December, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (12), 3533—3539 (1975)

Studies of the Coagulation Flotation of Bentonite and Its Application to the Removal of Co^{2+} Ions and Fission Products, Ce and Eu

Koichi Kobayashi,* Hiroshi Sato,** Kosei Kachi,*** Masao Nakamura,****
and Tsunetaka Sasaki****

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo 158

(Received July 11, 1975)

The regions of dispersion, coagulation precipitation, coagulation flotation, and redispersion were determined for aqueous bentonite-cationic surfactant and bentonite-cationic surfactant-polyacrylamide(PAA) systems. The region of coagulation flotation was markedly extended by the addition of PAA to both the lower and higher concentration regions of the cationic surfactant, hexadecyldimethylbenzylammonium chloride(HDBAC), and to the lower concentration region of bentonite. The phenomenon of coagulation flotation was investigated in detail and was applied to the removal of Co^{2+} ions and nuclear fission products, ^{144}Ce and ^{155}Eu, from an aqueous solution. The composition of the reagents for the maximum efficiency of bentonite flotation corresponded to that of the maximum efficiency of Co^{2+}-ion flotation. The effect of the pH on the flotation efficiency was studied in particular. The maximum flotation efficiency of 96% was obtained at pH 11 for Co^{2+} ions, 86% at pH 9.7 for ^{144}Ce, and 93% at pH 10.5 for ^{155}Eu. These radioactive elements were almost completely adsorbed on the surface of bentonite particles and were floated with them in the pH region of the maximum flotation efficiency. It was confirmed that Co^{2+} ions could be floated also from an extremely low concentration (10^{-9} mol/l) of Co^{2+} ions with nearly the same efficiency of flotation and with the additives in the same condition. Co^{2+} ions could also be effectively removed by using the step-by-step flotation, showing as high a flotation efficiency as 99.8%.

The importance of coagulation flotation is well known, as has already been discussed in a previous paper.[1] Coagulation flotation is of interest as a means for the rapid removal or separation of suspended particles from suspensions, since the velocity of flotation is faster than that of coagulation precipitation. Also, coagulation flotation is an effective means for the removal of coexisting ions from the solution when the coagulating particles have an ion-exchange capacity, like bentonite; this process is called adsorbing particle flotation,[2] or "piggy-back" flotation.[3] As has been pointed out in a previous paper,[4] the region of coagulation flotation is extended by the addition of PAA towards the higher and lower concentrations of the cationic surfactant and toward the lower-concentration region of bentonite. Therefore, the addition of PAA is considered to be effective for the removal of bentonite or radioactive cations.

Recently, the removal of substances from an aqueous solution has drawn increasing attention in connection with the problem of water pollution. The radioactive decontamination or the removal of radioactive elements is one of the most important problems involved in the processing of radioactive elements; it is also concerned with public health. Various methods for the removal of these contaminating elements have been employed—for instance, adsorption including ion exchange, coagulation precipitation, evaporation concentration, foam separation, and flotation.[5] Among these methods, the flotation method is considered to be the most effective and the least expensive. However, a comparatively limited number of works have reported on the ion flotation of radioactive elements.[6] For these reasons, it is of importance to investigate the basic parameters to be considered in the flotation process.

In the present study, the coagulation flotation of bentonite, the effect of PAA upon the flotation, and its application to the separation of Co^{2+} ions and some fission products were investigated in detail. The amount of bentonite, the cationic surfactant, PAA, and the effect of the pH on the flotation efficiency were studied in particular.

Experimental

Materials. The cobalt chloride used was a reagent-grade $CoCl_2 \cdot 6H_2O$, which was used without further purification. The stock solution of Co^{2+} ions (1×10^{-4} mol/l) was prepared by dissolving cobalt chloride in triply distilled water, with the addition of a small amount of ^{60}Co as a radiotracer. The ^{144}Ce and ^{155}Eu, which had been obtained by processing fission products, were supplied by the Japan Atomic Energy Research Institute. The initial activities of the aqueous ^{144}Ce and ^{155}Eu solutions were 2×10^{-2} and 1.5×10^{-2} μCi/ml respectively. The bentonite powder(Bt) used as an ion exchanger was supplied by the Wako Pure Chemical Co., Ltd.; the fraction passing through a 350-mesh sieve was collected and dried under reduced pressure. A suspension of the desired Bt content was made before each experiment and was used after shaking.

The hexadecyldimethylbenzylammonium chloride (HDBAC, 95% purity) was supplied by the Nippon Oils and Fats Co., Ltd., recrystallized from acetone, and dried under reduced pressure. The critical micelle concentration of HDBAC in an aqueous solution was found from surface-tension measurements to be about 8×10^{-5} mol/l. Polyacrylamide (PAA) with an 87% amide content was used as a coagulating agent; it was the product of the Nitto Chemical Co., Ltd., and had been dried under reduced pressure. The Bt, HDBAC, and PAA were all kept in a desiccator. The water was triply

---

[*] Address all correspondence to the present address: Laboratory of Chemistry, Musashi Institute of Technology, 1-28-1, Tamatsutsumi, Setagaya, Tokyo 158.

