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Selectivity Indexes as a Function of pH on a Mixture of Goethite and Clay Minerals

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Introduction and Summary

The previous report¹⁾ was mainly concerned with the flotation characteristics of clay minerals, kaolinite and montmorillonite which were significantly changed by previous roasting, due to the changes of their crystalline structure. In the flotation test of montmorillonite, for example, the mineral originally nonfloatable with a certain collector concentration with respect to the cationic collector became floatable when the specimen had been previously roasted. Determining the floatability of such a single, or nearly pure mineral is helpful in understanding further investigations on the separative properties of a two-mineral system.

The purpose of the present work was to obtain comprehensive information on the separation behavior of two minerals, goethite and clay minerals, under flotation conditions in a laboratory scale.

To determine the influence of roasting on the separative property, a previously roasted specimen was used and the result was compared with that of the non-roasted, or natural specimen. The value of the selectivity index²⁾ was taken as an indicator for measuring the result of the relative separation of the two minerals involved.

Upon achieving successful separation, a new experimental method was

devised, and the data obtained from this method were compared with those obtained from the Hallimond tube method.

Materials

Goethite Sample

The goethite sample was obtained from the Nittetsu Mines, Kutchan, Hokkaido. A hand-picked sample of about 2 kg was crushed and ground into powder, with a particle size less than 65 mesh. To eliminate any clay-like inclusions from the sample, the product was repeatedly washed with demineralized water until the "yellowish turbidity" completely disappeared from the solution. The remaining part, which had a brownish black color, was wet-screened at 200-mesh; the 100/200-mesh fraction was used for the flotation test. The cleaned goethite after treating with 15 percent hydrogen peroxide was stored under demineralized water. Chemical analysis of the sample is given in table 1.

The identification of the goethite sample was carried out by x-ray diffraction,

TABLE 1. Chemical Analyses of the Samples

| | Goethite | Theoretical | Kaolinite | Theoretical |
|--------------------------------|---------------|-------------|--------------|---------------|
| Fe ₂ O ₃ | 79.41 | 89.9 | nd. | — |
| SiO ₂ | 0.52 | — | 47.34 | 46.54 |
| Al ₂ O ₃ | 2.49 | — | 37.05 | 39.50 |
| H ₂ O (+) | | | 1.60 (130°C) | — |
| H ₂ O (—) | 12.27 (750°C) | 10.1 | 5.70 (600°C) | 13.96 (600°C) |
| Na ₂ O | — | — | n. d. | — |
| Total | 94.69 | 100.0 | 91.69 | 100.0 |

TABLE 2. X-ray diffraction of Goethite Samples

| ASTM Data for Goethite | | Specimen | No. indicated in Fig. 1 |
|------------------------|------|----------|----------------------------|
| I | 2θ | 2θ | |
| 60 | 21.0 | 21.0 | (1) |
| 100 | 24.7 | 24.8 | (2) |
| 60 | 31.1 | 31.0 | (3) |
| 70 | 38.7 | 39.0 | (4) |
| 55 | 41.0 | 41.0 | (5) |
| 80 | 43.0 | 43.0 | (6) |

