

Effects of Collector Ion Concentrations and Hydrogen Ion Concentrations on the Floatability of Non-Sulphide Minerals

By

Shigeru MUKAI*, Gentarō KANŌ* and Takahide WAKAMATSU*

(Received January 31, 1962)

The floatability of non-sulphide minerals such as quartz, hematite, barite, calcite, scheelite and wolframite was measured in various collector concentrations with various pH values by using dodecyl ammonium acetate, sodium dodecyl benzene sulphonate, and sodium oleate as collectors. From experimental results, it was recognized that the floatability of non-sulphide minerals correlates with the ratio of the concentration of the collector ion to that of hydrogen ion or hydroxyl ion in the solution. The relationships, $[R^+]/[H^+]^a = K$ with the cationic collector and $[R^-]/[OH^-]^a = K$ with the anionic collector, were obtained under critical flotation conditions. Next, the relationships above mentioned were derived from theoretical considerations of the competitive adsorption of collector cations and hydrogen ions or collector anions and hydroxyl ions onto a mineral surface and the significance of the two constants, a and K , in the above relationships was confirmed.

1. Introduction

The flotation of sulphide minerals has already been studied in detail, and many fundamental facts regarding their flotation characteristics have been clarified. However, there are only a few studies which have been systematically done on the flotation of non-sulphide minerals, and so the fundamental facts in this area are not fully clarified.

The purpose of this study is to clarify fundamental matters on the flotation of non-sulphide minerals by confirming the effects of collector and hydrogen ion concentrations on the floatability of non-sulphide minerals and by considering theoretically the action of collector ions and hydrogen ions or hydroxyl ions on a mineral surface.

2. Preparation of Mineral Samples

Quartz and scheelite from the Ōtani mine in Kyoto Prefecture, wolframite from the Kaneuchi mine in Kyoto Prefecture, barite from the Matsukura mine

* Department of Mining Engineering

in Otaru, Hokkaidō, calcite from the Chichibu mine in Saitama Prefecture, Japan, and hematite from Malaya were used in this experiment.

High grade coarse pieces of each of the above mentioned minerals were selected and crushed, and then pure mineral particles were picked up and ground in an agate mortar. The ground state of each mineral was sieved and the 35~48 mesh fraction was prepared. Each mineral sample was washed repeatedly in pure water to eliminate fine particles and was stored under pure water.

Qualitative analysis of the mineral samples was done with a Shimazu Quartz Medium Spectrograph (type NQM-60). The results of the spectro-chemical analysis of the mineral samples are shown in Table 1.

Table 1. Spectro-chemical analysis of mineral samples.

Elements Mineral	Ca	Si	W	Ba	Fe	Al	Mg	Mn	Ti	Cu	Sn	Other elements
Quartz	min. tr.	+++	—	—	min. tr.	min. tr.	min. tr.	—	—	min. tr.	—	—
Barite	+	+	—	+++	tr.	+	±	±	+	+	—	—
Calcite	+++	±	—	+	tr.	±	+	+	+	tr.	—	—
Scheelite	+++	min. tr.	+++	—	min. tr.	min. tr.	tr.	tr.	tr.	min. tr.	—	—
Wolframite	+	+	+++	±	+++	+	+	+++	+	+	+	—

Sign: (+)…present, (—)…none detected, tr…trace, min. tr…minute trace,
(±)…barely visible.

From the results of Table 1, it may be said that each mineral sample was pure enough for the purpose of this study. As the hematite may have contained some limonite and magnetite, the identification of the hematite was carried out by using a Philips Norelco X-Ray Diffraction Apparatus with results confirming the fact that the hematite sample used in this experiment was a pure hematite.

3. Collectors

Dodecyl ammonium acetate, sodium dodecyl benzene sulphonate, and sodium oleate were used as collectors in this study. Dodecyl ammonium acetate was prepared in the authors' laboratory from dodecyl amine and glacial acetic acid which were chemically extra pure. Sodium dodecyl benzene sulphonate and sodium oleate were produced at the laboratory of the Kaō Soap Co. Ltd., and the active ingredient of each of them was 94.6% and 94.7%, respectively. Sodium hydroxide and hydrochloric acid which were chemically extra pure were used as pH regulating agents.

4. Method of the Experiment

The floatability of mineral particles was evaluated by measuring the amounts of mineral particles picked up by air bubbles, adopting the bubble pick-up method of Cooke¹⁾.

Measurement procedures were as follows: an amount of mineral sample was taken into a bubble pick-up tube, a solution containing no collector with a constant pH value (100 ml) was added to it, the tube was kept in a thermostat ($25 \pm 1^\circ\text{C}$) for 5 min., an amount of collector was added to it, the tube was kept again in the thermostat for 5 min., and the amounts of mineral particles picked up were determined. The results recorded are the average value of three measurements. The pH value of the solution was measured with a glass electrode.

The critical bubble pick-up of mineral particles was determined by means of the standard visual method under various collector concentrations and pH values. Critical contact curves were determined from the critical pick-up point.

5. Experimental Results and Considerations

5.1 Effects of Collector and Hydrogen Ion Concentrations on the Floatability of Non-Sulphide Minerals.

The amounts of the mineral particles picked up by air bubbles were measured in the solutions of various collector concentrations with various pH values by using dodecyl ammonium acetate, sodium dodecyl benzene sulphonate, and sodium oleate as collectors, and then the effects of the collector ion concentrations and hydrogen ion concentrations on the floatability of the non-sulphide minerals were considered.

(1) Flotation by Dodecyl Ammonium Acetate

The results obtained are shown in Fig. 1, 2, 3, 4, 5 and 6 in which the amounts picked up of quartz, hematite, barite, calcite, scheelite, and wolframite are plotted respectively for various concentrations of dodecyl ammonium acetate, as a function of pH value.

Fig. 1 shows the results obtained with quartz.

Quartz starts to adhere to air bubbles at pH 3~5.5, and the amount picked up increases with the increase of pH value and becomes maximum at pH 9.5~10.5. In the more alkaline solutions, it decreases remarkably with the increase of pH value and becomes zero at pH 11.5~12.3.

Fig. 2 shows the results obtained with hematite.

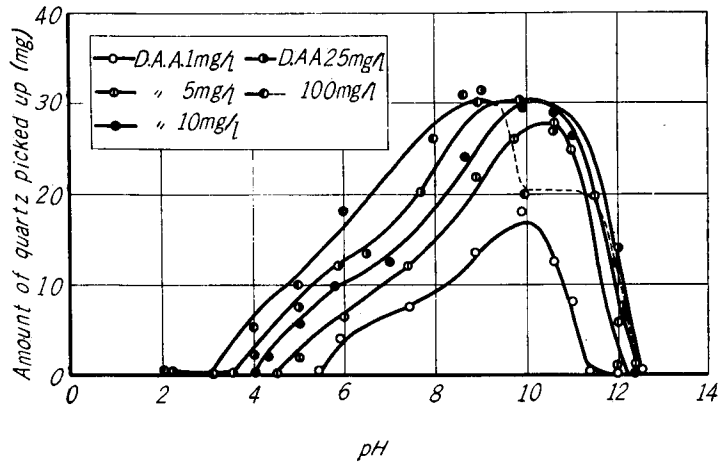


Fig. 2. Flotation curves for quartz in solutions of various concentrations of dodecyl ammonium acetate.

