

YANG AO\*

## THE INFLUENCE OF GRINDING AIDS ON THE FLOATABILITY OF THE FINE CASSITERITE

The article presents the study of the grindability of cassiterite and discusses the relationship between grinding additives and the floatability of the cassiterite. The addition of surface activator and inorganic electrolyte is helpful in the reduction of grinding energy consumption and in the increase of grinding efficiency, but it is limited to certain conditions. Among the five grinding aids, which we used in our tests, surface activators such as ammonium acetate, benzyl arsenic acid and copper sulphate, had promoting grinding function only at concentration of 0.05 kg/Mg. Sodium hexametaphosphate was helpful for grinding only at concentration of 0.5 kg/Mg. Sodium trimetric phosphate can be helpful at different concentrations but it produces the best results at concentration of 0.05 kg/Mg. Among the above five grinding aids benzyl arsenic acid appeared to be the best one and the next was sodium tripolyphosphate. When benzyl arsenic acid was applied as a collector for cassiterite flotation in our experiments, efficiency was much higher than the flotation productivity while adding grinding aids. Therefore, we think it is better not to use the grinding aids in that case.

### INTRODUCTION

Today, the main problem in tin ore processing is its low grade (0.01–1% Sn abroad and 0.01–0.5% in China), fine embedding grain size (75% cassiterite embedded in –44  $\mu\text{m}$  grain size) and the difficulty in separation the cassiterite from gangue (being difficult to recover –19  $\mu\text{m}$  and the percentage of the loss in tailings on gravity separation is 30–50%) (Trahar 1976). To solve this problem, the principal way is to process the ore by flotation after fine grinding, i.e. flotation of the fine cassiterite. However, fine grinding is a process which has the lowest energy efficiency. It consumes more energy and thus increases the cost of grinding. On the other hand, it creates the particle size too fine and brings about difficulties in flotation. Therefore, the study of grinding conditions under which we can achieve a rapid liberation, a high efficiency in grinding, and good results in flotation will be of great significance in the flotation of cassiterite.

This article starts with the study of the grindability of cassiterite and then discusses the relationship between grinding additives and the floatability of cassiterite.

There are two points of view on the grindability of cassiterite. One is that the hardness of cassiterite,  $f$ , should be in the range of 6–7. According to the general classification of the grindability of ores, if  $f$  is less than 8, an ore is regarded as easy to

---

\* Kunming Institute of Technology, 38 Bei Huan Road, Kunming, Yunnan, China 650093.

be ground. So cassiterite is brittle, easy to be ground and easy to be slimed. The other viewpoint is that as the crushing work index of the cassiterite is  $W_i = 10.81 \text{ kW} \cdot \text{h/t}$  (Zeng 1983), it is recognized of middle grindability. According to the general classification of ore grindability, for  $W_i = 10-14$  the grindability of an ore is identified as middle. Nevertheless, it is to be noticed that recently there is another viewpoint which holds that fine cassiterite is an ore which is rather difficult to be ground. The same conclusion has been reached both from the mass production in the plants and in laboratory testing, which utterly alters the previous viewpoints.

Since numerous investigators claim that cassiterite is easy to be ground and crushed, not enough attention has been paid to the addition of grinding additives and to its functional mechanism.

This article is a valuable study on the grindability of the cassiterite, its grinding aids and their influence on the floatability.

## TEST MATERIALS, REAGENTS, EQUIPMENT AND INSTRUMENTS

### 1. Test materials

Cassiterite; produced in Wenshan County, Yunnan province. Composition: 74% Sn, 4.3%  $\text{SiO}_2$ , 0.1% CaO, 0.04% MgO.

Quartz: from the Can Zhuang Gold Mine in Zhao Yuan County, Shandong province.

### 2. Reagents

The grinding aids: ammonia acetate, sodium tripolyphosphate, sodium hexametaphosphate, copper sulphate, chemical pure, available on the market. The benzyl arsenic acid was provided by Zhuxhou Flotation Reagent Plant.

The collector: benzyl arsenic acid with the concentration of 1%.

The frother: pine oil emulsified with alcohol with the concentration of 1%.

### 3. Equipment and instruments:

Ball mill driven by double-roller with the volume of 500 ml.

