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Structure-activity of chelating depressants for chalcopyrite/pyrite separation: DFT study and flotation experiment

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Abstract: Three types of chelating depressants were studied for chalcopyrite/pyrite separation, including S-S, S-O, and O-O types, via density functional theory calculations and microflotation. The calculation results indicate that the depressant's chelating atoms have large coefficient and great activity according to the molecular frontier orbital (HOMO and LUMO) and the orbital coefficients. For S-S type of depressant, S atom in both keto or enol forms won't affect their HOMO and LUMO patterns and the orbital contributions. For S-O type, the presence of N atom in the ring structure of a molecular will increase the reactivity of O-Cu while weak S-Cu. For O-O type, the electron supply capacity of benzene ring is higher than strain chain, and atom N in strain chain increased their electron supply capacity. The microflotation results basically confirmed the prediction based on the calculation. The simulation results demonstrate that the interaction of a depressant with metals and minerals are affected obviously by the spatial structure and electronic structure of an atom in its molecular.

Keywords: chelating depressants, activity, pyrite, DFT calculations, frontier orbitals

1. Introduction

Pyrite (FeS₂) often associates with chalcopyrite as a common gangue mineral in copper flotation (Fletcher, 2020). In order to obtain a qualified concentrate during chalcopyrite/pyrite separation, depressants are regularly needed to restrain the float of low economic value pyrite. Traditional inorganic depressants, such as cyanide, sulfides, and lime are widely used in industry (Guo, 2016; Zhao, 2015; Cao, 2018; Rinelli, 1973). But there are several drawbacks for using these depressants, for example, cyanide is harmful to the environment, lime using at extremely high alkaline environment also depresses chalcopyrite and associated precious metals, lime requires long conditioning time during flotation and will cause blockage of flotation pipeline. In short, traditional inorganic depressants inevitably causes low selective depression on various sulfide minerals flotation separation.

Organic depressants have become one of the research focus in recent years, owing to their much greater flexibility, biodegradability, excellent selectivity, abundant sources, and potential modificty. Chelating reagents can chelate with metal ions in solution forming insoluble chelate complex. Due to the high selectivity, chelating reagents can be adopted in sewerage treatment and metallic mineral flotation. Various organic chelating reagents have been conducted as the depressant of pyrite and provided valuable results. Previous researches have confirmed that many depressants such as starch, dextrin, carboxymethylcellulose and guar gum, show significant depress effects on pyrite flotation (Filippov, 2013; Valdivieso, 2004; Bogusz, 1997; Liu, 2006; Bicak, 2007; Wang, 2010; Rath, 2000; Zhao, 2017).

In addition to the reagents above, tannic acid, lactic acid and salicylic acid were also found to be effective depressants of pyrite in chalcopyrite/pyrite separation (Han, 2020a; Han, 2020b; Han, 2019). The adsorbed tannic acid, lactic acid or salicylic acid dramatically hindered xanthate's adsorption on pyrite surfaces. X-ray photoelectron spectroscopy measurements and time-of-flight secondary-ion mass spectrometry revealed a strong interaction between the depressants and Fe sites. Moreover, a starch's derivative tricarboxylate sodium starch (TCSS) combined with calcium oxide (CaO) could depress pyrite's flotation greater than that of chalcopyrite at low alkaline pH 9 (Khosro, 2019). The mechanism analysis demonstrated that the dissolved calcium species adsorbed on the pyrite surface in preference to chalcopyrite, which increased its positive charge and promoted TCSS's adsorption. Khosro et al (Khosro, 2019) also found polyglutamic acid (PGA) depressed pyrite's flotation more significantly than chalcopyrite in pH range of 8-12. All of the surface analysis techniques demonstrated that PGA mostly adsorbed on pyrite surface in preference to chalcopyrite, and the prior adsorbed PGA significantly hindered the collector's adsorption on pyrite surface.

Although lots of reagents had been tested for their depression effect during chalcopyrite/pyrite separation, the relationship between the depression performance of the depressants on chalcopyrite and pyrite and their chelating performance and molecular configuration was still not clear. With the development of infrared spectroscopy, XPS spectra, and electron paramagnetic resonance spectroscopy (Leppinen, 1986; Nowak, 1993; Cases, 1991; Vreugdenhil, 1999; Mielczarski, 1996; Laajalehto, 1993), the interaction mechanism and the relationship between depression performance and chelating performance were more clear and understood. For example, the mineral surfaces would form metal-depressant salt during depressant adsorption.

Although chemical equilibriums are usually applied to predict the selected reagent's functionality, this theoretical study may be limited because of the complex system for flotation. Plenty of chelating reagents have been found effective for chalcopyrite/pyrite separation as depressant. Density functional method (DFT) simulation is one of the most widely used methods for a molecule atomic-scale structure investigation in condensed matter physics, computational materials and computational chemistry. In this work, the frontier orbitals of three types of chelating depressants (Table 2) and two minerals (chalcopyrite and pyrite) were studied based on DFT calculations. The interactions of the three types of chelating depressants with Cu and Fe cations were also investigated.

