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UNIVERSITY OF ALBERTA

SURFACTANT EFFECTS ON BUBBLES AND COLUMN FLOTATION OF COAL

BY

ZHI-ANG ZHOU



A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE

IN

MINERAL ENGINEERING

٠

DEPARTMENT OF MINING, METALLURGICAL AND PETROLEUM ENGINEERING

EDMONTON, ALBERTA SPRING 1992



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c/o Mrs. Wanglian Luo

Shaodong Medical School, Shaoyang City,

Hunan Province, P. R. China

DATED: Feb. 3rd 1890

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled SURFACTANT EFFECTS ON BUBBLES AND COLUMN FLOTATION OF COAL submitted by ZHI-ANG ZHOU in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in MINERAL ENGINEERING.

Dr. N. O. Egiebor, Co-supervisor

Professor L. R. Plitt, Co-supervisor

Dr. J. M. Whiting

Dr. L. W Sigurdson

Dr. S. A. Bradford

It's tasteless to eat bread which has been chewed by others.
———— Chinese saying
Scientific research = imagination + creation + devotion.
The author
TO:
All those who — gave me help, even a little bit, either directly or indirectly; — devoted themselves to the understanding of flotation fundamentals

ABSTRACT

There is much discrepancy between theoretical models and experimental data for the rise velocities of bubbles (1 << Reb < 500) in aqueous media, due to the difficulties in evaluating the surfactant effects on bubbles. A new approach is used in this study, which considers the virtual mass of a bubble and utilizes the virtual thickness of the liquid film surrounding the bubble to explain the added mass effect on bubbles. The concept of contamination factor, a function of the surfactant type and concentration, is introduced to illustrate the retardation effect exerted by different surfactants on bubbles. Theoretical models were therefore developed to predict single bubble rise velocity in the absence and presence of surfactants. The models were found to agree with the literature data and the direct measurement for bubble rise velocities in single bubble systems in pine oil, MIBC and Dowfroth 250 solutions. The results indicate that bubbles behave like solid spheres only at the contamination factor of about 195. Bubbles move more slowly than solid spheres when their surfaces are completely immobilized by surfactants in the dynamic situation.

Based on Marrucci's equation and Nicklin's work, the average bubble rise velocity in a swarm is modelled and verified; a drift-flux model for gas/liquid two-phase systems is proposed; and a simple method to predict bubble size in a swarm in the presence of frothers, which agrees quite well with the literature data and the photographic measurement, is suggested.

Column flotation tests of coal have shown that particle hydrophobicity and particle size have great effects on froth stability and bubble coalescence. Adding collectors increase the particle surface hydrophobicity, thus accelerating the froth collapse, bubble coalescence and reducing the gas holdup. It was found that using Dowfroth 250 as frother can give higher recovery and flotation rate constants, as well as recover bigger particles than using MIBC. It is believed that this results from the stronger molecular interaction between Dowfroth 250 and kerosene than that between MIBC and kerosene.

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LIST OF SYMBOLS

```
bubble radius;
a
        constant (Eq. 2-27);
A
        surface area of a sparger:
A_{\varsigma}
        cross-sectional area of a column:
A_c
        a coefficient (Eq. 6-8)
A_r
        the distance between the center of a bubble and the orifice plate from which the
b
        bubble is ascending;
        the radius of liquid envelop surrounding a bubble;
bı
        coefficient (Eq. 5-11);
B_{c}
        coefficient (Eq. 5-14);
B_d
С
         frother concentration in liquid;
C_{c}
         contamination factor (Eq. 2-22);
C_{d}
         drag coefficient;
         coefficient relating to the reagent type and its diffusion property;
 C_r
         average particle size;
 dan
         bubble diameter,
 db
         diameter of a column;
 d_{c}
         gas sphere diameter;
 d_g
         particle diameter;
 d_{p}
         visual bubble diameter;
 d_{\mathbf{v}}
          Sauter mean diameter;
 d32
          gas holdup;
 \mathbf{E}_{2}
          Eotvos number (Eq. 2-4);
 Eo
          maximum force registered on torsion-balance scale in the measurement of surface
 f
          tension on gas-liquid interface by ring method;
          correction factor due to shape of liquid held up and the ring dimensions by ring
 F
          method:
          the attachment force;
  Fan
          bubble buoyancy;
  F_{bv}
           fluid drag force acted on a bubble;
  F_{db}
          fluid drag force acted on a particle;
  F_{dp}
          the particle gravity force;
  F_{pg}
           _ravitational accelerating constant;
  g
```

```
gas flowrate per hole on a sparger;
G
        coefficient (Eq. 2-3);
H
        the height of a bubble of interest from a sparger;
h
        critical thickness of liquid film;
h_c
        height of top liquid level in a column in the absence of gas flow;
H_0
        height of top liquid level in the presence of gas flow;
H_c
        coefficient (Eq. 2-2);
J
        superficial gas velocity;
J_{g}
        drift-flux for a gas-liquid system;
J_{gl}
        superficial liquid velocity;
J_1
J_{S}
        superficial slurry velocity;
        drift-flux for a solid-liquid system;
J_{sl}
        the superficial tailings rate;
J,
        retardation constant;
K
        the rate constant for particle-bubble attachment in column flotation systems;
K_f
         constant;
\mathbf{k}_{\mathbf{l}}
         constant (i = 1, 2, 3, 4);
k_i
         gas holdup correlation;
k_g
         the length of the column collection zone;
L_{\rm c}
         the thickness of virtual liquid film surrounding a bubble;
 Lf
         an exponent coefficient (Eq. 4-14);
 m
         Morton number (Eq. 2-5);
 M
         the mass of a gas sphere;
 M_2
         the mass of liquid displaced by sphere;
 Мį
         the mass of a solid sphere;
 M_{S}
         the virtual mass of a gas sphere moving in liquid;
 Myb
         the virtual mass of a solid sphere moving in liquid;
 M_{vs}
         the molar number of gas in the bubble;
 N
         the number of bubbles produced by a sparger per unit time;
 N_{bo}
         the total number of bubbles in a column;
 Nhr
         the number of effective holes on a sparger;
 Nh
          the number of bubbles with diameter dv;
 ni
          number of particles captured by a bubble;
 N_{\rm D}
  Patm
          atmospheric pressure;
          external hydrodynamic pressure acted on a bubble;
  P_{DE}
          external hydrostatic pressure acted on a bubble;
  P_{E}
```

Pe the Peclet number,

P_I internal pressure in a bubble;

P_K particle collection efficiency:

Qg gas flowrate (L/min);

 Q_{gc} critical gas flowrate, i.e., for gas flowrate larger than Q_{gc} , bubbles collapse.

rH hole radius in cm;

R thermodynamic constant;

Reb bubble Reynolds number in single bubble system;

Rebs bubble Reynolds number in a swarm;

Rg radius of a virtual gas sphere within the bubble;

Ri radius of a bubble under the ideal conditions; i.e., no liquid film and no viscosity difference between bulk liquid and bubble surface;

R_{org} the fractional recovery of organic materials in the coal;

rp particle radius;

R_r mean radius of the ring in ring method for surface tension measurement;

R_s radius of a solid sphere;

Ry radius of a visual bubble;

Spb total surface area occupied by the particles attached on bubble surface;

t time;

T kelvin temperature;

Uba average bubble rise velocity in a swarm;

Ubd bubble drift velocity;

Ubo bubble rising velocity, by buoyancy, in the absence of surfactants, which obeys Levich's equation;

Ubs bubble rising velocity, to buoyancy, in the presence of surfactants;

Uen velocity of an ensemble of spheres;

Ugl slip velocity for gas-liquid systems;

U_l average liquid velocity;

Up the particle settling velocity;

U_s Stokes' velocity;

U_{sl} slip velocity for solid-liquid systems;

U_T terminal velocity of a sphere;

V_b bubble volume at time t, cm³;

 V_{bo} bubble volume at time t = 0, initial size;

V_c the volume occupied by gas-liquid mixture in a column;

V_D dispersion energy;

```
expanded liquid volume in a column in the presence of gas flow;
V_{c}
        electrostatic energy;
V<sub>E</sub>
        the final volume of a bubble;
VF.
        hydrophobic interaction energy;
V_{H}
        the liquid volume in the absence of gas;
V_{o}
         structural energy;
V_{S}
        potential energy between two spheres interacting in an aqueous medium;
V_{T}
         the total volume of particles captured by a bubble;
V_{1D}
         weight of a gas oubble;
W_{h}
         the total weight of particles captured by a bubble;
W_{m}
          cumulative wt% passing;
Y
\epsilon_{\rm g}
         gas holdup;
         gas holdup defined by Macrruci (\varepsilon_{gm} = a^3/b_1^3);
\epsilon_{
m gm}
\varepsilon_{\rm s}
         solid holdup;
ε
         liquid holdup;
\rho_{G}
         density of gas;
         density of liquid;
\rho_{L}
         density of a mineralized bubble;
\rho_{mb}
         the amount of frother molecules adsorbed by a bubble per unit area, which obeys
 \Gamma_{\rm m}
          Gibbs' adsorption equation;
          the total amount of frother molecules adsorbed by a bubble;
 \Gamma_{\rm mt}
          retardation coefficient due to the presence of surfactants, \gamma = -(1/3)K(\partial \sigma/\partial C);
 γ
          the particle retention time in the flotation cell;
 \tau_{\rm p}
          bulk liquid viscosity;
 μ
          viscosity of the continuous phase;
 \mu_{c}
          viscosity of the dispersed phase;
 \mu_{\mathbf{d}}
          surface tension of gas-liquid phase;
 σ
          the volumetric dispersed-phase holdup fraction;
 Ø
 θ
          contact angle;
          virtual mass coefficient;
 α
 0/9d<sub>p</sub>
         the differentiation on particle size;
```

CHAPTER 1 INTRODUCTION

Air bubbles are ubiquitous and unique. The extensive application and vital importance of air bubbles in human life can be well illustrated by the following memorable words [Harper, 1972]: "Chemical engineers, metallurgists, geologists, brewers and cooks all try to understand processes in which bubbles or drops move through liquids". Jameson [1984] added mineral processing engineers to the above list, for bubbles are an indispensable part of the froth flotation process, and it appears likely that the thorough understanding of the interaction between bubbles and particles could give results of practical importance in the design of flotation cells and the optimization of flocation process, the typical examples being the research and development of flotation columns and Jameson cells [Jameson, 1991, 1988]. Therefore, air bubbles, which are regarded as the heart of the particle-bubble collection process in flotation [Dobby, 1984], deserve much more attention and intensive study.

Air bubbles in flotation systems are generally in the size range of 0.05 - 0.2 cm in diameter [Pal and Masliyah, 1990; Dobby et al.,1988]. They are basically spherical because of the dominant effect of surface tension on their shape, and rise smoothly in the unpurified water. Bubbles which are too small do not have enough buoyancy to carry the valuable mineral particles to the top of the flotation cell [Leja, 1983; Hu et al.,1980], or will be swept out of the column through the tailings effluent by the down-flow slurry, in the case of column flotation [Luttrell et al.,1987]. Bubbles which are too large can not give the required high flotation rate, due to the unfavorable hydrodynamic conditions surrounding the bubbles [Yoon and Luttrell, 1989], and to the fact that the rapid oscillations of bigger bubbles could probably repel any impinging mineral particle from the bubble surface [Fuerstenau and Wayman, 1958].

Another important characteristic of air bubbles in flotation is that the bubbles are normally formed in an aqueous solution containing surface-active reagents. Fig. 1-1 shows statistical results of single bubble rise velocity in aqueous media [Jameson, 1984; Leja, 1983; Clift et al.,1978; Fuerstenau and Wayman, 1958; Gaudin, 1957]. The areas enclosed by the curves are the data points, which are not shown for the sake of clarity. It can be seen from this figure that for bubbles less than about 0.05 cm and larger than about 1.5 cm, there is no difference between bubble rise velocities in contaminated water and in the distilled water obtained by conventional methods. The motion of small air bubbles (Reb <

1) can be predicted by Stokes' law, and they behave like solid spheres up to a Reynolds number of about 40, or a bubble diameter of 0.05 cm [Fuerstenau and Wayman, 1958]. While between bubble diameter in the range of 0.05 to 1.5 cm, there is much discrepancy in the rise velocities between different investigators, and between theoretical models and measurement data. Unfortunately, the air bubbles used in flotation systems just lie in this size range. Although froth flotation has been commercially employed in the mineral industry for about 80 years, until now, the behavior of bubbles in flotation system has not been fully understood. The strong turbulence induced in mechanical flotation cells impedes the theoretical analysis of bubbles in flotation, above all, one of the greatest difficulties in

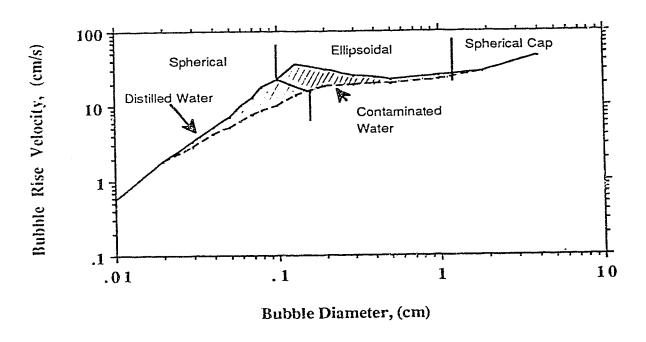


Figure 1-1 Statistical results of Bubble rise velocity in aqueous media

dealing with bubbles is the effect of surface-active materials in water, even when in undetectable amounts.

1.1 MECHANISMS OF FROTH FLOTATION

Froth flotation is a physico-chemical hydrodynamic process involving the three-phase interactions between gas, solid and liquid in the presence of different inorganic and organic

reagents. Fig. 1-2 shows the schematic diagram of a mechanical flotation cell. Bubbles are produced by intaking air, and then dispersing it through the rotation of the impeller. Ore

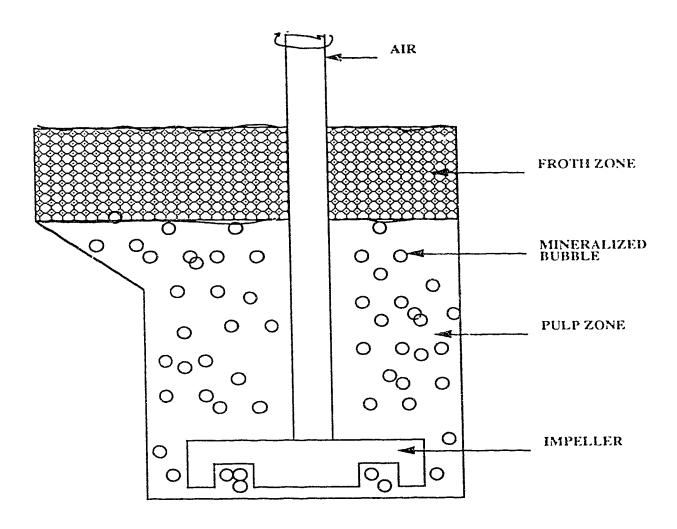


Figure 1-2 Schematic diagram of a mechanical flotation cell

particles are suspended by the mechanical agitation, and the valuables and gangues are separated according to differences in their surface properties. Particles are collected upward to the froth for further enrichment mainly by two mechanisms [Dobby, 1984]: (1) attachment to the rising bubbles, which is a function of bubble size and particle hydrophobicity; and (2) mechanical entrainment, which is a function of water recovery and applies to either hydrophobic or hydrophilic particles without discrimination. In flotation of

very fine particles, the coherence between valuable and gangue particles, or heterocoagulation, may contribute to another mechanism for particle collection. In this case, slime coating, i.e., the surface of the valuable particles covered by the fine gangues, can even entirely depress the flotation process. Therefore, a de-sliming of the pulp before flotation is the most common step in practice [Fuerstenau et al.,1985; Leja, 1983].

In order to enhance the flotation efficiency, chemical reagents are generally employed according to the different functions of the reagents and particle surface characteristics. Collectors, which are organic surfactants, composed of polar-group and non-polar hydrocarbon chains, selectively make the wanted valuable particles hydrophobic. Frothers, which are usually nonionic surfactants, ensure the formation of bubbles with suitable size, elasticity and strength. In this way the froth formed is sufficiently stable so that the mineralized bubbles will not be ruptured before leaving the cell, but break down immediately after entering the froth product collection trough, thereby avoiding transportation problems [Harris, 1982; Booth and Freyberger, 1962].

In order to improve selectivity, inorganic chemicals (sometimes organic chemicals [Dobias and Orthgieß, 1991; Suttill, 1991]) are often used as regulators to control and modify the particle surface properties and slurry conditions. They can be used as modifiers to adjust pulp pH, or depressants to selectively render certain mineral particles hydrophilic at the differential flotation stages, or activators to make the previously depressed components floatable in subsequent flotation operations [Wallis, 1988].

The rate of froth flotation depends on the product of particle-bubble collision and attachment probabilities. Mechanical agitation can increase the collision between particles and bubbles. But at the same time strong turbulence caused by the stirrer is deleterious to the particle-bubble attachment process, hence the captured particles may detach again, thus influencing flotation rate and recovery.

It is desirable in flotation that the mechanical entrainment and heterocoagulation between particles should be minimized, or eliminated to ensure high purity and grade of the product. However, an inherent limitation with flotation of fine particles in conventional cells is the recovery of hydrophilic (gangues) particles by mechanical entrainment in the water reporting to the froth. The commonly used method to minimize entrainment [Dobby, 1984] is to create a 5 - 30 cm thick froth at the slurry surface. The froth permits the gangues to drain back to the pulp while retaining the hydrophobic particles, which are eventually

discharged over the cell lip. But it is impossible to completely eliminate the entrainment in a single cell. Therefore banks of cells have to be used to increase the cleaning and recleaning effect, in order to obtain the required quality of the final product. Thus, higher capital and operating costs are incurred to provide for the cleaning stages.

1.2. FLOTATION COLUMN AND ITS OPERATION

One of the biggest breakthroughs in mineral industry in recent years is the adoption of column flotation. Invented by two Canadians, Boutin and Tremblay [Boutin and Wheeler, 1967] in the early 1960's, this method has been commercially employed to treat metallic ores, precious metal ores, phosphate and coal [Sastry, 1988]. Most of these practices have shown that higher recoveries and grades can be obtained by the columns than by the mechanical cells [Yianatos et al., 1988].

Fig. 1-3 schematically shows a flotation column, which is typically 9 - 15 m high, 0.5 - 3.0 m in diameter for commercial units, 3 - 5 m high and 2 - 5 cm in diameter for laboratory scale [Finch and Dobby, 1990; Dobby et al.,1988]. Bubbles are generated at the bottom of the column through either internal spargers, which are made from perforated pipe clad usually in fabric (e.g. filter cloth) or perforated rubber, or external spargers, in which air and water are mixed under pressure and released through an injection system [Mckay et al., 1988]. Feed slurry enters about one-third way down from the top and descends against a rising swarm of bubbles generated by the sparger. The bubbles collect the floatable particles in the collection or recovery zone, which is from the sparger to the pulp-froth interface, upward to the froth or cleaning zone, the area above the froth-pulp interface and consisting of a froth stabilized by the wash water. Wash water is added usually from an array of perforated pipes located just below the overflow lip, which cleans the froth by driving the entrained gangue particles back to the pulp, thus permitting high upgrading.

Therefore, a flotation column can be regarded as a compacted flotation circuit, with the collection zone as the rougher and scavenger stages to ensure a higher recovery, and the froth zone as the cleaning or recleaning stages to obtain a purified final product.

Typical ranges of operating variables of column flotation are: superficial gas velocity, the gas flow rate per unit sectional area of the column, $J_g = 1.5 - 2.5$ cm/s, superficial slurry

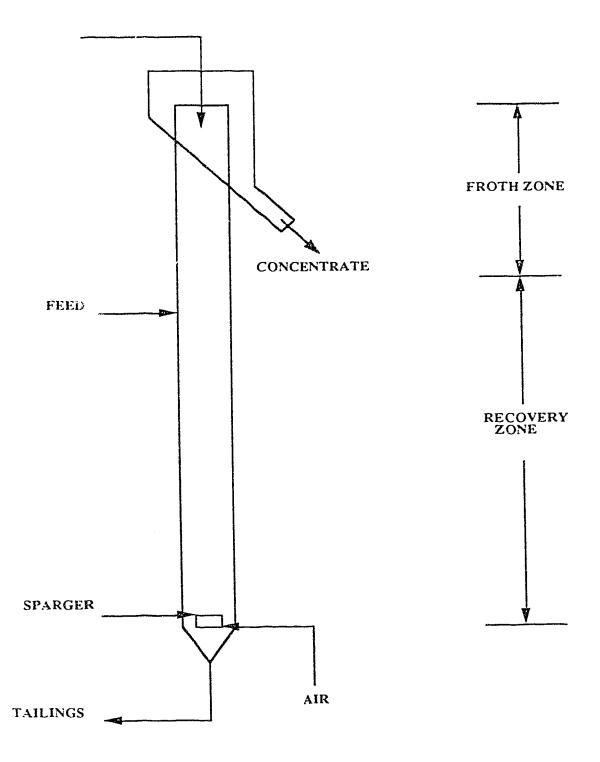


Figure 1-3 Schematic diagram of a flotation column

column, $\varepsilon_g = 5$ - 30%, average bubble diameter $d_b = 0.05$ - 0.2 cm. In practice, the slurry flow in the column is often kept at positive or zero bias, i.e., the tailings flowrate is larger than or at least equal to the feed flowrate, to prevent the feed slurry reporting to the floatable product.

The distinctive features of flotation columns from mechanical cells can then be summarized as follows:

- 1. counter-current contact between the solid particles and air bubbles and no mechanical agitation in the column. Thus the desorption of the attached particles from bubbles are minimized, or eliminated. This salient operating feature provides an ideal situation for theoretical study on bubbles and on flotation kinetics.
- 2. addition of wash water at the top of the froth zone. This means that the entrained gangue particles can be washed back to the pulp, permitting higher grades in the froth product.
- 3. multiple recleaning action in the column. If a particle is returned from the froth zone to the collection zone, it repeats the process of collection (just as when first fed into the column), and is available for 100% of the original retention time. Contrast this to a bank of mechanical cells, where each collection event subsequent to dropping back from the froth has a reduced retention time [Dobby, 1984].

Consequently, flotation columns offer several mechanical and operational advantages including simplicity of construction, absence of moving parts, feasibility of computer control, low operating and maintenance costs, and, most important, better recovery and higher grades than conventional machines [Sastry, 1988].

1.3 OBJECTIVES AND ORGANIZATIONS OF THE THESIS

1.3.1 Objectives

As mentioned earlier, without air bubbles, no froth flotation process is possible. Furthermore, the behavior of air bubbles is directly related to the particle-bubble collision

The size of air bubbles has been found to influence flotation rate drastically. In order to predict the separation performance and optimize the operation, it is necessary to know, at least approximately, the average bubble size in the column. Hence the second objective was to establish a convenient and reliable method to estimate the average bubble size in different kinds of flotation columns, e.g., conventional columns and Jameson cells [Jameson, 1988; 1991] in the presence of different frothers at varied dosages.

While the froth flotation involves the three-phase interaction process, the nature of particles and the presence of different chemicals may affect the flotation operation. So the third objective was to investigate the solidand chemical effects on column flotation characterization of coal.

1.3.2 Organizations

The paper format [Anon..1991] is adopted in this thesis. The first chapter is the general introduction to the entire thesis, which provides a general literature review, the objectives, and organization of the thesis.

From Chapter 2 to Chapter 6, each chapter deals with an independent, but related subject. Starting from a short introduction to every chapter, the previous work on the topic concerned is reviewed, followed by the approach used in this study. The models established are then compared with the literature data and the direct experimental measurements carried out in this study.

The second and third chapters are focused on the theoretical and experimental investigations of the single bubble motion (1<<Reb <500) in aqueous media. A model is developed to predict the rise velocity of bubbles in water with, and without addition of frothers. The results of experimental verifications with the commonly used frothers, MIBC, Dowfroth 250 and pine oil, are presented, and the relationship between contamination factors and the concentrations of these three frothers is established.

In order to simulate a real column flotation process, the frother effect on bubble motion in a swarm is investigated in Chapter 4. Based on this and the previous work, a model is

Different methods are employed to determine the frother effects on bubble rise velocity in a swarm, and to verify the established models.

