Electrokinetic Property and Flotation Characteristics of Scheelite

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灰重石의 水溶液中에 있어서의 界面現象과 浮選特性에 關한 硏究

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ABSTRACT

The fundamental investigations of surface properties of scheelite were made by electrophoretic mobility adsorption and contact angle measurements, and results have been correlated with its floatability obtained by Hallimond tube flotation test.

The role of the interfacial electrical condition on the adsorption of collectors on mineral surfaces is discussed with the flotation of scheelite. From electrokinetic measurements made on scheelite, Ca^{++} and WO_4^{--} are identified to act as potential-determining ions, thus controlling the surface properties on this mineral. Therefore, at the fixed pH, the scheelite surface become to be less negatively charged with increasing Ca^{++} concentration and more negatively charged with increasing WO_4^{--} concentration in the pulp. Adsorption of collectors then depends strongly on the concentration of Ca^{++} or WO_4^{--} in the solution; anionic collectors are adsorbed on less negatively charged surfaces and cationic collectors on more negatively charged surfaces, which in turn defines the effective flotation range with respective collectors for this mineral.

要 約

本硏究에서는 韓國產 灰重石($CaWO_4$)에 關하여 固相─液相界面에 있어서의 電氣化學的 性質을 電氣泳動法으로 調査하고 한便 浮遊性에 關하여서는 捕收劑로 Dodecyl ammonium chloride(D.A.C.라 略稱)와 Sodium dodecyl sulfate(S.D.S.라 略稱)를 使用하여 Hallimond tube 試驗, 接觸角測定 及 吸着量測定等으로 捕收劑 이온이 鑛物表面에 吸着하는데 있어서 電氣的인 相互作用이 重要한 役割을 하고 있다는 것을 實證하였다. 即 電氣泳動法으로 鑛粒의 水溶液中에 있어서의 mobility를 測定한 結果 灰重石의 境遇에는 Ca^{++} 或은 WO_4^{--} 이 界面 電氣特性을 決定하는 potential determining ion이라는 것이 確認되었고 水溶液中에 있는 Ca^{++}의 增加는 鑛粒界面의 陰電荷를 減少하며 WO_4^{--}의 增加는 그 陰電荷를 增加한다는 것을 알수 있다. 이와같은 表面에 "陰이온系"의 S.D.S.或은 "陽이온系"의 D.A.C.를 作用시키면 當然히 S.D.S.는 Ca^{++}의 增加에 따라 吸着量이 增加되어 浮遊性이 增大되고 한便 D.A.C.때는 反對로 WO_4^{--}이 增加하는데 따라 吸着量이 增加되며 따라서 浮遊性도 增大된다고 볼수 있고 實地로 捕收劑吸着量의 測定 및 Hallimond tube 試驗은 이것을 立證하고 있다. 이러한 基礎的인 究明은 灰重石浮選理論의 根幹이 되는 것이고 從來의 浮選法 改良에 對한 指針이 될수 있다고 生覺한다.

Introduction

In view of the importance of the development of natural resources, the fundamental research of metallurgical processes such as the beneficiation of the tungsten ore is urgently necessary in our country.

In recent years, Sangdon mine, one of the most

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important tungsten mines in the world is confronted with difficulty of treating low grade tungsten ore and molybdenum-bearing scheelite[$Ca(W, Mo)O_4$] which is increasing in deeper part of main ore bed.

Accordingly, those facts stimulate interests of the fundamental investigation of scheelite flotation. It would be, therefore, certainly essential to study the physical and chemical properties of scheelite.

It is well known that mineral particles show electrical charge in aqueous suspensions,1,2) and that most collectors are ionized in solution. It is natural to presume, therefore, that the electrokinetic property of the mineral would play an important role in governing the adsorption characteristics of collectors; the scheelite flotation being no exception.

The experimental verification that the adsorption of various ions on mercury and on some solid surfaces is strongly dependent on its electrical condition was reported by a number of investigators. 3,4,5)

For most oxide minerals, it has been postulated6) that their electrical conditions at the surface are greatly affected by hydrogen or hydroxyl ions, and subsequently the floatability of oxide minerals will be governed by the pH of the pulp.

