

Article

Metal Ion Release in Bastnaesite Flotation System and Implications for Flotation

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Abstract: Ca^{2+} , Mg^{2+} , Sr^{2+} and Fe^{3+} were found to be commonly released into bastnaesite flotation pulp from minerals with relatively high concentrations. The influence and corresponding mechanism of Ca^{2+} , Mg^{2+} , Sr^{2+} , Fe^{3+} and Al^{3+} , on bastnaesite flotation, have been studied by micro flotation tests, induction time measurements, adsorption measurements and solution chemistry analysis. It was found that all aforementioned metal ions depressed bastnaesite flotation. The order of depression ability was $\text{Fe}^{3+} > \text{Al}^{3+} > \text{Mg}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+}$ and the depression ability changed along with pH. The depression was mainly attributed to the adsorption of metals ions, which hindered collector adsorption. The species diagrams of metal ions changed along with pH, consequently changing the adsorption of metal ions on mineral surfaces, and therefore leading to different influences on flotation.

Keywords: bastnaesite; metal ions; flotation; adsorption

1. Introduction

The special electron structure of rare earth elements (REEs) leads to their unique fluorescent, magnetic and chemical properties; therefore, REEs play an irreplaceable role in many fields such as metallurgy, petrochemical industry, fine ceramics, luminescent materials and medical industry [1]. With technological development, REEs are becoming more and more important for the upgrading of traditional industries and development of high-tech industries. The REEs consist of fifteen metallic elements of the lanthanide series, plus yttrium and scandium. These elements are typically split into two sub-groups, the light rare earth elements (LREEs), which include La to Eu, and the heavy rare earth elements (HREE), which include Gd to Lu and Y [2,3]. Bastnaesite is the primary source of REEs [4]; Bayan Obo mine in China and the Mountain Pass mine in the United States are the main deposits of bastnaesite [4,5].

Froth flotation is the most important method for the beneficiation of bastnaesite from gangue minerals [1,3]. In practical flotation, various metal ions present in flotation pulp. They are released into the liquid phase during mineral liberation, pulp conditioning and flotation processes. The metal ions inevitably change solution chemistry, mineral surface properties and therefore affect mineral flotation. Many studies have indicated that these ions are mainly released by the dissolution of minerals [6–8]. In addition, fluid inclusions [9,10] and the addition of metal salt regulators [11] also contributes to the presence of metal ions in flotation pulp. Bastnaesite and common gangue minerals such as fluorite, calcite, barite, celestite, and dolomite can be classified as semi-soluble minerals [12,13], which are characterized by relatively high solubility. Therefore, the release of metal ions from these minerals into

liquid is inevitable. It is well known that the ionic environment in bastnaesite flotation pulp is quite complicated; however, the actual variety and abundance of metal ions in bastnaesite flotation pulp is still unclear.

The influence of metal ions on flotation is very complicated; it changes along with different metal ions and different minerals, and the solution pH also plays an important role. Different metal ions may exert different influences on the flotation of a given mineral, and the influence of a metal ion on the flotation of different minerals may be different or even opposite. For example, fatty acid collectors can hardly be adsorbed on pure quartz surfaces, leading to the poor floatability of quartz [14]. The adsorption of metal ions such Fe^{3+} on quartz surfaces provides adsorption sites for the collector and hence increases quartz floatability [15]. However, in the flotation of smithsonite, the presence of Fe(III) not only deteriorates sulfuration but also inhibits collector adsorption on smithsonite surfaces, attributed to a sharp decrease of floatation recovery even at low concentrations [16]. In the flotation of cassiterite, Pb^{2+} is adsorbed onto mineral surfaces through the interaction between lead species and oxygen sites of cassiterite surfaces to form Sn-O-Pb^+ ; this phenomenon increases collector adsorption and, hence, increases the floatability of cassiterite [17], while the adsorption of Fe^{3+} on cassiterite surfaces inhibits collector adsorption and depresses cassiterite flotation [18]. Ca^{2+} and Mg^{2+} commonly presents in flotation process waters and effect the flotation of many minerals: Ca^{2+} , Mg^{2+} was found to significantly reduce flotation recovery of Cu activated sphalerite when pH exceeded that for the formation of the corresponding hydroxide precipitate [19], while the adsorption of calcium hydroxide on spodumene surfaces effectively activates the flotation of spodumene [20]. Although the influence of metal ions on mineral flotation has been widely studied, nevertheless, the implications of metal ions for bastnaesite flotation are still unclear and minimal information is available in published literature.

In the present work, the composition of metal ions in practical bastnaesite flotation pulp was determined, and dissolution experiments of bastnaesite and common gangue minerals including calcite, dolomite, fluorite, celestite and iron minerals in open environment were conducted to investigate the release of metal ions in a bastnaesite flotation system. Then the influence of primary metal ions on bastnaesite flotation was studied by micro flotation tests, induction time measurements, adsorption experiments, and solution chemistry analysis.

2. Materials and Methods

2.1. Materials

The tested practical flotation pulp was derived from a concentrating mill in Zaozhuang, China. The suspension was subjected to solid-liquid separation using a centrifuge, the separated liquid was then collected to analyze the composition of metal ions using an inductively coupled plasma (ICP-OES/MS, Perkinelmer, Waltham, MA, USA).

Bastnaesite sample was derived from Zaozhuang, China. The high grade raw ore was crushed and ground to -1 mm, then the ground product was enriched by gravity separation. The sample was then ground to -74 μm , and washed by ultrasonic cleaning using deionized water to remove surface contaminates [21]. Some of the samples were ground continuously and received a proportion finer than 5 μm for zeta potential determination. According to the X-ray diffraction (XRD, Bruker, Karlsruhe, Germany) pattern (Figure 1), bastnaesite sample with a purity above 95% was finally obtained, meeting experiment requirements; the primary impurities are barite and quartz.

The purity of calcite, fluorite, dolomite and celestite are all above 95%; the iron ore is mainly composed of magnetite, associated with a little hematite. Each of these minerals were ground to -74 μm and then ultrasonic cleaning was used to remove surface contaminates in deionized water.

