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Historical perspective

Chemical and colloidal aspects of collectorless flotation behavior of sulfide and non-sulfide minerals

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ABSTRACT

Flotation has been widely used for separation of valuable minerals from gangues based on their surface characterizations and differences in hydrophobicity on mineral surfaces. As hydrophobicity of minerals widely differs from each other, their separation by flotation will become easier. Collectors are chemical materials which are supposed to make selectively valuable minerals hydrophobic. In addition, there are some minerals which based on their surface and structural features are intrinsically hydrophobic. However, their hydrophobicities are not strong enough to be floatable in the flotation cell without collectors such as sulfide minerals, coal, stibnite, and so forth. To float these minerals in a flotation cell, their hydrophobicity should be increased in specific conditions. Various parameters including pH, Eh, size distribution, mill types, mineral types, ore characterization, and type of reaction in flotation cells affect the hydrophobicity of minerals. Surface analysis results show that when sulfide minerals experience specific flotation conditions, the reactions on the surface of these minerals increase the amount of sulfur on the surface. These phenomenons improve the hydrophobicity of these minerals due to strong hydrophobic feature of sulfurs. Collectorless flotation reduces chemical material consumption amount, increases flotation selectivity (grade increases), and affects the equipment quantities; however, it can also have negative effects. Some minerals with poor surface floatability can be increased by adding some ions to the flotation system. Depressing undesirable minerals in flotation is another application of collectorless flotation.

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1. Introduction

Flotation concept has been widely used to efficiently and quickly separate gangue minerals from valuable minerals. This phenomenon happens based on their difference in natural or induced hydrophobicity. Three main principles including physical phenomena, chemical reaction, and mechanical parameters strongly control the possibility of floatability and finally separation of mineral from each other. Also, contact angle between three phases at the interfaces of minerals including liquid, solid, and gas critically determines the hydrophilic or hydrophobic properties of mineral surfaces [1–4].

Collectorless flotation depends on surface tension controlling forces in flotation medium and accordingly wettability differences of floating minerals [5]. The collectorless flotation of sulfide minerals plays an important rule which has been recognized since virtually the beginning of this century [6].

Changes in surface composition of sulfide minerals can be explained by electrochemical properties including mineral rest potentials and system redox potentials as well. Up to now, some crucial factors such as elemental sulfur, sulfur-enriched metal-deficient sulfide or a metal polysulfide are responsible for improving the rate of collectorless flotation. However, the intensity of floatability strongly depends on various circumstances in which flotation process is carried out [7].

Most sulfide minerals do not exhibit natural floatability. They have, however, collectorless floatability in specific pulp potential ranges, under the condition of which the sulfide mineral surface has been rendered hydrophobic by surface self-oxidation [8]. It is now well established that collectorless flotation of most sulfide minerals requires superficial oxidation of the sulfides leading to the formation of sulfur, sulfur-excess or polysulfide layers on their surfaces [9].

Some researchers stated the importance of pulp potential (Eh) which is a critical factor in the collectorless flotation [10]. It has been found that there is a clear distinction between flotation and non-flotation, which appear to be pH and Eh dependent [8].

The proper conditions have been discussed by some authors and it has been suggested that the collectorless flotation was possible with the addition of sodium sulfide (Na_2S) to the pulp [10].

Floatability of chalcopyrite depends on the state of oxidation which is controlled by the electrochemical reactions. In order to float chalcopyrite in the absence of a collector, a positive potential is required [11]. Also, a combination of surface sensitive analytical techniques for collectorless flotation investigation is used in order to determine the type and proportion of species on the surface. Research done on sphalerite collectorless flotation has revealed that Cu(II) addition can either increase or decrease the collectorless flotation of sphalerite, depending on the solution conditions (pH, Cu(II) concentration) [12].

Pyrite is one of the most common sulfide minerals encountered in nature. Pyrite often exists in sulfide mining and coal mines, where it is usually undesired and is often removed by the flotation method. The flotation behavior of pyrite is greatly influenced by the pH of the pulp [13].

More recently, with single minerals and in anaerobic laboratory conditions, researchers reported that galena, chalcopyrite, chalcocite, pyrite and copper-activated sphalerite were almost completely floatable without collector in water [7].

Floatability of the coals increases with the increase in carbon content. It is observed that higher-rank coal can usually be floated without the use of a collector, but not so with oxidized or weathered coal. The process, however, may require extensive conditioning to minimize reagent consumption [14]. The flotation results suggest that under some specific test conditions the coal product can be recovered in chloride salts without using any frother or collector [15].

Although talc and talc-carbonate ores have been well investigated by researchers worldwide in terms of surface characteristics, flotation kinetics, collectorless flotation and size dependent flotation kinetics as well, it is more necessary to put some efforts on the possibility of collectorless flotation of talc from talc carbonate ore with respect to particle size [16].

In this paper, we put our efforts to first scrutinize the most basic causes of collectorless flotation including hydrophobicity of minerals, contact angle, surface properties, and other effective factors leading to collectorless flotation. Moreover, purbe diagram and its applications were carefully studied for each mineral. Proper conditions for collectorless flotation of sulfide minerals such as chalcopyrite, sphalerite, galena, pyrite, etc. were analyzed and meticulously highlighted the most basic and brief information about them. In addition, requisite conditions for collectorless floatation for non-sulfide minerals such as coal, talc, pyroxene, and so forth were investigated. According to our findings, further investigations and experiments in the field of super-hydrophobicity, non-synthetic collectors (using minerals as collector instead of chemical materials), and surface analysis techniques will be so helpful and promising area to improve collectorless floatation concepts.

2. Basic concepts of collectorless flotation

2.1. Hydrophobicity

Hydrophobicity plays an important role in biological, chemical, and physical processes [1]. Hydrophobic and hydrophilic are frequently used as descriptors of surfaces [3]. Hydrophobic solid surfaces are often naturally non-wettable by water. Such surfaces are also typically air attracting, known as aerophilic surface [2]. Hydrophobicity and floatability of solids have been already analyzed from the standpoint of properties of solid–water and solid–water vapor interfaces, chemical bonds, bulk properties, crystal structure of the solid, and reactivity of the solid with water [1]. A surface is hydrophobic if it tends not to adsorb water or be wetted by water. A surface is hydrophilic if it tends to adsorb water or be wetted by water [3].

Wettability studies require the measurement of contact angles as a representative of the degree of wetting when a solid and liquid interact. Small contact angles (<90°) correspond to high wettability while large contact angles (>90°) correspond to low wettability [17,18]. The angle formed between a tangent to the drop and a tangent to the solid–water interface, both originating from the point of the three-phase contact, depends on the energetics of the three interfaces involved and is given by the following formula which is referred to as the Young equation (Eq. (1)) [1,17]:

$$\gamma_{sv}-\gamma_{sw}=\gamma_{wv}\,\mathrm{cose}(\theta) \tag{1}$$

where γ_{sv}, γ_{sw}, and γ_{wv} represent the interfacial free energy of the solid–air, solid–water, and water–air interfaces.

Consider a liquid drop resting on a flat, horizontal solid surface (Fig. 1). The contact angle is defined as the angle formed by the intersection of the liquid–solid interface and the liquid–vapor interface (geometrically acquired by applying a tangent line from the contact point along the liquid–vapor interface in the droplet profile) [18]. Fig. (3) displays certain measured contact angles for different materials. Based on this information, Teflon has the highest contact angle (stronger