Chapter 5 deals with bubble size estimation in a swarm. The general technique to estimate bubble size in a swarm is reviewed. A new and simple method is proposed to predict the average bubble size in a flotation column, and the results of experimental verifications are presented and discussed.

Chapter 6 is concerned with the solid and chemical effects on column flotation of coal. The results of the particle hydrophobicity, particle size, collector and frother addition effects on the froth stability and bubble coalescence have been presented and discussed. The frother effects on flotation rate are also presented.

General discussion and conclusions for the whole study are given in Chapter 7. The suggestions for further work are discussed in Chapter 8.

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CHAPTER TWO THE MOTION OF SINGLE BUBBLES _THEORETICAL*

2.1 INTRODUCTION

Air bubbles are essential components in froth flotation of minerals and coal, in which hydrophobic particles are attached to, and carried upward by the rising bubbles to the froth zone, leaving the hydrophilic particles in the liquid phase to go down with the tailings effluent. This separation process depends on the collision of particles with bubbles in the slurry and their ability to remain in contact long enough for three-phase aggregates to be formed. In order to thoroughly understand the mechanics of particle-bubble collision and attachment, it is necessary to know the nature and behavior of bubbles. Limited quantitative research work has been done on air bubbles in flotation systems. The difficulties in such studies may be attributed to the problem associated with the determination of the degree of mobility of the phase boundary of the bubble, and the effect of surface-active materials on such mobility. Two extreme cases are often assumed for such studies [Schulze, 1984]:

- 1.) that if the bubble is small and covered by an adsorption layer it behaves approximately as a solid particle; and
- 2.) that if it does not bear an adsorption layer, e.g., a bubble formed in pure liquids, its surface moves freely.

However, in froth flotation, different surface-active reagents at varied concentrations are employed to improve the separation efficiency, therefore, the surface characteristics of the bubbles may be different from the above two cases. Moreover, an agreement between the theoretical models, based on the above assumptions, and the experiment data was seldom obtained [Jameson, 1984].

In this Chapter the effects of surface-active chemicals on bubble rise velocities are briefly reviewed. A new approach to this problem is proposed, and the expressions derived are

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used to analyze literature data in comparison with other theoretical and empirical models for a single bubble system.

2.2 REAGENT EFFECTS

The effect of surface-active materials on bubble rise velocity has long been recognized [Jameson, 1984; Hu, et al., 1980; Clift, et al., 1978; Fuerstenau and Wayman, 1958]. Fuerstenau and Wayman may be the first to systematically measure the effect of flotation reagents on bubble motion. Their results are listed in Table 2-1.

Table 2-1. Effect of various reagents on shape and terminal velocity of bubbles with an equivalent radius of 0.082 cm (Fuerstenau and Wayman, 1958)

Aqueous Solution	Bubble Shape	
Distilled Water	Oblate spheroid	31
KOH, 7 mg/L	Oblate spheroid	29
KOH, 20 to 60 mg/L	Oblate spheroid	27
KCl, 15 to 40 mg/L	Oblate spheroid	27
Terpineol, 3.7 mg/L	Flattened spheroid	18
Terpineol, 7 to 88 mg/L	Spheroid	14
Potassium ethyl xanthate, 20 mg/L	Oblate spheroid	27
Potassium amyl xanthate, 25 mg/L	Oblate spheroid	21
25 mg Potassium amyl xanthate plus 3.7 mg terpineol/L	Spheroid	14

Table 2-2 shows the relative bubble rise velocities for different reagent systems, by assuming the bubble rise velocity in the presence of butyl xanthate as 100%. These measurements show that adding a surfactant retards the bubble motion, and this retardation varies with the different reagents. For a homogeneous series of surfactants present in

water, bubble rise velocity decreases with the increase of the number of carbon atoms in the molecule. The effects of salts, inorganic reagents and short chain collectors on bubble motion are minor, at least in the concentration ranges indicated in Table 2-1.

Table 2-2. Comparison of relative bubble velocities in the presence of different reagents (Hu et al., 1980)

Reagents	Relative Bubble Velocity (%)
butyl xanthate	100.0
phenol	93.4
cresol	90.8
pine oil	88.3
hexyl alcohol	76.2
octyl alcohol	75.8
TEB	72.3

The decrease in bubble rise velocity due to the surface-active agent is quite pronounced. It has been observed [Klassen and Mokrousov, 1963] that at lower coverage of the bubble surface by adsorbed frother, the retarding effect increases in proportion to the square of the amount adsorbed. For large bubbles the ascent of bubbles in the presence of surface-active agents is a third to a half as fast as compared to the rise of bubbles in water alone. For small bubbles the rising velocity in the presence of surfactants was reported to be less than half of that in pure water. Fuerstenau and Wayman [1958] found that the presence of a frother tends to maintain sphericity and smoothness in the shape of air bubbles rising up a column of water. In the absence of the frother, bubbles of the same size assumed very much more distorted shapes and underwent oscillations which could probably cause particles to be repelled from the bubbles.

One of the significant changes in the presence of surfactants is the sharp decrease of the gas-water interfacial tension. Therefore, a lot of the previous work has been done to relate

the bubble rise velocity to the changes in surface tension of aqueous media [Patel et al., 1990; Clift et al., 1978, Wallis, 1969]. Levich [1962] measured bubble rise velocities in pure water and in the presence of small amounts of alcohol, and the same phenomena caused by the addition of surfactants as mentioned earlier were observed. He concluded from the measurements that the effect of such surfactants on bubble rise velocity cannot be mainly related to the changes in surface tension or to the corresponding bubble deformation, since the alcohol concentration in water was extremely low and the change in surface tension would not exceed 0.5 dyne/cm.

From the direct measurement of more than 700 data points for bubbles in the size ranges of 0.06 - 0.3 cm in diameter, Clift et al.[1978] established an empirical expression relating bubble rise velocity to the surface tension as:

$$U_{T} = \frac{\mu M^{-0.149}}{\sigma d_{b}} (J - 0.857)$$
 (2-1)

where

$$J = 0.94 \text{ H}^{0.757} \qquad (2 < H \le 59.3) \tag{2-2}$$

$$H = (4/3) E_0 M^{-0.149} (\mu/0.009)^{-0.14}$$
 (2-3)

in which Eo is the Eotvos number given as

$$E_0 = g(\rho_I - \rho_G) d_b^2 / \sigma \tag{2-4}$$

M is the Morton number given as

$$M = \frac{g\mu^{4} (\rho_{L} - \rho_{G})}{\rho_{r}^{2} \sigma^{3}}$$
 (2-5)

From Equation (2-1), the bubble rise velocities at different surface tensions are plotted in Figure 2-1. It shows that there is almost no difference in bubble rise velocities at the surface tensions of 72 dynes/cm and of 50 dynes/cm in the solution. This indicates that surface tension cannot be used as a criterion to determine or satisfactorily explain the effect of surfactants on bubble ascent.

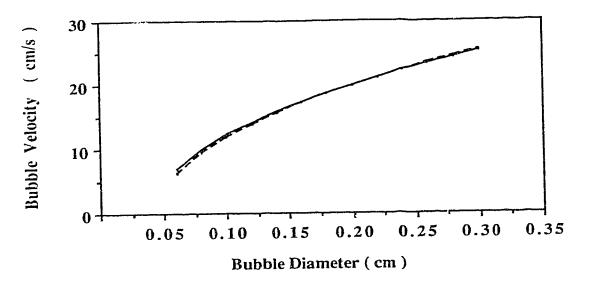


Figure 2-1 Effect of surface tension on bubble rise velocity $\sigma = 72$ dynes/cm; $\sigma = 50$ dynes/cm.

From the dynamic adsorption point of view, Frumkin and Levich [Clift et al., 1978; Klassen and Mokrousov, 1963] have established that molecules of surface-active agents which adsorb on the surface of bubbles are shifted to the bottom portion of the air bubbles during their upward movement in the liquid, leaving the front region relatively uncontaminated. The increased concentration of surface-active agent at the lower portion of the air bubble lowers the surface tension in this region so that the surface tension in the upper part of the bubble is greater than in the lower. Along the surface of the bubble appear forces attempting to equalize the surface tension, so as to prevent further shift of surface-active molecules on the surface of the air bubble and lower the mobility of bubbles. This decrease in mobility makes the bubbles behave like solid spheres. Therefore, the expressions for solid sphere terminal velocities are often employed to estimate the bubble rise velocity in flotation systems[Finch and Dobby, 1990; Dobby, et al., 1988; Dobby, 1984; Anfruns and Kitchener, 1977, 1976]. But the major drawback is that these equations cannot reveal the effect of different surfactants at varied dosages on the bubble motion, only being applicable to certain frother conditions.

It was also suggested and observed [Clift et al., 1978] that all bubbles, no matter how small, will show internal circulation within the bubble if the system is sufficiently free of surface-active contaminants. In the presence of surfactants, there is no such internal

circulation. Boussinesq[Clift et al.,1978] proposed that the lack of internal circulation in bubbles is due to an interfacial monolayer which acts as a viscous membrane.

Fuerstenau and Wayman [1958] employed the principles of the molecular interaction to explain this phenomenon. According to them, in the absence of surfactants, water molecules are strongly attracted to each other within the liquid through dipole interactions (the energy of association of water dipoles in the liquid state being about 6 kcal per mole) but are attracted only weakly to the bubble. Water molecules would have such affinity for themselves that they would tend not to travel with the bubble, consequently, the boundary layer is mobile. If a heteropolar organic compound is dissolved in the water, adsorption of these molecules takes place at the air-liquid interface in such a way that the hydrocarbon chain sticks into the gaseous phase, while the polar group remains in the water. Thus, when an air bubble moves through a dilute aqueous solution containing surfactants, the surfactant molecules move with the bubble (in a manner similar to the movement of a sailboat on water). Since a film of water molecules is held to the polar group of the surface-active reagent, they travel with the bubble. Thus the movement of a bubble in a dilute aqueous solution containing surface-active agents would be similar to the movement of a solid sphere through water because water molecules now travel with the bubble. In this case, viscous effects become significant in a thin layer near the surface, in other words, a peculiar boundary layer, or thin liquid film (or hydrated layer), appears near the gas-liquid interface, in which a manifestation of viscosity, in an actual liquid, is inevitable [Levich, 1962].

Efforts have been made to measure the thickness of liquid film on the bubble surface and the viscosity of hydrated layers under different conditions. It was found [Xu and Yoon, 1989; Schulze, 1984; Klassen and Mokrousov, 1963] that the thickness of the film was much less than 1 μm, and a definite increase in the viscosity of the hydrated layer is always present. The properties and the role of thin layers of water surrounding mineral particles and air bubbles in flotation have been studied extensively and confirmed by Russian scientists [Klassen and Mokrousov, 1963].

The above discussions show that the functions of surfactants on bubbles contribute to the immobilization of boundary layer, the formation and change of a thin liquid film surrounding the bubble, and the increase of bubble surface viscosity. Frother molecules form an "armoring layer" on the bubbles surface, which attract the water dipoles in the liquid, thus increasing the resistance to bubble motion [Hu et al., 1980]. The liquid films

formed at the air/liquid interface may be liquid expanded, liquid condensed or even solidified, depending on frother molecular structure and concentrations [Leja, 1984]. Therefore, in order to understand the behavior of bubbles in flotation systems, it is important to investigate the effect of different types and concentrations of frothers on bubble motion.

2.3 MODEL DEVELOPMENT

2.3.1 The Virtual Liquid Film of a Bubble

From the above discussion it can be reasonably assumed here that a real bubble (or visual bubble) formed in water consists of two parts:

- (1) the gas sphere with the virtual radius, Rg, (or virtual diameter dg); and
- (2) the thin liquid film with the virtual thickness, L_f, surrounding the gas sphere.

Therefore, the radius of the visual bubble, R_v, which can be obtained from the photographic technique, is given as:

$$R_{v} = R_{g} + L_{f} \tag{2-6}$$

or the diameter of the visual bubble, dv, given as:

$$d_{v} = d_{g} + 2L_{f} \tag{2-7}$$

Most of the previous theoretical treatments dealing with bubbles were done with the assumption of an ideal situation, i.e., the thickness of the liquid film is assumed to be zero and no viscosity difference between the bulk liquid and the bubble surface. However, in practice, as discussed earlier, a thin liquid film is attached to the rising bubble. As a result of the formation of the liquid film and the changes in the bubble surface viscosity, the net lifting force acting on the bubble will be smaller than that in the ideal situation. In order to account for the effect of the liquid film and the surface viscosity on a bubble, the virtual mass of the bubble is adopted here. This can be estimated in the following way [Ramakrishan et al.,1969; Davidson and Schuler, 1960; Milne-Thomson, 1960]:

Assume that a solid sphere with radius R_s and mass M_s is moving in water in a direction perpendicular to a wall, the virtual mass of the sphere M_{vs} can be given by

$$M_{VS} = M_S + M_1/2 \div 3M_1R_S^3/(16b^3)$$
 (2-8)

where M_1 is the mass of liquid displaced by the sphere; b is the distance of the center of the sphere from the wall. The sum of the last two terms on the right hand side of Eq. (2-8) is defined as hydrodynamic mass or added mass [Milne-Thomson, 1960]. If the sphere is a gas sphere, then $M_S = M_g$, where M_g is the mass of the gas sphere with the virtual radius R_g . When $b = R_S = R_g$, the average virtual mass for the bubble M_{vb} can be written as

$$M_{vb} = M_g + M_1/2 + 3M_1/16$$

$$= M_g + (11/16)M_1$$
(2-9)

Therefore, the virtual mass of the bubble is the sum of the mass of the gas sphere and 11/16th of the mass of liquid displaced by the gas sphere. From the assumptions made earlier, it is obvious that the second term on the right hand side of Eq. (2-9) should be equivalent to the mass of the liquid film surrounding the gas sphere, i.e.,

$$(11/16)(4\pi/3)\rho_{\rm L}R_{\rm g}^{3} = (4\pi/3)(R_{\rm v}^{3} - R_{\rm g}^{3})\rho_{\rm L}$$
 (2-10)

Solving Eq. (2-10) gives

$$R_g = 0.84R_v$$
 (2-11)

From Eq.(2-6), the thickness of this virtual liquid film is

$$L_{f} = R_{v} - R_{g} = 0.16R_{v} \tag{2-12}$$

Eq. (2-12) shows that the thickness of the virtual liquid film increases with the bubble size. Therefore, it should be expected that the effect of the virtual liquid film on the behavior of bubbles will be more pronounced for larger bubbles.

2.3.2 Bubble Rise Velocity

2.3.2.1 In the Absence of Surfactarits

Levich [1962] analyzed the single bubble rising velocity by the concept of boundary layer, based on the following assumptions:

- (1) that the bubble's shape is strictly spherical;
- (2) that no surface-active materials are present on its surface;
- (3) that the range of Reynolds numbers $1 << Re_b < 1500$, which corresponds to the bubble diameters less than 0.2 cm apply.

The expression for drag force, Fdb, is given as:

$$F_{db} = 12\pi\mu R_i U_{bo} \tag{2-13}$$

where R_i is the bubble radius under the ideal conditions, U_{bo} is the bubble rising velocity by buoyancy, μ is the viscosity of the bulk liquid.

The buoyancy force on a rising bubble, Fby, is given as:

$$F_{by} = (4\pi/3)(P_L - P_G)R_i^3/\mu \tag{2-14}$$

where ρ_L and ρ_G are the densities of the liquid and gas phase, respectively.

Equating Eq.(2-13) and (2-14) leads to an expression for the bubble rise velocity given as:

$$U_{bo} = \frac{g(\rho_L - \rho_G)R_i^2}{9\mu}$$
 (2-15)

Under the ideal conditions, $R_i = R_g = R_v$, U_{bo} can also be expressed as:

$$U_{bo} = \frac{g(\rho_L - \rho_G)R_g^2}{9\mu}$$
 (2-16)

Comparing this rise velocity of a bubble with Stokes' law for a solid sphere, it indicates that it is only half the velocity of a solid sphere with the same size and density. But measurements show that the bubble rise velocity predicted from Levich's equation is still about 30% higher than the observed values [Levich, 1962], as indicated in Fig. 2-2.

Now, consider the effect of the virtual liquid film on bubble velocity. In this case, Substituting Eq. (2-11) into Eq.(2-16) gives

$$U_{bo} = \frac{g(\rho_L - \rho_G)(0.84R_v)^2}{9\mu}$$

$$= (0.0784/\mu)g(\rho_L - \rho_G)R_v^2$$
(2-17)

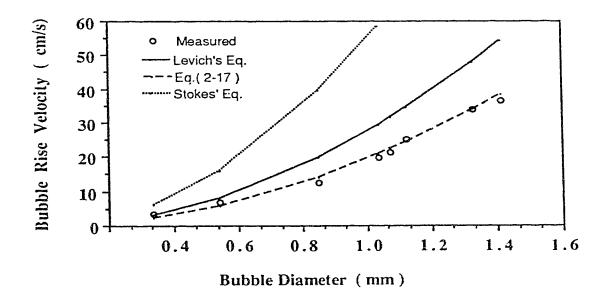


Figure 2-2 Comparison of bubble rise velocity in the absence of surfactants

Fig. 2-2 shows the comparison of the predictions from Stokes' equation, Levich's equation and Eq. (2-17) with the experimental results of bubble rise velocities in pure water which had been boiled with permanganate and then double distilled water [Levich, 1962]. It can be seen that Eq. (2-17) corresponds to the data very well, more closely than either Stokes'

explained by the effect of the virtual liquid film on the bubble, and it is equivalent to a decrease of the actual bubble size to a fraction of 0.84 of the original one, in the absence of surfactants. Since the bubble size R_i is ideal and conceptual, in order to use Levich's equation to estimate bubble rise velocity, it is necessary to convert the measured bubble size R_v to R_i . The above discussion shows that R_g can be regarded as equal to R_i in an ideal case or in an actual situation.

2.3.2.2 In the Presence of Surfactants

Experiments with liquid having clean surfaces are relatively rare in actual practice. Usually, the liquid is covered with surface-active substances to a greater or lesser degree [Levich, 1962]. In a flotation process, a frother is usually added to the slurry to form bubbles with suitable size and stability. Therefore, it is necessary to investigate the bubble rising velocity in the presence of surfactants.

In order to simplify the analysis, the changes in the bubble surface characteristics, due to the addition of surfactants, is assumed to be equivalent to the changes of the virtual liquid film thickness. The virtual thickness of the liquid film will depend on the number of frother molecules adsorbed on the bubble surface. The adsorption in dilute solution can be expressed by Gibbs' equation [Li, 1983]:

$$\Gamma_{\rm m} = (C/RT)(-d\sigma/dC) \tag{2-18}$$

where Γ_m is the molar number of molecules adsorbed on the bubble per unit area, C is the frother concentration in the solution, σ is the surface tension.

The total amount of frother molecules, Γ_{tm} , adsorbed on the gas sphere surface, is therefore

$$\Gamma_{\rm tm} = 4\pi R_{\rm g}^2 (\text{C/RT})(-\text{d}\sigma/\text{dC}) \tag{2-19}$$

It is assumed that the maximum virtual thickness of the liquid film is obtained when the bubble surface is completely immobilized. Further addition of frother will not increase the amount of the molecules on the bubble surface due to the repulsive forces exerted by the

unchanged. Thus the relationship between the virtual thickness of liquid film and the adsorption of frother molecules can be written as

$$L_{f} = (0.16 + C_{r}\Gamma_{tm})R_{v}$$
 (2-20)

where C_r is a coefficient related to the frother type and its diffusion property. In the absence of frother, $\Gamma_{trn} = 0$, and Eq. (2-20) reduces to Eq. (2-12).

Substituting Eqs. (2-6) and (2-19) into (2-20), we have

$$L_{f} = [0.16 + 4\pi R_{g}^{2}(C_{r}C/RT)(-d\sigma/dC)]R_{v}$$

$$= [0.16 + C_{c}(R_{v}^{2} - 2R_{v}L_{f} + L_{f}^{2})]R_{v}$$
(2-21)

where Cc is defined as the contamination factor given as

$$C_c = (4\pi C_r C/RT)(-d\sigma/dC) = 4\pi C_r \Gamma_m$$
 (2-22)

Rearranging Eq. (2-21) gives

$$R_{v}C_{c}L_{f}^{2} - (2C_{c}R_{v}^{2} + 1)L_{f} + 0.16R_{v} + C_{c}R_{v}^{3} = 0$$
(2-23)

Solving this equation, by assuming $L_f < R_v$, gives

$$L_{f} = \frac{2C_{c}R_{v}^{2} + 1 - [(2C_{c}R_{v}^{2} + 1)^{2} - 4R_{v}C_{c}(0.16R_{v} + C_{c}R_{v}^{3})]^{0.5}}{2R_{v}C_{c}}$$

$$= \frac{1 + 2C_{c}R_{v}^{2} - (1 + 3.36C_{c}R_{v}^{2})^{0.5}}{2C_{c}R_{v}}$$
(2-24)

Now, by substituting Eq. (2-6) and Eq. (2-24) into Eq. (2-17), the rising velocity of bubbles in the presence of frother or surfactant, U_{bs} , is obtained as:

$$U_{bs} = g(\rho_L - \rho_G)(R_v - L_f)^2/(9\mu)$$

$$= \frac{g(\rho_L - \rho_G)[(1 + 3.36C_cR_v^2)^{0.5} - 1]^2}{9\mu(2C_cR_v)^2}$$
(2-25)

or

$$U_{bs} = \frac{A[(1+3.36C_cR_v^2)^{0.5}-1]^2}{(2C_cR_v)^2}$$
(2-26)

where

$$A = g(\rho_{L} - \rho_{G})/(9\mu)$$
 (2-27)

All the variables in the equation (2-26), except C_c , can be determined experimentally. Thus, for a given frother, C_c can be estimated from measuring velocities of different bubble sizes at a fixed concentration.

2.4 APPLICATION OF THE MODEL

One of the most important information which can be obtained from Eq. (2-26) is the degree of contamination of the solution by surface-active materials. Using the data obtained by Fuerstenau and Wayman (Table 2-1) and Eq. (2-26), it was found that the distilled water used by them had a contamination factor of about 66.5, indicating that there were still some surface-active materials in the water.

Fig. 2-3 presents a comparison of Equation (2-26) with some existing models used for predictions of terminal velocities of solid spheres [Concha and Almendra, 1979; White, 1974; Schiller and Naumann, 1933], and which are generally adopted to estimate bubble rise velocities. It is clearly shown that there is little difference between these equations when the contamination factor is about 195. This implies that only when the contamination factor of the solution is about 195, does the bubble behave like a solid sphere at this intermediate Reynolds number range (1 << Reb < 500).

Fig. 2-4 shows a comparison between the measured data and predicted results from Eq. (2-26) for bubble rising velocities versus size, in the presence of n-amyl alcohol (10-4 M). The experimental data for this plot were obtained from Klassen and Mokrousov [1963]. It can

be seen that at a contamination factor, C_c , of 235, the prediction from Eq. (2-26) fits the data very well.

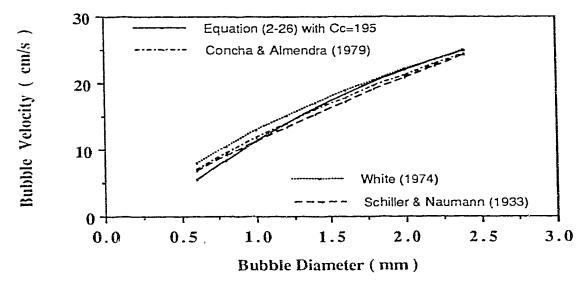


Figure 2-3 Comparison of bubble rise velocity in the presence of surfactants

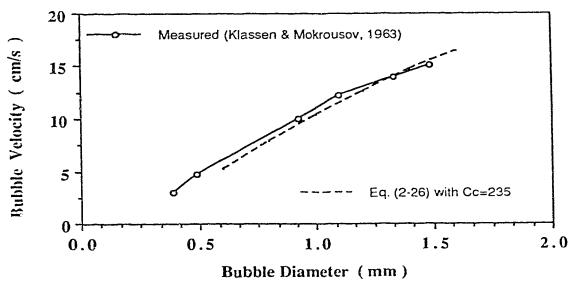


Figure 2-4 Bubble rise velocity in the presence of n-amyl alcohol (10⁻⁴ M) (data from Klassen and Mokrousov, 1963)

Fig. 2-5 shows the simulated results from Eq. (2-26) for the comparison of bubble rise velocity in pure water with that in the presence of surfactants. It can be seen that, for bubbles less than 0.1 cm in diameter, the rising velocity of bubbles in the aqueous media with a contamination factor of 195, is slower but less than half as fast when compared with the bubble ascent in pure water, whereas for bubbles with diameter larger than 0.1 cm, the ascent of bubbles in the presence of surfactants is only a third to a half as fast in pure water. This prediction agrees with the observation of the previous researchers [Klassen and Mokrousov, 1963]. It also indicates that the ratio of bubble rise velocity, Ubo/Ubs, increases with the contamination factor.

