

Collector matching in origin potential flotation^①

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Abstract: Through thermodynamic calculation and electrochemistry analysis, taking the galena as example, the basis for collector matching in origin potential flotation (OPF) was studied. The results of thermodynamic calculation show that the upper limit value of pH and flotation potential of diethyldithiocarbamate (DDTC) is higher than that of xanthogenate (KBX), which indicates that the collecting ability of DDTC for galena is better than that of KBX. The results of the interface capacitance analysis show that lead diethyldithiocarbamate (PbD_2) is more steady than lead xanthogenate ($Pb(BX)_2$) on the galena surface under the oxidation condition; the resistance analysis shows that D_2 (DDTC oxidizes into its dimmer) and dioxanthogen ($BX)_2$ will occur non-faradic desorption on the pyrite electrode surface when the potentials are above 0.13 V and 0.2 V respectively. A synthetical criterion ΔE of collecting ability and selectivity was proposed. The results predicted by this criterion are confirmed through flotation experiments of ore.

Key words: origin potential flotation; collector; galena

CLC number: TD 923.6

Document code: A

1 INTRODUCTION

Two types of potential controlled flotation methods have been developed: control by the addition of oxidants and reductants, and control by an outside-polarized electrode connected with a potentiostat. The former results in a big consumption of reagents and chemical side-reactions. The latter is complex in application and has low efficiency of polarized potential. So, pilot-scale and plant-scale tests of potential controlled flotation of ores have little progress^[1-8]. Origin potential flotation(OPF)^[9-11] is a new technology of potential controlled flotation developed by Central South University and Guangdong University of Technology in these years, which has been already applied in practice in many mines in Guangdong, Guangxi, Jiangshu province etc in China.

OPF makes use of potential caused by varies of intrinsic redox reactions in grinding-flotation system, achieves potential control flotation, and promotes flotation process through adjusting traditional flotation operation parameters. OPF technology has two key points: one is adjusting and controlling traditional flotation operation factors including pulp pH, type and dosage of collector, flotation time and flow structure etc; the other is not exerting outside electric field and not adding redox reagents for controlling electropotential. These two points are of advantage for OPF technology to be applied and extended in exist-

ing flotation systems. The main scientific inclusion and technical key of OPF are: combining parameters of traditional flotation with pulp origin potential (E_{op}), studying the effects of E_{op} on flotation and finding out the optimum matching plan among each of factors, then the optimum flotation conditions including economic reagent institution, the best hydrophobic conditions and separation selectivity, were established.

In the process of OPF, the matching of collector with pulp pH and pulp E_{op} is an important factor. Taking OPF of lead-zinc-iron complex multi-metal sulfide as an instance, the matching relation between collector with pulp pH and pulp E_{op} in the prior flotation of galena was investigated, and the basis of selection collector in OPF was proposed.

2 THERMODYNAMICS OF COLLECTOR MATCHING IN OPF

The study results of electrochemistry show that the chemical environment of high pH and low E_{op} for lead-zinc-iron complex multi-metal sulfide benefits to the flotation of galena, meanwhile, benefits to the depression of sphalerite and pyrite due to their self-oxidation. The matching relationship between pH and E_{op} is: $pH \geq 12$, $E_{op} 0.13 - 0.20 V$ ^[12-14].

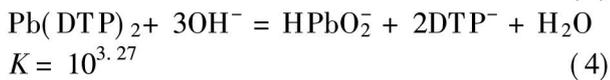
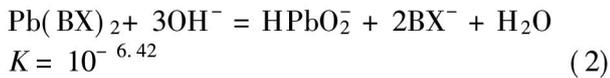
① **Foundation item:** Project(200145) supported by a Foundation for the Author of National Excellent Doctoral Dissertation of China; project supported by the Teaching and Research Award Program for Outstanding Young Teachers in Higher Education Institutions of MOE

Received date: 2003 - 07 - 18; **Accepted date:** 2003 - 11 - 18

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2.1 Selection of collector in prior flotation of galena

In the flotation of sulfide minerals, the common collectors are potassium ethyl xanthogenate (KEX), potassium butyl xanthogenate (KBX), diethyldithiocarbamate (DDTC), diethyldithiophosphate (DDTP) etc. The reaction products of collector on galena surface are collector metal salts. The upper limit value of pH in the flotation of galena with collectors is decided by the following reactions:



Given the ionic concentration of 10^{-4} mol/L, the upper limit values of pH for galena flotation with kinds of collectors are: KEX 10.98, KBX 12.14, DDTC 13.49, DDTP 8.91, respectively. According to the matching requirement of pH and E_{op} in OPF, the collector for the prior flotation of galena is DDTC or KBX.

