ADSORPTION OF FATTY ACID AND FUEL OIL ON IRON-TITANIUM MINERALS

Thesis
Submitted for the degree
of
Doctor of Philosophy
of
The University of London

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M. B. E. Lapidot

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ABSTRACT

An analytical procedure was developed for the determination of the concentration of fatty acid and fuel oil adsorbed on iron-titanium mineral. The oils were desorbed by means of a 5N sulphuric acid solution in 40% ethanol and extracted into pure iso-octane. The fatty acid was saponified by N/50 NaOH in 40% ethanol and determined in 60% ethanol by potentiometric titration with aqueous HCl. The fuel oil was determined by optical density measurements at 224 mμ.

An electrical test assembly, based on the d.c. shunt wound motor with separate excitation, was developed for control of the conditioning process at high pulp density and for measurement of the nett power consumption in the conditioning tank.

The flotation results were found to be correlated to the pattern of the power consumption variation during conditioning and to the concentrations of the fatty acid and the fuel oil in the flotation products. These correlations have disclosed the sorption processes taking place during conditioning.

The reagents were gradually adsorbed and then randomly distributed on the ore particles during a brief period of bulk flocculation. At the flocculation peak, the power consumption was at a maximum, and maximum per cent weight rougher

concentrate was obtained at practically no flotation selectivity. A "quasi-continuous" oil film on the surface of the particles, analogous to the oil film in "water-in-oil" emulsions, permitted rapid re-distribution of the reagents from gangue to values. The reagents were then desorbed from the gangue particles during a period of bulk deflocculation, at the end of which initial power consumption levels were regained, and maximum ilmenite recovery was obtained at maximum flotation selectivity. Further conditioning resulted in desorption of the reagents from the ilmenite particles as well. The initial fatty acid/fuel oil ratio was always maintained in the rougher concentrate.

These flotation results were determined by the pattern of the power consumption variation and not by the energy consumption during conditioning, by the impeller speed used, or by the conditioning time; the latter three factors were, however, interdependent in the shaping of the pattern mentioned.

The influence of different additional factors on the reagent sorption processes, in relation to the power consumption pattern, was also studied. These factors were: the fatty acid/fuel oil ratio, other neutral hydrocarbons, the addition of sulphuric acid, the addition of ferric chloride, and the addition of the initially removed slimes.

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Two papers on industrial flotation of ilmenite were presented at the International Mineral Processing Congress in London (April, 1960). Runolinna (1) described a technique applied to this process, which involved long conditioning time at high pulp density without desliming. The conditioning caused a flocculation of the mineral and a dispersion of the gangue, resulting in selective flotation. It was considered that fuel oil played an essential part, both in flocculating ilmenite on the oil droplets and in removing the soap film formed on the gangue in the initial stages.

Eidsmo (2) described the technique used for flotation of the Tellnes ilmenite, which also involved conditioning at high pulp density with desliming. In this process however the fuel oil was claimed to be a froth modifier only. In addition it was found necessary to recondition the pulp at 70% solids between each cleaning step.

Many interesting points were raised in the discussion following these papers, referring especially to the phenomenon of the selective flocculation of ilmenite grain and to the rather doubtful analytical results of the reagent contents in the rougher concentrates and tailings. The relative importance of tall oil and fuel oil in the ilmenite flotation was still open to question.

Additional data was presented in the above mentioned discussion to illustrate the different phenomena observed in the flotation conditioning of metal oxides with fatty acids and other organic acids combined with hydrocarbons such as fuel oil and kerosene.

In a paper by Kun Li (5) on laboratory flotation of iron ore similar question were raised in connection with the phenomena occuring during conditioning and flotation of such ores. An overall mechanism of reversible reagent transfer between ore and silica particles was postulated. It was suggested that the process involved in the conditioning of iron ore began with all solids completely floatable, and ended up with only ore particles floatable and silica particles non-floatable. It was claimed that this was contrary to what was generally believed to take place.

Many questions were raised in the following discussion in connection with the phenomena observed and especially in connection with the effects of slimes and of acid on the flotation results and the effects of energy input during conditioning on these results.

The process of Tellnes ilmenite flotation had been modified in 1960. The new flowsheet (4) involved conditioning of the crude ilmenite at 70% solids and at pH 6.5 with a 3:2 tall oil/fuel oil mixture, followed by flotation at 6.5. The rougher concentrate containing all the ilmenite and part of the gangue was reconditioned at pH 5.5 and refloated at the same pH. This reconditioning in the cleaner flotation process was repeated twice more at the respective pH values of 4.5 and 3.5, resulting in a final concentrate containing ilmenite and part of the pyrite. The latter was floated at pH 1 together with a major part of the adsorbed reagents, leaving a clean ilmenite as tailing.

The complexity of this process and the many questions raised in the above mentioned discussions have suggested an investigation of the phenomena occuring during conditioning and flotation of metal oxides with fatty acids and fuel oil. In this study it was decided to establish the correlation between the flotation results and the sorption of the two reagents on the values and gangue particles as well as with the power consumption during conditioning. High accuracy in the experimental approach was emphasized.

The system chosen consisted of an iron-titanium mineral - the Tellnes ilmenite - and as reagents - oleic acid or tall oil in mixture with fuel oil.

To make possible the desired correlation it was necessary to develop two experimental tools :

a. an analytical method permitting accurate assay of the reagent contents of the flotation products, and

b. an electrical power assembly permitting sensitive and accurate control of the impeller speed, accurate determination of the net power consumption in the conditioning tank, and highly sensitive reaction to small changes in the power consumption due to reagent adsorption or desorption processes.

The development of the analytical methods follows in part 1. The development of the electrical power assembly and the actual conditioning and flotation tests are described in part 2.

PART I

1. DEVELOPMENT OF ANALYTICAL METHODS FOR THE DETERMINATION OF FATTY ACIDS AND FUEL OIL ADSORBED ON ILMENITE FLOTATION PRODUCTS

1.1. INTRODUCTION

1.1.1. Expected range of reagent concentrations on the flotation products.

Tall oil and fuel oil are the particular reagents employed in the flotation of ilmenite. These reagents are usually applied in quantities of 900g tall oil and 600g fuel oil per ton solid feed (4). Assuming that 95% of the reagents are adsorbed on the values and 5% on the gangue minerals, and that the weight of the flotation concentrate and tailings are 35 and 65% respectively of the initial feed, the following reagent concentrations could be expected:

2.5g tall oil and 1.6g fuel oil per kilo flotation concentrate,
0.07g tall oil and 0.05g fuel oil per kilo flotation tailings.

The methods to be developed for assay of these reagents should cover these expected ranges of concentrations. Concentrations of this order of magnitude require sensitive assaying methods of semi-micro or micro type.

1.1.2. Literature survey.

An analytical method for the determination of tall oil and fuel oil contents of ilmenite flotation products was applied by Runolinna et al (1). It consisted essentially in extracting the organic matter with ether from samples dried at 50°C, followed by potentiometric determination of the fatty acids and gravimetric determination of the fuel oil.

Examination of the results obtained (1) raised many doubts in connection with the applied procedure, since less than 50% of the reagents were accounted for. It was concluded on the basis of these assays that the adsorption of tall oil on the mineral surface was unaffected by the conditioning time, while the adsorption of fuel oil increased with conditioning time. It was shown in other experiments (1) that the adsorption of tall oil required long conditioning time while the adsorption of fuel oil took place rapidly. These findings appeared to contradict those revealed by the analytical procedure. No evidence was presented to the effect that the strongly adsorbed reagents were completely extracted by the ether. Consequently the method was considered unsatisfactory.

A literature survey was therefore carried out in order to find an appropriate method for desorption of the reagents as well as analytical methods for determination of the two reagents, tall oil representing fatty acids and fuel oil.

* * *

Desorption of organic matter from mineral surfaces is achieved by several methods. One of the standard methods is combustion of the organic matter. This was applied by Balint (5) to the case of oleic acid adsorbed on pure quartz and hematite. The CO_2 produced was adsorbed in an Orsat type unit allowing determination of the carbon content of the initial mineral sample. This method was not suitable for a mixture of two organic reagents as it was desirable to differentiate between the tall oil and the fuel oil. In addition, the industrially processed minerals might contain varying amounts of organic matter.

Steam distillation has been used for removal of organic matter from solids or from aqueous pulps. The possibility of adapting this method to the desorption of tall oil and fuel oil from ilmenite flotation products was not investigated.

A considerable part of the reagents adsorbed on the surface of the Tellnes ilmenite flotation concentrate is removed by a flotation process at a pH value of 1 (4). It should therefore be possible to strip the organic reagents adsorbed on the flotation products by using a strongly acidic medium. The desorbed reagents could then be extracted into an organic solvent which should be immiscible with the aqueous pulp.

Acidification of Kraft black liquors and treatment with petroleum ether have enabled the desorption of the tall oil (6). Oleic acid was desorbed from magnetite by extracting with ethyl ether in the presence of 2N sulphuric acid (7).

Determination of fatty acids has been achieved by many methods which include potentiometric, complexometric, and conductimetric titrations, spectrophotometric and colorimetric measurements, and paper and gas chromatography.

A standard method for determination of the saponification value of oils involved heating in a N/2 alcoholic KOH solution followed by titration with N/2 HCl solution, using phenol-phthalein as indicator (8). Cold saponification of fatty acids was also possible:

the solution of fatty acids in petroleum ether was mixed with an equal volume of alcoholic KOH solution and was left standing for 12 hours at room temperature, when the excess KOH was determined with HCl solution(9). Both methods were suitable for the determination of 1-4 grams fatty acid.

The first method could be modified to permit direct titration with a N/2 aqueous NaOH solution by dissolving the fatty acids in neutral alcohol. This modified method was adapted to microdetermination of fatty acids by using N/100 aqueous NaOH solutions free of CO_2 (10).

In addition to these aqueous or semi-aqueous media employed for acidimetric titration of fatty acids various organic media were also shown to be applicable. Fatty acids contained in petroleum products were dissolved in 1:1 benzene-isopropanol and were titrated with N/10 KOH in dry isopropanol, using α-naphtholbenzene as indicator (11). Weak organic acids were determined in the above mentioned medium or in 1:4 benzene-methanol, using alcoholic KOH or sodium methoxide solutions as titrants, in the presence of thymol blue or bis(2,4-dinitrophenyl)-methane respectively (12). A slightly modified procedure was introduced by dissolving the weak organic acids in 1:5 methanol-benzene and by titrating with N/10 sodium methoxide in 1:5 methanol-benzene, in the presence of thymol blue 13).

In most cases the same media could be employed either for direct determination of the fatty acids with NaOH or for indirect determination of the alkali excess.

Oleic acid and sodium oleate solutions were analysed by precipitating with standard $CaCl_2$ solution followed by complexiometric determination of the $CaCl_2$ excess with EDTA in the presence of iminoxide (14).

Small amounts of monobasic fatty acids were determined by converting them to their methyl esters in methanol solutions in the presence of sulphuric acid as catalyst; the esters were then determined colorimetrically as the ferric hydroxamates (15).

Aqueous solutions of N/20 carboxylic acids were titrated conductometrically with N/25 $FeCl_3$ solutions (16).

Infrared spectroscopy was used in order to determine the various fatty acids (17,18) and in order to investigate the changes in the oleic acid caused by adsorption on quartz, hematite, limonite and magnetite (19,7).

Paper and gas chromatography were applied for the determination of the various fatty acids and resin acids in tall oil (20,21).

Determination of fuel oil by spectrophotometric measurements was indicated by preliminary experiments (22). Measurement of the optical density of fuel oil solutions in iso-octane in the ultraviolet range has made possible the determination of small concentrations of the standard No.1 tractor oil used.

* * *

1.1.5. Proposed research for development of the analytical methods.

The above literature survey indicated that acid stripping in the presence of an organic solvent would make possible the recovery and the desorption of the reagents from ilmenite flotation products. This must be followed by determination of the two reagents contained in the organic solvent.

Spectrophotometric measurements might provide a solution for the separate determination of the tall oil and the fuel oil. In case of mutual interference the tall oil must be separated from the fuel oil. A likely method for this purpose involves saponification with an aqueous alkaline solution into which the organic acid content is transferred. The two reagents could then be determined in their respective hydrocarbon and aqueous media.

As tall oil consists of a mixture of fatty acids and resin acids it was necessary to develop the analytical method for a pure fatty acid such as oleic acid. This might then be extended to determination of tall oil.

