



## Physical and chemical interactions in coal flotation

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### Abstract

Coal flotation is a complex process involving several phases (particles, oil droplets and air bubbles). These phases simultaneously interact with each other and with other species such as the molecules of a promoting reagent and dissolved ions in water. The physical and chemical interactions determine the outcome of the flotation process. Physical and chemical interactions between fine coal particles could lead to aggregation, especially for high rank coals. Non-selective particle aggregation could be said to be the main reason for the selectivity problems in coal flotation. It should be addressed by physical (conditioning) or chemical (promoters) pretreatment before or during flotation. Although the interactions between the oil droplets and coal particles are actually favored, stabilization of the oil droplets by small amounts of fine hydrophobic particles may lead to a decrease in selectivity and an increase in oil consumption. These problems could be remedied by use of promoters that modify the coal surface for suitable particle–particle, droplet–particle and particle–bubble contact while emulsifying the oil droplets. The role of promoters may be different for different types of coals, however. They could be employed as modifiers to increase the hydrophobicity of low rank coals whereas their main role might be emulsification and aggregation control for high rank coals. In this paper, a detailed description of the various phases in coal flotation, their physical and chemical interactions with each other in the flotation pulp, the major parameters that affect these interactions and how these interactions, in turn, influence the flotation process are discussed.

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### 1. Introduction

Conventional froth flotation for fine coal cleaning suffers mainly from two problems: (i) a lack of

selectivity for fast floating high rank coals due to the flotation of middlings and entrainment of mineral fines in the froth, and (ii) low recoveries for heavily oxidized or low rank coals due to poor adhesion between bubbles and particles. These shortcomings can be addressed appreciably by selection of better process control and by use of multi-stage flotation circuits (Olson and Aplan, 1984; Arnold, 2000), which, in turn, requires a good understanding of the roles and behavior of various components in the flotation pulp and the mechanisms involved.

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In this paper, a detailed description of the various phases in the coal flotation pulp, their interactions with each other and how these interactions affect the flotation process are discussed.

## 2. Disperse phases in coal flotation

There are three dispersed phases that constitute flotation pulp: coal particles, oil droplets and air bubbles. These phases interact in water as the medium through various sub-processes during flotation which are identified in Fig. 1. Several parameters affect these sub-processes and hence the outcome of the flotation process. These parameters are divided into four groups as illustrated in Fig. 2. These are: material, chemical, operational and equipment parameters. The parameters that might fluctuate and need adjustment on a regular basis (e.g. daily) are referred to as Level I parameters. Those that are set during the design stage or after a major renovation are referred to as Level II

parameters. Some parameters are not controlled due to inherent material characteristics and practical limitations, and they are referred to as the Level III parameters. Some examples of these parameters are listed in Fig. 2. A detailed discussion of various phases and the effect of their interactions on the flotation process are presented below.

### 2.1. Coal

Coal is defined as a heterogeneous combustible sedimentary rock formed from plant remains in various stages of preservation by processes, which involved the compaction of the material buried in basins, initially of moderate depth (IHCP, 1963) with an ash content of less than 50% (ECE-UN Document, 1991). Some other classifications of coals are also given in the literature (Lemos de Sousa et al., 1992). Three main parameters are considered in classifying coals, namely *type*, which refers to the petrographic composition, *rank*, which refers to the level of coal-

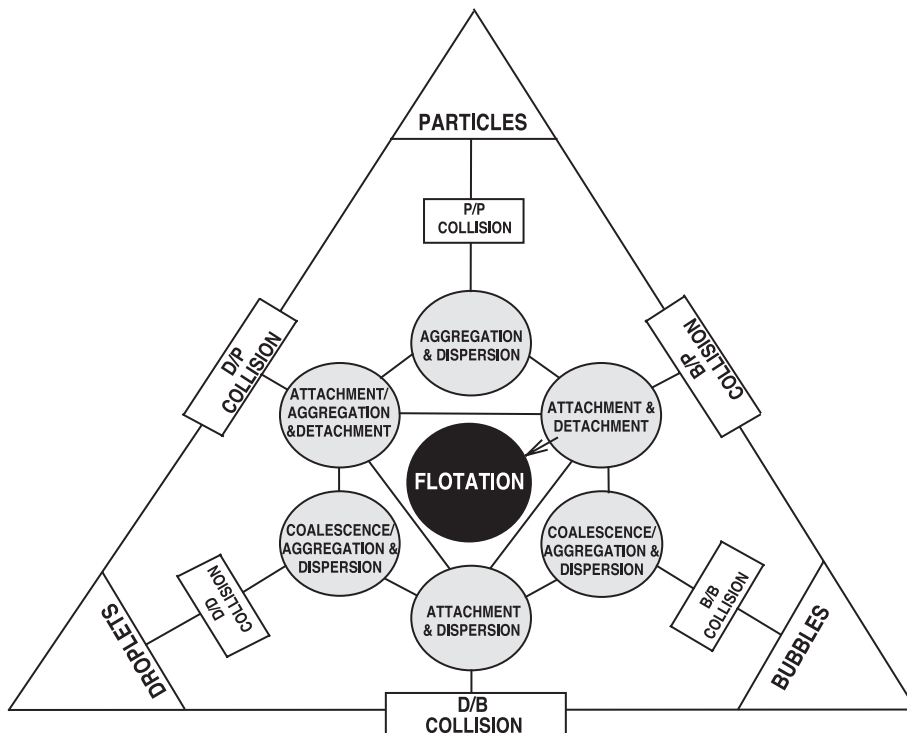


Fig. 1. A schematic representation of various sub-processes in coal flotation.

