FLOTATION OF CASSITERITE BY ALKYL SUBSTITUTED NITRO PHENOLS AND NITRO RESORCINOL ETHERS

By

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Percent Recovery and Enrichment as a Function of pH

Percent Recovery and Enrichment as a Function of Collector Concentration

Pounds Tin Recovered per Pound of Collector and Improvement Factor as a Function of pH

LIST OF FIGURES (Cont.)

PAGE

Pounds Tin Recovered per Pound of Collector and Improvement Factor as a Function of Collector Concentration

Solid Surface Graphs, Percent Recovery, Enrichment, pounds Tin Recovered per Pound Collector, and Improvement Factors Varying with pH and Collector Concentration

INTRODUCTION

INTRODUCTION

Tin generally exists as an oxide. Tin oxide is commercially known as Cassiterite. Its chemical formula is SnO_2. Economically important deposits of comparatively pure cassiterite are found in Bolivia, Malaya, and China. In the United States of America there exists a large quantity of tin ore which contains less than 3 percent of tin.

With the increasing use of tin metal in war production and the fact that rich tin ores will presently not be available in large quantities in these countries, a method should be developed to concentrate the low grade tin ores.

One of the easiest and the cheapest methods for the concentration of cassiterite is froth-flotation. Froth flotation has been used quite successfully for some time in the separation of non-ferrous minerals. The method is particularly well adapted to the recovery of the insoluble sulfides of the metals. It has also been extended to the separation of the other oxide ores. Work has been done on the flotation of cassiterite using organic chemicals as frothers and collectors, but the work has not yet been put on commercial basis.[41]

PURPOSE AND SCOPE

The purpose of this investigation was to show that the Nitro alkyl Phenols, and the Nitro resorcinol ethers act as collectors in the flotation of cassiterite. Three chemicals of each series are used having a carbon atom chain of 6, 8 and 10 carbons, for each series.

For identification, the following short designations are employed for the chemicals which are used as collectors.

(1) 2-Nitro 4-hexyl phenol - - - - - - - - - - - - - - - - - - NAP-6
(2) 2-Nitro 4-octyl phenol - - - - - - - - - - - - - - - - - - NAP-8
(3) 2-Nitro 4-decyl phenol - - - - - - - - - - - - - - - - - - NAP-10
(4) 2-Nitro hexyl resorcinol ether - - - - - - - - - - - - - - NRE-6
(5) 2-Nitro octyl resorcinol ether - - - - - - - - - - - - - - NRE-8
(6) 2-Nitro decyl resorcinol ether - - - - - - - - - - - - - - NRE-10

THEORY

Although the term flotation might lead one to believe that the separation depends upon the densities of various particles, this is certainly not the case in froth flotation. The fact is true, of course, that gravity separations are still in use, but since[50] 1912, differential froth flotation has increased in importance until it is now used in the concentration of many economic minerals.

Several steps are involved in the froth flotation process. These steps are as follows: (1) the ore is crushed to a state where the mineral particles are free of the accompanying gangue materials; (2) the crushed ore is suspended in water which contains various reagents, and these reagents together with agitation and air, cause the mineral particles to cling to the inside of the rising stabilized air bubbles; (3) the bubbles, lined with the mineral particles, are then skimmed from the surface. The concentrated mineral may be further concentrated by the same process or it may be suitably treated for the recovery of metal.[9]

The four functional reagents; the frother, the collector, the activator and the depressant; used in froth flotation are defined by Wark and DeWitt[9] as follows:

FROTHERS:

A frother is a substance (generally organic) which when dissolved in water, enables it to form more or less stable froth with air.

Frothers are almost entirely organic compounds whose molecules contain one polar group and one nonpolar group. These frothers act upon the gas-liquid interface, and not at the surface of solids. They should not ionize appreciably, as this will give them collecting properties. Several investigators have shown that the frothing power of a reagent is related to the lowering of surface tension, when that reagent is added to water. For example, DeWitt and Makens[8] found that the frothing agent with the most negative slope on a surface tension-molar concentration curve was the most effective frother.

Some of the commonly used frothers are: pine oil, eucalyptus oil, terpeniol, amyl alcohol, and soaps. The frother should not act as a collector, nor should it be used in excess. An excess of frother has a tendency to coat the ore particles thus excluding the collector and decreasing the efficiency of flotation. The amount of frother commonly used lies between 0.05 and 0.20 pounds per ton.

COLLECTORS:

A collector for any mineral is a substance (generally organic) which induces it to float at the air water interface, and, in the presence of frother to form more or less a stable mineralized froth.

Taggart[47] states that the collectors must be soluble in water at least to a small degree.

Collectors are similar to frothers, but the collectors should be ionized to a greater extent. Furthermore, the polar part of the collector should have a specific affinity for specific minerals, whereas the polar part of the frothers should have affinity for water only.[15] The purpose of the collector[9] is to attach itself to the mineral and present an outward oily film to the air bubble. One end of the collector contains an active polar group, and the other end is a hydrocarbon chain (non-polar group). The length of the hydrocarbon group on a collector which permits flotation depends upon both the mineral to be recovered and upon the active polar group in the collector molecule.

The present day views about the mechanism of the collector action are given by two hypotheses. (1) The chemical reaction hypothesis, and (2) the adsorption hypothesis.

The chemical reaction hypothesis is stated as follows by Taggart, Taylor and Knill[48]. "All dissolved reagents which in flotation pulp, either by action on to-be-floated or on not to-be-floated particles affect their flotability function by reason of chemical reaction of the well recognized types between the reagent and the particles affected."

The adsorption hypothesis which as adapted by Wark[50] may be stated as follows: The ions dissolved in a flotation pulp liquor adsorb at the mineral surface. The adsorption of each dissolved ion is specific, i.e. it depends on the dissolved ion on the mineral. This specific ion adsorption is also a function of the concentration of the dissolved ion under consideration, as related to that of the other dissolved ions. If and when a sufficient proportion of the mineral surface is covered by the effective collector ions, the particles become flotable.

The film that is formed, has non-polar groups projecting away from the mineral. These non-polar groups will seek out the non-polar air in preference to polar water, with the result that the mineral particles adhere to the air bubbles. In other words, the object of coating a mineral with an insoluble organic film is to give it the property of exhibiting a finite contact angle in the presence of air, i.e., to make it possible for the air to displace the water partially from the coated mineral surface in order to make the mineral particle surface less easily wetted by water.[9]

In case of collectors, as in the case of frothers, the collector possessing the most negative slope of surface tension - concentration curve will be the most effective.

ACTIVATORS

An activator for any mineral is a substance (generally inorganic), the addition of which induces flotation in the presence of some collector that otherwise is without any effect on the mineral. Heavy metal sulfides are readily caused to float by the use of xanthate collectors. The oxidized minerals do not have this property.

DEPRESSANT

When two minerals from an ore are concentrated together in the froth, depressants may be used to restrict the flotation of one of them. A depressant for any mineral is a substance (generally inorganic), the addition of which prevents a collector from functioning as such for that mineral. Their action should be specific and their concentration in the pulp must be closely governed, because an excess may cause complete depression of the minerals. Some of the commonly used depressants are: sodium silicate, sodium cyanide, sodium carbonate, sodium bicarbonate, sodium pyrophosphate, tartaric acid, citric acid, etc.

Gaudin[15] states that the optimum quantities of the reagents to be used in froth flotation cannot be predicted, but that depends on such a variety of circumstances as to defy classification. However, the following points may be useful.

(1) Increasing the fineness of grinding requires an increase of all reagents except frothers which may or may not have to be decreased.

(2) Use of thick pulps result in some economy of the reagents.

(3) Desliming the ore may permit a considerable reduction in the quantity of reagents of the type which are active at the mineral surface.

(4) Changes in type of flotation machine may require some adjustment in the quantity of the reagents. The same is likewise true for changes in place or time or physical method of addition.

A word of explanation might be added here, with regard to a few of the other terms used in this investigation. HEADS refers to the charge into the flotation cell. CONCENTRATE refers to the material collected in the overflow, and the solids remaining in the liquid are called the TAILS. The percentage recovery refers to the fraction of the total mineral in the heads that is present in the concentrate.

PREVIOUS WORK ON CASSITERITE

The investigation on the flotation of cassiterite began as early as 1920, when Edser[10] used the following flotation method and reagents. He took a sample of black Nigerian cassiterite and mixed it with white quartz gangue. He used a small amount of sodium oleate solution together with an alkaline gangue modifying reagent. There was no difficulty observed by him in flotation. He obtained 90 percent recovery.

In 1927, A. C. Vivian[49] obtained as high as 90 percent recovery using 0.10 pound per ton of cupferron as a collector; and coal tar and creosote as the frothing agents.

In 1939, O. C. Ralston[41] used oleic acid, linseed oil, and fish oil as the collectors; and tar oil, anthracene oil, and crude cresol as the frothers; and obtained 97 percent recovery. At the same time, Handy and Beard[25] reported the use of soaps as the collectors.

In 1941, Oberbillig and Frink[39] reported the use of oleic acid, palmitic acid and sodium oleate as collectors; and sodium hydroxide, and sodium carbonate as depressing agents. It was found that the above two inorganic chemicals showed greater depressing effect at higher concentrations but at lower concentrations they were not so powerful. They also reported the use of sodium silicate and tannin as powerful depressants for cassiterite. At lower concentrations ferric chloride, lead acetate and silver nitrate showed good depressing quality.

In 1941, Brown[5] added oleum, cresote, (a crude blast furnace grade) pine oil, and potassium amyl xanthate respectively in the flotation of cassiterite and obtained satisfactory results.

In 1944, Dean and Ambrose[7] reported that according to French Patent 755,895, a mixture of sodium oleate and the sodium salt of the butyl ester of ricinoleic acid is effective in the cassiterite flotation. Two hundred grams of sodium oleate, and 200 grams of the sodium salt of the ricinoleic acid per ton gave 99.7 percent recovery, with 35 times enrichment. They also reported the successful flotation of cassiterite with the use of 0.25 pound sodium oleate, 0.10 pound Ninol 431, and 1 pound of oleic acid per ton. Frother 40 (du Pont) could be substituted for Ninol 431 with slightly inferior results.

Gaudin et al[21] reported the satisfactory use of sodium oleate as a collector in the presence of a frothing agent. The amount of sodium oleate used was 0.20 pound per ton. It was also reported that six pounds of heptylic acid or one pound of nonylic acid per ton is required to obtain complete recovery of pure cassiterite. Cassiterite had a tendency to float before quartz, when these reagents were used, perhaps, due to the relative higher adsorption of the fatty acids. Better separation was obtained by increasing the amount of the reagents. Thirty hundredths pound per ton of cupferron was also used in a neutral circuit in the presence of 0.50 pound per ton of terpineol as the frothing agent.

In 1946, Gaudin et al[19] discovered oleic acid, saturated long chained fatty acids, lauryl pyridinium iodide, lauryl amine, and lauryl amine hydrochloride to be very good flotation reagents, and[17] hydrocarbon oil such as Nujol as useful collecting agents. Better results were obtained with smaller particle size (325 mesh). Sodium cyanide, sodium silicate were used as the modifying agents. Satisfactory pH range was found to be 6.75 to 7.10.[21]

In 1947, Hergst et al[26] advanced the idea that a polar group like $-SO_4^=$, or $-SO_3^=$ was needed in a reagent for it to be an excellent tin collector. They stated that pH up to 9 was quite satisfactory, but pH below 5 gave less recovery. They presented no data supporting this view, nor has any such data been found in the literature of cassiterite flotation.

In 1950, Graham, Thomson[23] concluded that the typical non-polar structure like that of parrafin chain salts was needed in collectors for the flotation of cassiterite.

EXPERIMENTAL WORK

DESIGN OF THE COLLECTOR

In designing the collector for the flotation of cassiterite, consideration was first given to the general physical and the chemical properties of the mineral. The specific gravity of the cassiterite is 7.3 grams per cubic centimeter, while that of silica is 2.3 grams per cubic centimeter. Large particles of cassiterite and silica are readily amenable to gravity separation. However, flotation separation is indicated when the particles are fine. It is with the latter size material that this presentation is actually concerned.

On the basis of the article by Hergt, Rogers, and Sutherland,[26] reagents containing either $-SO_4^=$ or $SO_3^=$ are excellent collectors, these investigators present no data to support their conclusions. It was found that the use of 4 alkyl 2 sodium benzene sulfonate was later patented by Commonwealth Council[6]. There seems to be no connection between the previous paper[26] and this patent.

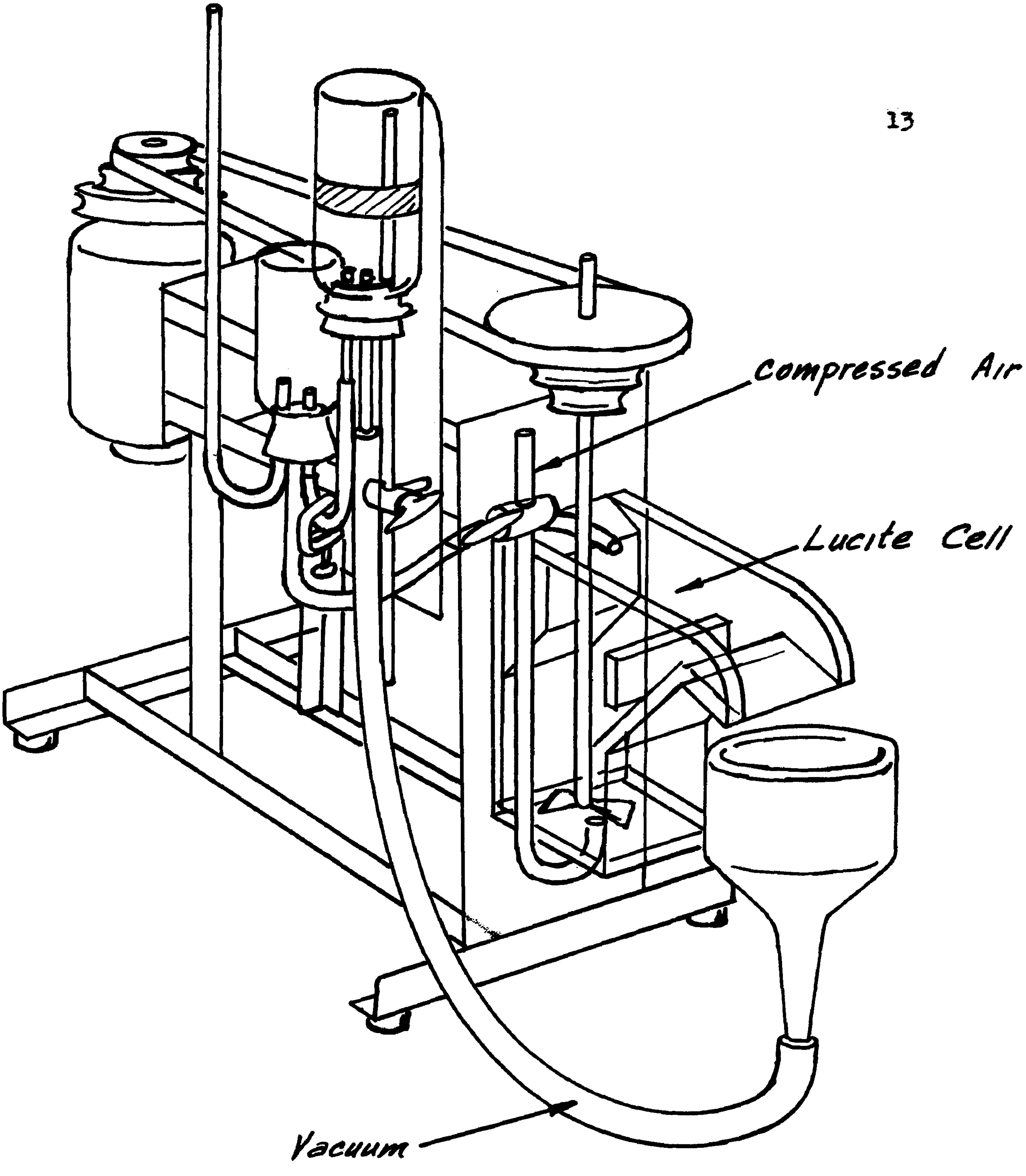
Gaudin and Sun[16] stated that hydrated hydrogen, hydroxyl, and sulfate ions fit particularly well into the contimuation of cassiterite lattice, the oxygen of these various ions has the same dimensions as the oxygen ion of the cassiterite. Otto, Neunhoeffer[38] suggested that a compound containing a phenyl radical with a nitro group in ortho, and methyl group in para positions would be the best for this work. He used the xanthates of the above in his investigation. From these two ideas it was concluded that a compound named 2-Nitro 4 alkyl phenol might also serve as a collector. The problem was thus resolved into a study of 2 Nitro resorcinol ethers and the 2 Nitro 4 alkyl phenols as flotation collectors for cassiterite. The substituted alkyl groups for each series were n-hexyl, n-octyl and n-decyl.

FLOTATION MACHINE

The flotation cell used for this investigation was a laboratory size sub-aeration type cell, made of lucite; whose details are shown in Figures 1 and 2. The agitator was driven through a V-belt from an electric motor, step pulleys made possible variation in the agitator speed. Froth overflowed from the cell into a Buchner funnel, the filtrate from the Buchner funnel was conducted to the suction bottle connected to a small vacuum pump, the suction bottle was so arranged that by cutting off the vacuum, it was possible to drain the filtrate into the feed bottle. Liquid contained in the feed bottle was fed into the cell during a run to maintain constant pulp level. Air was supplied to the bottom inlet of the cell from a low pressure blower. Reagents were added to the cell from a special titrating burette, having a long curved tip which made it possible to introduce the reagents well below the actual liquid surface, into the zone where they would be promptly dispersed into the pulp.

PARTICLE SIZE

Gaudin, Groth, and Henderson[20] state that the usual particle size for flotation of any mineral varies between 50 and 100 microns. This corresponds to about 150 to 300 mesh. For this investigation minus -120 - mesh was used because Gaudin[15] states that for cassiterite,



100 GM. FLOTATION CELL

FIGURE 1

FLOTATION CELL

Fig. 2

particle size below 100 mesh gives less recovery. It is also stated that when the particle size is reduced below 5 microns, a slime is formed, which does not respond to flotation action. While this theory lacks complete confirmation[31a] removal of the slime particles is generally good flotation practice.