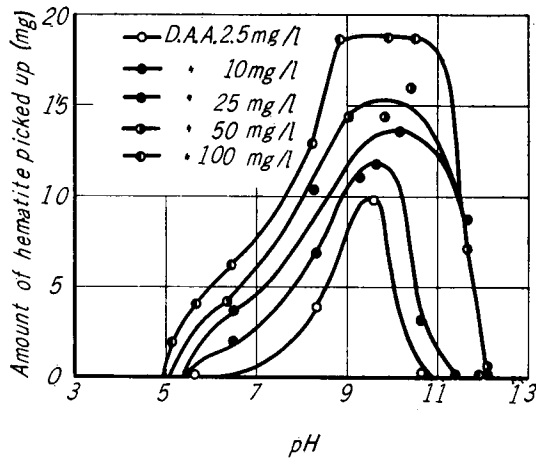


Fig. 3. Flotation curves for hematite in solutions of various concentrations of dodecyl ammonium acetate.

Hematite begins to adhere to air bubbles at pH 5~6, and the amount picked up increases with the increase of pH value and becomes maximum at pH 9~10. In the more alkaline solutions it abruptly decreases and becomes zero at pH 10.8~12.1.

Fig. 3 shows the results obtained with barite.

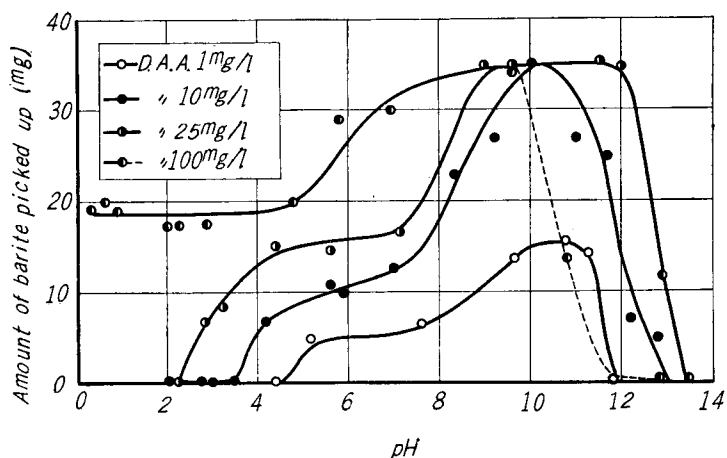


Fig. 3. Flotation curves for barite in solutions of various concentrations of dodecyl ammonium acetate.

Barite adheres to air bubbles at pH 2.2~4.5, and the amount picked up increases with the increase of pH value and becomes maximum at pH 9.5~11. In the more alkaline solutions it decreases remarkably and becomes zero at pH 11.8~13.5.

Fig. 4 shows the results obtained with calcite.

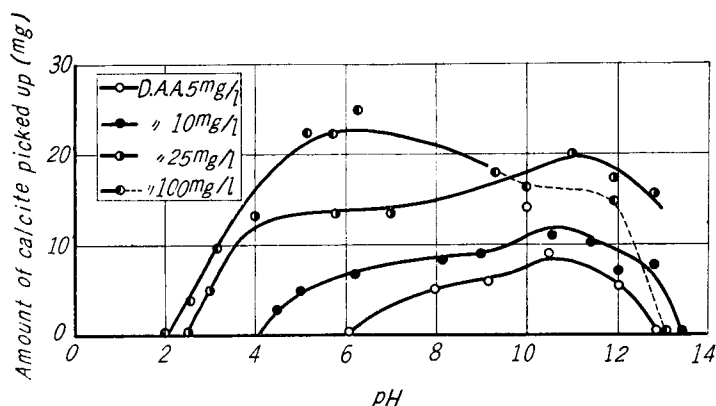


Fig. 4. Flotation curves for calcite in solutions of various concentrations of dodecyl ammonium acetate.

Calcite starts to adhere to air bubbles at pH 2~6, and the amount picked up increases with the increase of pH value and becomes maximum at about pH 10.5. In the more alkaline solutions it decreases and becomes zero at pH 12.8~13.5.

Fig. 5 shows the results obtained with scheelite.

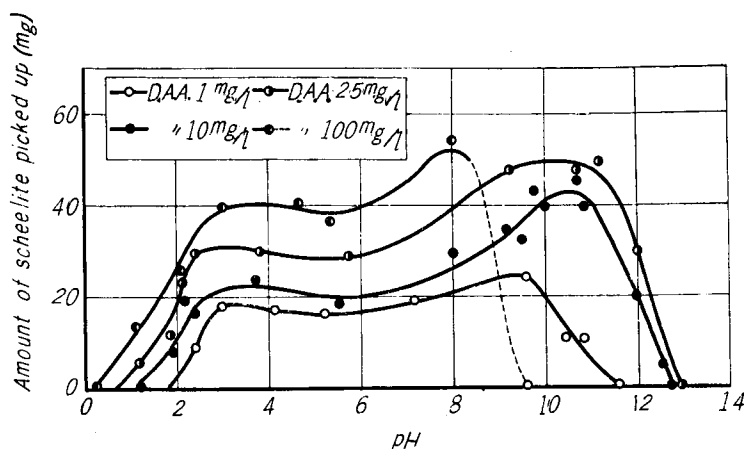


Fig. 5. Flotation curves for scheelite in solutions of various concentrations of dodecyl ammonium acetate.

Scheelite begins to adhere to air bubbles pH 0.2~2, and the amount picked up increases with the increase of pH value and becomes maximum at pH 10~11. In the more alkaline solutions it decreases remarkably and becomes zero at pH 11.5~13.

Fig. 6 shows the results obtained with wolframite.

