Eliminating the adverse effect of the lime on the gold-bearing pyrrhotite flotation using the isopentyl xanthate as collector at low alkalinity

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Abstract: Flotation optimal conditions and mechanism of regulator lime, isopentyl xanthate and butyl xanthate on pyrrhotite were investigated by flotation test, contact angle, zeta potential and infrared spectroscopic analysis. It is found that there is a certain relationship between the regulator lime and the collector isopentyl xanthate. The results of flotation indicate that lime can indeed inhibit pyrrhotite, and isopentyl xanthate can decrease the depression effect of lime on pyrrhotite in low alkalinity. The results of adsorption mechanism of lime and isopentyl xanthate show that after lime adsorbed on the pyrrhotite surface, Ca^{2+} inhibit the adsorption of collector with the form of $Ca(OH)_2$ precipitates. Compared with butyl xanthate, isopentyl xanthate could reduce the generation of hydrophilic $Ca(OH)_2$ and generate less hydrophilic $CaCO_3$ as well to decrease the negative effect of gold-bearing pyrrhotite flotation depressed by lime.

Keywords: pyrrhotite, flotation, pH regulator, collector

1. Introduction

The pyrite-arsenopyrite-pyrrhotite are the most common gold-bearing sulfide minerals (Dunne, 2005), and the flotation is a favorite method for concentrating gold (Arvidson et al., 2013; Forrest et al., 2001; Yalcin and Kelebek, 2011). Flotation as a physical-chemistry process is a mature technology that has been practiced successfully for more than a century. The physicochemical surface properties of minerals, which have a strongly influence on the effect of flotation, can be changed by reagent selection and flowsheet configuration (Bulatovic, 1997; Xiao et al., 2018a; Xiao et al., 2018b) .

In recent years, the majority studies on gold flotation have mostly focused on pyrite and arsenopyrite, including the mineralogical characteristics, processing flowsheets and application of agents and their interactions (Allan and Woodcock, 2001; Gul et al., 2012; Guo et al., 2016b; Sun et al., 2006). Affected by the electrochemical conditions of the flotation pulp (Buswell et al., 2002; Gu et al., 2010), the surface of pyrite could become hydrophobic because of the oxidation of xanthates to hydrophobic dixanthogen and their adsorption on pyrite surface (Qin et al., 2015). The increasing of pH value would reduce the floatability by affecting the oxidation of xanthate, but this negative effect could be ameliorated by increasing the amount of collector and much stronger collector (Moslemi and Gharabaghi, 2017). The study about pyrrhotite was mostly about how to depress pyrrhotite on the flotation of copper-lead-zinc (Agorhom et al., 2015; Guo et al., 2016a; Guo et al., 2016b) and how to float pyrrhotite from magnetite (Yu et al., 2016). It has been confirmed that the flotation behavior of pyrrhotite is most affected by pulp pH and potential (Sun et al., 2006). The lime, not only plays the role of pH regulator, but also acts as a common inhibitor of pyrrhotite, and when adjusted by lime, the pyrrhotite would be depressed in high alkalinity. However, the flotation behavior of pyrrhotite as a gold-bearing mineral in low alkalinity has been rarely researched. In order to recover the gold present

in pyrrhotite, after balancing the gains and losses of all the parties, most gold concentrators choose the lime as the pH regulator, and a certain relationship between lime and collectors is found.

This paper was based on a certain Nielsen concentrator gravity tailings that gold is mainly existed in pyrrhotite as the micro-grained particles with a grade of 3.50 g/Mg, reclamation of which is of high commercial value, the more and more attention should be given for the recovery of pyrrhotite flotation in order to recover gold as much as possible. This paper aims to optimize the existing pyrrhotite flotation process and explore the flotation behavior and mechanism of pyrrhotite under the condition of low alkalinity with lime as regulator. The flotation behavior of pyrrhotite in lime system was studied by flotation test, contact angle test, zeta potential test and infrared spectroscopy, which provided technology and theoretical basis for economic and reasonable recovery of pyrrhotite as gold-bearing mineral in actual production.