Analytical grade calcium chloride, magnesium chloride, strontium chloride, aluminium chloride and ferric chloride were used as metal ion source, analytical grade salicylhydroxamic acid (SHA) was used as collector. Industrial pine oil is used as frother. Analytical grade sodium hydroxide and hydrochloric acid was used to regulate solution pH. De-ionized water was used throughout testing.

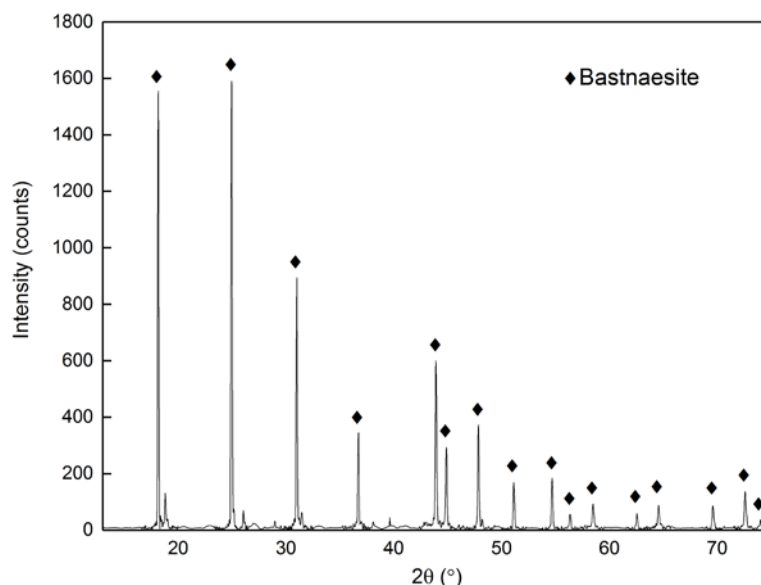


Figure 1. XRD pattern of single bastnaesite.

2.2. Metal Ions Released from Minerals

The experiments were conducted in a 100 cm³ beaker. Mineral samples (2 g) were dispersed in 40 cm³ of deionized water. After magnetic stirring for a certain time, the liquid was collected by centrifugation to analyze the concentration of metal ions using an Inductively Coupled Plasma (ICP-OES, OPTIMA8300). While investigating the influence of grinding on metal ion release, the mineral samples were dry ground for a certain time by a laboratory scale agate grinder before 40 min of magnetic stirring.

2.3. Flotation Experiments

Flotation experiments were conducted at room temperature in a small-scale flotation machine, and 2.0 g of bastnaesite samples were added into a 40 cm³ flotation cell. The pH of mineral suspension was adjusted, metal ions, collectors and frother were added in sequence, and the flotation pulp was conditioned for 3 min before the addition of subsequent reagent. After the collected flotation products were filtered and dried, the weight distribution between the floated and unfloated bastnaesite particles was calculated to determine the corresponding recovery.

2.4. Induction Time Measurements

A home-made system composed of a high speed camera, a light source, a displacement stage, a micro-syringe, a capillary tube and a piezomotor piezo linear actuator was used to measure the induction time (Figure 2). An air bubble was generated by the micro-syringe at the tip of the capillary tube, which submerged in water, the air bubble was then moved down till the bubble is retracted and remained in contact with sample for a given time, then the air bubble moved up. The camera was used to record whether successful attachment between sample and air bubble can occur, and the minimum time for successful attachment is defined as the induction time. It should be noted that, due to the limitation of time control accuracy of our system, the actual induction time obtained is not the same as the induction time in real flotation; however, the variation trend of induction time under different flotation condition is identical.

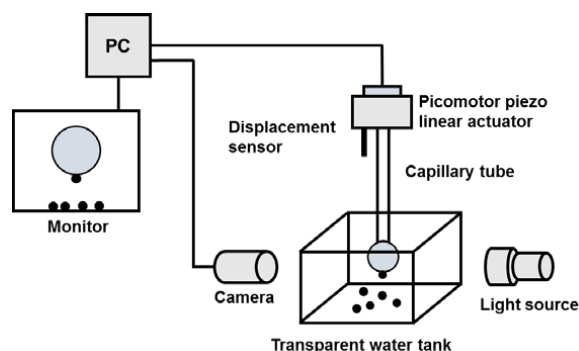


Figure 2. Induction time measurement system.

2.5. Adsorption Experiments

The adsorption experiments were conducted in a thermostatic water bath at 298 K. Bastnaesite samples (1 g) were dispersed in 40 cm³ of metal ion solution with various concentrations of 0.0–25.0 mg/dm³. The mineral suspensions were stirred for a certain time, then the resultant suspension was subjected to solid-liquid separation using a centrifuge, and the separated liquid was collected to quantitatively analyze the concentration of metal ion using an inductively coupled plasma (ICP-OES, OPTIMA8300). The equilibrium adsorption capacity was calculated according to the following formula.

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where Q_e is adsorption capacity (equilibrium adsorption capacity) (mg/g), C_0 is the initial concentration of metal ions (mg/dm³), C_e is the equilibrium concentration of ions, m is the mass of bastnaesite sample (g), and V is the volume of solution (dm³).

2.6. Zeta-Potential Determination

The zeta potential of the bastnaesite samples was determined using a ZetaPlus instrument (Brookhaven, New York, NY, USA). The mineral suspension (0.125% mass fraction) was dispersed and fully vibrated for a desired time by a constant temperature bath oscillator. This step was performed in the presence of desired reagent concentrations at a determined pH. After 30 min of the resultant suspension settling, the pH was measured and recorded, and the fine mineral particles were transferred to measure zeta potentials.

3. Results and Discussion

3.1. Determination of Metal Ions in Practical Flotation Pulp

There were abundant and various metal ions in the practical bastnaesite flotation pulp (Table 1). It can be seen from Table 1 that the primary metal ions were divalent alkaline-earth metal ions, Ca²⁺ had the highest concentration of 32.44 mg/dm³, followed by Mg²⁺ and Sr²⁺, with a concentration of 19.71 mg/dm³ and 18.58 mg/dm³, respectively. In addition, Fe³⁺, K⁺ and Na⁺ also presented in the pulp with relatively high concentrations compared with Ba²⁺, Cu²⁺, Zn²⁺, Pb²⁺ etc. All rare earth ions had low concentrations of below 0.1 mg/dm³.

