check sensitivity and reproducibility. Fig. 4.2 shows the data for the two light sources essentially fall on the same curve. The velocity where $I/I_0$ starts to deviate from 100% indicates the onset of bubble formation. The light transmission method proved to be a reliable way to determine this velocity for two-phase systems. For each test, two sets of data for both light sources were collected. No attempt was made at this stage to estimate the size of bubbles formed in the stream, due to their small size and the inherent difficulties in such measurements.
Figure 4.2 Comparison of two light sources for light transmittance measurement ($d = 1.65$ mm, 30 ppm DF250, no air addition)
To examine the effect of solids on bubble formation by cavitation, fine silica \( (d_{50} = 1.6 \text{ \upmu m}, \text{US-Silica Company}) \) was used without further purification. A portion of the silica sample was methylaed by trimethylchlorosilane (TMCS) (Fisher Scientific), using a procedure similar to that described by Laskowski and Kitchener [1969], to examine the effect of particle hydrophobicity on cavitation.

Both hot (> 55 °C) and cold tap water (22 °C) were used for the tests. Chemicals used included two kinds of surfactants: polypropylene glycol methyl ether (Dowfroth 250 or DF250, Dow Chemicals) and dodecylamine (DDA, Kodak), and sodium hydroxide (NaOH, Fisher Scientific) for pH adjustment.

To compare the bubble formation visually, a CCD camera was used to record the cavitation phenomena under the different conditions.

4.3. RESULTS

4.3.1. Effect of Chemical and Solid Particle Additions

Bubble formation by cavitation in water results from rupture of the water structure. Therefore, formation of bubbles should occur at "weak points" in the water. Consequently, additives which alter the local water structure may affect bubble formation by cavitation. Such additives are usually hydrophobic (e.g., surfactants in solution or solids in suspension), since the interaction between hydrophobic entities and water is weaker than that of water itself.

In these tests, the cavitation tube was placed downstream of the pump. Figure 4.3 shows the effect of Dowfroth 250 on bubble formation. As can be seen, only when the liquid flow velocity reached a critical value, did bubbles form, but the presence of frother did
Figure 4.3  Effect of Dowfroth 250 (DF250) on bubble formation by cavitation
(d = 1.3 mm, no air addition)
not change this velocity. The frother, however, did reduce the transmittance more, suggesting an increase in the number of bubbles formed (or possibly a change in bubble size). An increase in the number of bubbles could be due to stabilization of the cavities by adsorption of frother [Wu, 1969], as claimed in the case of gas aphrons [Sebba, 1989].

The effect of DDA was similar to that of DF250 (Figure 4.4): There is virtually no change in the onset of cavitation, but the number of bubbles apparently increased with concentration, at least up to $10^{-4}$ M. Hemmingsen [1978] also noted little effect of surfactant (and electrolyte) on the onset of cavitation.

Figure 4.5 shows the effect of pH on bubble formation in the presence of $10^{-3}$ M DDA. No changes were observed in bubble formation for the three pH values tested, although it was observed that DDA formed precipitates at pH $> 10$, which are known to be hydrophobic [Yalamanchili et al., 1993]. From the work of Pease and Blinks [1947] and Gerth and Hemmingsen [1980], such hydrophobic precipitates would be expected to promote bubble formation in gas supersaturated systems. While it may be argued that the amount of hydrophobic precipitates are insufficient to cause the macroscopic changes in bubble formation to be detected, adding hydrophobic methylated silica into the above solution also showed no change in bubble formation (Fig. 4.6). This observation seems contrary to that of Hemmingsen and Hemmingsen [1990] and Dean [1944]: they found that hydrophobic particles made bubble formation easier in gas-supersaturated systems. One reason for this difference may be that in gas supersaturated systems, gas molecules accumulate on the hydrophobic particle, which increases the probability of bubble formation. Under the conditions in this study, the accumulation of gas molecules on hydrophobic particles may not be sufficient to promote bubble formation. In addition, the light transmittance technique used may not be suitable to detect the changes in three-phase systems, due to different light reflective indices of particles and bubbles. The effect of solids with different surface properties on bubble formation in gas-supersaturated systems is discussed in Chapter 5.
Figure 4.4  Effect of DDA on bubble formation by cavitation

(d = 1.3 mm, no air addition, pH = 4 - 5)
Figure 4.5 Effect of pH on bubble formation by cavitation

(d = 1.92 mm, 1 x 10^{-3} M DDA, no air addition)
Figure 4.6  Effect of methylated silica addition on bubble formation by cavitation (d = 1.92 mm, 1 x 10^{-3} M DDA, pH = 11.5, 0.1% methylated silica, no air addition)
4.3.2. Effect of Physical Variables

The results to this point have shown that addition of chemicals and the presence of hydrophobic particles have little effect on bubble initiation in water. This suggests that cavitation did not involve rupture of the water structure, but rather the expansion of pre-existing gas nuclei.

Fig. 4.7 shows that when the cavitation tube was put on the up-stream (or suction side) of the pump, bubbles formed at a lower liquid flow velocity compared with when the cavitation tube was placed down-stream of the pump. To investigate this observation, the static pressures around the pump were measured. As can be seen (Fig. 4.8), pressure was lower up-stream (curve 3), than down-stream (curve 4). The lower pressure on the up-stream side means a lower cavitation number defined by Eq. (2-4):

\[ k_c = \frac{P_{loc} - P_{vap}}{\frac{1}{2} \rho \cdot V_{loc}^2} \]  

where \( k_c \) is the ratio of static pressure opposing cavitation to dynamic pressure inducing it [Young, 1989; Trevena, 1987]. The higher the cavitation number, the less likely the cavitation is to occur. Eq. (2-4) suggests that reducing the static pressure in a stream reduces the cavitation number, thus facilitating cavitation.

Fig. 4.9 shows, for the downstream cavitation tube, that the presence of pre-existing gas nuclei (generated by placing a cavitation tube up-stream of the pump) reduced the on-set velocity of cavitation. This is interpreted as expansion of pre-existing nuclei upon passage through the tube.
CHAPTER 4 GENERATION OF SMALL BUBBLES BY HYDRODYNAMIC CAVITATION

Figure 4.7 Effect of location of cavitation tube on bubble formation by cavitation (30 ppm DF250, no air addition)
Figure 4.8 Bubble formation and static pressure in the stream  
(d = 1.65 mm, 30 ppm DF250)

1 - cavitation tube up-stream;  
2 - cavitation tube down-stream;  
3 - pressure up-stream;  
4 - pressure down-stream.
Figure 4.9 Effect of pre-existing gas nuclei on bubble formation
by cavitation ($d = 1.3$ mm, 30 ppm DF250)
Fig. 4.10 shows the effect of water temperature on bubble formation. Increased temperature caused bubble formation at lower liquid flow velocities. This is due to the increased water vapor pressure and consequently reduced cavitation number.

Fig. 4.11 shows the effect of nozzle orifice diameter and length on cavitation. For a given length, higher liquid flow velocities were needed to initiate cavitation with the small orifices compared with the large ones, probably due to a higher energy loss resulting from the flow contraction and friction in the former. The tip length of cavitation tubes may also be a factor: for example, comparing \( d = 1.65 \) mm, tip length \( 10 \) mm, with \( d = 1.92 \) mm, tip length zero, the nozzle with the shorter tip length and larger diameter gave fewer bubbles. The same phenomenon was also found by Ross [1976]. His explanation was that gas nuclei in the stream need time to expand sufficiently to be detected. If the nozzle is too short, gas nuclei do not have enough time to expand in the low pressure region before reaching a region of higher pressure where they may collapse (re-dissolve). Knapp et al. [1970] also noticed that for cavitation to occur, the pressure has to be reduced and maintained for sufficient time below a critical value, which depended on the physical properties and conditions of the liquid. This indicates that a minimum length of tip is needed to promote cavitation.

Fig. 4.12 shows the effect of added gas on cavitation (as opposed to the presence of gas nuclei as in Fig. 4.10) was to reduce the velocity for onset of bubble formation. (Note, the figure shows the production of bubbles by cavitation superimposed on those already present due to the added gas). When air is added, some dissolves in the stream and is available for diffusing into the pre-existing gas nuclei, thus stabilizing them and enhancing cavitation. The effect of increased air content on enhancing cavitation was also reported by Holl [1960a].
CHAPTER 4  GENERATION OF SMALL BUBBLES BY HYDRODYNAMIC CAVITATION

Figure 4.10  Effect of temperature in the stream on bubble formation by cavitation (no chemicals added)
Figure 4.11 Effect of nozzle orifice diameter and length on bubble formation by cavitation (30 ppm DF250, downstream)
CHAPTER 4  GENERATION OF SMALL BUBBLES BY HYDRODYNAMIC CAVITATION

Figure 4.12  Effect of air addition on bubble formation by cavitation

(d = 1.3 mm, no chemicals added)
Fig. 4.13 shows the bubble formation recorded by a CCD camera. At low liquid flowrate ($V < 15$ m/s, liquid flows from the right to the left) through the nozzle ($d = 1.3$ mm), no bubbles are seen (Fig. 4.13a); when $V$ exceeded $15$ m/s, bubbles formed first at the tip, and then extended downstream, as indicated by the milky white color (Fig. 4.13b). In the presence of added air, the whole tube became milky (Fig. 4.13c).

4.4. DISCUSSION

4.4.1. Bubble Formation by Cavitation

4.4.1.1. Cavitation: General Observation

The phenomenon of bubble formation by a fast flowing liquid was first observed by Reynolds about 100 years ago [Trevena, 1987]. He noticed that bubbles formed when the flow velocity of water through a constriction reached about 16.5 m/s, which is of the order found in this study. Velocities about 8 - 15 m/s were required for bubbles formation, depending on the size and length of nozzles. This velocity range, interestingly, corresponds to typical slurry velocities through the feed nozzles of some new flotation cells [Finch, 1994, 1995], suggesting that cavitation may be playing a role.

Cavitation occurs when a bubble is formed due to the rupture of a liquid-liquid or a liquid-solid interface caused by reduction of local static pressure [Ross, 1976]. As discussed in Chapter 2, water is always undergoing very rapid fluctuations in molecular density and structural configuration due to molecular motion, which leads to a continuous formation of voids on a molecular scale [Hemmingsen, 1975]. In addition, in a flowing system, due to shear and turbulence, local liquid accelerations cause pressure fluctuations which may result in local pressures being below water vapor pressure (0.023 atm at 20 °C), and hence water vapor cavities may form [Trevena, 1987]. However, experimental measurements have shown that pure liquids can withstand very high tension without rupture [Ross, 1976]. It has been reported [Yount, 1989] that pure water can withstand
CHAPTER 4 GENERATION OF SMALL BUBBLES BY HYDRODYNAMIC CAVITATION

Figure 4.13 Bubble formation by cavitation recorded by a CCD camera (d = 1.3 mm)

a). $V < 15$ m/s; b). $V \geq 15$ m/s; c). $V \geq 15$ m/s with air addition.
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more than 50 - 200 atm (both negative and positive) pressures.

The ability of water to sustain such large stresses is related to the effect of surface tension. To illustrate, for a molecular void with a diameter of 2 nm surface tension develops a Laplace pressure of above 1000 atm. This means that even if molecular voids or vapor cavities form, they collapse immediately due to this large pressure. Therefore, in pure water, no stable bubbles form even when the pressure is less than water vapor pressure [Knapp, et al., 1970].

The actual low threshold stress of water - as demonstrated again in this study - indicates the presence of impurities such as gas nuclei in all real liquids [Ross, 1976; Ryan, 1991]. Although the presence of gas nuclei in water is well accepted, the reason they exist is difficult to comprehend from at least two viewpoints, as discussed in Chapter 2: first, bubbles larger than a few micrometers (meaning Brownian motion can be ignored) should, given time, rise to the surface and disappear; second, if the bubble is small enough, so that the bubble remains in suspension by thermal motion, the high capillary pressure caused by surface tension, as indicated above, suggests that the bubble should dissolve and disappear.

