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Danish Atomic Energy Commission
Research Establishment Risø

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Abstract

As part of the work aimed at the exploitation of the uraniferous rock in southern Greenland a flotation process has been developed. The uranium- and thorium-bearing minerals, mainly lanthanide phospho-silicates, can be floated selectively with oleic acid as collector and sodium silicate as a regulating agent. Experiments indicate that linoleic acid is a more efficient collector than oleic acid.

A characteristic feature is the sensitivity to cations in the process water, which excludes the use of tap water for the experiments. On the other hand this has led to the utilization of lanthanum as an activator.

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Introduction

Since 1956 the radioactive rocks in the Ilimaussaq intrusion in southern Greenland have attracted considerable attention as a possible source of uranium for Denmark's future energy supply.

The uranium-bearing rock is a lujavrite with inclusions of other nepteline syenites and lavas. Lujavrite has a large content of the dark minerals arfvedsonite and aegirine. Besides it is a host rock for many rare minerals among which steenstrupine and monazite account for the thorium and uranium content (see table 1). The grain size of the rock varies from 0.5 to several mm, but a considerable part of the uranium is associated with tiny particles more or less included in other minerals. The highest radioactivity is found in contact zones between lava intrusions such as appear most typically on the Kvanefjeld plateau. Here a small exploratory mine was opened in 1962.

Steenstrupine is named after the Danish geologist K. J. V. Steenstrup. Basically it is a sodium-lanthanide phospho-silicate, but its stoichiometry is not easily grasped because of the many accessories. Its dark brown colour is due to radiation damage of the crystal lattice. Kvanefjeld monazite is more yellowish than, but of an elemental composition much similar to that of steenstrupine, that is to say, it has a higher U/Th-ratio than monazite from most other sources.

The estimated reserves are 8000 t of uranium metal, but as the average grade is only 400 ppm, a major task has been the beneficiation of the raw ore before chemical treatment. Among the prevalent separation methods, froth flotation has proved by far the most promising.

The present investigation was undertaken to study some parameters which were likely to influence the process. For a brief introduction to the concept of flotation see the appendix.

Experiments and Results

The rock is crushed and mixed thoroughly to level the variation of properties. The hardness on Mohs's scale is 5-6, but the structure is rather brittle, and milling down to -100 mesh is performed with reasonable ease. Further comminution requires a fast rising power per ton and produces excessive amounts of superfine material, which is generally disadvantageous to flotation.

Table 1

The most important minerals in Kvanefjeld lujavrite

	Name	Formula
Light minerals 50-60%	Analcime	$\text{Na Al Si}_2\text{O}_6 \cdot \text{H}_2\text{O}$
	Sodalite	$\text{Na}_8 (\text{AlSiO}_4)_6 \text{Cl}_2$
	Nepheline	$\text{KNa}_3 (\text{Al SiO}_4)_4$
	Albite	$\text{Na Al Si}_3\text{O}_8$
	Microcline	$\text{K Al Si}_3\text{O}_8$
Dark minerals 30-40%	Arfvedsonite	$\text{Na}_3(\text{Fe}^{\text{II}}, \text{Mg})_4 \text{Fe}^{\text{III}} \text{Si}_8\text{O}_{22}(\text{OH}, \text{F})_2$
	Aegirine	$\text{Na Fe}^{\text{III}} \text{Si}_2\text{O}_6$
	Neptunite	$\text{Na}_2\text{Fe}^{\text{II}} \text{Ti Si}_4\text{O}_{12}$
Radioactive minerals	Monazite	$\text{Ce PO}_4 (\text{ThO}_2, \text{UO}_2, \text{SiO}_2)$
	Steenstrupine	see below
	Thorite	$\text{Th SiO}_4 (\text{UO}_2)$
Other minerals of possible economic interest	Villiaumite	NaF
	Sphalerite	ZnS
	Beryllium and niobium minerals	

Steenstrupine: SiO_2	R. E. ^{x)}	Na_2O	P_2O_5	ThO_2	MnO	Fe_2O_3	UO_2	H_2O
% 25	30	10	4-8	2-7	7-9	3	0.2-0.7	3-8

^{x)} Lanthanides, predominantly Ce_2O_3 and La_2O_3

The flotation apparatus used is a modification of the so-called Fagergren cell as shown in fig. 1. The special stirrer arrangement ensures effective agitation along with intake of air and distribution of fine bubbles.