PULP DENSITY

An increase in the apparent density of the pulp causes particles to rise to the surface more easily. Thus a higher concentration of the minerals in the suspension tends to aid flotation; but it also increases harmful effect of slime. The usual amount of solids in the pulp varies from 20 to 30 percent for optimum condition. In this investigation 25 percent solids were used.

ADDITION OF REAGENTS

Reagents were added to the pulp in the following order: Frother, Collector and Depressing agent or Activator. Excess addition of the collectors and frothers was avoided.

Dean and Ambrose[7] show that a conditioning period for certain cationic agents may seriously decrease the extent of flotation. The reagent is more effective immediately after addition than any other time. Their data show that 90 percent yield may be decreased to 10 percent by an eight minute conditioning period before flotation.

In this investigation a conditioning period of five minutes was allowed for each run before adding any reagents, but after adding the reagents no conditioning period was allowed. Collection of the froth followed immediately after the reagent addition.

The cassiterite and silica sand were dry ground in a one foot by one foot Abbe porcelain ball mill; pebbles were used as the grinding medium. The ground materials were separated using Tyler standard sieves which pass minus -120 - mesh. Proper care was taken to avoid overgrinding of the materials. In preparing a synthetic mixture the appropriate quantities of the ground cassiterite and silica sand were added separately to the cell and mixed therein. The total charge in the cell was 100 grams of solids and 300 grams of water for each run.

The frother used in all the runs was steam distilled pine oil. It was added in small quantity as required. Not more than 0.2 pound per ton of solids was used.

The collectors tested were made up as alcoholic solutions, 0.0005 grams of the chemical per milliliter of the solution.

Reagents used for adjusting pH were C.P. hydrochloric acid, and C.P. potassium hydroxide, both as 5 percent solutions. All the pH measurements were made using Hydrion test papers from a set of narrow range papers providing at least two checks on any single pH figure.

EXPERIMENTAL PROCEDURE

In most of the following flotation tests only a frother, a collector and the pH adjusting agents were used. Approximately 70 milliliters of water, the pH of which was adjusted to that specified for run were placed into a feed bottle. The agitator, air and the vacuum were turned on. The water and the samples were introduced into the clean cell, in such quantities as to leave a space of 5 to 10 milliliters for frothing blanket. The pH was adjusted at once to that desired. A conditioning period of five minutes was then allowed, at the end of which one small drop of pine oil was added. When the froth was reestablished, the collector was added at a regular dosage every minute from the dispensing burette for six to ten minutes of period as desired. The froth for this period was collected on a medium filter paper in the Buchner funnel. Water was drained from the funnel by vacuum filtration, and the froth was removed to evaporating dish, and dried at 115°C. The tailings from the cell were removed and the cell was well washed. Tin was determined by the volumetric method of Pearce-Lource.[36] Volumetric determination of Tin.

One gram of froth (dry basis) was weighed exactly, and was taken into a nickel crucible. To this was added three grams of sodium carbonate and both were mixed well. This mixture was then covered by the addition of seven grams of sodium peroxide, and fused and allowed to cool. The crucible with the fused content was placed into a beaker and the content was taken up with 50 milliliters of water and 100 milliliters of concentrated hydrochloric acid. The solution was transferred to a flask and a nickel coil, was introduced. The solution was boiled for 30 minutes, to reduce iron, the reduction was indicated by a color change from yellow to green. The solution in the flask was cooled; a carbon dioxide atmosphere was maintained by the addition of sodium carbonate. The nickel coil was washed with an acid solution and removed. With the temperature of the solution below 22°C., tin was determined by titrating the solution with standard 0.10N iodine using starch as the indicator.

DATA AND RESULTS

TABLE 1

FLOTATION OF CASSITERITE BY NAP-10

(Figures 3-6,7,13-16,17,23,24)

Synthetic ore: 98 grams sand and 2 grams cassiterite
Tin in synthetic ore: 0.032 percent
Time of run of experiments: 6 minutes
Synthetic ore size: minus 120 mesh

pH	Collector Lbs. per Ton	Concentrate gms.	Concentrate % Tin	Enrichment	Percent Recovery	Derived Data Lbs. Tin per lb. Collector	Derived Data Improvement Factor
3	.2	12.586	.200	6.26	80.5	2.56	504
6	.2	8.585	.374	11.70	99.7	3.22	1166
9	.2	9.58	.300	9.38	89.7	2.87	850
12	.2	9.145	.200	6.25	57.2	1.82	357
3	.1	9.37	.374	9.37	87.6	7.00	822
6	.1	8.075	.398	12.40	99.6	6.37	1235
9	.1	5.46	.450	14.05	76.5	4.91	1075
12	.1	8.57	.300	9.38	80.5	5.14	755
3	.06	9.11	.200	6.25	57.0	6.08	356
6	.06	9.154	.300	9.38	85.8	9.15	806
9	.06	6.87	.351	10.94	75.2	8.05	823
12	.06	7.7	.200	6.26	48.2	5.13	302
3	.03	10.285	.050	1.56	16.05	3.42	25
6	.03	7.58	.415	12.94	82.8	21.0	1073
9	.03	7.42	.351	10.94	81.2	15.05	890
12	.03	8.86	.250	7.82	69.2	14.75	541

TABLE 2

FLOTATION OF CASSITERITE BY NAP-8

(Figures 3-6,8,13-16,18,23,24)

Synthetic ore: 98 grams sand and 2 grams cassiterite
Tin in synthetic ore: 0.032 percent
Time of run of experiments: 6 minutes
Synthetic ore size: minus 120 mesh

pH	Collector	Concentrate				Derived Data	
	Lbs. per Ton	gms.	% Tin	Enrichment	Percent Recovery	Lbs. Tin per lb. Collector	Improvement Factor
3	.2	8.643	.175	5.47	47.4	1.51	259
6	.2	14.68	.175	5.47	80.0	2.57	438
9	.2	7.0	.402	12.50	87.5	2.82	1096
12	.2	13.6	.200	6.25	85.0	2.72	532
3	.1	6.22	.450	14.05	87.5	5.60	1230
6	.1	9.22	.300	9.37	86.2	5.53	807
9	.1	8.05	.350	10.94	87.2	5.63	955
12	.1	13.73	.200	6.25	86.0	5.50	538
3	.06	8.175	.250	7.8	63.8	6.82	497
6	.06	6.31	.350	10.94	69.0	7.36	755
9	.06	4.405	.450	14.05	61.8	6.61	890
12	.06	4.8	.374	11.7	56.2	5.98	658
3	.03	6.75	.402	12.5	84.5	18.10	1060
6	.03	5.096	.200	6.25	31.8	6.80	198
9	.03	5.45	.350	10.94	59.5	12.70	653
12	.03	5.025	.350	10.94	55.0	11.70	603

TABLE 3

FLOTATION OF CASSITERITE BY NAP-6

(Figures 3-6,9,13-16,19,23,24)

Synthetic ore: 98 grams sand and 2 grams cassiterite
Tin in synthetic ore: 0.032 percent
Time of run of experiments: 6 minutes
Synthetic ore size: minus 120 mesh

pH	Collector	Concentrate				Derived Data	
	Lbs. per Ton	gms.	% Tin	Enrichment	Percent Recovery	Lbs. Tin per lb. Collector	Improvement Factor
5	.2	10.785	.175	5.47	59.0	1.88	323
7	.2	11.245	.250	7.81	87.8	2.81	684
10	.2	6.97	.300	9.37	65.3	2.09	613
5	.1	9.32	.200	6.25	58.3	3.73	364
7	.1	11.685	.225	7.02	82.1	5.26	576
10	.1	9.95	.200	6.25	62.2	3.98	384
5	.06	9.145	.200	6.25	57.2	6.2	357
7	.06	9.75	.200	6.25	60.9	6.5	381
10	.06	9.31	.225	7.03	51.4	6.98	361
5	.03	8.655	.150	4.68	40.6	8.65	190
7	.03	8.77	.150	4.68	41.2	8.77	193
10	.03	5.16	.250	7.81	40.3	8.60	314

TABLE 4

FLOTATION OF CASSITERITE BY NRE-10

(Figures 3-6,10,13-16,20,25,26)

Synthetic ore: 98 grams sand and 2 grams cassiterite
Tin in synthetic ore: 0.032 percent
Time of run of experiments: 6 minutes
Synthetic ore size: minus 120 mesh

pH	Collector	Concentrate				Derived Data	
	Lbs. per Ton	gms.	% Tin	Enrichment	Percent Recovery	Lbs. Tin per lb. Collector	Improvement Factor
5	.2	8.19	.325	10.15	83.2	2.66	845
7	.2	11.692	.270	8.42	98.5	3.15	850
10	.2	9.50	.300	9.37	89.0	2.85	835
5	.1	8.512	.325	10.15	86.4	5.14	870
7	.1	9.045	.325	10.15	91.4	5.88	930
10	.1	11.075	.252	7.82	86.2	5.14	673
5	.06	8.445	.275	8.60	72.5	7.72	623
7	.06	10.40	.285	8.90	92.5	9.87	823
10	.06	7.78	.383	11.94	85.2	9.92	1020
5	.03	7.155	.300	9.38	67.0	14.3	628
7	.03	8.635	.300	9.38	81.0	17.25	760
10	.03	7.435	.325	10.15	75.4	16.10	767

TABLE 5

FLOTATION OF CASSITERITE BY NRE-8

(Figures 3-6,11,13-16,21,25,26)

Synthetic ore: 98 grams sand and 2 grams cassiterite
Tin in synthetic ore: 0.032 percent
Time of run of experiments: 6 minutes
Synthetic ore size: minus 120 mesh

pH	Collector	Concentrate				DERIVED DATA	
	Lbs. per Ton	gms.	% Tin	Enrichment	Percent Recovery	Lbs. Tin per lb. Collector	Improvement Factor
5	.2	8.44	.305	9.39	79.2	2.57	745
7	.2	7.865	.374	11.70	92.3	2.94	1083
10	.2	6.08	.350	10.94	66.5	2.13	727
5	.1	9.5	.200	6.25	59.4	3.80	371
7	.1	9.765	.250	7.80	76.2	4.88	594
10	.1	10.61	.150	4.70	49.8	3.18	234
5	.06	7.0	.1535	7.80	61.0	3.59	476
7	.06	8.90	.1535	7.80	69.6	4.65	542
10	.06	7.40	.300	9.38	69.3	7.40	650
5	.03	8.055	.250	7.81	62.8	13.40	490
7	.03	8.51	.260	8.13	69.0	14.75	562
10	.03	5.8	.250	7.81	45.3	9.66	354

TABLE 6

FLOTATION OF CASSITERITE BY NRE-6

(Figutes 3-6,12,13-16,22,25,26)

Synthetic ore: 98 grams sand and 2 grams cassiterite
Tin in synthetic ore: 0.032 percent
Time of run of experiments: 6 minutes
Synthetic ore size: minus 120 mesh

pH	Collector	Concentrate				Derived Data	
	Lbs. per Ton	gms.	% Tin	Enrichment	Percent Recovery	Lbs. Tin per lb. Collector	Improvement Factor
5	.2	10.235	.250	7.82	80.0	2.56	626
7	.2	8.20	.300	9.38	76.7	2.46	720
10	.2	6.315	.225	7.03	44.3	1.42	311
5	.1	9.40	.275	8.60	80.7	5.17	702
7	.1	6.875	.350	10.94	75.3	4.82	826
10	.1	6.25	.250	7,81	48.7	3.12	381
5	.06	7.435	.372	11.60	87.0	9.20	1010
7	.06	5.86	.300	9.38	55.0	5.86	515
10	.06	3.875	.300	9.38	36.3	3.87	350
5	.03	6.485	.150	4.69	30.4	6.48	143
7	.03	5.52	.200	6.25	34.5	7.38	216
10	.03	4.365	.200	6.25	27.3	5.55	171

TABLE 7

FLOTATION OF CASSITERITE BY NAP-10 AND NRE-10

In this table the effect on final concentration is shown by increasing the original percent of tin in the synthetic ore.

Time of run of experiments: 6 minutes
Synthetic ore size: minus 120 mesh

pH	Collector		% Tin in synthetic mixture	Na_2SiO_3 #/Ton	Concentrate		Percent Recovery
	Type	Lbs. per Ton			gms.	Enrichment	
5	NRE-10	.20	.10	None	8.13	11.25	91.5
7	NRE-10	.20	.10	None	8.64	11.50	99.3
5	NRE-10	.20	.953	None	41.275	1.84	76.0
7	NRE-10	.20	.953	None	34.575	2.47	85.2
5	NAP-10	.20	.10	None	4.50	18.00	81.0
7	NAP-10	.20	.10	None	7.08	14.0	99.2
5	NAP-10	.20	.953	None	29.90	1.416	42.3
7	NAP-10	.20	.953	None	38.80	2.44	94.7
5	NAP-10	.20	.953	1	11.71	2.52	29.5
7	NAP-10	.20	.953	1	18.615	2.36	44.0
7	NAP-10	.20	.953	.2	18.20	2.25	41.0
7	NAP-10	.20	.953	.5	25.44	2.52	63.7
7	NAP-10	.20	1.60	.75	16.10	4.67	75.3
7	NAP-10	.20	1.60	.75	15.70	4.72	74.2

TABLE 8

In this table, the Bolivian ore and the black ore of high percent tin is used.