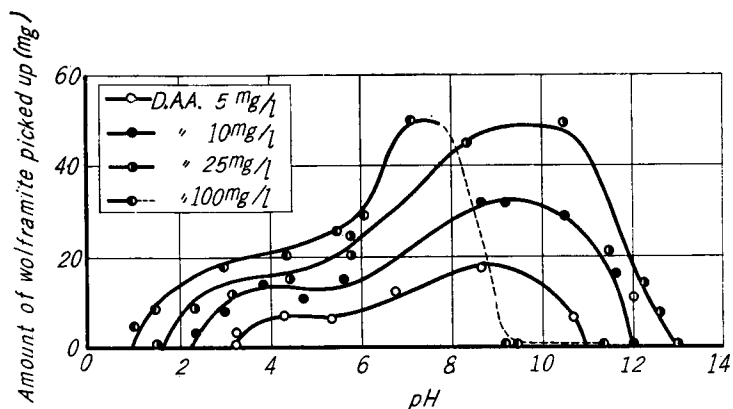


Fig. 6. Flotation curves for wolframite in solutions of various concentrations of dodecyl ammonium acetate.

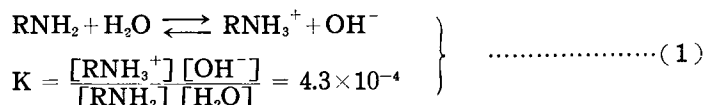
Wolframite adheres to air bubbles at pH 1~3, and the amount picked up increases with the increase of pH value, and becomes maximum at pH 9~10.5. In the more alkaline solutions it decreases remarkably and becomes zero at pH 10.8~12.1.

The dotted lines shown in Fig. 1, 2, 3, 4, 5 and 6 represent the unstable

adhesion of mineral particles to air bubbles.

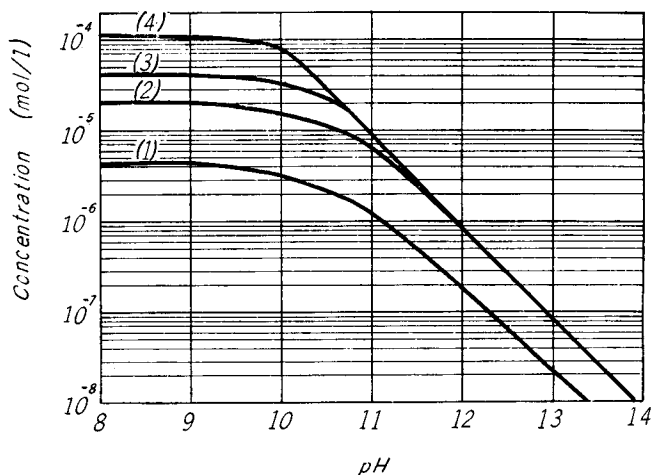
It is generally recognized from the above results that each mineral starts to contact air bubbles at certain acid pH values, and the amount picked up increases with the increase of pH value and becomes maximum at pH 9~10.5 and then decreases abruptly with the stronger alkaline solutions.

In the solutions of dodecyl ammonium acetate the following equilibrium²⁾ comes into existence,



where RNH_3^+ and RNH_2 represent the dodecyl ammonium ion and amine molecule respectively. K is the dissociation constant.

For the collector concentrations, 4.08×10^{-6} , 2.04×10^{-5} , 4.08×10^{-5} and 1.02×10^{-4} mol/l, the concentrations of dodecyl ammonium ion were calculated from equation (1) considering the solubility in water of dodecyl amine (2×10^{-5} mol/l)³⁾. The result calculated is shown in Fig. 7.



Concentration of dodecyl ammonium acetate (mol/l) :
(1) 4.08×10^{-6} (2) 2.04×10^{-5} (3) 4.08×10^{-5} (4) 1.02×10^{-4}

Fig. 7. Relation between pH value and dodecyl ammonium ion concentration.

As can be seen from Fig. 7, the concentrations of dodecyl ammonium ion can be regarded as nearly constant in the pH ranges of less than 9 at a given collector concentration. Accordingly, the quantity of $[\text{RNH}_3^+]/[\text{H}^+]$ increases

with the increase of pH value in the pH ranges of less than 9. Under such solution conditions, the floatability of mineral particles increases with the increase of pH value as shown in Fig. 1, 2, 3, 4, 5 and 6.

From these facts it is generally found that the floatability of non-sulphide minerals is correlative with the quantity of $[\text{RNH}_3^+]/[\text{H}^+]$.

On the other hand, the concentration of dodecyl ammonium ion becomes extremely low in the strong alkaline solutions as shown in Fig. 7. Under such solution conditions, the floatability of mineral particles decreases remarkably as seen in Fig. 1, 2, 3, 4, 5 and 6.

These facts may indicate that the floatability of non-sulphide minerals is influenced by collector ion concentrations.

(2) Flotation by Sodium Dodecyl Benzene Sulphonate

The results obtained are shown in Fig. 8, 9 and 10 in which the amounts picked up of barite, calcite, and wolframite are plotted respectively for various concentrations of sodium dodecyl benzene sulphonate, as a function of pH value.

Fig. 8 shows the results obtained with barite.

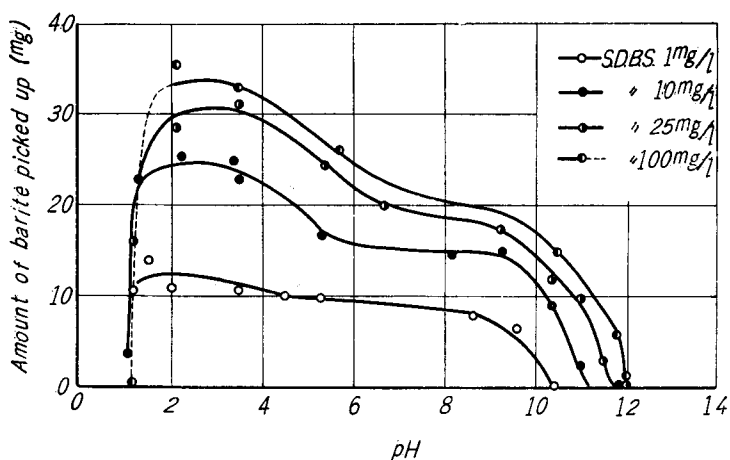


Fig. 8. Flotation curves for barite in solutions of various concentrations of sodium dodecyl benzene sulphonate.

Barite starts to adhere to air bubbles at pH 10.3~12, the amount picked up increases with the decrease of pH value and becomes maximum at about pH 2.5. In the lower pH ranges, it abruptly decreases and becomes zero at about pH 1.

Fig. 9 shows the results obtained with calcite.