[**] Present address: Takeda Chemical Industries Ltd., 2-17-85, Jiyusouhonmachi, Yodogawa, Osaka 532.

[***] Present address: Japan Automobile Research Institute, 2530, Karima, Yatabe-cho, Tsukuba, Ibaraki.

[****] Present address: Department of Chemistry, Faculty of Science, Tokai University, Hiratsuka, Kanagawa 259-12.

distilled using a borosilicate glass apparatus after it had been refluxed overnight with a sulfuric acid-potassium permanganate solution.

Apparatus and Procedure. The procedure used for the measurements of the dispersion state of Bt by HDBAC was the same as that described in the previous paper.[1] The apparatus and method used for flotation were likewise the same as those described previously.[7] A humidified nitrogen gas was introduced through a sintered glass plate of No. 4 into a 10-ml sample solution held in a glass tube (1.0 cm in inner diameter and 32.0 cm in length) for 1 or 2 min at a gas-flow rate of 10 ml/min, unless otherwise specified. Experiments were run under the condition of bubble flotation—namely, flotation using only ascending bubbles, without the aid of foam formation. The concentration of Bt was determined by turbidity measurements using a photoelectric colorimeter, Spectronic 20, of Bausch and Lomb, Inc. The light absorbance was measured at 440 mμ. The concentration of the stock solution of Co^{2+} ions was determined by the chelate titration method with EDTA[8], using murexide as an indicator. For the measurement of the flotation efficiency, a constant amount of the sample was pipetted out of the solution and dried in a stainless steel planchet, and the radioactivities of ^{60}Co, ^{144}Ce, and ^{155}Eu were measured by using the Geiger-Muller counter tube. From the radioactivity of the solution before and after the flotation, the flotation efficiency was calculated.

The flotation efficiency, F, was calculated according to this equation:

$$F = (1 - C_f/C_i) \times 100\%$$

where C_i and C_f are the concentrations or radioactivities of the solution before and after the flotation respectively.

The centrifugation was carried out in a 15-ml cell at 3000 rpm for 10 min; the concentration or radioactivity of the supernatant solution was similarly determined. The efficiency of centrifugation, R, was calculated as follows:

$$R = (1 - A_f/A_i) \times 100\%$$

where A_i and A_f are the radioactivities of the solution before and after the centrifugation respectively.

The pH of the solution was adjusted by means of a sodium hydroxide solution, which had been prepared by the dilution of a saturated NaOH solution. All the experiments were carried out at room temperature (about 25 °C).

Results and Discussion

Change of Dispersion State of Bt by HDBAC and/or PAA. The coagulation-dispersion and precipitation-flotation behavior is shown in Fig. 1 as a function of the amount of HDBAC and Bt added. The regions of dispersion, coagulation precipitation, coagulation flotation, and redispersion may be seen distinctly. Especially the change from coagulation precipitation to coagulation flotation is very sensitive to the slight addition of HDBAC under a constant Bt concentration.

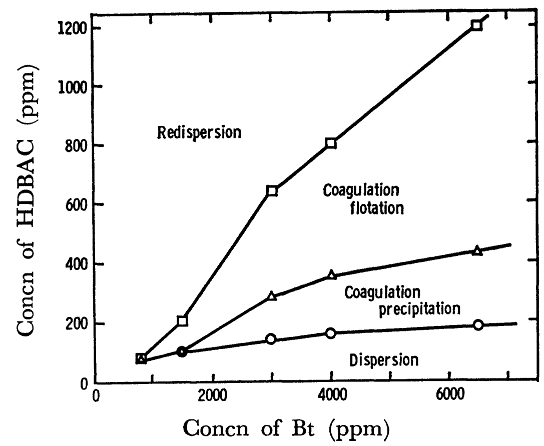


Fig. 1. Effect of HDBAC on dispersion state of Bt suspension.

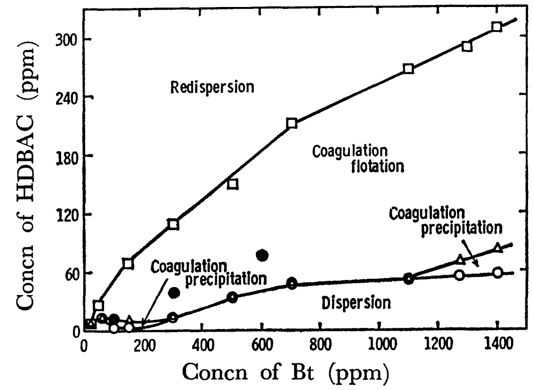


Fig. 2. Effect of HDBAC on dispersion state of Bt suspension in the presence of PAA. ●: composition of maximum flotation efficiency of Bt as shown in Fig. 4.