Fig. 2-6 shows the effect of the value of C_c on the bubble rise velocity. Because C_c is the product of the frother type coefficient C_r and the adsorption amount Γ_m , for a given frother, increasing the concentration of the frother will increase the adsorption Γ_m , thus giving a higher value of C_c . From Fig. 2-6 it can be seen that larger C_c , or higher concentration will slow the bubble velocity more profoundly. For the same reason at a given adsorption rate Γ_m a frother with higher C_r will yield bigger C_c , resulting in larger reduction in the bubble rise velocity.

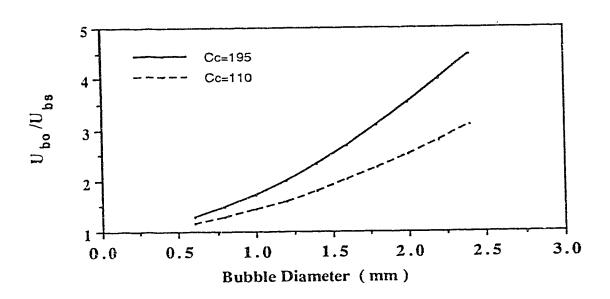


Figure 2-5 Comparison of bubble rise velocity in the absence and in the presence of surfactants

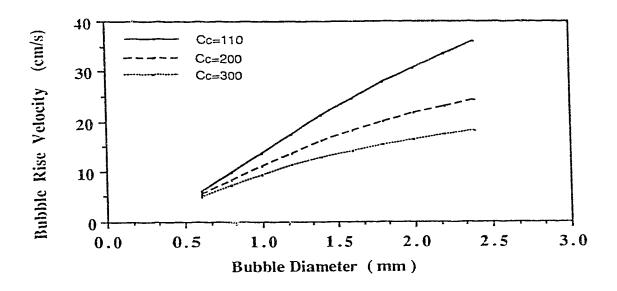


Figure 2-6 Effect of contamination factor on bubble rise velocity

2.5. SUMMARY OF CHAPTER

- 1. A model has been developed to predict the relationship between the rise velocity and the size of single bubbles in aqueous media with or without surfactant addition, which agrees with the literature data very well.
- 2. By considering the virtual liquid film of a bubble, the discrepancy between Levich's equation and experimental data can be reasonably explained.
- 3. The concept of contamination factor, C_c , of the solution is introduced, which is a function of the frother type and the amount of frother molecules adsorbed on the bubble surface. The surfactant effects on bubbles and on the solution purity can be characterized by the value of C_c . Larger C_c means higher contamination of the solution by surface-active materials and higher retardation effects on bubble motion.

- 4. A bubble behaves like a solid sphere only at the contamination factor of about 195. The motion of bubbles ascending in the solutions with contamination factors larger or less than 195 will deviate from that of solid sphere with the same size and density.
- 5. The retarding effects of surfactants on bubbles can be attributed to the immobilization of the boundary layer, the formation and change of a thin liquid film surrounding the bubble, and the increase of the bubble surface viscosity.

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CHAPTER 3 THE MOTION OF SINGLE BUBBLES _EXPERIMENTAL*

3.1 INTRODUCTION

The motion of single bubbles in aqueous media has been the subject of many theoretical and experimental investigations. Unfortunately, experimental data have shown significant deviation from the theoretical models. Wide ranges of bubble rise velocities for a given bubble size under the same conditions have been reported by different investigators, as indicated in Figure 1-1 in chapter 1. Jameson [1984] ascribed this to the "wall effect", i.e., the diameter of tubes which were used to study bubble motion was not large enough to have a negligible effect on the results, and to the surface active materials dissolved in the water. While the wall effect can be easily minimized by using tubes with larger sizes, it is almost impossible to get rid of those nearly undetectable trace surface active contaminants in water. Because of the different procedures used to obtain an aqueous solution and its history, as well as the cleanness of the apparatus used, the degree of the contamination of the system will be different. Therefore, in order to measure and compare the bubble rise velocity for different solution systems, it is necessary to know the degree of the contamination of the aqueous media.

The theoretical study in Chapter 2 provides a basis for this approach. The degree of the contamination of the solution by surfactants can be evaluated by the magnitude of the contamination factor. The higher the contamination factor, the higher the degree of contamination. Thus this Chapter deals with the experimental verifications of the established model regarding the contamination factors in Chapter 2, and the determination of the degree of contamination of the solution.

3.2 EXPERIMENTAL METHOD AND MATERIALS

3.2.1 Measurement of Bubble Size and Bubble Rise Velocity

^{*} The extended version of this chapter has been accepted for publication by Canadian Metallurgical Quarterly.

The experimental apparatus used for measuring bubble rise velocity and bubble size is presented diagrammatically in Fig. 3-1. It is basically similar in design and in technique to that used by Anfruns and Kitchener [1977, 1976], Yoon and Luttrell [1986] for the measurement of bubble rise velocity and bubble sizes. Before each measurement the water in the column was first saturated with air. Individual bubbles were produced by a syringe at the bottom of the cylinder. A piece of transparent polymer film was placed and floated on the top surface of the liquid. When the bubble reaches the top level of the cylinder, it attaches to that film and it is fixed. The bubble size was then measured by a microscope from the top. A calibrated scale was put into the eyepiece so that bubble size could be

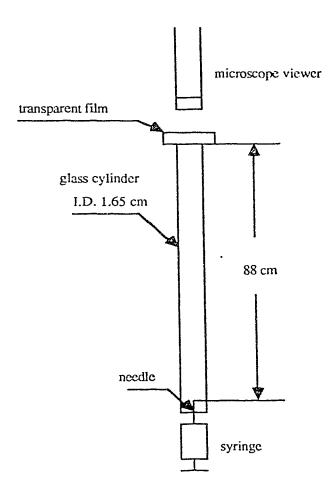


Figure 3-1 Schematic diagram of the apparatus used for measuring bubble rise velocity and bubble size

determined. The bubble rise velocity was estimated by measuring the time required for a bubble to rise from the bottom to the top of the cylinder. In this study the terminal velocities of single bubbles were measured as a function of bubble size, frother type and concentration.

In order to produce bubbles with the diameter less than 0.2 cm, a piece of rubber was pierced by the tip of the needle fixed on the syringe. By changing the position of the rubber on the needle, the size of the tip orifice of the needle is changed, and then the desired size range of bubbles can be obtained. According to Clift et al.[1978] and Wallis [1969], the wall effect is negligible if the ratio of bubble size to the tube diameter $d_b/d_c < 0.125$. Hence, in this study, the wall effect on bubble rise velocity can be ignored with the bubble sizes less than 0.2 cm.

It was found that, in the measurement of bubble size by this method, only the area of the bubble attached to the transparent film can be viewed. Therefore, attention was paid to the contact angle of the bubble attaching to the film. If the film material is too hydrophilic or hydrophobic, the contact angle will be either smaller or greater than 90 degrees, giving false results. Glass plates, polypropylene plastic films and polystyrene film were tried. Visual observations showed that the first two materials gave contact angles less than 90 degrees. The polystyrene film gave a contact angle of approximately 90 degrees, and reasonable results were obtained. Therefore, the polystyrene film was used in all the measurements.

3.2.2 Measurement of Surface Tension

Basically, there are four different methods generally used to measure surface tension in gas-liquid systems [Li, 1983; Anon.,1980; Daniels et al.,1956]. These are the capillary-rise, ring, drop-weight and bubble-pressure method. These methods are based on the principle that the molecules at the interface of gas-liquid are subject to the strong attractive forces of the interior molecules of liquid, due to the unbalanced attractive forces exerted by the molecules in gas. A resultant force, whose direction is in a tangential plane to the surface at a particular point, acts to make the interface area as small as possible. The magnitude of this force acting perpendicular to a unit length of a line in the surface is defined as the surface tension.

The ring method was used in this study because it provides a faster way to obtain reliable results, compared with other methods. The instrument used is the Du Nouy Tensionmeter (upward pull-type) made in Germany.

In the ring method, a platinum-iridium ring in the surface of the liquid is supported by a stirrup attached to the beam of a torsion balance (see Fig. 3-2). The ring is pulled upward from the liquid by turning the torsion wire, thus applying a force which is known from calibration of the instrument.

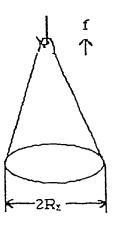


Figure 3-2 Principle of ring method for surface tension measurement

For an idealized system, the force just necessary to separate the ring from the liquid is equal to $4\pi R_r \sigma$, where R_r is the mean radius of the ring and σ is the surface tension. Doubling of the perimeter $2\pi R_r$ arises from the fact that there are two boundary lines between liquid and wire, one on the outside and the other on the inside of the ring. So the force balance is

$$f = 4\pi R_f \sigma F \tag{3-1}$$

where f is the maximum force registered on the torsion-balance scale; F is a correction factor which is related to the shape of liquid held up and the ring dimensions, and is normally taken to be close to unity.

The surface tension is thus given by the equation

$$\sigma = f/(4\pi R_r) \tag{3-2}$$

The value of σ can be directly read from the torsion-balance scale.

In order to simulate the actual situations, tap water from the city of Edmonton was used in all the experiments. MIBC, pine oil and Dowfroth 250, which are commonly used frothers in flotation of minerals and coal, were tested. All the measurements were done at room temperature (20-22 °C).

3.3. RESULTS AND DISCUSSIONS

3. 3.1. Bubble Rise Velocity

Fig. 3-3 shows the bubble rise velocities in tap water without frothers, and with pine oil addition of 3 cc/100 L. The continuous curves indicate the theoretical predictions with the given contamination factors.

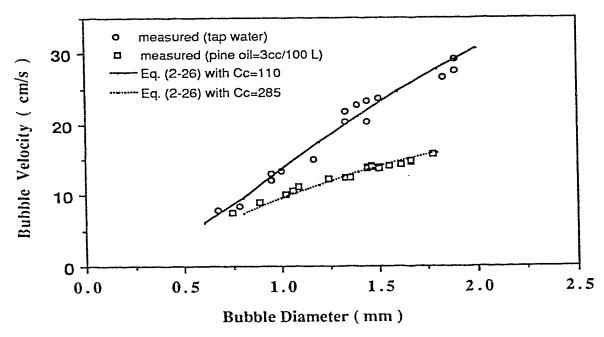


Figure 3 -3 The rise velocities of bubbles in tap water with and without pine oil addition

It can be seen from Fig. 3-3 that the experimental data fit the theoretical curves very well. The measurements show that the tap water from the city of Edmonton has a contamination factor of 110, which indicates that some organic surface-active materials are present in the water. The tap water with the addition of 3 cc/100 L pine oil has a contamination factor of 285.

It is observed in Figure 3-4 that at a similar concentration of MIBC and Dowfroth 250 of 1.5 cc/100 L, the retardation of bubble ascent varies for the different surfactants, which agrees with the measurements by other researchers [Hu, et al.,1980; Fuerstenau and Wayman, 1958]. This can be explained by the difference in the contamination factors. Dowfroth 250 solution gave a contamination factor of 245, while MIBC gave a contamination factor of 135, at the same concentration of 1.5 cc/100 L. Hence Dowfroth 250 retards bubbles more profoundly than MIBC.

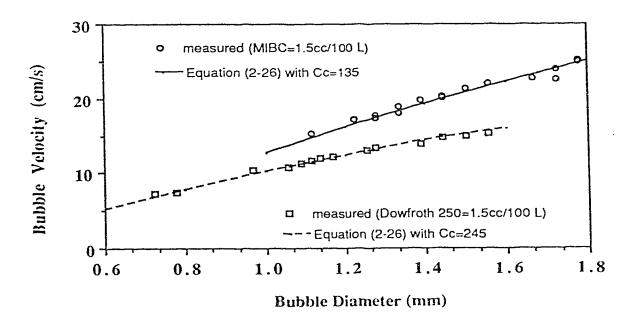


Figure 3-4 Bubble rise velocities in different frother solutions

Fig. 3-5 presents the effect of different pine oil concentrations on bubble rise velocity. From Eqs. (2-19), (2-22) and (2-26), it can be expected that increasing the concentration of frothers will increase the contamination factor, thus slowing bubbles more severely. These

measurements verify this prediction. The contamination factors obtained are 135 and 255 for pine oil concentrations of 0.18 cc/100 L and 1.5 cc/100 L, respectively.

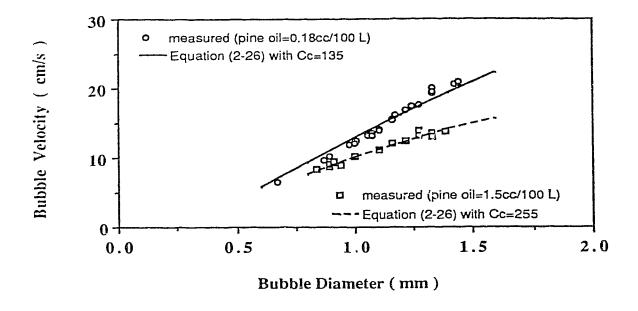


Figure 3-5 Effect of pine oil concentration on bubble rise velocity

3.3.2. Drag Coefficient and Reynolds Number

Now, consider the effect of the contamination factor on the drag coefficient and Reynolds number. The general relationship between the terminal velocity of spheres U_{bs}, when moving in liquid, and drag coefficient C_d can be written as [Dobby, 1988]:

$$U_{bs} = \frac{[8g(\rho_L - \rho_G)R_v]^{0.5}}{(3\rho_L C_d)^{0.5}}$$
(3-3)

or,

$$U_{bs} = [24A\mu R_v/(\rho_L C_d)]^{1/2}$$
 (3-4)

therefore, the drag coefficient of a bubble is given as:

$$C_{d} = \frac{24A\mu R_{v}}{\rho_{L}U_{bs}^{2}}$$
(3-5)

Substituting Equation (2-26) into (3-5) gives

$$C_{\rm d} = \frac{384\mu C_{\rm c}^4 R_{\rm v}^5}{\rho_{\rm L} A[(1+3.36C_{\rm c}R_{\rm v}^2)^{0.5} - 1]^4}$$
 (3-6)

It can be seen from Eq. (3-6) that the drag coefficient is also dependent on the contamination factor. Fig. 3-6 shows the relationship between drag coefficient C_d and contamination factor C_c .

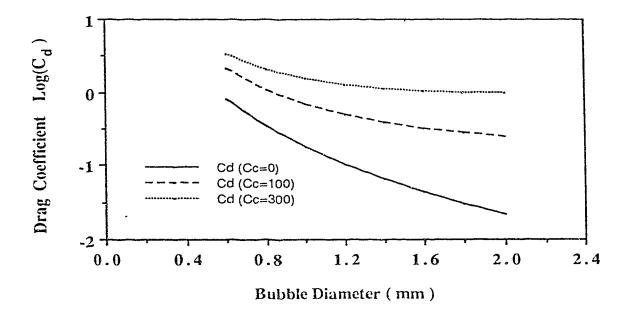


Figure 3-6 Effect of contamination factor on bubble drag coefficient

A higher C_c results in a larger C_d , thus a bigger drag force. For a bubble with diameter of 0.2 cm, the drag coefficient at a contamination factor of 300 is about 100 times larger than the bubble without adsorption layer, i.e., at $C_c = 0$. This indicates that one of the reasons for bubble retardation in the presence of surfactants is an increase in the drag force to the bubble motion, due to the interaction between the polar group of frother molecules

adsorbed on the bubble surface and water dipoles. This interaction presumably leads to the changes in bubble surface viscosity and the thickness of the virtual liquid film of the bubble.

The Reynolds number, Reb, can then be expressed as

$$Re_b = 2R_v U_{bs} P_L / \mu$$

$$= \frac{\Lambda P_L [(1+3.36C_c R_v)^{0.5} - 1]^2}{2\mu C_c^2 R_v}$$
(3-7)

Fig. 3-7 shows the effect of contamination factor on bubble Reynolds number. It can be seen that increasing C_c will reduce Re_b.

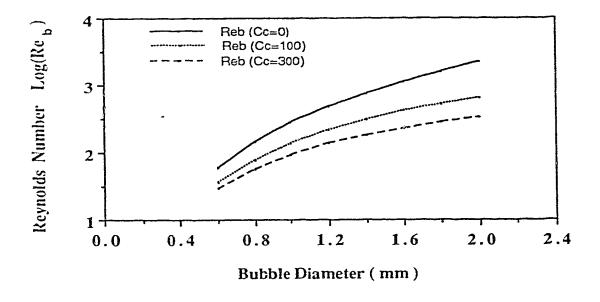


Figure 3-7 Effect of contamination factor on bubble Reynolds number

This implies that for the same size of bubbles, higher C_c , or adding a frother will make the bubble move less violently. It was observed during experimental measurements that for bubbles with diameter larger than about 0.15 cm the ascent in the water column occurred

more smoothly in the presence of frothers. The same phenomena were also found by other researchers [Leja, 1983; Klassen and Mokrousov, 1963; Fuerstenau and Wayman, 1958]. This can be partly attributed to the reduction of bubble Reynolds number with the addition of frothers.

3.3.3. Adsorption Rate

It is generally accepted that adding a surface active agent into water lowers the surface tension of the solution as a result of the heteropolar nature of the molecules. Thus the surface tension of a solution is usually used as an indication of the activity of a frother, with chemicals that strongly lower the surface tension producing more stable (persistent) froths [Klimpel and Hansen, 1988; Harris, 1982]. However, for the different frothers studied here, the results showed that surface tension cannot be used as a criterion to predict the effect of frothers on the bubble rise velocities (the same conclusion was obtained in Chapter 2). For example, for the same contamination factor of 235, MIBC solution (with a concentration of 6 cc/100 L) has a surface tension of about 75 dynes/cm; while Dowfroth 250 solution (with the concentration of 1.5 cc/100 L) has a surface tension of 65 dynes/cm.

The contamination factor, from Eq. (2-22), is dependent on the frother type and adsorption rate. Therefore, it is the frother molecular structure factor, C_r , and the adsorption rate, Γ_m , or the surface activity, $d\sigma/dC$, rather than surface tension, σ , alone, that influences the bubble rise velocity.

Fig. 3-8 shows the changes in surface tension of solutions with frother concentration. The surface tension of tap water without adding frothers was 77 dynes/cm, larger than the standard value of surface tension for pure water (72 dynes/cm at 20 °C). This is attributed to some inorganic ions and salts present in the tap water. It is observed that the surface tension of pine oil solution reduces sharply with increasing concentration, indicating much higher surface activity, do/dC, at the dilute concentration range, hence higher adsorption rate can be expected. The surface tension of MIBC solution does not change much with the concentration, so the adsorption rate will be expected to be low compared with pine oil and Dowfroth 250 solutions. One of the reasons may be attributed to the different solubilities of the frothers, resulting from the different molecular structures [Klimpel and Hansen, 1988]. Pine oil has a low solubility in water (2 g/L), so when pine oil is added into water most of the molecules will be arranged at the gas-liquid interface, thus lowering the surface tension very sharply. MIBC has a higher solubility in water (17 g/L), therefore most of them will

be dissolved in the bulk liquid, and only a small proportion can be adsorbed on the bubble surface. In order to reach the same adsorption rate, or to achieve the same retardation effect, as the pine oil solution, a much higher MIBC concentration has to be used. Measurements show that MIBC solution with a concentration of 6 cc/100 L has almost the same contamination factor as pine oil solution with concentration of 1.0 cc/100 L, as indicated in Figure 3-9.

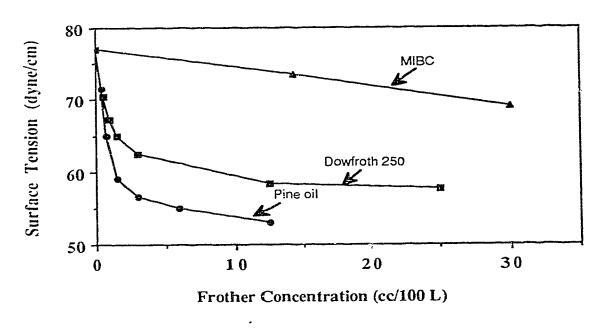


Figure 3-8 Surface tension of solutions at different frother concentrations

3.3.4. Contamination Factor

The above discussion has shown that the motion behavior of bubbles depends on the contamination factors of the aqueous solution. If we know the relationship between contamination factor and the frother concentration, then the bubble rise velocity under different concentrations of frothers can be estimated from Eq. (2-26). Because the usage of frothers in flotation practice is usually in the low concentration range, typically less than 3 cc /100 L [Booth and Freyberger, 1962], the effect of frother concentrations on the contamination factor was examined only at that dosage range.

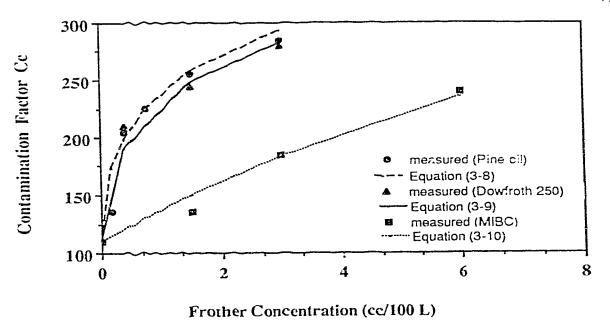


Figure 3-9 Variations in contamination factors with different frother concentrations

It was found from Fig. 3-9 that the contamination factors can be expressions for the three frothers studied:

For pine oil solution:

$$C_c \approx 110 + 285[1-\exp(-0.59C^{0.5})]$$
 $(0 \le C \le 3 \text{ cc/}100 \text{ L})$ (3-8)

For Dowfroth 250 solution:

$$C_c \approx 110 + 280[1-\exp(-0.55C^{0.5})]$$
 $(0 \le C \le 3 \text{ cc}/100 \text{ L})$ (3-9)

For MIBC solution:

$$C_c \approx 110 + 260[1-\exp(-0.11C)]$$
 $(0 \le C \le 5 \text{ cc}/100 \text{ L})$ (3-10)

3.5 SUMMARY OF CHAPTER

- 1. The direct measurement of single bubble rise velocity in a water column clearly shows that the frother effect on bubble motion can be conveniently explained in terms of the changes in a contamination factor.
- 2. One of the practical applications of the model established in this study is that it provides a simple method to check the reliability of the purified water and the degree of contamination by trace amount of surfactants, which may be difficult or even impossible to be detected by other physical or chemical methods.
- 3. The higher the contamination factor, the larger the drag coefficient and drag force, thus the lower the bubble rise velocity and Reynolds number.
- 4. At similar sizes, bubbles rise more smoothly in the presence of surfactants or at higher contamination factors, due to the reduction of the Reynolds number.
- 5. Frother molecular structure and urface activity, $d\sigma/dC$, or the adsorption rate, Γ_m , rather than surface tension alone, determine the effect of frothers on bubble rise velocity.

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CHAPTER 4 THE MOTION OF BUBBLES IN A SWARM

4.1 INTRODUCTION

Due to the difficulties in evaluating the effect of the surface-active materials on bubble behavior, the bubbles in flotation systems are often treated as solid spheres, and the bubble rise velocities in a swarm are usually estimated either from models for solid sphere hindered settling velocities [Finch and Dobby, 1990; Yoon and Luttrell, 1989; Pal and Masliyah, 1989; Dobby et al., 1988; Dobby, 1984; Schulze, 1984], or by empirical expressions for single bubble systems [Patel et al., 1990, 1989]. The previous chapters provide a simple method to determine the surfactant effects on single bubble motion, and the expressions for bubble rise velocities in MIBC, Dowfroth 250 and pine oil solutions have been experimentally determined. Therefore, the rise velocities of bubbles in different type and concentration of frothers can be predicted.