Flotation machine: Type XFG-80 suspending cell type flotation machine made in Chang Chun Exploring Machinery Plant.

## EXPERIMENTAL

### Investigation on the grindability of cassiterite

#### a) The sieve analysis of cassiterite and quartz.

As quartz composition is steady and it is easy to get, the grindability of ore is generally compared with that of quartz (Duan 1981). Figure 1 shows the result of the sieve test on cassiterite and quartz.

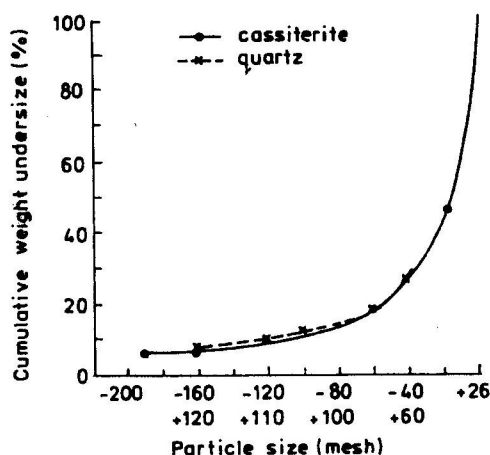


Fig. 1. Analytical curve of the sieve test on cassiterite and quartz

b) The determination of grindability of cassiterite and quartz:

The results of experimental reference examination are shown in Figs 2 and 3. It can be seen from the figures that with an increase of the grinding time, the grain size becomes finer and the quartz curve does not increase as much as the cassiterite curve. This shows that cassiterite is easier to be ground and crushed. Thus the viewpoint that cassiterite is hard to be ground and crushed has its limitations, as can be proved either by  $-0.074$  mm grain size curve or by  $-0.04$  grain size curve. The above viewpoint can only be adapted to the particular ore being studied. From the figures it can also be seen that rougher grains, in comparison, are easier to be ground than fine grains.

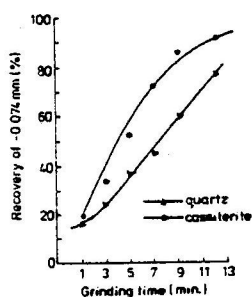


Fig. 2. The comparison of grindability of cassiterite and quartz (I)

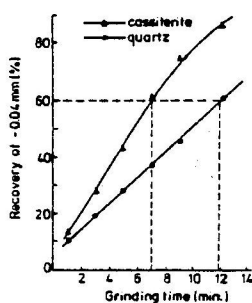


Fig. 3. The comparison of grindability of cassiterite and quartz (II)

### The influence of concentration on the fines of the ore being ground

During grinding, water is to be supplied to the ore to provide the required solid/liquid ratio. The efficiency of grinding becomes low without water addition. It is

reported in a number of literature that wet grinding is more effective than dry grinding. The grinding efficiency in moist air was found to be higher than that in vacuum. More fine grain size will be produced during grinding with tap water than with distilled water (Li 1982). This is because the fine grain continues to be in the state of suspension in water, and the buffering action produced in the fine grain layer is smaller in water than in dry grinding, and because there are various kinds of ions present. Lin and Mitzmager think that the function of water is due to the reversal action between the unsaturated surface bond of grain and the water molecules (Somasundaran 1983).

It has been reported (Klimpel 1977) that before grinding, the ore should be immersed in water for some period of time to improve the effect of subsequent grinding. This is because water penetrates into the porous zone of the ore grain and promotes further crushing action. Therefore we chose wet grinding for our research tests and performed our experiments at different slurry concentrations. The result of our experiment shows that the concentration of slurry has an influence on the grinding process. When the concentration of solid in pulp is below 75%, with the increase of the concentration the resultant grain size becomes small, when it is over 85%, the grain size does not become finer.

In a certain range of slurry concentration, with the increase of pulp concentration the ore grains are relatively packed, which increases effective strike of the ball of ball mill, and the striking kinetic energy will be transferred to crushing energy to the utmost. If the concentration is increased further, ore grains become packed too much, and a part of ore grains is struck so lightly that they could not be crushed. Besides, as the viscosity of the slurry is too high, a certain amount of resistance is thus produced and slows down the rolling and rotation of the balls. A part of kinetic energy is then turned into the heat of sticking friction and the efficiency of grinding is considerably reduced.