The approach to the solution of the above mentioned problems involved the following steps:

a. determination of fuel oil, oleic acid and tall oil, in iso-octane solutions, and possible mutual interference of these constituents;

b. determination of oleic acid by the potentiometric titration with alkali;

c. saponification of the oleic acid with aqueous NaOH solution and determination of the NaOH excess by potentiometric titration with HCl;

d. saponification of the oleic acid while in iso-octane by means of an aqueous NaOH solution and its extraction into the latter;

e. acid stripping of oleic acid and fuel oil from the mineral surface and their extraction into iso-octane;

f. application of the above steps to crude tall oil and fuel oil mixtures.

1.2. DETERMINATION OF FUEL OIL.

1.2.1. Introductory remarks.

The optical density of fuel oil, oleic acid and refined tall oil in iso-octane solutions has been measured before (22) in the ultra-violet range. The absorption spectra of fuel oil, oleic acid and refined tall oil showed a maximum at 225mμ. At this wavelength the values of the optical densities of these three substances at equal concentration were in the ratio of 30:1:100 respectively.

Fuel oil could therefore be determined by this method in the absence of tall oil. It should be pointed out that the optical density of crude tall oil might be even higher than that of the refined tall oil. The possibility of applying this method for the determination of the fuel oil was investigated in detail.

1.2.2. Suitability of iso-octane as solvent.

Spectroscopically pure iso-octane was prohibitively expensive for an analytical procedure consuming large amounts of solvent. For this reason the absorption spectrum of ordinary analytical grade iso-octane was first determined and presented in fig. 1.1. The spectrum obtained shows that the optical density of the analytical grade iso-octane was negligible at 225mμ and it was therefore suitable as solvent for the fuel oil determination.

All optical density measurements were carried out in a Unicam SP 500 spectrophotometer. Two milimeter fused silica cells were used and the optical density of iso-octane was measured against air. In all other tests the optical density of iso-octane solutions was measured against pure iso-octane.

Very slight contaminations affected the optical density measurements. Evaporation of the highly volatile solvent also caused an increase in the optical density, possibly because of an enrichment in the light absorbing contaminant present in the analytical grade iso-octane.

A high degree of cleanliness of the apparatus employed in the method was therefore imperative. It was also found necessary to use well stoppered cells and containers, to use in all tests only glass apparatus, and to calibrate frequently the absorption of the reference solvent. The precautions taken in this manner have ascertained satisfactory accuracy in the measurements of the optical density in iso-octane solutions.

1.2.3. Absorption spectrum of fuel oil in iso-octane solutions.

The optical densities of fuel oil in iso-octane solutions were measured at different wavelengths. The absorption spectrum of one of these solutions is presented in fig. 1.1. The spectrum in

FIGURE 1.1

ABSORPTION SPECTRA OF PURE ISO-OCTANE (AGAINST AIR) AND OF FUEL OIL SOLUTIONS (AGAINST ISO-OCTANE) IN THE ULTRA VIOLET RANGE.

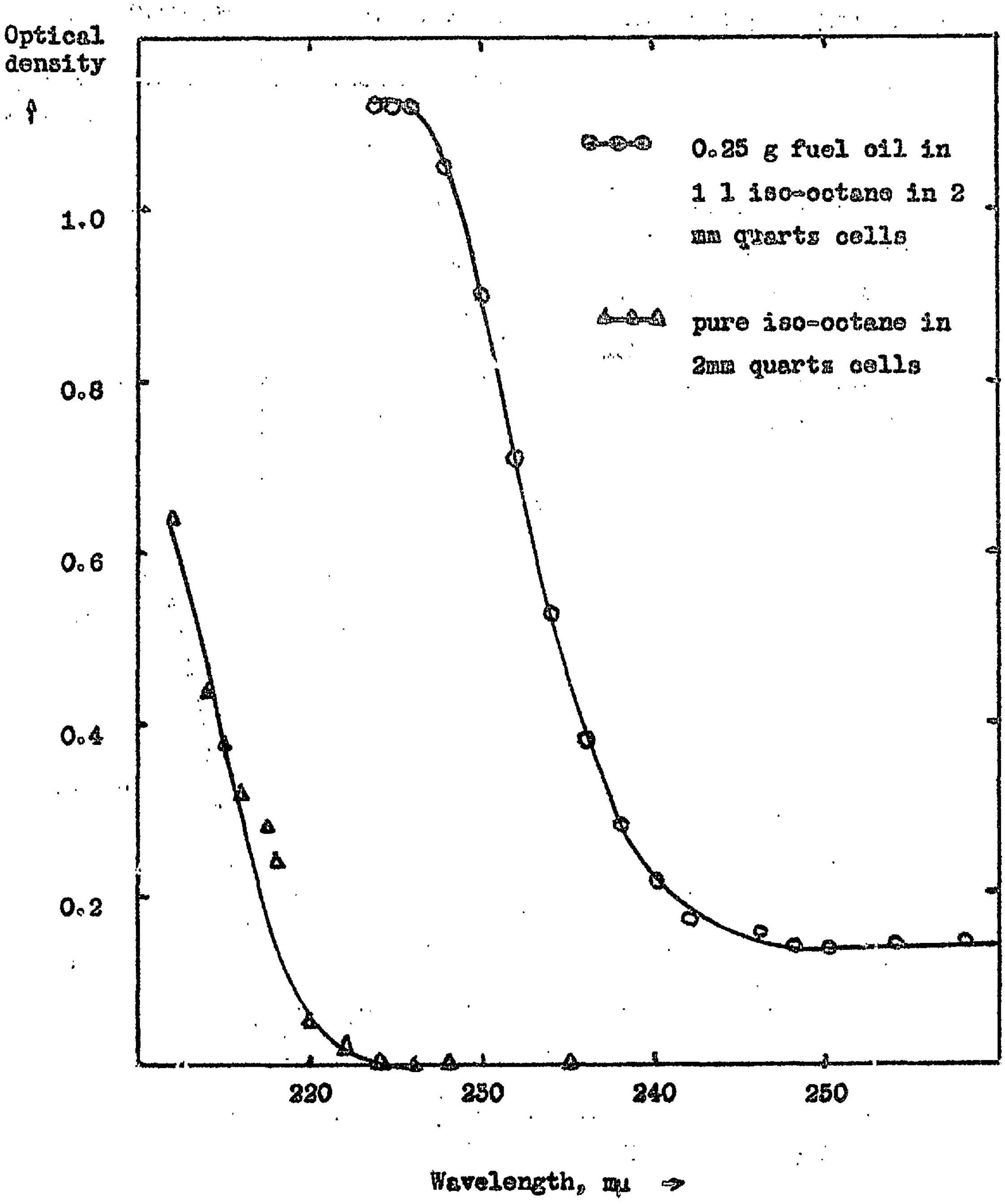


FIGURE 1.2

OPTICAL DENSITY OF FUEL OIL AT 224mμ AS A FUNCTION OF ITS CONCENTRATION IN ISO-OCTANE SOLUTIONS.

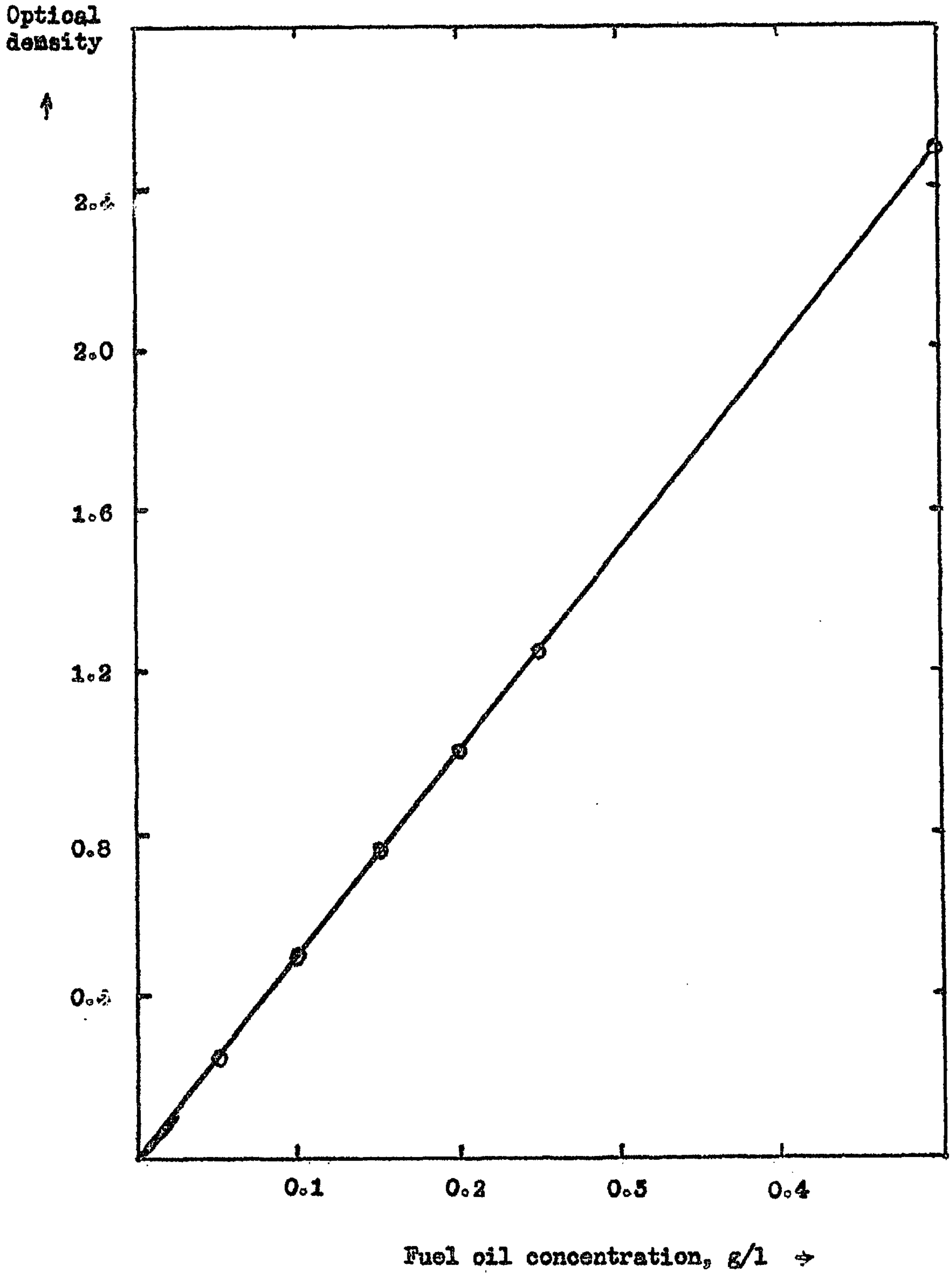


fig. 1.1. indicates that a concentration of fuel oil below 0.25g/l is required for accurate determination. The maximum optical density was attained in the wavelength range 224-226mμ.

The range over which the Beer-Lambert law was valid was determined by measuring the optical density of iso-octane solutions containing 0.05-0.5g/l fuel oil at the wavelength 224mμ. The optical densities were presented as a function of the fuel oil concentration in fig. 1.2. Fig. 1.2. shows a linear relationship between the optical density and the fuel oil concentration in the range below 0.5g/l. This relationship was expressed by the formula:

optical density = 5 . concentration (in g/l).

1.2.4. Absorption spectrum of oleic acid in iso-octane solutions.

It was necessary to assess the possible interference of oleic acid with the fuel oil determination. The absorption spectrum of oleic acid in iso-octane solutions was determined in the ultraviolet range and is presented in fig. 1.3. The spectrum obtained shows that the optical density of oleic acid was a maximum at the wave length interval 224-226mμ. Consequently oleic acid might interfere with the fuel oil determination.

Evaluation of the validity of the Beer-Lambert law at the maximal absorption wavelength established the order of magnitude of this interference. The optical density of iso-octane solutions containing 0.05-5.0g/l oleic acid was measured at 224mμ. The optical densities of the oleic acid solutions are presented as a function of the concentration in fig. 1.4.

FIGURE 1.5

ABSORPTION SPECTRUM OF OLEIC ACID IN ISO-OCTANE SOLUTIONS (IN U.V.)