In practice, a swarm of bubbles, as opposed to single bubbles, is used in the flotation of minerals and coal. It is a well-known fact that swarms of moving bubbles have velocities which are different from those for the case of single bubbles. This is mainly due to the fact that in the case of an ensemble of bubbles, the distribution of velocities, temperatures, and concentrations in the vicinity of one bubble is influenced by its neighbors [Galor and Waslo, 1968]. The flow characterization of bubble columns has been investigated extensively [Xu et al., 1991; Pal and Masliyah, 1989; Dobby et al., 1988; Yianatos et al., 1988; Shah et al., 1982; Rulev, 1977; Wallis, 1969; Marrucci, 1965; Nicklin, 1962]. However, the effects of different surfactants at varied dosages on bubble rise velocities have not been considered in most of these investigations. Therefore, it is the objective of this chapter to extend the study of frother effects on bubbles in single bubble systems to that in bubble swarm systems, and to establish an expression which relates the average bubble rise velocity in a swarm to other column flotation variables, such as superficial gas and liquid velocities, gas holdup and contamination factor due to the addition of frothers. Hence the frother effects on bubble rise velocity in a flotation column can be evaluated.

4.2 THEORETICAL

In column flotation, bubbles are produced by either internal porous spargers or external spargers. Due to the different pore sizes on the sparger and bubble coalescence after leaving the sparger, the bubbles in the column will be different in size and in rise velocity. In order to investigate the motion of bubbles in a swarm, the average bubble rise velocities are used in this study.

4.2.1 Average Bubble Rise Velocity

Nicklin [1962] established that the motion of bubbles in two-phase bubble flow arises partly from buoyancy and partly from the superficial velocity caused by the entry of the two phases into the column. Thus, in the case of counter-current column flotation process, at least three main factors continue to the actual average bubble rise velocity: (a) buoyancy; (b) superficial gas velocity, J_g ; and (c) superficial liquid velocity, J_1 . Therefore, the average bubble rise velocity, U_{ba} , can be written as:

$$U_{ba} = U_{bd} + J_g - J_1 \tag{4-1}$$

where U_{bd} is the bubble rise velocity by buoyancy in liquid, which is also known as "energy-destroying velocity", as defined by Nicklin [1962], or "drift velocity", as defined by Wallis [1969], or "collective velocity" as defined by Rulev [1977]. U_{bd} can be determined by measuring the rising velocity of the bottom line of demarcation of a bubble swarm, or the declining velocity of the top liquid level [Nicklin, 1962], or by dynamic gas disengagement techniques[Patel et al. 1990, 1989].

Assuming that the gas flowrate is Q_g (L/min.), the average size of bubbles produced by a sparger is R_v in radius, the expanded liquid level in the column is H_e , then the number of bubbles produced per unit time, N_{bo} , by the sparger can be written as:

$$N_{bo} = Q_g/[(4\pi/3)R_v^3]$$
 (4-2)

and the time, t, for a bubble rising from the sparger to the top liquid level is given as:

$$t = H_0/U_{ha} \tag{4-3}$$

Therefore, the total number of bubbles in the column, N_{bt} , is

$$N_{bt} = N_{bo}t = H_e Q_g / [(4\pi/3)R_v^3 U_{ba}]$$
 (4-4)

Note that the gas volume in the column, $V_e^{\varepsilon}_g$, equals the sum of the total bubble volumes, i.e.,

$$V_e \varepsilon_g = H_e A_c \varepsilon_g = (4\pi/3) R_v^3 N_{bt}$$
 (4-5)

where $V_c = H_c A_c$, is the expanded bed volume in the column; A_c is the cross sectional area of the column; ε_g is the gas holdup.

Substituting Eq. (4-4) into Eq. (4-5) gives

$$H_e A_c \varepsilon_g = \frac{(4\pi/3) R_v^3 H_e Q_g}{(4\pi/3) R_v^3 U_{ba}}$$

Rearrangement of the above equation results in another familiar expression for the bubble rise velocity U_{ba} given as

$$U_{ba} = Q_g/(A_c \varepsilon_g) = J_g/\varepsilon_g$$
 (4-6)

This is also equal to the average velocity of gas in the column. Nicklin [1962] experimentally verified Eqs.(4-1) and (4-6), by directly measuring average bubble rise velocity, bubble drift velocity and gas holdup in a stagnant liquid. Figure 4-1 presents Nicklin's results. It is clearly shown from this figure that for a certain range of gas holdup, the bubble rise velocities measured by three methods agree very well. This indicates that Eq. (4-6) provides a very convenient and reliable method to estimate the average bubble rise velocity in a swarm.

However, the major disadvantage of Equation (4-6) is that it cannot directly predict the bubble size and frother effects on the rise velocity, which are important in the analysis of flotation kinetics and process optimization. Therefore, it is necessary to establish the relationship between the rise velocities and the sizes of bubbles in a swarm, in the presence of different types and dosages of frothers.

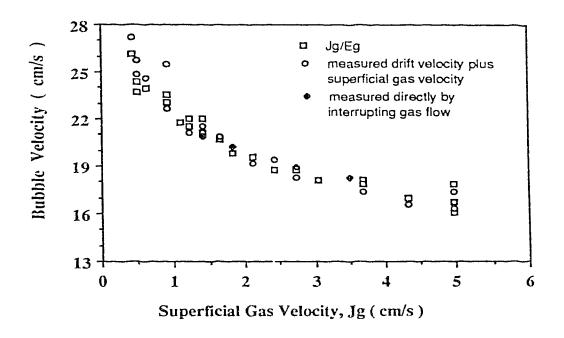


Figure 4-1 Effect of superficial gas velocity on bubble rise velocity

4.2.2 Bubble Drift Velocity

Galor and Waslo[1968] conducted a detailed hydrodynamic study on an ensemble of bubbles rising in a swarm in the presence or absence of surfactants under the Stokes' flow regime ($Re_b < 1$). They obtained an equation for the bubble rise velocity in a swarm, U_{cn} , given as

$$U_{en} = \frac{U_s[3\mu_c(1-\emptyset^{1/3})(1-\emptyset^{5/3})+(3-4.5\emptyset^{1/3}+4.5\emptyset^{5/3}-3\emptyset^2)(\mu_d+\gamma)]}{2\mu_c(1-\emptyset^{5/3})+(3+2\emptyset^{5/3})(\mu_d+\gamma)} \tag{4-7}$$

where U_s is Stokes' velocity; μ_c and μ_d are the viscosities of the continuous phase and dispersed phase, respectively; \emptyset is the volumetric dispersed-phase holdup fraction; γ is retardation coefficient due to the presence of surfactants, $\gamma = -(1/3)K(\partial\sigma/\partial C)$, in which C is the interfacial concentration of surfactants, K is retardation constant, σ is the surface tension of the solution.

In fact, this expression is a general equation for the terminal velocity of a sphere (including solid, liquid drop and bubble) moving in the presence or absence of surfactants. Under

different conditions, the corresponding sphere velocities, such as Stokes' equation for a solid sphere, Levich's equation for a single drop, etc., can be easily obtained.

Rulev et al.[1977] adopted this equation in flotation systems for $Re_b \le 0.5$ (or $d_b \le 0.01$ cm). In this case, bubbles rise like solid spheres because their surface is completely retarded by an adsorbed surfactant layer which is always present unless the liquid is specially purified. Therefore, Eq. (4-7) can be simplified as

$$U_{en} = \frac{U_s (3 - 4.5\%^{1/3} + 4.5\%^{5/3} - 3\%^2)}{3 + 2\%^{5/3}}$$
(4-8)

However, they inadequately took Eq. (4-8) for actual bubble rise velocity to analyze the bubble-particle contact in flotation. From the initial conditions assumed for deriving Eq. (4-7), it is obvious that Eq.(4-8) may be suitable for estimating the bubble drift velocity in the case of dissolved air flotation (where bubbles are about $100 \, \mu m$ in diameter), but it cannot be employed in flotation columns where average bubble sizes are much larger.

Based on Nicklin's idea, Marrucci [1965] proposed an expression relating the velocity of rise of a swarm of spherical bubbles to the velocity of a single bubble. The analysis, which employed a cellular spherical model, is restricted to the range of high but subcritical Reynolds numbers (1<< Re $_b<$ 300). The equation derived by Marrucci can be written as:

$$U_{bd} = U_{bo} \frac{(1 - \varepsilon_{gm})^2}{1 - \varepsilon_{gm}^{5/3}}$$
 (4-9)

where ε_{gm} is the gas holdup defined by Marrucci as $\varepsilon_{gm} = a^3/b_l^3$, in which a and b_l are the radii of a bubble and the fluid envelop surrounding the bubble, respectively; U_{bo} is the Levich's expression [Levich, 1962] for the single bubble rising velocity given as:

$$U_{bo} = \frac{(\rho_L - \rho_G)gR_g^2}{9\mu}$$
 (2-16)

According to Marrucci, the dependency on the holdup is weaker for bubbles than for solids [Marrucci, 1965; Happel, 1958], when Eq. (4-9) is compared with expressions for solids hindered settling velocities. This implies that some deviation may occur when using models for solids settling velocity to estimate bubble rise velocity, as treated by other researchers [Dobby et al.,1988; Schulze, 1984]. This equation was also inadequately adopted by Rulev et al.[1977] as the average bubble rise velocity in flotation system.

Whether Equation (4-9) agrees with experimental data has not been verified, because according to Marrucci [1965], a valid experimental confirmation of Eq.(4-9) is made difficult by the impossibility of keeping a constant volume of the bubble with increasing gas flowrate.

4.2.3 Slip Velocity

One of the most commonly employed methods to describe bubble flow is to use slip velocity, which is defined as the relative velocity of two phases, e.g., gas-liquid phase. In the case of counter-current flow employed in column flotation, the slip velocity of gas-liquid phase, Ugl, can be written as:

$$U_{gl} = U_{ba} + U_{l}$$

$$= J_g/\varepsilon_g + J_l/(1 - \varepsilon_g)$$
(4-10)

For bubble sizes of $d_b \le 0.2$ cm (Re_b ≤ 500), Yianatos et al.[1988] adapted an expression for multi-species hindered settling equation of Masliyah [1979], combined with Richardson and Zaki's expression [1954] for solid-liquid systems to give the gas-liquid slip velocity as

$$U_{gl} = \frac{gd_b^2 \rho_L (1 - \epsilon_g)^{m-1}}{18\mu (1 + 0.15Re_{bs}^{0.687})}$$
(4-11)

where

$$Re_{bs} = d_b U_{gl} P_L (1 - \varepsilon_g) / \mu$$
 (4-12)

$$m = (4.45 + 18d_b/d_c)Re_b^{-0.1}$$
 $1 < Re_b < 200$ (4-13)

or

$$m = 4.45 Reb^{-0.1}$$
 $200 < Reb < 500$ (4-14)

and

$$Re_b = d_b U_T \rho_L / \mu \tag{4-16}$$

where d_b and d_c are the diameters of bubbles and the column, respectively; Re_{bs} and Re_b are the bubble Reynolds number in bubble swarm and in single bubble systems, respectively.

However, this analysis is entirely based on the assumption that bubbles behave like solid spheres. It has been shown in the previous chapters that bubbles behave like solid spheres only under certain frother conditions at the intermediate Reynolds number ranges.

4.2.4 Drift Flux

The drift flux theory is widely used to analyze the flow characterization in solid-liquid and gas-liquid systems [Pal and Masliyah, 1989; Dobby et al., 1988; Wallis, 1969]. For a flotation column, the drift flux for a gas-liquid system, $J_{\rm gl}$, can be defined as:

$$J_{gl} = (1 - \varepsilon_g)J_g \pm \varepsilon_g J_l \qquad (4-17)$$

where + refers to counter-current and to co-current two phase flow.

Because $J_g = \epsilon_g U_{ba}$, $J_l = (1 - \epsilon_g) U_l$, the drift-flux can also be expressed as (from Eq. 4-10):

$$J_{gl} = \varepsilon_g (1 - \varepsilon_g)(U_{ba} \pm U_l)$$

$$= \varepsilon_g (1 - \varepsilon_g)U_{gl}$$
(4-18)

This equation shows that the drift flux is proportional to the slip velocity.

For solid-liquid systems, Richardson and Zaki [1954] experimentally established the relationship between slip velocity and single particle terminal settling velocity, U_{sl} , as follows:

$$U_{sl} = U_T (1 - \varepsilon_s)^{m-1}$$
 (4-19)

This idea has also been applied to gas-liquid systems [Dobby et al. 1988]. Therefore,

$$U_{g1} = U_T (1 - \varepsilon_g)^{m-1}$$
 (4-19')

By combining Eq. (4-19') with Eq. (4-18), a familiar empirical relationship is obtained as

$$J_{g1}/U_T = \varepsilon_g (1 - \varepsilon_g)^{m} \tag{4-20}$$

where U_T is the terminal velocity of a single sphere moving in an infinite stationary liquid, m is an exponent which differs for various studies in gas-liquid system [Pal and Masliyah, 1989; Wallis, 1969], ranging from 0 to 3. According to Pal and Masliyah [1989], the main reason for this appears to be the fact that most experimental studies reported in the literature are restricted to low values of gas holdups. As at low ε_g , $1 - \varepsilon_g \approx 1$, the drift-flux given by Eq. (4-20) becomes insensitive to the value of m. They tested the flow characterization of a flotation column and concluded that the Richardson-Zaki correlation at Re_b > 500 (m = 2.39 in Eq. 4-20) was suited to both the bubbly and the froth zones.

The second reason for this wide range of m may be attributed to the unsuitable assumption that bubbles behave like solid spheres at the intermediate Reynolds number ranges. If bubbles behave like solid spheres, m should be a function of the bubble Reynolds number, as indicated earlier. For most column flotation systems, bubble diameters lie in the ranges of 0.05 - 0.2 cm, which corresponds to $1 << Re_b < 500$. Consequently, Eqs. (4-13) and (4-14) should apply, and m should be a variable, instead of a constant, in the range of 2.39 - 4.45.

Another reason for this wide range of m may result from the inadequate estimation of bubble terminal velocity. Unlike the motion of solid spheres, the ascent of bubbles is significantly influenced by the surface-active materials present in the liquid. Different empirical expressions for bubble velocities are employed in drift-flux analysis. Wallis [1969] used Peebles and Garber's equation [1953], Pal and Masliyah [1989] adopted the empirical expression of Clift et al [1978] to estimate bubble terminal velocity. However, from the discussions in Chapters 2 and 3, it has been shown that Clift's expression cannot explain the effect of different surfactants on bubble rise velocity, and the surface tension

alone cannot be used as a criterion to determine different surfactants at varied dosages on bubble motion. If a suitable expression for bubble terminal velocity is not obtained, the deviation will certainly arise.

4.2.5 Model Development

4.2.5.1 Average Bubble Rise Velocity in a Swarm in Flotation Columns

It can be concluded from the above discussion that Marrucci's expression, Equation (4-9), is expected to give the most suitable description of bubble motion in flotation systems, because it considers the differences between bubbles and solid spheres, and the applicable Reynolds number ranges for flotation-sized bubbles. For practical purposes, it is not necessary to keep the strict conditions mentioned by Marrucci to verify the equation (4-9). The reason is that for a given gas flowrate, there would be a corresponding average bubble size, gas holdup and U_{bd}. All of these parameters can be measured, therefore the bubble drift velocity can be verified experimentally.

However, there are some drawbacks in Equation (4-9). First of all, Levich's expression is used to predict the single bubble rise velocity, U_{bo}, which does not consider the effect of the virtual liquid film and surface-active reagents on bubble motion, as discussed in the previous chapters. In order to take these factors into consideration, a model established in Chapter 2 can be incorporated into Eq.(4-9). The expression is given as:

$$U_{bs} = \frac{A[(1+3.36C_cR_v^2)^{1/2} - 1]^2}{(2C_cR_v)^2}$$
 (2-26)

Secondly, the definition for the gas holdup used by Marrucci when deriving Eq. (4-9) may be inadequate in actual situations. The arrangement of bubbles in a swarm should be, for the most commonly encountered cases, in the cubic, hexagonal and other compacted arrangements. Considering the gas holdup correlation and substituting Eq. (2-26) into Eq. (4-9) lead to an equation for the bubble drift velocity in a swarm:

$$U_{bd} = U_{bs} \frac{(1-k_g \varepsilon_g)^2}{1 - (k_g \varepsilon_g)^{5/3}}$$
(4-21)

where k_g is a gas holdup correlation related to Marrucci's assumption, which depends on the bubble arrangement in a swarm and gas holdup.

Therefore, by substituting Eq. (4-21) into Eq.(4-1), another expression for the actual average bubble rise velocity in a swarm can be written as:

$$U_{ba} = J_g + \left\{ \frac{A[(1+3.36C_cR_v^2)^{0.5}-1]^2}{(2C_cR_v)^2} \right\} \frac{(1-k_g\varepsilon_g)^2}{1 - (k_g\varepsilon_g)^{5/3}} - J_1$$
 (4-22)

Eq. (4-22) relates the average bubble rise velocity in a swarm to I_g , I_l , bubble size, gas holdup and contamination factor. A comparison of bubble velocities predicted from Eq. (4-22) with those from Eq. (4-6) is shown in Table 4-1, based on the literature data from Dobby et al. [1988] and Yianatos et al. [1988]. It was found that for the bubble systems used by Dobby et al. and Yianatos et al., a gas holdup correlation k_g of 0.7 gives reasonable estimation of bubble rise velocity for gas holdup less than 30%, while using the contamination factors previously determined in Chapter 3 for single bubble system. The deviation at the higher gas flowrates may be attributed to the different bubble arrangement at higher gas holdups, in which case the value of k_g may change and can only be determined experimentally.

Fig. 4-2 presents the simulated results from Eq. (4-21) ($k_g = 0.7$) for the comparison of single bubble rise velocity with the motion of bubbles at the different gas holdups. It can be seen that gas holdup has a great effect on bubble drift velocity, almost 35% lower in the case of 30% gas holdup than in single bubble system. This decrease in bubble velocity will contribute to the changes in particle-bubble collision, bubble retention time and flotation rate.

Figure 4-2 also shows that for gas holdups less than 30%, the bubble drift velocity can be simplified as:

$$U_{bd} = U_{bs} (1 - 1.06\epsilon_g)$$
 (4-23)

Table 4-1. Comparison of bubble rise velocity from Eq.(4-6) and Eq.(4-22) (Data from Dobby et al.[1988] and Yianatos et al.[1988])

Frothers	ppm	J _g (cm/s)	J_1	d _o (mm)	ε _g (%)	C _c	Bubble velocity (cm/s)	
			(cm/s)				measured	predicted(Eq.4-22)
Dowfrot	h							
250	15	0.5	1.0	0.61	12.3	247.24	4.07	4.08
	15	0.8	1.0	0.67	17.0	247.24	4.71	4.63
	15	1.0	1.0	0.70	20.0	247.24	5.00	4.94
	15	1.2	1.0	0.74	23.4	247.24	5.13	5.30
	15	1.5	1.0	0.81	28.0	247.24	5.36	5.92
	15	1.8	1.0	0.88	32.0	247.24	5.63	6.51
	5	1.0	0.91	1.20	9.5	200.22	10.53	12.09
	10	1.0	0.85	0.86	12.9	228.45	7.75	7.48
	15	1.0	0.82	0.77	15.8	247.24	6.33	6.13
	20	1.0	0.85	0.69	15.5	261.37	6.45	5.20
	25	1.0	0.77	0.73	16.2	272.65	6.17	5.56
	10	2.1	0.30	1.51	15.7	228.45	13.38	15.02
	15	1.5	0.30	1.13	14.0	247.24	10.71	10.82
MIBC	20	1.0	0.90	0.78	13.2	161.35	7.58	7.20
	30	1.9	0.90	0.75	13.3	183.08	7.52	6.58
	45	1.0	0.91	0.80	13.6	211.51	7.35	6.87
	60	1.0	0.91	0.73	15.3	235.62	2. 6.54	5.74

Fig. 4-3 presents the simulated results from Eq.(4-22) for the contamination factor effect on bubble rise velocity. It indicates that at the gas holdup ranges used in column flotation, the effect of contamination factor on bubble rise velocity is significant, with higher contamination factor slowing bubble ascent more profoundly.

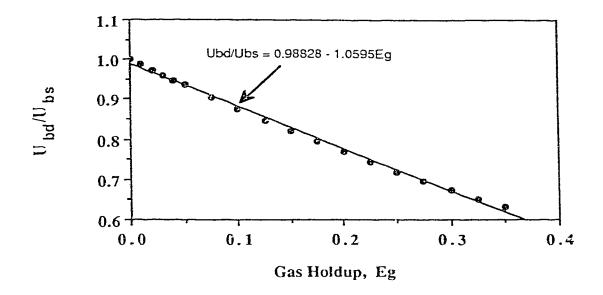


Figure 4-2 Comparison of single bubble rise velocity with the motion of bubbles at different gas holdups

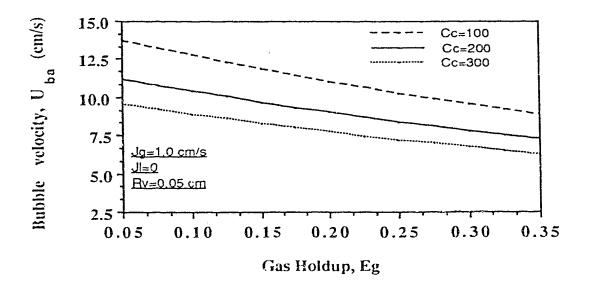


Figure 4-3 Effect of contamination factors on bubble rise velocity

4.2.5.2 A Drift-flux Model for Gas-liquid Systems at Subcritical Reynolds Numbers

The drift-flux analysis employed by the previous workers for gas-liquid systems was entirely adopted from the method for the solid-liquid system. Because the motion of air bubbles is sensitive to the surfactants present in the liquid, and is not identical to that of solid spheres at the subcritical Reynolds number ranges, it can be reasonably concluded that the drift flux should also be different. Based on Nicklin's idea and Marrucci's expression, a theoretical model for the drift-flux in a counter-current flotation column can be derived. From Eqs. (4-1) and (4-6), we have

$$J_g/\varepsilon_g = J_g + U_{bd} - J_l \tag{4-24}$$

or

$$J_g(1 - \varepsilon_g) - \varepsilon_g J_1 = \varepsilon_g U_{bd}$$

According to Eqs. (4-9) and (4-17), the above equation can be written as (let $\varepsilon_{gm} = \varepsilon_g$):

$$J_{gl} = \epsilon_g U_{bd}$$

$$= \frac{U_{bo} \, \varepsilon_{g} \, (1 - \varepsilon_{g})^{2}}{1 - \varepsilon_{g}^{5/3}} \tag{4-25}$$

Therefore,

$$J_{gl}/U_{bo} = \frac{\varepsilon_g (1 - \varepsilon_g)^2}{1 - \varepsilon_e^{5/3}}$$
 (4-26)

Comparing this equation with Eq. (4-20), the difference in the drift-flux expressions between solid-liquid system and gas-liquid system can be clearly shown. Figure 4-4 presents the changes in the ratio of the drift-flux to terminal velocity between gas-liquid phase (Eq. 4-26) and solid -liquid phase (Eq. 4-20), with the void fraction of the dispersed phase.

It can be seen from this figure that the drift-flux of gas-liquid system is larger than that of solid-liquid system at the same void fraction, especially at gas holdup above 10%. This indicates that using the solid-liquid drift flux model (Eq. 4-20) to predict the drift-flux in

gas-liquid systems will underestimate the void fraction effect on the ratio of drift-flux to the terminal bubble rise velocity.

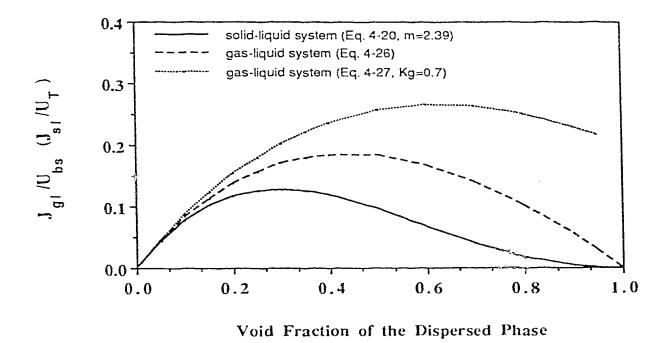


Figure 4-4 Comparison of the void fraction effect on drift-flux in gas-liquid and solid-liquid systems

In considering the surfactant effects on bubble rise velocity and gas holdup (as discussed earlier), a correlated expression for the drift flux in gas-liquid systems can be written as:

$$J_{g1}/U_{bs} = \frac{\varepsilon_g (1 - k_g \varepsilon_g)^2}{1 - (k_g \varepsilon_g)^{5/3}}$$
(4-27)

Therefore, instead of determining an exponent parameter m in solid-liquid systems, as shown in Eq. (4-20), both the contamination factor C_c and the gas holdup correlation k_g in gas-liquid systems should be determined. The gas holdup effect, in the presence of surfactants, on the ratio of the drift-flux to bubble terminal velocity (Eq. 4-27) (where k_g =

0.7) is also presented in Figure 4-4. It shows that the ratio increases much faster with the holdup in gas-liquid systems than in solid-liquid systems.

