University of Alberta

Froth Phase Study using a Naturally Hydrophobic Coal in a Mechanical Flotation Column

by

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ABSTRACT

The correlation between froth recovery and air recovery was established in a top-feeding mechanical flotation column. It was also found that the particles were stratified in froth layer, with hydrophobic particles (organic phase) concentrated in the upper region, and hydrophilic particles (quartz) in the lower region.

Subsequently, wash water and polyethylene oxide (PEO) were used to lower entrainment of the hydrophilic minerals. In the batch flotation tests of -15 µm quartz, the addition of both wash water and PEO were found to reduce the entrainment within a certain range of superficial water flow rate or PEO concentration, but it increased the entrainment beyond the range. In the batch flotation of 1:1 mixtures of the -15 µm quartz and oxidized coal, wash water improved the separation efficiency somewhat, but the combined use of wash water and PEO dramatically increase the separation efficiency from about 30% to over 70%.

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Table of Contents

List of Tables

List of Figures

1. INTRODUCTION

Froth flotation is a complex physicochemical process that is accomplished in two distinct phases in a flotation cell: a pulp phase and a froth phase. The pulp phase is a mixture of an aqueous suspension composed of finely ground particles of ore minerals, water and air bubbles, along with dissolved chemical species such as frother, collector, etc. The froth phase consists of mainly air bubbles, as well as intervening water films and ore particles. In the froth flotation process, the hydrophobic mineral particles attach to air bubbles in the pulp phase. The particle-bubble aggregates rise to enter the froth phase, move up the froth layer and are eventually scrapped off as the froth product (flotation concentrate), while the hydrophilic particles stay in the pulp phase and are discharged as flotation tailings.

Obviously, portions of the minerals, water and air contained in the flotation pulp will each be recovered in the flotation concentrate, and these are termed mineral recovery, water recovery and air recovery. As the objective of the froth flotation of ores is to recover the value minerals into the concentrate, the value mineral recovery is more important than the other recoveries. The value mineral recovery can be further divided into “pulp phase recovery” and “froth phase recovery” (or “froth recovery” for short). The former describe the percentage of value minerals in the pulp phase that are attached to air bubbles and enter the froth phase, while the latter describe the percentages of these minerals that survive the cleaning actions of the froth phase and eventually enter the flotation concentrate. The overall value mineral recovery is equal to the product of the pulp phase recovery and froth recovery.

Although relatively less important, water recovery has also drawn attention as it is found to be related to the entrainment of fine and ultrafine (hydrophilic) gangue minerals. Theoretically speaking these hydrophilic particles cannot attach to air bubbles and should stay in the flotation pulp. However, by virtue of their small sizes which make them prong to follow flow streamlines, these particles can be carried to the froth phase by the swarms of value mineral-bubble aggregates. In this fashion the amount of the entrained gangue particles is proportional to water recovery.

Air recovery is a relatively new term that has been defined in froth flotation. Ultimately the air bubble streams that are injected into a flotation cell will all leave the cell. Most of them burst at the top of the froth layer and enter the atmosphere. However, a small portion of the air bubbles, which are covered by water and mineral particles, are scrapped off or overflow into the flotation concentrate. This portion of the air bubbles, as a fraction of the total air injected into the flotation cell, is called “air recovery”.

At this point, air recovery is a notoriously difficult quantity to determine. In addition, how the air recovery affects value mineral froth recovery, as well as water recovery and gangue entrainment, has not been studied.

The purpose of the experimental work carried out in this thesis research is to determine air recovery in a hybrid mechanical flotation column and relate it to value mineral froth recovery. The rationale for the study is to understand the correlation and investigate the possibility to improve (or predict) value mineral recovery by changing air recovery (or air flow rate), and examine how water recovery and gangue entrainment will change at the same time.

Chapter 2 contains a literature review which presents a general overview of the froth flotation process, technical terms used therein and factors that affect the froth flotation process. Chapter 3 describes the objectives of the research project. Chapter 4 describes the experimental procedures and testing materials. Chapter 5 presents the major results from the experimental work together with in-depth discussions of the results, which are followed by Chapter 6 presenting the conclusions of the present study and recommendations for future work.

2. LITERATURE REVIEW

2.1 Froth Flotation

Froth flotation is a process to separate value minerals from gangue minerals by making use of differences in their surface hydrophobicity. The differences in hydrophobicity between value minerals and gangue minerals can be enlarged by using flotation collectors and modifiers. The flotation process is widely used for the separation of essentially all types of minerals.

Ore flotation begins by comminution (i.e., crushing and grinding), which is used to reduce particle sizes and liberate the value minerals from the gangue minerals. The ground ore is treated by different flotation reagents. The value minerals are rendered hydrophobic by the addition of collectors and possibly an activator, while the gangue minerals are either naturally hydrophilic or made hydrophilic by depressants. An air stream is then introduced to the slurry which is broken into small air bubbles. The hydrophobic mineral particles attach to the air bubbles and rise to the surface of the slurry to form a froth layer, while the hydrophilic minerals remain in the flotation cell. The froth layer is continuously removed to form the flotation concentrate, which contains hydrophobic minerals, while the minerals remain suspended in the flotation cell is discharged as flotation tailings (Figure 2.1). In a so-called “reverse flotation” process, the exact opposite is true, i.e., the gangue minerals are made hydrophobic and floated away while the value minerals are made hydrophilic and remain in the flotation cell.

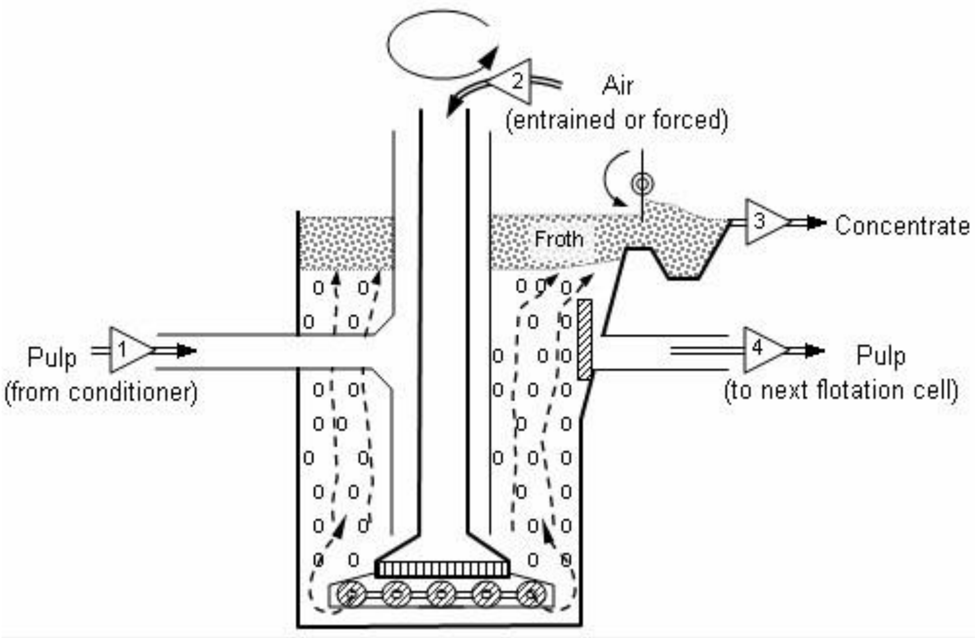


Figure 2.1 Schematics of froth flotation process (Webster's-online-dictionary).

2.1.1 Flotation Reagents

Reagents used in froth flotation can be divided into three types: collectors, frothers and regulators (Lovell, 1982).

1) Collectors

Collectors are the reagents that render the valuable mineral hydrophobic. They comprise a polar or ionizable thus hydrophilic functional group, through which they attach to mineral surface, and a non-polar hydrophobic group, by which they attach to the bubble. In this way, minerals were adhered to bubbles.

2) Frothers

Frothers are used to provide a stable froth layer giving the floated mineral particles sufficient residence time before they are removed into the flotation concentrate. They are usually surface-active and only contain hydroxyl groups (-OH) as the polar groups, i.e., they are usually alcohols.

3) Regulators

Regulators are used to ensure that the value minerals can be floated selectively with the rejection of gangue. They can further be divided into three types: activators, depressants and pH modifiers. Activators can enhance collector attachment to the value mineral surface. Depressants are used to enhance the hydrophilicity of gangue minerals so that they do not float. Finally, pH modifiers are used to adjust the pH of the pulp phase to an optimum condition for collection, activation and depression.

2.1.2 Flotation Recovery versus Entrainment

During the froth flotation of an ore, the value minerals are made hydrophobic and float to the concentrate, while the hydrophilic gangue minerals are left in the pulp phase. For the value minerals, the Overall Recovery k is the product of Pulp Zone Recovery, k_c, and Froth Recovery, R_f, i.e., $k = k_c \times R_f$ (Vera et al., 1999) (Figure

2.2). The Pulp Zone Recovery k_c represents the fraction of value minerals entering the froth phase, while the Froth Recovery R_f is the fraction of minerals that survive in the froth phase and move to the concentrate (Figure 2.2).

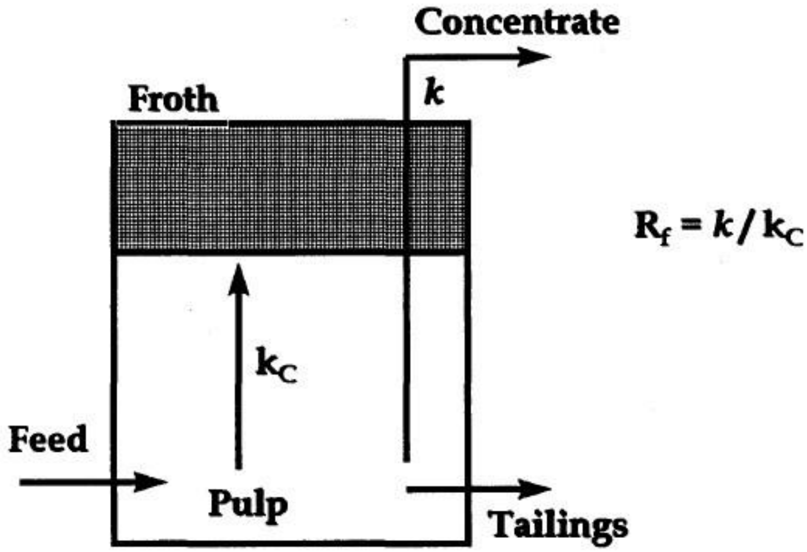


Figure 2.2 Two-phase model description of flotation (Vera et al., 1999).

Hydrophilic mineral particles can be carried to the froth phase by bubble swarms or piggybacking on hydrophobic particles through slime coating. Indeed they can even enter the final flotation concentrate in this fashion. This is called Hydraulic or Mechanical Entrainment. Entrainment is not true flotation and should be prevented.

In the froth flotation process, one can also determine the fraction of water that reports to the flotation concentrate from the pulp as “Water Recovery”. As has been shown by Warren (1984), entrainment becomes significant when particle size was below about 30 μm, and it is proportional to water recovery.

2.2 Effect of Froth Properties on Flotation Performance

2.2.1 Froth Height

The essential role of froth depth in determining flotation performance has been recognized by researchers for many decades. Woodburn et al. (1975) and Feteris et al. (1987) showed that froth stability depended on froth height, and bubbles would eventually collapse as they rose in an increasingly deeper froth layer because of liquid film thinning by drainage. Bisshop and White (1976) suggested that the drainage of hydrophilic particles from the froth zone back to the pulp phase was dependent on the froth residence time which was directly proportional to the froth height. Moys (1984) also reported that deeper froth provided longer time for liquid and particles to drain back to the pulp. Moreover, Feteris et al. (1987) found that there was a linear relationship between the probability for a particle to survive the cleaning action of the froth and the inverse of froth height. Subsequently, Tao et al. (2000) also reported this correlation in mechanical flotation tests of coal, and they demonstrated that there was a linear dependence of combustible recovery, ash recovery and water recovery on the froth depth in the column flotation of the coal samples.

According to previous studies on the effect of froth depth (Yianatos et al., 1988; Ynchausti et al., 1988), the fluctuations in the level of the pulp-froth interface were most likely to affect the grade of flotation concentrate. As it is generally accepted, the pulp-froth interface should be controlled at a certain level for effective operation of column flotation. When the level of interface became too low, the total froth recovery would reduce due to the decreased residence time of particles in the froth. While if the interface became too high, the concentrate would have a low grade as the selectivity of the froth phase was weakened.

2.2.2 Bubble Size

Bennett et al. (1958) were the first to point out the effect of bubble size on flotation. They observed that smaller bubbles were more efficient in the froth flotation of coal. However, Pryor (1965) demonstrated that bubbles less than 0.5 mm in diameter did not show any difference in their adhesion power, and they were all able to form a stable froth layer. However, when bubbles were extremely small, they may stay in the pulp and cannot enter into the froth phase. De Vivo and Karger (1970) later drew similar conclusions by utilizing two bubble sizes in column flotation of colloidal kaolinite and montmorillonite particles. Ahmed and

Jameson (1985) studied bubble sizes in the range of 75-655 μm and found that the efficiency of particles' removal from pulp phase was strongly affected by the bubble size. The collection efficiency of the 75 μm bubbles was about two orders of magnitude higher than the 655 μm bubbles.

Dobby and Finch (1986) reported that smaller bubbles with higher overall bubble surface areas would cause more stable froths and a greater carrying capacity. They observed that water recovery (and gangue entrainment) increased when bubble size was reduced.

On the other hand, Diaz-Penafiel and Dobby (1994) found that collection efficiency was insensitive to bubble size for very fine silica particles (d ≤ 3-5 μm). This observation is important since it argues against the general belief that smaller bubbles are more efficient in collecting fine particles.

2.3 Effect of Air Flow Rate on Flotation Performance

Klassen and Mokrousov (1963) pointed out that an increase in air flow rate resulted in more stable froth and higher water recovery. Laplante et al. (1983a) theoretically predicted and experimentally demonstrated that, in a flotation system without a froth phase in a specifically designed batch flotation cell, the flotation rate constant increased to a maximum and then decreased as air flow rate (AFR) was increased. They explained that the air flow rate had two counteracting effects on the flotation rate constant. Higher air flow rate generated more bubbles, enhancing the flotation rate. On the other hand, higher air flow rate increased bubble size, leading to a drop in the flotation rate.

