Invited Review

Interactive effect of minerals in the flotation of complex ores: A brief review

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Abstract: Froth flotation is the most effective industrial method used for the separation of fine-grained minerals. The main problem for the flotation of complex ores, obviously, is the negative effect of the interactions among minerals in slurry, which leads to the variation of surface properties in the process of separation. In this review, the studies of interactive effect among minerals in the flotation of iron ores, magnesite ores, and scheelite ores are summarized and the main problems and mechanisms that diminish the separation efficiency of minerals are revealed in detail. The recent research achievements in flotation of those ores confirmed that the mineral aggregation, coating, and dissolution, among other factors caused by interacting behavior explains the depressing effects of fine particles on minerals separation. In addition, the solvable methods for these effects were further discussed. There is good reason to believe that the novel flotation processes and more selective reagents are critical for the further investigations into various approaches to improving the beneficiation efficiency of those ores. This paper is intended to provide a good reference for studies related to the flotation of complex ores.

Keywords: interactive effect, flotation; iron ores; magnesite ores; scheelite ores

1. Introduction

Over the past few decades, rapid growth of the world economy has greatly increased the requirement to exploit natural resources to meet metals and energy demands from all fields of society [1-3]. With the excessive exploitation of high-grade ore deposits, especially for those complex ores, this has been a great challenge due to
available low-grade mineral reserves [4,5]. In recent years, various efficient methods have been explored to enhance the minerals separation, such as improving mineral liberation [6], developing high-efficient separation reagents, processes, equipment [7,8], and so on. Compared with other existed technologies, froth flotation did show a significant advantage and has undoubtedly become the most important method in separation of low-grade refractory ores [9,10]. However, the limitations of separation efficiency and product quality are the main problems in flotation process [11]. This is mainly due to the complex mineral compositions and the associated relationship between valuable minerals and gangue minerals in fine grain sizes [12,13]. At this point, finer grinding is needed to improve the mineral liberation, which is particularly important [14]. But on the other hand, it is of course what makes the fines particles more common in flotation system [15,16].

Interactive effect between valuable minerals and gangue minerals, which serves as one of the most important factors in the flotation of complex ores, has been a topic of great interest [17-20]. Interactive effect of minerals represents the inter adsorption and surface conversion behaviors of two or more minerals in flotation separation [17,19], which often leads to the reduction of separation possibility. In recent years, the research on the interactive effect of minerals includes the interaction pattern, interaction mechanism, as well as the methods of utilizing or eliminating the interaction effect [17-19]. With the results discussed above, major properties of the interaction effect between the fine and coarse particles can be stated as follows and shown in Fig. 1:

1. Fine valuable minerals adhere to the coarse gangue minerals, which leads to the passive loss of valuable minerals. In hematite (Fe₂O₃) flotation, for example, fine hematite particles can be adsorbed on the surface of quartz, resulting in a reduction of hematite recovery [19];

2. Fine valuable minerals adhere to the coarse valuable minerals and it is also known as carrier flotation [21,22]. In the research of Ateşok et al., the highly hydrophobic coarse coal particles were used as the carrier which helps to improve the floatability of the extremely hydrophilic low-rank coal particles [20];

3. Fine gangue minerals adhere to the coarse valuable minerals, which reduces the grade of concentrate. For
example, the fine feldspar particles easily cover the surface of coarse quartz in quartz flotation, which shows an adverse effect on the concentrate grade;

(4) The aggregation of fine gangue minerals and fine valuable minerals, which leads to the formation of coarse particles and they will be part of the froth product or tailings;

(5) Effect of mineral dissolution on flotation result [23].

Fig. 1. Types of interactive effect among minerals in flotation.

The interactive effect is more prominent when the mineral dissemination size getting smaller. The interaction effect is the influence of mineral adsorption, activation and inhibition on separation in complex ores flotation [24]. It mainly caused by the fine disseminated grain size of valuable minerals and the complex symbiosis with gangue minerals. To realize the monomer dissociation between minerals, the ore sample should be finely ground which results in the serious sliming and covering between minerals, then the separation becomes extremely difficult.

