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YANG AO*

A STUDY ON FLOCCULATION OF FINE CASSITERITE, HEMATITE, AND QUARTZ WITH HUMATE

The flucculation of hematite, quartz and cassiterite separately, and the selective flocculation of their mixtures with sodium humate in the absence and presence of various modifying reagents ($CuSO_4$ $Pb(NO_3)_2$, $CaCl_2$, hexametaphosphate, citric acid, sodium tripolyphosphate, water glass) have been described in the paper. Also, the mechanism of flocculation of these minerals is discussed.

Introduction

Selective flocculation is one of the methods used to solve the problem of fine-grained ore separation. Selective flocculation is not only widely studied theoretically, but also applied to ore-dressing practice. Flocculation-flotation of non-magnetic ferroflint has been put into commercial application [1]. Many years'experience has proved it feasible to separate fine-grained ore by means of selective flocculation [2], but the problems of power consumption in fine-grinding and the costs of flocculant should be taken into account.

Studies of the flocculation of fine-grained cassiterite are now being carried out in many places. But how to chose a cheaper and safer flocculant is still an unsolved problem. Studies of sodium humate emerge along with the production activities. However, there is little information available on separating fine cassiterite with sodium

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* The Ore-dressing Research Section of Kunming Institute of Technology Kunming, China

humate, which is still in the preliminary stages of study.

Sodium humate is a kind of highly oxidized lignin and a macromolecular compound with a complex composition and structure. It consists of varous cationic activating group such as: -CH, -COOH, $-OCH_3$, $-NH_2$, $-SO_3H$ and $-PO_3H$, etc. It occurs in solution as free-spirochete polymer, and acts as a linear-polymeric electrolyte. Salt humate is of soil, river and coal origin, and is at its highest content level in brown coal. It is a sort of non-toxic and odourless reagent which is easy to prepare and low in cost, and has found a wide application in ore-dressing.

There are different electric properties on the surface of various minerals [3], which can be adjusted with activating and disoersing agents. The macromolecule of sodium humate shall be used to "bridge chain" the minerals to be processed in order to achieve selective flocculation by the action of its activating group.

Samples, reagents and equipment

The samples come from mines in Yunnan. Their compositions are shown in Table 1.

Table 1

The Compositions of minerals

Minerals	Main compositions %					
	Fe	SiO_2	Sn	CaO	MgO	Al_2O_3
Cassiterite		4.3	74	0.1	0.04	
Quartz		97.3		0.23	0.2	
Hematite	67.2	3.7		1	0.2	0.1

Flocculant —— Sodium humate is supplied from Qu Jing, Yunnan. The compositions are shown in Table 2.

Table 2

The content of active groups in humate

Free humic %	Acid active group mN/g	Caxboxyl group mN/g	Phenolic hydroxyl group mN/g
28.55	4.05	1.20	2.89

Equipment and method

Zeta - potential Analyzer, Type 2P - 10B, manufactured by SHIMADZU Corp., Japan.

Grading Analyzer, manufactured by SHIMADZU Corp., Japan.

All of the flocculating testes were done in deep beakers. The adsorbed amount of the flocculants was assayed according to „The Standards Issued by the Coal Industry Ministry of P.R.C."

Test and Research

1. An analysis of the grading characteristics of the tested minerals

Measured by hydrolysis process, over 97% of all three minerals —— cassiterite, quartz and hematite, were of $-20\,\mu m$. The minerals were later assayed with the grading analyzer made by SHIMADZU Corp., Japan. The results obtained are indicated in Figures 1 and 2.

