The Study
Of
Flotation on Taconites

By

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A THESIS

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INTRODUCTION

The process of selective flotation originated by William Haynes (112) as a result of his recognition of the difference in wettability of minerals by water. His patent, granted in 1860, described this new flotation technique. In the succeeding fifty years flotation practices passed through various phases of development: such as skin flotation, bulk oil flotation, froth flotation, and more recently gross flotation. The development of these unique flotation techniques has been nourished by the depletion of the rich ores.

Flotation, as applied to the selective separation of mixtures of relatively finely divided solids suspended in the liquids (generally in water), is a surface phenomena. There exists in the flotation literature a healthy difference of opinion as to the exact nature of this surface phenomena. This controversy is concerned mainly with the relative importance of flotation reagent compound formation at the surface of the economic solids, or adsorption of the reagent at the solid surface. Examination of the structural characteristics of known flotation reagents indicates that whether compound formation at the surface, or adsorption occurs, these compounds have in their molecules, an element of groups Vb and VIb of the periodic table. Such atoms in their lower valence states have extra electrons to share with the surface metallic atoms of the solids. The application of these fundamental physico-chemical principles should contribute much to a better understanding of the exact nature of the surface phenomena active in flotation practice related to the concentration of economic values in low grade ores.

PURPOSE AND SCOPE

Coal and steel are the backbone of our industrial civilization. As the high grade and intermediate iron ores become more and more difficult to obtain, the low grade taconites constitute a nationally major source of iron for the future. Until now, the taconites were regarded a useless nuisance in the beneficiation of the economic iron ores. Taconites are most abundant in iron range areas and have been exceedingly difficult to concentrate.

The flotation of taconites is very typical of the ferrous and nonferrous minerals. Minerals, such as kyanite ore (quartz, pyrite, rutile mixture), ceramic grade feldspar , micas, garnets, tourmaline, hornblende, glass sands, alumina, have been successfully concentrated by the same types of reagents. The chemical nature of iron oxides and silicate minerals, is quite similar to that of other compounds containing of nickel, cobalt, uranium, thorium, vanadium, aluminium, cerium, and, copper. These mineral compounds can be concentrated with similar anionic type flotation collectors.

This investigation was concerned with the use of the foregoing physico-chemical principles in the design of a flotation reagents for the separation of the oxides, carbonates and silicates of the iron minerals. Polar chelating groups of the salicylic acid type proved not efficient. Alkylated salicylic acid, β-resorcylic acid and mono-alkyl ether of the latter were studied in detail. The work was also extended to study the effect of the chain length, ore concentration, pulp density, pH effect and the variation of collector concentration.

THEORY

In the froth flotation, mineral particles should become attached at the interface of air-liquid (36, 40A, 40, 48, 103, 109). The relative density of the mineral particles with the air bubble becomes less, and these particles are carried to the surface of the pulp on the inside of the air bubble. Thus, they become part of the stable froth and are skimmed off with the froth by mechanical device.

The following steps are involved in the flotation:

(1) Grinding the ore to liberate the valuable minerals from accompanied materials.

(2) The creation of the buoyant medium (air bubbles) with which to float the valuable minerals.

(3) Creation of conditions favorable to the formation of stabilized froth by the addition of a frothing agent.

(4) Creation of conditions favorable for the adherance of the mineral particles to air bubbles.

CONDITIONING AGENTS

A. FROTHER:

Frother is generally an organic compound, which enables the solution to form more or less stable froth with air. Frother molecules consist of one or more polar groups and one non-polar group. Polar groups have an affinity for water. These frothers act upon the interface of gas, liquid and solid. For the specific flotation the frother should not have the properties of the collectors.(48, 103) Several investigators have shown that the frothing power is related to the lowering of surface tension. DeWitt and Makens (42) found that the frothing agents having the most negative slope on a surface tension-molar concentration curve are the most effective frothers.

Some of the commonly used frothers are: pine oil, terpineol, cresol, n-amyl, and higher alcohols. An excess of frother decreases the efficiency of flotation.

B. COLLECTORS:

Collectors are usually organic compounds which promote the contact between the minerals and air bubbles by surface chemical reaction (chelation) or adsorption.

A collector reagent should have a specific selective action on the desired mineral. The collector reagent should impart water repellancy to the mineral. This water repellancy is attributed to the non-polar aliphatic portion of the collector molecule. Taggart (103) states that the collectors must be soluble in water, at least to a small degree. The chemical structure of the collector may be similar to the frother. The polar group of the collector contains elements from groups Vb and VIb of the Periodic Table.(40B) Certain collectors such as oleic acid contain unsaturated linkages which likewise contribute sharable electrons.

To explain the behavior of the collectors, various hypotheses have been put forward. The most important of these are: (1) the chemical (solubility) hypothesis (109) and (2) the adsorption hypothesis (112). Neither of these hypotheses is wholly acceptable for the complete explanation of the flotation phenomena. A co-ordination of the several flotation theories has been presented by DeWitt (40B) on the basis of electron sharing.

C. DEPRESSORS:

Since the collector coating is an indispensable factor in flotation, depressors accomplish their purpose of inhibiting flotation of gangue materials by eliminating the coating of the collectors on gangue particles. The common depressors in use are: silicates, hydroxides, cyanides, sulfides, and sulphates of the alkali metals.

D. ACTIVATORS:

Activators are the substances which alter the surfaces of a mineral. These compounds enhance the film formation by the collector which otherwise would have no effect on the mineral.

E. pH REGULATORS:

The effectiveness of all classes of flotation reagents, depends primarily upon the degree of alkalinity or acidity of the pulp. The pH regulators common in use are: caustic, lime, soda ash, and mineral acids.

PREVIOUS WORK:

The initial patents of William Haynes (112) and Bessel and Bessel (10) proposed the use of small amounts of various oils or organic compounds for selective wetting and floating of graphite. Everson(43) described the use of hydrocarbons and/or sulfonated fatty oils in combinations with air or gases introduced by chemical reactions for flotation.

Very little has been published on the flotation of taconites. However, a number of patents have been issued on the flotation of other types of iron ores (sulfides) and oxidized ores. Differential flotation with xanthates as the collector modified by addition of alkali compounds, cyanides and alkali sulfates have been used for the flotation of sulfide minerals containing copper, zinc, nickle, iron, lead.(94, 98) Brinker (13,14) proposed the use thiocarbanilide as the collector for iron. Hodges (88) recommended black liquors,"floating soap", a byproduct of the sulfate and soda-cellulose industry, as a collector for sulfide and oxidized iron ores.

Work of various investigators (28,33,49,50,79,91,95,96) showed that in flotation, silica gangue is activated by the presence of iron, calcium, barium, aluminium and tin atoms in the minerals. Silica (quartz) gangue materials are much easier to float with oils, especially with fatty acids, resin-acids, tall oil, and their soaps or the cationic type collectors (primary or secondary amines).

The patent issued to Kirby and Gilson (72) in 1941, included the uses of Betaine type compounds of the general formula- $R\cdot CH_2\overbrace{N(CH_3)_2CHR'COO}$ as a collector for silica. (R is a long chain aliphatic radical of 8-18 C atoms, R' is generally H). Various patents have been issued to Brown and Tartaron (19, 20) describing the use of fatty acids or resin acids and their soaps as the collectors, and the gelatinized starch as the depressor at pH about 1.6-3. Starch is gelatinized by boiling with caustic or acids, or by boiling one minute with oxidizing agents without allowing the degradation of starch to dextrin.

Brown's patent (17) covered the use of xanthated carbohydrates such as starch, cellulose, dextrin as a modifier in the flotation of siliceous gangue from iron ores, using calcium salts as the activators and anionic agents, such as fatty acids, resin acids and their soaps as the collectors. His another patent (18) covered the uses of xanthated carbohydrates as the depressors for the oxidized iron ores, using cationic collectors such as long chain amines, resin amines and quarternary ammonium compounds.

Clemmer and Clemmons (28) patented the process for floating siliceous gangue with anionic collectors, while retarding flotation of hematite with a metaphosphate in a solution of pH greater than ten. Sodium silicate, dextrin, starch, various tannins, as well as ortho-phosphates or pyrophosphates were specified as depressors; oleic acid, sodium oleate, sulfate soap or tall oil were the collectors. A 96% recovery of iron in flotation and reflotation of the concentrates by this technique was reported. (30) Clemmors and Williams in their various patents described the use of tannin extract or causticized starch as the depressors for iron oxides and/or lime as the activator for silica with the addition of anionic collector - fatty acids, tall oils, and their soaps, the sulfate soaps, the latter two groups. At the same time, Clemmers and Rempacek (29) patented the use of alkali sulfates as a hematite depressor; 70-75% of the silica gangue was floated.

These same anionic types of collectors have been patented by Morton (83), Sullivan (100A), Herkenhoff (60, 17, 18), for the flotation of siliceous gangue from iron bearing ores. In contrast to this work cationic reagents (primary and secondary amines) have been patented by Devaney (39), Christmann (25), Cohn (30A) for the flotation of siliceous gangue. In addition, various minerals have been floated with those same anionic collectors (2,3) such as: fatty acids, tall oil (mixture of palmitic, oleic, linolenic and linoleic acids) and their soaps. Among other minerals are illmenite, rutile, magnetite, hematite, silica, feldspar and various other non-ferrous oxides and silicates.

Patents have been issued to Booth and/or Herkenhoff (60,61,62) for the beneficiation of iron minerals by floating the iron oxides or silica. They cover anionic reagents, such as various sulfated and sulfonated oils: tall oil, aliphatic saponifiable oils, mahogany acids, linoleic acid, fatty acids, linseed, cotton seed, soyabean, corn, castor, glyceryl mono-laurate, sorbitan trioleate, aromatic sulfonic acids, etc., and various aliphatic mono- and/or dibasic acids, aromatic acids and their soaps. These patents described the various stages of the operations - rougher, cleaner etc. and the use of the combinations of other cationic type of collectors for removing silica from the concentrate of the various flotation stages.

Other patents have been granted to Barr (8), and Bates(9), which cover the use of sulfonated derivatives as the collector. Other interesting works include the use of (1) amino acids as collector for nonsulfide iron ores by Gregoire Gutzeit (56), (2) low temperature tar oils for oxidized iron ores by Taisaku et al.(105) and (3) cationic reagents of the type RRNP(:O)XX for nonsulfide, non-silicate iron ores by Cole and Duke (31); where R=H or amido group (-CONH) or functioning hydrocarbon groups such as octyl.......octadecyl, octadecenyl,.........

abietyl groups, naphthanyl groups - ($C_hH_{2n-2}O_2$; n=8-13; and $C_nH_{2n-4}O_2$ and $C_nH_{2n-6}\ O_2$ where n= 14 - 25), X = OR, NRR, OY or a helogen; Y=Salt forming group or element and at least, R in molecule is a functioning hydrocarbon group.

DESIGN OF A COLLECTOR:

Since flotation is a surface phenomena, surface energy is to be considered first. Scratching, breaking or grinding of solids requires an expenditure of energy. The major portion of this energy is transformed to heat and to some extent to sound. Only a minute fraction remains as surface energy. The increase in surface energy is proportional roughly to the increase in the surface area.(35) Wet grinding requires less energy, a fact which was observed a long time ago (55,100). The proportionality of the increase in surface area (surface energy) and energy consumed is expressed in "Rittinger's law", which is discussed in detail in DallaValle's book (35).

The relative wettability of the various solids has been studied systematically by measuring the contact angles (33,90). It was observed that the greater the contact angle, the greater will be the driving force and the greater will be the probability for the flotation. But there are various limitations to this which are due to variations in the size, shape and roughness of the particles. The latter causes variations in the surface area and contact angles. Also the contact angle depends on various other factors such as thickness of the film, impurities of surfaces. This makes the interpretation of the contact angle measurements and prediction of the behavior of various collectors very difficult.

The works of various investigators, Vivan (108), DeWitt (40,41,42), Holman (63), Peterson (89), etc. (92,103,109) reveal their attempts to interpret the results of their experiments with various collectors for the specific minerals. They indirectly suggested that the collectors may form the chelate or complex compounds with the metallic ions. According to this view various analytical reagents and dyes might be used as collectors. However, practical economic considerations and desired selectivity often preclude such usage.

Sutherland (92) and DeWitt with various coworkers (41,86,87) considered this point of view and the crystal lattice continuation in conjunction with the calculation of the dimensional size of polar and non-polar groups of collectors.

According to Grout (54) taconites were formed by leaching, oxidation, precipitation and conglomeration through the ages, taconites are mixtures of carbonates and oxides of iron and siliceous gangue.

When the freshly formed particles of minerals including taconites come in contact with water, the active iron atoms may form some hydrates on the surface. Hydrated iron oxides are weakly basic in chemical nature.

Considering this and the views of Sutherland (92), and DeWitt, (41,86,87) and a survey of the literature on complex compounds of iron, (4,5,6,11,22,32,34,46,57,65,68,70,97,99,110,111) many polar groups are found to be prospectively available for the flotation of iron. Among these are hydroxyl, carboxyl, sulfonic, sulfate or ortho-hydroxy aromatic nitro, nitroso, keto, aldehyde, thiocompounds. However, none of these references give any indication as to which of these polar groups will be the most effective for the flotation of iron bearing minerals.

The theory of classical quantum mechanics is the most logical one to be considered for selecting the collectors. However the computations become quite complicated which necessitate the consideration of the following simplified views based on the physico-chemical principles.

(1) The main driving force in any phenomena is the electrostatic and magnetic force. The electrostatic force is the predominant one.

(2) Dipole moment is an indirect measure of the residual electrostatic forces of the molecules.

(3) The electron sharing principal of the elements of Groups V_b and VI_b of the Periodic Table is related to the electrostatic principle. The shared electron is a part of the organic collector. Whether or not a compound is formed at the surface or chemisorption occurs, electrons are shared. (40B)

(4) Surface tension, adsorption, chemical reactions and many other physical and chemical phenomena depend on this residual electrostatic forces of the molecules and ions.

(5) Consideration of classical thermodynamic laws, gives a relationship $(K = e^{\frac{-\Delta E_{\circ}}{RT}})$ between equilibrium constants and free energy; free energy is definitely related to electrostatic forces.

(6) The dissociation constants of the collectors and stability constants or the complex formation constants are the true indirect yardsticks for the measurements of the electrostatic (or driving) forces.

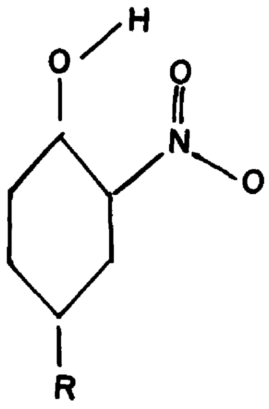
(7) The probability of chelate formation should be considered. Five or more membered chelate rings are the most stable.

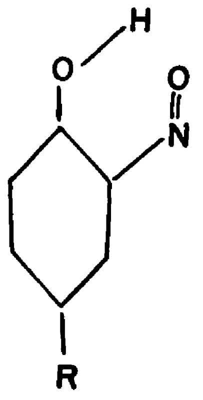
(8) Dimensional sizes of the various polar and non-polar groups will predict the steric hinderance if any.

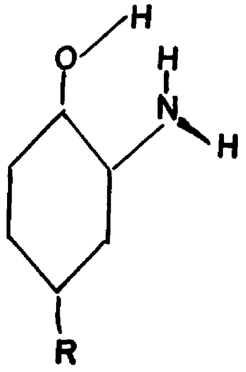
(9) Adsorption will be more pronounced, if there is any definite chemical reaction or complex chelate compound formation possibility with the collector and/or some compounds of the mineral element under consideration.

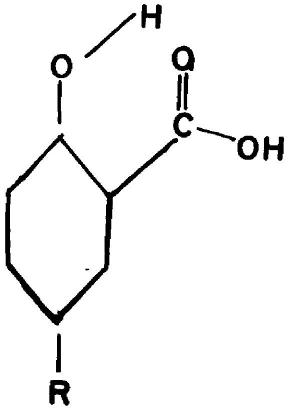
(10) The electro-magnetic proton resonance study will be the most useful since it makes possible the calculation of the residual electro-static forces of the various compounds.

The literature survey (4,5,6,11,22,32,34,46,57,65,68,70, 97,99,110,111), and consideration of above view points gave the following possibilities for the collector.


(1)


(2)


(3)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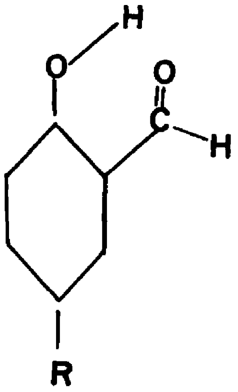
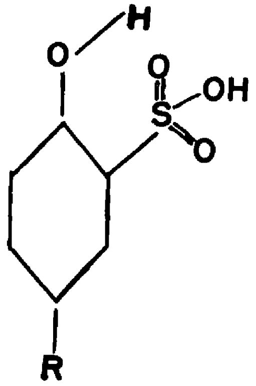

(5)


(6)

The constants as given in table 1, page 15 suggest most desirable the polar grouping of salicylic acid. It is also very interesting to consider the stability constants or equilibrium constants of the complex formation. There is very little information in the literature on the stability constants. (See table No. 2). These stability constants can be studied by the colorimetric, potentiometric, conductometric, photometric or spectrometric method.

TABLE NO. I

Dissociation constants of some organic compounds $^{(45)}$p.633

Phenol	$1.0x10^{-10}$	benzoic acid	$6.8x10^{-5}$
o-cresol	$4.2x10^{-8}$	o-toluic acid	$1.3x10^{-4}$
p-cresol	$1.1x10^{-8}$	p-toluic acid	$4.5x10^{-5}$
o-chrolophenol	$7.7x10^{-10}$	Salicylic Acid	$1.0x10^{-3}$
o-nitrophenol	$6.2x10^{-8}$	o-chloro-benzoic acid	$1.3x10^{-3}$
p-nitrophenol	$7\ x10^{-8}$	o-Bromobenzoic acid	$1.5x10^{-3}$
2,4-dinitrophenol	$1x10^{-4}$	o-nitrobenzoic acid	$6.2x10^{-3}$
Catechol	$4x10^{-10}$	3,5-dinitrobenzoic acid	$1.6x10^{-3}$
Guaicol	$1x10-^{7}$	Anisic acid	$3.2x10^{-5}$
resorcinol	$4x10^{-10}$	Anthranilic acid	$1.0x10^{-5}$
Hydroquinone	$1x10^{-10}$	Phthalic acid	k,=$1.0x10^{-3}$
Pyrogallol	$1x10^{-7}$	Phenylacetic acid	$6.0x10^{-5}$
Phloroglucinol	$1x10^{-7}$	x-naphthoic acid	$2x10^{-4}$
o-aminophenol	$2x10^{-10}$	Sulfinic acid	$6.2x10^{-4}$
x-naphthol	$1x10^{-8}$		
Formic acid	$2.1x10^{-4}$	oxalic acid	$^{K1}3.5x10^{-2}$
Propionic acid	$1.32x10^{-5}$	Malonic acid	$1.6x10^{-3}$
n-valeric acid	$1.5x10^{-5}$	Succinic acid	$6.8x10^{-5}$
Caproic acid	$1.40x10^{-5}$	Glutaric acid	$4.7x10^{-5}$
n-heptylic acid	$1.30x10^{-5}$	Adipic acid	$3.7x10^{-5}$
Caprylic acid	$1.41x10^{-5}$	Suberic acid	$3.0x10^{-5}$
Pelargonic acid	$1.1x10^{-5}$	Azelaic acid	$2.9x10^{-5}$

TABLE NO. 2

Equilibrium constants or the stability constants of the complex compounds.

(1) Iron: (11,2,32,70)

Salycilic acid	K=$10^{+16.35}$
P-Hydroxy benzoic acid	$10^{+15.2}$
Citric acid	$10^{+11.7}$
Lactic acid	$10^{+6.9}$
Glycolic acid	$10^{+4.7}$
Phenol	$10^{3.1}$
Salicylaldehyde	$10^{4.9}$
O-Hydroxy acetophenone	$10^{5.14}$
O-Nitro phenol	10^{4}

(2) Copper: (22)

Salicylaldehyde	$10^{6.5}$		
3-n-propyl-2-(OH)- "		2,1-naphtholdehyde	$10^{7.0}$
5-methyl-2-(OH) "	$10^{6.7}$	2,3- "	$10^{5.8}$
4,6-dimethyl- "	$10^{7.2}$	Acetyl Ac̄....	$10^{8.7}$
3-ethoxy- "	$10^{7.1}$	Tri-flouro Ac̄....	$10^{6.1}$
3-methoxy- "	$10^{6.6}$	Furoyl Ac̄........	$10^{8.4}$
4-methoxy- "	$10^{6.9}$	Benzoyl Ac̄.......	$10^{9.0}$
3-nitro- "	$10^{4.1}$	Acetoacetic acid.	$10^{7.1}$
4-nitro- "	$10^{4.6}$		
5-nitro- "	$10^{4.4}$		
3-fluoro- "	$10^{5.7}$		
3-chloro- "	$10^{5.3}$		
5-chloro- "	$10^{5.7}$		

(3) O-Amino phenol(11)

Cu	4.388x10^4
Zn	9.9 x 10^3
Ni	9.16x10^3
Co	9.16x10^3
Pb	9.16 x 10^3

(4) O-Nitro phenol. (11)

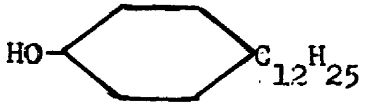
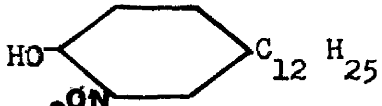
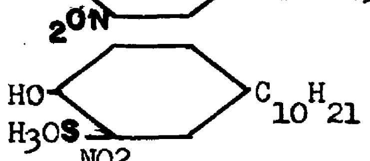
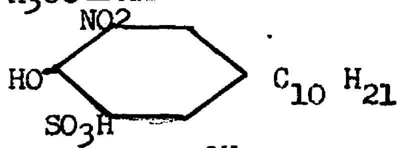
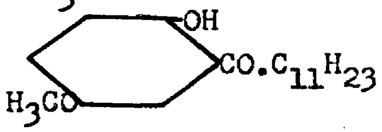
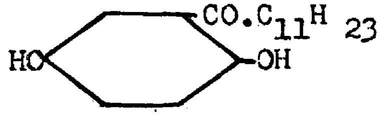
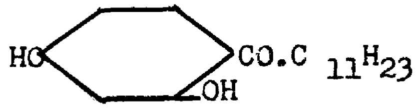
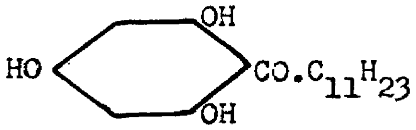
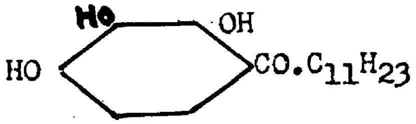
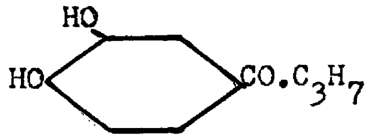
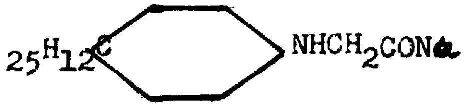
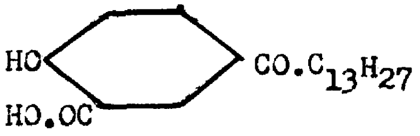
Ni	4.1x10^3
Cu	7.1x10^3
Mn	4.2x10
Cr	1.5-2.2x10^3
Al	1.5x10^3
Zn	3.3x10^3
Th	4x10^2
Co	1x10^3 Appro.
Ce	9x10^2

Pb - O-Amino Benzothiol (11) 1.678x10^4

Zn - O - " " 1.678x10^4

From a consideration of the foregoing tables and physico-chemical considerations previously set forth, the compounds of the nature 4,1,6, and a combination of 1 and 6 seemed a logical selection. The results of this study, selection and experiments are given in table No. 3. From these results, alkylated salicylic acid and β-resorcylic acid were selected for further investigation.