2.2 Thermodynamic condition of flotation of galena using DDTC as collector

Fig. 1 shows the relation of potential $-pH$ in the galena-DDTC-water and galena-KBX-water (partly) systems (the solid line for the concentration of soluble KBX and DDTC 10^{-4} mol/L; the dashed line for the concentration of DDTC 10^{-3} mol/L).

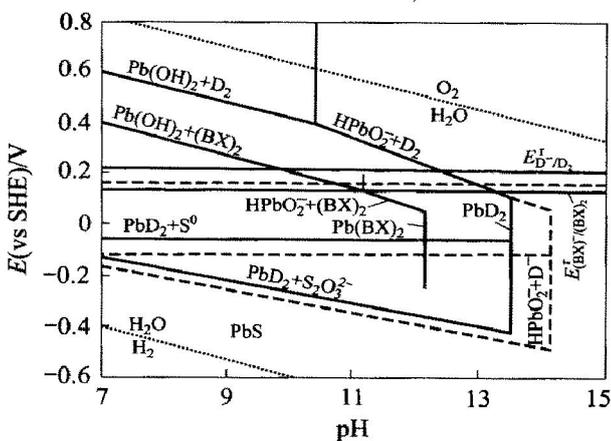


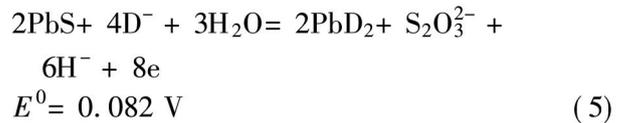
Fig. 1 $E-pH$ diagram for galena-collector-water system

It can be seen from Fig. 1 that the upper limit value of pH and flotation potential of DDTC are higher than those of KBX, which indicates that the collecting ability of DDTC for galena is better than that of KBX.

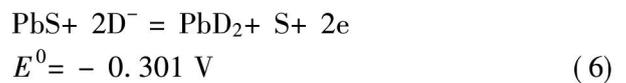
The thermodynamic condition of the flotation of galena using DDTC as collector is as follows.

1) The pH value of flotation. The upper limit value of pH is 13.49 when the concentration of DDTC is 10^{-4} mol/L; the theoretical upper limit of pH is 14.15 when the concentration reaches to 10^{-3} mol/L

2) Flotation potential. The lower limit value of potential: seen from the potential $-pH$ curve in Fig. 1, if the reaction product of collector on the galena surface is $\text{PbD}_2 + \text{S}_2\text{O}_3^{2-}$ (to abbreviate the DTC^- to D^-):

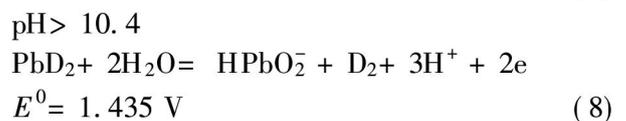
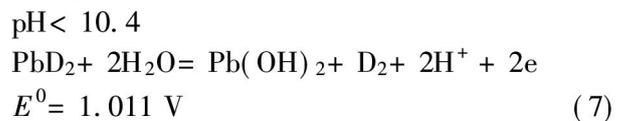


then the lower limit of the flotation potential is very low. But the $\text{S}_2\text{O}_3^{2-}$ formed makes reaction energy obstacle^[15], so the product of collector on the galena surface should be PbD_2 and S:



At that time, when the concentrations of DDTC are 10^{-4} mol/L and 10^{-3} mol/L, respectively, the lower limit value of flotation potential is -0.065 V and -0.124 V, correspondingly.

The upper limit value of potential for galena flotation with DDTC as collector is decided by the decomposing of PbD_2 , and the reactions are as follows:



The upper limit value of the flotation potential does not change with changing the concentration of agents, but decreases with increasing pH. When pH is above 12, the upper limit value of the flotation potential is about 0.25 V. Furthermore, the reversible potential line ($E_{\text{D}^-/\text{D}_2}^0$) of the D^- oxidized to D_2 shows that, the upper limit value of the flotation potential should be controlled at about 0.2 V to prevent the oxidation of D^- .

