Physicochem. Probl. Miner. Process., 54(4), 2018, 1172-1190 | Physicochemical Problems of Mineral Processing

http://www.journalssystem.com/ppmp | ISSN 1643-1049

Received May 31, 2018; reviewed; accepted July 18, 2018

The effect of particle size on coal flotation kinetics: A review

Jovica Sokolovic [1], Sanja Miskovic [2]

[1] University of Belgrade, Technical faculty in Bor, Vojske Jugoslavije 12, 19210 Bor, Serbia

[2] University of British Columbia, Norman B. Keevil Institute of Mining Engineering, Faculty of Applied Science, 508B-6350 Stores Road, Vancouver, Canada

Corresponding author: jsokolovic@tfbor.bg.ac.rs (Jovica Sokolovic)

Abstract: Coal flotation is a complex multiphase process governed by different sub-processes and interphase interactions. The coal cleaning efficiency by flotation is largely affected by many different physical and chemical factors that can be roughly classified into three main group: coal feed properties, pulp chemical and rheological properties, and machine and operational properties. A great number of flotation kinetic model have been proposed in literature but a vast majority uses three parameters to describe the flotation kinetics, which are the ultimate recovery, the flotation rate constant, and flotation time. The models expand on the classical theory of flotation proposed by Zuniga (1935) that is based on the assumption that the particle–bubble collision rate is first-order with respect to the number of particles in the system, while bubble concentration remains constant. The flotation rate constant is directly proportional to available bubble surface area and probability of flotation, which is strongly dependent on particle size. Therefore, particle size is one of the most important parameters in coal flotation because it affects gas bubble mineralization and froth stability, bubble size distribution and air holdup, bubble-particle collision, attachment, and detachment rates, and reagent adsorption. Numerous researchers have studied the effect of particle size on flotation kinetics over years. This paper provides a comprehensive review of coal flotation kinetics models with a special focus on the effect of particle size on coal kinetic rate, recovery, and product quality. A particular emphasis will be put on research findings reported over the last three decades.

Keywords: coal, flotation, kinetic, model, particle, size, review

1. Introduction

Coal is the most widely available fossil fuel and energy resource worldwide and it accounts for around 30% of primary energy and 41% of global electricity production worldwide (WEC, 2017). Despite environmental concerns, coal will still play the most important role in the energy supply until 2050 (BP, 2017) due to its abundance, relative ease of recovery, and low cost. The known coal reserves in the world are over 1140 billion tons, which is sufficient to satisfy global energy demands for more than 153 years at current rates of consumption (BP, 2017). Coal reserves reported by the World Coal Association (WCA) are significantly lower – about 860 billion tons, which is equivalent to 112 years of coal output (WCA, 2012).

Run-of-mine (ROM) coal must be processed using different technologies to achieve the desired product quality in terms of particle size and ash, sulfur, and moisture content. To produce a high quality coal with the highest economic value, a number of coal preparation technologies acting in concert have to be applied. Which coal preparation technologies are applied depend on ROM coal physical and chemical properties, such as coal rank (intrinsic ash and sulfur content) and particle size. Gravity separation technologies are commonly used for treating coarse coal. On the other hand, coal flotation is widely used to treat fine coal – typically below 0.5 mm in size (Polat et al., 2003; Bu et al., 2016) but efficient coal cleaning of coarser particles (-1 mm) have also been reported in literature (Brozek and

DOI: 10.5277/ppmp18155

Mlynarczykowska, 2013). According to Laskowski et al. (2010), the maximum particle size the feed coal can have to be considered highly floatable is generally about 28 mesh (0.589 mm).

Some of the first laboratory studies reporting the application of froth flotation to clean coal date back to 1915 (Lynch et al., 2007). The first coal flotation circuit was developed and applied in the United Kingdom in 1920, while the first coal preparation plant utilizing flotation in the USA was established in 1930 (Aplan, 1999; Parekh, 2000). Nowadays, flotation process is widely applied in many different countries, such as China, USA, Australia, Canada, and India (Aksoy and Sagol, 2016) - about 40% of ROM coal is processed by flotation (Dube, 2012).

In the past, a common approach to treating coal fines (slimes) was to discard and direct them to the refuse ponds. According to a study conducted by the USA's National Research Council, over 70 to 90 million tons of coal fines were deposited in refuse ponds in the USA annually (NRC, 2002). Froth flotation is considered to be one of the rare commercially available technologies for cleaning and recovering of coal fines (Yoon and Aksoy, 1999).

Coal flotation is a very complex process that is characterized by a large variation in physical and chemical properties of treated material, i.e. coal and mineral matter. It is the most efficient separation method for coal particles within a narrow size range, normally from 50 µm to 600 µm (Trahar and Warren, 1976; Humeres and Debacher, 2002). A number of models have been developed to describe the coal flotation process. The flotation kinetic model is the most commonly used flotation model that relates different process parameters, which are related to particle, slurry, and hydrodynamic properties, to flotation rate constant. Particle size is known to be one of the most important parameters in coal flotation due to its significant effect on flotation rate. The relationship between particle size and coal flotation kinetics was frequently studied by different researchers (Panopoulos et al., 1986; Vanangamudi and Rao, 1986; Rao et al., 1989; Vanangamudi et al., 1989; Mohns,1997; Humeres and Debacher, 2002; Abkhoshk et al., 2010; Kor et al., 2010; Brozek and Mlynarczykowska, 2013; Bedekovic, 2016; Li et al., 2013; Ni et al., 2016; Liao et al., 2017; Bu et al., 2017b; Sahoo et al., 2017b) which proposed different flotation kinetc models. This paper provides an overview of coal flotation kinetics models proposed in literature, summarizes findings of selected studies that investigated the effect of particle size on flotation recovery, flotation kinetics (rate constant), and product quality, and it highlights results and advances in this field that have been obtained over the past few decades.

2. Coal flotation

Coal flotation is based on the difference in the surface properties between hydrophobic coal and hydrophilic mineral matter. It is a complex three-phase process involving coal particles, oil droplets, and air bubbles, whose behavior is governed by a number of sub-processes as a result of their interactions as shown in Fig.1 (Polat et al., 2003). The process is affected by a large number of factors that can be divided into three main groups: coal properties, chemistry, and machine (Wills, 2006; Liang et al. 2015; Peng et al. 2015). The theory of coal flotation is complex, which has been described in detail by Laskowski (2001). That is a first monograph on the coal flotation and fine coal utilization. It is affected by a very large number of variables.

For a better understanding of the coal flotation process, the knowledge of the chemical composition, physical structure, surface characteristics, and floatability of coal is of great importance. Coal is an organic sedimentary rock, which is composed of a variety of organic macerals and inorganic minerals (Lynch et al. 1981; Hower et al. 1984; Arnold and Aplan 1989; Laskowski et al., 2010). It is a very heterogeneous material, whose composition changes via coalification process - the process of plant material conversion into coal by diagenesis and metamorphism. Organic and mineral matter in coal have different surface characteristics, typically expressed through their hydrophobicity level. It has been reported that the coal floatability varies widely depending on the coal rank (Hower et al., 1984; Laskowski, 2001), petrographic composition, degree of oxidation, and size distribution (Vanangamudi et al., 1989).

An analysis of the coal floatability as a function of coal rank was offered by Klassen (1963 and was extensively discussed by Laskowski, 2001. Coal with a high degree of coalification is naturally hydrophobic (Xia et al., 2013); the high volatile bituminous coals are the most hydrophobic, whereas lignite has lower hydrophobicity (Hower et al., 1984). It has also been reported that anthracite coal has lower hydrophobicity due to the increase of its specific surface area (Zhang, 2004).

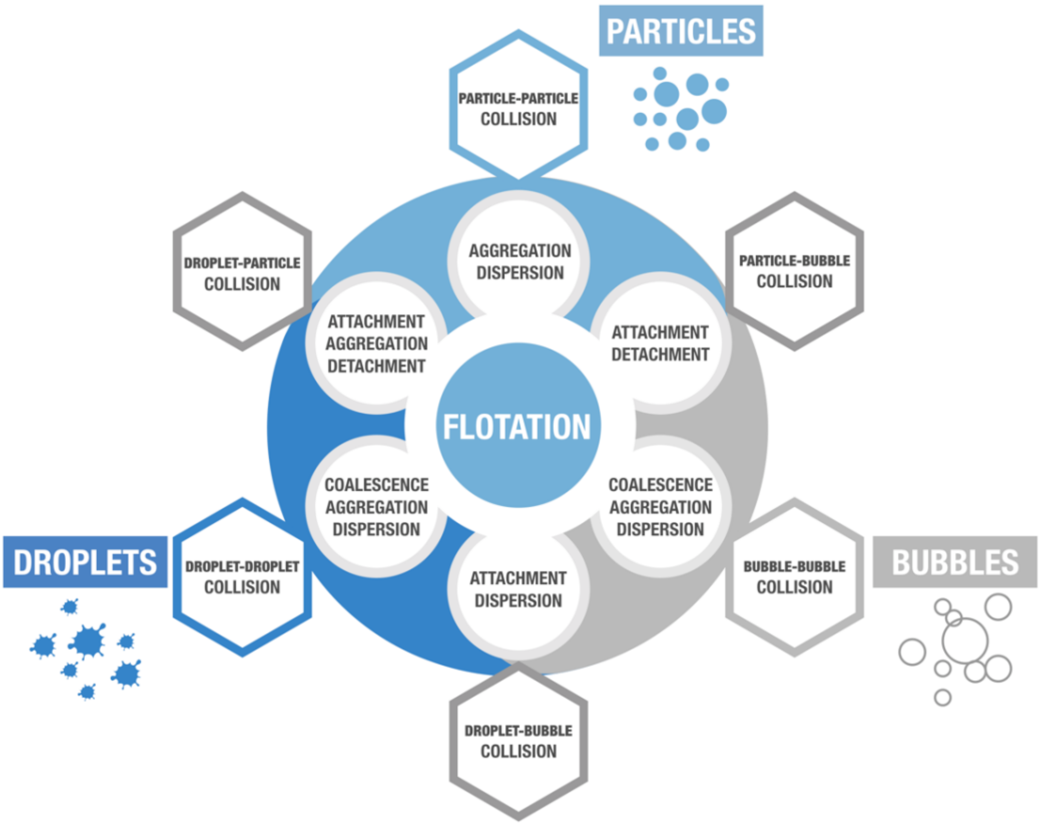

Fig. 1. Sub-processes in coal flotation (after Polat et al., 2003)

There is a strong dependence between coal floatability and its petrographic composition. Coal macerals are generally classified into three major maceral groups, such as vitrinite, liptinite, and inertinite. Since coal macerals have different structure and chemical composition, their chemical (Kessler, 1973) and physical properties (Laskowski, 2001) differ widely and change with coalification. It is generally known that the organic (macerals) matter is hydrophobic. Arnold and Aplan (1989) found that the hydrophobicity order of coal macerals can be given as: exinite > vitrinite > inertinite. These coal macerals have typical ranges of contact angles of 90-130°, 60-70° and 25-40° respectively (Arnold and Aplan, 1989). In another study (Sahoo et al., 2017a), coal macerals were arranged according to their first order flotation rate constant, k, and the reported order is liptinite > vitrinite > inertinite, with k = 0.118 s^{-1}, 0.113s^{-1} and 0.112 $^{s-1}$, respectively (Sahoo et al., 2017a).