Table No. 3

	Collector	Froth collected	ml 0.1 NKMNO4 Soln.
1.		10.313	4
2.		5.011	6.8
3.		6.313	5.3
4.		14.353	11.2
5.		7.012	3.5
6.		6.515	3
7.		10.02	6.4
8.		11.595	13.2
9.		13.40	12.0
10.		8.00	3.4
11.		4.617	18
12.		20.935	22.4

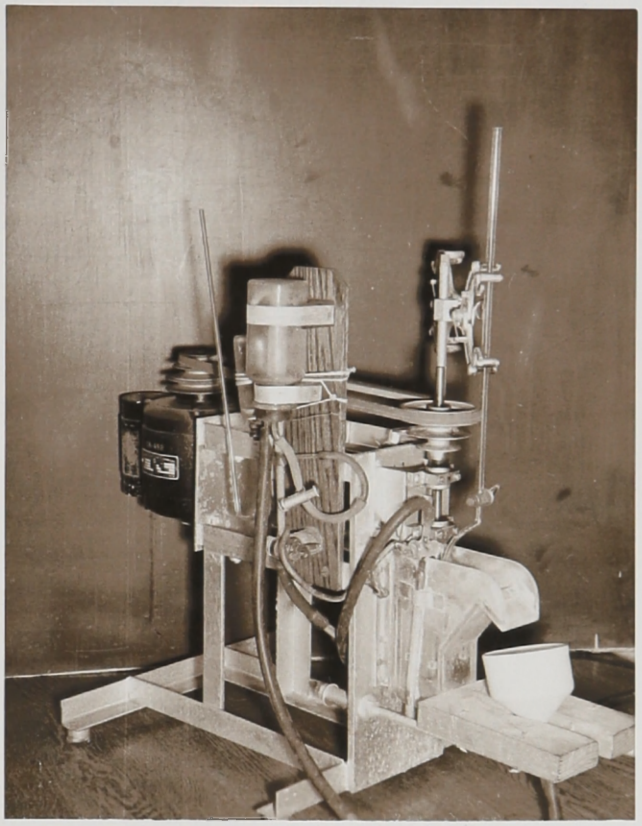
FLOTATION MACHINE:

The flotation machine used in this investigation was a laboratory size, sub-aeration type cell made of lucite. The unit details are shown in figures 1 and 2. The agitator was driven by an electric motor. The cell provided for variation in the agitator speed by using various size pulleys. Air was blown under the stirrer by a low pressure blower. The stirrer action broke up the air stream into appropriately sized bubbles.

The overflowed froth was collected on an eight centimeter Buchner funnel; the filtrate from the Buchner funnel was conducted to a suction bottle. The suction bottle was placed at a height so that on cutting off the vacuum, the filtrate was fed into the cell so as to maintain the constant pulp level. The collector was added to the cell from a burette, having a long curved tip, which made it possible to introduce the collector in small portions, at a point well below the pulp surface, where it dispersed readily into the pulp body.

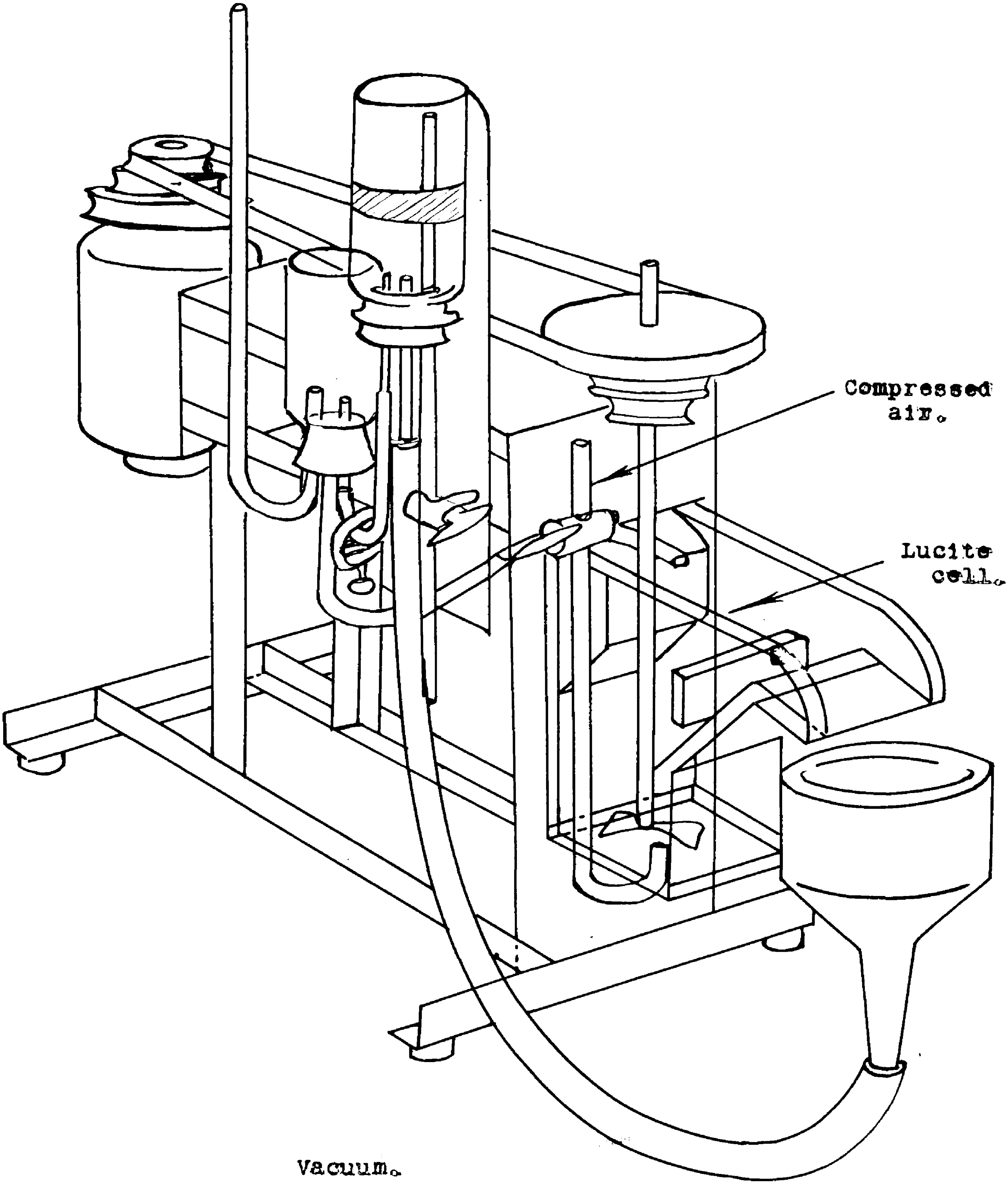
SYNTHETIC ORE PREPARATION:

The ore and the sand were dry ground in a ball mill. Pebbles were used as the grinding media. Ores and sands were ground separately without any type of reagent addition to avoid contamination. Ground materials were screened by Taylor Standard Sieves of -120 to +200 mesh sizes. This mesh size was used, because the work of Gaudin, Groth, and Henderson (51) stated that the usual particle size for flotation of any mineral varies between 50 and 100 microns, which corresponds to about 150 to 300 mesh. The finer



FLOTATION CELL.

FIG. 1.



100 GRAMM - FLOTATION CELL.

FIGURE NO. 2.

the particles the greater will be the activation and the lower will be the efficiency of separation. Gaudin (50) stated that when the particle size is reduced below five microns, a slime is formed, which does not respond to flotation action. This theory lacks complete conformation (50). Generally removal of the slime particles is a good flotation practice.

The flotation cell was made ready by putting in water and starting the stirrer. The ground ores and sand were weighed and total of 100 grams was added. The liquid level was adjusted by adding water so that the froth could be skimmed off easily. The stirred suspension containing about 25% solids.

ADDITION OF REAGENTS:

The reagents used were mainly frothers, pH regulators and collectors. A small drop of steam distilled pine oil was used as a frother; this amount corresponded to not more than 0.2 pounds per ton. After three minutes stirring the air was bubbled through the suspension. Two minutes later one milliliters of the collector solution was added and stirring was continued for one minute more.

Dean and Ambrose (36) showed that, a conditioning period for certain cationic reagents may seriously decrease the extent of flotation. In this investigation the conditioning period was six minutes for each run. Then the collection of the froth followed for five minutes. The addition of the collector was distributed during the collection period in such a way that the desired quantity could be added. The collector solution contains 0.001 gram of the reagent in absolute alcohol. Ten milliliters of the collector solution addition corresponds to 0.2 pounds of collector per ton of dry ore feed.

pH regulators were added before the addition of any reagents to adjust the desired pH. pH regulators were the C. P. hydrochloric acid and C. P. potassium hydroxide in 5% solution. All the pH measurements were carried out using pH Hydrion narrow range test papers. At least two checks were made on each pH figure.

Froth was collected in a Buchner funnel. The collected froth was filtered and the filtrate was fed back into the cell regularly. Then the concentrate was dried with the filter paper, weighed and labeled.

QUANTITATIVE DETERMINATION:

A) Decomposition of taconite ore samples:

Various methods for the decomposition of the iron bearing ores were tried. The best and the most suitable one was found to be: 0.5 grams of the ore sample weighed accurately and mixed with three to four grams of sodium peroxide. The mixture was fused in a porcelain crucible by heating on a small flame which was gradually increased until the sample fused. This operation should be done carefully, since long heating dissolves part of the crucible. The fusion period was about 5 minutes. The fused liquid mass was spread on the side of the crucible. After cooling the fused mass was dissolved in the beaker with water.

TABLE NO. 4

Flotation of taconite by decanoyl salicylic acid (S-102)

(Figures: 3-5) 8;11-13; 16;)

Synthetic ore: 4grams taconite + 96 grams sand.

Iron in synthetic ore: 1.5%.

Ore size: + 120 - 200 mesh.

pH.	Collector #/Ton.	Concentrates. Grams.	%Fe	Enrichment	%Recovery	Derived Data #Fe/#coll.	Improvement factor.
3.	0.0.2	6.1604	9.45	6.85	38.67	58.2	265.
6.	0.2	5.2962	24.3	21.0	85.5	128.	1795.
8.	0.2	7.0013	17.8	14.2	82.9	125.	1176.
3.	0.1	4.8849	13.5	10.24	43.8	132.	449.
6.	0.1	6.0325	17.2	13.7	69.3	208	950.
8.	0.1	5.3247	16.4	12.86	58.1	174.6	746
3.	0.05	4.673	7.14	5.05	22.2	133.5	112
6.	0.05	3.418	14.4	11.04	33.1	200.	365
8.	0.05	2.618	21.7	18.2	37.5	227.	682

TABLE NO. 5

Flotation of taconite by dodecanoyl salicylic acid (S-12).

(Figures: 3-5; 7; 11-13; 15; 25; 26)

Synthetic ore: 4 grams taconite + 96 grams sand.

Iron in synthetic ores: 1.5%.

Ore size: +120 - 200. mesh

pH.	Collector #/ton	concentrates grams.	%Fe	Enrichment	%Recovery	Derived Data #Fe/#coll.	Improvement Factor.
3.	0.2	8.6521	8.38	6.0	48.3	72.5	290
6.		7.7628	18.4	14.8	95.1	143.	141
8.		9.0485	14.8	11.4	89.1	134	1016
3.	0.1	8.471	13.1	10.06	73.6	222	740
6.		5.5122	24.0	20.8	88.0	265	1830
8.		5.3161	23.25	20.0	82.5	248	1650
3.	0.05	5.0447	9.88	6.4	32.7	198	209
6.		5.5304	18.52	14.9	68.2	410	1019
8.		5.0610	13.9	10.6	46.8	281	496

TABLE NO. 6

Flotation of taconite by tetradecanoyl salicylic acid (S-14).

(Figures: 3-5, 6, 11-14)

Synthetic ores: 4 grams taconite --- 96 grams of sand.

Iron in the synthetic ore: 1.5%.

Ore size: + 120 -200 mesh.

pH	Collector #/ton	concentrates. grams.	%Fe.	Enrichment.	%Recovery	Derived data #Fe/#coll.	Improvement factor.
3.	0.2	13.494	6.25	4.38	56	84	247
6.		11.4755	12.44	9.32	95.2	142	887
8.		10.084	14.8	11.4	99.2	149	1130
3.	0.1	5.296	17.5	13.8	61.9	185	855
6.		8.068	17.57	14.0	94.0	283	1316
8.		7.503	15.7	12.23	78.4	235	958
3.	0.05	6.046	11.5	8.54	46.2	277	394
6.		7.233	18.4	14.82	94.0	533	1392
8.		5.442	18.4	14.82	70.6	322	1047

TABLE NO. 7

Flotation of taconite by decanoyl B-Resorcylic acid.

(Figures: 3-5; 9, 11-13)

Synthetic ore: 4 grams taconite + 96 grams sand.

Iron in the synthetic ore: 1.5%

Ore size: + 120 -200 mesh.

	Collector	Concentrates		Enrichment.	%Recovery	Derived	Data
pH	#/ton	grams.	%Fe.			#Fe/#coll.	Improvement factor.
3.	0.2	5.5903	4.8	3.3	17.84	27	59
6.		8.733	10.39	7.6	60.2	91	457
8.		7.7657	9.55	6.6	49.5	74	326
3.	0.1	3.3269	3.35	2.27	7.5	22	16.9
6.		5.3112	10.43	7.63	36.9	111	758
8.		5.7672	9.26	6.7	34.9	107	234
3.	.05	4.1353	2.9	2.98	8.0	48.0	24
6.		4.6854	5.1	3.5	15.8	95.1	55
8.		2.4860	9.6	6.98	15.9	95.5	111

TABLE NO. 8

Flotation of taconite by 4-octoxy β-resorcylic acid.

(Figures: 3-5, 10, 11-13; 18)

Synthetic ore: 4 grams taconite + 96 grams sand.

Iron in synthetic ore: 1.5%

ore size: + 120 -200 mesh.

	Collector	Concentrates		Enrichment	%Recovery	Derived Data	
pH	#/ton	grams.	%Fe.			#Fe/#coll.	Improvement factor.
3.	0.2	5.9116	12.56	9.53	49.4	74	524
6.		10.8382	12.18	9.1	98.0	132	890
8.		11.8423	9.89	7.2	78.0	117	560
3.	0.1	5.6208	8.72	6.4	32.7	98.5	209
6.		5.5335	11.0	8.1	40.5	121.5	328
8.		4.9728	12.18	9.1	40.3	121.0	366
3.	0.05	3.574	5.02	3.48	12.0	71.6	41
6.		3.586	13.4	9.92	31.9	192	316
8.		6.521	5.15	3.57	22.4	134	80

TABLE NO. 9

Flotation of taconite ore by dodecansyl salicylic acid (S-12)

(Figures: 19; 20;)

Synthetic ore: 20 grams taconite + 80 grams sand.

Iron in the ores: 7.84%

Ore size: +120 - 200 mesh.

pH	Collector #/ton	Concentrates grams.	Concentrates %Fe.	Enrichment	%Recovery	Derived Data #Fe/#coll.	Derived Data Improvement factor
4	0.2	20.238	15.17	2.1	39.2	307	82.4
7		27.555	20.2	2.98	71.0	550	212
10		37.618	13.35	1.9	64.2	502	122
4	0.1	12.556	23.4	3.6	37.4	586	134.5
7		8.771	25.2	3.97	28.0	441	112
10		8.463	27.0	4.35	29.2	456	127
Trimethyl amine as depressor used:							
4	0.2	25.328	24.3	3.78	78.5	615	297
6		18.205	28.5	4.7	69.8	519	328
10		43.30	10.4	1.36	57.5	450	78.5
4	0.1	14.414	23.1	3.53	42.5	664	150
7		7.546	25.8	4.1	24.8	390	102
10		8.639	24.0	3.72	26.45	414	98.5

TABLE NO. 10

(Figures: 21-24; 25,26)

Flotation of taconite by tetradecanoyl salicylic acid.

Synthetic ore: 20 grams taconite + 80 grams of sand.

Iron in synthetic ore: 7.84%

Ore size: + 120 -200 mesh.

pH	Collector #/ton	Concentrates grams.	Concentrates #Fe	Enrichment.	%Recovery	Derived Data #Fe/#coll.	Derived Data Improvement factor
4	0.2	13.288	23.5	3.62	39.8	312	144
7		23.757	31.1	5.32	94.0	738	500
10		21.656	27.6	4.48	76.4	598	342
4	0.1	15.012	24.3	3.78	46.5	728	176
7		18.631	33.8	6.02	56.5	1258	340
10		26.7161	20.3	3.0	69.4	1084	208
4	0.05	7.7275	1495	2.07	14.74	462	31
7		9.432	22.9	3.17	27.6	863	87
10		6.842	24.7	3.8 7	21.6	675	83

Collector: decanoyl salicylic acid.

pH	Collector #/ton	Concentrates grams.	Concentrates #Fe	Enrichment.	%Recovery	Derived Data #Fe/#coll.	Derived Data Improvement factor
4	0.2	20.270	27.8	4.53	72.0	564	336
7		9.256	29.6	4.96	34.9	274	173
10		21.752	22.0	3.33	61.0	478	203
4	0.1	17.154	11.1	1.46	24.3	379	35
7		9.900	17.15	2.44	21.6	339	53
10		26.343	24.1	3.75	81.0	634	303

TABLE NO. 11

(Figures: 21-24;25- 26)

Taconite	Sand	Fe in	Collector		pH	Concentrates		%Recovery	Enrichment
grams	gram	ore	#/ton			grams.	%Fe		
50	50	19.9	S-12	.2	4	35.835	38.4	70.3	2.55
50	50				7	20.438	38.7	25.9	2.59
					10	30.834	35.2	27.7	
10	90	3.98	S-10	.2	4	10.220	26.4	69.0	8.7
					7	9.998	25.8	65.6	8.45
					10	31.348	7.9	65.5	2.07
40	40	19.9	S-12	.2	4	8.113	24.7	12.8	1.73
					7	37.116	35.5	84.3	2.91
					10	38.039	34.6	84.0	2.8
				.1	4	7.679	23.8	11.7	1.65
					7	20.160	42.6	54.8	3.93
					10	25.498	38.8	61.9	3.35
20	80	7.84	S-12	.2	4	20.238	15.17	39.2	2.10
					7	27.555	20.2	71.0	2.98
					10	37.618	13.34	64.3	1.90

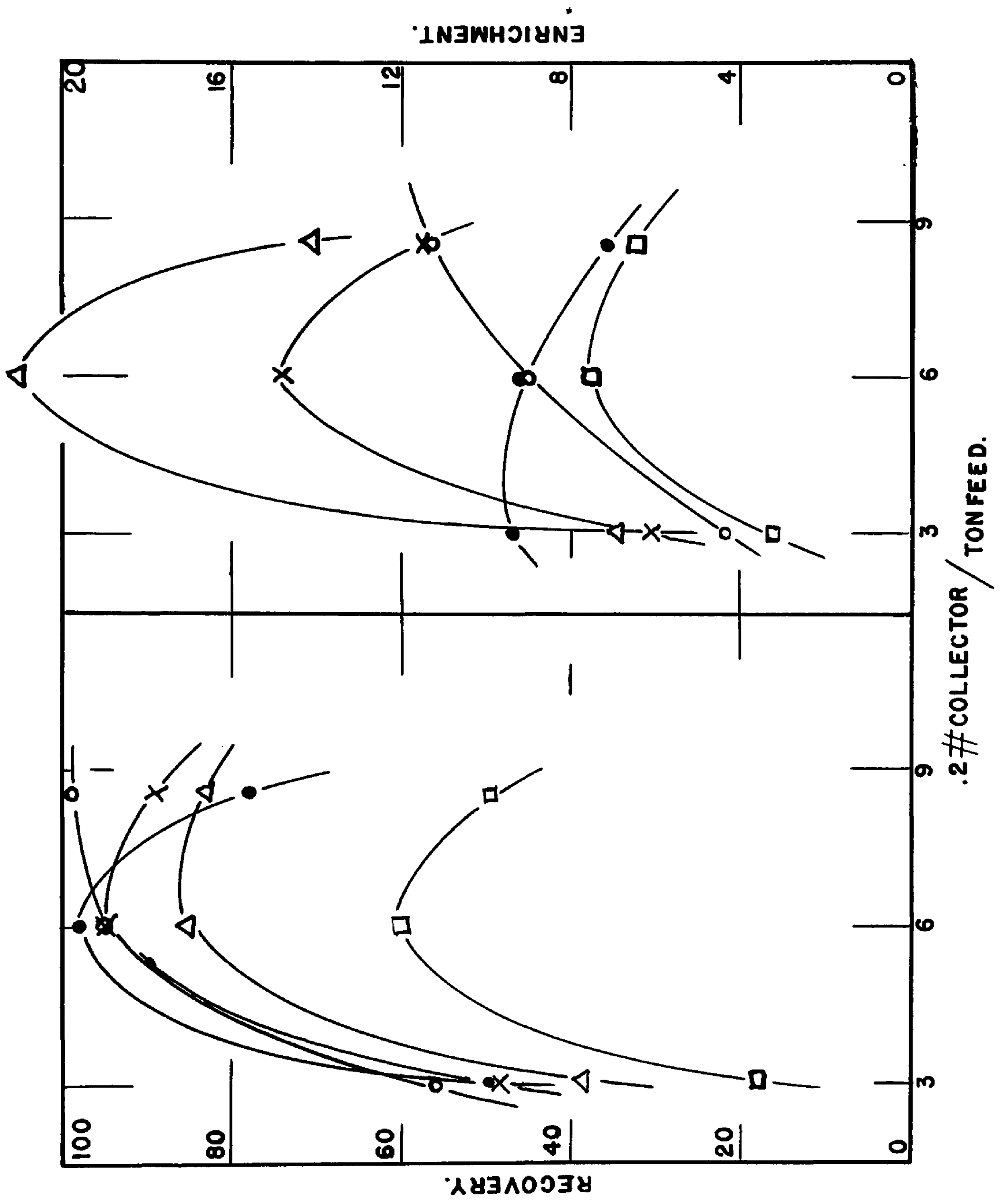

ENRICHMENT.
20
16
12
8
4
0
RECOVERY.
100
80
60
40
20
0
3
6
9
3
6
9
.2# COLLECTOR / TONFEED.

