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Review

Recent advances in effective collectors for enhancing the flotation of low rank/oxidized coals

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ABSTRACT

Coal plays an important role in energy supply. However, low rank/oxidized coals are difficult to float with the common oily collectors, and hence effective collectors are urgently needed to be found or created. The difficult-to-float reason of low rank/oxidized coals primarily includes two aspects, i.e. abundant oxygen-containing groups on coal surface and porous surface of coal particle. The common oily collectors are difficult to adsorb on hydrophilic sites on low rank/oxidized coals surface and a porous structure of coal surface needs large consumption of collectors. This review is to highlight recent advances in the effective collectors for enhancing the flotation of low rank/oxidized coals, especially an overview of effective collectors proposed in the past decade. The effective collectors are achieved through the emulsion of common oily collectors, the mixture of several collectors/surfactants, the special collectors and bio-collectors. Throughout this review, the mechanism of the effective collectors enhancing the flotation of low rank/oxidized coals is discussed and the development directions of effective collectors in the future are also recommended.

Contents

1. Introduction

As the demand for energy growth, coal plays an important role in energy supply and hence fine coals are urgently needed to be effectively recycled. Froth flotation is usually considered to be the most effectual method to upgrade the fine coal (<0.5 mm) [1]. On a worldwide basis, there are from 0 to 40% of the coal which are normally upgraded by flotation [2]. In the conventional coal flotation, the coal usually has natural hydrophobic surface while the mineral has natural hydrophilic surface. Exactly, flotation uses this difference in the surface properties of coal and mineral to separate the coal by bubbles from the minerals in the flotation pulp. Most of the coal enters into the froth product becoming the concentrate, while most of the mineral stays in the pulp becoming the tailings. In the froth flotation, a few coals cannot become the concentrate, which causes the loss in the combustible matter recovery as well as clean coal yield. However, a few minerals can also enter into the froth product, namely, the entrainment of high-ash minerals [3,4]. The coal is made up of the organic compositions, such as aliphatic hydrocarbons and aromatic series [5]. In contrast, the mineral in raw coal primarily consists of clays, such as carbonate minerals, gypsum, quartz, and pyrite. These minerals in the coal are normally hydrophilic. In a word, the coal is normally easy to float and separate from the

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minerals based on the difference in natural hydrophobicity between the coal and the minerals.

However, there are lots of low rank coals which are difficult to float with typical oily collectors in moderate additions [6–10]. A delegate for low rank coals is lignite. Lignite is generally hydrophilic due to the presence of a large amount of oxygen-containing groups. Meanwhile, the high-rank coal is easy to be oxidized in the air. The oxidation processes result in the formation of oxygen-containing functional groups on the high-rank coal surface, which reduces the hydrophobicity of the high-rank coal surface [11,12].

In other words, low rank and oxidized coals are similar in the surface properties and the role of collectors in the flotation of low rank coal is also similar to that in the flotation of oxidized coal. This review is to highlight recent advances in the effective collectors for enhancing the flotation of low rank/oxidized coals. The mechanism of the effective collectors enhancing the flotation of low rank and oxidized coals will be also discussed. This review does not focus on the reverse flotation collectors of low rank/oxidized coals because an overview of reverse flotation process for coal has been published [13].

2. Characters of low rank/oxidized coals surface

Low rank coals include peat, lignite and some sub-bituminous coals. All of these coals are characterized by low metamorphic degree. Coal is formed from plant materials after the long periods of compression and hardening. During the periods of the formation of coal, the oxygen content is reduced while the carbon content is increased. The carbon content/oxygen content ratio decreases with the increase of coal rank. The carbon content of anthracite coal reaches the highest value while the oxygen content is the lowest compared with other coals at different ranks, i.e. lignite, sub-bituminous coals and bituminous coals. The oxygen exists in the coal as the primary forms of oxygen-containing functional groups. Carboxyl, phenolic and carbonyl are the primary oxygen-containing functional groups in low rank coals. These oxygen-containing functional groups can be bonded with water molecules by hydrogen bonding, which reduces the hydrophobicity of low rank coal surface. Therefore, low rank coals are difficult to float with common oily collectors. The common oily collector cannot easily spread on the surface of low rank coals. According to this situation, the collectors containing the oxygenated functional groups have an important role on the flotation of low rank coals [14,15]. In addition, the surface topography of low rank coal is rough and porous. When low rank coal is pre-wetted in the flotation pulp, a thick water film will cover its surface [16]. The conventional oily collector is prevented to effectively adsorb on low rank coal surface. The porous surface properties of low rank coals also increase the consumption of collectors and flotation costs [17–19].