The most common mineral matter that occur in coal are: clay minerals (kaolinite and montmorillonite), carbonates (dolomite, calcite, siderite), oxides (quartz) and sulfides (pyrite) (Laskowski et al., 2010). Coal flotation is also dependent on the surface properties of high-ash mineral matter. In his study, Aplan (1997) found that pyrite has hydrophobic surface property, while the other minerals are generally hydrophilic. Coal flotation can be drastically affected by oxidation (Sokolovic et al., 2012a) and by the presence of various inorganics (Somasundaran et al., 2000).

The physical and chemical properties of coal usually change as a result of oxidation (Fuerstenau et al., 1983; Fuerstenau and Diao, 1992; Pietrzak and Wachowska, 2006; Xia et al., 2014.), which leads to the formation of oxygen functional groups, such as carboxyl (–COOH), phenolic (–OH) and carbonyl (C=O) on the coal surface (Somasundaran et al., 2000; Jia et al., 2000; Sokolovic et al., 2006; 2012a). These groups, which are normally hydrophilic (Beafore et al., 1984), significantly influence coal surface properties, hydrophobicity, and its floatability. The influence of oxidation processes on coal floatability was investigated by many researchers (Fuerstenau et al., 1983; Somasundaran et al., 2000; Wang et al., 2003; Dey, 2012). It has been widely reported that oxidation reduces the hydrophobicity and floatability of coal (Sun, 1954; Swann et al., 1972; Wen and Sun, 1981; Fuerstenau et al., 1983, Fuerstenau and Diao, 1992; Laskowski, 1995; Sokolovic et al., 2006; 2012b; Xia et al., 2013; Wen et al., 2017). Fuerstenau et al. (1983) found that oxygen functional groups control coal wettability through the balance of hydrophobic/hydrophilic sites, thus affecting the kinetics of flotation. Other studies have shown that coal oxidation has a great impact on coal flotation recovery (Sokolovic et al., 2012a; Xia et al., 2013).

3. Coal flotation kinetic model – general model description

Kinetic models are common fundamental models used for flotation process assessment and analysis and can be easily developed using standard release analysis tests for any considered coal (Lynch et al., 1981). They are very important for optimization, simulation, and control of the flotation process (Chander and Polat, 1995).

The first flotation kinetic model was developed by Zuniga (1935) and is based on the assumption that the particle–bubble collision rate is first-order with respect to the number of particles and that the bubble concentration in the system remains constant (Sutherland, 1948). A number of different flotation kinetics models have been proposed and published in the literature over the years, however, the first-order kinetic model introduced by Zuniga (1935) has been used the most extensively. This kinetic model can be used to describe flotation processes in both batch (Kelsall, 1961; Tomlinson and Fleming, 1963; Imaizumi and Inoue, 1963; Harris and Chakravarti, 1970; Jameson et al., 1977; Dowling et al., 1985; Agar et al., 1998; Xu, 1998; Oliveira et al., 2001; Cilek, 2004; Brozek and Mlynarczykowska, 2007; 2013) and continuous flotation systems (Jowett and Safvi, 1960).

Imauzimi and Inoue (1963) studied the kinetic of coal flotation and have shown that the flotation kinetics is too complex to be entirely portrayed by kinetic equations. Huber-Panu et al. (1976) developed a first-order flotation model for batch and continuous flotation which, for the first time, assumed the distribution of floatability and particle size distribution. This first-order model was applied to coal flotation kinetics by Klimpel et al. (1979).

The first-order kinetics equation can be given by following expression (Tsai, 1985; Vanangamudi and Rao, 1986; Rao et al., 1989; Govindarajan and Rao, 1991; Polat and Chander, 2000):

$$R = R_{\infty}[1 - e^{-k \cdot t}] \quad (1)$$

where, R is the combustible matter recovery in %; k is the first-order rate constant [s^{-1}], t is the flotation time [s], and R_{∞} is the ultimate (theoretical maximum) recovery.

As shown in Eq. (1), the classical first-order model uses two parameters, the ultimate recovery and the first-order rate constant, to describe the flotation kinetics. For any feed material, parameters can be easily determined from the experimental data reported through the recovery-time curve using simple model fitting and regression analysis approach. The ultimate recovery is dependent on chemical variables, such as collector dosage, while the first-order kinetic rate constant is strongly affected by physical variables of the process, such as feed particle size, gas flow rate, and power input (Nguyen and Shulze, 2003). The kinetic rate constant is often used to reflect the floatability of coal (Cheng et al., 2013). Both of these parameters can be effectively used to evaluate variables affecting the flotation process (Xu, 1998) are discussed further in the following section.

Xu (1998) and Sripriya et al. (2003) used the classical first-order flotation model to optimize the batch coal flotation process using the "modified flotation parameters", k_{mod} and SI, where k_{mod} is a modified flotation rate constant and is calculated from R_{∞} and k as $k_{mod} = R_{\infty} \cdot k$, while SI is the selectivity index and is defined as the ratio of the modified rate constant of coal to the modified rate constant of ash, $SI = k_{mod\_coal}/k_{mod\_ash}$. Sripriya et al. (2003) developed polynomial equations for predicting the selectivity index, combustible recovery, and ash recovery for different operating parameters. These studies also confirmed that "modified flotation parameters"can be used for coal flotation optimization.

More recently, Vapur et al. (2010) made an attempt to optimize the batch coal flotation process using the first-order kinetic model. They used "modified flotation parameters" to determine optimal values of operation variables of the Jameson flotation cell. This study also examined the effects of particle size distribution (i.e., d_{80} = 0.250 and d_{80} = 0.106 mm) on the flotation behavior of coal collected from an Omerler coal washing plant in Kutahya, Turkey. Based on the first-order kinetic analysis, authors found that the optimal particle size of feed coal should be around d_{80} = 0.250 mm.

Table 1. A list of mathematical models of flotation kinetics (Drzymala, 2018)

Family of kinetic curves	Kinetic curve type	Mathematical equation for approximation of a set of data points	Source
General n^{th} order with kinetic constant	0^{th} order	$R = k_o \cdot t$	Zuniga, 1935
	1^{st} order	$R = R_\infty[1 - e^{-k_1 t}]$	Zuniga, 1935
	n^{th} order	$R = R_\infty \left[1 - \frac{1}{(1 + (n-1)R_\infty^{n-1}Kt)^{\frac{1}{1-n}}}\right]$ n - integer and non-integer, order n≠1	Bu, 2016
	fractional order (α)	$R = R_\infty[1 - E_\alpha(-k_\alpha t^\alpha)]$ α - any integer or non-integer number E_α - Mittag-Leffer function	Vinnett et al., 2015
1^{st} order with kinetic constant distribution	gamma	$R_\infty\left[1 - \left(\frac{1}{1+at}\right)^p\right]$	Imaizumi and Inoue, 1963
	bimodal gamma	$R_\infty\left\{\gamma_1\left[1-\left(\frac{1}{1+a_1 t}\right)^{p_1}\right] + \gamma_2\left[1-\left(\frac{1}{1+a_2 t}\right)^{p_2}\right]\right\}$	Harris and Chakravarti, 1970
	triangular	$R = R_\infty\left[1 - \frac{1+e^{-2bt} - e^{bt}}{(bt)^2}\right]$	Harris and Chakravarti, 1970
	rectangular	$R = R_\infty\left[1 - \frac{1-e^{-ct}}{c\ t}\right]$	Huber-Panu et al., 1976
	sinusoidal	$R = R_\infty\left[1 - \frac{1 - 2dt\frac{e^{-dt}}{\pi}}{\left(1+\frac{2dt}{\pi}\right)^2}\right]$	Diao et al., 1992
	exponential	$R = R_\infty\left(1 - \frac{1}{t/\lambda}\right)$	Imaizumi and Inoue, 1963
	normal	$R = R_\infty\left[1 - \frac{\mathrm{erf}\left(\frac{\left(\sigma t + \frac{\mu}{\sigma}\right)}{\sqrt{2}}\right) - \mathrm{erf}\left(\frac{\left(\sigma t - \frac{\mu}{\sigma}\right)}{\sqrt{2}}\right)}{2e^{\mu t\frac{(\sigma t)^2}{2}}}\right]$	Chander and Polat, 1994
2^{nd} order with kinetic constant distribution	rectangular	$R = R_\infty\left\{1 - \left[\frac{1}{K_9 t}\ln(1+K_9 t)\right]\right\}$	Klimpel, 1980
Adopted chemical reactor models	Fully mixed reactor model	$R = R_\infty \cdot \left(1 - \frac{1}{1+\frac{t}{k_b}}\right)$	Imaizumi and Inoue, 1963; Jowett, 1969
	Gas/solid adsorption model	$R = R_\infty \cdot \left(\frac{k_c \cdot t}{1 + k_c \cdot t}\right)$	Bu et al., 2016 (Langmuir eq.)
Other	1^{st} order with two rates	$R = R_\infty[(1-\phi)(1 - e^{-k_s t}) + \phi(1 - e^{-k_f t})]$ ϕ - fraction of slow separating component k_s - 1^{st} order rate constant of fast separating component k_f - 1^{st} order rate constant of slow separating component	Kelsall, 1961; Jowett, 1974 Bu et al., 2016
	1^{st} order reversible model	$R = R_\infty \frac{K_5}{K_5 + K_5^*}\left[1 - e^{-(K_5+K_5^*)t}\right]$	Ek, 1992
	Rosin-Rammler's model	$R = R_\infty(1 - e^{-K_3 t^m})$	Tarjan, 1986.; Ahmed, 1995.