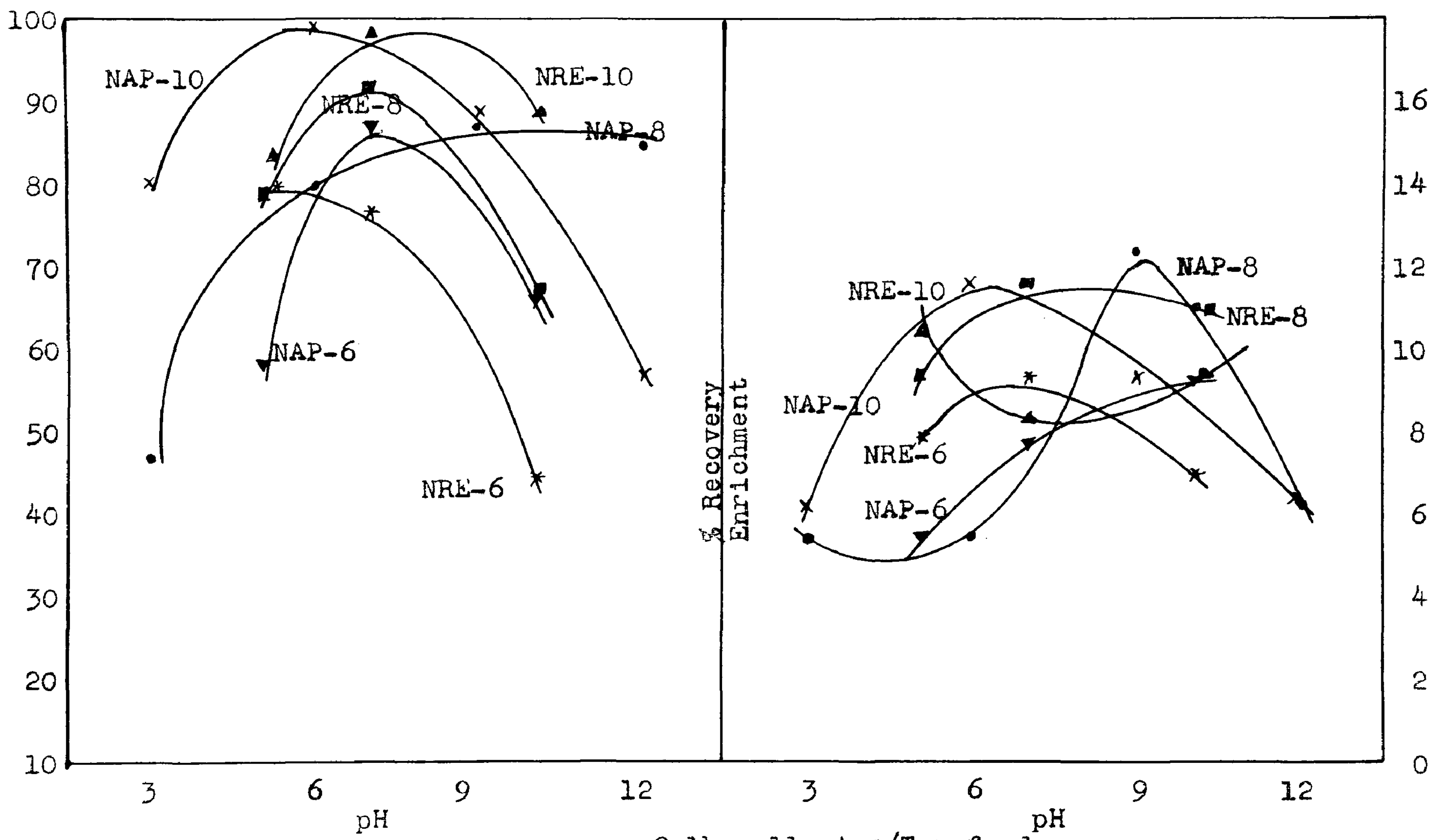
Time of ruh of experiments: 6 minutes

Synthetic ore size: minus 120 mesh

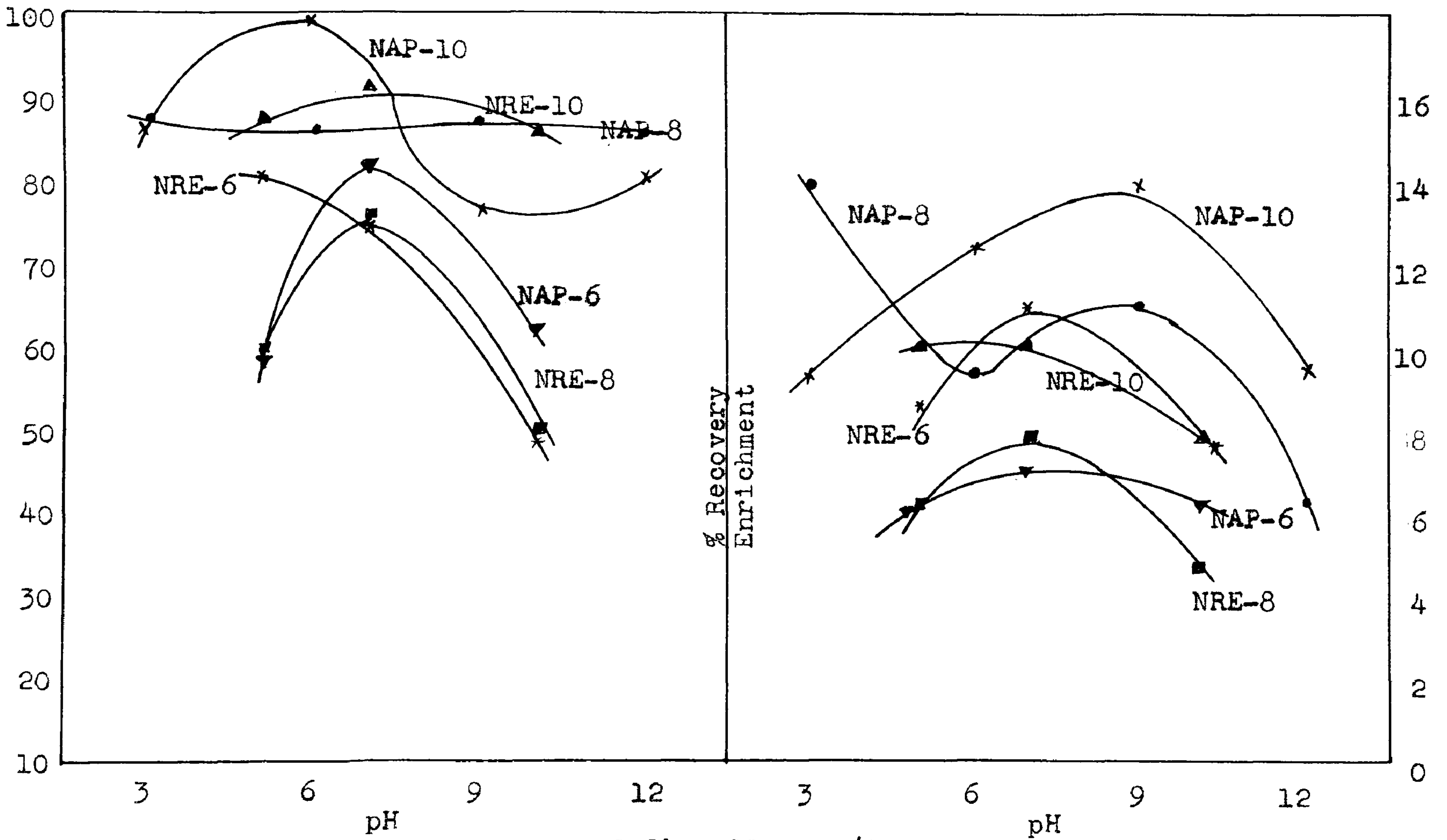
Collector used: .20 pound per ton

FLOTATION OF CASSITERITE BY NAP-10

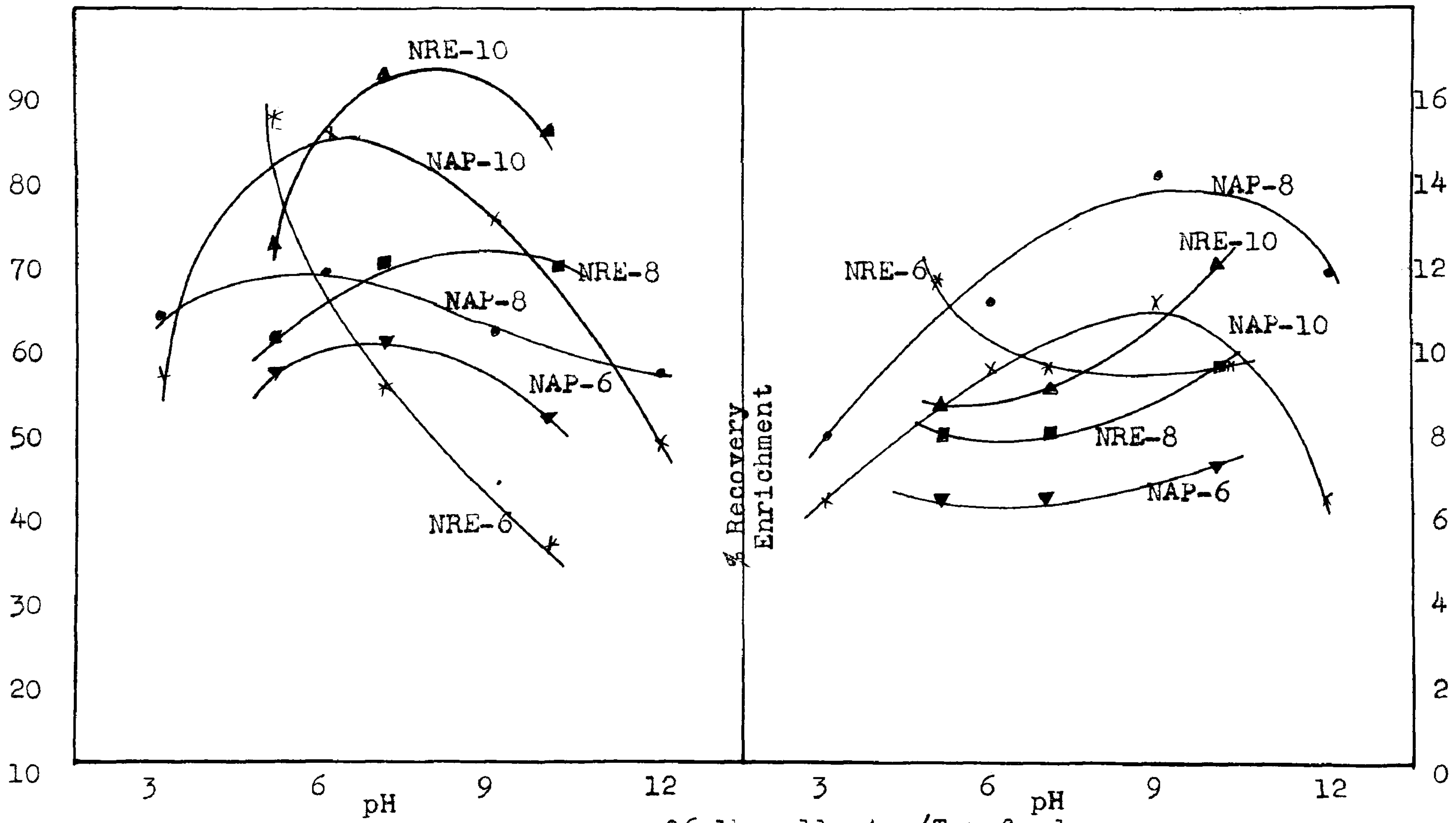
pH	Type of Ore	% Tin in mixture	Na_2SiO_3 #/Ton	Concentrate gms.	Concentrate Enrichment	Percent Recovery
5	Bolivian	.44	1	8.53	2.90	24.74
7	Bolivian	.44	1	10.10	2.40	24.24
7	Black	13.20	None	17.84	3.70	66.00
7	Black	13.20	None	16.10	4.47	73.20



