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# Influence of Organic and Inorganic Modifiers on the Selective Flotation of Fluorite from Calcite with Sodium Oleate

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**Abstract**

Flotation tests of fluorite-calcite mixture were carried out to elucidate the practical optimum conditions, using sodium oleate as collector and five kinds of modifiers.

Soluble starch, sodium lignin sulfonate, tannic acid and sodium metasilicate selectively depressed calcite and the optimum pH region for good separation lay at around pH8. Sodium phosphate depressed fluorite above pH12, however, its depressing action was not so strong. A suitable combination of plural modifiers such as soluble starch and tannic acid, and sodium lignin sulfonate and sodium metasilicate improved selectivity, limiting the optimum pH to a narrower region.

## 1. Introduction

Salt-type minerals such as fluorite, calcite, apatite and scheelite have higher solubilities in an aqueous system compared with sulfides, oxides and silicate minerals. When salt-type minerals coexist, the ions derived from the minerals markedly affect the surface and flotation properties of them, [1,2,3] and predictions for flotation separation based on single mineral tests often fail[1,2,4]. However, most of the fundamental studies concerning modifiers in the selective flotation of salt-type minerals were carried out only in the single mineral systems[5,6,7], and the critical actions of modifiers in flotation practice are not so clear.

Recently, the demand for high grade flouorite concentrate has increased[8]. Selective flotation of fluorite from calcite is not easily achieved[5,6,7] and it is a key to upgrade fluorite concentrate, because of the increasing calcite contents in some run-of mine ores[9].

In the present investigation, the influence of modifiers on the flotation separation of fluorite-calcite was studied to elucidate practical optimum conditions. Flotation tests in a mixed minerals system were conducted, and synergetic actions of plural modifiers were also studied.

## 2. Experimental Materials and Methods

The minerals used were high grade hand-picked specimens of fluorite from the Hiraiwa mines and calcite from the Todoroki mines. The 43-104 $\mu$m fraction was used for the.

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flotation test.

Sodium oleate and methyl isobutyl carbinol (MIBC) were used as the collector and frother, respectively. Organic modifiers used were soluble starch, sodium lignin sulfonate (Na-LS) and tannic acid. Inorganic modifiers used were sodium metasilicate and sodium phosphate.

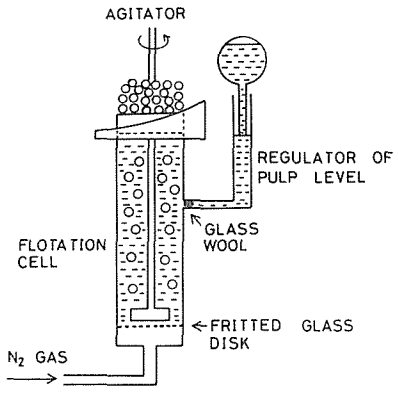



**Fig. 1.** Apparatus for flotation experiments.

Flotation tests were performed using the flotation cell shown in Fig. 1. An 8 g of fluorite-calcite (1 : 1) mixture was conditioned for 10 min in 500 ml of aqueous solution adjusted to the desired pH. A modifier, followed by a collector, then a frother were added to the system, which was conditioned for 5 min after each addition. Then, the system was allowed to settle for 5 min. The settled particles were transferred to the flotation cell with the supernatant. Flotation was conducted for 10 min at 300 ml/min of nitrogen gas flow rate and with 20 $\mu$l/l of MIBC addition. The froth and tailing products were dried, weighed and analyzed[10] for calculating recovery.

## 3. Results and Discussion

Fig. 2 shows the effect of starch addition on the flotation separation of fluorite-calcite with 40 mg/l sodium oleate. Selective depression of calcite was observed at around 1.5 mg/l of starch addition. The effect of oleate addition on the separation is shown in Fig. 3. When starch addition was fixed at 1.5 mg/l, fluorite was preferentially floated with an increase in the oleate concentration.