2. Experimental

2.1. Materials and reagents

The samples of chalcopyrite and pyrite used in this paper were obtained from the Yunnan province, China. Lumps of high-grade chalcopyrite and pyrite were firstly crushed and hand-picked to gain high-purity samples. The purified samples were then pulverized into smaller particle size in an agate mortar before sieving to different size fractions. The -74+38 μm size fraction sample was chosen for flotation.

The X-ray diffraction pattern (XRD) of the two minerals were shown in Fig. 1, which reveals that peaks correspond to crystal phase of chalcopyrite and pyrite. As shown in Table 1, the chemical analysis results indicate the relatively high purity of the chalcopyrite and pyrite samples.

The collector sodium ethyl xanthate and frother terpenic oil was obtained from Zhuzhou Flotation Reagents Ltd., China and Sinopharm Chemical Reagent, respectively. As shown in Table 2, three types of chelating depressants, including S-S (glycerine-xanthate, 2,3-dihydroxypropyl-xanthate, lactic acid-xanthate and propionic acid-xanthate), S-O (thiosalicylic acid and 2-mercaptonic acid), and O-O (lactic acid, salicylic acid, salicylhydroxamic acid and 3,4-dihydroxybenzohydroxamic acid) types, were chosen as depressants. HCl and NaOH were used as the pH modifiers, and all the reagents talked above were acquired from Adamas-beta® (Shanghai Titan Scientific Co.).

Table 1. Chemical composition results of chalcopyrite and pyrite (mass fraction, %)

Components	Fe	S	Cu	SiO ₂	Al ₂ O ₃	CaO
Chalcopyrite	30.26	35.69	33.13	0.12	0.13	0.11
Pyrite	45.82	52.23	0.26	0.09	0.08	0.06

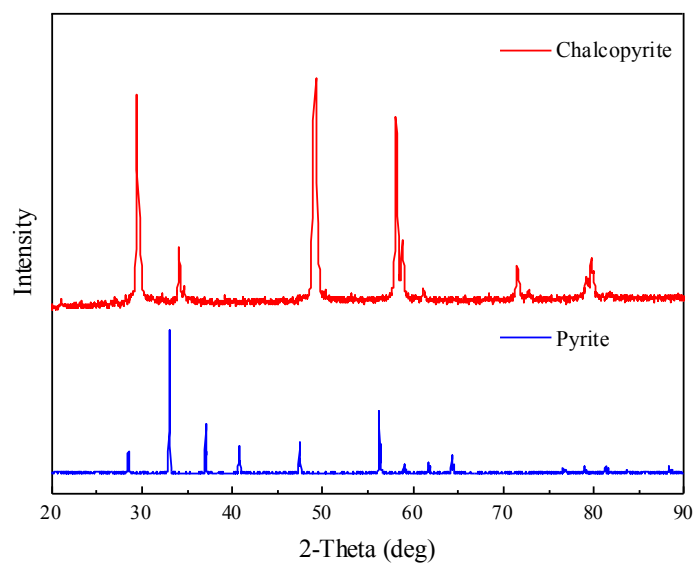


Fig. 1. XRD spectra of chalcopyrite and pyrite

Table 2. The molecular structures of depressant

Types	Names	Molecular structures
S-S	Glycerine-xanthate (GCX)	
	2,3-Dihydroxypropyl-xanthate (DHPX)	
	Lactic acid-xanthate (LAX)	
	Propionic acid-xanthate (PAX)	
S-O	2-Mercaptonicotinic acid (MCCA)	
	Thiosalicylic acid (TSA)	
O-O	Lactic acid (LA)	
	Salicylic acid (SA)	
	Salicylhydroxamic acid (SHA)	
	3,4-dihydroxybenzohydroxamic acid (DBDA)	

2.2. Methods

2.2.1. Computation

DFT simulation was conducted to achieve the frontier orbital calculation, including two minerals (chalcopyrite and pyrite), and three types of flotation chelating depressants with DMol³ module (Delley, 1990; Delley, 2000). During the calculations, GGA-PBE was chosen as the DFT exchange-correlation potential. The convergence precision of energy change, max force, max displacement, max step size and self-consistent field was 2.0×10^{-5} Ha, 1.0×10^{-3} Ha $\cdot \text{\AA}^{-1}$, 4.0×10^{-3} \AA , 0.3 \AA and 2.0×10^{-6} eV/atom, respectively. In the calculation, all electrons were included with DNP atomic orbital basis set. The conductor-like screening model (COSMO) with a dielectric constant of 78.54 was adopted to achieve the more scientific and reasonable metal-depressant interaction model (Klamt, 1993).

