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Invited Review

Reagent types and action mechanisms in ilmenite flotation: A review

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(Received: 15 April 2021; revised: 12 November 2021; accepted: 12 November 2021)

Abstract: Ilmenite is an essential mineral for the extraction of titanium. Conventional physical separation methods have difficulty recovering fine ilmenite, and dressing plants have begun applying flotation to recover ilmenite. The interaction of reagent groups with Ti and Fe sites on the ilmenite surface dramatically influences the ilmenite flotation. However, the investigation on Fe sites has received more attention because the activity of Ti is lower than that of Fe. For the activators on ilmenite flotation, most are metal ions but typically lead ions. The metal ions of activators promote ilmenite flotation by increasing the active sites on the ilmenite surface. Combined reagents have a better selective separation of ilmenite than single reagents due to their synergistic effect. Combining the lead ion (Pb^{2+}) and the benzyl hydroxamic acid (BHA) into a Pb–BHA complex has a marked effect on ilmenite flotation, which puts forward a new idea of developing combined reagents for ilmenite flotation. This review considers reagent types and action mechanisms in ilmenite flotation. On the basis of the analysis of previous research, a brief future outlook of reagent types and action mechanisms in ilmenite flotation is also proposed in this study.

Keywords: ilmenite; flotation; reagent; action mechanism; combined reagents

1. Introduction

Titanium is positioned on the fourth subgroup of the fourth period (element symbol: Ti; atomic number: 22; relative atomic mass: 47.88). As an important industrial metal, titanium [1] has the reputation of "space metal" for its high strength, low density, and remarkable corrosion resistance. Therefore, it is widely used in aerospace, military, and medical fields. The abundance of titanium in the earth's crust is 0.61%, ranking ninth among all elements and fourth in metal elements behind iron, aluminum, and magnesium. Titanium is distributed in the earth's crust extensively. At present, more than 100 titanium-containing minerals are found in nature. The main ones with industrial value are ilmenite, rutile, red ilmenite, white titanium ore, and anatase. Of these minerals, ilmenite is the most critical mineral resource for extracting titanium [2].

The chemical composition of ilmenite is $FeTiO_3$, which has a theoretical TiO_2 content of 52.66% [3]. Ilmenite has an enormous specific gravity of 4.72 and a Mohs hardness in the range of 5–6. Ilmenite crystals usually occur in the shape of thick plates, whereas other forms include flakes, blocks, compacts, and granules. The color of ilmenite is typically black or brownish black, and its streak color is black or brownish red.

Gravity separation, high-intensity magnetic separation, and electrostatic separation are the primary conventional methods to recover ilmenite due to its properties such as high density, paramagnetism, and electrical conductivity [4–5]. Furthermore, the combined process of "gravity separation, magnetic separation, and electrostatic separation" has been frequently used in dressing plants [6–7].

However, with the exploitation of ilmenite resources, they appear to have the characteristics of poorer in grade, finer in grain size, and more complex in mineralogy. In some cases, ilmenite is closely associated with gangue, which may significantly compromise the effectiveness of the abovementioned recovery methods [5,8]. The principle of flotation separation is based on the differences in surface chemistry and hydrophobicity on the mineral surface [9–10]. Therefore, flotation has become a research hotspot in recent years for it can effectively recover fine ilmenite minerals [11]. Flotation technologies, such as autogenous carrier flotation [12] and flocculation–flotation [13–14], have been recently reported for the flotation of microfine ilmenite, which has sound beneficiation effects on ilmenite flotation.

Commonly, ilmenite displays moderate floatability under conventional flotation conditions [15]. Hence, physical or

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chemical methods are usually used to modify the surface of ilmenite and gangue minerals for realizing the separation of ilmenite from gangue minerals [16–17]. These surface modification methods include microwave pretreatment, ultrasonic pretreatment, and roasting. One interesting work is conducted by Fan *et al.* [18–19]. They indicated that microwave irradiation can increase ilmenite flotation recovery by 20%.

During the ilmenite flotation process, reagents, including collectors, activators, and depressants, are added to modify the hydrophobicity of minerals in the system, which is critically important [4]. Chen *et al.* [20] found that the recovery of ilmenite in the presence of a Fe–BHA complex is 46% higher than that when using BHA alone at pH value of 8. Luo *et al.* [21] demonstrated that BHA/dodecylamine mixed collectors successfully separate ilmenite from titanaugite at a molar ratio of 8:1. Deng *et al.* [22] designed and synthesized a novel dendritic surfactant called 2-decanoylamino-pentanedioic acid (DPA). They found that DPA has a superior collecting activity, adsorbs better on the ilmenite surface than oleic acid, and can effectively recover ilmenite from titanomagnetite at a pH value of approximately 7.

Despite extensive studies, reviews to summarize the flotation reagent types and their action mechanisms of ilmenite are lacking. Herein, combined with the solution chemical calculation of ilmenite and reagents, the action mechanisms of flotation reagents for ilmenite are systematically summarized. This work also provides guidelines for selecting a suitable reagent system and developing new potential reagents for ilmenite flotation.

2. Surface properties and solubility of ilmenite

Flotation is a complicated physicochemical process, and many factors can affect the flotation process [23]. For example, the flotation reagent system, ore properties, and water quality impact the flotation operation because the flotation generally involves chemical reaction processes among the mineral, the flotation reagent, and air [24–25]. Understanding the effect of mineralogical composition on the mineral surface properties is critical [5,26].

The floatability of ilmenite is closely related to its crystal surface structure [27]. Fig. 1 shows the unit cell structure of ilmenite [28]. Ilmenite ($FeTiO_3$) is a mineral of the ABO_3 type, where Fe and Ti are cations in the ilmenite crystal lattice. A mixture of Fe^{2+} and Ti^{4+} forms each cation layer. Given that elements such as Mn, Mg, and Cr may substitute for Fe or Ti in the original ilmenite lattice, the formula of ilmenite can be generally expressed as $(Fe,Mg,Mn)TiO_3$ [5]. In general, ilmenite has a significant surface polarity and high solubility in water. After crushing or grinding, the Ti–O and Fe–O bonds are broken, and the surface lattice of Ti^{4+} and Fe^{2+} is easily unsaturated [29]. Unsaturated bond energy remains on the surface, which tends to interact with OH^- in water that is easily formed on a hydroxylated surface [10]. Surface dissolution can make differences in these properties and affect the flotation behavior of minerals. The surface activity

of ilmenite is determined by the ability of Fe^{2+} and Ti^{4+} to form hydroxyl compounds and their dissolution degree in water [30–31]. Only one kind of metallic ion on the ilmenite surface is reported to provide an active site on which surfactants are adsorbed [18].
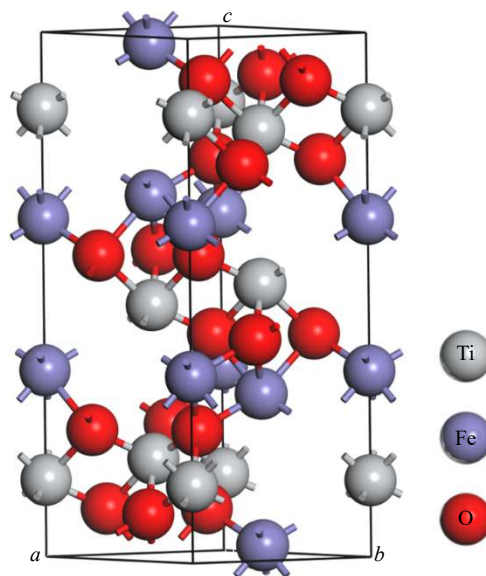

Fig. 1.   Unit cell structure of ilmenite.