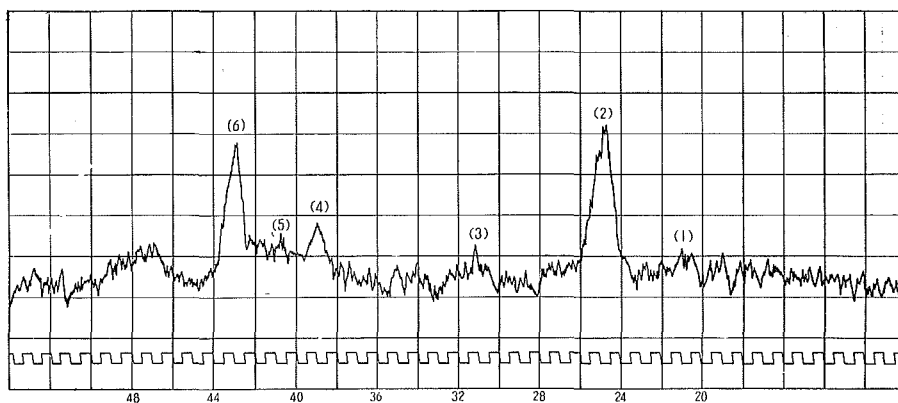


Fig. 1. X-Ray Diffraction Pattern of Goethite Sample

the automatically recorded diffraction pattern of the powder is presented in Fig 1. The result, which gives diffracted intensity vs. diffraction angle 2θ , shows that the material is comparable with the ASTM data for goethite as shown in table 2.

Clay minerals

The kaolinite sample obtained from the Takadama Mines in the Fukushima prefecture, was washed with demineralized water by decantation until free of foreign electrolyte. Chemical analysis and X-ray diffraction of the sample are presented in table 1 and Fig 2 (also table 3), respectively.

From the result of chemical analysis (table 1) and X-ray diffraction (table 3) of the clay mineral, the major constituent is believed to be kaolinite.

A high purity sample of montmorillonite was obtained, as bentonite, from the Kanto Chemical and Co.

TABLE 3. X-ray diffraction of Kaolinite Sample

| ASTM Data for Kaolinite | | Specimen | No. indicated in Fig. 2 |
|-------------------------|-----------|-----------|----------------------------|
| I | 2θ | 2θ | |
| 100 | 14.4 | 14.5 | (1) |
| 60 | 23.8 | 23.8 | (2) |
| 100 | 29.1 | 29.2 | (3) |
| 70 | 41.1 | 41.2 | (4) |
| 80 | 42.2 | 42.2 | (5) |
| 70 | 44.2 | 44.2 | (6) |
| 90 | 45.2 | 45.5 | (7) |