2.2.2. Flotation

Microflotation tests of single minerals, namely, chalcopyrite and pyrite were carried out using an XFG-5 flotation machine with a 40 mL suspension cell operating at 1460 rpm to evaluate the performance of depressants. For each test, 2 g chalcopyrite or pyrite was mixed with 30 mL deionized water. After adjusting the slurry pH to a specific value using NaOH or HCl, depressant, sodium ethyl xanthate, and terpenic oil was added into the flotation cell and followed by 5 min of conditioning in sequence. The adjusted slurry was floated for 5 min and then the concentrate and tailings were collected, dried, and weighed to calculate the recovery. Each test was repeated three times with the same condition, and the mean value was adopted as the final result.

3. Results and discussion

3.1. Analysis of frontier orbital

The frontier molecular orbital theory holds that a molecule's reactivity is determined by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (Fukui, 1952). Due to the electron of a molecule on HOMO has the highest energy in all the occupied orbital, thus the electrons in HOMO is the most active and easiest to lose. While the LUMO is the most receptive orbital to electrons as the lowest energy in all the unoccupied orbitals. Therefore, the reactivity between any two molecules is determined by their HOMO and LUMO. The smaller the absolute energy difference between the HOMO of one molecule and the LUMO of another molecule, the easier for electrons transfer from HOMO to LUMO. Hence the energy difference between HOMO and LUMO orbitals can be applied to predict the reactivity between the two molecules.

The two minerals' and three types of depressants' HOMO and LUMO energies were shown in Fig. 2. The results indicate that most of the HOMO energies of the depressants, except for TSA from S-O type and LA from O-O type, are extremely close to the LUMO orbital of pyrite, indicating that these chelating depressants would interact with pyrite strongly. In other words, most of these depressants would show depression effect on pyrite.

The HOMO orbitals of both chalcopyrite and pyrite are far away from the LUMO orbitals of all the depressants, and the LUMO orbitals of these two minerals are close to each other. In addition, the HOMO orbitals of S-S type, MCCA in S-O type, SHA and DBDA in O-O type depressants are very close to the LUMO orbitals of the two minerals. Moreover, the LUMO orbital of SHA in O-O type is most close to the HOMO orbital of the two minerals, especially close between chalcopyrite and SHA. It can be predicted that SHA in O-O type would have considerable chelating effect to the two minerals, especially to chalcopyrite. Additionally, it is notably that the HOMO orbitals of the four S-S type depressants are comparably with the two minerals' LUMO orbitals, which indicates that S-S type depressants could chelate with chalcopyrite and pyrite sensibly, especially with pyrite. This is consistent with the practice that molecules including xanthate group are effective reagents sulfide minerals flotation.

The Fig. 3-5, show the orbital configurations and coefficients of the chelating depressant molecules. The results were calculated to further analyze the frontier. According to the frontier molecular orbital theory, the frontier orbital coefficients can affect the regioselectivity of a reaction. The larger coefficient

is the more contribution of the atom to the frontier orbital and the greater activity of the atom (Houk, 1973; Sauer, 1980). It is obviously can be seen for the S-S type depressant that S atoms contribute much more to the HOMO than that of other atoms, especially for the double-bond S in these depressants. Additionally, the hydroxyl (-OH) and carboxyl (-COOH) groups in the S-S type depressants don't have contribution either to HOMO or LUMO, while the ether groups only have a little contribution to HOMO.

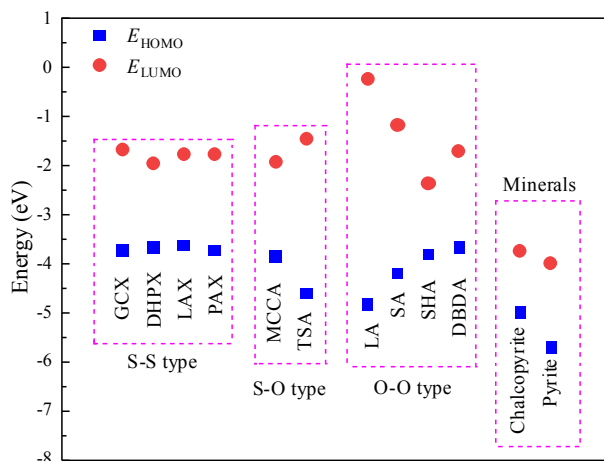


Fig. 2. The HOMO and LUMO energies of the three types of depressants and the two minerals