FIG. 3.

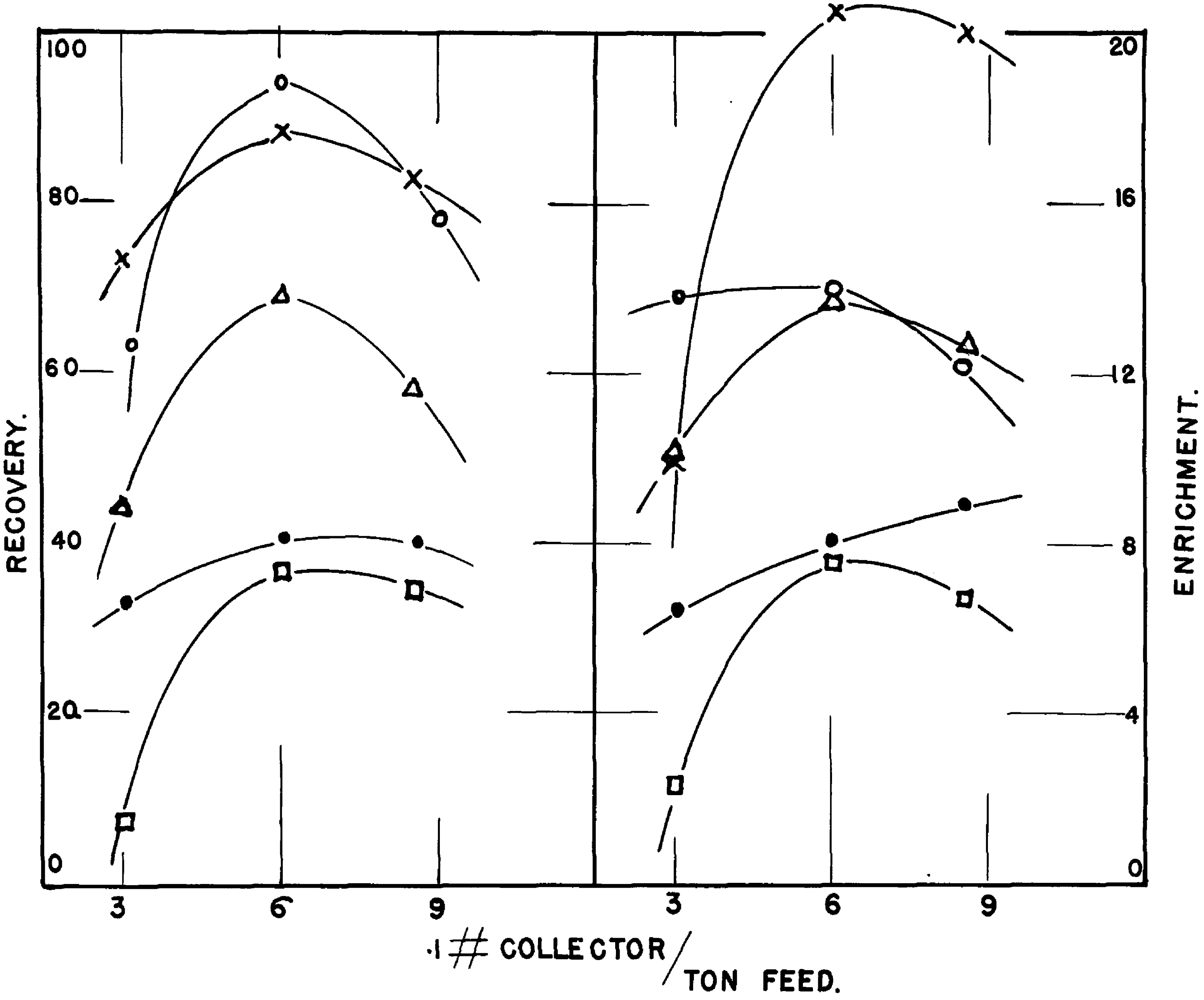

RECOVERY.
100
80
60
40
20
0
ENRICHMENT.
20
16
12
8
4
0
3
6
9
3
6
9
·1 # COLLECTOR/TON FEED.

FIG. 4.

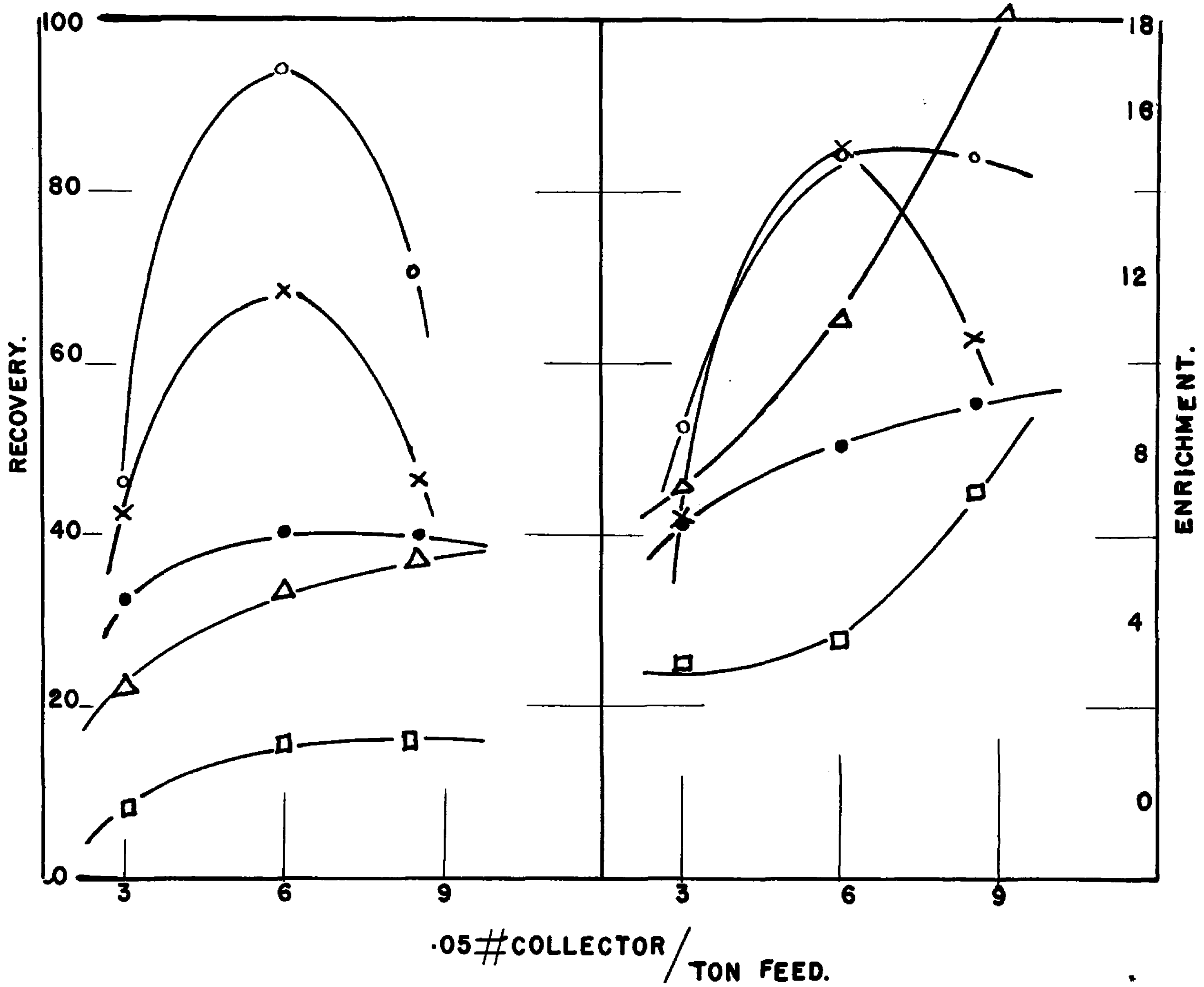

RECOVERY.
100
80
60
40
20
0
3
6
9
3
6
9
18
16
12
8
4
0
ENRICHMENT.
·05#COLLECTOR/TON FEED.

FIG. 5.

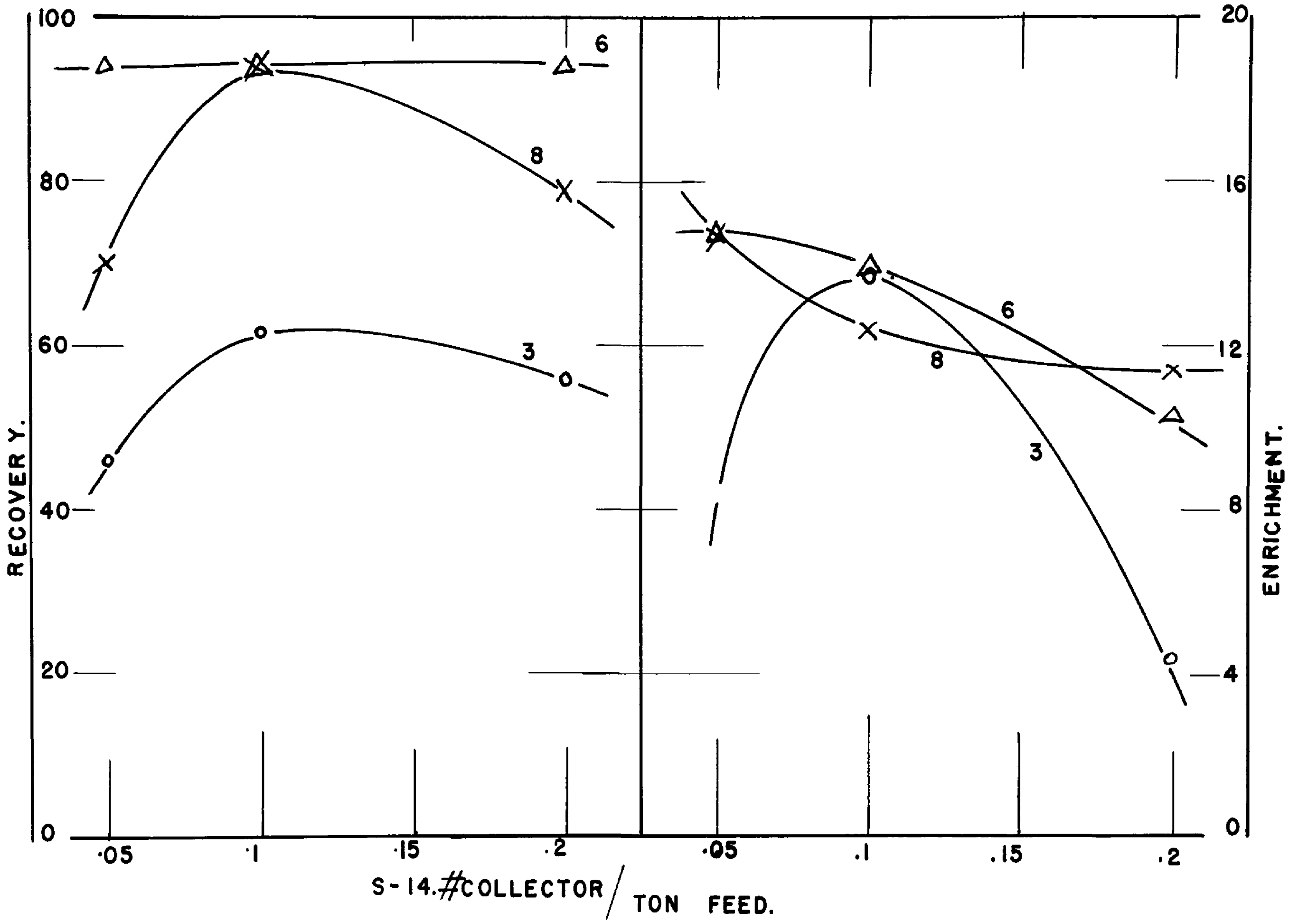

100
80
60
40
20
0
RECOVERY.
20
16
12
8
4
0
ENRICHMENT.
6
8
3
6
8
3
·05
·1
·15
·2
·05
.1
.15
.2
S-14.#COLLECTOR/TON FEED.

FIG. 6.

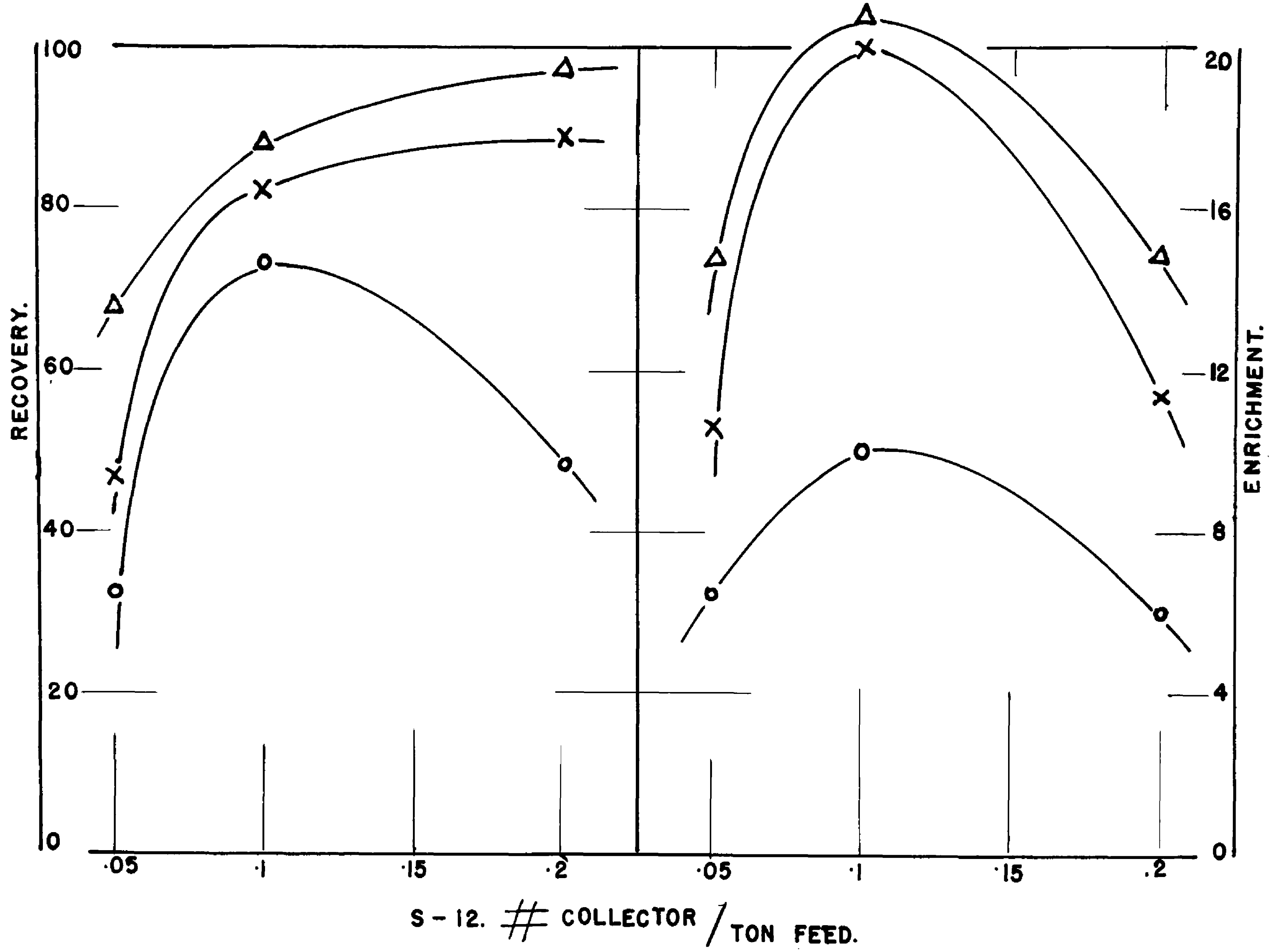

RECOVERY.
100
80
60
40
20
0
ENRICHMENT.
20
16
12
8
4
0
·05
·1
·15
·2
·05
·1
·15
·2
S – 12. # COLLECTOR / TON FEED.

FIG. 7.

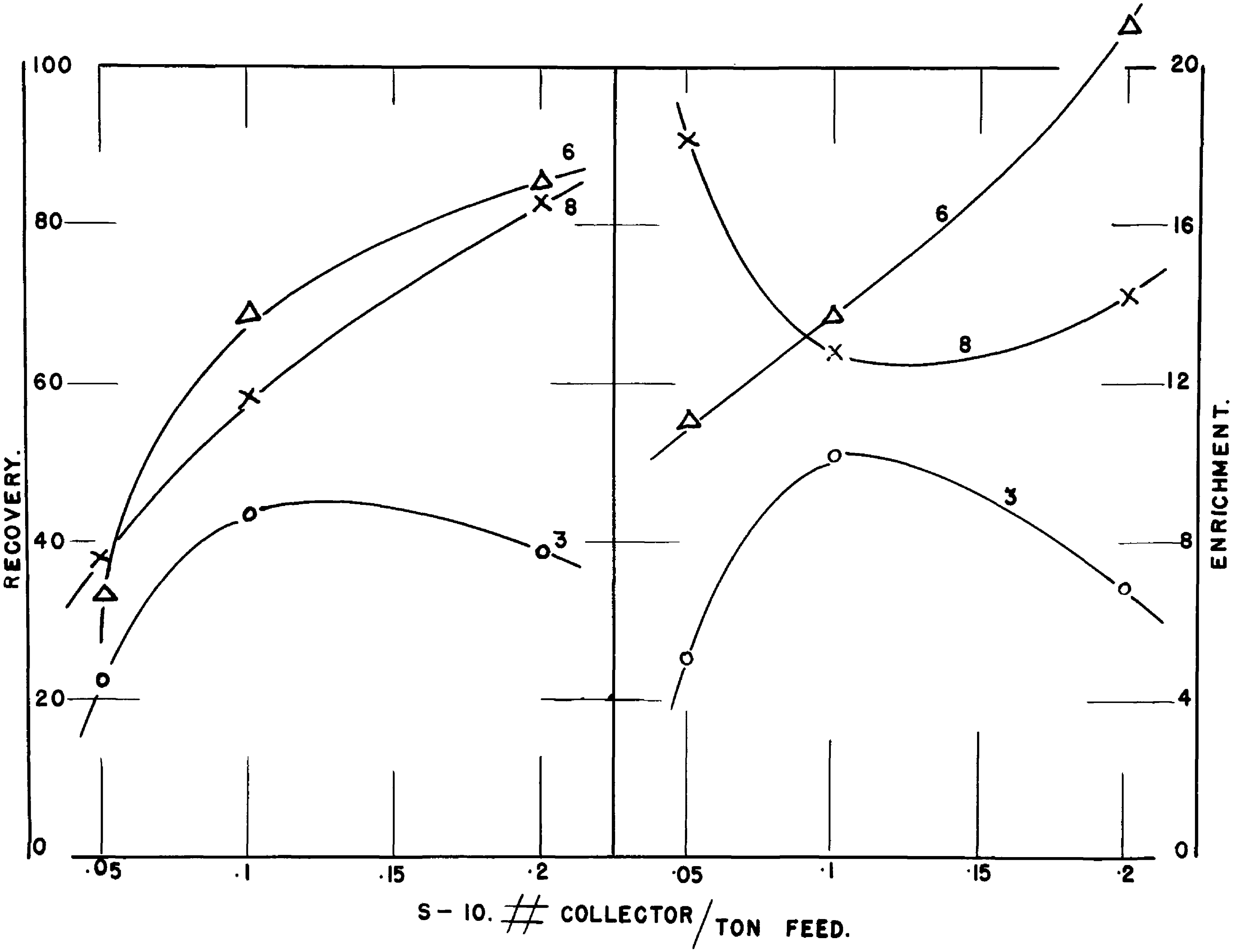

RECOVERY.
100
80
60
40
20
0
ENRICHMENT.
20
16
12
8
4
0
·05
·1
·15
·2
·05
·1
·15
·2
6
8
3
6
8
3
S - 10. # COLLECTOR/TON FEED.

FIG. 8.

