Fizykochemiczne Problemy Mineralurgii, 20 (1988) 145—156

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EFFECT OF γ-RAY IRRADIATION ON THE FLOATABILITY OF FINE CASSITERITE AND HEMATITE

The present paper describes the floatability of fine-grained cassiterite, hematite, and quartz, irradiated by γ-ray. First, we irradiated the minerals by Co-60. Then we made the flotation experiment, investigated the effect of irradiation on flotation, and explored the possibility of separating the minerals. We also studied the mechanism of the process by measuring the adsorbed amount of the flotation reagent, the zeta-potential, and the specific magnetization coefficient. The outcome of the research shows that the γ-ray irradiation can improve the effectiveness of separating cassiterite, hematite and quartz. As a new process of ore dressing it could find a wide application.

1. Introduction

Forty years ago gravitational methods were the only way to collect cassiterite effectively. Hovever, its result on recovering tinstone was so bad that sometimes no cassiterite could be recovered. In the last twenty years, the flotation method has been adopted and good results in recovering fine cassiterite have been achieved. Flotation on tin ore has not only been adopted in the field of experimental research but is also applied in the main process of big scale production.

To improve the flotation results and strengthen the flotation process, research is being made into the flotation mechanism, flotation reagent, working system and technological process on one hand (Yang Ao, 1982), and new technological processes and methods on the other hand. For example, selective flocculation is a new process of separation of fine divided minerals. Besides, based on ionizing irradiation sources, mineral processing combined with nuclear physics is also the latest method to process minerals (Tatarenkov, 1974) .

The study of mineral processing through nuclear physics began in

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the 50's and it was applied to industry in the 60's. Up to now, due to the varying degrees of the development of this processing, some have been or are going to be used in industry; others are still in the stage of experimentation and research (Zhang Wen-bim, 1981), but it can be predicted that mineral processing by nuclear physics will be applied more and more to non-ferrous metals, coal and other raw material processing (Yu Xiao-zhong, 1981).

According to its characteristics, nuclear physical mineral processing can be divided into four kinds: absorbtion, separation by detection of primary radiation, scattering radiation and other kinds of radiation which occur during the atomic interaction of the matter, and separation by prompt detection of radiation of nuclear reaction. In the process of flotation, absorption is mainly used.

There are three kinds of radiation sources in the irradiation of ores. They are isotopic sources, reactor sources and accelerator sources. The isotopic sources can be further divided into α, β, γ and neutron sources. Isotopic sources are often used in flotation processes and its theoretical study. Among these sources γ sources are mainly used. Of the ten common γ sources Co-60 is most of then used (Jian Bai-xi, 1981).

The reason why Co-60 is an ideal radiation source is that it has the following advantages: like other γ sources it is a kind of high energetic photon stream irradiated during nuclear decay. It is a nuclear particle and is also an electromagnetic wave. It transfers with light speed. It has a short wave-length and strong penetration. Besides, Co-60 is available at home and abroad. It can be used in industry. Its half-life is rather long (5.25 years). Quantum γ has the highest energy (1.17-1.33 million electron volt). When in use it does not make the irradiated ore produce radiation. It can be operated from a distance and its price is the cheapest compared with other γ sources (Horn, 1974).

This study is to use Co-60 (1.25 mililion electron volt) as source of radiation to irradiate fine cassiterite and its associated hematite and quartz. Then the flotation process, mineral absorption of the reagent and streaming potential are used to study the effect of radiation on floatation, to explore a new process of separating fine cassiterite and to look for the possible mechanism of flotation.

2. Materials, reagents, equipment and method

2.1. Materials

Cassiterite, hand-picked coarse grained crystal mineral, produced in Wenshan Country, Yunnan Province. Composition: 74% Sn, 4.3% SiO_2, 0.1% CaO, 0.04% MgO.

Hematite, produced in Wang Jia Tan Mine of Kunming Iron-Steel Corporation. Composition: 67.2 Fe, 3.7% SiO_2, 0.1% Al_2O_3, 1.0% CaO, 0.2% MgO.

Quartz, supplied by Yunnan Iron-Alloy Plant. Composition: 97.8% SiO_2, 0.23% CaO, 0.2% MgO.

All these minerals were ground separately in the pebble mill to -20 mesh (over 95%). To increase the purity, the sample of cassiterite was treated in hydrochloric acid, and then purified in distilled water until the pH was neutral.