Various hypotheses have been proposed to account for the apparent stability of gas nuclei, as discussed in Chapter 2, but none of them are completely satisfactory. Nevertheless, there is an agreement that gas nuclei do exist, and that the largest ones in a population determine the tensile strength of the liquid [Ross, 1976; Rood, 1991]. The existence of gas nuclei in water has been directly observed by numerous researchers [Flynn, 1964; Johnson and Cooke, 1981; Youm, et al., 1984; Youm, 1989]. To enhance cavitation and generate more tiny bubbles, it is necessary to understand both how to reduce the local pressure to permit the nuclei to grow, and how to prevent the cavity thus formed from collapsing.
4.4.1.2. Cavitation: Theoretical Considerations

To provide insight into bubble formation, the static pressures and flow velocities upstream of the tip were measured (Figure 4.14), and the results showed that a much higher upstream pressure (thus a larger driving force) was required for bubble initiation in the smaller nozzles compared to the larger ones. Due to the small size of the tip used, it is difficult to measure the local pressure inside the tip during cavitation. To estimate the static pressure within the nozzle, $P_2$, the following energy balance was made (Figure 4.15):

$$
\sum W = \frac{P_1}{\rho_1} + \frac{1}{2} V_1^2 = \frac{P_2}{\rho_1} + \frac{1}{2} V_2^2 + \sum H_L + \sum F \quad (J/kg)
$$

where $\sum W$ is the total energy consumed in the flow, $\sum H_L$ is the energy losses due to flow contraction, expansion and/or friction, $\sum F$ is the energy consumed for bubble formation in the tip, which can be expressed as [Takahashi et al., 1979; Ward et al., 1970]

$$
\sum F = \sum n_{ni} (\mu_{bi} - \mu_{li}) - (P_b - P_2) \sum V_b + \sigma \sum A \quad (J/kg)
$$

where $n_{ni}$ is the number of molecules of species $i$ within a bubble; $\mu_{bi}$ and $\mu_{li}$ are gas molecular chemical potential of species $i$ within a bubble and in the bulk liquid, respectively; $P_b$ and $P_2$ are bubble internal pressure and static pressure of liquid, respectively; $V_b$ is the bubble volume; $\sigma$ is the liquid-air surface tension; and $A$ is bubble surface area.
CHAPTER 4 GENERATION OF SMALL BUBBLES BY HYDRODYNAMIC CAVITATION

On-set of cavitation

Liquid flow velocity through nozzle (m/s)

Figure 4.14 Static pressures up-stream of the tip for different tip sizes
CHAPTER 4  GENERATION OF SMALL BUBBLES BY HYDRODYNAMIC CAVITATION

Figure 4.15
Energy balance around the tip
Assuming that air is the only component in the bubbles, and that the number of bubbles generated per liter of water passing the nozzle is \( N_h \). Eq. (4-2) can be written as

\[
\sum F = \left( P_2 + \frac{4 \sigma}{d_b} \right) \frac{\pi}{6} d_b^3 N_h \ln \left( \frac{P_2 + \frac{4 \sigma}{d_b}}{P_2} \right) + \frac{1}{3} \pi d_b^2 \sigma N_h \quad (\text{J/kg})
\]  

Taking a bubble diameter of 100 \( \mu \text{m} \) and gas holdup of 1\% at the tip [Jackson, 1994], in the present case without air addition, the number of bubbles \( N_h \) is

\[
N_h = 0.01 \times 1000 \text{ cm}^3 / \left( \pi \times (100 \times 10^{-4} \text{ cm})^3 / 6 \right) = 1.9 \times 10^7 \quad \text{(per liter liquid)}
\]

For energy losses due to contraction of the flow, we have [Walshaw and Jobson, 1979; Anon. 1980]

\[
H_t = \left[ \frac{1}{C_c} - 1 \right] \frac{V_z^2}{2} \quad (\text{J/kg})
\]

where \( C_c \) is a coefficient related to the contraction of flow, a value of 0.6 being suggested [Walshaw and Jobson, 1979].

For the cavitation tubes used in this study, the calculated static pressures within the tips for bubble initiation are listed in Table 4.2. It is observed that the energy loss increases with reducing tip diameter, as expected, and the energy involved in bubble formation, \( \Sigma F \), only accounts for a very small portion in the absence of added gas, compared with the total input energy, \( \Sigma W \). For a tip of \( d = 1.3 \text{ mm} \), the pressure \( P_2 \) has to be negative.
for bubble initiation, because a large portion of the input energy is lost in flow contraction and friction. For larger size tips, bubbles formed even when the pressures were much larger than the water vapor pressures (2.3 kPa at 20 °C). This finding indicates that cavitation was not principally due to vapor bubble formation but rather the expansion of pre-existing gas nuclei.

Table 4.2  Estimation of static pressure $P_1$ within nozzles for bubble initiation

<table>
<thead>
<tr>
<th>Nozzle diameter (mm)</th>
<th>$P_1$ (kPa)</th>
<th>$V_1$ (m/s)</th>
<th>$V_2$ (m/s)</th>
<th>$\Sigma H_1$ (J/kg)</th>
<th>$\Sigma F$ (J/kg)</th>
<th>$P_1$ (kPa)</th>
<th>$\Sigma W$ (J/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.30</td>
<td>140.6</td>
<td>0.339</td>
<td>14.5</td>
<td>46.72</td>
<td>0.038</td>
<td>-11.2</td>
<td>140.7</td>
</tr>
<tr>
<td>1.65</td>
<td>122.5</td>
<td>0.337</td>
<td>10.0</td>
<td>22.22</td>
<td>0.043</td>
<td>50.3</td>
<td>122.5</td>
</tr>
<tr>
<td>1.92</td>
<td>123.6</td>
<td>0.536</td>
<td>10.5</td>
<td>24.50</td>
<td>0.042</td>
<td>44.1</td>
<td>123.7</td>
</tr>
<tr>
<td>2.35</td>
<td>119.2</td>
<td>0.612</td>
<td>8.0</td>
<td>14.22</td>
<td>0.043</td>
<td>73.2</td>
<td>119.2</td>
</tr>
</tbody>
</table>

Other conditions: $d_b = 100 \, \mu m$, gas holdup within the tip $\varepsilon_g = 1\%$, surface tension of liquid $\sigma = 70 \, mN/m$.

Based on Eq. (4-1) and the experimental results, the changes in static pressure within the tip as a function of liquid flow velocity after bubble formation are shown in Figure 4.16. With increasing velocity, the static pressure reduces, eventually becoming less than the water vapor pressure and then becoming negative. Consequently, the bubbles formed may consist of both gas and water vapor. The importance of water vapor in bubbles on flotation was identified by Klassen and Mokrousov [1963]. Comparing Figure 4.16 with
Figure 4.16 Effect of liquid flow velocity on static pressures within the tip after bubble initiation
Figures 4.7 and 4.11, a conclusion is that the increase in bubble formation with liquid flow velocity is due to the reduction of the pressure within the nozzle, thus permitting more pre-existing gas nuclei to expand into bubbles of a detectable size.

4.4.1.3. **Role of Surfactants, Dissolved Gases and Gas Nuclei**

Although no change in the onset of cavitation was shown whether surfactants were present or not, surfactants do promote the formation of more bubbles at the same flow velocities. Unlike bubbles in air-sparged systems (e.g., used in flotation columns), where the internal pressure is larger than the ambient pressure, cavitation-formed bubbles may have internal pressures less than their surroundings or may even be negative [Yount, 1989], as demonstrated in the above analysis. Thus they tend to shrink, even collapse, especially when carried to regions of high pressure. In this regard, surfactant molecules play a role: they prevent the immediate collapse of the cavity by providing mechanical strength to the surface, which encourages the formation of more bubbles, as evidenced by Figures 4.3 and 4.4; and, in addition, the adsorbed surfactant film retards the diffusion of gas out of the bubble.

In the presence of dissolved gas, gas molecules actually diffuse into the cavity created, thus contributing to its stability [Shafer and Zare, 1991; van de Ven and Dukhin, 1992]. As shown in Figure 4.12, more bubbles were stabilized when gas was added up-stream, which suggests this "diffusion in" phenomenon.

From this study, it is concluded that cavitation was initiated from the expansion of pre-existing gas nuclei in water, and the more gas nuclei are present, the lower the liquid velocity required for cavitation (Figure 4.8).

### 4.4.2 Potential Applications in Flotation

The possible roles of cavitation in small bubble formation and flotation were discussed
in Chapter 2. One role in flotation was indirectly identified in experiments on hydrophobic coagulation, which will be discussed in Chapter 6. It was found that on removing gas nuclei from water by degassing, particles became more dispersed, indicating that small bubbles promoted aggregation. Since aggregation represents an increase in apparent particle size this will increase the collision probability with flotation-size bubbles.

Flotation is an energy-dependent process in that all the sub-processes - solid suspension, particle-bubble interaction, and bubble formation - are energy-dependent. It is desirable, therefore, that as much of the energy input as possible should be directed to the main function of flotation: particle collection by bubbles. One of the major energy sources is pumping but this is not directly related to the collection process. The study here has suggested a simple way to include pumping energy more directly, namely using it as a method of producing tiny bubbles by cavitation. By suitable designs, bubble formation and slurry transport could be combined without incurring extra energy costs.

4.5. SUMMARY OF CHAPTER

1. Bubble formation by cavitation in water is argued to be mainly due to expansion of pre-existing gas nuclei resulting from either the reduction of local pressure in a flowing stream or increased vapor pressure. More bubbles formed as the following increased: liquid flow velocity, the number of gas nuclei, the dissolved gas content, and temperature.

2. The presence of surfactants enhanced bubble formation probably by providing some mechanical strength to prevent the immediate collapse of cavities formed, and retarding gas diffusion out of the cavity.

3. By adding gas, more bubbles were formed which was attributed to diffusion of
dissolved gas into pre-existing gas nuclei.

4. Both the size and the length of nozzle tip affected cavitation: Smaller diameter tips required a higher liquid flow velocity and a higher driving force to generate cavities; a certain length of tip was needed for cavitation probably to allow time for gas nuclei to expand to detectable sizes.

5. Pumping used for slurry transport could be combined with bubble formation to direct more of the energy expended in flotation to particle collection.
CHAPTER 5

GENERATION OF SMALL BUBBLES BY GAS-SUPERSATURATION*

5.1. INTRODUCTION

The results in the previous chapter suggest that to enhance bubble formation a high dissolved gas content is required. This can be done either by bubbling gas into a slurry, or more efficiently, by forcing gas to dissolve in the system, as in dissolved air flotation. Dissolved air flotation is now a standard technique in potable/waste water treatment. It provides an efficient way to generate tiny bubbles. In this process, an aqueous solution is saturated with air at pressures of 3 - 5 atm. and then released through a nozzle or a needle valve where sudden pressure drop occurs and the solution becomes supersaturated. Microbubbles are generated, with mean diameter ($d_{m}$) in the range of 50 - 80 $\mu$m [Solari and Gochin, 1992], by cavitation during liquid release. Besides the bubble size, the population of bubbles, or the gas holdup, and most importantly, the total air-water interfacial area created in the system, also play an important role in improving flotation performance. There is a growing trend in applying a pressure reduction step in mineral

* A revised version of this chapter, co-authored by Z. A. Zhou, Zhenghe Xu and J. A. Finch, has been submitted to *Colloid & Surfaces* for publication (1996)
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and coal flotation machines [Amelunxen, 1993; Parekh and Groppo, 1990], to enhance fine particle flotation rates. To make use of the useful features inherent in dissolved air flotation, this chapter discusses the effect of some factors, such as gas-saturation procedure, surfactant addition, presence of solids and different gases, on the generation of microbubbles in gas-supersaturated systems.

5.2. EXPERIMENTAL

A pressure chamber made of stainless steel with an inside diameter of 10.5 cm and height of 15 cm was used (Figure 5.1). Compressed gas (extra dry air or carbon dioxide, Produits de Soudure Ltée, Montréal) from a gas cylinder was introduced to the chamber via tygon tubing (I.D. = 3.5 mm) with punched holes of ca. 0.5 mm in diameter. Two release valves were installed: one for liquid (slurry) release, and the other for gas release. A pressure gauge (ranging from 0 - 450 kPa) was used to indicate the pressure inside the chamber. In the center of the top lid there was a glass window which allowed the phenomena occurring within the chamber to be observed. A magnetic stirrer was used to mix the chamber contents.

Solids tested included fine silica (the same as used in Chapter 4) and a low rank coal (1.4% mineral matter) from Malaysia. Silica was used without further purification. Coal chunks were broken by hammer, then dry-pulverized. The minus 400 mesh (-38 μm, with \( d_{50} \approx 5 \mu m \) determined from the particle size distribution [Zhou, et al., 1996]) portion was obtained by dry screening, and stored in a freezer to retard oxidation. Film flotation results showed [Xu, et al., 1995] that the coal had a critical surface tension of 29.5 mN/m for complete wetting, and 39.5 mN/m for non-wetting.

To stabilize the bubbles formed in the system and to change the particle surface properties, a non-ionic surfactant, polypropylene glycol methyl ether, Dowfroth 250C or
Figure 5.1 The set-up used for bubble generation by gas supersaturation
CHAPTER 5 GENERATION OF SMALL BUBBLES BY GAS-SUPER Saturation

DF250 (Dow Chemical Canada, Inc.) and a cationic surfactant, dodecylamine. DDA (Prospect Chemicals Ltd., Fort Saskatchewan) were used. The stock DDA solution of $1.25 \times 10^{-2}$ M was prepared with the addition of HCl. Both distilled water and tap water were used in the experiments.

In each measurement, 500 mL water was mixed with chemicals (DDA or DF250) at given dosages in a 600 mL glass beaker for about 10 min, after which the beaker was placed in the pressure chamber for 20 min. The saturation procedure was shown in Figure 5.2 and the liquid (slurry) was stirred during gas saturation. About 400-mL of the gas-supersaturated solution was then released into a 345-mL porcelain vessel (or 400-mL glass vessel) (I.D. $\approx$ 7 cm) placed in a 2.5-L container which was used to collect overflow. The release time and the pressure in the chamber were recorded. The volume of water that overflowed into the 2.5-L container, that retained in the 345-mL vessel, and that left in the 600-mL beaker were all measured.