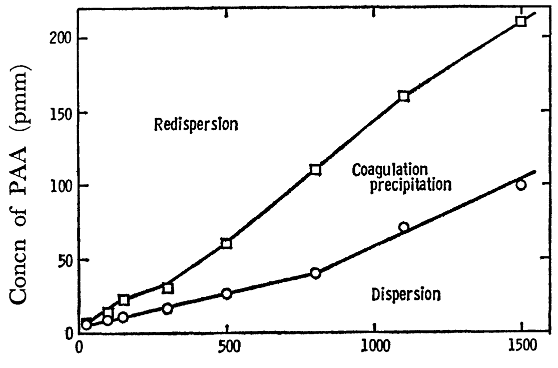


Fig. 3. Effect of PAA on dispersion state of Bt suspension.

Figure 2 shows the effect of HDBAC on the Bt suspension in the presence of 10 ppm PAA. As may be seen in Fig. 2, the region of coagulation flotation extended towards lower and higher concentrations of HDBAC and a lower concentration of Bt compared with the case of the Bt–HDBAC system. Also, the addition of PAA markedly clarifies the turbid solution and markedly increases the floating velocity of the coagulum by increasing the size of the aggregates. The transition from the region of dispersion to that of coagulation flotation is more distinct in the presence of PAA than in the system without PAA. In Fig. 2 a second region of coagulation precipitation appears, though it is somewhat indistinct at the low-concentration regions of Bt and HDBAC.

Figure 3 shows the change in the dispersion state in the PAA–Bt system in the absence of HDBAC.

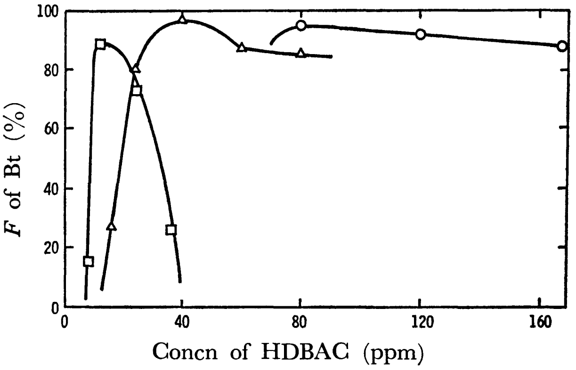


Fig. 4. Effect of HDBAC on flotation efficiency of Bt in the presence of PAA. PAA: 10 ppm, pH: 5—7, gas-flow time: 1 min, Bt: 100 ppm(□), 300 ppm(△), 600 ppm(○).

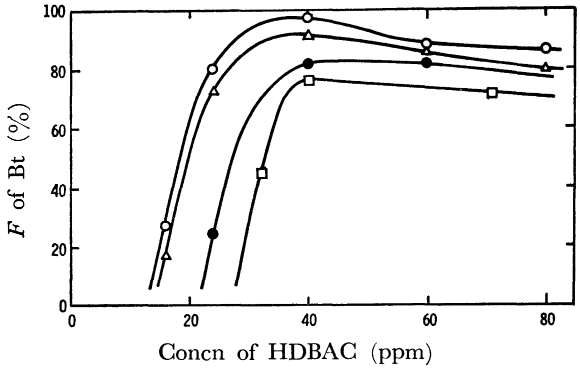


Fig. 5. Effect of PAA on flotation of Bt by HDBAC. Bt: 300 ppm, pH: 7, gas-flow time: 1 min, PAA: 0 ppm(□), 5 ppm(●), 10 ppm(○), 26 ppm(△).

As expected, the region of coagulation flotation disappears in Fig. 3. The fact that the lines separating each region are nearly linear and pass through the point of origin may suggest that the coagulation-dispersion change occurs at constant compositions of the Bt–PAA complex.

Effect of HDBAC on the Efficiency of Coagulation Flotation. In order to study the behavior of the Bt suspension in the region of coagulation flotation in detail, the efficiency of the flotation of Bt at various concentration levels of HDBAC was studied in the presence of 10 ppm of PAA. The results are shown in Fig. 4. It may be seen that the maximum efficiency of flotation appears and that the maximum becomes flatter with the increase in the concentration of Bt. The concentration ratio of Bt/HDBAC at the maximum flotation is nearly constant, as may be seen from the plots shown by filled circles in Fig. 2. This constancy may also indicate the constancy of the aggregate composition at the maximum flotation efficiency. Values of more than 90% were observed at the maximum of flotation. Beyond the maximum points of the flotation efficiency, redispersion began to occur and the supernatant become opaque or turbid. Although the composition of the floated Bt-surfactant aggregates was not determined, it must be similar to what has been reported for Bt–HTAC.1) In the case of the low concentration of Bt, the flotation efficiency of Bt rapidly decreased beyond a sharp maximum and the region of coagulation flotation became narrow.