2.2. Reagents

Styrene phosphonic acid: the effective content is more than 80%. Heat it when dissolved and make 1% concentration for use. Oleic acid: pure in chemical content. Use alcohol to dissolve it and dilute with water to 1% concentration. Pine oil: Dissolve it with alcohol and dilute with water to 1% concentration for use.

2.3. Equipment

Zeta-potential Analyzer, Type ZP-10B, manufactured by SHIMADZU Corporation, Japan. Irradiation Source: Co-60 Medico-Irradiation Meter, made by Shanghai No 2 Medical Instrument Factory.

2.4. Method

Cassiterite, quartz and hematite should be processed in a flotation cell before and after irradiation. The pulp temperature is 25°C and the pulp concentration is 25%. The pulp is added with reagent and is stirred and floated. The product is dried and weighed. The flotation effect is shown as productivity.

The measurement of absorption: Use the method of acid-sulfuric acid macro analysis of phosphate to measure the absorption of the collector on the mineral surface.

3. A study on the effect of γ-ray irradiation on the flotability of fine cassiterite and its associated minerals

3.1 The determination of floation factors

According to the effect of the study made before, when styrene phosphonic acid and oleic acid are used for the flotation of cassiterite, with a hematite and quartz system as the collector, the amount of styrene phosphonic acid is 1920, 1280, 1600 mg/l, respectively. In the flotation of cassiterite, oleic acid quantum is 400 mg/l. Pine alcohol oil quantum is 80 mg/l. The flotation machine runs at 2800 rev./min; pH of pulp is 3-4.

3.2. The influence of the dose of γ-ray irradiation on the flotation of cassiterite

When γ-ray irradiation is applied there are many factors which influence the property of flotation, such as the variety of minerals which determines the property of ores, the form of crystallization, the types and density of lattice defects, the electronic structure on mineral surfaces and the characteristics of irradiation source, depending on the circumstances of irradiation, irradiation dose, the percentage of the dose and irradiation conditions (Kittel, 1979). But irradiation dose is the most influential and can be controlled and made use of. So this investigation is primarily made on the effect of irradiation on flotation. When the irradiation dose reaches 70 rad/min, the results of the experiment are shown in Fig. 1 and Fig. 2.

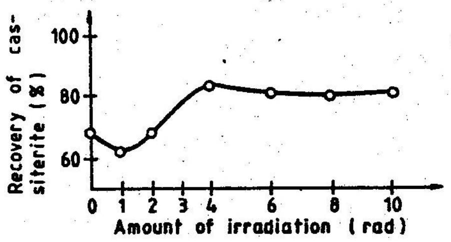

Fig. 1. Effect of amount of irradiation on the flotation of cassiterite.

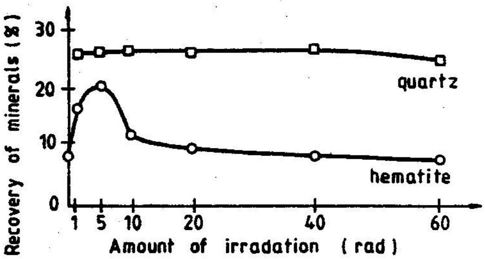

Fig. 2. Effect of amount of irradiation on the flotation of hematite and quartz.

From Fig. 1 it may be seen that under the same percentage of irradiation dose different irradiation doses have different effects on the behavior of cassiterite flotation. When the dose is small, the recovery percentage of cassiterite decreases as the irradiation dose increases. When the irradiation dose is 1000 rad, the recovery percentage decreases from 68% to 63%. After that, the recovery percentage of cassiterite increases as the dose rises. The recovery is the highest when the irradiation dose reaches 4000 rad (15% higher than before irradiation). Then the recovery is steady after the irradiation dose is further increased.

In Fig. 2 it may be seen that when hematite is under a small irradiation dose (below 500 rad) the percentage of flotation recovery rises as the dose increases. The best recovery occurs under the dose of 500 rad (rising from 8% to 21% as compared with that before irradiation). Then the recovery decreases if the dose further increases. When the dose comes over 2000 rad the recovery of hematite is almost 10%.

In Fig. 2. it may be also seen that no matter how large the dose is the recovery of quartz is almost the same after irradiation.

3.3. The influence of irradiation dose rate on mineral floatation

Here the irradiation dose rate means the increment of irradiation dose per unit interval. The dose rate has an effect on mineral flotation. The effect differs with different kinds of minerals. The dose rate changes with the adjustment of the distance between the cobalt source and the irradiated object. If the fixed irradiation dose is 2000 and 4000 rad, the distance should be adjusted accordingly to 45, 50, 55, 60, 65 and 70 cm. Then calculate with the formula concerned and the corresponding dose percentage is obtained.