4.3 EXPERIMENTAL

A laboratory Plexiglas flotation column with the inside diameter of 6.35 cm and the height of 366 cm was used for all the measurement in this study. A given dosage of frothers was added into, and mixed with 200 liters of tap water in a conditioning tank for about 10 minutes. The solution was then pumped into the column and the flowrate was controlled by a magnetic flow meter. The liquid level in the column was kept at about 220 cm from the sparger in the absence of gas flow. The gas was introduced at the bottom of the column and the flowrate was adjusted by a rotameter. A stainless steel porous tube sparger was used to generate bubbles. Figure 4-5 shows the schematic diagram of the apparatus used.

Water manometers were used to measure the gas holdup. In order to clearly show the changes in gas holdup caused by different operating variables, e.g., the addition of different frother dosages, the superficial gas and liquid velocities, the overall gas holdups, i.e., the expansion of the whole bed, instead of the local ones, were determined. For each operating condition at least three measurements were made, and then the average value of gas holdup for that point was obtained. In the case of high gas flowrate, the liquid level in the manometer tube was fluctuating, so the water head measured was kept at a deviation of ± 1.5 cm. Two of the most commonly used frothers in flotation, MIBC and Dowfroth 250, were tested under different concentrations.

The bubble size was determined by photographic technique. Detailed descriptions are presented later in Chapter 5.

The rise velocities of bubbles at the different frother concentrations were estimated from Eq. (4-22). The contamination factors determined in Chapter 3 are used for this study, i.e.,

For pine oil solution:

$$C_c = 110 + 285[1 - \exp(-0.59C^{0.5})]$$
 (C \le 3 \cc/100 L) (3-8)

For Dowfroth 250 solution:

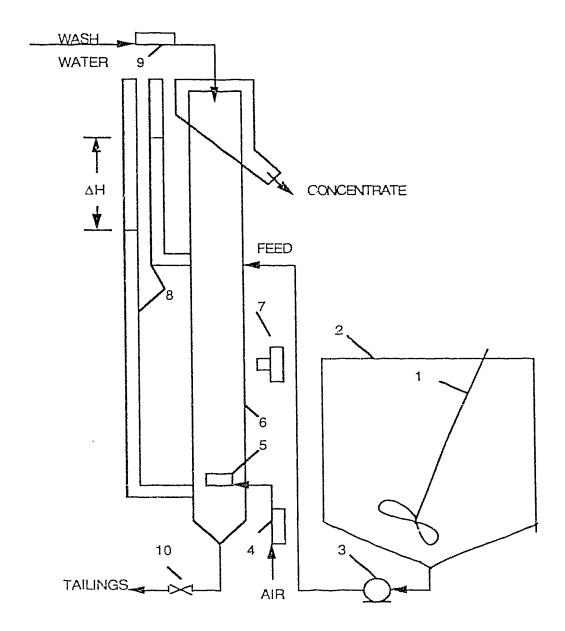


Figure 4-5 Schematic diagram of a flotation column used in this study

1 - stirrer; 2 - conditioning tank; 3 - feed pump; 4 - air rotameter; 5 - sparger; 6 - column; 7 - camera; 8 - water manometer; 9 - water rotameter; 10 - tailings adjusting valve.

$$C_c = 110 + 280[1 - \exp(-0.55C^{0.5})]$$
 (C \le 3 \cc/100 L) (3-9)

For MIBC solution:

$$C_c = 110 + 260[1 - \exp(-0.11C)]$$
 (C \le 6 \cc/100 L) (3-10)

4.4 RESULTS AND DISCUSSION

4.4.1 Frother Addition Effect

Because Eqs.(4-1) and (4-6) provide very convenient and simple methods to test the frother effect on bubble rise velocity, most of the measurements in this study were intended to be done by these two techniques. However, it was found in the measurement that the Nicklin's method (Eq. 4-1) can only be effectively used for the cases without frother additions. Fig. 4-6 clearly shows that Nicklin's method cannot be satisfactorily used to measure the bubble drift velocity in the presence of frothers, because there is significant deviation in bubble velocities measured between the two methods indicated in Eqs.(4-1) and (4-6).

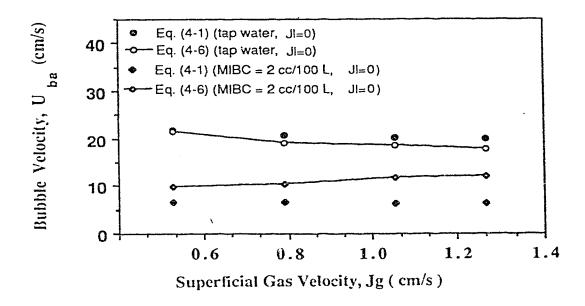


Figure 4-6 Effect of frother addition on the estimation of bubble rise velocity

One of the possible reasons for this phenomenon may be attributable to the fact that in the absence of frothers, there is almost no difference for the phenomenon of bubble coalescence before and after shutting off the gas. When frothers are added, this difference does occur, because at that moment when gas is shut off, the gas velocity passing through the pores on the sparger decreases, therefore, the chance for bubble coalescence reduces, thus generating smaller bubbles. In this case it is almost impossible to determine whether the liquid level in the tube has been completely returned to the static state. In addition, heavy foam was formed on the top level of the liquid. The foam does not collapse even when the liquid level returns to the static state after shutting off the gas supply. Thus, it will also be difficult to use the gas disengagement technique to measure the declining velocity of the top liquid level. Therefore, the two methods indicated in Eqs. (4-6) and (4-22) were used for estimating the bubble rise velocity in a swarm, as shown in Fig. 4-7. It is observed that Eq. (4-22) coincides with Eq.(4-6) quite well.

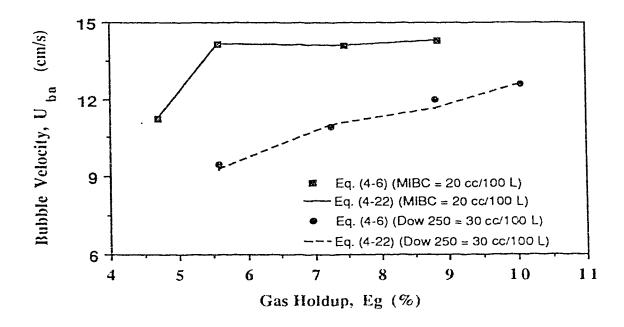


Figure 4-7 Comparison of the predicted and measured bubble rise velocity

4.4.2 Superficial Gas Velocity Effect

Fig. 4-8 shows the average bubble rise velocities under different gas flowrates. It is interesting to note that the bubble rise velocity in the absence of frothers decreases with the gas flowrate, which agrees with Nicklin's measurements. Nicklin attributed this decrease in bubble velocity to the increase of gas holdup in the column. However, Fig. 4-8 also shows that when frothers were added into water, bubble rise velocity either decreases or increases with the gas flowrate, depending on the frother concentration and type. The data of Dobby et al. and Yianatos et al also showed opposite trends of bubble rise velocity from Nicklin's, as indicated in Table 4-1.

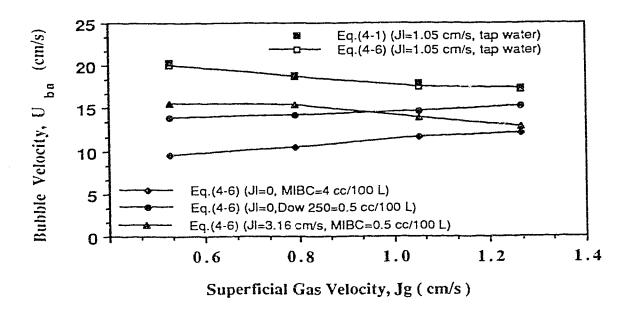


Figure 4-8 Effect of superficial gas velocity on bubble rise velocity

The reasons for this can be explained by Eq. (4-22) and Fig. 1-1. From this equation, we know that if other conditions are fixed, bubble rise velocity is dependent on both gas holdup and bubble size. Increasing gas flowrate will increase both parameters. Therefore, whether the bubble rise velocities increase or decrease depend on the relative incremental ratio of bubble size, or individual bubble rise velocity, and gas holdup. One of the reasons for the increase of bubble size with the gas flowrate is related to the coalescence of bubbles, which depends on the resistance of thin liquid film between bubbles to rupture. The ability

to resist the rupture and coalescence of bubbles is stronger in the presence of frothers than in the absence of frothers. Therefore, the critical gas flowrate value for bubble coalescence is much smaller for the liquid without surfactants than in the presence of surfactants. For a certain gas flowrate range used in this experiment, bubbles formed are much bigger in the absence of frothers, due to the coalescence of bubbles. Measurement has shown that, with $J_1 = 3.16$ cm/s, the bubble diameters are 0.43 cm and 0.36 cm (the change of bubble size is about 16%), under the gas flowrates of 1.264 cm/s and 0.79 cm/s, respectively, which gives gas holdups of 8.594 and 4.839% (the change of gas holdup is 77.6%), respectively. For bubbles in the size ranges of 0.2 - 1.0 cm in diameter, according to Fig. 1-1, there is almost no difference in bubble rise velocity. This implies that the increase of gas holdup is mainly attributed to the increase of the number and the size of bubbles in the column at higher gas flowrate. Therefore, bubble rise velocity decreases with the increase of gas flowrate. While in the case of adding a frother, it has been experimentally determined [Dobby and Finch, 1986; Xu and Finch, 1989] that bubble diameter is proportional to $J_g^{0.25}$, and individual bubble rise velocity is proportional to d_b^2 (Fig. 1-1), which may contribute to the different phenomena observed.

4.4.3 Superficial Liquid Velocity Effect

Figure 4-9 and Table 4-2 show the effect of superficial liquid velocity on bubble ascent.

Table 4-2. Effect of superficial liquid velocity on bubble motion

		J_{l}	Bubble	ε _g (%)	Cc	Bubble	Velocity (cn√s)
Frother	ppm	(cm/s)	Diameter (cm)	(%)		Measured	Predicted (Eq.4-22)
MIBC	20	0.0	0.122	7.47	161.35	14.10	14.86
MIBC	20	2.11	0.106	10.12	161.35	10.41	10.20

Note: $J_g = 1.053$ cm/s

Both of these results show that increasing the superficial liquid velocity reduces the actual average bubble rise velocity, as expected. This reduction in bubble velocity may be due to

the following factors: (1), reducing the average bubble size due to the dynamic pressure exerted on the bubbles by moving liquid. As indicated in Table 4-2, bubble diameter reduced to 0.106 cm ($J_1 = 2.11$ cm/s) from 0.122 cm ($J_1 = 0$); (2), slowing the individual bubble motion and increasing the gas holdup by increasing the bubble retention time and the total number of bubbles in the column. It can be seen from Table 4-2 that the gas holdup increases from 7.47% ($J_1 = 0$) to 10.12% ($J_1 = 2.11$ cm/s). Therefore, from Eq.(4-22), the bubble rise velocity can be expected to decrease with an increase in J_1 . Table 4-2 also shows that the prediction from Eq.(4-22) agrees well with the measurement.

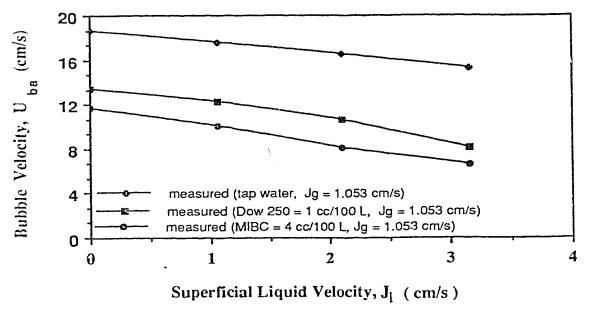


Figure 4-9 Effect of superficial liquid velocity on bubble rise velocity

4.4.4 Contamination Factor Effect

The effect of frothers on bubbles are multi-fold. Besides reducing the bubble size by lowering the air-water interfacial tension, preventing bubble coalescence and increasing the gas dispersion, which, of course, decreases the bubble rise velocity, the adsorption of frother molecules on the bubble surface also increases contamination factors, which retard the motion of bubbles. Therefore, in column flotation, at least two main parameters, bubble size and contamination factor, contribute to the reduction of bubble rise velocity and the increase of gas holdup. For a single bubble system, it is easy to quantitatively distinguish the bubble size effect from the contamination factor effect on bubble motion, as treated in

distinction, because the gas holdups also contribute to the reduction of the bubble rise velocity. In this study, different frothers were used to explain the effect of contamination factors on gas holdup and bubble rise velocity, by generating almost the same size of bubbles or gas holdups for different frother systems. Table 4-3 shows the comparison of measured and predicted bubble rise velocity with MIBC and Dowfroth 250 frothers.

Table 4-3. Comparison of bubble rise velocities for different frothers

Fuethore		J _g	bubble	ε _g (%)	C_c	Bubbl	e Velocity (cn/s)
Frothers	ppm	(cm/s)	diameter (cm)	(%)		measured	predicted (Eq. 4-22)
Dowfroth 250	30	0.527	0.100	5.58	282.00	9.44	9.39
MIBC	20	0.527	0.103	4.69	161.35	11.24	12.19
MIBC	40	0.527	0.086	5.53	202.55	9.53	8.95

Note: $J_1 = 0$

It can be seen from Table 4-3 that Dowfroth 250 solution (30 ppm) gave bigger bubbles than MIBC solution at concentration of 40 ppm, which indicates that lower gas holdup should be expected for Dowfroth 250 solution, if the contamination factor did not have any effect on bubbles. But the measurement did show that Dowfroth 250 solution gave a little bit higher gas holdup. This can only be explained by the effect of different frother molecular structure, or contamination factor, on bubbles. Dowfroth 250 has higher contamination factor, in this case $C_c = 282$, than MIBC solution, ($C_c = 202.55$). Therefore, Eq.(4-22) applies, and the average bubble rise velocity depends on the bubble size, contamination factor and gas holdup, if the gas and liquid flowrate are kept the same. For the same reason, even if Dowfroth 250 solution gave the same bubble size as MIBC solution, the gas holdups and bubble rise velocities for the two systems would be different, depending on the values of the contamination factor. In the case shown in Table 4-3, for almost the same bubble diameter (0.1 cm), Dowfroth 250 solution (30 ppm) gave lower rise velocities, and thus a longer retention time and higher gas holdup than MIBC solution

(20 ppm), due to the fact that Dowfroth 250 solution (30 ppm) has a higher contamination factor ($C_c = 282$) than MIBC solution ($C_c = 161.35$).

4.5 SUMMARY OF CHAPTER

- (1). Based on Marrucci's equation and Nicklin's idea, a model has been developed in bubble swarm systems to relate average bubble rise velocity to bubble size, gas holdup, contamination factor, superficial gas and liquid velocities, and found to agree well with literature data and experimental measurements.
- (2). A drift-flux model for gas-liquid systems at subcritical Reynolds numbers is derived, which shows that the void fraction effect is less than that in solid-liquid system, especially at higher holdup ranges.
- (3). Nicklin's method can only be effectively used to measure bubble rise velocities in the absence of surfactants.
- (4). Without frother addition, the average bubble rise velocity decreases with increasing gas flowrate; while adding a frother into water, the bubble velocities either increase or decrease with gas flowrate, depending on frother type and concentration.
- (5). Three functions of superficial liquid velocities on bubbles can be recognized in the presence of surfactants: (a) reducing bubble size by exerting a dynamic pressure on the bubble; (b) minimizing the bubble coalescence by driving liquid between the bubbles to prevent fast liquid drainage between them; and (c) decreasing the individual bubble rise velocity;
- (6). Contamination factors contribute to the reduction of bubble rise velocity and to the increase of gas holdup in the column. If other conditions are fixed, higher gas holdups in the column do not necessarily mean that smaller bubbles are produced for different frothers used, due to the effect of contamination factors on bubble.
- (7). For gas holdup less than 30%, a gas holdup coefficient, k_g , of 0.7 gives reasonable prediction of bubble rise velocity by Eq.(4-22).

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5.1 INTRODUCTION

The importance of bubble size in improving flotation efficiency has long been recognized and confirmed by various investigations [Finch and Dobby, 1990; Yoon and Luttrel, 1989; Miller and Ye, 1987; Yoon and Luttrell, 1986; Dobby and Finch, 1986; Ahmed and Jameson 1985; Dobby, 1984]. A number of methods have been described for determining the sizes of bubbles in two- and three-phase systems. These include: photographic techniques [Miller, 1985], electroresistivity measurements [Yasumishi et al., 1986], gas holdup and pressure measurements [Dobby and Finch, 1987], dynamic bubble-disengagement technique [Standish et al., 1991], and calculations using empirical or semi-empirical correlations etc. [Tsuge et al., 1981; Sada et al., 1978]. Among these methods, the photographic technique is the most common and reliable method used to measure the bubble size in a column. But it is tedious and restricted to vessels with transparent walls and relatively low bubble concentrations. Therefore, in an operating column, it is almost impossible to measure bubble sizes by the photographic technique, and other methods have to be employed. From a practical point of view, estimation of bubble size through the use of well-established models will be the most feasible and the simplest.

In this chapter the commonly used techniques and models for estimating average bubble size in a swarm will be reviewed. Based on the investigation in the previous chapters, a simple method is described, which employs the relationship between the average bubble rise velocity, the bubble drift velocity and the contamination factor. Comparisons with the photographically measured mean bubble size and literature data are made to confirm the feasibility of the proposed method.

5. 2 PREVIOUS WORK

In general bubbles produced by a sparger submerged in water are mainly influenced by the following parameters: the size and the number of pores on the sparger from which bubbles are generated; gas and liquid flowrate; hydrodynamic head, surface tension of the air-liquid interface, etc.[Jackson, 1964; O'Connor et al.,1990]. Thus, one of the commonly used methods to predict bubble size is related to the formation of bubbles at the orifice, which

should be a function of the pore size and gas flowrate on the sparger [Geary and Rice, 1991; Xu and Finch, 1989; Bowonder and Kumar, 1970]. On the other hand, the nature of bubbles affects the bubble ascent and the gas holdup in the column. Therefore, another method which can be used to estimate bubble size is to establish the relationship between bubble motion, bubble size and gas holdup [Dobby et al, 1988; Yianatos et al, 1988].

5.2.1 Models Based on Force Balance on a Forming Bubble

Davidson and coworkers [1960] pioneered the technique to predict the sizes of bubbles formed from a single orifice in viscous flow by the force balance method. Bowonder and Kumar [1970] extended this technique to multi-orifice and porous sparger. Recently, Geary and Rice [1991] proposed a model to predict bubble size for rigid and flexible spargers. However, the expressions obtained for bubbly column systems were very complicated.

Generally, the models derived using this technique are based on the following fundamental equations:

(1) force balance on a bubble for the initial bubble forming stage (where $\rho_G << \rho_L$)

$$V_b \rho_L g + G^2 \rho_G / (\pi r_H^2) - 2\pi \sigma r_H \cos \theta - F_{db}$$
 bouyancy gas momentum surface tension drag

$$= \frac{d(\alpha P_L V_b U_{bs})}{dt}$$
inertia
(5-1)

where V_b is the bubble volume in cm³ at time t, G is the gas flowrate per hole, r_H is the hole radius in cm, θ is the contact angle, α is the virtual mass coefficient.

(2) mass balance on the bubble for the second stage (bubble growth), under the usual circumstance of constant gas flow used in column flotation

$$dV_b/dt = G \quad \text{or} \quad V_b = V_{bo} + Gt \tag{5-2}$$

where the initial state is taken to be V_{bo} at t = 0.

(3) convert the bubble size produced in a single nozzle into a porous sparger according to the following expressions:

$$N_{h} = \frac{A_{s}[3V_{F}/(4\pi)]^{-2/3}}{2*30.5}$$
 (5-3)

and

$$G = Q_{\underline{u}}/N_{h} \tag{5-4}$$

where A_s is the area of the sparger used, V_F is the final volume of the bubble, N_h is the number of effective holes on the sparger.

If V_F can be explicitly expressed in terms of G, one can then directly obtain the value of N_h by using Eq. (5-3). If V_F is an implicit function of G, as is the actual case, iterative methods must be used for evaluation of N_h , that is, until the assumed N_h in Eq. (5-4) and calculated N_h in Eq. (5-3) are equal.

However, one of the important parameters in this technique is that the hole size has to be known. It is usually assumed that the properties of the holes are the same, and evenly distributed on the sparger. While for the porous spargers used in indexing, it would be difficult to know the actual average pore size on the sparger due to the surface corrosion, and the active number of pores under the different operating conditions because of the different pore sizes on the sparger. Futhermore, external spargers are now widely used in flotation columns, in which case, bubbles produced are not related to the pores. Hence, estimation of bubble size according to the bubble flow characterization is more practical.

5.2.2 Models Based on Bubble Flow Characterization

Dobby et al.[1988] proposed a method to calculate average bubble diameter in a flotation column from holdup phase velocity data. By using the drift flux relationship of Richardson and Zaki [1954], bubble terminal rise velocity is first determined as

$$U_{T} = \frac{J_{g}}{[\epsilon_{g}(1 - \epsilon_{g})]^{m}} + \frac{J_{g} + J_{l}}{(1 - \epsilon_{g})^{m}}$$
(5-5)

in which m is a function of bubble Reynolds number, Reb:

$$m = (4.45 + 18d_b/d_c)Re_b^{-0.1} 1 < Re_b < 200 (4-14)$$

$$m = 4.45 Re_b^{-0.1}$$
 $200 < Re_b < 500$ (4-15)

and,

$$Re_b = d_b U_T \rho_L / \mu \tag{4-18}$$

Using the drag coefficient, Cd, determined by Schiller and Naumann [1933],

$$C_d = 24(1 + 0.15Re_b^{0.687})/Re_b$$
 (Re_b < 800) (5-6)

Substituting Eq. (5-6) into Eq. (3-3), and replacing Reb by Rebs, the average bubble d ameter in a bubble swarm can be expressed by

$$d_b = [18\mu U_T(1+0.15Re_{bs}^{0.687})/(g\Delta\rho)]^{0.5}$$
 (5-7)

Where

$$Rc_{bs} = d_b U_{gl} P_L (1 - \varepsilon_g) / \mu$$
 (4-13)

and

$$U_{el} = U_T(1 - \varepsilon_g)^{m-1}$$
 (4-19)

By iterating on m and combining the above equations, db can be finally determined.

Yianatos et al. [1988] used the slip velocity r, l er than the terminal bubble velocity to give a direct estimation of bubble diameter d_b . In a gas-liquid system such as a countercurrent flotation column, the slip velocity, U_{gl} , is defined as the mean relative velocity of both phases, i.e.,

$$U_{gl} = J_g/\varepsilon_g + J_V(1-\varepsilon_g)$$
 (4-12)

By adapting Masliyah's expression for hindered settling velocity of spherical particles in a multispecies system [1979], the slip velocity can be estimated from the following expression

$$U_{g1} = \frac{gd_b^2 f(\varepsilon_L) \varepsilon_L(-\rho_L)}{18\mu(1 + 0.15 Re_b^{0.687})}$$
(5-8)

where ε_L is the liquid holdup in the column, and

$$f(\mathcal{E}_{L}) = \mathcal{E}_{L}^{m\cdot 2} \tag{5-9}$$

The solution for d_b is determined by repeated substitution of estimates of d_b in Eq. (5-8) until the calculated U_{g1} equals the measured U_{g1} .

Both methods, which is volve iterating and repeated back calculations, have been claimed to be quite reasonable to predict bubble size in a swarm for the size range of less than 0.2 cm, with deviation within 15%, as compared to the photographic technique. The methods were also extended to the solid-liquid-gas three phase systems to simulate the real case in flotation and to explore theoretically the effect of solids on bubble rise velocity and gas holdup.