According to the particle size classification proposed by Sivamohan and Forssberg, the terms “fines” refers to particles less than 100 μm [25]. The problem of fine particles in the flotation process has drawn researchers’ attention and understanding the limits in flotation of fine particles is the key to obtain the selective separation [26,27]. To date, some specific flotation schemes such as shear flocculation flotation and carrier flotation have
been proposed to improve flotation efficiency of fine minerals [28,29]. There is a lot of experimental evidence showed that the fine particles in flotation have low collision efficiencies with gas bubbles and very slow float speed [30-32]. In other words, the existing of slimes would result in significant adverse impacts on both direct and reverse flotation. To solve these problems, the current research mainly focuses on the following three aspects: 1) Reducing the size of bubbles to enhance the possibility of collision and adhesion of the bubbles with fine minerals, such as theoretical and applied research of micro-bubble flotation column [33]; 2) Increasing the apparent particle size of fine minerals to achieve the flotation under conventional conditions [34]; 3) Searching for the appropriate reagent system and flotation process, and removing the fine particles preferentially.

At present, researches on the interaction effect of minerals are mainly focused on the influence of fine particles on other minerals in different size fractions. The concepts of carrier flotation, flocculation flotation, dispersive flotation, and step flotation are all related to the interaction effect of minerals. Among them, the carrier and flocculation flotation are embodied in strengthening the interactions, while the dispersive and step flotation are embodied in weakening the interactions. In this review, the research work of interaction effect in the flotation of complex iron ores, magnesite ores and tungsten ores in recent years were summarized. It mainly includes the regularity and mechanism of the interactive effect, and methods of weakening the interactive effect. This review emphasized the important influence of the interactive effect of minerals in various flotation system. The study can be used to establish the theoretical system of interactive effect in flotation and the flotation separation can be significantly optimized.

2. Interactive effect in iron ores

Iron ore is a very important mineral resource, which has been widely used in the construction of machine tools and as structural components for buildings. Although there are over 300 types of minerals containing iron in the world, the iron sources mainly include hematite, magnetite (Fe₃O₄), limonite (FeO(OH)·n(H₂O)), goethite
((FeO(OH)), and siderite (FeCO₃) [35], among which the fully oxidized hematite ranks the first [36]. The major issue associated with iron ores is that the impurity (e.g., silica, phosphorous, alumina, sulfur) is contained normally [37]. In addition, quartz is generally considered to be the commonest gangue mineral in iron ores in China as well as in other countries [38].

Iron resources with high concentration are distributed in a few countries and regions, and above 75% of the world's reserves are distributed in Russia, Ukraine, Australia, etc. [39]. It is estimated that the global iron ore resources exceed 800 million kilotons of raw ores and it contains more than 230 million kilotons of iron [40]. On the world scale, the iron ore production and deposits are shown in Table 1, according to data from the US Geological Survey in 2018 [41]. The top 5-ranked countries in iron ore production are Australia, Brazil, China, India, and Russia, producing 81% of the world total.

<table>
<thead>
<tr>
<th>Country</th>
<th>Iron ore reserves (million metric tons)</th>
<th>Iron ore production (thousand metric tons)</th>
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<tbody>
<tr>
<td>Australia</td>
<td>54000</td>
<td>817000</td>
</tr>
<tr>
<td>Brazil</td>
<td>23000</td>
<td>397000</td>
</tr>
<tr>
<td>China</td>
<td>23000</td>
<td>375000</td>
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<tr>
<td>India</td>
<td>8100</td>
<td>156000</td>
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<td>Russia</td>
<td>25000</td>
<td>101000</td>
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<tr>
<td>Ukraine</td>
<td>6500</td>
<td>67000</td>
</tr>
<tr>
<td>USA</td>
<td>12000</td>
<td>46000</td>
</tr>
<tr>
<td>Others</td>
<td>18000</td>
<td>130</td>
</tr>
<tr>
<td>World total</td>
<td>190000</td>
<td>2290000</td>
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2.1. Iron ore flotation

With the continuous consumption of high-grade iron ores, various methods have been proposed to deal
with iron ores in lower grade to meet the rapidly growing demand. In industry cases, the iron ores containing less than 2.0% SiO$_2$ will be required [42]. In practice, however, the enriched primary concentrates still contain a certain amount of SiO$_2$, even after repeated magnetic separations. It is exactly with this in mind that flotation has been proposed to remove gangues rapidly from iron ores to further improve the final concentrate indices [43,44], which has rapidly been used as a primary method in the iron ore industry [45].