Brozek and Młynarczykowska (2006) studied the application of the stochastic model for analysis of the flotation kinetics of several coal samples, differing by the ash content. The flotation rate constant in the stochastic model achieves the interpretation of the resultant adhesion rate constant, which is the sum of the permanent adhesion rate constant and the detachment rate constant.

Chaves and Ruiz (2009) evaluated five different kinetic flotation models, namely classical first-order model, first-order model with rectangular distribution (Klimpel's), fully mixed reactor model, second-order kinetic model and second-order model with rectangular distribution, for modeling of flotation rate of coal contained in tailings from a Colombian coal preparation plant. Based on the experimental data, it was found that the best fitted model was classical first-order model confirming early notion. Klimpel's model also showed good adherence to experimental results.

Sokolovic et al. (2012a) considered classical first-order model and modified Kelsall model for modeling raw and waste anthracite coal flotation. The nonlinear model fitting approach was used and both models showed good correlation with experimental data, while modified Kelsall model provided the best fit. The mathematical form of a modified Kelsall's model (Jowett, 1974) is similar in form with original Kelsall's model (Kelsall, 1961). Here, the kinetics of fine coal flotation can be approximated by two first-order rate constants, namely fast flotation rate constant, k_f, and the slow flotation rate constant, k_s, taking into account the fraction of slow floating components in the feed, ϕ. Authors reported that k_f was greater than k_s - k_f was found to be 6.7566 min^{-1} for raw coal and between 1.1105 and 2.8562 min^{-1} for waste coal, while k_s was found to be constant and about 1 min^{-1}. This agrees very well with findings made by Tsai (1985), who concluded that k_f was about one order of magnitude greater than k_s. In general, the fast floating component can be recovered within the first 0.5 to 1 minute of flotation.

Drzymala (2007; 2018) evaluated a number of different flotation kinetic models available in literature (Zuniga, 1935; Bu et al., 2016; Vinnett et al., 2015; Imaizumi and Inoue, 1963; Harris and Chakravarti, 1970; Huber-Panu et al., 1976; Diao et al., 1992; Chander and Polat, 1994; Klimpel, 1980; Jowett, 1969; 1974; Kelsall, 1961; Ek, 1992; Tarjan, 1986; Ahmed, 1995), which are summarized in Table 1.

A review of literature (Lynch et al., 1981; Polat and Chander, 2000; Nguyen and Shulze, 2003; Brozek et al., 2003; Mavros and Matis, 2013; Bu et al., 2017a) has shown that a development of kinetic models is usually associated with the distribution of flotation rate constants. A number of different flotation rate constant distribution functions, *k(t)*, have been proposed in literature. The first-order flotation kinetics models with distribution of flotation rate constants were analyzed by Polat and Chander, 2000, Nguyen and Shulze, 2003 and Bu et al., 2017a. These include gamma (Imauzimi and Inoue, 1963; Loveday, 1966), Kelsall (Kelsall, 1961), rectangular (Huber-Panu et al., 1976; Klimpel, 1980), triangular (Harris and Chakravarti, 1970), Dirac delta function (Lynch et al., 1981; Yianatos et al., 2010), and sinusoidal (Diao et al., 1992) distributions. In their papers, Jowet (1974) and Diao et al., (1992) argued that there is a disagreement about which function is better suited to represent the actual distribution of flotation rate, especially for a wide range of flotation conditions.

Imaizumi and Inoue (1963) concluded that the same mineral has different *k(t)* and that it reflects the immediate changes in the flotation rate constant with the flotation time. The authors studied the kinetics of coal flotation and have shown that the flotation kinetics is too complex to be entirely portrayed by the kinetic equations. Soon after, Woodburn and Loveday (1965) found that the flotation rate constant of the same mineral follows gamma distribution function trend. Kalinowski and Kaula (2013) investigated and compared the mathematical models based on the distribution of gamma and proposed triangular model for the batch coal flotation process.

In Table 1, symbol R stands for either recovery (ε) or yield (γ) while R_∞ denotes ultimate (maximum) recovery. In literature R usually means recovery and k represent flotation rate constant.

4. The main factors controlling flotation kinetics

Coal flotation kinetics and, hence, flotation rate constant are affected by a number of physical and chemical factors, including type and dosage of reagents, pulp pH and density, particle size, gas flow rate (superficial gas velocity), bubble size, temperature, impeller speed, froth depth, flotation cell design, among many others (Laskowski, 2001; King, 2001; Polat et al., 2003; Sokolovic et al., 2012a; Fan et al., 2013).

For a process running under steady state conditions, it was found that the flotation rate constant is directly proportional to the probability of flotation, P, and bubble surface area flux, S_b, which can be written as (Yoon and Mao, 1996; Gorain et al., 1997, 1998):

$$k = \frac{1}{4} S_b \cdot P \tag{2}$$

Bubble surface area flux is a factor describing the amount of bubble surface area available for particle attachment and can be calculated from the measured mean bubble size, d_b, and superficial air velocity, J_g, as $S_b = d_b/6J_g$. The overall probability of flotation is given by the following equation (Schumann, 1942; Sutherland, 1948; Tomlinson and Fleming, 1963):

$$P = P_c \cdot P_a \cdot (1 - P_d) \tag{3}$$

where, P_c represents the collision probability, P_a is the probability of attachment, and P_d is the probability of detachment.

Mechanisms of particle-bubble interaction in the flotation process is given in Figure 2.

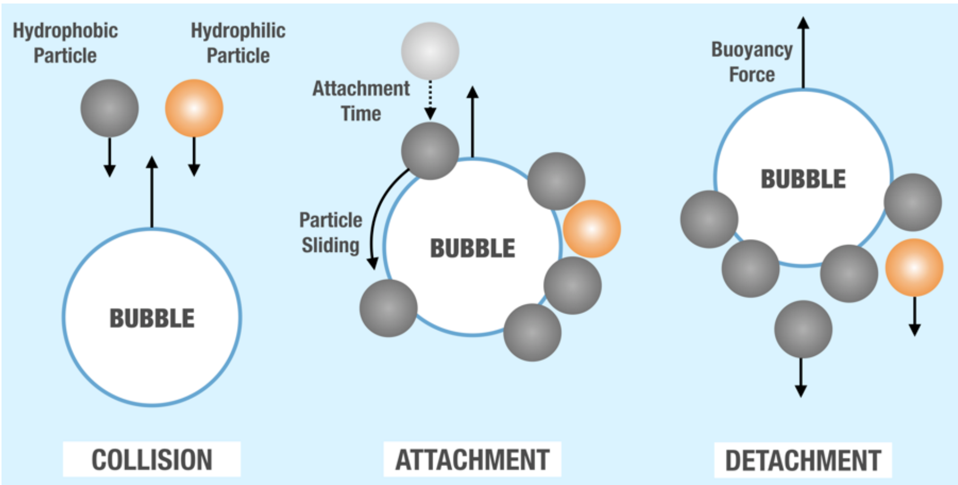

Fig. 2. Mechanisms of particle-bubble interaction

The overall probability of flotation and, thus, the flotation kinetic rate are strongly dependent on particle size; the probability of collision is directly related, while the probabilities of attachment and detachment are inversely related to particle size (Trahar, 1981). The following equation represents a general model of particle-bubble collision probability as proposed by Sutherland (1948):

$$P_c = A\left(\frac{R_p}{R_b}\right)^n \tag{4}$$

where, R_p and R_b are particle and bubble radii, A and n are parameters that depend on bubble Reynolds number and, hence, flow fields around the bubbles. Sutherland (1948) obtained the parameters values for potential flow conditions, Yoon and Luttrell (1989) for intermediate flow conditions, and Gaudin (1957) for Stokes flow conditions. This general expression is in agreement with the experimental results obtained by Collins and Jameson (1976), who reported the following expression for probability of collision (P_c) as a function of particle and bubble diameters:

$$P_c = \left(\frac{d_p}{d_b}\right)^2 \tag{5}$$

From Eq. 5, it can be concluded that with increasing particle size the probability of collision is also increasing.

According to the model developed by Glembotskii et al. (1972), the flotation rate constant is proportional to the probability of particle-bubble collision and the probability of adhesion.

Stokowski and Freyberger (1985) proposed an alternative empirical model for the flotation rate constant as a function of critical operating parameters, namely particle size, d_p, bubble size, d_b, air holup, C_a, air flow rate, J, and pulp or slurry volume, V_s, which can be written as:

$$k = A\frac{d_p(0.806\, C_a^{-0.33} - 0.5) \cdot J}{(V_s\, d_b)^2} \tag{6}$$

5. The effect of particle size on coal flotation kinetics

The particle size is an important parameter in the flotation process because it affects gas bubble mineralization, bubble size distribution and air holdup, stability of bubble-particle aggregates (expressed through particle attachment and detachment rates), and reagent adsorption (Bedekovic, 2016). Particles of various sizes behave differently in flotation system, directly affecting flotation recovery and overall performance (Gaudin, 1932; Chander and Polat, 1995; Nguyen and Shulze, 2003; Markovic et al., 2008).

The pioneer work on the relationship between particle size and flotation recovery was carried out by Gaudin et al. (1931). Figure 3, which has been adapted from the work of Gaudin et al. (1931), shows flotation recovery by size for a variety of mineral systems.