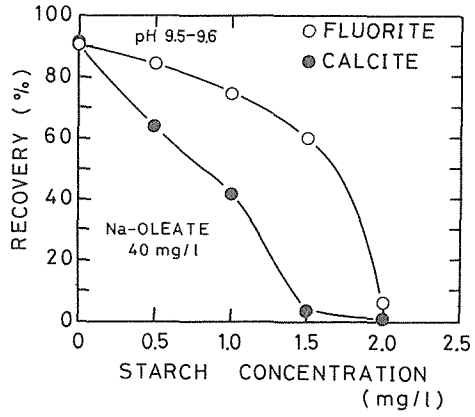



**Fig. 2.** Effect of starch addition on the flotation of fluorite-calcite mixture.

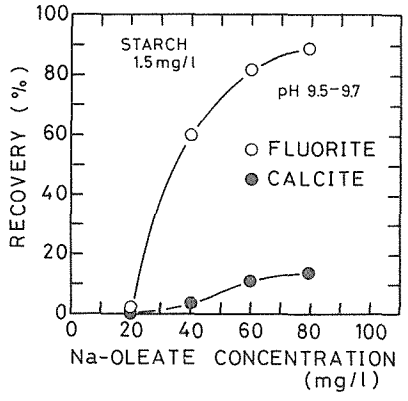



**Fig. 3.** Effect of sodium oleate addition on the flotation of fluorite-calcite mixture in the presence of starch.

Fig. 4 shows flotation recovery of fluorite and calcite as a function of pH in the presence of 60 mg/l sodium oleate and 1.5 mg/l starch. Over a wide pH range, the recovery of fluorite was higher than that of calcite. The recovery of both minerals was minimal at around pH 8. This corresponds to the adsorption behavior of soluble starch. Adsorption of starch on fluorite and calcite is maximal at around pH 8[11]. The calcite content in fluorite concentrate increased above pH 8. Good selectivity was limited in the pH range of 7 to 9.

Figs. 5, 6 and 7 show flotation results with sodium lignin sulfonate as a modifier. Lignin sulfonate selectively depressed calcite even at small addition levels. With decreasing pH, the recovery of calcite fell and was very low below pH 9. On the other hand, fluorite was strongly depressed only below pH 7.2. The difference in the flotation recovery of both minerals was maximum at around pH 8.

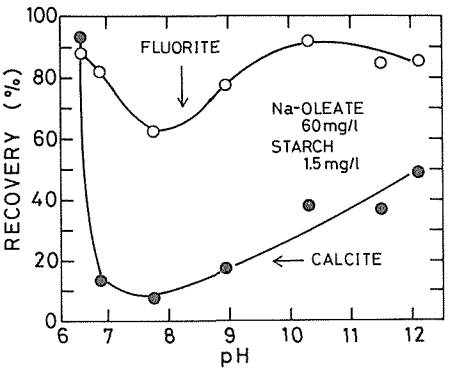



**Fig. 4.** Effect of pH on the flotation of fluorite-calcite mixture in the presence of starch.

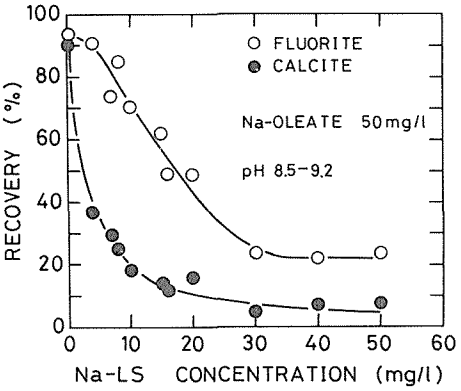



**Fig. 5.** Effect of sodium lignin sulfonate addition on the flotation of fluorite-calcite mixture.

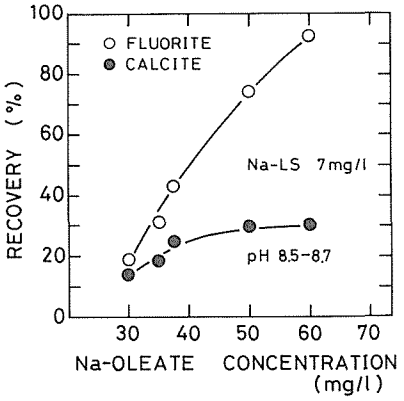



**Fig. 6.** Effect of sodium oleate addition on the flotation of fluorite-calcite mixture in the presence of sodium lignin sulfonate.