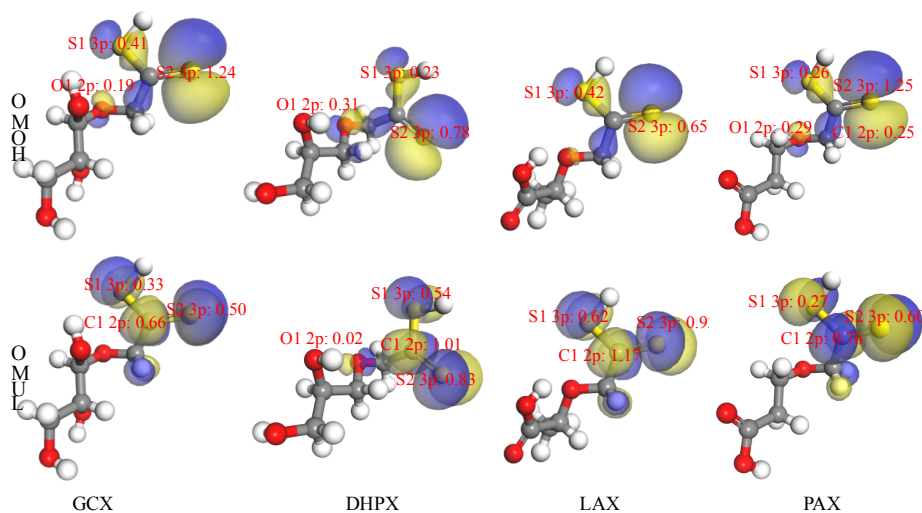


Fig. 3. Frontier orbital configurations and coefficients of S-S type of depressant molecules

MCCA and TSA have been adopted as the representative for S-O type chelating depressants. Keto and enol form MCCA were applied to investigate the contribution difference between these two forms. The single coordinated atom S in enol form is sort of single-bond, whereas that in keto form is sort of double-bond. It is demonstrated that the contributions of atoms to the orbitals and the HOMO and LUMO patterns of both keto and enol forms MCCA are almost the same. For HOMO, the single coordinated atom S contributed the most, followed by the C and N atoms, and the O atoms in carboxyl group contribute very little. It is dissimilar for LUMO, the S atom has almost no contribution, while the largest contribution derives from the C and N atoms in the annular molecule. Moreover, the two O atoms in carboxyl group also contribute little. Compared the TSA with enol form MCCA, it is found that there is no significant distinction between the frontier orbital coefficients of these two depressant molecules, except that the O atoms in carboxyl group contribute a little more than that of MCCA. This maybe because the electronic mobility of benzene ring of TSA is higher than of MCCA. Moreover, the coefficient of S in HOMO of MCCA is bigger than that of TSA indicating that N atom has more electron-donating effect than C atom.

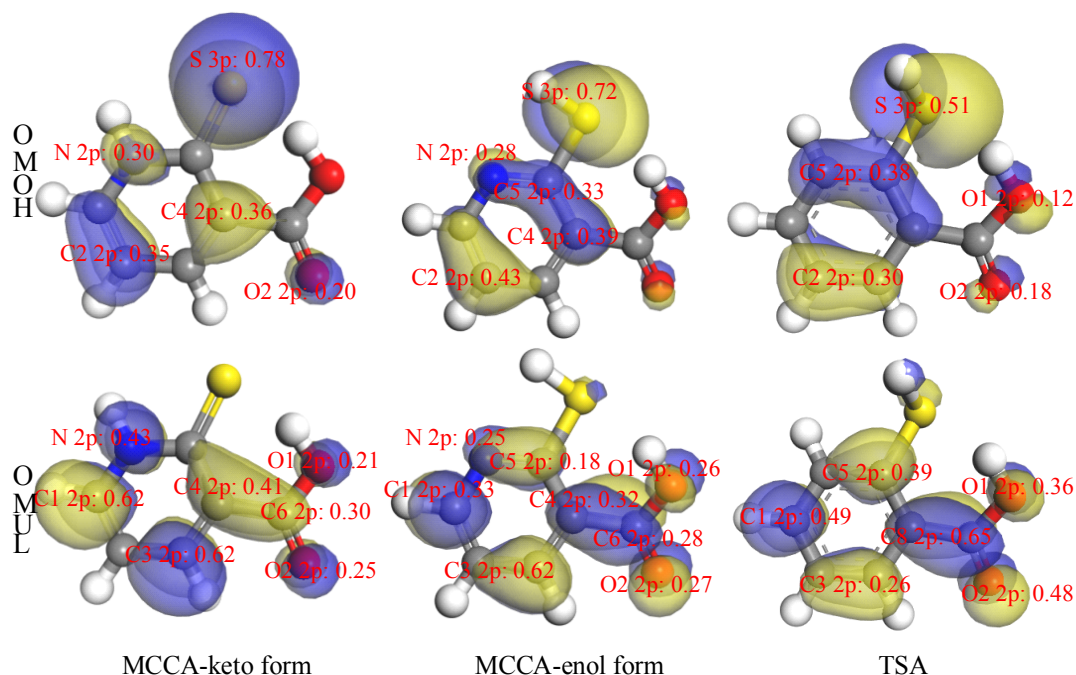


Fig. 4. Frontier orbital configurations and coefficients of S-O type of chelating depressant molecules