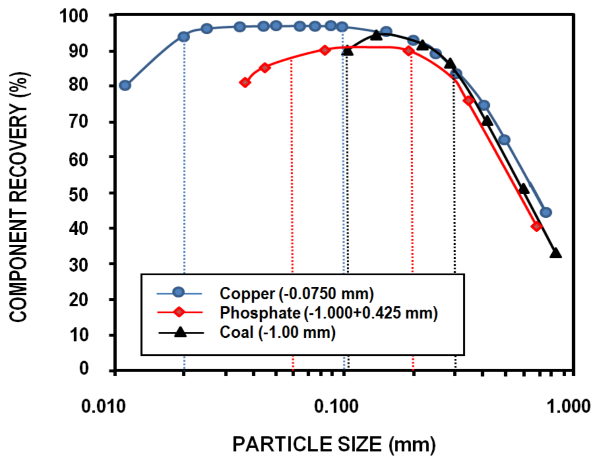

Fig. 3. Flotation recovery by size for a variety of mineral systems (after Gaudin et al., 1931)

They found that particle of different sizes exhibited different flotation kinetics under the same chemical conditions. The maximum flotation recovery of copper minerals was between 20 and 100 µm size range as well as for phosphate minerals between 60 and 200 µm. The optimum particle size in coal flotation is generally smaller than 1 mm.

Trahar (1981) reported that the flotation recoveries of fine and coarse particles follow different trends and that the recovery of coarse particles is more sensitive to the changes in surface hydrophobicity than the fine particles.

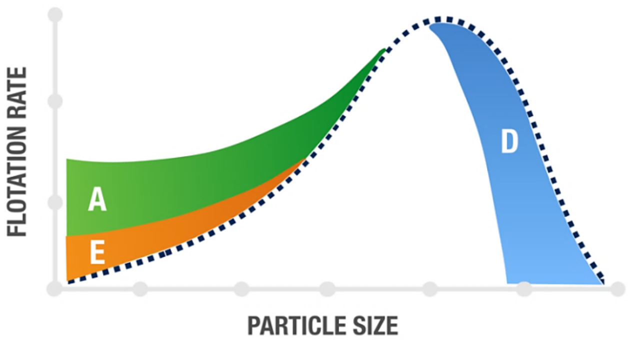

Fig. 4. A schematic representation of the effect of particle size on flotation rate (after Chander and Polat, 1995)

Numerous researchers have studied the effect of particle size on general flotation kinetics (Morris, 1952; Trahar and Warren, 1976; Varbanov, 1984; Polat et al., 1993; Chander and Polat, 1995; Rubinstein and Samygin, 1998; Hernainz and Calero, 2001; Yoon et al., 2002; Graeme, 2012). The relationship between particle size and flotation rate constant was firstly studied by Morris (1952). In his study, Morris (1952) concluded that maximum flotation rate was obtained in an intermediate size range and that the flotation rate constant was decreasing for fine and coarse particle size. The flotation rate constant of fines is lower in comparison with other particle sizes, primarily as a result of the decreased probability of collision between particles and bubbles as the particle size is decreased (Mohns, 1997). A schematic representation of the effect of particle size on flotation rate marking the regions dominated by the three phenomena having a detrimental effect on particle recovery, namely aggregation (A), entrainment (E), and detachment (D), is given in Figure 4.

The following relationship, given by Trahar (1981), defines the flotation rate constant as a function of particle size:

$$k = A \cdot {d_p}^n \quad (7)$$

where, A is the coefficient of proportionality and n is a parameter that takes value between 1 and 2.

In coal flotation, a fair number of studies have been conducted to determine the effect of feed coal particle size on the coal flotation recovery, product quality, and coal flotation kinetics (Firth et al., 1978; Panopoulos et al., 1986; Vanangamudi and Rao, 1986; Rao et al., 1989; Vanangamudi et al., 1989; Abdel-Khalek and Stachurski, 1990; Chander and Polat, 1995; Mohns, 1997; Humeres and Debacher, 2002; Abkhoshk et al., 2010; Kor et al., 2010; Brozek and Mlynarczykowska, 2013; Bedekovic, 2016; Li et al., 2013; Ni et al., 2016; Liao et al., 2017; Bu et al., 2017b; Sahoo et al., 2017b).

In one of the first studies, Firth et al. (1978) found that flotation of coarse particles (+0.25 mm) is significantly reduced when the amount of ultrafine coal (-0.063 mm) is increased. Abdel-Khalek and Stachurski (1990) investigated the flotation recoveries of six coals of different rank. They found that the coal flotation recovery is strongly dependent on particle size. Maximum recoveries were observed at intermediate sizes, while lesser amount of coarse and fine size fractions was recovered.

The relationship between coal particle size and flotation rate is particularly complex and still not quite well understood. One of the first studies that made an attempt to define a relationship between the probability of collision and flotation rate constant was given by Al Taweel et al. (1986). For strongly hydrophobic coal, they found that the flotation rate is governed by the probability of collision (P_c), which increases with particle size. Chander and Polat (1995) argued that the key phenomena causing such effect over fine partice sizes is the aggregation of fine particles in coal flotation. The difference in flotation rate kinetics constants of various size fractions can also be explained by the combined effect of the collision and attachment/detachment sub-processes in flotation. The low flotation rate of fine particles is mainly due to the low probability of bubble–particle collisions, whereas the poor flotation rate of coarse particles is due to the high probability of detachment of such particles from the bubble surface (Tao, 2005).

Mohns (1997) proposed a second order polynomial model for flotation kinetic rate as a function of particle size, given by Eq. (8)

$$k = a + b \cdot d_p + c \cdot {d_p}^2 \quad (8)$$

where a, b and c are coefficients which depend on the material and reagent concentration.

The particle size effects also depend on the applied reagents. Rastogi and Aplan (1985) showed that the flotation rate of coal increases with decreasing particle size for a pulp modified only by frother. The upper particle size limit for coal flotation using novel flotation reagents increases the combustible yield (Yoon et al., 2002).

The effect of particle size distribution on the flotation of two South African coals was investigated by Panopoulos et al., (1986). Based on the relationship between flotation recovery and particle size, they found that the maximum recovery peak occurring between 100 and 200 μm. The flotation recovery of coal rapidly fall-off above 200 μm and decreased to almost zero at a particle size of 1 mm. The difference in flotation rate is very small for particles ranging in relative density from 1.3 to 1.7, and ash content from 2 to 31%. The maximum specific flotation rate constant of the floatable component was found in the -500+425 μm size fraction. It was also noted that recovery significantly varies with the particle density for coarser coal particles and, at the fine end, high-density particles are effectively depressed.

Vanangamudi and Rao (1986) developed the model for batch coal flotation, which showed that an increase in particle size results in a decrease in the flotation rate constant. A mathematical equation has been developed to predict the combustible yield and ash content of the flotation product with the changes in the reagent dosage. However, the effects of feed size distribution have not been taken into account, which is a limitation of the model.

In their following study, Rao et al. (1989) developed a simple kinetic model for batch coal flotation defined by independent parameters. The model has been tested over widely varying feed characteristics and reagent dosages and operating conditions. Experiments were carried out in a batch flotation cell using four different coals. It has been found that the flotation rate constant for any size fraction is dependent on the average value of the size fraction, as well as on the proportion of ash and non-ash fractions within each particle size range and -75 μm fraction in the feed. For any coal, the flotation rate constant of non-ash material in the feed was reported to have the following form:

$$\ln k_n = Y_1 - C_1 \cdot X_n \tag{9}$$

where, n is denoting n^{th} size fractions of the feed; X_n is mean particle size of n^{th} fraction; k_n is rate constant of a non-ash component of n^{th} fraction; Y_1 is the intercept value of k_n versus X_n linear curve, which is defined as a product of X_n, weight fraction of non-ash material in the n^{th} size range, and weight fraction of non-ash material in fines below 75 μm; and C_1 is the slope of the same curve and is a characteristic constant for any coal. The correlation coefficients for all obtained k_n versus X_n curves have been found to be larger than 0.9.

The authors also proposed a model describing a relationship between ultimate recovery and particle size for two considered conditions:

$$R_\infty = 100\ \mathrm{e}^{-a \cdot d_p{}^b} \tag{10}$$

where, a and b are fitting constants depending on coal type and operating conditions. This model has an advantage in that the material characteristics and the process variables are defined by measurable parameters. They found that the model predicts flotation recovery satisfactorily for feeds having varying amounts of coal fines. According to the model, increase in -75 μm fraction in the feed results in a decrease in the flotation rate constant. Based on the results of another study by Vanangamudi et al., (1989), the authors concluded that the recoveries of non-ash and ash material follow first-order kinetics for both tested coals. They found that the maximum recoveries and the first-order rate constant decreased with an increase of fines content (-75 μm) in the feed. This decrease is due to the lower yield of the coarse size fractions in the coal feed. For the first coal they considered, the ultimate recovery of non-ash material decreased from 83.6% to 77.1% and the first-order rate constant from 0.0653 to 0.0470 s^{-1} as the fines content in the feed increased from 0 to 27.7%, respectively. Further, as the content of fines increased from 0 to 27.7%, the ultimate recovery of non-ash material for the coarser size fraction (-500+355 μm) decreased from 63.2% to 38.1% with a decrease in the rate constant from 0.0605 to 0.0338 s^{-1}. The intermediate size fractions, namely -355+250, -250+150, and -150+75 μm, also showed a similar trend even though the decrease in recovery was only 16%, 5.7%, and 0.4%, respectively. Similar observations were noted for other considered coals. Kinetic studies revealed that the flotation rate constant decreased from 0.0682 to 0.0356 s^{-1}, 0.0736 to 0.0435 s^{-1}, and 0.0779 to 0.0522 s^{-1} as the content of fines in the feed increased. The finer size fraction in the feed showed a different trend as the percentage of -75 μm material in the feed increased. They found that the highest recovery and the first-order flotation rate constant was obtained for intermediate, -150+75 μm, size fraction.

The ratio of maximum recovery of non-ash material, $R_{non\text{-}ash}$, to that of the ash material, R_{ash}, has been used for estimating the relative recoveries, R_r, at different levels of fines content in the feed. It has been found that the ratio increased with square of particle size. A change of R_r with average particle size is found to be parabolic, which can be expresed as:

$$R_r = a + b \cdot d_p{}^2 \tag{11}$$

where, a and b are fitting constants.

Holuszko et al. (1991) considered the effect of four different size fractions of vitrain particles, namely -500+300 μm, -300+212 μm, -212+150 μm, and -150+74 μm, on floatability of vitrain. Film flotation experiments and small scale dynamic flotation tests were used. The obtained results indicate that particle size does not influence the thermodynamics (i.e. wettability) as much as it does the kinetics of coal flotation.