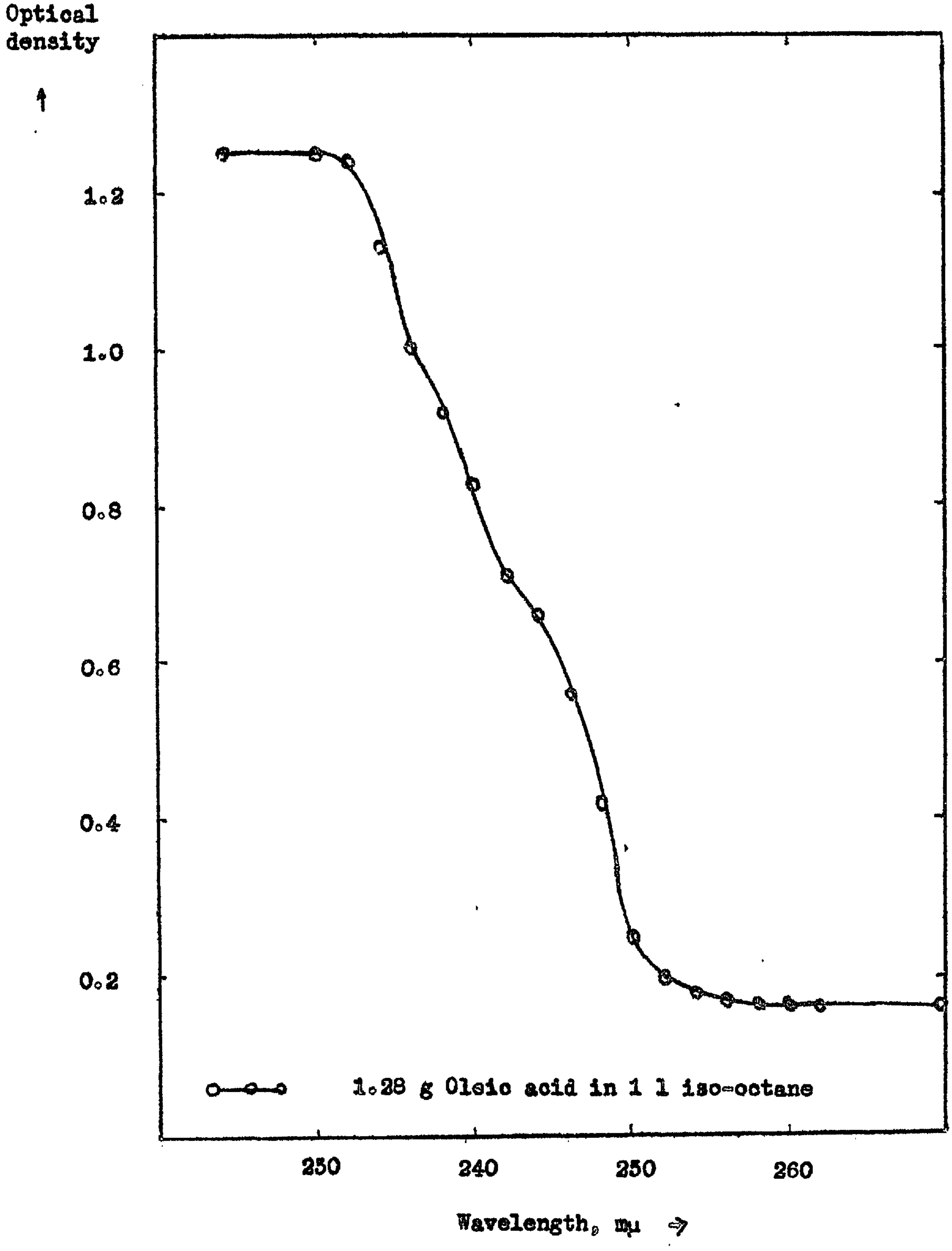


FIGURE 1.4

OPTICAL DENSITY OF OLEIC ACID AT 226mμ AS A FUNCTION OF ITS CONCENTRATION IN ISO-OCTANE SOLUTIONS.

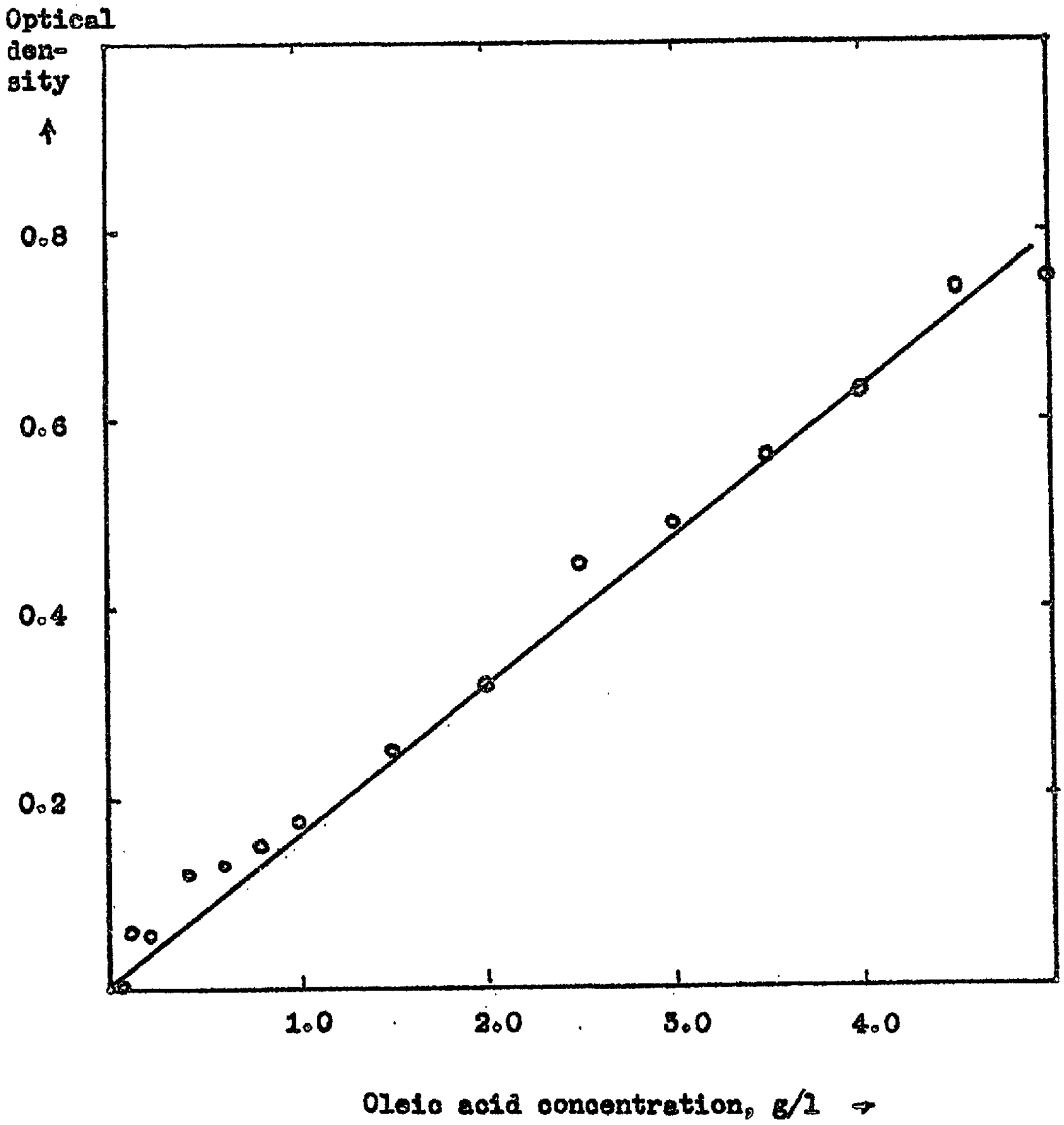


Fig. 1.4. shows a linear relationship between the optical density and the concentration of oleic acid in iso-octane solutions over the range studied. This relationship was expressed by the formula:

optical density = 0.16 . concentration (in g/l).

* * *

Comparison of the two formulae correlating the optical density and the concentration of fuel oil and oleic acid respectively in iso-octane solutions, demonstrated that the optical density of fuel oil was 30 times higher than that of the oleic acid at equal concentration. Since the oleic acid/fuel oil ratios employed in ilmenite flotation vary from 3:2 to 1:1, oleic acid could not be determined by this method in the presence of fuel oil, and it also interfered to a small extent with the determination of fuel oil. At oleic acid/fuel oil ratios of 1:1 the additional optical density due to the oleic acid was 3% of the total optical density.

1.3. DETERMINATION OF THE OLEIC ACID.

1.3.1. Saponification of oleic acid by aqueous NaOH solutions.

Small quantities of oleic acid were treated with an excess of aqueous N/10 NaOH solution and agitated with a magnetic stirrer. Visual observation indicated that small flakes of saponified oleic acid remained undissolved. Whereas heat is used in normal saponification procedures (8) to facilitate dissolution, it could not be used in the present case where the aim was saponification of the oleic acid while in iso-octane solution.

The suspensions of undissolved oleate were titrated potentiometrically with a N/10 HCl solution and the pH values were measured after reaching equilibrium. The results of some of these titrations are presented graphically in fig. 1.5. It was observed that the oleate ion can not be distinguished from the carbonate ion but is easily distinguished from the free alkali.

The end points of the titrations were presented in table 1.1. In all titrations reported in this part the end points were set at the midpoints of the respective inflections in the potentiometric titration curves as shown in fig. 1.5.

TABLE 1.1

End point results of the potentiometric titrations of sodium oleate suspensions in water with aqueous N/10 HCl solution.

Initial oleic acid, meq.	N/10 NaOH total, ml.	N/10 NaOH excess, ml	N/10 Na_2CO_3 ml.	Oleic acid found, meq.
1.6	24.5	16.0	1.0	0.75
0.8	24.75	15.8	1.0	0.795
0.55	10.0	6.55	0.4	0.315

FIGURE 1.5

POTENTIOMETRIC TITRATION CURVES OF OLEATE SUSPENSIONS WITH HCl.

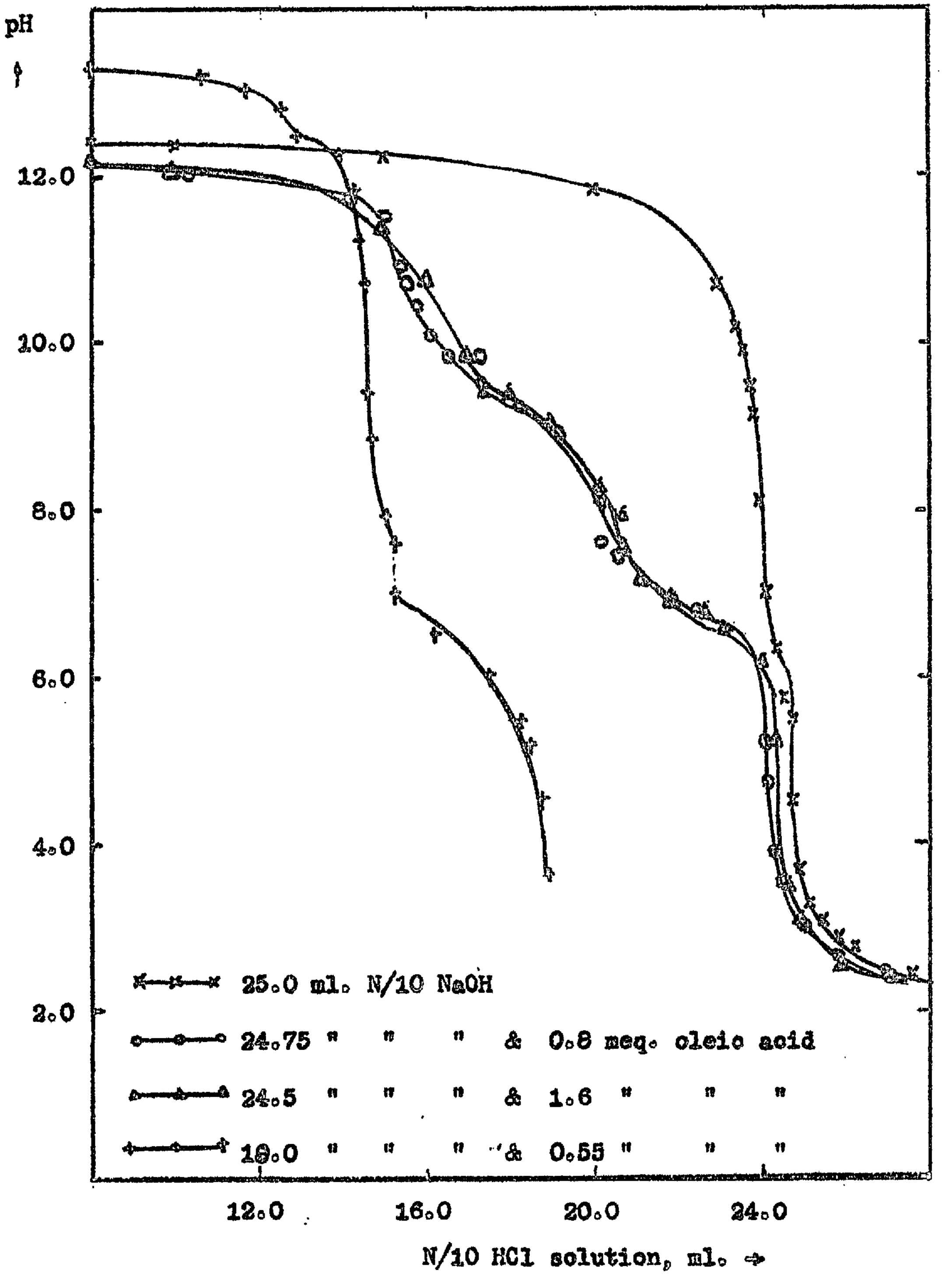


Table 1.1 shows that the oleate ion was only partially accounted for by the potentiometric titration with HCl. The amount of oleate was determined by correcting for the carbonate content of the NaOH aliquot used for the saponification.

