Full Length Article

Exploration on the mechanism of oily-bubble flotation of long-flame coal

Songjiang Chen\textsuperscript{a,b}, Longfei Tang\textsuperscript{a,b}, Xiuxiang Tao\textsuperscript{a,b}, Huan He\textsuperscript{a,b}, Zhao Yang\textsuperscript{b}, Liang Chen\textsuperscript{b}

\textsuperscript{a} China University of Mining and Technology, Key Laboratory of Coal Processing and Efficient Utilization, Ministry of Education, Xuzhou 221116, PR China
\textsuperscript{b} School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, PR China

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A B S T R A C T

The interaction between long-flame coal particles and oily bubbles controls the crucial processes of attachment and mineralization in oily-bubble flotation thus dominates the recovery of coal. In this study, the interaction energy between long-flame coal particles and diesel oily bubbles was estimated by both DLVO and EDLVO theories, while the attachment of coal particles to oily bubbles was evaluated by induction time measurements and oily-bubble flotation tests. The results indicated that the isoelectric points of oily bubbles and coal particles were observed at about pH 3.5 and 2.3, respectively. Over the entire range of pH 2–11, the attachment between coal particles and oily bubbles was confirmed by the results of the induction time and oily-bubbles flotation tests. Additionally, it was found that the flotation recovery of coals was inversely related to the induction time. The attachment could be accurately predicted by the EDLVO theory over the tested pH range. On the contrary, it showed a great deviation for the DLVO theory to predict the attachment over the tested pH range except at pH 3. The reason for the deviation in prediction may be that the hydrophobic force on the interface of coal particles and oily bubbles is too great to be ignored.

1. Introduction

China as the largest energy consumer in the world accounted for 23% of global energy consumption in 2016 and 27% of global energy consumption growth. Coal is the major primary energy source and its primary energy consumption is 62% in 2016 \cite{1}. Moreover, the exploitation and utilization of low-medium rank coals (i.e., lignite, long-flame coal, weakly caking coal, and non-caking coal) and other coals that are difficult to float have been an important strategy for China’s sustainable development of the coal industry. Low-medium rank coals accounting for about 50% of total coal production capacities provide an important guarantee for China’s economic and social development and security of energy supply \cite{2}.

Gravity separation including wet and dry density-based separation technologies are applicable for the effective separation of low-medium rank coals with particle sizes more than 0.5 mm \cite{3}. Whereas froth flotation that is based on the differences of the mineral surface properties, such as surface physical and chemical properties, is widely used for the beneficiation of minerals less than 0.5 mm \cite{4,5}. After particles-bubbles collision in flotation cell, hydrophobic enough coal particles strongly adhere to the rising bubbles hence float to the froth zone, while hydrophilic gangue particles can’t attach themselves to bubbles thus are discharged as tailings. However, owing to the high surface hydrophilicity, large amount of collector is required to achieve satisfactory yields. Therefore, it is difficult to achieve the economic recovery of low-medium rank coals using common oily collectors, such as diesel oil and kerosene \cite{6-10}. In order to enhance the flotation of low-medium rank coals, oily-bubble flotation technology was proposed in which oily bubbles (i.e., bubbles coated by a thin layer of oily collector, such as diesel oil, kerosene, and dodecane) instead of air bubbles were taken as a carrier \cite{11-13}. Compared to the conventional flotation, the oily collector was spread on the surface of air bubbles in the form of oil film in the oily bubble flotation, making the dispersion of oily collector improved in pulp. As a result, the collecting power of bubbles was enhanced owing to the increased concentration of collector molecules localized on the oil-water interface. It has been proven to be an effective technology for the mineral separation by various researchers \cite{14-16}.

In this method, collector was heated and produced into oil vapor, then air with the oil vapor was inhaled into the flotation pulp to generate oily bubbles \cite{11-13}. In the present work, an improved experiment device for oily bubble flotation was put forward to improve its security and adjustability, as shown in Fig. 7. In this technology, diesel oil was dispersed into micro oil droplets by an air-compressed atomizer to generate oily bubbles, avoiding the high temperature process.

Flotation efficiency is determined by oily bubble-coal particle attachment and mineralization processes, while the attachment process is controlled by the interaction, i.e., surface forces, between oily bubbles and coal particles. These processes involve the fields of colloid and...
interfacial chemistry. In flotation pulp, when coal particles and oily bubbles collide and approach each other closely to about 100 nm, various surface forces begin to play a role that include the London-van der Waals attractive force, the electrostatic double layer repulsive force, the hydrophobic force and so on [17,18]. The classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory was widely used to estimate and describe the interactions between particles as well as colloid stability [19,20]. However, it should be noted that there exists a kind of special interaction energy, i.e., a polar surface interaction energy, between the hydrophilic or hydrophobic particles, which plays a decisive role in the aggregation and dispersion between mineral particles [17,18,21]. As a result, the extended DLVO (EDLVO) theory is proposed, which suggests that the colloid stability is determined by the sum of London-van der Waals attractive force, electrostatic double layer repulsive force and polar surface interaction force.