For tiny bubbles formed in gas-supersaturated systems, the measurement of their size and population is a difficult task. To examine the effect of different factors on bubble generation and simplify the analysis, a method similar to that of Jordan and Spears [1990] was adopted to estimate the gas content or the gas holdup. During each test, the gas holdup, (i.e., the amount of gas molecules in the form of gas bubbles,) of the gas-supersaturated solution was measured by releasing the solution into the 345-mL vessel. After all the bubbles had risen and burst, and the foam collapsed, the volume of water was measured, and the content of gas in the form of bubbles of the released solution per unit volume (i.e., the gas holdup) was estimated. Because the receiving vessel used can actually hold 345 mL (or 430 mL in the case of glass beaker) of water without overflowing, the gas holdup $\varepsilon_g$ is then estimated by

$$\varepsilon_g = 100 \times \frac{(345 - V_f)}{345} \%$$ (5.1)
CHAPTER 5 GENERATION OF SMALL BUBBLES BY GAS-SUPER SATURATION

Figure 5.2  gas-saturation procedure

1). Step saturation: slowly raising the pressure to the final value while bubbling (i.e., the gas inlet tube is immersed in the liquid);

2). Fast saturation: directly raising the pressure to the final value while bubbling;

3). Direct pressurization: directly raising the pressure to the final value without bubbling (i.e., the gas inlet tube is above the liquid).
or in the case of 430-mL glass vessel.

\[ \varepsilon_r = 100 \times \frac{(430 - V_f)}{430} \quad (\%) \]

where \( V_f \) is the volume of water (slurry) remaining in the 345-mL (430-mL) vessel after all the bubbles had disappeared and the foam collapsed. Using this technique, the measured gas holdup reflects the combined effect of the number and size of bubbles in the released liquid and bubble rise velocities in the receiving vessel.

5.3. RESULTS

Upon releasing the gas saturated solution from the pressure chamber into the receiving vessel, a hissing sound from the release tube, due to cavitation, was frequently heard, and a milky-looking solution was obtained. The bubbles formed were so small, in the case of air, that they could not be distinguished by eye. In the absence of surfactant and at low pressures (102 kPa), tiny bubbles appeared occasionally in the release tube and around the outlet of the tube immersed in the beaker.

Fig. 5.3 shows the effect of liquid release velocity from the pressure chamber on gas holdup. It can be seen that there is a sharp increase in gas holdup at gas supersaturation pressures above \(\sim 170\) kPa, suggesting on-set of cavitation. On comparing this figure with Figs. 4.2 and 4.11, it is observed that the critical velocity of 10 - 15 m/s needed for cavitation in the absence of added gas is reduced to 5 - 7 m/s in the presence of dissolved gas. This indicates that dissolved gas enhances cavitation. Stabilization provided by the diffusion of gas molecules into the bubbles is likely responsible for this observation.

Fig. 5.3 also suggests that a higher saturation pressure, (and therefore, a higher dissolved gas content in the solution), does not guarantee the production of more bubbles and high
Figure 5.3  Effect of liquid release velocity on gas holdup

(1.25 x 10^{-4} M DDA, 20 ppm DF250; CO_{2}; bubbling and stirring.
Note: dotted lines connect points of equal gas saturation pressure)
CHAPTER 5 GENERATION OF SMALL BUBBLES BY GAS-SUPERSATURATION

It is also shown in Fig. 5.3 that at the same supersaturation pressures (e.g., 310 kPa), gas holdup increases with liquid release velocity. This suggests that more cavities were formed in the stream at higher velocities, with sufficient dissolved gas being present to diffuse into the cavities to prevent their collapse. This is consistent with the observation by Takahashi, et al. [1979] and Jackson [1994] that the number of bubbles produced was strongly influenced by air saturation pressure and increased with increasing liquid release rate.

Fig. 5.4 shows the effect of stirring the liquid on gas holdup in the presence and absence of surfactants. In both cases, the gas holdup increased upon stirring. This suggests that the associated shear may generate some cavities, which could be stabilized by the increased amount of gas dissolved in the liquid resulting from the stirring. Therefore, the total amount of gas nuclei in the system increases. The gas holdup was much higher in the presence of surfactants, suggesting that the cavities generated are preserved by surfactant adsorption at the freshly-created gas/water interface.

The effect of different gases on gas holdup is presented in Figure 5.5. Much higher gas holdup was obtained when using CO$_2$ compared to air, under the given conditions. This is attributed to a much higher solubility of CO$_2$ than air in water [Geankoplis, 1983, Tong, et al., 1990]. It was observed that in the case of air, no individual bubbles could be distinguished by eye in the vessel. The foam that formed was more stable than that with CO$_2$, as observed by a longer period of the milky appearance. Bubbles were visible on the top of the vessel when CO$_2$ was used. However, these bubbles collapsed quickly. The foam formed was much thicker but less stable, compared to that formed with air.

Figure 5.6 shows the effect of coal and silica addition on gas holdup at different saturation pressures. It was noted that both tap water and distilled water gave similar gas
CHAPTER 5  GENERATION OF SMALL BUBBLES BY GAS-SUPER SATURATION

Figure 5.4 Effect of stirring liquid on gas holdup

\((1.25 \times 10^{-4} \text{ M DDA}; 20 \text{ ppm DF250}; \text{CO}_2; \text{bubbling}; \text{release tube d} = 1.5 \text{ mm})\)
Figure 5.5 Effect of different gases on gas holdup

(1.25 x 10^{-4} M DDA, 20 ppm DF250; CO\(_2\); bubbling and stirring; release tube \(d = 1.5\) mm)
Figure 5.6 Effect of solids on gas holdup

(30 ppm DF250; 20 min saturation time; release tube d = 1.5 mm)
holdup, although the number of pre-existing gas nuclei in tap water would be expected to be greater than in distilled water [Jackson, 1994; Keller, 1972], due to the presence of impurities. This indicates that in gas-supersaturated systems the effect of pre-existing gas nuclei in the original liquid on overall bubble formation may not be significant.

Fig. 5.6 also shows that adding solids, whether silica or coal, decreased gas holdup. In the case of coal at 2% (w/w), more than a 50% decrease in gas holdup occurred. Visual observation indicated that the behavior of bubbles and the froth formed were different for the coal and silica. In the case of silica, there were no obvious changes in bubble size and froth, but larger bubbles and faster froth collapse were observed in the case of coal. This observation suggests that the mechanism causing the decrease of gas holdup by solids might be different for the two solids studied.

In order to confirm this, the effect of different amounts of coal particles on gas holdup in gas-supersaturated systems was examined. Figure 5.7 shows that gas holdup actually increased initially with addition of a small quantity of coal, reaching a maximum at a slurry concentration of 0.05% w/w. A further increase in the amount of coal particles decreased gas holdup sharply, corresponding to the observed presence of large bubbles. This indicates that the coalescence of bubbles is induced by coal particles above a certain solid content, and suggests that coalescence may be the dominant factor in modifying gas holdup.

Figure 5.8 shows the effect of silica content on gas holdup in the presence of $1.25 \times 10^{-4}$ M DDA or 30 ppm DF250. The pH of the released slurry in the receiving vessel was about 3. In the presence of DDA gas holdup initially increased sharply, from about 20% to more than 40% at 2% w/w solids. Further solids addition reduced gas holdup, but it was still higher than in the absence of solids. In the presence of DF250 gas holdup decreased progressively to about 10% with increasing solid content above 5% (w/w).
CHAPTER 5 GENERATION OF SMALL BUBBLES BY GAS-SUPERSATURATION

Figure 5.7 Effect of solid % (w/w) on gas holdup (-38 μm coal)

(30 ppm DF250; release tube d = 1.5 mm; CO₂; 20 min. gas saturation)
Figure 5.8  Effect of silica addition on gas holdup under different conditions

(30 ppm DF250; release tube d = 1.5 mm; CO2; 20 min. gas saturation)
Silica in the presence of DDA at pH -3 is moderately hydrophobic (the reported contact angle is about 15 - 20° [Smith and Akhar, 1976]), as evidenced by the solids floating on the liquid surface and forming a much more stable froth. Therefore, a reduced rise velocity of a bubble with attached particles may act to increase gas holdup.

To examine whether a reduced bubble/particle aggregate rise velocity could account for the increased gas holdup, two comparative tests were conducted (see Figure 5.9): a) 500-mL slurry with a given silica content in the pressure chamber was gas-saturated for 20 min, and then ~400 mL was released into a 600 mL beaker containing 400 mL solution with the same chemical composition and pH, and the gas holdup was measured; b) a solution (500 mL) with given chemicals was saturated in the pressure chamber for 20 min, and was released (~400 mL) into a 600 mL beaker containing 400 mL suspension of a given silica content with the same chemical composition and pH. The results in Fig. 5.10 show that when releasing solution into a slurry (case b) there was essentially no effect of solids content on gas holdup, indicating that a reduced bubble rise velocity due to attached particles was unlikely to be the main reason for the increase in gas holdup in the presence of chemically-induced hydrophobic particles.

The effect of different gas saturation procedures (see Fig. 5.2) on bubble formation in the presence of solids is shown in Table 5.1. At the given pressure (313 kPa) and saturation time (20 min), raising the pressure directly by bubbling from zero to the final value (i.e., the "fast saturation" procedure) produced a lower gas holdup than by a slow increase in the pressure to the final level during bubbling (i.e., "step saturation" procedure). Increasing the saturation pressure with no bubbling (i.e., "direct pressurization" procedure) resulted in a lower gas holdup. However, even without bubbling, a similar gas holdup was obtained by using a longer saturation time (90 min), suggesting that the total amount of gas dissolved in liquid may play a role.
Figure 5.9 Schematic of set-up for different tests
Figure 5.10 Effect of solid % (w/w) on gas holdup (-5 μm silica)

(1.25 x 10^{-4} M DDA; release tube d = 1.5 mm; CO_{2}; 20 min. gas saturation)
Table 5.1 Effect of different saturation procedures on bubble formation

\(P = 313 \text{ kPa}\)

<table>
<thead>
<tr>
<th>Saturation Procedure</th>
<th>Saturation Time, (min)</th>
<th>Gas Holdup (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step Saturation</td>
<td>20</td>
<td>41.5</td>
</tr>
<tr>
<td>Fast Saturation</td>
<td>20</td>
<td>17.7</td>
</tr>
<tr>
<td>Direct Pressurization</td>
<td>20</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>40.9</td>
</tr>
</tbody>
</table>

Conditions: - 5 \(\mu\)m 1\% (w/w) silica. \(1.25 \times 10^{-4} \text{ M DDA}\). the slurry remained stirring during gas-saturation.

5.4. DISCUSSION

5.4.1. Energy Effects

To form a cavity in bulk water the structure of water has to be broken. The forces which hold water molecules together are intermolecular cohesive forces and external positive pressures [Knapp et al., 1970]. If the pressure is reduced below zero, water is under tension, and the structure of water will rupture to form a cavity when the tension is stronger than the intermolecular attractive forces. According to Bernoulli’s principle, the reduction of pressure in a liquid stream can be achieved by converting the kinetic energy of the flow. When the velocity reaches a critical value, the weakest location in the stream
will rupture and cavity bubbles will form. In a real liquid, such weak points can be: pre-existing gas nuclei; gases trapped in crevices of solid particles and cracks in the container walls; or particulate impurities. Because of this, the energy required to initiate cavitation is much less than that predicted from the theory of either homogeneous or heterogeneous nucleation (see Chapter 2). In addition, it has been reported [Dean, 1944] that cavitation can be initiated at less than one-tenth of the energy necessary to produce a pressure as low as the vapor pressure, due to pre-existing gas nuclei. As shown in Fig. 4.9, cavitation is easier in the presence of gas nuclei (i.e., occurs at lower liquid flow or release velocities).

The existence and stability of free gas nuclei in normal liquids are not well understood. These gas nuclei do not form spontaneously, because nucleation involves creation of new interface and hence an increase in system energy. If gas nuclei are formed in water under external activation, such as supersaturation and agitation, the changes in free energy in the system, $\Delta F$, can be calculated using Eq. (4-2) [Takahashi et al., 1979; Ward et al., 1970]:

$$\sum F = \sum n_{ni} (\mu_{bi} - \mu_{li}) - (P_b - P_a) \sum V_b + \sigma \sum A$$

(4-2)

Assuming that air is the only component in the bubble or gas nuclei, the critical radius $R_{bc}$ for a bubble to stabilize can be given by

$$R_{bc} = \frac{2\sigma}{P_a - P_b} = \frac{2\sigma}{H(c_s - c_p)}$$

(5-1)
where $P_s$ and $P_o$ are the supersaturation pressure and atmospheric pressure, respectively; $c_s$ and $c_o$ are the saturation concentration of the gas in liquid at $P_s$ and equilibrium concentration of the gas in liquid at $P_o$, respectively; and $H$ is Henry's constant.

For an air-supersaturation pressure of $3 \times 10^5$ Pa (gauge) in pure water, bubbles have a critical radius of $0.48 \times 10^{-6}$ m, which is sufficiently small for them to remain in suspension by Brownian motion. This indicates that gas nuclei and tiny bubbles can be generated and stabilized in gas-supersaturated systems under high shear. The formation of cavity bubbles by mechanical agitation in a flotation cell has been shown by Grainger-Allen [1970]. As indicated in Fig. 5.4, gas holdup was much higher when stirring the liquid than without stirring, partly resulting from the formation of more cavities.

When decompressing a solution, or releasing the solution from a pressure chamber, the expansion of gas nuclei breaks the equilibrium between the mass of gas within gas nuclei and that in the bulk liquid. Therefore, the gas nuclei may grow to visible bubbles through the diffusion of gas molecules into and consequent expansion of the nuclei [Shafer and Zare, 1991; van de Ven and Dukhin, 1992]. Considering the effect of adsorbed films of surface-active materials, which build barriers to mass transfer, the model of Libermann [1957] can be modified to estimate the process of bubble growth as:

$$ R_t^2 = R_{bc}^2 + \frac{2D_L}{\rho_g} (c_s - c_o) t - \frac{2D_L \delta}{D_u} (R_t - R_{bc}) $$

in which $R_t$ is bubble radius after time $t$; $D_L$ and $D_u$ are the gas diffusion coefficients in

---

**The original model was used to estimate the dissolution rate of a bubble in water under both stationary and free rising conditions.**
the absence and presence of adsorbed films at the gas/liquid interface, respectively; and, 
δ is the thickness of the adsorbed film.