However, Kuehn Walker et al.[1991] recently reported that the calculated mean bubble size by the above methods was 100% to 200% larger than that measured by using a Reynolds bubble measurement cell. The reasons for this may be attributed to the facts that (1) the narrower entry port (7 mm) through which bubbles enter the measurement cell may not be able to guarantee that bigger bubbles have the same probabilities to be captured as smaller ones, thus, the measured bubble size is smaller than the calculated; (2) a big column with diameter of 91.4 cm was used for the bubble diameter measurements, in which case, radial effects on bubbles have to be considered. Smaller bubbles will be near the wall and larger bubbles in the central area above the sparger. Therefore, for a large column, bubbles at the different radial distances from the center would have to be measured to obtain a representative average bubble size in the column. However from their measurements, it seems that only the bubbles at a given dist, and near the value are sampled, which may be the another reason why a smaller bubble size was obtained.

It is also claimed by Sapnchez-pino and Moys [1991] that the drift-flux methods established by Dobby et al. [1988], Pal and Musliyah [1989] cannot give a suitable estimation of bubble size in co-current downwards flotation columns, such as Jameson cells. One of the main reasons for this is that the previous investigation on bubbly flow is based on the assumption that bubbles behave like solid spheres, and the frother effect on bubbles has not been considered. It has been determined in the early chapters that bubbles behave like solid spheres only at certain frother concentration ranges. Furthermore,

retardation effects on bubble ascent vary for different frothers [Fuerstenau and Wayman, 1958; Hu et al., 1980]. Therefore, it can be expected that, for the same superficial gas velocity, J_g , and liquid velocity, J_l , gas holdups will be different for the various frothers used, even when using the same average bubble size in the column. What this implies is that higher gas holdups do not necessarily mean that smaller bubbles are produced with the different frother systems, as has been verified in chapter 4. It was also shown from the measurements done by Yianatos et al [1988] that under the same J_g (=1.0 cm/s) and J_l (=0.91 cm/s), adding TEB (15 ppm) had a gas holdup of 14.4% and average bubble diameter of 0.085 cm; while adding MIBC (45 ppm) gave a lower gas holdup (13.6%) and a smaller bubble diameter (0.080 cm), which contradicts the generally accepted idea that higher gas holdups give smaller bubbles for the fixed operating conditions. This phenomenon can not be predicted and explained by the existing techniques.

5.3 PROPOSED METHOD

5.3.1 Counter-current Flotation Columns

It has been established in Chapter 4 that the average bubble upward velocity, U_{ba}, in a counter-current flow system, like those in conventional column flotation, can be written as

$$U_{ba} = J_g/\varepsilon_g \tag{4-6}$$

or

$$U_{ba} = U_{bd} + J_g - J_i \tag{4.1}$$

Bubble drift velocity can be determined by

$$U_{bd} = A \frac{[(1+3.36C_cR_v^2)^{0.5}-1]^2}{(2C_cR_v)^2} \frac{(1-k_g\epsilon_g)^2}{1-(k_g\epsilon_g)^{5/3}}$$
(4-22)

For gas holdups less than 30%, $k_g = 0.7$, and equation (4-22) can be simplified as

$$U_{bd} = A \frac{[(1+3.36C_cR_v^2)^{0.5}-1]^2}{(2C_cR_v)^2}$$
 (4-22')

Substituting Eqs. (4-22) and (4-6) into (4-1) gives the bubble radius as

$$R_v = B_c^{0.5}/(0.84 - C_c B_c)$$
 (5-10)

where

$$B_{c} = [J_{g}(1 - \varepsilon_{g})/\varepsilon_{g} + J_{1}]$$

$$= \frac{1 - (k_{g}\varepsilon_{g})^{5/3}}{(5-11)}$$

$$= \frac{1 - (k_{g}\varepsilon_{g})^{5/3}}{(5-11)}$$

O.

$$B_{c} = \frac{J_{g}(1 - \varepsilon_{g})/\varepsilon_{g} + J_{1}}{A(1-1.06\varepsilon_{g})} \qquad (0 \le \varepsilon_{g} \le 30\%)$$

For different frothers used in single bubble systems, it has been determined in Chapter 3 that C_c can be given as

For pine oil solution:

$$C_c = 110 + 285 \exp(-0.59 C^{0.5})$$
 $(0 \le C \le 3 \text{ cc}/100 L)$ (3-8)

For Dowfroth 250 solution:

$$C_c = 110 + 280 \exp(-0.55 C^{0.5})$$
 $(0 \le C \le 3 \text{ cc/100L})$ (3-9)

For MIBC solution:

$$C_1 = 110 + 260 \exp(-0.11C)$$
 $(0 \le C \le 6 \operatorname{cc/1(X)L})$ (3-10)

The gas holdup, superficial liquid and gas velocities can be easily measured, therefore, the bubble size can be conveniently predicted and calculated by a hand calculator.

Table 5-1 shows the comparison of Eq. (5-10) with the measurement data from the literature [Dobby et al.,1988; Yianatos et al.,1988] (where $k_g = 0.7$). It can be observed that the predicted bubble diameters agree with the literature data quite well, with an error

less than 15%, which is about the limit of experimental error [Yianatos et al.,1988]. It can also be noted that the deviation increases with the gas flowrate, this may be attributed to the higher probability of bubble coalescence at higher gas flowrate, while in the theoretical treatment of the study bubble coalescence has not been taken into account. Another reason is that the arrangement of bubbles in a swarm will vary for different gas holdups, which means that k_g has to be experimentally determined for gas holdups larger than 30%.

Table 5-1. Comparison of bubble size estimation with measurement (data from Dobby et al.[1988] and Yianatos et al.[1988])

		J_{g}	J_1	ε _g (%)	C_c	Bubble d	liameter (mm)
Frothers	ppm	(cm/s)	(cm/s)	(%)		Measured	Predicted(Eq.5-10)
Dowfroth							
250	15	0.5	1.0	12.3	247.24	0.62	0.62
	15	0.8	1.0	17.0	247.24	0.67	0.68
	15	1.0	1.0	20.0	247.24	0.70	0.70
	15	1.2	1.0	23.4	247.24	0.74	0.72
	15	1.5	1.0	28.0	247.24	0.81	0.75
	15	1.8	1.0	32.0	247.24	0.88	0.78
	5	1.0	0.91	9.5	200.22	1.20	1.06
	10	1.0	0.85	12.9	228.45	0.86	0.88
	15	1.0	0.82	15.8	247.24	0.77	0.79
	20	1.0	0.85	15.5	261.37	0.69	0.81
	25	1.0	0.77	16.2	272.65	0.73	0.79
	10	2.1	0.30	15.7	228.45	1.50	1.34
	15	1.5	0.30	14.0	247.24	1.13	1.12
MIBC	20	1.0	0.90	13.2	161.35	0.78	0.81
	30	1.0	0.90	13.3	183.08	0.75	0.82
	45	1.0	0.91	13.6	211.51	0.80	0.84
	60	1.0	0.91	15.3	235.62	0.73	0.80

5.3.2 Co-current Downwards Flotation Columns

In the case of a co-current downward flotation column, the bubbly flow can be regarded as the same as the counter-current flow, except that the superficial liquid velocity is larger than the bubble rise velocity, hence bubbles move downwards. Therefore, the following relationship can be used

$$-U_{ba} = J_g + U_{bd} - J_1 (5-12)$$

the minus sign in the equation means that the direction of motion is downward.

Using the same treatment as in counter-current flotation columns, the bubble size can be estimated as

$$R_{v} = B_{d}^{0.5}/(0.84 - C_{c}B_{d})$$
 (5-13)

where

$$B_{d} = [J_{l} - J_{g}(1 - \varepsilon_{g})/\varepsilon_{g}] \frac{1 - (k_{g}\varepsilon_{g})^{5/3}}{A(1 - k_{g}\varepsilon_{g})^{2}}$$
(5-1.4)

Unfortunately, there are no literature data available to verify Eq. (5-13).

5.4 EXPERIMENTAL

As discussed earlier, if bubbles are produced in a big column by a tube sparger, the size of bubbles would be different in the radial direction. For a small column, the bubble size in the column can be regarded as almost the same. Therefore, in order to verify the model, a smaller diameter column can be used. In this study, a Plexiglass flotation column with 6.35 cm inside diameter and a length of 366 cm was employed. All the installation of the apparatus and the gas holdup measurement procedures are the same as discussed in Chapter 4. The effect of two commonly used frothers, MIBC and Dowfroth 250, on bubble sizes were tested.

A photographic technique was employed to measure bubble size. A Nikon camera with micro-lens and Tmax-40() film were used. The light source was provided by two 600-W bulbs. It was found that a good picture can be obtained at a shutter speed of 1/1000 and focus length of 8 to 11. In order to minimize the optical distortion caused by the curved wall of the column, the focused area was kept as small as possible. All the photographs were taken at a fixed height of about 100 cm from the sparger. A calibrated ruler was attached to the column wall and in the field of view of the camera so that the bubble size could be estimated. The photographs were enlarged to 8" x 10", and then measured and counted manually. All the bubbles which could be recognizable on the picture were About 300-900 bubbles were measured at every operating condition, except measured. at very low gas flowrate and frother dosages, in which cases the total number of bubbles shown on the picture was less than 300. The Sauter mean diameter, d₃₂, which is the volume to surface area ratio of bubbles, and considered as the most consistent representation of mean bubble size [Dobby et al., 1988; Yianatos et al., 1988], was used, i.e., $d_{32} = \sum n_i d_v^3 / \sum n_i d_v^2$.

The apparatus used for measuring the bubble size is schematically shown in Fig. 4-5. Fig. 5-1 presents a typical cumulative number passing vs. bubble diameter result from the photographic measurements.

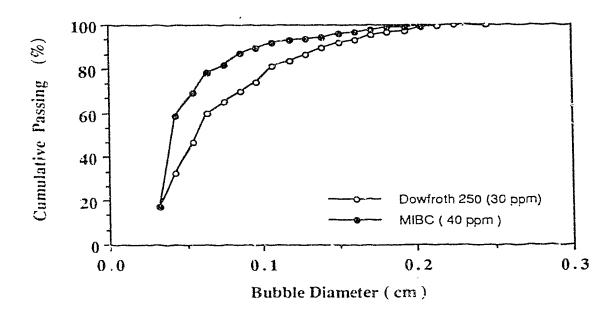


Figure 5-1 Bubble size distribution in a flotation column $(J_g = 1.05 \text{ cm/s}, J_1 = 0)$

5.5 RESULTS AND DISCUSSIONS

5.5.1 Gas Flowrate Effects

Table 5-2 shows the results of hubble size under different gas flowrates. As was expected, bubble diameter increases with the gas flowrate. The relationship between bubble size and gas flowrate for a single bubble system has been theoretically established by Davidson and Schuler [1960] as

For a viscous liquid,

$$d_b = k_1 G^{6.25} \tag{5-15}$$

For an inviscid liquid,

$$d_b = k_2 G^{0.4} (5-16)$$

where k_1 and k_2 are constants. The same relationship as Eq. (5-15) has been experimentally found for bubbles $d_b < 0.1$ cm generated from porous spargers by Dobby and Finch [1986], and Xu and Finch [1989] as

$$d_b = k_3 J_g^{0.25} = k_3 (Q_g/A_s)^{0.25}$$
 (5-17)

The measurement of O'Connor et al.[1990] showed that for bubble diameter larger than 0.2 cm the relationship between bubble size and the gas flowrate can be given as

$$d_b = k_4 J_g^{0.4} (5-18)$$

Comparing these equations, it seems that for bubble swarm systems, if $d_b < 0.1$ cm, bubbles can be regarded as produced in the viscous liquid; if $d_b > 0.2$ cm, bubbles are moving in an inviscid liquid.

In this study the relationship between bubble size and gas flowrate approximately obeys Eq. (5-17).

T		J _g	J _i	ε _g (%)	C _c	Bubbl	e diameter (cm)
Frothers	ppm	(cm/s)	(cm/s)	(70)		Measured	Predicted(Eq.5-19)
Dowfroil	n						
250	30	0.527	0.0	5.58	282.00	0.100	0.100
	30	0.790	0.0	7.24	282.00	0.119	0.118
	30	1.053	0.0	8.80	282.00	0.128	0.132
	30	1.264	0.0	10.05	282.00	0.141	0.141

Table 5-2. Effect of gas flowrate on bubble size

161.35

161.35

0.103

0.125

0.098

0.120

5.5.2 Superficial Liquid Velocity Effect

0.0

0.0

4.69

8.85

Table 5-3 shows the effect of superficial liquid velocity on bubble size. It indicates that bubble size decreases with the increase of J_I. Ghosh and Ulbrecht [1990] have also observed the same trend. One of the reasons may be that bubble coalescence is minimized by forcing liquid into the layers between bubbles, i.e., the same mechanism as the bubbles in the froth zone, in which adding wash water reduces the bubble rupture by providing liquid for the liquid film between bubbles, thus having smaller bubbles. Another reason may be attributed to the increase of the dynamic pressure exerted by the flowing liquid, which changes the force balance of the bubble and affects the bubble size.

The pressure balance inside and outside a rising bubble in counter-current two-phase flow can be written as:

$$P_{I} = P_{E} + P_{DE} \tag{5-19}$$

where

MIBC

20

20

0.527

1.264

$$P_{\rm I} = \frac{NRT}{(4\pi/3)R_{\rm v}^3}$$
 (5-20)

is the bubble internal pressure, in which N is the molar number of gas in the bubble, R is a gas constant, T is Kelvin temperature, R_V is the bubble radius.

$$P_E = P_{atm} - [H_0(1 + \varepsilon_g) - h]P_L g + 2\sigma/R_v$$
 (5-21)

is the bubble external static pressure, in which H₀ is the liquid height from sparger in stagnation, h is the height of the bubble of interest from the sparger, P_{atm} is atmospheric pressure.

$$P_{DE} = k_1 \mu U_{gl} / R_v$$
 (5-22)

is the bubble external dynamic pressure [Anon.,1982, Clift et al.,1978].

Combining (5-19) - (5-22) gives

$$R_{v}^{3}\{P_{atm} + [H_{o}(1+\epsilon_{g}) - h]P_{L}g\} + R_{v}^{2}(k_{l}\mu U_{gl} + 2\sigma) = NRT/(4\pi)$$
 (5-23)

For the constant gas flow condition, which is usually the case for a porous sparger used, the bubble internal pressure is changeable, depending on different operating conditions, i.e., the molar number of gas in the bubble will be different. Therefore, the bubble size will be dependent on the balance of Eq. (5-23).

Table 5-3. Effect of superficial liquid velocity on bubble size

		J _g (cm/s)	J_1	ε _g (%)	Cc	Bubbl	e diameter (cm)
Frothers	ppm	(cm/s)	(cm/s)	(%)		Measured	Predicted (Eq.5-10)
MIBC	20 20	1.053 1.053	0.0 2.106	7.47 10.12	161.35 161.35	0.122 0.106	0.118 0.107

5.5.3 Contamination Factor Effect

Table 5-4 Shows the results of bubble size under different MIBC concentrations. Increasing the frother concentration yields smaller bubbles, as expected. What was unclear is the fact that smaller bubbles were obtained in MIBC solution than in Dowfroth 250 solution (Table 5-5), although Dowfroth 250 solution has lower surface tension than MIBC solution under the same concentrations, which contradicts the results of Klassen and Mokrousov[1963] for single bubble systems, and those of Yianatos et al [1988] for bubble swarm systems. However, the measurements done by Pal and Masliyah [1990, 1989] also showed the same phenomena as observed in this study, with the surfactants having lower surface tension giving bigger bubbles. It was observed in the experimental work that much heavier foam was formed for Dowfroth 250 solution than MIBC for the same concentrations. One of the possible reasons may be attributed to the fact that Dowfroth 250 molecules are more easily carried up to the froth after entering the column, due to the strong frothing capability, thus, fewer molecules than MIBC are kept in the liquid phase. Another reason may be attributed to the different gas flow conditions used. For single bubble systems, as used by Klassen and Mokrousov [1963], gas is usually introduced under a constant pressure condition, in which case the pressure balance for the bubble can be written as

$$P_I = P_{atm} + (H_o - h)P_L g + 2\sigma/R_v$$
 (5-24)

or

$$R_v = 2\sigma/[P_I - P_{atm} - (H_0 - h)\rho_L g]$$
 (5-25)

For the constant pressure condition the bubble internal pressure P_I is constant, thus lower surface tension gives smaller bubbles, as indicated in Eq. (5-25). While for the bubble swarm system, in which case a porous sparger is used, gas passes through the pores on the sparger under the constant flow condition, which means that pressure drop across the sparger, or the bubble internal pressure, varies according to different operating conditions. Whether bubble size increases or decreases depends on the balance of the different variables, such as gas and liquid velocities, contamination factor, gas holdup, and bubble coalescence, etc., as indicated in Eq. (5-23).

The effect of contamination factor on the relationship between bubble size and gas holdup is shown in Table 5-5.

Table 5-4. Effect of frother concentrations on bubble size

		Ĵg (am/a)	J _l	ε _g	C _c	Bubble di	ameter (cm)
Prothers	ppm	(cm/s)	(cm/s)	(%)	-	Measured	Predicted (Eq.5-10)
			<u>, </u>				
MIBC	20	1.053	0.0	7.47	161.35	0.122	0.118
	40	1.053	0.0	9.03	202.55	0.114	0.110

Table 5-5. Effect of contamination factor on bubble size

		Jg	Jį	$\epsilon_{ m g}$	C _c	Bubble	e diameter (cm)
Frothers	ppm	(cm/s)	(cm/s)	(%)	-	Measured	Predicted(Eq.5-10)
Dowfroth	1			· · · · · · · · · · · · · · · · · · ·			
250	30	0.527	0.0	5.58	282.00	0.100	0.100
MIBC	20	0.527	0.0	4.69	161.35	0.103	0.098
Dowfroth	h						
250	30	1.053	0.0	8.80	282.00	0.128	0.132
MIBC	40	1.053	0.0	9.03	202.55	0.114	0.110

With approximately the same bubble diameter of 0.1 cm, Dowfroth 250 solution gives higher gas holdup ($\epsilon_g = 5.58\%$) than MIBC solution ($\epsilon_g = 4.69\%$). The commonly accepted theories and the previous models cannot explain and predict this phenomenon. However, it can be explained by the effect of the contamination factors on bubbles.

Dowfroth 250 solution with the concentration of 30 ppm has a contamination factor of about $C_c = 282.0$, larger than that of MIBC solution ($C_c = 161.35$). This indicates that a much larger retardation effect is exerted by the Dowfroth 250 molecules on bubbles; therefore, the bubble has lower rise velocity in Dowfroth 250 solution than in MIBC solution and a higher gas holdup can be expected for the Dowfroth 250 solution. For the same reason, at a similar gas holdup ($\varepsilon_g = 9\%$), Dowfroth 250 solution should produce bigger bubbles than in MIBC solution, as indicated in Table 5-5.

5.5 SUMMARY OF CHAPTER

- 1. In order to obtain a representative average bubble size in a flotation column, attention should be paid to the fact that in big columns with tube spargers, the size of bubbles produced may be different in the radial direction, with the larger bubbles in the center, and smaller bubbles near the wall.
- 2. A simple method for estimating average bubble size in a flotation column has been proposed, which can account for the effect of different frother type and concentrations on bubbles. A good agreement between the prediction from the established model and the literature data, as well as the data from direct photographic measurement, was obtained.
- 3. Increasing superficial liquid velocity tends to reduce the size of bubbles produced, due to the increase of dynamic pressure on the bubble and the minimization of bubble coalescence by forcing liquid between the layers of bubbles.
- 4. With different frothers, the gas holdup can be different for the same bubble sizes, or a higher gas holdup does not mean that smaller bubbles are produced under the same operating conditions, due to the different frother retardation effects on bubble ascent.

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6.1 INTRODUCTION

The previous chapters have mainly dealt with the bubble flow in gas-liquid two-phase systems. In order to study the actual flow characterization in column flotation of minerals and coal, it is necessary to investigate the interaction between the solid, liquid and gas three-phase system. Unlike the conventional multi-phase flow encountered in chemical engineering, the column flotation system involves the interaction between the different wettabilities of solid particles and bubbles in the presence of various chemical additives, and the valuable mineral (hydrophobic) particles are transported to the froth by attaching to the rising bushles, leaving the hydrophilic particles in the slurry. Therefore, the effects of solids and chemical reagents on the characteristical of both froth zone and collection zone have to be considered. It has been reported that the addition of solid particles to a bubble column may either increase or reduce bubble coalescence and froth stability, depending on the hydrophobicity of particles adhering to the bubbles [Jamialahadi and Muller-steinhagen, 1991; Finch and Dobby, 1990; O'Connor, 1990; Espinosa-Gomez et al, 1988; Dippenaar, 1982, 1978]. However, it seems that only a limited amount of work has been done regarding the effects of chemical additives on the bubble coalescence in (column) flotation systems. While the addition of a collector into a flotation cell enhances the hydrophobicity of the particle surface, thus reducing the induction time and increasing the particle-bubble attachment probabilities, adding a frother reduces the bubble size and the rise velocity, and increases the gas dispersion and gas holdup. All these changes will influence the actual number of particles captured by the rising bubbles, and hence, the flotation rate and recovery. On the other hand, both the structure of collector and frother, and the character of particles captured by the bubbles also affect the stability of the froth and bubbles, which in return, will influence the separation and process control. The objective of this chapter is to experimentally investigate the solid and chemical addition effects on flow characterization in the column flotation of coal.

6.2 EXPERIMENTAL

6.2.1 Description of Samples

In order to test the effects of solid and chemical reagents on column flotation characteristics of coal, about 100 kg of coal were collected directly from the minus 28-mesh stream in the coal cleaning plant at Smoky River Coal Mine, located at Grande Cache, Alberta. The coal is low volatile bituminous coking coal. The minus 28-mesh fraction (about 35% of the total) is cleaned by froth flotation in the plant.

The sample was mixed, split by cone and quartering and then riffled to a size about 5 kg per sub-sample. These sub-samples were bagged and stored. The size distribution of the sample was obtained by a wet sieve analysis. The particle size distribution results and the ash contents for each size fraction are shown in Table 6-1 and Fig. 6-1.

Table 6-1 Particle size distribution and ash analysis

Mesh	Size (µm)	Wt%	Cum.Wt% passing	Ash%	Cum. Ash% retained
35	500	9.94	90.06	7.90	7.90
48	300	27.84	62.22	8.29	8.19
65	212	15.13	47.09	7.89	8.10
100	150	11.60	35.50	8.40	8 16
150	106	9.54	25.96	8.38	8.19
200	75	6.40	19.56	8.80	8.24
-200		19.56		12.76	9.12
total		100.0			9.12

note: all the ash analyses in this study were duplicated, and the duplicated head ash analyses done were 9.11% and 9.06% ash, respectively.

It is observed from Fig. 5-1 that the Cumulative wt% passing, Y, of the coal sample obeys Gaudin-Schuhmann model very well, with the size distribution modulus given as 0.79, i.e.,

$$Y = 100(d_p/577)^{0.79} \quad (\%) \tag{6-1}$$

The weight mean particle size of the coal sample, d_{ap} , can then be estimated as (the integration ranges $0 \le d_p \le 577 \ \mu m$)

$$d_{ap} = (1/100) \int d_p (\partial Y/\partial d_p) \partial d_p$$
$$= (1/100) \int 0.52 d_p 0.79 \partial d_p$$
$$= 255 \ \mu m$$

where $\partial Y/\partial d_p$ denotes the differentiation on particle size.

While flotation columns are mainly superior to the mechanical cells in flotation of fine particles, the sample used for the experiments might be too coarse for testing the flotation efficiency.

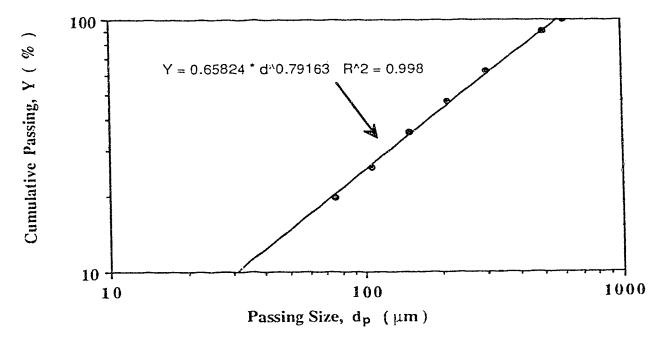


Figure 6-1 Particle size distribution of the coal sample

6.2.2 Experimental Materials and Procedure

A Plexiglas column as described in Chapter 4 was used for all the column flotation tests. A different sparger from the one used in the previous chapters was employed in this study to give higher gas holdups. The reagents used for the tests were kerosene as collector and Dowfroth 250 and MIBC as frothers. In order to use frothers effectively and efficiently, two requirements have to be satisfied, i.e., frothers should be mixed well and completely dispersed in the liquid, and no foam is formed when mixing. Two different methods to add frothers into the column were tested. Method (1) involved adding a frother into the conditioning tank and mixing it with slurry, while method (2) involved injecting the frother into the column with a RUSKA pump, which can give a very accurate injection rate, ranging from 2 to 240 cc/hour. It was observed that with method (1), a heavy foam was formed on the top of the slurry, due to the strong stirring intensity. The injection method by the RUSKA pump was therefore employed in all the column flotation tests.