Laplante et al. (1983 b) studied the flotation rate of galena as a function of air flow rate (AFR) and froth height (from 0 to 6 cm) in a batch flotation cell. The overall rate constant (ORC) was found to increase with increasing AFR and decreasing froth thickness. By using multi-linear regression method to fit the data, a correlation between ORC and AFR was found:

$$\mathrm{ORC} = K_1 + K_2G + K_3G^2 + K_4D \tag{1}$$

Where: G = AFR (L min^{-1}); D = froth thickness (cm); $K_1 = 0.293 \pm 0.11$; $K_2 = 0.281 \pm 0.045$; $K_3 = -0.0134 \pm 0.004$; and $K_4 = -0.140 \pm 0.011$.

This equation suggested that the ORC increases as AFR is increased. However, this relation is not linear, which is inconsistent with the results of Woodburn et al. (1975), who reported that in the presence of a froth phase, ORC would increase with AFR monotonically.

Tao et al. (2000) mentioned that an increase in air flow rate stabilized the froth layer and improved froth recovery during coal flotation. But they also observed a sharp increase in ash recovery when the superficial air flow rates (i.e., volumetric air flow rate divided by the cross-sectional area of the flotation cell) were higher than 2 cm/s, due to increased non-selective hydraulic entrainment. Although Barbian et al. (2003) did not believe that increasing air flow rate would always strengthen froth stability, they also agreed that a high air flow rate would lead to high gangue entrainment.

2.4 Air Recovery

Woodburn et al. (1994) were the first to propose a concept to express the fraction of total injected air overflowing the weir of a flotation cell, and Barbian et al. (2007) coined the phrase “Air Recovery” to describe this fraction. There are currently two methods to measure air recovery. They were the “image analysis” method and the “relative froth height” method.

It follows that based on Bikerman’s study on the dynamic stability of froth (Bikerman, 1973), when a sufficiently high column was used to hold the equilibrium froth preventing it from overflowing, the air recovery would be zero. However, when the height of the column was adjusted to below the equilibrium froth height, the froth will overflow, and the overflow rate is related to the ratio of the column height against the equilibrium froth height. Barbian et al. (2003) argued and showed that the fraction of air overflowing the cell weir (i.e. air recovery) correlated well with the ratio of the actual froth height (H) against the maximum equilibrium froth height (H_{max}), based on which the "relative froth height" method was generated. They observed that the fraction of air expected to overflow (β) was related to the difference between the maximum and the actual froth heights, the froth stability factor τ and the air flow rate by:

$$\beta = \frac{(H_{max} - H)/\tau}{Q/A} = (1 - \frac{H}{H_{max}}) \tag{2}$$

where H_{max} and τ are the equilibrium froth height and the characteristic average bubble lifetime, obtained from the froth growth rate curve ($H = H_{max}\,(1 - e^{\frac{t}{\tau}})$), Q and A are respectively the air flow rate introduced to the cell and the cross sectional area of the cell. H is the actual froth height at which the experiment is carried out. And the actual fraction of air overflowing the weir (i.e., air recovery α) is directly related to the fraction of air expected to overflow (β) when operating at column heights below the maximum. Moreover, Figure 2.3 (Barbian et al., 2003) shows the relationship between the fraction of air overflowing the weir (i.e., air recovery α) and the different froth height ratios at 50 g/ton frother concentration and two different air flow rates. It is clear that air recovery is negatively related to (H/H_{max}). Therefore, the air recovery could be calculated by ($1\text{-}H/H_{max}$) based on this method.

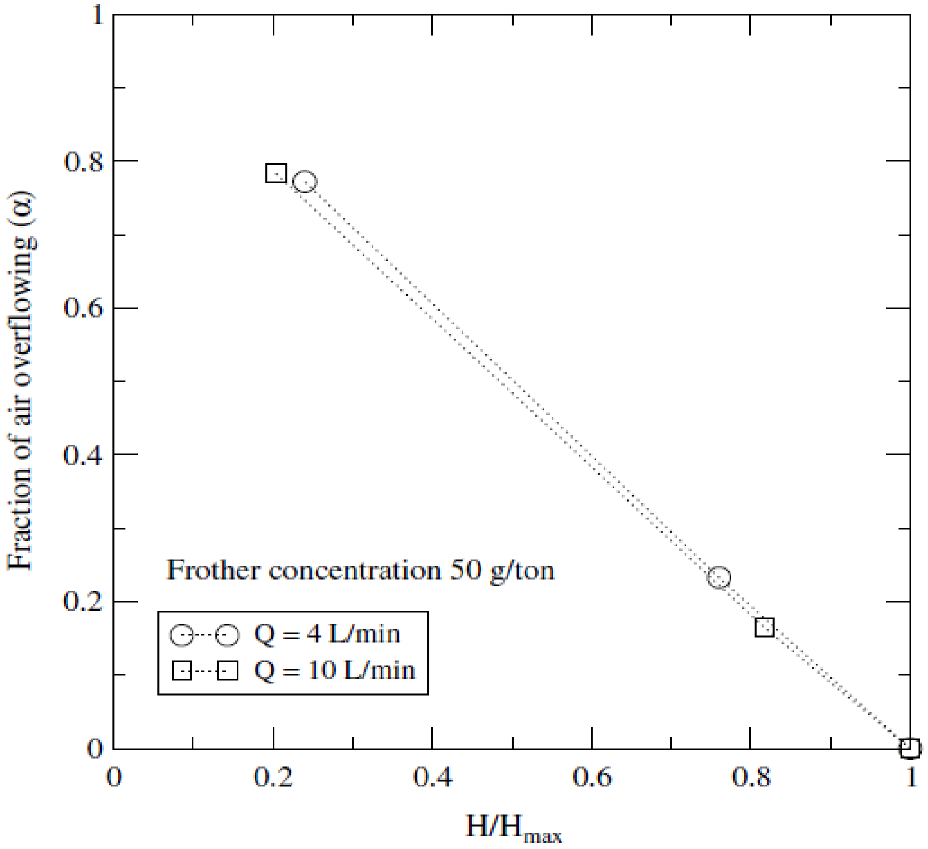


Figure 2.3 Measured fraction of air overflowing the weir (α) as function of the ratio H/H_{max} at 50 g/ton frother concentration and 4 and 10 L/min aeration rate (Barbian et al., 2003).

The “image analysis” method was based on the assumption that the overflowing froth contains 100% air, which is obviously an overestimate since the froth contains water and particles besides air. However, Barbian et al. (2007) proposed that air recovery could be calculated by the following equation:

$$\alpha = \frac{Q_{out}}{Q} = \frac{\zeta \times v_f \times h_w \times W}{Q} \tag{3}$$

Where α is the air recovery expressed as a fraction; Q is the volumetric flowrate of air injected into the flotation cell; ζ is the fraction of air in the overflowing froth; v_f is the linear flowrate of the overflowing froth; h_w is the depth of overflowing froth above the weir; and the W is the weir lip length. Here Q, h_w and W could be measured directly; v_f is found from froth image analysis and ζ is assumed to be unity (Barbian et al., 2007) as stated earlier.

In general, air recovery well reflects the froth stability: at a certain froth overflowing height, higher air recovery means more stable froth phase.

2.5 Relationship between Froth Stability and Flotation Performance

It is widely accepted that an unstable froth leads to losses of value minerals from the froth phase to the pulp, and consequently low froth recovery. Conversely, an excessively stable froth would cause problems in entrainment and pumping operations, and adversely impact mineral separation in subsequent flotation stages.

Barbian et al. (2006) conducted a series of experiments using an automated version of Feteris et al. (1987)'s froth stability column under different operating conditions. They reported that air flow rate significantly changed froth stability, and consequently affected flotation performance. They also reported that the high froth stability conditions occurred at medium air flow rates, which is similar to the results of Laplante et al. (1983a).

Figure 2.4 (Barbian et al., 2006) shows the platinum-group-metal (PGM) relative grade/recovery for two types of froth: the unstable froths, for which β < 5%, and the stable froths, β > 5%, at the lowest air flow rate tested (6 m^3/min). It suggested that the froth stability and flotation performance are related. The conditions corresponding to high froth stability (β > 5%) led to an overall higher PGM recovery, while low froth stability (β < 5%) resulted in lower PGM recovery.

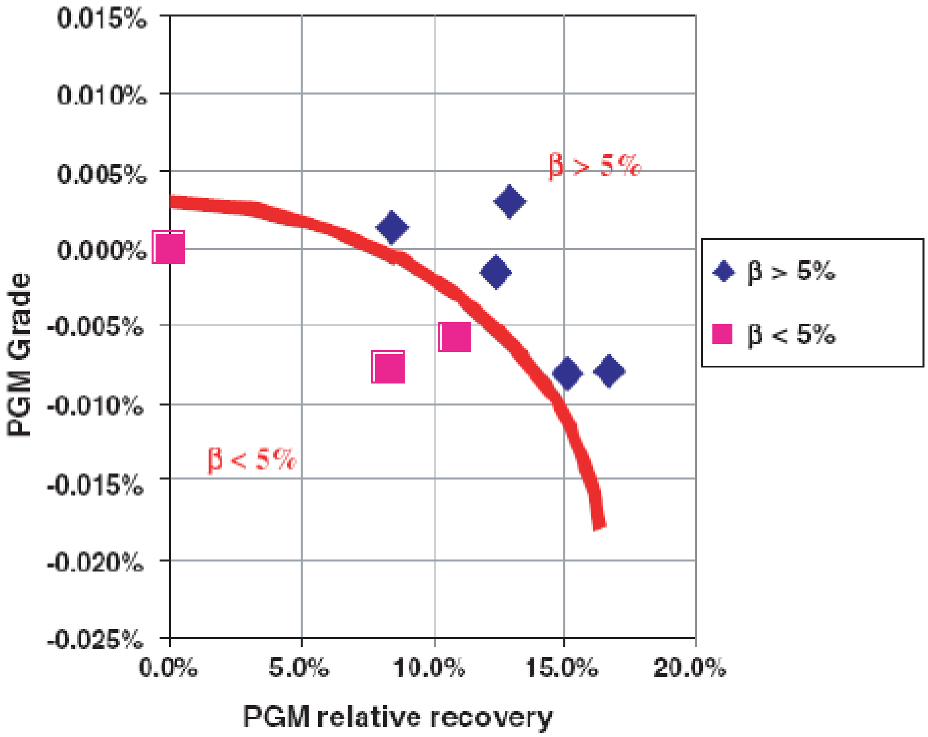


Figure 2.4 Grade-recovery plot showing different stability regions (Barbian et al., 2006)

Subsequently, Hadler and Cilliers (2009) carried out experiments on the first four cells of the rougher flotation bank at a South African platinum mine, with the objective of finding out the relationship between froth stability and flotation performance as a function of air flow rate. Figure 2.5 (Hadler and Cilliers, 2009) shows the effect of air flow rate on air recovery. As can be seen, air recovery peaked at a superficial air flow rate (i.e., the volumetric air flow rate divided by the cross-section of the flotation cell) of 1.0 cm/s for all the four cells. Figure 2.6 (Hadler and Cilliers, 2009) shows the effect of air flow rate on the grade and recovery of the flotation cells. It reveals that concentrate grade decreased at both high and low superficial air flow rates. The highest concentrate grade was achieved at a medium superficial air flow rate (1.0 cm/s), where the air recovery peaked. This reveals the link between froth stability and flotation performance.

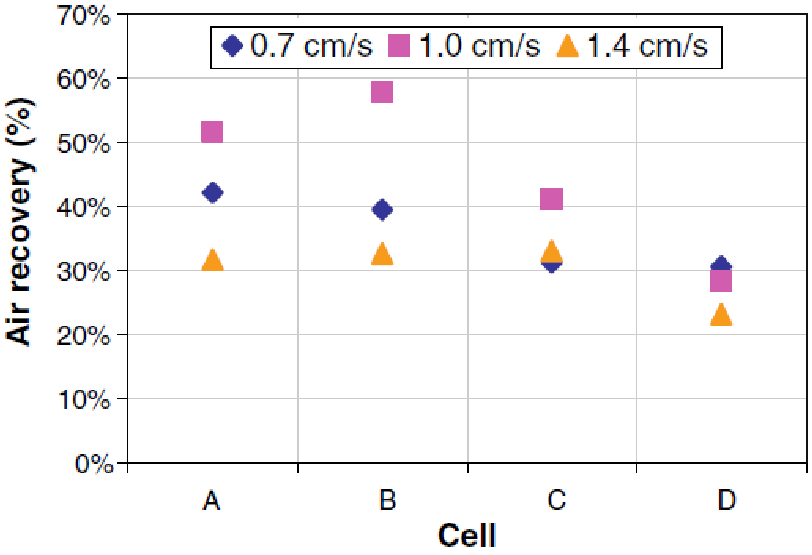


Figure 2.5 Variations in air recovery in the flotation bank at different air flow rates (Hadler and Cilliers, 2009)

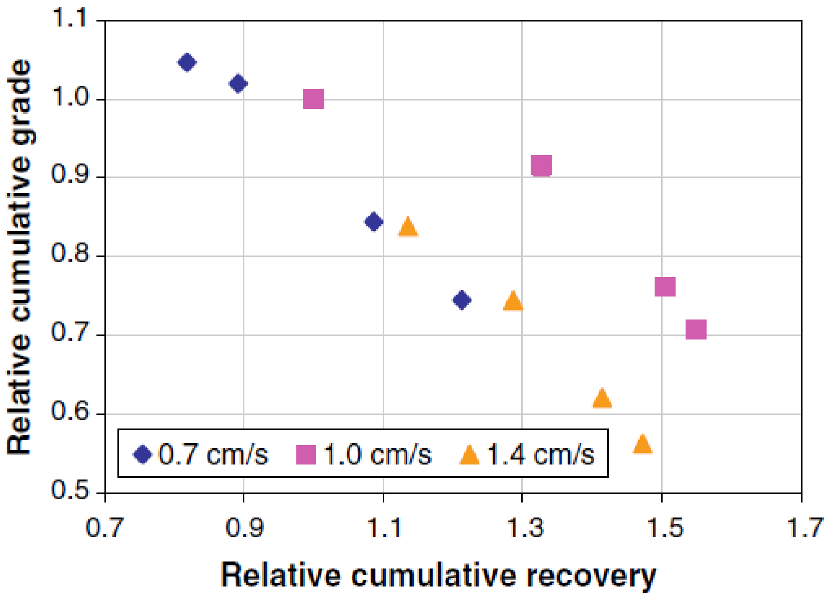


Figure 2.6 The effect of air flow rate on flotation bank performance (Hadler and Cilliers, 2009)

2.6 Gangue Entrainment

Gangue entrainment is one of the most intractable obstacles in product upgrading in flotation, especially for fine and ultrafine flotation (Warren, 1984). Consequently, clarifying the mechanism and effects of entrainment is of great importance for flotation operation.

