[Article ID] 1003 - 6326(2000)06 - 0798 - 06

Surface chemistry of activation of lime-depressed pyrite in flotation①

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[Abstract] The depression of pyrite by lime is attributed to the surface formation of $Ca(OH)_2$, $CaSO_4$ and $Fe(OH)_3$ as determined by XPS analysis. Xanthate flotation tests show that oxalic acid and other organic acids, as well as sulphuric acid and other inorganic acids and their salts can restore xanthate flotation of pyrite after depression by lime. In terms of XPS analysis, solution chemistry calculations and electrochemical measurements, it is evident that these chemicals act as activators to reduce pulp pH, prevent further oxidation of pyrite, and dissolve surface calcium or iron species to create a fresh surface. Activation efficiency was quantitatively discussed based on an activation index related to the polar group functionality of the activators. The results for activation flotation of pyrite are very well explained using the activation index. Oxalic acid which exhibited the greatest activation index can be substituted for sulfuric acid, which may solve potential environmental and maintenance problems associated with calcification/scaling reaction expected with sulfuric acid.

[Key words] pyrite; surface chemistry; activation flotation
[CLC number] TD923; TD952 **[Document code]** A

1 INTRODUCTION

The fundamental behavior of pyrite flotation has been widely investigated. The self-induced flotation of pyrite occurs only in strongly acidic solution[1]. The poor self-induced flotation of pyrite is usually due to its surface oxidation to oxy-sulphur species[1~5]. However, pyrite exhibits good sulphur-induced floatability, when the formation of elemental sulphur is accomplished by oxidation of hydrosulphide ion[4,6,7]. Pyrite also shows good collector-induced floatability[8~11]. The formation of dixanthogen has been considered to be the dominant mechanism for the pyrite-xanthate interaction although there is some evidence to show the ferric-xanthate compounds existed at pyrite surface[8~16]. The depression of pyrite flotation by various depressants and related mechanisms have also been extensively studied[17~21].

However, in the flotation of poly-metallic sulphide minerals, especially complex sulphide ores, the pyrite can only be depressed at very high additions of lime (at > 12), such is the case at the Fankou Mine in China where the pyrite is very floatable. After flotation of galena and sphalerite, the activation and reflotation of pyrite caused a predicament due to the extremely high pH. Sulfuric acid is the main activator for the flotation of lime-depressed pyrite, which causes environmental and calcification problems due to the large additions of sulfuric acid. Although the adsorption reactions of pyrite with collectors such as xanthate and dithiocarbamate and with depressants such as lime and sodium sulphite, have been widely studied, as described above, the surface chemistry of activation flotation of depressed pyrite remains obscure. In this regard, a search for new activators and the analysis of the corresponding surface reaction is justified. In this paper, some organic acids, inorganic acids and their salts have been tested as the activators for the flotation of lime-depressed pyrite. Surface reaction mechanism and the molecular structure of the activator for the flotation of lime-depressed pyrite are discussed.

2 EXPERIMENTAL

Pyrite, taken from Fankou Lead-Zinc Mine, was ground in a laboratory porcelain mill. The 0.18 ~ 0.063 mm fraction was prepared by wet screening with distilled water using standard sieves. In other experiments, pyrite ore was taken from the flotation tailing at Fankou Mill. The reagents used were analytical grade except for xanthate, which was a commercial grade. Distilled water was used throughout for the flotation of the pyrite mineral.

Flotation tests were conducted in a micro flotation cell with a volume of 100 mL. Prior to flotation, 2 g pyrite mineral sample was put in a beaker containing 50 ml distilled water, and placed in an ultrasonic bath in order to clean the pyrite surface. Then the sample was transferred to the flotation cell and conditioned by addition of lime, activator and collector for 8 min, the flotation time was 3 min. Ore experiments

① [Foundation item] Project (59925412) supported by the National Science Fund for Distinguished Young Scholars of China
[Received date] 2000 - 02 - 25; [Accepted date] 2000 - 04 - 27

were conducted in a 1.5 L XFD flotation cell.

Voltammograms were measured by PARC Model 273 potentiostat/galvanistat and a conventional three-electrode system. The working electrode was made from a pyrite crystal. A saturated calomel electrode was used as the reference electrode. The potentials are expressed on the standard hydrogen scale. An XPS system Model Microlab MKH was used for surface analysis.