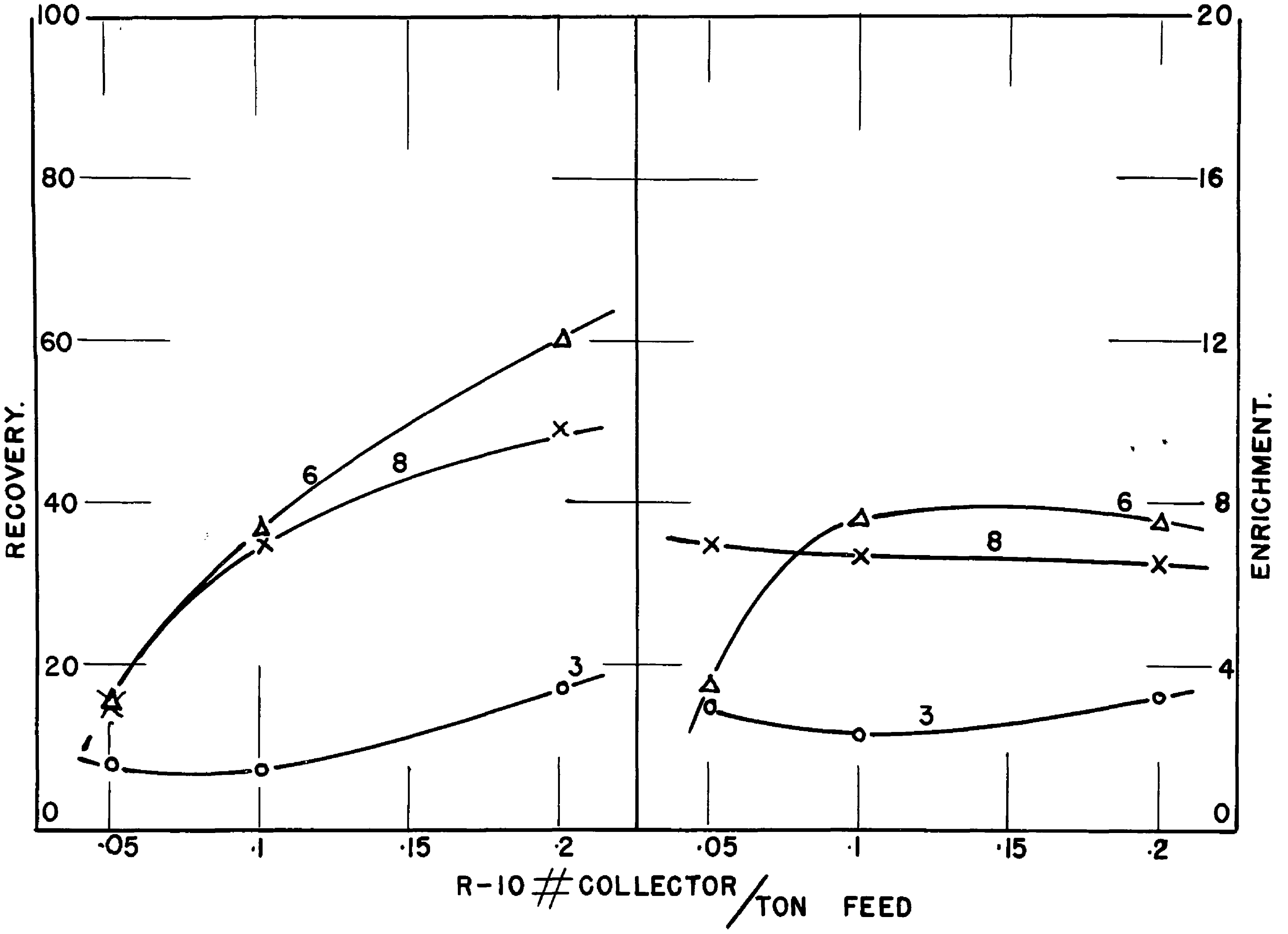

RECOVERY.
ENRICHMENT.
100
80
60
40
20
0
20
16
12
8
4
0
·05
·1
·15
·2
·05
·1
·15
·2
6
8
3
6
8
3
R-10 # COLLECTOR/TON FEED

FIG. 9.

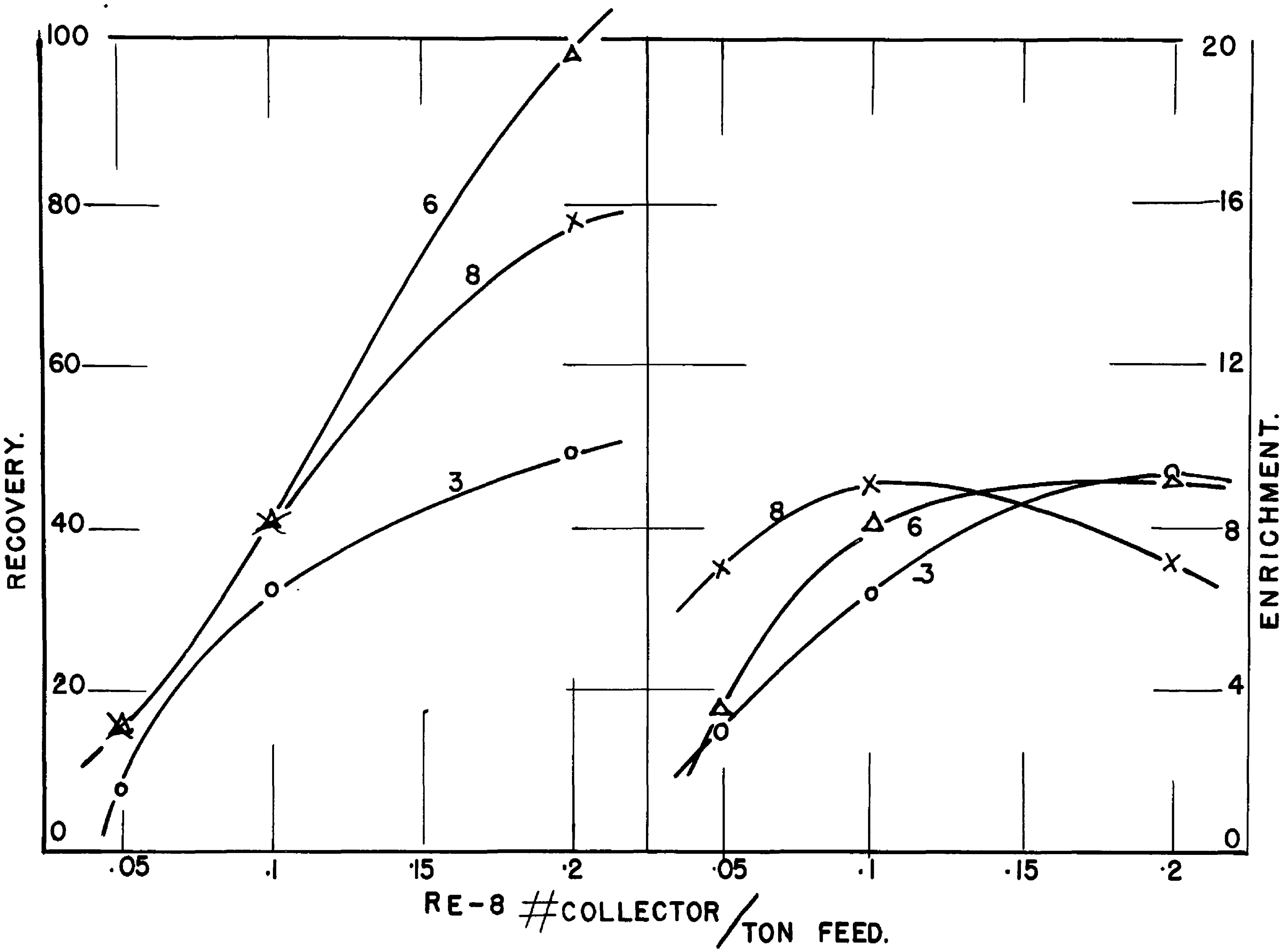

100
80
60
40
20
0
RECOVERY.
·05
·1
·15
·2
6
8
3
20
16
12
8
4
0
ENRICHMENT.
·05
·1
·15
·2
8
6
3
RE-8 #COLLECTOR/TON FEED.

FIG. 10.

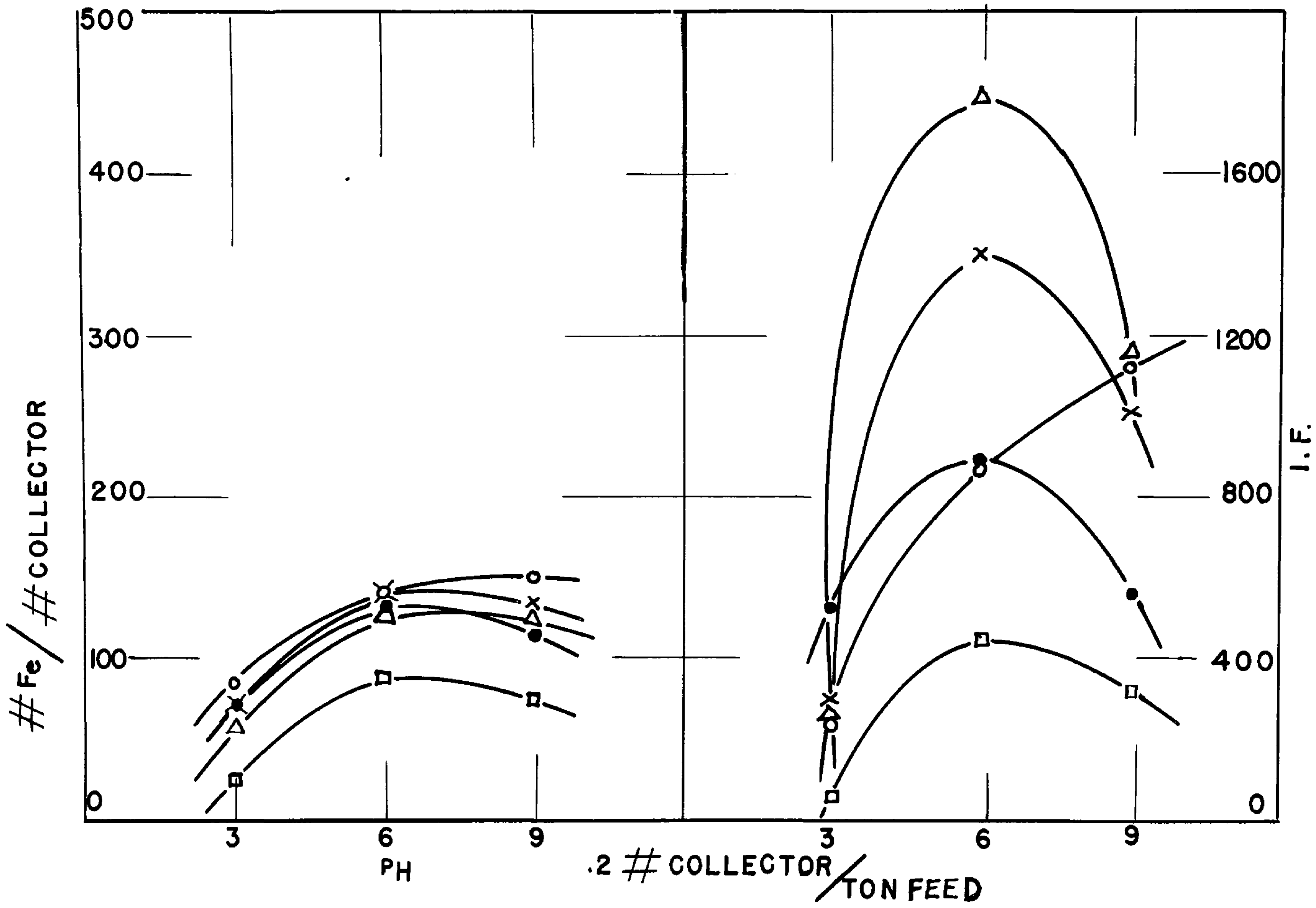

#Fe/#COLLECTOR
500
400
300
200
100
0
3
6
9
PH
.2 # COLLECTOR/TON FEED
3
6
9
1600
1200
800
400
0
I.F.

FIG. 11.

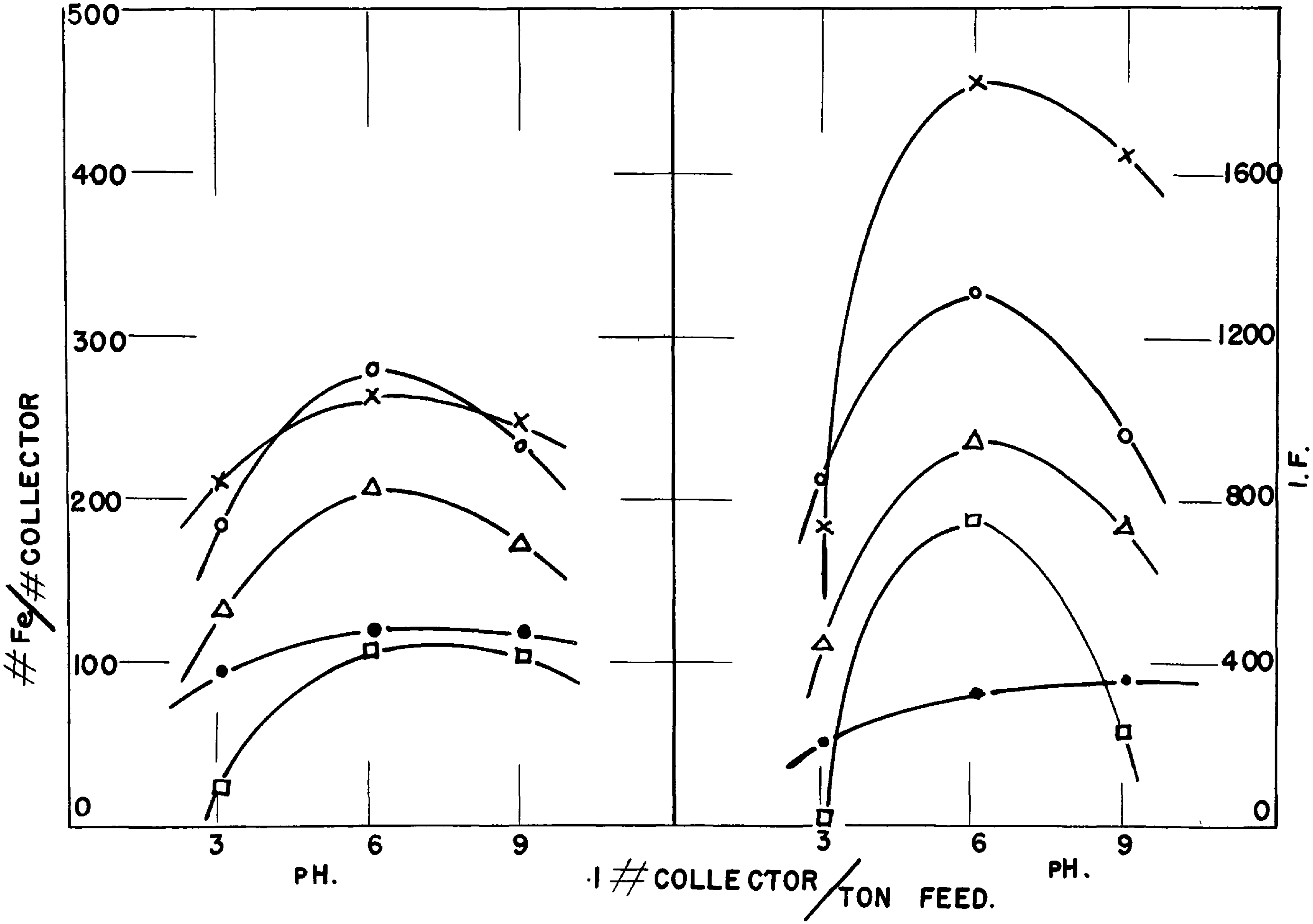
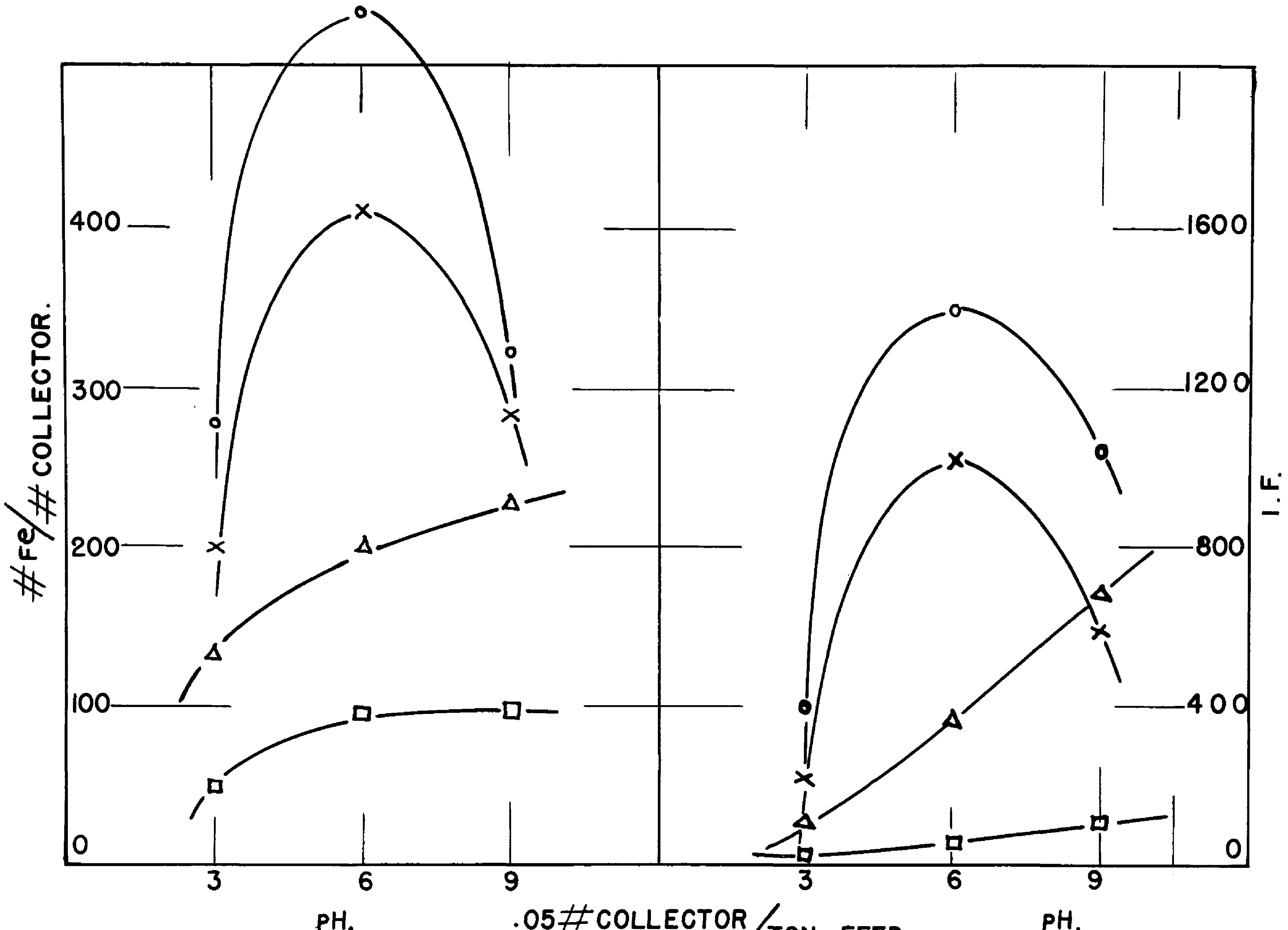

500
400
300
200
100
0
#Fe/#COLLECTOR
3
6
9
PH.
·1 #COLLECTOR/TON FEED.
1600
1200
800
400
0
I.F.
3
6
9
PH.

FIG. 12.



.05# COLLECTOR/TON FEED.

FIG. 13.

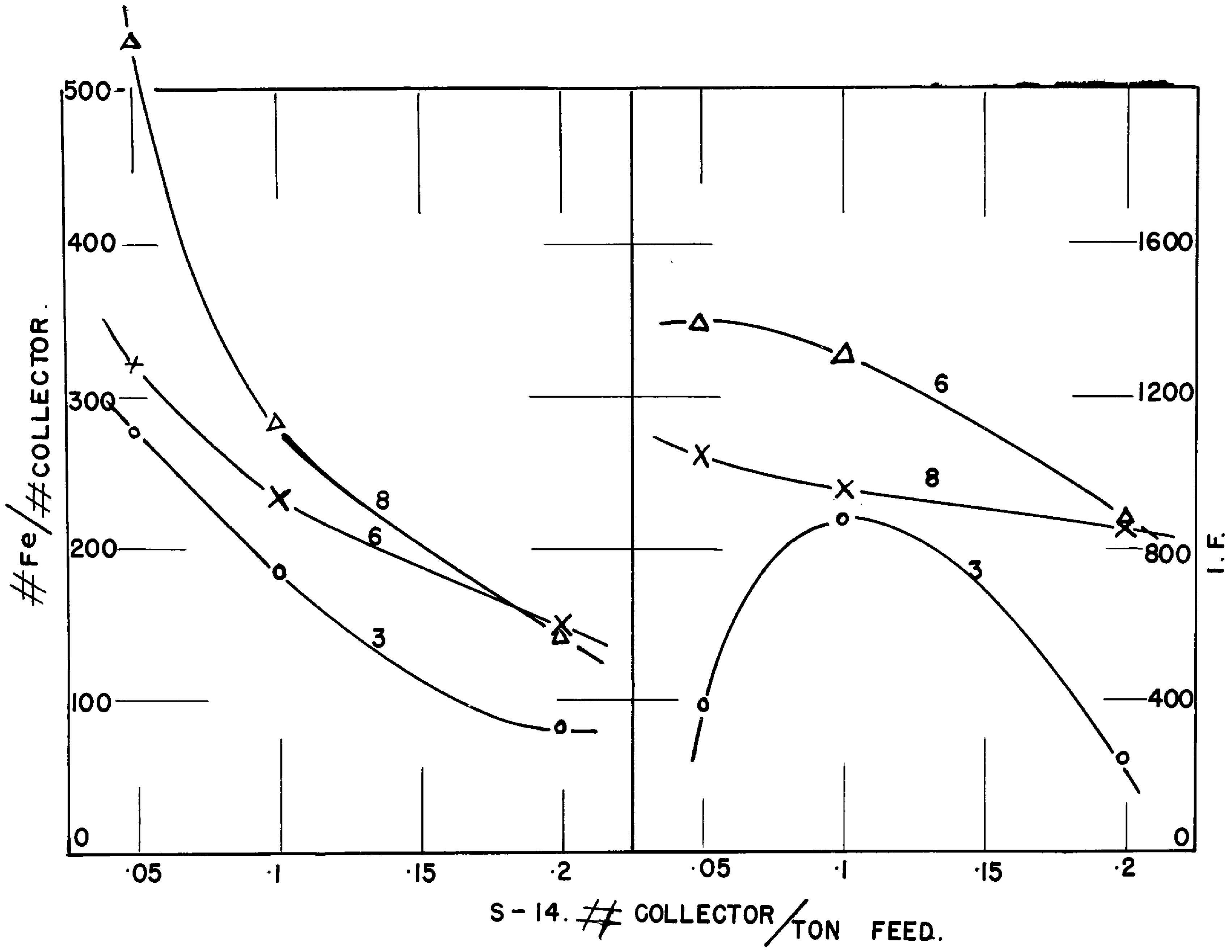

#Fe/#COLLECTOR.
500
400
300
200
100
0
1600
1200
800
400
0
I. F.
8
6
3
6
8
3
·05
·1
·15
·2
·05
·1
·15
·2
S - 14. # COLLECTOR/TON FEED.