The interaction of flotation reagent and ilmenite is closely related to the pH of the flotation pulp; the two main different action sites of ilmenite, that is, Fe and Ti, also have various forms as the pH changes [32]. Therefore, analyzing the surface properties of ilmenite is essential.

Solution chemistry calculations provide a powerful analytical method and have been widely used to study the effective components of flotation reagents in flotation [33]. A solution chemical analysis has been performed on the ilmenite [18], and Fig. 2 illustrates the composition of the ilmenite solution. The results show that the Ti and Fe sites on the ilmenite surface can form various complex ions and neutral complexes after the Ti and Fe sites are dissolved in an aqueous solution and hydrated. Fig. 2 indicates that Fe on the ilmenite surface is selectively dissolved in a strong acid medium, whereas Ti becomes the main active site on the sur-
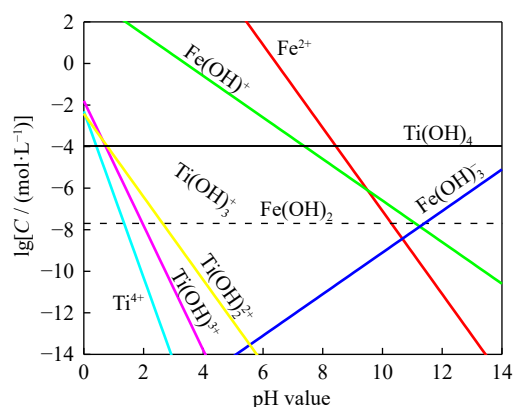

Fig. 2.   Logarithmic distribution diagram of surface species on ilmenite as a function of pH value (*C* is the concentration of a component).

face. In weak acid and alkaline medium, Ti^{4+} and Fe^{2+} mainly exist on the ilmenite surface as hydroxyl compounds $Ti(OH)_n^{4-n}$ and $Fe(OH)_n^{2-n}$, respectively.

At low pH value, the possible location ions on the ilmenite surface mainly include Ti^{4+}, $Ti(OH)^{3+}$, $Ti(OH)_2^{2+}$, and Fe^{2+}. When pH value is greater than 4, the hydroxyl compound of titanium ion is very stable and is difficult to become an active site of the ilmenite surface. Moreover, the ferrous ion and its hydroxyl compounds are more active and can easily become an active site of the ilmenite surface. Under the condition of a weak acid or a weak base, the location ions on the ilmenite surface are $Ti(OH)_4$, $Fe(OH)^+$, and $Fe(OH)^{2+}$. However, $Ti(OH)_4$ is much more stable at this pH range, and the hydroxyl compounds of iron become the main active sites on the ilmenite surface.

3. Collectors

The typical collectors used in ilmenite flotation mainly include fatty acid, phosphonic acid, arsonic acid, and hydroxamic acid. These collectors usually interact with the metal ions on the ilmenite surface and then make the ilmenite surface hydrophobic. A summary of collectors for ilmenite flotation is given in Table 1. Xi [34] studied the collecting ability of common collectors used in ilmenite flotation. The results of single mineral tests showed that the ranking of collecting ability is: sodium oleate > benzyl hydroxamic acid (BHA) > styrene phosphonic acid > benzyl arsonic acid.

Table 1. Summary of collectors for ilmenite flotation

Reagent	Major component	Optimum pH range	Action mechanism	Feature
Oxidated paraffin soap [34]	RCO_2Na	6–8	Long-chain fatty acids react with metal ions that form complexes	Sensitive to temperature, poor collecting ability, foamability
Tall oil [34]	Fatty acid salt, rosinate	4–10	Similar to oleic acid	Similar to oleic acid
Arsonic acid [34]	Organic compound with AsO_3H_2 functional group	4–6	van der Waals action; reaction with metal ions to form chelate compound	Good selectivity, toxicity
Oleic acid and its oleate [35]	RCOOH (Na,K)	4–8	Reaction with metal ions to form ferric oleate compounds	Sensitive to temperature, high collecting ability, poor selectivity, foamability
Phosphonic acid [36]	Organic phosphorous compounds with C and P atoms	5.82–7.2	Reaction with the Fe and Ti of ilmenite to form an organic phosphonate	Better selectivity, expensive
Hydroxamic acid [37]	RC(=O)NHOH	5–9	Reaction with metal ions to form chelate compound	Low dosage, high selectivity, expensive

3.1. Fatty acids

In general, fatty acid collectors used in dressing plants mainly include oleic acid and its oleate, tall oil (soap), and oxidized paraffin soap [38–39].

Given that fatty acids have a good collecting ability, a low cost, and a good foaming ability, the collecting mechanism of oleic acid and its oleate for ilmenite has been widely investigated by mineral processing researchers [40]. Oleic acid is sensitive to temperature and can obtain better separation results for ilmenite when the temperature is above 20°C. The flotation index of ilmenite may deteriorate at a low temperature. Parkins [41] found that the recovery of ilmenite increases gradually as flotation temperature increases, whereas the concentrate grade decreases as temperature increases. Regarding the action mechanism of sodium oleate and ilmenite, Parkins [41] confirmed that the action mechanism of ilmenite and oleate ions differs owing to the different adsorption densities of oleate. Oleate adsorption on the ilmenite surface is a physical adsorption process at low adsorption density, which is an exothermic process. It becomes a chemisorption process at high adsorption density, which is an endothermic process. Fan and Rowson [15] believed that the action mechanism of oleate ions and ilmenite is the substitution process of oleate ions on the ilmenite surface.