The adapted beneficiation methods of an iron ore depend on the nature of the main valuable minerals and the associated gangue minerals, which should concentrate on its composition, physical and chemical properties, and the liberation degree. In many cases, conventional methods of gravity, magnetic, and flotation separations are mainly applied to enrich the Fe grade of the iron ores [46,47]. Among these, gravity and magnetic separations are the most widely used beneficiations to handle the iron ores with high Fe grade, while froth flotation method is essential for further upgrading. In general, the major task of flotation of iron ores is to improve the concentrate quality by decreasing the contents of silicon, phosphorus, and alumina containing minerals [40]. The removal of silicate impurities by reverse flotation, during the processing of iron ores, has been reported successfully with using an anionic or cationic collector [48]. In fact, the flotation process will be changeable, relying on types of valuable and gangue minerals. Besides, floatation reagents and particle size are also important parts to the flotation process of iron ores.

### 2.2. Regularity of the interactive effect

The flotation efficiency of iron ores is likely to be passive and easily influenced by the ore particle size, which is limited to a narrow particle size range of feed (approximately 10–100 µm). The flotation of iron ores with a high enough efficiency is often limited to a narrow particle size range of feed (approximately 10–100 µm). The finer slimes are usually removable as overflow in classification cyclone units. According to the results from plant practice, the effect of particle size on the flotation was confirmed [49]. Moreover, the fine slimes
have greater specific surface area, which may decrease the adsorption probability of collector on those coarser particles when the two fractions are mixed in a pulp system. However, it was easily found from references that the interactions (e.g., electrostatic interactions) between mineral particles in an iron ore flotation involving ultrafine particles is identified as well [50,51]. It was reported in 1981 that a widely established passive effect of ultrafine particles in flotation of the iron ore is the adhering of ultrafine quartz particles to the surface of coarser hematite particles and the adhering of ultrafine hematite particles to the surface of coarser quartz particles [51].

![Graph of Fe grade and SiO2 recovery vs. content of added siderite](image-url)

Fig. 2. The effect of added siderite on the flotation results: (a) Fe grade and (b) recovery of SiO2 in the concentrate.

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Work carried out by Luo et al. demonstrates the effect of the carbonate minerals, such as siderite and dolomite (MgCa(CO3)2) on the reverse flotation of hematite using sodium oleate (NaOl) and dodecylamine (DDA) as the collectors. Fig. 2 shows the grade of hematite and recovery of quartz, respectively, as a function of content of added carbonates (siderite) in reverse flotation. The results confirmed the presence of siderite negatively affected the flotation in the mixed minerals (hematite and quartz at 4:5 ratio) [19,51,52]. Fig. 3 shows the scanning electron microscope (SEM) analysis results of pure feed minerals (see Figs. 3(a) and 3(c)) and flotation concentrate of mixed minerals (see Figs. 3(b) and 3(d)). It shows that the fine siderite particles were adsorbed on the surfaces of coarse hematite and coarse quartz, which led to the convergence of the surface
characteristics between the two minerals, resulting in the reduction of separation differences [53].

Fig. 3. SEM images of the pure hematite (a), the concentrate of mixed minerals with -106+45 μm hematite and -18μm siderite (b), pure quartz (c), and the concentrate of mixed minerals with -106+45μm quartz and -18μm siderite (d). Reprinted with permission from Ref. [53].

Besides the theoretical calculations, the real-time measurement method has been reported to assess the interaction [54]. For more information about agglomeration formation of particles in solution during flotation, the focused beam reflectance measurement (FBRM) technique has been inserted directly into a slurry to investigate how the particle size and count distribution change over time, which made it possible for the measurement of interactions between fine and coarse hematite particles [55]. More details about this instrument can be found in the literature [56].