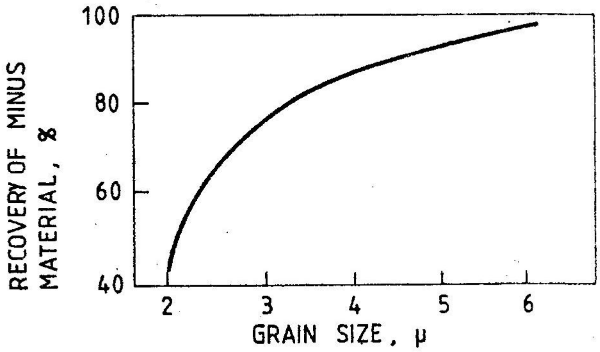

Fig. 1. Particle distribution curve of cassiterite

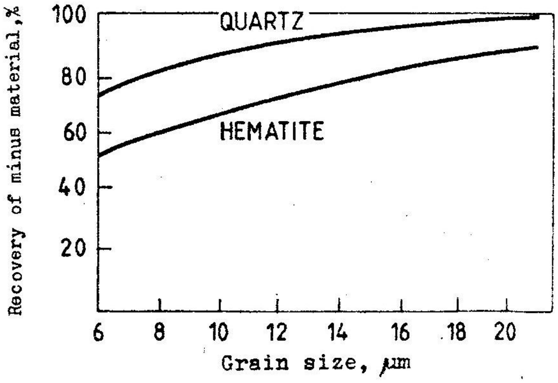

Fig. 2. Particle distribution curves of quartz and hematite

From the results, we came to the conclusion that during the process of fine grinding, cassiterite was easy to grind, while hematite difficult and quartz just intermediate. However, these three minerals were ground finely. Over 68% of them reached -10 μm. Almost all the cassiterite was -10 μm and 95% of the others was -5 μm; thus, the grain size of the ores met the requirements of flocculation.

2. The determination of pulp pH

When flocculating minerals, pH is the most important factor. In order to flocculate ore selectively, a prerequisite is that the minerals must be in a state of stable suspension. Some selective flocculants should be added to flocculate the objective minerals selectively, while the nonobjective minerals remain in a good dispersion state [4]. The whole procedure is aimed at adjusting the electric properties of the mineral surface. Dispersion may lead to the phenomenon that the mineral surface and the ions in the solution have the same electric properties, but flocculation results in the formation of opposite charges. Those of the same charge repel each other, while those of different charges attract each other.

These three kinds of minerals - cassiterite, hematite and quartz - are all oxidized minerals. H^+ and OH^- in pulps are their positioning ions. Therefore, dispersion and flocculation are also the procedures for adjusting the pH of the pulps.

In order to adjust pH value and control the dispersion and flocculation of the minerals, the electric properties of the minerals surface should first of all be clarified. The relatioship between the pulp pH and the kinetic potential of the mineral surface assayed by means of streaming potentiometry is shown in Fig. 3.

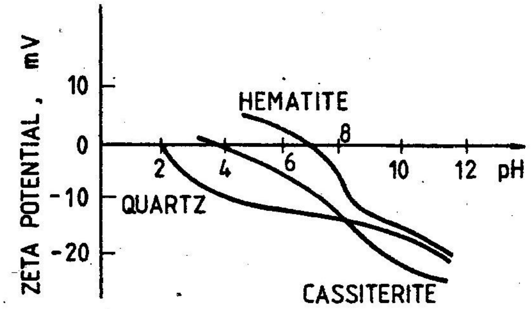

Fig. 3. The relation of pH value with mineral zeta potential

From the figures above, it can be seen that under various pH conditions the electropositivity of the three minerals is very weak, but the electronegativity is strong. When pH varies between 2.5 and 7.5, heterogeneous flocculation will likely occur among the three minerals, so in this case selective flocculation is impossible. Only when pH is below 2 or above 7.5 the minerals can be stably disperse in the pulps. When the adopted pH of the pulps is below 2, the consumption of acid is high and the corrosion of the equipment serious, which would be harmful to the health of the workers and should be used only on rare occasions. Therefore, during the test , it is better to use weak-alkaline pulps with a pH of 8, which is favorable in the test as well as in production.

When the pH of the tested pulp equals[8], the surface streaming potentials of hematite, quartz and cassiterite are -7.36,-11.57 and -16 (mV), respectively. Under such conditions, the surfaces of the three minerals are negatively charged. However, there are certain differences and strength in the electrical properties. For this reason, the minerals are all in stable suspension states and their dispersion and flocculation conditions can be adjusted with other reagents and electrolytes.