The experimental results suggested that the oleic acid was not completely saponified before the titration. A suitable reaction medium had to be used for complete dissolution of both the oleate and the free oleic acid. The medium should be immiscible with the iso-octane in order to permit extraction of the oleic acid from the iso-octane solution. Mixtures of water and ethanol could fulfil these requirements.

1.5.2. Saponification of oleic acid by NaOH solutions in ethanol-water.

Oleic acid was completely dissolved in N/10 NaOH solutions to which 20% by volume ethanol was added. The solutions were titrated with aqueous N/10 HCl solutions and the end point results are presented in table 1.2. The table shows that almost all the oleic acid was accounted for. Liberation of free oleic acid as a turbid emulsion was however observed in the course of the titration. It was therefore necessary to determine the minimal proportion of ethanol required.

The ethanol/water ratios needed for complete dissolution of oleic acid were determined as a function of the oleic acid concentration in water. The results are presented in fig. 1.6 which shows that an 1.6:1 ethanol/water ratio was a minimum for the titra-

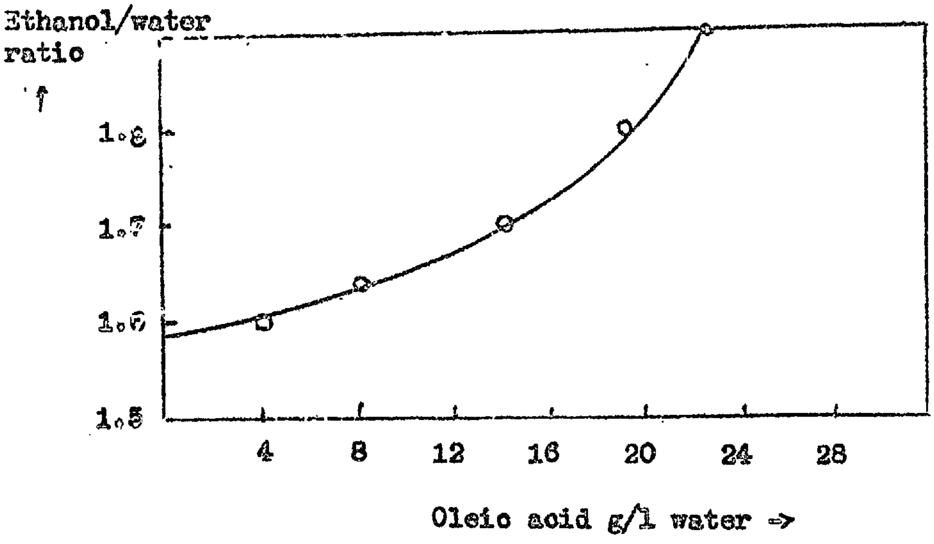
TABLE 1.2

End-point results of the potentiometric titrations of sodium oleate solutions in 20% ethanol with aqueous N/10 HCl solution.

Initial oleic acid, meq.	N/10 NaOH total, ml.	N/10 NaOH excess, ml.	N/10 $CO_3^{=}$ ml.	Oleic acid found, meq.
0.68	9.5	2.8	0.4	0.66
0.545	9.5	6.0	0.4	0.525

FIGURE 1.6

ETHANOL/WATER RATIO NECESSARY FOR COMPLETE DISSOLUTION OF 0 - 24 GRAMS OLEIC ACID IN 1 LITER WATER.



tion of sodium oleate with aqueous HCl solution. The volumetric ratio was reported in relation to the sum of the NaOH and HCl volumes consumed.

The suitability of this minimal volumetric ethanol/water ratio for the potentiometric titration of sodium oleate was examined in the following tests. In each of these tests 52 ml ethanol were added to 10 ml of aqueous N/10 NaOH solution, oleic acid was introduced, and the solutions were titrated with aqueous N/10 HCl solution. The potentiometric titration curves are presented in fig. 1.7 and the end-point results in table 1.5.

This procedure was cross-checked in the following manner: samples of oleic acid were dissolved in mixtures of ethanol and water and were titrated with N/10 aqueous NaOH solution; the excess of NaOH was then back titrated with aqueous N/10 HCl solution. The potentiometric titration curves are presented in fig. 1.8. The difference between the titration end-points was equal to the Na_2CO_3 content of the N/10 NaOH aliquot.

Examination of figures 1.7 and 1.8 shows that the potentiometric titration curves were smooth and that distinct end-points could be obtained for both free NaOH and sodium oleate in the pH intervals 11-9 and 5-4 respectively. Table 1.5 shows that the entire oleic acid content was determined by this titration.

FIGURE 1.7

POTENTIOMETRIC TITRATION CURVES OF SODIUM OLEATE SOLUTIONS IN 1.6:1 ETHANOL/WATER WITH N/10 AQUEOUS HCl SOLUTION.

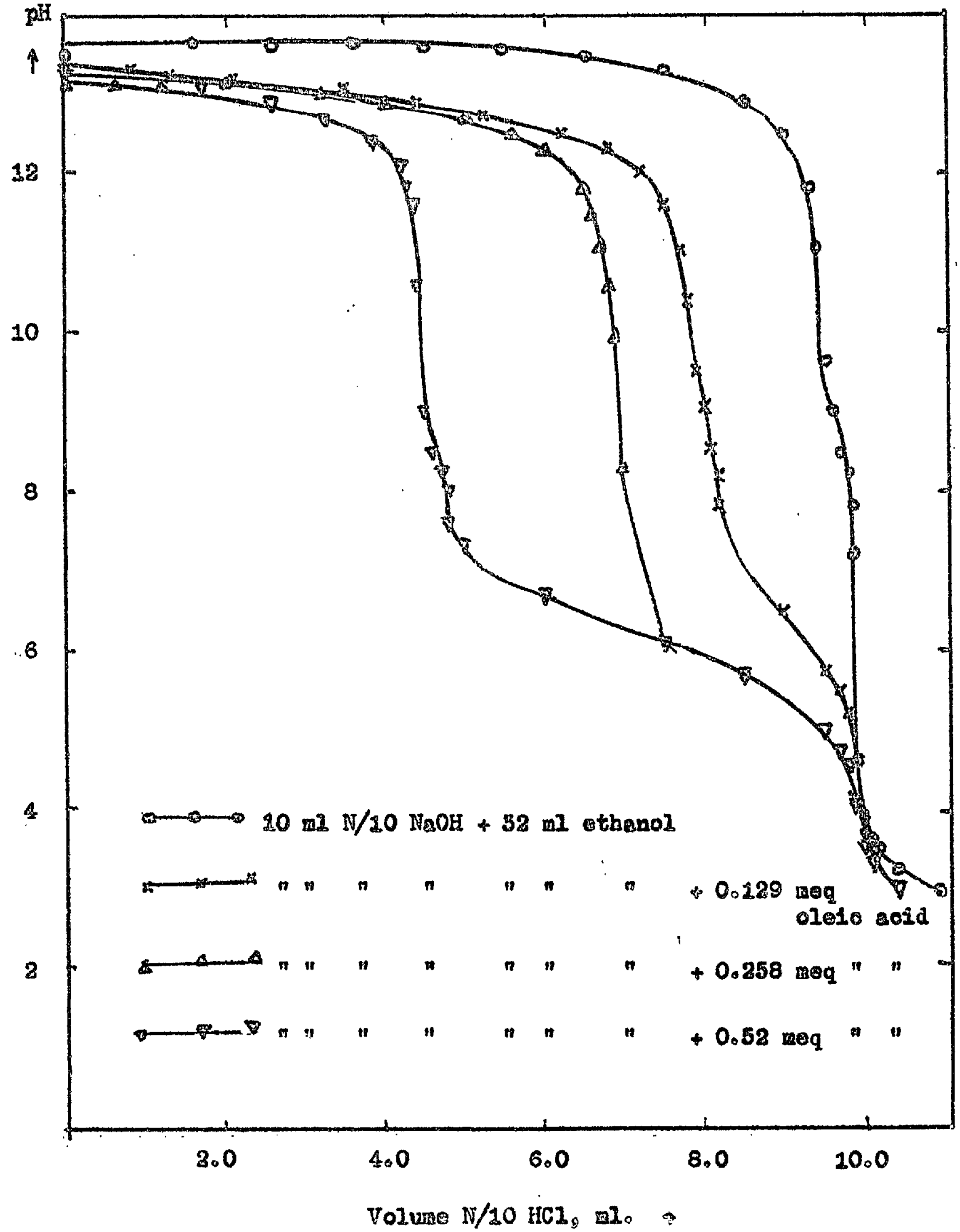


FIGURE 1.8

POTENTIOMETRIC TITRATION CURVE OF OLEIC ACID IN 1.6:1 ETHANOL/WATER WITH AQUEOUS N/10 NaOH AND BACK TITRATION WITH AQUEOUS N/10 HCl.

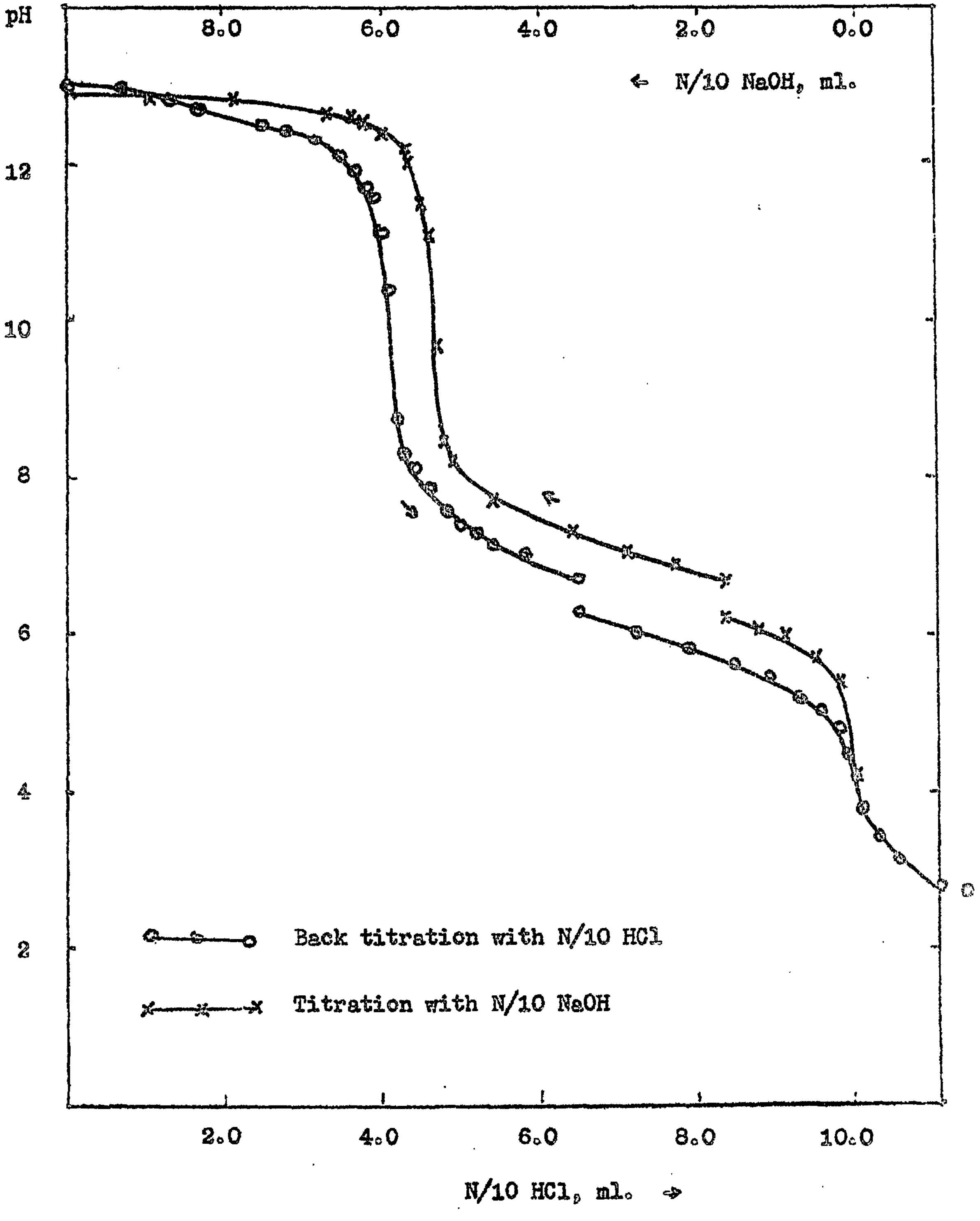


TABLE 1.3

End-point results of the potentiometric titrations of sodium oleate solutions in 1.6:1 ethanol/water with aqueous N/10 HCl.