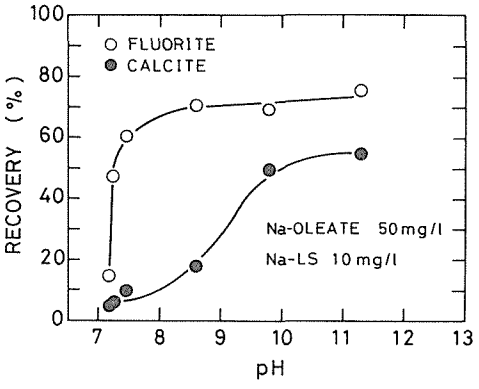



**Fig. 7.** Effect of pH on the flotation of fluorite-calcite mixture in the presence of sodium lignin sulfonate.

The flotation results obtained with tannic acid are shown in Figs. 8 and 9. Tannic acid was an effective modifier that depressed calcite at a concentration as low as 0.2 mg/l. Selective flotation of fluorite occurred in the pH range of 7.5 to 9.

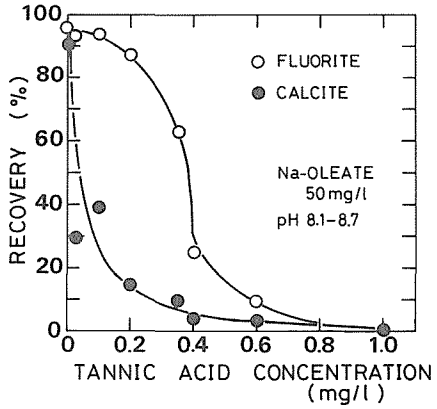



**Fig. 8.** Effect of tannic acid addition on the flotation of fluorite-calcite mixture.

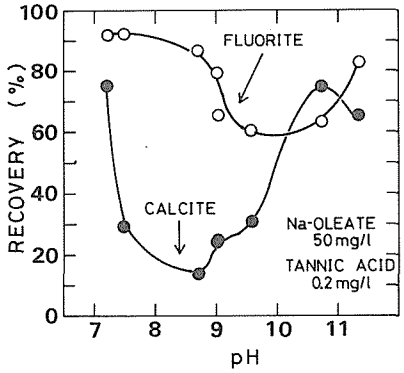



**Fig. 9.** Effect of pH on the flotation of fluorite-calcite mixture in the presence of tannic acid.

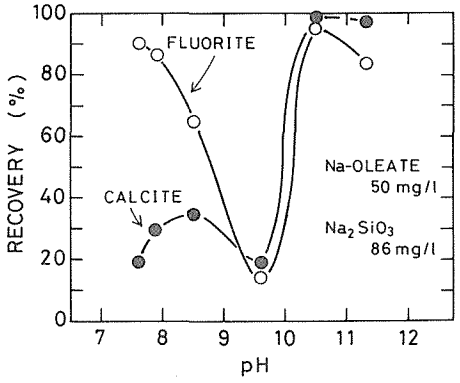



**Fig. 10.** Effect of pH on the flotation of fluorite-calcite mixture in the presence of sodium metasilicate.

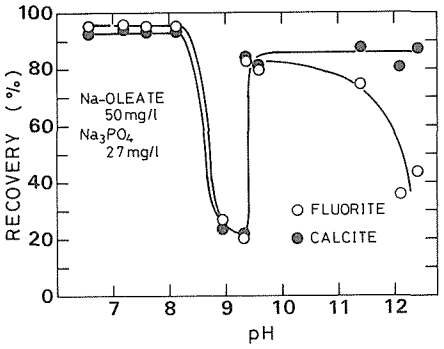
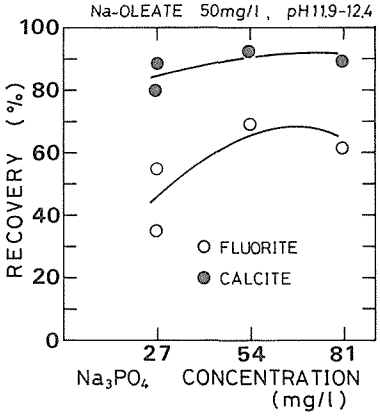



**Fig. 11.** Effect of pH on the flotation of fluorite-calcite mixture in the presence of sodium phosphate.




Figs. 10 and 11 show flotation results of fluorite-calcite mixture with sodium metasilicate and sodium phosphate as a modifier, respectively. In the case of sodium metasilicate, both minerals were strongly depressed in the pH range of 9 to 10, and fluorite was preferentially floated with decreasing pH. Good selectivity was obtained at around pH 8. Sodium phosphate selectively depressed fluorite above pH 12. However, as shown in Fig. 12, the difference in the

**Fig. 12.** Effect of sodium phosphate addition on the flotation of fluorite-calcite mixture at around pH 12.

recovery did not become large even with increasing sodium phosphate addition.