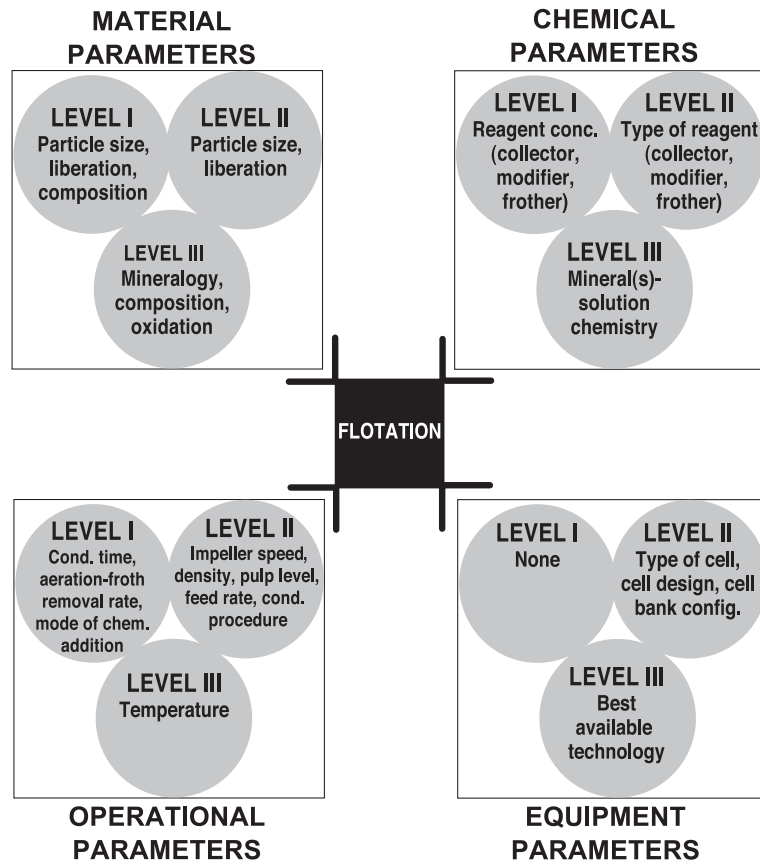


Fig. 2. Process variables in flotation.

ification, and *grade*, which refers to the amount of inorganic matter content.

Microscopically, coal has a cross-linked network structure of polymeric macromolecules as indicated by insolubility and swelling of coal in an organic solvent (Iino, 2000; Marzec, 2002). Macroscopically, it is made up of finely mixed discrete organic entities known as macerals, which fall into three main groups with different physical and chemical properties: vitrinite, exinite (liptinite) and inertinite (Jimenez et al., 1998). The bands of these macerals, which can be distinguished by naked eye, are called lithotypes. The main lithotypes are vitrain (vitrinite rich), fusain (inertinite rich), clarain (vitrinite and exinite rich) and durain (inertinite and exinite-rich). Vitrinite is the major maceral group in humic coals and contributes significantly to their behavior in

industrial processes ranging from flotation to combustion to coking.

Although differences in wetting behavior of various macerals is well recognized, the quantification of wetting behavior of a given coal sample remains a formidable task. For example, vitrain and fusain differ in elemental composition, oxygen-containing functional groups, hydrophobicity and electrokinetic behavior (Shu et al., 2002), therefore, display different degrees of floatability (Burdon, 1962; Sun and Cohen, 1969; Sarkar et al., 1984; Arnold and Aplan, 1989; Holuszko and Laskowski, 1996; Agus, 1997; Zheng, 1997). Aplan and Arnold (1986) who studied various US coals using contact angle to quantify the hydrophobicity of coal macerals found that the order of hydrophobicity from the highest to the lowest was as follows: liptinite>vitrinite>inertinite with typical

contact angles ranging from  $90^\circ$  to  $130^\circ$ ,  $60^\circ$  to  $70^\circ$  and  $25^\circ$  to  $40^\circ$ , respectively. Nearly the same ordering of lithotypes and macerals for floatability was observed in conventional and column flotation tests (Sun and Cohen, 1969; Brown, 1979; Arnold and Aplan, 1988; Kizgut, 1996; Attia, 1999; Barnwall, 2000; Hower et al., 2000). Hydrophobicity of coal depends strongly on its rank as was shown by the contact angle measurements (Gutierrez-Rodriguez et al., 1984). The captive bubble contact angle varied from  $0^\circ$  for the lignites to  $55^\circ$  for the bituminous coals, decreasing down to around  $30^\circ$  with further increase in rank to anthracite.

It should be noted however that a given coal would display a distribution of contact angles owing to its heterogeneous structure. In a recent study, Polat and Chander (1999) showed, using a modified contact angle measurement method, that the surface of a hvA bituminous coal displayed a distribution of captive bubble contact angles ranging from  $40^\circ$  to  $58^\circ$  (Fig. 3a–c). The same figure also contains the case where the contact angles are measured in the presence of a PEO/PPO block copolymer. It can be observed that adsorption of a promoter not only

changes the hydrophobicity of the surface, but it also seems to make the surface more uniform with respect to its wetting character (Fig. 3d).