For O-O type, SA, SHA and DBDA all have one benzene ring, and one $-\text{COO}^-$ for SA, $-\text{COONO}^-$ for SHA and DBDA, respectively. The different between SHA and DBDA is the $-\text{OH}$ number and location which SHA has only one $-\text{OH}$ while DBDA has two. LA and SA both have a $-\text{COO}^-$ and $-\text{OH}$ in molecule, but LA has not benzene ring. It is shown that the $-\text{COO}^-$ and $-\text{OH}$ in LA both contribute to HOMO and LUMO, the $-\text{OH}$ in SA mostly contributes to HOMO while the $-\text{COO}^-$ mostly to the LUMO. For SHA and DBDA, it is the same to the contribution of $-\text{OH}$, while the $-\text{COONO}^-$ shows much more contribution on to the LUMO than that of HOMO. Compared with the SA, SHA and DBDA, it is obviously that the benzene ring in these three molecules both contributes to HOMO and LUMO, and the existence of $-\text{OH}$ increases the contribution to the HOMO.

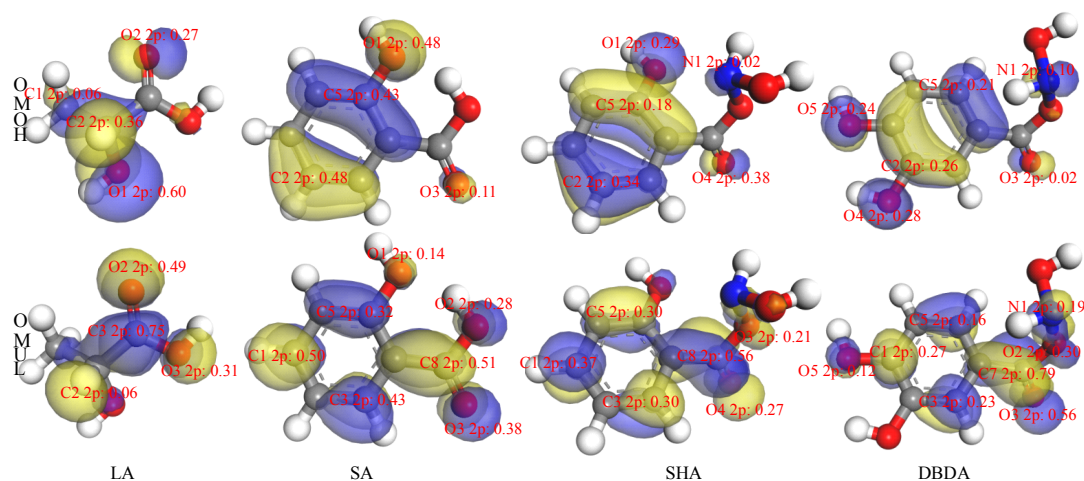


Fig. 5. Frontier orbital configurations and coefficients of O-O type of chelating depressant molecules

3.2. Interactions of chelating depressants with Cu and Fe ions

It has been approved that the chemisorbed surface film which is produced by the interaction of metal ions and chelation reagents would be responsible for flotation (Rinelli, 1973). The interaction configurations of metal ions (Cu^{2+} and Fe^{2+}) with these chelating depressants (two depressant molecules are bonded with one metal ion) are shown in Figs. 6-9.

As shown in Fig.6, S-S type depressants can chelate Cu^{2+} and Fe^{2+} ions via S-S in a form of a four-coordinated structure. The mean S-Cu bond distance of these four depressants was 2.395 Å, 2.402 Å, 2.402 Å and 2.398 Å, and S-Fe bond distance 2.188 Å, 2.282 Å, 2.238 Å and 2.270 Å, respectively, indicating that the interaction of GCX and PAX with Cu^{2+} and Fe^{2+} was stronger (longer distance) than that of DHPX and LAX. Compared with DHPX, GCX has one more hydrophilic group -OH showing stronger affinity to these two ions. While for LAX and PAX, although they both have one hydrophilic group -COOH, the methyl in LAX weakened the electron supplying capacity of hydrocarbon chain and decreased its reaction affinity.

For S-O type of depressants, it is indicated the interaction of Cu^{2+} and Fe^{2+} with atom S and O occurred, while the interaction of atom N in MCCA with the two ions was not observed. The mean S-Cu bond distance of MCCA and TSA was 2.252 Å and 2.212 Å, O-Cu bond distance 1.907 Å and 1.923 Å, respectively. This suggested that, compared with TSA, the substitution of atom N increased the reaction affinity of O-Cu, while the S-Cu decreased. Because the electron supplying capacity of atom N is higher than C, thus the substitution of atom N contributed more effective electron to atom O than S. The interaction of the two depressants with Fe^{2+} was similar to Cu^{2+} . Moreover, the mean S-Cu and S-Fe bond distance of S-O type depressant was shorter than that of S-S type, indicating that ring functional groups show more electron supplying capacity than chain.