3 ELECTROCHEMISTRY OF COLLECTOR MATCHING IN OPF

3.1 Interface capacitance of galena electrode

In strong alkaline media (pH = 12.8), the relationship between the interface capacitance and potential for galena electrode is shown in Fig. 2.

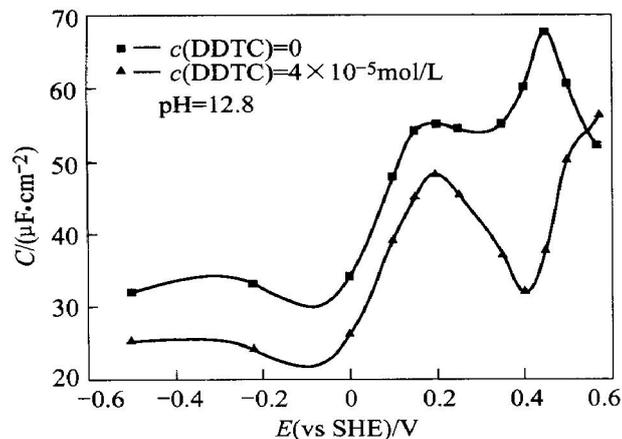
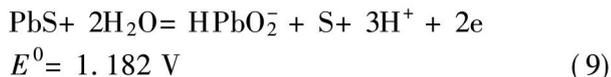


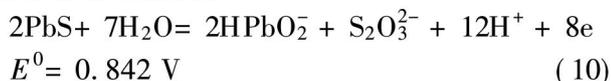
Fig. 2 Interface capacitance vs potential curves for galena electrode.

Background solution: pH 12.8 buffer solution plus 0.5 mol/L KNO₃ at 298 K

It can be seen from Fig. 2 that in the test results without collector (line 1), the interface capacitance for galena electrode has little change when the potential is below 0 V, while it increases when the potential is above 0 V, and the surface of galena is oxidized to form HPbO₂⁻. When the potential is at about 0.2 V, the capacitance curve appears a flat step, which indicates that the product of oxidation of electrode surface has element sulfur. The reaction is as follows:



When the potential is above 0.2 V, the capacitance rises slowly. There is S₂O₃²⁻, with high dielectric constant, appearing on the electrode surface. The reaction is as follows:



Adding DDTC into liquid phase, PbD₂ is formed on the surface of galena, which does not change the curve shape but decreases the interface capacitance. Under the reduction potential, the interface capacitance rises slowly when potential is below -0.4 V, which indicates that the surface product PbD₂ formed according to Eqn. (6), tends to be reduced, and this trend stops on -0.88V (not shown in Fig. 2) due to a Faradic desorption of PbD₂ on the electrode surface. Under the oxidation potential, the curve intersect at 0.55 V with the one without collector, which implies that only the potential is above 0.55 V, will PbD₂ be oxidized further according to Eqn. (8) (proved by the measuring interface resistance). The difference of the oxidized potential of PbD₂ between these test results and the thermodynamic analyzing (seen from Fig. 1) mainly owes to the action of over-potential, and the high over-potential (0.35 V) denotes that PbD₂ is

firmly adsorbed on galena surface under oxidation condition.

The test result after adding KBX is similar to that of DDTC. The remarkable difference lies in that the interface capacitance curve of adsorbed Pb-(BX)₂ on galena intersects at 0.43 V with the one of pure surface, which is 0.12 V lower than that of DDTC. Thus it can be seen that PbD₂ is more steady than Pb(BX)₂ under the oxidation condition.

3.2 Interface resistance for pyrite electrode

The test result of interface resistance for pyrite electrode at pH= 12.8 is shown in Fig. 3, where line 1 stands for electrode pre-covered with D₂ and line 2 stands for electrode pre-covered with (BX)₂.