### 2.1.1. Effect of the size and locking of coal particles on flotation

Many studies have been conducted to determine the effect of particle size, shape and degree of particle-locking (liberation) on coal flotation. For example, Varbanov (1984) concluded that the flotation rate depends strongly on particle size but not as much on particle shape. The particle size, where a maximum in the flotation rate and the final recovery is obtained, varies widely depending on the conditions of operation (Robinson, 1960; Rastogi and Aplan, 1985; Polat et al., 1993, 1994a,b). The flotation rate increases initially, reaches a maximum and decreases afterwards with increasing particle size. This is due to the combined effect of the collision, and attachment/detachment sub-processes, dominant in small and large sizes, respectively (Al Taweel et al., 1986). Nevertheless, the exact relationship between the particle size and flotation rate is complex and not well understood, most probably due to the aggregation of

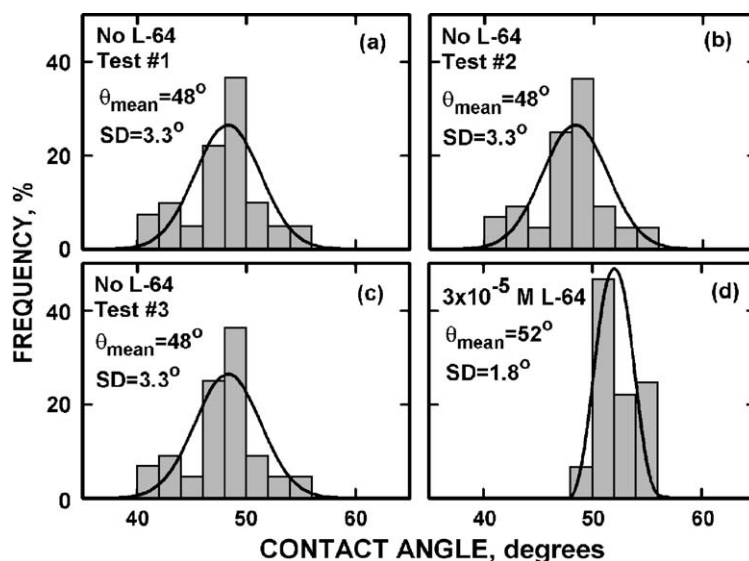


Fig. 3. The captive bubble contact angles on a hvA bituminous coal by the modified contact angle method Polat and Chander (1999). The coal sample was from Pittsburgh seam. Data in each figure correspond to a different set of contact angle measurements from 40 bubbles. Graphs a, b and c are repeat test to demonstrate the reproducibility of the method. Graph d is under identical conditions except for the presence of the block copolymer L-64.

fine particles in flotation (Chander and Polat, 1995; Chander et al., 1995). Hence, it is difficult to determine the effect of primary particle size on the rate of flotation of fine coal particles.

Interpretation of flotation results for coals where oily collectors are used require knowledge of the emulsification behavior of the oily collector and the effect of fine coal particles on emulsification process. The oily collector is introduced into an environment with many fine particles, some of which are strongly hydrophobic even for medium rank coals. Polat and Chander (1994) observed that oil droplets aggregated strongly in the presence of fine hydrophobic particles, while hydrophilic particles enhanced dispersion by preventing the coalescence of droplets through a retardation of film thinning.

The association between the organic and mineral matter in coal, which goes from merely physical association to true chemical bonding, is also important. Pusz et al. (1997) who studied the density fractions of coals using vitrinite reflectance, X-ray diffraction, FTIR and Mossbauer spectroscopy found that for low volatile coals carbonates and for high-volatile bituminous coals sulfides especially associated with organic matter. The most important impurity in coal is sulfur, which is present in the raw coal as organic, sulfatic or pyritic forms. Of these, pyritic sulfur is often the major form and, if reasonably well liberated, is the most readily removable. For successful removal of mineral matter from coal for better froth quality, these impurities must be liberated. In most cases, this could be achieved only at extremely fine sizes (Olson and Aplan, 1984).

Though the mineral particles decrease the floatability of the associated coal particles due to an increase in the particle density which leads to poor attachment efficiency and higher detachment rates, locked particles do possess a finite probability for flotation since a small fraction of hydrophobic surface is sufficient for attachment to air bubbles (Lynch et al., 1981). Within a given size fraction, the particles of lower specific gravity (relatively pure coal particles) float much faster than the locked coal–pyrite or coal–ash particles or liberated pyrite. The use of oil improves the flotation rate of particles of all sizes and specific gravities though the effect is more for the locked or mineral particles (Olson and Aplan, 1987; Polat et al., 1993, 1994a,b; Zhou et al., 1993).

### 2.1.2. Effect of the oxidation of coal particles in flotation

The oxidation of coals starts with the physical adsorption of oxygen on the surface to form an oxy-complex. Then, chemical adsorption of oxygen takes place to form polar phenolic–OH, carbonyls, phenols and peroxide type oxygenated moieties by the rupture of cyclic rings (Schlyer and Wolf, 1981; Tekely et al., 1987; Ramesh and Somasundaran, 1989; Somasundaran et al., 2000). These polar species leads to the formation of humic acids, which then degrade into soluble acids (Fuerstenau et al., 1987). Adsorption of oxygen is exothermic and, besides the moieties formed on the coal surface, such reaction products as CO, CO<sub>2</sub> and H<sub>2</sub>O may be released from the structure (Itay et al., 1989). The most susceptible linkages to oxidation were found to be the  $\alpha$ -CH<sub>2</sub> groups to polyaromatics using a variety of techniques such as FTIR, UV Fluorescence and DRIFT spectroscopy (Calemma et al., 1988; Kochi, 1973; Kister et al., 1988; Xiao et al., 1990). An interesting point on oxidation was revealed by Mitchell et al. (1996) who showed that blue-light irradiation was also a strong agent in oxidizing the vitrinite surfaces.