2. Materials and methods

2.1. Materials

In this study, the lime (calcium oxide in terminology) was used as pH regulators; terpenic oil was used as the frother; isopentyl xanthate, butyl xanthate and ammonium dibutyl dithiophosphate (ADD) were used as collectors. And all the tests were conducted at room temperature.

Pure pyrrhotite used in this study was obtained from the iron ore at Dachang town in Guangxi Province, China. The XRD analysis indicates 96.73 wt% pyrrhotite as shown in Fig. 1.

The actual ore used in flotation tests was Nielsen concentrator gravity tailings supplied by a mine in Lingbao, Henan Province, China. The results of elemental composition of the gravity tailings analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Fisher Scientific Inc., Waltham, MA, USA) are given in Table 1, and the chemical composition of the tailings analyzed by process mineralogy are given in Table 2. As can be seen in Tables 1 and 2, main recyclable elements in the ore is Au, pyrrhotite is recovered occur as major minerals. By high magnification microscopy, the gold in the gravity tailings is mainly present in pyrrhotite attached. The pictures were shown in Fig. 2.
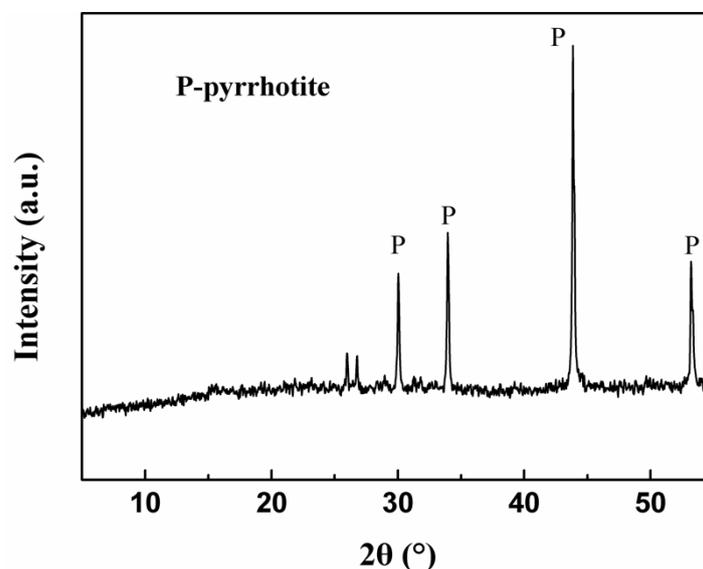

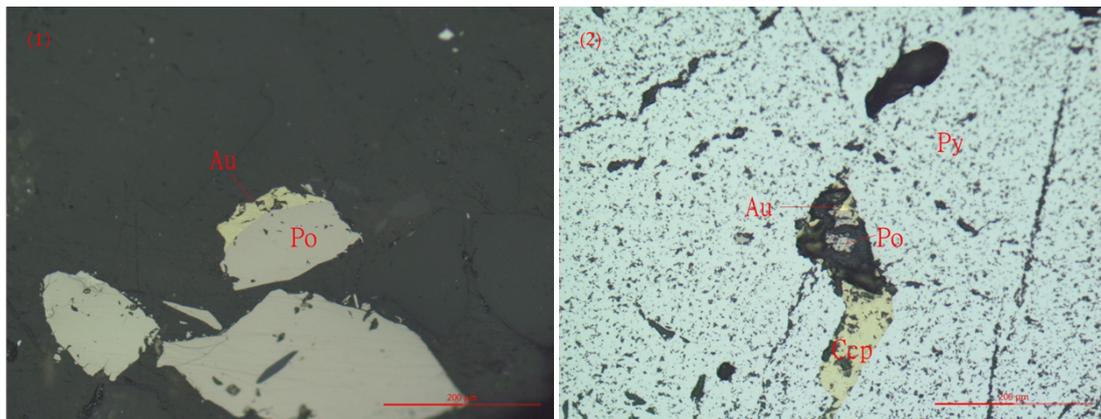Fig. 1. X-ray diffraction (XRD) analysis of the pure pyrrhotite sample