When using a RUSKA pump to inject the frothers, a given dosage of frother was first mixed with the tap water in a beaker for about 10 minutes by a magnetic stirrer, then the solution was added into the RUSKA pump cylinder with a maximum volume of 1 liter, and the solution was injected out by automatically pushing a piston inside the cylinder. In this method, attention was paid to the following factors:(1) the contamination of the frother solution by the oil, which is used to lubricate the interface between the piston and the cylinder wall. In order to get rid of the oil on the wall before adding frother solution into the cylinder, the cylinder was washed by detergent, and then cleaned by tap water several times until no visible oil contaminants appeared in the water. (2) the maximum solubility of the frothers. For example, if a concentration of 6cc/100 L(or 60 ppm) MIBC and a feed rate of 3L/Min are to be used, the corresponding concentration prepared in the RUSKA pump cylinder would be 54 cc/L (using the injection rate of 200cc/hour). This concentration exceeds the maximum solubility of MIBC in water (17 g/L). In this case, it was observed that the solution was turbid. A lot of MIBC drops were formed in the solution. Measurements for gas-liquid systems have shown that the gas holdup obtained in the presence of 60 ppm MIBC is almost the same as that in 20 ppm MIBC, indicating that the MIBC at 60 ppm was not dissolved in the liquid in the column and the frother molecules were directly carried up to the top level by the rising bubbles. (3) the injected solution should be well mixed with the slurry. In order to ensure good mixing of the frother with the slurry, the frother solution was injected upstream of the feed pump so that the frother and the feed slurry could be mixed by the action of the rotation of the feed pump.

Before running each test, about 3.5 kg of coal sample was mixed with 100 L of tap water in the conditioning tank in the presence of 3 cc kerosene for about 10 minutes. Frother solution was prepared in the RUSKA pump. During the test runs, the feed rate was kept at 3 L/min, wash water rate at 0.5 L/Min, and frother solution injection rate at 200 cc/h. Gas flowrates used were 1.0, 1.5 and 2 L/Min, which correspond to superficial gas velocities of 0.527, 0.79 and 1.053 cm/s, respectively. The static liquid level in the column was controlled by adjusting the tailings flowrate. Feed sample for the flotation test was obtained from the mixing tank for ash analysis. After the first froth overflowed into the overflow launder, about 5 to 10 minutes were allowed for the system to stabilize, and then both the tailing and froth samples were collected continuously for about 3 to 7 minutes at the same time. The gas holdups at that condition were measured. Then the samples were weighed, filtered, dried, and duplicated ash analysis for each sample was done.

6.3. RESULTS AND DISCUSSION

6.3.1 Column Flotation Efficiency

In general, flotation efficiency is evaluated by two parameters: recovery and grade (or yield and clean coal ash% in the case of coal cleaning). Ideally, it is hoped that higher recovery and grade can be achieved at the same time. However, the practical trend is that higher recovery is sacrificed for the grade, or vise visa, thus making the flotation efficiency comparison difficult and complicated.

Recently, the tree analysis method [Nicol et al.,1991; Pratten et al.,1989] was adopted to evaluate coal flotation efficiency by comparing the actual flotation results with the ideal or theoretical response of coal to flotation. This is achieved by the repeated flotation of both froth and tailings products obtained from the previous operation in a mechanical flotation cell, and a final product is obtained if it is less than 2% of the feed. In this way, the ideal cumulative yield-ash curve of coal flotation can be generated.

In this study, the column flotation efficiency under different chemical conditions was evaluated by the tree analysis method. The results are shown in Fig. 6-2. The cumulative yield-ash curve was obtained by repeated flotation of froth and tailing products 24 times in a Lab Wemco flotation cell.

It is observed from Fig. 6-2 that when using the flotation column, the tests using both collector and frother almost reached the limiting separation point which requires 24 repeated flotations in the mechanical cell. This shows how efficient the flotation column is, and it should be expected that if using a flotation column to do the tree analysis, the ideal cumulative yield-ash curve can be obtained more quickly, maybe in less than 10 repeated tests to define the ideal curve.

It can also be seen from Fig. 6-2 that when running column tests, chemicals have pronounced effect on the operation. In order to achieve the same results, more cleaning and recleaning operations should be done in the case of no collector or frother addition than that in the presence of frother and collector. What this implies is that the chemicals play a significant role in accelerating the process to approach the ideal yield-ash curve. This shows that a suitable combination of frother and collectors can give a higher flotation efficiency.

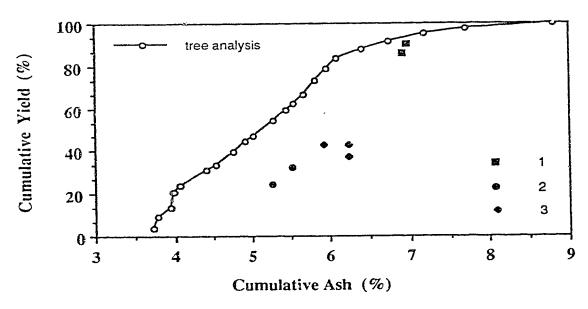


Figure 6-2 Chemical effects on column flotation efficiency ($J_g = 0.527, 0.79$ and 1.053 cm/s, $J_l = 1.58$ cm/s, wash water = 0.5 L/M)

- 1 Dowfroth 250 = 20 ppm, kerosene = 4 cc, 3% solids.
- 2 no frother, kerosene=3 cc, 3.5% solids.
- 3 Dowfroth 250=20 ppm, no collector, 3% solids.

6.3.2 Particle Size Effect

Particle size has a great effect on flotation recovery. Whether a particle can be recovered to the froth product depends on two requirements:

(1) the attachment force is large enough to fix the particle on the bubble surface, i.e.,

$$F_{att} \ge (F_{dp} + F_{pg}) \tag{6-2}$$

(2) the bubble is big enough to carry the particle upward to the froth, or,

$$F_{by} > (F_{dp} + F_{pg}) \tag{6-3}$$

where F_{by} is bubble buoyancy, F_{att} is the attachment force, F_{dp} is fluid drag force acted on the particle, F_{pg} is the particle gravity force. For a given size of bubbles, F_{by} is fixed. Thus, only when the attachment force, which is related to the particle hydrophobicity, collector and frother used, and the bubble buoyancy is larger than the particle gravity and drag force, can this particle be carried upward by the bubble. Therefore, either too coarse or too fine particles will affect the particle-bubble collection process, due to the hydrodynamic and physico-chemical conditions in the cell. It has been found [Hu and Liu, 1988] that flotation columns are superior to the mechanical cells only in the flotation of fine particles. One of the reasons may be that the wash water added in the froth zone of the column may drive the coarser particles captured by the bubbles back to the slurry, due to the increase of detachment force acting on the particles.

In this study, the particle size effect on column flotation was examined by analyzing the particle size distribution in the clean coal products. Figure 6-3 shows the particle size distribution of clean coal products obtained under different frother conditions. Two conclusions can be drawn from this figure: (1) the sizes of froth products are finer than the feed, indicating that the sample used might be too coarse; (2) when a frother is added, a greater fraction of the coarse particles is floated. This may be attributed to the increase of attachment force resulting from an interaction between the frother and collector.

The attachment force should be a function of frother type and proportional to the dosages. This can be clearly verified from Table 6-2. Using Dowfroth 250 as frother, the average

particle size in the froth product is bigger than when using MIBC. This implies that the molecular interaction between Dowfroth 250 and kerosene is stronger than that of MIBC with kerosene.

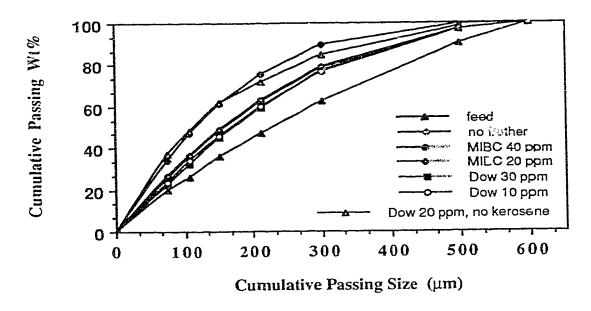


Figure 6-3 Particle size distribution of products (3.5% solids, 3 cc kerosene feed rate: 3 L/Min., wash water: 0.5 L/Min.)

Table 6-2 Average particle size of products

Product	Frother type	Dosage (ppm)	Average d _p (μm)	
Feed	None	None	255	
Clean coal None		None	115	
Clean coal	MIBC	20	189	
Clean coal	MIBC	40	192	
Clean coal	Dow*	10	199	
Clean coal	Dow	30	201	

Note: Dow* denotes Dowfroth 250

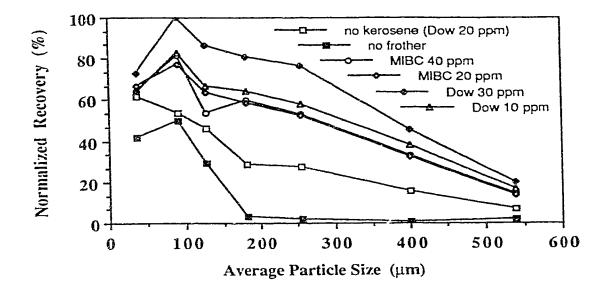


Figure 6-4 Normalized size recovery in the clean coal products (3.5% solids, 3 cc kerosene, feed rate: 3 L/Min., wash water: 0.5 L/Min.)

The effect of specific particle size ranges on column flotation can be illustrated by comparing the recovery of particles in different size ranges. The results are presented in Figure 6-4. This figure shows that for very coarse or too fine particles the recovery decreases, as expected. The highest recoveries were obtained for particles in the size ranges of 75-150 μm. It should be noted that for particles larger than about 200 μm, recovery was very poor in the absence of frother, due to the bigger bubbles formed in the column, and thus giving a lower collection efficiency for coarser particles [Finch and Dobby, 1990]. Adding frother increases the recovery of the coarser particles, resulting from the increase of the attachment force acting on the particles. However, irrespective of frother type and concentration in the presence of collector, the size recovery always peaks at about $100 \ \mu m$. In the absence of kerosene, the peak of recovery is at about 40 μm at the frother dosage rate of 20 ppm Dowfroth 250. What this implies is that the recovery peak is mainly related to the particle hydrophobicity or the dosages of collector. Adding more collector shifts the recovery peak to a coarser particle size ranges, due to the increase of particle surface hydrophobicity and the reduction of induction time. This phenomenon has also been predicted and observed by other researchers [Finch and Dobby, 1990].

6.3.3 Particle Hydrophobicity Effect

6.3.3.1 Froth Zone

In column flotation, both the froth and collection zones are affected by the particle addition and its hydrophobicity. The presence of solid particles incorporated within the froth structure has a profound effect on the characteristics of the froth and its stability. A most informative account of the role played by hydrophobicity of the particles (as measured by contact angles on particles and on plates of the same solid kept in the same solutions), the shape of the particles, particle roughness and size, the type of frother, etc., has been prepared by Dippenaar [1982, 1978]. He found that highly hydrophobic particles with contact angles greater than 90° will destabilize froth as a result of facilitated thinning of the interbubble liquid bridged by the particle. In practice, it is very common to add collectors to enhance the hydrophobicity of certain mineral particles, which means that a collector also affects the stability of the froth by increasing the contact angle of the particles. It was found by Espinosa-Gomez et al.[1988] that fatty acid concentration up to 30-40 ppm collapsed the froth regardless of frother type.

The effect of particle size and collector addition on froth stability can be observed from this study. Under the conditions of 30 ppm Dowfroth 250 and superficial liquid velocity of 1.053 cm/s, a heavy foam of more than 70 cm thick was formed in the gas-liquid two phase system. When 3-5% coal particles were added into the above system, the thickness of the froth reduced to about 40 cm. This reduction of the froth thickness was mainly caused by the coarser particles used (rather than the hydrophobicity, which will be discussed later). If bubbles carry these coarse particles to the froth zone, the froth is not strong enough to support them, and the particles may rupture the bubbles by the action of wash water and gravity. When the coal particles were mixed with 3 cc kerosene in the conditioning tank, and then introduced into the column, there was no visually apparent froth zone. It was observed that the froth which formed immediately collapsed. Therefore, frothless column flotation was carried out under these conditions. While the cleaning effect in column flotation is ensured by the froth zone and its thickness, the reduction and collapse of the froth zone will therefore affect the purity of the product. This indicates that the control of the particle surface hydrophobicity by chemicals directly influences the flotation separation. It was suggested by Finch and Dobby [1990] that a column sometimes requires less collector than does a mechanical cell, and the reduced hydrophobicity permitting a deep column froth to be stabilized, or adding frother into the wash water is sometimes used to stabilize the froth.

6.3.3.2 Collection Zone

Bubble Coalescence: While at least the rupture of the liquid film in the froth zone can be qualitatively explained by the contact angles of the particle, its size and shape, it seems that no investigation has ever been carried out to examine the particle hydrophobicity and chemical effect on bubble coalescence in the collection zone of flotation columns. The bubble coalescence will affect the particle-bubble collection process. The average bubble size may change with the addition of solids.

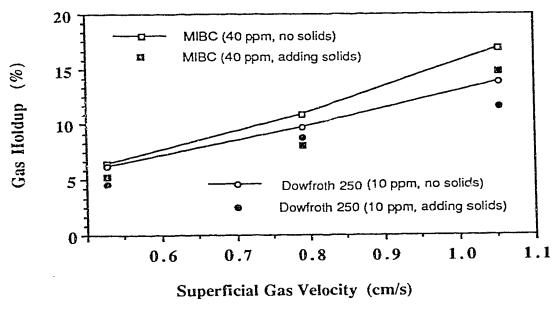


Figure 6-5 Solid addition effect on gas holdup (3.5% solids, 3 cc kerosene in the presence of solids, feed rate: 3 L/Min.)

Fig. 6-5 presents the coal particle effect on gas holdup in the collection zone. It is shown that gas holdup decreases in the presence of coal particles, thus indicting bubble coalescence and bigger bubbles formed in the column.

If we assume that 50% of the bubble surface area is occupied by the particles (the maximum loading of bubbles is reached when 70% of the bubble surface area is occupied by the particles [Dobby, 1984]), and the density of coal particles is 1.35, the changes of bubble size can be estimated by Eq. (4-26). In order to do so, the density of the mineralized bubbles have to be known, which can be estimated in the following way:

The total surface area occupied by the particles, Spb, is

$$S_{i:b} = 0.5*4\pi (R_v + r_p)^2$$
 (6-4)

where r_p is the mean radius of particles adhering on the bubble surface. The number of particles captured by the bubble is N_p given as

$$N_{p} \approx \frac{0.5*4\pi (R_{v} + r_{p})^{2}}{4\pi r_{p}^{2}}$$
 (6-5)

Therefore, the mineralized bubble density, ρ_{mb} , can be estimated as (ignoring the weight of gas bubble)

$$\begin{split} \rho_{mb} &= (W_b + W_{tp})/(V_b + V_{tp}) \\ &\approx 1.35 N_p (4\pi/3) r_p^3 / [4\pi (R_v + r_p)^3/3] \\ &= 1.35 * 0.5 r_p / (R_v + r_p) = 0.675 r_p / (R_v + r_p) \end{split} \tag{6-6}$$

From Eq. (4-26)

$$A = \frac{(2C_cR_v)^2[1-(K_g\varepsilon_g)^{5/3}](U_{ba} - J_g + J_1)}{[(1+3.36C_cR_v^2)^{0.5} - 1]^2(1 - k_\gamma\varepsilon_g)^2}$$

$$= \frac{g(\rho_L - \rho_{mb})}{9u}$$
(4-27)

so,

$$\rho_{mb} = \rho_{L} - \frac{9\mu(2C_{c}R_{v})^{2}[1-(k_{g}\varepsilon_{g})^{5/3}][J_{g}(1-\varepsilon_{g})/\varepsilon_{g} + J_{1}]}{g[(1+3.36C_{c}R_{v}^{2})^{0.5} - 1]^{2}(1-k_{g}\varepsilon_{g})^{2}}$$
(6-7)

The bubble size and the density of the mineralized bubbles can be obtained by iterating Eq. (6-6) and (6-7) on R_v until the density for both equations are approximately the same. The results are listed in Table 6-3.

Table 6-3 Solid addition effect on bubble size

	<u> </u>	J_g	$arepsilon_{ ext{g}}$	(%)	d _v (cm)
type	ype (ppm) (cm/s)		no solids	with solids	no solids	with solids
MIBC	40	0.527	6.452	5.30	0.093	0.116
MIBC	40	0.790	10.83	8.756	0.088	0.108
Dow	10	0.527	6.221	4.608	0.099	0.151
Dow	10	0.790	9.67 7	8.065	0.097	0.120
Dow	30	0.527	7.604	5.30	0.088	0.131
Dow	30	0.790	12.44	8.765	0.084	0.114

Note: kerosene=3 cc in the presence of coal. $d_p = 0.02$ cm

Table 6-3 shows that the bubble size increases 20-50% in the presence of coal particles. What should be noted here is that the bubbles produced in the lower gas flowrate (0.527 cm/s) are bigger than that at the higher gas flowrate (0.79 cm/s). This may be caused by the gas leaking at the joint point connecting the sparger with the gas inlet. Because of this, most of the gas will come out from the joint point to form big bubbles at the lower gas flowrate, due to the bigger holes and lower capillary pressures than those on the sparger. When increasing the gas flowrate, more smaller bubbles can be formed from the sparger by overcoming the external pressures so the ratio of smaller bubbles increases, thus the average bubble size decreases with the gas flowrate in the range indicated in Table 6-3. Due to the problems relating to the design of the sparger connecting system, it was difficult to prevent gas leaking by using this sparger.

Collector Effect: The collector effect on particle hydrophobicity, and thus the bubble coalescence, can be illustrated by Figure 6-6. It shows that in the absence of collector, gas holdup increases with the solids addition, indicating that the original coal particles are not hydrophobic enough to increase the bubble coalescence, or the contact angle is less than 90°. Therefore, the bubble size can be assumed to be unchanged after adding solids, and the bubble rise velocity would decrease because now the bubble is mineralized and the density of the bubble increases, thus increasing the retention time in the column. Consequently, the gas holdup increases. Hence, the reduction of the froth thickness in the absence of collector, as discussed earlier, cannot be attributed to the particle hydrophobicity, but the particle size effect. When adding 3 cc of kerosene, the gas holdup decreases in the presence of coal particles. This implies that at this time the particle surface hydrophobicity has been increased to such a level to induce bubble coalescence, or the contact angle may be larger than 90°. Because of this feature, it is questionable whether frother addition into the wash water, as suggested by Finch and Dobby [1990], can effectively stabilize the froth. The reason is that the bubble surface hydrophobicity has not been reduced, and bubbles in the froth zone can still coalesce.

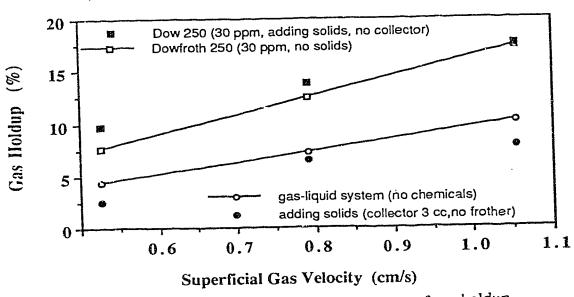


Figure 6-6 Chemical effects on the changes of gas holdup (3.5% solids, feed rate: 3 L/Min., wash water: 0.5 L/Min.)

6.3.4 Frother Effect

It is observed that frothers obviously influence the kinetics of particle-bubble attachment, and therefore flotation rate. An addition of a frother is capable of decreasing the induction time, the time elapsed from particle-bubble contact to the true attachment, i.e., forming a three-phase aggregate, by more than one or two orders of magnitude [Leja, 1983]. For practical purposes the most important of all effects is the change in flotation recovery resulting from frother additions. A systematic investigation on frother effects on flotation performance done by Lekki and Laskowski [1971] has clearly shown a progressive improvement in the recovery with the increase of frother dosages (obtained under constant additions of a collector at constant pH). The manner in which this influence is exerted has been neither unequivocally identified nor agreed upon [Leja and He, 1984]. The flotation rate constants determined experimentally were only in reasonable agreement with those based on the interceptional collision model without addition of frothers [Yoon, 1991].

In this study, the frother effect on flotation rate and recovery is discussed by comparing the flotation results under different frother types and dosages. The recovery of coal particles from the collection zone of a flotation column can be estimated using Levenspiel's equation [1972]:

$$R_{\text{org}} = 1 - \frac{4A_r * \exp(Pe/2)}{(1 + A_r)^2 \exp(A_r Pe/2) - (1 - A_r)^2 \exp(-A_r Pe/2)}$$
(6-7)

and

$$A_{r} = (1 + 4K_{f}\tau_{p}/Pe)^{1/2}$$
(6-8)

where R_{org} is the fractional recovery of organic materials in the coal, K_f is the rate constant for particle-bubble attachment. τ_p is the particle retention time, and Pe is the Peclet number. The empirical expressions established by Adel et al. [1991] for the retention time of particles in the collection zone and the Peclet number are adopted here:

$$\tau_{p} = L_{c}(1 - \varepsilon_{g})/(J_{t} + U_{p}) \tag{6-9}$$

$$Pe = 0.91(L_c/d_c)^{0.53}[J_t/J_g(1 - \varepsilon_g)]^{0.35}$$
(6-10)

the superficial tailings rate, and U_p is the particle settling velocity, which can be estimated by Stokes' equation:

$$U_{p} = \frac{g(\rho_{p} - \rho_{L})d_{p}^{2}}{18\mu}$$
 (6-11)

 K_f can be estimated by comparing the calculated and observed recoveries from the above equations. Some of the results are listed in Table 6-4.

Table 6-4 Recovery and flotation rate constant

Frother type	Dosage (ppm)	ε _ε (%)	d _b (cm)	J _t (cm/s)	R _{org} . (%)	Ash (%)	K _f (Min. ⁻¹)
MIBC	40	5.30	0.116	1.534	66.84	5.07	0.477
MIBC	40	8.756	0.108	1.365	69.55	5.43	0.504
Dow	10	4.608	0.151	1.478	72.50	5.49	0.548
Dow	10	8.065	0.120	1.370	73.60	5.33	0.569
Dow	30	5.30	0.131	1.128	83.90	5.48	0.693
Dow	30	8.765	0.114	0.122	89.45	5.91	0.930

Note: L = 366 cm, D_c =6.35 cm, d_p =0.02 cm, ρ_p =1.35, ρ_l =1.00

Table 6-4 shows that for almost the same conditions the recovery and flotation rate constant increases with the frother dosages, and Dowfroth 250 gives higher recovery than MIBC. One of the reasons is the increase of the critical thickness of thin films h_c (i.e., at this critical thickness, the liquid film will be ruptured spontaneously) in the presence of frothers. It was found that [Schulze, 1984] the influence of the surfactant concentration on the critical thickness of thin films h_c is appreciable. The investigation yielded the surprising result that even extremely low surfactant concentrations lead to film instability. Therefore, the increase of the recovery with the addition of frothers can be explained by the effect of

function of frother type and concentrations. Therefore, higher dosages of frother increase h_c , thus increasing the recovery. The reason that MIBC gives lower recovery than Dowfroth 250 may be due to the different frother structure and the contamination factor, so h_v is different.

As shown in Fig. 6-4 and Table 6-2, bigger particles can be recovered by Dowfroth 250 than MIBC, which cannot be explained by the increase of h_c and the reduction of induction time. As discussed earlier, this can only be attributed to the stronger interaction between Dowfroth 250 molecules adsorbed on the bubble surface and kerosene molecules adsorbed on the coal particles than MIBC, thus increasing the attachment force to capture the coarser particles.

This can also be verified by Fig. 6-7, which shows the reduction ratio of gas holdup in solid-gas-liquid system to that in gas-liquid system in the presence of different frothers.