Moreover, it was reported that induction times were a more sensitive marker than contact angles in predicting the attachment efficiency and closely correlated with the flotation recovery [22–24]. For a successful flotation, the mineralization process, i.e., the attachment of hydrophobic particles onto air bubbles, should be accomplished after collision process in flotation pulp. Particle-bubble attachment involves a series of events, as seen in Fig. 1. The hydration film or wetting film between them forms when particles closely approach to bubbles after collision. In the first stage, the hydration film interposed between particles and bubbles is drained to a critical thickness owing to great enough attractive surface forces. After that, the film ruptures to form a three-phase contact line with a critical radius as the distance between further declines. At last, the expansion of the three-phase contact line conducts to form a wetting perimeter needed by a stable attachment. The time period required for accomplishing the attachment processes is referred to as the attachment time or induction time [22]. In fact, the induction time of a mineral is inherently constant, which is closely related to the surface properties of mineral particles and bubbles.

A method to measure the induction time is particle dropping techniques in which sliding interaction between a particle and a bubble is observed by a high-speed camera, as shown in Fig. 2a. In this method, the induction time can be considered as the duration for a particle sliding from the touching point on the bubble surface to the bubble bottom (i.e., sliding time), as shown in Fig. 2b. If the sliding time is lower than the induction time, the attachment of the particle to the bubble will not occur. On the contrary, with the sliding time greater than the induction time, the attachment between them is expected to occur [26]. To sum up, it was concluded that induction time and sliding time can be used to characterize attachment efficiency. Greater sliding times required by the attachment process mean larger induction times, which indicates that it is difficult for the mineral particles to adhere onto bubbles. In the present work, another method to measure the induction time, bubble pick-up technique, was employed, and the detailed description for this measurement method can be found in the Section 2.6. Induction time measurements.

Although the oily bubble flotation has been proven to be an efficient technology for the beneficiation of low-medium rank coal and the minerals difficult to float, its mechanism is still not well understood. In this study, we focused on the interaction and attachment between particles and oily bubbles to explore the mechanism of oily bubble flotation of low-medium rank coal. The characteristics of the low-medium rank coal were investigated based on its SEM, XPS, and XRD analyses, the interaction between low-medium rank coal particles and oily bubbles was studied by both DLVO and EDLVO theories, and the attachment of coal particles to oily bubbles was evaluated by the induction time and oily bubble flotation tests.

2. Theory and experimental

2.1. EDLVO theory for calculating the interaction energy between coal particles and oily bubbles

The extended DLVO theory takes into consideration the London-van der Waals energy ($V_{\text{LV}}$), the electrostatic double layer energy ($V_{\text{ED}}$) and the polar surface interaction energy ($V_{\text{PT}}$), and the total interaction energy between colloidal particles ($V_{\text{T}}$) in a dielectric medium calculated by the theory is

$$V_{\text{T}} = V_{\text{PV}} + V_{\text{H}} = V_{\text{LV}} + V_{\text{ED}} + V_{\text{PT}}$$

where $V_{\text{PV}}$ is the total energy calculated by DLVO theory. The case of $V_{\text{PV}} > 0$ is corresponding to a mutual exclusion between particles as well as a system in dispersion. In contrast, the case of $V_{\text{PV}} < 0$ is corresponding to a mutual attraction between particles as well as a system in aggregation.

For two spherical particles of radii $R_1$ and $R_2$, the London-van der Waals attractive energy is given by:

$$V_{\text{LV}} = \frac{A}{6H} \times \frac{R_1 R_2}{R_1 + R_2}$$

where $A$ (unit, J) is the Hamaker constant and $H$ is the distance between particles, m.

$A_{12}$ is the Hamaker constant when material 1 and 2 is in the medium 3, which can be expressed as the follow:

$$A_{12} = (\sqrt{A_{11}} - \sqrt{A_{13}})(\sqrt{A_{22}} - \sqrt{A_{13}})$$

where $A_{11}$, $A_{22}$ and $A_{33}$ are the Hamaker constants of material 1, 2 and medium 3 in vacuum respectively. The Hamaker constants of materials in vacuum are listed in Table 1 [20,28].

Table 1 and Eq. (3) can be used to calculate the effective Hamaker constant between oil bubbles and coal particles in water, $A_{12} = 1.08 \times 10^{-21}$ J.

For two spherical particles of radii $R_1$ and $R_2$, the electrostatic double layer energy is given by:
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