The flotated minerals are dried, weighed and analysed. Current analyses are most easily made by measuring the radioactivity of a sample, while chemical determinations are carried out from time to time.

As steenstrupine and monazite have varying contents of the metals to be extracted, it is most convenient to present the results by plotting the percentage of radioactivity recovered against the percentage of material flotated. In such a graph a simple mass transfer corresponds to a diagonal from (0, 0) to (100, 100), while a completely selective flotation of uniformly composed material is depicted by a steeper line, the slope of which indicates the enrichment factor (fig. 2).

The minerals to be concentrated are essentially rare-earth minerals which can be flotated with fatty acids as collectors. Oleic acid was chosen for the first series of experiments, and a comparison was made between addition of the free acid and of sodium oleate. In consequence of the marked alkalinity of lujavrite a suspension of the powdered rock in de-ionized water assumes a pH of 8-9. The free oleic acid was added as a 10% solution in methanol in order to obtain a fine dispersion in the pulp. As the alkali salts of the higher fatty acids form micelles when left in aqueous solutions with the result that part of the collector effect is lost, the sodium oleate used was freshly prepared by adding oleic acid to the equivalent amount of hot 0.1 m NaOH solution.

Experiment 1 (table 2, fig. 3)

Cell volume: 12.5 l
Feed: 5 kg of lujavrite, -100 mesh
Collector: 5 g of oleic acid
Air: 1.7 l/min
Temp.: 15°C

Successive fractions collected in the time intervals stated:

Table 2

	Weight %	(Th + U) %	Time in minutes
1	13.64	27.6	3
2	12.68	20.1	5
3	10.70	12.9	7
tail.	62.98	39.4	

Experiment 2 (table 3, fig. 3)

Collector: sodium oleate from 5 g of oleic acid; other conditions as above.

Table 3

Weight %	(Th+ U) %	Time in minutes
8.40	30.75	2
13.40	27.75	3
8.98	10.75	5
69.22	30.75	

Inspection of the flotated material showed that in the first experiment it was highly impure and the output low. The performance of sodium oleate was much better, and, especially at the beginning, a real concentrate was obtained. The interfering minerals were mostly the iron-containing arfvedsonite and aegirine. To be sure, the higher pH in the second experiment causes a suppression of the collector adsorption by iron, but a more pronounced effect is seen after the addition of sodium silicate, which is a widely used modifying reagent.

Experiment 3 (table 4, figs. 4 and 6)

Before the sodium oleate, 15 ml of $\frac{1}{2}$ M Na_2SiO_3 is added. This corresponds to 1.5 moles of SiO_3^{--} per ton of feed. Other conditions as in exp. 2.

Table 4

Weight %	(Th+ U) %	Time in minutes
9.10	55.1	$7\frac{1}{2}$
1.74	4.5	$7\frac{1}{2}$
89.16	40.4	

Experiment 4 (table 5, fig. 4)

0.7 mole of SiO_3^{--} per ton. Other conditions as in exp. 2.

Table 5

Weight %	(Th+ U) %	Time in minutes
11.96	55.3	5
5.30	12.0	$7\frac{1}{2}$
4.52	5.5	10
78.22	27.2	

It is seen that the silicate accelerates the flotation of monazite and steenstrupine, while the entrainment of other minerals is more or less quenched.

The first concentrate, which is clearly brownish or yellowish, is followed at a lower rate by a less pure material. Graphically this is expressed by a bend of the curve. This bend does not occur at higher silicate concentrations, but the total yield becomes lower although the purity is high.

In the following experiment a higher pulp concentration was tried in order to enhance the capacity of the flotation unit.

Experiment 5 (table 6, fig. 5)

Feed: 10 kg
 Modifier: 14 ml of $\frac{1}{2}$ M Na_2SiO_3
 Collector: 9 g of oleic acid in the form of sodium oleate
 Air: 1.7 l/min
 Temp.: 15°C

Table 6

Weight %	(Th+ U) %	Time in minutes
6.13	39.6	10
4.48	14.2	12 $\frac{1}{2}$
4.79	6.3	10
84.60	39.9	

The advantage of a higher solid concentration is neutralized by the relatively slower flotation. Furthermore the selectivity, which at first is excellent, deteriorates too soon.