Table 1. Metal ion concentration in practical flotation pulp (mg/dm³).

Ions	Ca ²⁺	Mg ²⁺	Sr ²⁺	Cu ²⁺	Zn ²⁺	Pb ²⁺	Ba ²⁺
Concentration	32.44	19.71	18.58	0.20	0.33	0.15	0.74
Ions	Fe ³⁺	Al ³⁺	Na ⁺	K ⁺	Ce ³⁺	La ³⁺	Nd ³⁺
Concentration	1.40	<0.001	2.89	3.11	0.071	0.043	0.025

3.2. Concentration of Metal Ions Released from Pure Minerals

As the determined concentration of metal ions in practical flotation pulp was the equilibrium results of metal ions-mineral surfaces-flotation reagents interactions, there are still some knowledge limitations with respect to the contribution of minerals to the abundance of corresponding metal ions in flotation pulp. Therefore, the intrinsic metal ions released from pure minerals was investigated; minor factors such as impurities and fluid inclusions were not considered in this work. According to technological mineralogy research, the primary calcium minerals in raw ore are fluorite, calcite and dolomite, the primary magnesium mineral is dolomite, and the primary strontium mineral is celestite. The occurrence of iron minerals cannot be detected in raw ore, the Fe^{3+} in practical flotation pulp might be released from the dissolution of low content soluble salt or amphibole containing iron in raw ore. However, considering the fact that rare earth minerals are closely associated with high content of iron minerals in some other deposits such as bayan obo mine [22,23], the Fe^{3+} released from iron minerals was also worth investigating. Although the concentrations of rare earth ions were quite low in practical flotation pulp, before interacting with minerals and reagents, the initial concentrations of rare earth ions released into pulp from semi soluble bastnaesite is also worth considering. The monovalent K^+ and Na^+ have little influence on flotation [24,25] hence they were not selected in the following research. Above all, fluorite, calcite, dolomite, celestite, iron minerals and bastnaesite were selected to investigate the contribution of minerals on the abundance of Ca^{2+} , Mg^{2+} , Sr^{2+} , Fe^{3+} and rare earth metal ions (represented by Ce^{3+}) in bastnaesite flotation environment.

As shown in Figure 3, all calcium minerals, calcite, dolomite and fluorite showed strong releasing ability of Ca^{2+} , the concentration of Ca^{2+} increased rapidly to 35.53 mg/dm^3 , 32.60 mg/dm^3 and 17.61 mg/dm^3 in 60 min, respectively. The strong dissolubility and high content of calcium minerals in raw ore led to the highest concentration of Ca^{2+} in practical flotation pulp. The dolomite's capacity of releasing Mg^{2+} was lower compared with that of Ca^{2+} , the released Mg^{2+} reached saturated after 120 min, with a concentration of 7.10 mg/dm^3 . Among all the minerals, celestite exerted the strongest dissolubility, the concentration of Sr^{2+} in solution increased rapidly to 63.72 mg/dm^3 in 30 min, then the concentration increased gradually to 75.53 mg/dm^3 at 180 min. Therefore, the high concentration of Sr^{2+} in practical flotation pulp was released from celestite due to its high dissolubility. Fe^{3+} were released from iron minerals during the stirring process, the concentration of Fe^{3+} increased gradually and reached 10.53 mg/dm^3 at 180 min. Bastnaesite exerted the lowest capacity of releasing intrinsic metal ions, the concentration of Ce^{3+} was below 0.70 mg/dm^3 across the whole dissolution time.

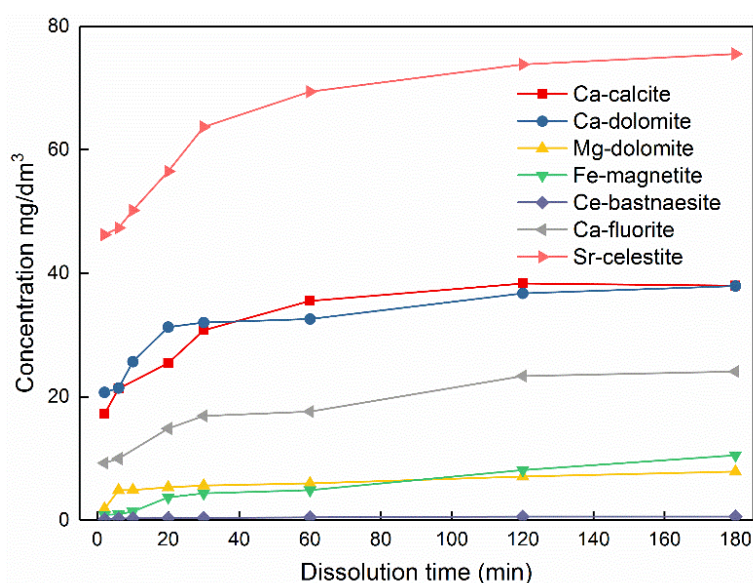


Figure 3. Concentration of metal ions release from minerals.

Grinding is an essential process before flotation, and is generally accepted to be able to change ionic environment in flotation pulp [26–28]; therefore, the influence of grinding on metal ion release was investigated. As shown in Figure 4, for all the minerals, the concentration of metal ions increased with grinding time, this may be attributed to the reduction of particle size, which increased surface area of particles exposed in solution [26]. As for calcite, dolomite, fluorite, celestite and iron minerals, the concentration of released intrinsic metal ions has been improved significantly, which indicates that the release of metal ions were remarkable enhanced by grinding before flotation. While for bastnaesite, grinding had little influence on the release of Ce^{3+} , even when the particles were ground to $d_{50} = 10.82 \mu\text{m}$, the concentration of released Ce^{3+} was still below 0.9 mg/dm^3 ; therefore, the release of rare earth ions from bastnaesite into flotation pulp could be negligible.