Effect of PAA on Efficiency of Coagulation Flotation. Figure 5 shows the effect of PAA on the relation between the coagulation-flotation efficiency and the HDBAC concentration in the system of 300 ppm Bt. As may be seen in the figure, the HDBAC concentration at the maximum efficiency of Bt flotation is nearly independent of the PAA concentration, but the flotation efficiency itself is markedly influenced by the concentration of PAA. From Fig. 5, the concentration of 10 ppm PAA was found to be optimum in the case of 300 ppm Bt. From this result, together with the results obtained from Fig. 4, it may be concluded that an optimum concentration ratio of Bt : HDBAC : PAA, and therefore an optimum composition of the aggregate, exists which gives a maximum efficiency of flotation. The concentration ratio is estimated to be 300 : 40 : 10 (in the case of 300 ppm Bt).

Effect of the Heat Treatment on the Flotation Efficiency of Bt. In Fig. 6, the flotation efficiencies of Bt are compared between two samples; one was heated at 110 °C for 48 h, while the other had no heat treatment. In the case of pH 7 (solid curves), a flat maximum appeared in the *F vs.* HDBAC concentration curve for the system of untreated Bt, while a distinct maximum of a larger value was observed for the heat-treated Bt. In the case of pH 11 (dashed curves), both curves show a flat maximum and the effect of heat treatment disappears.

Effect of the Coexistence of PAA and HDBAC on the Flotation Efficiency of Bt and Co^{2+} Ions. From the enhancement of the flotation efficiency of Bt by the simultaneous addition of HDBAC and PAA, it may be presumed that the Co^{2+} ions can also be effectively floated under such conditions. To confirm this, the flotation efficiencies of Bt and Co^{2+} ions were investigated for the Co^{2+}–Bt–HDBAC–PAA, Co^{2+}–Bt–HDBAC, and Co^{2+}–HDBAC–PAA systems. The results are shown in Table 1. As may be seen in Table 1, both Bt and Co^{2+} ions are best floated by the simultaneous addition of PAA and HDBAC, while the

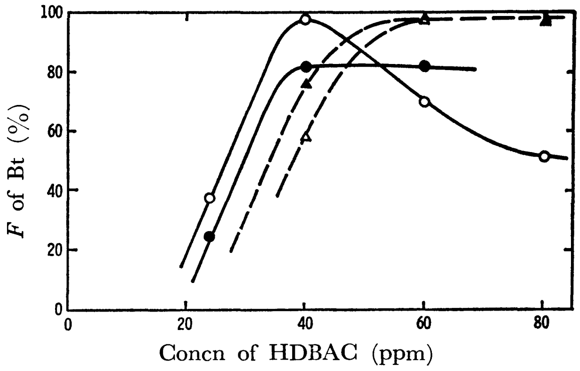


Fig. 6. Effect of heat treatment of Bt flotation.
Flotation efficiencies of untreated Bt (●, ▲) and Bt treated at 110 °C for 48 h (○, △).
Solid curves; Bt: 300 ppm, PAA: 5 ppm, pH: 7, gas-flow time: 1 min.
Dashed curves; Bt: 300 ppm, PAA: 100 ppm, pH: 11, gas-flow time: 1 min.

Table 1. Effect of PAA, HDBAC, and Bt on the flotation efficiency of Co^{2+} ions and Bt

Bt (ppm)	PAA (ppm)	HDBAC (ppm)	pH	F	
				Co^{2+}(%)	Bt(%)
200	10	20	10.9	72.6	77.5
200	0	20	10.7	56.3	38.0
0	10	20	10.8	15.6	0
750	0	88	10.9	51.3	30.1

Co^{2+}: 1×10^{-5} mol/l.

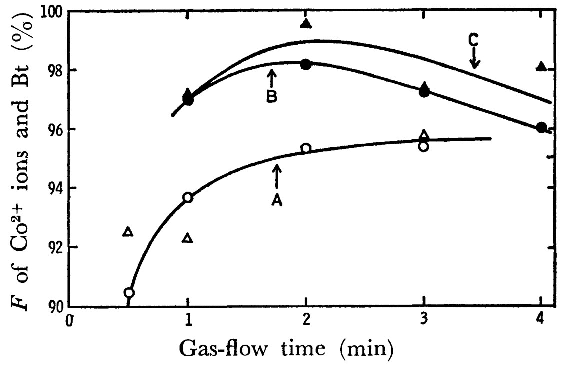
Table 2. Effect of Bt concentration on the flotation efficiency of Co^{2+} ions and Bt

Bt (ppm)	pH	F	
		Co^{2+}(%)	Bt(%)
100	9.5	87.0	86.9
100	10.1	95.0	92.7
110	10.1	97.3	94.4
130	10.0	99.2	96.0
140	9.8	97.1	89.3
130[a]	10.0	96.2	93.9

Co^{2+}: 1×10^{-5} mol/l, HDBAC: 20 ppm, PAA: 3 ppm.
a) Heated at 110 °C for 48 h.

flotation efficiencies markedly fall for the system lacking either PAA or Bt. In particular, the flotation efficiency of Co^{2+} ions in the absence of Bt is quite poor. The decrease in flotation efficiency due to the lack of PAA does not completely recover even if the concentration of HDBAC is increased. Further, the comparision of the flotation efficiencies of the Co^{2+} ions and Bt shows that the Co^{2+} ions may be considered to float by combining with Bt at the optimum flotation, as will be shown in Table 2, while some Co^{2+} ions can float without the aid of Bt in other systems.