In order to overcome this drawback a very small amount of $\text{La}(\text{NO}_3)_3$ is added to the pulp before any other reagent. The idea is that an enrichment of the mineral surface with lanthanide ions might improve the adsorption of collector molecules and thus increase the flotation rate.

Experiment 6 (table 7, fig. 5)

Feed: 10 kg
 Activator: 0.12 g of La as $\text{La}(\text{NO}_3)_3$
 Modifier: 14 ml of $\frac{1}{2}$ M Na_2SiO_3
 Collector: 9 g of oleic acid in the form of sodium oleate
 Air: 1.7 l/min
 Temp.: 15°C

Table 7

Weight %	(Th+ U) %	Time in minutes
7.0	44.5	7 $\frac{1}{2}$
8.7	21.5	7 $\frac{1}{2}$
9.3	9.5	7 $\frac{1}{2}$
9.15	5.1	7 $\frac{1}{2}$
65.85	19.4	

The desired effect is obtained without any loss of selectivity. This indicates that the lanthanum is chiefly attached to the steenstrupine and the monazite. In any case the fastest-floating minerals are those which show the greatest uptake of lanthanum, as seen from the tracer experiment mentioned below (table 8). The relative lanthanum content is determined by counting a unit sample of each fraction and subtracting the known contribution from immanent natural radioactivity.

Table 8

	Weight %	Uptake of La ¹⁴⁰ (arbitrary units per gram)
1	10.7	75
2	8.2	59
3	6.2	41
tail.	74.9	23

In a paper by Viswanathan et al.¹⁾ an investigation of flotation of beach sand monazite is described which shows parallels to the present work. An interesting feature is the finding that linoleic acid is a still better collector than oleic acid, whereas a saturated fatty acid salt, sodium laurate, is a rather poor one.

As linoleic acid was not available in this laboratory at the time concerned, a fatty acid mixture was prepared from crude linseed oil. Application of this instead of oleic acid gave the following result:

Experiment 7 (table 9, fig. 6)

Feed: 5 kg
 Modifier: 15 ml of $\frac{1}{2}$ M Na₂SiO₃
 Collector: Sodium salt of 4 g of the above fatty acid
 Air: 1.7 l/min
 Temp.: 15°C

Table 9

Weight %	(Th + U) %	Time in minutes
10.6	50.2	4
6.15	16.6	4
3.75	7.0	7
79.5	26.2	

Two things speak in favour of linoleic acid. One is the high flotation rate, which means increased cell performance. The other is the persisting selectivity expressed by the slight bend of the curve. In addition the amount of collector can be decreased, which may compensate for a possible higher price.

After a properly performed flotation only small traces of steenstrupine and monazite are found in the tailings, but a substantial radioactivity remains. Unfortunately this is due chiefly to uranium. Fig. 7 shows how the usual flotation curve based on counting results splits into a thorium- and a uranium-distribution curve when the percentages of Th and U as determined by analysis are plotted. Especially one notes that more than 90% of the thorium is collected in a 22% fraction.

Discussion

The regulating effect of sodium silicate is well known and is utilized especially in the flotation of non-sulphide minerals. It is assumed that the depression is caused by absorbed hydrolysis products of silicate which lead to an increased wettability. A similar but inopportune effect is observed after storage of wet-ground lujavrite for more than a few hours. All species are suppressed, presumably because the surfaces are hydrolyzed, liberating silicic acid. Also after dry milling and keeping in bags the minerals undergo surface alterations, although at a much lower rate. In the plant, however, the flotation department will be run in close connection with the mill without the necessity of any storage in between.

Sodium silicate can activate the flotation of apatite (Beloglazov²⁾), and monazite and steenstrupine show certain analogies with apatite.

Klassen and Mao-Tse-Fan³⁾ have shown that small amounts of sodium silicate used to activate the flotation of hematite sharply decrease the negative electro-kinetic potential. According to Borisov⁴⁾, collectors interact more strongly with minerals if their electro-kinetic potential is brought to a minimum by the addition of suitable electrolytes. From that point of view lanthanum should be a favourable additive because of its high positive charge. However, an excessive La^{+3} -concentration leads to increasing flotation of arfvedsonite and aegirine. Correspondingly, the Ca- and Mg-ions present in ordinary water disturb the flotation, wherefore de-ionized water is always used under laboratory conditions.