As we know from Fig. 3, each of the three minerals has its own point of pH, in this case, the electrokinetic potential is zero, which is the so-called zero electric point [4] . The zero electric points of the three minerals are shown in Table 3. It is known that the surface electric properties of oxide ore change with pH, according to this regularity, the heterogeneous agglutination of the mineral particles occurs near the zero point. At this pH value, the particles originally having positive or negative charges are no longer charged. The different kinds of particles agglutinate with each other and become coase-particle floccule because of the electrostatic gravitational force or chemical adsorption. In order to further ascertain this phenomenon, observation was made of these three minerals under the condition of adding no reagents when pH was at the zero electric point, and it was found that the ore particles were of coarse floccules which sedimentated quickly, leaving clear solution above. The spectrometer showed that the transmissivity of the three minerals usually varied at 85 - 95%, and 100% in max, which clearly indicated that near the zero point, all of the three minerals would agglutinate heterogeneously.

The zero electric points of the. three minerals measured are some different from those obtained by D.W. Fuerstenau [6], which might be caused by the differences both in the origin of the ore and the measuring conditions adopted (e.g. we used redistilled water, and NaOH and HCl for pH adjustment).

Besides, there are some advantages when pH is set at 8 e.g. the activating group of the flocculant is easy to separate completely (after ionizing, the activating group of humic acid becomes acid). And the function of the anionic selective flocculation of the activating group can be brought into full play, but not in strong base, because the strong base may cut the macromolecule of humic acid into micromolecules, thus decreasing the flocculating effect of the flocculant.

Table 3

PZC of minerals

Mineral	PZC	Grain size(mesh)	Remarks
Cassiterite	3.6(4.5)	-40 + 60	Distilled water
Hematite	7.2(8.6)	-30 + 60	"
Quartz	2.0(2-3)	-30 + 40	"

The data in brackets are from M.C. Fuerstenau

3. A test of the effect of humate on the flocculation properties of cassiterite, hematite and quartz

The results of the test regarding the effect of sodium humate on the flocculation properties of cassiterite, hematite and quartz are shown in Fig. 4.

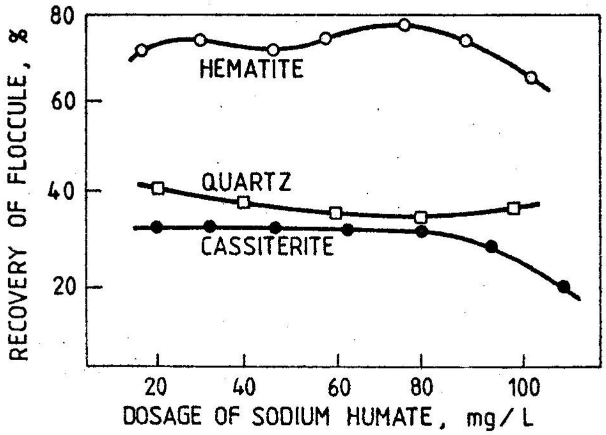

Fig. 4. The influence of sodium humate on mineral flocculability

It can be seen in the above figure that before the activator is added and when the pH of pulp equals 8, the most efficient among the results obtained by flocculation is humic sodium to hematite. Its recovery from floccule is more than 65%, while the recovery of cassiterite and quartz are below 40%. So it is proved that humic acid possesses a greater affinity to hematite, while the other two minerals are harder to flocculate then hematite.

4. Observation of the role of the activator in flocculating cassiterite and quartz with sodium humate

A negatively charged hydroxylic surface of oxidized minerals being put into the solution blocks or weakens the effect of the negatively charged radical of humic acid. But when the activated ions of high valency metal are added in pulp, they are adsorbed on the surface of mineral, weakening the electronegativity on the surface or changing the potential from negative to positive, and causing the mineral to fully react with sodium humate, so that selective flocculation is achieved.