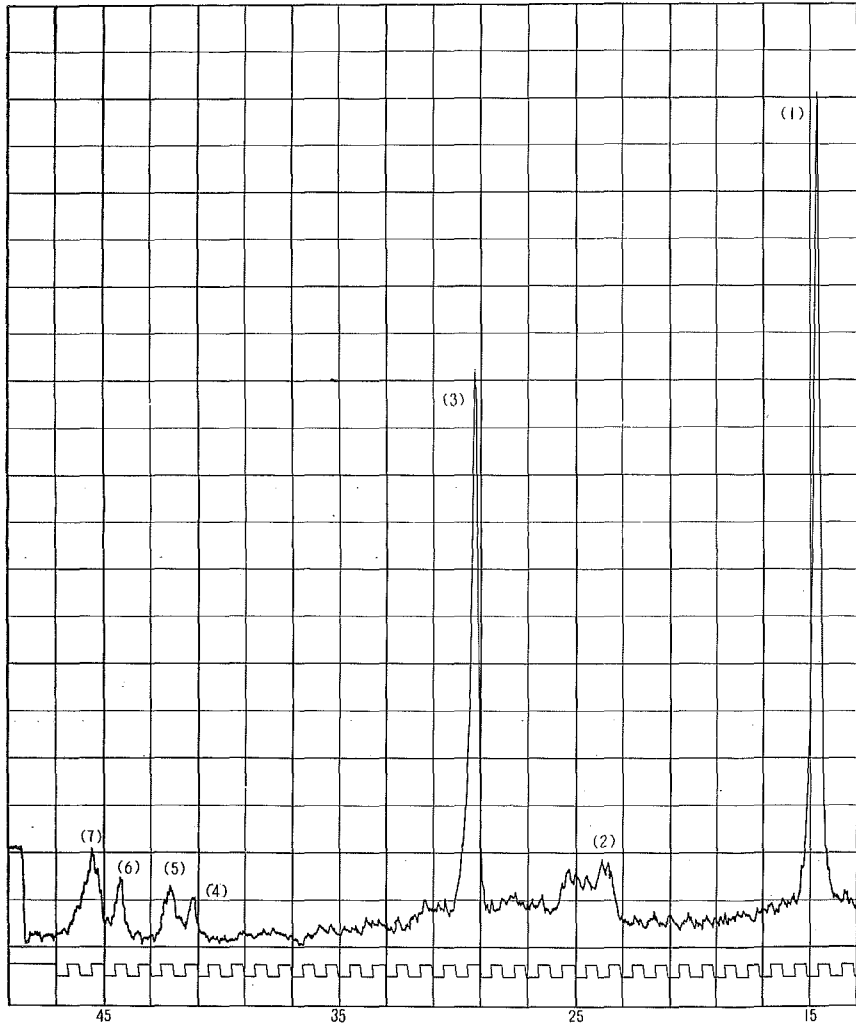


Fig. 2. X-Ray Diffraction Pattern of Kaolinite Sample

The samples of goethite, kaolinite and montmorillonite were used for the flotation tests in the natural state and in the state roasted for 1 hour at 400°C, 600°C and 800°C, respectively.

Reagents

Dodecyl amine acetate having a reported purity of 99.9 percent was received from Dr. T. Yamazaki, the Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Sendai, Japan. Sodium lauric sulfate

having a reported purity of 99.8 percent was obtained from Daiichi Kogyo Seiyaku Co. Reagent grade sodium hydroxide and hydrochloric acid were used as pH regulators.

Experimental Procedure and Results

K-Flot Cylinder Method

The quantitative studies on the floatabilities of clay minerals and "panit rocks" have been carried out in miniature with the modified Hallimond tube method as described in the previous paper". To test the applicability of the results obtained with the Hallimond tube, a new flotation system was devised. The arrangement of this flotation system (hereinafter referred to as K-Flot cylinder system) is schematically shown in Fig. 3. The system consists mainly

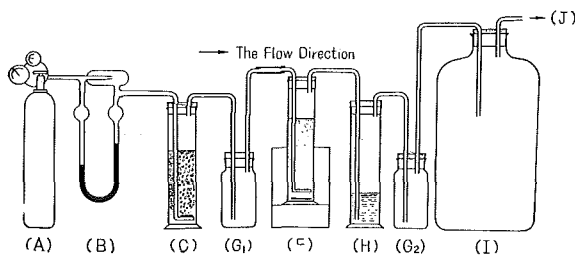


Fig. 3. The K-Flot Cylinder Unit

of the gas-washing part, the K-Flot cylinder, the froth settling cylinder and the aspiration part. Nitrogen gas for aeration is sent from a compressed gas tank (A) to the K-Flot cylinder (F) through the fluid-paraffine manometer (B) and the gas washing cylinder (C) containing 30 percent KOH solution. The K-Flot cylinder (F) is set to obtain the desired isothermal and regular agitation conditions by means of the thermostat (D) and the magnetic stirring mechanism (E),

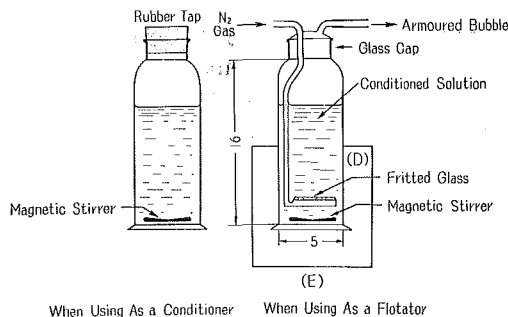


Fig. 4. The K-Flot Cylinder, cm

respectively, as shown in Fig 4. When the armoured bubble produced by sub-aeration bulks and fills up the K-Flot cylinder entirely, the bubbles move toward the froth settling cylinder (H) through the rubber tube connected. Higher than 95 percent of methyl alcohol contained in the froth settling cylinder immediately breaks the armoured bubbles to separate the mineral product from the froth. After a number of preliminary tests, about 30 ml of methyl alcohol was found to be enough to extinguish the bubbles completely.