Fortunately the water in streams and lakes around the Kvanefjeld deposit originates from glacier melting and rainfall. Investigations have as yet shown that it is fit for use.

Examination of the temperature dependence gives the result for the oleic acid case that below 14°C the bubble mineralization takes place more slowly and the output diminishes substantially.

The water in Greenland is generally very cold, but in view of the high solid concentration possible in the pulp it will not be very expensive to maintain a temperature of 15°C . Furthermore the energy consumption of the grinding process is converted to heat in the material being broken, thus causing a temperature rise of $5-6^{\circ}\text{C}$.

Not quite satisfactory is the considerable hold-back of uranium in the tailings. Probably this uranium is found in very fine-grained material of less defined composition and partially amorphous structure. It was earlier recognized that macroscopic crystals of steenstrupine have a higher Th/U-ratio than has the bulk of lujavrite. The same has now proved to be true of the flotation concentrates. The thorium, evidently contained in more regular mineral grains, is recovered much more easily.

Acknowledgement

The authors want to express their appreciation of the technical assistance of Mr. Sven Persson and Miss Birthe Hougaard.

Appendix

In flotation the varying wettability of minerals is utilized for separation purposes. When a sufficiently finely ground sample in water suspension is passed by a stream of air bubbles, the least wettable grains will tend to adhere to the bubbles and float to the surface. This tendency may be supported by the addition of chemicals which are selectively adsorbed by certain types of minerals and aid their attachment to bubbles. Such chemicals are termed collectors and will generally be found among organic, long-chained compounds with a polar group at one end. On reaching the surface the bubbles must remain for a while as a brittle froth which facilitates the removal of the collected mineral grains by skimming. In some cases the collector has frothing properties itself, but often the froth formation requires the addition of another chemical which is termed a frother and as a rule belongs to the higher alcohols.

The adsorption of the collector is due to interaction between its polar group and the atoms on the crystal faces of the mineral. The relative affinities may be thoroughly altered by the addition of complexing agents or pH-regulators or by ion exchange on the mineral surface, whereby one type is depressed and another made to float. Chemicals which show effects of this kind are called modifying reagents and are of great importance for the development of flotation into a versatile tool in mineral dressing.

References

1. K. V. Viswanathan, T. R. Madhavan and K. K. Majumdar, Selective flotation of beach sand monazite. *Mining Magazine* 113 (1965) 17-23.
2. K. F. Beloglazov and G. A. Osolodkov, Effect of the alkalinity of the pulps on flotation of apatite. *Rep. Leningr. Min. Inst.* 9, (1936) 1.
3. V. I. Klassen and Mao-Tse-Fan, Action mechanism of sodium silicate in flotation of non-sulphide minerals. *Non-ferrous Metals*, Moscow, No. 9 (1959).
4. V. M. Borisov, Method of the physico-chemical evaluation of the reagent interaction with the mineral grain surfaces during flotation. *Khimicheskaya Promyshlennost* No. 6 (1954) 336-338.