Ore samples for the test are cassiterite, hemitite and quartz. Sulfuric copper, nitric lead and calcium chloride (varied in amount) are used as activator. The dosage of sodium humate is 20 mg/l.

The results of test are shown in figure 5, 6, 7.

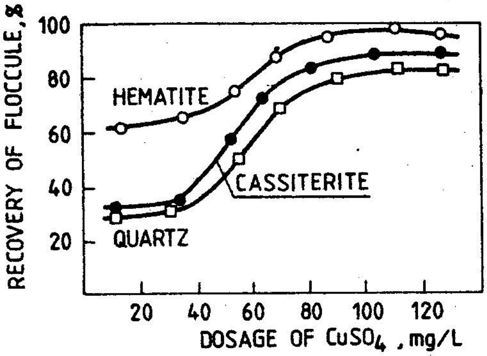

Fig. 5. The influence of copper sulphate on mineral flocculation

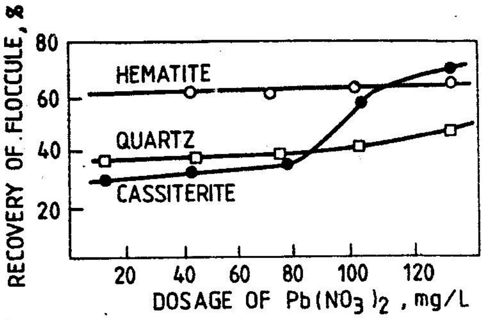

Fig. 6. The influence of lead nitrate on mineral flocculation

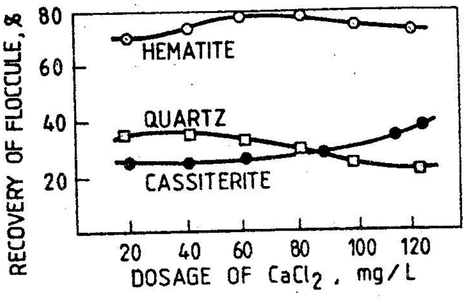

Fig. 7. The influence of calcium chloride on mineral flocculation

It is obvious from the above figures that the activated efficiency varies widely among the three minerals. Sulfuric copper gives a remarkable activatory efficiency to all three of these minerals. The recoveries of floccules are raised as the amount of activator increases. When little activator is added (45 mg/l), the recovery of hemitite remains on a high level, meanwhile the recoveries of cassiterite and quartz are low. This means that when the activator is used in smaller amounts, the majority of hematite is still flocculated, but the greater part of the other two minerals is dispersed. However, in comparison with Figure 4, when the activator is used in smaller amounts, the activability of all three of these minerals is low, and vice versa. There was not really much difference among these three minerals, so they are difficult to separate.

Nitric lead promotes flocculation of cassiterite only in high concentrate, but not in other circumstances.

Calcium chloride has effects the flocculation of hematite but not of quartz and cassiterite.

Oxidized ore is somewhat soluble in water. Its surface is easily hydroxylable [7], and its solubility is the product of the solubility of the different minerals. The solubility depends on the pH of the pulp. When the mineral adsorbs H^+ or OH^- and other ions on its surface, the latter will get potential, forming electric double layers. By measuring the adsorbed amount of H^+ or OH^-, the change of agent on the surface of mineral before and after floatation can be observed. The floatation mechanism can be explained, provided we know the change of electrokinetic potentials and the adsorbed amount of agent on the surface of minerals.