2.3. Elimination of interactive effect

To reduce the influence of carbonate minerals on the flotation of iron ores, step-flotation [57,58] and
dispersion flotation [53] technologies were proposed, which proved to help eliminate the typical interactive effect among minerals in carbonate-bearing iron ores. Further, Fig. 4 displays the details of step-flotation flowsheet and it shows that the whole technique is mainly composed of two parts, direct flotation (the first step) and reverse flotation (the second step). For this first step, the flotation separation of fine siderite was carried out under neutral conditions. It can help to reduce the impact on the subsequent separation. Then, without the distraction from fine siderite particles, in the second step, the conventional reverse flotation for hematite separation becomes easier to be conducted under alkaline conditions.

![Step-flotation flowchart of carbonate-bearing iron ores.](image)

In addition to the prior separation of siderite, some physical dispersion methods such as properly increasing the rotational speed of the impeller of flotation machine, were used to reduce the influence of slime mineral covering [59,60]. On the other hand, the addition of chemical dispersants, e.g., sodium silicate, sodium carbonate, citric acid, was declared to weaken or eliminate the adverse effect [61,62]. In another work by Luo et al. [61], it was suggested that the dispersants can play a decisive role in the separation of hematite from quartz, and an iron ore concentrate with Fe grade of 66.20% and recovery of 71.52% can be obtained by adding sodium
carbonate and sodium silicate as the dispersants. Han et al. [63] explained the dispersion mechanism of the citric acid during the hematite flotation. According to her paper, with a concentration of 200 mg·L⁻¹ NaOl as the collector, fine siderite lowered the hematite flotation. Nevertheless, the addition of citric acid producing the adsorption onto the surfaces of siderite and hematite, which help to decrease the surface charge and enlarge the total repulsion energy between siderite and hematite particles. Further, it was observed that in the absence of any dispersant, numerous fine siderite particles adhered to the coarse hematite surface (see Fig. 5(a)). In contrast, the surface of hematite has become much cleaner after treated with 20 mg·L⁻¹ citric acid (see Fig. 5(b)), suggesting the exactly weakened of the covering state.

It is well known that the flotation of iron ores is a complicated procedure. According to above results, the presence of fine or ultrafine particles was considered to result in obvious adverse effects in flotation of iron ores which was probably due to the heterocoagulation and covering of those fines and it leads to the variation of mineral surfaces, resulting in the low separation efficiency. By optimizing flotation process, and reagent system, these problems, to some extent, can be resolved. Further research is in progress.

![Fig. 5. SEM images of particles before (a) and after (b) treated with citric acid as a dispersant. Reprinted with permission from Ref. [63].](image)

3. Interactive effect in magnesite ores

Magnesite (MgCO₃) is a preponderant magnesium mineral resource, which has been widely used in
refractory material, construction material, and other fields [64,65] (see Fig. 6). From a global perspective, magnesite is an important non-metallic mineral resource, and 98.6% of which is distributed in China, North Korea, Russia, etc. Mainly distributed in China's Liaoning and Shandong Province, Chinese proven magnesite reserves are about 3.564 billion tons.

![Fig. 6. Industrial applications of magnesite and its products.](image)

Magnesite in natural ore deposits is associated with other carbonates and silicates that represent gangue minerals [66]. Among them, calcium-bearing and magnesium-bearing minerals are the most common ones present in large amounts [67-69]. With the continuous development of magnesite resources, the purification of magnesite ores has been paid more and more attention, and different methods such as gravity separation [70], magnetic separation [71], electrostatic separation [72], chemical beneficiation [73], thermal separation [68], and froth flotation [23,74,75] are used in accordance with different associated minerals. For the magnesite particles +1.0 mm in size, a good separation result can be obtained by using the dense medium separation when bromoform/tetra-bromoethane was used as the organic medium, expect certain particles with porous structures
In a certain pH range of the pulp and the presence of surfactants, the selective magnetic coating could be obtained on serpentine particles, which helps with the selective separation between fine magnesite and fine serpentine [71]. In addition, Moudgil [76] reported another physical method (fluorescence sorting) for the separation of magnesite from associated carbonate minerals as the coupling agent and the fluorescent dye coexists. With the development of beneficiation techniques, more and more magnesite resources are being developed. As shown in Fig. 7, the magnesite mine productions of China and the world has been increasing gradually, especially over the last three years [77].