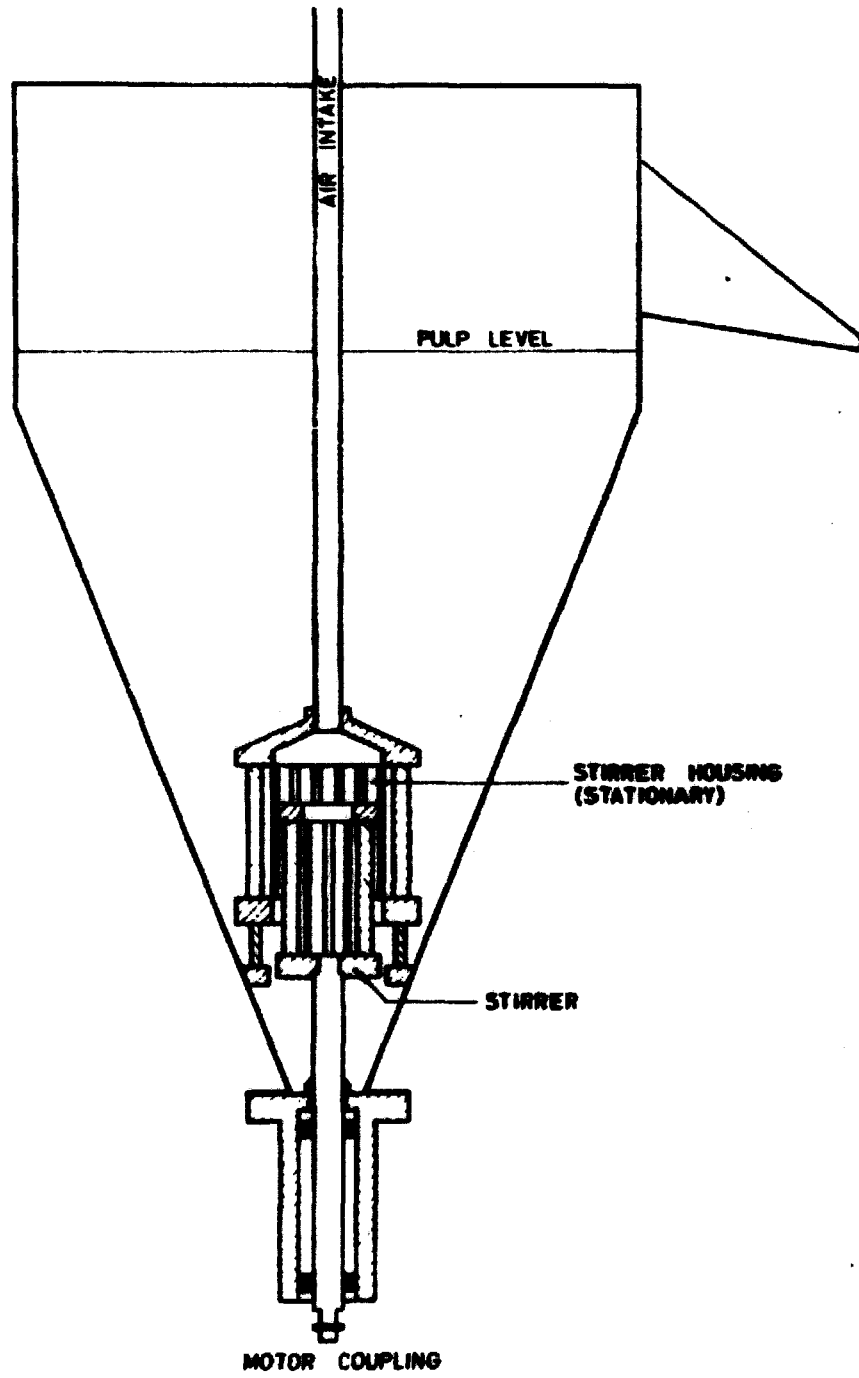


Fig. 1

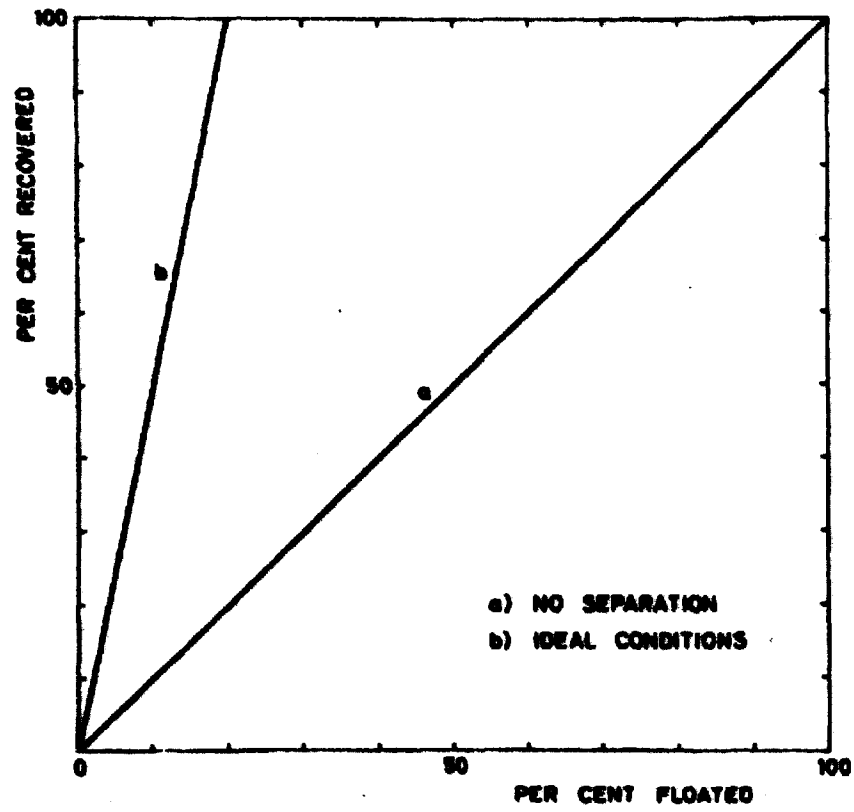