Presently, flotation solution chemistry is an effective means of studying the surface properties of minerals and reagent species during the flotation process [35]. Fig. 3 shows a logarithmic diagram of the oleate hydrolysis components of sodium oleate.
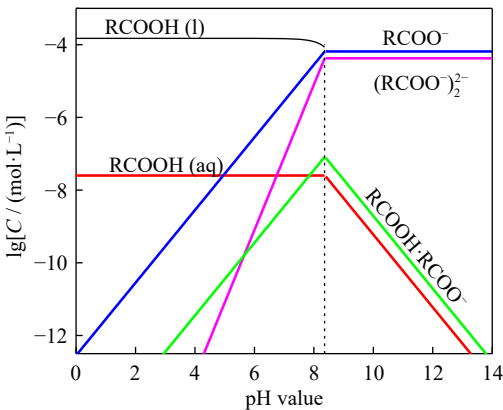

Fig. 3. Logarithmic diagram of oleate hydrolysis components with sodium oleate ($C_{Sodium\ oleate} = 1.5 \times 10^{-4}$ mol/L, C is the concentration of a component).

When the concentration of sodium oleate is 1.5×10^{-4} mol/L, the components of sodium oleate solution include oleic acid (RCOOH), oleate ($RCOO^-$), oleic acid dimer [$(RCOO)_2^{2-}$], and acid soap complex [$(RCOO)_2H^-$]. Oleic acid (RCOOH) is the dominant component at low pH value.

Under weakly acidic and neutral conditions, the dominant component becomes the acid soap complex $[(RCOO)_2H]^-$ [42]. The oleic acid dimer $[(RCOO)_2^{2-}]$ is the dominant component in an alkaline environment. Chen *et al.* [35] found that $RCOO^-$, $(RCOO)_2^{2-}$, and $[(RCOO)_2H]^-$ are generated on the ilmenite surface when sodium oleate is the collector for ilmenite at pH value of 6 by X-ray photoelectron spectroscopy (XPS). In addition, Kulkarni and Somasundaran [43] revealed that the unique solubility characteristics of oleate, together with its tendency to form ionic–molecular complexes, are responsible for the observed complex flotation behavior.

On the basis of previous studies on the solution chemistry calculation of sodium oleate and ilmenite, Zhang *et al.* [44] explored the action mechanism between microfine ilmenite and sodium oleate through pure mineral flotation experiments, zeta potential measurements, and infrared spectroscopy analysis. The results showed that the ilmenite has good floatability within pH value of 4–10 when the dosage of sodium oleate is 2×10^{-4} mol/L. When the pH value of the flotation pulp is 4–6, the chemical interaction is dominant between the oleate ion and Fe active sites on the ilmenite surface, and some ferric oleate forms on the ilmenite surface. At pH value of 6–10, the chemical interaction between oleate ions and ilmenite is weakened, but the ilmenite maintains good floatability, caused by the increased concentration of the highly surface-active component, ionic–molecular association, in the sodium oleate solution. Fan and Rowson [30] confirmed that Ti^{4+} and Fe^{2+} cannot simultaneously serve as active sites that interact with the collector at specific pH values, even though Ti and Fe are active sites on the ilmenite surface. These metal ions interact with oleate ions at different pH ranges; Ti^{4+} interacts with sodium oleate in the strong acid medium at pH value of 2–3, whereas Fe^{2+} interacts with sodium oleate in the pH range of weak acid and weak base. Therefore, the active sites of flotation on the ilmenite surface are strongly dependent on the pH of the pulp [15,18,45].
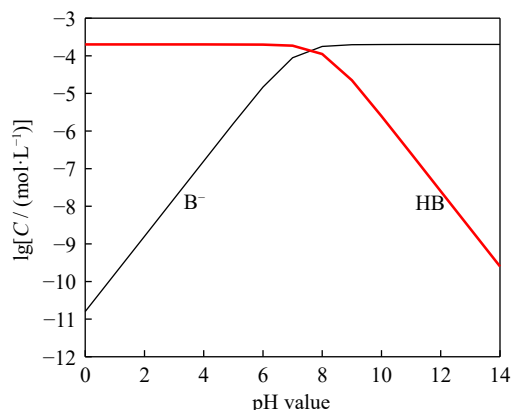
3.2. Hydroxamic acids

Hydroxamic acid has a keto form [RC(=O)–NHOH] and an alcoholic form [R–COH(–N)–OH]; both forms are considered to exist simultaneously [46–47]. The –C(O)NHOH group can form stable chelates with metal ions, which provide good collecting ability and high selectivity. It has been proven to be an efficient collector in the flotation of oxidized minerals, such as cassiterite, tungsten ore, malachite, and rare earth minerals.

Fig. 4 displays the logarithmic diagram of BHA solution as a function of pH. BHA mainly exists in molecules (HB) in an aqueous solution when the pH of the pulp solution is acidic. In an alkaline slurry solution, BHA exists in the form of ions (B^-). Under neutral conditions, the concentration of dissociated hydroxamic acid anions (B^-) and neutral molecules (HB) is roughly equal [48].

The –C(O)NHOH group in the hydroxamic acid molecule is well known for its ability to form highly stable chelates with metal ions. At the same time, the mineral surface of il-

menite is readily hydrolyzed in an aqueous solution to form a hydroxylated surface. Hydroxamic acids possess a strong chelating ability, where it chelates with metal ions (Fe and Ti) on the surface to form a four-membered O–N ring chelate or a five-membered O–O ring chelate (the majority). Then, ilmenite flotation is achieved through the hydrophobization of a nonpolar group (hydrocarbyl group) in the hydroxamic acid molecule [48].

Fig. 4. Logarithmic distribution diagram of BHA as a function of pH value ($C_{BHA} = 2 \times 10^{-4}$ mol/L, C is the concentration of a component).

Liu [48], Zhang and Zhong [49], and Wen [50] found that the effect of hydroxamic acid on the flotation behavior of ilmenite is related to the hydrophobic structure of the hydroxamic acid. With the increase of the length of the carbon chain in the hydrophobic group of a hydroxamic acid collector, the critical micelle concentration of the collector decreases gradually, and the hydroxamic acid collector has a better collecting effect on ilmenite. Moreover, ilmenite mainly undergoes chemical adsorption, followed by physical adsorption. When salicylic hydroxamic acid is used as the collector of ilmenite, Dong and Chen [51] found that the adsorption between ilmenite and salicylhydroxamic acid is related to the concentration of salicylhydroxamic acid. The adsorption is mainly chemical adsorption when the concentration of salicylhydroxamic acid is low in the pulp. The chemical and physical adsorptions of salicylhydroxamic acid coexist onto the ilmenite surface under a high concentration of salicylhydroxamic acid in the solution.