FIG. 14.

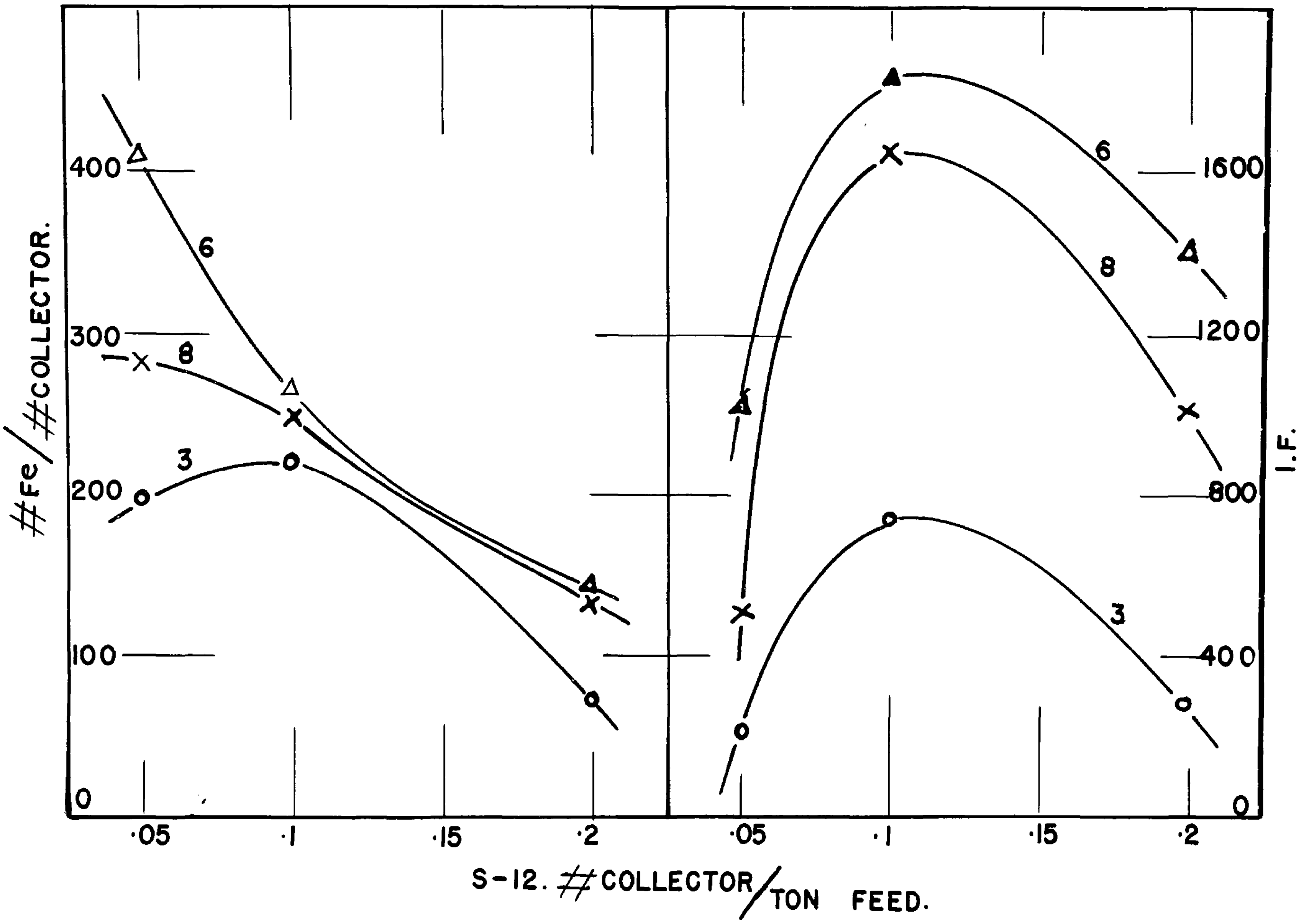

#Fe/#COLLECTOR.
400
300
200
100
0
6
8
3
·05
·1
·15
·2
S-12. #COLLECTOR/TON FEED.
1600
1200
800
400
0
I.F.

FIG. 15.

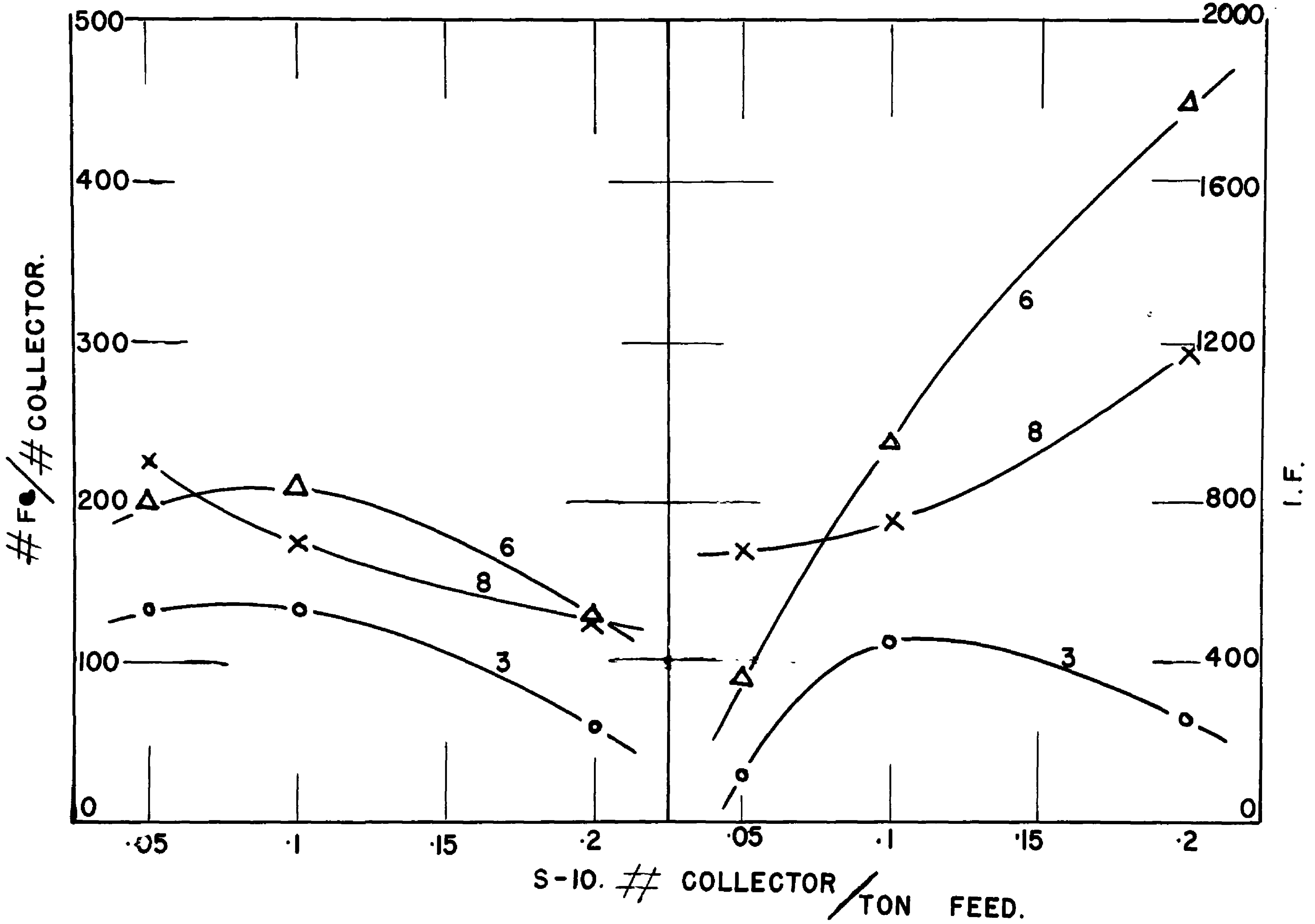

500
400
300
200
100
0
Fe/# COLLECTOR.
2000
1600
1200
800
400
0
I.F.
6
8
3
6
8
3
·05
·1
·15
·2
·05
·1
·15
·2
S-10. # COLLECTOR/TON FEED.

FIG. 16.

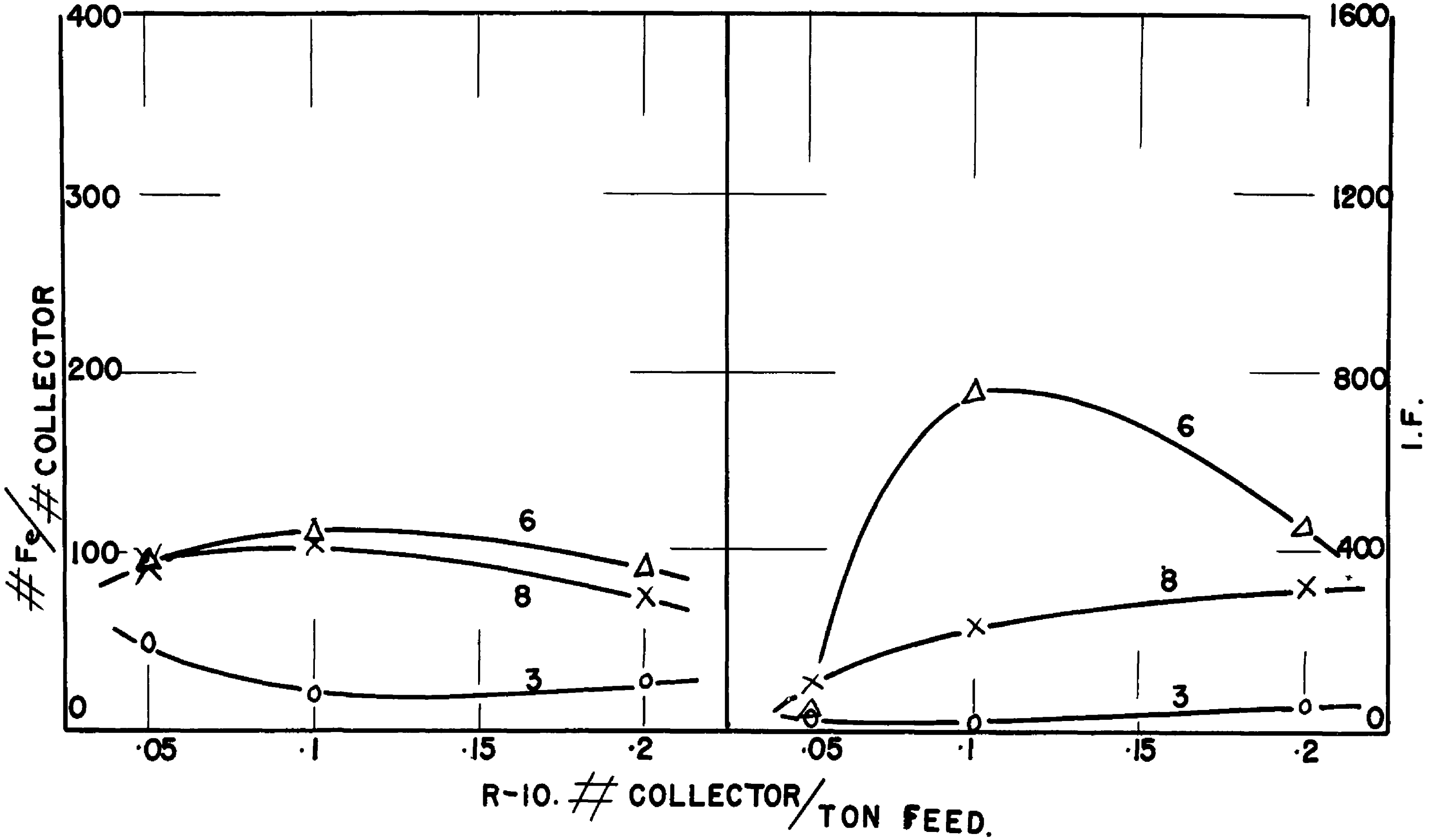

#Fe/# COLLECTOR
0
100
200
300
400
I.F.
0
400
800
1200
1600
·05
·1
·15
·2
·05
·1
·15
·2
6
8
3
6
8
3
R-10. # COLLECTOR/TON FEED.

FIG. 17.

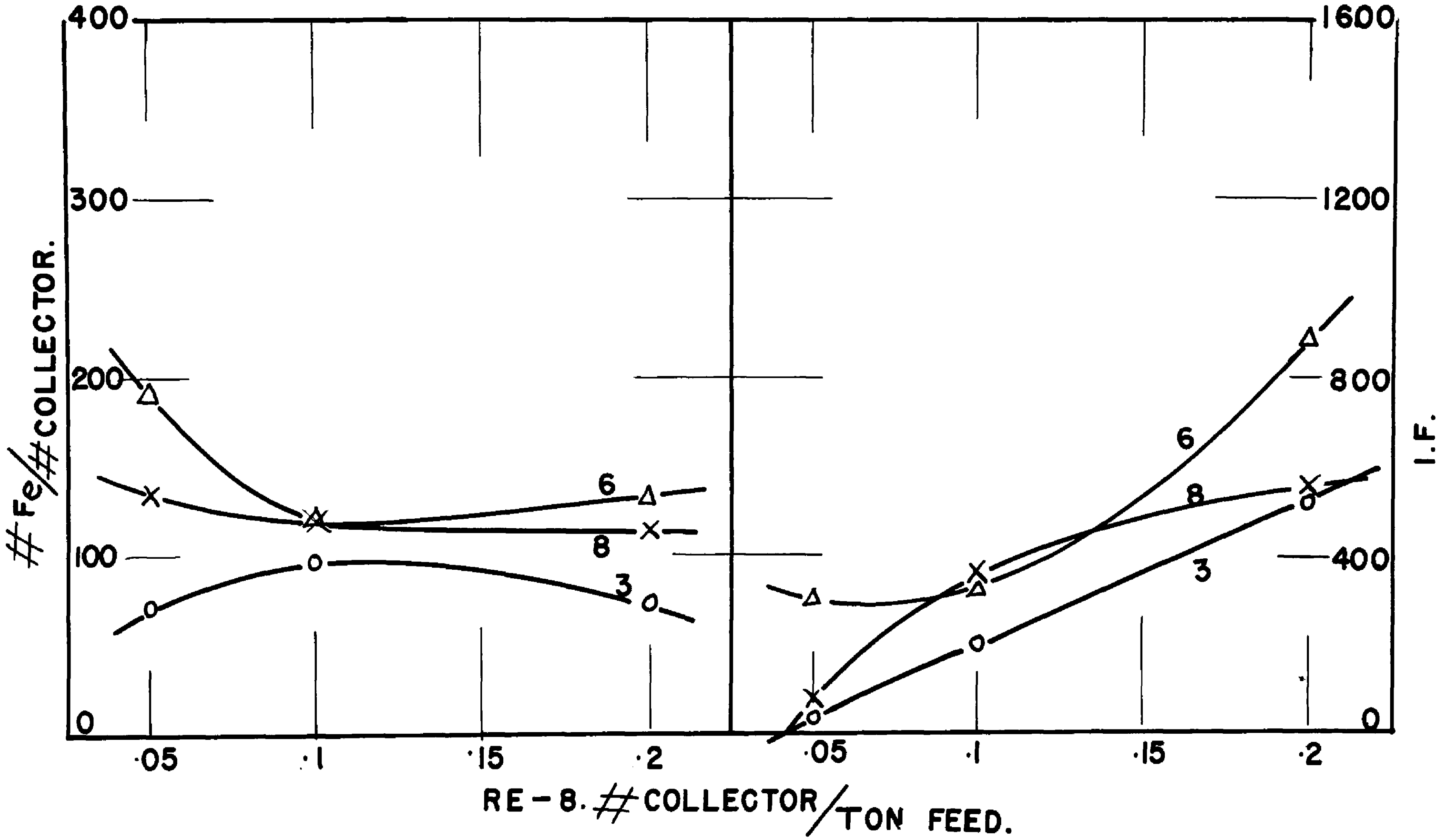

400
300
200
100
0
Fe/# COLLECTOR.
6
8
3
1600
1200
800
400
0
I.F.
6
8
3
·05
·1
·15
·2
·05
·1
·15
·2
RE-8. # COLLECTOR/TON FEED.

FIG. 18.

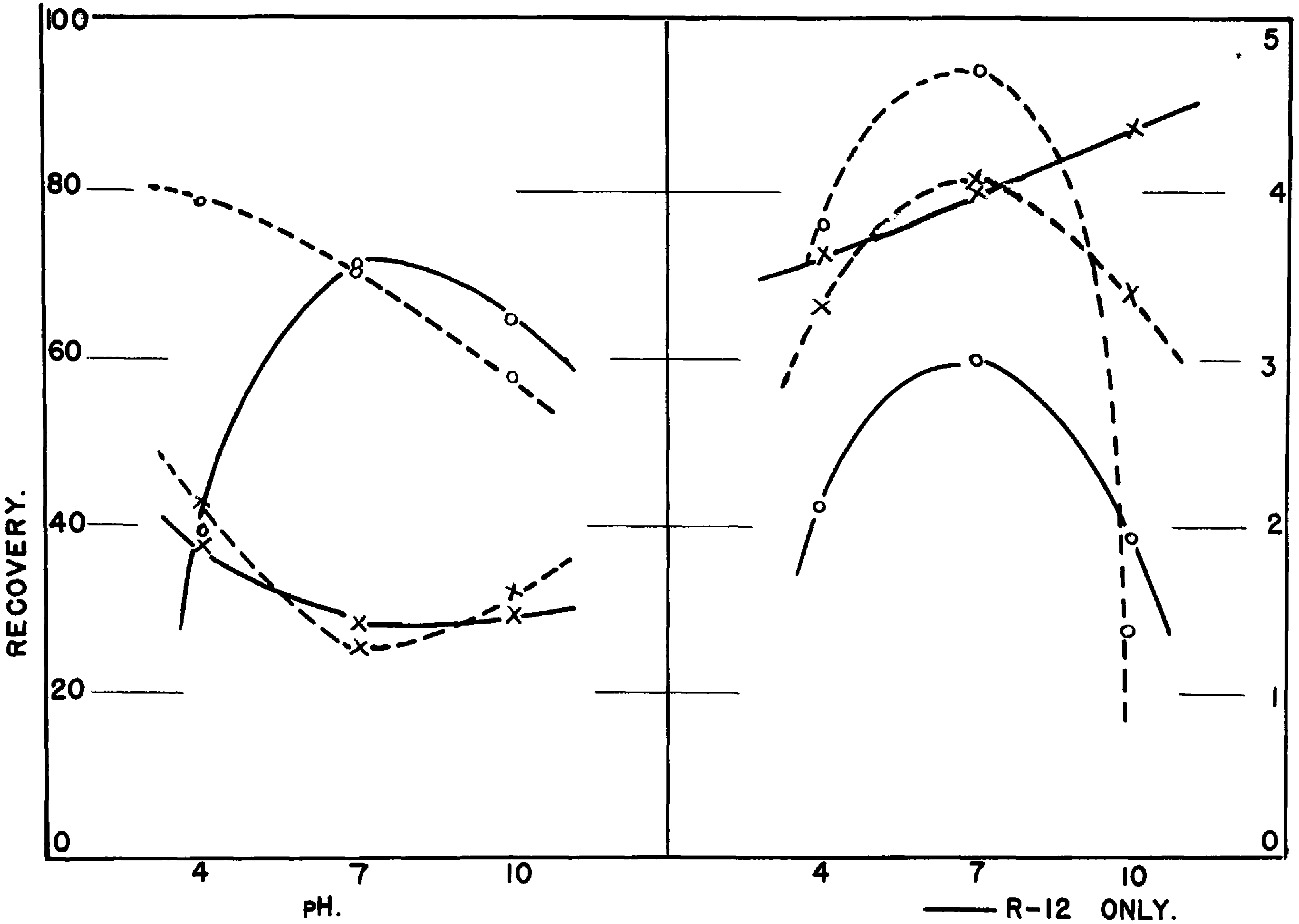

100
80
60
40
20
0
RECOVERY.
4
7
10
pH.
5
4
3
2
1
0
ENRICHMENT.
4
7
10
—— R-12 ONLY.
- - - - R-12 + TRIMETHYL AMINE.
o o o .02 # COLLECTOR/TON.
x x x .1 # "

FIG.19.

