UTILIZATION OF FISH OILS IN ORE FLOTATION

By S. R. B. Cooke* and M. E. Stansby**

ABSTRACT

RESEARCH IS BEING CONDUCTED TO RETURN FISH OILS TO THEIR PREVIOUS USE AS FLOTATION AGENTS FOR THE SEPARATION OF METALS FROM ORES. POTENTIAL FLOTATION USAGE OF SUCH OILS AT ONE-HALF POUND PER TON OF IRON ORE IS ABOUT 5,000,000 GALLONS A YEAR. STUDIES HAVE BEEN CONDUCTED ON THE EFFECTS OF CONCENTRATION, FATTY ACID CARBON-CHAIN LENGTH, AND UPON THE DEGREE OF UNSATURATION OF SUCH COMPOUNDS ON THEIR EFFICIENCY AS FLOTATION AGENTS. FATTY ACIDS WITH IODINE VALUES OF 70-115, INDICATING MODERATE UNSATURATION, HAVE GIVEN THE GREATEST EFFICIENCY. SEPARATION OF THE INDIVIDUAL FATTY ACIDS FROM THE OILS HAS BEEN COMPLETED AND WORK ON THE EFFECTS OF CARBON-CHAIN LENGTHS ON FLOTATION EFFICIENCY IS IN PREPARATION.

Although at one time fish oils were used to a small extent in ore flotation, this is no longer the case. Research carried out by competing oil producers has resulted in the development of oil derivatives such as alkyl amines, that in some cases are superior to the aliphatic acids, although oleic acid is still widely employed as a flotation collector.

FIG. 1 - H. S. CHOI USING A FAGERGREN FLOTATION CELL TO INVESTIGATE THE USE OF FISH OIL FATTY ACIDS IN ORE CONCENTRATION. THE HEAVY GLASS CELL CONTAINS AN AQUEOUS PULP OF FINELY-GROUND IRON ORE. FATTY ACIDS SELECTIVELY COAT THE IRON OXIDE MINERAL PARTICLES, MAKING THEM HYDROPHOBIC. MECHANICAL STIRRING OF THE PULP AND SIMULTANEOUS ADMISSION OF AIR PERMITS THE COATED IRON OXIDE PARTICLES TO BECOME ATTACHED TO AIR BUBBLES, WHICH RISE TO THE SURFACE AND ARE SCRAPED INTO THE PAN IN FRONT OF THE OPERATOR, THUS PRODUCING AN IRON-RICH "CONCENTRATE." THE SILICEOUS GANGUE MINERALS, BEING HYDROPHILIC, REMAIN IN THE PULP AND DO NOT CONTAMINATE THE "CONCENTRATE," THUS PRODUCING A "TAILING."

The flotation process is currently employed for sulfide ores (using sulphydric collectors), as well as in many applications to other types of ore. The flotation process can be applied to the concentration of low-grade iron ores. At the present time, the high-grade iron ores are nearing exhaustion, and these lower-grade ores, which are very abundant, will be the principal future source of iron production in this country. The School of Mines and Metallurgy and the Mines Experiment Station at the University of Minnesota have carried out research for the past 30 years to develop methods for concentrating these ores. Based on this research, plants valued at over 500 million dollars are now under construction.

There are two general types of iron-concentration methods that can be used and that are being considered at the present time. One of these involves magnetic separation; the other flotation. Although the magnetic-separation process has been widely investigated and most of the plants now under construction make use of this method, there are many iron ores to which the magnetic-separation process is not directly applicable and for which flotation may well be the favored method. Should the flotation process eventually be adopted for this purpose there would be a very great expansion in demand for flotation agents. Less than one-half pound of oil or oil derivative is required for flotation of a ton of iron ore, but since nearly 100 million tons of iron ore are processed annually, the amount of oil required for the flotation of this amount of ore is considerable (about 5 million gallons).

* PROFESSOR OF MINERAL DRESSING AND METALLURGY, SCHOOL OF MINES AND METALLURGY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINN.
** CHIEF, PACIFIC COAST AND ALASKA TECHNOLOGICAL RESEARCH, FISHERY TECHNOLOGICAL LABORATORY, BRANCH OF COMMERCIAL FISHERIES, U. S. FISH AND WILDLIFE SERVICE, SEATTLE, WASH.