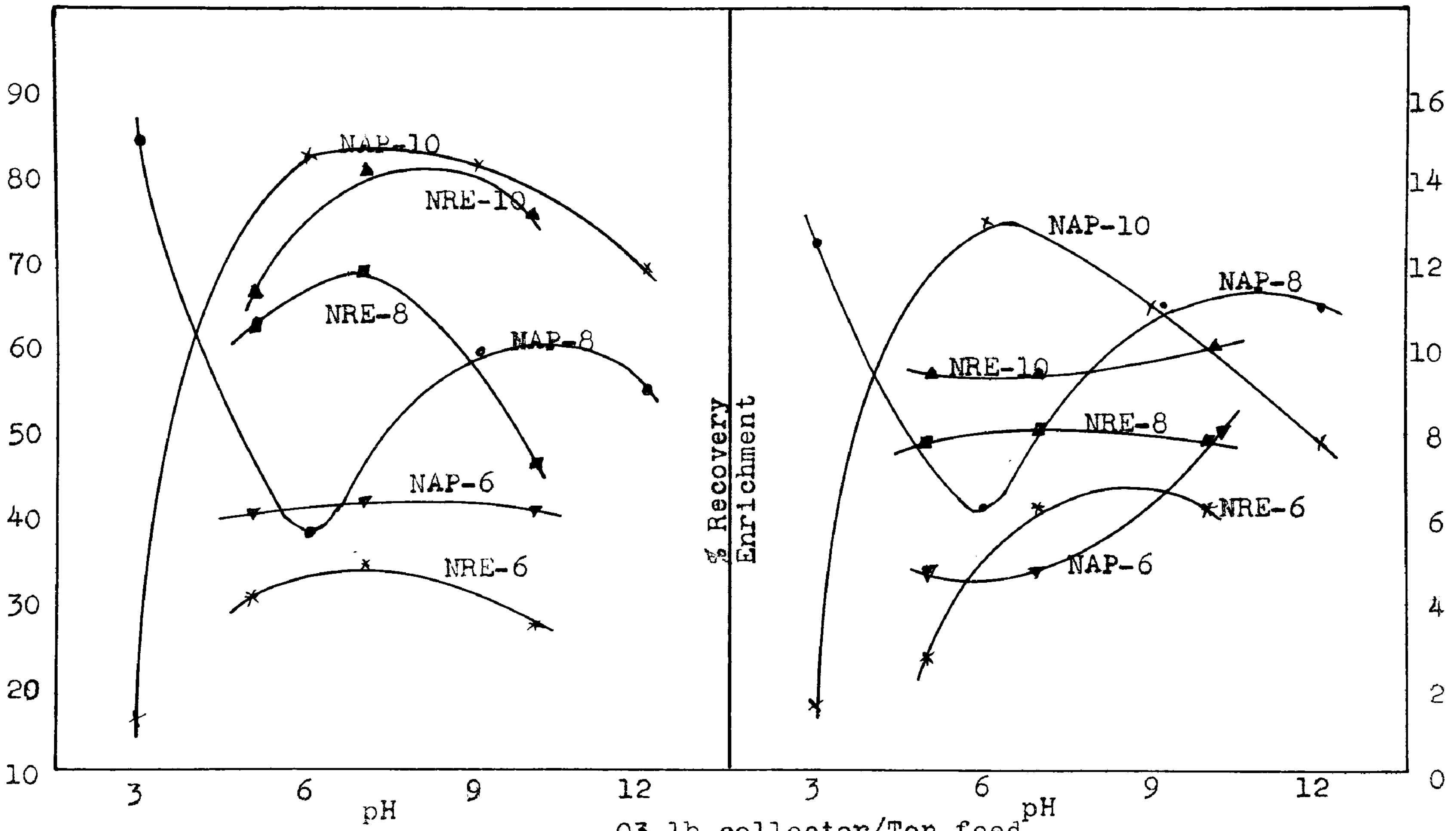
.2 lb.collector/Ton feed
Figure 3



.1 lb.collector/Ton feed
Figure 4



.06 lb. collector/Ton feed
Figure 5



.03 lb.collector/Ton feed
Figure 6

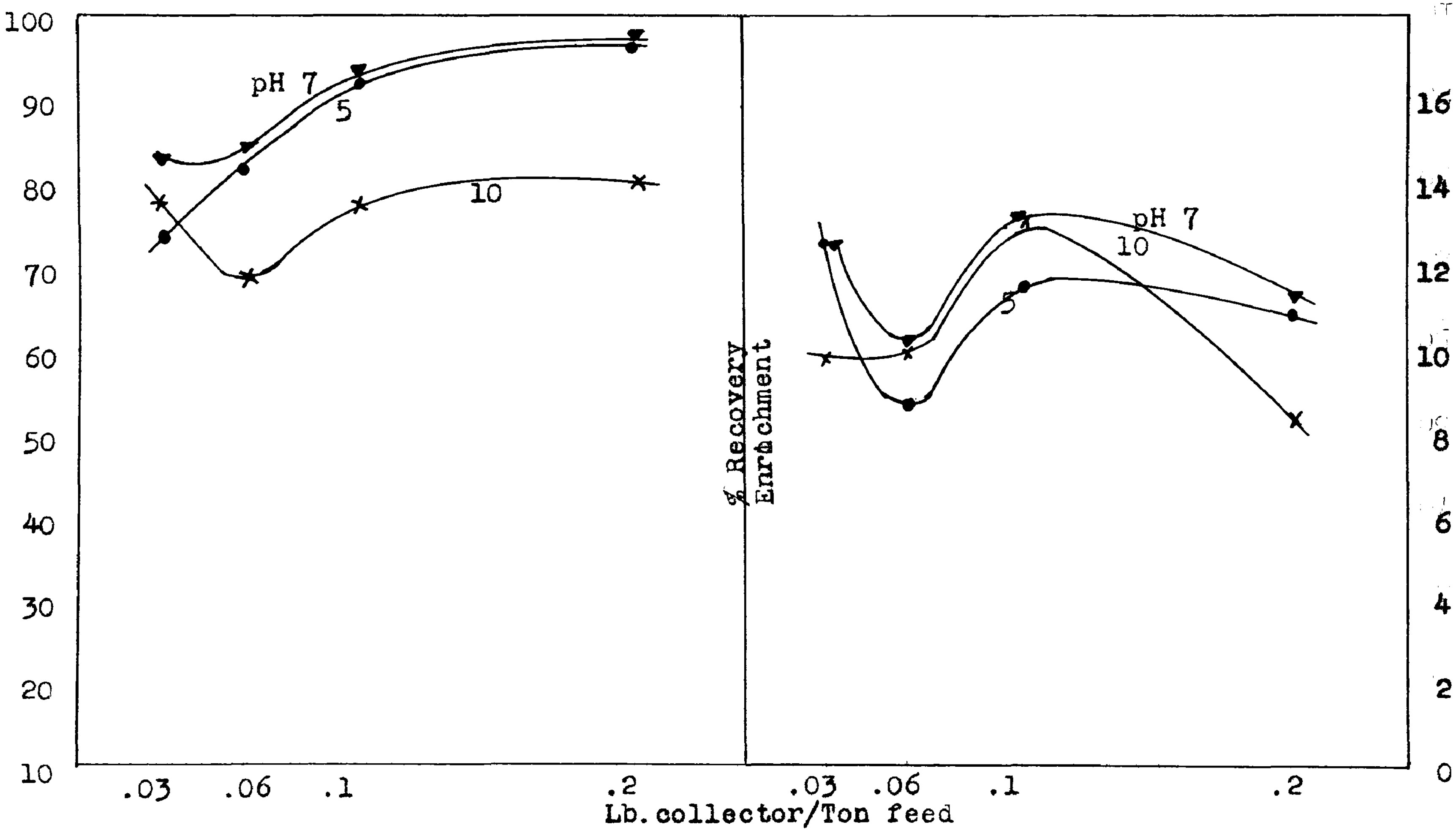


Figure 7
NAB-10

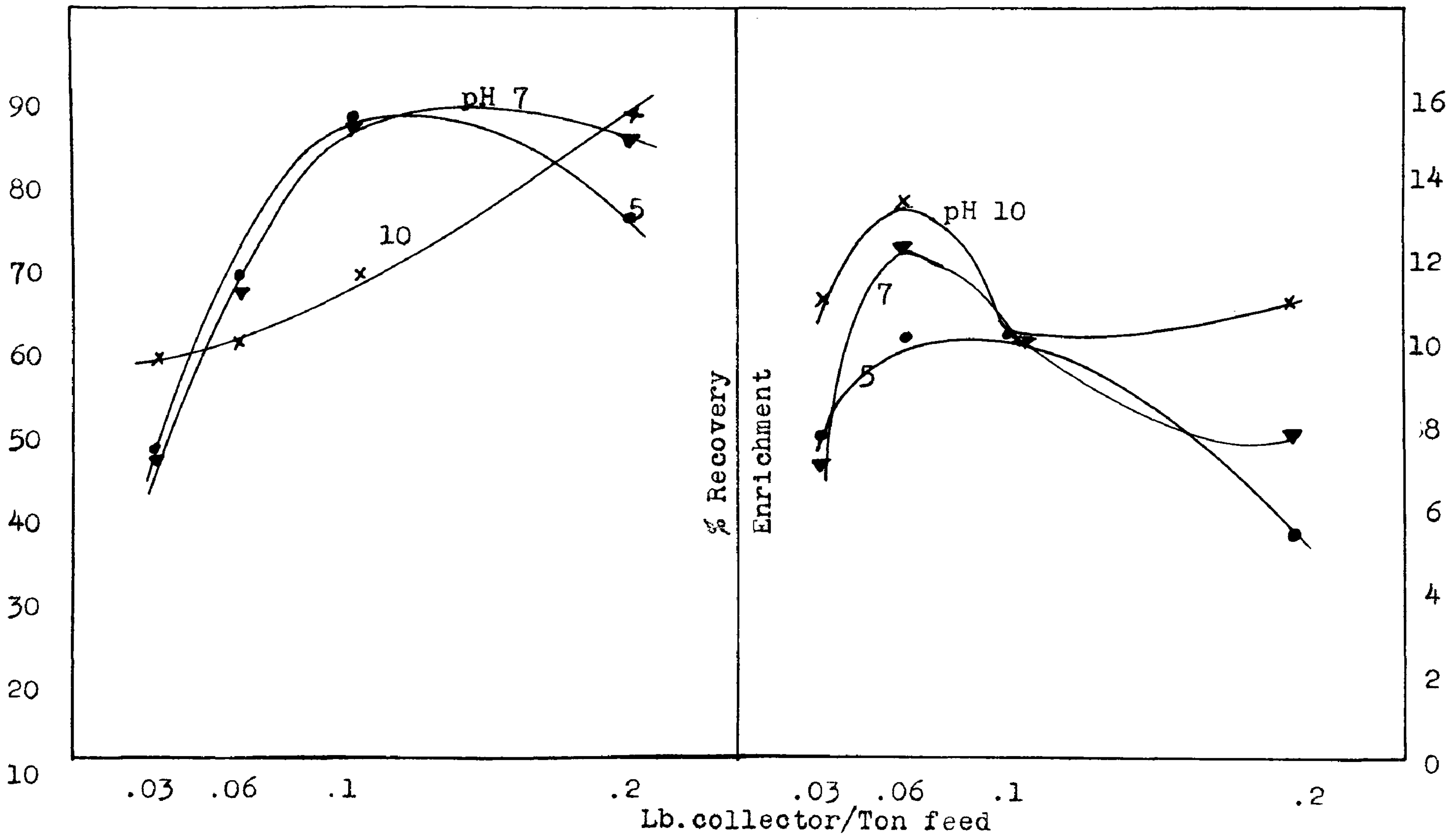


Figure 8
NAP-8

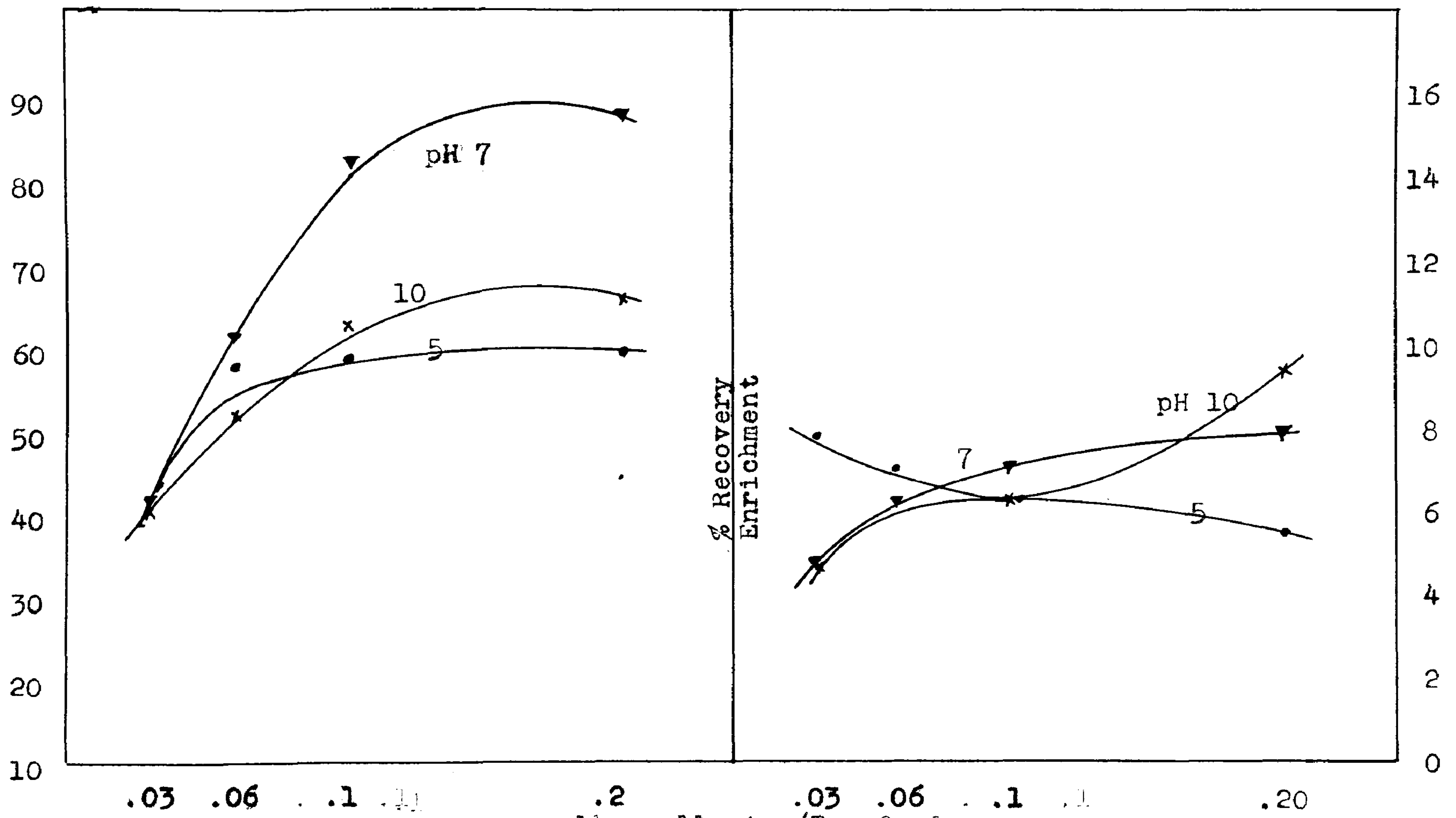


Figure 9
N AP-6

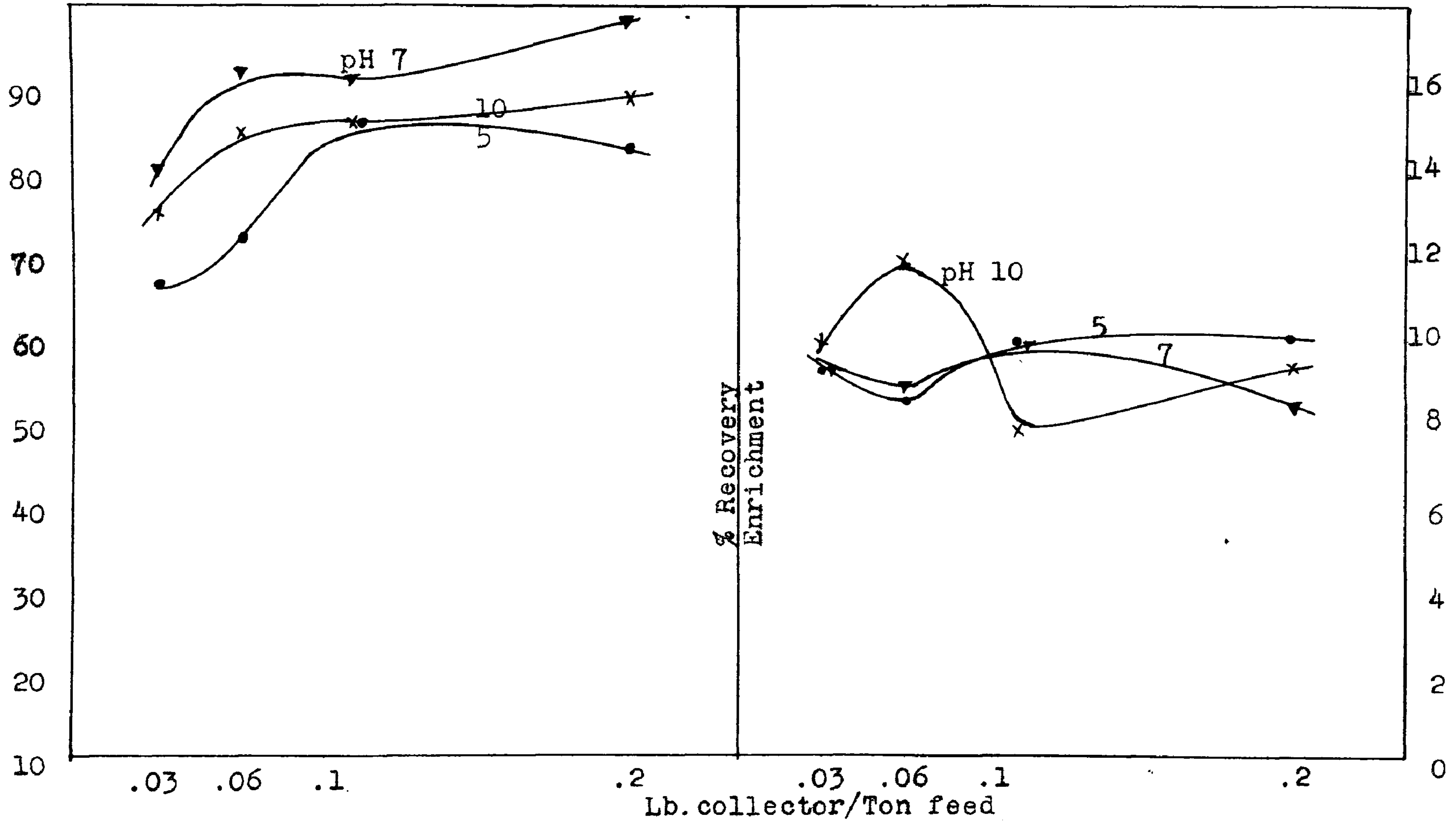


Figure 10
NRE-10

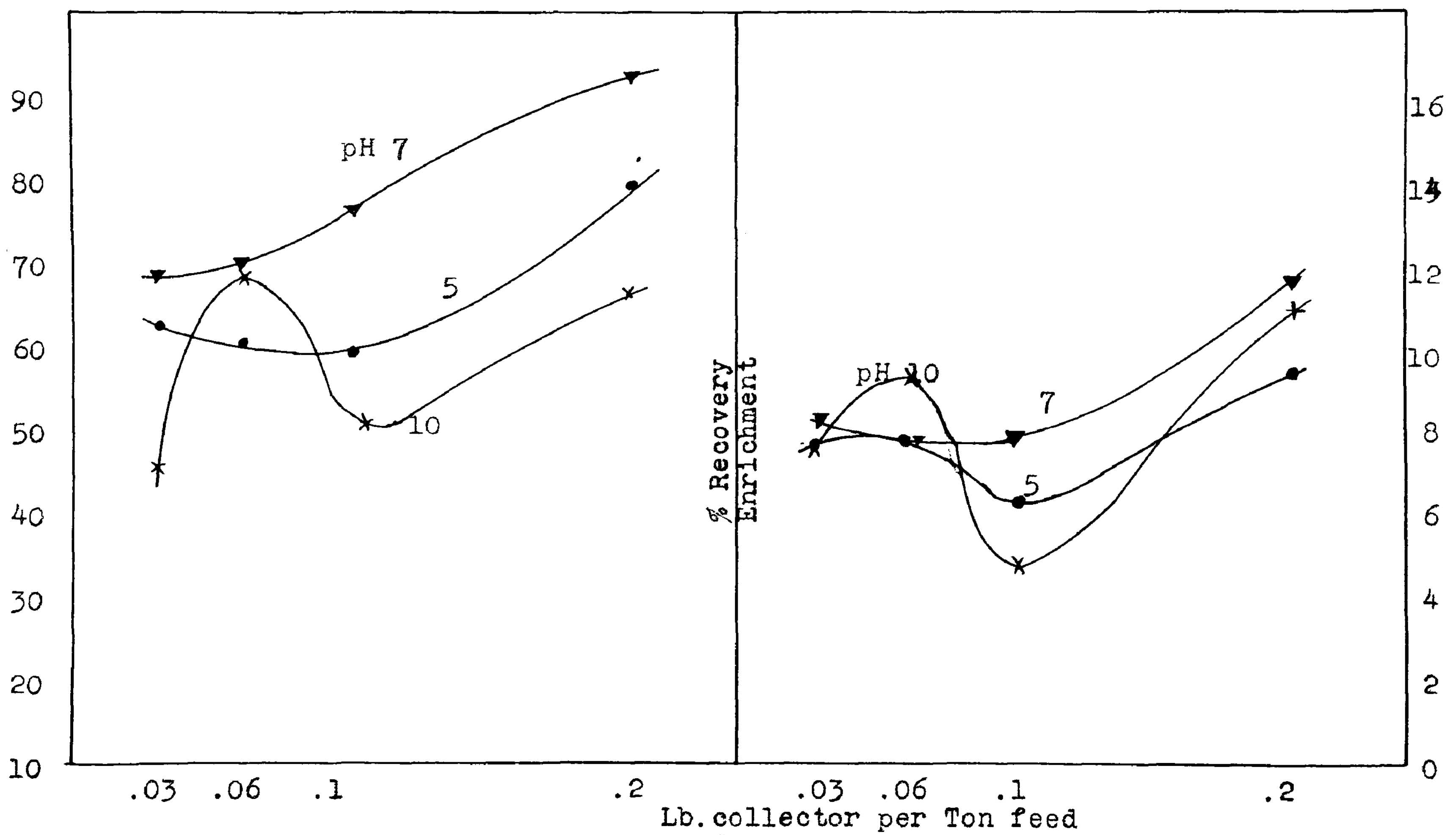


Figure 11
NRE-8

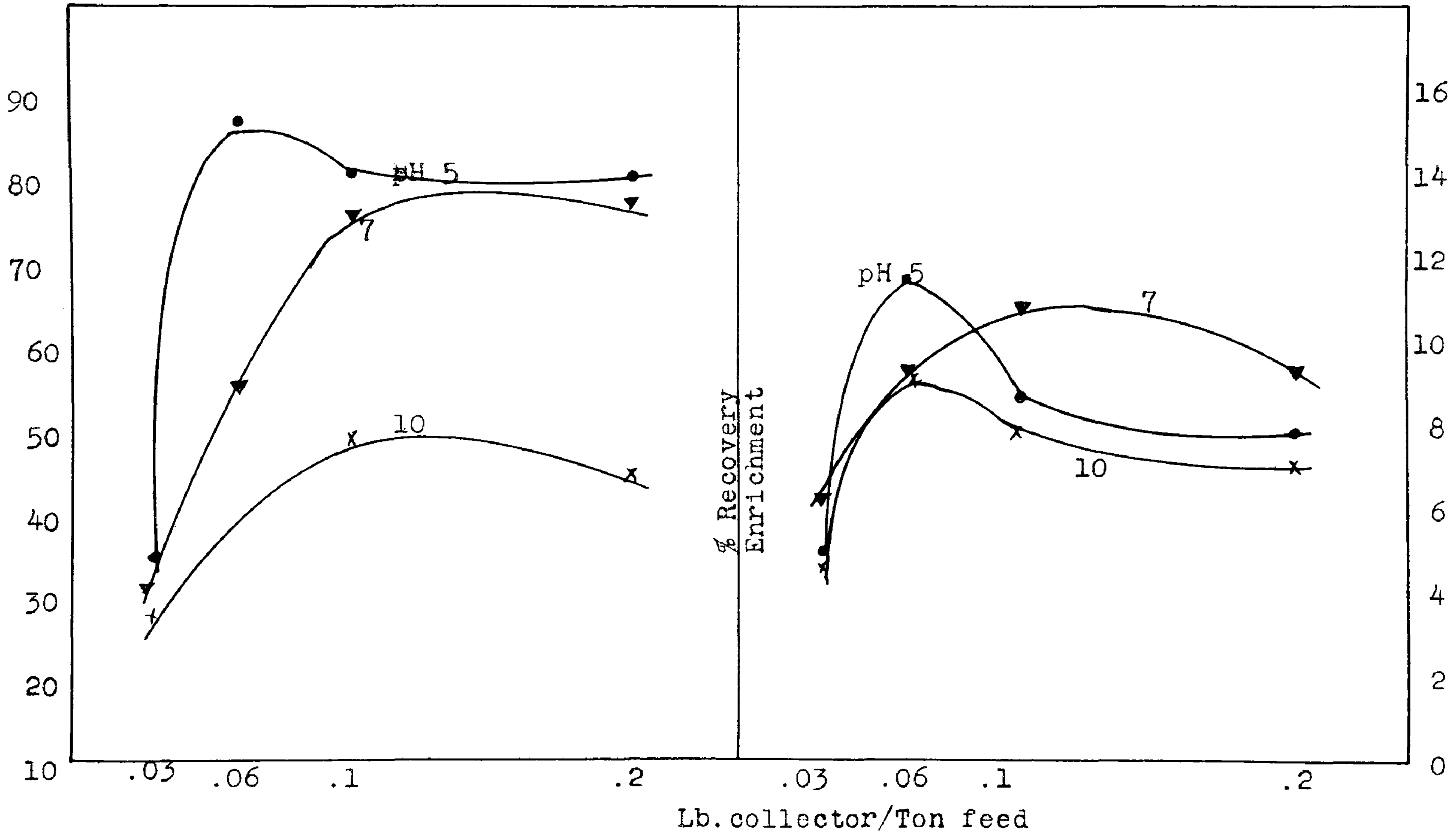


Figure 12
NRE-6

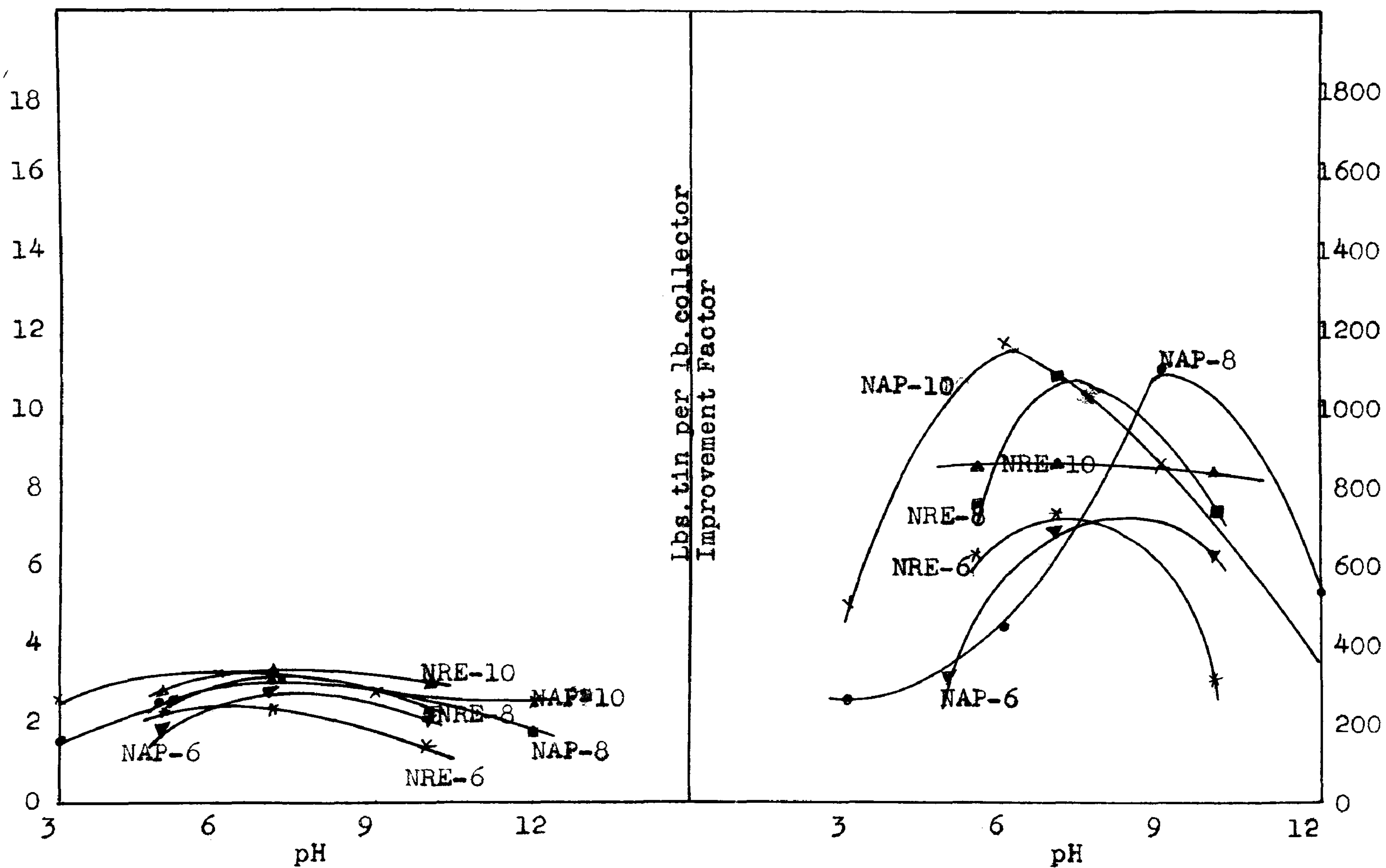


Figure 13