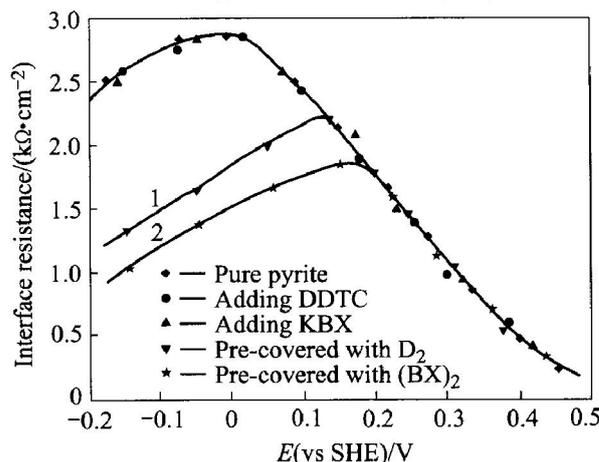


Fig. 3 Interface resistance vs potential for pyrite electrode at pH= 12.8

It can be seen from Fig. 3 that, in strong alkaline media, the interface resistance for pure pyrite electrode decreases gradually above 0 V, which indicates that strong oxidation happens on the pyrite electrode surface. Under this condition, the interface resistance with adding collector is identical with that without collector, which shows the collector does not react with mineral. While the potential is higher, collector will be oxidized to form collector dimer, and the collector dimer cannot be adsorbed on the mineral surface. It also can be seen from Fig. 3 that the curve 1 with D₂ coating and the curve 2 with (BX)₂ coating intersects with the resistance curve of surface pure pyrite electrode at about 0.13 V and 0.2 V, respectively, which implies that D₂ and (BX)₂ will occur non-faradic desorption on the electrode surface when the potentials are above 0.13 V and 0.2 V, respectively.

4 SYNTHETICAL CRITERION OF COLLECTOR MATCHING IN OPF

In original potential prior flotation of galena, two factors are taken into account for selecting collector: the collecting ability and selectivity of collectors. Collecting ability can be decided by the thermodynamic stability of collector metal salt (PbD_2 , $\text{Pb}(\text{BX})_2$ for example) formed on galena surface, also judged by the oxidized decomposing potential E_1 of collector metal salt. The higher the E_1 is, the stronger the collecting ability is. Selectivity can be decided by the thermodynamic stability of collector dimer formed on the surface of pyrite, also judged by desorption potential E_2 of collector dimer. The lower the E_2 is, the better the selectivity is. Considering these two factors, the difference of E_1 and E_2 (ΔE), acts as synthetical criterion of collecting ability and selectivity for collector. The bigger the ΔE is, the better collecting ability and selectivity are.

The results of electrochemical test for galena with DDTC or KBX are shown in Fig. 4. It can be seen that the value of ΔE_{DDTC} is bigger than that of ΔE_{KBX} , so DDTC is a more suitable collector for selective flotation of galena.

5 FLOTATION TEST RESULTS OF COLLECTOR MATCHING IN OPF

The flotation flow has one rougher and three cleaners, and the tailing of cleaner is combined as lead middling. The test results in Guangdong Fankou lead-zinc mine are listed in Tables 1 and 2.

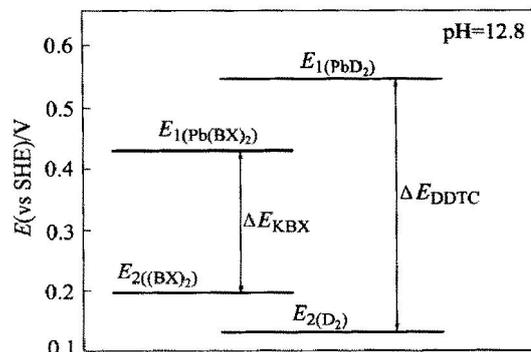


Fig. 4 Synthetical criterion of ability and selection for collector

E_1 —Oxidized decomposing potential of PbD_2 or $\text{Pb}(\text{BX})_2$;
 E_2 —Desorption potential of $(\text{BX})_2$ or D_2

Table 1 Fankou mine test results of OPF with diethyldithiocarbamate as collector in galena flotation system ($\text{pH}=12.7$, $E_{\text{op}}=0.16\text{ V}$)