Initial oleic acid, meq.	N/10 NaOH total, ml.	N/10 NaOH excess, ml.	N/10 CO_3^{--} ml.	Oleic acid found, meq.
0.52	9.85	4.4	0.45	0.5
0.258	9.85	6.8	0.45	0.26
0.129	9.85	7.8	0.45	0.16

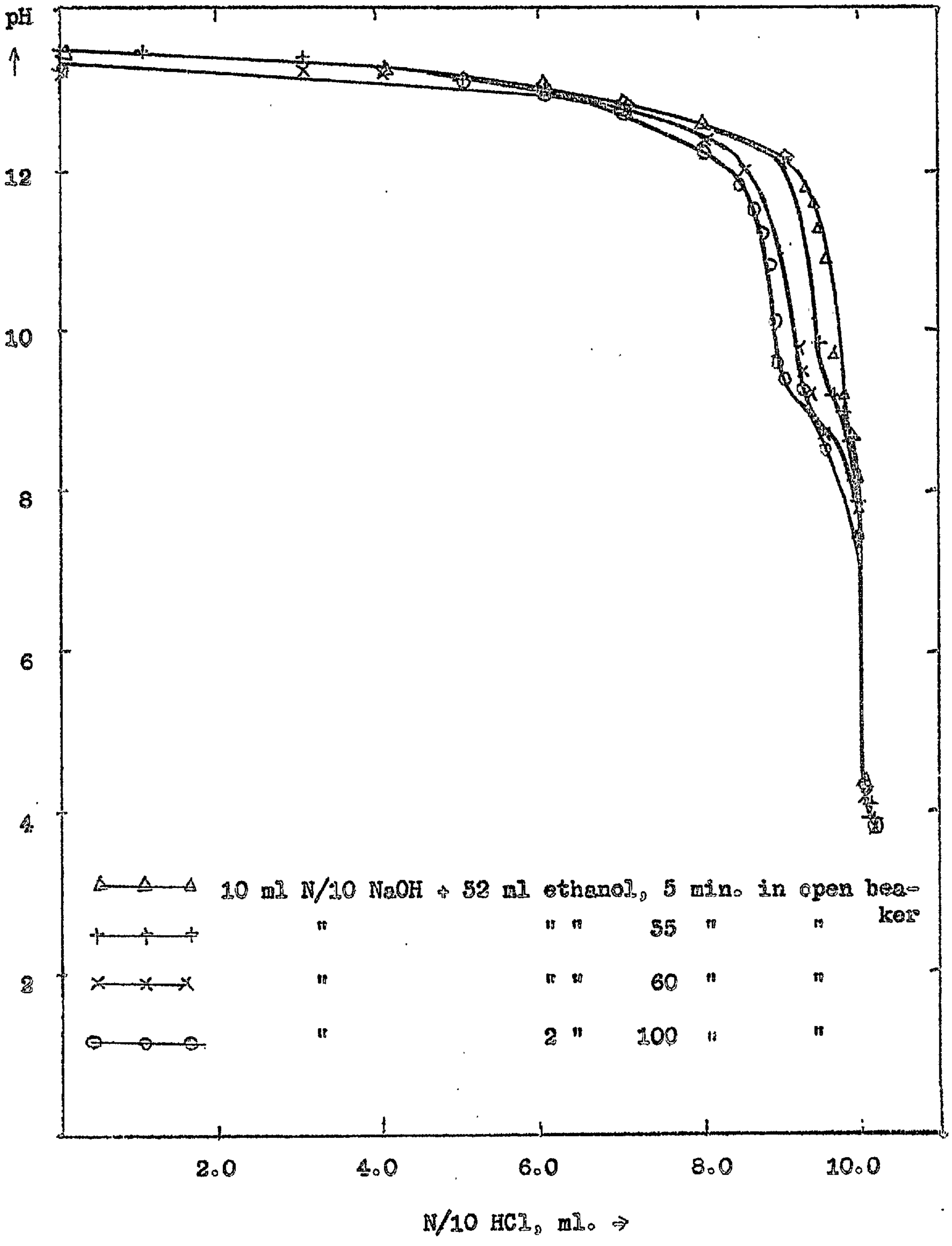
TABLE 1.4

End-point results of the potentiometric titrations of sodium hydroxide solutions in 1.6:1 ethanol/water, left in open beakers for different periods

Period before titration, min.	N/10 NaOH total, ml.	N/10 NaOH excess, ml.	N/10 CO_3^{--} ml.	CO_3^{--} meq.
5	10.0	9.55	0.45	0.045
55	10.0	9.50	0.70	0.07
60	10.0	9.05	0.95	0.095
100	10.0	8.8	1.2	0.12

FIGURE 1.9

POTENTIOMETRIC TITRATION CURVES OF N/10 NaOH IN 1.6:1 ETHANOL/WATER WITH N/10 HCl. THE CO_2 ABSORPTION AS A FUNCTION OF TIME.



1.5.3. The rate of CO_2 absorption by the alkali solution in 1.6:1 ethanol/water.

It was necessary to determine the rate of CO_2 absorption from the atmosphere by NaOH solutions in 1.6:1 ethanol/water. Mixtures of 10 ml N/10 NaOH solution and 52 ml ethanol were left standing in open beakers for different periods and were then titrated with N/10 HCl solution. The potentiometric titration curves are presented in fig. 1.9 and the end-point results in table 1.4.

These results show that the CO_2 was absorbed from the atmosphere at a rate of 0.05 meq per hour and in order to avoid errors in the oleic acid determination the oleate solutions in 1.6:1 ethanol/water must be titrated as soon as prepared.

It was found unnecessary to use special CO_2-free NaOH solutions because standard N/10 NaOH solutions, containing 3-5 equivalent % of CO_2, did not significantly absorb further CO_2 when kept in ground-glass stoppered bottles. As a further precaution it was necessary always to withdraw the NaOH aliquots by means of mechanical pipettes and to calibrate frequently the CO_2 content of the N/10 NaOH solution.

1.5.4. The NaOH excess required for quantitative saponification.

Various quantities of oleic acid were added to a series of 10 ml aliquots of N/10 NaOH solution to neutralise 10-90 equivalent % of the NaOH present. The solutions were diluted with 32 ml ethanol and were titrated with N/10 HCl. The potentiometric titration

TABLE 1.5

End-point results of the potentiometric titrations of sodium oleate solutions in 1.6:1 ethanol/water at different NaOH excesses with aqueous N/10 HCl solution.

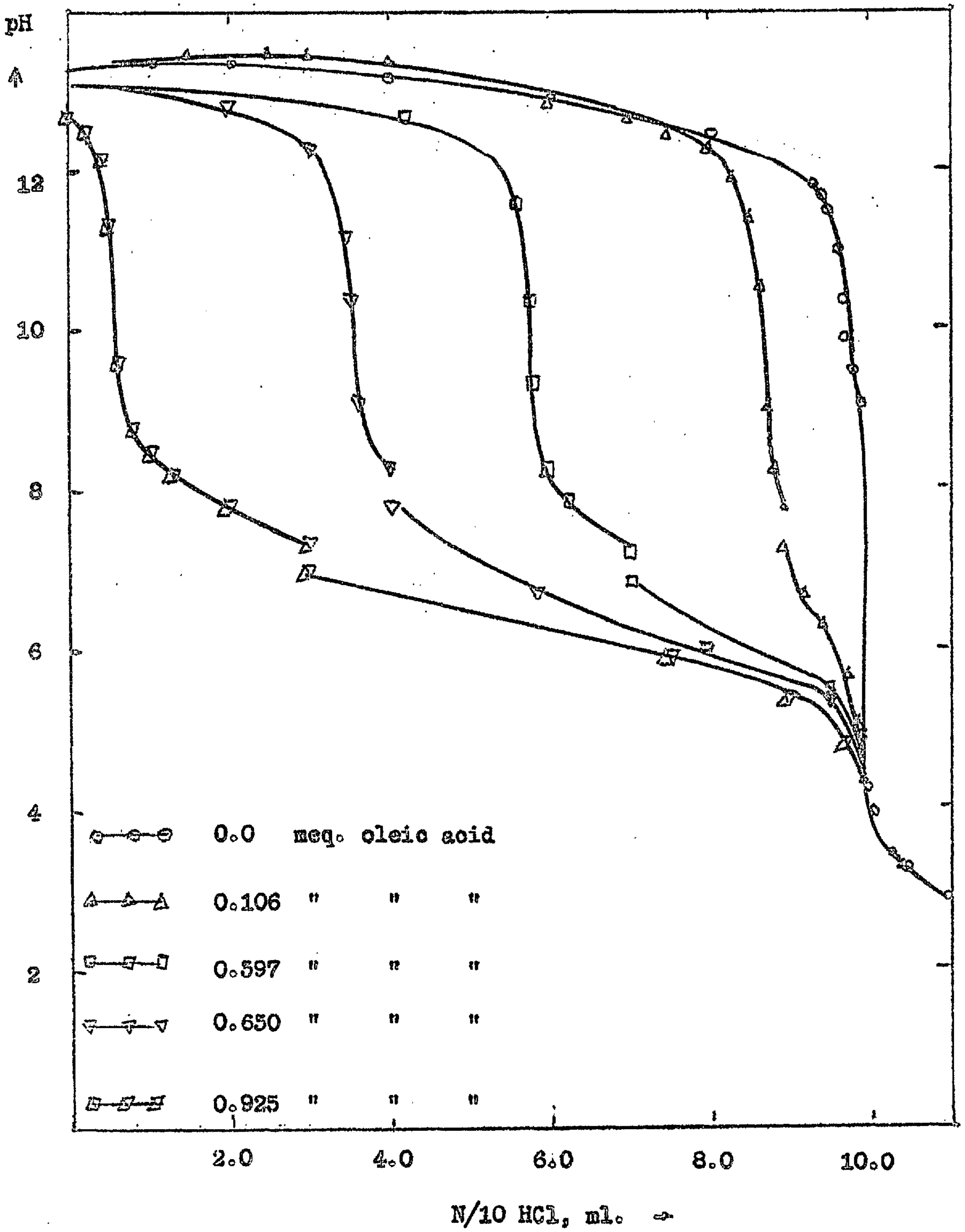
N/10 NaOH total, 9.95 ml.;	N/10 CO_3^{--}, 0.3 ml.			
Initial oleic acid, meq.	N/10 NaOH excess, ml	N/10 oleate found, ml.	Oleic acid found, meq	Error, %
0.0	9.65	0.0	0.0	0
0.106	8.60	1.05	0.105	-1
0.222	7.50	2.15	0.215	-3
0.288	6.85	2.80	0.280	-3
0.397	5.75	3.90	0.390	-2
0.515	4.55	5.10	0.510	-1
0.630	3.50	6.15	0.615	-2.5
0.728	2.45	7.20	0.720	-1
0.791	1.95	7.70	0.770	-2.5
0.925	0.55	9.10	0.910	-1.5

curves are presented in fig. 1.10 and the end-point results in table 1.5.

