QUANTUM CHEMICAL MECHANISM ON THE SURFACE OXIDATION AND FLOTATION OF SULPHIDE MINERALS①

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ABSTRACT

The surfaces of galena and pyrite, the adsorption of oxygen, and the reactions of ethyl xanthate on the sulfides were studied using quantum chemical calculations. In addition, the surface electron structures of the minerals were discussed. According to the results, the mechanisms of ionic exchange reaction and dixanthogen adsorption for the xanthate flotation of galena and pyrite were explained. The important role of oxygen in collector and collectorless flotation processes was also investigated.

Key words: sulphide minerals, oxidation, flotation, galena, pyrite, quantum chemistry

1 INTRODUCTION

Flotation theories of sulphide minerals have been studied widely[1-3]. Natural floatability of sulfide minerals, role of oxygen and xanthate collector adsorption mechanism have been three key subjects for a long time. The studies on the three aspects have made great progress since 1950 through the use of modern electrochemical and surface analysis techniques and others. The electrochemical investigations on sulfide-collector-oxygen systems have shown that there are two kinds of collector adsorption[4]. The coupling of anodic collector oxidation with cathodic oxygen reduction results in the formation of dixanthogen which is responsible for pyrite flotation. The coupling of anodic oxidation of a sulphide surface with cathodic reduction of oxygen followed by the adsorption of xanthate ion on the surface causes the formation of metal xanthate, which is responsible for galena flotation. The comparison between the rest potential of a sulphide electrode and the Nernst potential of xanthate oxidation may determine whether the dixanthogen or the metal xanthate is formed[5]. Therefore, the electrochemical activity of sulfide minerals has a great effect on xanthate adsorption. Systematic studies of sulfide-collector-oxygen systems have shown that there are two typical characteristics of sulfide minerals which can be represented by galena and pyrite respectively.

Collectorless flotation of sulphide minerals has been an interesting research topic recently. Some sulphide minerals, such as chalcopyrite, galena, arsenopyrite and pyrite can be floated well in the absence of xanthate collector when the redox potential is controlled within a suitable range[6]. Compared to traditional

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collector flotation, the electrochemical conditions in the collectorless flotation of sulfide minerals are most important. The collectorless flotation of galena can be carried out in the absence of Na_2S under suitable electrochemical conditions. But for the collectorless flotation of pyrite, the presence of Na_2S is necessary.

Molecular oxygen plays an important role in sulphide flotation. Many reports have indicated that oxygen is necessary to either collector or collectorless flotation[7-12]. But there are different views on the role of oxygen, which has not completely understood yet.

In this paper, the calculations for two kinds of sulphide minerals (pyrite and galena) and their flotation systems were carried out using CNDO/ 2 method of quantum chemisty. The results are used to discuss the role of oxygen, xanthate collector adsorption and mechanism of collectorless flotation.

2 QUANTUM CHEMICAL CALCULATIONS

2. 1 *Geometrical Structure Models f or Calculation*

According to Lindquist's view[13], the (100) face of a mineral is the most important for flotation. Fig.1 shows the structures of the (001) face of cubic lattices of galena and pyrite which are used as calculation models. The calculation model of ethyl xanthate ion is given in Fig. 2.

Figs. 3 and 4 show the calculation models for the adsorption of oxygen molecule on the (001) face of galena and pyrite crystals. Although many other models can be constructed, the models given in Figs. 3 and 4 possess the lowest total energy, and they are most stable and possible. Fig.5 is the calculation model for interaction between oxidized galena surface and ethyl xanthate ion. Fig. 6 is the model for catalytic oxidation of xanthate ion on pyrite surface forming dixanthogen. The two models are the most probable at the lowest energy.