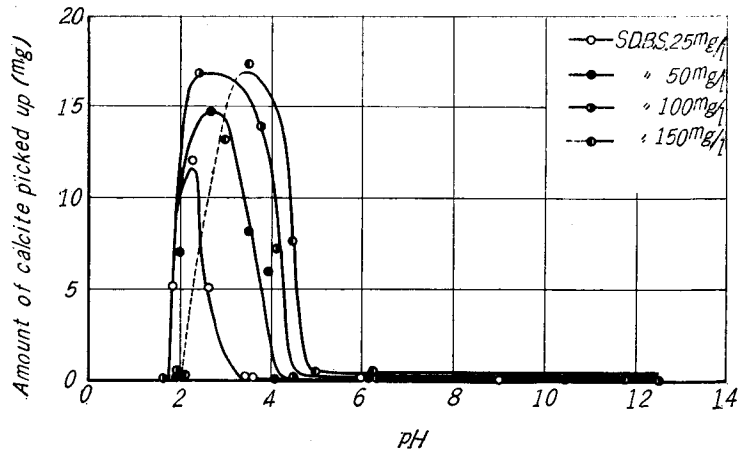


Fig. 9. Flotation curves for calcite in solutions of various concentrations of sodium dodecyl benzene sulphonate.

Calcite begins to adhere to air bubbles at pH 3.5~5, and the amount picked up increases with the decrease of pH value and becomes maximum at about pH 2.5. In the lower pH ranges, it abruptly decreases and becomes zero at pH 1.8~2.

Fig. 10 shows the results obtained with wolframite.

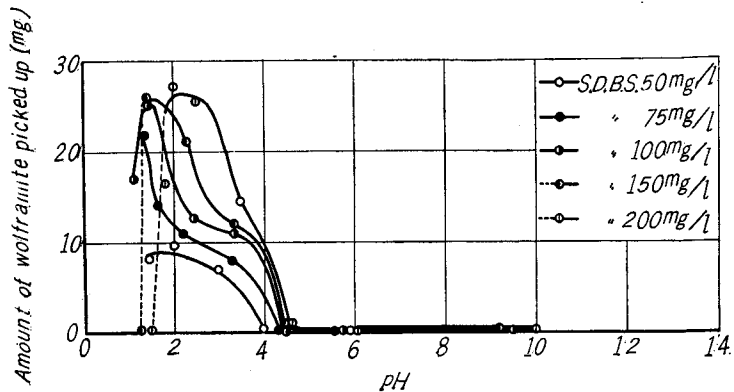


Fig. 10. Flotation curves for wolframite in solutions of various concentrations of sodium dodecyl benzene sulphonate.

Wolframite begins to adhere to air bubbles at pH 4~4.5, and the amount picked up increases with the decrease of pH value and becomes maximum at about pH 1.5~2. In the lower pH ranges, it decreases remarkably and becomes zero pH 1.2~1.5.

It is generally recognized from the above results that each mineral starts to contact air bubbles at certain alkaline or weak acid pH values, and the amount

picked up increases with the decrease of pH value and becomes maximum at pH 1.5~3 and then decreases abruptly at the stronger acid solutions.

Comparing Fig. 8 with Fig. 3, Fig. 9 with Fig. 4, and Fig. 10 with Fig. 6 respectively, it is found that the effect of hydrogen ion concentration on the floatability of non-sulphide minerals is opposite in the case of cationic collectors and anionic collectors.

(3) Flotation by Sodium Oleate

The results obtained are shown in Fig. 11, 12, 13 and 14 in which the amounts picked up of barite, scheelite, wolframite, and calcite are plotted respectively for various concentrations of sodium oleate, as a function of pH value.

Fig. 11 shows the results obtained with barite.

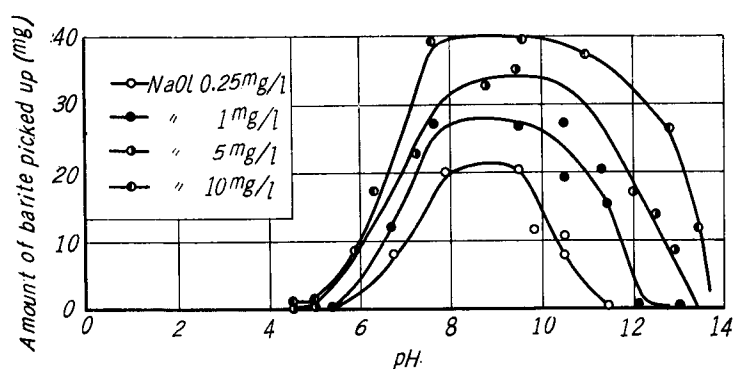


Fig. 11. Flotation curves for barite in solutions of various concentrations of sodium oleate.

Barite starts to adhere to air bubbles at pH 11.5~13.5, and the amount picked up increases with the decrease of pH value and becomes maximum at about pH 9. In the pH ranges less than 8, it decreases remarkably and becomes zero at pH about 5.

Fig. 12 shows the results obtained with scheelite.

Scheelite begins to adhere to air bubbles at pH 11.5~13.4, and the amount picked up increases with the decrease of pH value and becomes maximum at about pH 9.5. In the pH ranges of less than 8, it decreases remarkably and becomes zero at about pH 5.5.

Fig. 13 shows the results obtained with wolframite.

Wolframite adheres to air bubbles at pH 10~10.5, and the amount picked up increases with the decrease of pH value and becomes maximum at pH 8~9. In the lower pH ranges, it decreases remarkably and becomes zero at about pH 5.

Fig. 14 shows the results obtained with calcite.

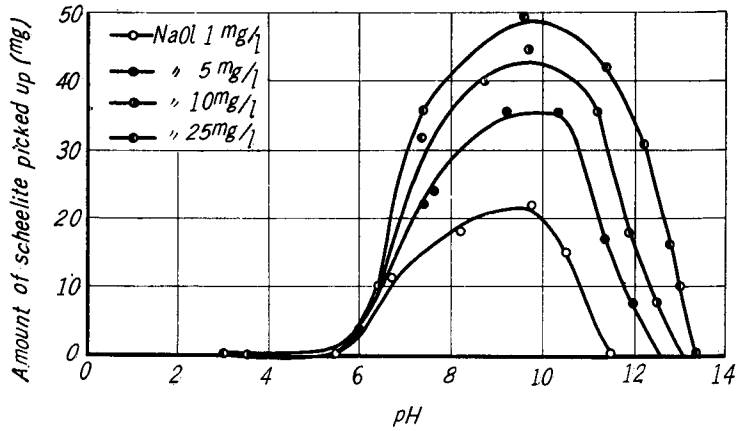


Fig. 12. Flotation curves for scheelite in solutions of various concentrations of sodium oleate.

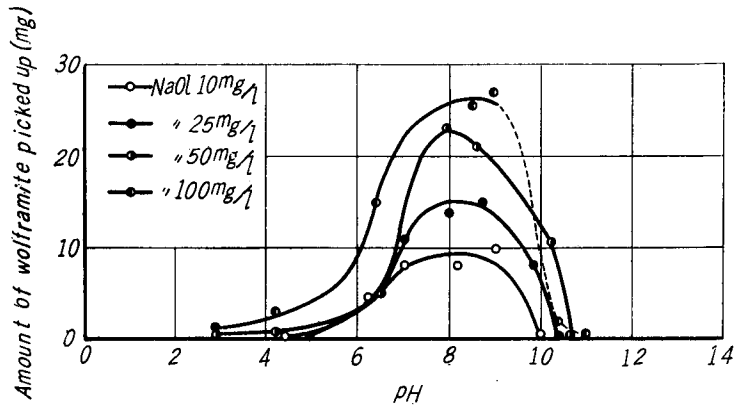


Fig. 13. Flotation curves* for wolframite in solutions of various concentrations of sodium oleate.