Moving the armoured bubbles from the K-Flot cylinder to the froth settling cylinder is carried out not only by sub-aeration but also by aspiration, which is equipped with a water tap. To stabilize the pressure of both aeration and aspiration, a 20-liter empty bottle (I) is laid between the froth cylinder and an aspirator (J).

Prior to flotation, conditioning is carried out in the K-Flot cylinder by inserting a rubber tap, as shown in Fig. 4.

To obtain good reproducibility, special care must be given for the flotation test on the following points :

- (1) No air-leakage is detectable through the system.
- (2) The stirring speed in flotation should not exceed the point where the centrifugal current breaks the armoured bubbles created. Reversely, the speed should not be too slow to agitate the heavy mineral settled in the bottom.
- (3) At the end of flotation, the valve of the nitrogen gas flow, the magnetic stirrer and the aspirator are stopped. One end (G_1) of the rubber tube between the empty bottle (G_1) and the cylinder (F) is removed off and quickly put into water in a beaker, so that the water flowing through the fritten glass in the cylinder can push the remained armoured bubbles out of the cylinder. As the water level increases, the vacancy in the cylinder decreases. Filling water is thus continued until the water completely occupies the vacancy.
- (4) The armoured bubble remaining in the rubber tube between the K-Flot cylinder and the froth settling cylinder should be thoroughly washed out by taking one end (F) of the tube and pouring in washing water. The aspiration power which is still retained in the big empty bottle (I) after stopping the aspirator, is applicable for the operations (3) and (4) mentioned above.

After a number of preliminary tests, the K-Flot cylinder was standardized to operate with approximately 2 grams of the mineral sample per 200 ml of the solution with a flotation time of 5 minutes. The sample has been conditioned at 25°C for 60 minutes in the K-Flot cylinder.

To test reliability of the apparatus employed, the experimental results obtained from the K-Flot cylinder and the Hallimond tube methods are

compared against each other on their floatabilities.

Fig. 5 shows the effect of pH on the floatabilities of the roasted montmorillonites, Wyoming and Kanto bentonites when 10^{-3} M. of dodecylammonium chloride and dodecyl amine acetate were respectively used. The former data for the floatability was reproduced from the previous paper¹⁾ and the latter was obtained from the present work. It is clearly shown that these two characteristic curves are nearly identical, indicating that the flotation characteristics are little affected by the differences in the descriptions of the minerals prepared or in the negative electrolytes dissociated from the collectors.

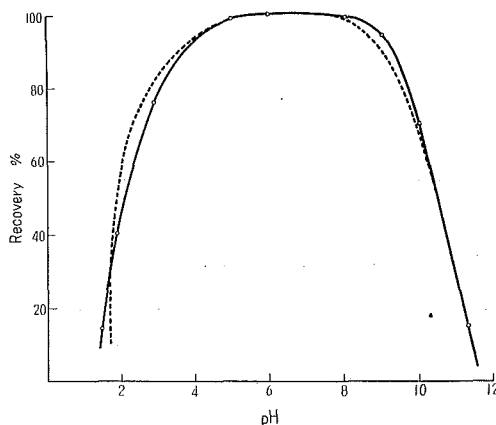


Fig. 5. Effect of pH on Recovery of Montmorillonite Roasted at 800°C , with 10^{-3} M. of DAA, when the Present Technique was Used, and with 10^{-3} M. of DACl when the Hallimond Tube Unit was Employed (Dotted Line)

Fig. 6 shows the effect of pH on the floatability of goethite when 10^{-3} M. of dodecyl amine acetate and sodium lauric sulfate (hereinafter referred to as DAA and NaLS respectively) were used. The dashed curves in Fig. 6 were reproduced from the published data³⁾. The floatability curve of NaLS crosses the DAA curve at about pH 7.0, being approximately the same pH value as that of the dashed curves. As illustrated by I. Iwasaki et. al., this value corresponds to the isoelectric point of goethite⁴⁾.