Table 4

Condition Zeta potential (mv) Minerals	unactived	$CuSO_4$		$CaCl_2$		$Pb(NO_3)_2$		Remarks
		Activated	Washed	Activated	Washed	Activated	Washed	
Cassiterite	-11.57	-2.29	-3.32	-8.6	-10.5	-6.7	-7	10^{-3}KCl
Quartz	-16	-3.2	-14	-12	-15.3	-7.3	-15	〃
Hematite	-7.35	+10	+5	3.44	1.5	-6	-6.6	〃

Condition: Humate 20mg/L Concentration of pulp 100:1
Ore sample 5g Activator 60mg/L

Table 5

Minerals Adsorbed amount Condition	Cassiterite	Hematite	Quartz
Unactived	0.0392	0.0810	0.0112
Adding $CuSO_4$	0.11415	0.1598	0.0267

Condition; $CuSO_4$ 60 mg/L · Humate 100 mg/L
Ore sample 5 g Concentration of pulp 100;1

Table 4 shows that in the case of activating cassiterite and quartz, sulfuric copper gets the greatest decrease of electronegativity among the three different activators. This means that after activation by sulfuric copper, minerals are easy to flocculate. The change of electrokinetic potential after washing in distilled water shows the adsorption of these three activators and flocculants. is physical adsorption. Its effects are limited in the dispersed layer of electrical double layers. Both before and after washing, the negative values of the electrokinetic potentials of cassiterite and qartz activated by sulfuric copper are lower than when activated by the other two activators; evidently, minerals activated by the former are easy to flocculate. After hematite has been activated by sulfuric copper and calcium chloride its electrokinetic potential is changed from negative to positive. This means that the ions of copper and calcium affect humic sodium, causing chemical adsorption on the surface of hemitite, and after washing, the electrokinetic potential remains positive, showing that their adsorbability is strong. In addition, surface adsorption untilizing sulfuric copper as an activator is stroger than that activated by calcium chloride. According to theory of chemical adsorption of activated ions, it may be concluded that Ca^{++} Cu^{++} and humic acid are adsorbed on the inner layer of electrical double layers.

Fig. 5 shows that humic sodium has lower adsorbed amounts on the surface of cassiterite, quartz and hemitite before being activated, but right after activation, the adsorbed amounts of humic sodium increase more than 100%. Such an increase on the surface of hematite is the highest.

5. Observation of the effect of disperser in flocculating cassiterite, hematite and quartz with humic sodium

In the test sodium hexametaphosphate, citric acid, sodium tripolyphosphate, sodium silicate and EDTA were used as dispersers. pH of the pulp equals [8], and the amount of humic acid is 20 mg/l.

Results of the test are shown in Figures 8 - 12.

From the above figures, it may be concluded that the dispersion efficiency of sodium hexametaphosphate, citric acid, sodium silicate and EDTA is better for cassiterite, but lower than for hematite; and is medium for quartz. Tripolyphosphate has an identical law, but is not as remarkable as the former.

From these result, it can be seen that by using the dispersing agent mentioned above to adjust the pulp, it is also possible to separate