However, very few investigations of surface properties and floatabilities of minerals having ionic crystal structure have been made and the mechanism of collection of these minerals is not well understood.

Scheelite has ionic crystal structure and may be considered to be ionized to Ca^{++} and WO_4^{--} at its surface, and therefore the Ca^{++} and WO_4^{--} ions in aqueous solution would act as potential determining ions for this mineral.

The purpose of this investigation is to study the surface properties of scheelite through electrophoretic mobility measurements and adsorption measurements; and the results were correlated with the results of floatability obtained with scheelite in the simplified flotation test using a modified Hallimond tube.

Experimental Materials

A. Samples for Tests

Scheelite sample was obtained from Okpang Mine, located near Sangdong Mine.

This sample is a highgrade ore(WO_3: 79.9%) which was obtained from pegmatite deposits. The gangue minerals were rejected by vanning and followed by the sedimentation and decantation for the further purification.

A 100/150 mesh fraction was obtained for flotation sample and was cleaned with warm 1.0 N hydrochloric acid and washed with absolute dehydrated alcohol. Lastly the sample was washed repeatedly with demineralized water and was stored under demineralized water in a pyrex bottle.

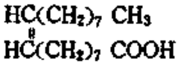
Minus 200 mesh scheelite fraction was cleaned and washed with hydrochloric acid and demineralized water respectively. And the sample was ground in an agate mortar and minus 3 micron fraction of the finely ground scheelite was obtained by sedimentation and decantation method. This was used for the electrophoretic mobility measurements.

B. Reagents

The following collectors were used in this investigation:

$C_{12}H_{25}NH_3Cl$ ……… Dodecylammonium chloride

$C_{12}H_{25}SO_4Na$ ……… Sodium dodecyl sulfate



$$\begin{matrix} HC(CH_2)_7\,CH_3 \\ \| \\ HC(CH_2)_7\,COOH \end{matrix}$$

……… Oleic acid

Dodecylammonium chloride and sodium dodecyl sulfate were obtained from Armour and Co., Chicago, Ill., U.S.A.

Pure oleic acid was obtained from the Hrom Foundation, Austin, Minn., U.S.A.

The fatty acid was converted to water soluble sodium-soap before use, by adding 50 percent excess amount of the stoichiometric requirements of sodium hydroxide, and digesting at 60°C, until all the acid was in the soluble soap form.

Analytical-reagent grade sodium hydroxide was used for the conversion of fatty acid pH adjustment. Chemically-pure reagent grade hydrochloric acid was used for pH adjustment.

Demineralized water containing less than 0.1 p.p.m. of salts as sodium chloride was used in the preparation of all solutions and for all test work.

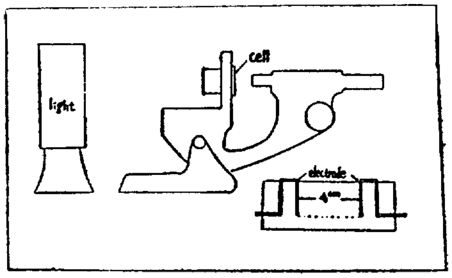


Fig. 1 Apparatus of electrophoretic mobility measurement

Experimental Apparatus and Procedure

A. Electrophoretic Measurements

The apparatus of the electrophoretic mobility measurements is a flat type, vertical microelectophoretic cell made of two pieces of microscope slides. The experimental apparatus of the electrophoretic mobility measurements is shown in Fig. 1.

A sample of scheelite suspension having the desired pH was prepared and conditioned for 10 minutes by shaking with hand and settled for 5 minutes.

The rectangular glass cell filled with the prepared suspension was fixed on the stage of the microscope.

To avoid the suspended particlse to move vertically downwards due to the gravitational pull, the suspended solution was settled for 5 minutes after fixing on the microscope stage. Then the measurement of the electrophoretic mobility was begun.

The electric flow reversed freely by using the reversal switch, so that the velocities in opposite direction were also determined at the same time. The results were averaged after twenty measurements were taken. The voltage applied between the two electrodes was 15 volts. Then the calculated mobilities were expressed in terms of "cm/sec/volt/cm."