Various models of gangue entrainment have been reported in the past thirty years. As has been shown by several researchers, mechanical entrainment generally became significant for particles smaller than about 30 µm. Woodburn et al. (1975) found a relationship between ash recovery and water recovery which suggested that the recovery of hydrophilic species was directly proportional to the water recovery. The results of Tao et al. (2000) partly agreed with that of Woodburn et al. (1975). Tao et al. (2000) carried out a series of flotation tests in which air flow rate, feed solid concentration, and froth height were selected as variables to obtain different froth stabilities. They also observed a linear dependence of ash recovery on water recovery. However, unlike Woodburn et al. (1975), Tao et al. (2000) found that this line did not cross the origin. This difference between the two studies was thought to be due to the different samples used in their experiments.

Based on an understanding of the mechanisms of gangue entrainment and influencing factors, including water recovery, air flow rate and froth thickness, methods have been developed to lower the hydraulic and mechanical entrainment, such as wash water spray to the froth layer, and vibration of froth phase.

2.6.1 Wash Water

Wash water is usually utilized in column flotation, and only found occasional use in the operation of conventional mechanical flotation to reduce gangue entrainment.

Klassen and Mokrousov (1963) gave examples of froth washing. They found that the thickness of aqueous films around bubbles and the wash water rate played a crucial part in reducing mechanical entrainment, and reported that the decrease of entrainment brought by froth washing was mainly due to the drainage of gangue particles. Besides, they claimed that froth washing would increase value mineral recovery since the froth layer was stabilized by the wash water.

Kaya (1989) utilized wash water in conventional mechanical flotation cells. In her study, several kinds of wash water distributors were designed to obtain gentle and even water addition, such as garden sprinklers, spargers and copper pipes. Finally, she found that wash water at an optimum superficial flow rate of 0.03 to 0.07 cm/s could reduce entrainment in mechanical flotation cells, but excess wash water increased gangue entrainment due to high water recovery.

Considering the importance of wash water in upgrading flotation concentrate, further research has been done in recent years. Among these studies, the work of Tao et al. (2000) drew much attention. In their study, a series of laboratory flotation tests were carried out to examine the effect of froth stability on column flotation of finely pulverized coal. A significant positive bias rate (≥ 0.2 cm/s) was required to eliminate hydraulic entrainment. The appropriate wash water rate depended on air flow rate, frother concentration and coal properties, etc. Tao et al. (2000) suggested that bias rate just above zero was not enough to obtain the best product grade, which was in agreement with Yianatos et al. (1987) who claimed that bias rate of 0.3-0.4 cm/s was required to prevent gangue entrainment into the froth.

Tao et al. (2000) also observed that at high wash water rate, upgrading occurred primarily at the pulp-froth interface, while at low wash water rates, upgrading took place in the drainage zone (froth zone). The ash profiles along the depth of the froth layer at high wash water rate remained relatively constant from the pulp-froth interface to the top of froth, which was similar to the observations of Szatkwoski et al. (1985). Tao et al. (2000) further observed that lowering the wash water addition point into the froth increased bias water rate, which could improve the effectiveness of wash water and enhance the product grade. However, excessive drainage of froth along with low wash water addition position induced an unstable froth which adversely affected froth performance.

Banisi et al. (2003) reported that the optimum wash water superficial rate was found to be 0.06 cm/s in the flotation circuit of the Sarcheshmeh copper mine, which agreed with the results of Kaya (1989). In their study, a shower type system was found to be the best for adding wash water. Based on continuous sampling of the re-cleaners over a period of two months, the grade of the final concentrate was enhanced by 1.5% when wash water was used in the flotation circuit. However, it was not clear from the paper whether it was a 1.5% increase, or a 1.5 percentage point increase.

However, the usefulness and mechanism of the action of wash water are not well understood even though some interesting results were reported. Many investigations indicate that wash water could create a downward counter-flow (i.e. positive bias) to the entrained liquid and flush the gangue particles back to the pulp, thus upgrading the froth product. But some researchers did not agree with this point of view. For instance, Aliaga et al. (2006) obtained a high grade fluorite concentrate under negative bias regime (i.e., wash water was added from the bottom of the flotation column and flowed upward). Thus, the function of wash water addition in flotation requires further study.

2.6.2 Polymer Depressants

Fine hydrophilic particles are carried into the froth layer due to their small size and mass. It is therefore logical to enlarge their particle sizes to decrease gangue entrainment. Liu et al. (2006) reported the dual functions of polymer depressants in reducing fine particle entrainment: the polymer depressants could not only render the particles hydrophilic but also enlarge their sizes. In the meantime, Liu and Cao (2006) showed that the entrainment of fine and ultrafine hydrophilic sphalerite particles could be reduced by enlarging their sizes through the coagulating functions of inorganic depressants such as zinc sulfate. Recently, polyethylene oxide was used to flocculate and depress fine silicate gangue in the flotation of a Au-Cu ore using potassium amyl xanthate (KAX) in batch flotation (Gong et al., 2010). They observed that PEO alone caused non-selective flocculation of both the silicate gangue and the sulfide minerals. But the addition of KAX caused the sulfide mineral to break off from the hetero-aggregates.

2.7 The Use of Polymers in Coal Flotation

With the growing demand for resources and concerns on environmental protection, it is essential to develop techniques to process fine coal, so as to product clean coal with low ash and sulfur contents. Among the techniques investigated, selective flocculation, in which only small amounts of polymers are employed to flocculate particles, has shown its important role in reducing the ash content of fine coal. In a number of previous investigations, several flocculants including polyacrylamides and polyethylene oxide (PEO) have been used in coal flotation. Spencer and Brookes (1987) found that polyacrylamide polymers could selectively flocculate coal from coal/shale slurries so as to depress coal. Similarly, Williams et al. (1987) reported that the presence of polyacrylamide flocculants in coal reverse flotation increased ash recovery and reduced ash content in tailings for all four different coal samples tested. And polyacrylamide flocculants were also observed to lead to a more stable froth. Whereas, Ding and Laskowski (2007) argued that the addition of polyacrylamides (with a low degree of anionicity) could selectively flocculate gangue minerals only after sufficient conditioning in coal reverse flotation, otherwise, it resulted in a total flocculation of the coal and gangue particles.

Polyethylene oxide (PEO) is widely used as a flocculant for its bridging function between particles, especially in the pulp and paper industry. Van de ven et al. (2004) observed that flocculation induced by PEO was due to the presence of entanglement of PEO molecular chains. Freshly-dissolved PEO solution, rather than aged one, works much better in inducing flocculation. Moudgil (1983) studied the functions of both polyacrylamide and PEO in coal flotation. And he observed that at higher dosage of polyacrylamide, coal particles were completely depressed, while in the case of PEO, the coal recovery was first decreased and then increased with the increasing dosage of PEO. Gochin et al. (1985) suggested that the adsorption of PEO on coal was almost independent of pH but dependent on the degree of oxidation of the coal, and the amount of adsorption was basically unchanged in the presence of H-bonding competitors. Therefore, they claimed that the mechanism of adsorption of PEO on coal is by a hydrophobic interaction.

3. RESEARCH OBJECTIVES

According to the literature review in Chapter 2, the relation between froth recovery and air recovery has not been studied, and it is unclear if the recovery/grade of flotation could be improved by changing air recovery based on this correlation. Besides, the effects of polymers in coal flotation (both direct flotation and reverse flotation) have not been fully exploited. Therefore, the objective of this study is to use coal as a naturally floatable solid and quartz as a naturally hydrophilic (non-floatable) mineral, to study

1) if and how the froth recovery of valuable minerals is related to air recovery under different flotation conditions;
2) the effects of wash water and polyethylene oxide (PEO) on the water recovery–gangue entrainment relationships, as well as on froth recovery.

The rationale to use coal as a naturally hydrophobic solid is such that no collectors would be needed to avoid their roles in affecting the froth behavior. Also, quartz of different particles sizes can be used to examine their entrainment behavior and the effect of wash water and polymer depressants.

4. EXPERIMENTAL MATERIALS AND METHODS

4.1 Research Methodologies

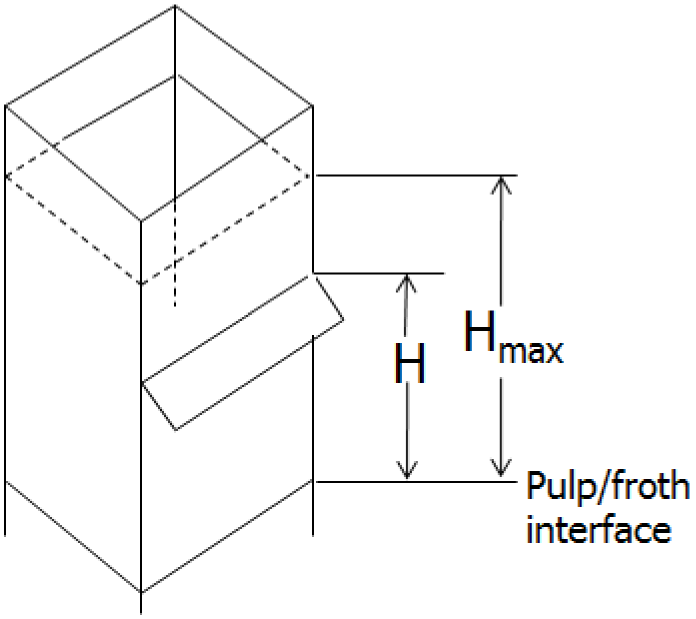
4.1.1 Froth Flotation

Flotation tests were conducted using a JKTech flotation machine along with a specially constructed cell designed to hold up a pulp volume of 3 L and a froth column up to 600 mm high. Figure 4.1 shows the hybrid mechanical flotation column. The front side of the column was made up of Perspex weir bars, each with different heights such as 20, 50, 120 and 250 mm. These bars could be removed to adjust the height of the overflowing weir from 0 to 600 mm above the pulp/froth interface. The perspex column is 150 mm wide and 160 mm long, with a cross-sectional area of 24,250 mm^2.

Figure 4.1 The hybrid mechanical flotation column.

In a typical flotation test, a 240 g of sample was mixed with 1 L distilled water by a magnetic stirring bar for 5 min at the natural pH. At the same time, the flotation cell was filled with distilled water and a pre-determined amount of DF250 was added to form a stable two-phase froth in the Perspex column. The two-phase froth was generated at a chosen air flow rate and the air was allowed to flow for 2 to 3 minutes to ensure a stable froth layer. The conditioned mineral slurry was then dripped to the top of the froth layer by a peristaltic pump at a rate of 200 mL/min. When half of the slurry sample was loaded onto the froth, the pump was stopped and the froth would reach a new equilibrium height. This was recorded as H_{max}. Tests had shown that further addition of the mineral slurry led to small but insignificant increase in H_{max}. At this point, the pump was restarted and the front weir bars removed to allow the froth to overflow by itself at the designated froth height (H). A plastic plate was inserted from the top to about 50 mm below the surface of the froth to avoid short-circuiting. Two or three minutes later, the remaining mineral slurry was loaded completely. The flotation machine was turned off and the wet and dry weights of the froth product and tailing were measured and used to calculate water and mineral recoveries.

Using the above flotation procedures, the flotation recovery into the froth product could be considered as “froth recovery”. This is because the “pulp zone recovery” could be assumed to be 100% - as conditioned mineral particles were dropped on top of the froth layer, they should have “attached” to the bubbles in the froth layer. Based on previous research, two methods can be used to determine air recovery (section 2.4). However, the “Image Analysis” method did not work in the flotation tests in this study although a VisioFroth imaging system was kindly donated by Metso Cisa Minerals. The first thing was that the froth layer was too deep to set up the laser beam for froth height measurement, as the VisioFroth system is designed for conventional mechanical flotation machines, which have a shallow froth layer. Other difficulties encountered included changing distances between the froth top to the camera, and inadequate contrast of the froth surface, especially when quartz was used. Thus the “Relative Froth Height” method was used in the study. As shown in Figure 4.2, air recovery was calculated by $1–H/H_{max}$, where H is the overflowing froth height and H_{max} is the equilibrium three-phase froth height.



Air Recovery = $1-H/H_{max}$

Figure 4.2 Schematic description of “Relative Froth Height” method to calculate air recovery (Barbian et al., 2003)

To measure solids distribution in the froth phase, the conditioned mineral slurry was pumped to the top of the two phase froth, and a full length front plate was inserted so that the froth did not overflow. After the froth layer reached the equilibrium height, a dip tube, which was connected to a vacuum line through a collecting flask, was used to collect solids at a certain froth height. The siphoning speed of the dip tube was kept sufficiently low such that it did not cause the collapse of the froth layer above.

In the flotation tests in which wash water was used, the wash water distributor was made by a perforated copper tube with a 2 mm inner diameter. The 1 mm holes on the pipe were drilled at about 20 mm intervals. In order to control the pulp/froth level height when using wash water, a hole was drilled on the Plexiglas window of the stainless steel flotation cell to allow excess water to flow out (Figure 4.3). A cloth mesh was used to block mineral particles.

Figure 4.3 Outlet for controlling the level of pulp/froth interface

4.1.2 Small-scale Flotation

A flotation tube (Figure 4.4) was used in this study to measure the floatability of coal particles. It was a modified Hallimond tube that was able to float fine particles with low entrainment. The bottom of this tube was a sintered glass frit with a pore size of 1.6 μm on which a magnetic stirring bar could be used to agitate the flotation pulp. The top of the flotation tube was modeled after Siwek et al. (1981). The throat that connects flotation tube and the collection bulb was so narrow that only one gas bubble could pass through it at one time when no frother was used. Therefore, only hydrophobic particles attached to air bubbles could pass through the throat and enter the collection bulb.

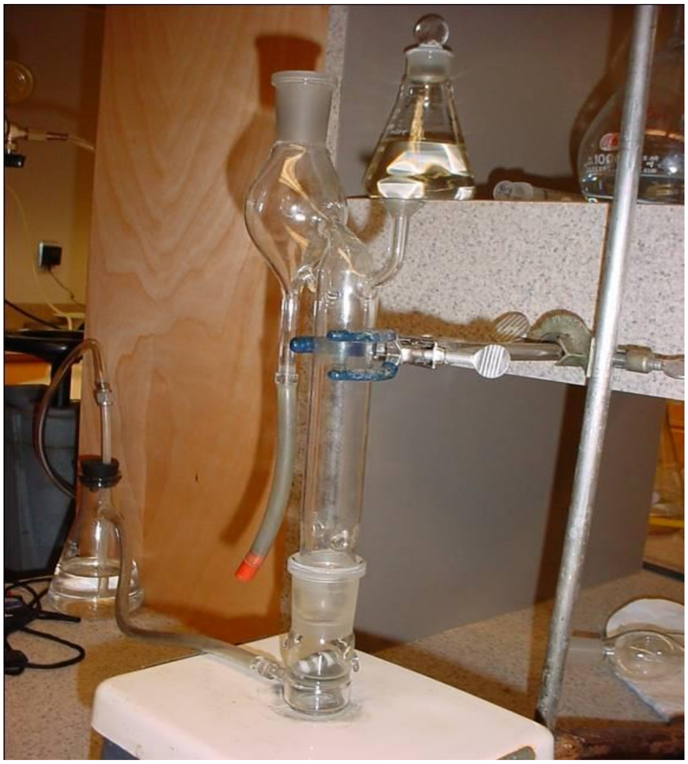


Figure 4.4 Small scale-flotation tube

In this study, a typical small- flotation test procedure was as follows: 1.5 g sample was mixed with 150 mL distilled water and agitated in a 250-mL beaker for 2 min at natural pH. Subsequently, the conditioned pulp was transferred to the flotation tube and floated for 1 min. Both the concentrate and tailing were collected, and their dry weights were measured and used to calculate recovery.