Fig. 2

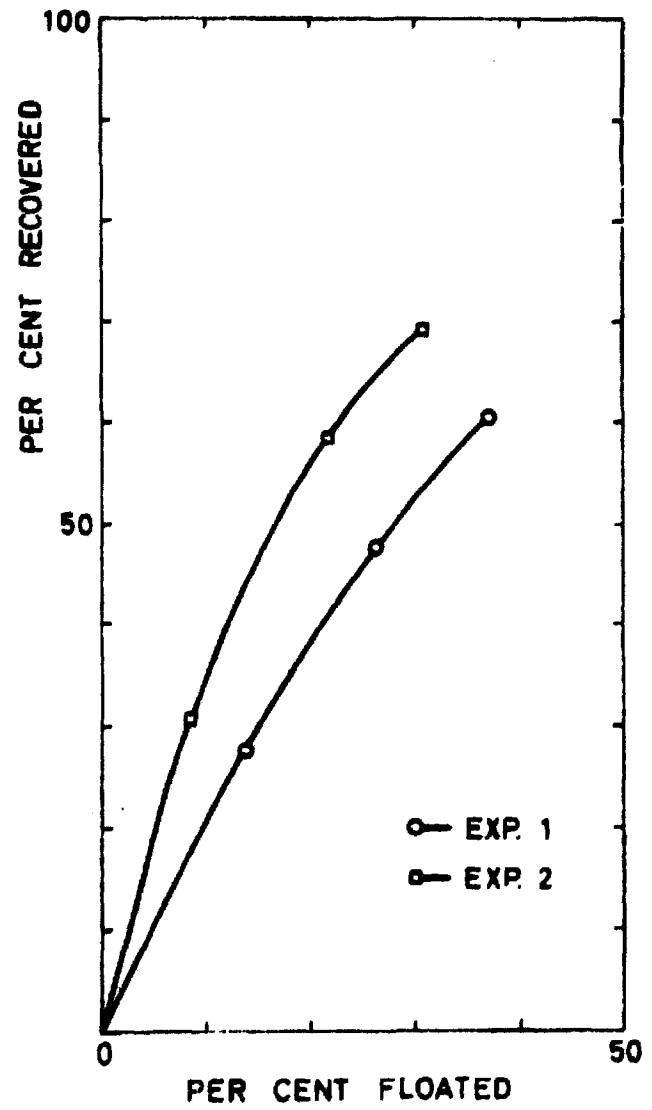


Fig. 3

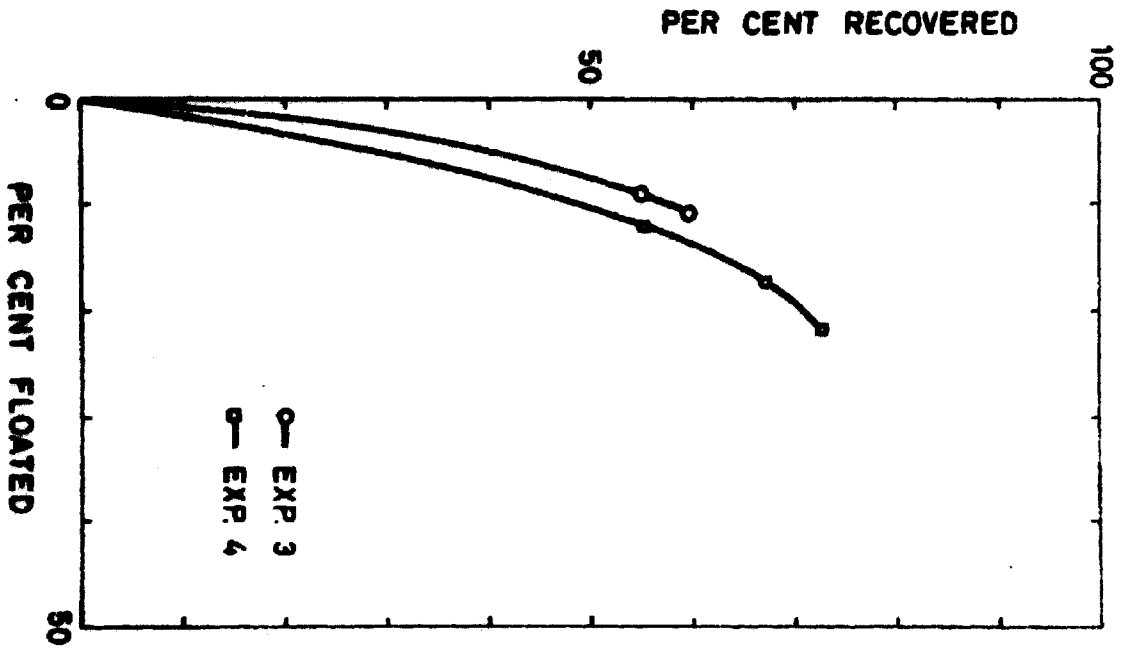