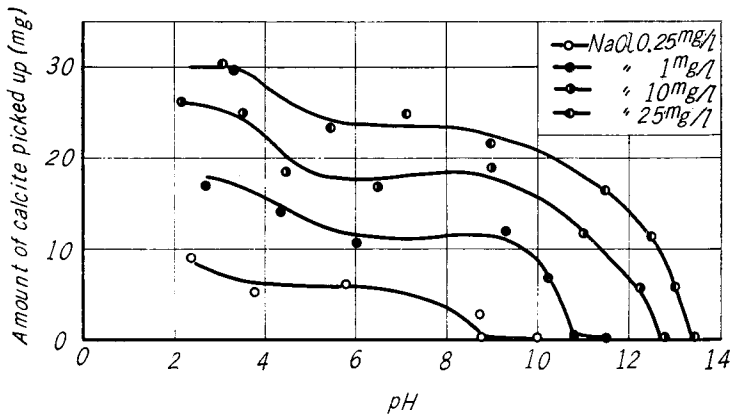
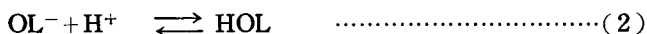


Fig. 14. Flotation curves for calcite in solutions of various concentrations of sodium oleate.

Calcite begins to adhere to air bubbles at pH 8~13.4 and the amount picked up increases with the decrease of pH value until about pH 3.

It is recognized from the above results that each mineral starts to contact air bubbles at certain alkaline pH values, and the amount picked up increases with the decrease of pH value and becomes maximum at about pH 9 in the case of barite, scheelite and wolframite, and then decreases abruptly with the more acid solutions.

In the solutions of sodium oleate the following equilibrium comes into existence.



where OL^- , HOL and HOL_2^- are oleic ion, oleic acid and an acid soap, respectively. The value of pK_a on equation (2) may be 5.5, and equation (3) may proceed at less than pH 9⁴⁾. From equation (2) and (3), the concentrations of oleic ion may be considered as nearly constant in the pH ranges of more than 9 at a given collector concentration. Accordingly, the quantity of $[OL^-]/[OH^-]$ increases with the decrease of pH value in the pH ranges 9~13.5. Under such solution conditions, the floatability of mineral particles increases with the decrease of pH value as shown in Fig. 11, 12, 13 and 14.

From these facts it is found that the floatability of non-sulphide minerals correlates with the quantity of $[OL^-]/[OH^-]$.

On the other hand, the concentration of oleic ion is extremely reduced in the acid solution. Under such solution conditions, the floatability of barite, scheelite and wolframite becomes very low.

As mentioned above, it is recognized that the floatability of non-sulphide minerals, as a rule, is governed by the quantity of $[R^+]/[H^+]$ with cationic collectors or $[R^-]/[OH^-]$ with anionic collectors in the pH ranges in which each collector ion concentration is kept nearly constant.

5.2 Relationship between Concentration of Collector and Critical pH Value.

The critical contact curves of the systems above described were obtained, and the relationships between the concentration of collector and the critical pH value were quantitatively determined.

The critical contact curves of each system are summarized in Fig. 15, 16 and 17. These contact curves represent the relationships between the concentration of collector and the critical pH value of each mineral, when dodecyl ammonium acetate, sodium dodecyl benzene sulphonate, and sodium oleate are used as collectors.

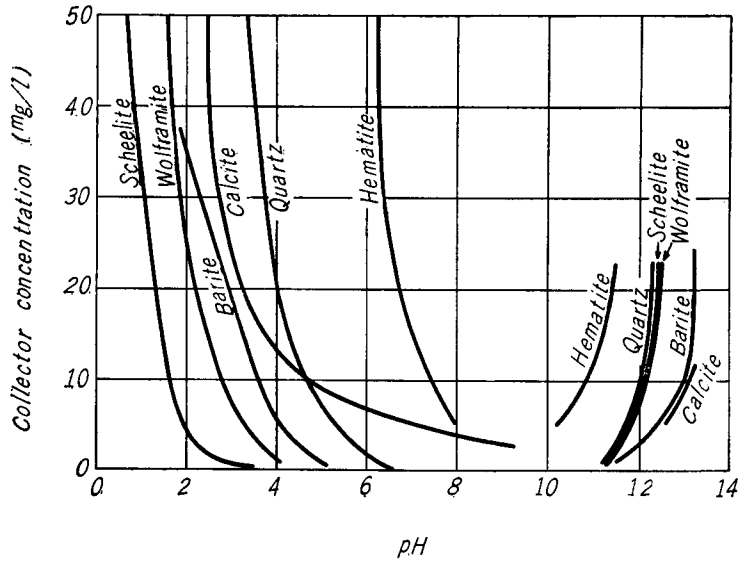


Fig. 15. Critical contact curves for various non-sulphide minerals, using dodecyl ammonium acetate as collector.

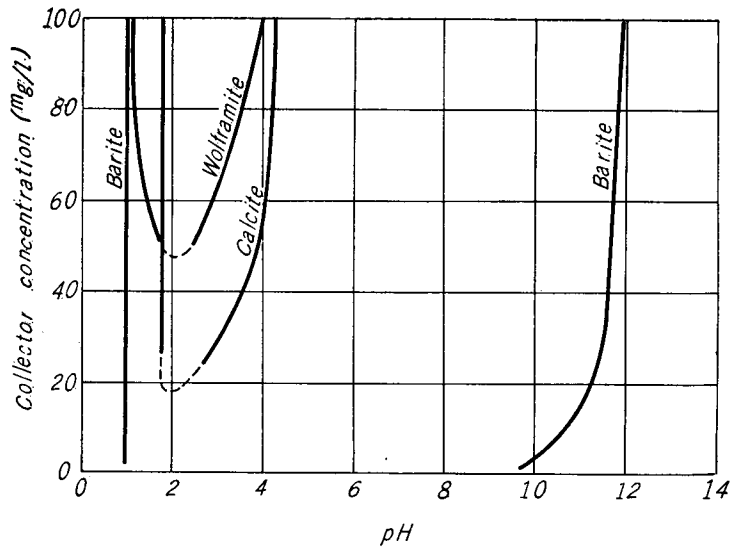


Fig. 16. Critical contact curves for various non-sulphide minerals, using dodecyl benzene sulphonate as collector.