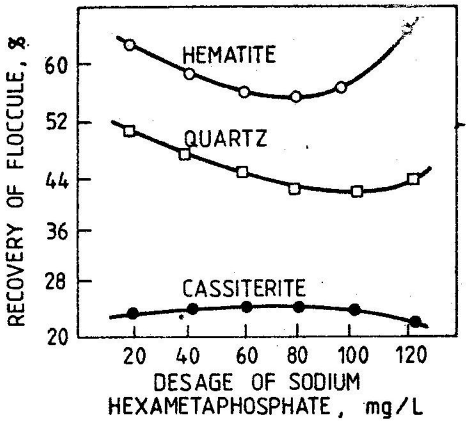

Fig. 8. Dosage of sodium hexemetaphosphate, mg/L

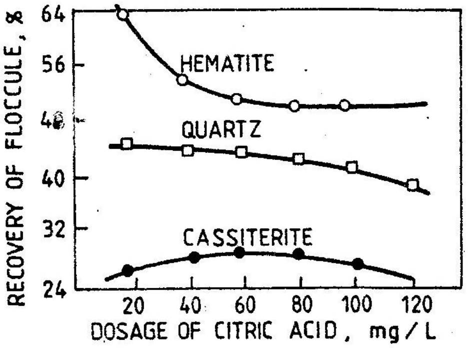

Fig. 9. Dosage of citric acid mg/L

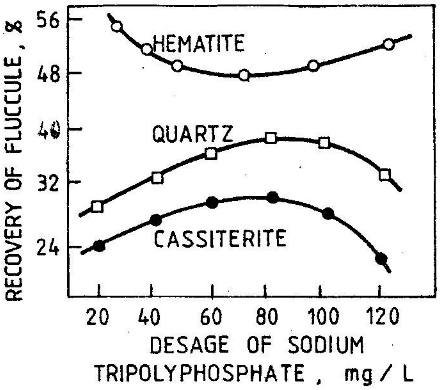

Fig. 10. Dosage of sodium tripolyphosphate, mg/L

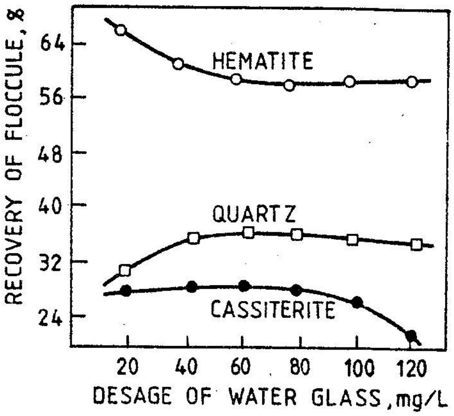

Fig. 11. Dosage of water glass mg/L

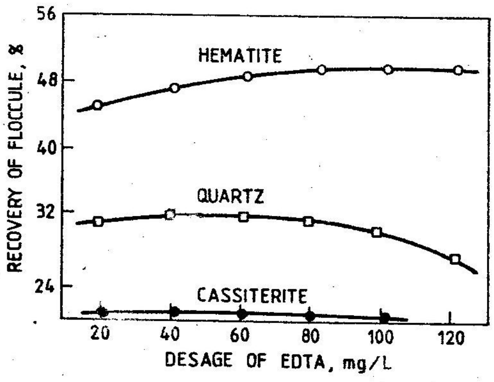

Fig. 12. Dosage of EDTA mg/L

quartz, cassiterite and hematite while for separating cassiterite and quartz, only hexametaphosphate, citric acid, sodium tripolyphosphate and EDTA can be used.

The above conclusion can be verified by measuring the adsorbed amount of flocculant on the mineral surface and the kinetic electrical potential.

Tables 6 and 7 indicate that cassiterite, hematite and quartz in distilled water or a solution of sodium humate have negative kinetic electrical potential, but the negative value differs greatly with or without sodium humate. Adding sodium humate in pulp will reduce the negative value due to the competition of ions, or the "bridge chain" effect of sodium humate. As negative value decreases to some extent, homophase flocculation will occur. Without adding sodium humate, the negative value will increase, so flocculation does not easily occur, or the degree of flocculation is lower. As seen in Tables 6 and 7, whatever dispersing agent has been added, the negative kinetic electric potential

Table 6

The influences of dispersing agents on the Zeta potential

Conditions Zeta potentials (mV) Minerals	Distilled water	Reagent amount 10 mg/L					Remark
	pH = 8	1	2	3	4	5	
Cassiterite	-11.57	-20.45	-18.60	-17.63	-22.08	-22.62	10^{-3}KCl
Hematite	-7.36	-12.15	-12.45	-11.56	-18.72	-16.4	
Quartz	-10.10	-15.36	-13.80	-14.27	-19.83	-18.46	

1. Hexametaphosphate 2. Citric acid 3. Sodium tripolyphosphate
4. EDTA 5. Water glass

Table 7

The influence of dispersing agent on kinetic electric potential

Conditions Zeta potentials (mV) Minerals	Sodium humate	Reagent amount 10 mg/L					Remark
		1	2	3	4	5	
Cassiterite	100	-17.87	-16.36	-14.34	-18.97	-16.32	10^{-3}KCl
Hematite	100	-10.52	-10.10	-11.68	-14.91	-14.4	
Quartz	100	-15.87	-13.15	-12.27	-16.15	-15.22	

of hematite is low, while quartz is slightly higher and cassiterite the highest. When sodium humate, is added, the phenomenon is about the same.