Mohns (1997) investigated the effect of particle size on the flotation kinetics of tailings and run-of-mine (ROM) coals. He concluded that the particle size has a major influence on the flotation rate constant. For both coals studied, the relationship between flotation rate constant and particle size was found to be similar; the flotation rate constants were lowest for fine, -44 µm, fraction and increase in the ascending order for the following micron sizes fractions: -710+300 µm, -149+44 µm, and -300+149 µm. The flotation rate constant of tailings coal is found to be 0.002, 0.071, 0.104, and 0.034 s^{-1} for -325, 100x325, 48x100, and 28x48# fractions, respectively. Similar trends were identified for ROM coal, and reported values of the flotation rate constants are 0.028, 0.177, 0.260, and 0.113 s^{-1}.

Humeres and Debacher (2002) studied the flotation kinetics of coarse coal particles in a modified Hallimond tube using nitrogen as the carrier gas in the pH range between 2 and 12. A series of experiments were carried out by changing feed coal particle size in the range from 505 to 127 µm. They found that the first-order rate constant can be represented as the product of separable constants and three newly defined functions, which are f_D, f_V and f_{pH}, that depend on particle size, gas flow rate, and dispersion pH, respectively. The correlation between the flotation rate constant and particle size was found to be linear and strongly negative with an increase in particle size. The proposed function describing this relationship can be written as:

$$f_D = e^{-1.56 \cdot d_p} \tag{12}$$

Abkhoshk et al. (2010) studied the effect of particle size on the flotation kinetics of coal in a batch flotation cell. They used a fuzzy logic model to predict the cumulative recovery of different particle sizes of coal from the Zarand coal plant in Iran. Particle size was considered as the independent input variable and the first-order rate constant and ultimate flotation recovery were established as output variables. The tests were conducted using five distinct fractions: -75+0, -150+75, -300+150, -500+300, and -850+500 µm. The relationship between flotation rate constant and cumulative recovery, R_∞, with particle size was found to be non-linear and was described by the following equations:

$$k = -3.02 \cdot 10^{-6} \cdot {d_p}^2 + 0.0055 \cdot d_p + 0.6827 \tag{13}$$

$$R_\infty = -8.8904 \cdot (\ln(d_p))^2 + 92.65 \cdot \ln(d_p) - 149.25 \tag{14}$$

Using fuzzy logic model, they achieved a good correlation with experimental results, which were expressed through R^2 values as 0.986, 0.993, 0.983, 0.977, and 0.972 for 37.5, 112.5, 225, 400, and 625 µm average particle sizes, respectively. In the following study, Kor et al. (2010) investigated the particle size effect on coal flotation kinetics applying different regression analysis approaches. Their results revealed that the quadric regression model showed better correlation than the other considered regressions models for different particle size fraction, which was consistent with the results of previous research.

Brozek and Mlynarczykowska (2013) carried out a series of batch flotation tests using several different sizes fractions of coal samples: –200+100, –315+200, –400+315, 500+400, and -630+500 µm. Flotation kinetics of narrow size fractions were compared with the overall flotation kinetics of the wide size fraction –630+100 µm. According to obtained results, it appears that particles with different sizes float independently from each other. They found that the concentrate recovery increased with the decrease in the particle size, as well as with an increase in the flotation rate. The highest recovery and rate constant was obtained for a -200+100 µm size fraction, while the rate constant was decreasing for coarser particle sizes. Based on the obtained flotation results, the particle detachment probability was calculated using a ratio between the mass of particles with the density below 1.6 kg/m^3 in tailings and the mass of the same type of particles present in the feed. The probability of detachment was reported as 0.68, 2.52, 11.94, and 43.17% for –200+100, –400+315, 500+400, and -630+500 µm fractions, respectively. A similar trend was demonstrated by using the dependency of real and theoretical degree of heterogeneity as a measure of flotation efficiency over particle size. They found that the degree of heterogeneity increases with the increase in particle size and reaches the highest value for particles in –400+315 µm fraction, which then decreases for coarser particles.

Li et al. (2013) studied the flotation kinetics and separation selectivity of three narrow coal size fractions. The values of R_∞ and k were determined using Matlab software. They assert that during coal flotation, organic component floats according to the first-order kinetics, while the inorganic component floats according to the second-order kinetics. The flotation rate constant of both combustible matter and ash forming minerals increase with the particle size. The flotation rate constant of -500+250, -250+75, and -75+0 µm particles for the combustible matter fraction were 3.52, 2.47, and 2.17 s^{-1} and for ash forming minerals 0.16, 0.09, and 0.05 s^{-1}, respectively. On the other hand, the Fuerstenau upgrading curves (Drzymala and Ahmed, 2005; Drzymala, 2006) for the investigated size fractions showed different trends. The best selectivity was obtained for the middle size fraction of -250+75 µm, which was significantly lower for coarser particles. Authors also concluded that the combustible matter recovery increased with the particle size. The fine particles have low collision efficiencies due to their low mass and inertial force, while the coarse particles have a higher degree of heterogeneity.

Brozek and Mlynarczykowska (2013) found the increase in the ash content in the concentrate with a decrease in particle size. The tests were carried out on the same particle fractions as in previous study: -500+250, -250+75, and –75+0 µm. Lower ash content and higher recoveries were reported for coarse particles and high ash content and low recoveries for fine particles.

Ni et al. (2016) conducted flotation tests to investigate the difference in the flotation kinetics of various size fractions of bituminous coal between rougher and cleaner flotation processes. The relationship between flotation rate constant, maximum combustible recovery, and particle size was also studied. Six different flotation kinetic models, namely the classical first-order model, the first-order model with rectangular distribution of flotabilities, the fully mixed reactor model, the improved gas/solid adsorption model, the second-order kinetic model, and the second-order model with rectangular distribution of flotabilities, were applied to model the results from the flotation tests using Matlab software. They found that the rougher flotation process can be described accurately using both the first-order and second-order models, while the first-order model was found to be more suitable for the cleaner flotation process modeling. Among all six tested models, the first-order model with rectangular distribution of floatabilities was shown to provide the best fit to both rougher and cleaner experimental data considering various particle size fractions of bituminous coal. This was ascribed to an intrinsic nature of the rectangular distribution of flotabilities model, which provides an added flexibility. The reported flotation rate constants for -500+250, -250+125, -125+74, -74+45, and -45+0 µm size fractions were 0.0585, 0.1096, 0.1030, 0.0673, and 0.0382 s^{-1} in the rougher flotation tests. The corresponding rates were shown to increase by 58.97%, 15.97%, 38.16%, 63.60%, and 114.14%, for the cleaner flotation tests. The results also showed that the highest combustible recovery and flotation rate constants were obtained for intermediate particle size in both rougher and cleaner flotation applications. The highest combustible recovery of 87.15% and rate constant 0.1096 s^{-1} were obtained for −250+125 µm size fraction in a rougher, and 95.65% and 0.1423 s^{-1} for −125+74 µm size fraction in cleaner application.

Bedekovic (2016) studied the effect of particle size, air flow rate, and pulp density on the combustible matter recovery and the ash content using laboratory flotation column. The tests were conducted using five different coal size fractions: -450+400, -400+300, -300+200, -200+100, and -100+63 µm. The author found that the combustible matter recovery is higher for coarse particles, i.e. the increase in particle size increased the combustible matter recovery. The ash content in the concentrate was reported to go from 4.61% to 9.62% with the combustible matter recovery from 17.43% to 81.98%. Based on the p-level, or values of the level of importance, of conducted test, a significant linear effect ($p = 0.008$) of particle size on concentrate ash content was demonstrated, as well as quadratic (p=0.092) and cubic effects ($p = 0.001$). An effect of particle size on the combustible matter recovery ($p = 0.0015$) was also presented.

In the study of Liao et al., (2017), the effect of particle size on the flotation kinetics of a low-rank coal was compared using conventional air bubble flotation (ABF) and oily bubble flotation (OBF) processes, which were proposed and designed by Xia and Yang (2013). The flotation tests were conducted using five particle size fractions: +500, -500+250, -250+125, -125+74, and -74+0 µm. Five kinetic models were considered to determine parameters of the flotation kinetic model and evaluate the relationships between rate constant, ultimate recovery, and particle size. They found that the first-order model with rectangular distribution and the classical first-order model provide the best fit to the experimental data for ABF and OBF, respectively. The correlation coefficients for combustible recovery were 0.9970 and 0.9971, which were obtained for the best fit models. The flotation rate constants for OBF process were found to be higher over all size fraction and operating conditions considered. The rate constant was observed to first increase and then decrease with a decrease in particle size, with the highest rate reported for -125+74 µm fraction, which was 1.217 s^{-1} for ABF and 0.689 s^{-1} for OBF process. The modified rate constants, k_{mod}, and the selectivity index, SI, were also used to compare the selectivity between ABF and OBF. The highest modified rate constants were obtained for intermediate size fractions, which coincides with the previously reported findings.

Table 2. The effect of particle size on coal flotation kinetics and recovery – summary of reported findings

Considered flotation kinetic model	**Proposed models**	**Particle size range for highest flotation rate constant**	**Source**
General 1st order kinetic model		-200+100 μm -500+425 μm	Panopoulos et al., (1986).
General 1st order kinetic model	$R_r = a + b \cdot {d_p}^2$	-150+75 μm	Vanangamudi and Rao (1986) Vanangamudi et al., (1989)
General 1st order kinetic model	$R_\infty = 100\ e^{-a \cdot {d_p}^b}$	-150+75 μm	Rao et al. (1989)
General 1st order kinetic model	$R = 100 \cdot \left\{1 + \left[\frac{1}{(0.5 \cdot kt)}\right]^2\right\}$ $k = a + b \cdot d_p + c \cdot {d_p}^2$	-300+149 μm	Mohns (1997)
General 1st order kinetic model	$R_\infty = -8.8904 \cdot (\ln(d_p))^2 + 92.6 \cdot \ln(d_p) - 149.25$ $k = -3.02 \cdot 10^{-6} \cdot {d_p}^2 + 0.0055 \cdot d_p + 0.6827$	-150+75 μm	Abkhoshk et al. (2010) Kor et al. (2010)
General 1st order kinetic model		-500+250 μm	Li et al. (2013)
1st order kinetic model with rectangular distribution		−250+125 μm	Ni et al. (2016)
General 1st order and 1st order with rectangular distribution kinetic models		-125+74 μm	Liao et al., (2017)
1st order kinetic model with rectangular distribution		-188+100 μm	Bu et al. (2017b)
1st order and 2nd order kinetic models with rectangular distribution		-250+150 μm	Zhang et al. (2013

Bu et al. (2017b) conducted a series of flotation tests to investigate the order of kinetic models in coal fines flotation. Matlab software was used to calculate the model parameters. In this study, six different kinetic models with different orders were used following a series of flotation tests. Tests were conducted on fine coals with different average particle sizes, namely 375, 188, 100, and 37 μm. They found that the first-order kinetic model with a rectangular distribution of floatabilities gave the best fit to the experimental data under the average coal particle size of 375 and 37 μm. It is also observed that the non-integer order equation fit the test data of fine coal with average particle sizes of 188 and 100 μm. Also, the results showed that a non-linear relationship existed between the order of the flotation process and the average particle diameter; they reported a non-integer order for intermediate particles (188 and 100 μm) and first order for coarse and fine particles (375 and 37 μm).