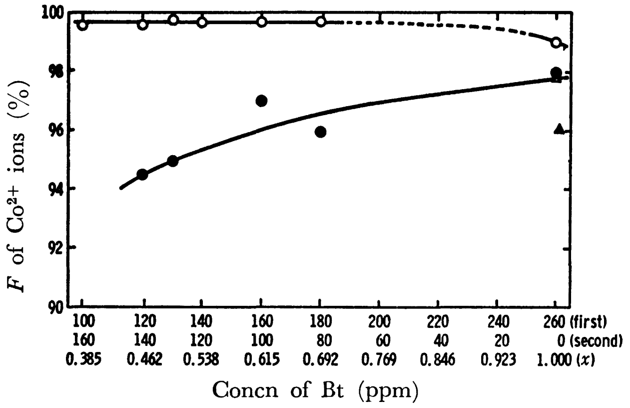
Relation between the Coagulation Flotation and the Concentration of Bt. The relation between the Bt concentration and the flotation efficiency was investigated under the conditions of 3 ppm PAA and 20 ppm HDBAC at pH 9. The results are shown in Table 2. It may be seen that the flotation efficiencies of 99.2% for the Co^{2+} ions and 96% for Bt are obtained at Bt : PAA= 130 : 3 (wt). Thus, the optimum conditions of Co^{2+}-ion flotation were found to be 130 ppm Bt, 20 ppm HDBAC, and 3 ppm PAA for Co^{2+} of a 1×10^{-5} mol/l concentration; these conditions are in agreement with the ratio listed in the former section.



Gas-flow time (min)

Fig. 7. Effect of gas-flow time on flotation efficiency of Co^{2+} ions and Bt. Co^{2+}: 1×10^{-5} mol/l, pH: 10—11, gas-flow rate: 10 ml/min,

(A) Bt: 130 ppm, HDBAC: 20 ppm, PAA: 3 ppm, } Co^{2+}(○), Bt(△)
(B) Bt: 260 ppm, HDBAC: 40 ppm, PAA: 6 ppm, } Co^{2+}(●)
(C) Bt: 260 ppm, HDBAC: 40 ppm, PAA: 6 ppm, } Bt(▲)



Concn of Bt (ppm)

Fig. 8. Stepwise flotation of Co^{2+} ions.
Co^{2+}: 1×10^{-5} mol/l, pH: 10—11, gas-flow time: 2 min. Amount of Bt, HDBAC, and PAA are variable for the first and second flotations, but the total amount of each of these additives must sum up to 260 ppm, 40 ppm, and 6 ppm, respectively.
●: first flotation efficiency, ○: first plus second flotation efficiencies. △, ▲: results of one step flotation process under the condition of 260 ppm Bt, 40 ppm HDBAC, and 6 ppm PAA(△ is for gas-flow time of 2 min, ▲ is for gas-flow time of 4 min)

Effect of the Time of the Gas-Flow on the Flotation Efficiency of Co^{2+} Ions and Bt. Figure 7 shows the floatation of Co^{2+} ions and Bt from the Co^{2+}–Bt–HDBAC–PAA system of the composition listed in each figure as a function of the time. The effect of the gas-flow time on the flotation efficiency of Bt closely resembles that of Co^{2+} ions, as is shown by Curve A in Fig. 7. In this case, the flotation efficiencies of both Co^{2+} and Bt increase with the gas-flow time. About 95.5% of the flotation efficiency was attained after 2—3 min. When the amount of additives is doubled, as is shown by Curve B, a maximum of $F=$ 98.2% also appears after 2 min, but this gradually decreases on a further increase in the gas-flow time. The decrease is perhaps due to the partial redispersion of a scum once floated by continued bubbling. A similar curve was obtained for Bt, as is shown by Curve C. Therefore, the gas-flow time of 2 min was used as the optimum condition for all subsequent investigations.

Effect of the Step-by-step Flotation of Co^{2+} Ions. In the practice of flotation, a step-by-step method is often adopted.[9] Here, the effect of such a method will also be discussed. First, the flotation of Co^{2+} ions from a solution containing 1×10^{-5} mol/l Co^{2+}

ions, 260x ppm Bt, 40x ppm HDBAC, and 6x ppm PAA was run at pH 10—11, where $x(\leqq 1)$ is a variable. After the underlying liquid had been removed from the flotation cell as completely as possible, the second flotation of the solution was carried out with the further addition of $260(1-x)$ ppm Bt, $40(1-x)$ ppm HDBAC, and $6(1-x)$ ppm PAA. The F value for the first flotation and the sum of the F-values for the first and second flotations are plotted against the initial Bt concentration of 260x ppm in Fig. 8, together with the flotation efficiency obtained for the one-step flotation process of 260 ppm Bt with the gas-flow times of 2 and 4 min, for comparison. It is evident in Fig. 8 that the step-by-step flotation is far more effective than the simple flotation; it is especially so when we compare the open circles with the filled triangle, which indicates the F-value of the simple flotation with a total gas-flow time of 4 min. In the case of the step-by-step flotation, a flotation efficiency as high as 99.6—99.8% was obtained at pH 10—11.