Since the diffusion coefficients of most gases $D_L$ are similar (in the order of $10^{-10}$ m$^2$/s) [Dean, 1944; Houghton et al., 1962], the rate at which gas enters a bubble [Eq. (5-2)], will be largely controlled by any surfactant films and by the solubility of the gas. Therefore, more small bubbles are produced, resulting in a higher gas holdup in the presence of surfactants, as shown in Fig. 5.4. In addition, the expansion rate of a bubble may also depend on the experimental procedure employed (consider the consequences of shaking a bottle of carbonated water compared with one left undisturbed before opening). The strong shear and high turbulence present in most new flotation cell designs may serve to accelerate bubble formation, by increasing the number of the nuclei generated, and the rate of gas diffusion into the nuclei resulting from the distortion or disturbance of the surface film of adsorbed surfactants on the gas nuclei (Fig. 5.3-5.4).

5.4.2. Solids Effect

Adding solids increases the liquid density, $\rho$, and viscosity, $\mu$, simultaneously. If this was all that changed, the analysis of Banisi et al., [1995] showed that the predicted effect is a slight increase in gas holdup. This suggests that the present observations (i.e., gas holdup can decrease or increase, depending on the surface properties and the amount of solids added), can not be satisfactorily explained by changes in these two physical parameters alone. They must, therefore, be also related to the events occurring during gas saturation inside the pressure chamber and during slurry release.

In gas supersaturated systems, the rate of bubble evolution in the presence of solids may be governed by the nucleation process, by the rate at which nuclei grow, by a combination of both, or by the kinetics of detachment of bubbles from solid surfaces [Carr et al., 1995]. Consequently, increasing either the number of gas nuclei or the
quantity of gas molecules dissolved in water under dynamic conditions may enhance bubble formation and give rise to a higher gas holdup.

5.4.2.1 Natural Hydrophobic Particles (Coal)

In the presence of naturally hydrophobic particles, the total number of gas nuclei is the sum of free gas nuclei in the water and the gas nuclei entrapped on the surface. When coal particles are mixed with water, "entrapped" gas nuclei form, due to the low wettability of (unoxidized) coal. In addition, some of the gas nuclei generated by the vigorous mixing employed here during gas saturation may attach to coal particles in suspension, and thus remain in the slurry. Because of these two contributions, the number of bubbles and therefore, the gas holdup may increase in the presence of coal particles, thus explaining the increase in gas holdup (from 15.5% to 18.5%) at the low solids content indicated in Fig. 5.7.

In gas/liquid/solid systems, hydrophobic particles tend to induce bubble coalescence as bubbles spread across the solid surface to achieve the characteristic contact angle of the system [Dippenaar, 1982]. Such coalescence is observed in water only (i.e., surfactant free water [Van Weert and Ruizendaal, 1995; Jamiahadi and Muller-Steinhagen, 1991]). It can also be observed when surfactants are present [Dippenaar, 1982; Cilliers and Bradshaw, 1996], but this is sometimes due to hydrophobic surfaces adsorbing surfactant by hydrophobic interaction, and thus removing it from the water. For example, a significant reduction of gas holdup in the presence of coal particles (15% v/v, $d_{54} = 53 \mu m$), compared to that without solids, was reported by Banisi et al., [1995], which was attributed to the reduction of frother concentration in the liquid phase. Due to the different conditions used in this study, it is difficult to evaluate the effect of coal particles on frother reduction in the liquid. In addition, the hydrophobicity of coal may have different effects on bubble coalescence, and thus on gas holdup [Zhou, et al., 1993]. Now the question is whether the presence of coal particles induces bubble coalescence in the present study. To simplify the evaluation, it is assumed here that all frother molecules are
adsorbed on coal particles, then the measured gas holdup should be similar to that without frother addition in the absence of coal, i.e., $\varepsilon_g \geq 10.5 \pm 0.5\%$ at $P = 313$ kPa (Fig. 5.4); however, the measured gas holdup at 2% w/w coal particles is only about 7% (Fig. 5.7), suggesting some bubble coalescence. Further work is needed to determine which factor (i.e., induced bubble coalescence, or frother adsorption) dominates the reduction of gas holdup in the presence of natural hydrophobic particles.

5.4.2.2. Natural Hydrophilic Particles (Silica)

According to Wilt [1986], the nucleation rate for heterogeneous nucleation reduces to that for the homogeneous case when the contact angle equals zero. Since there should be no change in the total amount of gas nuclei in water after addition of hydrophilic silica (there being no entrapped gas nuclei on a hydrophilic surface), the bubble nucleation rate should remain unaffected. However, the gas holdup reduced in the presence of hydrophilic silica (Figs. 5.6 and 5.8). The thermodynamic analysis by Yount and Kunkle [1975] indicated that the probability of forming a bubble decreases in the presence of hydrophilic solids, which seems to agree with the present findings, but the event of bubble formation is a non-equilibrium process and is generally not regarded as amenable to thermodynamic treatment [Dean, 1944].

One possible reason for the reduction of gas holdup may be related to the total number of gas molecules dissolved in water. It was reported that the amount of dissolved gas in solution reduced in the presence of hydrophilic solid particles, which was explained by the adsorption of gas molecules on the particle surfaces [Klassen and Mokrousov, 1963; Gregg and Sing, 1976]. This is only applicable for a sealed system (i.e., the initial amount of gas dissolved in the liquid is fixed), which is not the situation here. It is possible, nevertheless, that the formation of a water film on the silica particle surface may have an effect on the dissolved gas content. Because of the strong interaction with silica, water molecules near the surface will exhibit some order, forming a solid-like film [Drost-Hansen, 1969; Derjaguin and Churaev, 1986]. Such a film has features distinct
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from bulk water, with increased viscosity and density, reduced dielectric permeability and
dissolving power [Derjaguin and Churaev, 1987; Churaev, 1991]. The last point suggests
a lower gas solubility is expected within this film. The consequence is that both the total
free water in the system and the total amount of gas molecules dissolved are reduced.
However, the calculation of the total amount of water attached on the particle surfaces
is complicated by the uncertain thickness of water films (the reported values ranging from
100 Å to 0.1 - 0.3 µm ([Klassen and Mokrousov, 1963; Drost-Hansen, 1969; Derjaguin
and Churaev, 1987])). Therefore, the exact reason for this reduction in bubble formation
in the presence of hydrophilic silica is unclear.

5.4.2.3. Chemically-Induced Hydrophobic Particle (DDA + Silica)
In this case the stability of froth formed depended on the %solids in the slurry. When the
solid content was low, e.g., 0.2%, the froth was thin (~1 cm) and unstable, only
persisting for a few seconds, which was similar to the case with no solid addition. At
higher solid concentrations the froth was thicker (up to ~5 cm, i.e., about the half vessel
was occupied by froth) and stable, persisting for several minutes. This indicates the
bubbles formed were stabilized by chemically-induced hydrophobic silica particles, which
was opposite to the case with coal particles.

Hydrophobic particles provide gas nucleation sites. The number of sites depends on the
number of particles and their degree of hydrophobicity. Consequently, in the absence of
coalescence, increasing gas holdup with solids addition is expected. This is the situation
here up to 2% (w/w) but with a further increase in solids, gas holdup decreased (Fig.
5.8). Gas holdup, therefore, reduces in two systems after a certain solids addition -
naturally hydrophobic coal and chemically induced hydrophobic silica - but the origin may
be different. Evidence for this is that while there were no obvious changes in the stability
of the froth formed when silica (> 2% w/w) was added, for coal, large bubbles and fast
froth collapse were observed. One reason for the reduction in gas holdup with increasing
solid content in the DDA-silica system may be caused by a reduced concentration of
CHAPTER 5  GENERATION OF SMALL BUBBLES BY GAS-SUPERSATURATION

An increased rate of gas evolution in water in the presence of chemically-induced hydrophobic particles, compared to that without solids, was demonstrated by Klassen and Mokrousov [1963]. This phenomenon appears to be related to the low wettability of these particles, resulting in gas molecules and nuclei being accumulated at the interface. The ability of hydrophobic particles to “trap” gas nuclei is also evident in this study. After releasing about 400 mL slurry, the remaining slurry (~100 mL) was kept in the beaker within the pressure chamber. The beaker was removed after releasing the pressure inside the chamber by opening the gas release valve. Virtually no bubbles were observed. However, shaking the beaker produced an abundance of bubbles, which formed a thick foam. In contrast, only a few bubbles formed in the case without solids. A tentative explanation is that without stirring bubbles were temporarily stabilized by being attached to the hydrophobic particles and shaking introduced sufficient shear to detach them. (It is not known whether this phenomenon is similar to the cases of copious bubble formation in beer [Shafer and Zare, 1991] and in salt solutions upon shaking [Hofmeier, et al., 1995].)

Now the question arises as to how gas nucleates on chemically-induced hydrophobic particles, with contact angles about 15 - 20° [Fuerstenau, 1957; Smith and Akbar, 1976], as encountered here. According to heterogeneous nucleation theory [Winterson, 1977; Wilt, 1986], among other requirements, a contact angle of greater than 90° is required for the surface to act as a nucleation site. Although the macroscopic contact angle of particles under the present conditions was low, it is possible that DDA molecules adsorb as localized clusters (hemimicelles) which exhibit higher local contact angles at the microscopic level. Kitchener [1984] found that some areas may become more hydrophobic than others reflecting the microscopic heterogeneity of almost all real mineral surfaces. Recent investigation by Carr et al. [1995] revealed a distribution of active nucleation
sites. Also, in the presence of adsorbed gas or vapor, the contact angle was shown to increase significantly [Klassen and Mokrousov, 1963], indicating the difficulty in evaluating the microscopic properties of the particle surface from macroscopic measurements. On the other hand, the results also suggest that for hydrophobic particles to act as nucleation sites, contact angles can be less than 90° under dynamic conditions.

Dean [1944] proposed that although an adsorbed monolayer of gas on a particle surface would not be expected to promote bubble formation, there is considerable evidence that multilayers of gas adsorbed on or accumulated near the surface in supersaturated solutions may act as nuclei. Theoretical analysis [Yount and Kunkle, 1975] indicated that the direct accumulation of gas molecules on hydrophobic particles to form a gas nucleus requires a high degree of supersaturation (~1000 atm), which does not correspond to the situation here. Therefore, some mechanism must exist whereby energy can be concentrated at a point to an extent that the high attractive forces between neighboring molecules can be overcome and a cavity be generated [Hayward, 1970]. One possibility may be the dynamic conditions used in this study, which is considered next.

5.4.3. Stirring and Dissolved Gas

Under dynamic conditions, the turbulence generated by strong stirring causes pressure fluctuations so that at some locations the pressure drops to the water vapor pressure, and thus a water vapor cavity forms. The formation of a cavity would be facilitated in the presence of solid particles due to the pronounced changes in pressure around a particle. Therefore, some cavities may form at low pressure regions on hydrophobic particles, into which dissolved gas would migrate. If the liquid is not saturated with gas, or the concentration of gas molecules in the liquid is not sufficient, mechanical equilibrium may not be reached between the cavity and the surrounding liquid, and the incipient cavity will collapse. (This may explain the different effect of solids on bubble formation in gas-supersaturated systems compared to ambient pressure conditions, as shown in Chapter 4.)
Therefore, the formation of bubbles by mechanical agitation is a function of stirring intensity and the concentration of dissolved gas.

Besides generating cavities, the continuous stirring employed during the saturation period in this study also served to promote gas dispersion and dissolution. This may increase the diffusion rate of gas molecules into any newly-generated cavities, thus preserving them and giving a higher gas holdup for the same gas supersaturation pressure compared to that with no stirring. The results in Table 5.1 support this contention: a high gas holdup was obtained both by bubbling in gas (indicating efficient dispersion and dissolution of gas) and, by using a long saturation time. This suggests that stirring generated cavities, and that a long saturation time allowed more gas molecules to dissolve and migrate into the cavities.

More importantly, the fast release of slurry may have further enhanced cavity formation and gas diffusion, due to pressure fluctuations in the stream as predicted from Bernoulli’s principle. Fig. 5.3 clearly showed that although the saturation pressures were similar, faster liquid release velocities produced more bubbles, which agreed with the recent work by Jackson [1994]. Since gas holdup is a measure of the concentration of gas bubbles in the system, the increased gas holdup in the liquid released from the pressure chamber suggests that more gas is present in the form of nuclei or small bubbles, rather than in the form of individual molecules. Formation of nuclei/small bubbles would appear to be the desired situation for most solid/liquid and mineral separation technologies based on gas-supersaturated systems such as dissolved air (gas) flotation and vacuum flotation.

5.5 SUMMARY OF CHAPTER

1. Large quantities of microbubbles are generated by the fast release of gas-saturated solutions in the presence of surfactants. Higher gas holdups were obtained using CO₂ than
that using air, due to the higher solubility of CO₂.

2. Bubble formation in gas-supersaturated systems under dynamic conditions is affected by the amount of gas nuclei, the total amount of dissolved gas and the liquid release velocity. Strong stirring of the liquid, slow increase of the saturation pressure by bubbling, and fast release of the liquid from the pressure chamber, as well as addition of a small amount of hydrophobic particles enhanced bubble formation significantly.

3. Gas holdup decreased upon addition of hydrophilic silica. The exact reason for this is unknown.

4. In the presence of a small quantity (< 0.1% w/w) of natural hydrophobic coal particles, gas holdup increased. This was attributed to an increased number of gas nuclei and nucleation sites. In the presence of > 0.1% w/w coal, gas holdup reduced by up to 50%. This was attributed to the coalescence of bubbles induced by the hydrophobic nature of the solids, and the adsorption of frother by coal particles.

