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CASSITERITE FLOTATION VS THE ELECTRICAL NATURE OF ITS SURFACE

Styrene phosphonic acid and benzyl arsonic acid were used for flotation of cassiterite. It was established that a good flotation takes place at a low pH of aqueous solution. Small amount of $CuSO_4$ activates cassiterite flotation at pH=8 while EDTA may be used as a depressant in a strong alkaline environment. The influence of the electrical nature of cassiterite surface on its flotation is also discussed.

1. Introduction

Tin was discovered long ago. It is an important metal which supports the livelihood and production activities of human beings. Its uses and applications are continuously expanding with the development of science and technology. Now, however, the shortage of tin supply is increasing owing to its limited reserves. In this paper the influence of different collectors, activators, depressants, and pH on the flotation of cassiterite is presented.

2. Experimental

2.1. Materials and methods

Cassiterite, hand-picked coarse grains of a crystalline mineral, was obtained from Wenshan Country, Yunnan Province. The composition of the cassiterite sample was as follows: SnO_2 (94%), SiO_2 (4.3%), CaO (0.1%), MgO (0.01%). The mineral for flotation was ground in a pebble mill to -20 μm (over 95%). To increase the purity of the cassiterite samples, they were treated in hydrochloric acid, and then, washed several times in distilled water until the pH was neutral. HCl and NaOH

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were used as pH regulators. All chemicals were analitical grade. The following reagents were used: collectors - benzyl arsonic acid, or styrene phosphonic acid; activators - cupric sulphate, lead nitrate; depressants - EDTA, citric acid, water glass, and sodium hexametaphosphate. Zeta potential was measured with Zeta-potential analyzer (type ZP-10B) manufactured by SHIMADZU Corporation, Japan. Flotation machine with pendant cell and agitator model XFGC-80, made by Exploration Machinery works, (CHANG-CHUNG, CHINA), was used for flotation tests. Samples used for measuring the electrokinetic potentials was prepared in a deep beaker with sufficient agitation of the slurry with reagents.

3. Flotation test

3.1. Determination of the isoelectric point (i.e.p.) of cassiterite.

It is seen from Fig.1 that the surface of cassiterite is positively charged at low pH and negatively charged above pH 4.7. This value is only slightly higher than that obtained by D. W. Fuerstenau(1978) (pH=i.e.p 4.5). This difference may be caused by the origin of the cassiterite used and different measuring conditions (NaOH and HCl were used to regulate pH value of the slurry, and measured in distilled water in our measurements).

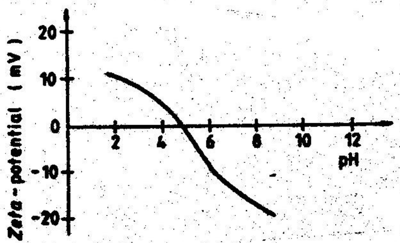

Fig.1 The relation between pH and Zeta potential of cassiterite surface

3.2 Relationship betwen pH of slurry and cassiterite flotation.

As we know so far either from literature or from our tests, the collecting power of collectors used in cassiterite flotation can be arranged in the following order: styrene phosphonic acid > mixture of toluene arsonic acid > benzyl arsonic acid > salts of oxime acid > reagent S-3903 > oleic acid. According to the current state of research and production practice, styrene phosphonic acid and benzyl arsonic acid are the best collectors for cassiterite flotation. They show strong collective power towards cassiterite fines. Therefore benzyl arsonic acid was mainly used as the collector in our flotation tests and styrene phosphonic acid was chosen as the supplementary collector. Test condition were: slurry temperature 23°C, slurry concentration20%frothing agent: 80mg/dm. A constant agitation level was maintained in the flotation machine. Hydrochloric acid and sodium hydroxide were used to regulate the pH of slurry. The result is shown in Fig.2.

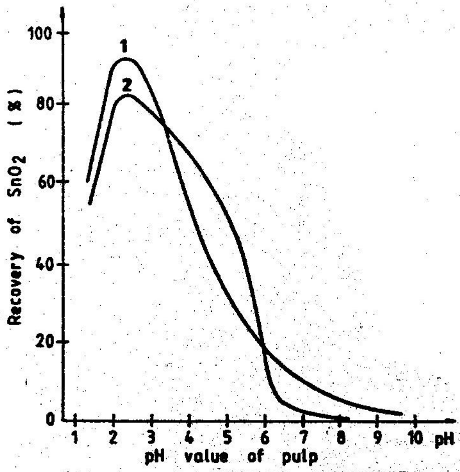

Fig.2 The relationship between recovery of cassiterite and pH value: 1-styrene phosphonic acid (1920 mg/dm^3); 2-benzyl arsonic acid (2240 mg/dm^3)

A satisfactory flotation of cassiterite occured at pH 1.5-3.0 for the two studied reagents. The recovery of cassiterite decreases rapidly when pH is below 4. No flotation occurs at pH>8. Thus, the optimun pH value was around 2 with these two agents. This result corresponds well with the electrokinetic potential of cassiterite.