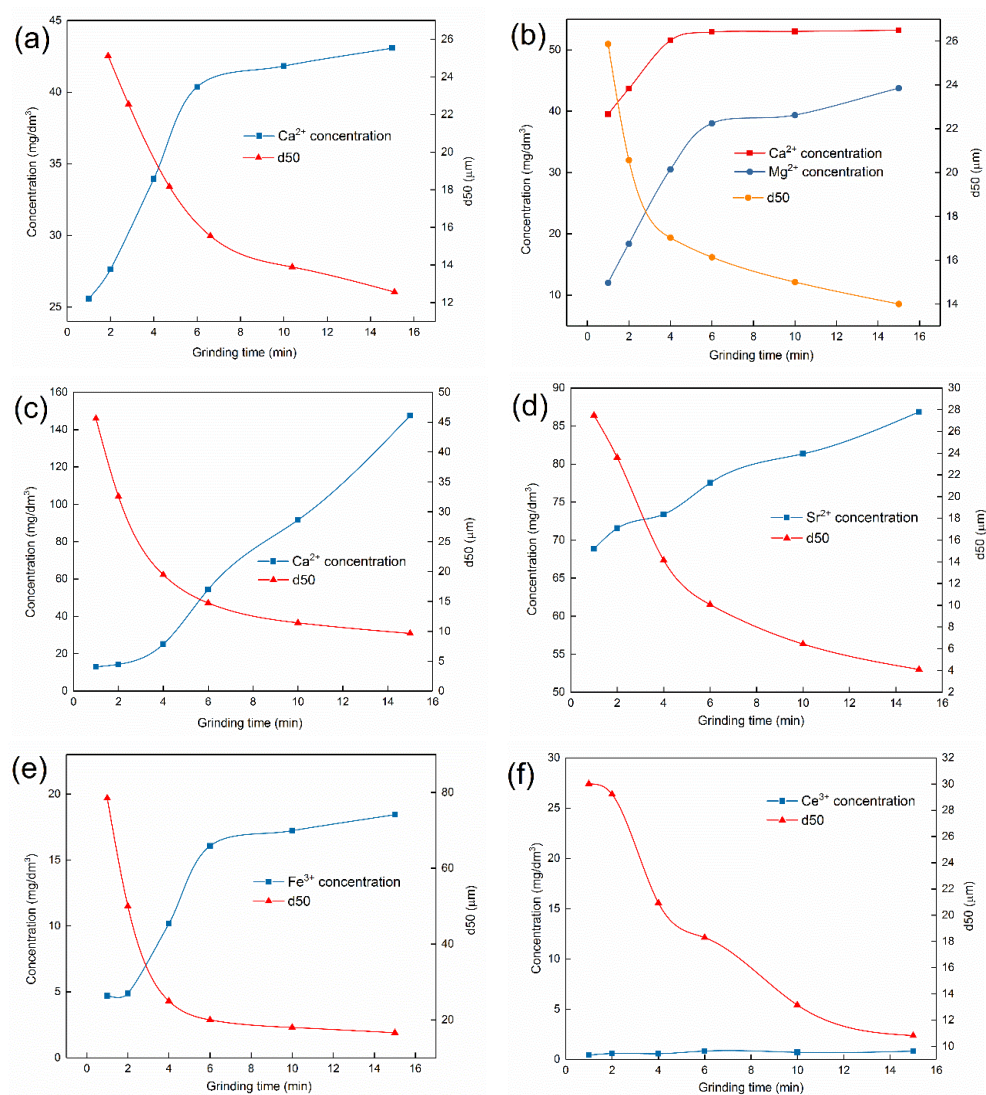


Figure 4. Metal ion release from minerals in the presence of grinding: (a) calcite; (b) dolomite; (c) fluorite; (d) celestite; (e) iron minerals; (f) bastnaesite (Stirring time: 40 min).

3.3. Influence of Metal Ions on Bastnaesite Flotation

According to the results of the metal ion release study, Ca^{2+} , Mg^{2+} , Sr^{2+} and Fe^{3+} were selected because they presented in flotation pulp with relatively high contents and had a potentially major influence on bastnaesite flotation. In addition, although Al^{3+} was not found in practical flotation pulp and there was no aluminum minerals in raw ore, aluminium salt is an important depressant used in the

separation of bastnaesite from monazite [11]; therefore, the influence of Al^{3+} on bastnaesite flotation was also investigated. The influence of metal ions under different pH and different concentration was investigated by micro flotation. As shown in Figure 5, the flotation recovery of bastnaesite increased gradually at $\text{pH} < 8$, and reaching a maximum of 72.30% at about $\text{pH} 8.0$. At $\text{pH} > 8$, the flotation recovery decreased rapidly with the increase of pH , and dropped to 42.10% at $\text{pH} = 11$. In the acidic environment, the collector mainly present as molecules, which limited collector adsorption; the ionization of SHA increased incrementally with rising pH , and therefore the flotation recovery increased at $\text{pH} < 8$. In heavy alkaline solution, the electrostatic repulsion between anionic collector ions and negative bastnaesite surfaces as well as competitive adsorption between collector ions and hydroxyl ions decreased flotation recovery, leading to the decrease of flotation recovery at $\text{pH} > 8$ [17]. It can be seen from Figures 5 and 6 that all of the five metal ions depressed bastnaesite flotation; the order of depression ability was $\text{Fe}^{3+} > \text{Al}^{3+} > \text{Mg}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+}$. The influence of metal ions on flotation varied with pH , Ca^{2+} , Mg^{2+} and Sr^{2+} exerted stronger depression at high pH than at low pH , for example, at $\text{pH} = 6.5$ the gaps between recoveries in the absence of metal ions and in the presence of Ca^{2+} , Mg^{2+} and Sr^{2+} were 8.39%, 18.92% and 12.15%, while at $\text{pH} = 11$, the gaps increased to 23.00%, 28.79% and 24.85%, respectively. However, Al^{3+} and Fe^{3+} exerted stronger depression at low pH ; for example, at $\text{pH} = 6.5$ the gaps between recoveries in the absence of metal ions and in the presence of Al^{3+} and Fe^{3+} were 35.99% and 51.60%, while at $\text{pH} = 11$, the gaps decreased to 15.35% and 26.86%, respectively.