3 RESULTS AND DISCUSSION

3.1 XPS analysis of pyrite surface at high pH as established with lime

The extended Ca XPS spectrum of the pyrite surface exposed to high lime concentration of 320 mg/L is shown in Fig.1. Usually, chemical shifts of the peak position are observed resulting from changes in the structure and oxidation state of the surface compounds. It can be seen from Fig.1 that the formation of $Ca(OH)_2$ and $CaSO_4$ takes place at the pyrite surface because of the high pH and the oxidizing atmosphere. At high pH, formation of $Fe(OH)_3$ is also expected[4,21]. These hydrophilic species account for the complete depression of pyrite by lime treatment.

Fig.1 Extended spectrum of XPS for Ca on pyrite surface at high pH as established by high dosage of lime

3.2 Activation flotation of lime-depressed pyrite

A series of organic acids, inorganic acids and their salts have been tested as possible activators for the flotation of lime depressed pyrite. The results are presented in Figs.2, 3 and 4. It can be seen from Fig.2 that oxalic acid is the strongest activator in the organic acid series. When the concentration of oxalic acid is greater than 5×10^{-3} mol/L, the flotation of lime depressed pyrite can be restored and its recovery reaches to 94%. The activating efficiency decreases in the order of: oxalic acid > butyl bicarboxylic acid > propionic acid > acetic acid > poly amino phosphonic acid.

For the inorganic acid series, it follows from

Fig.2 Curves of recovery of lime-depressed pyrite activated by organic acids vs concentration of activators
($\rho(CaO) = 320$ mg/L; $c(BuX) = 10^{-5}$ mol/L)

Fig.3 Curves of recovery of lime-depressed pyrite activated by inorganic acids vs concentration of activators
($\rho(CaO) = 320$ mg/L; $c(BuX) = 10^{-5}$ mol/L)

Fig.3 that sulfuric acid is the strongest activator. The activation flotation of lime depressed pyrite can reach to 80% with 5×10^{-3} mol/L. The activating efficiency decreases in the order of: sulfuric acid > poly-phosphoric acid > phosphoric acid > carbonic acid > hydrochloric acid.

At a high dosage, phosphoric acid and carbonic acid also exhibit good activation ability.

Fig.4 shows that the corresponding salts are not as effective activators as the acids except ammonium oxalate which exhibits better activation action at a high dosage.

According to the results above, the activating efficiency of oxalic acid and sulphuric acid on the lime-depressed pyrite ore (flotation tailing from the Fankou Pb-Zn circuit) has been tested. The results

Fig.4 Curves of recovery of lime-depressed pyrite activated by salts vs concentration of activators (ρ(CaO) = 320 mg/L; c(BuX) = 10^{-5} mol/L)

are compared in Table 1. It can be seen that both oxalic acid and sulphuric acid can be used as effective activators for the flotation of lime-depressed pyrite. A pyrite concentrate with a high sulphur grade and recovery can be obtained. Table 1 also shows that the dosage of oxalic acid is half that of sulphuric acid, which suggests that organic acids compete with sulphuric acid and reduce the environmental impact as well as calcification of pipelines.

3.3 Effect of activator acidity on flotation of lime-depressed pyrite

The results in Figs.2 ~ 4 also reveal the following activation orders on lime-depressed pyrite at a 10^{-2} mol/L concentration of activators: $H_2SO_4 > FeSO_4 > (NH_4)_2SO_4$; $H_2C_2O_4 > (NH_4)C_2O_4$; $H_2CO_3 > Na_2CO_3$.

These results show that the greater the acidity of the activator containing the same compelling group, the greater the activating action. Thus it is expected that the best activator should have a pK_a value as low as possible. Acidic activators can remove the hydroxides from the pyrite surface, and in effect, clean the surface. However, the activation phenomenon can not be simply attributed to the decrease in pulp pH because the strong acid—hydrochloric acid does not exhibit a good activating efficiency. The activation efficiency of moderately strong acids such as oxalic acid is better than that of sulfuric acid and much better than that of hydrochloric acid at the same dosage. And even the activation efficiency of weak acids such as phosphoric acid at high dosage is much better than that of hydrochloric acid. Therefore, factors other than activator acidity must be considered in the activation of lime depressed pyrite.