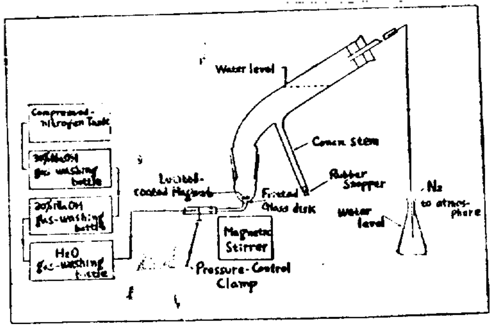


Fig. 2 Hallimond tube system

B. Hallimond Tube Tests

Quantitative study of flotation behavior on a miniature scale may conveniently be carried out with a modified Hallimond tube which was originally designed by Hallimond and modified by Fuerstenau.[7]

Fig. 2 shows the Hallimond tube set-up. The magnet bar which is in the lower part of the Hallimond tube gives an adequate stirring to the sample with a rotating mechanism according to the rotating magnet which is fixed under the tube. Purified nitrogen gas was used for aeration; and purification was carried out by passing two bottles of 30 percent of potassium hydroxide solution, to remove carbon dioxide and then washed by bubbling through water.

The Hallimond tube was standardized to operate with approximately 1 gram of the mineral sample at a gas flow of 30 ml. per minute and with a flotation time of 5 minutes.

About 1 gram of 100/150 mesh scheelite was transferred from the storage bottle to milliliter volumetric flask and filled with a prepared collector solution. After the pH of solution is adjusted to the desired value, it was conditioned for 20 minutes by tumbling at a speed of 35 r.p.m.

After conditioning, the sample and solution were transferred into the Hallimond tube and the flotation was performed for 5 minutes. Both float and nonfloat products were dired and the flotation recovery was calculated by weighing.

C. Contact Angle Measurement

The captive bubble technique was used to measure the contact angle on an inverted scheelite specimen mounted in lucite.

A collector solution of adjusted concentration and pH was transferred to the 180 milliliter optical cell, in which the polished and cleaned specimen was conditioned for 5 minutes by rotating it with a motor. After conditioning, pH readings were taken.

A bubble was placed on the specimen by means of a bubble holder.

The contact angle of a bubble on the mineral was measured for each side of the bubble separately and an averaged value was taken.

D. Adsorption Measurements

The adsorption of dodecylammonium chloride and sodium dodecyl sulfate on scheelite was measured. The scheelite sample used in this experiment was the same as that used in the flotation test. For each test, exactly 1 gram of the sample was taken and transferred into a 100 ml. volumetric flask and then prepared solution was filled to make 100 ml. volume. The volumetric flask was conditioned for 20 minutes. It was left for one hour to attain equilibrium before measurement, and then the residual concentration in the solution was colorimetrically analyzed. The dodecylammonium chloride in aqueous solution was analyzed colorimetrically by precipitating it as amine picrate, extracting the precipitate with chloroform and then measuring the transmittancy at 510 mμ. Concentrations of sodium dodecyl sulfate were measured in a similar way by precipitating with rosaniline hydrochloride and extracting the precipitate with a 1 : 1 chloroform-ethyl acetate mixture.

Experimental Results

Since scheelite has ionic crystal structure and it is essential to investigate the role of Ca^{++} & WO_4^{--} in the solid-solution interface, the effects of Ca^{++} and WO_4^{--} were observed on electrophoretic mobility, adsorption, contact angle measurements and Hallimond tube tests.

Calcium chloride($CaCl_2 \cdot 2H_2O$) and sodium tungstate($Na_2WO_4 \cdot 2H_2O$) were used as electrolytes of Ca^{++} and WO_4^{--} ions respectively.

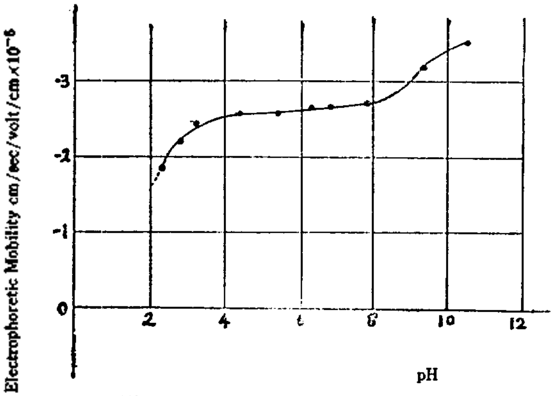


Fig. 3 Electrophoretic mobility of scheelite (-3μ) as a function of pH

A. Measurements of Electrophoretic Mobility

The results of the electrophoretic mobility measurements on scheelite as a function of pH are given in Fig. 3. It shows that the particles are negatively charged in the entire pH range. The curve shows mobility of negatively charged mineral particles decrease slightly up to pH 8 and stay almost constant until pH 3. Below pH 3 the mobility decrease again rather abruptly.

