

# Interactive effect of minerals on complex ore flotation: A brief review

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## **Invited Review**

# Interactive effect of minerals on complex ore flotation: A brief review

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**Abstract:** Froth flotation is the most effective industrial method used to separate fine-grained minerals. The main problem of complex ore flotation is the negative effect of interactions among minerals in slurry, leading to variation in surface properties during separation. In this review, studies on the interactive effect among minerals on 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. Recent research progress on the flotation of these ores has confirmed that mineral aggregation, coating, and dissolution, as well as other factors caused by interacting behavior, explain the depressing effects of fine particles on mineral separation. Solvable methods for these effects are further discussed. Novel flotation processes and more selective reagents are critical for further investigations on various approaches to improve the beneficiation efficiency of these ores. This review aims to provide a good reference for conducting studies related to complex ore flotation.

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

#### 1. Introduction

The rapid growth of the world economy has greatly increased the requirement to exploit natural resources to meet metal and energy demands from all fields of the society [1–3]. The excessive exploitation of high-grade ore deposits, especially complex ores, has increasingly caused the waste of low-grade ore resources. Furthermore, the rapid reduction in ore quality has made it difficult to improve the utilization of those minerals [4-5]. Various efficient methods, such as improving mineral liberation [6], developing high-efficient separation reagents, processes, and equipment [7–8], have been explored to enhance mineral separation. In comparison with other existing technologies, froth flotation has a significant advantage and has become the most important method for separating low-grade refractory ores [9–10]. However, the limitations of separation efficiency and product quality are the main problems in flotation [11] mainly because of complex mineral composition and the associated relationship between valuable minerals and gangue minerals in fine grain sizes [12–13]. Fine grinding is needed to improve mineral liberation for finely disseminated ores, which is particularly important [14]. However, some associated minerals with brittle nature are easily over-ground in the grinding process which causes the formation of fine particles [15–16].

An interactive effect between valuable minerals and

gangue minerals, which serve as one of the most important factors in complex ore flotation, has been widely explored [17–20]. The interactive effect of minerals represents the inter adsorption and surface conversion behavior of two or more minerals in flotation separation [17,19], which often leads to the reduction of separation possibility. Studies on the interactive effect of minerals include the interaction pattern, interaction mechanism, and methods of utilizing or eliminating the interaction effect [17–19]. The major properties of the interaction effect can be described as follows (Fig. 1).

- (1) Fine valuable minerals adhere to coarse gangue minerals, leading to the passive loss of valuable minerals. For example, in hematite (Fe<sub>2</sub>O<sub>3</sub>) flotation, fine hematite particles can be adsorbed on the surface of quartz, resulting in the reduction of hematite recovery [19].
- (2) Fine valuable minerals adhere to coarse valuable minerals, and they are also known as carrier flotation [20–22]. Ateşok *et al.* [20] used highly hydrophobic coarse coal particles as a carrier that helps improve the flotability of extremely hydrophilic low-rank coal particles.
- (3) Fine gangue minerals adhere to coarse valuable minerals, thereby reducing the grade of concentrate. For example, fine feldspar particles easily cover the surface of coarse quartz in quartz flotation, which adversely affects the grade of concentrate.
  - (4) The aggregation of fine gangue minerals and fine



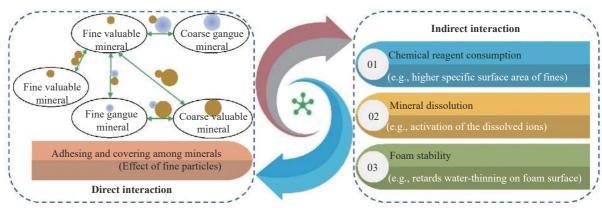


Fig. 1. Types of interactive effect among minerals on flotation.

valuable minerals, leading to coarse particle formation, and they will be a part of froth products or tailings.

### (5) Mineral dissolution affects flotation results [23].

The interactive effect is more prominent when the mineral dissemination size decreases. The interaction effects include the influence of mineral adsorption, activation, and inhibition on separation in complex ore flotation [24]. It is mainly caused by the fine disseminated grain size of valuable minerals and complex symbiosis with gangue minerals. An ore sample should be finely ground to achieve monomer dissociation between minerals, resulting in serious sliming and covering between minerals. Consequently, separation becomes extremely difficult.