4.1.3 Small-scale Flotation Column

A small-scale flotation column (Figure 4.5) with a volume of 200 mL was used in this study. The procedure of small-scale flotation column was similar to that of small-scale flotation tube, but 15 g of sample was used and DF250 (200 mg/L) was added as a frother followed by 1 minute of conditioning. After 2 minutes of flotation, the concentrate and tailing were filtered and dried, and the dry weights measured and used to calculate recovery.

Figure 4.5 small-scale flotation column

4.1.4 Ash Analysis

Ash analysis was determined by weighing the residue remaining after burning the coal under rigidly controlled conditions of sample weight, temperature, time, atmosphere and equipment specifications. The equipment for ash analysis is an electric muffle furnace. The furnace was equipped with a temperature display and a vacuum outlet to release the combustion gases.

The procedure of ash analysis was as follows: approximately 2 g of the coal sample was accurately weighed and placed in a weighed capsule, which was covered up quickly. When the temperature of the muffle furnace reached 900 ℃, the capsule was placed in the furnace. After heating for eighteen hours, the capsule was removed from the muffle furnace, cooled in air and weighed. The ash content of the sample was calculated from the following equation:

$$\text{Ash content, } \% = [(A - B)/C] \times 100 \quad (4)$$

Where:

A= weight of capsule, cover and ash residue, g;

B= weight of empty capsule and cover, g;

C= weight of sample used, g.

4.1.5 XPS Analysis

X-ray Photoelectron Spectroscopy (XPS) measurements were done using an AXIS 165 (Kratos) XPS Spectrometer at the Alberta Centre for Surface Engineering and Sciences, University of Alberta. The base pressure in the sample analytical camber (SAC) was lower than 1×10^{-9} torr. A monochromatized Al Kα source (hν = 1486.6 eV) was used at 210 W. Survey scans spanned from binding energy of 1100 to 0 eV, collected with an analyzer pass energy of 160 eV and a step of 0.3 eV.

4.1.6 XRD Analysis

X-ray diffraction (XRD) is a technique which is able to characterize the crystallographic structure, crystallite size and preferred orientation. It is commonly used to identify unknown substances by comparing diffraction data against a database maintained by the International Centre for Diffraction Data (Ramesh, 2009).

In this study, the equipment for conducting XRD analysis was a RIGAKU Rotation anode XRD system. The X-ray source utilized in this study was Cu-Kα, and Jade software was used to identify minerals.

4.2 Test Samples and Reagents

Quartz and a metallurgical coal were used in this work. The latter represented naturally hydrophobic and floatable solid without the need of a flotation collector, while the former represented typical hydrophilic gangue mineral. The coal sample was prepared by blending 10 kg of G1-20 with 20 kg of Q1-4, both of which were from Elk Valley Coal, Teck Metals Ltd. The blended coal sample contained 1.6% moisture, 9.8% ash and 26.1% volatile matter. The coal sample was dry ground by a mild steel ball mill, and the -300 μm size fraction from the ground sample was screened out for flotation tests. To change its hydrophobicity, the coal sample was heated at 180 ℃ in an oven.

Quartz with two different particle sizes, -15 µm (90% passing 10 µm, 98% SiO_2) and -90 µm (80% passing 45 µm, 98% SiO_2), were used in the experiment as the hydrophilic gangue mineral. Both quartz samples were purchased from U.S. Silica. Artificial mixtures of coal and quartz were prepared by blending, at a weight ratio of 1:1, the -15 µm quartz with coal sample that was heated at 180 ℃ for 4 h. Figure 4.6 shows the X-ray diffraction patterns of the quartz sample. The narrow XRD peaks indicated the presence of the highly crystalline quartz.

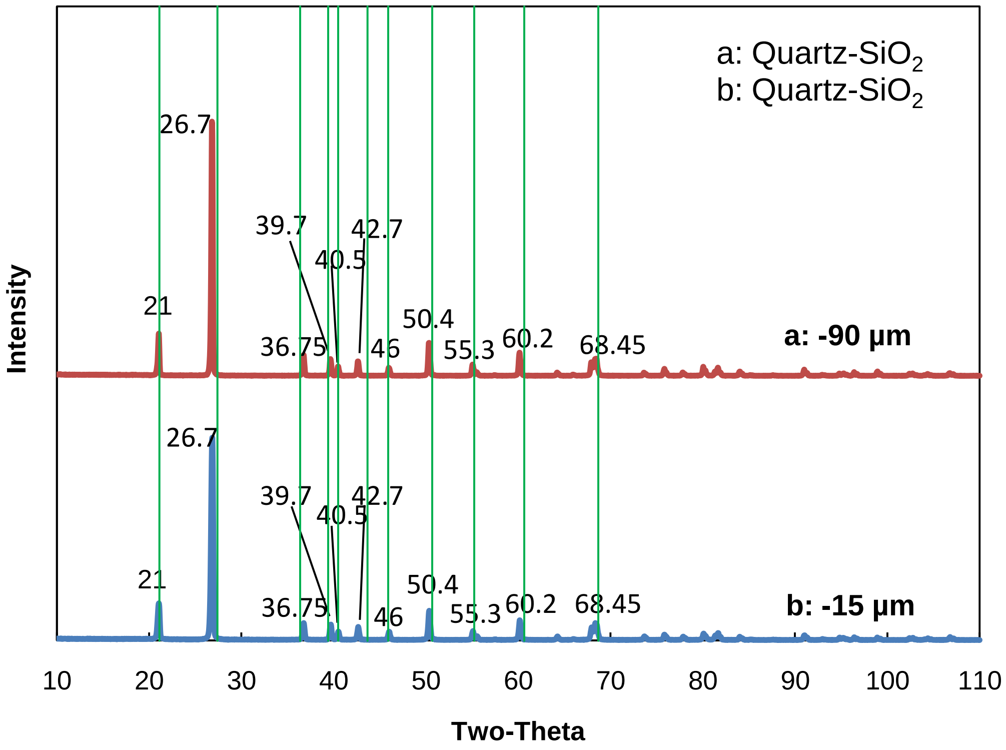


Figure 4.6 X-ray diffraction patterns of quartz with two different particle sizes: a. -90 μm; b. -15 μm. The thin vertical blue lines show the peak positions of pure quartz from the Jade database.

Polyethylene oxide (PEO), with a specified molecular weight of 8 million, was obtained from Polysciences, Inc. The PEO stock solution was prepared by slowly sprinkling 0.1 g PEO onto the stirring vortex of 100 mL distilled water. The stirring was continued for 10 min after the powder was completely mixed with water. The 0.1% stock PEO solution was added to mineral slurry under agitation at about 1 mL/min using a syringe.

Dowfroth 250 (DF250) from Dow Chemical Canada Inc was used as a frother. It was used directly without dilution and was added by a syringe.

5. RESULTS AND DISCUSSION

5.1 Effect of Oxidation on Hydrophobicity of Coal

5.1.1 Heating time

Coal can be oxidized when exposed to air. When oxidation happens, coal becomes less hydrophobic due to the hydroxyl groups formed on the surface, which results in lower recovery in flotation. Therefore, in this study, the coal was oxidized deliberately to change its hydrophobicity (and floatability) to examine its effect on the froth recovery – air recovery correlation.

Figure 5.1 shows the effect of heating time on the floatability of the coal sample and the oxygen/carbon ratio on the coal surface. The coal sample was heated at 180 ℃ for different time periods. As can be seen, the floatability of the untreated coal sample was almost 100%. The floatability progressively dropped with increasing heating time at 180 ℃. After heating for 10 hours, the floatability was reduced to around 20%. As the flotation tests were conducted with no frother and no collectors, and all samples with the same particle sizes, the decrease in floatability reflects a decrease in the surface hydrophobicity of the coal samples.

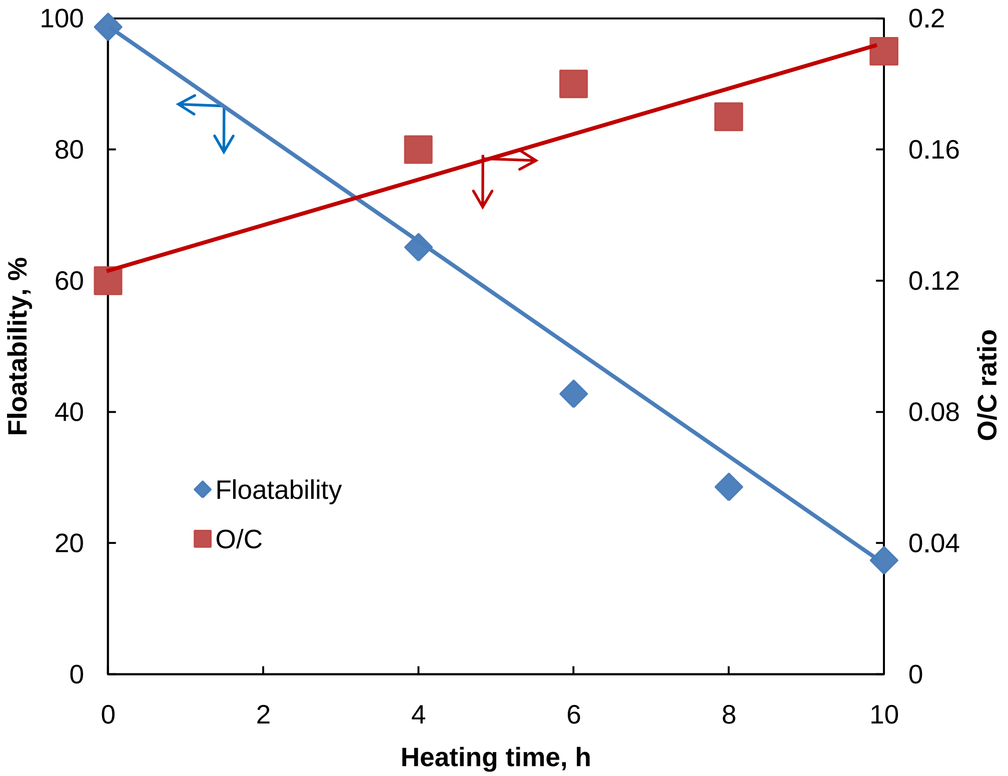


Figure 5.1 Floatability and O/C ratio of coal samples with different lengths of heating time. Micro-flotation tube; Solids: 1.5 g; Water: 150 mL; Flotation time: 1 min.

5.1.2 XPS Analysis

X-ray photoelectron spectroscopic (XPS) analysis of the coal samples identified only two peaks, corresponding to C and O (Figure 5.2). The intensities of the two peaks changed with different lengths of heating time. From the peak intensities, the relative atomic concentrations of the surface C and O were calculated and tabulated in Table 5.1 and plotted in Figure 5.1.

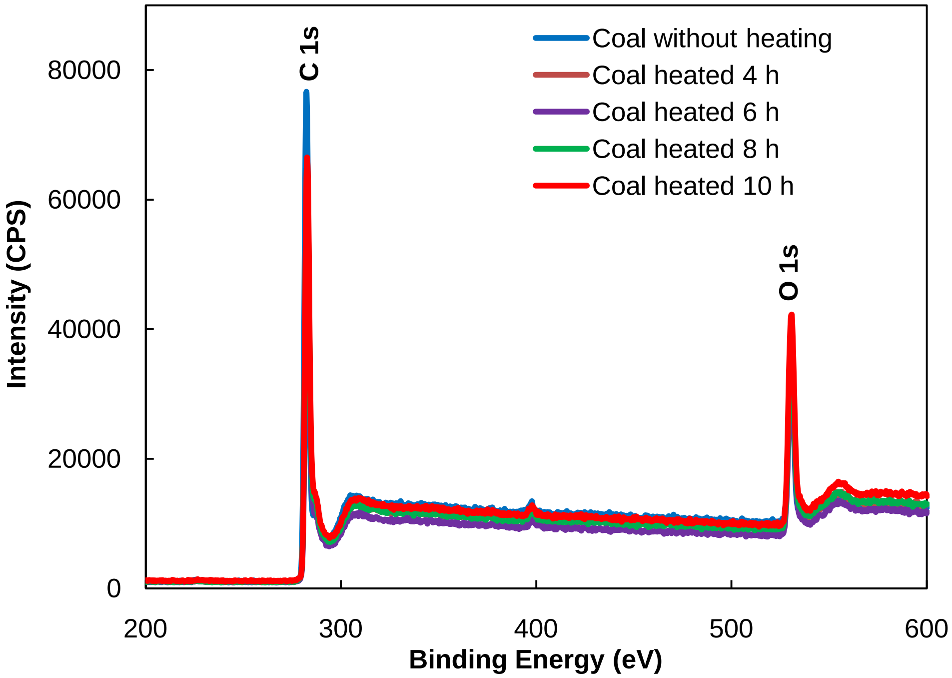


Figure 5.2 XPS analysis of coal with different lengths of heating time

As can be seen, the atomic concentration of oxygen on the surface was increased with increasing length of heating time. And so was the oxygen/carbon ratio (Figure 5.1). The higher oxygen concentration at the coal surface was probably the result of oxidation products, such as carboxylic acids, from the oxidation of coal hydrocarbons.

Table 5.1 Atomic concentrations of oxygen and carbon on the surface of coal samples

	Atomic Conc of O1s, %	Atomic Conc of C1s, %	O/C
Coal without heating	10.58	87.8	0.12
Coal heated 4 h	13.85	84.63	0.16
Coal heated 6 h	15.03	83.44	0.18
Coal heated 8 h	14.48	84.24	0.17
Coal heated 10 h	15.5	83.16	0.19

5.2 Froth Recovery-Air Recovery Correlation

5.2.1 Solid Hydrophobicity

Figure 5.3 shows the variation of froth height before and after loading conditioned mineral slurries from the top of froth phase. As can be seen, the froth height (of the two-phase froth) was at a relatively low level (around 10 cm) before loading the minerals. The froth layer rose continuously as slurries were added into the flotation column. Two minutes after loading the minerals, the froth would stabilize at a new level that was called the equilibrium froth height. It can be seen from Figure 5.3 that the equilibrium froth height was progressively lower for less hydrophobic solids.