It was shown using contact angle, film flotation and flotation tests that oxidation of coals lowers floatability and that lower rank coals were influenced more by oxidation (Fuerstenau et al., 1983, 1987, 1994; Gutierrez-Rodriguez and Aplan, 1984; Bolat et al., 1998). The reason for the decrease in floatability is due to the generation of polar phenolic and carboxylic groups, which are known to increase the wettability and increase the surface charge, both of which are known to be detrimental to flotation (Wen, 1977). The effect could be substantial. Sarikaya (1995) reported that upon oxidation the flotation yield dropped from an initial 95% down to 24% for a bituminous coal using alcohol type frother only.

Small amounts of residual oxygen are sufficient to bring about oxidation (Korobetskii et al., 1990). Natural oxidation mainly affects the external surfaces of coal, hence, for better flotation results the size reduction must be retarded as long as possible (Fuerstenau et al., 1994). Polat et al. (1994a,b) demonstrated that upon weathering coal particles developed cracks whose extent was a function of coal rank. Low rank coal particles developed extensive cracks where as high rank coals did not seem to be affected

physically. This suggests that for low rank coals oxidation might have its adverse effect at relatively larger particle sizes due to the development of cracks which help the transfer of oxygen into interior of the particles. Formation of cracks during oxidation can also result in the production of finer particles, which may be difficult to float.

In determining the effect of oxidation on coal floatability, the behavior of the associated mineral matter, especially pyrite, should also be taken into account. Oxidation of pyrite leads to the generation of various soluble inorganics that can adsorb on the coal surface and modify its wettability while pyrite itself was reported to show improved hydrophobicity upon oxidation (Tao et al., 1994).

### 2.1.3. Effect of coal particle–promoter interactions on flotation

Promoters act as surface modifiers and may alter hydrophobicity depending on the rank of coal and promoter concentration (Laskowski, 1993; Laskowski and Miller, 1984; Laskowski and Romero, 1996; Onlin and Aplan, 1987, 1989; Chander et al., 1994, 1996; Polat and Chander, 1998, 1999; Polat et al., 1994a,b; Celik and Seyhan, 1995; Vamvuka and Agridiotis, 2001). A change in the surface properties of the coal particles affects their attachment and detachment characteristics with other dispersed phases in flotation pulp. In the flotation of low rank or oxidized coals with highly negative surfaces in the pH range of 3–5, the use of cationic promoters enhance flotation (Campell and Sun, 1970; Aplan, 1989; Zheng, 1997; Vamvuka and Agridiotis, 2001). Bustamante and Woods (1984) found that adsorption of dodecylammonium on non-polar parts of the coal surface decreased its hydrophobicity, while adsorption on the mineral matter caused an increase in hydrophobicity. On weathered coal where both the carbonaceous and the mineral matter were extensively negatively charged, dodecylammonium was adsorbed with the polar group interacting with surface and therefore all types of composite grains became hydrophobic.

Non-ionic surfactants and water-soluble polymers have been utilized to modify the coal surface (Harris, 1995). Li et al. (1992) who used a comb-like polymer found that the coal became more hydrophobic with increasing promoter concentration regardless of its

original floatability. The PEO/PPO/PEO triblock copolymers were also found to improve coal flotation and the mechanism of polymer action was a function of the coal rank (Polat and Chander, 1995, 1998, 1999; Polat et al., 1994a,b, 1997; Chander, 1997). These reagents had double effect on flotation: they modified the coal surface and also they improved the emulsification of the oily collector. For high rank coals, which usually require relatively small amounts of the collector, the surface modifier function of the polymers was dominant over their emulsifier function. The polymer increased ash rejection in flotation primarily because the coal agglomerates, which were observed in the flotation cell, were smaller and considered to be more selective. For medium and low rank coals, where larger oil concentrations were required, the polymer acted both as an emulsifier and a surface modifier. It was suggested based on the surface tension and contact angle studies that adsorption of the block co-polymers at coal/water interface occurred by adsorption of PPO groups by hydrophobic attraction on the most hydrophobic sites, and adsorption of PEO groups by hydrogen bonding on the hydrophilic sites. The coverage of the hydrophilic sites on the surface by the promoter molecules was proposed to be the mechanism by which hydrophobicity increased. For the high rank coals, which contain a relatively small number of hydrophilic sites, the polymer adsorbed on hydrophobic sites, rendering coal less hydrophobic. This was the reason for the observed increase in selectivity for high rank coals since it caused a decrease in the size of the coal agglomerates, hence, in the amounts of ash particles entrapped in the agglomerate structure.

Even though it is common practice to float coal from the associated mineral matter, several investigators have suggested the flotation of pyrite from coal with simultaneous depression of coal. Some coal depressants used in the literature are sulphhydryl collectors, natural and modified starches such as dextrans and nonionic polymers polyacrylamide and polyethylene oxide (Miller, 1973; Aplan, 1976, 1977; Moudgil, 1983). Nearly all coal depressants are also pyrite depressants at a similar or somewhat higher concentration. Several pyrite depressants have been used in the literature; oxidizing agents such as potassium dichromate and sodium hypochlorite, reducing agents such as sodium sulfide and sodium

thiosulfate, physically adsorbed colloids such as starches, various dyes such as congo red and nigrosine, dispersing agent such as sodium silicate and Aerosol OT and Quebracho, complexing agents such as citric acid and sodium cyanide, hydrolyzed ions such as various ferric and ferrous chlorides and sulfates, bacteria such as thiobacillus ferrooxidans and surface tension modifiers such as methanol and butylbenzaldehyde are some examples (Chander and Aplan, 1989). Use of such depressants assumes that the pyrite is naturally hydrophobic floats along with the bituminous material.

