

Influence of metal cations on cassiterite flotation^①

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Abstract: Flotation of cassiterite has been studied on pure minerals performed in a microflotation cell with various collectors. The results indicate that sulphosuccinamate demonstrates strong collection, good selectivity on cassiterite in the region around pH 6, and that lead ions have certain activation whereas other ions such as ferric, aluminum, manganese, ferrous, calcium have strong depression on cassiterite flotation. In addition, X-ray photoelectron spectroscopy (XPS) was applied to study the flotation systems of cassiterite-sulphosuccinamate in the presence and absence of metal cation, and a chemisorption mechanism through chemically bonding between stannum species on the cassiterite surface and oxygen from sulphosuccinamate is proposed. The chemical environment of stannum species would be changed in the presence of lead ions in the flotation systems and therefore improve the activity of the stannum species, while ferric ions show strong depression due to the formation of steady complexes between ferric species and collector.

Key words: cassiterite flotation; sulphosuccinamate; tin

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1 INTRODUCTION

Cassiterite flotation has been the subject of considerable research since the forties of 20th century. The studies are concentrated on the aspects of reagents, flotation chemistry and advanced technology, which led to the introduction of flotation to most tin ore concentrators in Germany, Bolivia, U. K., Australia, South Africa and China since early 1970's^[1~6]. The collectors of commercial application for cassiterite flotation are mainly phosphonic acids^[7~9], arsenic acids^[1,3,10], and sulphosuccinamates^[1,11~13]. However, subsequent progress has been limited owing to the complicated bulk systems and interfacial chemistry of the reagents.

XPS is a surface sensitive technique, capable of revealing the elemental and chemical composition of the surface and near the surface up to a maximum depth of 50~100 Å and has been introduced extensively to the basic research of various fields such as physics, material science, environmental science and quantum chemistry. XPS has recently been used to characterize surfaces of minerals, and some useful information about surface chemical reactions and products during flotation can be obtained^[14]. However, most studies are involved in sulphide minerals and relatively fewer in oxide minerals. This paper presents some results on cassiterite flotation with sulphosuccinamate and by the XPS analyses pertaining to mineral surface chemistry of complicated flotation systems.

2 EXPERIMENTAL

The cassiterite, quartz and calcite were obtained from Dachang mine, Guangxi province, China^[15]. They have been ground in a ceramic ball mill and submitted to a high intensity magnetic separator, gravity separator, subsequently dried and screened in laboratory sieves, yielding the various size fractions of pure minerals, (74+30) µm for cassiterite, (100+30) µm for quartz and calcite. The chemical composition of these pure minerals is given in Table 1. The relative lower purity of calcite was due to the existence of magnesite.

The collectors included tetrasodium octadecyl sulphosuccinamate (A-22) from Kunming Institute of Metallurgy, styrene phosphonic acid (SPA) from Changsha Institute for Mining and Metallurgy, and salicylhydroxamic acid (SHA) from Guangzhou Research Institute for Nonferrous Metals. The depressants were carboxymethyl cellulose (CMC) prepared in our laboratory at General Research Institute for Nonferrous Metals and water glass with a model number of 2.5 from Beijing Chemical Reagents Corporation. Sodium hydroxide and hydrochloric acid were used as pH modifier, while other regulators included lead acetate, ferrous chloride, ferric chloride, calcium chloride, aluminum chloride and manganese chloride. The A-22 was industrial agent and has been purified in advance. The others were chemical agents.

The flotation tests were carried out in a micro-

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Table 1 Chemical composition of pure minerals

w / %

Mineral	Element or oxide										
	Sn	Pb	Zn	Fe	Cu	Bi	S	SiO ₂	CaO	MgO	Al ₂ O ₃
Cassiterite	77.34	< 0.10	< 0.017	0.38	< 0.017	< 0.002	0.0067	0.22	< 0.07	< 0.01	< 0.05
Quartz	0.001	0.006	0.009	0.04	< 0.002	< 0.020	0.025	98.48	1.32	0.18	0.10
Calcite	< 0.0005	0.018	0.019	0.22	< 0.002	< 0.002	0.20	0.14	47.60	3.50	< 0.004

flotation cell with a volume of 30 ml, using 2.0 g mineral, a conditioning time of 6 min and flotation time of 5 min. XPS spectra were recorded on an ESCALAB MK II type spectrometer, using MgK α radiation (1253.60 eV) at 280 W and an operating pressure of 10^{-5} Pa. The electron analyzer pass energy was 20 eV or 50 eV. All binding energies were calibrated with reference to the C_{1s} peak of graphite.