.2 lb. collector per ton feed

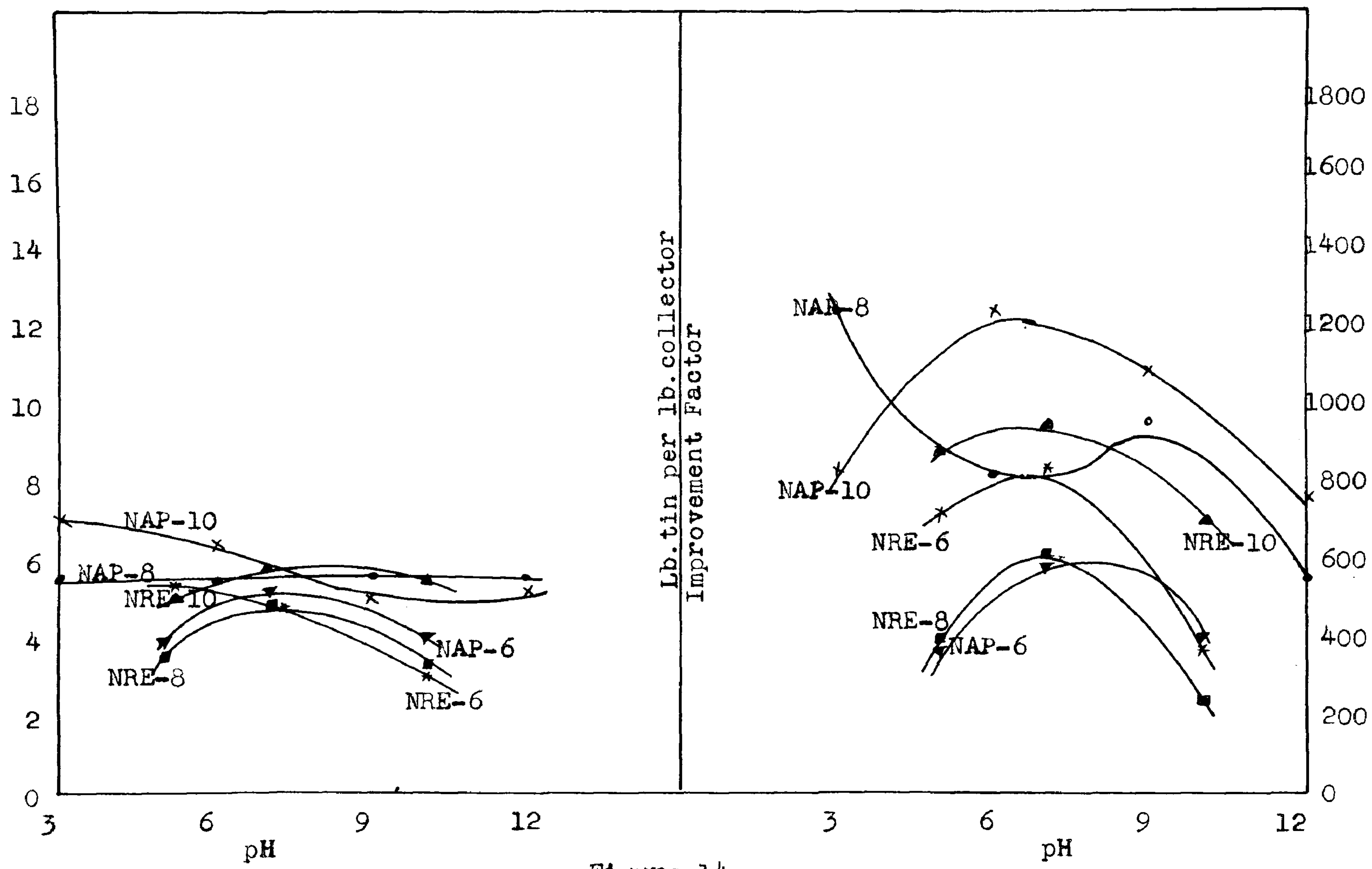


Figure 14
.1 lb.collector per ton feed

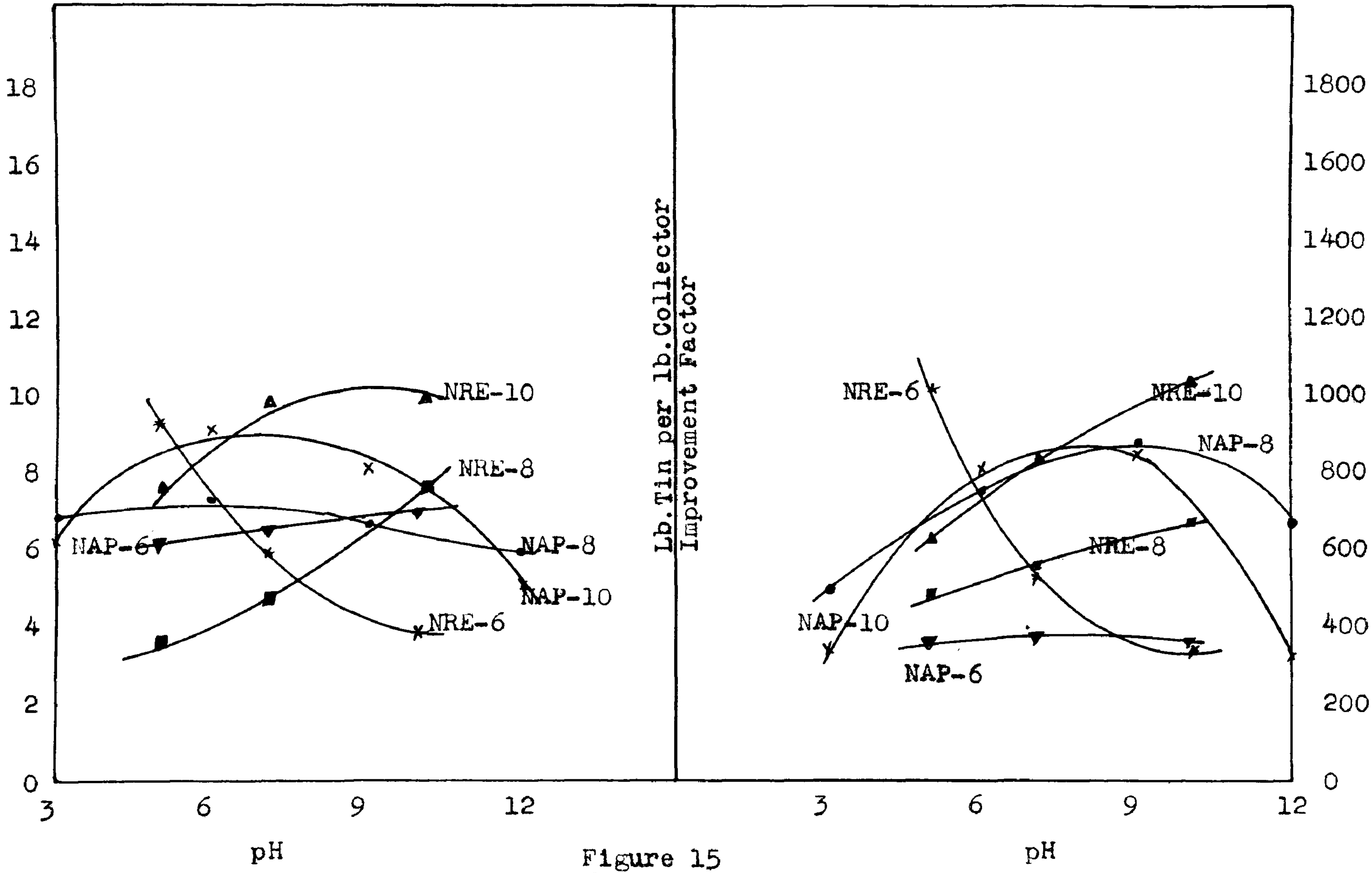


Figure 15
.06 lb.per ton feed

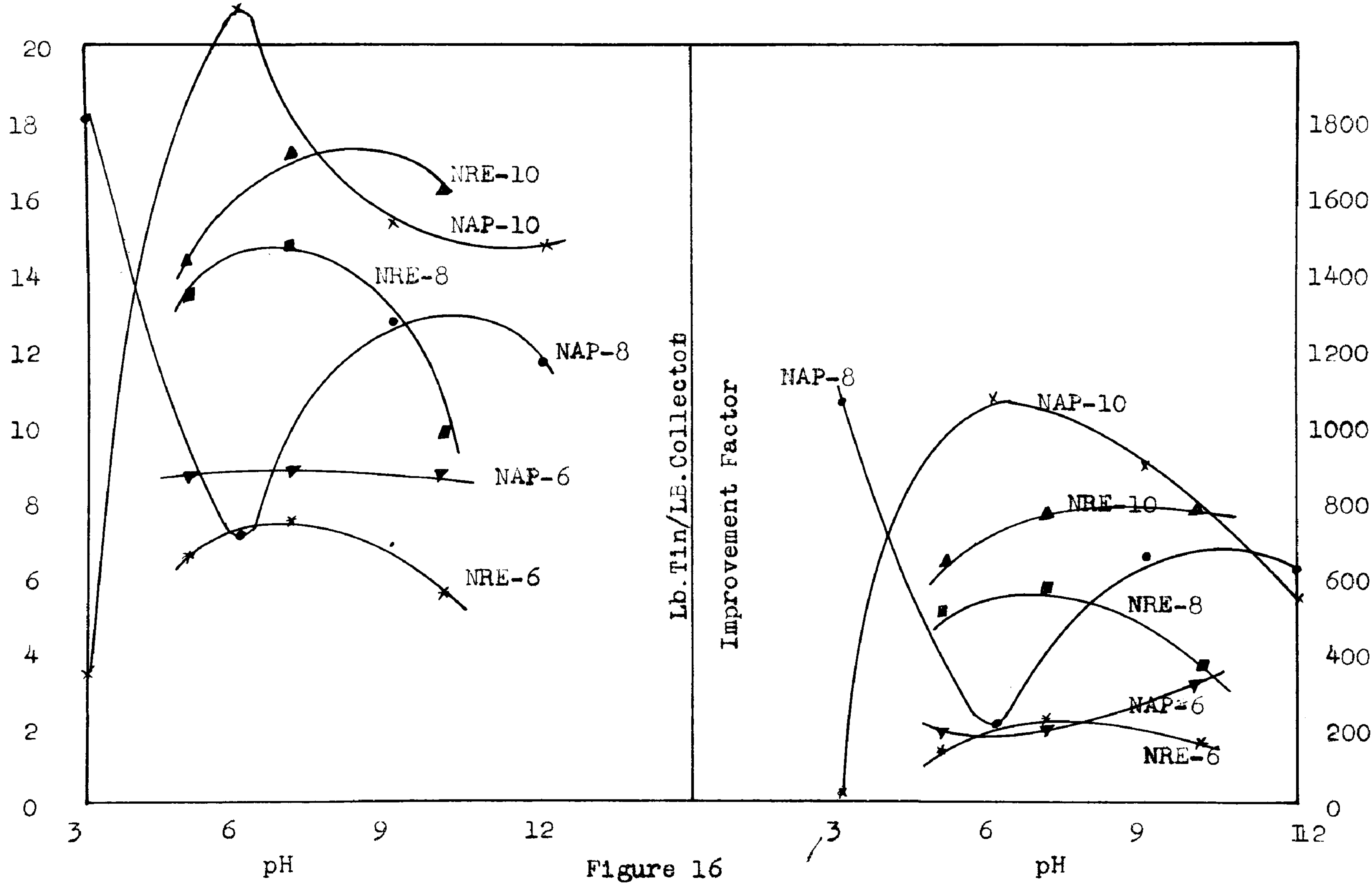


Figure 16
.03 lb.collector per ton feed

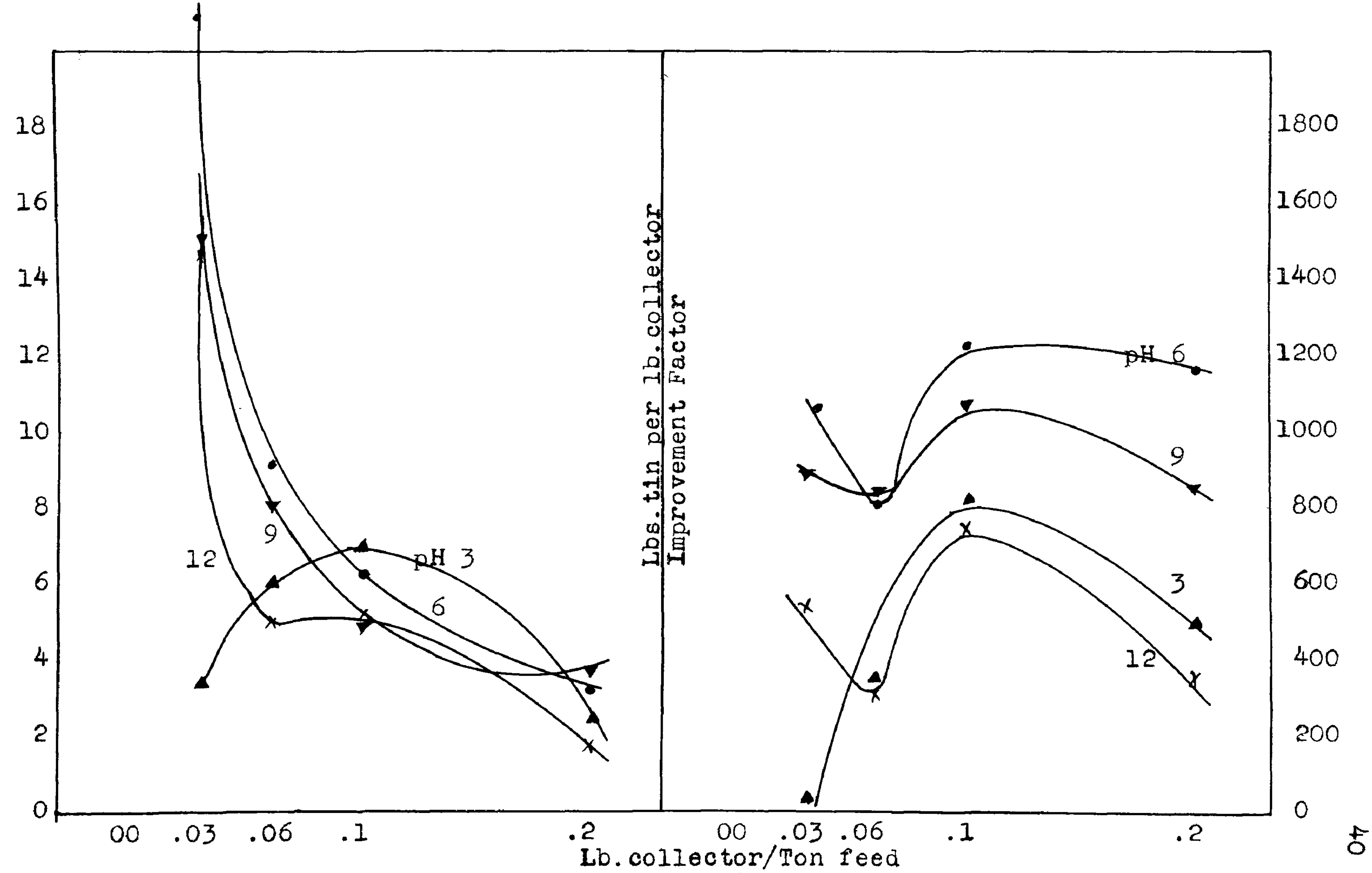


Figure 17
NAP-10

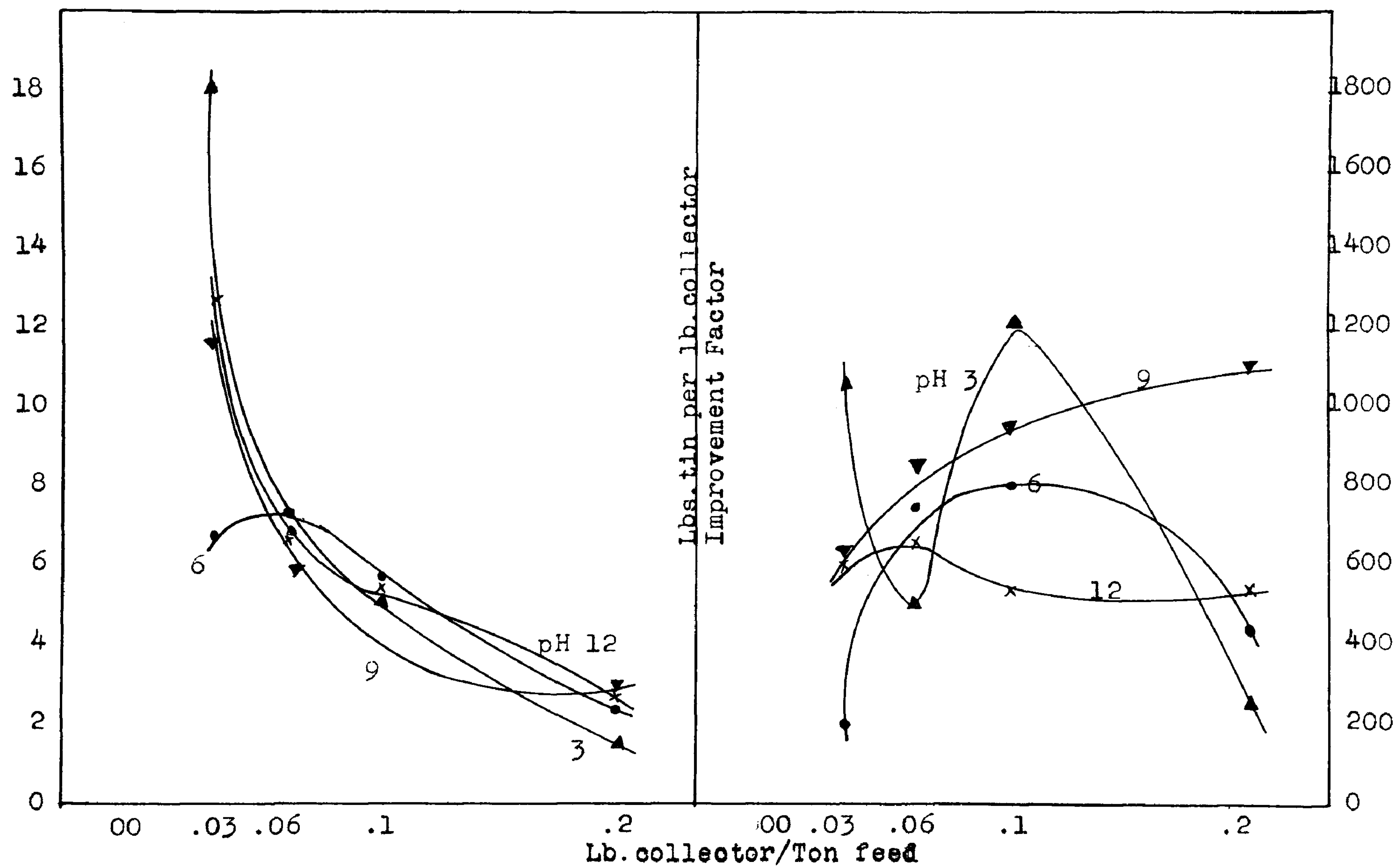


Figure 18
NAP-8

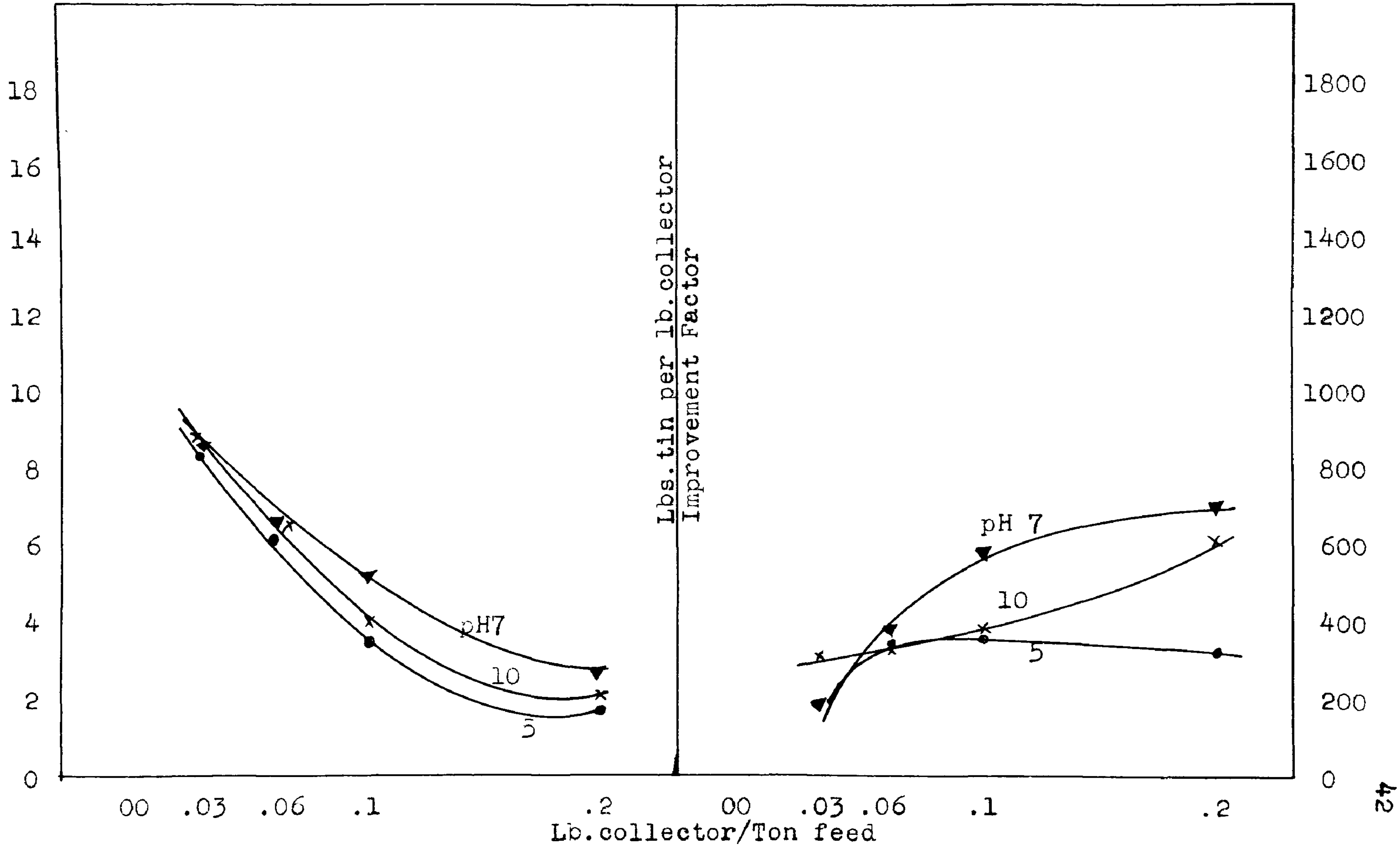


Figure 19
NAP-6

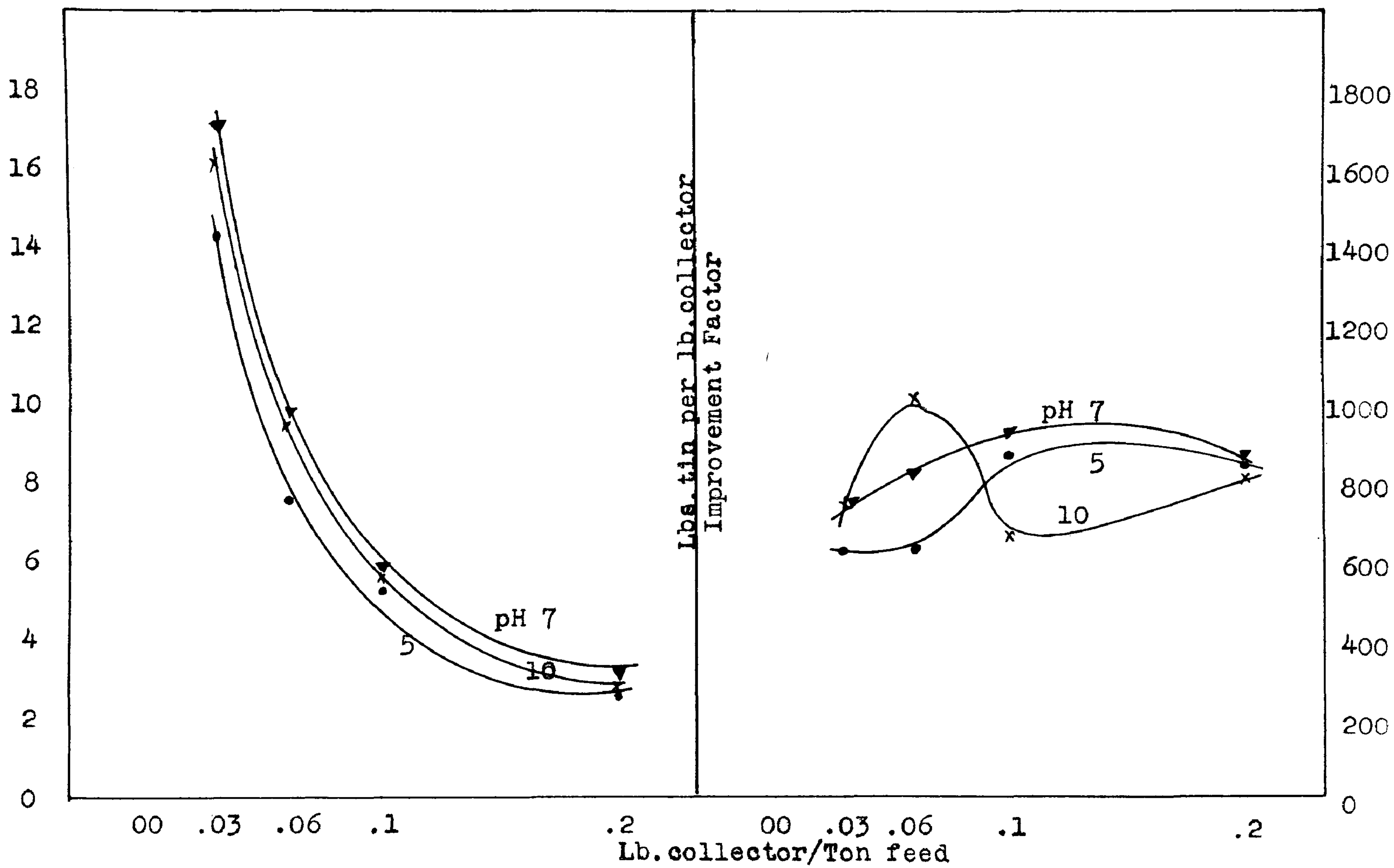


Figure 20
NRE-10

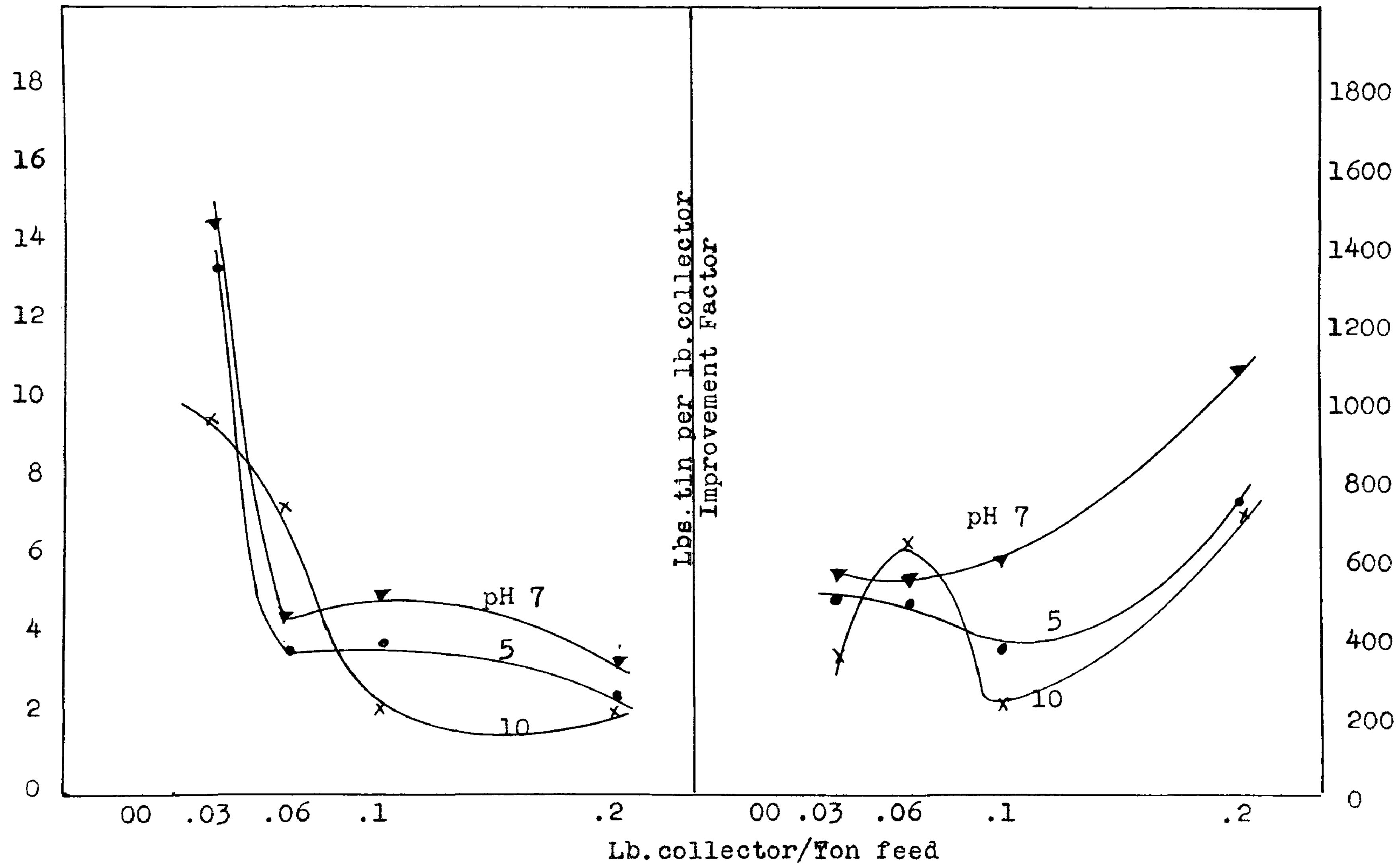


Figure 21
NRE-8

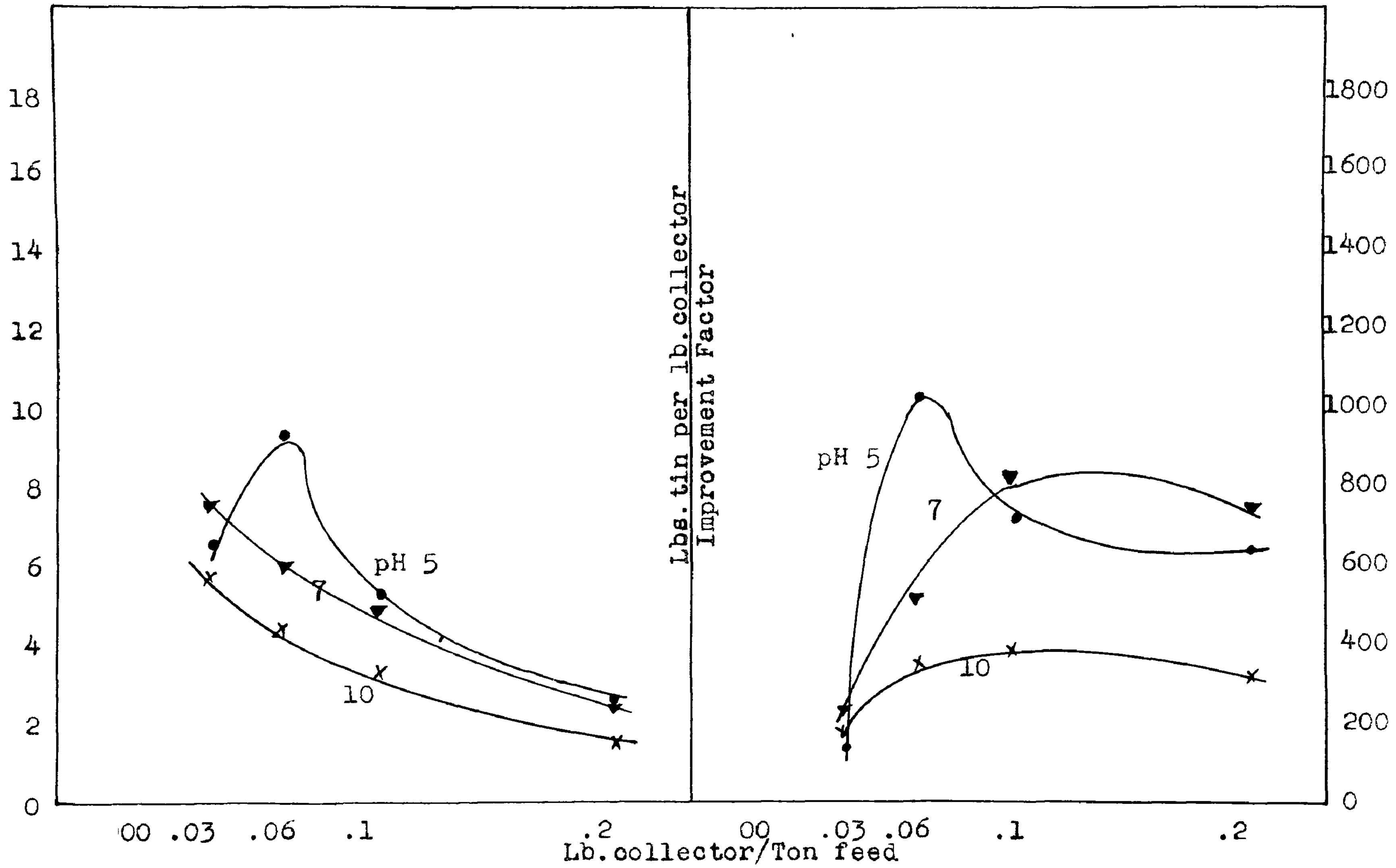


Figure 22
NRE-6

DISCUSSION OF RESULTS

Examination of Tables 1-8, and Figures 3-12 indicates that every series of tests shows good recovery and enrichment of tin dioxide from the synthetic mixture. The enrichment and recovery are due to the presence of the collector because without using the collector no enrichment or recovery was obtained. Some investigators have stated that carryover of collector from one run to another will have beneficial influence on recovery and enrichment. In this investigation care was taken to flush the flotation cell between runs so that carryover of collector and froth was avoided.