3.3. Phosphonic acids

Phosphonic acids, organic phosphonic acid compounds, are directly connected to carbon and phosphorus atoms. The commonly used phosphonic acid collectors include monophosphonic and bisphosphonic acids and their derivatives. Phosphonic acids can be divided by their structure as alkylphosphonic and alkylarylphosphonic acids. Styrene phosphonic acid is insensitive to calcium and magnesium ions and exhibits excellent collectability and selectivity on ilmenite compared with sodium oleate. Meanwhile, the application of phosphoric acid collectors is still limited in dressing plants due to their high price [52].

Most researchers believed that the action mechanism

between phosphoric acid and ilmenite is mainly chemical adsorption [40], accompanied by physical adsorption through electrostatic force and hydrogen bonding [53]. Yang *et al.* [54] explored the effects of styrene phosphonic acid on the flotation behavior of ilmenite. They found that the oxygen atom in the phosphonic acid group of styrene phosphonic acid and the unsaturated lattice cation of the ilmenite surface can form a four-membered chelate ring or insoluble compound. The chemical reactivity of the active sites on the ilmenite surface acting with styrene phosphonic acid are ranked as $Fe^{3+} > Fe^{2+} > Ti^{4+}$ [54]. Bulatovic and Wyslouzil [55] and Hu and Zhang [56] reported the action mechanism between phosphoric acid collectors and ilmenite. They believed that the phosphonic acid collectors can have a chemical interaction with the Fe and Ti sites of the ilmenite surface, forming a hydrophobic organic phosphonate at the solid–liquid interface.

A novel collector, α-hydroxyoctyl phosphonic acid (HPA), is synthesized by Li *et al.* [36]. It has an excellent collecting effect on ilmenite. The results of density functional theory and XPS analysis revealed that three O atoms in the $PO(OH)_2$ group are of the reactive center of the three HPA species, which bond with the active sites (Ti and Fe) on the ilmenite surface. Their chemical reactivity follows the order as $HPA^{2-} > HPA^- > HPA$. In addition, HPA weakens the influence of water molecules on the interfacial tension of ilmenite particles, thereby improving the hydrophobicity of il-

menite for flotation. A schematic model of HPA adsorption on the ilmenite surface is shown in Fig. 5.
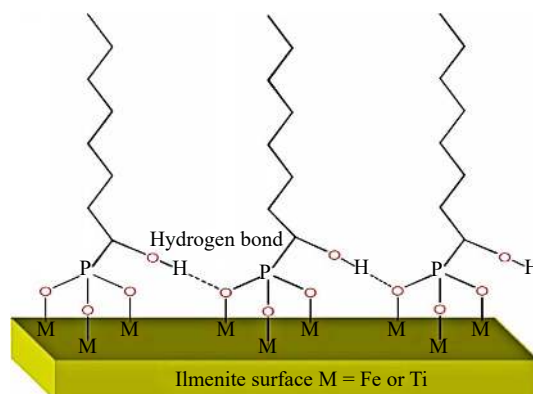

Fig. 5.   Recommended model of α-HPA adsorbed on the ilmenite surface [36]. Reprinted from *Colloids Surf. A Physicochem. Eng. Aspects*, 490, F.X. Li, H. Zhong, G. Zhao, S. Wang, and G.Y. Liu, Adsorption of α-hydroxyoctyl phosphonic acid to ilmenite/water interface and its application in flotation, 67-73, Copyright 2016, with permission from Elsevier.

4. Regulators

Regulators in ilmenite flotation can be roughly divided into three categories: pH regulators, activators, and depressants (Table 2).

Table 2.   Summary of regulators for ilmenite flotation

Reagent	Major component	Action mechanism	Feature
Sulfuric acid [57]	H_2SO_4	Electrostatic adsorption, oxidation	pH regulator, activator
Metal ions of copper and lead [35,58]	$Pb(NO_3)_2$, $CuSO_4$	Physical adsorption and chemisorption	Widely used in dressing plants
Sodium silicate [52,59]	$Na_2O \cdot mSiO_2$	H_2SiO_3 and $HSiO_3^-$ generate the depression effect as they are adsorbed on the mineral surface.	Depressant of gangue minerals and dispersing the slurry
Oxalic acid (OA) [60–61]	$H_2C_2O_4$	OA reacts with metal ions to form a stable complex.	Preferentially interact with Ca on the surface of gangue minerals
Carboxymethyl cellulose (CMC) [62]	Obtained by the carboxymethylation of natural cellulose	The hydroxy anion reacts with the cation on the gangue mineral surface through electrostatic adsorption; Chemical adsorption	Depress the magnesium-containing silicate minerals
Sodium hexametaphosph-ate [52]	$(NaPO_3)_6$	Its anions interact with the polyvalent metal ions in the pulp to form insoluble salts, which are then converted into stable soluble complexes.	Used with sodium silicate to achieve better depression

4.1. pH regulators

The pH regulators for ilmenite flotation involve lime, soda, sulfuric acid, and caustic soda. Yan [63] and Zhu *et al.* [64] studied the effects of pH regulators (H_2SO_4–NaOH, HCl–Na_2CO_3, HNO_3, and H_3PO_4) and the pH of the pulp on the flotation index of ilmenite. Their results indicated that when H_2SO_4, HCl, and HNO_3 are used as pH regulators for ilmenite, the recovery of ilmenite has little difference; however, when H_3PO_4 is used as a pH regulator of ilmenite, the floatability of ilmenite is poor. Compared with other acids and bases, when pH value is greater than 5.5, the use of

H_2SO_4–NaOH to adjust the pH of the pulp is more conducive to the separation of ilmenite and gangue minerals.

Sulfuric acid is the most commonly used pH regulator for ilmenite flotation. It is considered to have the following functions: (1) adjusting the pH of the pulp; (2) changing the density distribution of the ilmenite particles on the surface; and (3) causing characteristic adsorption on the ilmenite surface to change the electric double layer of ilmenite, which is beneficial to the adsorption of the collector on the ilmenite surface [11,36]. Researchers [65] demonstrated that sulfuric acid can adjust the pulp's pH in ilmenite flotation and oxidize the Fe^{2+} on the ilmenite surface to Fe^{3+}. The electric double layer

on the ilmenite surface can also be changed by SO_4^{2-} and HSO_4^- in the solution, enhancing the adsorption of the collector on the ilmenite surface.

Zhang *et al.* [66] confirmed that the pH of the pulp can affect the active sites on the ilmenite and titanaugite surface. Liu *et al.* [67] illustrated that under acidic conditions, Fe^{3+} (the oxidation of Fe^{2+} produces Fe^{3+} in the presence of sulfuric acid) and Ti^{4+} on the ilmenite surface and Ca^{2+}, Mg^{2+}, and Al^{3+} on the titanaugite surface can react with sodium oleate chemically; while in an alkaline environment, the active sites on the titanaugite surface mainly include Ca^{2+} and Mg^{2+}, generating the chemical bonding effects with sodium oleate.