Fig. 4

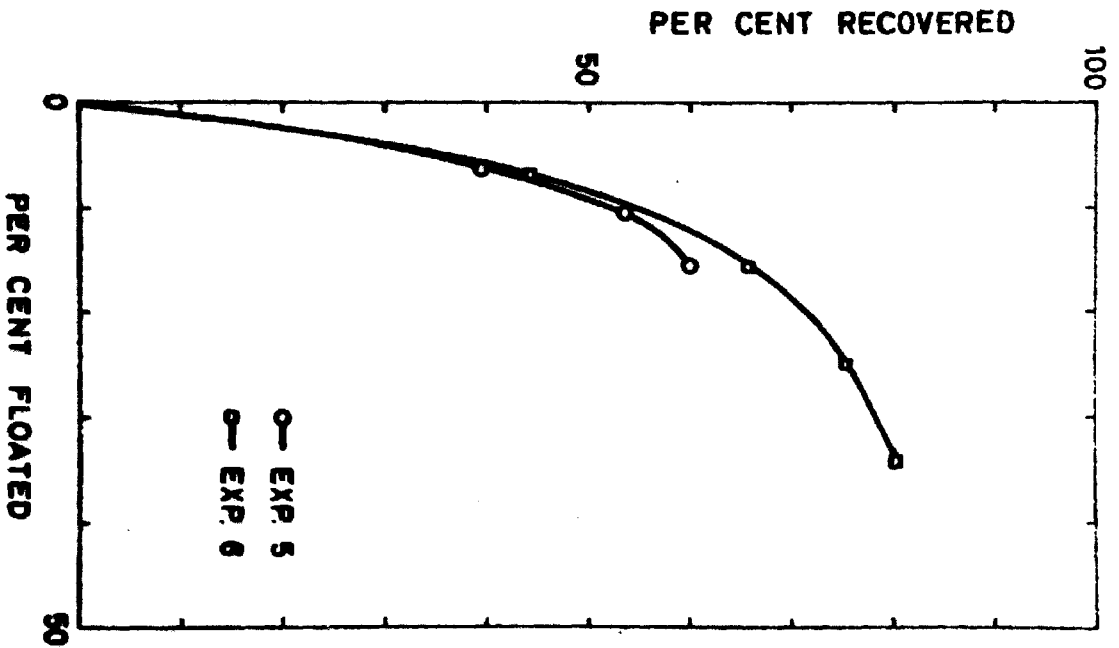


Fig. 5