Table 1.5 shows that an error (max. deviation from the mean) of ±1% was obtained if oleic acid of 98% purity was assumed, and therefore 1 meq. oleic acid equalled 289mg. This accuracy was exceeded in the range below 100% excess NaOH, and the most suitable

FIGURE 1.10

POTENTIOMETRIC TITRATION CURVES OF N/10 NaOH IN 1.6:1 ETHANOL/WATER PARTIALLY NEUTRALISED BY OLEIC ACID WITH AQUEOUS N/10 HCl.



range was 20-100% excess NaOH with respect to the oleic acid present.

Fig. 1.10 shows that distinct end-points were obtained for both free NaOH and sodium oleate, at pH 11-9.5 and pH 4.4-5.8 respectively, over the entire range of 10-900% excess NaOH.

These results demonstrate that 50-200mg oleic acid could be quantitatively saponified in a mixture of 10 ml N/10 NaOH solution and 52 ml ethanol, and that the amount of oleic acid could be accurately determined by potentiometric titration with aqueous N/10 HCl solution.

1.4. SEPARATION OF OLEIC ACID AND FUEL OIL DISSOLVED IN ISO-OCTANE.

1.4.1. Saponification of oleic acid dissolved in iso-octane.

It was necessary to separate the oleic acid from the fuel oil by quantitative transfer from the iso-octane phase to the aqueous alkaline solution. The feasibility of such a process was examined in the following tests.

Mixtures of oleic acid solutions in iso-octane and of NaOH solutions in ethanol-water media were strongly shaken by hand in 30 ml ground-glass stoppered test tubes, and the emulsions obtained were rapidly transferred into centrifuge test tubes and centrifuged for 45 minutes at 3000 r.p.m.

Samples of the iso-octane phase were analysed by measuring the optical density at 224mμ. Samples of the alkaline layer were subsequently pipetted into beakers containing 50 ml ethanol and were then titrated with N/10 HCl solution. The results are presented in table 1.6.

TABLE 1.6

Results of the saponification of oleic acid in iso-octane solutions by N/10 NaOH solutions in ethanol-water.

N/10 NaOH ml.	Initial oleic acid, ml	Ethanol ml.	Iso-octane/(NaOH + Ethanol) ratio	Oleic acid found meq	Error %	Optical density 224mμ
8	0.502	0	2.5:1	0.506	-0.8	0.185
5	0.251	0	5.0:1	0.250	-0.4	0.136
5	0.251	0	4.0:1	0.241	-4	0.101
5	0.251	1	2.5:1	0.247	-1.6	0.160
5	0.251	2	2.1:1	0.255	+1.6	0.136
5	0.251	4	1.7:1	0.247	-1.6	0.125

A highly stable emulsion was formed when attempting the saponification in the absence of ethanol. Prolonged centrifugation produced a cloudy NaOH phase and a clear iso-octane phase with a jelly like interface. Addition of ethanol to the system resulted in less stable emulsions which separated in the course of 2-5 minutes centrifugation. The minimum amount of ethanol necessary for good phase separation was 40% by volume of the alkaline phase.

Optical density measurements of the iso-octane phase showed the presence of a residue which was proportional to the initial concentration of oleic acid and inversely proportional to the amount of ethanol added. The optical density of this residue corresponded to 10-15% of the initial oleic acid concentration (see 1.2.4.). The contribution of this residue could be neglected, since the contribution of oleic acid itself to the optical density of fuel oil was only 8% of the total at customary 1:1 oleic acid /fuel oil ratios. The residue itself was not an organic acid since the results in table 1.6 indicate complete saponification of the oleic acid.

The distribution of ethanol between the aqueous alkaline phase and the iso-octane phase was examined in the absence and in the presence of oleic acid. It was found that practically no ethanol was left in the iso-octane at 2:1:5 ethanol/water/iso-octane ratios, in the presence of 0-10g oleic acid per l. iso-octane.

Contact with alkali solutions in 40% ethanol did not affect the optical density of iso-octane when oleic acid was absent.

1.4.2. The NaOH excess required for quantitative extraction of oleic acid from iso-octane solutions.

In order to determine the necessary excess of NaOH, several 10 ml aliquots of iso-octane solutions containing varying amounts of oleic acid were shaken with 5 ml N/10 NaOH solution and

5 ml ethanol. After centrifugation the iso-octane layer was analysed by optical density measurements and the alkaline layer by potentiometric titrations.

The results are presented in tables 1.7 and 1.8. Table 1.7 shows that the optical density of the impurity left in the iso-octane layer was roughly proportional to the initial oleic acid concentration but was negligible from the view point of fuel oil determination.

Table 1.8 shows that an excess of 50% NaOH was sufficient for quantitative extraction of the oleic acid. The difference between the initial quantity of the oleic acid and the quantity found was ±1% over the entire range of NaOH excess.

1.4.3. Saponification of oleic acid in iso-octane solutions in the presence of fuel oil.

The saponification procedure described in 1.4.2. was applied to aliquots of iso-octane solution containing varying amounts of oleic acid and fuel oil. After centrifugation the iso-octane phase was analysed for fuel oil and the alkaline layer was analysed for oleic acid.

The results presented in table 1.9 show that the NaOH, the ethanol, the oleic acid, and the oleate residues in the iso-octane did not affect the accuracy of the fuel oil determination. The error was ±1%. The results presented in table 1.10 show that the fuel oil did not interfere with the oleic acid determination. The

TABLE 1.7

Optical density of iso-octane solutions after saponification of the oleic acid.

Initial oleic acid, g/l	Optical density at 224mμ	Equivalent oleic acid concentration, g/l	% of initial oleic acid
0.945	0.05	0.19	20
1.89	0.025	0.16	8.5
2.84	0.059	0.37	13
3.78	0.075	0.46	12
4.73	0.105	0.645	13.5
5.67	0.125	0.78	13.7
6.65	0.198	1.24	18.5

TABLE 1.8

End-point results of the potentiometric titrations of alkaline saponification mediums after extraction of the oleic acid from iso-octane.

Initial oleic acid, meq.	N/20 NaOH total, ml.	N/20 NaOH excess, ml.	N/20 $CO_3^{=}$ ml.	Oleic acid found, meq	Error %
0.0492	9.2	7.85	0.45	0.049	-0.4
0.0985	8.95	6.75	0.45	0.0978	-0.7
0.1475	9.2	6.05	0.45	0.147	-0.4
0.197	9½1	5.1	0.45	0.195	-1.0
0.246	9.35	4.25	0.45	0.2485	+1.0
0.295	9.05	3.25	0.45	0.295	0
0.344	8.85	2.35	0.45	0.342	-0.6
0.00	8.85	8.4	0.45		
NaOH blank	10.05	9.65	0.4		

TABLE 1.9

Fuel oil content of the iso-octane layer after saponification of oleic acid.

Iso-octane ml.	N/10 NaOH ml.	Ethanol ml.	Oleic acid g/1	Fuel oil g/1	Optical density 224mμ.	Fuel oil found, g/1	Error %
5.0	0.0	0.0	0.0	5.08	2.50	5.0	-1.6
4.0	0.0	0.0	0.0	5.81	1.95	5.85	+1.0
15.0	5.0	5.0	0.0	2.54	1.58	2.525	-0.6
15.0	5.0	5.0	0.0	5.08	2.62	5.025	-1.1
15.0	5.0	5.0	4.74	2.54	1.55	2.52	-0.8
15.0	5.0	5.0	2.57	2.54	1.55	2.52	-0.8
15.0	5.0	5.0	2.57	5.08	2.76	5.045	-0.7
20.0	5.0	5.0	5.55	5.81	1.90	5.80	-0.25

TABLE 1.10

End-point results of the potentiometric titrations of saponification mediums after extraction of the oleic acid from the iso-octane layer.

Initial oleic acid, meq.	N/20 NaOH total, ml.	N/20 NaOH excess, ml.	N/20 CO_3^{--} ml.	Oleic acid found, meq.	Error %
0.0					
0.0					
0.0	8.9	8.25	0.65		
0.0	9.05	8.5	0.55		
0.2505	9.5	4.05	0.6	0.2525	+0.8
0.125	8.2	5.7	0.6	0.123	-1.6
0.125	9.0	6.5	0.6	0.1255	+0.4
0.2505	8.95	5.9	0.6	0.2525	+0.8
NaOH blank	10.1	9.75	0.55		

It was thus demonstrated that the saponification method made possible an effective separation of oleic acid and fuel oil, while the individual analytical methods permitted accurate determination of their concentrations in the respective phases.

1.5. DETERMINATION OF TALL OIL.

1.5.1. Direct determination of the organic acid content of tall oil.

It was desirable to study the adsorption of fatty acids and fuel oil on ilmenite flotation products in the case of crude tall oil. The analytical procedure was therefore adapted to the determination of tall oil and fuel oil mixtures, and in this adaptation the following steps were considered: potentiometric titration of tall oil solutions in ethanol-water media, saponification of tall oil in iso-octane, and the possibility of interference of the tall oil and the fuel oil.

Small amounts of tall oil and oleic acid were dissolved in ethanol, HCl and NaOH were added, and the resulting solutions were titrated with N/20 NaOH solution. Tables 1.11 and 1.12 show the potentiometric titration end-point results. The amount of organic acid contained in the tall oil was found to be equivalent to 80% of its weight expressed in oleic acid.

1.5.2. Indirect determination of the organic acid content of tall oil.

Small amounts of tall oil were dissolved in 25 ml ethanol,

TABLE 1.11

End-point results of the potentiometric titrations of oleic acid solutions in 1.6:1 ethanol/water with aqueous N/20 NaOH solution

Initial oleic acid, mg	N/20 NaOH consumed, ml	N/20 CO_3^{--} ml	Oleic acid found meq	Oleic acid found mg	Error %
0	0.5	0.3			
80	5.9	0.3	2.83	81	+1.2
82	6.05	0.3	2.90	83	+1.2
94	6.8	0.3	3.28	94	0

TABLE 1.12

End-point results of the potentiometric titrations of tall oil solutions in 1.6:1 ethanol/water with aqueous N/20 NaOH solution.

Initial tall oil, mg	N/20 NaOH consumed, ml	N/20 CO_3^{--} ml	Oleic acid found meq	Oleic acid found mg	Oleic acid/tall oil ratio
11.2	0.95	0.3	0.0325	9.2	0.82
35.1	2.25	0.3	0.0975	27.6	0.785
85.6	5.15	0.3	0.2425	68.5	0.8
135.7	7.9	0.3	0.38	107.7	0.795

excess of N/20 NaOH solution was added, and the solutions were titrated potentiometrically with N/20 HCl solution. The potentiometric titration curves obtained for tall oil were similar to those obtained for oleic acid, as can be seen from fig. 1.11 and fig. 1.10.

The end-point results presented in table 1.15 show that the organic acid content of tall oil could be accurately determined by the potentiometric titration. Each gram of tall oil contained 2.75 meq. organic acids, which is equivalent to 0.8 gram oleic acid. By using the factor 1 meq. = 364 mg tall oil, the amount of tall oil present could be calculated from the difference between the titration end-points, expressed in miliequivalents. The error was ±2.0%. It was impossible to differentiate between the fatty and resin acids by means of the potentiometric titration.

Visual observation indicated complete dissolution of the tall oil in the ethanol or in the alkaline solutions in ethanol-water. The tall oil remained dissolved in the course of the titration with the HCl solution.

1.5.5. Saponification of tall oil in iso-octane solutions.

It was impossible to dissolve tall oil completely in iso-octane. A 180mg sample of tall oil was therefore treated with 50ml iso-octane and the resulting suspension was centrifuged. Two 20ml aliquots were withdrawn from the clear solution. These aliquots as well as the remaining solution, containing the entire residue, were saponified with N/20 NaOH solution in ethanol-water, as described

FIGURE 1.11

POTENTIOMETRIC TITRATION CURVES OF N/20 NaOH IN 1.6:1 ETHANOL/ WATER CONTAINING TALL OIL WITH AQUEOUS N/20 HCl SOLUTION.