Sivamohan and Forssberg [25] proposed particle size classification and used the terms "fines" to refer to particles less than 100 µm. Problems associated with fine particles in flotation have been widely explored, and limits in the flotation of fine particles is a key to obtaining selective separation [26–27]. Some specific flotation schemes, such as shear flocculation flotation and carrier flotation, have been proposed to improve the flotation efficiency of fine minerals [28–29]. Experimental evidence has shown that fine particles in flotation have low collision efficiencies with gas bubbles and slow float speed [30-32]. The existence of slimes results in significant adverse effects on direct and reverse flotation. Current research mainly focuses on the following aspects to solve these problems: (1) reducing the size of bubbles to enhance the possibility of the collision and adhesion of bubbles with fine minerals, such as theoretical and applied research on a microbubble flotation column [33]; (2) increasing the apparent particle size of fine minerals to achieve flotation under conventional conditions [34]; (3) searching for the appropriate reagent system and flotation process; (4) preferentially removing fine particles.

Studies on the interaction effect of minerals have mainly focused on the influence of fine particles on other minerals in different size fractions. The concepts of carrier flotation, floculation flotation, dispersive flotation, and step flotation are related to the interaction effect of minerals. Among them,

carrier and flocculation flotation are embodied in strengthening interactions, whereas dispersive and step flotation is involved in weakening interactions. This review summarized studies on the interaction effect on the flotation of complex iron ores, magnesite ores, and tungsten ores, the regularity and mechanism of the interactive effect, and the methods of weakening the interactive effect. This review emphasized the important influence of the interactive effect of minerals on various flotation systems. This review could be used to establish the theoretical system of the interactive effect on flotation, and flotation separation could be significantly optimized.

### 2. Interactive effect on iron ores

Iron ore is an important mineral resource widely used to construct machine tools and serve as structural components for buildings. Although over 300 types of minerals containing iron in the world, iron sources mainly include hematite, magnetite (Fe<sub>3</sub>O<sub>4</sub>), limonite [FeO(OH)·*n*(H<sub>2</sub>O)], goethite [FeO(OH)], and siderite (FeCO<sub>3</sub>) [35]. Among them, fully oxidized hematite is the main source [36]. However, iron ores have impurities (e.g., silica, phosphorus, alumina, and sulfur) [37]. Quartz is generally considered a common gangue mineral in iron ores in China [38].

Iron resources with a high concentration are distributed in few countries and regions, and above 75% of the world's reserves are distributed in Russia, Ukraine, Australia, Brazil, Kazakhstan, and China [39]. Global iron ore resources exceed 800 billion tons of raw ores, and they contain more than 230 billion tons of iron [40]. On a world scale, iron ore production and reserves in 2018 are shown in Table 1 according to data from the US Geological Survey in 2019 [41]. The top five ranking countries in iron ore production are Australia, Brazil, China, India, and Russia, producing 81% of the world's total production.

#### 2.1. Iron ore flotation

With the continuous consumption of high-grade iron

ores, various methods have been proposed to deal with low-grade iron ores to meet the rapidly growing demand. In industrial cases, iron ores containing less than 2.0wt% SiO<sub>2</sub> are required [42]. However, the enriched primary concentrates still contain a certain amount of SiO<sub>2</sub> even after magnetic separations are repeatedly conducted. Flotation has been proposed to rapidly remove gangues from iron ores and further improve the final concentrate indices [43–44], and this technique has been rapidly used as a primary method in the iron ore industry [45].

Table 1. Word production and reserves of iron ore in 2018

Country	Reserves / Mt	Production / kt
Australia	54000	900000
Brazil	32000	490000
China	20000	340000
India	5400	200000
Russia	25000	95000
Ukraine	6500	60000
USA	2900	49000
Others	24200	366000
World total	170000	2500000