### **The effect of grinding aid on the formation of fines during grinding**

Surface activator is an efficient grinding aid, and its function was widely reported. For example, the addition of 0.3% Flotigan-P has increased the specific surface area of quartz and limestone two times. The use of ammonium salt can also improve the grinding effect of quartz, but if oleic acid is used as grinding aid, it will lead to the reduction of the surface area.

Adding inorganic electrolyte is also beneficial in grinding. It effects the hardness of the solid material and also has an impact on the flocculation and dispersion of grains. Nevertheless, its addition makes the grinding process worse, according to other reports.

The grinding aids we use in this work are of two kinds. First is an organic surface activator including ammonium acetate and benzyl arsenic acid. The other one is an inorganic electrolyte including sodium tripolyphosphate (STPP), sodium hexametaphosphate (SHMP) and copper sulphate. The result of grinding experiments with various concentrations of additives are given in Table I.

According to Table I, the organic surface activator and copper sulphate can be efficient only when used in small quantity (0.05 kg/Mg). If used in large quantity, the effect of additive decreased. Effective quantity for sodium hexametaphosphate is only

0.5 kg/Mg, otherwise it will be less effective. Sodium tripolyphosphate can be used in any quantity. Of course, it is more effective when used in a small quantity (0.05 kg/Mg). Among the five grinding additives mentioned above, benzyl arsenic acid gives the best results when used in the quantity of 0.05 kg/Mg. Sodium trimeric phosphate has an inhibitive effect on cassiterite in flotation process, whereas benzyl arsenic acid is the best grinding aid.

Table 1. The experimental results of the addition of various kinds of grinding aids during grinding

Dosage	-0.075 mm grain size productivity, %					-0.04 mm grain size productivity, %				
kg/Mg	ammo- nium acetate	benzyl arsenic acid	sodium tripoly- phosphate	sodium hexameta- phosphate	copper sulpha- te	ammo- nium acetate	benzyl arsenic acid	sodium tripoly- phosphate	sodium hexameta- phosphate	copper sulpha- te
0.05	71.36	75.00	74.83	62.97	71.54	62.15	63.71	63.88	60.89	61.14
0.1	70.73	64.15	71.79	68.15	71.03	62.13	53.95	61.94	54.89	61.51
0.5	68.81	61.92	73.32	73.20	69.83	60.23	52.62	64.48	63.63	59.34
1.0	67.47	58.00	71.23	70.52	69.70	60.09	48.34	61.97	50.32	59.20
1.5	64.19	53.49	70.95	66.36	69.49	59.09	52.34	62.48	58.16	58.17
0.0	70.53						60.09			

In Japan, ammonium acetate is commonly used and its grinding effect is satisfactory (Somasundaran 1983). It was effective only in small quantity in our experiment, which corresponds with R. Klimpel's opinion about surface activator. He thinks that each grinding aid has its limited concentration and that it will have less effective influence on the fines of the ore when it exceeds its optimal concentration. Some data (El-Shall et al. 1979) show that sodium silicate, sodium tripolyphosphate, and sodium hexametaphosphate reduce the grinding effectiveness when their pH is 10.5 in aqueous alkali but they have no obvious influence when pH is other than 10.5. Results of our experiments differ from the above conclusion. In our experiments, sodium tripolyphosphate has its grinding effect at various concentrations, but other grinding aids have their grinding effect only at a certain concentration. It was also shown that each grinding aid has its promoting effect in grinding of the specific ore only in a certain range of pH.

As surface activator has both polar and non-polar radicals, it is preferentially adsorbed on the mineral surface in the pulp and thus lowers the surface tension of the grain during comminution. As its free energy is reduced, so it is possible for the surface active material to penetrate into the fine cracks and go deeper into it, producing a chopping and splitting effect, just like wedging into a crack (Karmazin 1975). As the grains adsorb surface active species, they do not attach each other easily and the grain surfaces are smooth, easy to roll, to be ground off and to be hammered by the balls. Rebinder once said that if the surface free energy of a solid was reduced for some reason, the same amount of energy could be used to produce more surface area and reduce the possibility of surface recombination. Microbubbles may occur in the grinding process and they can be stabilized by the added surface active compounds.