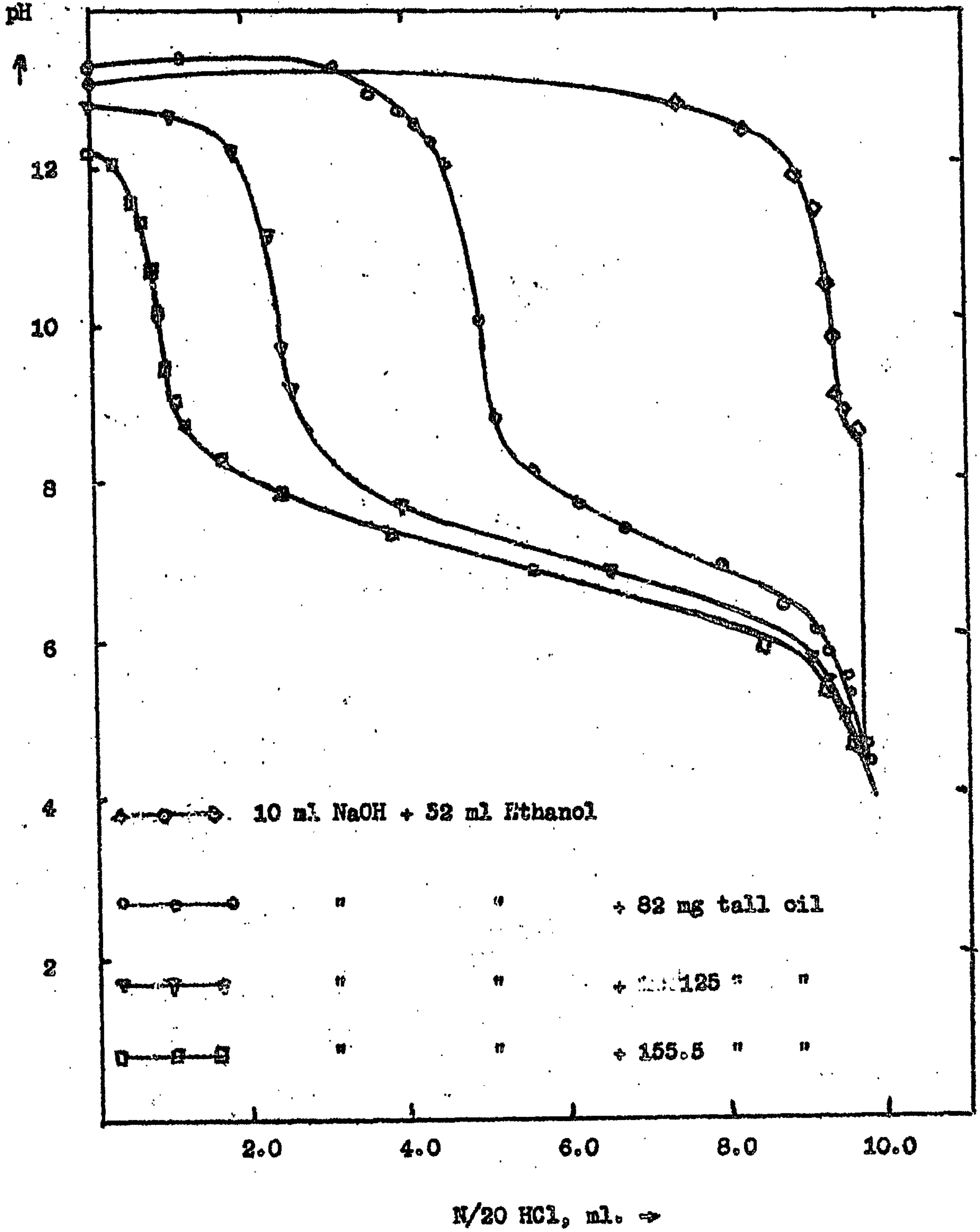


TABLE 1.13

End-point results of the potentiometric titration of saponified tall oil solutions in 1.6:1 ethanol/water with aqueous N/20 HCl solution.

Initial tall oil mg.	N/20 NaOH total, ml	N/20 NaOH excess,ml	N/20 CO_3^{--} ml	Tall oil found, meq	Equivalence factor meq./g	Error %
32	6.0	3.95	0.35	0.087	2.72	-1.0
81	9.8	4.9	0.35	0.2275	2.80	+1.8
82	9.8	4.95	0.35	0.225	2.75	0
111	9.8	3.3	0.35	0.3075	2.77	+0.8
124.5	9.7	2.45	0.35	0.345	2.77	+0.8
155.5	9.7	0.9	0.35	0.4225	2.72	-1.0

TABLE 1.14

End-point results of the potentiometric titrations of saponification mediums after extraction of the tall oil from iso-octane suspensions.

Initial tall oil mg	N/20 NaOH total,ml	N/20 NaOH excess,ml	N/20 CO_3^{--} ml	Tall oil found meq	mg	Error %
72	6.7	3.75	0.25	0.198	71.4	-1.0
72	6.7	3.75	0.25	0.198	71.4	-1.0
36	4.75	2.55	0.125	0.101	36.5	+1.0

in 1.4.2. The organic acid content in the alkaline layer was determined and the results were presented in table 1.14.

The results in table 1.14 show that it was possible to saponify the entire organic acid content of the tall oil in iso-octane solutions, analogous to the saponification of oleic acid in iso-octane solutions. The organic acid concentration in the clear iso-octane solution corresponded to complete dissolution of the entire organic acid content of the original tall oil sample. This indicated that the entire organic acid content of tall oil samples, adsorbed on ilmenite flotation products, could be dissolved in the iso-octane, if they have been successfully desorbed by some agent.

The optical density of the iso-octane solutions left after the saponification was measured at 224mμ. The optical density of all three samples was the same, and it corresponded to a fuel oil content equivalent to ½% of the tall oil content, which was a negligible error at customary tall oil/fuel oil ratios around 1:1.

1.5.4. Saponification of tall oil in iso-octane solutions in the presence of fuel oil.

The applicability of the saponification procedure to the separation of tall oil and fuel oil in iso-octane solutions was investigated.

Small amounts of a 3:2 tall oil/feul oil mixture were administered by means of a syringe to 20ml iso-octane aliquots, in the range 0.205-2.29g/l tall oil and 0.155-1.525g/l fuel oil. The resulting solutions were saponified with alkali solutions in ethanol-water as described in 1.4.2. Samples were withdrawn from the two layers and they were analysed for tall oil and fuel oil.

It was concluded from the results presented in table 1.15 that saponification separated the tall oil from the fuel oil as effectively as it separated the oleic acid from the fuel oil, when in iso-octane solution. The presence of fuel oil did not interfere with the determination of tall oil by the potentiometric titration.

Measurement of the optical density of the iso-octane solutions left after the saponification has shown the presence of an impurity, originating in the tall oil, which contributed 4% of the total optical density. This relative contribution was constant over the entire range of fuel oil and tall oil concentration, at constant tall oil/fuel oil ratio.

The above mentioned tests show that it is possible to determine tall oil and fuel oil contents of iso-octane solutions by means of the analytical procedure developed.

1.6. DESORPTION OF OLEIC ACID AND FUEL OIL FROM ILMENITE.

1.6.1. Introductory remarks.

It was mentioned in section 1.1.3. that acidification of the ilmenite pulps would result in desorption of the flotation

TABLE 1.15

Results of the separation of tall oil and fuel oil dissolved in iso-octane by means of saponification.

Initial reagents, mg		Tall oil found, mg	Error %	Fuel oil found, mg	Error %
tall oil	fuel oil				
4.1	2.7	3.7	-9.8	2.8	+4-0.5
8.9	5.9	8.4	-5.6	6.0	+4-2.5
13.6	9.1	14.6	+7.35	9.4	+4-0.7
17.6	11.7	17.7	+0.57	12.2	+4+0.5
22.9	15.5	24.1	+5.2	16.0	+4+0.6
27.7	18.5	26.9	-2.9	19.4	+4+0.8
33.5	22.4	34.4	+2.7	23.5	+4+0.9
37.6	25.0	36.7	-2.4	26.2	+4+0.8
42.1	28.1	41.0	-2.6	29.2	+4-0.1
45.8	30.5	46.6	+1.75	32.0	+4+0.9

reagents from the minerals. These reagents could then be extracted with iso-octane.

A pure ilmenite sample (< 1mm) was first washed with pyridine and then rinsed with iso-octane in order to remove the organic impurities. The sample was then ground to a size distribution equivalent to that of actual flotation concentrates.

The finely ground material was stored in ground-glass stoppered jars in order to prevent contamination. Treatment of this ilmenite with the flotation reagents, at 70% solids, produced frothy and agglomerated pulps which were similar in appearance to the actual flotation concentrates, and these pulps were termed "simulated flotation concentrates".

In the tests described below the flotation reagents were introduced by means of a hypodermic syringe, permitting accurate determination of the initial reagent content of a "simulated flotation concentrate". Since the extraction of the flotation reagents from "simulated flotation concentrates" was not quantitative in open vessels, because of the high iso-octane volatility, all tests described below were carried out in closed containers.

A preliminary test was performed in order to establish the possibility of extracting the reagents from "simulated flotation concentrates" by acidification of the pulp and by treatment with iso-octane. A ground-glass stoppered flask containing 500g pure ilmenite, 150ml water, 524mg tall oil and 548mg fuel oil, was vigorously shaken for 5 minutes to allow adsorption of the reagents on the ilmenite surface. A "simulated flotation concentrate" was thus produced. The pulp was acidified to an H_2SO_4 concentration of 12N, and 200ml iso-octane was added. The flask was shaken again for 5 minutes and left to stand. After separation of the two layers, samples were withdrawn from the iso-octane layer and were analysed for tall-oil and fuel oil. The results showed the presence of 104% of the initial oleic acid and 107% of the initial fuel oil.

Having established that the entire content of oleic acid and fuel oil adsorbed on "simulated flotation concentrates" can be determined by the method suggested, it was necessary to examine the effects of the individual parameters: the H_2SO_4 concentration, the proportion of iso-octane, and the concentration of the two reagents.

1.6.2. Effects of the sulphuric acid concentration on the desorption.

A standard procedure was adopted in the desorption tests:

Ground-glass stoppered containers, into which ilmenite and water at 70% solids and a given quantity of the reagents were added, were shaken vigorously for 5 minutes to produce a "simulated flotation concentrate". Various amounts of H_2SO_4 and iso-octane were then added and the bottles were shaken again for 5 minutes to allow extraction of the reagents. After 10 minutes standing the liquid phases were transferred to centrifuge test tubes for phase separation at 3000 r.p.m. After 10 minutes' centrifugation samples were withdrawn from the iso-octane extracts and were analysed for oleic acid and fuel oil content.

In the first series of tests the H_2SO_4 concentration was varied over the range 0.0465-1.6N, and the other parameters were 150g ilmenite, 75g water, 0.5-0.55 g/kg oleic acid and 0.20-0.22 g/kg fuel oil, and a 1:5 iso-octane/solids ratio (vol./wt.). In some of these tests the iso-octane/solids ratio was decreased to 1:4. The results are presented in fig. 1.12 and the related data in table 1.16.

Fig. 1.12 shows that the reagent desorption was complete at an H_2SO_4 concentration of 1.5N, when the iso-octane/solids ratio was 1:5. On lowering the iso-octane/solids ratio to 1:4 the recovery of the reagents was reduced.

Table 1.16 shows that the oleic acid recovery was higher than the fuel oil recovery at iso-octane/solids ratios of 1:4. The ratios of the respective reagents recoveries were on an average 1.1 in the first case and only 0.98 in the second case. The correlation of this difference with the iso-octane/solids ratio is examined in the following section.

1.6.5. Effects of the iso-octane/solids ratio on the desorption.

In the first series of tests the desorption was carried out in two stages:

a. the reagents were desorbed at 1:4 iso-octane/solids ratio, and

b. the volume of iso-octane extract removed at stage a was replaced by an equal volume of fresh iso-octane and the desorption was repeated (no further acid was added at this stage).

The parameters in this series were 100g ilmenite, 50g water,

FIGURE 1.12

RECOVERY OF OLEIC ACID AND FUEL OIL FROM PURE ILMENITE AS A FUNCTION OF THE NORMALITY OF THE AQUEOUS SOLUTION.