The effects of coal type and particle size on rate constant and ultimate recovery for different macerals (vitrinite, liptinite and inertinite) were investigated by Sahoo et al., (2017b). The sub-bituminous rank coals with -500+150 and -74+36 μm particle size was used in ths study. Experimental results showed that rate constant and ultimate recovery increase for liptinite and decrease for vitrinite and inertinite macerals with increase in particle size. The authors reported that for the coarser fraction liberated vitrinite component have higher rate constant (0.046 s^{-1}) and ultimate recovery (95.6%) than inertinite component. These results showed that the flotation rate constant is a function of the maceral percentage in coal particle.

Most of the previously published research has been focused on direct coal flotation, whereas studies on the effect of particle size on reverse coal flotation kinetics have been quite rare. Zhang et al. (2013) investigated the effects of five distinct particle size fractions (-425+250,-250+150,-150+74, -74+45, and -45 μm) on lignite reverse flotation considering samples with various fines content in the presence of sodium chloride. Six different kinetic models considered by Ni et al., 2016 as explained before, were also tested in this study using the 1st Opt statistical analysis software for modeling of the lignite reverse flotation kinetics. It has been shown that the reverse flotation of lignite in the presence of sodium chloride can be described with the first-order and second-order models with rectangular distribution, but it should be noted that all tested kinetic models gave an excellent fit to the experimental data (correlation coefficients, R^2, were all higher than 0.99, except the classical first-order model). The authors found that the particle size of lignite strongly affects the reverse flotation kinetics. The highest flotation rate constant was obtained with intermediate, -250+150 µm size fraction. The summary of findings reported in selected research studies are given in Table 2.

Many studies have been conducited to determine the effect of particle size on coal flotation kinetics. In general, studies found that the highest flotation rate can be obtained over an intermediate particle size range while it is decreasing sharply for fine and coarse particle sizes.

Flotation rate constant increased with particle size up to a maximum value before decreasing for coarser particles. The flotation rate constant of fines is lower in comparison with other particle sizes, primarily as a result of the decreased probability of collision between particles and bubbles as the particle size is decreased.

6. Conclusions

Coal flotation is a very complex three-phase process that involves many different sub-processes and interactions. The coal flotation kinetics is affected by a number of factors of which particle size is considered to be one of the most important. The effect of particle size on coal flotation has been studied extensively and a number of flotation kinetic models have been developed and proposed in the past. This review paper summarizes some of the current challenges associated with the effect of particle size on coal flotation kinetics and discusses current state of the art in this field.

The main conclusions of this paper can be summarized as follows:

- Based on worldwide coal flotation practice, the optimum particle size in coal flotation is generally smaller than 0.6/0.5 mm or 0.25mm.
- Coal flotation recoveries of fine and coarse particles follow different trends. Recovery of coarse particles is more sensitive to the changes in surface hydrofobicity than the fine particles. The maximum coal recovery was found in the 75 to 300 µm particle size range.
- A number of kinetic models have been developed and tested for the coal flotation process. Based on available literature to date, it is found that the coal flotation follows the first-order kinetics model. Also, the relationship between flotation rate constant and cumulative recovery with particle size was found to be nonlinear.
- In general, the best fit kinetic model varies for different coal types and flotation conditions. Studies showed that the first-order kinetic model with a rectangular distribution of floatabilities gave the best fit to the rougher and cleaner flotation experimental data at particle size between 37 and 375 µm.
- The flotation rate constant is strongly dependent on particle size. The highest flotation rate was obtained over an intermediate particle size range while the rate is decreasing significantly over fine and coarse particle size range. These trends could be well explained by a low collision efficiency of fine particles with bubbles and high detachment probablity of coarse particles from bubbles. A second order polynomial model for flotation kinetic rate as a function of particle size is proposed. It is also found that the flotation rate constant is a function of the maceral percentage in coal particle.
- For the case of reverse flotation, the highest flotation rate constant was obtained with intermediate, -250+150 µm, size fraction.

References

ABDEL-KHALEK, N.A., STACHURSKI, J., 1990. *Role of grain size on the flotation of coals of different rank.* Miner. Metall. Proc. 7 (1), 38.

ABKHOSHK, E., KOR, M., REZAI, B., 2010. *A study on the effect of particle size on coal flotation kinetics using fuzzy logic.* Expert Syst. Appl. 37 (7), 5201-5207.

AGAR, G.E., CHIA, J., REQUIS, C.L., 1998. *Flotation rate measurements to optimize an operating circuit.* Miner. Eng. 11 (4), 347-360.

AHMED M.M., 1995. *Kinetics of Maghara coal flotation.* Unpublished MSc Thesis, Assiut University, pp. 3–33.

AKSOY, D. O., SAGOL, E., 2016. *Application of central composite design method to coal flotation: Modelling, optimization and verification.* Fuel 183, 609-616.

AL TAWEEL, A.M., DELORY, B., WOZNICZEK, J., STEFANSKI, M., ANDERSEN, N., HAMZA, H.A., 1986. *Influence of the surface characteristics of coal on its floatability.* Colloids Surf. 18 (1), 9 – 18.

APLAN F.F, 1997. *Use of flotation process for desulfurization of coal*, in: Wheelock, T.D. (Ed.) Coal Desulfurization: Chemical and Physical Methods. American Chemical Society, Symposium Ser., 64-70.

APLAN, F.F., 1999. *The historical development of coal flotation in the United States.* Advances in flotation technology. B. K. Parekh and J. D. Miller. Littleton, Colorado, Society for mining, metallurgy, and exploration, Inc.

ARNOLD, B.J., APLAN, F.F., 1989. *The hydrophobicity of coal macerals.* Fuel 68, 651-658.

BEAFORE, F.J., CAWIEZEL, K.E., MONTGOMERY, C.T., 1984. *Oxidized coal-What it is and how it affects your preparation plant performance.* J. Coal Qual. 3, 17-24.

BEDEKOVIC, G., 2016. *A study of the effect of operating parameters in column flotation using experimental design.* Physicochem. Probl. Miner. Process. 52 (2), 523−535.

BP, 2017. *BP statistical review of world energy 2017.* Available at: https://www.bp.com/content/ dam/bp/en/corporate/pdf/energy-economics/statistical-review-2017/bp-statistical-review-of-world-energy-2017-full-report.pdf

BROZEK, M., MLYNARCZYKOWSKA, A., TURNO A., 2003. *The relationships between deterministic and stochastic models of flotation.* Arch. Min. Sci. 48 (3), 299-314.

BROZEK, M., MLYNARCZYKOWSKA, A., 2006. *Application of the stochastic model for analysis of flotation kinetics with coal as an example.* Physicochem. Probl. Miner. Process. 40, 31-44.

BROZEK M., MLYNARCZYKOWSKA A., 2007. *Analysis of kinetics models of batch flotation.* Physicochem. Probl. Miner. Process. 41, 51-65.

BROZEK, M., MLYNARCZYKOWSKA, A., 2013. *An analysis of effect of particle size on batch flotation of coal.* Physicochem. Probl. Miner. Process. 49, 341–56.

BU, X.N, XIE, G.Y, PENG, Y.L. CHEN, Y.R. 2016. *Kinetic modeling and optimization of flotation process in a cyclonic microbubble flotation column using composite central design methodology.* Int. J. Miner. Process. 157, 175-183.

BU, X. XIE, G, PENG, Y., GE, L., NI, C, 2017a. *Kinetics of flotation. Order of process, rate constant distribution and ultimate recovery.* Physicochem. Probl. Miner. Process. 53 (1), 342−365.

BU, X., XIE, G., CHEN, Y., NI, C., 2017b. *The order of kinetic models in coal fines flotation.* Int. J. Coal Prep. Util. 37 (3), 113-123.

CHANDER S., POLAT M., 1994. *In quest of a more realistic flotation kinetics model.* In: Proceedings of the IV Meeting on the Southern Hemisphere on Mineral Technology and III Latin American Congress on Froth Flotation, Castro, S., Alvares, J. (Eds.), Chile, 481-500.

CHANDER, S., POLAT, M., 1995. *Coal flotation kinetics: Interactions between physical and chemical variables.* In: Plenary Lecture, Proc. Int. Conf. on Mineral Proc.-Recent Advances and Future Trends, Kanpur-India, 615–631.

CHAVES, A. P., RUIZ, A. S., 2009. *Considerations on the kinetics of froth flotation of ultrafine coal contained in tailings.* Int. J. Coal Prep. Util. 29 (6), 289-297.

CHENG, G., MA, L.Q., GUI, X.H., LIU, J.T., WANG, Y.T., 2013. *Study on kinetic modelling for fine coal flotation.* Int. J. Coal Prep. Util. 33 (1), 12-25.

CILEK, E.C., 2004. *Estimation of flotation kinetic parameters by considering interactions of the operating variables.* Miner. Eng. 17 (1), 81-85.

COLLINS, G. L., JAMESON, G.L., 1976. *Experiments on the flotation of fine particles. The influence of particles size and charge.* Chem. Eng. Sci. 31, 985-991.