Effect of the pH on the Flotation Efficiencies of Co^{2+} Ions and Bt. According to Table 2, the optimum conditions of Co^{2+} ion flotation are presumed to occur at the composition of 130 ppm Bt, 20 ppm HDBAC, and 3 ppm PAA. The subsequent flotations were carried out under these conditions and under varying pH values. Figure 9 shows the results concerning the flotation efficiencies of Co^{2+} ions and Bt from a solution containing 1×10^{-5} mol/l Co^{2+} ions. It may be seen that the flotation efficiency of Co^{2+} ions begins to increase sharply at around pH 8 and that the maximum F of 95% is recorded in the pH range from 9 to about 11. The flotation efficiency is seen to decrease gradually with a further increase in pH. The flotation efficiency of Bt shows a curve with a flat maximum which coincides with that of Co^{2+} ions in the pH region of 9—11. As the cobalt hydroxide begins to form in the vicinity of pH 9, Co^{2+} ions are considered to float as polynuclear species,10) similar to the flotation of Cu^{2+},7) and Cd^{2+} ions.7) In this pH region, Co^{2+} ions are considered to combine almost completely with Bt and are floated together with Bt with the aid of a surfactant, while in other pH regions, especially in the acid region, a large amount of Bt is floated without adsorbing Co^{2+} ions. The effect of Bt is clearly shown by comparing the flotation efficiencies of Co^{2+} ions for the system containing HDBAC with and without Bt, as is shown in Figs. 9 and 10, where Fig. 10 shows the flotation efficiency of Co^{2+} ions from solutions each containing 1×10^{-5} and 7.4×10^{-9} mol/l of Co^{2+} ions and 20 ppm of HDBAC. It is evident that the flotation efficiency of Co^{2+} ions decreases from about 95% for the system with Bt to 5% for the system without Bt, although the latter system also lacks PAA. This decrease in flotation efficiency is more remarkable than in the case of Cu^{2+}-ion flotation.7) Further, we can observe a remarkable foam formation in the case of the system lacking Bt; this renders the bubble flotation impossible.7) From these facts, it may be concluded that the addition of Bt acts both to bridge Co^{2+} ions and HDBAC and to suppress foam, thus ensuring bubble flotation.

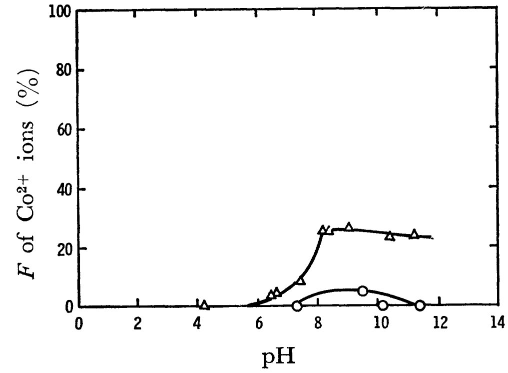


Fig. 10. Foam flotation of Co^{2+} ions.
HDBAC: 20 ppm, gas-flow time: 2 min, ○: 1×10^{-5} mol/l Co^{2+} ions, △: 7.4×10^{-9} mol/l Co^{2+} ions.

A similar flotation experiment was carried out for such a dilute solution of Co^{2+} as 7.4×10^{-9} mol/l. The system was studied since the behavior of Co^{2+} ions in such a dilute solution may give information concerning that of the carrier-free state or of radioactive contamination. The measurements of the flotation efficiency of the Co^{2+} ions and Bt were made for the systems with the same conditions as those listed in

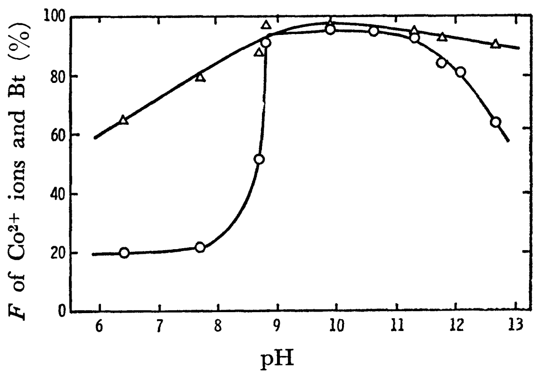


Fig. 9. Effect of pH on flotation efficiency of Co^{2+} ions and Bt.
Co^{2+}: 1×10^{-5} mol/l, Bt: 130 ppm, HDBAC: 20 ppm, PAA: 3 ppm, gas-flow time: 2 min, ○: F of Co^{2+} ions, △: F of Bt.