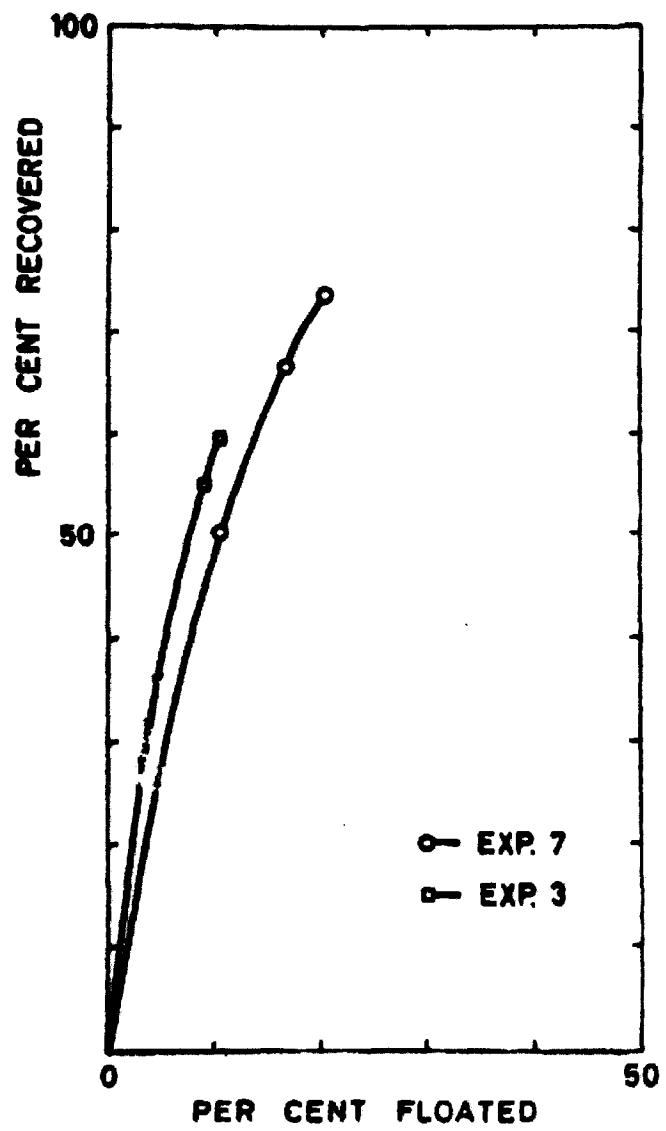


Fig. 6

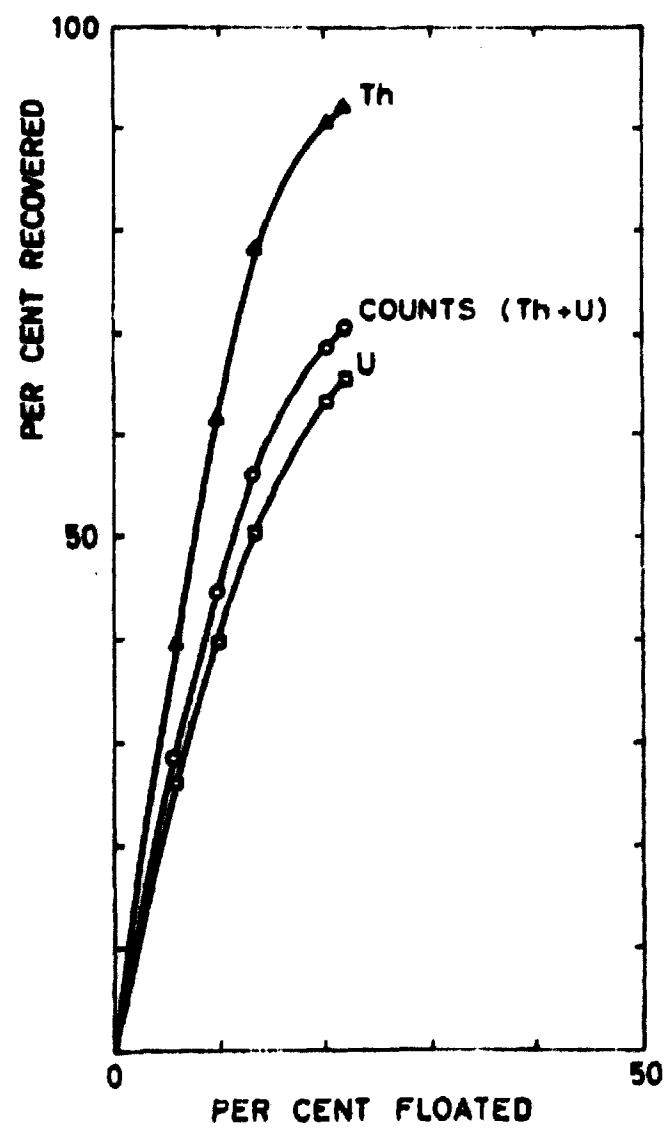


Fig. 7