DEY, S., 2012. *Enhancement in hydrophobicity of low rank coal by surfactants – a critical overview.* Fuel Process. Technol. 94, 151–158.

DIAO, J., FUERSTENAU, D.W., HANSON, J.S., 1992. *Kinetics of coal flotation*, In: SME-AIME Annual Meeting, Phoenix, AZ, vol. 92.

DOWLING E.C., KLIMPEL R.R, APLAN F. F., 1985. *Model discrimination in the flotation of a porphyry copper ore.* Miner. Metall. 2 (2), 87-101.

DRZYMALA, J., AHMED, H.A. M., 2005. *Mathematical equations f or approximation of separation results using the Fuerstenau upgrading curves.* Int. J. Miner. Process. 76, 55–65.
DRZYMALA, J., 2006. *Atlas of upgrading curves used in separation and mineral science and technology.* Physicochem. Probl. Miner. Process. 40, 19–29.
DRZYMALA, J., 2007. *Mineral Processing. Foundations of theory and practice of minerallurgy.* 1st edition., Ofic. Wyd. PWr., Wroclaw.
DRZYMALA, J., 2018. *Mineral processing. Foundations of theory and practice of minerallurgy.* 2nd edition., Ofic. Wyd. PWr, Wroclaw, Poland.
DUBE, R.M., 2012. *Collectors for enabling flotation of oxidized coal*. Theses and Dissertations-Mining Engineering. 1.
EK, C., 1992. *Flotation kinetics*. In: Innovations in Flotation Technology (Mavros P., Matis K.A. Eds.). Kluwer Academic Publisher.
FAN, M., TAO, D., ZHAO, Y., RHONAKER, R., 2013. *Effect of nanobubbles on different particle size coal flotation*. Miner. Metall. Process. 30 (3), 157-167.
FIRTH, B.A., SWANSON, A.R., NICOL, S.K., 1978. *The influence of feed size distribution on the stage flotation of poorly floating coals*. Aust. IMM. 267, 49-53.
FUERSTENAU, D.W., ROSENBAUM, J.M., LASKOWSKI, J.S., 1983. *Effect of surface functional group on the flotation of coal*. Colloids Surf. 8, 153–174.
FUERSTENAU, D.W., DIAO, J., 1992. *Characterization of coal oxidation and coal wetting behavior by film flotation.* Coal Prep. 10 (1–4),1–17.
GAUDIN, A.M. GROH, J.O. HENDERSON, H.B., 1931. *Effect of particle size in flotation.* Am. Inst. Min. Metall. Eng., Tech. Publ. 414, 3-23.
GAUDIN, A. M., 1932. *Flotation.* 1st Edition, McGraw-Hill, New York.
GAUDIN, A.M., 1957. *Flotation.* 2nd Edition, McGraw-Hill, New York.
GLEMBOTSKII, V.A., KLASSEN, V.I., PLAKSIN, I.N., 1972. *Flotation.* 2nd Edition, McGraw-Hill, New York.
GORAIN, B.K., FRANZIDIS, J.P., MANLAPIG, E.V., 1997. *Studies on impeller type, impeller speed and airflow rate in an industrial scale flotation cell. Part 4: Effect of bubble surface area flux on flotation kinetics*. Miner. Eng. 10, 367-379.
GORAIN, B.K., MUNN, N., FRANZIDIS, J.P., MANLAPIG, E.V., 1998. *Studies on impeller type, impeller speed and air flow rate in an industrial scale flotation cell. Part 5: Validation of k-S_b relationship and effect of froth depth.* Miner. Eng. 11, 615-626.
GOVINDARAJAN, B., RAO, T.C., 1991. *An empirical model for batch coal flotation.* Coal Prep. 9, 155–168.
GRAEME, J.J. 2012. *The effect of surface liberation and particle size on flotation rate constants.* Miner. Eng. 36-38, 132-137.
HARRIS, C.C., CHAKRAVARTI, A., 1970. *Semi-batch flotation kinetics: species distribution analysis*. Trans. AIME. 247, 162-172.
HERNAINZ, F., CALERO, M., 2001. *Froth flotation: Kinetic models based on chemical analogy.* Chem. Eng. Process. 40 (3), 269–275.
HOLUSZKO, M.E., 1991. *Wettability and floatability of coal macerals as derived from flotations in methanol solutions*. M. Sc. Thesis, UBC.
HOWER, J.C., FRANKIE, K.A., WILD, G.D., TRINKLE, E.J., 1984. *Coal microlithotype response to froth flotation in selected western Kentucky coal.* Fuel Process. Technol. 9, 1–20.
HUBER-PANU, H., ENE-DANALACHE, E., COJOCARIU, D.G., 1976. *Mathematical models of batch and continuous flotation.* In: MC Fuerstenau (ed.), Flotation, AIME, New York, 675-724.
HUMERES, E., DEBACHER, N. A., 2002. *Kinetics and mechanism of coal flotation.* Colloid Polym. Sci. 280, 365-371.
IMAIZUMI, T., INOUE, T., 1963. *Kinetic considerations of froth flotation.* In: Proceedings of the 6th International Mineral Processing Congress, Cannes, Ed. A. Roberts, 581-593.
JAMESON, G.J., S. NAM, S., YOUNG, M.M., 1977. *Physical factors affecting recovery rates in flotation.* Miner. Sci. Eng. 9 (3), 103–118.
JIA, R., HARRIS, G.H., FUERSTENAU, D.W., 2000. *Improved class of universal collectors for the flotation of oxidized and/or low-rank coal.* Int. J. Miner. Process. 58 (1), 99-118.
JOWETT, A., 1969. *The development of studies in froth flotation kinetics.* De Ingenieur (Niderl), 81 (38), M11-M17.
JOWETT, A., 1974. *Resolution of flotation recovery curves by a difference plot method.* Trans. Am. Soc. Min. Metall. Eng. 85, C263-C266.
JOWETT, A., SAFVI, S.M., 1960. *Refinements in methods of determining flotation rates.* Trans. AIME 217, 351–357.

KALINOWSKI, K., KAULA, R., 2013. *Verification of flotation kinetics model for triangular distribution of density function of flotability of coal particles.* Arch. Min. Sci., 58 (4), 1279–1287.

KELSALL, D.F., 1961. *Application of probability in the assessment of flotation systems*. Trans. Inst. Min. Metall. 70, 191-204.

KESSLER, M.F., 1973. *Interpretation of the chemical composition of bituminous coal macerals.* Fuel 52 (3), 191-197.

KING, R.P., 2001. *Modeling and simulation of mineral processing systems.* Butterworth-Heinemann, Oxford, Great Britain.

KLASSEN, V.I., 1963. *Coal flotation*, Gosgortiekhizdat, 2nd Edition, Moscow. (In Russian).

KLIMPEL, R.R., HANSEN, R.D., MEYER, W.C., NIMERICK, K.H. 1979. *Laboratory characterization of the influence of reagent changes on coal flotation.* Presented at the AIME Meeting, New Orleans.

KLIMPEL, R.R., 1980. *Selection of chemical reagents for flotation*. In: Mular A., Bhappu R. (Eds.)., Mineral Processing Plant Design, 2nd Ed. SME, Littleton, CO., 907-934.

KOR, M., ABKHOSHK, E., GHARIBIE, K. H., AND SHAFAIE, S. Z., 2010. *An investigation of the particle size effect on coal flotation kinetics using multivariable regression.* Int. J. Min. Env. Iss. 1 (1), 41-47.

LASKOWSKI, J.S., 1995. *Coal surface chemistry and its effects on fine coal processing.* In: Kawatra, S.K. Ed., High Efficiency Coal Preparation: An International Symposium. SME, Littleton, CO, 163–176.

LASKOWSKI, J.S., 2001. *Coal flotation and fine coal utilization*, Elsevier, Amsterdam.

LASKOWSKI, J.S., G.H. LUTTRELL, G.H., ARNOLD, B.J., 2010. *Coal flotation.* XXV International Mineral Processing Congress (IMPC 2010), Brisbane, Australia.

LI, Y., ZHAO, W., GUI, X., ZHANG, X., 2013, *Flotation kinetics and separation selectivity of coal size fractions.* Physicochem. Probl. Miner. Process. 49, 387-395.

LIANG, L., LI, Z., PENG, Y., TAN, J., XIE, G., 2015. *Influence of coal particles on froth stability and flotation performance.* Miner. Eng. 81, 96–102.

LIAO, Y., CAO, Y., LIU, C., ZHAO, Y., ZHU, G., 2017. *Comparison of the effect of particle size on the flotation kinetics of a low-rank coal using air bubbles and oily bubbles.* J. S. Afr. Inst. Min. Metall. 117 (6), 561-566.

LOVEDAY, B.K., 1966. *Analysis of froth flotation kinetics*. Trans. Am. Soc. Min. Metal. Eng., C219-C225.

LYNCH, A.J., JOHNSON, N.W., MANLAPIG, E.V., THORN, C.G., 1981. *Mineral and coal flotation circuits—their simulation and control.* Elsevier, Amsterdam, Netherland.

LYNCH, A. J., WATT, J. S., FINCH, J. A., HARBORT, G. E., 2007. *History of flotation technology.* Chapter in: Froth flotation: A century of innovation by Fuerstenau, M. C., Jameson, G. J., & Yoon, R. H. (Eds.). SME., 65-91.

MARKOVIC, Z. S., JANKOVIC, A., TOMANEC, R., 2008. *Effect of particle size and liberation on flotation of a low grade porphyry copper ore.* J. Min. Metall. Sect. A 44 (1), 24 – 30.

MAVROS, P., MATIS, K.A., 2013. *Innovations in flotation technology.* (Vol. 208). Springer Science & Business Media.

MOHNS, C.A., 1997. *Effect of particle size on coal flotation kinetics.* MSc. Thesis. Department of Mining Engineering, Queen's University, Kingston, Canada.

MORRIS, T.M., 1952. *Measurments and evaluation of the rate of flotation as a function of particle size.* Miner. Eng. 4, 794-798.

NATIONAL RESEARCH COUNCIL (NRC), 2002. *Coal waste impoundments.* National Academy Press, Washington DC.

NGUYEN, A., SCHULZE, H. J., 2003. *Colloidal science of flotation*. Vol. 118. CRC Press.