Effects of Ca^{++} and WO_4^{--} on electrophoretic mobility of scheelite at pH 9.0-8.5 are shown in Fig. 4. The mobility of particle decreases with increase of concentration of Ca^{++}.

When the Ca^{++} concentration is more than 5×10^{-3}M., no mobility was observed due to liquid movement.

The increase of concentration of WO_4^{--} shows increase of mobility, but the mobility drops abruptly at 3×10^{-3}M. of WO_4^{--} addition and stays content above that concentration. This may due to the compression of double layer.

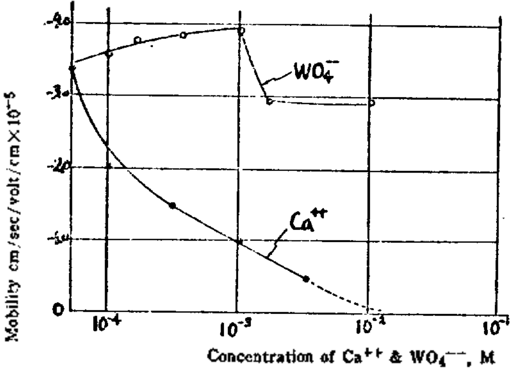


Fig. 4 Effect of Ca^{++} and WO_4^{--} on electrophoretic mobility at pH 9.0

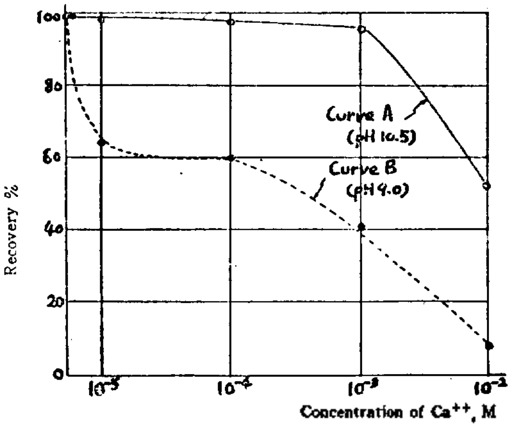


Fig. 5 Effect of Ca^{++} on scheelite flotation with dodecylammonium chloride 10^{-4} M. at pH 9.0

B. Hallimond Tube Flotation Tests

The results of flotation of scheelite using 10^{-4} M of dodecylammonium chloride are shown in Fig. 5 in terms of recovery v.s. Ca^{++} concentration.

The curve A shows the effect of Ca^{++} at pH 10.5 and the curve B at pH 9.0. The recovery, generally, decreases with increase of Ca^{++} concentration. The recovery without Ca^{++} is 100 percent, but it drops to 52 per cent at pH 10.5 and only 8 percent at pH 9.0 when 10^{-2}M. of Ca^{++} is added.

Fig. 6 shows the effect of Ca^{++} on scheelite flotation with 10^{-4}M. sodium dodecyl sulfate at pH 9.0. The recovery increases gradually from 4 percent to 40 percent by adding 10^{-2}M. of Ca^{++}.

Fig. 7 shows the effect of Ca^{++} on scheelite flotation with 10^{-4}M. of oleic acid at pH 4.7. As shown in this figure, the recovery increases with increase of the concentration of Ca^{++}.

On the other hand, Fig. 8 shows the effect of WO_4^{--} and MoO_4^{--} on floatability of scheelite with 10^{-4}M. of dodecylammonium chloride at pH 7.0. The recovery increases with increase of the concentration of WO_4^{--}, showing very similar characteristics of WO_4^{--} and MoO_4^{--}.