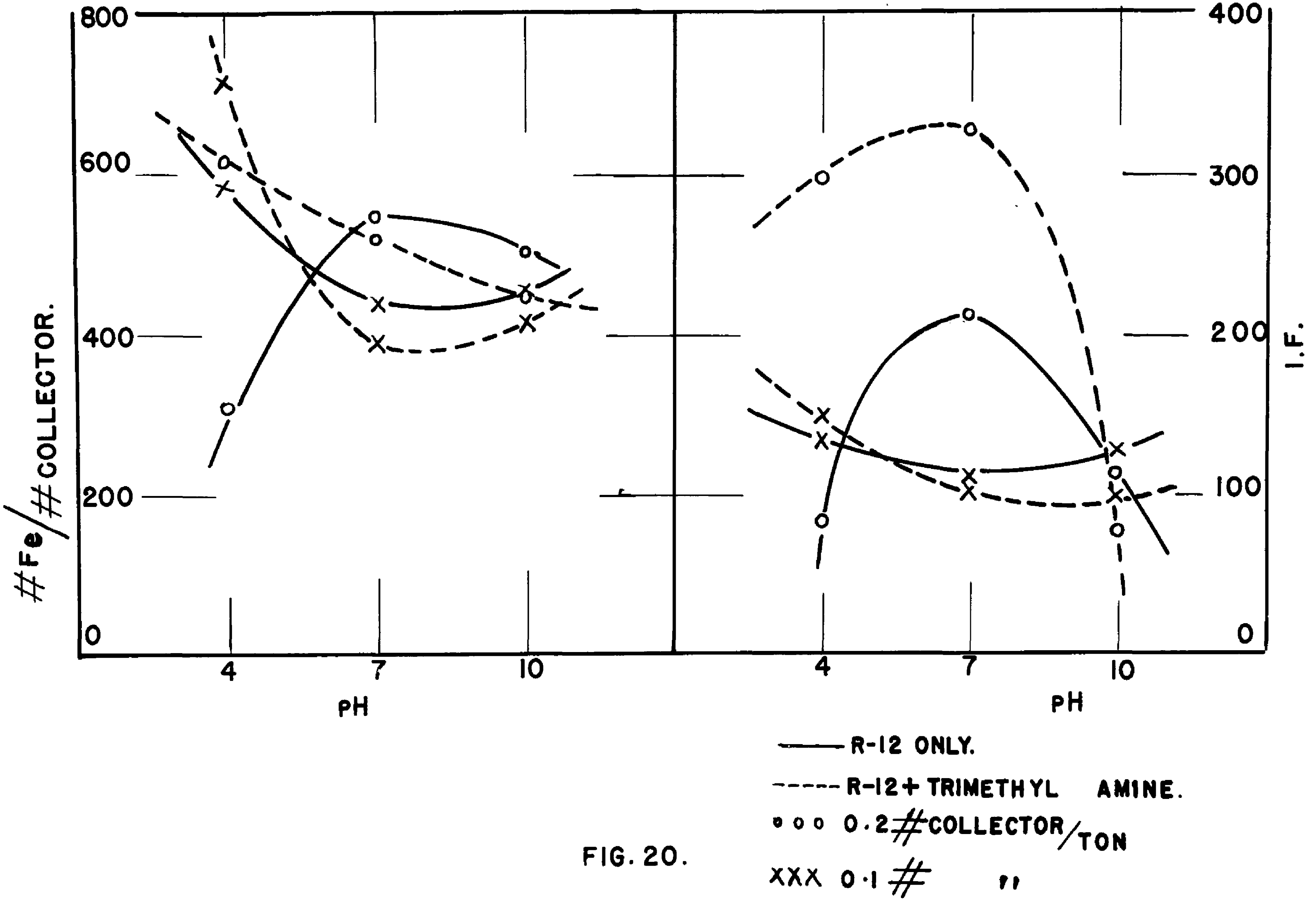

#Fe/#COLLECTOR.
800
600
400
200
0
4
7
10
pH
I.F.
400
300
200
100
0
4
7
10
pH
R-12 ONLY.
R-12+ TRIMETHYL AMINE.
○ ○ ○ 0.2#COLLECTOR/TON
XXX 0.1# "

FIG. 20.

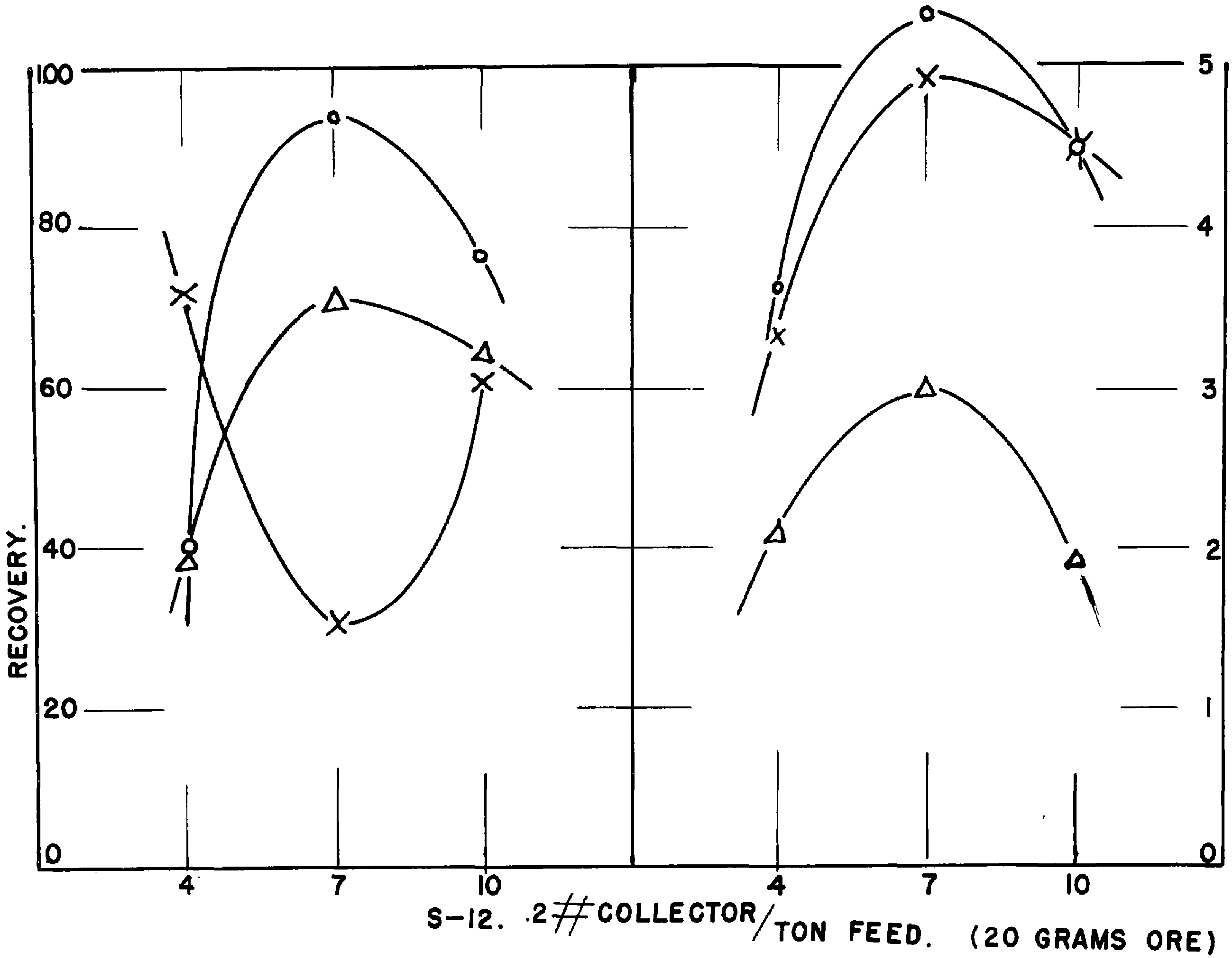
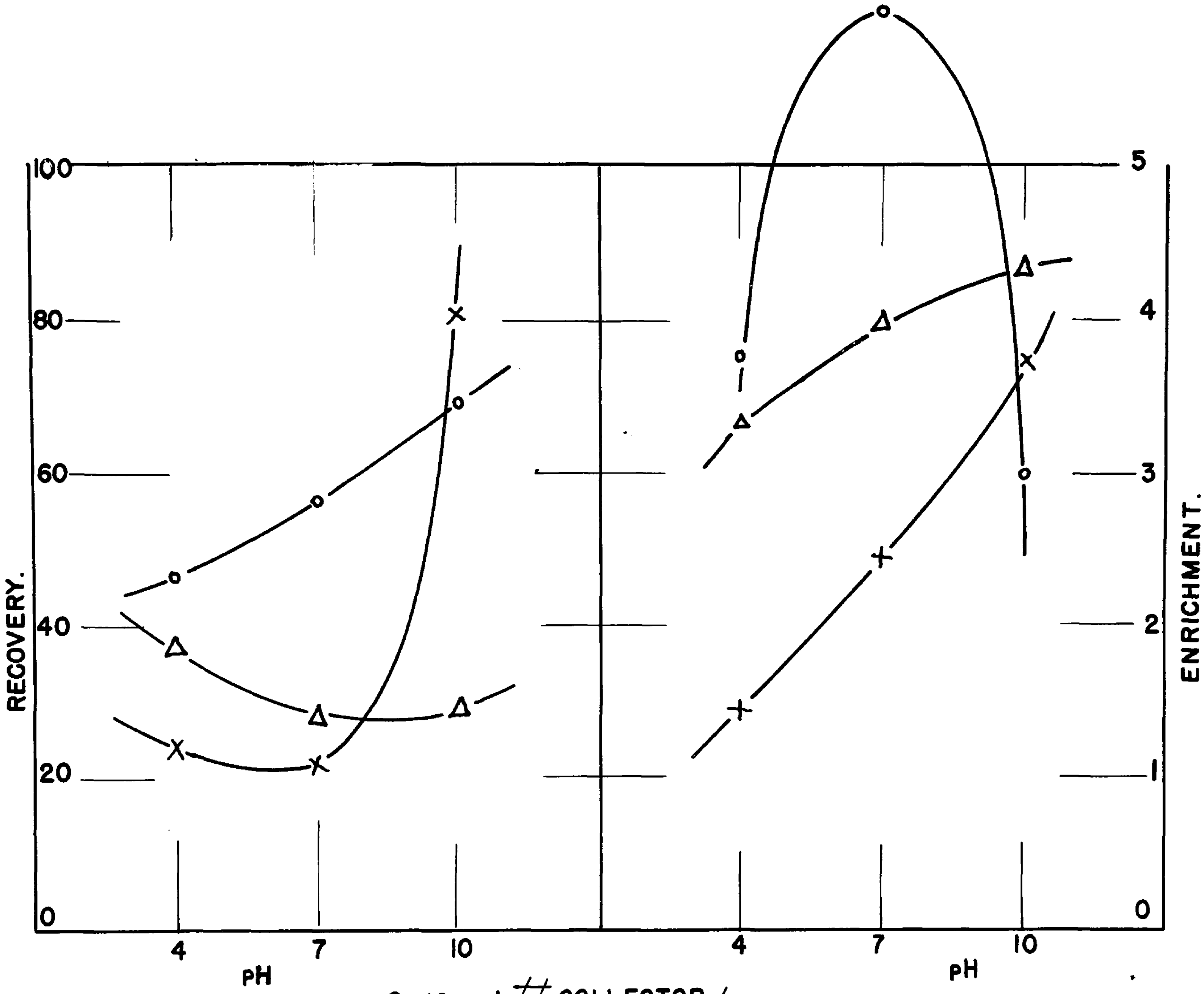
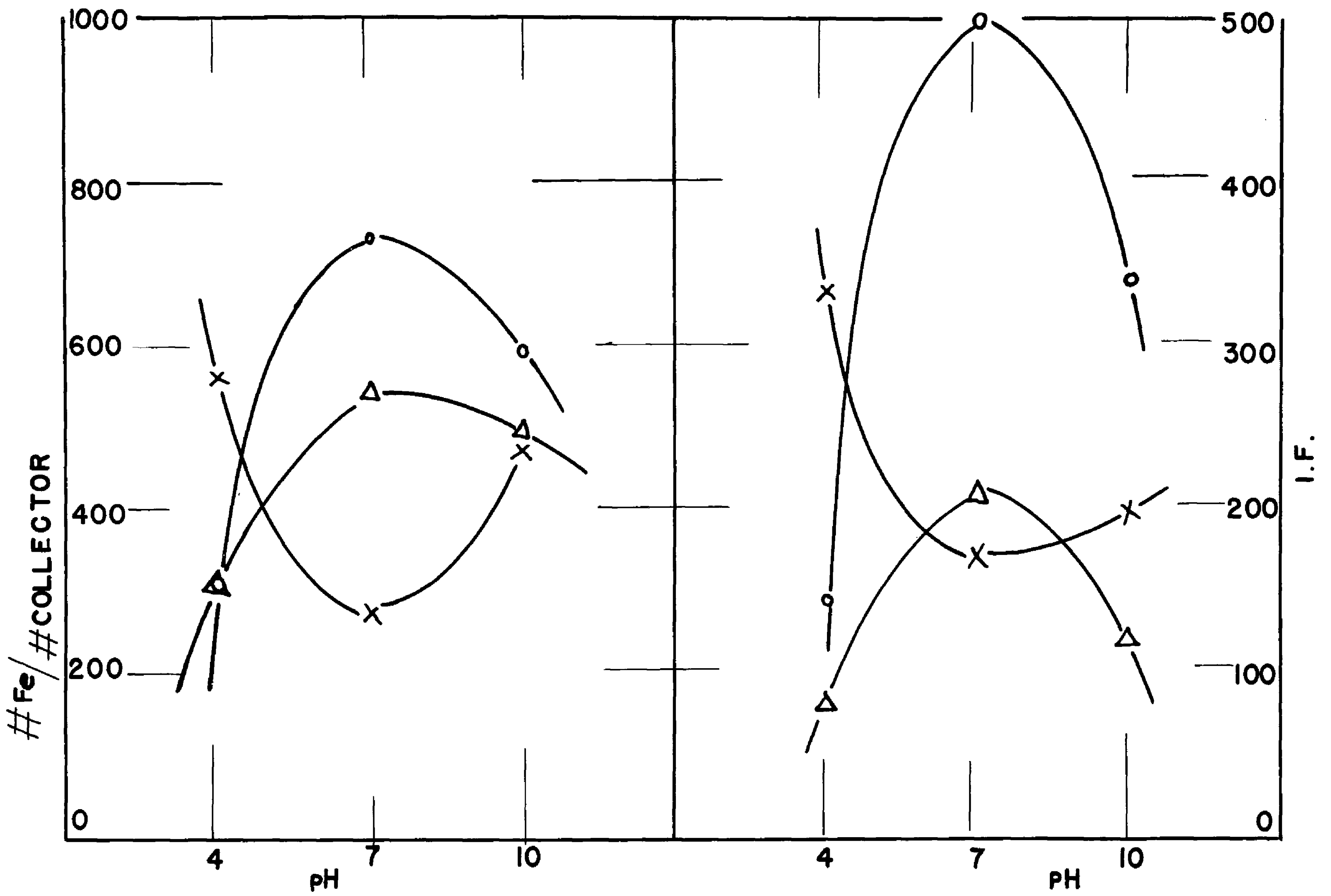

RECOVERY.
100
80
60
40
20
0
ENRICHMENT.
5
4
3
2
1
0
4
7
10
4
7
10
S-12. .2# COLLECTOR/TON FEED. (20 GRAMS ORE)

FIG. 21.



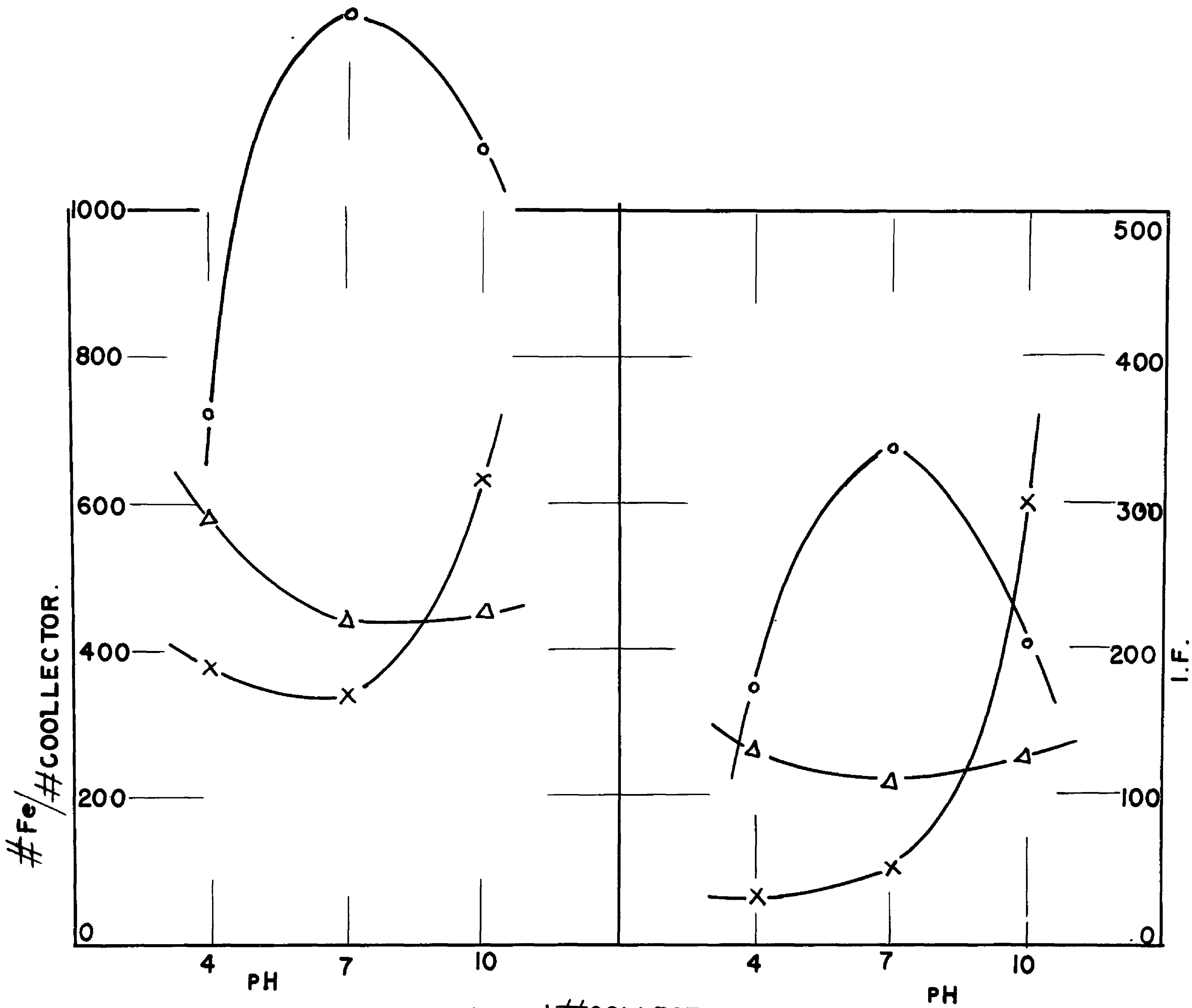
S-12. ·1 # COLLECTOR/TON FEED. (20 GRAMS ORE.)

FIG. 22.



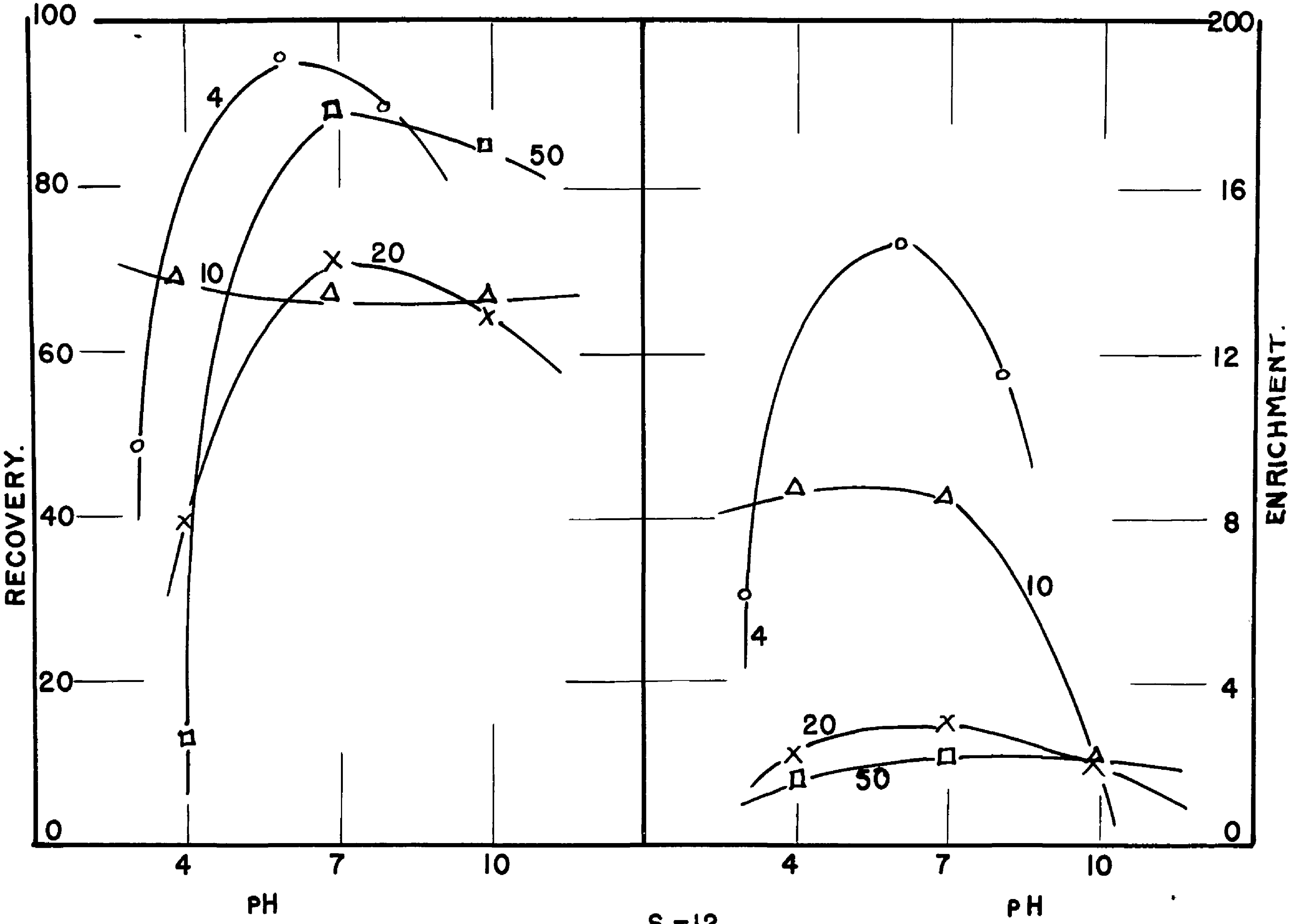
S-12. .2#COLLECTOR/TON FEED.

