AN EFFICIENT ACTIVATION ON FLOTATION OF FINE ANTIMONY OXIDE

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Abstract  The effects of Mn$^{2+}$ on the flotation behaviour of fine refractory antimony oxide and its flotation separation from silicified limestone were studied. The principal gangue mineral, under the condition of pH=7.5 and in the presence of modified water glass through flotability test, measurements of interracial potential and adsorption, and X-ray diffraction technique were described. The activation mechanism of Mn$^{2+}$ in antimony oxide flotation is fully discussed via modern molecular orbit theory.

Key words  antimony; flotation; activator

Recovery of fine antimony oxide with froth flotation is one of the most difficult problems. The oxide mineral is not only to be slimed easily, but also tends to form colloid in water solution, and to its hydrolysis, on its surface, there exists SbO$_2^-$ in alkaline solution and SbO$_2^+$ in acidic solution.

Up to now, traditional gravity concentration method has been universally used to recover antimony oxide. Now some antimony mills still use shaking table technique, but the recovery is only about 20%. In flotation system, the colloid of antimony oxide is easily adhered on the surface of silicified limestone, and it is difficult to separate them.

1 SAMPLE AND EXPERIMENTAL METHOD

Samples are antimony oxide and silicified limestone obtained from Xikuangshan Mine, Hunan, China, purified by physical separation methods, and finally ground to $-0.076$ mm in pocielian mill. The antimony oxide is 95% pure. Flotation test has been carried out in 30 mL flotation cell for 5 min. Interracial potential is measured with microelectrophorsis of MRK model made in Japan. The adsorption quantity of Mn$^{2+}$ is measured by means of atomic absorption spectrophotometer, then the adsorption density (mol/cm$^2$) calculated. Size analysis of samples is done by laser particle size analyzer Microtrac of model 7991, made in the U. S. A. The specific surface areas of the sample for antimony oxide and silicified limestone are determined.

2 RESULTS AND DISCUSSIONS

2.1 Effect of Mn$^{2+}$ on the Flotation Behaviour of Antimony Oxide

Test shows that when a combined collector containing hydroxamic acid is used, antimony oxide floats readily. The recovery is increased because of the presence of Mn$^{2+}$. However, in the absence of manganous salt, the recovery is only 42%. When the dosage of Mn$^{2+}$ is kept at 30 mg/l, the recovery increases up to 95%. And there exists obvious interrelationship between the increase of antimony oxide recovery with the adsorption density of Mn$^{2+}$ and the change of Zeta-potential. But under the same condition, the effect of Mn$^{2+}$ on the recovery of silicified limestone may be negligible (Fig. 1).

According to the solution chemistry calculation, in Mn (II) solution there may be Mn$^{2+}$, Mn(OH)$^+$, Mn(OH)$_2^{aq}$ and Mn(OH)$_3^-$, etc. Mn$^{2+}$ is counted as 99.97% (pH=7) in the total. Therefore, it may be said that the increase of recovery of antimony oxide is mainly due to the activation of Mn$^{2+}$ on the surface of antimony oxide. Because Mn$^{2+}$ exists as a form of complex adsorption on the surface of antimony oxide.
de, it can change the surface potential of the mineral and consequently enhance the action of collector. X-ray diffraction spectra of flotation concentrate of antimony oxide shows that there are not only Sb$_2$O$_3$ and Sb$_2$O$_5$, but also MnSb$_2$O$_6$ in it (Fig. 2). There exist antimonic acid (HSbO$_3$) and antimonious acid (HSbO$_2$) on the surface of antimony oxide in the solution. According to the theory of coordination chemistry, the electron layer structure of Mn$^{2+}$ (centre ion) is $ls^22s^22p^63s^23p^63d^4$. On the 3d orbit it is unsaturated and the outer layer is empty. When complex adsorption is carried out, a lone pair electron gained from antimonic acid and antimonious acid group can be held, forming a ligand bond. Therefore Mn$^{2+}$ ion is adsorbed easily on the surface of antimony oxide to form a stable complex compound. According to the modern theory of molecular orbit there are 9 orbits of valence electrons for Mn$^{2+}$; 6 orbits of them with 6 orbits of 6 ligands can be made up of 6 bonding molecular orbits ($a_{1g}, t_{2g}, e_g$) and 6 antibonding molecular orbits ($a_{1g}, t_{2g}, e_g^*$); other 3 are nonbonding molecular orbits ($t_{2g}$). They are 6 pr. electrons of 6 ligands entering 6 bonding molecular orbits ($a_{1g}, t_{2g}, e_g$); 5 electrons on the 3d orbits of Mn$^{2+}$ have to enter non-bonding $t_{2g}$ and antibonding $e_{g}^{*}$ orbits (when $P>\Delta_0$, there are 3 electrons entering $t_{2g}$ and 2 electrons entering $e_{g}^{*}$. $P$-paired energy, $\Delta_0$-separation energy).

They all obey the Pauli exclusion principle or Hund's rule, and filled in these orbits, so as to form the complex compound structure of octahedron (Fig. 3). It is essential that Mn$^{2+}$ brings forth the complex adsorption reaction and activation mechanism on the antimony oxide surface. As a result, the surface character of antimony oxide is changed and the collector action strengthened, so the oxide mineral is activated to make flotation more effective in selectivity. It should be pointed out that because of the hydrolysis of antimony oxide, in the flotation pulp the milky colloid may be seen, and it can interfere with flotation separation between antimony oxide and gangue mineral. However, when in the presence of Mn$^{2+}$ in solution the milky colloid may be quickly flocculated and precipitated. Therefore the harmful effect is decreased obviously. This is why Mn$^{2+}$ can enhance the flatability and selectivity of antimony oxide.

Fig. 1 The effect of Mn$^{2+}$ on the flatability of antimony oxide and silicified limestone

(a)—Effect of Mn$^{2+}$ on the flatability of antimony oxide and silicified limestone
(b)—Amount of adsorption and Zeta-potential of mineral as a function of concentration of Mn$^{2+}$

Fig. 2 X-ray diffraction spectra of flotation concentrate of antimony oxide

Fig. 3 Energy level diagram of molecular orbits of Mn$^{2+}$ and HSbO$_3$ or HSbO$_2$ group role on the surface of antimony oxide