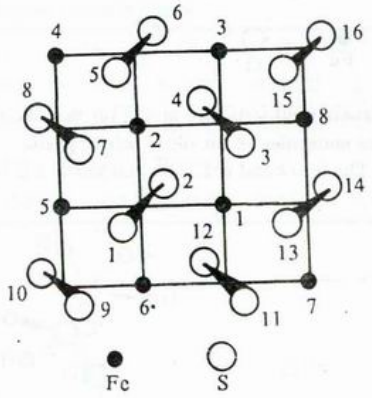

Fig.1 (001) faces of pyrite and galena crystals as calculation model

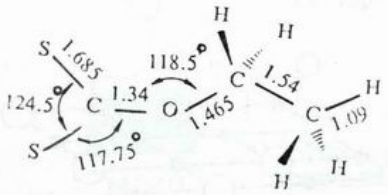

Fig.2 Calculation model of ethyl xanthate ion

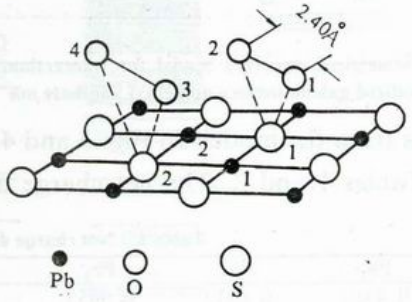

Fig.3 Geometrical structure model for the adsorption of oxygen molecule on the (001) face of galena crystal
The 0–0 bond length is 2. 40Å and the 0–S 2. 0Å

2. 2 *Calculation Results*

The electron structure of galena and pyrite surfaces is calculated first. The net charge density of the atoms on the two mineral

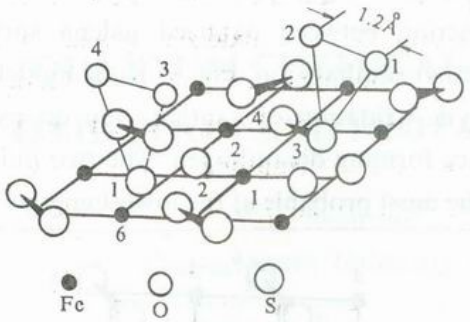

Fig.4 Geometrical structure model for the adsorption of oxygen molecules on the (001) face of pyrite
The 0–0 bond is 1. 20Å and the 0–S 2. 47Å

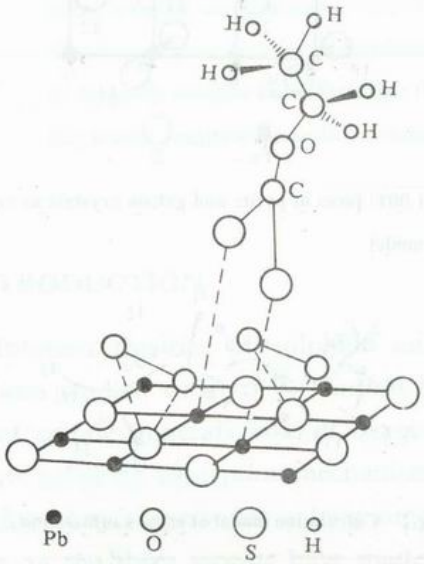

Fig.5 Geometrical structure model for interaction between oxidized galena surface and ethyl xanthate ion

surfaces from the models in Figs.3 and 4 is listed in Tables 1 and 2. The net charge density and Wiberg's bond order of some atoms on the oxidized mineral surfaces (Figs.3 and 4) are shown in Tables 3 and 4.

Fig. 7 shows the energy level of molecular orbitals of galena and pyrite surfaces and the energy level of common oxygen, activated oxygen and ethyl xanthate ion. The two kinds of oxygen are different models used in the calculation, one of which is common oxygen with a O–O bond length of 1.2Å, and the other is activated oxygen with a O–O bond length of 2.4Å.

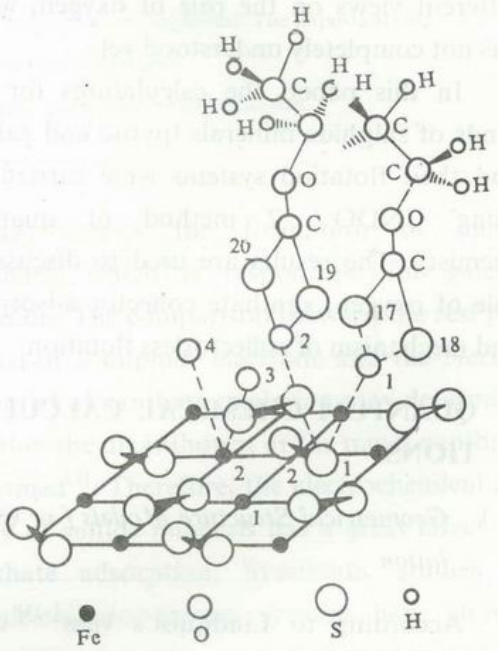

Fig.6 Geometrical structure model for catalytic oxidation of ethyl xanthate ion on pyrite surface forming dixanthogen