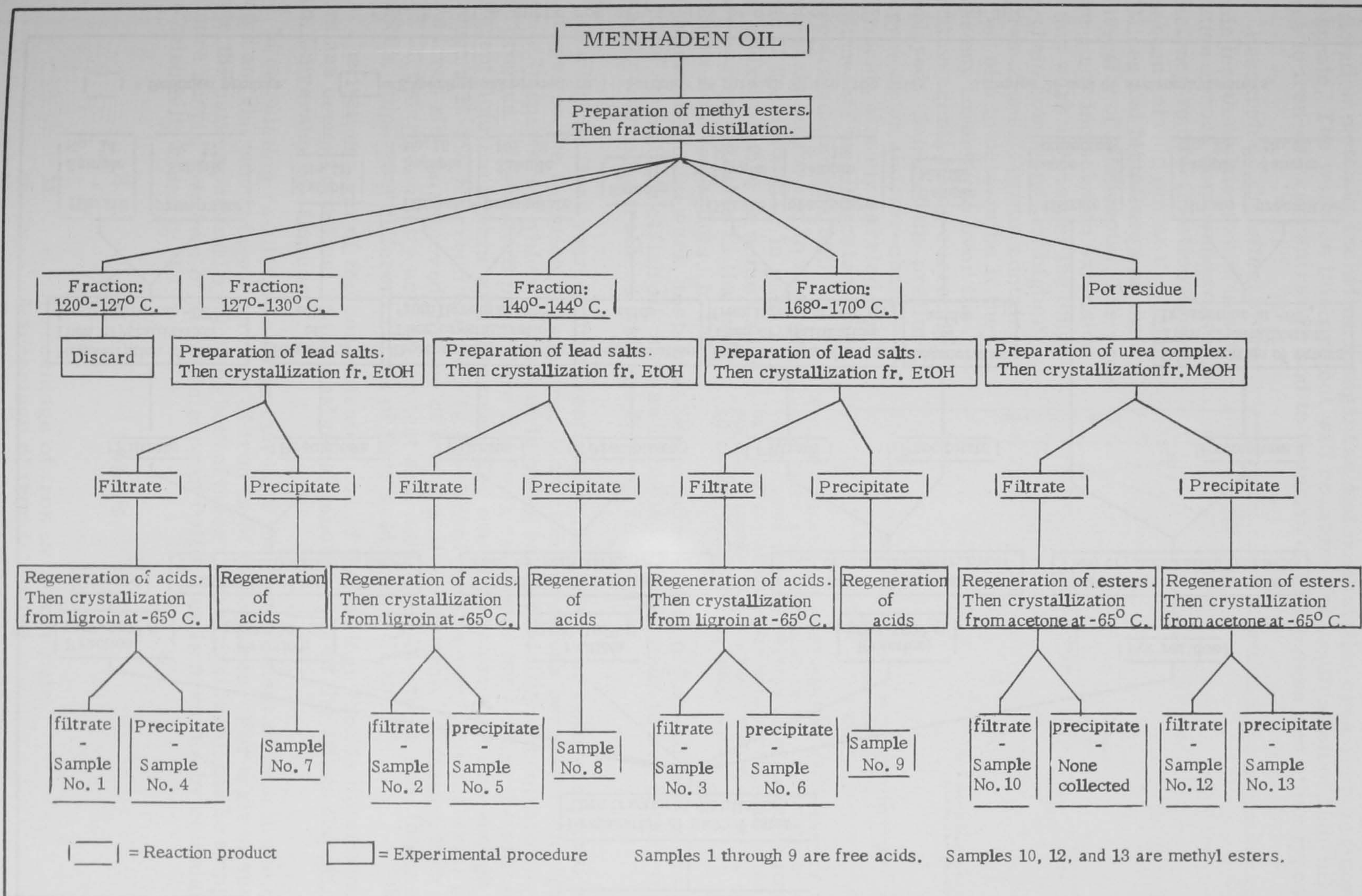

FIG. 2 - FLOW SHEET FOR SEPARATION OF THE COMPONENTS OF MENHADEN OIL.