4.2. Activators

Activators are the flotation reagents that enhance collectors' adsorption capacity on the mineral surface [68]. Surface modification is widely used to activate the target mineral [69]. In general, two methods can be used to activate the target mineral. One approach is to change the structure or valence state of the target mineral surface in specific ways (e.g., roasting or microwave irradiation). Another is to introduce the required active components or ions into the surface of the target mineral. The active sites on the target mineral surface can be increased with the two methods, thereby achieving the activation of the mineral [35,70–73].

In practice, the addition of various metal ions (e.g., Pb^{2+}, Cu^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}) on the mineral surface is currently the more common activation method [74–77]. Gao and Wang [78] studied the effects of Fe^{3+}, Cu^{2+}, Al^{3+}, and Pb^{2+} on the ilmenite flotation behavior of the particle size less than 20 μm. The four metal ions have activation effects on ilmenite in the pH range of their respective action, which can increase the recovery rate of ilmenite flotation by 20%–30%.

Li *et al.* [79] studied the activation mechanism of Cu^{2+} in ilmenite flotation by using HPA as a collector. Their results illustrated that the mechanism of Cu^{2+} activation is mainly based on ion exchange, metal hydroxide precipitation, and redox reactions. In addition, the Fe–HPA and Cu–HPA complexes are formed on the ilmenite surface after introducing Cu^{2+} and HPA.

The above studies confirm that Cu^{2+} and Fe^{3+} have activation effects on ilmenite. However, in dressing plants, Pb^{2+} (as an activator) is extensively used in ilmenite, cassiterite, and tungsten flotation [80–83].

Researchers generally believed that the activation mechanism of Pb^{2+} for ilmenite flotation is that Pb^{2+} can be selectively adsorbed on the electric double layer of the ilmenite surface and make the surface potential of ilmenite shift to more positive values, which are conducive to the adsorption of anionic collector, thereby activating the ilmenite [30,57,65].

Further studies have investigated the adsorption mechanism of lead ions on the ilmenite surface [32,35,84] through zeta potential analysis, adsorption density calculation, Fourier transform infrared (FT-IR) spectroscopy, and XPS analysis. They believed that the activation of Pb^{2+} on ilmenite and

the action with collectors are based on (1) physical adsorption and (2) chemical adsorption, where chemical adsorption plays a dominant role. In the case of physical adsorption, lead ions are adsorbed on the ilmenite surface in the form of Pb–O–H or Pb^{2+}. These ions then bond with the collectors (NaOl in Fig. 6 and BHA in Fig. 7) to form a hydrophobic substance. In the case of chemical adsorption, the Fe–O–Pb complex, formed by the lead ions adsorbed on the ilmenite surface, is chemically bonded to the collectors (NaOl and BHA) to form a hydrophobic surface. The Fe sites on the ilmenite surface and the Pb^{2+} in the pulp are active sites on the ilmenite surface. The addition of Pb^{2+} increases the number of active sites on the ilmenite surface. Moreover, when BHA and lead ions are added to the flotation system, lead ions either adsorb on the surface of ilmenite to increase the number of active sites or react with BHA in the solution to form a Pb–BHA complex. Both interactions improve the ilmenite floatability [58].

Many researchers have studied the effects of oxidation on ilmenite flotation, such as microwave irradiation [85–88], calcination, acid dissolution [45,64], oxygen oxidation [89], and ultrasonic pretreatment [90]. The oxidative activation of ilmenite is based on an oxidation method to facilitate the conversion of Fe^{2+} to Fe^{3+} on the ilmenite surface, which enhances the adsorption between ilmenite and collectors [91–92].

Therefore, oxidative activation and ion-induced activation are effective means to activate ilmenite. The difference between oxidation activation and ion-induced activation is that oxidative activation forms the active component on the mineral surface. By contrast, ion-induced activation is the adsorption of the active component added from the outside on the mineral surface.

4.3. Depressants

In general, ilmenite is always associated with titanaugite, plagioclase, chlorite, serpentine, hornblende, and sericite [93]. Thus, the impurity removal from ilmenite is mainly to remove the above calcium and magnesium-bearing minerals. The commonly used depressants in ilmenite flotation include sodium silicate, CMC, starch, OA, and sodium hexametaphosphate [94].

Wang [95] summarized the effects of various depressants on the floatability of ilmenite and titanaugite. These depressants include inorganic depressants (sodium silicate and sodium hexametaphosphate), complex organic depressants (oxalic and citric acids), and organic polymer depressants (CMC and starch). Investigation results show that each of these depressants has a good depression effect on titanaugite at a suitable dosage. Sodium silicate can effectively depress titanaugite but has little effect on the floatability of ilmenite. Researchers suggested that the depression mechanism of sodium silicate is due to the adsorption of H_2SiO_3 and $HSiO_3^-$ (Fig. 8) on the mineral surface, which causes the hydrophilicity of the mineral. However, the extended DLVO (Derjaguin–Landau–Verwey–Overbeek) theory calculations suggest
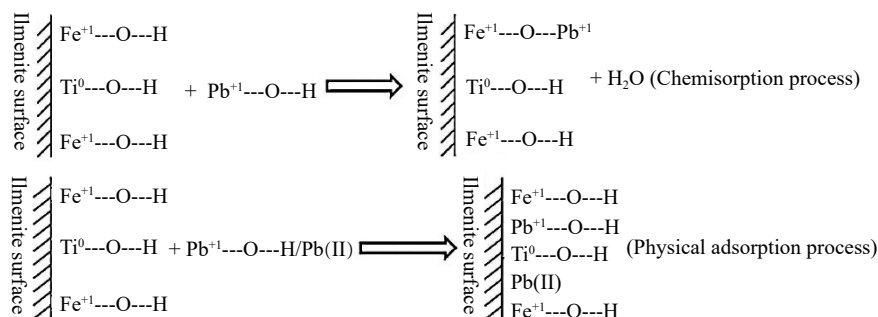
Scheme 1: The adsorption of lead ions onto ilmenite surface.
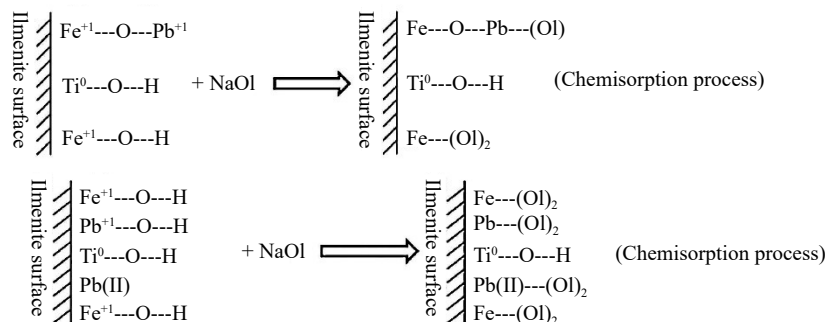
Scheme 2: The adsorption of sodium oleate onto ilmenite surface pretreated with lead ions.