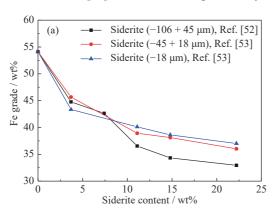
The adapted beneficiation methods for an iron ore depend on the nature of the main valuable minerals and the associated gangue minerals, which should concentrate on their composition, physical and chemical properties, and liberation degree. In many cases, the conventional methods of gravity, magnetic, and flotation separations are mainly applied to enrich the Fe grade of iron ores [46–47]. Among these factors, gravity and magnetic separations are the most widely used beneficiation methods to handle high-Fe-grade iron ores, whereas froth flotation is essential for further upgrading. In general, the major task of iron ore flotation aims to improve concentrate quality by decreasing the contents of silicon-, phosphorus-, and alumina-containing minerals [40]. Silicate impurities through reverse flotation during iron ore processing have been successfully removed by using an anionic or cationic collector [48]. Flotation is changeable, relying on the types of valuable and gangue minerals. Flotation reagents and particle size are also important parts of iron ore flotation.

#### 2.2. Regularity of the interactive effect

The flotation efficiency of iron ores is likely to be passive and easily influenced by ore particle size, which is limited to a narrow particle size range of feed (approximately  $10-150 \mu m$ ). The fine slimes (<10  $\mu m$ ) are usually removed as overflow in classification cyclone units [49]. Plant practice results have confirmed the effect of particle size on flotation [50]. Fine slimes have a great specific surface area, which may decrease the adsorption probability of collectors on coarse particles when two fractions are mixed in a pulp system. However, interactions (e.g., electrostatic interactions) between mineral particles in an iron ore flotation involving ultrafine particles have been identified [51]. In 1981, a widely established passive effect of ultrafine particles on iron ore flotation is the adherence of ultrafine quartz particles to the surface of coarse hematite particles and the adherence of ultrafine hematite particles to the surface of coarse quartz particles [51].

Luo *et al.* demonstrated the effect of carbonate minerals, such as siderite and dolomite [MgCa(CO<sub>3</sub>)<sub>2</sub>] on the reverse flotation of hematite by using sodium oleate (NaOl) and dodecylamine (DDA) as collectors [52]. Fig. 2 shows the grade of hematite and the recovery of quartz as a function of the content of added carbonates (siderite) in reverse flotation. The presence of siderite negatively affects flotation in mixed minerals (hematite and quartz with a mass ratio of 4:5) [19,51–52]. Figs. 3(a) and 3(b) present the SEM analysis results of the flotation concentrate of mixed minerals. Fine siderite particles are adsorbed on the surfaces of coarse hematite and coarse quartz, leading to the convergence of surface characteristics between the two minerals, resulting in the reduction of separation differences.

In addition to theoretical calculations, real-time measurement has been used to assess the interaction [54]. Focused



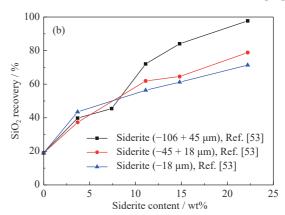
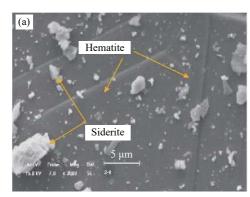


Fig. 2. Effect of the added siderite on flotation results of hematite and quartz mixed minerals: (a) Fe grade; (b) recovery of  $SiO_2$  in the concentrate. (Flotation condition: pH = 11.3; NaOl, starch, and CaCl<sub>2</sub> dosages are 160, 60, and 100 mg·L<sup>-1</sup>, respectively).



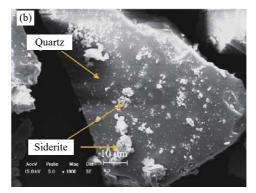


Fig. 3. SEM images of concentrate of mixed minerals flotation (a) with  $-106 + 45 \mu m$  hematite and  $-18 \mu m$  siderite, and (b) with  $-106 + 45 \mu m$  quartz and  $-18 \mu m$  siderite [18].

beam reflectance measurement is conducted directly with a slurry to investigate how particle size and count distribution change over time and to obtain more information about the agglomeration of particles in solutions during flotation; thus, interactions between fine and coarse hematite particles can be determined [55]. Further details about this instrument can be found in previous studies [56].