At the same time, the flotation of oxidized coal is a key issue. The two types of coal, i.e. bituminous and anthracite coals are usually easy to float with the common oil collectors due to their high natural hydrophobicities. However, they can be oxidized in the air. The oxidation reduces the hydrophobic sites on the coal surface. The oxidation reaction also results in the formation of oxygenated functional groups on the coal surface and hence the natural hydrophobicity of the coal will be reduced after the oxidation. The oxidation of the coal surface makes the coal difficult to float using common oily collectors [20,21]. Coal oxidation includes three major aspects, namely, the adsorption of oxygen on coal surface, the release of reaction products (like H_2O, CO_2 and CO), and the release of heat [22–27]. Sometimes, the release of heat may cause the coal to be oxidized to a further extent. For the mild oxidation, the oxidation only occurs on the coal surface and the surface properties of coal can be significantly changed. However, for the heavy oxidation, the oxidation can occur in the inner of coal particles and hence the whole coal is oxidized [28,29]. After the oxidation, the surface properties of oxidized coal are similar to those of low rank coal. As shown in Fig. 1, XPS and SEM pictures of lignite and oxidized coal surface are similar [30,31]. Both lignite and oxidized coal surface have abundant oxygen-containing groups and porous structure.

The grinding pretreatment has been widely used in the recovery of the hydrophobicity of oxidized coal. The oxidized layer on coal surface can be removed and the fresh and hydrophobic surfaces are exposed. After the grinding or attrition pretreatments, the surface hydrophilicity of the oxidized coals is generally reduced [32–37]. However, the heavy oxidized coal is difficult to obtain a good hydrophobicity through the grinding or attrition pretreatments [28]. In this case, the effective collector is the only way to float them effectively.

3. Common oily collectors

In coal flotation industry, the common oily collectors are fuel oils, such as kerosene and diesel oil. In the experimental study, the common oily collectors are dodecane and hexadecane. The oily collectors primarily consist of carbon and hydrogen elements. In some cases, the common oily collectors are named as hydrocarbon oils. The carbon and hydrogen elements usually exist as the forms of —CH_3, —CH_2, —CH in the oily collectors. The groups, —CH_3, —CH_2 and —CH are hydrophobic and can spread easily on the hydrophobic sites on the high-rank coal surface [38]. While the coal is low rank or the coal is oxidized, there are only a few hydrophobic sites on the coal surface. The oily collectors are difficult to have an effective spread or adsorption on the low rank/oxidized coal surface [16,39,40]. Therefore, the hydrophobicity or floatability can be hardly enhanced by the oily collectors.

In addition, the dosage of oily collectors is also very high in order to create a high reagent concentration for the effective spread or adsorption of the oily collectors on the coal surface. Especially for low rank and oxidized coals, the high reagent concentration is somewhat useful for obtaining the high flotation recovery [7]. Therefore, the reagent dosage in the flotation of low rank/oxidized coals is usually much higher than the reagent dosage in the flotation of bituminous and anthracite coals. Many coal preparation plants usually adopt this method (increasing collector dose) to enhance the flotation recovery of low rank and oxidized coals [14]. However, a high reagent dosage can also somewhat decrease the selectivity, which increases the ash content of clean coal because the hydrophobicity of some ash minerals will be also enhanced at a high collector dosage condition [4]. Furthermore, a high dose of oily collectors in coal flotation is not economic. Therefore, it is urgent that the effective collectors should be found to enhance the flotation of low rank and oxidized coals.

4. Effective and special collectors

4.1. Emulsion and mixture of common oily collectors and others

Usually, the common oily collectors spread on the coal surface as the form of small oil drops. The oily collectors, such as kerosene and diesel oil are broken into amounts of small oil drops by the impeller or stirring devices. The diameter of small oil drops is usually several microns. The hydrophobicity of coal surface can be enhanced by the adsorption of the small oil drops on its surface. In recent years, the emulsion technology for the effective distribution of the oily collectors is widely applied in the conditioning and flotation processes. Benefiting from this emulsion technology, the collector dosage is decreased as well as the distribution condition is improved [41]. Ahmed and Drzymala [42] compared the flotation behavior of oxidized coal by the direct contact with pure (anhydrous) flotation reagent or microemulsion, and they found that mixing dry oxidized coal with microemulsion droplets achieved higher clean coal yield.

Shen et al. [43] used fatty acids emulsions in the reverse flotation of Pingsuo gas coal fines and found the emulsions not only reduced the clean coal ash content but also save the reagents consumption. They used two types of emulsions obtained from oleic acid and dodecanoic acid emulsified by dodecylamine hydrochloride (DDA-HCL),