Table 1 Net charge density of the atoms on galena surface in Fig. 1

Pb_1	Pb_2	Pb_3	Pb_4	Pb_5	Pb_6	Pb_7	Pb_8
0. 4910	0. 4910	0. 3055	0. 2518	0. 3055	0. 3055	0. 2518	0. 3055
S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
−0. 3425	−0. 3425	−0. 3372	−0. 3367	−0. 3372	−0. 3372	−0. 3367	−0. 3372

Table 2 Net charge density of the atoms on pyrite surface in Fig. 1

Fe_1	Fe_2	Fe_3	Fe_4	Fe_5	Fe_6	Fe_7	Fe_8
−0. 2787	−0. 2711	−0. 1020	−0. 1188	−0. 0403	−0. 0646	−0. 0981	−0. 0698
S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
0. 1188	−0. 0774	0. 0277	0. 0401	0. 0278	−0. 0018	−0. 0661	0. 0610
S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}	S_{16}
−0. 0124	−0. 0333	0. 0553	−0. 0524	0. 0305	−0. 0322	0. 1032	0. 4216

Table 3 Net charge density and Wiberg's bond order of some atoms in Fig. 3

		Pb_1	Pb_2	S_1	S_2	O_1	O_2	O_3	O_4
net charge density		0.6634	0.6634	0.2536	0.2536	−0.4717	−0.4717	−0.4717	−0.4717
				Pb_1-S_1		Pb_3-S_1		O_1-S_1	
Wiberg's bond order	before oxidation			0.4717		0.5757			
	after oxidation			0.2017		0.2676		0.9165	

Table 4 Net charge density and Wiberg's bond order of some atoms in Fig. 4

		Fe_1	Fe_2	S_1	S_2	S_3	S_4	O_1	O_2	O_3	O_4
net charge density		−0.2825	−0.2430	0.1235	−0.0885	0.0270	0.0408	0.0172	0.0224	0.0222	0.0275
				Fe_2-S_2	Fe_2-S_4	Fe_1-S_3	Fe_6-S_1	S_1-S_2	S_3-S_4	O_1-S_3	O_3-S_1
Wiberg's bond order	before oxidation			0.4643	0.3796	0.3665	0.7073	0.9518	0.9512		
	after oxidation			0.4649	0.3829	0.3274	0.7420	0.9324	0.9371	0.0131	0.0083