The flotation effects on cassiterite, hematite and quartz under different irradiation dose percentages are shown in Fig. 3.

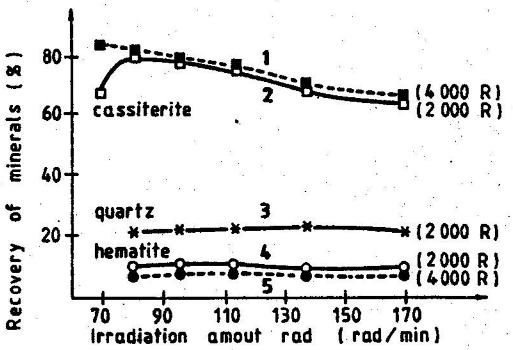

Fig. 3. Effect of irradiation amount rate on mineral recovery.

Curve 1 and Curve 2 in Fig.3 show that the recovery of cassiterite is rather low when the dose (2000 R) is as small as 70 rad/min, and that the recovery of cassiterite first rises and then falls a little as the dose rate rises but its range is small (less than 10%). From Curves 3, 4, 5 it is visible that no matter how much the dose is, the change of the dose rate has no obvious effects on the flotation of hematite and quartz. This also indicates that under the same irradiation dose the change of the dose rate percentage has little or no influence on effect, i.e. when under the same irradiation dose, the effect of mineral flotation is the same on the whole.

3.4. The influence of mineral lay-aside time on flotation after irradiation

Generally speaking, mineral lay-aside time after irradiation has some influence on cassiterite flotation which is shown in Fig. 4. In Fig. 4 Curve 1 indicates some decrease in the cassiterite recovery as the lay-aside time is prolonged. Curve 2 indicates a little increase in the recovery of cassiterite as the lay-aside time is prolonged. But its value is small whether rising or falling. So we can say that the time effect of cassiterite after irradiation is steady. At least it has no obvious influence on floatation over half a month.

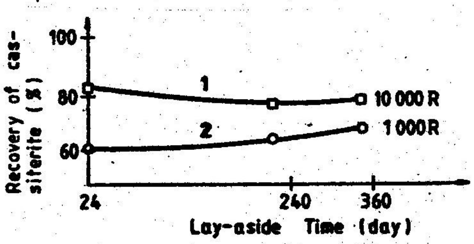

Fig. 4. Influence of the cassiterite lay-aside time after irradiation on its flotation

3.5. The study of the rate of mineral flotation

In order to know the effect of irradiation on flotation we have studied the change of the mineral flotation rate before and after irradiation. The result is shown in Fig. 5. Figure 5 is drawn by means of sectioning the flotation forth. It take 1 min for the forth to collect in the front four sections and 2 min in the back two sections. As it is shown in Fig. 5, there is an obvious change in the flotation effect and flotation rate on cassiterite and hematite after irradiation but only a slight difference on quartz after irradiation.

Fig. 5. The change of the mineral flotation rate before and after irradiation.

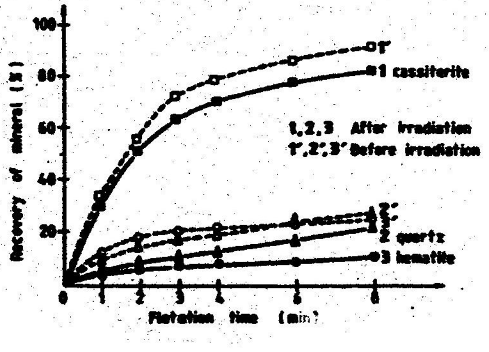

Fig. 5 also shows that after irradiation there is a big difference in flotation effects and rates among cassiterite, hematite and quartz, which shows that irradiation is helpful in the separation of cassiterite and hematite.

3.6. Tests on the separation of the two products

In order to further investigate the effect of the separation experiments have been made on tin-iron mixed materials of which the proportion of SnO_2 to Fe_2O_3 is 3:2.

The result is as follows:

Table 1.