Fig. 6.   Potential interaction scheme for the adsorption of lead ions onto the ilmenite surface (Scheme 1: Adsorption of lead ions on the ilmenite surface) and its influence on the adsorption of sodium oleate (Scheme 2: Adsorption of sodium oleate on the ilmenite surface pretreated with lead ions) [84]. Reprinted from *J. Ind. Eng. Chem.*, 53, P. Chen, J.H. Zhai, W. Sun, Y.H. Hu, Z.G. Yin, and X.S. Lai, Adsorption mechanism of lead ions at ilmenite/water interface and its influence on ilmenite flotability, 285-293, Copyright 2017, with permission from Elsevier.
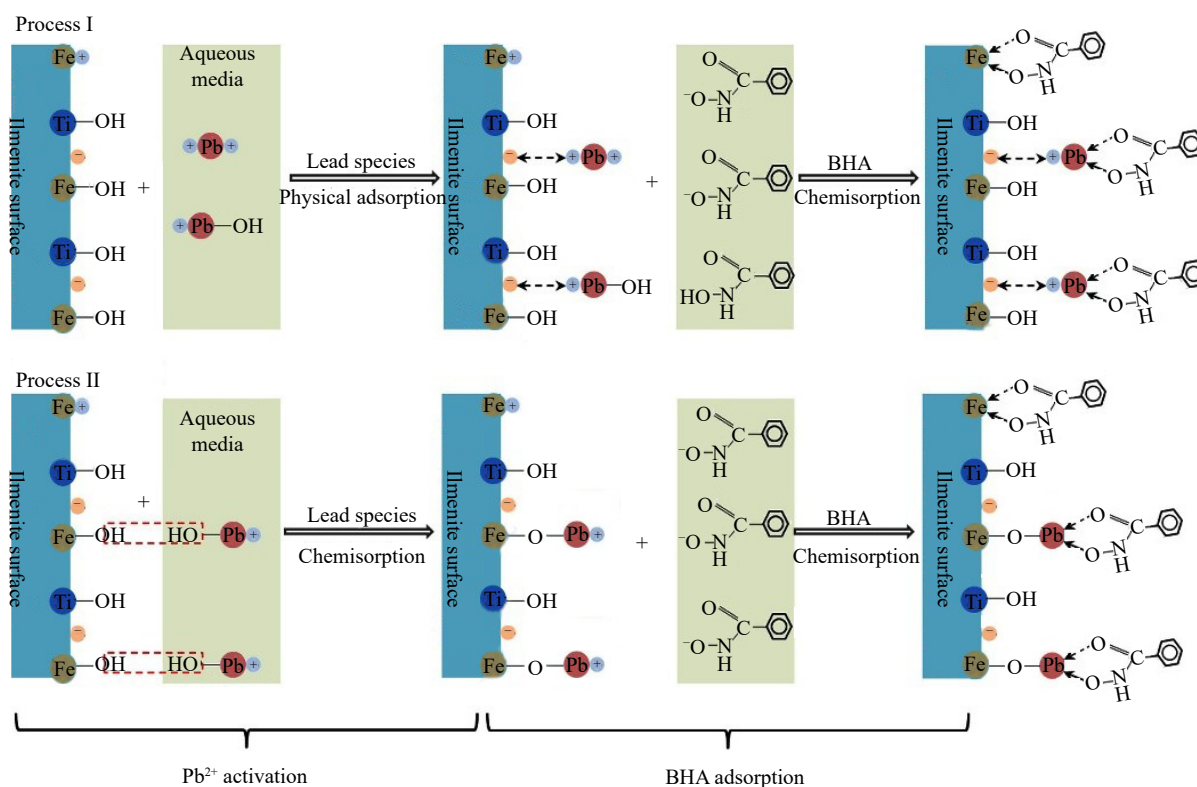
Fig. 7.   Potential mechanisms for Pb^{2+} activation and BHA adsorption on the ilmenite surface [32]. Reprinted from *J. Ind. Eng. Chem.*, 62, Q.Y. Meng, Z.T. Yuan, L. Yu, Y.K. Xu, and Y.S. Du, Study on the activation mechanism of lead ions in the flotation of ilmenite using benzyl hydroxamic acid as collector, 209-216, Copyright 2018, with permission from Elsevier.

that the depression mechanism of sodium silicate is based on its ability to enlarge the difference in wettability and weaken the attraction energy of hydrophobic interaction between ilmenite and titanaugite. Thus, the repulsive force between ilmenite and titanaugite is increased, whereas the attraction force is decreased.
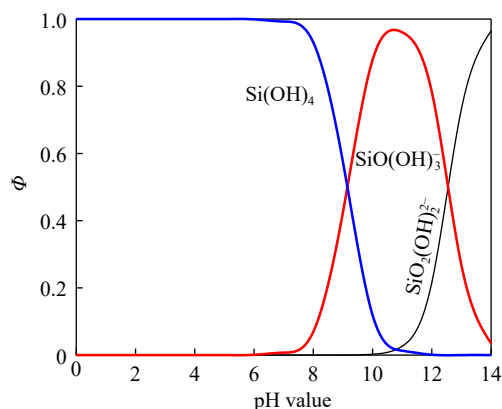

Fig. 8.   Effects of pH value on the species distribution of sodium silicate (Φ is the amount of a component).

Deng *et al.* [59] analyzed the action mechanism of sodium silicate in ilmenite flotation through single mineral flotation tests, zeta potential measurement, and infrared spectroscopy. They confirmed that under weakly acidic conditions, more sodium oleate is adsorbed on the ilmenite surface because the adsorption strength of sodium silicate and ilmenite is less than that of titanaugite. Therefore, the depression of titanaugite by sodium silicate has good selectivity. Moreover, sodium silicate has a good dispersion effect on the flotation system.

Acidified sodium silicate, the mixture of acid or acid salt and sodium silicate, is reported to have a better depression effect on the mineral than that of ordinary sodium silicate [96]. In addition, ordinary sodium silicate can be modified with various metal salts to obtain saline sodium silicate, which exhibits a better selective depression effect on the mineral surface [52,97].

Ma [52] found that the depression effect of acidified sodium silicate on ilmenite and titanaugite is better than that of ordinary sodium silicate. Still, the acidified sodium silicate loses the ability of selective depression effect on the two minerals.