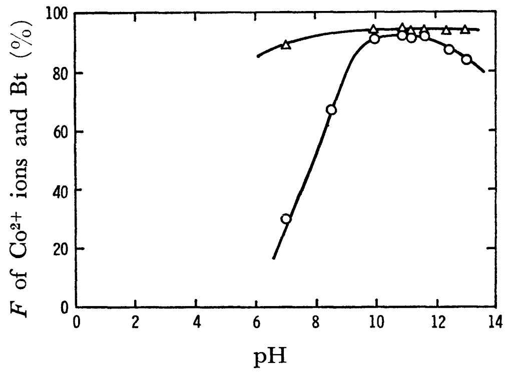


Fig. 11. Effect of pH on flotation efficiency of Co^{2+} ions and Bt.
Co^{2+}: 7.4×10^{-9} mol/l, Bt: 130 ppm, HDBAC: 20 ppm, PAA: 3 ppm, gas-flow time: 2 min.
○: F of Co^{2+} ions, △: F of Bt.

Fig. 9 except that the concentration of the Co^{2+} ions was 7.4×10^{-9} mol/l. The results are shown in Fig. 11. It may be seen that the plots are similar as a whole to those of Fig. 9, though somewhat lower maxima. Also, in this case, the coincidence of the maxima of the flotation efficiency of the Co^{2+} ions and Bt indicates that the Co^{2+} ions are adsorbed on Bt particles and are removed with them.

Removal of Co^{2+} Ions by Centrifugation. It may be considered likely, on the basis of the above observations, that Co^{2+} ions combine with Bt particles under the optimum conditions of flotation. To further confirm this mechanism, the centrifugation of the Co^{2+} ions was carried out at 3000 rpm for 10 min at varying pH values, and the efficiency of the centrifugation or efficiency of the adsorption of Co^{2+} ions on Bt was measured and was plotted against the pH (*cf.* Fig. 12).

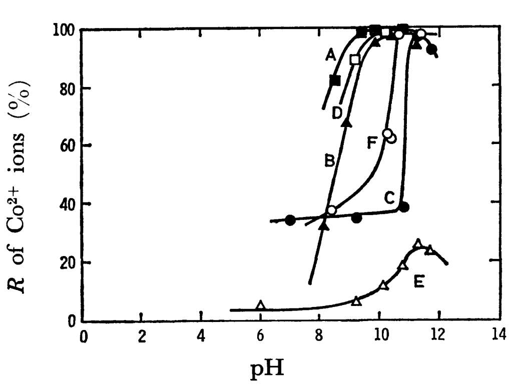


Fig. 12. Effect of pH on R or adsorption of Co^{2+} ions.
Co^{2+}: 1×10^{-5} mol/l, Bt: 130 ppm, HDBAC: 20 ppm, PAA: 3 ppm, centrifugation: 3000 rpm for 10 min.
A: Co^{2+}-Bt-HDBAC-PAA system,
B: Co^{2+}-Bt-HDBAC system,
C: Co^{2+}-Bt-PAA system,
D: Co^{2+}-Bt system,
E: Co^{2+}-PAA system,
F: Co^{2+} system.

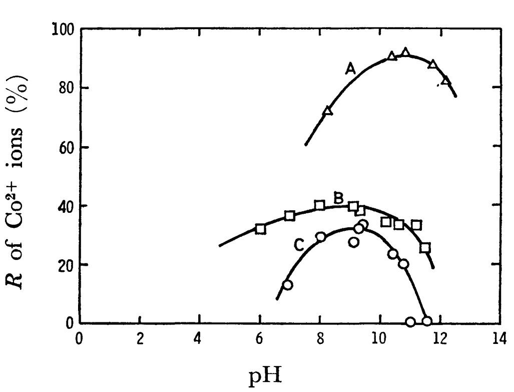


Fig. 13. Effect of pH on efficiency of centrifugation of Co^{2+} ions.
Bt: 130 ppm, HDBAC: 20 ppm, PAA: 3 ppm, centrifugation: 3000 rpm for 10 min.
A: Co^{2+}-Bt-HDBAC-PAA system, Co^{2+}: 3.1×10^{-9} mol/l,
B: Co^{2+}-Bt-PAA system, Co^{2+}: 7.4×10^{-9} mol/l,
C: Co^{2+}-PAA system, Co^{2+}: 7.4×10^{-9} mol/l.

As may be seen in Fig. 12, high R values were obtained for the Co^{2+}–Bt–HDBAC–PAA system(A), the Co^{2+}–Bt–HDBAC system(B), and the Co^{2+}–Bt system(D). It is confirmed that the R value of the system containing PAA but lacking HDBAC is very low up to high pH values, while the system containing Co^{2+} ions alone still shows a large R value in a sufficiently high alkaline region. It seems likely that, in the absence of HDBAC, the Co^{2+} ions are protected by PAA against adsorption on Bt and hydroxide formation. The centrifugation was carried out further for solutions containing 7.4×10^{-9} mol/l of Co^{2+} ions or 3.1×10^{-9} mol/l of Co^{2+} ions, with other constituents similar to those of Systems (A), (B), and (E), shown in Fig. 12. The results are shown in Fig. 13. The tendencies are similar to those of Fig. 12, and the Co^{2+}–Bt–HDBAC–PAA system is seen to be most effective in removing the Co^{2+} ions from this dilute solution.