#### 2.3. Elimination of interactive effect

Step-flotation [57–58] and dispersion flotation [53] technologies have been proposed to reduce the influence of carbonate minerals on iron ore flotation. These technologies

help eliminate the typical interactive effect among minerals in carbonate-bearing iron ores. Fig. 4 displays the details about step-flotation flowsheet and shows that the whole technique is mainly composed of two parts, namely, direct flotation (the first step) and reverse flotation (the second step). In the first step, fine siderites are separated through flotation under neutral conditions. This technique can help reduce the effect on subsequent separation. In the second step, conventional reverse flotation for hematite separation can be easily conducted under alkaline conditions without distraction from fine siderite particles.

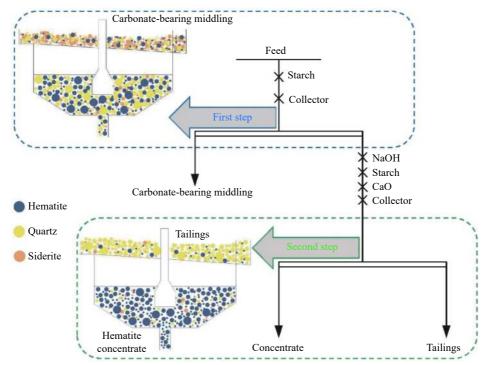


Fig. 4. Step-flotation flowchart of carbonate-bearing iron ores.

In addition to the prior separation of siderite, some physical dispersion methods, such as properly increasing the rotational speed of the impeller of the flotation machine, have

been used to reduce the influence of slime mineral covering [59–60]. The addition of chemical dispersants, e.g., sodium silicate, sodium carbonate, and citric acid, weakens or elim-

inates adverse effects [61-62]. Luo et al. [61] suggested that dispersants can play a decisive role in the separation of hematite from quartz, and an iron ore concentrate with an Fe grade of 66.20% and a recovery of 71.52% can be obtained by adding sodium carbonate and sodium silicate as dispersants. Han [63] explained the dispersion mechanism of citric acid during hematite flotation. With a concentration of 200 mg·L<sup>-1</sup> NaOl as a collector, fine siderite decreases the flotation of hematite in the absence of any modifier. Nevertheless, citric acid addition induces adsorption onto siderite and hematite surfaces, which help decrease the surface charge and enlarge the total repulsion energy between siderite and hematite particles. In the absence of any dispersant, numerous fine siderite particles adhere to a coarse hematite surface. By contrast, hematite surface has become much cleaner after it is treated with 20 mg·L<sup>-1</sup> citric acid. This result suggests the weakened covering state. Readers interested in learning more about the phenomenon should consult the SEM images in Ref. [63].

Iron ore flotation is a complicated procedure. The presence of fine or ultrafine particles adversely affects iron ore flotation, which is probably due to the heterocoagulation and covering of fines. This process leads to variation in mineral surfaces, resulting in a low separation efficiency. To some extent, these problems can be resolved by optimizing the process and reagent system of flotation. Further research should be performed.

# 3. Interactive effect on magnesite ores

Magnesite (MgCO<sub>3</sub>) is a preponderant magnesium mineral resource, which has been widely used in refractory materials, construction materials, and other fields [64–65] (Fig. 5). From a global perspective, magnesite is an important non-metallic mineral resource, and most of this resource is distributed in China, North Korea, and Russia. Mainly distributed in Liaoning and Shandong Provinces in China, Chinese-proven magnesite reserves are about 3.564 billion tons.

Magnesite in natural ore deposits is associated with other carbonates and silicates that represent gangue minerals [66]. Among them, calcium- 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 widely explored, 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], have been used in accordance with different associated minerals. For magnesite particles with a size of >1.0 mm, a good separation result can be obtained through dense medium separation when bromoform or tetrabromoethane is used as an organic medium except certain particles with porous structures [70]. In a certain pH value range of the pulp

and the presence of surfactants, selective magnetic coating can be obtained on serpentine particles, which help with selective separation between fine magnesite and serpentine [71]. Moudgil [76] reported another physical method (fluorescence sorting) for the separation of magnesite from the associated carbonate minerals because a coupling agent and a fluorescent dye coexists. With the development of beneficiation techniques, numerous magnesite resources have been developed. In Fig. 6, magnesite mine production in China and other countries has been increasing gradually, especially over the last 3 years [77].



Fig. 5. Industrial applications of magnesite and its products.