All modifiers used, except sodium phosphate, indicate that the optimum pH region for selective flotation of fluorite lies at around pH 8. Then, the synergetic action of plural modifiers in the flotation separation of fluorite-calcite at around pH 8 were examined using both tannic acid and starch, and both sodium lignin sulfonate and sodium metasilicate in combination. The results obtained are shown in Figs. 13-16. Figs. 13 and 15 show that a suitable combination of plural modifiers improved selectivity and smaller additions of both modifiers were sufficient for better separation than those required in single modifier systems. However, the optimum pH region became narrower as shown in Figs. 14 and 16. Care must be taken to determine and control the flotation pH.

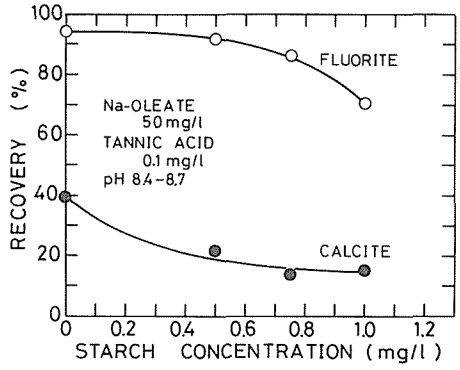



**Fig. 13.** Effect of starch addition on the flotation of fluorite-calcite mixture in the presence of tannic acid.

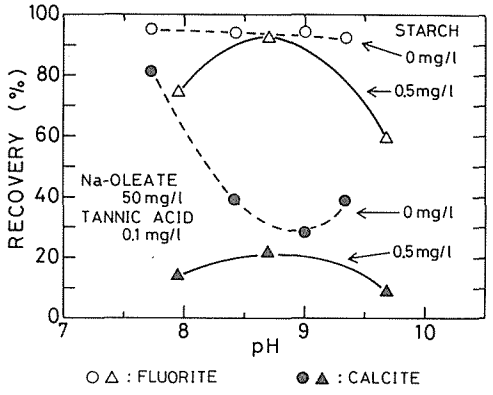



**Fig. 14.** Effect of pH on the flotation of fluorite-calcite mixture using tannic acid with and without starch.

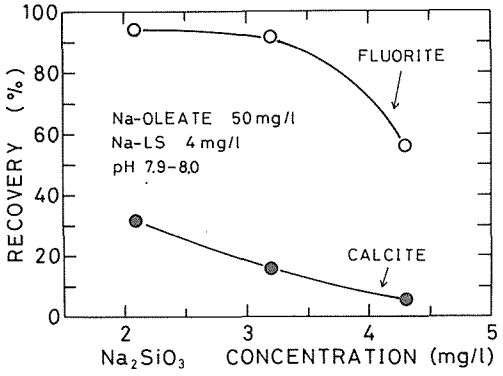



**Fig. 15.** Effect of sodium metasilicate addition on the flotation of fluorite-calcite mixture in the presence of sodium lignin sulfonate.

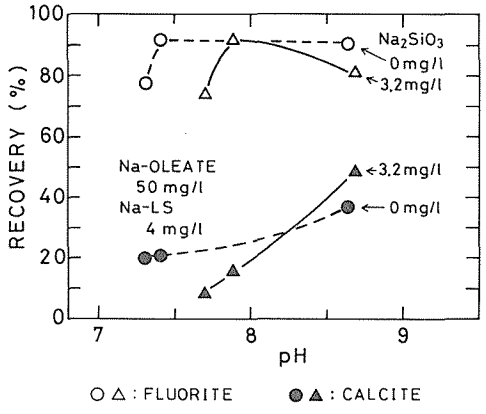



**Fig. 16.** Effect of pH on the flotation of fluorite-calcite mixture using sodium lignin sulfonate with and without sodium metasilicate.

## 4. Summary

The influence of modifiers on the flotation separation of fluorite-calcite was studied by conducting flotation tests in a mixed minerals system, using sodium oleate as the collector and five kinds of organic and inorganic modifiers.

Soluble starch, sodium lignin sulfonate, tannic acid and sodium metasilicate selectively depress calcite and the optimum pH region for separation lies at around pH 8. Sodium phosphate depresses fluorite above pH 12, however, its depressing action is not so strong.

A suitable combination of both tannic acid and starch, and of both sodium lignin sulfonate and sodium metasilicate improves selectivity at around pH 8. Though a small addition of both is sufficient for better separation, the optimum pH region becomes narrower.

## Acknowledgment

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