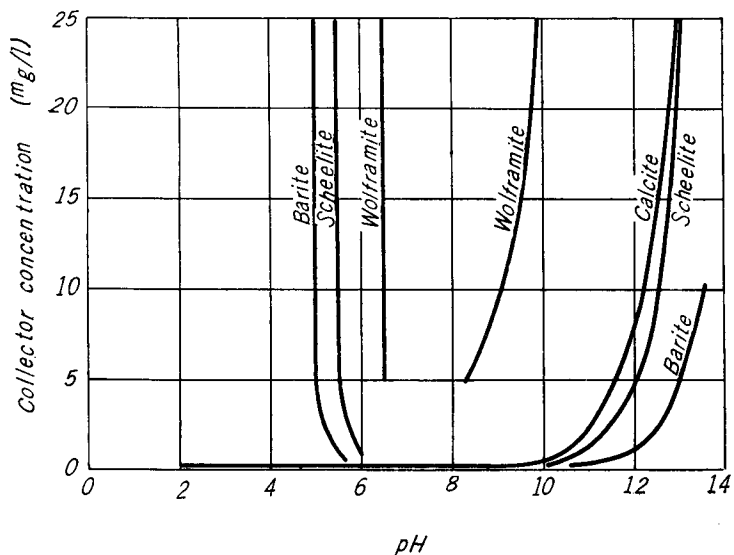


Fig. 17. Critical contact curves for various non-sulphide minerals, using sodium oleate as collector.

As can be seen from Fig. 15, when a cationic collector is used, the critical pH value of each mineral in the acid side becomes lower according to the increase of the collector concentration. On the other hand, as can be seen from Fig. 16 and 17, when an anionic collector is used, the critical pH value of each mineral on the alkaline side becomes higher with the increase of the collector concentration. However, on the alkaline side in Fig. 15 and on the acid side in Fig. 16, and 17, the critical pH values are nearly free from the concentrations of each collector and appear to be nearly constant. This may be based upon the fact that each collector ion concentration is reduced notably in such pH ranges as previously described.

The relations between the concentration of the collector and the critical pH value on the acid side in Fig. 15 and on the alkaline side in Fig. 16 and 17 are generally expressed by the following equation,

$$\log [R] = a \text{ pH} + b \dots\dots\dots(4)$$

where R represents a collector, and a and b are constant.

The values of a and b for each system were determined. The results calculated are summarized, as the relationships of $[DAA]/[H^+]^a = K$, $[SDBS]/[OH^-]^a = K$ and $[NaOL]/[OH^-]^a = K$, in Table 2, 3 and 4, and their graphic representations, as the form of equation (4), are shown in Fig. 18, 19 and 20. The value of K is a characteristic constant depending upon the kind of collector and mineral.

Table 2. Relationship between concentration of dodecyl ammonium acetate and critical pH value.

Hematite	:	$[\text{DAA}]/[\text{H}^+]^{0.53} = 10^{-0.4}$
Quartz	:	$[\text{DAA}]/[\text{H}^+]^{0.67} = 10^{-1.3}$
Calcite	:	$[\text{DAA}]/[\text{H}^+]^{0.15} = 10^{-3.6}$
Barite	:	$[\text{DAA}]/[\text{H}^+]^{0.58} = 10^{-2.4}$
Wolframite	:	$[\text{DAA}]/[\text{H}^+]^{0.72} = 10^{-2.5}$
Scheelite	:	$[\text{DAA}]/[\text{H}^+]^{0.83} = 10^{-3.0}$

Table 3. Relationship between concentration of sodium dodecyl benzene sulphate and critical pH value.

Barite	:	$[\text{SDBS}]/[\text{OH}^-]^{0.19} = 10^{-1.2}$
Calcite	:	$[\text{SDBS}]/[\text{OH}^-]^{0.39} = 10^{0.24}$
Wolframite	:	$[\text{SDBS}]/[\text{OH}^-]^{0.20} = 10^{-2.5}$

Table 4. Relationship between concentration of sodium oleate and critical pH value.

Wolframite	:	$[\text{NaOL}][\text{OH}^-]^{0.53} = 10^{-1.9}$
Scheelite	:	$[\text{NaOL}][\text{OH}^-]^{0.68} = 10^{-3.5}$
Calcite	:	$[\text{NaOL}][\text{OH}^-]^{0.49} = 10^{-3.7}$
Barite	:	$[\text{NaOL}][\text{OH}^-]^{0.57} = 10^{-4.3}$

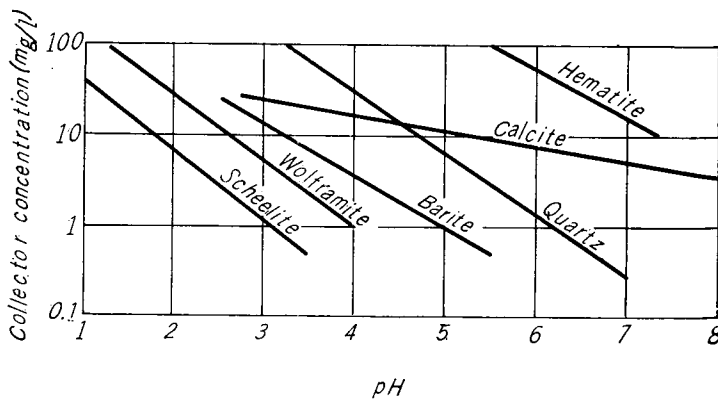


Fig. 18. Relation between concentration of dodecyl ammonium acetate and critical pH value.

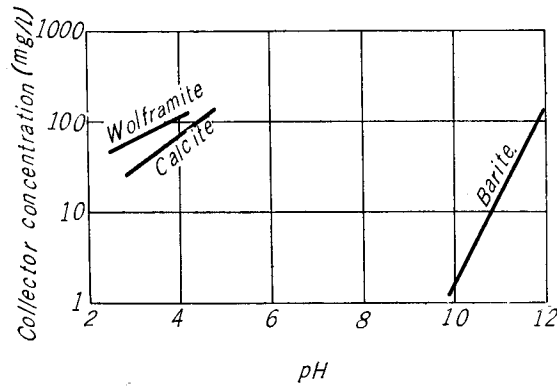


Fig. 19. Relation between concentration of sodium dodecyl benzene sulphonate and critical pH value.

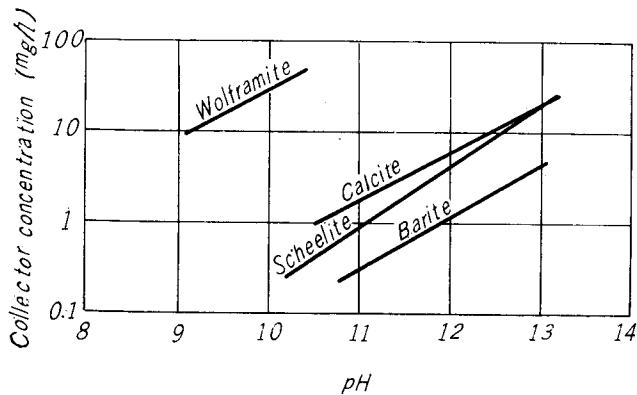


Fig. 20. Relation between concentration of sodium oleate and critical pH value.