The result of tests of the adsorption of humic acid on any kinds of minerals (see Tables 8 and 9) indicates that without the dispersing agent, the adsorbed amount on hematite is higher than that on quartz and cassiterite, while the adsorbed amount of quartz is less than that of cassiterite. After the dispersing agent has been added, the adsorbed amount of sodium humate on the three minerals decrease greatly, however, whatever dispersing agents are used, the results are always that the adsorbed amount on hematite is greater than that on cassiterite, and that on quartz is greater than that on cassiterite.

The measurment of the kinetic electrical potential and the adsorbed amount conforms to the testing of the dispersing agent. These fully indicate that the dispersing agent itself is a strong electrolyte, which can be adsorbed to the mineral surface, and makes the surface increasingly negatively charged, hindering and decreasing the flocculant adsorption ability. Thus,decreasing the adsorbed amount, will obviously reduce the floccule recovery.

Table 8

The adsorbed amount of sodium humate

Minerals	Cassiterite	Hematite	Quartz
Adsorbed amount m N/g	0.0392	0.0810	0.0112

Sodium humate 100 mN/g pH = 8

Table 9

The adsorbed amount of sodium humate

Minerals	Adsorbed amount mN/g				
	1	2	3	4	5
Cassiterite	0.0090	0.0167	0.0190	0.0112	0.0392
Hematite	0.07665	0.0879	0.0767	0.0542	0.0842
Quartz	0.0538	0.0577	0.0228	0.0577	0.0074

Ore sample 5 g Concentration of pulp 100:1
Dispersing agent 40 mg/L Sodium humate 100 mg/L

The adsorbed amount of flocculating agent on cassiterite is greater than on quartz when the dispersion reagent is absent (see Tables 8, 9), but the reverse is true if a dispersion reagent is present (no matter which of the above dispersion reagent is added): the strong negativity of quartz under the action of the dispersion reagent is the cause of this phenomenon.

Both the dispersion reagent and activating reagent are strong inorganic electrolyte, their electrical properties, adsorbed amount on the mineral surface as well as adsorptive characteristics all coincide with the DLVO theory and hetero-coagulation theory [8].

Physical adsorption is mainly affected by electrostatic force, but chemical adsorption is a result of the chemical adsorptive force of the hydroxyl complex ions which are produced by the slight solvation of cations from the mineral surface. Because of the strong surface activity, the hydroxyl complex ions are able to be adsorbed stably on the mineral surface. In case of high concentration, the sign of the electrokinetic potential can be changed: it even can be adsorbed on the surface with a positive charge.

Separation tests of cassiterite, hematite and quartz

The selective flocculation process is chosen for separation tests of cassiterite, hematite and quartz.

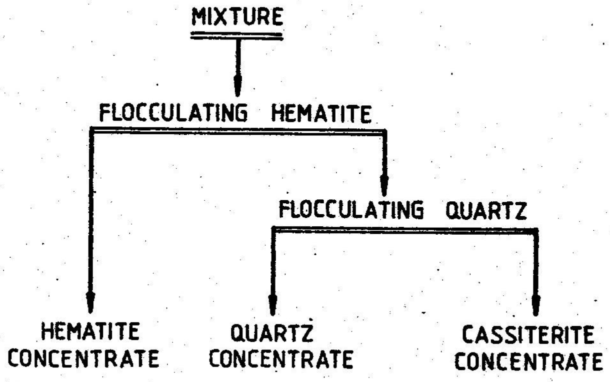

Fig. 13. Selective flocculation process flowsheet

Test condition: Ore mixture proportion; cassiterite; quartz; hematite = 2:4:4; pulp pH = 8; pulp concentration is 1%.