The representatives of O-O type, LA, SA, SHA and DBDA are shown in Fig. 8. It is suggested that LA and SA can react with Cu^{2+} and Fe^{2+} via atom O in a form of four-coordinated structure. The mean O-Cu and O-Fe bond distance of LA was 1.892 Å and 1.847 Å, respectively, while for SA 1.911 Å and 1.894 Å. The benzene ring of SA did not show obvious electron donating effect. For SHA and DBDA, four-membered ring structure is not observed as other depressants. The mean O-Cu and O-Fe bond distance of DBDA was 1.871 Å and 1.873 Å, respectively, which was shorter than SHA of 1.992 Å and 1.994 Å, although intramolecular hydrogen bond was observed in SHA. Compared with SHA, the two hydrophilic -OH on the benzene ring of DBDA increased its reaction activity.

The results above demonstrated that the interacting strengths of a metal ion with the chelating atom in different depressants are different. The reaction activity associated both with the ions' reactivity and the electronic and spatial structure of the functional group. The charge, radius and electronegativity of metal ions all together effect their complexation ability to ligands. The electrostaticly and covalently complexing capacity of metal ions to ligands depend on their radius and electronegativity. For the metal

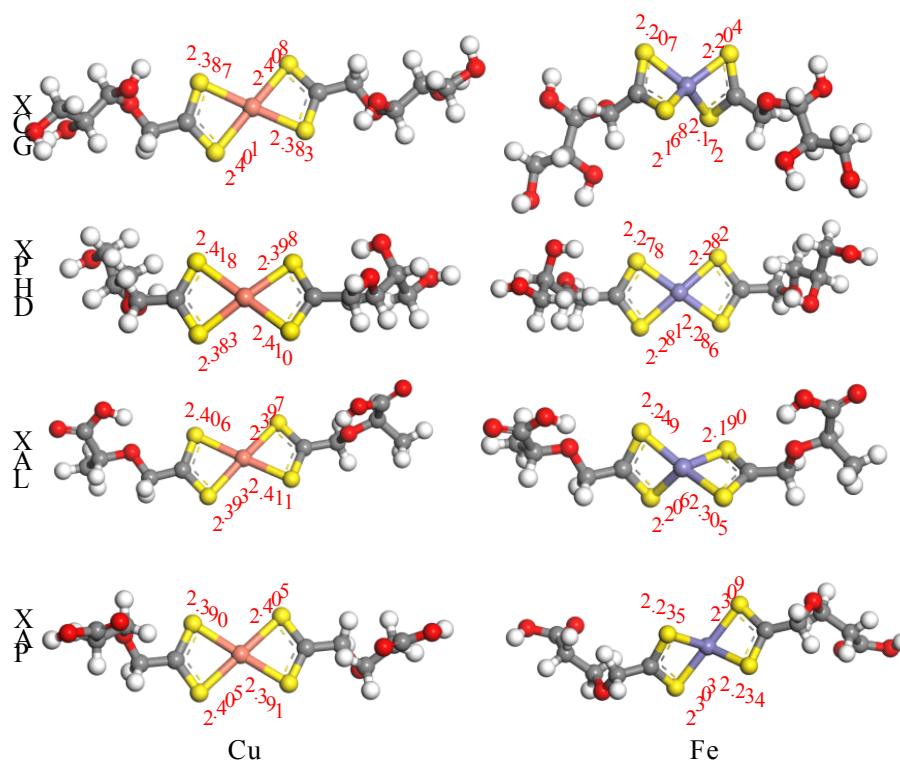


Fig. 6. Interaction configurations of Cu^{2+} and Fe^{2+} with S-S type of depressants

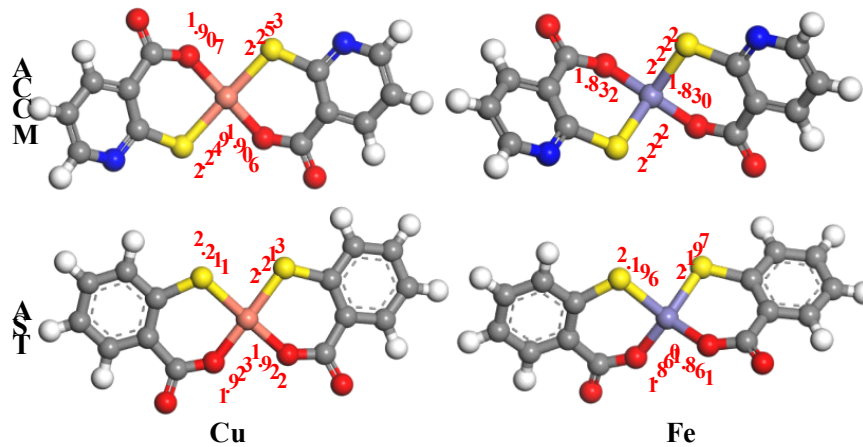


Fig. 7. Interaction configurations of Cu^{2+} and Fe^{2+} with S-O type of depressants