Dosage of collector/ ($\text{g}\cdot\text{t}^{-1}$)	Product title	Product ratio/ %	Grade/ %		Recovery/ %	
			Pb	Zn	Pb	Zn
50	Lead concentrate	1.37	71.63	2.39	24.05	0.36
	Lead middling	8.04	26.83	6.80	52.87	6.05
	Lead coarse concentrate	9.41	33.35	6.16	76.92	6.41
	Lead tailing	90.59	1.04	9.33	23.08	93.59
	Feed	100.0	4.08	9.03	100.0	100.0
100	Lead concentrate	2.93	67.87	3.79	48.86	1.23
	Lead middling	9.91	13.60	12.61	33.12	13.80
	Lead coarse concentrate	12.84	25.99	10.60	81.98	15.03
	Lead tailing	87.16	0.84	8.83	18.02	84.97
	Feed	100.0	4.07	9.05	100.0	100.0
150	Lead concentrate	3.53	62.52	4.99	54.90	1.94
	Lead middling	9.98	11.46	13.70	27.67	15.09
	Lead coarse concentrate	13.51	24.57	11.47	82.57	17.03
	Lead tailing	86.49	0.81	8.69	17.43	82.97
	Feed	100.0	4.02	9.06	100.0	100.0
200	Lead concentrate	3.09	67.81	4.22	51.98	1.45
	Lead middling	10.29	12.16	13.26	31.04	15.14
	Lead coarse concentrate	13.38	25.51	11.17	83.02	16.59
	Lead tailing	86.62	0.79	8.68	16.98	83.41
	Feed	100.0	4.03	9.01	100.0	100.0
250	Lead concentrate	2.87	69.22	3.83	49.54	1.22
	Lead middling	10.58	12.91	12.73	34.06	14.96
	Lead coarse concentrate	13.45	24.92	10.83	83.60	16.18
	Lead tailing	86.55	0.76	8.72	16.40	83.82
	Feed	100.0	4.01	9.00	100.0	100.0

Table 2 Fankou mine test results of OPF with buthylxanthate as collector in galena flotation system (pH= 12.7, E_{op} = 0.16 V)

Dosage of collector/($g \cdot t^{-1}$)	Product title	Product ratio/ %	Grade/ %		Recovery/ %	
			Pb	Zn	Pb	Zn
50	Lead coarse concentrate	2.56	7.10	10.56	4.48	3.00
	Lead tailing	97.44	3.98	8.97	95.52	97.00
	Feed	100.0	4.06	9.01	100.0	100.0
100	Lead coarse concentrate	5.23	29.77	6.60	37.98	3.82
	Lead tailing	94.77	2.68	9.17	62.02	96.18
	Feed	100.0	4.01	9.04	100.0	100.0
150	Lead concentrate	0.20	40.17	4.60	1.96	0.10
	Lead middling	13.45	24.62	9.78	80.76	14.57
	Lead coarse concentrate	13.65	24.85	9.70	82.72	14.67
	Lead tailing	86.35	0.82	8.92	17.28	85.33
	Feed	100.0	4.10	9.03	100.0	100.0
	Lead concentrate	0.51	55.99	5.32	7.03	0.30
200	Lead middling	17.26	18.34	14.56	77.98	27.86
	Lead coarse concentrate	17.77	19.42	14.30	85.01	28.16
	Lead tailing	82.23	0.74	7.88	14.99	71.84
	Feed	100.0	4.06	9.02	100.0	100.0
250	Lead concentrate	1.54	61.07	6.25	23.05	1.06
	Lead middling	22.18	11.81	18.31	64.21	44.68
	Lead coarse concentrate	23.72	15.01	17.53	87.26	44.74
	Lead tailing	76.28	0.68	6.47	12.74	54.26
	Feed	100.0	4.08	9.09	100.0	100.0

The test results show that, with DDTC as collector, the quality of lead concentrate is still high with the increase of the dosage of DDTC. This indicates that DDTC is a well selectivity collector of galena, and the optimal dosage is about 100 g/t, which is lower than that of KBX; with KBX as collector, the lead recovery of rougher is so low as 37.98% when the dosage of KBX is about 100 g/t, only when it is 150 g/t, the recovery is over 80%. However, the content of zinc in lead coarse concentrate rises with increasing the dosage of KBX. Apparently, the collecting ability and selectivity of KBX for galena is weaker than those of DDTC. The test results also show that, when the dosage of KBX reaches 250 g/t, the recovery of lead rougher can be as high as 87.26%, but the recovery of lead concentrate is just about 23% under three cleaners, and the most part of lead is in the middling, which causes the huge recycle of middling. Here, in order to insure the high recovery of galena, the collector must be added in cleaner, which causes the selectivity of the collector to decline.

6 CONCLUSIONS

1) The collecting ability is decided by the thermodynamic stability of the product on the aim mineral (galena for example) surface, also judged by the oxidized decomposing potential E_1 of collector metal salt.

2) Selectivity can be decided by the thermodynamic stability of collector dimer formed on the comitancy mineral (pyrite for example) surface, also judged by desorption potential E_2 of collector dimer.

3) The synthetical criterion ΔE ($\Delta E = E_1 - E_2$) of collecting ability and selectivity is proposed. The results forecasted by this criterion are confirmed through flotation experiments of ore.

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(Edited by LI Xiangqun)