Reagent dosage and procedure: dosage of water glass 40 mg/l and sodium humate 20 mg/l prior to hematite flocculation; dosage of calcium oxide 40 mg/l, sodium hexametaphosphate 60 mg/l and sodium humate 20 mg/l.

The results of the tests are shown in Table 10.

Table 10

The results of separating the mixture

Products	γ %	β Fe %	β Sn %	β Si %	ε Fe %	ε Sn %	ε Si %
Hematite	33.0	46.4	8.7	22.3	55.31	8.50	34.77
Quartz	7.2	25.2	18.0	40.5	6.60	3.80	13.78
Cassiterite	59.8	17.7	49.5	18.2	38.09	87.70	51.45
total	100.00				100.00	100.00	100.00

It is indicated in Table 10 that:

(1) Hematite concentration with recovery of 55.31 % and iron content of 46.4%, and also grade 49.5% tin concentration with recovery of 47.7% can be obtained by the selective flocculation process.

(2) The recovery and grade of the hematite concentrates are quite low, but both the tin content in the hematite concentrate and iron and iron content in tin concentrate are decreased (as compared with the preceding tests).

(3) Increasing the cleaning times, as well as feeding in rising water flow to minimize the mechanical impurities, would help the completeness of the tin and iron separation.

Conclusion

Humate is usually used in the flotation process as a desliming reagent and depressor, having the advantage of widespread resourse, low cost, safety and non-toxicity. In this study, it is used as a flocculant for tin —— iron —— silicon minerals mixture sample separation. A regularity in the separation process is found.

People involved in ore dressing have paid a lot of attention to the selective flocculation process which has been practically proved to be an economical and feasible new process for fine grain separation. Good results were reported from our preliminary study in which sodium humate was used as a flocculant for cassiterite and hematite separation.

The base for using sodium humate as a flocculant for cassiterite separation is not the same as for hematite separation. Acting with various minerals, the organic and inorganic electrolytes cause different surface electrical properties: some of the minerals are depressed, as others are activated. Mineral flocculation and dispersion are depended on the control of electrical properties, and the long chain molecule of sodium humate "bridge chain" the objective mineral and the action of its active group promotes the selective flocculation process.

Under the same pH conditions, the above three kinds of minerals have different streaming potential and different zero potential points; the sodium humate adsorbed amount of these minerals is different at various sodium humate concentrations. Affected by the activating reagent, the sodium humate adsorbed amount increases as the mineral streaming potential increases. On the other hand under the action of an depressor, the streaming potential and adsorbability of the mineral decrease. Different minerals have different increase and decrease amplitudes, so that various minerals can be separated.

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STRESZCZENIE

Yang Ao, 1986. Badania flokulacji zawiesin kasyterytu, hematytu i kwarcu przy użyciu huminianów. Fizykochemiczne Problemy Mineralurgii 18; 39-54.

Zbadano i określono warunki flokulacji drobnoziarnistych zawiesin, hematytu, kwarcu i kasyterytu oraz flokulacji selektywnej mieszanin tych minerałów. Jako flokulant używano huminianu sodu. Doświadczenia prowadzono bez dodatku i z dodatkiem różnych odczynników modyfikujących jak: $CuSO_4$, $Pb(NO_3)_2$, $CaCl_2$, sześciometafosforan sodu, kwas cytrynowy, trójpolifosforan sodu, szkło wodne. W pracy dyskutowano także mechanizm flokulacji wymienionych minerałów.

СОДЕРЖАНИЕ

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Исследованы и определены условия флокуляции мелкозернистых суспензий гематита, кварца и касситерита, а также селективной флокуляции смесей этих минералов. В качестве флокулянта использован гуминат натрия. Эксперименты проводились без добавлений и с добавлением различных модифицирующих реагентов как: $CuSO_4$, $Pb(NO_3)_2$, $CaCl_2$, шестиметофосфат натрия, лимонная кислота , триполифосфат натрия, жидкое стекло. В работе также обсужден механизм флокуляции представленных минералов.

Because of problems in correspondence with the Author in order to verify of manuscript , this paper is published in the original version.