Table 1. The elemental composition of the actual ore (wt %)

Compositions	Au*	Ag*	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	FeO	Mn	MgO
Content	3.50	2.29	60.34	0.34	8.32	3.03	4.62	0.14	1.44
Compositions	**CaO**	**Na$_2$O**	**K$_2$O**	**TC**	**S**	**As**	**Cu**	**Pb**	**Zn**
Content	2.65	4.45	1.50	0.54	4.51	1.43	0.04	0.02	0.02

* The unit of Au and Ag is g/Mg

Table 2. The mineralogical composition of the actual ore (wt%)

Compositions	Electrum	Chalcopyrite	Pyrite	Molybdenite	Hematite
Content	microscale	0.30	2.90	-	-
Compositions	**Pyrrhotite**	**Arsenopyrite**	**Magnetite**	**Limonite**	**Quartz**
Content	3.70	3.10	0.20	-	66.50
Compositions	**Plagioclase**	**Calcite**	**Chlorite**	**Illite**	
Content	4.90	2.90	6.80	7.80	

Po: pyrrhotite, Py: pyrite, Ccp: chalcopyrite, Au: gold

Fig. 2. Gold embedded features of actual ore: (1) Gold intergrowing in pyrrhotite (200X) (2) Pyrrhotite surrounded by pyrite and gold by pyrrhotite

2.2. Methods

2.2.1. Flotation

The flotation test was conducted in a RK / FGC 1L hitch groove flotation cell at a rotating speed of 1700 rpm to recover the main minerals pyrrhotite. In the flotation process, 373 g actual ore was added into the flotation cell after the grinding fineness reaches -0.074 mm accounting for 70%, followed by the addition of pH regulator, collector, and frother. After add the pH regulator, collector, frother and the mineral was conditioned for 2 min, the conditioned slurry was floated for the designed time. The grade of gold in the flotation concentrate is measured by Flame Atomic Absorption Spectrophotometer, and then calculated the recovery of gold.

2.2.2. Contact angle experiment

The wettability of regulator and collector on pyrrhotite were investigated by contact angle measurement and was measured with JY-82 Contact Angle Measuring. The surface of pure pyrrhotite was treated in a system of deionized water and the lime water of pH 8.0 with different types of collectors (6×10^{-4} mole/dm^3), following the volume of 1.0-2.0×10^{-3} cm^3 deionized water was injected into the treated surface pure of pyrrhotite by a micro syringe. The measurements were repeated three times and the average values and standard deviations were reported. Measured the contact angle of the mineral surface in deionized water and obtained an average value. After that, measured the value of the reagents, repeated washing the minerals surface until the contact angle of the mineral surface in the deionized water after washing is within 2 degrees of the initial contact angle error.

2.2.3. Zeta potential experiment

The absorption mechanism of collector on pyrrhotite at the lime condition was investigated by zeta potential and infrared spectroscopy. Zeta potential was measured with a zeta potential analyzer from Micromeritics Instrument Corp (Atlanta, GA, USA). The suspension containing 0.25 g pure pyrrhotite

with a particle size of 0.01 mm or less to 50 cm³ of deionized water at known pH, then conditioned for 15 minutes in different alkalinity with different collector solutions (the concentration of collector was 30 g/dm³). The suspension was then transferred to a sample vessel for the zeta potential measurement at a room temperature of 293.15 K. The measurement was repeated five times and the average zeta potential was reported.

2.2.4. IR spectrum

The Infrared spectroscopy (IR) spectra ranging from 4000 to 400 cm⁻¹ were measured by a NEXUS470 Fourier Transform Infrared Spectrometer at room temperature of 293.15 K. Put 1 g pure pyrrhotite with a particle size below 0.002 mm and 20 cm³ solution with lime into a 50 cm³ beaker, and then 0.2 g collector was added. They were mixed by a thermostatic oscillator for 5 min, and rinsed with deionized water 2 to 3 times and dried vacuum.