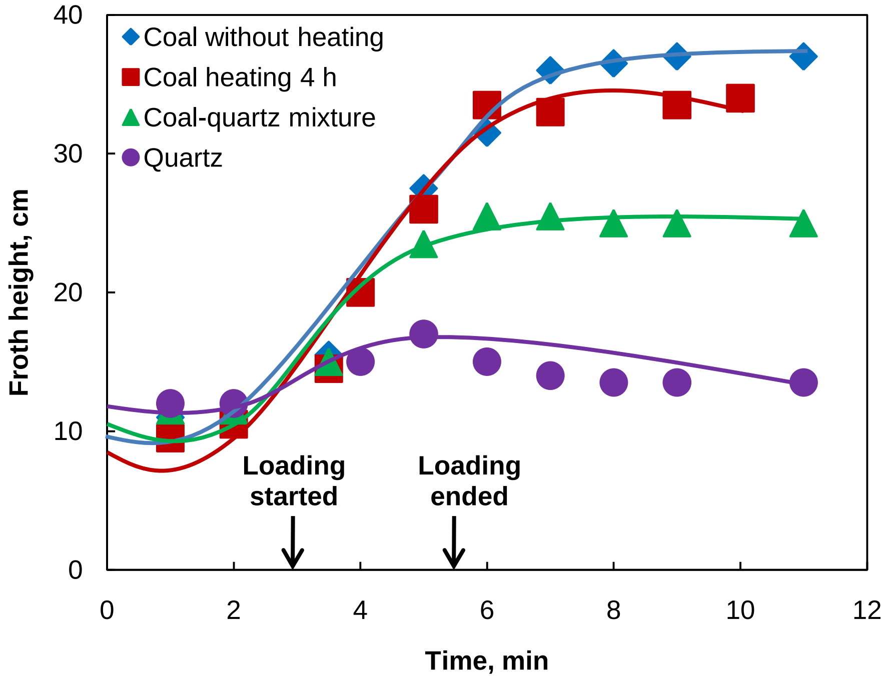


Figure 5.3 Effect of solid's hydrophobicity on froth height. Solid concentration: 8.0%. Impeller speed: 1000 rpm; DF250 concentration: 98 mg/L; Superficial air rate: 1.06 cm/s.

Figure 5.4 shows the correlation between froth recovery and air recovery of the coal samples tested. The froth recovery and air recovery were determined using method described in Section 4.1.1. As can be seen, there was a near linear relationship between froth recovery and air recovery, and the un-oxidized coal (more hydrophobic) had a steeper slope than the oxidized coal, i.e., the froth recovery of un-oxidized coal increased faster with increasing air recovery. For instance, at an air recovery of 40%, the froth recovery of un-oxidized coal was around 60%, whereas that of the coal heated for 4 hours was less than 40%.

One interesting feature of Figure 5.4 is that the lines do not extrapolate to the origin, and the (extrapolated) intercept at zero air recovery was higher for the sample that contained more hydrophobic solids (higher both in the degree of hydrophobicity and the quantity of hydrophobic solids), except for the pure quartz. That is, at very low air recovery, the froth recovery was much higher than air recovery and the difference was larger for more hydrophobic solids. This probably signifies that the solid particles were stratified in the froth layer, with the hydrophobic particles enriched at the top part of the froth phase.

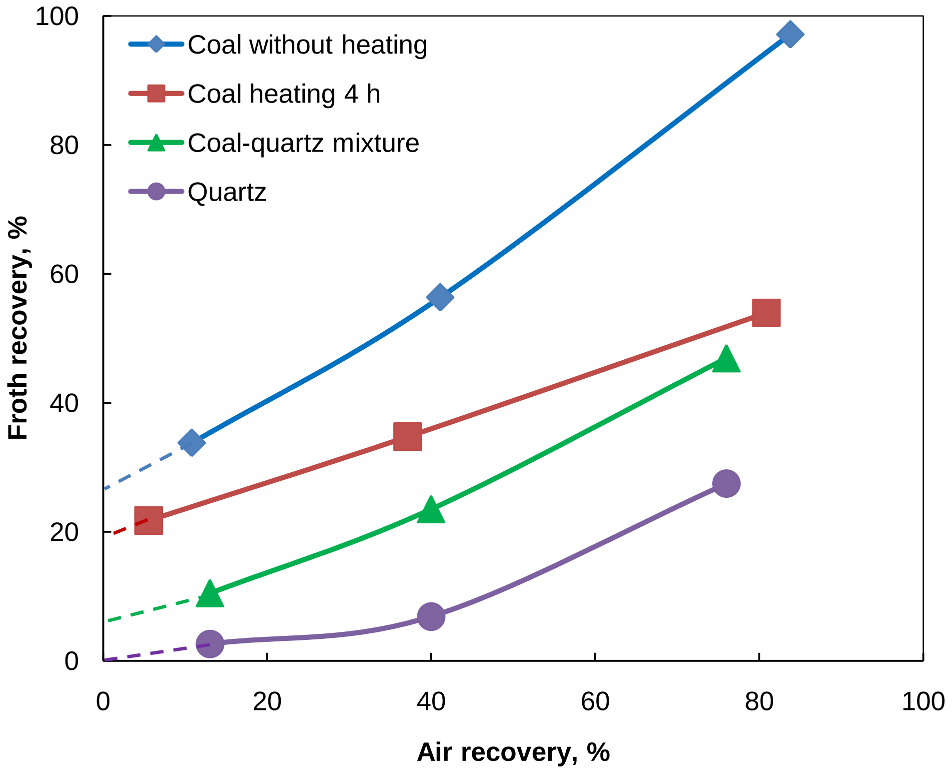


Figure 5.4 Froth recovery – air recovery correlation for different coal samples tested. Solid concentration: 8.0%. Impeller speed: 1000 rpm; Frother concentration: 98 mg/L; Superficial air rate: 1.06 cm/s; Flotation time: 4 min.

The stratification behavior was verified by the results shown in Figure 5.5, for a 1:1 coal:quartz mixture. The carbon content, an indication of hydrophobic organic particles in coal, was found to increase in solid samples collected from bottom to the top of the froth layer. While the total froth height was 44 cm, the carbon content of the solid sample collected in the top 16 cm was close to the carbon content of the oxidized coal, which suggested that solids in this region are mostly the hydrophobic organic phase. Conversely, the ash content followed an opposite trend, with the highest ash content observed close to the pulp/froth interface. Therefore, the hydrophilic particles are most likely to stay in the lower region of the froth phase.

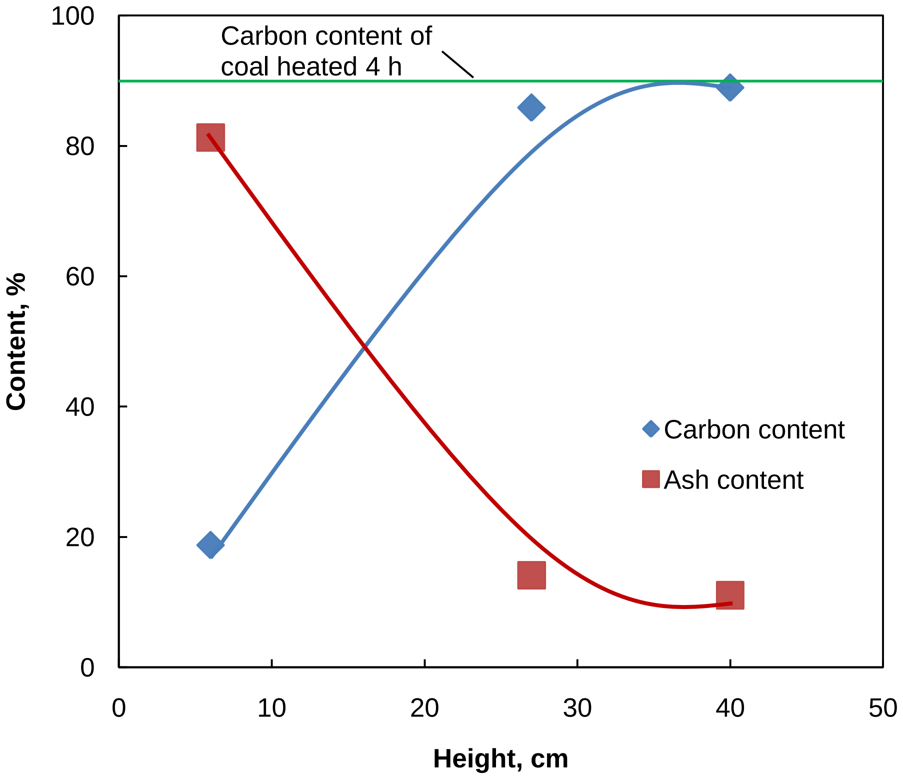


Figure 5.5 The distribution of hydrophobic/hydrophilic solids in froth phase. Sample: coal-quartz (1:1). Solid concentration: 8.0%. Impeller speed: 1000 rpm; DF250 concentration: 98 mg/L; Superficial air rate: 1.06 cm/s.

Based on the established relation between froth recovery and air recovery, the amount of solids contained in the entire froth phase was calculated for each coal sample by extrapolating froth recovery to 100% air recovery, and the results were plotted in Figure 5.6. As can be seen, the total amount of solids in the froth phase progressively reduced with the decrease of solids' hydrophobicity. For the most hydrophobic particles, the raw coal, the amount was over 200 g, while for the less hydrophobic particles (i.e., the oxidized coal and the coal:quartz mixture), the amount was much less (note that a total of 240 g of solids were used in each test). This suggested that hydrophobic particles were mostly retained in the froth phase, but the hydrophilic particles passed through the froth layer and dropped to the pulp phase.

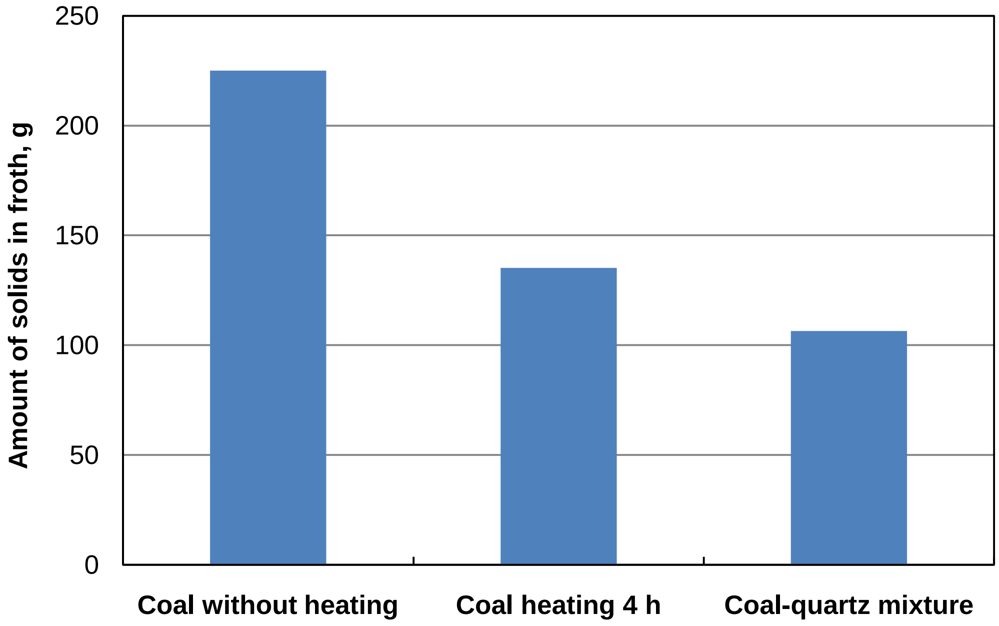


Figure 5.6 Amounts of solids in froth layer for three coal samples. Solid concentration: 8.0%. Impeller speed: 1000 rpm; DF250 concentration: 98 mg/L; Superficial air rate: 1.06 cm/s.

5.2.2 Effect of Air Flow Rate on Equilibrium Froth Height

Air flow rate has two contradictory effects on froth stability. On one hand, high air flow rate can generate more bubbles, which increase froth height and further enhance froth recovery. On the other hand, high air flow rate enlarges bubble size that leads to higher bubble burst rate and lower froth recovery. To find out if it is possible to enhance the recovery of coal by changing air flow rate, especially for oxidized coal (less hydrophobic), flotation tests were conducted on three different coal samples at different air flow rates.

Figure 5.7 shows how the air flow rate affects equilibrium froth height for the three different feed solid samples. As can be seen, the equilibrium froth height was lower for solids feed with lower hydrophobicity at both air flow rates. Also, a much higher equilibrium froth height could be achieved at the higher air flow rate (15 L/min).

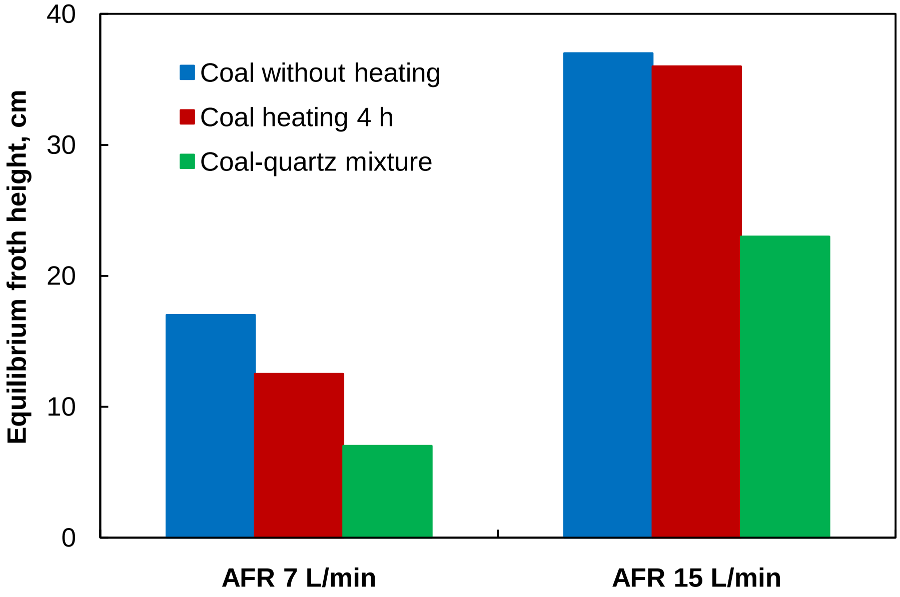


Figure 5.7 Effect of air flow rate (AFR) on equilibrium froth height for three tested coal samples. 3.0 L flotation cell. Solid concentration: 8%; Impeller speed: 1000 rpm; DF250 concentration: 98 mg/L.