C. Contact Angle Measurements

Fig. 9 shows the effect of Ca^{++} and WO_4^{--} on contact angle of scheelite with 10^{-4}M. of dodecylammonium chloride.

At fixed pH, the increase of concentration of Ca^{++} shows a decrease of contact angle. The contact angle without Ca^{++} is 27° and the angle decreases to 15° when 10^{-1}M. of Ca^{++} is added.

However, the contact angle increases with increase of concentration of WO_4^{--}, until it reaches a maximum of 42° at addition of 10^{-2}M. of WO_4^{--}. Beyond this concentration, dodecylamm-

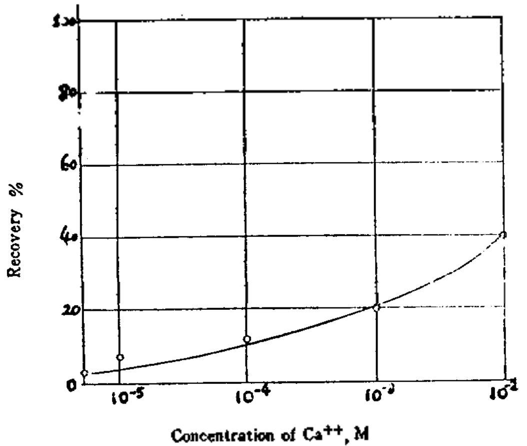


Fig. 6 Effect of Ca^{++} on scheelite flotation with sodium dodecyl sulfate 10^{-4} M. at pH 9.

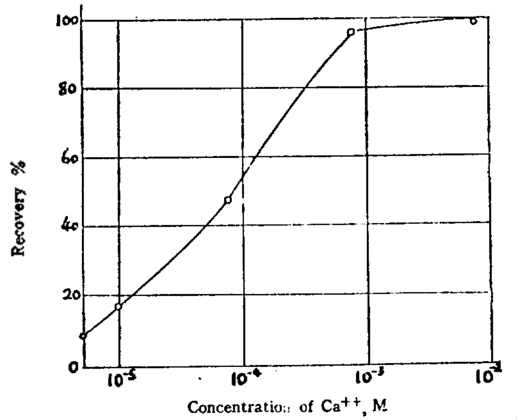


Fig. 7 Effect of Ca^{++} on scheelite flotation with oleic acid 10^{-4} M. at pH 4.7

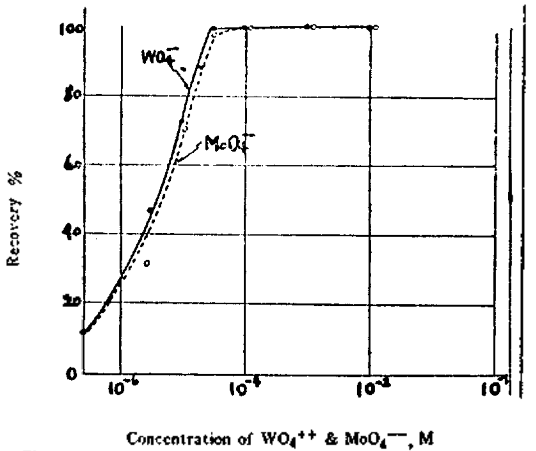


Fig. 8 Effect of WO_4^{--} & MoO_4^{--} on scheelite flotation with dodecylammonium chloride 10^{-4} M. at pH 7.0

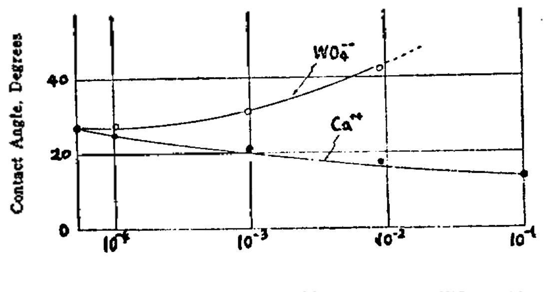


Fig. 9 Effect of Ca^{++} and WO_4^{--} on contact angle using 10^{-4}M. of dodecylammonium chloride at pH 8.5

onium chloride was precipitated with WO_4^- to form $(RNH_3)_2WO_4$.

D. Adsorption Measurements

The effects of Ca^{++} and WO_4^{--} on the adsorption of dodecylammonium chloride on scheelite are shown in Fig. 10.