3. Results and discussion

3.1. The flotation Tests

3.1.1. Effect of pH

Chose the lime as the pH regulator, the butyl xanthate as the collector at value of 60 g/Mg and the account of frother (terpenic oil) was 20 g/Mg. On the natural condition, the original pH of the pulp was 6.7. The influence of the pH on flotation was studied and the results were shown in Fig. 3.
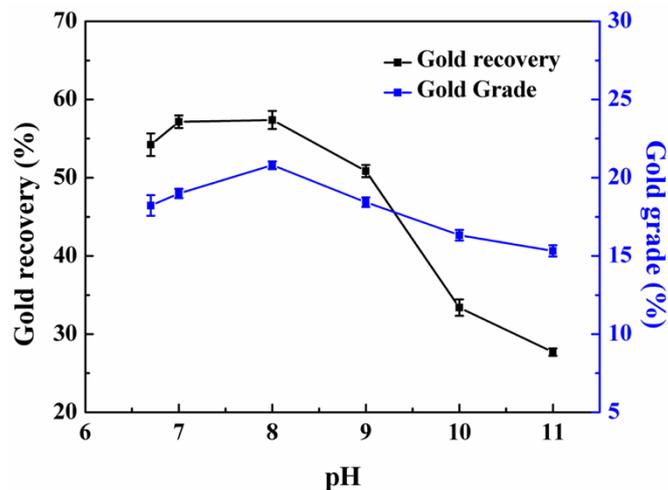

Fig. 3. Effects of pH on flotation index

As can been seen in Fig. 3, when lime was used to adjust the pH, the gold recovery and grade gradually increased as the alkalinity increased to 8.0. As the alkalinity continued to increase, the recovery and grade of gold began to decrease. The grade of gold reached its maximum of 20.80 g/Mg at pH=8.0, and the recovery rate of gold obtained under the conditions of pH=7.0 and pH=8.0 are not much different. From the experimental result, lime can inhibit the flotation of pyrrhotite, but the floatability of pyrrhotite still has a better state under low alkalinity. In addition, the equipment would be corroded at the acidic conditions. Considering that the xanthate collectors are suitable for use under the alkaline condition and the need to adjust the pulp pH to about 10.5 during subsequent cyanide leaching in the actual production situation, and then chose pH=8.0 as the pH value of slurry.

3.1.2. Effect of collector

At a collector dosage of 60 g/Mg and the combined collector (m (butyl xanthate): m (ADD) = 2: 1), the pH value was adjusted at 8.0 by using lime. The effect of different collectors was shown in Table 3. The recovery of gold in isopentyl xanthate condition was obviously higher than that in butyl xanthate and that in combined collector. When the isopentyl xanthate was used as a collector, the recovery of gold

was 7.07% higher than that when butyl xanthate was used, even using the ADD and butyl xanthate as a combined collector can increase the recovery of gold by 5.25% through synergetic effect, the recovery of gold was still at a disadvantage compared with the single collector use of isopentyl xanthate. It was shown that isopentyl xanthate could improve the flotation effect in lime condition about this ore.

Table 3. Effects of collectors on flotation index with different pH regulators

Species of collector	butyl xanthate	isopentyl xanthate	butyl xanthate+ ADD
Grade/(g/Mg)	20.80	20.60	18.10
Recovery/%	57.38	64.45	62.63

3.1.3. Closed-circuit floatation test

The flowsheet of closed-circuit flotation and results were shown in Fig. 4. and Table 4, respectively. The gold recovery of 80.94 % and the concentrate gold grade of 29.72 % could be obtained when only isopentyl xanthate was used as a collector.