5.2.3 Effect of Air Flow Rate on Coal Recovery-Air Recovery Correlation

Figure 5.8 shows the effect of air flow rate on the correlation of coal recovery and air recovery. The coal sample heat treated for 4 hours at 180 ℃ was used. The reason to use this coal sample was because it was not very hydrophobic, and could be used to find out if the flotation recovery of such a coal could be improved by changing froth properties. Two air flow rates, 7 L/min and 15 L/min were tested. As can be seen from Figure 5.8, at air recoveries lower than about 30%, an increase in air flow rate from 7 L/min to 15 L/min caused an increase in the froth recovery of the organic phase, with almost a parallel increase in ash recovery. The parallel increase in ash recovery was probably caused by entrainment and not due to poor liberation as better separation was observed at an air recovery of about 60% at the air flow rate of 7 L/min (Figure 5.8). At higher air recoveries (> 40%), the increase in air flow rate did not improve the froth recovery of the organic phase, but only caused an increase in ash recovery. As air recovery in commercial flotation circuits are usually very low, usually below 15% (Barbian et al., 2007), it seems logical to increase air flow rate in order to increase the recovery of the organic phase. The increased ash recovery, i.e. entrainment, needs to be dealt with.

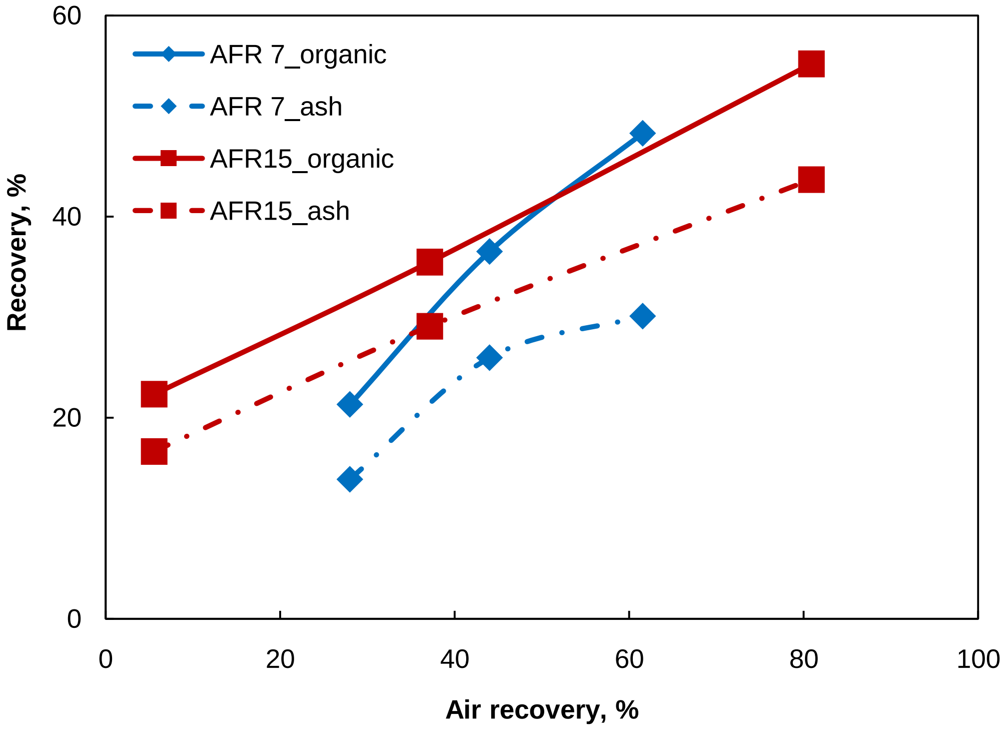


Figure 5.8 Effect of air flow rate (AFR) on organic recovery and ash recovery. Sample: coal heated for 4 h. Solid concentration: 8%; Impeller speed: 1000 rpm; DF250 concentration: 98 mg/L; Flotation time: 4 min.

5.2.4 Summary

1) There was a near linear relationship between froth recovery and air recovery for the different coal samples tested. Higher coal recovery could be obtained at high air recovery.

2) The results indicated that the particles were stratified in the froth layer in the batch flotation tests. The hydrophobic particles were mostly concentrated at the upper region of the froth layer, and the hydrophilic particles were mostly

concentrated at the lower part of the froth layer.

3) The froth recovery was positively related to solids hydrophobicity (both in the degree of hydrophobicity and the amount of hydrophobic solids).

4) The equilibrium froth height of more hydrophobic particles was higher than that of less hydrophobic ones, and it progressively increased with increasing air flow rate.

5) At low air recovery (< 30%), high air flow rate could enhance recovery of organic phase, with parallel increase in ash recovery; at high air recovery (> 40%), increasing air flow rate did not seem to affect recovery of organic phase, while ash recovery would increase significantly.

5.3 Effects of Wash Water and Polyethylene Oxide on Quartz Entrainment

5.3.1 Effect of Particle Size

In this project quartz was tested as a typical “ash phase” mineral to study its entrainment behavior in the hybrid mechanical flotation column. Two quartz samples, with sizes of -90 µm and -15 µm, were tested. The flotation tests were conducted following the procedures described in section 4.1.1, with the addition of DF250 as a frother. The flotation results of the two quartz samples are presented in Figure 5.9, in which the entrainment rate of the quartz, i.e., the ratio between quartz recovery and water recovery, is shown for the two quartz samples. It can be seen that the entrainment rate of fine particles (-15 µm) was much higher than that of coarse particles (-90 µm). This phenomenon was reasonable since large hydrophilic particles could easily drain from the intervening water films of bubbles due to their large masses and high inertia. While the fine hydrophilic particles were kept highly dispersed in the water films, even the froth draining behavior could not carry them down. And that is why the entrainment of fine particles is always an intractable issue in mineral flotation.

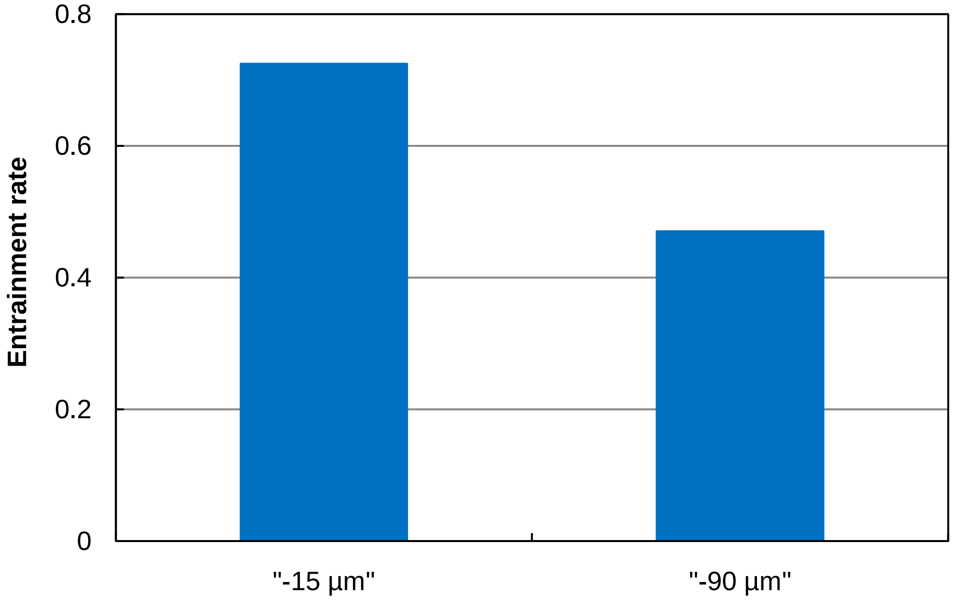


Figure 5.9 Effect of particle size of quartz on entrainment rate. 3 L flotation cell. Solid concentration: 8.0%; Impeller speed: 1000 rpm; Frother concentration: 0.6 mL (131 mg/L); Superficial air rate: 0.62 (9 L/min); Flotation time: 2.5 min.

5.3.2 Superficial Wash Water Rate

Wash water may be used to lower the entrainment of the fine quartz from the hybrid flotation column. However, a potential problem during froth washing was that the water recovery could increase if there was no positive bias wash water, which could cause higher entrainment. To ensure that the addition of wash water would not cause an increase in the pulp/froth level and water recovery, an outlet was drilled on the side of the flotation cell at the pulp/froth interface to maintain the level (Figure 4.3).

Figure 5.10 shows the water recovery at different superficial wash water rates (i.e., the volumetric flow rate of wash water divided by the cross sectional area of the flotation cell) with the drilled water outlet. As can be seen, the water recovery was constant at different superficial wash water rates. The constant water recovery into the froth product at different superficial wash water rates indicates that there was a positive downward bias water flow when wash water was used.

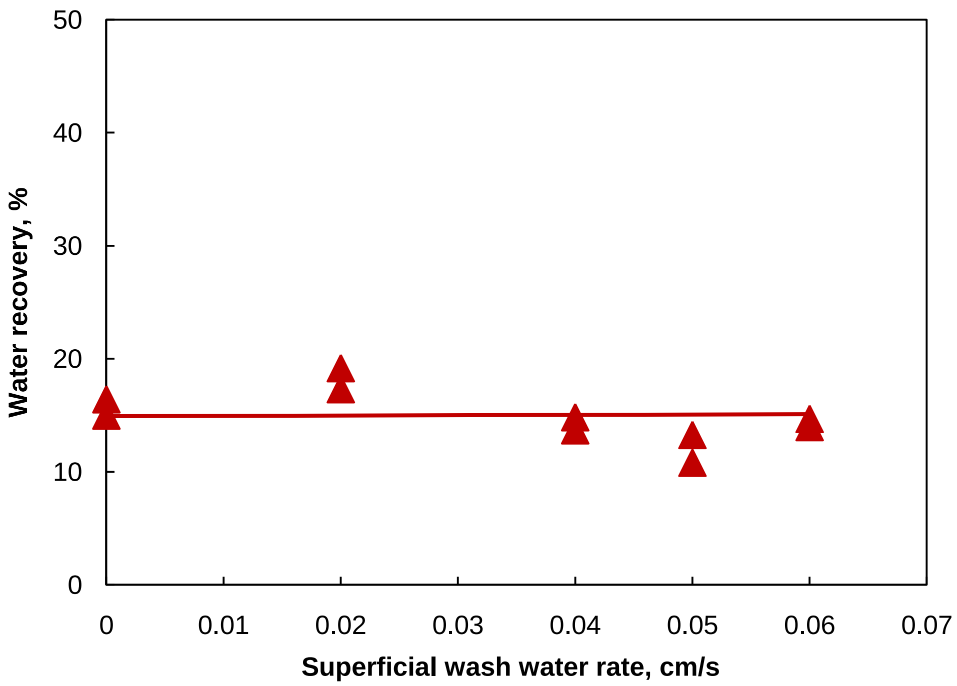


Figure 5.10 Water recovery at different superficial wash water rate. 3 L flotation cell. Solid concentration: 8.0%; -15 µm quartz; Impeller speed: 1000 rpm; Frother concentration: 0.6 mL (131 mg/L); Superficial air rate: 0.62 cm/s (9 L/min); Flotation time: 2.5 min.

Figure 5.11 shows the effect of superficial wash water rate on the entrainment of the two quartz samples. As can be seen, the wash water did not have any effect on the entrainment of the -90 µm quartz, and its recovery into the froth product stayed at about 6% within the superficial wash water flow rate range tested (up to 0.05 cm/s). On the other hand, the entrainment of -15 µm quartz was reduced by the wash water, especially at the superficial wash water rate of 0.05 cm/s. At this water flow rate, the quartz recovery dropped to 4.6% from about 13% when no wash water was used. While at higher superficial wash water flow rate, the entrainment of the -15 µm quartz started to increase, which suggested that too much wash water had an adverse effect on entrainment. In fact, the absolute weight of floated froth products at different superficial wash water rates decreased with increasing wash water initially and then started to increase at superficial wash water rate of 0.05 cm/s (Table 5.2). The results of Kaya (1989) on the effect of wash water flow rate were also plotted in Figure 5.11 and as can be seen the trend was the same, although the optimum superficial wash water rate was higher at 0.06 cm/s in Kaya’s case.

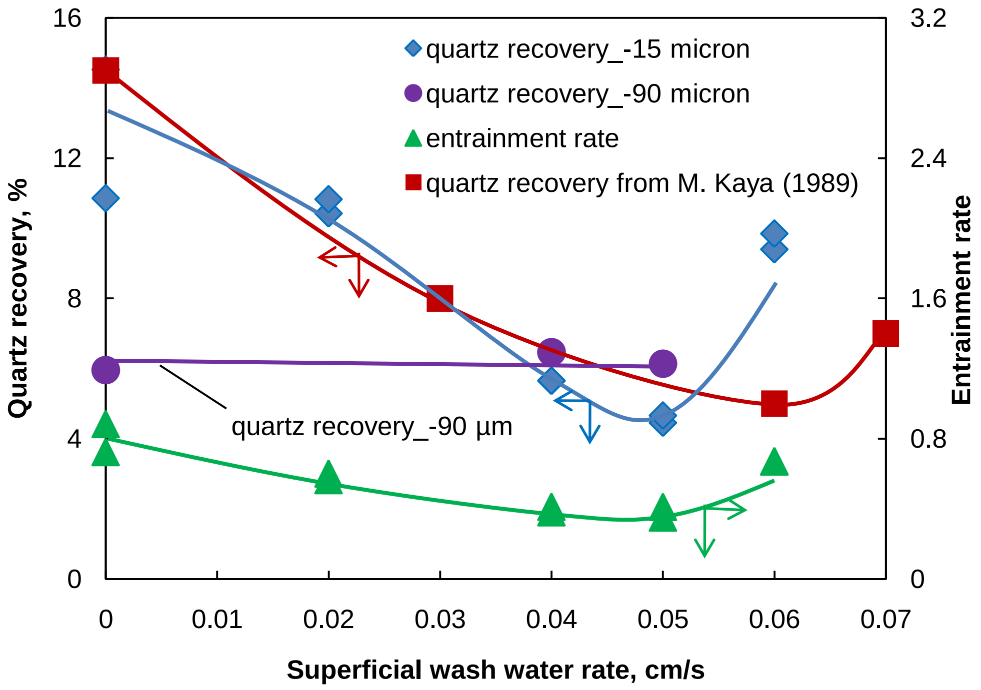


Figure 5.11 Effect of superficial wash water rate on quartz recovery and entrainment rate. 3 L flotation cell. Solid concentration: 8.0%; -15 µm quartz; Impeller speed: 1000 rpm; Frother concentration: 0.6 mL (131 mg/L); Superficial air rate: 0.62 cm/s (9 L/min); Flotation time: 2.5 min.