These two flotation tests indicate that the results obtained from the present experimental apparatus are sufficiently comparable with those of the Hallimond tube method. Consequently the former system is believed to be applicable to the proceeding experiment.

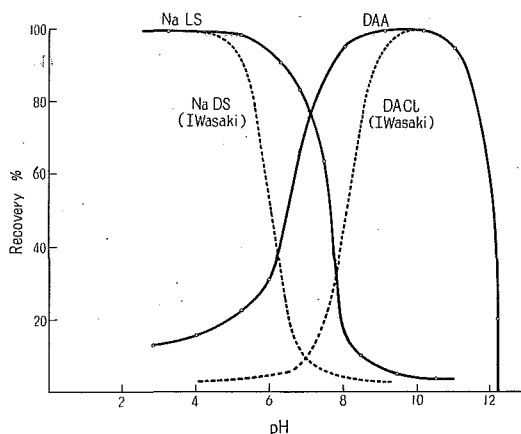


Fig. 6. Effect of pH on Recovery of Goethite, with 10^{-3} M. of NaLS and DAA, Comparing with the Iwasaki's Results (Dotted Lines)

Determination of the Selectivity Indexes On a Mixture of Goethite and Clay Minerals

The value of the selectivity index is taken as an indicator for measuring the effectiveness of the relative separation of the two minerals involved. Selectivity index, S I, is defined as follows²⁾:

$$SI = \sqrt{\frac{M}{m} \times \frac{n}{N}}$$

Where M is the percentage of Fe in concentrate, m is the percentage of Fe in tailing, N is the percentage of clay in concentrate, and n is the percentage of clay in tailing. If there is no separation, the selectivity index is unity; whereas if the separation is perfect, the selectivity index is infinite.

The first selectivity test in the present work was carried out by using an artificial mixture of goethite and montmorillonite. When using 10^{-3} M. of DAA as a cationic collector, the selectivity index is unity through the whole pH range tested. This was expected as long as the single mineral, montmorillonite, remained nonfloatable with this concentration of the collector. The extremely high adsorption capacity of montmorillonite toward the cationic collector, as illustrated in the previous paper, is obviously responsible for no selection. If, however, the excess amount of the collector was added to the solution of the montmorillonite in conditioning, some part of the collector, after mostly consumed for penetration between the layers of the montmorillonite structure, might be available to convert the mineral floatable.

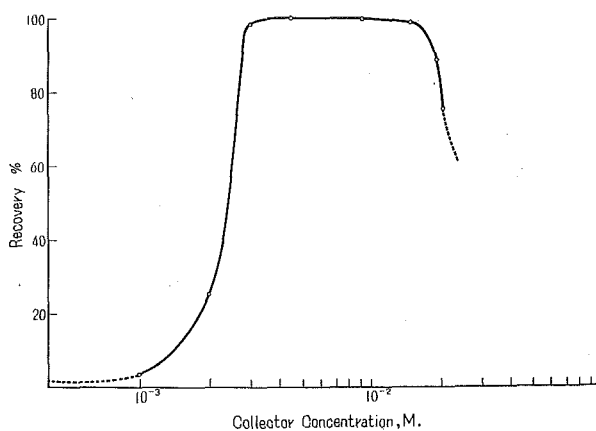


Fig. 7. Effect of Concentration of DAA on Recovery of Montmorillonite at pH 8.0 ± 0.5

Fig. 7 shows the percent recovery of montmorillonite (virtically) as a function of the initial concentration of DAA (horizontally). It now becomes clear that the concentration of the collector of 10^{-3} M. was insufficient to get a good recovery. It is interesting to note that when the concentration of the collector exceeds approximately 2×10^{-3} M. ie, the saturation capacity of the