Fig. 4. Flowsheet of flotation closed-circuit test

Table 4. Result of flotation closed-circuit test

Production	Concentrate	Tailings
Yield / (%)	9.53	90.47
Grade / (g/Mg)	29.72	0.74
Recovery / (%)	80.94	19.06

3.2. Absorption mechanism of reagent on pyrrhotite

3.2.1. Contact angle measurements

The result was shown in Fig. 5 that the collector and regulator could change the wettability of the minerals (Li and Gao, 2018). Compared with the deionized water system, the contact angle of the pyrrhotite was lower after adding the lime, which is due to the alkalinity of the pulp is increased and

formed a hydroxyl hydrophilic membrane on the minerals surface. In all deionized water system, the type of collector has little effect on contact angle. While in lime system, the contact angle will change to a greater extent by changing the type of collector. Isopentyl xanthate can increase the contact angle and hydrophobicity of minerals more obviously than butyl xanthate. As noted, adding xanthate collector can significantly improve the surface of pyrrhotite inhibited by lime.
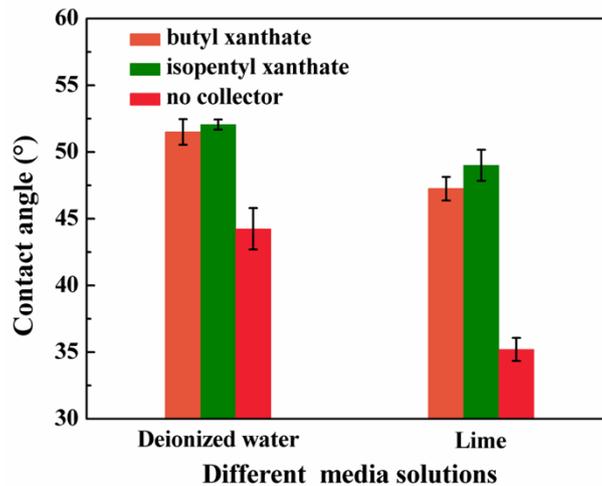

Fig. 5. Measurement of contact angle different medium solutions

3.2.2. Zeta potential measurements

The zeta potential of pure pyrrhotite in lime as a function of pH value was presented in Fig. 6. It can be seen from Fig. 6 that zeta potential of pyrrhotite is negative in all range of pH measurements. The results indicated that, the original pH and zeta potential of pyrrhotite in deionized water was 6.50 and -22.788 mV, in butyl xanthate system was 6.80 and -24.579 mV, in isopentyl xanthate system was 6.50 and -28.276 mV. In the pH range of 7.0-9.0 in low alkalinity, the zeta potential on pyrrhotite surface was moved in the negative direction which pH value adjusted by pH buffer, which meant that pyrrhotite surface could chemically absorb some xanthate anions and exist stably. The potential began to move positively at pH>10.0, meaning that under high alkalinity, the floatability of pyrrhotite was strongly suppressed. When adjusting the pulp with lime, the zeta potential of the three solutions is constantly shifting positively as the pH increases, some positive charges are adsorbed on the minerals surface and the solution system cannot exist stably. The degree of positive shift of the zeta potential can be slightly reduced by adding the collector. Compared with adding lime only, the zeta potential to shift negatively after adding the collector, which meant that the xanthate anions chemisorb on pyrrhotite surface. At low alkalinity, isopentyl xanthate is more effective than butyl xanthate in controlling the surface poten-
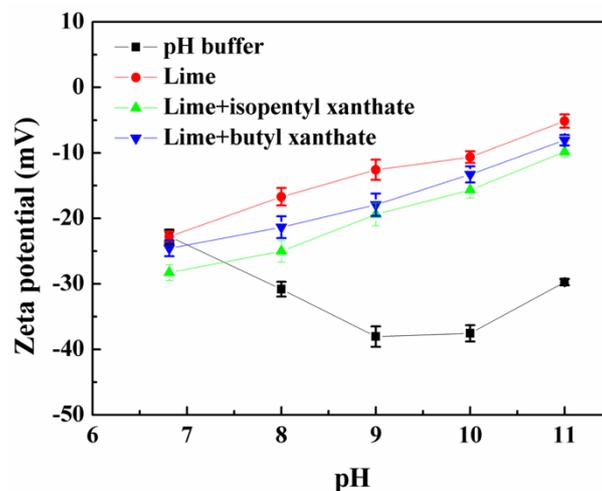

Fig. 6. Zeta potential of pyrrhotite in different conditions of reagents

tial of the mineral move in the positive direction, and it is not applicable at high alkalinity.