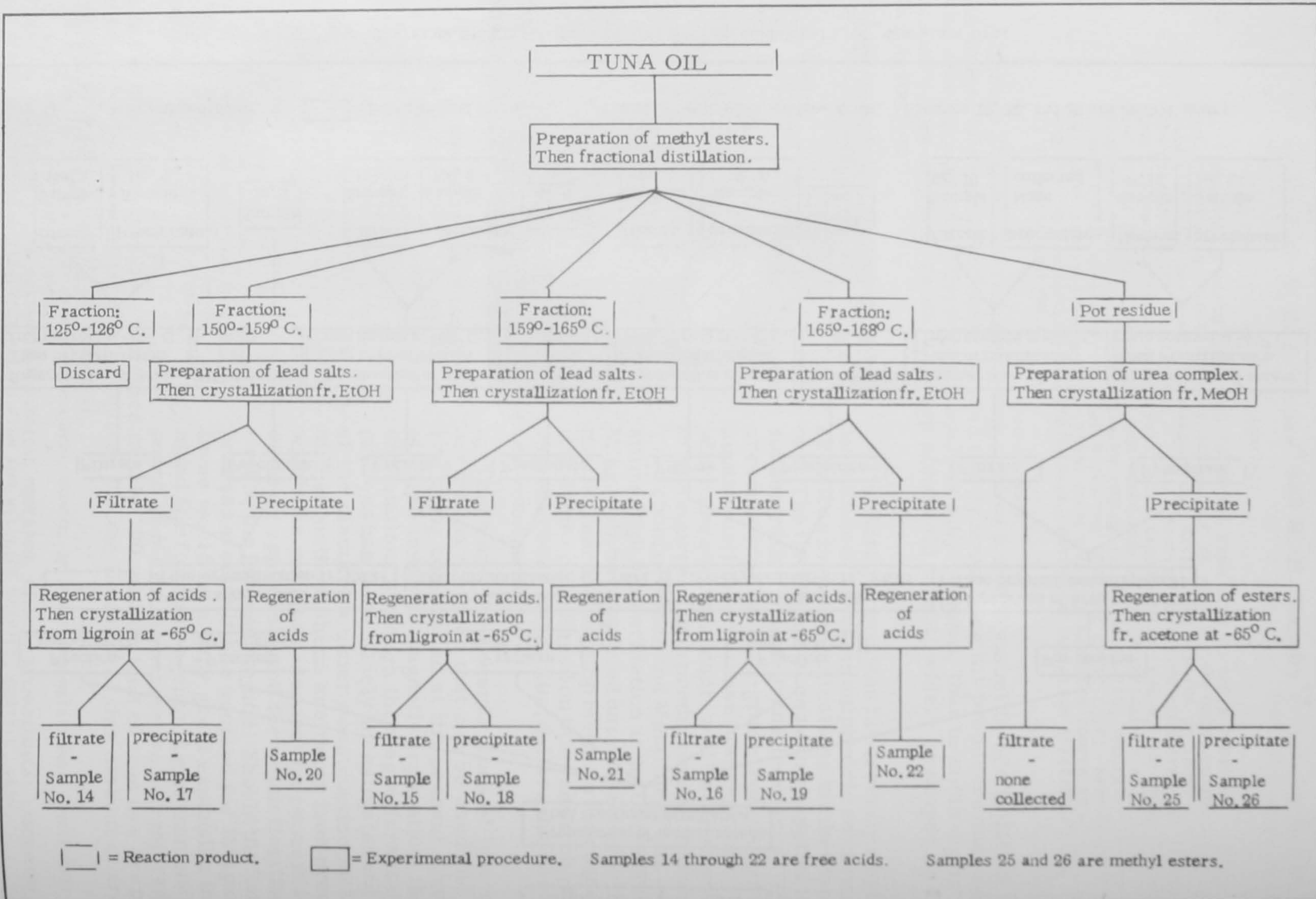

FIG. 3 - FLOW SHEET FOR SEPARATION OF THE COMPONENTS OF TUNA OIL.

In addition to this very large potential use of oils for the concentration of iron ore, there are sizable quantities of other ores that at present are being concentrated by flotation methods, including manganese and nonmetallic ores such as fluorite and phosphate. The work on this project will consider the application of fish-oil derivatives to iron-ore concentration and to flotation of manganese and other types of ores.

Research on the effect of the chain length and degree of unsaturation of such compounds on their efficiency as ore-flotation agents has been carried out at the School of Mines and Metallurgy of the University of Minnesota. The present study includes an extension of this work to consider the longer-chain compounds of higher degree of unsaturation contained in fish oils to determine if they offer any advantages over the flotation agents being currently employed. Some of the preliminary work on shorter-chain fatty acids already carried out at Minnesota has indicated that there are advantages both to long-chain length and to high degree of unsaturation. In past work, alkyl amines in some cases have proved superior to the fatty acids as flotation agents. In the initial experimental work, tests have been confined to use of fish-oil fatty acids. Some tests of derivatives of fish oil, such as alcohols, will be made to see if they will function as compatible frothers with the fish-oil fatty acids.