3 RESULTS AND DISCUSSION

3.1 Flotation tests

Flotation tests on cassiterite with A-22, SPA and SHA were carried out^[16]. The results shown in Fig. 1 indicate that flotation of cassiterite is improved with the increase of collector concentration. The relatively low concentration of collector and the sharp rise in floatability of cassiterite is found in the case of A-22. The recovery of cassiterite is up to 82% at a low concentration of 5.6×10^{-6} mol/L and then reached a stable recovery of about 90% above the concentration of 2.0×10^{-5} mol/L. Whereas a slow rise in floatability appears with SPA and SHA. Their maximum recoveries are 64% and 61% above the concentration of 2.0×10^{-4} mol/L, respectively.

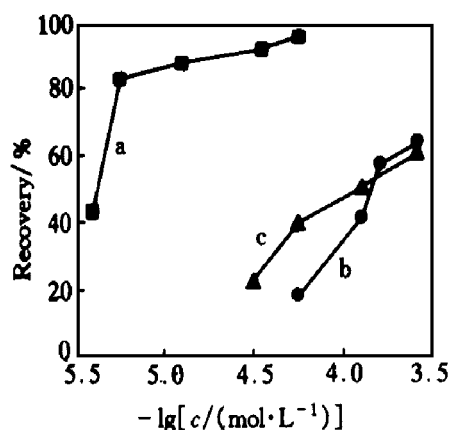


Fig. 1 Cassiterite flotation as a function of collector concentration

a—A-22, pH 6.0; b—SPA, pH 7.0; c—SHA, pH 6.0

Sulphosuccinamate was discovered by Arbiter as cassiterite collector and obtained wide application in Bolivian Concentrators, and ever in the Wheal Jane Concentrators (Cornwall). However, its selectivity appears in the range of pH 2~3, which limited somewhat its extensive application. Thus, flotation tests were performed at suitable concentration of collector.

As a results, an excellent flotation was obtained with A-22 in a broad range of pH 2~7. The recovery of cassiterite was over 80% and up to 95% around pH 6.0, whereas the floatabilities of cassiterite with SPA and SHA were relatively poor even in a high concentration and sharply decreased above pH 8.0.

The unavailable ions such as ferric, aluminum, calcium ions and their hydrolysis products, are one of the major factors that influence the flotation process^[17]. So it is worth investigating the effects of some ions on the cassiterite flotation to get a better insight into the process. Flotation tests in the presence of various metal cations were carried out. The results (Fig. 2) indicate that lead ions have certain activation which exceeds the laboratory errors of 2% and is similar to the results of other researchers. While other ions such as ferric, aluminum, calcium, ferrous, manganese ions, act as depressants for the process. Moreover, a shape reduce on flotation appears at 10^{-4} mol/L for ferric and aluminum ions and 10^{-5} mol/L for ferrous ions. Finally they become unfloated at a higher concentration.

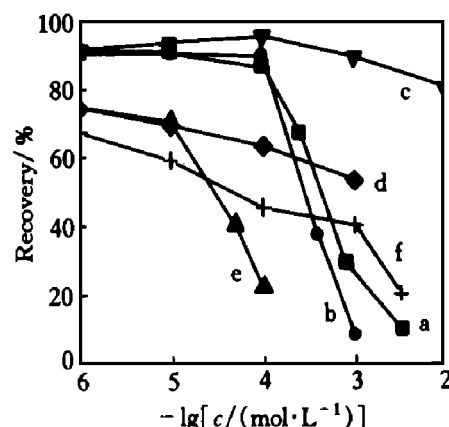


Fig. 2 Cassiterite flotation as a function of metal cation concentration with A-22 (4×10^{-4} mol/L for curve a, b, c; 2×10^{-5} mol/L for curve d, e, f) at pH 6
a—FeCl₃; b—Al₂(SO₄)₃; c—Pb(CH₃COO)₂;
d—CaCl₂; e—FeCl₂; f—MnCl₂