3.2.3. Infrared spectroscopy

The IR spectra were shown in Fig. 7. It can be seen that the characteristic peak at about 1091 cm^{-1}~1093 cm^{-1} were assigned to SO_4^{2-} (Wang et al., 2016) in spectra 1#, 2#, 3#, which was caused by the oxidation of the pyrrhotite surface to sulfate formation. The characteristic peak at 3440 ~ 3443 cm^{-1} and 1627 ~ 1636 cm^{-1} were assigned to OH^- in these four spectra (Zhang et al., 2013). 1# spectrum had characteristic absorption peak of OH^-, which was caused by adsorption of OH^- from distilled water in pyrrhotite surface. Compared with spectrum 1#, the intensity of characteristic peak of OH^- at spectrum 2# in lime condition was almost the same, but the characteristic peaks of OH^- at spectra 3# and 4# decreased after reacting with collector, and spectrum 4# decreased even more, which showed that pyrrhotite surface could generate hydrophilic substance $Ca(OH)_2$ in lime condition (Zhang et al., 2013), that the increase of xanthate could decrease the generation of $Ca(OH)_2$, and that the negative effect of lime under the condition of isopentyl xanthate was smaller than that of butyl xanthate.

The peaks at 1430 cm^{-1}、1423 cm^{-1}、1425 cm^{-1} and the peaks at 876 cm^{-1}、875 cm^{-1} were assigned to stretching vibration of CO_3^{2-} (Gao et al., 2017). The intensity of the characteristic peak of CO_3^{2-} at spectrum 2# was comparatively weaker, which probably indicated the combination of lime and CO_2 in the air could generate a hydrophilic substance $CaCO_3$ (Gao et al., 2017). The intensity of characteristic peak of CO_3^{2-} at spectra 3# and 4# were stronger than spectrum 2# after reacting with collectors, for xanthate could be oxidized into dixanthogen in solution, and the dithiocarbonate of dixanthogen would hydrolyze into CO_3^{2-}、HCO_3^-, etc., and when these ions reacted with Ca^{2+} in lime, they would generate $CaCO_3$, which would prevent mineral flotation. The larger the molecular weighed and the more stable xanthate was, the more difficult it would be to hydrolyze (Moncayo-Riascos and Hoyos, 2017). At isopentyl xanthate system, compared with butyl xanthate, the intensity of CO_3^{2-} was weaker and the adsorbing of CO_3^{2-} at pyrrhotite surface was less, meaning that the generation of $CaCO_3$ in isopentyl xanthate system was less than that in butyl xanthate. The adsorbing of $CaCO_3$ could lead to pyrrhotite surface hydrophilic. As a result, it was very difficult to adsorb collector on the mineral surface. It was inferred that isopentyl xanthate could improve the flotation effect of gold-bearing pyrrhotite because of generating less $CaCO_3$.
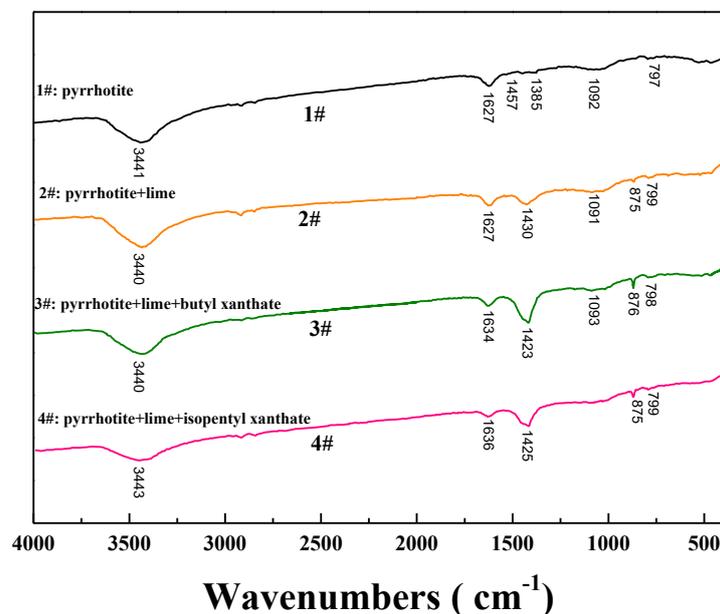

