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## Comparison of air and oily bubbles flotation kinetics of long-flame coal

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ARTICLEINFO	A B S T R A C T
A R T I C L E I N F O Keywords: Long-flame coal Oily-bubble flotation Flotation kinetics (models)	This paper focuses on the difference in kinetics of air and oily bubbles flotation of long-flame coal. Six flotation kinetic models were taken to fit the air and oily bubbles flotation results by the software MATrix LABoratory. The findings indicated that the conventional flotation was greater than the oily-bubble flotation in flotation rate in the early stage, and these two flotation processes exhibited different variation laws in cumulative concentrate yield with flotation time. Additionally, it was found that the classical first-order model could provide an excellent fit to the experimental data for the conventional flotation, yet all the studied kinetic models showed a great deviation in fitting to oily-bubble flotation data. Consequently, an improvement for flotation kinetic models was conducted by subtracting the delay constant in the oily-bubble flotation to attain an excellent fitting. Finally, the delay constant for the oily-bubble flotation was determined to be about 0.7500 min, while the improved classical first-order model was found to give the best fit to the oily-bubble flotation data. This study may contribute to a better understanding of the oily-bubble flotation characteristics.

#### 1. Introduction

Coal is a main energy fuel in the world, especially in China. It accounted for 62% of China's primary energy consumption in 2016 [1]. It is therefore important to achieve the efficient and clean utilization of coals so as to avoid the corresponding environmental pollution. In general, coal is recovered by gravity separation technologies, such as heavy media separator, heavy media cyclone, jigger, spiral separator, vet these methods are only applicable for beneficiation of coal more than 0.5 mm or larger in particle size [2]. Fine coal particles, however, have been ever-increasing with the deterioration of geological conditions and the continuous improvement in mining mechanization. Especially for low-medium rank coals, they are easy to break into fine particles in mining and gravity separation, thereby producing a great amount of coal slime. Compared with gravity methods, froth flotation is an effective physicochemical technique for upgrading fine coals less than 0.5 mm in particle size [3,4]. For high rank coals, they respond well to the conventional flotation processes owing to their natural surface hydrophobicity, and a high yield is thereby easy to attain. Nevertheless, low-medium rank coals are usually characterized by hydrophilicity due to abundant oxygenated functional groups on their surfaces [5–11]. As a result, it is difficult to achieve their economic recovery by conventional flotation and the dosage of common oily

collector is usually as high as 30–50 kg/t [7,12–14].

Inspired by the demonstrated success of oily-bubbles flotation for minerals, which exhibited a better flotation performance than air bubble flotation [15-17], a similar oily-bubble flotation method was proposed to enhance the flotation of oxidized coals [18]. In this technology, the oily collector, such as diesel oil, kerosene and dodecane, was first heated to form oil vapor, and then with air induced to the flotation cell to generate oily bubbles that replace air bubbles as a flotation carrier. In comparison to the conventional flotation, it improves the dispersion of oily collector by spreading the oily collector as a thin oil film on the air bubble surface. The oily-bubble flotation technology has been proven to be an effective technology for the beneficiation of low-medium rank coals, exhibiting a better collecting power and selectivity for low rank coal particles [6,12,18-21]. In the present work, an improved experimental device for oily bubble flotation was assembled by our team, as shown in Fig. 2, and the detailed description for this experimental device can be found in the Section 2.2.2.

Flotation is a complex physico-chemical process to separate concentrate (valuable minerals) from gangues, which is dependent on the difference in the surface properties of valuable minerals and gangues [7]. Whereas flotation kinetics is widely used to investigate the flotation behaviors, mainly involving the fluid environment of flotation, the

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collision and attachment between particles and bubbles, and the flotation rate [22,23]. In order to describe and simulate the flotation kinetics, various flotation kinetic mathematical models were proposed or improved, which is widely used to optimize operating parameters so as to improve the flotation process [24-28]. Based on these models, the effects of particle size and its distribution, the aeration rate, the type and dosage of flotation reagents, pulp density and other flotation parameters on flotation kinetics were comprehensively studied [29-38]. In addition, Ni et al. [39] investigated the difference in flotation kinetics of bituminous coal with different size fractions between rougher and cleaner flotation processes. It was found that both greater combustible recovery and flotation rate were attained in the cleaner flotation process compared with the rougher flotation process, and that the first-order and second-order models were suitable to describe the rougher flotation process while the first-order model was applicable to the cleaner flotation process. A similar research reported that the chosen kinetic models except the classical first-order flotation kinetic model could give good fits to experimental data in the reverse flotation of lignite with different size fractions [40]. However, these abovementioned studies only focused on the kinetics of air bubble flotation instead of oily bubble flotation. Although the oily-bubble flotation has been proven to be an efficient technology, its flotation kinetics is not yet well understood. The aim of this investigation is to explore the difference in the kinetic characteristics between air and oily bubbles flotation. What more important is that we tried to improve the flotation kinetic models to make them give a better fit to the oily-bubble flotation data, and therefore it was expected to provide a better description for the oily bubble flotation behaviors. As a result, this study may provide an invaluable insight into the oily-bubble flotation process of low rank coals.