Table 5.2 The amount of froth products at different superficial wash water rates

wash water rate cm/s	0	0.02	0.04	0.05	0.06
froth product 1, g	25.5	22.8	9.2	7.5	15.7
froth product 2, g	33.3	25.6	10.3	7.4	16.3

5.3.3 PEO Dosage

As has been shown in Figure 5.9, coarse particles had lower entrainment. Also, Figure 5.11 shows that the entrainment of coarse quartz particles was unaffected by wash water, probably because it was already sufficiently low. It was reasoned that a polymer depressant could be used to enlarge the particle sizes of the quartz, lowering entrainment without using wash water. In fact this concept was described earlier by Liu et al. (2006) and Gong et al. (2010). Thus polyethylene oxide (PEO) was used for this purpose. Figure 5.12 shows the effect of PEO dosage on quartz entrainment with and without the addition of wash water. As can be seen, the addition of PEO without wash water could reduce the quartz entrainment. Without PEO, quartz recovery was about 15%. At a PEO dosage of 4 mg/L, the quartz recovery was reduced to about 5%, which was very close to the lowest quartz recovery when wash water was added at the optimum superficial wash water rate of 0.05 cm/s (Figure 5.11). This result indicated that PEO had the similar function as wash water on alleviating quartz entrainment. Quartz recovery increased at PEO dosage above 4 mg/L, which might be due to the frothing property of PEO. Additionally, it is interesting to note that the entrainment rate of quartz at PEO dosage of 4 mg/L was 0.46, which was the same as the entrainment rate of the coarse quartz (-90 µm), i.e., 0.47 (Figure 5.9). This indicated that the sizes of the fine quartz were indeed enlarged by the addition of PEO.

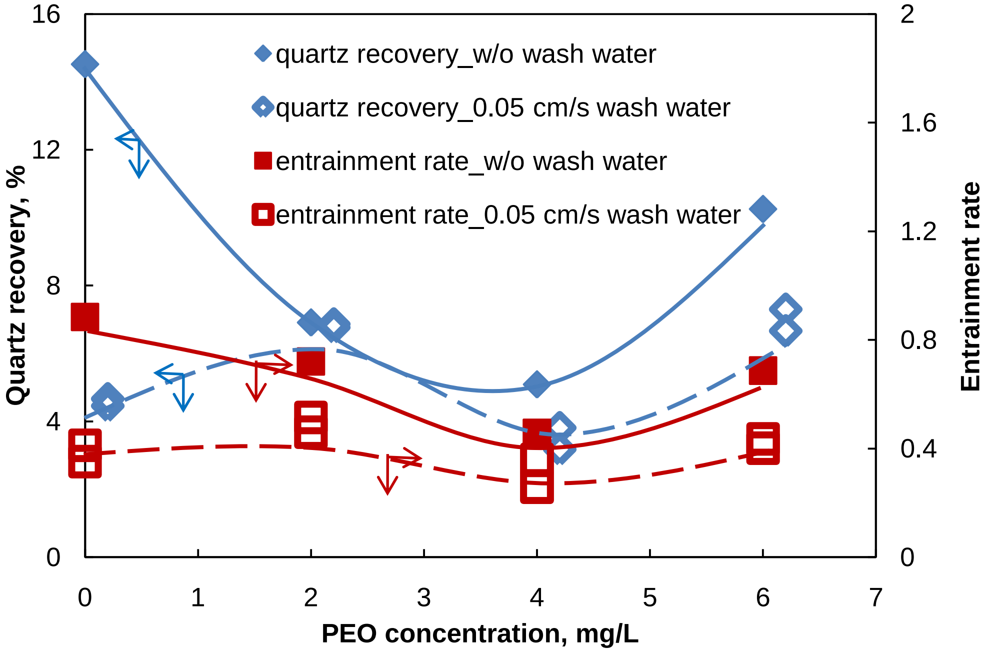


Figure 5.12 Effect of PEO dosage on quartz recovery and entrainment rate in quartz entrainment with and without the addition of wash water. 3L flotation cell. Solid concentration: 8.0%; -15 µm quartz; Impeller speed: 1000 rpm; Frother concentration: 0.6 mL (131 mg/L); Superficial air rate: 0.62 cm/s (9 L/min); Flotation time: 2.5 min.

Table 5.3 Amount of froth products at different PEO dosage with and without wash water

PEO dosage, mg/L	0	2	4	6
froth product (w/o wash water), g	25.5	16.8	11.9	24.4
froth product (w/ 0.05 cm/s wash water), g	7.5	11.1	6.3	11.3
froth product (w/ 0.05 cm/s wash water) -repeat, g	7.4	11.2	5.0	12.8

When PEO was added with wash water (at a superficial wash water rate of 0.05 cm/s), the quartz recovery was reduced further compared with results when no wash water was used, although the decrease was very slight. The same was true with the entrainment rate (Figure 5.12) and the absolute weight of froth product (Table 5.3).

5.3.4 Summary

1) Quartz entrainment was higher for fine particles (-15 µm) than the coarse (-90 µm) particles. For fine particles, the entrainment rate was around 0.8, whereas for coarse particles, the entrainment rate was 0.47.

2) Within a superficial wash water rate of 0.02~0.06 cm/s, wash water was found

to reduce the entrainment of the -15 µm fine quartz. Especially at wash water rate of 0.05 cm/s, the quartz recovery was decreased by as much as about 10 percentage points. However, excess wash water caused an increase in entrainment.

3) The addition of PEO also decreased quartz entrainment. At PEO dosage of 4 mg/L, the quartz entrainment was also lowered by around 10 percentage points. But the quartz entrainment started to increase at higher PEO dosage, possibly due to the frothing power of PEO.

4) The combined use of wash water and PEO could lead to a slight further reduction in quartz entrainment. Compared to the addition of PEO without wash water, the quartz recovery in this case was further decreased by three or four percentage points on average.

5.4 Effects of Wash Water and Polyethylene Oxide on Coal-Quartz Mixture Flotation

5.4.1 Superficial Wash Water Rate

In view of the beneficial roles of wash water and polyethylene oxide (PEO) in reducing quartz entrainment, an attempt was made to use wash water and/or the addition of PEO to lower ash recovery while trying to improve coal flotation by increasing air recovery. In these tests, the heat treated coal sample (180 ℃ for 4 h) and the -15 μm quartz sample were mixed at 1:1 weight ratio and floated in the hybrid mechanical flotation column.

To study the effect of wash water, the flotation tests were conducted at a fixed air flow rate of 9 L/min (i.e., superficial air rate of 0.62 cm/s). At this air flow rate, the equilibrium three-phase froth height was 12 cm when the 1:1 coal-quartz mixture was loaded to the froth layer. Three flotation tests were carried out by setting the overflow weir bars at 4, 6.5 and 9.5 cm, respectively. Figure 5.13 shows the effect of superficial wash water rate on ash recovery at the three different overflowing weir heights. As can be seen, ash recovery at overflowing weir heights of 6.5 cm and 9.5 cm was somewhat decreased with the addition of wash water. However, the ash recovery at the overflowing weir height of 4 cm dropped significantly at the superficial wash water rate of 0.04 cm/s, then increased at higher wash water rate. The results seem to indicate that froth washing was more efficient if the froth layer was shallow and the wash water rate was not too high. This would be particularly applicable to mechanical flotation cells as the froth layers in these cells are usually shallow compared with flotation columns. This is reasonable as hydrophilic particles were concentrated at the lower region of the froth layer (section 5.2.1). Thus in mechanical flotation, wash water is more likely to act directly on the hydrophilic gangue particles and bring them downward.

As can be seen from Figure 5.14, the recovery of organic phase from the coal:quartz mixture seemed to be independent of superficial wash water rate, except for the superficial wash water rate of 0.02 cm/s. A higher organic recovery was obtained at this particular wash water flow rate, and it consistently happened at all of the three overflowing weir heights. Similarly, Figure 5.15 revealed that the separation efficiency (i.e., organic recovery minus ash recovery) of coal:quartz mixture flotation was independent of superficial wash water rate except for a significant improvement at a superficial wash water rate of 0.02 cm/s. It seems that for the hybrid mechanical flotation column used in this work, the superficial wash water rate at 0.02 cm/s is a special case which not only caused higher organic recovery at all three weir heights tested, but also led to higher separation efficiency at all of the three overflowing weir heights. However, the reason for this behavior is not clear at this point. It might be due to the froth stabilization effect at this superficial wash water rate.

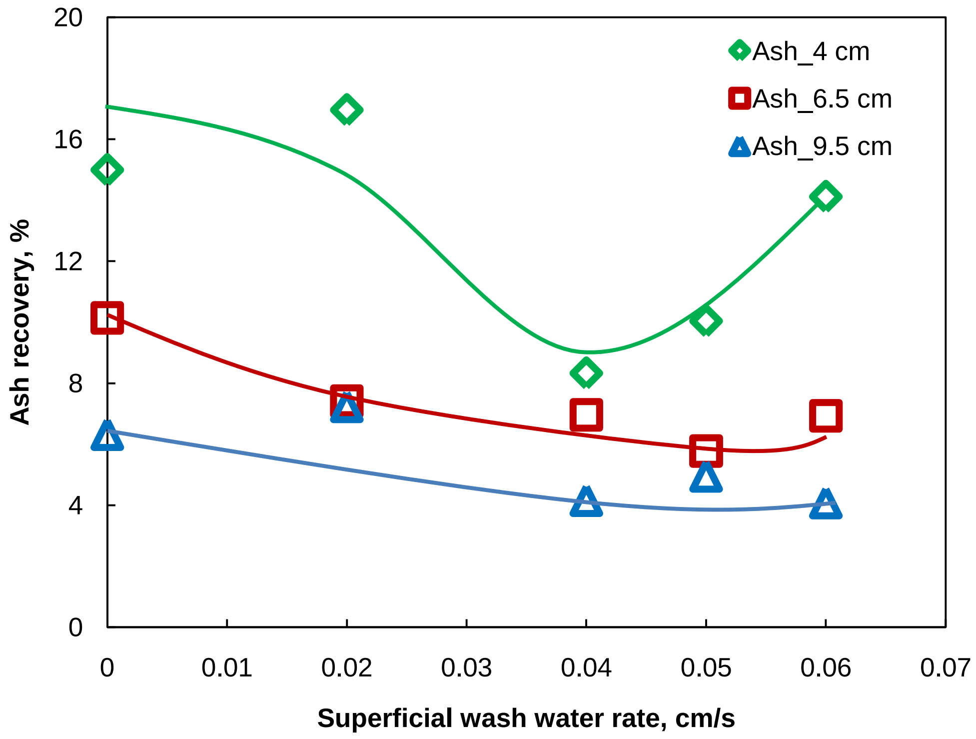


Figure 5.13 Effect of superficial wash water rate on ash recovery of coal-quartz flotation at three different overflowing weir heights. Solid concentration: 8.0%; coal-quartz. Impeller speed: 1000 rpm; Frother concentration: 0.6 mL (131 mg/L); Superficial air rate: 0.62 cm/s (9 L/min); Flotation time: 2.5 min.

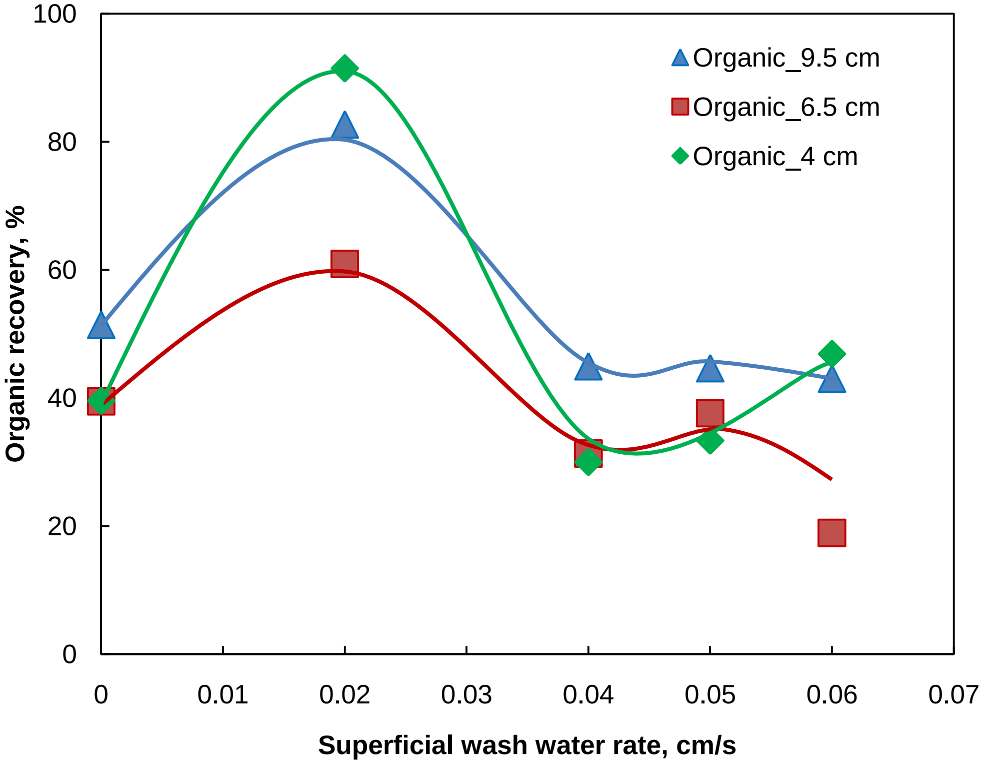


Figure 5.14 Effect of superficial wash water on organic recovery of coal-quartz flotation at three different overflowing weir heights. Solid concentration: 8.0%; coal-quartz; Impeller speed: 1000 rpm; Frother concentration: 0.6 mL (131 mg/L); Superficial air rate: 0.62 cm/s (9 L/min); Flotation time: 2.5 min.