![Fig.7. World and Chinese magnesite mine production from 2008 to 2018.](image)

**3.1. Magnesite ore flotation**

Nevertheless, even with the above methods, low efficiency was still the main problem in the selective separation of magnesite. As in the case of many non-metallics minerals, froth flotation is the dominant method in magnesite beneficiation [75]. The main impurities in magnesite ores are silicate minerals (e.g., quartz, serpentine, talc, olivine, chlorite) and carbonate minerals (e.g., dolomite, calcite) [78]. Therefore, during the flotation, effectively reducing contents of calcium and silicon items is key to improve the quality of magnesite [79]. The selection of flotation method greatly depends on the associated gangues in magnesite ore. Some
researchers have found that a favorable flotation result could be achieved through the reverse flotation when the silicate minerals are the dominant gangue minerals, while removal of carbonate minerals from magnesite ores still remains a challenge [23,80].

As the development of modern industries, the lack of appropriate technological means has emerged, which caused the waste of magnesium resources and environmental pollution. Therefore, the studying of magnesite flotation is highly desirable and beneficial from both economic and environmental perspectives. It has been reported that one of the essential challenges during magnesite flotation in the presence of carbonate gangues is the occurrence of slimes. In general, the slime problems are largely caused by the associated carbonates in low hardness. To interpret the mechanism which is responsible for the difficulty in separating of magnesite from carbonate minerals, the effects of crystal structure, fine or ultrafine particles, and the solubility of associated carbonates have been discussed successfully in both cationic and anionic systems during flotation [23,66,81]. It is observed that the selectivity is still a major problem in achieving sufficient separation effect due to the similarities in crystal structure, surface characteristics, and physiochemical properties [23,82].

3.2. Regularity of the interactive effect

The flotation behavior of a mineral is often consistent with the adsorption characteristics of collectors on mineral surfaces and depends in part on adsorption density of the collector on the target mineral. However, the adsorption behavior would be affected by the fines which could be either the same or different minerals. On one hand, according to the results of plant practice, coarse magnesite particles are thought to be relatively floatable, while the fines by flotation would have several difficulties [83]. Under conventional conditions, the fine particles float deficiently with little selectivity. On the other hand, the previous researches have demonstrated an intriguing pattern that the fine or ultrafine particles have shown interactive effects with coarse particles of other minerals, which showed detrimental effects on the recovery of other minerals. Although the interactive effect of
minerals in magnesite flotation has been studied by many investigators, the action mechanism of fines in flotation is still not clearly understood. The coating of slimes is an explanation which has been proved by the researchers [84].

In magnesite flotation, it has been confirmed that flotation of magnesite is highly sensitive to the added dolomite particles when using conventional oleate or amine as the collector [18,85]. Fig. 8 shows the influence of added dolomite and serpentine on floatability of the magnesite. With increasing content of added minerals, the flotation recovery of magnesite decreased gradually when NaOl was employed (see Fig. 8(a)). In contrast, dolomite increased the recovery of magnesite most while other minerals had minor effects when DDA was used as collector (see Fig. 8(b)). Also, another topic under investigation is the effect of particle size of added minerals on the magnesite flotation, has been studied by Yao et al. [86]. The recovery of magnesite with -0.067+0.045 mm size fraction was slightly reduced as the addition of dolomite with different size fractions (-0.10+0.067 mm, -0.067+0.045 mm, and -0.045 mm), among which the effect of the finest dolomite was obvious. Then, the influence mechanism of fine particles on magnesite was investigated through microscopic analysis and theoretical calculation studies. Fig. 9 displays the agglomeration response of particles from artificial mixed minerals flotation and the results of total interaction energy calculation based on the extended Derjaguin–Landau–Verwey–Overbeek (EDLVO) theory [87]. \( V_{T}^{ED} \) with a more negative value has a stronger hydrophobic aggregation ability [85]. As can be seen from Fig. 9 that the fine particles of dolomite and serpentine could aggregate to the surface of coarse magnesite (see Figs. 9(b) and (d)), which reduced the recovery of magnesite flotation approximately 5% and 60%, respectively [88]. The energy profiles exhibit an obvious attraction between coarse magnesite and fine dolomite, and between coarse magnesite and fine serpentine particles in the presence of collectors at pH 8.5, as shown in Figs. 9(a) and 9(c). Therefore, associated fine particles can cover the surface of other valuable minerals and change their surface properties.
According to Luo et al. [23], the difficulty of separation of magnesite from dolomite may lie in Ca\(^{2+}\) dissolved from dolomite, which can be adsorbed on the surface of magnesite and then change its surface.
properties. They indicated that a new component which is CaCO$_3$ can be formed on the surface of magnesite, so that both magnesite and dolomite were depressed without any selectivity. Others believe, however, that it is the consumption of collectors since Ca$^{2+}$ dissolved from dolomite can react with collectors and converted into undissolved matter [89].