FIG. 23.



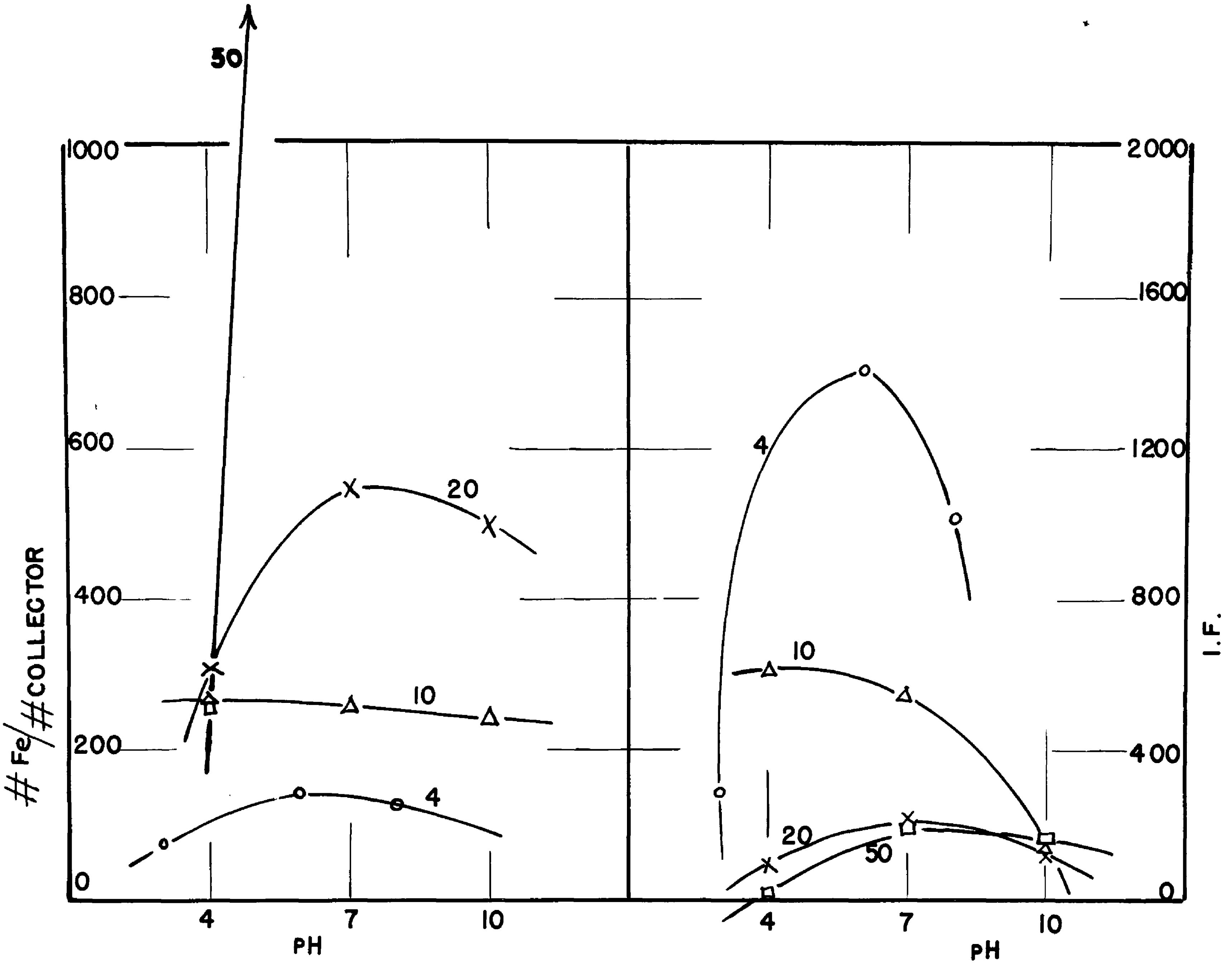
S-12. 1#COLLECTOR/TON FEED.

EIG. 24.


RECOVERY.
100
80
60
40
20
0
4
7
10
PH
4
10
20
50
ENRICHMENT.
200
16
12
8
4
0
4
7
10
PH
4
10
20
50

S-12.

FIG. 25.


50
1000
800
600
400
200
0
Fe/# COLLECTOR
20
10
4
4
7
10
PH
2000
1600
1200
800
400
0
I.F.
4
10
20
50
4
7
10
PH

S-12.

FIG. 26.

Hydroxides of the iron with other members of the same group were precipitated from the water. Most of the silica and other compounds of the alkaline metals remained in solution. The mixture was filtered, and precipitates were washed with water and taken up in beaker, and dissolved with dilute hydrochloric acid.

B) VOLUMETRIC ANALYSIS:

The iron was determined volumetrically by permagnate method.(74) The reduction was carried out with standard stannous chloride solution according to the modified Zimmerman-Reinhardt method. The results are tabulated in tables 4-11.

DISCUSSION OF THE RESULTS:

Table No. 3, shows fairly good agreement with the view points discussed on page No. 11 for the design of the collector.

Dodecyl phenol has a very small dissociation constant. There is no possibility for the chelate formation, except the complex formation with the active centers on the surface of the new surface area of the ground particles. The result showed very poor collecting power for taconite as expected.

Dodecyl ortho-nitro phenol shows the possibility of the six membered chelate complex compound formation. Its dissociation constant will not be noticeably larger than dodecyl phenol. The result showed little better collecting power than dodecyl phenol. For other types of oxides and silicate minerals it may be a good collector. The studying of the stability constants of various complexes with the various elements is necessary.

Ortho-sulfonic 4-decyl phenol will have slightly larger dissociation constant. It has a possibility of forming six membered chelated complex. At the same time, the complex compound formation with the calcium particles (naturally associated in taconites), will decrease the efficiency of the collector. Thus the efficiency of the dodecyl-O-sulfonic phenol as a collector, will vary according to the types of the ores. Sulfonated oils, fats, soaps and the petroleum products are patented as collectors for the flotation of oxidized iron ores and some taconites after desliming and other pretreatments.

Ortho-nitro -6-sulfonic -4-decyl phenol shows the possibility of forming a six membered chelate in two ways, but the same reasoning applies to sulfonic group as to o-sulfonic-4-decyl phenol. Thus, the efficiency of these compounds will depend on the type of taconites. Therefore, the results of these compounds will not be indicative.

Dodecanoyl hydroquinone and mono-methyl ether of the same have the possibility of the formation of six membered chelate. Their dissociation constants will be about the same as phenol (see table No. 1). Moreover the alkyl group as located, will have a steric hinderance effect. As a result of this, the molecular density of the collector per active atoms of the iron on the surface will be much smaller. Thus it is apparent, that these will be poor collectors for the taconites. This agrees with the author's experimental results.

The same reasoning appears to hold for the alkylated polyhydroxy aromatic compounds; but in these cases, there is a possiblity of two types of complex compound formation. One is with ortho-carboxyl group and hydroxyl group- (a six membered chelate formation) and the other will be with hydroxyl groups. The dissociation constants will be slightly larger than the phenols and hydroquinones. Thus alkylated polyhydroxy aromatic derivatives should show good possibilities as collectors for iron ores. This agrees with the results shown in the table No. 3.

Propanoyl catechol has a possibility of complex compound formation. The complex compound will not be of the six or more membered chelate type. It has a very small aliphatic chain (non-polar group). Moreover the source of it was not known. Thus, the result of it is not reliable.

Sodium N-(dodecyl phenyl) glycenate has a possibility of forming five membered chelate, which will be less stable than the six or more membered chelate, but it will be more stable than the unchelated complex compounds. Its dissociation constant was not reported in the literature. It gave very preferential collection of the iron ores. The much smaller amount of the froth was obtained. Thus, it gave a lower percentage of recovery. It may be improved by desliming and pretreatment of the ores.

Tetradecanoyl salicylic acid shows six membered chelate complex compound to be the most stable.(11) Besides, dissociation constant of salicylic acid is considerably larger (see table 1).

Also according to the lattice structure, continuation of the taconite particles (carbonate and oxides mixtures of iron) should be logically the best collector for the taconites. Preliminary survey of the results of table No. 3 showed the same trend.

Examination of tables 4-11, and figures 3-26, indicates that every series of tests show good recovery and enrichment of the iron ores from the synthetic mixtures of taconites. This enrichment and recovery are due to the presence of the collector, since without the use of a collector no enrichment or recovery was obtained. On the contrary siliceous gangue particles were floated due to the activation of silica by the presence of elements, such as ferrous, calcium, aluminium, etc. This phenomena is well discussed in the literature (28,33,49,50,79,91,95,96).

To facilitate the discussion, the following designations are employed for the different collectors:

(1) 4-Decanoyl salicylic acid................△△△........S-10

(2) 4-Dodecanoyl salicylic acid..............××××......S-12

(3) 4-Tetradecanoyl salicylic acid...........○○○........S-14

(4) 4-Decanoyl β-resorcylic acid.............□□□........R-10

(5) 3-octoxy β-resorcylic acid...............●●●........RE-8

4-ALKANOYL SALICYLIC ACID: (Tables 4-6; Fig. 3-5)

Several general trends are indicated as follows:

Maximum recoveries are obtained at neutral pH 7, for the collector concentration of 0.20 pounds per ton of the dry feed. The lower the amount of collector, the lower the degree of enrichment and recovery. In practically all cases (in each series), enrichment decreases considerably by increasing pH above 7. This is due to the increased amount of froth. At higher pH, the alkalinity condition activates everything including siliceous gangue. This tends to float and carry over (entraps) all mineral particles. At pH below 7, (in the acidic condition of the pulp) recovery is decreased to some extent and enrichment increased slightly. This may be due to the slime effect, which can be reduced by desliming and pretreatment of the ores.

The imprevement factor is better at pH 7-9; when 0.1 pound of collector per ton of taconite is used. The enrichment drops at the same time. As the amount of pounds of iron collected in froth per pound of collector used increases, the enrichment and recovery drops.

The higher the alkyl chain of the alkylated salicylic acid, the better are the results of recovery, enrichment, improvement factor and pounds of iron in froth collected per pounds of collector used.

Table 4-11 and figures 3-26; reveal that higher concentration of the synthetic ore reduces the recovery, enrichment, improvement factor and pounds of iron in froth per pound of collector used. This may be due to the increased activation of the siliceous gangue by higher concentration of the ferrous and non-ferrous elements. This should be improved by using a depressant for the siliceous gangue. Cationic type of reagents, particularly trimethyl amine and di-n-butyl amine were tried in few runs. These showed the desired effect, but not enough so to compensate for the increased cost of the reagents. The effect of reducing the pulp density was tried in several runs for higher concentration of the synthetic ores. Some improvement was noted but the consumption of the collector was increased. Further investigation along this line is necessary before any definite conclusions can be drawn.

Gaudin, (51) DeWitt with co-workers(41), and various other investigators (96) proved that using finer particles (-200 mesh or finer) decreased the flotation efficiency. The same effect was found in the various runs, which are not included in the results.

β-RESORCYLIC ACID DERIVATIVES: (Tables 7-8; fig. 3-5).

General trends for the various factors such as pH, amount of collectors with respect to recovery, enrichment, improvement factor and pounds of iron collected in froth per pound of collector used, are more or less similar to thoseof alkylated salicylic acid derivatives. The results of β-resorcylic acid derivatives showed a slightly lower percentages.

CONCLUSIONS

The following conclusions are drawn from the data presented.

(1) The design and prediction of the behavio~~u~~r of collectors can be accurately made by considering the following factors:

- (a) Relationship of chemical affinity, dipole moment, residual electrostatic forces of the molecules.
- (b) Chelate compound formation and chemical reactions.
- (c) Dissociation constants of collectors and stability constants or complex formation constants of the complex compounds. Relationship of free energy and equilibrium constants.
- (d) Electron sharing pairs and electron density of the polar groups, ions or molecules of the collector reagents. The position of the polar group electron sharing elements in the Periodic Table.
- (e) Size, dimensions and steric hinderance of polar and non-polar groups and dimensional properties of crystalline lattice.
- (f) Physical and chemical properties of the ores and collectors.

(2) Alkylated salicylic acid is one of the best collectors for iron particles from the siliceous gangue. It was possible to obtain 90-98% recovery of iron and about 15 enrichment for the synthetic taconites. For the higher concentration of the synthetic ores the recovery and enrichment drop.

(3) Alkylated β-resorcylic acid and 3-monoether of β-resorcylic acid showed good collecting powers for the synthetic ores. The recovery and enrichments are slightly lower than alkylated salicylic acid.

(4) Cationic types of depressors for silica, pulp density and higher concentration of the synthetic ores were studied, but further detail study is required to draw any conclusions.

(5) Various prospective collectors studied as shown in table No. 3, failed in the rough flotation of taconites, but their flotation efficiency may be improved by desliming and other pretreatments of the ores.

(6) Salicylic acid types collectors show the possibility of the flotation for various minerals of the oxides, carbonates and silicate mixtures of iron, nickel, cobalt, aluminium, cerium, uranium, thorium etc., but further study is required.

(7) Study of the dissociation constants, stability constants and/or complex formation constants showed good prospects for the flotation study.

THE SYNTHESIS OF COLLECTORS

(1) Dodecyl phenol.

In this research work, commercial grade dodecyl phenol was used. It was obtained from Sharple's corporation. The alkyl branch was the compact tertiary type.

(2) O-nitro-p-dodecyl phenols

Anisole was alkylated by the Friedel-Crafts method and reduction was subjected according to the Wolff-Kishner method. Then alkylated phenol was nitrated by a procedure similar to that reported by Cecyl M. Galloway (47). The details of this can be found in the author's previous work (87).

(3) O-sulfonic-p-decyl phenol:

O-sulfonic-p-decyl phenol was prepared by the procedure similar to that reported by Suter and Muffett (102). Fifty grams of p-decyl phenol were taken in a three necked flask equipped with stirrer and 30ccs. of concentrated sulfuric acid were added. The mixture was stirred at 100°C for one hour and then allowed to cool. After cooling the mixture was poured into a saturated solution of sodium chloride. The precipitate of sodium salt was recrystallized twice from hot water.

(4) 2-nitro-4-decyl-6-sulfonic phenol:

The procedure followed for the preparation of 2-nitro-4-decyl-6-sulphonic phenol was similar to the preparation of o-sulfonic-p-decyl phenol, which was modified from the preparation of the picric acid. In this case the starting compound was o-nitro-p-desyl phenol instead of p-decyl phenol.

(5) 2-hydroxy-5-methoxy undecyl phenol:

According to the report published by Mitizo Asano and Zyunity Hase (80), the method of Hasan and Stedman (C.A. 25 5669) for the synthesis of alkyl dihydroxy quinones does not work smoothly. Asano and Yamaguty obtained the same objective by a different method. (C,A. 34 50697). The procedure followed is similar to that reported by Mitizo Asano and Zyuniti.

One hundred and ten grams of dimethoxy hydroquinone were dissolved in a four hundred cubic centimeters of carbon disulfide solvent in a three necked flask equipped with stirrer and a reflux condensor with drying tube containing calcium chloride. Then 140 grams (1 mole) of anhydrous $AlCl_3$ were added while stirring. Then 208 grams of decyl bromide were added dropwise while stirring continuously. (5 hours). Hydrochloric acid fumes were given off.

The final reaction mixture was kept overnight. It was very viscous and orange brown in color. Next day, the mixture was poured in acidified cold water. Initially a yellow substance appeared but further stirring gave two layers after setting. The bottom layer was extracted with ether and mixed with the upper oily layer. Carbon disulfide solvent and ether was distilled off. The residue was purified from alcohol by crystallization. The crystals were pale yellow needles and gave about 78% yield.

(6) 2-5-dihydroxy undecyl phenone:

2-hydroxy-5-methoxy undecyl phenone was demethylated by

48% HBr solution in a three necked flask equipped with reflux condensor. Then the mixture was washed with water and crystallized from alcohol which gave very bright yellow needles. The yield was almost quantitative.

(7) 4-Dodecanoyl pyrogallol:

Various methods have been reported (91A) in use for the alkylation of polyhydroxy phenones. Frie's reaction, Nencki's reaction (modification of Frie's reaction), and Hoesch synthesis are the most common in use. Yields of the alkylation product or the reaction product will depend on the procedure used.

Hart and Woodruff (58) reportedthat they obtained 30-50% yield of the alkylation of pyrogallol by Nencki's reaction.

68 grams (0.5 mole of anhydrous $ZnCl_2$were dissolved in 220 grams (1.05 mole) of dodecyl acid with the aid of heat, whereupon 63 grams (0.5 mole) of pyrogallol were added. The mixture was heated at 130-140° for one and one-half hours. Unreacted acid was distilled off under vacuum. The residual heavy oil was washed with water several times and recrystalized from a mixture of toluene and petroleum ether. It gave white needle shaped crystals.

(8) 4-dodecanoyl phloroglucinol.

A 70-85% yield for the alkylation of phloroglucinol by Hoesh's synthesis was reported. Frie's reaction reportedly gave about 60%.yield. (91A)

Hoesch's reaction: Equimolar quantity of dodecyl nitrile and phloroglucinol in dry ether solvent was taken in a three necked flask equipped with condensor with drying tube containing $CaCl_2$. Dry hydrochloric acid gas was passed through using $ZnCl_2$ (anhydrous) as the catalysts till saturation at 0°C. The resulting mixture was hydrolysed and insoluble ketimine hydrochloride precipitates were filtered and washed with dry ether. The ketimine hydrochloride precipitates were boiled with water for three hours. The final mixture was cooled and the resulting crystals of ketone were boiled with alcohol and norite for a few minutes to decolorize. The details of this work are reported in previous work.(66)

(9) 4-Dodecanoylresorcinol.

The yield of the alkylation of resorcinol by Frie's reaction was reported to be better than Hoesch's reaction.(91A) The procedure followed was similar to that reported by Masao et al. (78). One and one half moles of dodecyl acid and 0.8 mole of anhydrous $ZnCl_2$ were heated in a flask at 125° for half hour. Then 0.5 mole of dry resorcinol was added in portions and the mixture was heated at 130° for two hours. The resulted product was kept over night and decomposed with acidified (2% Hcl) ice cold water. The aquaous layer was extracted with benzene. The benzene layer and oily layer were mixed and the benzene was removed. The unreacted fatty acid was removed by vacuum distillation. The residue was treated with petroleum ether and purified from it by crystallization. It gave leaflet crystals.

(10) 3,4-dihydroxy dodecyl phenone.

Frie's reaction and Nencki's reactions were tried, but without much success. The resultant product was a black gunk. (It may be due to the air oxidation in the presence of traces of the catalyst used). In the stock 3,4-dihydroxy propyl phenone was found but the source was unknown.

(11) Sodium n-(4-dodecyl phenyl) glycinate.

This compound was prepared by heating n-dodecyl aniline with chloroacetic acid in a mixture of water and alcohol at 80°C in a three necked flask for eight to ten hours. The resulting mixture was neutralized with sodium hydroxide and unreacted chloro acetic acid was distilled off. The residue was purified from alcohol by crystallization. This process was modified from the process for phenylene glycine reported by Alfred.(1)

(12) 4-tetradecanoyl salicylic acid.

Various methods were tried but the best one was found to be similar to that reported by Felix Seidel and Otto Engelfried. (44).

In a three necked flask equipped with reflux condensor, 310 grams of nitrobenzene, 32 grams of salicylic acid and 63 grams of tetradecyl chloride were placed. The stirrer was

~~was~~ started and 60 grams of anhydrous $AlCl_3$ were added slowly at room temperature (45 minutes). This mixture was kept overnight. The next day, it was heated on a water-bath for two hours, and then cooled and decomposed in acidified (HcL) ice cold water. The oily layer was separated, washed with water and the nitrobenzene was distilled off. The residual mass was purified by crystallization first from glacial acetic acid and then from alcohol. The crystals were dull white in color.

Similarly decanoyl and dodecanoyl salicylic acid were prepared.

(14) Alkylation of β-Resorcylic acid.

Alkylation was carried out by a modified procedure similar to the alkylation of salicylic acid.

Various investigators (37,38,70) have reported the acylation of methyl -β-resorcylate. They carried out the condensation of anhydrous aliphatic or aromatic mono- or dicarboxylic acid with anhydrous aluminium chloride. The previous works of Desai with coworkers (37,38) obtained the substitution in position five. Recent works of Trivedi and Sethna (107) obtained the various substitution products - 5-acyl, 3-acyl and also disubstitution by using various mole ratio of methyl - β-resorcylic acid, anhydrous aliphatic or aromatic acid and $AlCl_3$.

Comparison of these procedures indicates that the substitution is more likely to be in 5-position for the procedure used in the laboratory.

(14) 4-Octoxy-2-hydroxy benzoic acid.

Etherification of β-resorcylic acid was carried out according to the process described by Gootjes et al.(53) Methyl B-resorcylate was refluxed for eighteen hours in a solution of sodium in absolute alcohol, after dropwise addition of octyl bromide. Then the alcohol was removed and the mass was saponified with 2N sodium hydroxide solution. Then the solution was shaken with acetone. From the extracted solution acetone was removed and the resulted mass was washed with acidified water. It was purified further by crystallization from acetic acid and finally from alcohol.