These compounds adsorb as a surface activator and make the surface hydrophobic and grain can attach to the microbubbles. Therefore, the grains float up and the efficiency is lowered indirectly. The similar results observed Malat during his experiments in a wet rod mill.

The function of phosphate is such that when mineral surface adsorbs hydrolytic ions of phosphate, the transfer of dislocation of mineral surface occurs. Precipitation of complex calcium or magnesium phosphates takes place in the presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in the pulp. Subsequent adsorption of these species creates the surface tension leading to the decrease in solid hardness.

The copper sulphate hydrolyzes to copper ion and hydroxy copper ion which are adsorbed on the surface of cassiterite and, consequently, decrease the electronegativity of this mineral. According to the statement of Engleman and his colleagues and Westwood (1968), the hardness of solid depends on zeta potential. That is why when electronegativity decreases, the hardness of cassiterite is also reduced and the mineral becomes easier to be ground.

The addition of chemical grinding additives can raise the efficiency of crushing due to the following reasons:

- (1) Adsorption causes the change of surface free energy.
- (2) Adsorption causes the transfer of dislocation of lattice on the near surface.
- (3) The grinding aid can change the flow of pulp in the grinding process thus making newly-created fine grains coagulate again ( El-Shall 1979 ).
- (4) The pulp can produce frothiness during grinding process.
- (5) Mutual actions between balls and grains can occur.

### The effect of grinding aids on the floatability of cassiterite

1. Table 2 shows the effect of various grinding aids on the floatability of cassiterite in the experiments carried out under the following conditions: grinding pulp concentration – 65%, grinding time – 5 minutes, concentration of benzyl arsenic acid – 2240 mg/dm<sup>3</sup>, pH 2.7.

Table 2. Effect of grinding aids on floatability of cassiterite

Grinding aids	Dosage of aids kg/Mg	Grinding productivity, % of -0.074 mm	Grinding productivity, % of -0.04 mm	Flotation productivity, %
Water	0	70.53	61.09	51.60
Ammonium acetate	0.05	71.36	62.15	26.40
Benzyl arsenic acid	0.05	75.00	63.71	58.00
Sodium tripolyphosphate	0.50	73.32	64.48	17.80
Sodium hexametaphosphate	0.50	73.20	63.63	9.60
Copper sulphate	0.05	71.54	61.14	26.18

It is seen from Table 2 that during the cassiterite flotation, the productivity of floating products decreases with the addition of grinding aids, except of benzyl arsenic

acid. Among them sodium hexametaphosphate creates the most pronounced decrease. Less decrease was observed for sodium tripolyphosphate. It is also shown that inorganic electrolyte, sodium tripolyphosphate, and sodium hexametaphosphate are simultaneously dispersants and depressants. They are more or less helpful in grinding but they cause cassiterite to be hydrophilic and thus decrease the surface tension in the pulp and the floatability of cassiterite (Wang 1977). Copper sulphate, though it can activate cassiterite, needs a long time to be helpful in grinding and the activating part combines with hydrophilic ions, decreasing the floatability of cassiterite. Only benzyl arsenic acid appeared to be both the grinding aid and the collector of cassiterite. It reduces not only grinding work consumption but also remarkably raises the floatability of cassiterite.

2. The effect of concentration of collector on the floatability of cassiterite in the presence of grinding additives.

The experimental results at benzyl arsenic acid concentration of 50 mg/Mg, grinding pulp density of 65%, grinding time 5 min., and pH 2.7 are shown in Fig. 4.

It is seen from Fig. 4 that it is the best to select the collector with the concentration of 2240 mg/dm<sup>3</sup>. Productivity can be increased from 51.5% to 58%. Above or below this concentration, the flotation not only changes but also becomes depressed. Considering the past experiments, we can achieve no better result than that observed at the collector concentration of 2240 mg/dm<sup>3</sup>.