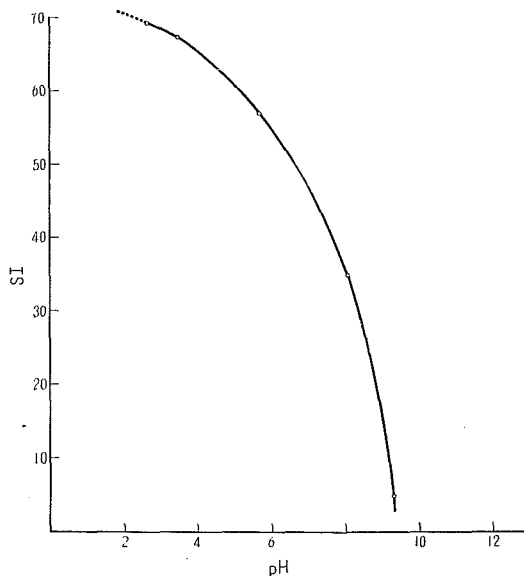


Fig. 8. Selectivity Index as a Function of pH on a Mixture of Goethite and Montmorillonite, with 3×10^{-3} M. of DAA

sample, the recovery suddenly increases to about 100 percent. This augments the previous illustration¹⁾ in which the collector penetrated (or adsorbed) into the mineral body is not available, but only the collector adsorbed by the mineral surface is available for flotation. When the collector concentration exceeds 1.5×10^{-2} M., however, the recovery rather tends to decrease, due probably to the micelle effect. It should be also added here that a strong flocculation phenomenon was observed at around this concentration of the collector.

The selectivity index as a function of pH on a mixture of goethite and montmorillonite, with 3×10^{-3} M. of DAA is presented in Fig. 8. It is clearly shown in Fig. 8. that the selectivity index is very high in the acid side where the montmorillonite is almost perfectly recovered, whereas the selectivity index rapidly decreases in the alkaline side where the goethite tends to float. This result agrees with the Hallimond tube tests; a cationic collector is useful to float goethite in the alkaline range which is basically correlated with the electrokinetic property of the mineral surface.

Fig. 9 shows the selectivity index as a function of pH on a mixture of roasted specimens of goethite and montmorillonite, with 10^{-3} M. of DAA. Inasmuch as the roasted sample of montmorillonite requires a less amount of the collector than that for the natural specimen, 10^{-3} M. of the concentration employed was considered to be sufficient to get the selectivity index on the roasted mixture. The dashed curves in Fig. 9 indicate the respective recoveries of roasted goethite and montmorillonite when tested separately in the Hallimond

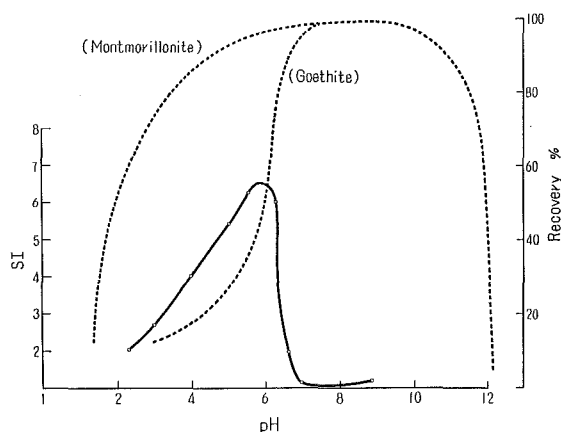


Fig. 9. Selectivity Index as a Function of pH on a Mixture of Roasted Goethite and Roasted Montmorillonite, with 10^{-3} M. of DAA (Dotted Lines Indicate the Respective Recovery)

tube with 10^{-3} M. of DACI (dodecylammonium chloride). The selectivity index reaches a maximum at pH 5.6, (the flotation product being clay), then the selectivity index rapidly drops to unity, or no selection at pH 7.0, where the flotation product (the clay) includes the goethite floated. The result again agrees with the Hallimond tube test.