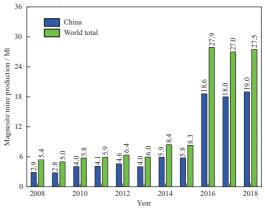


Fig. 6. World and Chinese magnesite mine production from 2008 to 2018.

### 3.1. Magnesite ore flotation

The main impurities in magnesite ores are silicate minerals (e.g., quartz, serpentine, talc, olivine, and chlorite) and carbonate minerals (e.g., dolomite and calcite) [78]. Therefore, effectively reducing the contents of calcium and silicon items is key to improving the quality of magnesite during flotation [79]. The selection of flotation method greatly depends on the associated gangues in magnesite ore. Some researchers found that a favorable flotation result can be

achieved through reverse flotation when silicate minerals are the dominant gangue minerals, but the 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 and caused the waste of magnesium resources and environmental pollution. Therefore, magnesite flotation should be studied in economic and environmental perspectives. One of the essential challenges during magnesite flotation in the presence of carbonate gangues is the occurrence of slimes. In general, slime problems are largely caused by the associated carbonates in low hardness. The effects of crystal structure, fine or ultrafine particles, and solubility of the associated carbonates have been discussed successfully in cationic and anionic systems during flotation to interpret the mechanism responsible for the difficulty in separating magnesite from carbonate minerals [23,66,81]. Selectivity is still a major problem in achieving a sufficient separation effect because of similarities in crystal structures, 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 partly on the adsorption density of collectors on target minerals. However, adsorption behavior is affected by fines, which can be either the same or different minerals. On the one hand, plant practice results have shown that coarse magnesite particles are relatively floatable, whereas fines produced via flotation likely have several difficulties [83]. Under conventional conditions, fine particles float deficiently with limited selectivity. On the other hand, previous studies demonstrated an intriguing pattern that fine or ultrafine particles have shown interactive effects with coarse particles of other minerals, which elicit detrimental effects on the recovery of other minerals. Although the interactive effect of minerals in magnesite flotation has been stud-

ied by many investigators, the action mechanism of fines in flotation is poorly understood. Nevertheless, slime coating is an explanation proven by researchers [84].

In magnesite flotation, magnesite flotation is highly sensitive to the added dolomite particles when oleate or amine is used as a collector [18,85]. Fig. 7 shows the influence of dolomite and serpentine on magnesite flotability. As the content of added minerals increases, the flotation recovery of magnesite decreases gradually when NaOl is employed, as shown in Fig. 7(a). By contrast, dolomite mostly increases the recovery of magnesite, whereas other minerals have minor effects when DDA is used as a collector, as presented in Fig. 7(b). Yao et al. [86] investigated the effect of the particle size of added minerals on magnesite flotation. The recovery of magnesite with -0.067 + 0.045 mm size fraction is 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). The effect of the finest dolomite is obvious. The influence mechanism of fine particles on magnesite has been investigated through microscopic analysis and theoretical calculation studies. Fig. 8 displays the agglomeration response of particles in the flotation of artificial mixed minerals and the results of total interaction energy  $(V_{\mathrm{T}}^{\mathrm{ED}})$  calculation based on the extended Derjaguin-Landau-Verwey-Overbeek (E-DLVO) theory [87].  $V_{\rm T}^{\rm ED}$  with a more negative value has a stronger hydrophobic aggregation ability, which related to the minimum separation distance (H) between two spheres [85]. In Figs. 8(b) and 8(d), fine dolomite and serpentine particles can aggregate to the surface of coarse magnesite, which reduces the recovery of magnesite flotation by approximately 5% and 60%, respectively [88]. 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. 8(a) and 8(c). Therefore, associated fine particles can cover the surface of other valuable minerals and change their surface properties.

Luo et al. [23] showed that separating magnesite from

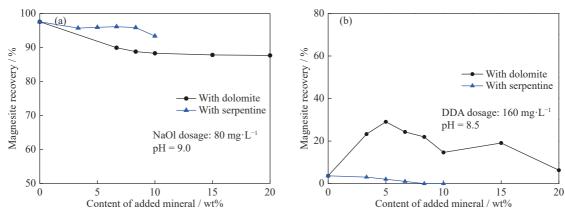


Fig. 7. Effect of added minerals on the recoveries of magnesite in NaOl (a) and DDA (b) flotation systems [86].