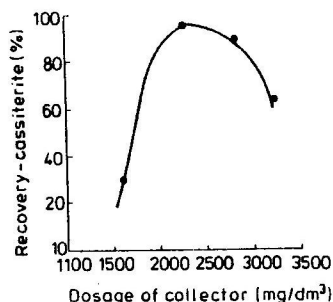


Fig. 4. Effect of dosage of collector on the flotation productivity when grinding additive is added

## Research on the floatability of ground products

### 1. Flotation experiments and products

For the following experimental conditions: tested materials – 5 grams, concentration of slurry – 65%, benzyl arsenic acid concentration in flotation – 2240 mg/dm<sup>3</sup>, and pH 2.7, grinding time and fines are to be tested if the former is changed. The result is that fines is increased as the time of grinding prolongs, which results in the increase of flotation productivity of cassiterite. It can be as high as 92.7% after 15 minute grinding, and –200 mesh grain size productivity is 96%. But then it goes down, to 63.2% after 16 minutes grinding when –0.074 mm (–200 mesh) productivity is 98.1%.

### 2. The effect of collector concentration (benzyl arsenic acid) on floatability of cassiterite

For the following experimental conditions: 5 grams of the ore, grinding time – 15 min., concentration of solid – 65%, and pH 2.7, different amounts of benzyl arsenic acid are added during the experiments. When the concentration of benzyl arsenic acid is

1000–3200 mg/dm<sup>3</sup>, the productivity of cassiterite is about 70% and even 92%, and when the above concentration is surpassed, the productivity decreases (compare Table 2 with Fig. 4). It is shown that when grinding aids are added at the fixed collector concentration, the productivity can be as high as 58% and when different amounts of the collector are added at the fixed concentration of grinding aids, the best productivity is 58%, too. Without grinding aids, the productivity can reach 76% when the concentration of benzyl arsenic acid is 2240 mg/dm<sup>3</sup> and the productivity is 92.7%. Therefore from these experiments we can come to the conclusion that it is better not to use grinding aids as far as cassiterite productivity is concerned. Besides, it can lower the cost of reagents.

### 3. The effect of pulp pH on cassiterite floatability

For the following experimental conditions: grinding time – 15 min., concentration of pulp – 65%, reagent concentration – 2240 mg/dm<sup>3</sup>, the experiments show that the effect of pulp pH on cassiterite is obvious. The cassiterite floatability is better in acidic pulp than in approximately neutral pulp which corresponds with our past experiments.

## CONCLUSIONS

1. Comparing cassiterite with quartz, the former is easier to be ground and crushed. The idea that cassiterite is difficult to be ground and crushed can only be limited to some particular or individual ore. Obviously, rough grains are easier to be ground than fine ones.

2. Wet grinding is more efficient than dry grinding. Different water content leads to the different grinding results: the more water is added, the better are the results of grinding. There is an optimum water content of 70–80%, while above or below this percentage the results were much worse.

3. The addition of surface activator and inorganic electrolyte is advantageous in the reduction of grinding energy consumption and in the increase of grinding efficiency, but this effect is limited to certain conditions. Grinding aids (surface activators) such as ammonium acetate, benzyl arsenic acid and copper sulphate exhibit grinding improvement only at low concentration (0.05 kg/Mg). Sodium hexametaphosphate is beneficial in grinding only at concentration of 0.5 kg/Mg. Sodium tripolyphosphate can be helpful at different concentrations but it produces the best result at 0.05 kg/Mg. Among the above five grinding aids benzyl arsenic acid is the best one, the next is sodium tripolyphosphate. As it has the function of restraint on cassiterite, so it is better to use benzyl arsenic acid as its grinding aid.

4. The addition of grinding aids has effects on the floatability of cassiterite. The foam products in flotation are better dealt with benzyl arsenic acid. The other four aids have less effects to some extent. Among them sodium hexametaphosphate and sodium trimeric phosphate have least effects.



5. From the experiments on the influence of concentration of collector on flotation it is shown that the best collector concentration is 2240 mg/dm<sup>3</sup> with or without the addition of grinding aids. But, when grinding aid is added, the productivity can be raised from 51.6% to 58%. Other amounts of collector cannot change its flotation activation or can even cause depression.

6. The grinding fines of cassiterite is increased with the increase of grinding time and flotation productivity increases with the increase of fines. But it can reach no more than 92.7% for the following conditions: grinding time 15 min. and -0.074 mm (-200 mesh) grain size productivity is 96%.