### 3.3. Elimination of interactive effect

Sodium hexametaphosphate (SHMP, (NaPO$_3$)$_6$) disperses slimes very well and has been widely used in mineral processing as a flotation regulator. Furthermore, there are a considerable amount of studies reporting the mechanism of SHMP in flotation. In the presence of conventional fatty acid collectors (e.g., NaOl), SHMP has been proved to be successful used as the modifier in the flotation of magnesite [18,90]. Yao et al. [86] investigated the effect of SHMP on the flotation of magnesite in the presence of dolomite or serpentine. The results showed that, with NaOl as the collector, after treatment with 40 mg·L$^{-1}$ SHMP, the adsorption of dolomite on the surface of magnesite could be significantly decreased, as well as the serpentine particles.

In order to reduce the negative effects of associated minerals, it was necessary to change the hydrophilicity of gangues [91]. In the case of cations dissolved from those minerals, the modifiers were considered to interact with those ions preferentially [89]. Work performed by Luo et al. [23] demonstrates the effect of the adding order of SHMP on magnesite flotation. They claimed SHMP was added before or after the pH modifier (Na$_2$CO$_3$) led to different results of separation, and the addition of 20 mg·L$^{-1}$ SHMP before Na$_2$CO$_3$ can eliminate the adverse effect of Ca$^{2+}$ on magnesite flotation. The flotation separation of magnesite from dolomite can be achieved with the magnesite grade increased to about 85.8% and that of dolomite decreased to about 20%.

### 4. Interactive effect in scheelite ores

Tungsten (W) is one of the most important metals with a wide application range, not only thanks to the
high electron emissivity of tungsten but also its high chemical stability [92]. Tungsten resources are widely distributed in the world, and China continued to rank first in terms of tungsten reserves. According to a report by the USGS the world total tungsten mine production in 2018 was 82000 tons, of which above 80% was from China (see Table 2). Portugal was the second-ranked producing country, with 9% of world total amount, which was followed by Vietnam, Russia and Bolivia [93]. Tungsten is mainly derived from scheelite (CaWO₄), wolframite ((Fe,Mn)WO₄), and monotungstates stolzite (PbWO₄). Among them, scheelite is the most main source of tungsten, which is found in above 60% of known tungsten deposits [94].

| Table 2. Production of tungsten ore and deposits among major regions of the world |
|-------------------------------|-----------------|--------------|
| Country          | Tungsten ore reserves (metric tons) | Tungsten ore production (thousand metric tons) |
| Australia       | 10000           | 980          |
| Bolivia         | --              | 1000         |
| China           | 19000000        | 67000        |
| Portugal        | 3100            | 7700         |
| Russia          | 2400000         | 2100         |
| Rwanda          | --              | 830          |
| Spain           | 54000           | 750          |
| United Kingdom  | 43000           | 900          |
| Vietnam         | 95000           | 6000         |
| Others          | 1000000         | 1400         |
| World total     | 3300000         | 82000        |

The challenge associated with various scheelite ores is the presence of different impurities such as calcite, fluorite and apatite. The gravity separation method can be used to deal with coarse scheelite, however, as a low hardness mineral (4.5–5.0 as measured by the Mohs scale), it tends to present too many slimes during comminution. Froth flotation is usually used to process the finely grained scheelite. In general, scheelite has a good floatability, however, the associated calcium-containing minerals show similar surface properties to
scheelite, and hence similar flotation response to conventional fatty acid collectors [95]. Thus, it is usually difficult to separate scheelite from calcium-containing minerals adopting traditional flotation scheme [96].