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

(1) 2 - Nitro 4 hexyl phenol - - - - - - - - - - - - - - - - - NAP-6
(2) 2 - Nitro 4 octyl phenol - - - - - - - - - - - - - - - - - NAP-8
(3) 2 - Nitro 4 decyl phenol - - - - - - - - - - - - - - - - - NAP-10
(4) 2 - Nitro hexyl resorcinol ether - - - - - - - - - - - - NRE-6
(5) 2 - Nitro octyl resorcinol ether - - - - - - - - - - - - NRE-8
(6) 2 - Nitro decyl resorcinol ether - - - - - - - - - - - - NRE-10

Percentage Recovery as a Function of pH at Varying Collector Concentrations

Nitro Alkyl Phenols: (Tables 1-3, Figures 3-6)

Several general trends are indicated. Maximum recoveries are obtained at pH 6 for the highest collector concentration, 0.20 pound per ton of feed. For lower collector concentrations, the optimum pH value was between six and seven for all collectors of this series. In practically all cases recoveries decrease by the variation of pH beyond the range of 6 to 7 pH. NAP-10 reagent gives the best results at pH6, 0.20 pounds per ton of feed.

Nitro Resorcinol Ethers: (Tables 4-6, Figures 3-6)

The best pH conditions for varying collector concentrations are the values between pH six and pH eight. Maximum percentage recoveries were obtained by using 0.20 pound per ton of collector; however, there is not too much difference between the recovery values by using 0.10 pound per ton of feed, and by using 0.20 pound per ton. NRE-10 reagent gives the best results at pH seven when 0.20 pound per ton collector is used.

Percentage Recovery as a Function of Collector Concentration at Varying pH

Nitro Alkyl Phenols: (Tables 1-3, Figures 7-9)

The majority of the curves indicate maxima at 0.20 pounds per ton. For NAP-8, at pH 5, maxima is obtained at collector concentration equal to 0.10 pounds per ton. Percent recovery in most cases runs between 80 and 100.

Chain Length: From Figures 6-8, it can be observed that increase in chain length from six carbon atoms to ten carbon atoms increases the percent recovery at constant reagent concentration.

Nitro Resorcinol Ethers: (Tables 4-6, Figures 10-12)

Maximum recovery in most of the cases is obtained at collector concentration equal to 0.20 pounds per ton. It can also be observed that increse in collector concentration increases the percentage recovery, except for NRE-8 where for pH 10, the percentage recovery drops at 0.10 pounds per ton.

Chain Length: It could also be observed from the curves that increase in chain length of the collector increases the percentage recovery. The percentage recovery is 80-100 percent in most cases.

Enrichment as a Function of pH at Varying Collector Concentrations

Nitro Alkyl Phenols: (Tables 1-3, Figures 3-6)

It is shown that variations in pH provides a maximum enrichment between pH seven and pH nine except for NAP-10, at 0.20 pound per ton and 0.03 pound per ton of feed, which shows maximum at pH six. At 0.10 pound per ton of feed, maximum appears for NAP-10, while at 0.06 pound per ton, maximum appears for NAP-8. At 0.20 pound per ton and at 0.03 pound per ton, maxima are shown by NAP-10.

Chain Length: Increased chain length has little influence on enrichment.

Nitro Resorcinol Ethers: (Tables 4-6, Figures 3-6)

Maximum enrichment is generally shown between pH six and pH nine. At 0.06 pound per ton, maximum is shown at pH ten for all collectors. The presence of maximum enrichment indicates an optimum pH for both Nitro Alkyl Phenols and Nitro Resorcinol Ethers.

Chain Length: Increased chain length has little influence on enrichment.

Enrichment as a Function of Collector Concentrations at Varying pH Values

Nitro Alkyl Phenols: (Tables 1-3, Figures 7-9)

In case of NAP-6, increase in collector concentration improves the enrichment. In case of NAP-8 increase in collector concentration up to 0.06 pound per ton increases the enrichment, but it decreases afterwards. In case of NAP-10, maximum enrichment is obtained by using 0.10 pound per ton of feed, while increase or decrease in collector concentration from 0.10 pound per ton decreases the enrichment.

Chain Length: There is a very little influence on enrichment due to chain length.

Nitro Resorcinol Ethers: (Tables 4-6, Figures 10-12)

In the case of NRE-6, enrichment increases from 0.03 pound per ton to 0.06 pound per ton, but then the enrichment decreases with increase in collector concentrations. In case of NRE-8, enrichment decreases from 0.03 pound per ton to 0.10 pound per ton, and it increases from 0.10 pound per ton to 0.20 pound per ton except at pH ten, where the enrichment increases 0.03 to 0.06 pound per ton, and then follows the NRE-8 trend. In case of NRE-10, increase in concentration from 0.03 to 0.06 pound per ton decreases the enrichment, except at pH ten, where it increases from 0.03 to 0.06 pound per ton, and then decreases. Increased collector concentration from 0.10 to 0.20 pound per ton increases the enrichment.

Chain Length: No definite influence by increased chain length.

Comparison of Corresponding Nitro Alkyl Phenols, and Nitro Resorcinol Ethers

Variation with Collector Concentration: (Tables 1-6, Figures 3-6)

In comparing variation of percentage recovery and enrichment with collector concentration, it is noted that enrichments are somewhat superior for the Nitro Alkyl Phenols as compared to Nitro Resorcinol Ethers of the same chain length. In case of recovery both are equally good.

Chain Length: Increased chain length improves the percentage recovery in both series, but there is no definite effect on enrichment.

Variation with pH:

Ph six to nine gives always good recoveries. In the case of enrichment, pH six to nine is satisfactory except for NRE-6, 8 and 10 at 0.06 pound per ton where pH ten is better. In case of NAP-6 and NAP-8 at 0.03 pound per ton higher enrichments are obtained at pH ten.

Pounds Tin Recovered Per Pound of Collector

Nitro Alkyl Phenols: (Tables 1-3, Figures 13-19)

The pounds of tin per pound of collector is a maximum at 0.03 pound collector per ton of feed. It is observed that increasing the amount of collector decreases the pounds of tin recovered per pound of collector. There is an indication that pounds of tin recovered per pound of collector is at a maximum at pH 7. It is indicated that increasing the chain length of the collector increases the pounds of tin recovered per pound of collector.

Nitro Resorcinol Ethers: (Tables 4-6, Figures 13-16, 20-22)

The pounds of tin recovered per pound of collector is maximum at 0.03 pound of collector per ton of feed. It decreases with increase in collector concentration. Increase in the chain length of the collector increases pounds of tin recovered per pound of collector. At various collector concentrations, pounds of tin per pound of collector is maximum at pH 7.

Improvement Factor

In considering this derived variable, it is arbitrarily assumed that an improvement factor of 400 would be a satisfactory flotation criterion. This corresponds to a 40 percent recovery with tenfold enrichment, or a fourfold enrichment with 100 percent recovery.

Nitro Alkyl Phenols: (Tables 1-3, Figures 13-19)

Generally improvement factor increases with increase in collector concentration. In practically all cases, improvement factor is satisfactory for pH between 6 and 9. Increase in chain length of the collector improves the improvement factor.

Nitro Resorcinol Ethers: (Tables 4-6, Figures 13-16, 20-22)

Here also, improvement factor increases with increase in collector concentration. Improvement factor is satisfactory at pH 7. The increase in the chain length of the collector increases the improvement factor.

Concentrated Synthetic Ore Tests (Tables 7-8)

In these tests only NRE-10 and NAP-10 were used, because from previous tests it was concluded that NRE-10 and NAP-10 were better than their corresponding short chained reagents. Tests were run on synthetic ore having 0.10 percent of tin, 1 percent tin and on pure ore. Collector concentration used in these tests was 0.20 pound per ton.

For NRE-10, when 0.1 percent synthetic tin ore was used, the obtained enrichment was 11.50 at pH seven, and the percent recovery was 99.3. At the same pH, when concentrated ore mixture containing 0.953 percent tin was used, enrichment obtained was 2.47 and the percent recovery was 85.2.

By using NAP-10, and 0.10 percent synthetic ore, enrichment obtained was 14.0, and percent recovery was 99.2 at pH seven. By using 0.953 percent tin ore and NAP-10 as a collector, obtained enrichment was 2.44 and recovery was 94.7 percent at pH seven.

By using pure tin ore which contained 1.60 percent tin, obtained enrichment was 4.72 and the percent recovery was 75 when sodium silicate was used as a depressant. By using sodium silicate as a depressant, enrichment was increased from 2.5 to 4.72; and the recovery was improved from 48 percent to 75 percent.

GENERAL SUMMARY AND DISCUSSION

The object of this investigation was to investigate the suitability of Nitro alkyl phenols, and Nitro alkyl resorcinol ethers as flotation collectors for cassiterite (tin oxide). It was found that these collectors are very good flotation agents. It was also found that depressing agents, such as sodium silicate, were not necessary for separation of the synthetic mixtures or for the natural ore which contained a low percentage of tin dioxide. However, with a rich ore the use of a depressant proved advantageous. The depressant used was sodium silicate, 0.20 to 1 pound per ton.

The increase in chain length of the collector increases the recovery as well as the enrichment. Maximum recovery of 99 percent, and enrichment of 14 times were obtained. The practical limit to the number of carbon atoms in a collector is the solubility of the resultant compound. Taggart[47] states that, a collector is an organic compound, either, acid, base or salt which must be soluble in water to at least a small degree. The longer the carbon chain, the less will be the solubility, therefore, in this investigation ten carbon atom straight chain was selected as the upper limit.

Generally better results for enrichments are obtained between pH 6 and pH 9 which agrees well with previous investigators.[26, 21, 6]

Increase in collector concentration does increase the recovery and enrichment. In this investigation it was found that by using longer chain length, collector concentration as low as 0.03 pound per ton was quite satisfactory, while by using shorter chain length collector concentration as high as 0.10 pound per ton was required.

The isometric three dimensional representation of this investigation is shown at the end of this thesis in a pocket; which gives better picture of this investigation.

CONCLUSION

CONCLUSION

The following conclusions are drawn from the data presented.

(1) It is shown that Nitro alkyl phenols and Nitro monoalkyl resorcinol ethers function as collectors for cassiterite in the synthetic mixture of cassiterite with silica sand.

(2) It is shown that these collectors are specific for pure and concentrated ores in presence of depressing agent like sodium silicate.

(3) It is shown that pH, collector concentration, and the length of carbon atom chain affect in varying degrees the flotation of cassiterite.

(4) Both series of the collectors are equally good, and easily prepared from commercially available raw materials.

(5) Variation of pH from six to nine gave satisfactory results in this investigation. pH seven is most desirable.

(6) Recovery as high as 99.7 percent was obtained. Enrichment as high as 14 times was obtained using synthetic mixture of cassiterite and silica sand.

APPENDIX

GENERAL DISCUSSION

The following two series of the organic compounds were prepared for this investigation:

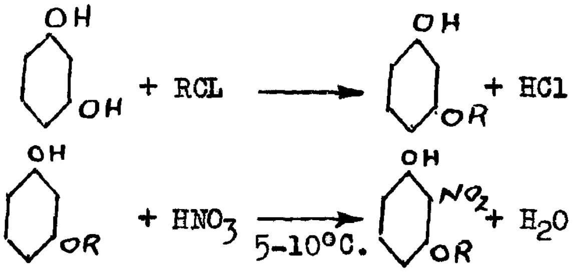
(1) 2 - Nitro 4 alkyl phenols,

(2) 2 - Nitro resorcinol ethers.

There are several methods for preparing these chemicals, but the easiest and the one which gives high recovery was selected for each series. For use as a flotation agent, a predetermined structure is desired but branch chain is not necessary.

SYNTHESIS OF 2 - NITRO RESORCINOL ETHERS

The complete reaction for preparing 2 - Nitro resorcinol ethers can be given by the following two steps:



In the above reactions R can be n-hexyl (C_6H_{13}), n-octyl (C_8H_{17}), or n-decyl ($C_{10}H_{21}$) group.

The resorcinol monoalkyl ethers were prepared according to Kharman, Ghatyas and Shternow.[30]

One mole of resorcinol (119 grams) was dissolved in 225 milliliters of absolute ethyl alcohol, in a one liter flask provided with an air tight stirrer, a reflux condenser, and a dropping funnel. One mole of n-octyl chloride (150 grams) was added and the mixture was heated to refluxing. Then one mole of potassium hydroxide (56.1 grams) in 168 milliliters of water, was added slowly over a period of about three hours. Separation was affected by a simple extraction method as discussed below.

Water was added to the cooled mixture which was placed in a separatory funnel. Then there was added 750 milliliters of diethyl ether followed by 400 milliliters of 6 N sulfuric acid to insure acid extraction. A copious précipitate of potassium sulfate was formed. The two liquid layers were separated from the funnel, and the acid layer was again extracted with 250 milliliters of diethyl ether. The combined ether extract was washed repeatedly with cold water until no reaction was given with ferric chloride solution. This was a test for the complete removal of the unreacted resorcinol. The etherial layer was extracted repeatedly with 5 percent sodium hydroxide solution. The alkaline extract was shaken with ether, the washed alkali was acidified with 50 milliliters of 6 N hydrochloric acid. The separated oil was shaken out again with pure ether. The evaporation of the ether gave about 25 milliters of heavy red oil.

Distillation of this material through a fifteen centimeter open fractionating column with an adiabatic jacket gave 20 milliliters (14.5 grams) of clear red product.

A similar procedure was used for decyl and hexyl resorcinol ethers. n-Decyl chloride, n-octyl chloride and n-hexyl chloride were prepared by the method given in organic synthesis, Coll. Vol. 1[29] for normal octyl bromides.

The following are some of the physical properties of these compounds:

No.	Compound	B.P.	Yield	Colour
1	Hexyl resorcinol ether	140-150°C (5 mm.)	21%	Light yellow
2	Decyl resorcinol ether	160-165°C (5 mm.)	16%	Red
3	Octyl resorcinol ether	155-158°C (5 mm.)	7%	Red

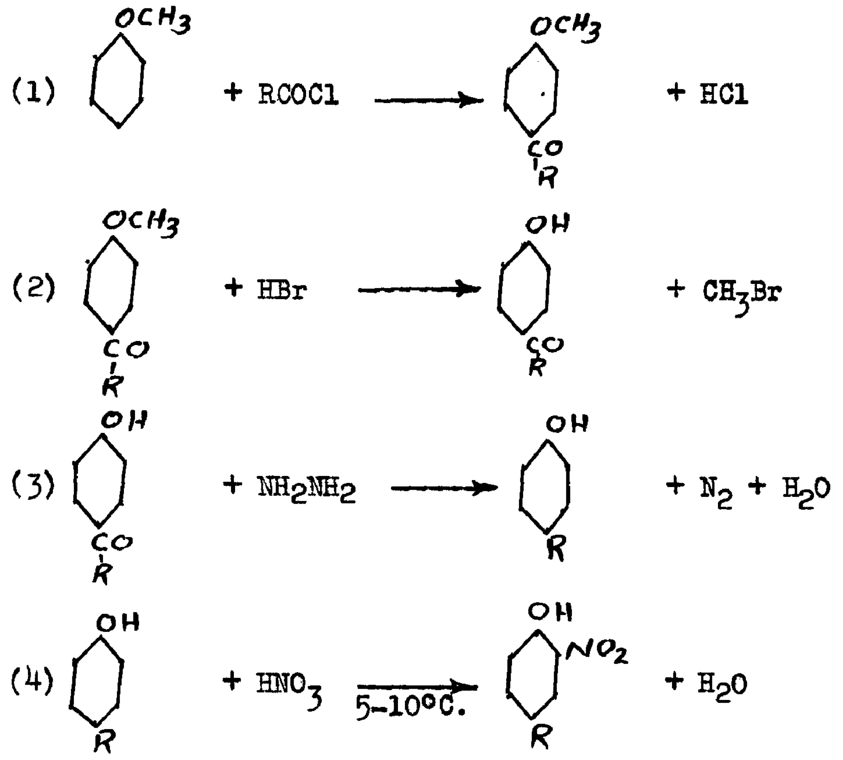
For preparing the nitro compounds from the above ethers the procedure followed was that of Cecil M. Galloway.[13]

0.17 mole of octyl resorcinol ether was dissolved in 80 milliliters of benzene; and the dissolved mixture was taken into a dropping funnel. 0.18 mole of nitric acid with 12 ml. of water was placed in a three necked flask fitted with a reflux condenser, an air tight stirrer, and a dropping funnel. The acid mixture was cooled by an external cooling down to 8°C. The mechanical stirrer was then started, and the octyl resorcinol ether solution was added dropwise from the funnel, maintaining the temperature of the mixture at 5-10°C. After completing the addition of the octyl ether from the funnel, the reaction mixture was stirred for half an hour. The reaction mixture was diluted with water and the benzene layer was separated. The bezene was separated by distillation. The residue was vacuum distilled.

The same procedure was followed for hexyl and decyl resorcinol ethers to obtain nitro compounds. The recovery in this step was as high as 80 percent.