These relationships can also be expressed as $[R^+]/[H^+]^a = K$, or $[R^-]/[OH^-]^a = K$, where R^+ and R^- represent collector cation and collector anion respectively, because each collector concentration is nearly equal to the collector ion concentration.

The relationships shown in Table 2, 3 and 4 give the quantitative relation between the collector concentration and pH value concerning the critical flotation conditions of various non-sulphide minerals. These data give the base of the separation of non-sulphide minerals by flotation.

6. Theoretical Consideration

The adsorption of the two ions, R^+ and H^+ or R^- and OH^- onto the same site of mineral surface was discussed theoretically and then the relation between the collector concentration and the critical pH value were considered.

(1) The Adsorption of Two Cations onto a Uniform Surface.

Considering that the two cations, R^+ and H^+ adsorb competitively on a mineral surface and that the rate of adsorption is equal to the rate of desorption in an equilibrium condition, the following equations are derived according to Langmuir's treatment⁵⁾

$$k'_{R^+}[R^+](1-\theta_{R^+}-\theta_{H^+}) = k''_{R^+}\theta_{R^+} \quad \dots\dots\dots(5)$$

$$k'_{H^+}[H^+](1-\theta_{R^+}-\theta_{H^+}) = k''_{H^+}\theta_{H^+} \quad \dots\dots\dots(6)$$

where θ_{R^+} and θ_{H^+} are the fraction of the surface covered by collector cation and hydrogen ion respectively.

Putting $k'_{R^+}/k''_{R^+} = a_{R^+}$ and $k'_{H^+}/k''_{H^+} = a_{H^+}$,

$$a_{R^+} = k_{R^+} e^{E_{R^+}/RT} \quad \dots\dots\dots(7)$$

$$a_{H^+} = k_{H^+} e^{E_{H^+}/RT} \quad \dots\dots\dots(8)$$

where E_{R^+} and E_{H^+} are the heat of adsorption of collector cation and hydrogen ion respectively.

From equation (5) and (6), the following equations are obtained.

$$\theta_{R^+} = \frac{a_{R^+}[R^+]}{1 + a_{R^+}[R^+] + a_{H^+}[H^+]} \quad \dots\dots\dots(9)$$

$$\theta_{H^+} = \frac{a_{H^+}[H^+]}{1 + a_{R^+}[R^+] + a_{H^+}[H^+]} \quad \dots\dots\dots(10)$$

The adsorption amount of R^+ ion, Γ_{R^+} , is proportional to θ_{R^+} .

Hence,

$$\Gamma_{R^+} = \frac{b a_{R^+}[R^+]}{1 + a_{R^+}[R^+] + a_{H^+}[H^+]} \quad \dots\dots\dots(11)$$

where b is a proportional constant. Equation (11) represents the adsorption amount of collector ion, R^+ under conditions where collector cations and hydrogen ions adsorb competitively on a mineral surface.

(2) The Adsorption of Two Cations onto a Nonuniform Surface.

The adsorption isotherm on a nonuniform surface is expressed by the following equation,

$$\Gamma = \int_{\epsilon_l}^{\epsilon_m} N(\epsilon)\theta(\epsilon)d\epsilon \quad \dots\dots\dots(12)$$

where $N(\epsilon)$ is the distribution function of the heat of adsorption, ϵ_l and ϵ_m are the lower and upper limits of the heat of adsorption on the surface, $\theta(\epsilon)$ is the fraction of adsorption on the adsorption site of which heat of adsorption is ϵ .

From equation (7), (8) and (9), the following relation is derived.

$$\theta(\varepsilon) = \frac{k_{R^+}[R]e^{\varepsilon_{R^+}/RT}}{1 + k_{R^+}[R^+]e^{\varepsilon_{R^+}/RT} + k_{H^+}[H^+]e^{\varepsilon_{H^+}/RT}} \quad \dots\dots\dots(13)$$

If it be assumed that the distribution function, $N(\varepsilon)$, can be expressed as an exponential function, it may be written as follows,

$$N(\varepsilon) = \beta e^{-\alpha\varepsilon} \quad \dots\dots\dots(14)$$

where β and α are constant. In the critical condition of mineral flotation, the adsorption of collector is equivalent to that of the hydrogen ion or hydroxyl ion and, therefore, it may be considered that

$$\varepsilon_{R^+} \cong \varepsilon_{H^+} = \varepsilon. \quad \dots\dots\dots(15)$$

Accordingly, equation (12) can be put in the form

$$\Gamma_{R^+} = \int_{-\infty}^{+\infty} \frac{k_{R^+}[R^+]e^{\varepsilon/RT}}{1 + (k_{R^+}[R^+] + k_{H^+}[H^+])e^{\varepsilon/RT}} \cdot \beta e^{-\alpha\varepsilon} d\varepsilon \quad \dots\dots\dots(16)$$

Putting $x = 1 + (k_{R^+}[R^+] + k_{H^+}[H^+])e^{\varepsilon/RT}$, equation (16) is

$$\begin{aligned} \Gamma_{R^+} &= RT\beta \frac{k_{R^+}[R^+]}{k_{R^+}[R^+] + k_{H^+}[H^+]} (k_{R^+}[R^+] + k_{H^+}[H^+])^{\alpha RT} \int_1^{\infty} (x-1)^{-\alpha RT} x^{-1} dx \\ &= RT\beta \frac{k_{R^+}[R^+]}{k_{R^+}[R^+] + k_{H^+}[H^+]} (k_{R^+}[R^+] + k_{H^+}[H^+])^{\alpha RT} \int_0^{\infty} \frac{t^{-\alpha RT}}{t+1} dt \quad \dots\dots\dots(17) \end{aligned}$$

When αRT is for $0 < \alpha RT < 1$, $\int_0^{\infty} \frac{t^{-\alpha RT}}{t+1} dt = \frac{\pi}{\sin[(1-\alpha RT)\pi]}$.

Hence, the integral of equation (17) becomes

$$\begin{aligned} \Gamma_{R^+} &= RT\beta \frac{\pi}{\sin[(1-\alpha RT)\pi]} \cdot \frac{k_{R^+}[R^+]}{k_{R^+}[R^+] + k_{H^+}[H^+]} (k_{R^+}[R^+] + k_{H^+}[H^+])^{\alpha RT} \\ &= C \frac{k_{R^+}[R^+]}{(k_{R^+}[R^+] + k_{H^+}[H^+])^\gamma} \quad \dots\dots\dots(18) \end{aligned}$$

where, $C = RT\beta \frac{\pi}{\sin[(1-\alpha RT)\pi]}$, $\gamma = 1 - \alpha RT$.