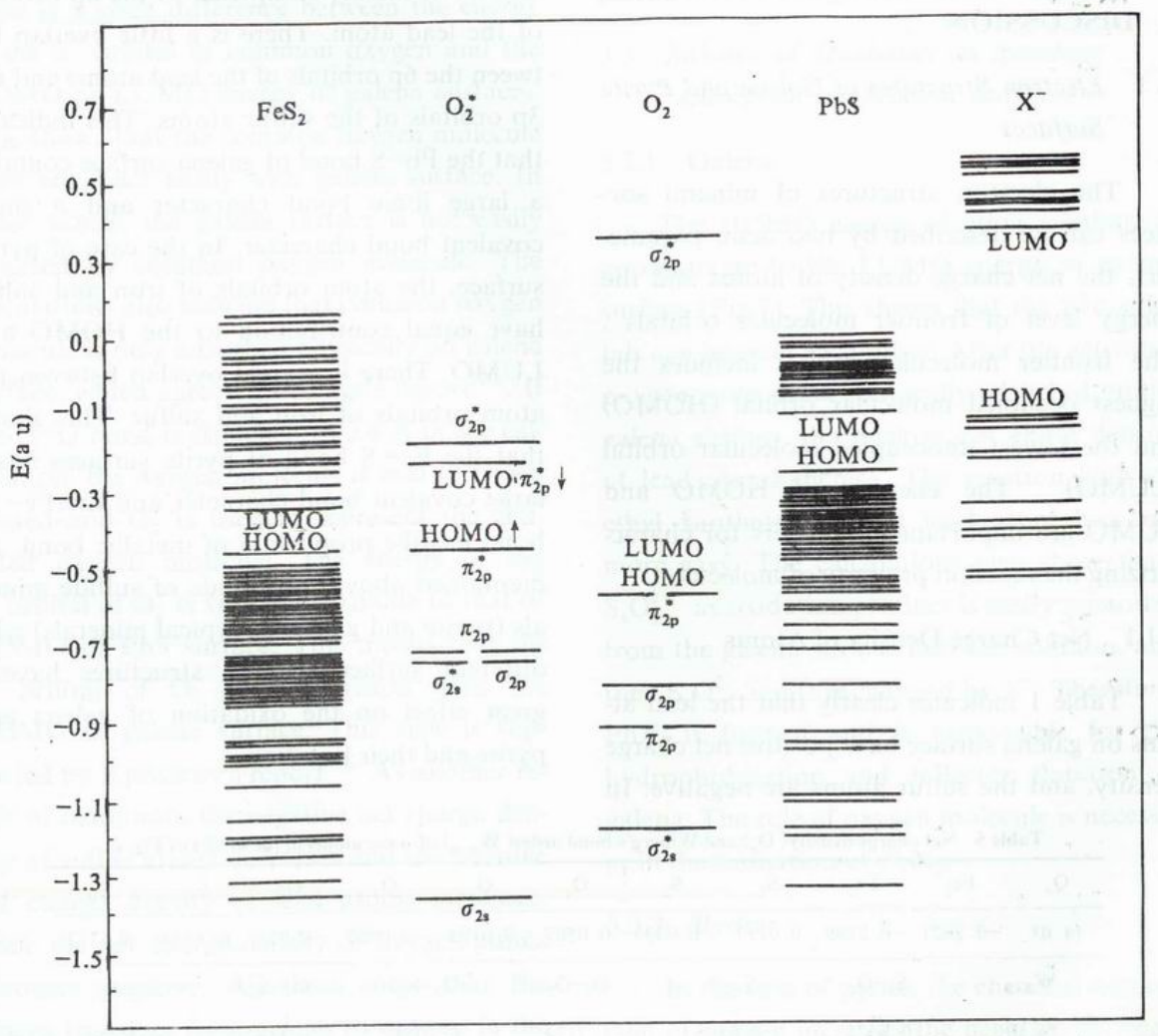

Fig. 7 Energy level diagram of molecular orbitals

(O_2—activated molecular oxygen with a bond length of 2.4Å; X^-—ethyl xanthate ion)

Fig.8 gives the net charge density of atoms in the polar group of ethyl xanthate ion. Table 5 shows the charge density and Wiberg's bond order of atoms in the model of Fig.6.

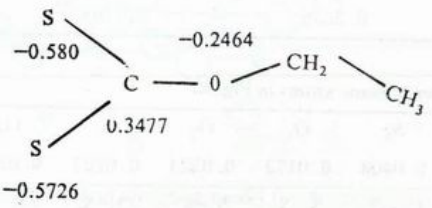

Fig. 8 Net charge density of atoms in the polar group of ethyl xanthateion

3 DISCUSSION

3.1 *Electron Structures of Galena and Pyrite Surfaces*

The electron structures of mineral surfaces can be described by two main parameters: the net charge density of atoms and the energy level of frontier molecular orbitals . The frontier molecular orbital includes the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) . The energies of HOMO and LUMO are important parameters for characterizing the reaction property of molecules.

3.1.1 Net Charge Density of Atoms

Table 1 indicates clearly that the lead atoms on galena surface have positive net charge density, and the sulfur atoms are negative. In opposition to galena, the iron atoms on pyrite surfaces have negative net charge density, and the sulfur atoms are positive (see Table 2) . This great difference mainly arises from the fact that the electron in disulfide ion S_2^{2-} of pyrite transfers to the 3d orbital of iron atom when it coordinates with sulfur.

3.1.2 Constitution of HOMO and LUMO

The quantu mechanical calculations show that the HOMO of galena surface mainly consists of 3p orbital of sulfur atoms, and the LUMO is mainly comprised of the 6p orbitals of the lead atom. There is a little overlap between the 6p orbitals of the lead atoms and the 3p orbitals of the sulfur atoms. This indicates that the Pb−S bond of galena surface contains a large ionic bond character and a small covalent bond character. In the case of pyrite surface, the atom orbitals of iron and sulfur have equal contribution to the HOMO and LUMO. There is a great overlap between the atom orbitals of iron and sulfur. This shows that the Fe−S bond of pyrite surfaces has a large covalent bond character and the Fe−Fe bond has the proportion of metallic bond. As mentioned above, two kinds of sulfide minerals (pyrite and galena as typical minerals) with different surface electron structures have a great effect on the oxidation of galena and pyrite and their flotation.