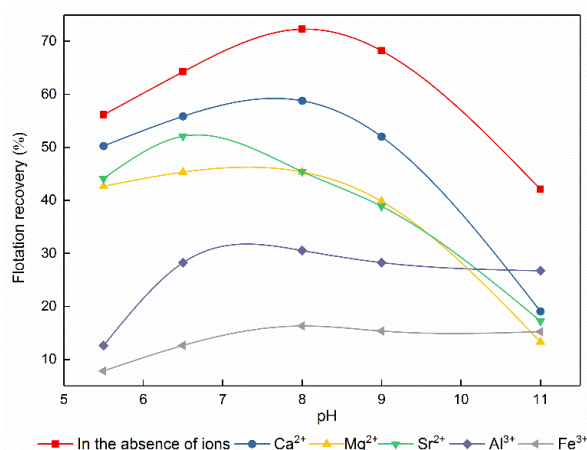


Figure 5. Influence of pH on bastnaesite flotation (Metal ion: $1 \times 10^{-4} \text{ mol/dm}^3$, salicylhydroxamic acid (SHA): $5 \times 10^{-4} \text{ mol/dm}^3$).

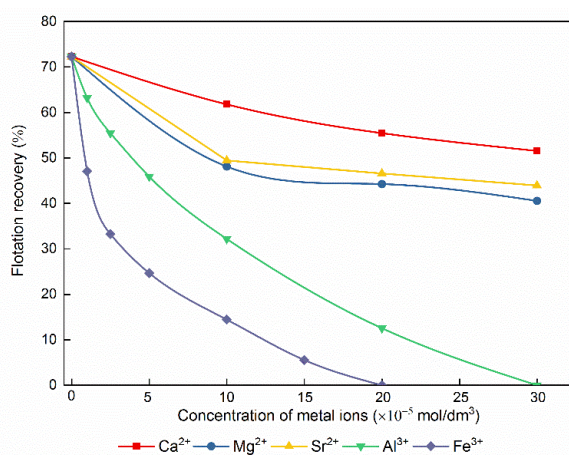


Figure 6. Influence of ion concentration on bastnaesite flotation (SHA: $5 \times 10^{-4} \text{ mol/dm}^3$, $\text{pH} = 8$).

3.4. The Influence Mechanism of Metal Ions on Bastnaesite Flotation

3.4.1. Induction Time Measurements

The attachment of mineral particles to air bubbles is the most fundamental requirement for successful flotation. This process includes film thinning and liquid drainage during the formation of a stable particle-bubble bond. The minimum time required to form an attachment between a particle and a bubble is defined as induction time [29]. Induction time is closely related with the floatability of mineral particles, when the particle-bubble contact time is longer than the induction time the bubble-particle attachment occur. As shown in Figure 7a, particles could not attach to air bubbles in 30 s, indicating the wetting film on bastnaesite surfaces was very stable and hence the inherent floatability of bastnaesite was poor. After SHA adsorption, the induction time decreased to 1.1 s (Figure 7b), suggesting that SHA adsorption improved hydrophobicity of bastnaesite and made the wetting film much more unstable; the wetting film became easy to break during the contact process. The presence of Ca^{2+} , Mg^{2+} and Sr^{2+} increased induction time slightly (Figure 7c–e); while in the presence of Al^{3+} increased the induction time remarkably to 17.5 s (Figure 7f) and in the presence of Fe^{3+} , the attachment between particles and air bubble could not occur in 30 s (Figure 7g), the influence of metal ions on induction time was in accordance with flotation results. The increase of induction time in the presence of metal ions with SHA as collector suggests that the presence of metal ions decreased SHA adsorption, leading to the surface wetting film becoming more stable, and hence decreased bastnaesite floatability.

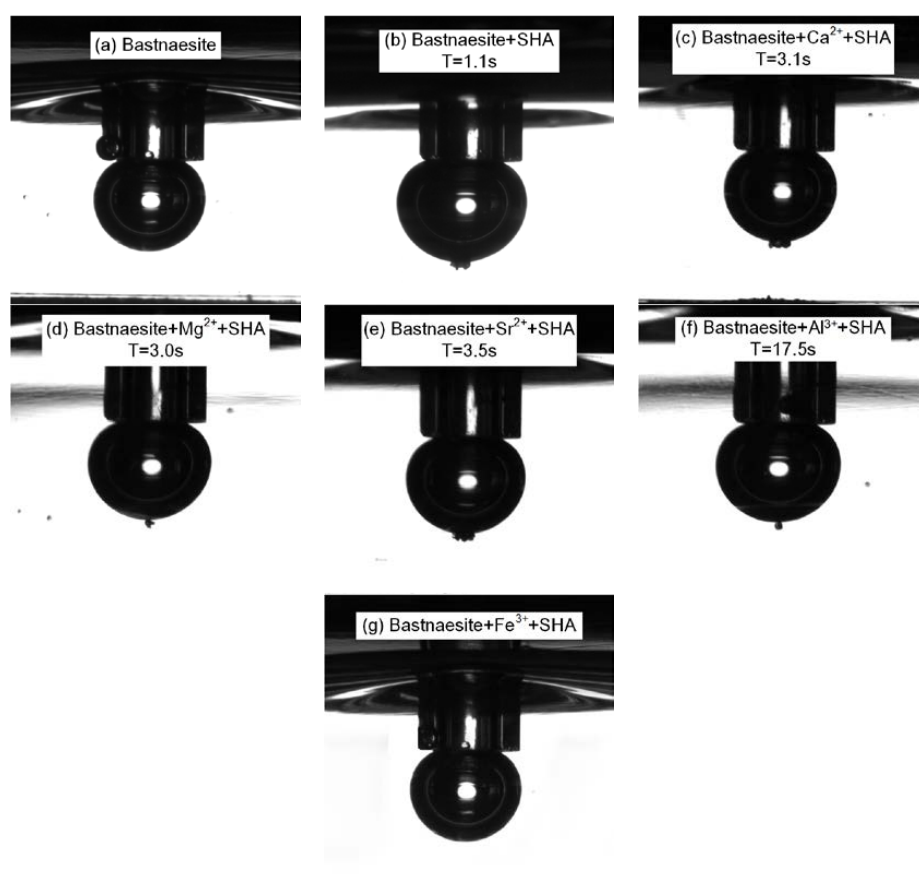


Figure 7. Influence of metal ions on induction time of (a) Bastnaesite; (b) Bastnaesite + SHA; (c) Bastnaesite + Ca^{2+} + SHA; (d) Bastnaesite + Mg^{2+} + SHA; (e) Bastnaesite + Sr^{2+} + SHA; (f) Bastnaesite + Al^{3+} + SHA; (g) Bastnaesite + Fe^{3+} + SHA (pH = 8, metal ions: 1×10^{-4} mol/dm³, SHA: 5×10^{-4} mol/dm³).