#### 2. Experimental and methods

#### 2.1. Materials

The coal sample used in this study, a long-flame coal, was collected from the Daliuta Mine in the Shendong mine area located in Shaanxi province, China. The proximate and ultimate analyses for the coal samples are given in Table 1. The coal sample is 36.68% in volatile matter content, 33.98% in ash content, and 24.55% in oxygen content in the coal organic matrix. Fig. 1 shows the chemical groups analyses for the coal sample. It was found from Fig. 1 that there are abundant hydrophilic groups on the surface, such as alcohol or phenolic hydroxyl groups at 3398 and 1099 cm<sup>-1</sup>, while the coal sample is low in hydrophobic groups, such as the stretching vibration of methylene group at 2919, 2850 and 1433 cm<sup>-1</sup>, C=C-stretching vibration absorption peak at 1597 cm<sup>-1</sup>, and the characteristic infrared absorption band of methyl group at  $1375 \,\mathrm{cm}^{-1}$ . In addition, the intensities of peaks at 1032, 1009, 913, 470, and  $425 \text{ cm}^{-1}$  for gangue minerals were found to be strong. These findings support the proximate and ultimate analyses of the coal samples. As a result, the coal sample is surface hydrophilic, with a contact angle of 56.5°. What's more, the other characteristics of the samples were comprehensively investigated. The results indicated that the ultrafine (-0.045 mm) particles with ash content of 45.07%accounted for more than 50% of the coal sample, which specific surface area was  $6.114 \text{ m}^2/\text{g}$ , and that the coal sample surface was very rough and rugged, with developed pores and cracks on the surfaces.

Table	1
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Proximate and ultimate	analyses of coal	l slime samples	[6].
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Proximate analysis, %			Ultimate analysis, %					
M <sub>ad</sub>	A <sub>ad</sub>	$V_{\mathrm{daf}}$	FC <sub>daf</sub>	$C_{daf}$	H <sub>daf</sub>	O <sub>daf</sub>	N <sub>daf</sub>	S <sub>daf</sub>
7.68	33.98	36.68	63.32	68.38	3.90	24.55	1.14	2.03

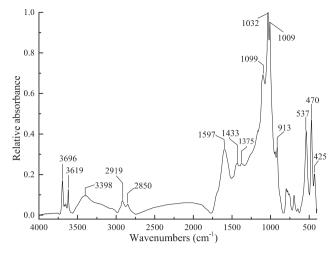


Fig. 1. FT-IR spectrum of coal sample.

Consequently, it was envisaged that the coal sample exhibits low floatability, and it will be difficult to achieve an economic recovery of the coal sample by the conventional flotation method.

#### 2.2. Conventional and oily-bubble flotation tests

#### 2.2.1. Conventional flotation test

The conventional (air bubble) flotation test was carried out in a 1.5 L XFD flotation cell, and diesel oil and methyl isobutyl carbinol (MIBC) were used as a collector and a frother, respectively. The dosages of both reagents were respectively 50 and 0.4 kg/t, and the aeration rate was kept constant at  $0.25 \text{ m}^3$ /h. First, 90 g of coal samples less than 0.5 mm in particle size were mixed with 1.5 L water in the flotation cell, and prewetted for 120 s at an impeller speed of 2200 rpm. Then, the collector and foaming agent were successively added into the pulp, and were conditioned for 120 and 60 s, respectively. After the conditioning processes, air was introduced into the flotation cell and six clean coals were collected at 15, 30, 60, 120, 180 and 300 s, respectively. Finally, the flotation products were filtered, vacuum dried, weighed, and collected for ash determination. The combustible matter recovery (E<sub>C</sub>) was calculated from Eq. (1) to analyze the flotation results.

$$E_{\rm C}(\%) = \frac{M_{\rm C}(100 - A_{\rm C})}{M_{\rm F}(100 - A_{\rm F})} \times 100$$
(1)

where  $M_C$  is the weight of the concentrate (%),  $A_C$  is the ash content of the concentrate (%),  $M_F$  is the weight of the feed (%), and  $A_F$  is the ash content of the feed (%).

#### 2.2.2. Oily bubble flotation tests

The oily bubble flotation test was conducted with the oily bubble flotation system shown in Fig. 2, which is mainly composed of a 1.5 L XFD flotation machine, an air compressor, an atomizer, a heating tube, a temperature control box, and a gas flowmeter. Unlike the conventional flotation, the oily collector was held in an atomizer instead of directly added into the flotation pulp. In this technology, the collector was first dispersed into fine oil droplets by the air compressed atomizer. In the heating tube that was preheated to 280 °C, the fine oil droplets form oil vapors almost for an instant due to the high temperature. Once the diesel oil vapors with air was induced to the flotation cell, they rapidly condensed into droplets in the flotation pulp while air was sheared into a lot of fine air bubbles that contain the oil droplets under the high-speed rotating impeller. Due to the molecular motions, the oil droplets spread and coated the air bubbles surface, generating oily bubbles. For a typical test, the dosage of diesel oil was 4.35 kg/t, and the frother dosage was kept consistent with the air bubble flotation. The mixed coal samples/water were conditioned for 240 s. Then, the frother

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