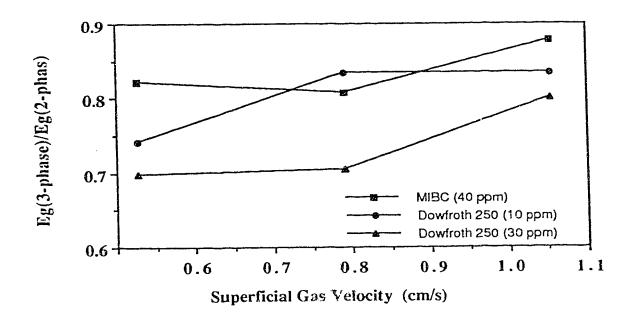


Figure 6-7 Solid effects on gas holdup changes in different frother systems (3.5% solids, 3 cc kerosene in the presence of solids, feed rate: 3 L/Min.)

profoundly. Due to the stronger molecular interaction between Dowfroin 200 and Kerosene, for the same size of bubbles, more particles are captured by the bubbles in Dowfroth 250 solution than in MIBC, or in the higher dosage system, so the chance for bubble coalescence increases.

Most of the previous flotation kinetics studies, which are based on the single bubble-single particle system, and did not consider the gas holdup and frother effects, predict that flotation rate constant increases with the decrease of bubble size. For the same type and concentration of frothers used, the results in Table 6-4 agrees with the prediction. If considering the frother and gas holdup effects, this prediction fails. Much higher recovery and flotation rate constant can be obtained at 30 ppm Dowfroth 250 with bigger bubbles than that at MIBC 40 ppm with smaller bubbles. It shows from Table 6-4 that the frother or chemical effect is far more important than the bubble size and gas holdup or hydrodynamic effects on flotation rate. That is why recently that it has been recognized by Yoon [1991] that a workable model for bubble-particle interactions can only be developed by considering both the hydrodynamic and surface forces involved, which will allow one to relate the surface chemistry information to the flotation rate constant.

6.4 SUMMARY OF CHAPTER

- 1. Particle hydrophobicity has a great effect on froth and bubble stability. Very hydrophobic particles will collapse the froth, induce bubble coalescence and reduce the gas holdup.
- 2. A collector enhances the hydrophobicity of the particles, thus increasing the instability of froth and bubbles.
- 3. Particle size affects the flotation. Adding a collector shifts the recovery peak to a coarser particle size range; adding a frother enhances the recovery of coarse particles.

captures bigger particles than MIBC.

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7.1 FROTHER EFFECTS ON BUBBLE MOTION

7.1.1 Single Bubble System

The motion of air bubbles in aqueous media is far more complicated than that of 1. solids. Two major factors contribute to this complexity: (1) the flow characterization of fluid passing through a rising bubble changes with the bubble size or bubble Reynolds number, and (2) the adsorption of surface-active materials on the bubble surface, or the boundary condition of the gas-liquid interface, varies with the bubble flow regime, the surfactant type and concentration in the liquid. For bubbles less than 0.01 cm, or Reb ≤ 0.5, the motion of bubbles is in the viscous flow condition, or Stokes' flow regime. The hydrodynamic drag is not big enough to influence the adsorption of surfactants on the bubbles; in other words, the adsorption of surfactants on the bubble surface can be regarded as in the static adsorption condition, thus the bubble surface is completely immobilized by an adsorbed layer which is always present unless the liquid is specially purified. Consequently, the type and concentration of surfactants present in water will not change the adsorption characteristics on the bubble surface. Therefore, there is no difference between the rise velocities of bubbles in the contaminated water and in the distilled water obtained by conventional methods. The motion of bubbles obeys Stokes' law, and bubbles behave like solid spheres, as indicated in Fig. 1-1.

For very big bubbles, or very large bubble Reynolds number, say $Re_b > 10^4$, potential flow condition applies [Yoon and Luttrell, 1989]. In this case, the liquid can be regarded as inviscid. The effects of surface tension and viscosity on bubble motion are negligible, compared to the inertia of bubbles and liquid [Wallis, 1969]. Therefore, the rise velocity of bubbles in the presence of surfactants should be the same as that in pure water, which is found to be proportional to the square root of the bubble size, as shown in Fig. 1-1 and reported by other researchers [Clift et al.,1978; Wallis, 1969; Levich, 1962].

For the bubbles used in froth flotation, which are in the size ranges from 0.05 to 0.2 cm in diameter (corresponding to $1 << Re_b < 500$), neither Stokes' nor potential flow streamline function can be used to reasonably describe the liquid flow surrounding the bubble. All the effects of liquid inertia, surface tension, viscosity and cleanness of the apparatus are

important and have to be considered. The most successful theoretical study in this bubble Reynolds number range was conducted by Levich [1962]. But it is restricted to the condition that the bubble surface is free from surfactants, and the theoretical prediction is 30% higher than experimental data. An empirical streamline function at this intermediate bubble Reynolds number range is proposed by Yoon and Luttrell [1989]. However, it is also based on the assumption that bubbles behave like solid spheres. Until now there is no suitable model which can describe the surfactant effect on bubble motion in froth flotation systems.

- For any kind of spheres moving in an inviscid liquid, the hydrodynamic mass, or 2. the added mass, of the sphere, which is due to the motion of the sphere and the attached water on the sphere surface, should be taken into consideration. In other words, the virtual mass, instead of the static mass, of the sphere, should be adopted in the analysis of the motion of the sphere. If the sphere is solid, this added mass is small compared with the mass of the solid sphere due to the higher density of the solid than that of water, and the surfactant effect on this added mass should be minor, resulting from the strong molecular bond between the solid surface and the water dipole. Thus the surfactant effect on the changes in the added rass is negligible. However, if the sphere is an air bubble, this added mass cannot be ignored because in this case, the added mass is much larger than the real mass of the gas sphere. In this study, the virtual mass effect of a bubble is explored by utilizing the virtual thickness of the liquid film surrounding the bubble. Hence, the rise velocity of the bubble was determined by considering the added mass of the bubble. It was found that the deviation between the bubble rise velocity from observation and prediction by Levich's equation is almost eliminated. This shows that the added mass does have great effect on bubble motion.
- 3. In practice, a lot of empirical expressions for predicting bubble rise velocities have been established, most of which are related to surface tension. But controversies arise in applying these expressions to different surfactant systems, due to the restricted conditions.

The effect of surface-active materials on bubbles is very pronounced, especially for the bubbles used in froth flotation. In this intermediate bubble Reynolds number range, the fluid flow around the rising bubbles will affect the adsorption of surfactants on bubble surface. The distribution of surfactants on bubble surface will not be even, with the lower adsorption in the upper hemisphere than in the static condition, and higher adsorption in the bottom. This dynamic adsorption of surfactants on bubble surface is also dependent on the

surfactant molecular structure or surface activity. Due to the complexity of the interaction of surfactant molecules with water dipoles and of the hydrodynamic conditions surrounding the bubble, the dynamic adsorption of surfactants on bubble surface in general cases is still unavailable [Schulze, 1984].

- 4. When surfactant molecules are adsorbed on bubble surface, the molecules will be oriented at the gas-liquid interface, with the non-polar group, the hydrocarbon chain towards the gas phase and polar group in the liquid. Due to the attraction of the polar group to the water dipole, at least two main changes caused by adding a surfactant into water can be observed: (1) the increase of the bubble surface viscosity and the shear force; and (2) more water will be attached to the rising bubble. Consequently, the added mass increases. Therefore, the rise velocity of bubbles in the water containing surfactants is lower than that in pure water, and surface tension alone cannot account for the surfactant effect on bubble motion, as has been observed by many investigators and in this study.
- 5. The amount of water attached on the surface of a rising bubble in the presence of surfactants will depend on the surfactant molecular structure and concentration. Therefore, the added mass should be a function of surfactant type and dosage. This idea is expressed by the concept of contamination factor in this study. The higher the contamination factor, the larger the thickness of the virtual liquid film and the bigger the added mass, thus the slower the bubble ascent. This indicates that the rise velocities of bubbles in various surfactant systems will be different for the same bubble size at the same concentrations.
- 6. Schulze [1984] conducted a theoretical analysis on the effect of adsorption layer on the hydrodynamic drag, and concluded that the hydrodynamic drag increases with increasing adsorption layer thickness on the bubble surface, but in the limit of a completely immobilized bubble surface it is only 4 times as great as for a bubble without an adsorption layer. This point has not been verified experimentally.

The reduction of bubble motion in the presence of surfactants is related to the increase of hydrodynamic drag, due to the interaction of surfactant molecules adsorbed on the bubble surface with the water dipoles. If the bubble surface is covered by an adsorption layer, it is generally accepted that the bubble behaves like solid, i.e., with a contamination factor of 195, as discussed in chapter 2. Fig. 2-6 illustrated the ratio of bubble rise velocity in pure water ($C_c = 0$) to that in the presence of surfactants ($C_c = 195$). It was seen that for bubbles less than 0.2 cm in diameter, the rise velocity of bubbles with a contamination factor

of 195 is one quarter of therise velocity in pure water. This difference agrees with the Schulze's prediction.

However, it has been experimentally determined that the contamination factor can 7. be far more greater than 195. Another unsolved problem is that the bubbles move even more slowly than solid spheres in the presence of surfactants, as reported by Fuerstenau and Wayman[1958] and other researchers [Clift et al., 1978; Gaudin, 1957] as well as observed in this study. This implies that the traditional idea that a bubble behaves like a solid sphere if bearing an adsorption layer cannot satisfactorily explain the surfactant effects on bubbles. The reasons for this may be that the generally considered cases are limited to the static adsorption condition, or very small bubbles (Reb <1), in which the surfactant molecules on bubble surface are uniformly distributed. But in an actual case for a bubble (with Reb >> 1) rising in contaminated water, the upper portion of the bubble surface will not be immobilized in the dynamic adsorption condition, even though the bubble surface might be completely immobilized in the static adsorption condition at the same surfactant concentration. The concept of contamination factor introduced in this study can explain this effect on bubbles very reasonably. If the bubble rise velocity for a given bubble size levels off, or the contamination factor becomes a constant, after a certain surfactant concentration, then it is said that the bubble surface is completely immobilized in the dynamic adsorption condition. This study shows that bubbles behave like solid spheres only at the contamination factor of about 195. This implies that even when the bubble surface has not been completely immobilized in the dynamic adsorption condition, bubbles move like solid spheres. If the adsorption layer is condensed on the entire bubble surface, or the bubble surface is completely immobilized in the dynamic adsorption conditions, i.e., the further addition of the surfactants does not affect bubble rise velocity any more, bubbles would move more slowly than solid spheres. This can only be explained by the differences in the added mass, resulting from the different surface structures of solid spheres and bubbles.

7.1.2 Bubble Swarm System

8. The motion of bubbles in a swarm is even more complex than that in a single bubble system, due to the interaction between the neighboring bubbles and the bubble coalescence. The average bubble rise velocity is the sum of the bubble drift velocity, superficial gas and liquid velocity, which can also be conveniently expressed by the average velocity of the gas passing through the column. The bubble drift velocity should be a function of bubble size

and gas holdup. Therefore, the two main factors, bubble size and gas holdup, will influence the average bubble rise velocity.

- 9. Increasing the gas flowrate will increase both the bubble size and gas holdup. In the absence of surfactants, bigger bubbles can be expected due to the coalescence of bubbles after leaving the sparger. The major factor affecting bubble rise velocity is the gas holdup, or the total number of bubbles in the column, because there is almost no difference between bubble rise velocity for bubbles in the size ranges of 0.3 1.0 cm in diameter, as indicated in Fig. 1-1 and observed by other researchers [Levich, 1962]. Therefore, the average bubble rise velocity should decrease with increasing gas flowrate. In the presence of surfactants, whether bubbles coalesce or not after leaving the sparger depends on the surfactant type and concentration.
- 10. One of the functions of the surfactants is to form bubbles with a certain elasticity and strength, thus increasing the ability of bubbles to resist rupture or coalescence. This ability, of course, depends on gas flowrate, the surfactant type and concentration. Therefore, under a given liquid flow conditions, for different surfactant systems, the critical gas flowrate, Q_{gc} , (i.e., for gas flowrate larger than Q_{gc} bubbles will be collapsed), will be different. For the same kind of surfactants, this critical gas flowrate will increase with the surfactant concentration. That may be the reason why the bubble rise velocities either increase or decrease with the gas flowrate, depending on the frother type and concentration, as observed in this study.
- 11. Because of the difference in boundary conditions, the motion of flotation sized bubbles in a swarm cannot be estimated by the expressions established in solid-liquid systems. Theoretical treatment has shown that the dependence on void fraction for sphere motion is less important in gas-liquid system than in solid-liquid system. The drift-flux obtained in this study for gas-liquid systems is greater than that in solid-liquid systems, especially at higher void fraction ranges.
- 12. Due to the different molecular structure, the interaction between frother molecules and water dipoles varies with the different frother system. The higher the contamination factor, the bigger the retardation effect, and the slower the bubble motion. Therefore, the bubbles of the same sizes in the aqueous media with higher contamination factors will remain in the column for a longer time than that in the solution with lower contamination factor. This implies that for the same size of bubbles in the column, the retention time and

the total number of bubbles, or the gas holdup in the column will be different for the different frother systems. For the given bubble sizes, the solution with higher contamination factor gives higher gas holdups.

7.2 FROTHER EFFECTS ON BUBBLE SIZE

- 13. The sizes of bubbles formed in liquid are mainly influenced by the gas flow conditions, liquid flow conditions and the surface tension of the liquid. For bubbles produced by a single orifice submerged in water, in which case, the constant gas pressure condition is used to compare the influence of other parameters on bubbles, the bubble size can be easily determined by photographic technique or using a video camera, or by employing a simple capillary equation (Eq. 5-25) to calculate the bubble size. In this case, bubble size decreases with the surface tension, or the surfactants with high surface activities produce smaller bubbles, as has been observed by many investigators [Klassen and Mokrousuv, 1963].
- 14. The bubble size estimation in a bubbly column is quite difficult. First of all, the bubbles in the column are different in size due to the bubble coalescence after leaving the sparger and the different hole sizes on the sparger. Thus only the statistical results of many bubble size measurements are recorded, then the average bubble size for that condition is said to be obtained. Therefore, the difficulties in obtaining the representative average bubbles size in a bubbly column lie in the facts that (1) the method to express the average bubble size; (2) the bubble size measurement technique. It has been found that for the size range of bubbles used in flotation, the Sauter mean diameter, the ratio of total bubble volume to the total bubble area, gives the most persistent and representative average bubble size in the bubbly column, and is widely adopted [Dobby et al., 1988; Yianatos et al., 1988].
- 15. The most commonly used method to determine the bubble size is the photographic technique. In order to get a truly representative bubble size in the column, attention should be paid to the problems related to the distortion caused by the curved surface of the column (if a small cylinder column is used), and the distribution of bubbles along the radial direction in a big column. Ideally, only the bubbles in the different points along the radial direction in the column has been determined, and the representative bubble size in the column is said to be obtained.

- 16. The surfactant effect on bubble size in a bubbly column is more complicated than in a single bubble system. A foam will be certainly formed at the top level of the liquid. Much of the surfactant molecules entering the column would be carried by the rising bubbles to the foam. Generally, a frother with higher surface activity tends to reduce the surface tension more sharply and more easily to be carried by the bubbles, thus forming a heavier foam. Because of this feature, it is difficult to determine the actual frother concentration in the column. Unlike in single bubble systems, whether the bubble sizes increase or decrease cannot be predicted from the measurement of static surface tension of the solution; it depends on the balance of all the variables and the flow conditions.
- 17. The existing models for predicting the bubble size in a flotation column have not considered the effect of surfactants on bubbles. Because the retarding effect on bubbles varies for different surfactants, for the same size of bubbles, the gas holdup will be different, or the same gas holdup will not give the same size of bubbles in different frother systems. This phenomenon cannot be predicted and explained by the existing models and theory. A model established in this study, by considering the contamination factor and bubble arrangement effects, gives a reasonable prediction of frother effects on bubbles.

7.3 CHEMICAL EFFECTS ON FLOTATION AND BUBBLES

7.3.1 Frother

- 18. Adding a frother will increase the flotation rate and recovery. Several mechanisms have been proposed to explain this phenomenon:
- (a) Because air bubbles themselves are usually negatively charged in pure water owing to a preferential adsorption of OH⁻ [Yoon and Yordan, 1986; Collins, 1978], it was found that the rate of flotation, and hence, the recovery is maximum when the zeta-potential of the particle to be floated is at a minimum, due to less electrostatic resistance experienced when the particle approaches the bubble. Hence one of the usually acceptable mechanisms for particle-bubble attachment is attributable to the electrical attraction-repulsion between bubbles and particles. Derjaguin and Dukhin [1960] suggested that when bubbles and particles have opposite charges, flotation is almost instantaneous. Therefore, Leja [1983] proposed that the main role of a frother-acting surfactant in flotation is to provide means of

replacing repulsive forces, whenever necessary, with attraction, owing to the ability of such surfactant molecules to align their dipoles appropriately and instantaneously at the moment of particle-bubble collision. However, the investigation done by Yoon and Yordan [1986], using microelectrophoresis technique, indicated that in the presence of nonionic surfactants, the zeta-potentials on the bubble surface change little with the surfactant concentration. While the commonly used frothers in flotation are nonionic surfactants [Klimpel and Hansen, 1988; Hu et al., 1980; Booth and Freyberger, 1962], such as MIBC, Dowfroth 250 and pine oil, the increase of recovery due to the addition of frothers cannot be fully explained by the above neutralization of bubble surface charge by frothers.

(2) Theoretical studies on flotation kinetics show that flotation rate increases sharply with the decrease of bubble size., i.e.,

$$K_f = 1.5 J_g P_K / d_b$$
 (7-1)

so the second hypothesis suggests that adding a frother will produce smaller bubbles, thus increasing flotation rate. However, the decrease of bubble size with the frother concentration levels off at a certain frother dosage, usually below 30 ppm, as reported by Finch and Dobby [1990], Klassen and Mokrousov [1963]. But the recovery still increases with the frother addition, as indicated by Lekki and Laskowski [1971]. Therefore, the increase of recovery by addition of frothers cannot be entirely attributed to the bubble size reduction in the presence of frothers, either.

(3) One of the acceptable explanations for the function of frothers on flotation rate is attributable to the synergistic effect between frothers and collectors [Leja, 1983]. This is very ambiguous, and cannot be visualized to explain the changes in particle-bubble attachment. Only when considering the dynamic adsorption of frothers on the bubble surface and the critical film rupture thickness, h_{crt}, can this process be reasonably explained. From the molecular point of view, this critical film rupture thickness is related to the interaction between the frother molecules adsorbed on bubble surface and the collectors on particles, more importantly, the hydrophobic force resulting from the interaction between the hydrocarbon chains in both frother and collector molecules. For a given collector dosage, this hydrophobic force increases with the frother addition, thus increasing h_{crt} and the attachment process is easier.

19. Recently, Xu and Yoon [1990, 1989] extended the classical DLVO theory to the following format:

$$V_T = V_E + V_D + V_S \tag{7-2}$$

where V_T is the potential energy between a bubble and a particle interacting in an aqueous medium, V_D is dispersion energy, V_E is electrostatic energy and V_S is structural energy. For hydrophilic surfaces $V_S > 0$ (i.e., repulsive), for hydrophobic surfaces $V_S < 0$ (i.e., attractive). In the latter case, the structural energy may be referred to as hydrophobic interaction energy, V_D . Since air bubbles are hydrophobic and only the hydrophobic particles adhere to air bubbles, the bubble-particle interaction may be viewed as a hydrophobic interaction [Yoon, 1991]. Therefore, it is obvious that adding a frother will increase the hydrophobic interaction between bubbles and particles, thus reducing the energy barrier between a bubble and a particle and increasing the attachment probabilities. The hydrophobic interaction in flocculation and flotation has been investigated and confirmed recently by Lu et al. [Lu and Song, 1991; Dai and Lu, 1991; Lu, 1991].

20. If we consider a homogeneous series of surfactants, say, n-alcohols, the hydrophobic force should be a function of the hydrocarbon chain length. The longer the non-polar group, the larger the hydrophobic force and h_{crt}, and easier attachment between particles and bubbles. Thus higher recovery should be expected for alcohols with longer hydrocarbon chains, as shown by Leja [1983].

However, on the other hand, the dissolution of alcohol in water is also related to the non-polar group length. the longer the hydrocarbon chain, the more difficult for it to be dissolved in water. If a surfactant cannot be dissolved in water, it is meaningless to talk about its functions on the attachment. Judging from this point, a surfactant with a branched hydrocarbon chain should be easier to dissolve in water than that with a straight chain with the same number of carbons. But at the same time, the surface activity will decrease, due to the reduction of the total length of the non-polar group. Thus the adsorption on the bubble surface decreases, so does the hydrophobic force. Therefore, evaluating whether a frother is good or not depends on the combination of its surface activity and solubility, besides the economical consideration and other factors. This may explain why the present trend in mineral industry is the wide adoption of Dowfrotl 250 and MIBC, and the declining utilization of pine oil as frothers.

21. For different types of frothers, the existing knowledge in surface chemistry cannot explain the effect of different functional groups in the frother molecules on the interaction between frother and collector, frother and water dipoles. Therefore, a suitable combination of chemical systems for a given kind of ore can only be obtained by numerous flotation tests. Compared with the collectors, to which much effort has been devoted, and therefore, the interaction between particles and different collectors can be at least qualitatively predicted, less attention has been paid to the function of frothers in flotation. If this problem is solved, another reagent revolution in mineral industry will certainly occur, just as the introduction of xanthate into froth flotation.

7.3.2 Collector

- 22. The major function of a collector is to increase the hydrophobicity of the desired mineral particles, thus reducing the induction time and increasing particle-bubble attachment probabilities. The effects of collectors, such as xanthates, on bubble behavior are minor. The measurements by O'Connor et al.[1990] and Klassen and Mokrousov [1963] clearly showed that neither collector type nor dosages have any effect on bubble size because the commonly used xanthate collectors have no frothing properties. Measurements done by Fuerstenau and Wayman [1958] indicated that the xanthates and other inorganic ions only had minor effect on bubble rise velocity. This is mainly due to the short hydrocarbon chains in the collector molecular structure. Furthermore, in a real flotation system, most of the collectors added would be adsorbed on the particle surface. Therefore, all the changes in bubble characteristics in flotation are dominantly caused by frothers, the effect of collectors and other reagents on bubbles can be ignored.
- 23. However, in the solid-gas-liquid three-phase systems, this effect cannot be ignored because the particle hydrophobicity also influences the stability of the froth and the bubbles. Too hydrophobic particles, or higher dosages of collectors, may collapse the froth, and induce bubble coalescence. This phenomenon is very obvious in the column flotation of coal as conducted in this study. In the presence of kerosene, column flotation of coal could only be conducted without a froth zone, due to the rapid collapse of mineralized bubbles; the gas holdup decreases, indicating bubble coalescence, and 20 to 50% bigger bubbles were formed than without solid addition.

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Because froth flotation is actually a physico-chemical hydrodynamic process involving solid-liquid-gas three-phase interaction in the presence of different chemicals, the following work is regarded as the key issues for fully understanding flotation separation, and need intensive investigations:

- 1. Hydrodynamics of Bubbles at the Intermediate Reynolds Number Ranges. Such study should provide the characterization of fluid flow surrounding the bubble, and establish a suitable streamline function by considering the surfactant effects.
- 2. Dynamic Adsorption of Surfactants on the Surface of a Flotation Sized Bubble. The study should resolve the problems relating to the relationship between the surfactant concentration at the different points on the bubble surface and the bulk concentration, and the effect of different surfactant structures on such adsorption.
- 3. Chemical Effects on Particle-bubble Attachment. This mainly involves the hydrophobic interaction of the hydrocarbon chains between collector and frother molecules. The study will finally solve the mysteries about how particle and bubble are brought together to form three-phase aggregates by the action of chemicals, and detailed expressions for induction time and critical film thickness can be obtained.
- 4. Particle Characters and Chemical Effects on the Froth Stability and Bubble Coalescence. This involves the effects of particle surface hydrophobicity, particle size and shape, and the chemicals on the interfacial interaction between solid/liquid, solid/gas, and liquid/gas, and will reveal the dynamic situation in a running column.
- 5. The Combined Effects of Bubble Size and Gas Holdup. Such study will provide information regarding the design and arrangement of spargers in the column to optimize the process.