The results of separating the two products

Reagents	Amount of irradiation (rad)	Products (concentrate)	Mineral recovery (%)	β_{Sn} (%)	β_{Fe} (%)	ε_{Sn} (%)	ε_{Fe} (%)
Styrene Phosphonic acid	4000	Cassiterite Iron	56 44	52.65 34.63	19.31 35.58	66 34	40.8 59.2
	0	Cassiterite Iron	52 48	49.82 35.64	22.33 34.64	60.23 39.77	41.11 58.89
Oleic acid	4000	Cassiterite Iron	84 16	44.31 35.96	27.90 36.18	86.62 13.38	80.19 19.81
	0	Cassiterite Iron	66 34	48.61 36.05	24.54 34.68	72.65 27.65	57.88 42.12

From Table 1 it is visible that with styrene phosphonic acid as the collector, the index after irradiation is better than that without irradiation. Especially in the difference between the tin concentrate index before separation and after irradiation there is a striking contrast.

With oleic acid as the mixed test of the material of the collector. although the grade of tin concentrate seems a little higher (from 72% to 86.6%) the grade of iron falls a little and it is evident that iron and tin have been combined. The recovery ratio of iron concentrate is raised but the grade of iron decreases. This shows that oleic acid and styrene phosphonic acid both are collectors for the tin mineral and they also have the effect of collecting for the iron mineral. The oleic acid has no selective effect on tin and iron while styrene phosphonic acid has an alternative effect on cassiterite, which is obviously shown i. single mineral flotation. As shown in Figs 2, 3, the recovery of hematite with styrene phosphonic acid as its collector is 10-20%, but with oleic acid the recovery of hematite has been reparted at 50-60% in some literature.

The index shown in Table 1 is not high because no activator or depressant has been used. As the purpose of this experiment is to show the effect of irradiation, so the above flotation reagents are not used. If they were used, the effect of irradiation would be much better.

4. Investigation of the function mechanism of g-ray irradiation and flotation of minerals

In order to reveal the mechanism of irradiation and flotation of minerals we measured the amount of absorbed collectors on the surface of the minerals, the zeta-potential and specific magnetization coefficient before and after irradiation.

Table 2.

The adsorbed amount of reagent before and after irradiation

	After irradiation (4000)	Before irradiation
Dasage of reagent (mg)	48	48
Reagent amount in liquid (mg)	11.65	16.13
Adsorbed reagent amount on cassiterite (mg)	36.35	31.87
(mg/g)	7.25	6.09
Washable amount (mg)	12.77	14.78
Unwashable amount (mg)	23.58	17.9

4.1. The adsorption of styrene phosphonic acid on the surface of cassiterite (shown in Table 2)

From Table 2 it is visible that after irradiation styrene phosphonic acid adsorption is apparently inreased (from the adsorption 6.09 before irradiation to 7.27 mg/g) and chemical adsorption is increased to 6.49 mg. This shows that after irradiation the ionization of the mineral surface has been increased and has greater absorbability to the ion-type collector. Thus, the adsorbing stability of the reagents on the mineral surface is improved so mineral floatability is improved through irradiation.

4.2. Effect of streaming potential of cassiterite surface before and after irradiation (shown in Table 3)

From Table 3 it is visible that for acid pulp the streaming potential of cassiterite after irradiation is greater than before irradiation.

Table 3.

The zeta-potential of cassiterite surface before and after irradiation

Particle size of cassiterite (mm)	- 0.3 + 0.15		- 0.45 + 0.3	
Condition of irradiation	Irradia-tion	Unirradia-tion	Irradia-tion	Uniradia-tion
pH of solution	3	3	3	3
Zeta-potential (mv)	2.05	1.47	5.26	1.23

This indicates a change in the electronnegativity of the mineral surface after irradiation. Either the positive charges or the negative charges are increased to pull more H^+ into the inner part of the electronic double-layer, which leads to an increase of the positive charges of zeta potential. In the range of the Cobalt source used, the photoelectric effect thus produced, or Compton effect quantum photon can transfer their energy to the electrons, which can than separate from the atoms and move on. So there is no doubt that the positive charges on the mineral surface are increased after γ irradiation. In addition to the effect of pH - of the pulp, the irradiated cassiterite has stronger positive charges and a larger zeta-potential. In Table 3 it is also shown that the difference is also influenced by grain size. The coarser the grain is, the greater the difference of streaming potential is before and after irradiation.

4.3. Specific magnetization effect

The specific magnetization coefficient is the magnetic moment produced by one gram of substance in the outer sphere of the magnetic field with the intensity of one oersted. The magnetism is bound to be affected by the changes of electrons before and after irradiation.