In a recent paper, Kawatra and Eisele (1997) concluded that pyrite floats mainly in the form of entrainment with water or in the form of locked particles with coal, not because of its inherent hydrophobicity. Their data are re-plotted in Fig. 4 to

establish various correlations. Combustible matter (CM), pyrite and ash-mineral recoveries are plotted as a function of water recovery in Fig. 4a. The data clearly shows that the selectivity follows the order: combustible matter>pyrite>ash-mineral up to a combustible matter recovery of 85–90%. For CM recoveries greater than ~ 85%, flotation of locked mineral particles is indicated. Since the slope of the curves is less one (shown by a light line) in the high recovery region, entrainment of mineral matter with water may be ruled out. These results are indicative of flotation of locked or unliberated particles, or entrapment of liberated particle with highly floating coal. For CM<85%, entrapment is the most likely mechanism where as for CM>85%, the pyrite and mineral matter might float is locked particles. This conclusion is based on the observation that the slope of the curves

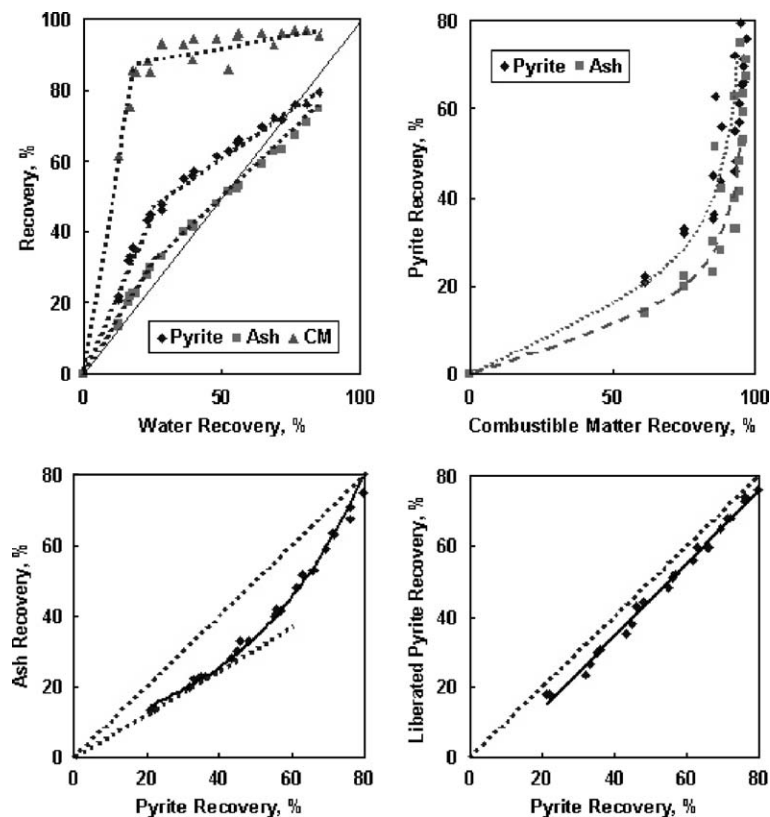


Fig. 4. Coal flotation results. The data was re-plotted from Kawatra and Eisele (1997). Top left—CM, pyrite and ash recovery as a function of water recovery. Top right—pyrite and ash recovery vs. CM recovery. Bottom left—ash recovery vs. pyrite recovery. Bottom right—liberated pyrite recovery vs. pyrite (total) recovery.

in Fig. 4b increases rapidly at CM recoveries greater than 85%. From Fig. 4b and c, one may also conclude that the pyrite has slightly higher floatability than the ash-forming minerals. These investigators also conducted a microscopic analysis to determine liberated and unliberated pyrite and their results are plotted in Fig. 4d. A linear correlation suggests that the liberated and unliberated pyrite floated similarly. The results are not surprising because the majority of pyrite seems to float under conditions where locked coal particles are floating.

## 2.2. Oil droplets

Water-insoluble hydrocarbons are widely used as collectors to increase the affinity of the coal particles towards the air bubbles. These collectors are basically non-polar oils such as kerosene, crude petroleum, fuel oil, gas oil and certain coal-tar distillates (Wojcik et al., 1990; Solov'eva and Muklakova, 1995; Petukhov, 1995). It is generally accepted that the collector disperses into droplets in the pulp and these droplets collide with, adhere to and spread on the coal particles to render them more hydrophobic. Moxton et al. (1987) observed that the effectiveness of saturated hydrocarbons in coal flotation was a function of the size of the hydrocarbon chain, dodecane giving the best results. The heavier hydrocarbons suffered from higher viscosity, leading to a decrease in their spreading ability, whereas the lighter hydrocarbons were lost in the pores of the coal structure by excessive spreading due to their low viscosity. On the other hand, Polat and Chander (1994) observed using high-speed photography that the oil droplets introduced into a flotation pulp containing a high rank coal were stabilized instantaneously by fine coal particles and produced large oil-coal aggregates. It is clear that oil in such form will not be available to carry out the functions attributed to them in the lines above. This suggests a more complex mechanism with respect to the wetting of the coal surfaces by collector droplets.