Table 5 Net charge density(Q_a) and Wiberg's bond order(W_{A-B}) of some atoms in the model of Fig. 6

Q_a	Fe_1	Fe_2	S_1	S_2	O_1	O_2	O_3	O_4	S_{17}	S_{19}
(a. u)	−0. 2821	−0. 2789	0. 0113	−0. 0339	0. 0507	0. 0195	−0. 0965	−0. 065	0. 1466	0.1372
W_{A-B}		S_1-O_2		S_1-O_1		O_1-O_2		O_2-S_{19}	O_1-S_{17}	$S_{17}-S_{19}$
(a. u)		0. 0371		0. 0305		1. 7124		0. 1054	0. 1182	0. 8979

3.2 *Oxidation of Sulfide Minerals*

3.2.1 Galena

Oxygen possesses the following molecular orbitals:

$$(\sigma_{1s})^2(\sigma_{1s})^2(\sigma_{2s})^2(\sigma_{2s}{}^*)(\sigma_{2p_x})^2(\pi_{2p_y})^2(\pi_{2p_z})^2$$
$$(\pi^*_{2p_z})^1(\pi^*_{2p_y})^1(\sigma^*_{2p_x})^0.$$

In its two anti-π orbitals(π^*), there are two single electrons. The orbital can either accept or donate one electron. So it can become HOMO or LUMO. It can be seen in Fig.7 that there is a great difference between the energy of the π^* orbital of common oxygen and the HOMO or LUMO energy of galena surfaces. This shows that the common oxygen molecule does not react easily with galena surface. In other words, the galena surface is not easily oxidized by common oxygen molecule. The calculations also indicate that common oxygen molecule is only adsorbed physically on galena surface, which agrees with Page's report[10]. If the O–O bond is stretched to 2.4 Å in the calculation, the oxygen molecule is said to be activated and O_2^* is used to represent the activated oxygen molecule. The energy of the π^* orbital of O_2^* is very approximate to that of HOMO of PbS surface. This means that the π^* orbital of O_2^* strongly reacts with the HOMO of galena surface. This view is supported by Kposikov's report[14]. As another result of oxidation, the negative net charge density of sulfur atoms decreases and the positive net charge density of lead atoms increases, while the net charge density of oxygen atoms becomes negative. All these show that the charge transfers from galena to oxygen in the oxidation process of galena surface

3.2.2 Pyrite

In the case of pyrite surface, it is clear from Fig. 7 that the energy of HOMO and LUMO is appoximate to that of common oxygen molecules. This shows that common oxygen molecule can be adsorbed chemically on pyrite surface. In this case, the charge transfers from the common oxygen molecule to the pyrite surface and as a result, the negative net charge density of iron atoms increases, but the positive net charge of sulfur atoms has only a little change. It seems that pyrite surface has great electron acception, and in opposition, galena surface has great electron donation.

3.3 *Influnce of Oxidation on Xanthate Adsorption on Mineral Surfaces*

3.3.1 Galena.

The HOMO energy of ethyl xanthate is approximate to the LUMO energy of galena surface (Fig.7). This shows that the two orbitals can interact each other. After the activated oxygen molecule is chemically adsorbed on the galena surface, the positive net charg density of lead atoms increas. The reaction between ethyl xanthate ion and lead atom becomes more easy. The calculations also show that $S_xO_y^{2-}$ as oxidation product is easily separated from the galena surface into the solution, and then $S_xO_y^{2-}$ ion is exchanged by X^-. Therefore, PbX_2 is formed and is responsible for the hydrophobization and collector flotation of galena. The role of oxygen molecule is necessary in the formation of PbX_2.

3.3.2 Pyrite

In the case of pyrite, the chemical adsorption of oxygen increases the negative net charge density of the iron atoms. Because of eletro-static repulsion, the ethyl xanthate ion

does not easliy interact with iron atom with negative charge. On the other hand, the oxygen molecule adsorbed on pyrite surface has a positive charge density. The charge will transfer from ethyl xanthate ion to oxygen. The ethyl xanthate ion (X^-) may be oxidized into neutral dixanthongen (X_2). It is clear in Table 5 that the oxygen molecule accepts the charges of sulfur atoms in X^- ion. The sulfur atoms of two X^- ions interact with each other and form S– S bond. The Wiberg's order of S_{17}–S_{19} bond in Fig.7 is 0.8979 which shows that X^- is really oxidized into X_2. The pyrite surface possesses an electrochemically catalytical function on the oxidation of X^-, so the oxidation rate of X^- is faster on pyrite surface than in solution.