3.4.2. The Adsorption of Metal Ions on Bastnaesite Surfaces

As shown in Figure 8, the saturated adsorption capacity of Fe^{3+} was much higher than that of other metal ions, reaching 0.32 mg/g at 20 °C, followed by Al^{3+} , reaching a saturated adsorption capacity of 0.18 mg/g, while the adsorption capacity of Ca^{2+} , Mg^{2+} and Sr^{2+} was much lower in comparison with that of Al^{3+} and Fe^{3+} . The results of adsorption capacity experiments were consistent with flotation and induction time measurement results, indicating the influence of metal ions on bastnaesite flotation was related to metal ion adsorption on bastnaesite surfaces. It should be noted that Ca^{2+} and Mg^{2+} could hardly be adsorbed on bastnaesite surfaces; however, they still exerted slight depression effects, and this may be attributed to the consumption of collector in solution by metal ions.

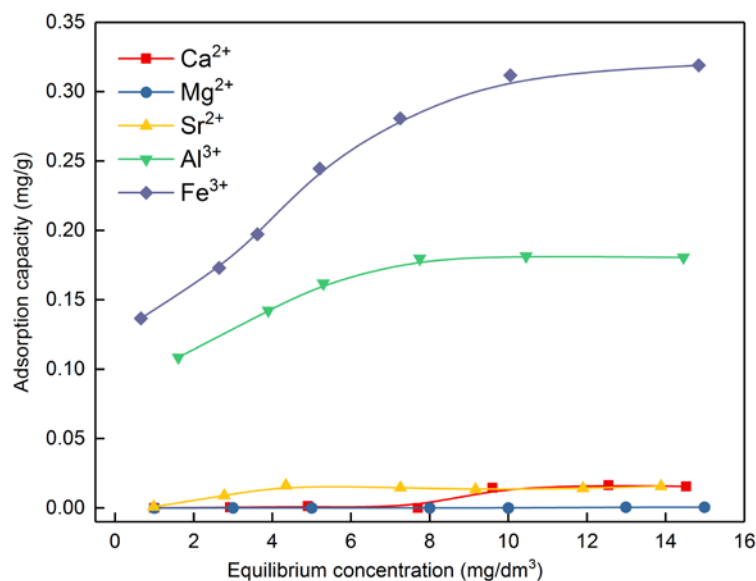


Figure 8. Adsorption capacity of metal ions on bastnaesite surfaces (pH = 8, 20 °C).

3.4.3. Effect of Metal Ions on Zeta Potential of Bastnaesite

The zeta potential is normally obtained in flotation to determine the electro-kinetic changes on mineral surfaces conditioned in aqueous system with flotation reagents. Figure 9 shows the zeta potential of bastnaesite surfaces treated and not treated with metal ions as a function of pH in the absence and presence of SHA. According to Figure 9, changing the pH from 5 to 11 decreased the zeta potential of bastnaesite, and the iso-electric point (IEP) was located at approximately pH 9.60. The bastnaesite surface was positively charged at pH < 9.60 and negatively charged at pH > 9.60. The primary functional groups on bastnaesite surfaces are $\equiv\text{F}-\text{Ce}-\text{OH}^0$ and $\equiv\text{CO}_3\text{H}^0$ [30], the bastnaesite surface is charged due to their different adsorption capacities for H^+ and OH^- . Therefore, the zeta potential was influenced primarily by pH. After SHA was added to the suspension, the zeta potential decreased for the entire pH range, and the IEP reduced from 9.60 to 8.05, indicating chemisorption of SHA ions on bastnaesite surfaces. The effect of metal ions on the zeta potential of bastnaesite in the presence of SHA is demonstrated in Figure 9. It can be seen that all of the five metal ions added prior to SHA decreased the negativity of the zeta potential of bastnaesite in the presence of SHA relative to that in the absence of metal ions. This finding suggests lower adsorption density of SHA on the mineral surface when bastnaesite was pretreated with metal ions, this phenomenon may be attributed to the hindering of active sites for SHA adsorption when bastnaesite was pretreated by metal ions before SHA addition.