5. Gas holdup initially increased significantly in the silica-DDA system with increasing solids content, more than doubling at 2% (w/w), compared with no solids. This was attributed to an increased number of nucleation sites and stabilization of the bubble dispersion in the presence of solids. A further increase in solids content reduced gas holdup, one reason may be attributed to a reduced surfactant concentration in the bulk liquid.
CHAPTER 6

INTERACTION BETWEEN GAS NUCLEI AND FINE PARTICLES*

6.1. INTRODUCTION

The thesis to this point has shown that the formation of bubbles by hydrodynamic cavitation is mainly due to the expansion of the pre-existing gas nuclei, and that the more gas nuclei that exist the more bubbles form. Although the existence of gas nuclei in water, even in highly purified water, has been demonstrated directly and indirectly, it involves sophisticated procedures in most cases [Flynn, 1964; Yount and Kunkle, 1975; Johnson and Cooke, 1981; Yount, et al., 1984; Yount, 1989]. To demonstrate the existence of gas nuclei in water in a simple way (which forms the basis for applying cavitation principles to flotation cell designs), and examine their effect on particle/particle, and particle/bubble interaction, coagulation, sedimentation, and filtration tests were used in this study.

6.2. EXPERIMENTAL

A Pittsburg #8 coal and a low rank coal from Malaysia (1.4% mineral matter) were used. The coal chunk was broken with a hammer, and then dry-pulverized in a bench-scale hammer mill. The minus 400 mesh (38 \mu m) fraction was obtained by dry screening, and stored in a freezer to minimize oxidation. The surface hydrophobicity of coal was estimated from the contact angle (measured by a goniometer). An advancing contact angle of about 65° was obtained by placing a water drop on a flat surface of a coal chunk. A similar value was reported by Drzymala and Wheelock [1995].

The second material used in this work was minus 10 \mu m silica (>99% pure, d_{50} \approx 3.5 \mu m), provided by the US Silica Company.

Chemicals used included dodecylamine hydrochloride, DAH (Kodak) as a surfactant, calcium chloride (Fisher Scientific) as a coagulant, and sodium hydroxide (Fisher) for pH adjustment. Distilled water was used for all tests, and the experiments were conducted at room temperature.

6.2.1. Coagulation/Sedimentation Test

For the coal, 15 g samples were mixed with 600 mL water (volume fraction, 1.85%) in a beaker for 15 to 20 min by magnetic stirring. (Caution was taken to avoid the entrainment of air and thus the formation of bubbles when stirring.) While still mixing, slurry was transferred to fill a Plexiglas cylinder (I.D. 3.8 cm and 16.5 cm high) with a volume of 187 mL, and the top of the cylinder was sealed by a piece of parafilm (Fig. 6.1). After shaking the slurry by turning the cylinder end over end, the particles (aggregates) were allowed to settle in the cylinder for a given period of time (the parafilm was removed at the beginning of settling). Then, the outlet tube (6 cm from the bottom) was opened and the upper portion of the slurry (referred as "supernatant") was drained
Figure 6.1 Settling cylinder used in tests:

a) immediately after mixing, sample gives C0;

b) after a given time of settling, supernatant gives C.
out and collected in a second beaker. Both the sediment and the supernatant were filtered, and the solids dried and weighed. This approach to obtaining settling data was used as no solids/supernatant interface was visible, and the supernatant still contained varying amount of suspended solids.

For the -10 \( \mu \text{m} \) silica sample, a 29.4 g sample was mixed with 600 mL water (volume fraction, 1.85%). A given dosage of dodecylamine hydrochloride (DAH, Kodak) was added to give a solution concentration of \( 10^{-1} \) M. The pH of the solution was adjusted to about 9.5 - 10.0 by sodium carbonate (Fisher Scientific). Under this condition, the reported contact angle of silica is about 80° [Fuerstenau, 1957; Smith, 1963]. The subsequent experimental settling procedure was the same as for coal.

To examine the effect of degassing on coagulation/sedimentation, the beaker containing the slurry was placed in a desiccator which was connected to a vacuum pump. During degassing, the slurry was stirred by a magnetic stirrer. Degassing continued until no visible bubbles formed in the slurry. Then the slurry was transferred to the cylinder for the settling test using the same procedure as described above.

The settling efficiency, \( E_c \), was evaluated using the "coagulation" efficiency formula introduced by Xu and Yoon [1989]:

\[
E_c = \frac{C_0 - C}{C_0} \times 100\%
\]

(6-1)

where \( C_0 \) and \( C \) refer to percent solids in the initial slurry and supernatant, respectively. The form of Eq. (6-1) implies that an increase in settling efficiency corresponds to an increase in settling rate, reflecting, for example, an increase in apparent particle size due to coagulation.
6.2.2 Filtration tests

The filter press used (Fig. 6.2) was the Model 3000 from Baroid Testing Equipment, Houston, USA. It was 9 cm high with a volume of about 420 mL. Filter paper of pore size 2.7 μm was used as the filter medium. The compressed air was set at a fixed value (136, 170 or 184 kPa).

During each test, a slurry containing a certain quantity of solids under given chemical conditions was mixed in a beaker for 15 min using a magnetic stirrer. The slurry was then transferred into the filter press and left for 5 - 8 min during which solids settled to develop a filter bed. Compressed air was then applied, and the filtrate collected in a beaker on an electronic balance. The filtrate weight was recorded as a function of filtration time. A second filtration was performed by pouring filtrate back on to the cake developed in the first filtration. This second filtration was conducted following the first filtration in two ways: (1) all the solution that could be filtered at the given pressure was removed; and (2) some solution was kept above the cake (i.e., before the air penetrated through the cake). Pressure was applied 5 minutes after the filtrate was re-introduced. The thickness of the cake was measured by a caliper after each test.

To examine the effect of degassing the slurry, the same set-up and procedure for slurry deaeration as described in coagulation testwork were used. The deaerated slurry was then transferred to the filter press, and subjected to the same filtration procedures as described above.

6.3. RESULTS

In the coagulation/sedimentation tests, a different settling behavior was observed for coal between the tests with and without degassing. Without degassing, some flocs floated on
Figure 6.2  Schematic of the apparatus used in filtration
the top, forming a thick layer. On opening the tube to allow the liquid to drain out, the inner wall of the top portion of cylinder was covered with a layer of coal. For degassed slurry, the coal was more dispersed; the apparent size of aggregates was observed to be smaller, compared to that without degassing, and essentially no aggregates floated on the top. For silica, there was no visible difference in behavior with or without degassing.

Figure 6.3 (a and b) shows the settling efficiency with and without degassing (or "natural", as referred to in the Figure). In the case of coal (Fig. 6.3a), degassing increased settling efficiency (i.e., deaeration increased the settling rate of coal) although visually (reported above) the flocs were smaller and particles more dispersed after degassing. In the case of silica (Fig. 6.3b), there was no settling without addition of DAH (i.e., the particles remained dispersed). With DAH, the particles settled, but in contrast to coal, deaeration reduced settling efficiency. The repeat tests shown in the Figure indicate that the experiments were reproducible.

In the coal filtration tests, thirty grammes of coal was mixed with 175 g of water. The natural pH of the resultant slurry was between 4.5-5.5, with or without deaeration. The results in Fig. 6.4 show that the filtration rate increased after degassing. Since the degassing procedure used will likely only remove gas nuclei present in the liquid and not those on the coal surface (the size of most cracks in which bubbles lodge is less than 300 nm [Owen, 1989]), one reason for the increased filtration rate could be attributed to reduced blockage of capillaries by bubbles entrapped in the cake.

To further explore the effect of gas and gas nuclei, air was bubbled through a previously deaerated coal slurry for 30 minutes prior to filtration. Fig. 6.5 shows that the filtration rate reduced (compared with the degassed sample), but remained higher than without degassing. Since the diameter of the bubbling tube was 3 mm, bubbling in the present case probably did not generate gas nuclei in the liquid. However, bubbling probably expanded gas nuclei entrapped on the coal surface through diffusion of gas molecules. It
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Figure 6.3  Effect of gas nuclei on coagulation

a). coal in water;  b). silica in DAH solution (10^{-4} M)
Figure 6.4  Effect of deaeration on coal filtration
(Malaysia coal, $P = 136$ kPa)
FIGURE 6.5 Effect of bubbling the slurry on coal filtration

(Pittsburg #8 coal, \( P = 184 \) kPa)
appears that an increase in the size of nuclei on the coal surface could account for the lower filtration rate observed, compared to the degassed sample not subjected to bubbling.

In the silica filtration tests, the slurry (10% w/w solids) was filled to the top edge of the filter press. The pH of the slurry was adjusted to 9.0 - 10.0 by NaOH. Fig. 6.6 shows the effect of deaeration on the filtration of silica in the presence of 10^{-2} M DAH. The filtration rate reduced after deaeration, which is opposite to the result for coal. The sedimentation results in Fig. 6.3b showed that the settling rate was reduced after degassing, suggesting a reduced aggregate size. The same effect here could increase the cake packing density and contribute to the reduced filtration rates as observed (more tortuous path for water removal due to smaller particles).

The possible dual role of gas nuclei in modifying aggregate size, as well as interfering with liquid flow through the channels in the cake, complicates the interpretation of the results. In an attempt to avoid changes in aggregate size and structure of the cake, the second filtration was performed at the same pressure as used in the first filtration. As shown in Fig. 6.7, the general trend in silica filtration was that the second filtration was slower initially, and then faster than the first filtration. This trend was different from that for coal, where the second filtration was always slower than the first (Fig. 6.8). Nemeth and Sirois also observed [1970], in their tests with distilled water filtering through a bed of cotton cloth, that the filtration rate increased when the filtrate was refiltered by vacuum filtration for all the 50 tests they conducted. This suggests that the interaction between gas nuclei and particles may depend on particle surface properties.
Figure 6.6  Effect of deaeration on filtration of silica in $10^{-4}$ M DAH
($pH = 9.0 - 10.0$, $P = 170$ kPa)
Figure 6.7  Comparison of the first and second filtration of silica
(pH = 9.0 - 10.0, P = 170 kPa, $10^{-2}$ M Ca$^{++}$, $10^{-4}$ M DAH.

data points in DAH and Ca$^{++}$ were not shown for the sake of clarity)
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Figure 6.8  Comparison of first and second filtration of coal
(Malaysia coal, \( P = 170 \) kPa)

Note: (1) and (2) indicate the repeated tests
6.4 DISCUSSION

6.4.1 Entrapment of Gas Nuclei

6.4.1.1 Coagulation/sedimentation

The existence of gas nuclei in water has been observed and demonstrated repeatedly, although the exact reason for their existence is still unknown [Brennen, 1995]. Due to their small size, they remain in suspension by Brownian motion. When mixing solids with water, these gas nuclei may interact with particles. To examine the effect of gas nuclei on the behavior of particle aggregates, the density of aggregates formed by the particles being bridged by gas nuclei was calculated. The following conditions were assumed: coal, density \( \rho_p = 1.35 \text{ g/cm}^3 \), size \( d_p = 10 \mu\text{m} \) (the sizes are relevant to the average particle aggregate size after degassing [Zhou et al., 1996]); silica, density \( \rho_s = 2.65 \text{ g/cm}^3 \), size \( d_s = 18 \mu\text{m} \) (determined from the sedimentation); gas nuclei, diameter \( d_n \leq 0 \mu\text{m} \) (\( d_n > 0 \)).

For simplicity the natural case considers two particles bridged by one gas nucleus, while for the degassed case, the two particles remain separate. The apparent density of the aggregate formed in the natural case \( \rho_a \) is:

\[
\rho_a = \frac{2 \times d_p^3 \rho_p}{2 \times d_p^3 + d_n^3}
\]

with a volumetric mean diameter of

\[
d_a = \left(2 \times d_p^3 + d_n^3\right)^{\frac{1}{3}}
\]

and an aggregate settling velocity given by Stokes' equation
Using equation (6-4), the settling velocity of aggregates in the presence of gas nuclei was calculated as a function of the diameter of gas nuclei entrapped (Fig. 6.9). (For $d_g = 0$, the settling velocity is for a single particle, i.e., the degassed case.) Note that for $d_g \geq -6.5 \mu m$, the natural coal (coal-I) aggregate (two particles with diameter of $10 \mu m$ bridged by a gas nucleus) has a settling velocity less than that of the coal with degassing (one particle with diameter of $10 \mu m$), and when the gas nuclei are larger than $9 \mu m$, the coal-I aggregate actually has a negative settling velocity, i.e., it rises. The decrease in settling rate, and the levitation of some particles observed corresponds to this prediction.

For silica, on the other hand, the natural sample (two particles with diameter of $18 \mu m$ bridged by a gas nucleus up to $17 \mu m$ in diameter) had a higher settling rate than the degassed sample, which again corresponds to the observation. To account for the observations for both coal and silica, the average diameter of gas nuclei therefore has to be in the range of $6.5-17.5 \mu m$ (shaded area in Fig. 6.9). Interestingly, this lies in the typical size range of gas nuclei found in unpurified water, according to Flynn [1964] and Mesler [1985].