The increase of the concentration of Ca^{++} indicates the decrease of the adsorption and the increase of concentration of WO_4^{--} shows the increase of adsorption amount.

The amount of adsorption of dodecylammonium chloride without addition of Ca^{++} and WO_4^{--} is 2.9×10^{-7} moles per gram at the concentration of 10^{-4}M. of dodecylammonium chloride. But the amount of adsorption decreases to 1.0×10^{-7} moles per gram by adding 10^{-2}M. of $Ca.^{++}$. However it increases to 6.92×10^{-6} moles per gram by adding 10^{-2}M. of WO_4^{--}.

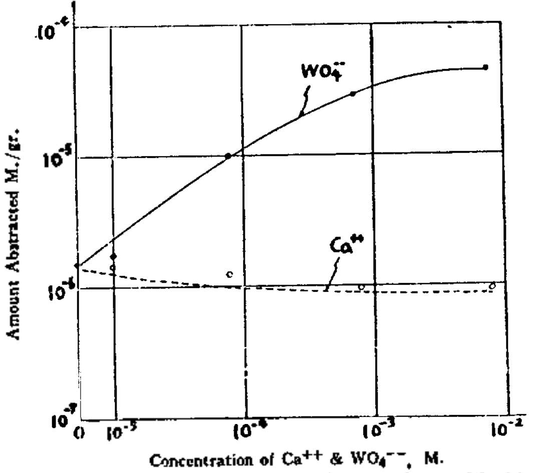


Fig. 10 Adsorption of dodecylammonium chloride as a function of Ca^{++} and WO_4^{--} concentration at pH 9.0

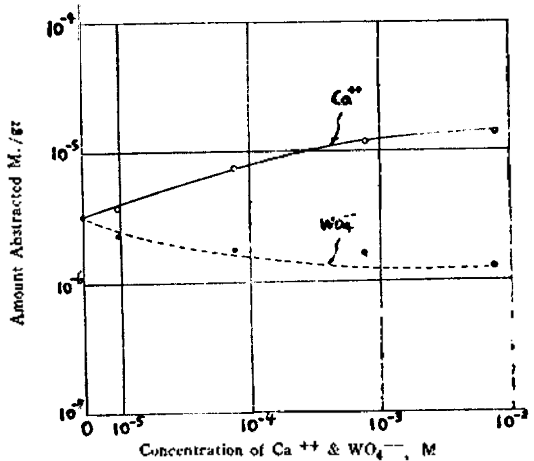


Fig. 11 Adsorption of sodium dodecyl sulfate as a function of Ca^{++} & WO_4^{--} concentration at pH 9.0

Fig. 11. shows the effects of Ca^{++} and WO_4^{--} on the adsorption of sodium dodecyl sulfate as a function of concentration at pH 9.0.

At the concentration of 10^{-4}M. of dodecyl sulfate, the amount of adsorption without addition of Ca^{++} and WO_4^{--} is 5.7×10^{-7} moles per gram.

The amount of adsorption increases to 1.62×10^{-6} moles per gram by adding 10^{-2}M. of Ca^{++} and decreases to 2.2×10^{-7} moles per gram by adding 10^{-2}M. of WO_4^{--}.

Discussion of Experimental Results

When mineral particles are dispersed in aqueous solution and an ionic equilibrium is reached, it is observed that the particles generally migrate under the influence of an electric field.[8]

The existence of an electrical charge at the mineral-solution interface has long been demonstrated by electrokinetic phenomena such as electrophoresis, electroosmosis, streaming potential, and sedimentation potential, depending upon the same phenomenon of selective ion distribution at interfaces.

Those ions, which establish equilibrium at the interface and which determine the potential drop between the solid and the liquid phases, are termed "potential determining ions" and are responsible for the electrical charge observed on the solid surface.

For most oxide minerals, it is thought that hydrogen and hydroxyl ions are the potential determining ions, and it is postulated [9,10,11] that the oxygen ions in the surface undergo the following reaction:

$$O^{--}(\text{surface}) + H_2O \rightleftharpoons 2OH^-(\text{solution}) \ldots\ldots(a)$$

According to equation(a) and increase in pH should drive the reaction to the left rendering the surface more negative. A decrease in pH should reverse the reaction, making the surface less negative. At a certain pH there will be a transition point where the surface is uncharged. This condition of electrical neutrality is referred to as an isoelectric point.