3.3. Effect of activators on flotation.

In order to investigate the effect of high valency metal ions on floatability of cassiterite, $CuSO_4$ and $Pb(NO_3)_2$ were used as activators for cassiterite and benzyl arsonic acid as collecting agent in our tests. The tests were carried out, under the same conditions as before except that the pH of the slurry was equal to 8. The result is shown in Fig.3.

It is seen from Fig.3 that the activating effect increases (enhances the recorvery). Howerver $CuSO_4$ is more active than $Pb(NO_3)_2$. Even at a high pH (=8), the condition under which cassiterite is not floatable without any activators, floatation can reach 60% when the activators are

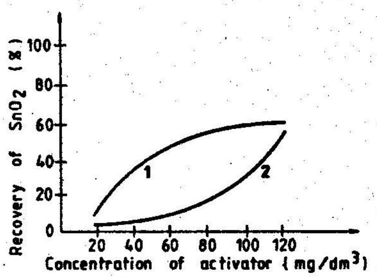

Fig.3 Recovery of cassiterite as a function of the dosage of the activators: 1-$CuSO_4$; 2-$Pb(NO_3)_2$. Collector : benzyl arsonic acid (2240 mg/dm^3)

used. This gives the evidence that added high valency metal activating ions such as Cu^{2+} or Pb^{2+} are adsorbed on the surface of ore grains and decrease the negative surface charge and facilitate adsorption of benzyl arsonic acid on cassiterite surface and cassiterite flotation.

3.4. Effect of depressant on floatability of cassiterite.

In this series of experiments depressants were used. Test conditions were the same as previously. Tests results are shown in Fig.4. All depressants depress the flotation of cassiterite. The inhibiting effect of EDTA is directly proportional to its dosage.

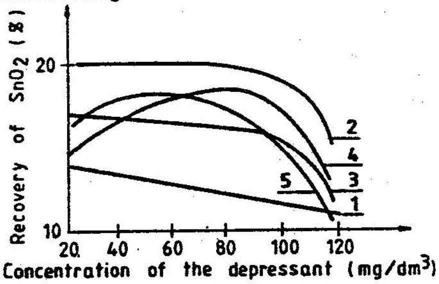

Fig.4 Flotation of cassiterite as a function of the depressant dosage: 1-EDTA; 2-Water Glass; 3-Sodium Hexametaphosphate; 4-Trimeric Phosphonic Sodium; 5-Citric acid.

3.5 .The relationship between activation, inhibition and pH value of slurry to flotation of cassiterite.

Tests conditions were the same as previously mentioned. The results are shown in Fig.5.

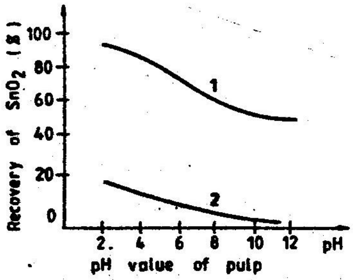

Fig.5 The relation between recovery of cassiterite and pH value when activactor or depresant is added. 1-$CuSO_4$-60mg/dm^3; 2-EDTA-40mg/dm^3.

The activating effect decreases with the increasing pH. When pH < 4 the recovery of cassiterite may be higher than 90%, which is greater than that when only the collector is used (83%). Inhibition effect increases with the increase of the pH value. Cassiterite is not floatable when pH > 11. This result is well confirmed by the electrokinetic potentials shown in Fig.1. So, at a high pH, the flotation of cassiterite can only be accomplished if the activator is used.

A high recovery of cassiterite can be obtained at low pH using arsonic acid as the collector as is shown in Figs.5 and 2. The recovery is even higher if an activator is used . Cassiterite can partially be recovered at high pH (pH > 8) if activators ($CuSO_4$,$Pb(NO_3)_2$) were used in an adequate quantity.

4. Electrokinetic potential measurements

For cassiterite, proper flotation conditions have been found and factors affecting its floatability have been investigated as described above . In order to determine the electrical character of cassiterite surface under previously determined conditions, the following studies were performed.