3.4 Solution chemistry studies

Under certain conditions, oxalic acid (let L^{2-} represent the oxalate anion) can form soluble complexes with calcium and iron ions[22]

$$Fe^{3+} + L^{2-} = FeL^{+} \qquad K_1 = 10^{7.56} \tag{1}$$

$$Fe^{3+} + 2L^{2-} = FeL_2^{-} \qquad K_2 = 10^{13.64} \tag{2}$$

$$Fe^{3+} + 3L^{2-} = FeL_3^{3-} \qquad K_3 = 10^{18.49} \tag{3}$$

$$Me^{2+} + L^{2-} = MeL$$

$$\beta_1: Ca^{2+}\ 10^{1.6};\ Fe^{2+}\ 10^{3.05} \tag{4}$$

$$Me^{2+} + 2L^{2-} = MeL_2^{2-}$$

$$\beta_2: Ca^{2+}\ 10^{2.69};\ Fe^{2+}\ 10^{5.15} \tag{5}$$

Let $[Fe^{3+}]$ express the total concentration of species containing Fe^{3+}, then

$$[Fe^{3+}] = [Fe^{3+}] + [FeL^{+}] + [FeL_2^{-}] + [FeL_3^{3-}] \tag{6}$$

Let Φ_0, Φ_1, Φ_2 and Φ_3 represent the percentages of various complexing species Fe^{3+}, FeL^{+}, FeL_2^{-} and FeL_3^{3-}, then

$$\Phi_0 = \frac{[Fe^{3+}]}{[Fe^{3+}]_T} = \frac{1}{1 + K_1[L^{2-}] + K_2[L^{2-}]^2 + K_3[L^{2-}]^3} \tag{7}$$

$$\Phi_1 = K_1[L^{2-}]\Phi_0 \tag{8}$$

$$\Phi_2 = K_2[L^{2-}]^2\Phi_0 \tag{9}$$

$$\Phi_3 = K_3[L^{2-}]^3\Phi_0 \tag{10}$$

If c_L represents the total concentration of oxalate anion, then

$$[L^{2-}] = \frac{c_L}{\alpha_L} \tag{11}$$

$$\alpha_L = 1 + \beta_1^H[H^+] + \beta_2^H[H^+]^2$$

$$\beta_1^H = 10^{4.27},\ \beta_2^H = 10^{5.52} \tag{12}$$

Table 1 Results of activation flotation of lime-depressed pyrite ore from tailing of flotation of Pb-Zn sulphide ores

Experimental	Product	Yield/ %	Grade/ %	Recovery/ %	pH
Oxalic acid 8 kg/t; Ethyl xanthate 220 g/t; Pine oil 130 g/t	S concentrate	52.23	48.92	94.84	7.8
	S tailing	47.77	2.91	5.16	
	S feed ore	100.00	26.94	100.00	
Sulphuric acid 16 kg/t; Ethyl xanthate 220 g/t; Pine oil 130 g/t	S concentrate	46.88	50.67	93.74	7.2
	S tailing	53.12	3.00	6.26	
	S feed ore	100.00	25.34	100.00	

where α_L is the coefficient for the protonation of oxalate.

The percentage distribution of various complexes in such systems can be calculated using the equations above and the results are presented in Fig.5. It may be seen that in the presence of oxalic acid, the dominant ferric complex is even at lower dosage; The dominant complexes of Fe^{2+}, FeL and FeL_2^{2-}, respectively, at concentration of oxalate greater than 10^{-3} mol/L and 10^{-2} mol/L. The formation of CaL occurs only at a concentration of oxalate greater than 10^{-2} mol/L.

Similarly, for the system of iron/calcium/phosphate, the percentage distribution of various complexes can also be calculated using solution equilibrium calculations as shown in Fig.6. It follows that depending on solution pH, the dominant complexes is $CaPO_4^-$ at pH 10, whereas $CaHPO_4$ (aq) and $CaH_2PO_4^+$ are dominant at pH 8.

Fig.5 Distribution of complexing species formed between oxalate and metal ions vs concentration of oxalate

Fig.6 Distribution of complexing species formed between phosphate and calcium ions vs concentration of phosphate

The soluble complexes formed by activators will desorb cation from the lime depressed pyrite surface, which will expose a fresh pyrite surface and activate pyrite flotation. Therefore, the moderately strong acids such as oxalic acid and phosphoric acid exhibit a strong activation action on lime-depressed pyrite because of their ability to decrease pulp pH and to form soluble complexes with hydrated surface cations.