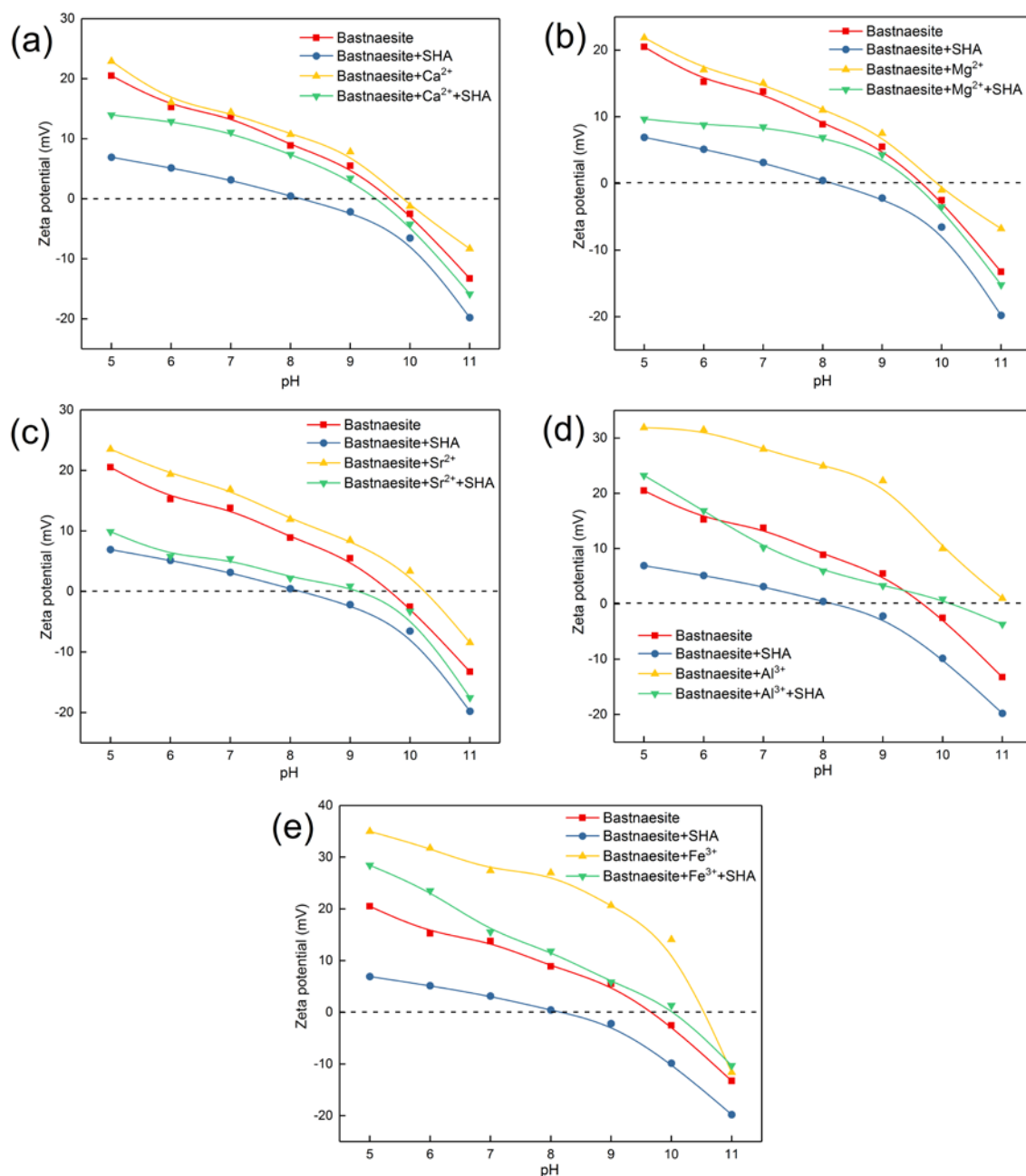


Figure 9. Zeta potential of bastnaesite treated and not treated with (a) Ca²⁺; (b) Mg²⁺; (c) Sr²⁺; (d) Al³⁺; (e) Fe³⁺ as a function of pH in the absence and presence of pH.

To further investigate the contribution of metal ions to the collector adsorption onto mineral surface, the determination of zeta potential of bastnaesite conditioned with metal ions as a function of pH was conducted (Figure 9). It can be seen that the addition of metal ions shifted the zeta potential of bastnaesite positively across the entire pH range, indicating that the bastnaesite surface was occupied by metal ions. It was consistent with the results of induction time measurements and flotation experiments that Fe³⁺ and Al³⁺ yielded a much more pronounced effect than Ca²⁺, Mg²⁺ and Sr²⁺. The diagrams of metal ion-species distribution as a function of pH based on solution chemistry calculation by Visual MINTEQ 3 Program were plotted in Figure 10. As it shows, the metal ions hydrolyzed and hydroxy complex(es) formed in aqueous solution. At a certain concentration of ions, the composition of ion species and there concentrations were pH-dependent.