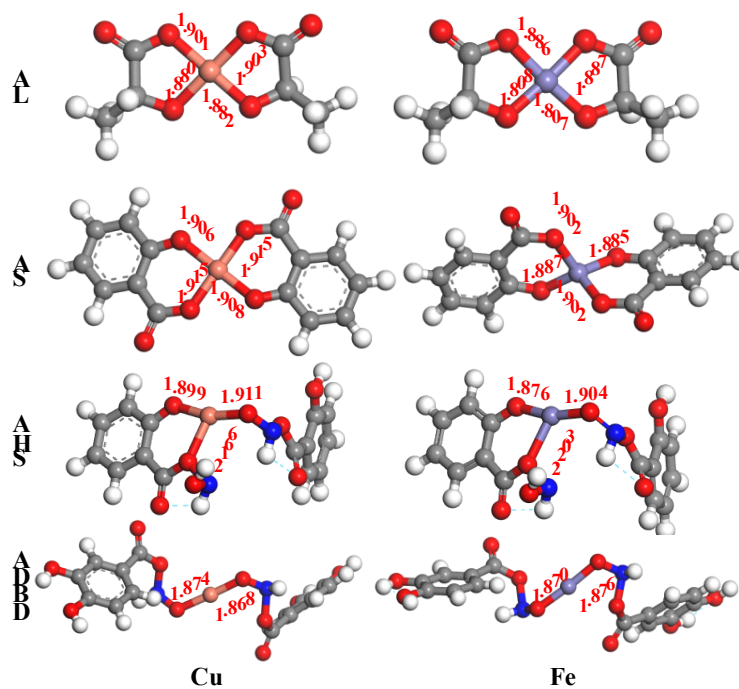


Fig. 8. Interaction configurations of Cu^{2+} and Fe^{2+} with O-O type of depressants

ions with the same valence state, the smaller radius and the larger electronegativity, the easier to form metal-ligand complex. The bivalent radius of Cu and Fe is 0.073 and 0.078, respectively. The modified Pauling electronegativity is 1.90 and 1.83, respectively (Li, 2020). Thus, the electrostatic complexing capacity of Cu^{2+} and Fe^{2+} is close, and their ability to N and O ligands is great. Due to water molecules have manifest influence on the electrostatic interaction between metal ions and atoms O and N, therefore their influence cannot be neglected.

3.3. Flotation

To verify the aforementioned simulation results, as shown in Fig. 9, microflotation were carried out to determine the depression effect of these reagents on the floatability of the chalcopyrite and pyrite. For all flotation tests, the relationships between the mineral recoveries and concentration of depressant were controlled at 8×10^{-5} mol/L SBX and pH 8.

As shown in Fig.9a, these two minerals were highly floatable without depressants, and their recoveries were more than 90% in the pH 8. This indicates that chalcopyrite and pyrite have good natural floatability, and this is consistent with the previous results (Mu, 2017; Guo, 2003). The recoveries

of the two minerals both decreased with the addition of S-S type depressants, and the floatability of chalcopyrite was higher than pyrite. This indicates that although the four S-S depressants could depress both chalcopyrite and pyrite, the depression effect on pyrite was stronger than chalcopyrite. Moreover, GCX and PAX showed more obvious depression effect than DHPX and LAX. The inhibitory potency of GCX against pyrite was greater than PAX, while against chalcopyrite was weaker, which indicated that the selectivity intensity of GCX was greater than PAX. LAX showed weaker inhibitory potency against chalcopyrite than DHPX, but the two reagents showed similar inhibitory potency against pyrite. Compared to LAX, the selectivity intensity of DHPX was greater. Therefore, the selectivity intensity order of the four depressants was $GCX > PAX > DHPX > LAX$.

The floatability of chalcopyrite and pyrite with different concentration of S-O typer depressant (TSA and MCCA) was shown as Fig. 9b. It is obvious that the floatability of the two mineral both decreased significantly with the increase of TSA and MCCA concentration. When the concentration of TSA and MCCA reached to 6×10^{-4} mol/L, the two minerals' recovery dropped to around 30%. The corresponding concentration of S-S depressants were about 21×10^{-4} mol/L to obtain around 30% recovery of pyrite. This result suggested that the inhibitory potency of S-O type depressant TSA and MCCA was much greater than that of S-S type. What should be noted that there was no obvious floatability difference between chalcopyrite and pyrite, suggesting although TSA and MCCA showed strong depression effect on the two minerals, either of them had good selectivity intensity.