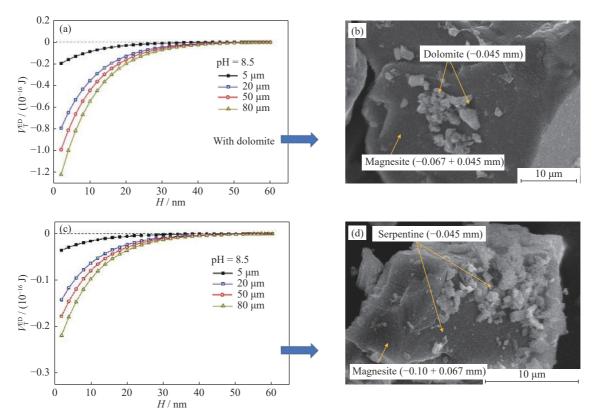


Fig. 8. E-DLVO theoretical calculation between magnesite and dolomite (a) and between magnesite and serpentine (c), and SEM images of fine dolomite (b) and fine serpentine (d) absorbed on the coarse magnesite surface [86].

dolomite may be difficult in Ca<sup>2+</sup> dissolved from dolomite, which can be adsorbed on the surface of magnesite and then change its surface properties. They indicated that a new component, namely, CaCO<sub>3</sub>, can be formed on the surface of magnesite so that magnesite and dolomite are depressed without any selectivity. However, other studies have shown that collectors were consumed because the Ca<sup>2+</sup> dissolved from dolomite can react with collectors and converted into undissolved matter [89].

#### 3.3. Elimination of interactive effect

Sodium hexametaphosphate (SHMP, (NaPO<sub>3</sub>)<sub>6</sub>) disperses slimes well and has been widely used in mineral processing as a flotation regulator. Furthermore, studies have reported the mechanism of SHMP in flotation. In the presence of fatty acid collectors (e.g., NaOl), SHMP has been successfully used as a modifier in magnesite flotation [18,90]. Yao *et al.* [86] investigated the effect of SHMP on magnesite flotation in the presence of dolomite or serpentine. The adsorption of dolomite on the surface of magnesite, as well as serpentine particles, can be significantly decreased with NaOl as a collector and 40 mg·L<sup>-1</sup> SHMP treatment.

In the case of cations dissolved from minerals, modifiers preferentially interact with these ions [89–91]. Luo *et al.* [23] demonstrated the effect of the addition order of SHMP on magnesite flotation. They claimed that adding SHMP before

or after a pH modifier (Na<sub>2</sub>CO<sub>3</sub>) leads to different separation results, and the addition of 20 mg·L<sup>-1</sup> SHMP before Na<sub>2</sub>CO<sub>3</sub> can eliminate the adverse effect of Ca<sup>2+</sup> on magnesite flotation. Magnesite can be separated from dolomite through flotation by increasing the magnesite grade to about 85.8% and decreasing the grade of dolomite to about 20%.

### 4. Interactive effect on scheelite ores

Tungsten (W) is one of the most important metals with a wide application because of the high electron emissivity and high chemical stability [92]. Tungsten resources are widely distributed worldwide, and China ranks first in terms of tungsten reserves. According to the report from United States Geological Survey (USGS), the world total tungsten mine production in 2018 was approximately 82000 tons, and >80% of this value was from China (Table 2). With ~9% of the total amount of global production, Portugal is the second-highest producing country, which was followed by Vietnam, Russia, and Bolivia [93]. Tungsten is mainly derived from scheelite (CaWO<sub>4</sub>), wolframite ((Fe,Mn)WO<sub>4</sub>), and monotungstate stolzite (PbWO<sub>4</sub>). Among them, scheelite is the main tungsten source, which is found in >60% of known tungsten deposits [94].