3.2 X-ray photoelectron spectroscopy studies

3.2.1 Cassiterite—A-22 flotation system

Fig. 3 shows the Sn_{3d}^{5/2} and O_{1s} peaks of primary cassiterite and A-22 treated cassiterite. The binding energy of Sn_{3d}^{5/2} peak is 486.49 eV; and reduced to 486.13 eV after treated with A-22 due to the increase

of electron cloud density and then the changes of chemical environment around the stannum species in cassiterite surface. Moreover, the binding energy of O_{1s} peak of primary cassiterite shifts from 530.69 eV to 530.38 eV, and two shoulder peaks due to the oxygen from carboxylic and sulphonic groups appear, their binding energies are 531.67 eV and 532.83 eV, and increased with 0.74 eV and 0.79 eV respectively on comparison with those of A-22. From this point of view, a chemical interaction between stannum species on cassiterite and oxygen from carboxylic and sulphonic groups of A-22 are proposed*.

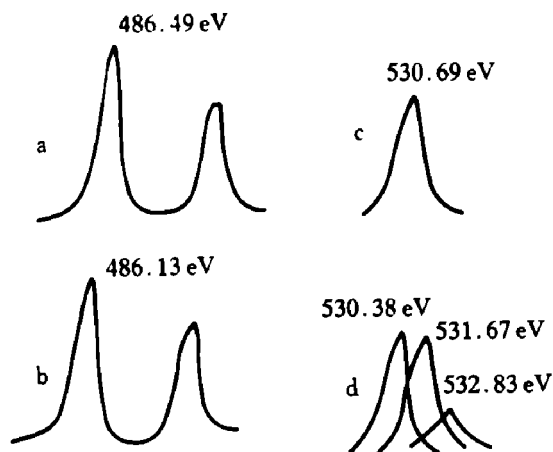


Fig. 3 XPS spectra of primary cassiterite and treated cassiterite

- a— $Sn_{3d}^{5/2}$, primary cassiterite;
b— $Sn_{3d}^{5/2}$, cassiterite treated with A-22;
c— O_{1s} , A-22; d— O_{1s} , cassiterite treated with A-22

3. 2. 2 Cassiterite—A-22—metal cation flotation systems

XPS studies were carried out mainly in the cases of lead and ferric ions. The spectra of different atoms are shown in Fig. 4. Compared with curve a in Fig. 3, the binding energy of $Sn_{3d}^{5/2}$ peak reduces from 486.40 eV to 486.20 eV, which indicates that the electron cloud density of stannum species has increased with the action of lead ions and thus has an influence on the chemical environment. In addition, as known from solution chemistry, the lead ions exist mainly in the forms of $PbOH^+$ and Pb^{2+} in the range of weak acidity. Consequently, the chemical binding between lead ions and stannum species through $-OH-$ and $-O-$ on cassiterite surface is considered. As the cassiterite treated with lead ions further reacts with A-22, the binding energy continuously reduces to 486.09 eV. Thus, the presence of lead ions would improve the interaction between cassiterite and A-22.

In the presence of ferric ions, the chemical environment around stannum species on cassiterite surface