3.5 Bonding of activator polar group with surface cation

In order to form stable complexes with calcium and iron ions, the activator must have a strong affinity for the cations. The bonding strength can be determined by the group electronegativity as[23]

$$x_g = 0.31\left(\frac{n^* + 1}{r}\right) + 0.5 \tag{13}$$

$$n^* = (N - P) + \sum 2m\frac{x_A}{x_A + x_B} + \sum s\left(\frac{x_A - x_B}{x_A + x_B}\right) + \sum \frac{2m_i + s_i}{a_i}\left(\frac{x_{i+1} - x_i}{x_{i+1} + x_i}\right) \tag{14}$$

where n^* is the effective valence electron numbers; r is the covalent radius of the bonding atom; N is the valent electron numbers of bonding; P is the electron numbers of bonding atom bonded by neighboring atom B; x is electronegativity of element; I is the order number of the group; m is the number of electron pairs for the bond between A and B; S is the number of electron pairs unbonded between A and B; a_i is the separated constant (usually taken as 2.7). The x_g value reflects the bonding ability of the activator with a particular cation. A better activator should have a greater x_g values for some activators are calculated and given in Table 2. Also shown in Table 2 are the pK_a values for the activators of interest. It can be seen from Table 2 that the activating ability is increased in the order of increase of x_g values, and of decrease of pK_a values.

Table 2 pK_a, x_g and pK_{sp} values of calcium salts of activators and their activity index A_i

Activator	x_g	pK_a[20]	A_i
$H_2C_2O_4$	3.74	1.27	2.94
H_2SO_4	3.69	1.9	1.94
$(HPO_4)_n$	3.6	1.94	1.86
H_3PO_4	3.59	2.12	1.69
H_2CO_3	3.62	6.39	0.57
HCl	2.69		

Therefore, the efficiency of an activator depends on its acidity which decreases pulp pH, and its bonding ability with cations which form soluble stable complexes with cations at the pyrite surface. In other words, a better activator should have a lower pK_a (stronger acidity) and a greater χ_g value (stronger affinity). A combination of these factors defines the activity index A_i as

$$A_i = \frac{\chi_g}{pK_a} \tag{15}$$

The greater the A_i value, the stronger the activating action of an activator. Table 2 demonstrates that the activating efficiency of activators is in the same order as the A_i value.

3.6 Surface analysis of lime depressed pyrite in presence of activator

Fig.7 shows the XPS spectra of the pyrite surface under different conditions. The characteristic peaks Ca2p, Ca2s and Fe^{3+} disappear by the addition of oxalic acid when compared to spectra in the absence of activator. In the XPS extended spectra for oxygen and carbon(present since the system is open to atmosphere) at the pyrite surface no change was found after the addition of oxalic acid, indicating that no adsorption of oxalate occurred at the pyrite surface. The results in Fig.7 also indicate that the soluble complexes formed by activators with cation hydroxides of $Ca(OH)_2$ and $Fe(OH)_3$ desorb from the pyrite surface.

Fig.7 XPS spectra of lime depressed pyrite in absence and presence of activator
(a) —320 mg/L CaO+10^{-3} mol/L $H_2C_2O_4$;
(b) —320 mg/L CaO

Fig.8 presents the anodic current of the pyrite electrode in different solution. The results show that the potential at which the anodic current begins to rise is greatly increased in the presence of activators, indicating that activators will inhibit the surface oxidation of pyrite due to the high dosage of CaO.

Fig.8 Anodic current of pyrite electrode in different solutions at scanning rate of 20 mV/s
(ρ(CaO) = 320 mg/L)

4 CONCLUSIONS

The flotation of pyrite at high addition of lime is completely depressed due to the formation of $Ca(OH)_2$ and $Fe(OH)_3$ at the pyrite surface. The activators such as oxalic acid and other organic acids, sulphuric acid and other inorganic acids and their salts can restore the flotation of lime depressed pyrite in different extent. The mechanism is attribute to that the activator decreases pulp pH and form the soluble complexes with cation at the pyrite surface, which remove hydroxide and oxide at the surface and expose fresh surface making the lime depressed pyrite flotation restore. A better activator should have pK_a value as low as possible and have stronger affinity with calcium and iron ion to form soluble complexes (a greater χ_g). The activity index A_i of an activator reveals its activating ability. The greater the A_i value, the greater the activating efficiency.

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(Edited by LONG Huai-zhong)