Besides the density effect, a contributing factor in the different coagulation behavior of silica and coal may be a lower concentration of gas nuclei in the case of the silica slurry, due to the hydrophilic nature of silica. The total number of gas nuclei in a slurry include the free nuclei already present in water plus those entrapped on particles. Natural hydrophobic particles with rough surfaces (like coal) tend to entrap more gas on their surface when dispersed in water [Hemmingsen and Hemmingsen, 1990; Ryan, 1991], than do hydrophilic ones such as silica. Using the same numerical example as above, but assuming that coal particles are bridged by two gas nuclei, and silica particles remain
Fig. 6.9  Effect of gas nuclei on the settling velocity of aggregates

Note: Coal-1 two particles are bridged by one gas nucleus
Coal-2 two particles are bridged by two gas nuclei
bridged by one gas nucleus, the settling behavior was recalculated (coal-2 in Fig. 6.9). This leads, as anticipated, to a further decrease in the settling rate of coal and suggest that nuclei finer than 7 \( \mu \text{m} \) could now cause aggregates to levitate. Since in practical situations, several gas nuclei may be entrapped between two particles, and the calculation is based on the volumetric mean diameter of all gas nuclei entrapped, it is expected that even gas nuclei with a size less than 1 \( \mu \text{m} \) that may exist in water could contribute to the settling behavior.

6.4.1.2 Hydrophobic interaction

Since the hydrophobic force is the major driving force for hydrophobic coagulation [Xu and Yoon, 1989, 1990], any changes in hydrophobicity are expected to affect coagulation. It is not known if gas nuclei affect the actual hydrophobicity of particles. What is important in the present work is that gas nuclei enhance the interparticle attractive force and increase coagulation rates. Parker and Claesson [1994] measured and analyzed the hydrophobic force as a function of hydrophobicity in the presence and absence of gas nuclei. They found that the presence of gas nuclei increased the magnitude of attraction. It was also reported that degassing gave increased stability of oil-in-water emulsions [Meagher and Craig, 1994]. Since oil droplets are destabilized by the hydrophobic interaction, the implication is that removal of the dissolved gas reduced this interaction. Applying these results to the current study, it appears that a higher coagulation rate in the presence of gas nuclei could also be due to the stronger attractive force resulting from the highly hydrophobic nature of the gas (vapor) phase, thus causing hydrophobic particles to experience an attractive force over a larger separation distance, than would be the case in the absence of gas nuclei.

6.4.1.3 Interaction between gas nuclei and particles

To develop a physical picture of the interaction between gas nuclei and particles for the systems studied here, Fig. 6.10 illustrates the probable effect of gas nuclei on coagulation, sedimentation, and filtration of particles with different surface properties.
CHAPTER 6  INTERACTION BETWEEN GAS NUCLEI AND FINE PARTICLES

a) interaction between gas nuclei and natural and induced hydrophobic particles
b) first vs second filtration for (hydrophobic and hydrophilic) silica

Fig. 6.10  Schematic of the interaction between gas nuclei and particles
For coal, since the total number of gas nuclei in the slurry is the sum of those present in water and those entrapped on the coal surface, deaeration may not be able to remove the entrapped gas nuclei. Thus the changes in the size of particle aggregates, pores and structure of the cake may be minimal before and after deaeration. But deaeration which removes the relatively large gas nuclei in water will have some effect on increasing the density of the aggregates and reducing the blockage of pores and channels, thus increasing the settling and filtration rate (Figs. 6.3 - 6.5).

In the case of chemically-induced hydrophobicity (silica with DAH), there is probably no gas nuclei entrapped on the particle surfaces, due to their originally hydrophilic nature. Consequently, aggregation is controlled mainly by the gas nuclei in the water. After degassing and removal of the gas nuclei the aggregates may break and re-arrange to give a more compact cake structure. This would result in a reduced aggregate and pore size, and therefore, lower settling and filtration rates (Figs. 6.3, 6.6 and 6.10).

To interpret the second filtration results with regard to the possible role of gas nuclei, the tenacity with which nuclei are held in the cake, and therefore, the number of nuclei in the filtrate relative to the feed liquor needs to be considered. In the case of coal, gas nuclei may remain trapped in the cake, due to their strong interaction with the coal surface. This helps explain why the filtration rate near the finishing point of the first filtration is almost the same as that at the start of the second filtration (Fig. 6.8). The reduced filtration rate of the second filtration with time, may be either due to the further compression of the cake or the accumulation of the trapped gas nuclei at the bottom of the cake, which will be discussed later.

Compared to coal, for silica (hydrophilic or chemically-induced hydrophobic) particles, some of the relatively large gas nuclei within the cake tend to be flushed out upon breakthrough at the end of the first filtration (Fig. 6.10b). Therefore, the total number of gas nuclei present is less during the second filtration, and the filtration rate is duly
To explore this possible "flushing out" effect, the two second-filtration procedures were compared, i.e., one where the first filtration was conducted to completion, and the second, where the first filtration was stopped with sufficient liquid to just cover the cake. Figure 6.11 shows that the first and second filtration rates were similar in the second procedure (i.e., "partial" in the figure), while a higher filtration rate was obtained in the second filtration for the first procedure (i.e., "full" in the figure). This reinforces the view that one of the reasons for the increased rate in the second filtration using the first procedure is due to the flushing out of gas nuclei from within the cake at the end of the first filtration.

### 6.4.2. Specific Resistance to Filtration

To further demonstrate the existence of gas nuclei in water and investigate their effect on filtration, an analysis of specific resistance to filtration was conducted. Conventionally, the filtration rate is expressed as [Carman, 1938]:

\[
\frac{dV_o}{dt} = \frac{P_T A_f}{\mu (x^* L_c + R)}
\]  

where \( V_o \) is the filtrate volume at time \( t \) (m³); \( P_T \) is pressure difference across the cake and the medium (Pa); \( A_f \) is the filtration area (m²); \( \mu \) the viscosity of slurry (N/s.m²); \( r^* \) the inverse of the permeability coefficient for the modified Darcy expression (1/m²); \( L_c \) the thickness of the cake at time \( t \) (m); and \( R \) is the support medium resistance (1/m²).
Figure 6.11  Effect of different procedures on filtration of silica

(pH = 9.0 - 10.0, P = 170 kPa, 10^{-2} M Ca^{++})

full: procedure 1, all the solution that could be filtered at the given pressure
was removed, then the filtrate was poured back for the second filtration;

partial: procedure 2, some solution was kept above the cake when the filtration
was stopped and the filtrate was then poured back for the second filtration.

"1st" and "2nd" refer to the first and second filtration.
Replacing \( r^* L_c \) by \( r_c \omega V_{o} / A_t \), under the assumption that the porosity of each successive layer of cake is the same and constant, and that the same volume of cake will be deposited by each unit volume of filtrate [Carman, 1938]. Eq. (6-5) becomes

\[
\frac{dV_{o}}{dt} = \frac{P \tau A_{f}^2}{\mu (x_{c} \omega V_{o} + PA_{f})}
\]  

(6-6)

where \( r_c \) is the cake specific resistance (m/kg), which is assumed to originate from the hydraulic resistance to water flowing through the pores of the filter cake; \( \omega \) is mass of cake deposited per unit volume of filtrate (kg/m³).

For constant pressure filtration, integrating Eq. (6-6) gives

\[
\frac{t}{V_{o}} = \frac{\mu x_{c} \omega}{2 P \tau A_{f}^2} V_{o} + \frac{\mu R}{P \tau A_{f}}
\]  

(6-7)

Eq. (6-7) indicates that the specific resistance \( r_c \) can be obtained from the slope of the curve \( t/V_{o} \) vs \( V_{o} \), which should be a straight line (reflecting the so-called parabolic behavior of rigid cake filtration [Christensen and Dick, 1985a, b], i.e., the curve \( t \) vs \( V_{o} \) is parabolic). This proved to be the case here (Fig. 6.12). The nonparabolic behavior at the initial filtration stage, apparent for coal without degassing (i.e., "natural"), is associated with sedimentation and consequent changes in the porosity of the cake with time [Christensen and Dick, 1985a; Tiller, et al., 1995].
natural degas • silica-water • silica
Pitl, #8 Pitl, #8 DAH, 10^{-4}M

Air flushing through the cake
Air flushing through the cake

Figure 6.12 Parabolic behavior of filtration demonstrated for samples studied here
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For constant rate filtration under constant pressure, if the cake has already been formed and \( \omega = 0 \), as in the second filtration tests, a horizontal line is expected when plotting \( t/V_0 \) vs \( V_0 \). A simple case is water flowing through a filter paper, as shown in Fig. 6.13.

Applying Eq. (6-6) to the results for the second filtration, Fig. 6.14 shows that the horizontal line is indeed observed, but only for the degassed samples. For samples without deaeration, the parabolic behavior remained in the second filtration. This is an indication of the effect of trapped gas nuclei. These gas nuclei tend to be pushed from the top to the bottom of the cake under the applied pressure (just like the deposition of solid particles on the filter medium). They may even coalesce during the filtration, thus forming bigger obstacles and reducing the effective surface area for filtration. The second filtration without degassing is akin to filtering gas nuclei from the filtrate, which produces a parabolic behavior, even though there are no solids in the feed.

6.5 SUMMARY OF CHAPTER

The results from coagulation and filtration tests have demonstrated the existence of gas nuclei in water and their effect on particle interaction, which has significance for the application of cavitation principles in flotation. The increased particle aggregate size through gas nuclei bridging may increase the collision probability of the aggregates with flotation-size bubbles; the strong interaction between gas nuclei and hydrophobic coal particles which resists break-up of gas nuclei/particle aggregates, as indicated by the second filtration results (Fig. 6.8), may reduce the detachment of the aggregates from the bubble surfaces. This may also provide further evidence to support the view that fine particle flotation should be conducted by fine bubbles under turbulent and shear conditions.
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Figure 6.13 Filtration of water through the filter press
Figure 6.14 Behavior of the second filtration of fine particles under different conditions.
CHAPTER 7

FINE PARTICLE FLOTATION AND
A FLOTATION REACTOR DESIGN

7.1. INTRODUCTION

Since the introduction of flotation into mineral processing at the turn of the century, numerous flotation cells have been developed; however, only a few have survived. Besides the basic requirements for flotation, there are many factors which affect the selection of cells [Flint, 1973]. One of the reasons that subaeration mechanical flotation machines have worked quite satisfactorily for the past seven to eight decades is related to processing relatively coarse particles associated with high grade ores. With their depletion, finely disseminated ores of low grade have to be treated. The feed preparation now requires extensive grinding to obtain adequate liberation. The processing of fine particles must therefore become routine, which poses a challenge to existing technology. Different solutions have been proposed. [Sivamohan, 1990; Fuerstenau, 1980]. However, the application of these techniques in practice often encounter difficulties, both technical and non-technical, especially for a flotation plant which has successfully run for years using the existing technology. Although flotation columns have shown their advantages during the last decade, they do not replace, but rather augment existing flotation technology. The role of technology in the minerals industry has recently been addressed by Batterham and Algie [1995]. They claim that it is innovation and modification of
existing techniques, rather than replacement by new technology, which may be the acceptable route. Therefore, this project does not aim to design a flotation cell to replace the existing ones, but to improve cell design and flotation circuits by adding useful features for accelerating particle-bubble collection rates, especially for fine particles, based on the fundamental work presented in the previous chapters. This chapter discusses the role of gas nucleation and cavitation in fine particle flotation and introduces a new flotation reactor designed to explore these phenomena.

7.2 FLOTATION BY GAS NUCLEATION

7.2.1 Mechanisms of Particle Collection

Particle collection by air bubbles in flotation is a multi-step process, involving three phases and interactions among solid/liquid, solid/gas and liquid/gas in the presence of various inorganic and organic species, while at the same time satisfying economical and mechanical constraints. A flotation cell should be designed to provide a favorable environment for fast particle collection by utilizing optimized collection mechanism(s).

At present, at least three mechanisms have been considered for particle-bubble attachment in flotation: gas precipitation or nucleation, impaction, and sliding [Klassen and Mokrousov, 1963], with only the latter being investigated in much detail over the last 40 years, due to the relative simplicity for theoretical treatment and experimental verification. However, the sliding mechanism alone does not explain the entire attachment process occurring in current flotation machines and certainly not in recently developed flotation cells. Conventional flotation columns present an ideal situation for particle-bubble attachment by the sliding mechanism. In mechanical flotation cells, sliding coupled with some degree of gas nucleation, contributes to the attachment (although it was over emphasized by Taggart [1927] that gas precipitation was the only mechanism for particle-
bubble attachment). In other non-mechanical cells, such as Jameson cells [1988], pneumatic cells [Bahr, 1985], and those using static mixers [Adel, et al., 1991; Jordan and Susko, 1992], the high flotation rate may be due to cavitation, or gas nucleation, coupled with strong particle-bubble impaction. This is because, from the kinetic point of view, particle collection by sliding is a slow process, which involves a particle contacting with, bouncing from and/or sliding on a bubble, and then attaching to the bubble by rupturing the intervening liquid film. It has been shown photographically that a hydrophobic particle can be captured by bubbles only after the particle has bounced off two or more bubbles, when the particle settles down against the rising bubbles in a water column [Whenan and Brown, 1956; Crozier and Klimpel, 1989]. The results in chapter 3 suggest that for the direct contact between a descending fine particle \( d_\text{p} < 10 \, \mu\text{m} \) and a rising swarm of bubbles, a collection zone as tall as 10 m is required to make sure that the particle does collide with a bubble once, which again implies an inefficient process. While particle attachment to bubbles by impaction is a faster process compared to sliding, due to the larger kinetic energy available to overcome the energy barrier, it has to satisfy the condition that the approach velocity of the particle to a bubble should not be greater than the thinning or drainage velocity of the intervening liquid film, or else the particle will bounce from the bubble surface, as evidenced from the photographs taken by a high speed moving camera [Whenan and Brown, 1956]. Gas nucleation on particles is instantaneous and avoids the collision stage. This indicates that the proper exploitation of gas nucleation/cavitation promises to improve the collection process to such an extent that new cell designs may emerge.