NI, C., XIE, G., JIN, M., PENG, Y., XIA, W., 2016. *The difference in flotation kinetics of various size fractions of bituminous coal between rougher and cleaner flotation processes.* Powder Technol. 292, 210-216.

OLIVEIRA, J.F., SARAIVA, S.M., PIMENTA, J. S., OLIVEIRA A.P.A., 2001. *Kinetics of pyrochlore flotation from Arax mineral deposits.* Miner. Eng. 14 (1), 99-105.

PANOPOULOS, G., KING, R. P., JUCKES, A. H., 1986. *The effect of particle-size distribution on the flotation of two South African coals.* J. S. Afr. Inst. Min. Metal. 86 (5), 141-152.

PAREKH, B.K., 2000. *Coal: flotation.* Encyclopedia of Separation Science. 2490-2496.

PENG, Y., LIANG, L., TAN, J., SHA, J., XIE, G., 2015. *Effect of flotation reagent adsorption by different ultra-fine coal particles on coal flotation.* Int. J. Miner. Process. 142, 17–21.

PIETRZAK, R., WACHOWSKA, H., 2006. *The influence of oxidation with HNO bsubN3b/subN on the surface composition of high-sulphur coals: XPS study*, Fuel Process. Technol. 87 (11), 1021–1029.

POLAT, M., ARNOLD, B.J., CHANDER, S., HOGG, R., ZHOU, R., 1993. *Coal flotation kinetics – effect of particle size and specific gravity.* In: B.K. Parekh and J.G. Groppo, Editors, Proc. and Utilization of High Sulfur Coals vol. V, Elsevier, New York, 161.

POLAT, M., CHANDER, S., 2000. *First-order flotation kinetics models and methods for estimation of the true distribution of flotation rate constants.* Int. J. Miner. Process. 58 (1-4), 145-166.

POLAT, M., POLAT, H., CHANDER, S., 2003. *Physical and chemical interactions in coal flotation.* Int. J. Miner. Process. 72 (1-4), 199-213.

RAO, T. C., GOVINDARAJAN, B., VANANGAMUDI, M., 1989. *A kinetic model for batch coal flotation.* Miner. Eng. 2 (3), 403–414.

RASTOGI, R.C., APLAN, F.F., 1985. *Coal flotation as a rate process.* Miner. Metall. Process. 2, 137–147.

RUBINSTEIN, J.B. AND SAMYGIN, V.D. 1998. *Effect of particle and bubble size on flotation kinetics.* Frothing in Flotation II: Recent Advances in Coal Processing. 2, 51-80.

SAHOO, S.K., SURESH, N., VARMA, A.K., 2017a. *Studies on separation of macerals from coal by froth flotation.* J. Energ. Nat. Resour. 6 (3), 38-44.

SAHOO, S.K., SURESH, N., VARMA, A.K., 2017b. *Kinetic studies on petrographic components of coal in batch flotation operation.* Int. J. Coal Prep. Util., 1-22.

SCHUMANN, R., 1942. *Flotation kinetics. Part 1. Methods for steady-state study of flotation problems*. J. Phys. Chem. 46, 891-902.

SOKOLOVIC, J., STANOJLOVIC, R., MARKOVIC, Z., 2006. *Effect of oxidation on flotation and electrokinetic properties of coal*, J. Min. Metall. Sect. A 42 (1), 69–81.

SOKOLOVIC, J., STANOJLOVIC, R., MARKOVIC, Z., 2012a. *The effects of pretreatment on the flotation kinetics of waste coal.* Int. J. Coal Prep. Util. 32 (3), 130-142.

SOKOLOVIC, J., STANOJLOVIC, R., MARKOVIC, Z., 2012b. *Activation of oxidized surface of anthracite waste coal by attrition.* Physicochem. Probl. Miner. Process. 48 (1), 5–18.

SOMASUNDARAN, P., ZHANG, L., FUERSTENAU, D.W., 2000. *The effect of environment, oxidation and dissolved metal species on the chemistry of coal flotation.* Int. J. Miner. Process. 58 (1), 85-97.

SRIPRIYA, R., RAO, P.V.T., CHOUDHURY, R.B., 2003. *Optimization of operating variables of fine coal flotation using a combination of modified flotation parameters and statistical techniques.* Int. J. Miner. Process. 68, 109–127.

STOKOWSKI, H., FREYBERGER, W.L., 1985. *Model describing mechanism of the flotation process.* T. I. Min. Metall. 94, C61-C69.

SUN, S.C., 1954. *Effects of oxidation of coals on their flotation properties.* Trans. Am. Inst. Min. Metall. Eng. 6, 396–401.

SUTHERLAND, K.L., 1948. *Kinetics of flotation process.* J. Phys. Chem. 52, 386–390.

SWANN, P.D., ALLARDICE, D.J., EVANS, D.G., 1972. *Low-temperature oxidation of brown coal: 1. Change in internal surface due to oxidation.* Fuel 53, 85–87.

TAO, D., 2005. *Role of bubble size in flotation of coarse and fine particles – a review.* Sep. Sci. Technol. 39 (4), 741–760.

TARJAN, G., 1986. *Mineral processing: concentration, flotation, separation, backup processes.* Vol. 2. Akademai Kiado, Budapest, 113–336.

TOMLINSON, H.S., FLEMING, M.G., 1963. *Flotation rate studies.* In: Proceedings of VI International Mineral Processing Congress, Cannes, Pergamon Press, Oxford – New York, 563-579.

TRAHAR, W. J., WARREN, L. J., 1976. *The floatability of very fine particles-a review.* Int. J. Miner. Process. 3, 103–131.

TRAHAR, W.J., 1981. *A rational interpretation of the role of particle size in flotation.* Int. J. Miner. Process. 8, 289–329.

TSAI, S. C. 1985. *Effects of surface chemistry, particle size and density on froth flotation of fine coal.* Colloids Surf. 16, 323–336.

VANANGAMUDI, M., RAO, T.C., 1986. *Modelling of batch coal flotation operation.* Int. J. Miner. Process. 16, 231-243.

VANANGAMUDI, M., KUMAR, S.S., RAO, T.C., 1989. *Effect of fines content on the froth flotation of coal.* Powder Technol. 58 (2), 99-105.

VAPUR, H., BAYAT, O., UCURUM, M., 2010. *Coal flotation optimization using modified flotation parameters and combustible recovery in a Jameson cell.* Energ. Convers. Manage. 51 (10), 1891-1897.

VARBANOV, R., 1984. *Trans. IMM* C93, 6–8.

VINNETT, L., ALVAREZ-SILVA, A., JAQUES, A., HINOJOSA F., YIANATOS, J., 2015. *Batch flotation kinetics: Fractional calculus approach.* Miner. Eng. 77, 167-171

WANG, H.H., DLUGOGORSKI, B.Z., KENNEDY, E.M., 2003. *Coal oxidation at low temperatures: oxygen consumption, oxidation products, reaction mechanism and kinetic modeling.* Prog. Energy Combust. Sci. 29, 487–513.

WEN, B., XIA, W., SOKOLOVIC, J., 2017. *Recent advances in effective collectors for enhancing the flotation of low rank/oxidized coals*. Powder Technol. 319, 1–11.

WEN, W.W., SUN, S.C, 1981. *An electrokinetic study on the oil flotation of oxidized coal.* Sep. Sci. Technol. 16, 1491-1521.

WILLS, B., 2006, *Handbook of mineral processing technology*, 7th Edn. Wiley, New York.

WOODBURN, E. T., LOVEDAY, B.K. 1965. *The effect of variable residence time on the performance of a flotation system*. J. South. Afr. Inst. Min. Metall. 12, 612–628.

WORLD COAL ASSOCIATION (WCA), 2012. *World Coal Association, Coal – energy for sustainable development 2012,* Available at: http://www.worldcoal.org/blog/coal-%E2%80%93-energy-for-sustainable-development/

WORLD ENERGY COUNCIL (WEC), 2017. *World energy resources 2016*. Available at: https://www.worldenergy.org/wp-content/uploads/2016/10/World-Energy-Resources-Full-report-2016.10.03.pdf

XIA, W., YANG, J., 2013. *Experimental design of oily bubbles in oxidized coal flotation.* Gospod. Surowcami Min. 29 (4), 129-136.

XIA, W., YANG, J., LIANG, C., 2013. *A short review of improvement in flotation of low rank/oxidized coals by pretreatments.* Powder Technol. 237, 1-8.

XIA, W., YANG, J., LIANG, C., 2014. *Investigation of changes in surface properties of bituminous coal during natural weathering processes by XPS and SEM*. Appl. Surf. Sci. 293, 293–298.

XU, M., 1998. *Modified flotation rate constant and selectivity index*. Miner. Eng. 11 (3), 271–278.

YIANATOS, J., BERGH, L., VINNETT, L., CONTRERAS, F., DIAZ, F., 2010. *Flotation rate distribution in the collection zone of industrial cells*. Miner. Eng. 23, 1030-1035.

YOON, R.-H., AKSOY, B.S., 1999. *Hydrophobic forces in thin water films stabilized by dedecylammonium chloride.* J. Colloid Sci. 211, 1-10.

YOON, R.H., LUTTRELL, G.H., 1989. *The effect of bubble size on fine particle flotation.* Miner. Process. Extr. Metall. Rev. 5, 101–122.

YOON, R-H., MAO, L, 1996. *Application of extended DLVO theory, IV: Derivation of flotation rate equation from first principles.* J. Colloid Interface Sci., 181, 613-626.

YOON, R.H., LUTTRELL, G.H., ASMATULU, R. 2002. *Extending the upper particle size limit for coal flotation.* J. South. Afr. Inst. Min. Metall. 102 (7), 411-415.

ZHANG, H., LIU, J., CAO, Y. WANG, Y., 2013. *Effects of particle size on lignite reverse flotation kinetics in the presence of sodium chloride.* Powder Technol., 246, 658-663.

ZHANG, S.Q., 2004. *Coal chemistry.* China University of Mining and Technology Press, Xuzhou. (In Chinese).

ZUNIGA, H.G., 1935. *Flotation recovery is an exponential function of its rate.* Bol. Soc. Nac. Min., Santiago, Santiago, Chile, 47, 83-86.