The challenge associated with various scheelite ores is the presence of different impurities, such as calcite, fluorite,

Table 2. World production and reserve of tungsten ore in 2018

Country	Reserves / t	Production / t
Australia	10000	980
Bolivia	_	1000
China	1900000	67000
Portugal	3100	770
Russia	240000	2100
Rwanda	_	830
Spain	54000	750
United Kingdom	43000	900
Vietnam	95000	6000
Others	1000000	1400
World total (approximate)	3300000	82000

and apatite. Gravity separation method can be used to deal with coarse scheelite. As a low-hardness mineral (4.5–5.0 of Mohs' scale hardness), it tends to present too many slimes during comminution. Froth flotation is usually used to process finely grained scheelite. In general, scheelite has good flotability; however, the associated calcium-containing minerals show similar surface properties to scheelite; hence, a similar flotation response to conventional fatty acid collectors is observed [95]. Thus, separating scheelite from calciumcontaining minerals adopting traditional flotation scheme is usually difficult [96]. Normally, the beneficiation of scheelite ores can be carried out with gravity methods involving the use of spirals and vibrating tables and often combined with froth flotation [97]. Magnetic separation is also used to remove magnetic gangue minerals from scheelite ores, and electrostatic separators are used only for scheelite-cassiterite mixtures [95,98]. Although scheelite separation has been widely explored, this process has been found to be challenging [99].

#### 4.1. Scheelite ore flotation

Scheelite usually coexists with calcite, and many efforts have been devoted to achieving more effective separation [100]. Fatty acids and oxidized paraffin soap have been widely used in scheelite flotation industries (e.g., oleic acid, linoleic acid, and NaOl) [101]. During the Petrov process flotation with fatty acids as the collectors, the response difference between scheelite and Ca-containing gangue minerals increases by increasing slurry temperature [102]. As a key factor of flotation, studies have explored various novel collectors, however, most of them only involve theoretical research or laboratory tests [99,103]. Han et al. [104] conducted flotation experiments on a complex scheelite ore and showed that benzohydroxamic acid (BHA) helps improve the scheelite recovery by 10% compared with that of using fatty acids as collector. The group of -CONHOH in hydroxamic acids shows a great metal chelating ability. Gao et al. [105] suggested that the selectivity of HXMA-8 is better than that of NaOl, which can be selectively adsorbed on a scheelite surface. A binary mixture collector of DDA and NaOl is then tested at a molar ratio of 2:1, which seems to show a stronger collecting ability, and a higher selectivity as well compared with each single collector [106]. A mixed collector has been proven to increase recovery and selectivity of scheelite flotation and visible collector consumption, which will be an indepth trend in future research [103].

The selectivity in scheelite flotation can be improved further by using appropriate depressants in addition to selective collectors. Kupka and Rudolph [100] summarized the effect of various depressants on Ca-bearing minerals, and they claimed that modified versions of sodium silicate and quebracho are considered the best depressants. Some promoters and modifiers enhance the collecting ability of collectors. Zhao *et al.* [107] successfully evaluated the effects of Pb(NO<sub>3</sub>)<sub>2</sub> as an activator on the scheelite flotation by using BHA as a collector.

The negative effects of fine particles, which are formed by comminution circuits, should be further explored. Up to 20% of the reported mined tungsten deposits in the world are lost as fine or ultrafine particles. Some specific flotation methods have been studied since the 1970s to improve the flotation efficiency of fine scheelite. Koh and Warren [108] reported that the flotation response of scheelite is possibly improved by treating ultrafine slurry with shear flocculation. Currently, the effect of the agitation speed of a flotation unit in scheelite flotation has been investigated when scheelite particles with a particle size less than 10 µm as a feed material. In carrier flotation, coarse polystyrene particles (50-100 um) have been successfully used as carriers of fine scheelite, which has been effectively recovered. As another specific process of ultrafine scheelite recovery, hydrodynamic cavitation method has been developed to generate small bubbles, which increase fine particle aggregates. In summary, these flotation processes are considered valid because of the hydrophobic aggregation of fine particles or in the presence of coarse particles.

### 4.2. Regularity of the interactive effect

The separation of scheelite from calcite and fluorite by using flotation, and the efficient recovery of fine scheelite particles has been a tough problem in mineral processing. Difficulties in separation are attributed to the similar flotability and interactive effects among different minerals with different particle sizes, which seriously decrease scheelite recovery and depressant selectivity.