7.2.2 Dissolved Gas (air, CO\(_2\)) Flotation

7.2.2.1 Experimental Procedures

To compare the different particle collection mechanisms, and the effect of gas nucleation on flotation recovery, dissolved gas (air, CO\(_2\)) flotation of fine silica was conducted. The set-up was shown in Fig. 5.1. In the tests, 425 mL DDA (1.25 \( \times \) \( 10^4 \) M) solution was prepared using distilled water in a 600 mL glass beaker, then a given weight of silica was
mixed in the solution for about 10 min., followed by the addition of 20 ppm Dowfroth 250C. The slurry prepared as such was placed in the pressure chamber for gas-saturation. The pressure increase rate and procedure followed set-schedules (Fig. 5.2). After holding for a given period (40 min.), the pressure was released by different methods. Flotation was conducted in a 400 mL beaker which was placed in either an 800 mL or 1000 mL beaker. The froth product was collected in the 800 mL (1000 mL) beaker, with the non-floats remaining in the 400 mL beaker. (In the case of CO₂, flotation was conducted in a 800 mL beaker which was placed in a 2.5 L container to avoid the overflow of the released slurry.) The samples were then dried and weighed. No attempt was made to optimize the flotation conditions. To exclude the entrained gas effect on particle collection, the slurry release tube was immersed under a solution (same concentration as the solution in the pressure chamber) in the 400 mL beaker. Therefore, all changes in recovery could be attributed to the gas supersaturation system.

7.2.2.2 Results and Discussions
The effect of slurry release velocity on silica recovery is shown in Fig. 7.1. It is noted from this figure that regardless of gas saturation pressure, the recovery of silica can be correlated to the slurry release velocity in the systems studied: higher slurry release velocities gave higher silica recoveries. Since for a given (air or CO₂) saturation pressure, the total amount of gas dissolved in the system is the same for the cases with different release velocities, the different recoveries obtained indicated that something occurred during slurry release. As shown in Chapter 5, this may result from the increase in gas holdups with increase in the liquid release velocity caused by gas nucleation and cavitation on particle surfaces and in the slurry (Figs. 5.3 and 5.8).

It is also evident from this figure that for a given slurry release velocity, a higher silica recovery was obtained when using CO₂ than using air. This may be due to the difference in the amount of gas dissolved in the slurry. Compared with air, CO₂ has a much higher solubility in water. As discussed in Chapters 4 and 5, a higher dissolved gas content in
Figure 7.1  Effect of slurry release velocity on silica recovery
(note: the dotted lines connect the points with same saturation pressures)
the slurry facilitates the bubble formation by cavitation, and their growth to form bubbles large enough to levitate particles, thus increasing the recovery.

To support this, the effect of different gases on silica recovery is shown in Fig. 7.2. As can be seen, a higher silica recovery was obtained using CO₂ than using air, for a given saturation pressure and slurry release velocity, indicating that the amount of dissolved gas also plays a role in enhancing flotation.

To examine the effect of bubble nucleation on particle surfaces on flotation, two different procedures, similar to those described in Chapter 5, were used (Fig. 5.9). In these tests, a receiving beaker of 800 mL was used to avoid overflow. After releasing slurry (liquid), the solids which floated on the top of liquid were collected, the subsequent procedures were the same as those mentioned earlier in the experimental part (7.2.2.1). The results presented in Figure 7.3 show that higher recoveries are obtained by releasing slurry from the pressure chamber into the solution, compared with that by releasing solution from the chamber into the slurry. This, as already indicated in Fig. 5.10, is because more bubbles nucleated on particle surfaces during gas-saturation and slurry release, suggesting that bubble nucleation does enhance particle collection rates. A similar trend was also reported by Shimoiizaka et al., [1982] in flotation of fine coal ( ~ 15 μm) with the addition of kerosine (< 30 kg/t) or under the condition of a solids content greater than 2% w/w.

To verify the two-stage attachment model proposed by Dzienisiewicz and Pryor [1950], flotation tests were conducted by releasing the slurry from the pressure chamber into a mechanical flotation cell (1.5 L Denver cell, with air on). The following procedures were used: about 750 mL solution was put in the mechanical cell, then 500 mL slurry from the pressure chamber, which had been air-saturated (306 kPa) for 40 min, was released into the cell. Flotation was timed from whenever overflow started.
Fig. 7.2  Effect of different gases on silica recovery

\[(1.25 \times 10^{-4} \text{M DDA} + 20 \text{ ppm DF250}, 1\% \text{ solids, release tube } d = 1.0 \text{ mm})\]
Figure 7.3 Effect of gas nucleation on silica recovery
For fine silica (≤ 5 μm) flotation, attention was paid to the silica recovery by mechanical entrainment. Flotation of fine silica in the presence of 10 and 20 ppm DF250 showed that silica recovery was more than 90% of water recovery, even reaching 100%, in the case of 10 ppm DF250 addition.

To allow for this entrainment and simplify the analysis, silica recovery due to the entrainment was assumed 100% of water recovery, and the "true" flotation recovery was calculated by subtracting the water recovery. The results shown in Fig. 7.4 suggest that a higher recovery was obtained by releasing the slurry into the mechanical flotation cell, although the amount of dissolved gas in the released slurry was negligible, compared with the volume of gas introduced by the impeller action in the mechanical cell. Releasing slurry above the liquid level as a jet plunging into the cell further increased the recovery by entraining air into the cell. When comparing the results with the work of Klassen and Mokrousov [1963] and Shimoiizaka et al., [1982], the difference between the recovery by mechanical cell alone and the recovery by mechanical cell plus gas nucleation was much smaller in this study. One reason may be due to the low solid content and smaller size of particles used here. However, when comparing the results with the nucleation tests in Fig. 7.1, it is observed that a similar recovery was obtained no matter whether the slurry was released into a beaker or into a mechanical flotation cell with its additional air. The possible reason may be that the strong turbulence associated with the mechanical cell may increase the probability of detachment. The important implication from this observation is that for recovering particle aggregates, the flow condition in the separation cell should be kept as quiescent as possible.

The above results indicate that gas nucleation and cavitation provide a favorable mechanism for fine particle flotation, and that application of the two-stage attachment process (as discussed in Chapter 2) may improve the particle collection rates and flotation kinetics.
Figure 7.4 Effect of different feed procedures on silica flotation

(1% (w/w) silica; 1.25 x 10^{-4} M DAH + 10 ppm DF250; 1.5 L Denver cell; impeller speed: 850 rpm)
7.3 DEVELOPMENT AND TESTING OF A NEW FLOTATION REACTOR

7.3.1 Description of the Design

Based on the above experimental work and discussion, a new flotation reactor was designed and constructed (Fig. 7.5). The design is based on the reactor-separator concept. An attempt was made to exploit the two-stage attachment mechanism, i.e., the generation and nucleation of small bubbles on particle surfaces followed by their attachment to relatively larger bubbles. It is achieved by combining the attributes of dissolved gas with dispersed gas flotation. Since the separator could be either a flotation column or a mechanical flotation cell (i.e., any available device), the present design focuses on the practicalities of how to incorporate the two-stage mechanism into mineral flotation of fine particles.

The design can be divided into three parts: gas dispersion, gas compression and dissolution, and slurry release. The role of the gas introduced here is different from other designs such as in the Microcell column [Yoon, 1993] and the cell described by Xu et al. [1994], where the air stream is sheared to form flotation-sized bubbles by in-line static mixers. Since in the case of fine particle flotation, small bubbles are required, using static mixers and introducing relatively high gas flow rates in the stream under conventional operating conditions may not generate bubbles that are fine enough (say, less than 50 μm). The purpose of introducing gas into the stream in the present design is to increase the solubility of gas in slurry and to enhance bubble formation by cavitation downstream. As demonstrated in Chapters 4 and 5, introducing gas up-stream and increasing dissolved gas content enhanced bubble formation by cavitation.

Therefore, unlike the other designs, the gas here is introduced up-stream of the pump, instead of down-stream. (It should be noted that although the cyclo-flotation cell [Yalcin, 1994] also introduces air on the suction side of the pump, the objective is again to generate
Figure 7.5 Schematic of a flotation reactor
One reason for introducing gas upstream is to achieve higher gas saturation rates, as reported by Rees, et al. [1980a,b]. That same study also showed that saturation rate is further increased by installing turbines in the stream. Based on this, static mixers were inserted in-line to increase the turbulence and shear effect to further disperse the air. Introducing the gas on the suction side also increases the interaction between particles and any bubbles generated, especially when the slurry passes through the pump. The effect of centrifugal pumps on bubble generation and particle-bubble interaction will be shown later.

A second reason for introducing gas upstream is that the pressure there is generally lower than down-stream of the pump. Therefore, the internal pressure of bubbles generated in the stream by injecting (or aspirating) air would be lower on the suction side, and these bubbles will be further compressed under the high pressures down-stream.

Thirdly, the amount of gas introduced at this stage should not be too high, since the solubility of gas in water is limited. At equilibrium, the gas in the slurry would be as gas molecules (or some undetectable gas nuclei). If the amount of gas introduced is higher than the saturation limit at a given pressure, the extra gas will be in the form of bubbles, and the more that gas is introduced, the larger the bubbles will be. Since the dissolution of gas in a liquid is a kinetic process and therefore time dependent, it is desirable to dissolve all the gas introduced into the slurry, which may necessitate a long retention time and increase the capacity requirements, a problem encountered in dissolved air flotation. Therefore, to have sufficient gas dissolved in water for small bubble generation, it may nevertheless be necessary to have gas in slight excess of the solubility limit.

On the down-stream of a pump, a certain pressure (e.g., 2 to 3 atms.) is desirable to force any remaining gas to dissolve. To accelerate this, static mixers are again used. Part of the rationale for this is the observation that in dissolved air flotation the air saturation efficiency in the pressure tank increased when packing materials were inserted [Zabel,
Since the dissolution of gas in water is time-dependent, it is desirable to retain the slurry at this stage as long as possible. In many practical situations, slurry transport pipelines are long, and if they are under pressure, the amount of gas dissolved could be significant, even compared with that in pressurized tanks used in dissolved air flotation. One example of long distance slurry pipeline transport is at the Syncrude oil sands treatment site, where flotation is conducted after slurry has been transported for more than 3 km. with slurry conditioning actively promoted in the pipeline [Cymerman and Leung, 1995]. It has been observed in the discharge that bitumen floated spontaneously due to the small bubbles generated by the addition of hot water and temperature changes during the transportation. Another source of bubble generation in the pipeline may come from the large slurry pumps operating at impeller peripheral speeds of 20 to 25 m/s [Cymerman and Leung, 1995]. In this case, bubble formation by cavitation may be significant. It is anticipated that performance would be even better if some gas was deliberately introduced and the slurry was transported under pressure.

For slurry release, flow contraction by a nozzle or a Venturi tube is used to reduce the static pressure within the nozzle so that small bubbles can be generated by cavitation. It has been demonstrated in Chapters 4 and 5 that the orifice size and length of the nozzle used have a great effect on bubble generation by cavitation. In general, a higher liquid flow velocity within the nozzle produces a lower static pressure at that point (following Bernoulli’s principle), and thus more bubbles may be expected to form by cavitation.

7.3.2 Experimental

To verify the role of bubbles formed by cavitation on fine particle flotation, a Lab-scale apparatus was built (see Fig. 7.6). Two wooden boards were used to hold the static mixers (12 elements for each static mixer, 10.16 cm long with the outside diameter of ~9.5 mm, from Cole Parmer), both down-stream and up-stream of the pump. Ten pieces of static mixer inserted into tygon tubing (inside diameter of ~9.5 mm) were installed.
Figure 7.6 Schematic of set-up by using a centrifugal pump
with copper tubes bent to connect the neighboring static mixers. On the suction side, a vacuum gauge was installed, and on the down-stream side, two pressure gauges were installed to indicate the pressure drop due to the static mixers and bends, and the pressure drop across the slurry release nozzle. The slurry release nozzle was made from stainless steel with inner diameters of 2, 3, 4, 5 mm, respectively, and a length of 10 mm (the expansion part, made of aluminum, was 45 mm long, and gradually expanded to ~ 9 mm).

In the experiment, a centrifugal pump was initially used. The liquid flow was controlled by by-passing slurry which was recirculated into the slurry container. Twenty liter slurry (1% (w/w) silica (~ 5 µm)) was prepared with given chemicals (1.25 x 10^-4 M DAH as collector, 10 ppm DF250 as frother) for each continuous flotation test.

A 3-L Lab AGITAIR flotation cell was used (Fig. 7.7). To run the flotation continuously, a hole was drilled on one side of the cell to allow the slurry to flow out (referred to as tailings). Another hole was inserted to detect the liquid level in the cell by means of a manometer.

To minimize the effect of operating variables, a pre-scheduled procedure was used: the slurry was introduced to the cell by pumping through the set-up shown in the figure, and agitation was started when the slurry just covered the impeller. When the slurry in the cell reached a given level, air was introduced in the mechanical cell. About 30 seconds later, froth and tailings were collected for a given time. The total volume of the collected products were measured to estimate the retention time of the slurry in the cell. Then the products were filtered, dried, and weighed. The recovery, \( R_e \), was calculated using:

\[
R_e = \frac{W_c}{W_c + W_t} \times 100 \quad (\%)
\]
Figure 7.7 Schematic of set-up for flotation tests

1% silica (-5 mm) (w/w)
10 ppm DF250
1.25 x 10^{-4} M DAH
pH = 7.5 - 7.8
where the $W_c$ and $W_t$ are the weight of concentrate and tailings, respectively.