Normally, beneficiation of scheelite ores can be carried out by gravity methods (involve the use of spirals and vibrating tables), often combined with froth flotation [97]. Magnetic separation is sometimes also used to remove magnetic gangue minerals from the scheelite ores, while electrostatic separators are used only for scheelite-cassiterite mixtures [95,98]. Despite attracting the interest of many researchers, the scheelite separation still has been found to be challenging [99].

4.1. Scheelite ore flotation

Scheelite usually coexists with calcite, and many efforts have been made to achieve more effective separation [100]. Up to now, fatty acids and oxidized paraffin soap have been widely used in scheelite flotation industries (e.g. oleic acid, linoleic acid, sodium oleate) [101]. During the Petrov process flotation [102] with fatty acids, the response difference between scheelite and Ca-containing gangue minerals was increased by raising slurry temperature. As the key factor of flotation, many efforts have been made to explore other novel collectors, such as cationic collector, amphoteric collector, anionic collector, and mixed collectors [99,103]. Nevertheless, most of them are still in the stage of theoretical research or laboratory tests. Flotation experiments carried out by Han et al. [104] on a complex scheelite ore showed that benzoxydroxamic acid (BHA) help to improve the scheelite recovery by 10% compare to that of fatty acid collector. It has also been certified that the group of –CONHOH in hydroxamic acids showed a great metal chelating ability. In the work by Gao et al. [105], they claimed that the HXMA-8 exhibits better selectivity than NaOl, which could be adsorbed selectively on scheelite surface. A binary mixture collector of DDA and NaOl was then tested at a molar ratio of 2:1, which seemed to show a stronger collecting ability, and a higher selectivity as well compared with each single collector [106]. Mixed collector has been proved to increase flotation recovery and selectivity for scheelite at
the same time as well as visible collector consumption, which will be an in-depth trend in future research [103].

In addition to selective collectors, efficiency and selectivity in scheelite flotation can be improved further by using appropriate depressants. Kupka and Rudolph [100] summarized the depressing effect of various depressants on the Ca-bearing minerals, and they claimed that modified versions of sodium silicate and quebracho were proven to be the best depressants. Some promoters and modifiers are considered to enhance collecting ability of the collector. Zhao et al. [107] have successfully evaluated the effects of Pb(NO₃)₂ as an activator for scheelite flotation using BHA as the collector, and it was confirmed that the binding ability difference is one of the primary causations.

Despite this, negative effects of fine particles, which caused by the comminution circuits, are still worth pondering. In the literature, up to 20% of the reported mined tungsten deposits in the world are lost as fine or ultrafine particles. In order to improve flotation efficiency of the fine scheelite, some specific flotation methods have been studied since the 1970s. Koh and Warren reported that the flotation response of scheelite is possibly improved by treating the ultrafine slurry with the shear-flocculation [108]. Currently, the impact of agitation speed of flotation unit in scheelite flotation were investigated when the scheelite particles with a particle size less than 10μm as feed material. In addition, in case of carrier flotation, coarse polystyrene particles (-100+50μm) were successfully used as the carrier of those fine scheelite which have been effectively recovered. As another specific process for ultrafine scheelite recovery, hydrodynamic cavitation method was proved to generate tiny bubbles which were found to increase the fine particles aggregates. To summarize, the above flotation processes had been considered valid, due to the hydrophobic aggregation of fine particles or with the coarse particles. However, there are few studies on the interactive effect between scheelite and other minerals.

4.2. Regularity of the interactive effect

The separation of scheelite from calcite and fluorite using flotation, and the efficient recovery of fine
Scheelite particles have always been a tough problem in minerals processing. The difficulties of separation lie in the similar floatability and interactive effect among different minerals with different particle sizes, which seriously decrease the recovery of scheelite and selectivity of depressants.