Jia et al. (2000) observed that the addition of oxygenated functional groups to the collector molecule markedly enhances the flotation of lower rank and oxidized coals. These non-ionic oxygenated promoters (THF series of ester) were more effective collectors than oily collectors for both oxidized and unoxidized coals, attaching to the coal surface through hydrogen

bonding for the oxygenated sites or hydrophobic bonding of the hydrocarbon chain for the hydrophobic carbonaceous sites on the coal. They also suggested that nonyl benzene was a better collector than dodecane for the high-sulfur coals, indicating strong interaction of the benzene ring with aromatic sites on the coal surface. Vamvuka and Agridiotis (2001) observed a superior separation when a combination of kerosene and dodecylamine were utilized.

### 2.2.1. Effect of oil droplet–promoter interactions on flotation

Size distribution of oil droplets depends on dispersion and coalescence sub-processes, which are determined by the intensity of mechanical agitation, presence of promoters and fine solid particles in the system. (Polat et al., 1999, 2000; Polat and Chander, 1994). Although promoters are commonly used in molybdenite flotation as oil emulsifiers, their use is not common in coal flotation. It was shown in full-scale industrial tests that emulsification of oil with frother resulted in a significant improvement in the overall flotation results (Laskowski, 1993; Laskowski and Romero, 1996).

Polat et al. (1999) investigated the effect of the addition of the PEO/PPO tri-block copolymeric promoters on the dispersion kinetics of oil (dodecane). Addition of promoter reduced the median oil droplet size significantly and the extent of this reduction was a strong function of promoter concentration, as can be seen in Fig. 5. The change in the median droplet size

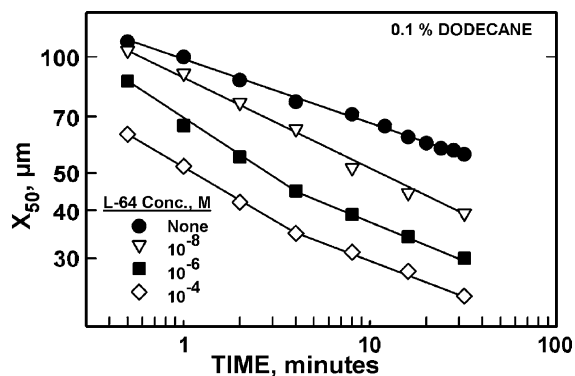


Fig. 5. Kinetics of emulsification of *n*-dodecane (0.1% by volume) at various concentrations of Pluronic L-64, a PEO/PPO/PEO tri-block copolymer.



could be divided into two distinct regions. The breakage rate was high initially, most probably due to continuous adsorption of the promoter molecules at the oil/water interface. A lower breakage rate was attained at longer times as the promoter molecules were depleted from the solution. The time of transition between the two was affected strongly by the concentration of the promoter added.

### 2.3. Air bubbles

Air bubbles are introduced into the system to capture and carry hydrophobic coal particles to the froth phase leaving hydrophilic ash minerals selectively behind. In a typical flotation cell the bubble size ranges from about 0.5 to 1.0 mm. An increasing amount of aeration air in the flotation widens the spectrum of floatability of the particles (Kalinowski and Kaula, 1997). Ahmed and Jameson (1983) have found a strong relation between the flotation rate and the bubble size. When bubble size was reduced from 655 to 75  $\mu\text{m}$ , the flotation rate increased up to 100-fold.

Adsorption of a promoting reagent at the air/water interface results in finer bubbles and a stable froth and therefore affects the collision and adhesion sub-processes. This is one of the most frequent uses of water soluble reagents in flotation (frothers). Some commonly used frothers in coal flotation are methyl isobutyl carbinol (MIBC), polypropylene glycol, methyl ethers (e.g., Dowfroth 250), phenol and cresylic acid. Laskowski (1993) argued that good frothers have branched hydrocarbon chains that make it impossible for such molecules to form close-packed (condensed) films at the liquid/gas interface. Their hydrophile–lipophile properties must be properly balanced and for most good frothers the HLB values are close to 6, which allow them to cooperate actively with the adsorbed collector in the moment of particle to bubble attachment. In addition to froth stabilization, frothers are known to reduce the induction time, hence, increase flotation kinetics.

Many commercial frothers are known to have both frothing and collecting properties. Horsley and Smith (1951) found very early that MIBC, which is not readily adsorbed by coal, has little collecting property. Recent studies have confirmed adsorption of frothers onto coals (Frangiskos et al., 1960; Klassen and

Makrousov, 1963; Jowett, 1980; Fuerstenau and Pradip, 1982; Aston et al., 1983; Gurses et al., 1992). For lignites, the adsorption increased with oxidation and decreased with demineralization, which suggests hydrophilic interactions between coal surface and the frother. For bituminous coals, the adsorption increased by demineralization and decreased by slight oxidation, which explained by hydrophobic interactions between coal surface and the frother molecule.

According to Saleh and Iskra (1997a,b), there was an optimum molecular weight of polyethylene glycol frothers to give best performance in low rank coal flotation. The better performance (i.e. high flotation rate, recovery, and selectivity) of PG 600 was attributed to its greater surface activity. The promoter–alcohol mixtures were found to float ultrafine coal at a rate three to four times faster than either pure alcohols or pure anionic promoters (Read et al., 1989). Pine oil, a mixture of terpene alcohols and hydrocarbons, was shown to be an exception to this finding; it exhibited higher rate constants than the pure aliphatic alcohols or other pure anionic promoters studied. This was explained by the fact that pine oil used acted as a frother/collector similar to alcohol/kerosene system. They also suggested that the commercially available promoter–alcohol mixtures are not as selective as pure alcohols such as 2-ethyl-1-hexanol or MIBC. Strydom et al. (1983) have also employed a promoter–alcohol mixture, sodium di-isobutyl sulfosuccinate with MIBC, and obtained the maximum recovery and grade at much lower reagent dosages than with MIBC alone.