7.3.3 Results and Discussion

Observations:
With the set-up as shown in Fig. 7.6, some problems were encountered: firstly, on the suction side, if too many static mixer and bends were used, the pump was not able to draw in liquid. Therefore, all the static mixers and bends installed upstream were removed.

Secondly, the energy loss on the down-stream side was found to be large. As indicated by the pressure gauges, more than half the pressure was lost through the mixers and bends. To reduce this energy loss, only two static mixers and one bend were used.

Thirdly, the slurry by-pass generated numerous gas bubbles by cavitation. It was evident that these bubbles were pumped to the cell, thus complicating the interpretation.

Fourthly, due to the bubbles formed by cavitation, particles floated in the slurry container, forming a heavy, stable froth. When introducing a small amount of air into the feed line, the slurry container filled with this particle-stabilized froth. This indicated that using a centrifugal pump tended to obscure the role of cavitation in the flotation tests. On the positive side, however, this was a direct evidence that bubbles formed by cavitation can be stabilized to float fine particles even in the absence of added air.

Despite these problems, the results in Table 7.1 did show an encouraging improvement in flotation recovery over "normal" operation (i.e., neither nozzle nor static mixer was used), especially when a small amount of gas was introduced in the feed stream.
Table 7.1  Effect of cavitation on silica (-5 μm) flotation (centrifugal pump, partial feed recirculation, nozzle diameter = 2 mm, feed rate = 2 L/min)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Retention time (min)</th>
<th>Air (L/min)</th>
<th>Velocity in nozzle (m/s)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal*</td>
<td>1.5</td>
<td>2</td>
<td></td>
<td>0.29</td>
</tr>
<tr>
<td>Nozzle</td>
<td>1.5</td>
<td>2</td>
<td></td>
<td>0.66</td>
</tr>
<tr>
<td>Nozzle</td>
<td>1.6</td>
<td>2</td>
<td>0.3</td>
<td>0.77</td>
</tr>
</tbody>
</table>

* No nozzle nor static mixer was used. A peristaltic pump was used, because in this case, it was very difficult to control the flow rate to feed the cell by the centrifugal pump.

** k is a flotation rate constant, a first order flotation kinetics and perfect mixing in the cell were assumed for the estimation of k.

To avoid the bubble generation problems caused by the centrifugal pump, a peristaltic pump was then used, and a static mixer was installed up-stream to disperse the aspirated air. The results, summarized in Fig. 7.8, suggest that there is an optimum velocity of slurry passing through the nozzle to maximize recovery (note: to keep the same retention time in the separator, the slurry velocity was adjusted by changing the orifice size of the cavitation tube). Although it was shown in Fig. 7.1, that silica recovery increased with the slurry release velocity in gas-supersaturated systems, the velocities there were all below 10 m/s. It was also shown in Chapter 4 that the amount of bubbles formed by cavitation may increase with the liquid flow velocity, which would favor particle collection and flotation. However, it seems that if the liquid flow velocities within the nozzle become too high, the high shear force developed may disrupt bubble/particle and
Figure 7.8 Effect of slurry flow velocity through the nozzle on silica recovery

1. normal condition

(1% (w/w) silica; 1.25 x 10^{-4} M DAH + 10 ppm DF250; 3-L AGTAIR cell; air rate in the cell 2 L/min; impeller speed: 850 rpm)
particle/particle aggregates, contributing to the reduction in recovery in the mechanical cell. It has been reported [Spears and Stanley, 1994; Bilgen, et al., 1994] that the size of particle aggregates decreases after a certain level of stirring or shear. This reduction in aggregate size may affect the collision and attachment efficiency of the aggregates with the flotation-size bubbles generated in the mechanical cell.

While it may be argued that the air introduced in the feed stream increases the total amount of air in the flotation process, a comparison test was conducted by increasing the amount of air introduced to the flotation cell from 2 L/min to 3 L/min. Since the retention time for each test was different, the flotation rate constant is a better criterion than recovery to compare the flotation performance and repeatability of the tests. The results (Table 7.2) show that increasing air in the cell does increase the flotation rate constant, but its effect on the flotation kinetics was less significant than the small amount of air in the feed stream (0.15 L/min). This indicated that small bubbles generated by cavitation did play a role in enhancing fine particle flotation.

Static mixers are now widely used to shear air for small bubble generation in flotation [Yoon, 1993; Xu, et al., 1994; Jordan and Susko, 1992]. Consequently, a comparative test was conducted to determine the effect of a static mixer and cavitation tube. The results in Table 7.2 indicate that compared with the normal conditions, a 20% increase in the rate constant is obtained by installing a static mixer with small amount of air added, but up to an 85% increase in flotation rate was obtained by installing a cavitation tube (i.e., "Nozzle" in Table 7.2) in the feed stream with less air (last line of Table 7.2). A similar conclusion was reached by Xu et al. [1994; 1996]. The possible reasons are: a). the liquid flow velocity in the static mixer was much lower than the velocity at the tip of cavitation tube, thus the number of bubbles formed in the feed stream by using static mixers was less. b). bubble formation by cavitation may not occur at this velocity (0.74 m/s) in the static mixer. The effect of slurry flow velocity on flotation can also be inferred from Table 7.2. It was observed that about 17% increase in flotation rate
constant was obtained by installing a nozzle in the feed line, even with no air, other conditions being the same. This again suggests that bubbles formed by cavitation played a role in accelerating particle collection.

Table 7.2 Effect of different operating variables on silica (-5 μm) flotation (peristaltic pump, feed rate = 2 L/min, which was equivalent to the average slurry velocity in the feed stream 0.59 m/s, and the velocity within the static mixer 0.74 m/s)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Retention (min)</th>
<th>air (L/min)</th>
<th>k (min⁻¹)</th>
<th>Velocity in nozzle (m/s)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>cell reactor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1.50</td>
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<td>0.291</td>
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<td>30.4</td>
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<tr>
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<td>1.57</td>
<td>2</td>
<td>0.307</td>
<td></td>
<td>32.4</td>
</tr>
<tr>
<td>Normal</td>
<td>1.34</td>
<td>3</td>
<td>0.361</td>
<td></td>
<td>34.8</td>
</tr>
<tr>
<td>Mixer</td>
<td>1.57</td>
<td>2</td>
<td>0.399</td>
<td></td>
<td>36.7</td>
</tr>
<tr>
<td>Nozzle</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d = 1.3 mm</td>
<td>1.56</td>
<td>2</td>
<td>0.353</td>
<td>23.2</td>
<td>35.4</td>
</tr>
<tr>
<td>d = 1.3 mm</td>
<td>1.37</td>
<td>2</td>
<td>0.340</td>
<td>26.3</td>
<td>31.9</td>
</tr>
<tr>
<td>d = 1.65 mm</td>
<td>1.30</td>
<td>2</td>
<td>0.352</td>
<td>17.2</td>
<td>31.5</td>
</tr>
<tr>
<td>Nozzle</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d = 1.3 mm</td>
<td>1.96</td>
<td>2</td>
<td>0.558</td>
<td>18.4</td>
<td>52.3</td>
</tr>
</tbody>
</table>
7.5 SUMMARY OF CHAPTER

1. A new flotation reactor, based on the fundamental work, has been designed to conduct fine particle flotation.

2. Bubble nucleation provides a better particle collection mechanism compared with the conventional collision mechanism; and the two-stage attachment mechanism offers a means in increase flotation kinetics.

3. The stability of particle/particle and particle/bubble aggregates is affected by the flow velocity within the nozzle. Too high a velocity may decrease the recovery due to aggregate break-up, even though small bubble generation continues to increase.
CHAPTER 8

GENERAL CONCLUSIONS,
CLAIMS FOR ORIGINAL RESEARCH AND
SUGGESTIONS FOR FUTURE WORK

8.1 GENERAL CONCLUSIONS

8.1.1 Effect of Gas Nuclei

1. The presence of gas nuclei in water has been indirectly verified from coagulation, sedimentation and filtration tests. Gas nuclei tend to increase hydrophobic coagulation and aggregate size by bridging particles together. Removal of gas nuclei by deaeration increased the settling rate of naturally hydrophobic coal, due to the increased density of aggregates, but reduced the settling velocity of chemically-induced hydrophobic silica, because of the break-up of aggregates.

2. Upon removal of gas nuclei by deaeration, the filtration rate increased for the naturally hydrophobic coal, but decreased for the chemically-induced hydrophobic silica. Compared with the first filtration, the rate of second filtration was always lower for coal, but for silica (either hydrophilic or hydrophobic), the second filtration rate was initially
lower, and then faster than in the first filtration. This was attributed to a "flushing out" effect at the end of the first filtration, which removes some trapped gas nuclei in the silica system, but has minimal effect in the coal system.

8.1.2 Bubble Formation

3. Small bubbles can be generated by hydrodynamic cavitation by creating a sufficiently fast flow of liquid through a nozzle, mainly due to the expansion of pre-existing gas nuclei. The generation of bubbles can be enhanced by increased temperature, reduced static pressure, creation of "pre-existing gas nuclei" and addition of gas.

4. Surfactants do not affect the on-set of bubble formation by cavitation, but increase the number of bubbles formed by stabilizing the cavities generated.

5. In gas-supersaturated systems, more bubbles are formed by stirring the liquid, and fast release of the supersaturated liquid from the pressure chamber.

6. The effect of solids on bubble formation in gas-supersaturated liquid was found to depend on the nature of the solids: hydrophilic solids tend to reduce bubble formation; chemically-induced hydrophobic particles increased bubble formation by nucleating bubbles; and, naturally hydrophobic particles enhanced bubble formation when present in a small amount, but reduced bubble formation when a large amount was present, due to the dominant effect of bubble coalescence induced by hydrophobic particles, and the adsorption of surfactant by the particles.

8.1.3 Fine Particle Flotation

7. For fine particle flotation, the collision between particles and bubbles is probably the rate limiting step. The quiescent flow conditions used in flotation columns limit collision frequency, and thus give low flotation kinetics. A certain degree of turbulence...
and energy dissipation is needed to increase collision frequency.

8. In flotation practice, bubble-bubble interaction coupled with the flow and mixing conditions complicates theoretical analysis of the particle-bubble collision process.

9. A two-stage attachment mechanism provides an exploitable means of conducting fine particle flotation. Fine silica (≤ 5 μm) recovery was increased when slurry was pre-saturated with gas, compared to without gas-saturation.

10. In gas-supersaturated systems, recovery increases with slurry release velocity, regardless of the saturation pressures applied, indicating that bubbles nucleate on hydrophobic particle surfaces during slurry release by hydrodynamic cavitation.

11. Releasing the slurry from a pressure chamber gave a higher recovery than releasing solution into a slurry, suggesting that bubble nucleation was a superior mechanism for enhancing particle collection compared with simple particle-bubble encounter.

12. The preliminary experimental results indicate that bubbles formed by hydrodynamic cavitation do improve flotation kinetics, even in the absence of added gas in the stream. Adding a small amount of air in the feed stream increased recovery significantly.

8.2. CLAIMS FOR ORIGINAL RESEARCH

1. The role of cavitation and gas nucleation in accelerating particle collection during flotation has been systematically analyzed theoretically and experimentally.

2. The effect of bubble-bubble interaction on particle-bubble collision has been
incorporated in a particle-bubble collision model applicable to bubble swarms.

3. The effect of different variables, related to the flotation process, on bubble formation by hydrodynamic cavitation has been shown, which was used to explain some features of recently developed flotation cells.

4. The enhancement of bubble formation in gas-supersaturated systems by stirring the solution and fast release of the liquid has been demonstrated.

5. The effect of solids with different surface properties on dynamic bubble nucleation in gas supersaturated systems has been demonstrated and the role of solids in bubble nucleation explained.

6. The effect of gas nuclei on enhanced hydrophobic coagulation has been demonstrated.

7. The different effect of gas nuclei on the sedimentation of naturally hydrophobic coal and chemically-induced hydrophobic silica has been shown and explained.

8. The effect of gas nuclei on the filtration of fine particles with different surface properties has been demonstrated, and a mechanism proposed.

9. Flotation of fine particles in gas-supersaturated systems has been correlated with the slurry release velocity from the pressure chamber, regardless of the pressures applied in this study.

10. The effect of gas nucleation on increasing flotation recovery has been shown in gas supersaturated systems.

11. A new flotation reactor based on cavitation principles was developed and
constructed; preliminary testing showed that hydrodynamic cavitation improved flotation recovery of fine silica.

8.3. SUGGESTIONS FOR FUTURE WORK

1. Systematic experimental work should be conducted to find the effect of different operating parameters (e.g., nozzle size and length, particle size and concentration, mixture of minerals, etc.) on the separation performance of the newly-designed flotation reactor.

2. Investigation should be conducted on the design and scale-up of the cavitation tube to minimize the energy loss while generating the maximum amount of tiny bubbles, and on the selection of suitable materials for nozzle construction to resist the abrasion in real systems.

3. A study on effect of bubble-bubble interaction on bubble rise velocities would provide useful information for the model of particle collection in bubble swarms.

4. A study on the coalescence of flotation-size bubbles (0.5 - 3.5 mm) with small bubbles (< 100 μm) is one way to explore the two-stage attachment mechanism.

5. A comparative study of the liquid film rupture between two bubbles and between a hydrophobic particle and a bubble under different chemical conditions is another way to explore the two-stage attachment mechanism.


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