(3) Theoretical Consideration of the Relation between Collector Ion Concentration and Hydrogen Ion Concentration at the Critical Condition of Mineral Flotation.

Equation (11) is simplified as follows under the condition, $1 \ll a_{R^+}[R^+] + a_{H^+}[H^+]$,

$$\Gamma_{R^+} = \frac{b a' \frac{[R^+]}{[H^+]}}{1 + a' \frac{[R^+]}{[H^+]}} \quad \dots\dots\dots(19)$$

in which $a' = a_{R^+}/a_{H^+} = k_{R^+}/k_{H^+} \cdot e^{(E_{R^+} - E_{H^+})/RT}$.

It follows that the adsorption amount, Γ_{R^+} , increases with increasing of the quantity $[R^+]/[H^+]$ from equation (19), and Γ_{R^+} increases with increasing of

the quantity $k_{R^+}[R^+]/(k_{R^+}[R^+] + k_{H^+}[H^+])^\gamma$ from equation (18), and Γ_{R^-} increases with increasing of $[R^-]/[OH^-]$ or $k_{R^-}[R^-]/(k_{R^-}[R^-] + k_{OH^-}[OH^-])^\gamma$.

The floatability of mineral particles increases with the increase of $[R^+]/[H^+]$ in the pH ranges of less than about 9 in the case of cationic collectors, as already shown in Fig. 1, 2, 3, 4, 5 and 6. Also the floatability of mineral particles increases with the increase of $[R^-]/[OH^-]$ in a solution of more than about pH 9 in the case of sodium oleate and more than about pH 3 in the case of sodium dodecyl benzene sulphonate, as shown in Fig. 8, 11, 12, 13 and 14.

From these facts, it is recognized that the floatability of mineral particles correlates with the adsorption density of the collector ion which is governed by the competitive adsorption of collector cations and hydrogen ions or that of collector anions and hydroxyl ions onto the mineral surface.

From the considerations on the competitive adsorption of the two ions, R^+ and H^+ or R^- and OH^- , onto the same site of mineral surface, equation (11) and (19) were derived.

$$\Gamma_{R^+} = \frac{b \cdot a' \frac{[R^+]}{[H^+]}}{1 + a' \frac{[R^+]}{[H^+]}} \quad \dots\dots\dots(19)$$

Under the critical condition of flotation, the adsorption of collector ion may be constant. Hence,

$$\frac{[R^+]}{[H^+]} = \frac{\Gamma_{R^+}}{a'(b - \Gamma_{R^+})} = \text{const.} \quad \dots\dots\dots(20)$$

From the considerations on the competitive adsorption of the two ions, R^+ and H^+ or R^- and OH^- , onto the same site of nonuniform surface, equation (18) was derived.

$$\Gamma_{R^+} = C \frac{k_{R^+}[R^+]}{(k_{R^+}[R^+] + k_{H^+}[H^+])^\gamma} \quad \dots\dots\dots(18)$$

Similarly, under the critical condition, the following relation is formed in many flotation systems,

$$\frac{[R^+]}{[H^+]^\gamma} = \frac{1}{C} \cdot \frac{(k_{H^+})^\gamma}{k_{R^+}} \cdot \Gamma_{R^+} = \text{const.} \quad \dots\dots\dots(21)$$

From equation (20) the following relation between R^+ and H^+ under the critical condition is confirmed

$$\frac{[R^+]}{[H^+]} = K \quad \dots\dots\dots(22)$$

K is shown as a function of the adsorption of the collector at the critical condition, b and $k_{R^+}/k_{H^+} \cdot e^{(E_{R^+} - E_{H^+})/RT}$.

From equation (21), the following relation between R^+ and H^+ under the critical condition is confirmed

$$\frac{[R^+]}{[H^+]^a} = K' \quad \dots\dots\dots(23)$$

K' is characterized as a function of the adsorption of collector at the critical condition and $\frac{1}{C} \cdot \frac{(k_{H^+})^{1-\alpha RT}}{k_{R^+}}$. Also the constant in equation (23), a , is characterized as a function of $(1-\alpha RT)$. In the case of the competitive adsorption of collector anion and hydroxyl ion, similar relations to equation (22) and (23) are obtained.

The significance of two constants, K and a , under the critical condition of flotation was confirmed by the considerations on the competitive adsorption of collector ions and hydrogen ions or hydroxyl ions onto mineral surface.

7. Summary

The floatability of the various non-sulphide minerals, such as quartz, hematite, barite, calcite, scheelite and wolframite were measured by using dodecyl ammonium acetate, sodium dodecyl benzene sulphate, and sodium oleate as collectors and then the effects of the collector ion concentrations and hydrogen ion concentrations on the floatability of these minerals were considered theoretically.

The results of this study are summarized as follows:

- (1) The effects of the hydrogen ion concentration on the floatability of each mineral were ascertained in the solutions of various concentrations of the collector.
- (2) The floatability of non-sulphide minerals, as a rule, is governed by the quantity of $[R^+]/[H^+]$ with cationic collector or $[R^-]/[OH^-]$ with anionic collector in the pH ranges in which each collector ion concentration is kept nearly constant.
- (3) The critical contact curves of each mineral were determined, and the results are shown in Fig. 15, 16 and 17.
- (4) The relationships between the collector concentration and the critical pH value were determined for each mineral and the following relationships under the critical condition $[R^+]/[H^+]^a = K$ in the case of cationic collector or $[R^-]/[OH^-]^a = K$ in the case of anionic collector were obtained. Both a and K are constant for each mineral, and their values are summarized in Table 2, 3 and 4.
- (5) The relationships between the collector concentration and the critical pH value under the critical condition of flotation were discussed theoretically on the

basis of the competitive adsorption of collector ions and hydrogen ions or hydroxyl ions on mineral surface in the case of both a uniform and a nonuniform surface, and the concept of two constant, a and K , under the critical condition of flotation was confirmed.

References

- 1) R. B. Cooke and M. Digre: *Min. Eng.*, **1**, 306~309, (1949).
- 2) A. M. Gaudin and D. W. Fuerstenau: *Min. Eng.*, **7**, 958~962, (1955).
- 3) P. L. de Bruyn: *Min. Eng.*, **7**, 291~297, (1955).
- 4) K. L. Sutherland and I. W. Wark: *Principles of Flotation*, **2nd**, 174~175, (1955).
- 5) H. S. Taylor: *A Treatise on Physical Chemistry*, **2nd**, Vol 2, 1072~1074, (1930).