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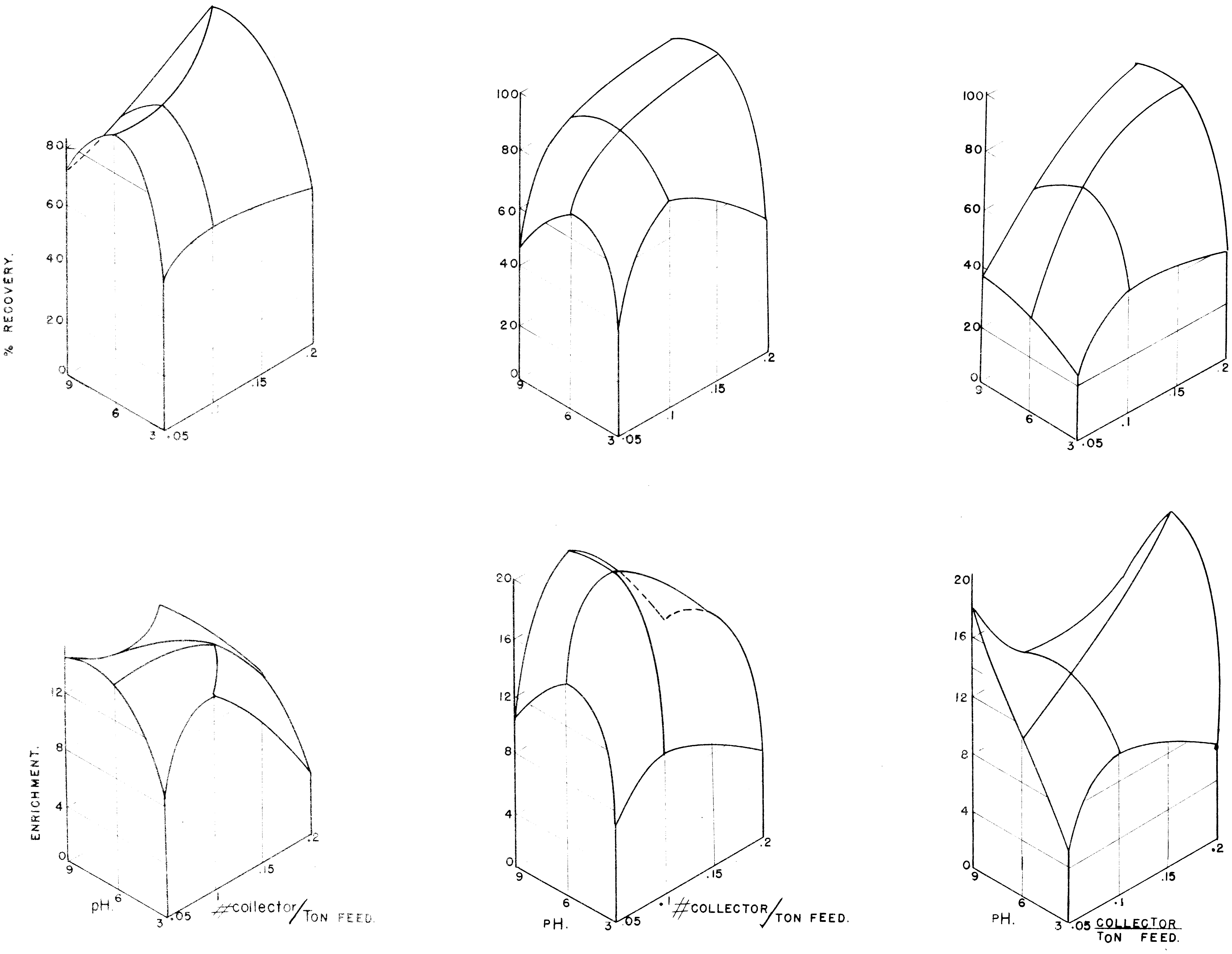
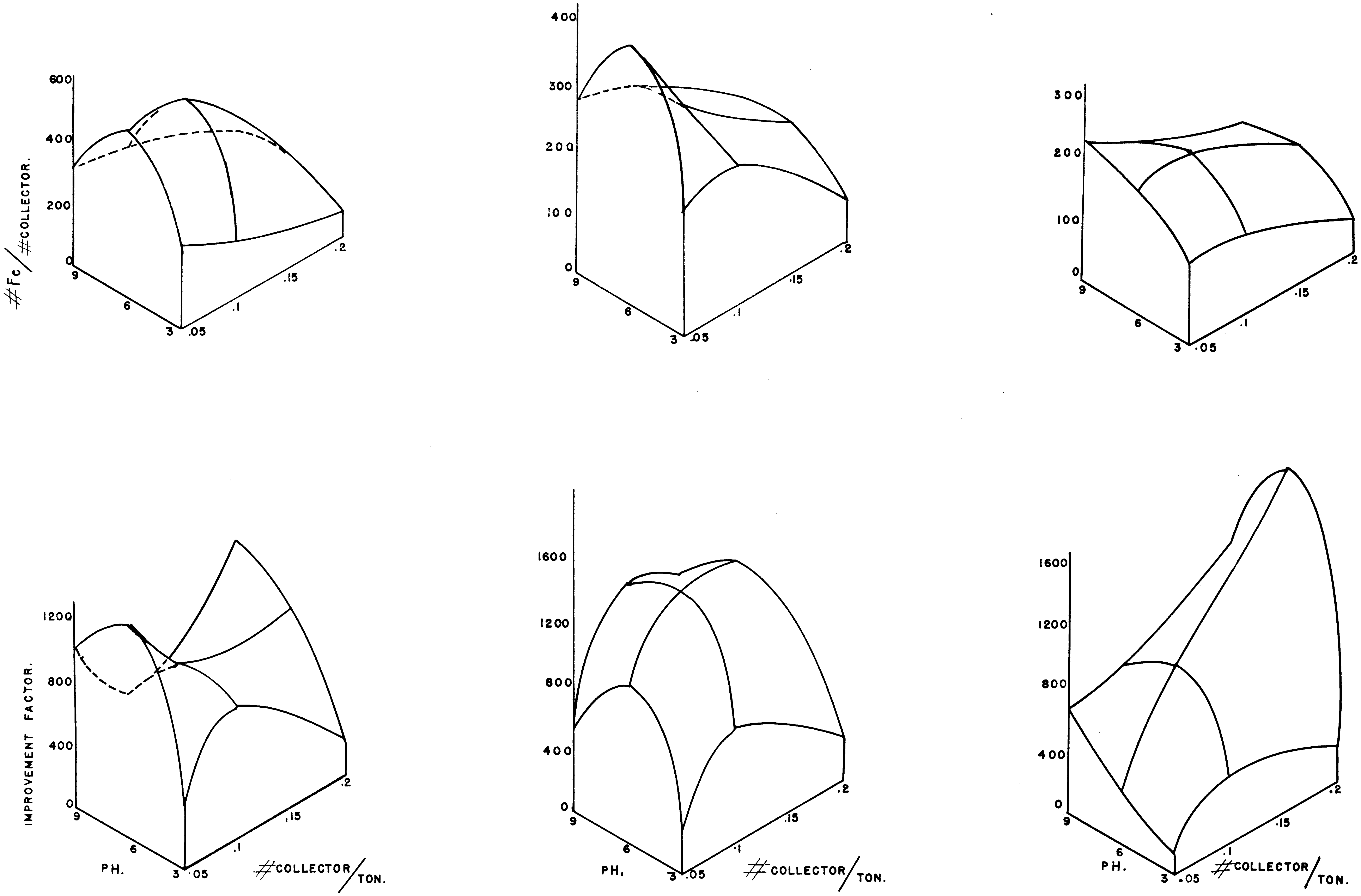


(S - 14.)

(S – 12.)

(S - 10.)

FIG. 27. FEED SIZE- -120 +200 MESH.

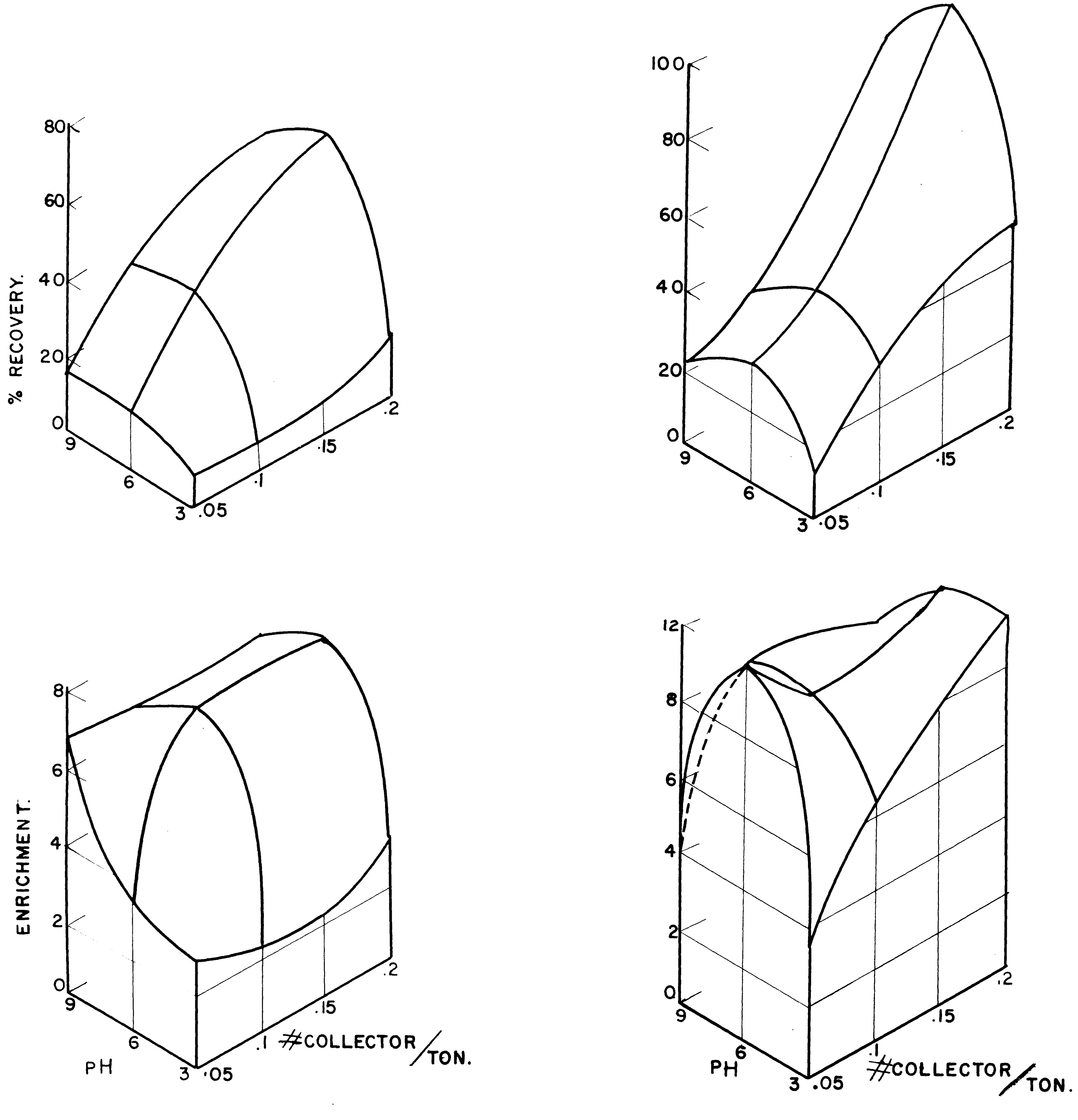


S - 14

S - 12.

S - 10.

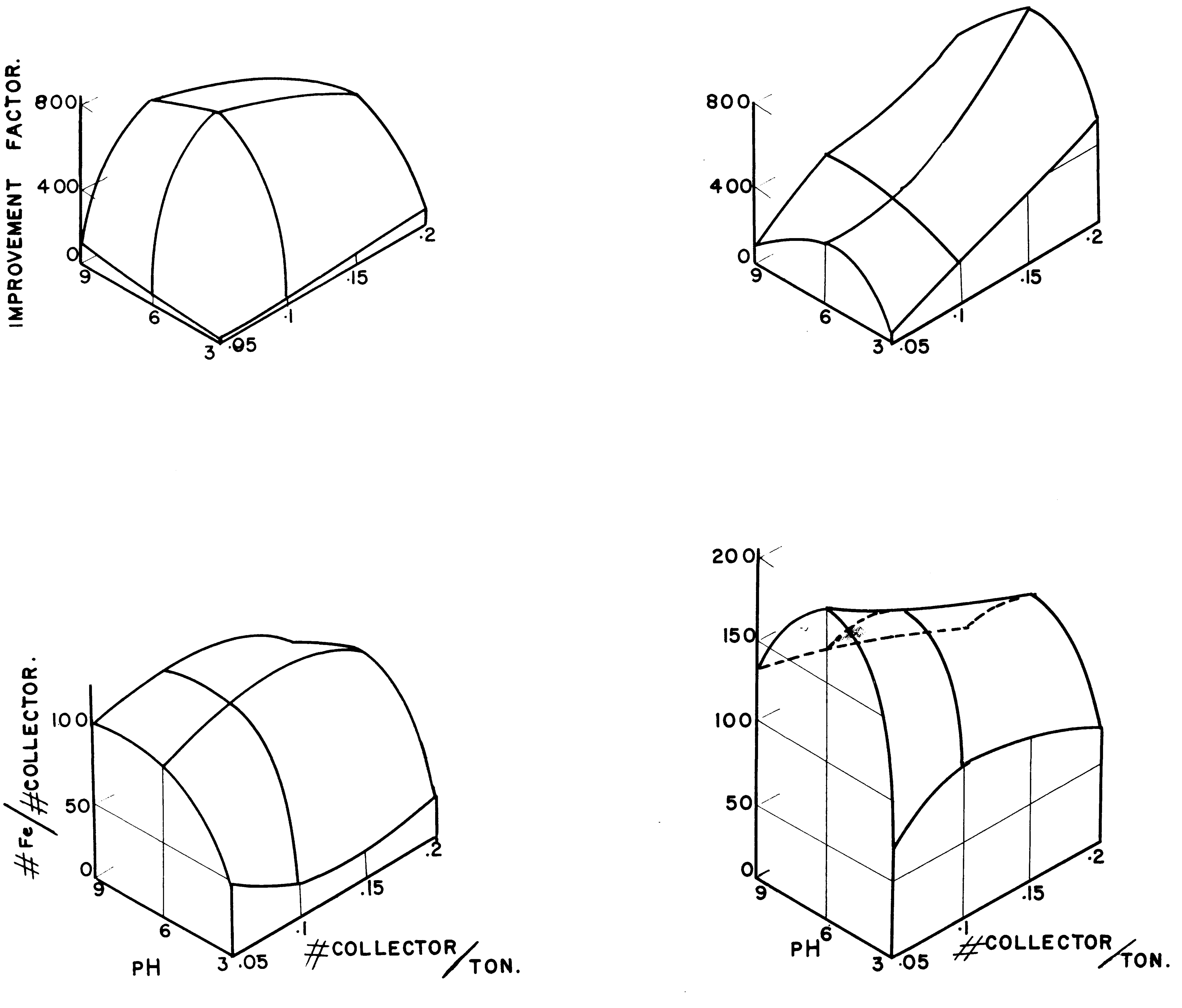
FIG - 28. -120 +200 MESH SIZE.



R-10.

RE-8.

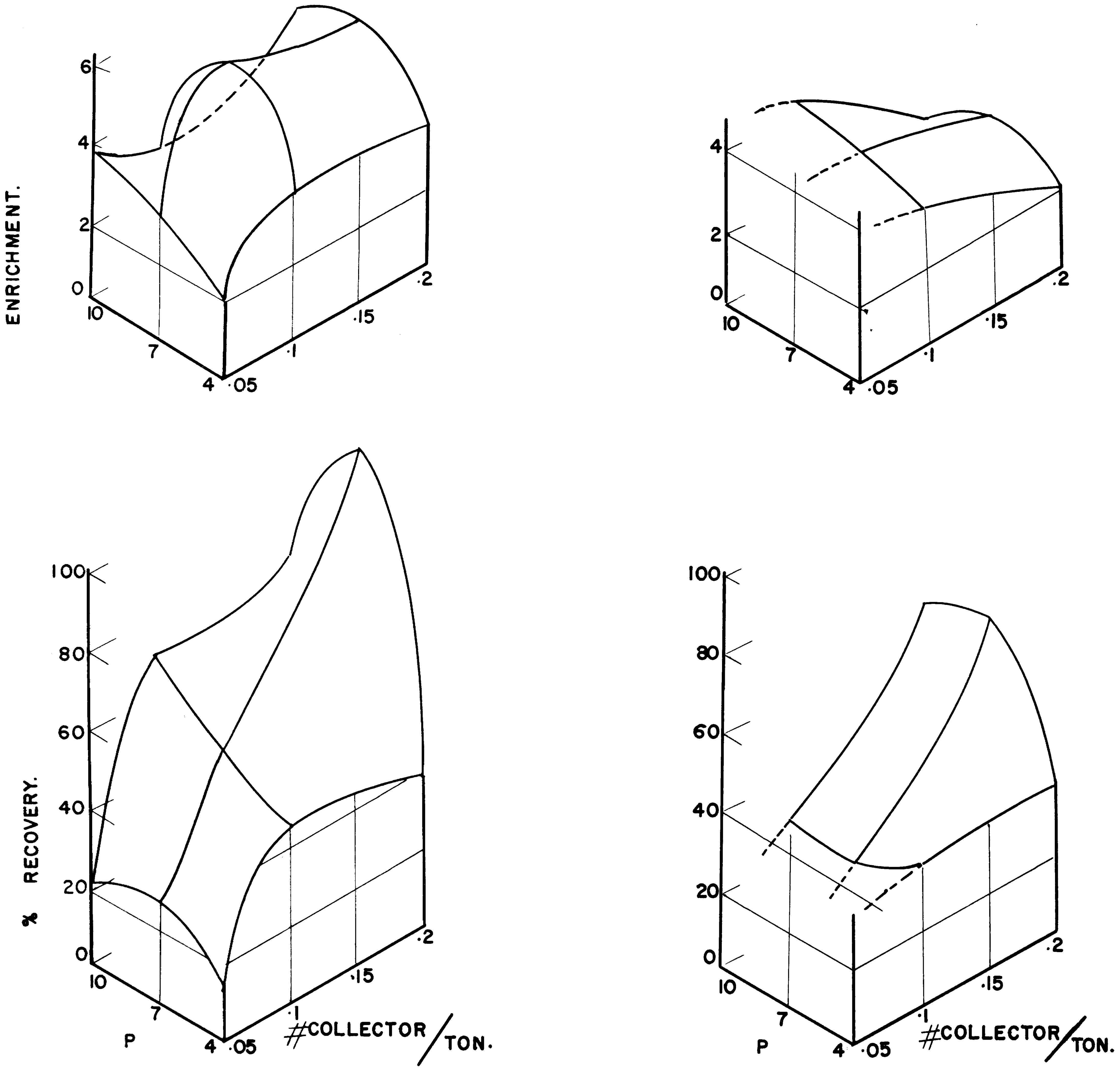
FIG. 29. TACONITES.



R-10.

RE-8.

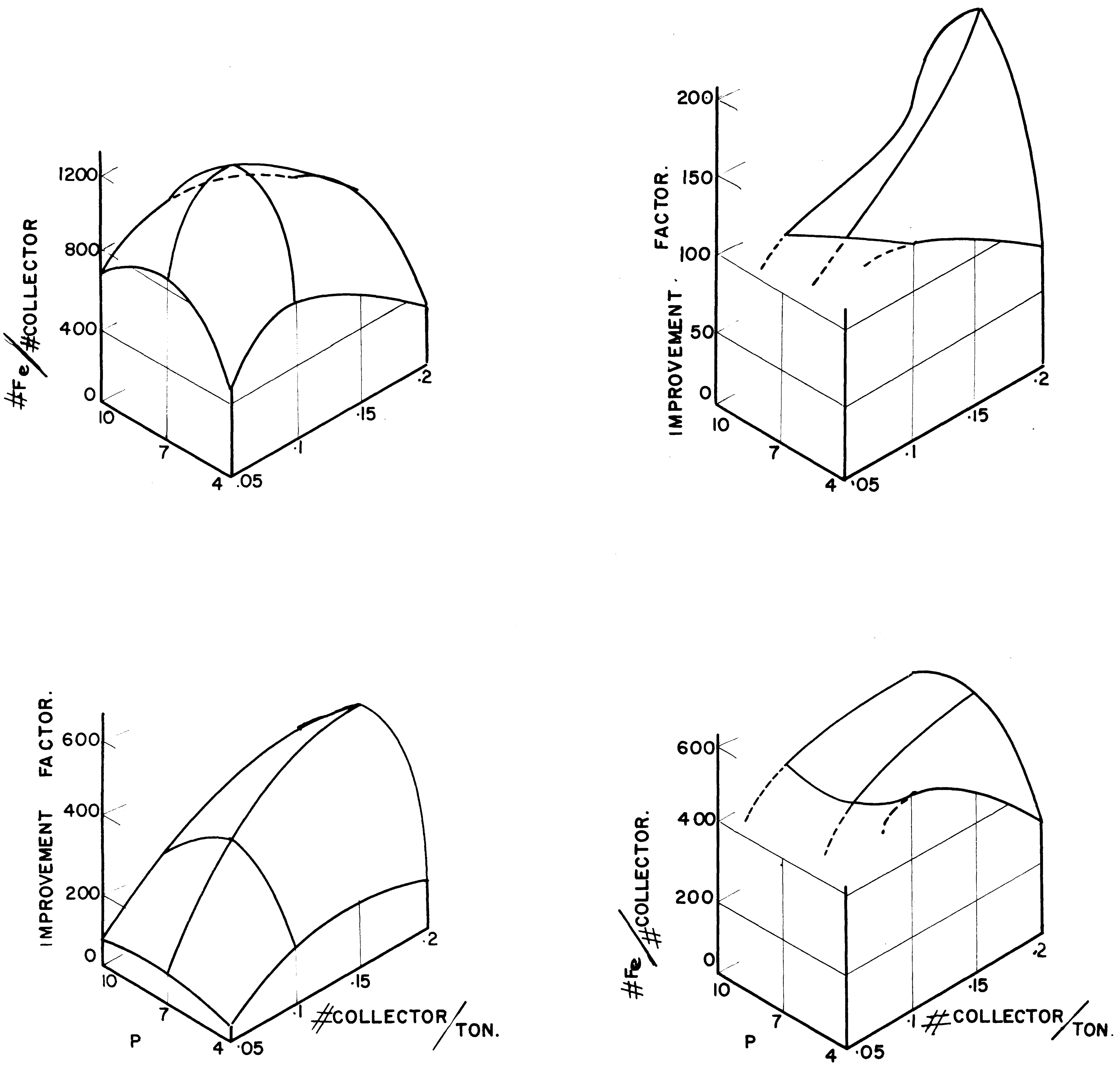
FIG. 30. TACONITES.



S - 14.

S - 10.

FIG. 31. TACONITES - 20 GRAMS.



S - 14.

S - 12.

FIG. 32. TACONITES - 20 GRAMS.