The texture of froth is generally accepted as a good qualitative indicator as the performance of the flotation process. It was observed by Hargrave et al. (1996) during the image analysis of froth textures that the gray level of coal froth can provide significant information with respect to the flotation performance. Image analysis of froth structure was also used by Banford et al. (1998) to define a desired bubble size in the concentrate and subsequently to use measured deviations to control bubble coalescence by the compensating addition of promoters (2-ethylhexanol, Triton X-405). Holtham and Nguyen (2002) discussed the metallurgical parameters that influence surface froth appearance and the progress that has been made in image analysis of flotation froths in their paper.

### 3. Effect of water chemistry on coal flotation

The floatability of coal is also affected by the presence of dissolved inorganics in the system (Somasundaran and Liu, 1998; Somasundaran et al., 2000). In a study of the effects of different hydrolyzable multivalent ions such as Ca and Al, it was observed that the adsorption of Ca increases slightly with pH up to 8 and then sharply above that value, while that of Al exhibits a sharp increase around pH 3–5 (Celik and Somasundaran, 1986). The sharp uptake of these metal ions appears to be governed by the formation of  $\text{CaOH}^+$  and  $\text{AlOH}^{2+}$ . These results show that the adsorption of multivalent species can drastically affect the hydrophobicity of coal and depress the flotation most probably due to such surface precipitation.

It was shown using film flotation and zeta potential measurements that the maximum flotation response for coal occurs close to its isoelectric point (Fuerstenau et al., 1983; Diao and Fuerstenau, 1991). The work of Harvey et al. (2002), where the effect of electrolyte ( $\text{NaCl}$  and  $\text{MgCl}_2$ ) concentrations on coal flotation was investigated using a modified Hallimond tube, supported this observation. The floatability of coal was seen to be not entirely controlled by the electrical double layer (EDL) interactions. Coal flota-

tion in low electrolyte concentrations decreased due to other effects dominating the EDL interactions, but increased at high electrolyte concentrations most probably due to the EDL depression. Since the addition of polyvalent cations decrease the zeta potential of coal close to zero, they could be used as a flotation aid within proper concentration range.

Besides the externally added organic and inorganic reagents, coal flotation is affected also by precipitation or adsorption of the dissolved mineral species released from the coal itself during grinding and pulping (Somasundaran et al., 2000). The release of mineral ions examined as a function of pH by Liu et al. (1994). The concentrations of dissolved Fe, Al, Ca and Mg decrease as the pH increase, with the mode of alkali addition being irrelevant. This result suggests that if the pH increases during coal processing, there will be precipitation of metal ion species whereas if the pH decreases, there will be dissolution of mineral species. The authors observed a decrease in the flotation recovery to a great extent under the precipitation conditions. They argue that the hydroxide precipitate from the dissolved mineral species adsorbs on the coal surface and makes surface hydrophilic. It was concluded that the presence of these species can be controlled by manipulating the pH at different stages of processing depending on coal type.

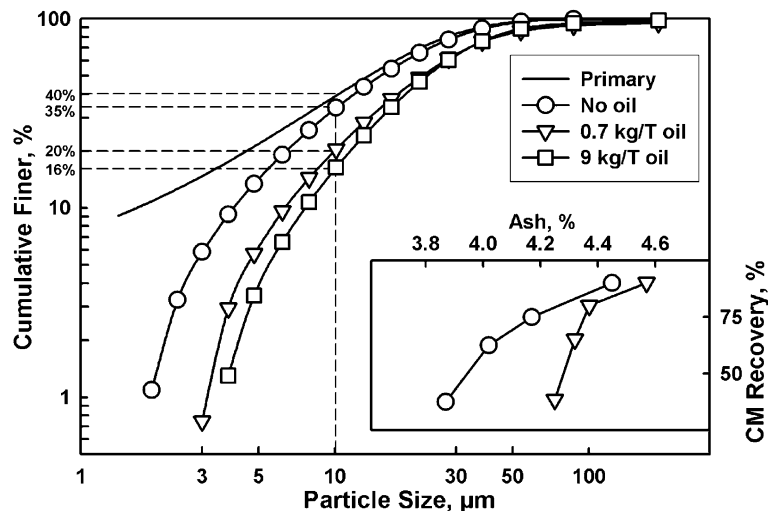


Fig. 6. The effect of oil on size distribution of particles in the flotation cell. The primary size distribution was determined by using a wetting agent to ensure particle dispersion. The inset shows the combustible matter ash recovery curves in the absence and presence of oil. The sample was a hvA bituminous coal from Lower Kittanning seam; dodecane was used as the collector; solids concentration in the pulp is 1.0%.

#### 4. Aggregation in the coal flotation pulp

Coal particles, oil droplets and air bubbles interact with each other and with water or with the promoters and dissolved inorganic species in water under a given set of flotation conditions. Though attachment between the dissimilar phases are desirable, those taking place between similar dispersed phases, such as particle/particle, droplet/droplet, bubble/bubble, are detrimental to flotation since the dispersed forms of all three phases are required for good flotation.