Liu *et al.* [60] and Nuri *et al.* [61] demonstrated that OA can selectively depress titanaugite and make titanaugite hydrophilic. When the pH value of the pulp is above 4.19, $C_2O_4^{2-}$ is the dominant component in the OA solution. Thermodynamic calculations revealed that Ca^{2+} preferentially reacts with $C_2O_4^{2-}$ in the pulp to form a cover layer on the gangue mineral surface, followed by a reaction with Fe^{2+} and Mg^{2+}.

Wei *et al.* [62] studied the effect of CMC on the floatability of ilmenite and titanaugite. They found that compared with ilmenite, CMC is preferentially adsorbed on titanaugite, owing to competitive adsorption. Moreover, the adsorption of CMC on titanaugite is mainly chemical adsorption, accompanied by electrostatic adsorption.

Meng *et al.* [98] found that carboxymethyl starch (CMS) can effectively enhance the floatability difference between ilmenite and titanaugite at pH value of 6–10. CMS is adsorbed on the titanaugite surface through hydrogen bonding and chemisorption. CMS exhibits a stronger interaction with titanaugite than that with ilmenite, and CMS tends to be adsorbed onto the titanaugite surface. The hydrophilic CMS coating occupies most of the active sites of titanaugite; hence, the adsorption of sodium oleate is limited.

A mixture of OA and sodium silicate (acidified water glass (AWG)) is tested at a molar ratio of 1:3 to show a higher selectivity depression on olivine. The depressant usage is reduced by 40% compared with that of single water glass (WG). The adsorption tests and zeta potential measurements indicated that the adsorption of AWG on the olivine surface at its optimal molar ratio is stronger than that of the ilmenite surface. The adsorption of AWG on the olivine surface weakens the interaction between the olivine and the collector [99].

5. Combined reagents

With the increasingly complex mineralogy of iron and titanium resources, the conventional single-reagent systems have difficulty in meeting the separation requirements. Compared with the development of new reagents, combined reagents are another effective way to improve selectivity and collectivity by leveraging the advantages of different reagents. Many investigators argued that the effect of combined reagents is typically better than that of single reagents, owing to the synergism of combined reagents [100].

The types of combined reagents reported in the ilmenite flotation include the combination of various collectors, combination of collectors and frothers, and combination of collectors and flocculants [40]. They are primarily reported in the form of codes, such as the TAO series [101], XT [102], ROB [103], R series [104], H717 [105], ZY [106], and F968 [107], including MOH [108] and MOS developed by researchers [109–112] (Table 3).

Hu *et al.* [116] studied the action mechanism on oxidized ores (e.g., tungsten and tin) with $Pb(NO_3)_2$ and BHA. They found that the premixing of $Pb(NO_3)_2$ and BHA is more capable of collecting oxidized minerals than conventional sequential dosing. That is, a combination of collector and activator can perform better than a single reagent. On the basis of the above findings, a new model, coordination of molecular assembly by metal ion, is proposed to improve the classical metal-activated flotation theory.

Tian *et al.* [33] investigated the premixing effect of $Pb(NO_3)_2$ and BHA on the flotation of cassiterite. The energy required for the reaction of the HO–Pb–BHA complex with the mineral surface is less than that of conventional sequential dosing, leading to a better flotation of the mineral (Fig. 9).

Based on classical solution chemistry calculations, lead species exists in the form of Pb^{2+}, $Pb(OH)^+$, $Pb(OH)_2$, and $Pb(OH)_3^-$ in pulp, rather than in the form of $Pb(H_2O)_n^{2+}$,

Table 3.   Summary of combined reagents for ilmenite flotation

Reagent	Major component	Feature
Salicylhydroxamic acid–alkyl bisphosphonate [56]	Hydroxamic and phosphonic acids	A good flotation effect can be obtained at a low dosage.
Salicylhydroxamic acid–oleic acid [111]	Hydroxamic and oleic acids	The combination of salicyl hydroxamic and oleic acids in a mass ratio of 9:1 has the optimal flotation effect.
Terpenic oil–styrene phosphonic acid [113]	Terpenic oil and phosphonic acid	The optimal flotation effect is obtained at about pH value of 3.5.
TAO [101]	Prepared by high fatty acid and nitrogen-containing organic compounds with different hydroxyl groups	Strong collecting ability
MOS/MOH [108]	Composed of three kinds of organic compounds of A, B, and C in a ratio	The collectivity of MOH is better than that of MOS.
ROB [103]	Prepared from organic acids with carboxyl and hydroxyl functional groups	Chemical and electrostatic adsorptions
RHB [114]	Prepared by combining TAO with fatty acid soap	Strong selectivity
RST [115]	Prepared by tall oil with some additives	A good flotation effect can be obtained with the depressant of OA.
XT [102]	Prepared by A, B, and C collectors in a certain ratio	Applied to the flotation of micro-fine ilmenite
ZY [106]	Prepared from the primary raw materials of oleochemicals and petrochemicals	Strong collecting ability, high selectivity, low price

$Pb(H_2O)_n(OH)^+$, $Pb(H_2O)_n(OH)_2$, and $Pb(H_2O)_n(OH)_3^-$. Essentially, the hydration behavior of lead ions is neglected in the solution. However, owing to the existence of the hydration of lead ions, BHA anion adsorption needs to replace hydrated water molecules within $Pb(OH)^+$ to make the mineral surface hydrophobic in conventional sequential dosing. By contrast, the combined reagents of $Pb(NO_3)_2$ and BHA can easily interact with mineral surfaces. The Pb–BHA complex

also works well in the flotation of scheelite [117–119], ilmenite [37,120], and wolframite [121].