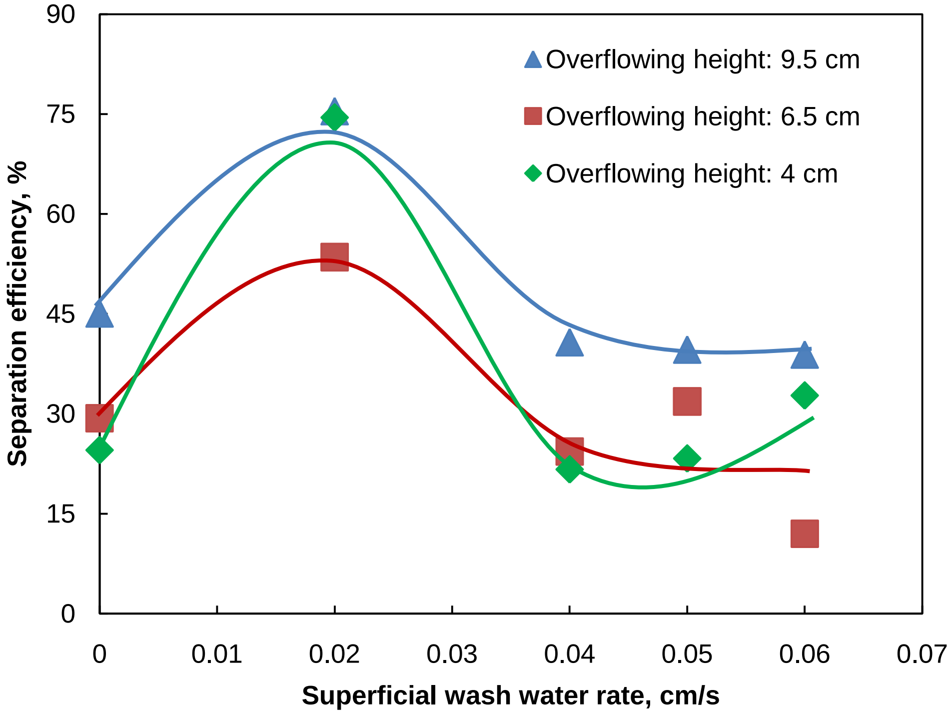


Figure 5.15 Effect of superficial wash water on separation efficiency of coal-quartz flotation at three different overflowing weir heights. Solid concentration: 8.0%; coal-quartz; Impeller speed: 1000 rpm; Frother concentration: 0.6 mL (131 mg/L); Superficial air rate: 0.62 cm/s (9 L/min); Flotation time: 2.5 min.

5.4.2 PEO Dosage

To verify the role that PEO played in the coal:quartz system, the effect of its dosage on coal:quartz mixture flotation with wash water was studied. Superficial wash water rate used here was kept identical with Section 5.3.3 for comparison, which was 0.05 cm/s. The weir height of 6.5 cm was selected in coal:quartz flotation even though the separation efficiency was much higher at 4 cm (Figure

5.15) when wash water was used alone. The reason that the 4 cm weir height was not used was because the data for the 4 cm weir height was unstable due to turbulence as the weir height was close to the pulp/froth interface. As can be seen from Figure 5.16, the organic recovery was dramatically enhanced with the addition of PEO, while the ash recovery increased slightly. The results suggested that the combined use of PEO and wash water could significantly improve the organic recovery of coal without a parallel increase of ash.

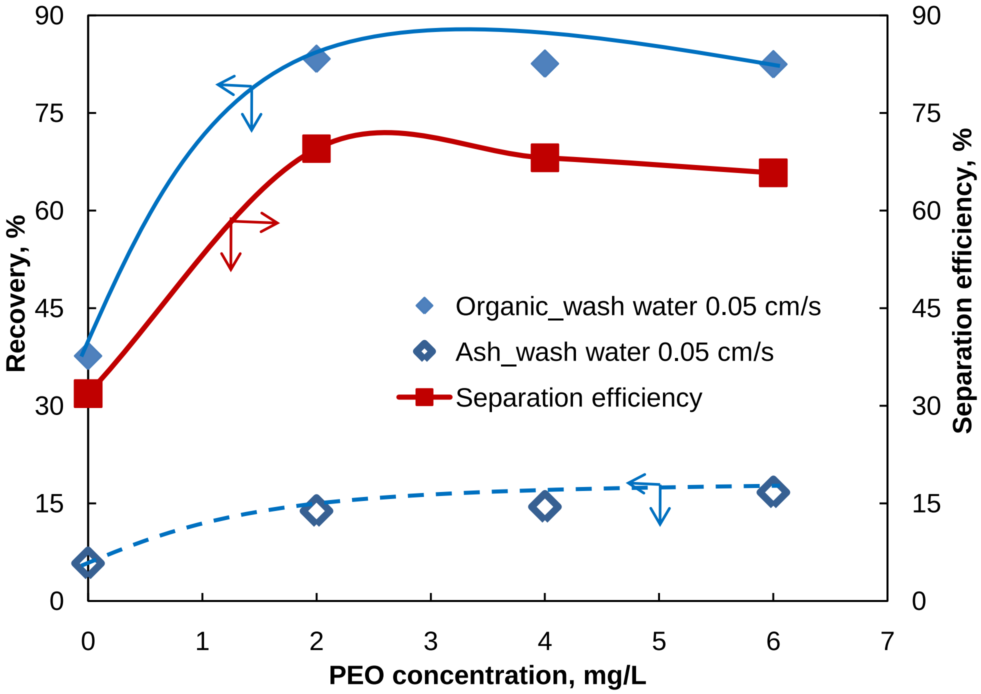


Figure 5.16 Effect of combined use of PEO and wash water on organic recovery, ash recovery and separation efficiency of coal:quartz flotation. Solid concentration: 8.0%; coal-quartz (1:1); Impeller speed: 1,000 rpm; Frother concentration: 0.6 mL (131 mg/L); Superficial air rate: 0.62 cm/s (9 L/min); Flotation time: 2.5 min; Overflowing height: 6.5 cm; Wash water superficial flow rate: 0.05 cm/s.

By taking the difference of organic recovery and ash recovery, which gives the separation efficiency, then plot it against the PEO dosage (Figure 5.16), it can be seen that the separation efficiency of coal:quartz mixture flotation was greatly improved by about 40 percentage points, from 30% without the PEO, to about 70% at a PEO dosage of 2 mg/L. While at the same overflowing weir height (6.5 cm), wash water alone only improved separation efficiency by about 15 percentage points, from 30% to about 45% (Figure 5.15).

5.4.3 Effect of PEO on Coal Recovery

According to the preceding results (Figure 5.16), the combined use of PEO and wash water was found to increase the separation efficiency of coal:quartz flotation. It is reasonable to assume that PEO played the role of increasing the organic recovery of coal, since wash water could not improve the organic recovery at the superficial wash water rate of 0.05 cm/s (Figure 5.12).

To verify this hypothesis, small scale-flotation column tests were conducted on two types of coal samples, as shown in Figure 5.17. As can be seen, the recoveries of these two coal samples were 52% and 71%, respectively, without the use of PEO. After adding PEO, the recovery of both coal samples reached close to 100%.

Therefore, the experimental results indicated that PEO had an interesting double role in the studied coal:quartz flotation system. When the coal and quartz was tested alone, PEO was able to lower the entrainment of quartz and increase the recovery of coal, both of which seemed to be the result of bridging flocculation. However, the question is: why did the PEO not cause hetero-flocculation of the coal with quartz, lowering separation efficiency? According to literature, PEO adsorbed on quartz through hydrogen bonding while it adsorbed on coal through hydrophobic bonding. It is likely that the different bonding mechanisms led to preferential adsorption of PEO on coal in the coal:quartz mixture, so that when used at starvation dosages, only coal was flocculated by PEO but not quartz.

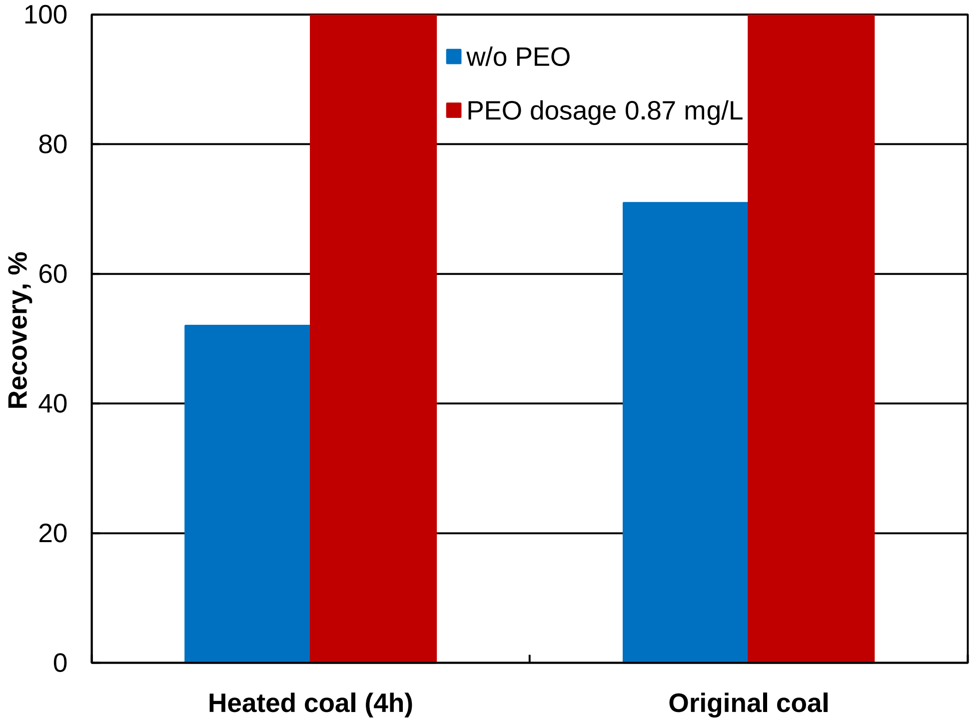


Figure 5.17 Effect of PEO on recoveries of two types of coal by micro-column flotation. Small-scale flotation column. Solid concentration: 7%; Frother concentration: 200 mg/L; Flotation time: 2 min.

5.4.4 Summary

1) The use of wash water was found to decrease ash recovery in coal:quartz system. The largest ash recovery reduction, at about 8 percentage points, was observed at the lowest overflowing weir height at a superficial wash water rate of 0.04 cm/s.

2) In the hybrid mechanical flotation column set up used in this work, wash water at the superficial water rate of 0.02 cm/s seemed to significantly improve separation efficiency of the coal:quartz mixture. Such an effect was not observed at other wash water flow rates.

3) The combined use of PEO and wash water significantly enhanced the recovery of oxidized coal with rejection of quartz. The separation efficiency was increased from 30% (without PEO) to 70% (after adding 2 mg/L PEO at a superficial wash water rate of 0.05 cm/s) in the batch flotation tests.

4) PEO was found to significantly increase the recovery of oxidized coal. After adding PEO, the recovery of oxidized coal was enhanced from 52% to 100% in small-scale flotation column tests.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 General Findings

1. Heating at 180°C was found to lower the hydrophobicity of coal samples. The longer the heating time, the lower the floatability of the coal. X-ray photoelectron microscopic analysis indicated that the oxygen/carbon atomic ratio at the coal surface increased with increasing heating time at 180 ℃.

2. Loading of conditioned -300 μm coal or -15 μm quartz samples to a stable two-phase froth led to an increase in the height of the (three-phase) froth layer. The equilibrium heights of the three-phase froth were higher for more hydrophobic solid samples.

3. By using the "relative froth height" method to determine air recovery, and by taking the overall mineral recovery as froth recovery when the conditioned mineral samples were top loaded to a two-phase froth, it was observed that there was a near-linear relationship between froth recovery and air recovery, and higher air recovery led to higher froth recovery. In addition, the lines for more hydrophobic solids are above the ones for less hydrophobic solids.

4. Samples were taken from a 1:1 mixture of -300 μm coal and -15 μm quartz at

different froth heights after the mixture was loaded to a two-phase froth layer. Total carbon analysis of the samples indicated that the solid particles were stratified in the froth layer. The hydrophobic solids (coal) were concentrated in the upper region of the froth and decreased in concentration down the depth of the froth layer. The hydrophilic solid (quartz) followed an opposite pattern of distribution.

5. Coal flotation tests performed at different air flow rates indicated that in the low air recovery range of <30%, a higher air flow rate could enhance the recovery of the (hydrophobic) organic phase. However, in the high air recovery range of >40%, increasing air flow rate did not increase the recovery of the (hydrophobic) organic phase but only increased the recovery of (hydrophilic) ash phase. This was consistent with the stratification of the solid particles in the froth layer.

6. The entrainment rate of the fine -15 μm quartz was found to be higher than that of the coarser -90 μm quartz. The corresponding entrainment rate was 0.8 and 0.47, respectively.

7. In the tested superficial wash water rate range (up to 0.06 cm/s), wash water did not change the entrainment rate of the coarse -90 μm quartz but it lowered

the entrainment rate of the fine -15 µm quartz when a positive bias was maintained. The optimum superficial wash water rate was found to be 0.05 cm/s, which lowered the quartz entrainment by about 10 percentage points, from about 14% to about 4%.

8. The addition of polyethylene oxide (PEO) was also found to lower the entrainment of the -15 µm quartz. At a dosage of 4 mg/L, the entrainment of the -15 µm quartz was reduced by about 10 percentage points, similar to the addition of 0.05 cm/s wash water. Also, the entrainment rate of the -15 µm quartz was reduced from 0.8 (without PEO) to 0.45 (4 mg/L PEO), which was the same as the -90 µm quartz without PEO. At higher PEO dosages, the entrainment rate started to increase.

9. In the batch flotation of the 1:1 coal:quartz mixture, wash water in general did not improve the separation efficiency except for a superficial wash water of 0.02 cm/s. At this particular superficial wash water rate, the separation efficiency could be increased.

10. Combined use of wash water and polyethylene oxide in the batch flotation of the 1:1 coal:quartz mixtures enabled a further increase in the separation efficiency. A 40 percentage point increase in separation efficiency was observed at a PEO dosage of 2 mg/L and a superficial wash water rate of 0.05

cm/s. The reason why PEO increased the separation efficiency by over 40 percentage points is not clear at this point. But previous researchers have reported that PEO adsorbed on coal through hydrophobic interaction. And it is widely accepted that the PEO adsorbed on quartz through hydrogen bonding. The different adsorption mechanism might have resulted in the preferential adsorption of PEO on coal but not on quartz in the coal-quartz mixture.

6.2 Recommendations for Future Work

1. Mathematical models can be developed to model the froth recovery – air recovery correlation, to better understand the behavior of the three-phase flotation froth layer.

2. The experimental facilities for conducting the flotation tests for froth phase study should be improved in the future. The current flotation system was only allowed for batch flotation. The system needs to be modified to carry out continuous flotation studies with automatic control of pulp/froth level and reagent metering.

3. The mechanism of why polyethylene oxide (PEO) improved the separation efficiency of coal flotation for ash rejection was not clear yet. Based on the results already obtained, there were several possible explanations: 1) PEO

enlarged the particle size of coal and thus increased the probability of particle-bubble interaction. 2) PEO increased the surface hydrophobicity of coal. Moreover, the interaction forces between coal, ash and PEO need to be studied.

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