For example, the particle/particle interactions lead to formation of particle aggregates, which may result in a loss of selectivity due to entrapment. Aggregation among coal particles has been reported previously to occur in a flotation cell (Gaudin et al., 1942; Morris, 1952; Chander et al., 1995). The degree of aggregation increases as a function of hydrophobicity of the coal particles and the amount of the oily collector present in the system. In the flotation of high rank coals, the particles are very difficult to disperse without the use of special wetting agents and dispersants. Hence aggregation most often means entrapment of ash particles. Use of oil should only worsen the aggregation problem between the coal particles. The size, structure and composition of aggregates will therefore determine the selectivity, which is the whole purpose of coal flotation. The extent of aggregation in the flotation pulp and its effect on the selectivity is given in Fig. 6 from the data of Polat (1995). It was observed that the primary size distribution of the coal sample was much finer when the coal was dispersed using chemical and mechanical dispersion methods compared to the size distribution of the same coal in the flotation cell. The weight percent of particles, which were finer than 10  $\mu\text{m}$ , decreased from 40% to 16% when the coal was in the flotation cell in the presence of oil. For measurement difficulties the solids concentration was kept at 1.0% in this test. If the concentration of coal in the flotation pulp were around 5% as is the case in coal flotation practice, the aggregation should be expected to be much more severe. The inset graph in the same figure shows the deleterious effect of oil addition on the selectivity in relation to aggregation in the flotation pulp.

On the other hand, how the oil droplets behave in a pulp of hydrophobic particles, many of which much finer than the droplets is not well understood.

Upon introduction of oil into flotation pulp, the oil droplets are assumed to be thoroughly dispersed to collide with, attach and spread over the coal particles to render them hydrophobic. However, the facts are different. The oil droplets, with or without a pre-emulsification stage, are instantaneously covered with very fine hydrophobic coal particles and become unavailable for flotation, as was shown to be the case by high speed photography and in-situ size measurements (Polat and Chander, 1994; Chander et al., 1995). The droplets stabilized in this fashion proceed to create large oil droplet/particle aggregates with time. The exact size, shape and structure of such aggregates were observed to be a strong function of coal rank, amount of oil and other reagents in the system. Then, use of oil, especially in coal flotation, should be done with extreme care, most probably with the introduction of special high-shear conditioning tanks, preferably in the presence of promoters. In this way, both the dispersion of oil and interactions between oil droplets and coal par-

Table 1

Association between coal particles and oil droplets as a function of coal rank, oil concentration and the presence of surfactant and its effect on flotation

Rank	Particle aggregation	Recovery	Selectivity	Surfactant effect
<i>No surfactant/low oil</i>				
High	small agglomerates	high	moderate	–
Low	No agglomerates	very low	low	–
<i>No surfactant/high oil</i>				
High	large agglomerates (entrapment)	very high	low	–
Low	small agglomerates	moderate	moderate	–
<i>Surfactant/low oil</i>				
High	moderate size agglomerates	high	high	surface modifier
Low	small agglomerates	low	low	surface modifier
<i>Surfactant/high oil</i>				
High	moderate size agglomerates	moderate–high	moderate–high	modifier/emulsifier
Low	small agglomerates	high	high	modifier/emulsifier

ticles can be controlled to a better degree. Another option is to de-slime very fine coal prior to oil addition.

These interactions are responsible for the mediocre selectivity in flotation at fine sizes. The lack of control on these interactions is, in some cases, simply due to complexity of the process, but in other cases is due to a lack of understanding of how these phases behave during the flotation. Use of suitable selected promoters may increase the floatability of coal particles, prevent excessive aggregation and emulsify the oil at the same time. A qualitative picture of these interactions in the presence of low and high oil concentrations is given in Table 1 for high and low rank coals. The effect of PEO/PPO/PEO block copolymers on this picture is also included in the table as an example.

## 5. Summary

Coal flotation system is quite complex since it involves multiple phases; coal particle, oil droplet and air bubbles, along with promoters and dissolved inorganic ions in water. A good understanding of these phases and the mechanism of the interactions among them is crucial for controlling coal flotation. This paper gives a qualitative account of these aspects. To summarize it could be said that:

- (1) Coal particles aggregate in the flotation pulp. Magnitude of aggregation depends on the coal rank and, the amount of oil and the presence of promoters in the system. Aggregation to a large level is the responsible reason for the selectivity problems, which hamper coal flotation.
- (2) Assumption that oil droplets collide with and spread over the coal particles is an over simplification. In coal floatation, it is quite possible that oil droplets are immediately stabilized by fine hydrophobic particles and become unavailable for flotation, especially in the case of high rank coals. This will reduce selectivity and increase oil consumption. Hence, it is extremely important to create conditions for better particle-oil droplet contact. This can be achieved by preconditioning in high-shear environment or by de-sliming the coal prior to oil addition, both of which have been reported to enhance selectivity.

- (3) Use of promoters is an effective way of manipulating particle–particle, particle–oil droplet and particle–air bubble contacts due to the multiple actions of these reagents: modification of the coal surface, improved emulsification of the oil droplets and dispersion of the air bubbles. These effects should be considered together in designing the coal flotation process. For example, the mode of promoter addition could be as important as the type and concentration of the promoter employed.
- (4) Selection of promoters should be made with extreme care. They may be used to increase recovery for low rank coals (through improved hydrophobicity), to enhance selectivity for high rank coals (through reduced aggregation) and/or to decrease oil consumption (through emulsification action). Some promoters, such as PEO/PPO/PEO block copolymers, which possess both hydrophilic and hydrophobic groups, seem to be good candidates for achieving any of these actions when they are properly used.

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