The effect of the addition of calcium-containing gangue mineral such as calcite on the scheelite recovery using NaOl as collector was systemically investigated [109]. According to Fig. 10(a), depression effect of scheelite increased with the addition of calcite, and then, the scheelite recovery increased to about 80% after further increasing dosage of NaOl. Along with the increase of NaOl concentration, the recovery of scheelite has greatly increased in the presence of calcite (see Fig. 10(a)). It was noticed that the depression behavior of scheelite can be considerately went well with that of the small amount of calcite added, which might be the consumption of collectors by dissolved Ca$^{2+}$ from calcite. While the activation performance of scheelite attributable to a considerable amount of calcite, which probably due to the covering of calcite and it led to the variation of scheelite surfaces, resulting in the higher floatability [109].

![Fig. 10. Effects of (a) calcite content and (b) concentration of NaOl on scheelite recovery. Reprinted with permission from Ref. [109].](image)

**4.3. Elimination of interactive effect**

Although some fundamental studies on the interactions between scheelite and the associated minerals have
been carried out, it still has the inadequacy knowledge about the elimination of the negative effect produced in response to the interactive effect [110]. It has been stated by Li and Li that the phosphates could be potential effective modifiers for the separation of scheelite from calcium-containing minerals selectively through flotation scheme [102]. Interestingly, the selective depressant action varied with the phosphate structure.

Wang [109] has made a comparative study on several depressants, namely sodium hexametaphosphate (SHMP), tannic acid, sodium silicate, and carboxy methyl cellulose (CMC), with disparate characteristics as depressants for calcium-bearing minerals in scheelite flotation using NaOCl as the collector. The results indicated that sodium carbonate could inhibit the dissolution of calcite and eliminated the negative effects of calcite on the selectivity of depressants. Flotation results confirmed that CMC can help to achieve effective separation of scheelite from calcite after treated with sodium carbonate. Moreover, sodium carbonate has an optimum dosage.

In the presence of sodium silicate, the selective separation of scheelite from calcite can be achieved in the alkalescent system by using mixed collectors of octyl hydroxamic acid (HXMA-8) and NaOCl (preferred mass ratio of 1:2). It indicated that HXMA-8 has been proven to adsorbed on scheelite surfaces significantly by chemisorption [97].

5. Conclusions and outlook

Overall, as a highly efficient technique, flotation shows broad application prospect in many fields. However, it still faces many challenges, including the interactive effect among minerals, poorly understood interaction mechanisms, and the elimination methods. Selective flotation of valuable minerals is very important and strongly depends on the types of associated minerals. The main objective of this review was to discuss the influences of interactive effect among minerals in flotation. In this paper, the regularity, the mechanism, and the eliminating methods of the interactive effect on removal of impurities from iron ores, magnesite ores, and scheelite ores were investigated. It also indicated that if addressed successfully, would make practical progress.
In fact, however, there are complex challenges to be overcome through a fundamentally solve the interactive
effect among minerals. According to the results emphasized by this review, the following conclusions can be
drawn:

(1) The presence of fine particles was proved to cause notable negative effects in the flotation of complex
ores. Therefore, a greater level of understanding of the effects has become a central issue to be solved.

(2) A commonly accepted adverse effect of fines in iron ores flotation, particularly the siderite particles, is
the agglomeration of slimes with coarser hematite particles and with coarser quartz particles. As a
typical interactive effect of different minerals, the agglomeration and covering of fines engendered
changes in surface properties of aimed minerals. To eliminate this adverse effect, the step-flotation
and dispersion flotation methods were successfully proposed, with which the separation efficiency has
been greatly improved.

(3) The fine dolomite/serpentine particles have been certified to be easily absorbed on the surface of
magnesite, which caused the difficulty of separation. To facilitate the removal of aggregates, an
appropriate dispersant, such as phosphates, is recommended. On the other hand, cations dissolved
from associated salt minerals have also been shown to cause adverse effect on magnesite flotation, and
it was expected to be solved by adjusting the adding order of modifiers.

(4) Mineral covering and dissolution also occur in flotation separation of scheelite from
calcium-containing minerals. CMC together with sodium carbonate as the pH modifier help to
strengthen the separation efficiency.

(5) Some reported novel reagents, such as new selective collectors, more effective depressants, in the
flotation separation of complex ores are not used on a large scale and most of the reported findings are
based on the micro-scale and lab-scale. Thus, on the basis of recent studies, the application of those
reagents to industrial-scale could be explored in future studies.

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