However, it may be thought easily that the lattice ions, are the potential determining ions, for the mineral having ionic crystal structure.[12]

Electrophoretic measurements on scheelite as a function of pH(Fig. 3) show that the scheelite particles are negatively charged in whole pH range. Therefore, other ions must be potential determining ions rather than hydrogen and hydroxyl ion.

Since scheelite has ionic crystal structure, it is soundly assumed that WO_4^{--} and Ca^{++} are the potential determining ions for this mineral. This assumption may be proved by the following various measurements concerned with the effect of Ca^{++} and WO_4^{--}.

A. Electrophoretic Mobility Measurements.

Fig. 4 shows that electrophoretic mobility charged scheelite particles become nearly zero with increase of the concentration of Ca^{++}, whereas it increases with increase of the concentration of WO_4^{--}, showing that Ca^{++} and WO_4^{--} are governing the surface potential of scheelite.

B. Hallimond Tube Flotation Test

Fig. 5 shows the effect of Ca^{++} on scheelite flotation in cationic collector at pH 9.0 and 10.5. It is easily presumed that the surface of scheelite is less negatively charged by the addition of Ca^{++}, so that the physical adsorption between scheelite surface and RNH_3^+ is dispelled.

On the other hand, Fig. 6 shows the effect of Ca^{++} in anionic collector. Here, the less negatively charged mineral particles give stronger adsorption of anionic collector.

Fig. 7 shows the effect of Ca^{++} on the anionic flotation when 18-carbon aliphatic acid is used as collector, showing the increase of recovery due to the less negatively charged mineral surface.

It also shows that the 18-carbon fatty acid has more powerful collectability in the scheelite flotation than the 12-carbon anionic collector.

Meanwhile, it was proved the effect of MoO_4^{--} on the cationic flotation of scheelite is very similar with the effect of WO_4^{--} (Fig. 8).

C. Contact Angle Measurements

Fig. 9 gives the relation between contact angle and concentration of Ca^{++} and of WO_4^{--} in 10^{-4}M. of dodecylammonium chloride at pH 8.5.

As shown by these figures, the addition of WO_4^{--} increases the adsorbing power between solid and collector, whereas adsorbing power decreases with increases of Ca^{++} in the solution of cationic collector. This is well correlated with adsorption measurements in the addition of Ca^{++} and WO_4^{--}.

D. Adsorption measurements

Fig. 10 and 11 shows that the effect of Ca^{++} and WO_4^{--} on the adsorption of a cationic collector and an anionic collector respectively on scheelite. The effective adsorption of the cationic collector, dodecylammonium chloride, appears on a more negatively charged surface of scheelite, and of the anionic collector, sodium dodecyl sulfate, on a less negatively charged surface. The results give good correlation with other observation.

Conclusions

The basic surface properties of scheelite were investigated by electrophoretic mobility, adsorption and contact angle measurements, and those results have been correlated with its flotation characteristics obtained by Hallimond tube flotation test. The experimental results have led to the following conclusions:

1. The potential determining ions of scheelite are Ca^{++} and WO_4^{--}.
2. The scheelite particles in aqueous solution are negatively charged in the entire pH range. However, at the fixed pH, the scheelite surface become to be less negatively charged with increasing Ca^{++} concentration and more negatively charged with increasing WO_4^{--} concentration in the pulp.
3. The amount of adsorption of the cationic collector increases wtth increasing WO_4^{--} concentration and the amount of adsorption of the anionic collector increases with increasing Ca^{++} concentration in the pulp.
4. Anionic collector, sodium dodecyl sulfate, is effective on less negatively charged scheelite and cationic collector, dodecylammonium chloride is effective on more negatively charged scheelite, in the flotation of scheelite.
5. The effect of MoO_4^{--} on the cationic flotation of scheelite is very similar with the effect of WO_4^{--}.
6. The 18-carbon fatty acid is more powerful collector in the flotation of scheelite, in comparison of the 12-carbon anionic collector, sodium dodecyl sulfate.

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