It can be seen from Fig. 6 that, before and after irradiation. The specific magnetization coefficient varies regularly with the increase in magnetic field intensity. The specific magnetization coefficient of cassiterite after irradiation is higher than before irradiation. When the magnetic field intensity is below four, there is a remarkable difference (over 1.5). When it is over six, there is a minor difference (below 0.5).

This result shows that after irradiation the magnetism of cassiterite (which is a mineral with weak magnetism) increases; and when the intensity of the magnetic field is four, the increase of magnetism is most remarkable. It shows that, owing to the motion of electrons around the nucleus and their rotation, a magnetic moment is generated in molecules, thus magnetizing the substance. The irradiation causes an excitation and ionization in the outer sphere of atoms, and changes the direction of motion of electrons, thus increasing the magnetism and raising the specific magnetisation coefficient.

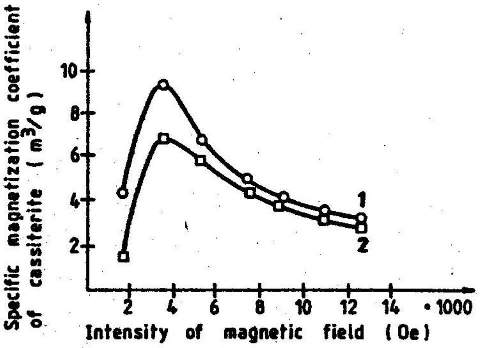

Fig. 6. The changes in specific magnetization coefficient of cassiterite before and after irradiation.

5. Conclusions

Either from the experiments on single minerals or from the experiments on separation of mixed mineral flotation, it is shown that the irradiation of γ-ray can improve the flotation index and can improve the flotation process of cassiterite and hematite. It is a new technology.

The best irradiation sources used in cassiterite flotation are γ-sources among which the cobalt source is the most convenient. It is cheaper and safer because of the smaller doses necessary.

When irradiated, cassiterite should be floated with phenylethylene phosphonic acid. Its effect on the separation of tin from iron is better than that of oleic acid. Irradiation can increase the adsorption of styrene phosphonic acid on SnO_2, can increase the positive value of the zeta-potential of cassiterite in acid pulp, can reduce the density of free electrons, which eventually can lead to the increase of electron-holes and the reduction of the fermi energy level. This may be the cause of the improvement on the flotation property of cassiterite and hematite after irradiation.

According to literature data (Huong Kun, 1958, Hu Wei-bei, Yang Ao etc., 1983), γ-ray is related to three forms of matter action: photoelectronic effect; Copton effect; and the occurrance of electron dipole. They are related to the energy of γ-ray and the atomic number of the matter. When different energies of γ quantum photons penetrates the matter with different atomic numbers, there is a great difference among the probabilities of the above three effects. It is also noted that for the γ-ray with a range of 1-4 megaelectronvolts, the Compton effect is most prominent and is almost unrelated to the atomic number of the matter.

For our study we adopt a cobalt source with a 1.25 magaelectronvolt as the irradiation source, so the Compton effect plays an important role when cobalt source acts with cassiterite and hematite. The effect takes place in the outer layer electrons of the atom (Seeger, 1980). When the quantum photon produces Compton diffusion, the electron is freed, therefore the electrons excited and ionized escape from the mineral, and there are more positive charges on the mineral surface, which attract a cathode ion collector with negative charges on the pulp. This leads to physical absorption even to chemical absprption. As a result, the irradiation improves the flotation process and increases the floatability of the mineral.

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STRESZCZENIE

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W pracy opisano flotowalność drobnych ziarn kasyterytu, hematytu oraz kwarcu napromieniowanych promieniami γ. Napromieniowane źródłem Co-60 minerały poddawano flotacji w celu określenia warunków ich flotacyjnego rozdziału. Badano także mechanizm procesu mierząc potencjały dzeta, adsorpcję odczynników flotacyjnych oraz współczynnik magnetyzacji. Wykazano, że promieniowanie zwiększa efektywność separacji magnetytu, hematytu i kwarcu. Jako nowy proces przeróbczy mógłby on znaleźć szerokie zastosowanie

СОДЕРЖАНИЕ

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В работе описана флотируемость мелких зерен касситерита, гематита, а также кварца, облученного γ- лучами. Облученные источником Со-60 минералы подвергались флотации для определения условий их флотационного раздела. Исследованы: механизм процесса путем измерения потенциалов дзета, адсорбция флотационных реагентов, а также коэффициент магнетизма. Определено, что излучение повышает эффективность сепарации магнетита, гематита и кварца. В качестве нового процесса переработки он мог бы найти широкое применение.