The effect of the addition of calcium-containing gangue minerals, such as calcite on scheelite recovery by using NaOl as a collector, has been systemically investigated [109]. As the calcite content increases, the recovery of scheelite has increased firstly and then decreased, as shown in Fig. 9(a). As the NaOl concentration increases, the recovery of scheelite has greatly increased in the absence and presence of calcite, as shown in Fig. 9(b). On the whole, the depression behavior

of calcite for scheelite flotation occurs when the small amount of calcite is added, which is probably because the collectors react with the dissolved Ca<sup>2+</sup> from calcite. However, the activation performance of scheelite increase

when a considerable amount of calcite added probably because of the covering of calcite, leading to the variation in scheelite surfaces and resulting in high flotability [109].

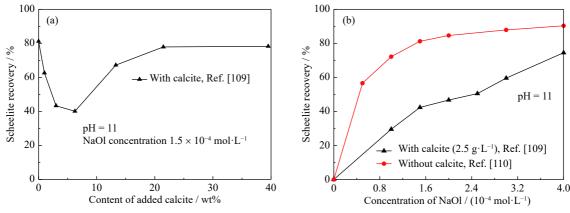


Fig. 9. Effects of calcite content (a) and NaOl concentration (b) on the scheelite recovery.

#### 4.3. Elimination of interactive effect

Although some fundamental studies on the interactions between scheelite and the associated minerals have been conducted, knowledge about the elimination of those effect is inadequate. Li and Li [102] demonstrated that phosphates can be effective modifiers for the selective separation of scheelite from calcium-containing minerals through a flotation scheme. Interestingly, a selective depressant action varies with phosphate structures.

Wang [109] and Wang *et al.* [110] studied 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 by using NaOl as a collector. Sodium carbonate can inhibit the dissolution of calcite and eliminate the negative effects of calcite on the selectivity of depressants. Flotation results have confirmed that CMC can help achieve the effective separation of scheelite from calcite after sodium carbonate treatment. Sodium carbonate has an optimum dosage.

In the presence of sodium silicate, the selective separation of scheelite from calcite can be achieved in an alkalescent system by using the mixed collectors of octyl hydroxamic acid (HXMA-8) and NaOl (preferred mass ratio of 1:2). This result indicates that HXMA-8 is significantly adsorbed on scheelite surfaces through chemisorption [97].

## 5. Conclusions and outlook

Flotation, as a highly efficient technique, shows broad application prospects in many fields. However, it still faces many challenges, including the interactive effect among minerals, poor understanding of interaction mechanisms, and

elimination methods. The selective flotation of valuable minerals is important and is strongly dependent on the types of associated minerals. This review mainly aimed to discuss the influences of the interactive effect among minerals on flotation. The regularity, mechanism, and elimination methods of the interactive effect on the removal of impurities from iron ores, magnesite ores, and scheelite ores were investigated. This review also indicated that these methods would make practical progress if they were addressed successfully. However, complex challenges should be overcome to fundamentally solve the interactive effect among minerals. Based on the results emphasized in this review, the following conclusions can be drawn.

- (1) The presence of fine particles was proved to cause notable negative effects on complex ore flotation. Therefore, enhanced understanding on the effects has become a major issue to be solved.
- (2) A commonly accepted adverse effect of fines on iron ore flotation, particularly siderite particles, is the agglomeration of slimes with coarse hematite particles and coarse quartz particles. As a typical interactive effect of different minerals, the agglomeration and covering of fines cause changes in the surface properties of the target minerals. Stepflotation and dispersion flotation methods are successfully proposed to eliminate this adverse effect. Thus, separation efficiency remarkably improves.
- (3) Fine dolomite/serpentine particles become easily absorbed on the surface of magnesite, which causes separation difficulty. An appropriate dispersant, such as phosphates, is recommended to facilitate aggregate removal. Cations dissolved from associated salt minerals adversely affect magnesite flotation, but this effect is addressed by adjusting the addition order of modifiers.

- (4) Mineral covering and dissolution also occur in the flotation separation of scheelite from calcium-containing minerals. CMC, together with sodium carbonate as a pH value modifier, helps strengthen separation efficiency.
- (5) Some reported novel reagents, such as new selective collectors and 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 micro- and lab-scale experiments. Thus, the industrial-scale application of these reagents should be further explored on the basis of recent studies.

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