SYNTHESIS OF 2 NITRO 4 ALKYL PHENOLS

The reactions involved are as follows:



Anisole ketone was prepared according to Fieser and Hershberg.[11] In a three necked flask fitted with a mechanical stirrer, a reflux condenser and a thermometer; one mole of anisole (108 grams), 600 milliliters of tetrachloroethane as a solvent and 1.2 moles of hexanoyl chloride (161 grams) were placed, and cooled to 5°C by an external cooling by ice salt mixture. The mechanical stirrer was started, and 1.4 moles of anhydrous aluminum chloride (187 grams) were added gradually over a period of three hours. It was allowed to stir for half an hour more, maintaining the reaction temperature 4-8°C. The red reaction mixture was allowed to stand for three days at room temperature.

The fatty acid chlorides were prepared according to the method of Armour Chemical Company.[2]

The reacting mixture after three days was poured into a four liter beaker containing hydrochloric acid and cracked ice. Brownish precipitate separated out when the mixture was allowed to stand for a few hours. The tetrachloroethane layer was separated and was extracted with 1200 milliters of diethyl ether. The ether extract was treated with concentrated sodium carbonate solution. The ether extract was distilled to boil off the ether, tetrachloroethane and unreacted anisole. The residue was treated with hydrobromic acid[31b] as follows:

In a three necked flask fitted with a stirrer, a reflux condenser and a thermometer, the above residue was taken and to this was added one mole of 48 percent hydrobromic acid. The mixture was allowed to reflux by external heating, and stirring begun. The reaction was allowed to go for three hours. Next day, the excess hydrobromic acid was removed, and the residue subjected to the Wolfe-Kishner reduction.[36]

In a three liter, three-necked flask, the above residue was placed with 1500 milliliters of diethylene glycol; 190 grams of potassium hydroxide and 130 milliliters of 85 percent hydrazine hydrate. A thermometer, a mechanical stirrer and a take off condenser were joined to the flask. The mixture was allowed to reflux for one and one half hours and then the water was drained off, by the take-off condenser until the temperature of the reaction mixture reached 195°C. Then it was allowed to reflux for four hours longer, and allowed to stand overnight.

The above reaction mixture was acidified by adding concentrated hydrochloric acid and extracted with 2000 milliliters of benzene. The benzene was evaporated out, and the residue was vacuum distilled.

The same procedure was followed for preparing 4 octyl phenol and 4 decyl phenol. The boiling points of these alkyl phenols are given below.

No.	Compound	B.P.	Pressure
1	4 hexyl phenol	118-122°C	4-5 mm.
2	4 octyl phenol	130-140°C	6-8 mm.
3	4 decyl phenol	146-150°C	6-8 mm.

The nitration of these compounds was carried out according to Cecil M. Galloway[13], as described for resorcinol ethers. The physical properties of the nitro compounds are as follows:

No.	Compound	B.P.	Pressure	Yield
1	2 Nitro 4 hexyl phenol	142-46°C	15 mm.	50%
2	2 Nitro 4 octyl phenol	152-55°C	15 mm.	55%
3	2 Nitro 4 decyl phenol	160-62°C	15 mm.	52%

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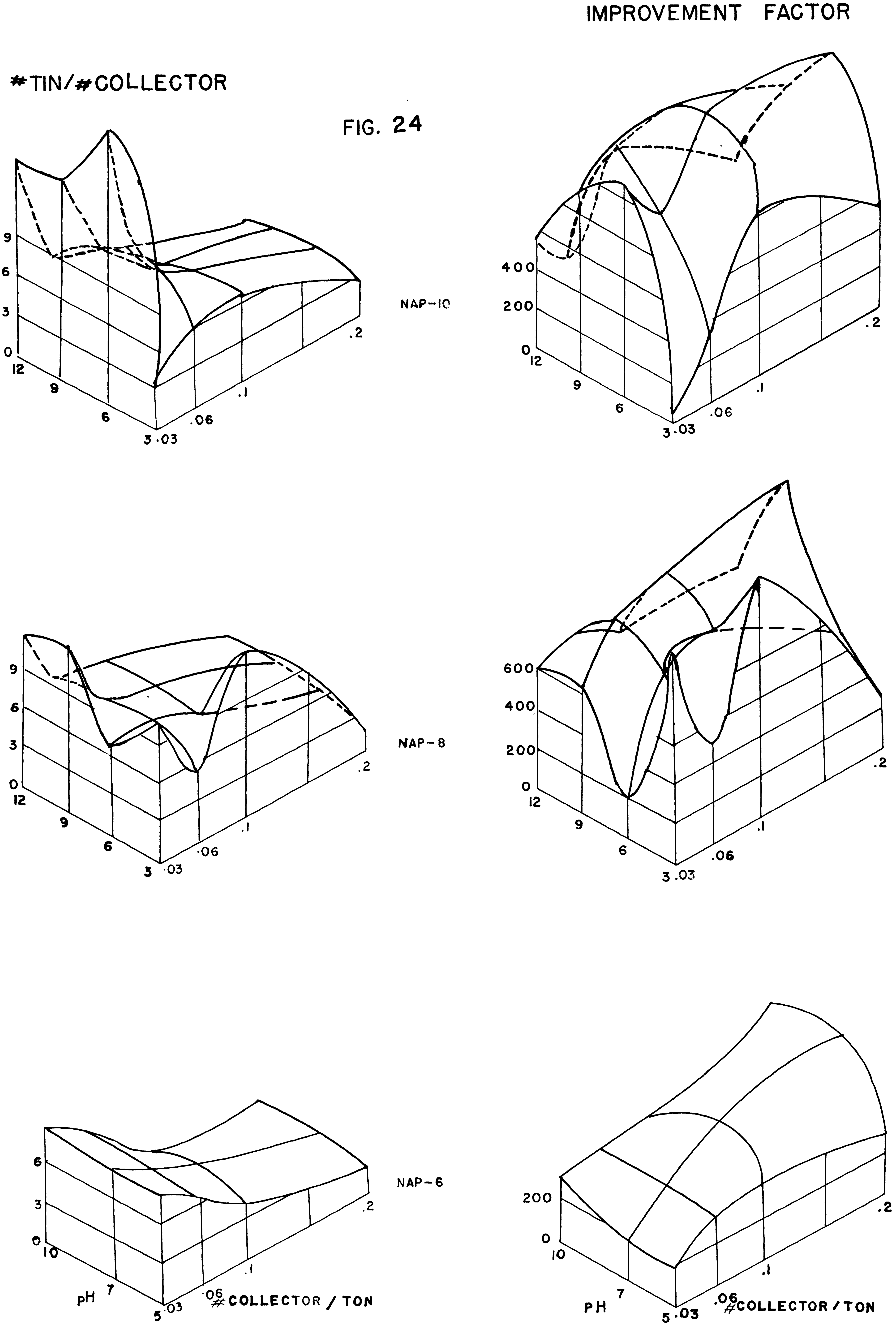
FIG. 24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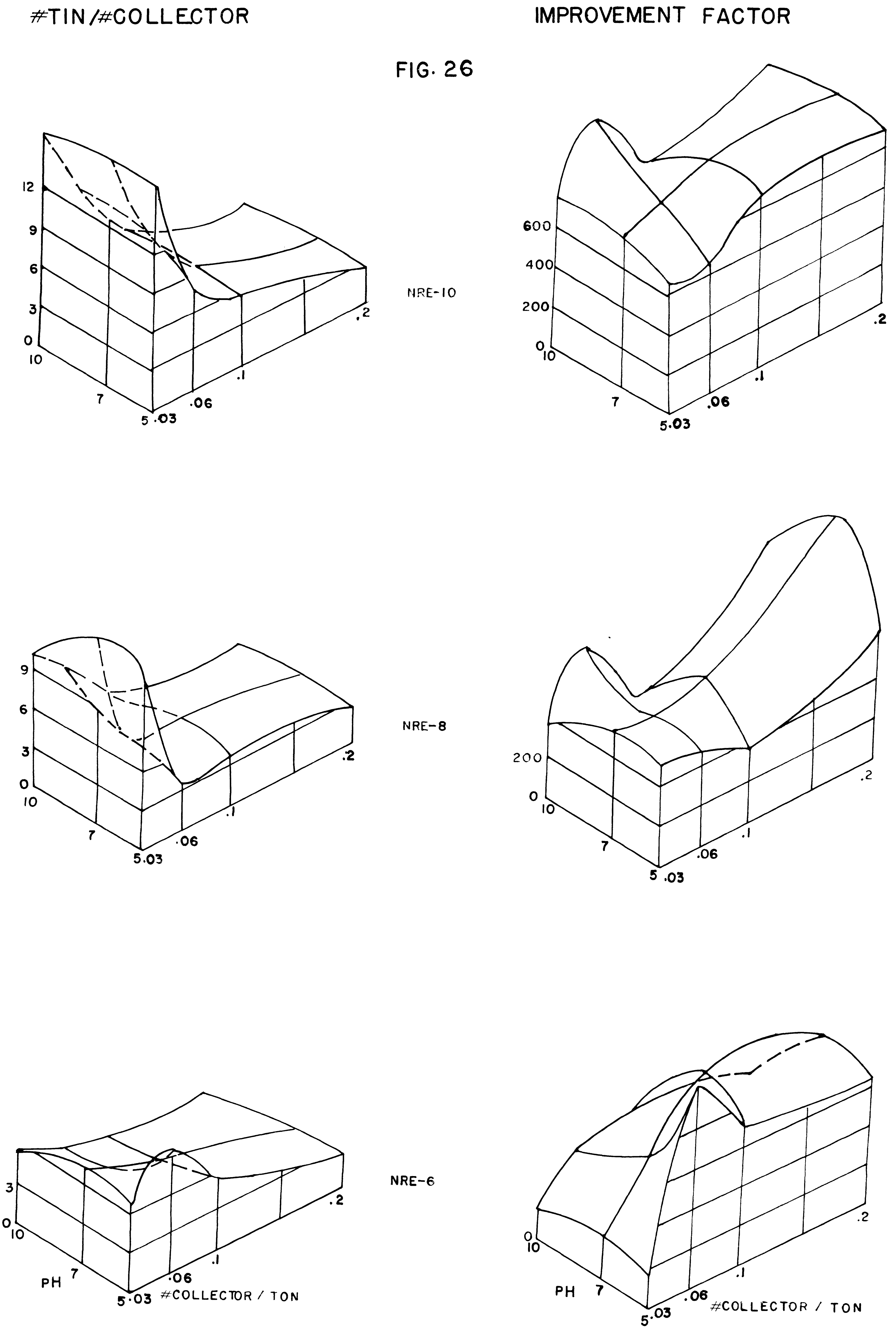

FIG. 26

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FIG. 25

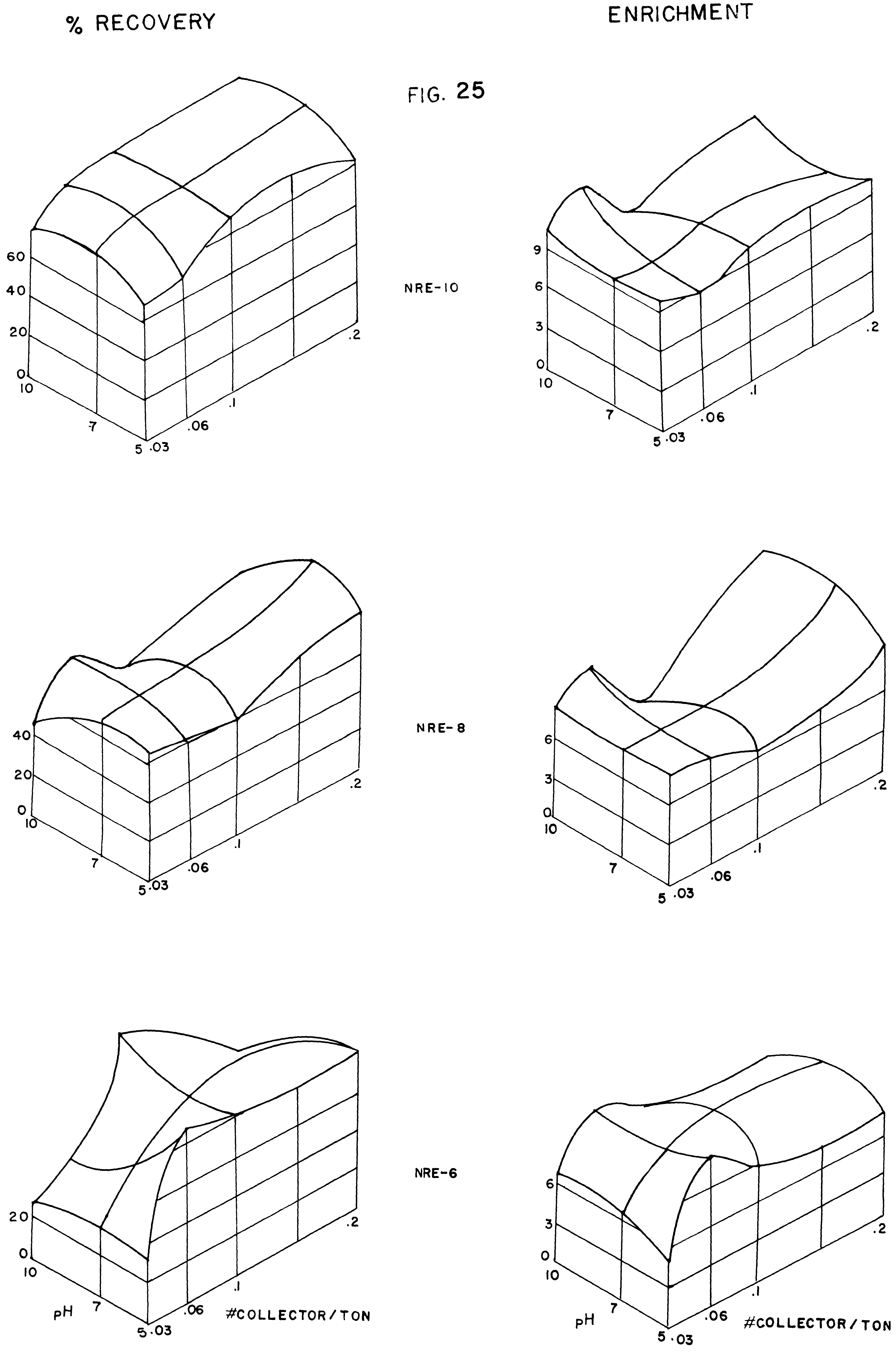
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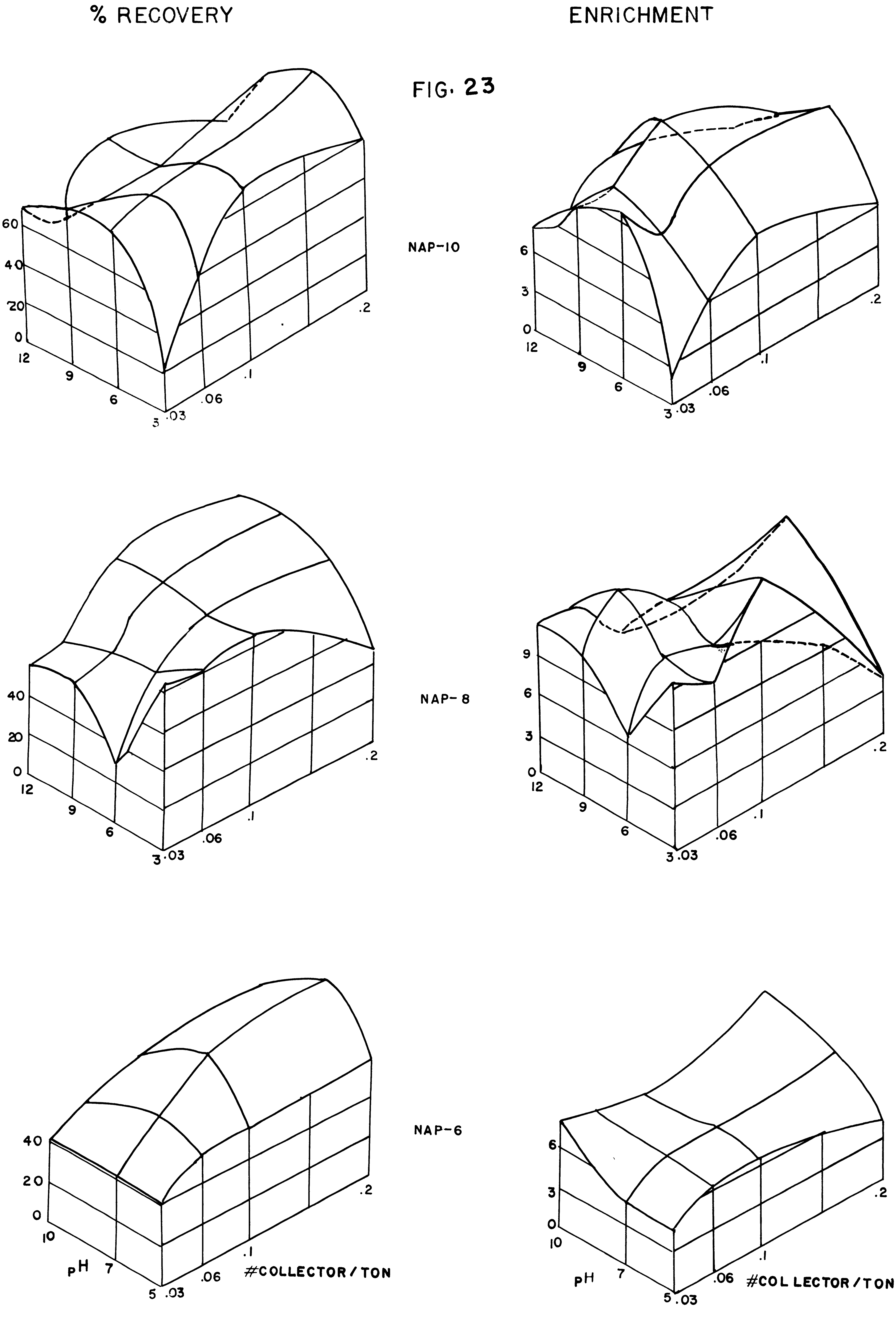
FIG. 23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