4.1. Zeta potential and pH value of the slurry.

For investigating the adsorbing nature of collectors on the surface of cassiterite, zeta potential of cassiterite was measured after agitation with the collector and after repeated washing of the sample which had been treated with benzyl arsonic acid. It resulted from our investigations that zeta potential changes only when pH is higher than 4.7 (above i.e.p.), and there is a slight difference in zeta-potentials between washed cassiterite and that cassiterite without the addition of a collector. This and the flotation results indicated that when pH < 4.7, the surface of cassiterite, existing in form of-SnOH, firmly adsorbs benzyl arsonic acid. When pH of slurry is above 4.7, a multi-layer physical adsorption of the reagent on cassiterite occurs, because the layers are easily removed from the surface by washing. According to Fig.1 and 2, when pH of the suspension is below 4.7, cationic surface groups facilitate the adsorption of the anionic collector, and the recovery is high. When pH >4.7, the surface of cassiterite has a negative charge, and its magnitude increases with the increase of pH value up to 7, while recovery decreases steadily. When pH > 7 the SnO_2 surfaces can not adsorb any reagent, and cassiterite is almost un-floatable. This indicates that both chemisorption and electrostatic sorption are responsible for cassiterite flotation. Similar conclusions were drawn by Wottgen (Senior, Poling, 1986).

4.2. Cassiterite recovery and electrokinetic potentials.

The electrokinetic nature of cassiterite surface depends on the pH value of the suspension as indicated in Fig.1. Therefore, an apropriate pH should be chosen to according the appropriate property of the collector for a successful flotation. A low pH value of the slurry can be mantained by using bezyl arsonic acid as the collector for cassiterite. When the pH value is less than 4.7 (below i.e.p) a high recovery can be obtained due to positive charges present on the surface of cassiterite fines. In contrary, when the charge is negative, the recovery rate of cassiterite decreases.

4.3 EDTA and zeta potential of cassiterite surface.

Today, EDTA is a widely used complexing agent. Structuraly, it is an inner-salt type compound and can form stable chelate compounds. Fig.6 shows the influence of EDTA on the zeta potential of cassiterite. It can be seen from this figure that the negative charge on the surface of cassiterite increases with the increase of EDTA, and approaches a constant equal to -22 mV.

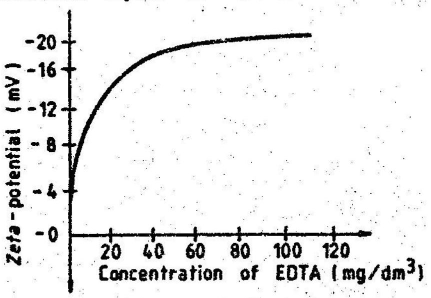

Fig.6 Recovery of cassiterite as a function of Zeta potential.

5. Summary

The following conclusions are possible:
Both styrene phosphonic acid and benzyl arsonic acid are effective collectors for cassiterite flotation a particularly good flotation was obtained at low pH. A small amount of $CuSO_4$ activated cassiterite when benzyl phosphonic acid was used as the collector. EDTA may be used as a depressant in a strong alkaline environment. The isoelectric point of SnO_2 occurred at pH 4.7. At pH<4.7 a strong chemical and electrostatic adsorption of the collector and cassiterite take place while a weak physical adsorption occurs in the pH range of 4.7 - 7.

6. References

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Shi Daomin.,1988. Flotacja kasyterytu a jego powierzchniowe właściwości elektryczne. Fizykochemiczne Problemy Mineralurgii 20; 157-163.

Kwas styrenofosfonowy oraz kwas bezylo-arsenowy użyto do flotacji kasyterytu. Ustalono, że dobra flotacja zachodzi przy niskich pH środowiska wodnego. Małe ilości $CuSO_4$ aktywowały flotację kasyterytu przy pH=8 podczas gdy EDTA działa jako depresant jeśli stosuje się go w środowisku silnie alkalicznym. W pracy przedyskutowano również wpływ stanu elektrycznego powierzchni kastyterytu na jego flotowalność.

СОДЕРЖАНИЕ

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Стиренофосфоновая кислота, а также бензило-мышьяковая кислота применялись для флотации касситерита. Определено, что хорошая флотация происходит при низких pH водной среды. Малое количество $CuSO_4$ активировало флотацию касситерита при pH=8,6, в то время как ЕДТА действует в качестве депрессанта, если он применяется в очень щелочной среде. В работе обсуждено также влияние электрического состояния поверхности касситерита на его флотируемость.