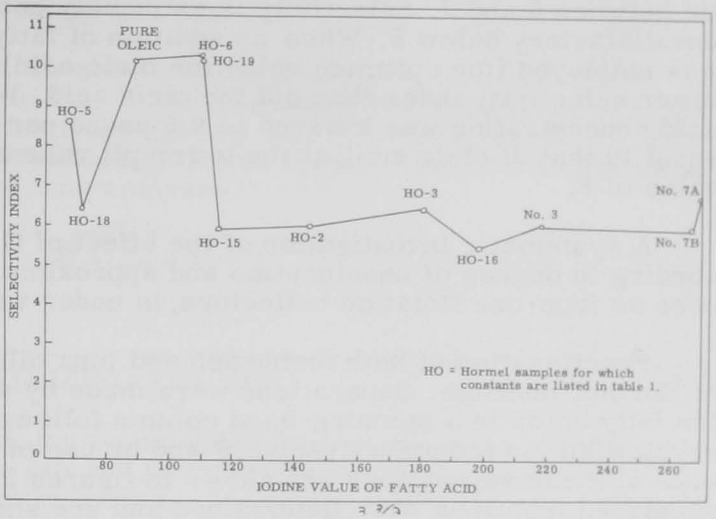

FIG. 4 - RELATIONSHIP BETWEEN THE EFFICIENCY OF THE VARIOUS FATTY ACID FRACTIONS IN THE COLLECTION OF ORE AND THEIR DEGREE OF UNSATURATION AS MEASURED BY IODINE VALUE. ORE WAS CONDITIONED WITH FATTY ACIDS AT 60 PERCENT SOLIDS, FLOATED AT 19-PERCENT SOLIDS AT PH 6, AND ROUGHER CONCENTRATES WERE CLEANED TWICE.

During the first year of the investigation, the work has been restricted entirely to studies on the flotation of iron ore. Most of the work has been with Michigan specularite (jasper ore), which at present is being commercially concentrated by a flotation process. A standard procedure has been developed for testing the efficiency of different flotation agents with this ore. The ore first is crushed fine enough to pass through a 20-mesh screen and then is de-slimed (that is, very fine material of minus 10-micron size is removed) by use of a hydraulic elutriator. Flotation then is carried out using each fatty acid under test at a series of pH values and, in some instances, employing different ratios of fatty acid to ore (figure 1).

The iron content of the concentrates and of the tailings then is determined. This work has been carried out in the analytical laboratories of the Mines Experiment Station, University of Minnesota.

In calculating results, one finds that both the final content of iron in the concentrates and the percentage recovery of iron is of importance. For a given series of tests, the curves obtained by plotting both of these factors against pH can be compared. A more simple measure of the efficiency of collectors is possible by calculation of the selectivity index (S. I.):

$$S.I. = \sqrt{\frac{M}{m} \times \frac{n}{N}} \quad \text{where}$$

M = Percentage of iron in concentrate
m = Percentage of iron in tailing
N = Percentage of insoluble in concentrate
n = Percentage of insoluble in tailing

The selectivity index varies from 1, when no concentration has been made, to infinity for complete concentration (never practically obtainable).

Concentration experiments have been completed at a series of pH values between 5 and 9, comparing the selective index when using oleic acid and the mixed fatty acids from pilchard oil. On the ores so far investigated, the optimum pH seems to lie between 6 and 7. Selectivity is extremely poor at pH 8 or higher, and frothing is unsatisfactory below 5. When an addition of fatty acid of one pound per ton of ore was employed (the optimum value for oleic acid), the pilchard fatty acids showed a lower selectivity index than did the oleic acid. When, however, the pilchard-oil fatty acid concentration was lowered to 0.5 pound per ton of ore, the selectivity index was equal to that of oleic acid, at the lower pH values, and was markedly higher, at a pH value of 8.

A systematic investigation of the effect of fish-oil fatty acids, fractionated according to degree of unsaturation and approximate chain length upon their effectiveness as iron-ore flotation collectors, is under way.