Fang *et al.* [37] studied the effect of Pb–BHA complexes on ilmenite flotation. The results indicated that Pb–BHA complexes exhibit better flotation characteristics than those of their sequentially dosed components; meanwhile, the collection properties of these complexes depend on their compositions. Microcalorimetric measurements revealed that the
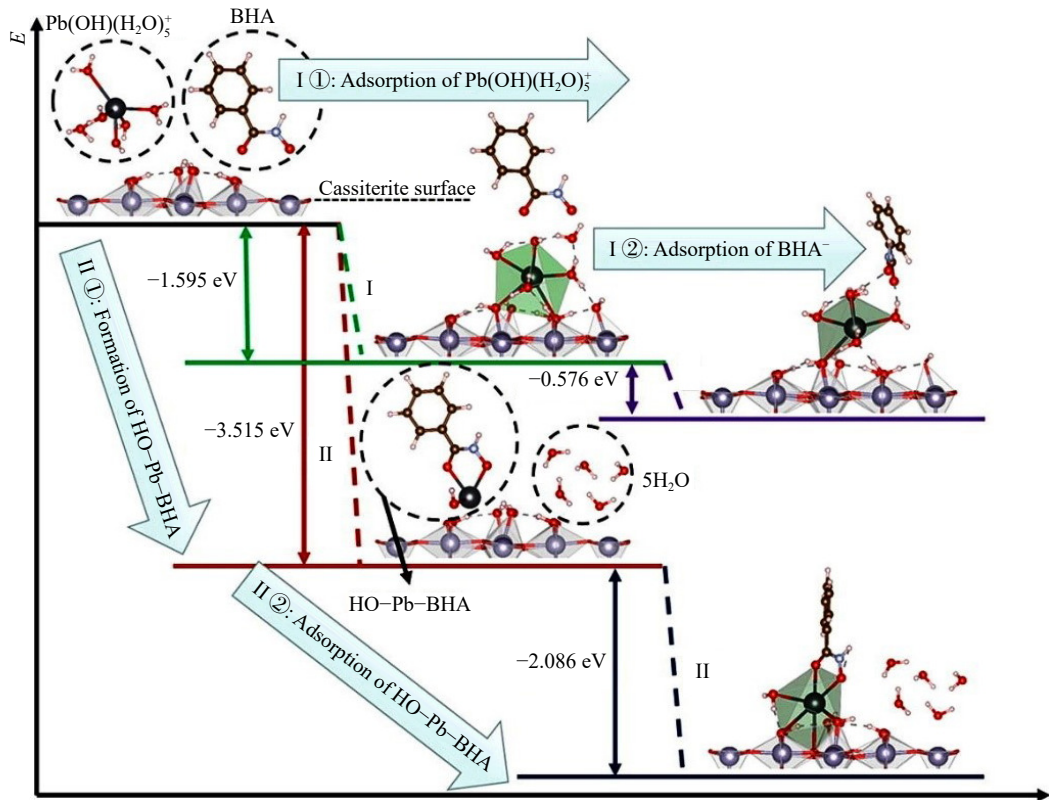

Fig. 9.   Comparison of thermodynamic differences between the two activation systems [33]. Reprinted from *J. Colloid Interface Sci.*, 529, M.J. Tian, Z.Y. Gao, W. Sun, H.S. Han, L. Sun, and Y.H. Hu, Activation role of lead ions in benzohydroxamic acid flotation of oxide minerals: New perspective and new practice, 150-160, Copyright 2018, with permission from Elsevier.

adsorption heats of the three reagents are ranked as $Pb^{2+} <$ BHA $<$ Pb–BHA (Table 4).

Furthermore, He *et al.* [122] investigated the effective surface microstructures and adsorption mechanisms for Pb–BHA on typical oxide mineral surfaces. They found that the thickness and area of the $Pb(BHA)^+$ cover layer on mica are thicker than those of $Pb(BHA)_2$. It indicates that the combined organic–metal collector can alter the mica surface more efficiently than that formed by the conventional method using metal ions as the activator.

Table 4.   Calorimetric analysis of the adsorption of various collector species on the ilmenite surface [37]. Reprinted from *Miner. Eng.*, 126, S. Fang, L.H. Xu, H.Q. Wu, J. Tian, Z.Y. Lu, W. Sun, and Y.H. Hu, Adsorption of Pb(II)/benzohydroxamic acid collector complexes for ilmenite flotation, 16-23, Copyright 2018, with permission from Elsevier

Species	C_0 / $(10^{-3}\ mol\cdot L^{-1})$	n_{ads} / $(mmol\cdot g^{-1})$	$-Q_{ads}$ / $(J\cdot g^{-1})$	$-\Delta_{ads}H$ / $(kJ\cdot mol^{-1})$
Pb^{2+}	1.2	0.053	0.864	16.30
BHA	1.2	0.043	4.099	95.33
Pb–BHA	1.2	0.046	6.069	131.93

Notes: where n_{ads} is the adsorbed amount of collector species per gram of ilmenite, C_0 is the initial concentration of the collector, Q_{ads} is the net heat, and $\Delta_{ads}H$ is the adsorption enthalpy change.

6. Conclusions and outlook

This review summarizes the progress made on the study of reagent types and action mechanisms in ilmenite flotation. According to the literature reviewed, the following conclusions can be drawn.

(1) The surface properties of ilmenite are closely related to its crystal surface structure and the pH of the flotation pulp. The action sites of ilmenite are Fe and Ti, which have various forms as the pH changes. Hence, the floatability of ilmenite is determined by the ability of Fe^{2+} and Ti^{4+} to form various hydroxyl complexes in the solution.

(2) Fatty acids are the widely used collectors in ilmenite flotation. They can easily adsorb on the ilmenite surface and form hydrophobic substances, which improve the floatability of ilmenite. Still, they have shortcomings, such as low selectivity and high sensitivity to temperature. Hydroxamic and phosphonic acids are chelating collectors with stronger collectability and selectivity on ilmenite than fatty acids. However, the application of hydroxamic and phosphonic acids is still limited in dressing plants due to their high price.

(3) Ilmenite displays moderate floatability, and surface modification can improve its floatability. The lead species, a commonly used activator for ilmenite flotation, is selectively adsorbed on the ilmenite surface and makes the surface potential of ilmenite shift to more positive values, which are conducive to the adsorption of the anionic collector. Given that ferric oleate is more insoluble than ferrous oleate, changing the valence state of iron atoms on the ilmenite surface in specific ways can also achieve the activation of ilmenite. The depressants in ilmenite flotation play a critical role in increasing the TiO_2 grade of ilmenite concentrate. Further attention has been paid to the modification of the ordinary depressant.

(4) Based on the synergistic mechanism of combined reagents, the combination of two or more reagents can achieve a better separation index and reduce the dosage of each reagent.

To recover ilmenite resources efficiently, future studies on ilmenite flotation can discuss the following.

(1) Given that Fe^{3+} is more active than Fe^{2+}, the amount of Fe^{3+} on the ilmenite surface largely determines the reactivity of the ilmenite and the collector. Therefore, the influence of more different oxidation methods on the ilmenite flotation must be investigated. Future research should also focus on exploring the effect of changing the iron valence on the crystal structure of ilmenite by using advanced analysis techniques. Doing so can enrich the basic theories of ilmenite flotation.

(2) Commonly, calcium and magnesium-bearing minerals are closely associated with ilmenite. The dissolved cations from calcium and magnesium-bearing minerals in the solution can reduce the selectivity of collectors and depressants. How to eliminate the influence of calcium and magnesium ions on the flotation behavior of ilmenite is still one of the important principles for the development of collectors and depressants of ilmenite flotation in the future.

All in all, surface chemistry (e.g., the reactivities of Ca, Fe, and Ti on Ti-containing mineral surfaces) must be studied and verified in the future to help design more selective collectors or depressants.

Acknowledgements

Conflict of Interest

The authors declare no potential conflict of interest.

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