3.4 *Collectorless Flotation of Galena and Pyrite*

Many test results have shown there are two kinds of flotation behaviors of sulfide mineral. One of them is a galena as typical and common reductants which can be used in collectorless flotation as potential modifiers. But for the other kind, pyrite is a typical, only sodium sulfide is used as reductant. Although the test phenomena can be explained through various views, quantum chemical calculation may be used in this disscussion

3.4.1 Galena

The negative net charge of the sulfur atoms on galena surface transfers easily to oxygen molecule. This finally results that the S^{2-} on galena surface is oxidized into neutral sulfur (S^0). The neutral sulfur formed on the surface may be regarded as a hydrophobic species for collectorless flotation without sodium sulfide.

3.4.2 Pyrite

In the case of pyrite, there exists a charge transfer between the surface and oxygen, but the oxidation product is not neutral sulfur under the conditions of flotation pulp. When Na_2S is added to the flotation pulp, the electrons of S^{2-} ions in Na_2S easily transfer to the sulfur atoms on the pyrite surface, and then to oxygen molecule. This charge transfer process causes the formation of neutral sulfur on pyrite surface and it is responsible for hydrophobization and collectorless flotation with sodium sulfide.

Fig.9 gives the experimental results of collectorless flotation of galena and pyrite without Na_2S. Galena has a good flotation behavior at pH 0–12, and pyrite has only a poor flotation behavior at pH > 5. The experimental results are in concordance with the discussion of quantum chemistry.

Fig.10 presents the test results of collectorless flotation of galena and pyrite with Na_2S as reductant. The addition of Na_2S can promote pyrite flotation and depress galena flotation. These test results confirm the above discussions.

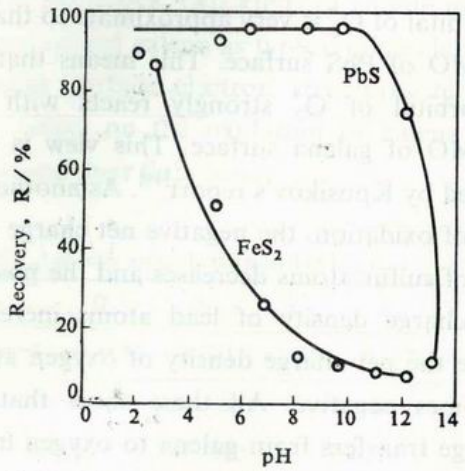

Fig.9 Collectorless flotation of galena and pyrite without Na_2S as a function of pH

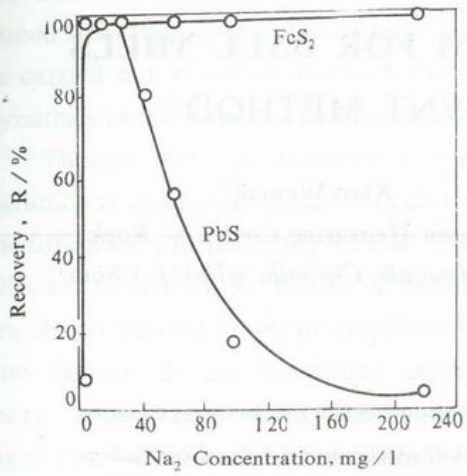

Fig.10 Collectorless flotation of galena and pyrite with Na_2S as a function of Na_2S concentration at pH 11

4 CONCLUSIONS

1 The electron structure of sulfide mineral surfaces were studied by the quantum chemical calculation. Galena is very different from pyrite in the surface electron structure. The sulphide minerals may be divided into two groups according to the surface electron structure. It is important for the explanation of mechanisms of collector and collectorless flotation.

2 The electron structures of mineral surfaces can be used to discuss the role of oxgen molecule, collector adsorption and collectorless flotation. The three aspects are different for galena and pyrite. In the former case, the charge transfers from the mineral to oxygen, in other words, the adsorption of oxygen molecule increases the positive net charge density of lead atoms on galena surfaces. Therefore,xanthate ions react easily with lead atoms, which forms PbX_2. This is known as the chemisorption mechanism of sulphide flotation.

In the case of pyrite, the charge transfers from molecular oxygen to the pyrite surface. The negative net charge density of iron atoms on the pyrite surface increases. X^- is easily oxidized into dixanthogen. This is also known as the electrochemical mechanism of sulphide flotation.

3 The oxygen molecule plays a great role in collectroless flotation of sulfide minerals. The charges transfer from galena surface to oxygen results in the formation of neutral sulfur and collectorless flotation of galena without Na_2S. The charges transfer from HS^- ions to oxygen through the pyrite surface, like a catalyst, inducss the collectorless flotation of pyrite with Na_2S.

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