Fractionation of both menhaden and tuna oils was carried out in the laboratories of Hormel Institute. Separations were made by distillation of the methyl esters of the fatty acids in a spinning-band column followed by lead-salt and low-temperature crystallization from Skellysolve F and by use of urea-complex separations. The details of these separations are shown in figures 2 and 3. Chemical constants of the separated fractions were determined and are shown in table 1.

Table 1 - Fractions of Fatty Acids or Methyl Esters Obtained from Menhaden and Tuna Oils

Menhaden Oil				Tuna Oil			
Sample No.	Quantity	Saponification Value	Iodine No.	Sample No.	Quantity	Saponification Value	Iodine No.
	Ml.				Ml.		
1	5	1/	1/	14	10	1/	1/
2	100	214.5	144.0	15	150	194.1	115.8
3	150	207.2	181.2	16	50	193.6	197.4
4	10	1/	1/	17	10	1/	1/
5	250	219.2	67.6	18	150	200.8	71.2
6	250	204.1	109.7	19	150	197.2	109.4
7		2/	2/	20		2/	2/
8		2/	2/	21		2/	2/
9		2/	2/	22		2/	2/
10	225	166.5	196.5				
12	50	179.7	202.2	25	25	175.8	149.8
13	50	175.2	111.1	26	75	170.8	69.7

1/ DENOTES SAMPLE TOO SMALL FOR ANALYSIS.
2/ DENOTES SOLID, SATURATED FRACTION AND THAT NO ANALYSIS WAS MADE.

Application of these various fractions of fish oils to the flotation of certain Mesabi Range wash-ore tailings are now under way. Although all fractions have not been completely tested, enough results for some preliminary conclusions have been obtained. Figure 4 shows the relationship between the degree of unsaturation of the various fractions, as expressed by iodine value, and their efficiency as ore collectors, as given by the selective index. These preliminary results indicate that the efficiency of fatty acids as collectors for iron ore is determined, at least in part, by the degree of unsaturation. Fatty acids having iodine values in the range of 70-115 give the greatest efficiency. This range includes the degree of unsaturation of oleic acid, which has been used as a standard in the work to date.

The oleic acid used has been a relatively pure product, whereas in the commercial flotation operation, an impure commercial grade oleic acid is employed. In some preliminary experiments, it was found that the efficiency of oleic acid was greatly affected by its purity. Accordingly, work is now under way to compare the efficiency of the oleic acid used in commercial iron ore flotation with that of the purer oleic acid used in this research. Work also will be started soon on derivatives of fish-oil fatty acids prepared at the Service's Seattle Fishery Technological Laboratory.

ACKNOWLEDGMENT

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FERTILIZING THE SEA

In different parts of the world, the technique of applying chemical fertilizers to increase the yield of fish in the sea has been used both experimentally and on a commercial scale in an attempt to increase the fish yield in the sea. Under natural conditions, the sea can only support a limited population of marine animals. The food chain in the sea is very complex, small animals feeding on small plants, larger animals feeding on the small animals, and in turn being fed upon by the fish. Theoretically if the abundance of any link in the chain could be increased, the fish would also increase in quantity. In most marine situations, it does not appear to be feasible to introduce a sufficient number of living organisms to have a significant effect on the food chain. The method which has been used is that of applying chemicals or organic waste to the water to increase the abundance of the lowest living link in the food chain, the tiny plants. If this were done in the open sea an enormous wastage would occur since the ocean currents would disperse the fertilizer and perhaps also the organisms feeding on it. Thus it seems that this experiment could only be successful if conducted in an enclosed area of water. Some water exchange may be necessary to maintain the oxygen supply.

An experiment of this type was carried out in an inlet on the west coast of Scotland. This technique has also been used in pond-culture work in Japan and elsewhere. While an increase in the yield of fish can be obtained using such methods, the gain is not usually in proportion to the amount of fertilizer applied. Some of the fertilizer may be wasted if it sinks to the bottom and became unavailable to living organisms. Some of the fertilizer will be taken up by organisms which do not enter into the food chain of the fish whose yield the experiment is intended to increase. Such organisms may prey upon the organisms in the food chain or on the fish themselves. Hence it is possible, under special circumstances, to increase the yield of marine animals, but "sea farming" will pay only rarely, if at all.

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The Marine Laboratory,
University of Miami,
Coral Gables, Fla.