7. When grinding time is 15 min., the examination of the concentration of benzyl arsenic acid shows that cassiterite flotation productivity is above 70% or even as high as 92%, provided that the concentration of benzyl arsenic acid is 1600 mg/dm<sup>3</sup>. Much higher efficiency of the flotation was observed when grinding aids were introduced. Thus, from our experiments we think that it is better not to use grinding aids. In addition, reagent concentration can be reduced and the cost can be lowered.

8. Generally, when pH was within the range of 2-4, the most satisfied results were obtained.

#### REFERENCES

- DUAN XIXIANG (1981), Yunnan Metallurgy, No. 2, pp. 17-26.
- EL-SHALL H., GORKEN A., SOMASUNDARAN P. (1979), *Effect of chemical additives on wet grinding of iron ore minerals*. Proceed. of XIII Intern. Mineral Process. Congr., (Warsaw), Vol. 1, ed. J. Laskowski, Elsevier, p. 695-726. pp. 451-481.
- EL-SHALL H., VIDINAGE S., SOMASUNDARAN P. (1979), *Grinding of quartz in amine solutions*. International Journal of Mineral Processing, Vol. 6, No. 2, pp. 105-117.
- KARMAZIN V.V. et al. (1975), *Study of some trends in selective grinding and their application to processing of fine-disseminated iron ores*. Proceed. of XI Intern. Min. Process. Congr., (Cagliari), special volume, Ente Minerario Sardo, pp. 11-33.
- KLIMPEL R., MANFROY W. (1977), *Development of chemical grinding aids and their effect on selection for breakage and breakage distribution parameters in the wet grinding of ores*. Proceed. of XII Intern. Mineral Process., Congr., (Sao Paulo), Meeting 1, Paper 3, Proceed. ed. D.N.P.M., Sao Paulo 1980, Vol. 1, pp. 65-91.
- LI QIHENG et al. (1982), Journal of Kunming Institute of Technology, No. 1, pp. 82-93.
- SOMASUNDARAN P. (1983), Journal of Central South Institute of Mining and Metallurgy, No. 2, (Supplement), pp. 185-194.
- TRAHAR W.J., WARREN L.J. (1976), *The floatability of very fine particle - a review*. International Journal of Mineral Processing, Vol. 3, No. 2, pp. 103-131.
- WANG WENQIAN (1979). Non-Ferrous Metal, No. 1, pp. 22-29.
- WESTWOOD A. R. C. (1968), *Effects of adsorption on hardness and the mobility of near-surface dislocations in non-metals*. Chapter in: *Advances in Materials Research*, 2, Microplasticity. New York, Interscience Publisher, pp. 365-382.
- ZENG XIANBIN (1983), Metallic Ore Dressing Abroad, No. 3, pp. 11-14.

**YANG AO, (1994), Wpływ środków wspomagających mielenie na flotowalność zawiesin kasyterytowych. *Fizykochemiczne Problemy Mineralurgii*, 28, 37–46 (English text)**

Badano wpływ różnych substancji, znanych jako wspomagające rozdrabnianie, na mielenie i flotację kasyterytu. Wiadomo, że dodatek pewnych środków powierzchniowo-czynnych lub elektrolitów nieorganicznych wpływa na zmniejszenie zużycia energii potrzebnej do rozdrabniania oraz może zwiększać skuteczność tego procesu. Zjawisko to występuje jedynie w ściśle określonych warunkach. Przebadano 5 substancji, które okazały się pomocne w procesie mielenia przy różnym ich dozowaniu do procesu. Dodatek octanu amonu, kwasu benzyloarsenowego i siarczanu miedzi wykazywał skuteczność jedynie w ilości 0,05 kg/Mg. Heksametrafosforan sodu okazał się skuteczny jedynie w ilości 0,5 kg/Mg. Trójpolifosforan sodu był natomiast skuteczny w różnych stężeniach, ale najlepsze wyniki gwarantował przy dozowaniu go do mielenia w ilości 0,05 kg/Mg. Najkorzystniejsze działanie wspomagające mielenie wykazywał kwas benzyloarsenowy, a następnie trójpolifosforan sodowy. Zauważono jednak, że podczas stosowania kwasu benzyloarsenowego jako kolektora we flotacji kasyterytu wszystkie badane substancje dodawane uprzednio do mielenia wpływały niekorzystnie na wyniki flotacji.