Fig. 7. IR spectra of pyrrhotite with collectors

To sum up, it can be seen from Fig. 8 that under low alkalinity conditions, the inhibition of lime on pyrrhotite is mainly manifested in the formation of hydrophilic substance $Ca(OH)_2$ on the mineral surface, which affects the flotation effect of pyrrhotite. The addition of xanthate collectors can

significantly reduce the formation of $Ca(OH)_2$, but the corresponding oxidative hydrolysis of xanthate will lead to the formation of hydrophilic substance $CaCO_3$. Compared with butyl xanthate, isopentyl xanthate can reduce the formation of $Ca(OH)_2$ more, and the amount of hydrophilic substance $CaCO_3$ produced by hydrolysis is relatively less, which indicates that isopentyl xanthate can improve the inhibition of lime on pyrrhotite.
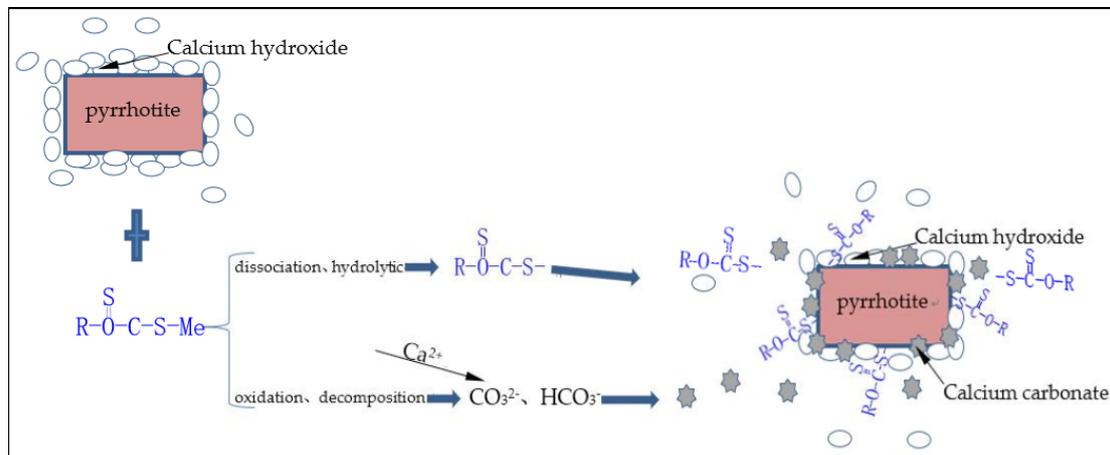

Fig. 8. The reaction process between pyrrhotite and collector

4. Conclusions

Through the flotation test, contact angle test, zeta potential test and infrared spectroscopy test, some conclusions about the relationships between pyrrhotite, lime and xanthate collectors can be drawn as follows:

(1) For gold-bearing mineral pyrrhotite, using isopentyl xanthate as a collector is better and the gold recovery is 7.07% and 1.82% higher than that of butyl xanthate and that of combined collector, respectively.

(2) Using lime as the pH regulator can indeed inhibit the flotation of pyrrhotite, but the floatability of pyrrhotite can be improved in neutral and low alkalinity by using xanthate collectors, and isopentyl xanthate is superior to butyl xanthate.

(3) Lime as pH regulator can affect the pyrrhotite by the generation of hydrophilic $Ca(OH)_2$ on the surface of pyrrhotite, which can cause negative effects on flotation. Worsely, the negative effects will increase with the rise of pH value. While isopentyl xanthate can improve the effect of pyrrhotite flotation on lime condition by reducing the generation of hydrophilic $Ca(OH)_2$ and generating less hydrophilic $CaCO_3$.

Acknowledgments

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