Fig. 10 shows the selectivity index on a mixture of goethite and kaolinite with 10^{-3} M. of DAA, where the dashed curves represent the respective recoveries on each single mineral with 10^{-3} M. of DACI. The first peak appears at pH 4.5, and above this point the selectivity index gradually decreases and finally reaches unity at pH 8.0, where the kaolinite concentrate is mixed with the goethite. The recovery curve of kaolinite intersects the recovery curve of goethite at pH 7.5, corresponding approximately to the minimum point on the

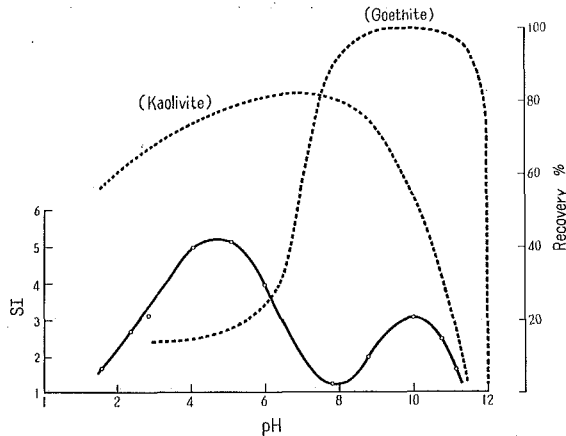


Fig. 10. Selectivity Index as a Function of pH on a Mixture of Goethite and Kaolinite, with 10^{-3} M. of DAA (Dotted Lines Indicate the Respective Recovery)

selectivity curve. At about pH 10, the selectivity index again reaches the second peak, where the flotation product is not goethite but kaolinite. From the recovery curves of kaolinite and goethite in Fig. 10, the flotation product at pH 10 was expected to be goethite. The selectivity exhibited in this pH range may be attributed to the nature of the froth; bubbles were smaller and not very persistent to keep the heavier particle of goethite at the surface. A small amount of MIBC as a frother was helpful to solve this unexpected problem.

Conclusions

The determination of the selectivity index, as a function of pH, on an

artificial mixture of goethite and the clay minerals was carried out by using a newly devised equipment. The system temporarily named as the K-Flot cylinder unit consisted of a gas washing system, the K-Flot cylinder, the froth settling cylinder and the aspiration system. To ascertain the reliability of this method, the flotation results obtained from the present method on goethite and roasted montmorillonite were compared with the Hallimond tube results; the former was shown to be sufficiently comparable with the latter.

The selectivity indexes on the mixtures of goethite-kaolinite, goethite-montmorillonite, roasted goethite-montmorillonite were investigated by measuring the respective weight of their flotation products.

The experimental results leads to the following conclusions :

(1) The flotation recovery curve of goethite with respect to an anionic collector (NaLS) intersects the curve for a cationic collector (DAA) at pH 7, the isoelectric point of goethite⁹.

(2) The flotation characteristics of roasted montmorillonite in the Hallimond tube test are almost identically reproduced by using the present method, without regard to the differences in the descriptions of the sample prepared and in the negative electrolytes dissociated.

(3) The montmorillonite sample retaining nonfloatable with 10^{-3} M. of the collector concentration can convert floatable with increase in the collector concentration; about 100 percent recovery of montmorillonite is obtained with 3×10^{-3} M. of the concentration at $\text{pH } 8.0 \pm 0.5$. The excess addition of the collector beyond 1.5×10^{-2} M. tends to decrease the recovery, due probably to the micelle formation.

(4) The selectivity index, as a function of pH, on the mixture of goethite and montmorillonite with 3×10^{-3} M. of DAA indicates that in the acid range, the separation of the two minerals is effective, whereas in the alkaline range, noneffective. A very strong flocculation is observed at around pH 2 with this collector concentration.

(5) The selectivity index on the roasted goethite-montmorillonite system with 10^{-3} M. of DAA reaches to the maximum point at pH 5.6 and rapidly drops to unity (or no selection) at pH 7.0, corresponding to the intersection point of the respective recovery curves. This result is in agreement with the Hallimond tube test.

(6) The selectivity index on the goethite-kaolinite system indicates a similar tendency to the roasted goethite-montmorillonite system, except at the peak point at pH 10, in which the weak persistence of the bubbles at high pH is responsible for this result.

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