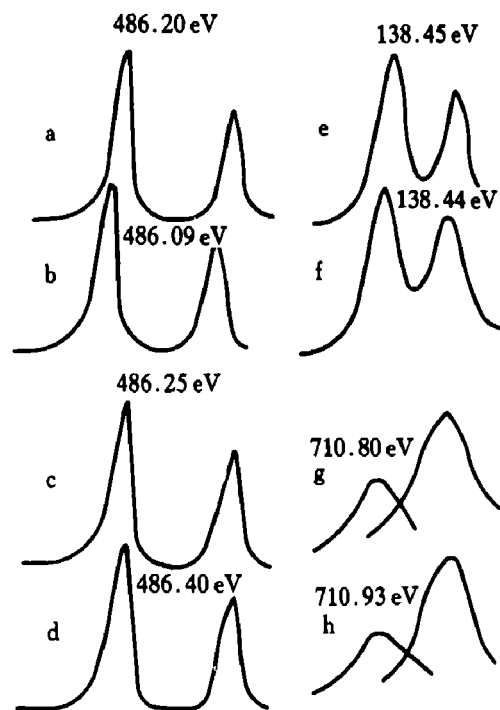


Fig. 4 XPS spectra of cassiterites under various treatment

- a— $Sn_{3d}^{5/2}$, lead acetate; b— $Sn_{3d}^{5/2}$, lead acetate and A-22;
c— $Sn_{3d}^{5/2}$, ferric chloride; d— $Sn_{3d}^{5/2}$, ferric chloride and A-22;
e— Pb_{4f} , lead acetate; f— Pb_{4f} , lead acetate and A-22;
g— $Fe_{2p}^{3/2}$, ferric chloride; h— $Fe_{2p}^{3/2}$, ferric chloride and A-22

is changed, which is indicated from the reduce of binding energy of $Sn_{3d}^{5/2}$ peak from 486.49 eV to 486.25 eV. However, as the cassiterite treated with ferric ions further reacts with collector, the binding energy conversely shifts from 486.25 eV to 486.40 eV. Thus, the interaction between A-22 and cassiterite is depressed because of the existence of ferric ions. In addition, the binding energies of Pb_{4f} and $Fe_{2p}^{3/2}$ peaks were measured. Little change is found for Pb_{4f} peak of lead ions treated cassiterite as further reaction with A-22, which indicates again that lead ions improve the interaction between cassiterite and collector, and its chemical environment is not influenced in the presence of A-22. Whereas the binding energy of $Fe_{2p}^{3/2}$ peak of ferric treated cassiterite increases from 710.80 eV to 710.93 eV as further reaction with A-22, which shows that ferric species adsorbed on cassiterite surface react in some context with collector. Senior *et al*^[13] proposed that a stable chelate was formed between A-22 and ferric ions on the cassiterite surface or in the bulk, which strongly depressed cassiterite flotation.

3. 2. 3 Element analyses on cassiterite surface

Due to the adsorption of A-22 and lead and ferric ions, the concentration ratio of stannum on cassiterite surface reduces from 18.4% to 6.19%, 13.01% and

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17.32%, respectively. The lead concentration ratio is 15.14% in the presence of lead ions and reduces to 14.04% with the addition of A-22, which contributes to the displacement of stannum species with lead ions in the forms of PbOH^+ and Pb^{2+} , and the interaction around the weak acidity region.

The concentration ratios of lead and stannum species on lead ion treated cassiterite reduce in the presence of A-22. However, the ratio of stannum species has a larger change than that of lead. Therefore, interaction between A-22 and lead ion treated cassiterite chiefly contribute to stannum species other than lead species. In the presence of ferric ions, the stannum concentration ratio is still 17.32% with a slightly reduce and the ferric species is 5.91%. Besides, the stannum species exposed to the cassiterite surface remain 13.91% after treated with A-22, which indicates only a little amount of collector is adsorbed on cassiterite surface. Therefore, the cassiterite is unfloated in the presence of ferric ions.

4 CONCLUSIONS

1) Sulphosuccinamate shows strong collection and excellent selectivity in cassiterite flotation at a wide range of pH, especially around pH 6.0.

2) The metal cations present in bulk would influence cassiterite flotation. The results indicate that lead ions have somewhat activation on the flotation system whereas other ions such as ferric, aluminum, ferrous, manganese and calcium strongly depress cassiterite flotation.

3) XPS was used to study the interaction mechanism in cassiterite flotation systems. A chemisorption of collector on cassiterite was examined through chemically binding between stannum species and oxygen from carboxylic and sulphonate groups.

4) Lead ions are adsorbed on cassiterite surface in the forms of PbOH^+ and Pb^{2+} , and improve the activity of stannum species, whereas ferric ions showed a strong depression on cassiterite flotation owing to the formation of stable chelates between A-22 and ferric ions.

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