For O-O type depressants, as shown in Fig. 9c, the four depressants LA, SA, SHA and DBDA all have no clear depression effect on chalcopyrite, but obvious depression effect on pyrite. The inhibitory potency of LA against chalcopyrite and pyrite was weaker than SA, which possibly due to the higher electron supply capacity of benzene ring in SA, although the hydrophilicity of LA is higher than SA. The atom N in SHA and DBDA increased their electron supply capacity, which results these two reagents show more obvious depression effect on pyrite than SA. Compared with SHA, molecular DBDA has one more -OH, resulting in a higher hydrophilicity and greater inhibitory potency against the two minerals.

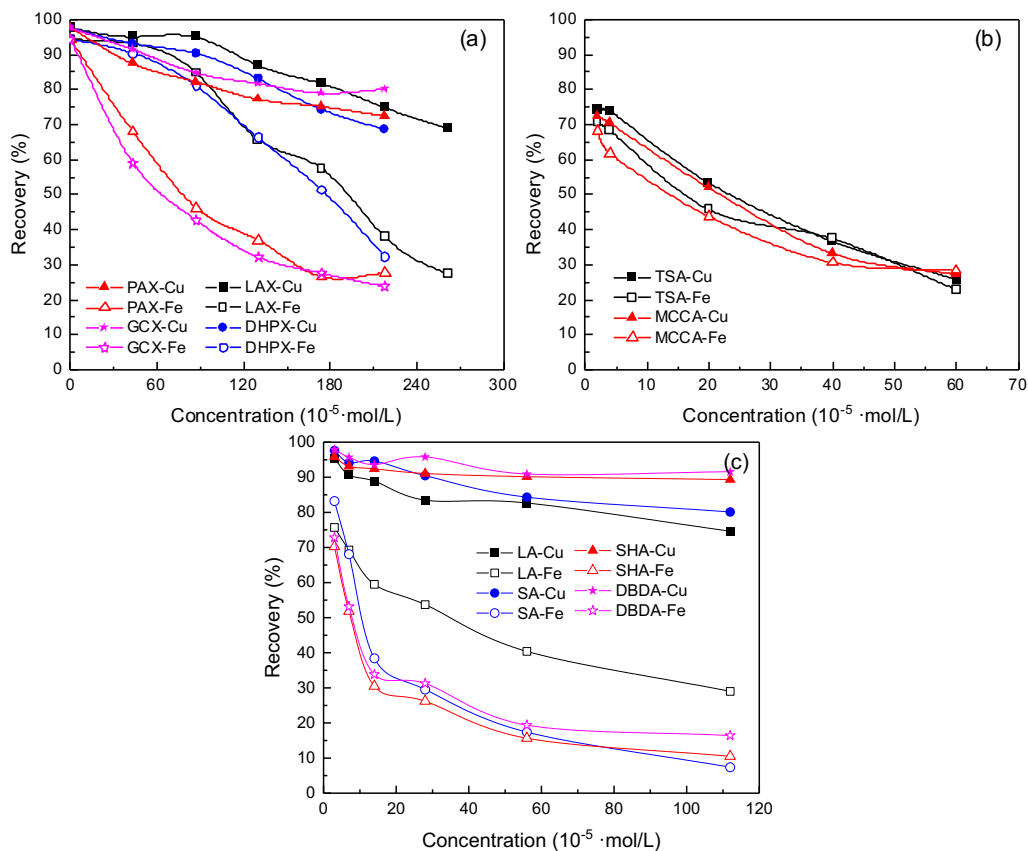


Fig. 9. Floatability of pyrite and chalcopyrite as a function of the depressant concentration at pH 8 with 8×10^{-5} mol/L SBX (a: S-S type, b: S-O type, c: O-O type)

4. Conclusions

The HOMO and LUMO patterns, the frontier orbital coefficients, the chelating effects of depressants to Cu and Fe metals, and the floatability of pyrite and chalcopyrite with different type of depressants have been investigated by DFT simulation.

The results of HOMO and LUMO demonstrated that most of the three types of depressants could depress pyrite, while the S-S type depressants could chelate with chalcopyrite and pyrite sensibly. S atom in both keto or enol forms of S-S type depressant won't affect their HOMO and LUMO patterns and the orbital contributions. It is found that the activity of a depressant is influenced significantly by the spatial structure of an atom. For instance, atom N in a ring will increase the activity of O-Cu while weak S-Cu. The differences of molecular structure result in the various chelating performances on the metal ions and minerals.

The flotation results indicate that the three type depressants inhibit both chalcopyrite and pyrite in a certain degree, and the selectivity intensity order was GCX>PAX>DHPX>LAX for S-S type, DBDA>SHA>SA>LA for O-O type, but no selectivity intensity was observed for S-O type.

The simulation results delineate the structure-activity relationship of three types of chelating depressants in details, which is mostly consistent with the flotation results. Simulation is useful for screening, development and synthesis of reagents as depressants. Further research on the adsorption of depressants on chalcopyrite and pyrite surface will focus on the effect of molecule structure on the adsorption mechanism.

Acknowledgements

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