Application of Adsorbing Particle Flotation to the Fission Product. Figure 14 shows the results of the flotation of ^{155}Eu from a solution containing 2×10^{-2} μCi/ml of ^{155}Eu ions, 130 ppm of Bt, 20 ppm of HDBAC, and 3 ppm of PAA. The flotation efficiency of ^{155}Eu ions is plotted against the pH. As may be seen in Fig. 14, the flotation efficiency increases from pH 3 with an increase in the pH and two maxima of 85% and 93% flotation efficiencies are observed, at

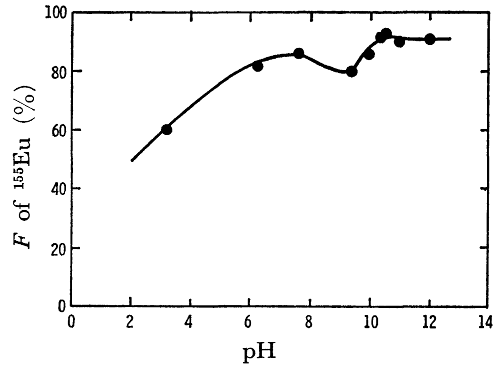


Fig. 14. Effect of pH on flotation efficiency of ^{155}Eu.
^{155}Eu: 2×10^{-2} μCi/ml, Bt: 130 ppm, HDBAC: 20 ppm, PAA: 3 ppm, gas-flow time: 2 min.

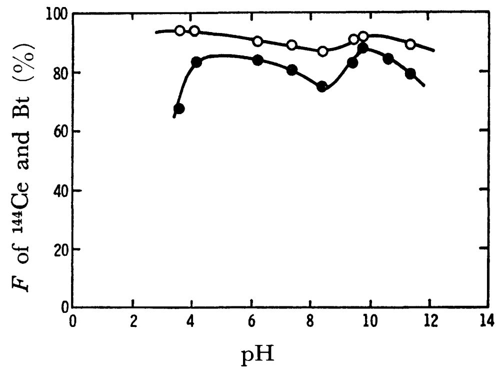


Fig. 15. Effect of pH on flotation efficiency of ^{144}Ce and Bt.
^{144}Ce: 1.5×10^{-2} μCi/ml, Bt: 130 ppm, HDBAC: 20 ppm, PAA: 3 ppm, gas-flow time: 2 min,
●: F of ^{144}Ce, ○: F of Bt.

pH 7.5 and 10.5 respectively. The former and the latter maxima may be explained by the formation of the radiocolloid of ^{155}Eu and of insoluble europium hydroxide respectively, but this requires further study.[11) Figure 15 shows the flotation efficiency of ^{144}Ce and Bt from a solution of 1.5×10^{-2} μCi/ml of ^{144}Ce ions, 130 ppm of Bt, 20 ppm of HDBAC, and 3 ppm of PAA as a function of the pH. In this case, the similar maxima of 85% at pH 5 and 80% at pH 9.7 are observed. The flotation efficiency of ^{144}Ce ions parallels that of Bt. Likewise, this may suggest that there is a relationship between the combining ratio of Bt and the cerium ion under its optimum flotation conditions.

The authors wish to thank Dr. Fujio Ichikawa of the Japan Atomic Energy Research Institute for the supply of fission products.

References

1) T. Inakazu, K. Kobayashi, and T. Sasaki, This Bulletin, **48**, 3008 (1975).

2) R. Lemlich, "Adsorptive Bubble Separation Techniques," Academic press, New York and London (1972), pp. 273—278.

3) R. Lemlich *Ind. Eng. Chem.*, **60**, 17 (1968).

4) K. Kobayashi, This Bulletin, **48**, 1750 (1975).

5) W. Rudolfs, "Industiral Waste," Reinhold, New York (1957), p. 454; J. E. Sabadell, "Traces of Heavy Metals in Water, Removal Process and Monitoring," Princeton University, Princeton, New Jersey, November 15—16 (1973).

6) B. M. Davis and F. Sebba, *J. Appl. Chem.*, **16**, 297 (1966); *ibid.*, **17**, 40 (1967); R. Lemlich, "Adsorptive Bubble Separation Techniques," Academic Press, New York and London (1972), pp. 243—248, pp. 285—288; Y. Koyanaka, *Nippon Genshiryoku Gakkaishi*, **7**, 621 (1965); Y. Koyanaka, *Radioisotopes*, 77 (1966).

7) K. Kobayashi, This Bulletin, **48**, 1180 (1975).

8) H. Flaschka, *Microchemie ver Mikorochim. Acta*, **39**, 38 (1952); K. Ueno, "Chelate Titration Method," Nankodo (1972), p. 292.

9) H. Kishimoto, *Kolloid-z.*, **192**, 66 (1963).

10) F. Sebba, "Ion Flotation," American Elsevier, New York (1966).

11) F. Ichikawa and T. Sato, *Radiochim. Acta*, **12**, 89 (1969).