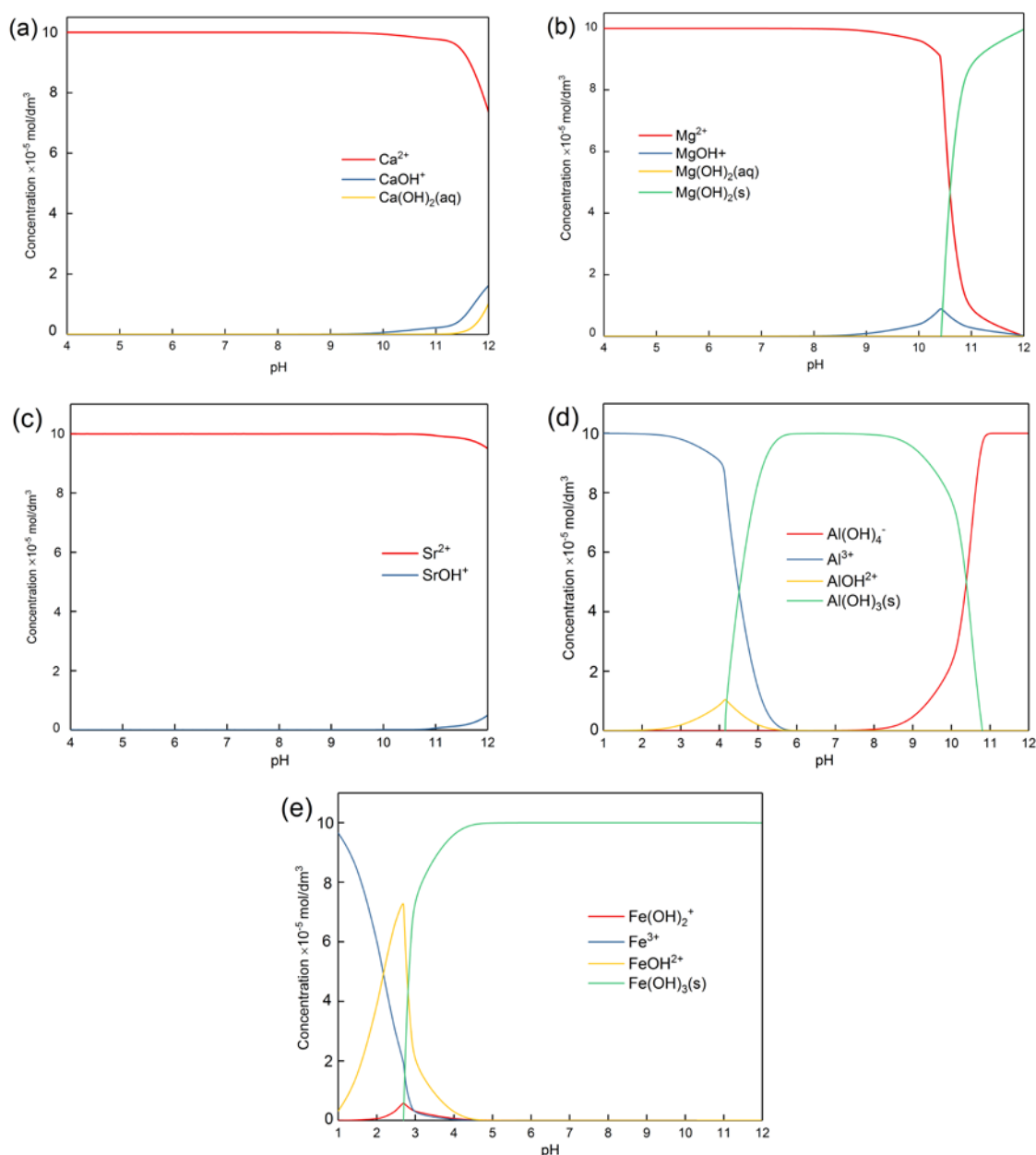


Figure 10. Distribution diagrams of (a) Ca^{2+} ; (b) Mg^{2+} ; (c) Sr^{2+} ; (d) Al^{3+} ; (e) Fe^{3+} as a function of pH ($1 \times 10^{-4} \text{ mol/dm}^3$).

It can be seen from Figure 9a–c that the zeta potential of bastnaesite shifted more positively at $\text{pH} > 9.6$ when treated with Ca^{2+} , Mg^{2+} and Sr^{2+} , while at $\text{pH} < 9.6$, the effects of these ions were limited. At $\text{pH} < 9.6$, the electrostatic repulsion between metal ions and bastnaesite surfaces leads to low adsorption capacities and limited influence on flotation. At $\text{pH} > 9.6$, the bastnaesite surfaces were negatively charged and hence increased the adsorption of cationic metal ion species. Meanwhile, the proportion of hydroxo complexes (CaOH^+ , MgOH^+ , $\text{Mg}(\text{OH})_2(\text{aq})$, SrOH^+) relative to the total metal ion content increased with pH (Figure 10a–c); they may complex with bastnaesite surfaces and hence further increased the adsorption of metal ions. Therefore, at high pH condition, Ca^{2+} , Mg^{2+} and Sr^{2+} exerts stronger depression than at low pH condition due to higher adsorption density. The hydrolyzation of Mg^{2+} is stronger than that of Ca^{2+} and Sr^{2+} , at pH 11 magnesium ions mainly presented as $\text{Mg}(\text{OH})_2(\text{aq})$ (Figure 10b); therefore, the effect of Mg^{2+} on zeta potential was more pronounced, leading to stronger depression on flotation [19,31]. The hydrolyzation of Sr^{2+}

is the weakest among Ca^{2+} , Mg^{2+} and Sr^{2+} , even at pH 11 the percentage of SrOH^+ relative to the total strontium content was still very low (Figure 10c). Sr^{2+} has been reported mainly adsorbed on bastnaesite surfaces by the complexation between free Sr^{2+} ions and surface $-\text{Ce}-\text{OH}$ groups [30]. Therefore the effect of pH on zeta potential of bastnaesite treated with Sr^{2+} was lower than that treated with Ca^{2+} and Mg^{2+} .

Al^{3+} and Fe^{3+} yielded a much more pronounced effect on zeta potential of bastnaesite than Ca^{2+} , Mg^{2+} and Sr^{2+} , this may be due to higher valence and higher adsorption capacities of Al^{3+} and Fe^{3+} . $\text{Fe}_2(\text{CO}_3)_3$ and $\text{Al}_2(\text{CO}_3)_3$ has been proven unstable in aqueous solution; therefore, aluminium ion species and ferric ion species could hardly be adsorbed by complexing with exposed CO_3^{2-} sites on bastnaesite surfaces [32,33]. As shown in Figure 10d,e, aluminium ions and ferric ions mainly presented in the form of hydroxo complexes in the flotation pH range, indicating they may be adsorbed by surface precipitation and complexation between bastnaesite surfaces and hydroxo complexes of metal ions [34]. On the one hand, the adsorption of aluminium ions and ferric ions hindered collector adsorption [18,35], leading Fe^{3+} to exert stronger depression than Al^{3+} due to higher adsorption capacity. On the other hand, the consumption of collector by residual metal ions in solution may further depress bastnaesite flotation [36]. At high pH, the electrostatic repulsion between negative mineral surfaces and negative hydroxo complexes of metal ions may decreased the adsorption of metal ions [37], and part of aluminium ions and ferric ions may have precipitated out from solution by the form of hydroxide [38]; therefore, the depression of Al^{3+} and Fe^{3+} on bastnaesite flotation was decreased.

4. Conclusions

1. The primary metal ions in practical flotation pulp were Ca^{2+} , Mg^{2+} , Sr^{2+} , Fe^{3+} , Na^+ and K^+ . Rare earth metal ions such as Ce^{3+} , La^{3+} and Nd^{3+} had low concentrations of below 0.1 mg/dm^3 .
2. The release of metal ions from calcite, dolomite, fluorite and celestite contributed to the high concentration of alkaline-earth metal ions in bastnaesite flotation pulp, Fe^{3+} could be released from associated iron minerals, while the release of rare earth ions from bastnaesite was negligible. Grinding significantly enhanced the release of metal ions (except rare earth ions) from minerals into pulp.
3. Ca^{2+} , Mg^{2+} , Sr^{2+} , Al^{3+} and Fe^{3+} all depressed bastnaesite flotation, and the order of depression ability was $\text{Fe}^{3+} > \text{Al}^{3+} > \text{Mg}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+}$. The Ca^{2+} , Mg^{2+} and Sr^{2+} exerted stronger depression at high pH while Al^{3+} and Fe^{3+} exerted stronger depression at low pH.
4. The depression of metal ions on bastnaesite flotation was mainly attributed to the adsorption of metal ions on mineral surfaces, which decreased collector adsorption. The species distribution diagrams of metal ions in solution changed along with pH, leading to changes of adsorption and zeta potential on mineral surfaces, and consequently resulting in different influences on bastnaesite flotation.

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