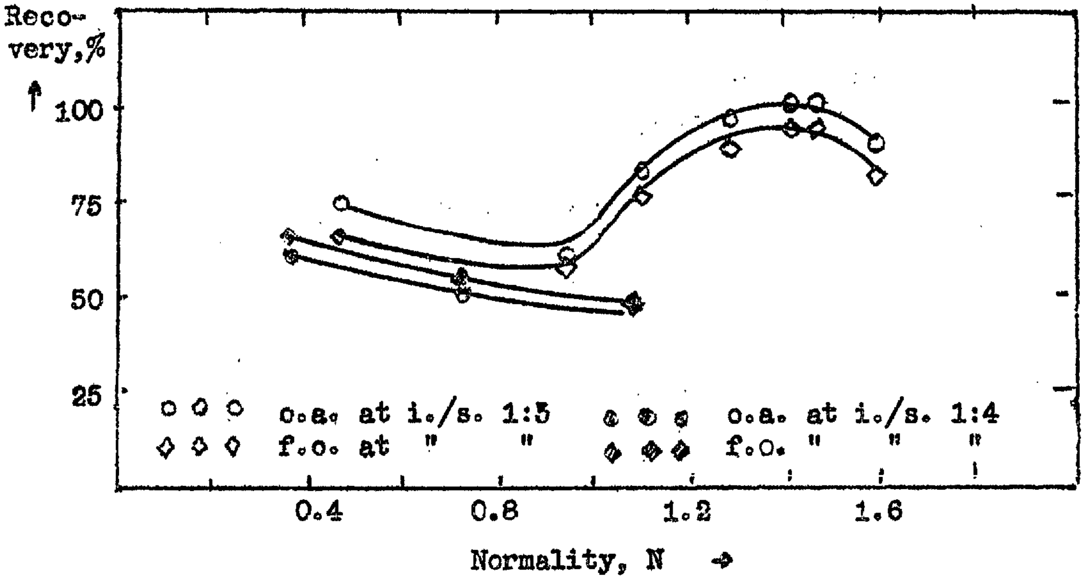
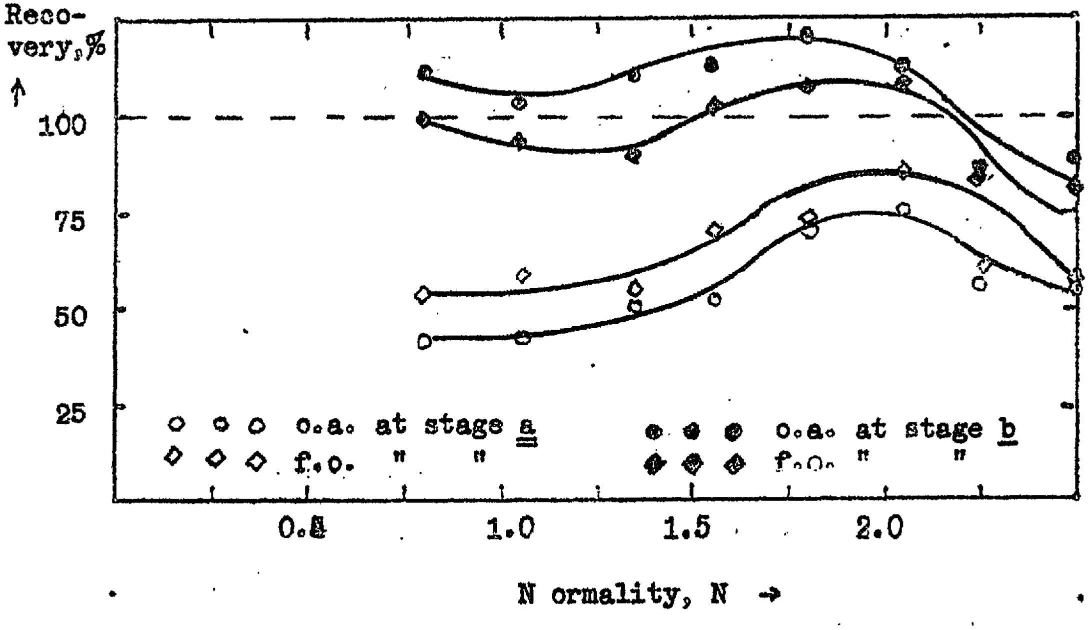


FIGURE 1.15

RECOVERY OF OLEIC ACID AND FUEL OIL ADSORBED ON PURE ILMENITE AS A FUNCTION OF THE NORMALITY OF THE AQUEOUS SOLUTION.



Note: o.a. - oleic acid, f.o. - fuel oil, i./s.-iso-octane/solids

TABLE 1.16

Results of the desorption of oleic acid and fuel oil from "simulated flotation concentrates" as a function of the normality of the aqueous solution.

Iso-octane/solids.	Normality N	Initial reagents		Found reagents		% recovered		Ratio
		o.a. mg.	f.o. mg.	o.a. mg.	f.o. mg.	o.a.	f.o.	
1:4	0.56	618	412	394	265	62	64	0.97
1:4	0.72	665	445	349	240	52	54	0.97
1:4	1.08	664	444	322	215	48	48	1.0
1:5	0.47	442	296	330	208	75	70	1.07
1:5	0.94	450	501	278	170	62	56	1.09
1:5	1.075	457	505	367	252	80	76	1.06
1:5	1.25	460	506	450	278	98	90	1.08
1:5	1.41	465	511	470	292	101	94	1.075
1:5	1.42	461	507	475	294	105	96	1.075
1:5	1.585	470	315	428	257	91	81	1.12

Note: o.a. - oleic acid, f.o. - fuel oil, ratio - of the % recoveries of oleic acid and fuel oil.

0.24-0.27g/kg oleic acid, 0.16-0.18g/kg fuel oil, and an H_2SO_4 concentration of 0.8-2.5N. The results obtained in stages a and b are presented in fig. 1.13 and the related data in table 1.17.

Fig. 1.13 shows that complete desorption of oleic acid and fuel oil from simulated flotation concentrates was impossible at iso-octane/solids ratio 1:4 over the entire range of H_2SO_4 concentration. The increase of the iso-octane/solids ratio in stage b has resulted in the complete desorption over the range of H_2SO_4 concentration of 1.6-2.0N. The ratios of the respective recoveries of oleic acid and fuel oil were 1.14±0.11 at stage b and only 0.86±0.12 at stage a where the iso-octane/solids ratio was 1:4.

Since it was preferable to extract the entire content of oleic acid and fuel oil in one stage, the second series of tests was carried out at a 1:2 iso-octane/solids ratio. The other parameters were 50mg ilmenite, 25g water, 2.1-5.1g/kg oleic acid, 1.4-2.05g/kg fuel oil, and a H_2SO_4 concentration of 0.5-5.5N. The results are presented in fig. 1.14 and the related data in table 1.18.

Fig. 1.14 shows that the reagent desorption was almost complete over the range of H_2SO_4 concentration 1.8-5.0N, while even at concentrations as low as 0.5N the desorption was considerably higher at this iso-octane/solids ratio.

Table 1.18 shows that the ratio of the oleic acid and fuel oil recoveries was an average of 1.15 at the 1:2 iso-octane/solids ratio. It also shows that the recoveries of oleic acid were over 100% while those of fuel oil were below 100%. The elimination of

TABLE 1.17

Results of the desorption of oleic acid and fuel oil as a function of the normality of the aqueous solution at low and high iso-octane/solids ratios (two stages)

Normality N	Initial reagents		First stage of desorption				
	o.a. mg.	f.o. mg.	o.a. mg.	f.o. found mg.	o.a. % recovery	f.o. % recovery	ratio
0.81	258	172	115	92.5	45.6	53.9	0.81
1.09	256	171	115	98.7	45.6	57.6	0.756
1.54	262	174	126	102.5	50	59	0.848
1.58	266	177	136	122.5	51	69.2	0.738
1.82	254	170	177	122.5	69.5	72	0.965
2.05	268	178	205	150	76.5	84.4	0.906
2.27	259	173	138	105	53.5	60.6	0.88
2.48	265	176.5	138	94	52	53.5	0.975
Standard	240	160	240	160	100	100	1.0

Second stage of desorption						
Additional found o.a. mg.	Additional found f.o. mg.	Additional % recovery o.a.	Additional % recovery f.o.	Total % recovery o.a.	Total % recovery f.o.	Ratio of recoveries
178	79	69	45.8	112.6	99.7	1.13
154	65	60.2	36.8	103.8	94.4	1.10
161	52.5	61.5	50.2	111.5	89.2	1.25
165	58	62	52.8	115	102.5	1.10
136	62	53.5	36.4	123	108.4	1.133
101	45	37.5	26.3	114	110.7	1.03
83	57.5	32	21.7	85.5	82.5	1.03
100.5	51.2	38	29	90	82.5	1.095

Note: o.a. - oleic acid, f.o. - fuel oil.

TABLE 1.18

Results of the desorption of oleic acid and fuel oil as a function of the normality of the aqueous solution at a 1:2 iso-octane/solids ratio.

Normality N	Initial reagents o.a. mg.	Initial reagents f.o. mg.	Reagents found o.a. mg.	Reagents found f.o. mg.	% recovery o.a.	% recovery f.o.	Ratio
0.55	155	88.5	109	82.5	82	95	0.88
1.07	157.5	91.5	124	85.7	90.2	91.5	0.985
1.56	144	96	151.5	78.5	91.5	82	1.115
1.80	128	85	124.5	76	97	89.5	1.08
2.05	155	90	157	82	101.5	91	1.115
2.24	129	86.5	152.5	77.5	102.5	89.5	1.145
2.46	155	105	148	87	95.5	84.5	1.15
2.87	107.5	71.5	110	68.6	102,5	96	1.07
5.25	124	85	120.5	72.5	97.2	87.5	1.115

Note: o.a. - oleic acid, f.o. - fuel oil, ratio - of the % recoveries of oleic acid and fuel oil.

FIGURE 1.14

RECOVERIES OF OLEIC ACID AND FUEL OIL AS A FUNCTION OF THE NORMALITY OF THE AQUEOUS SOLUTION AT 1:2 ISO-OCTANE/SOLIDS RATIO.

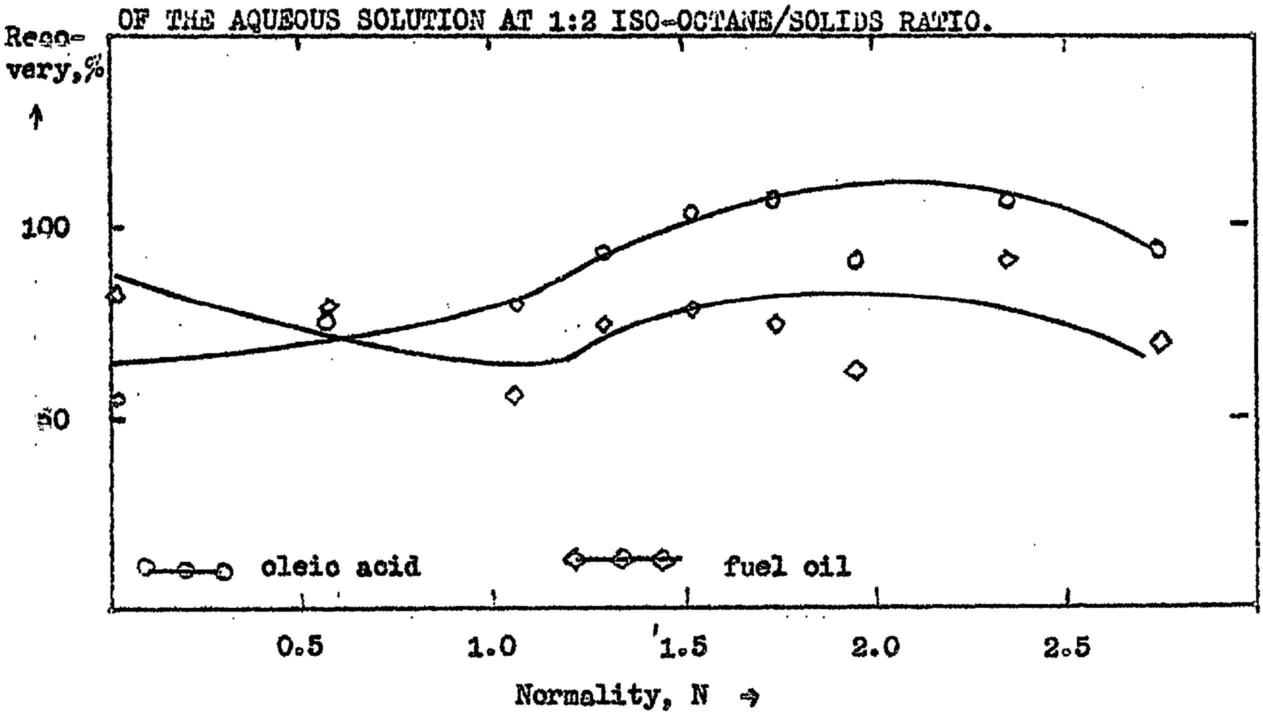
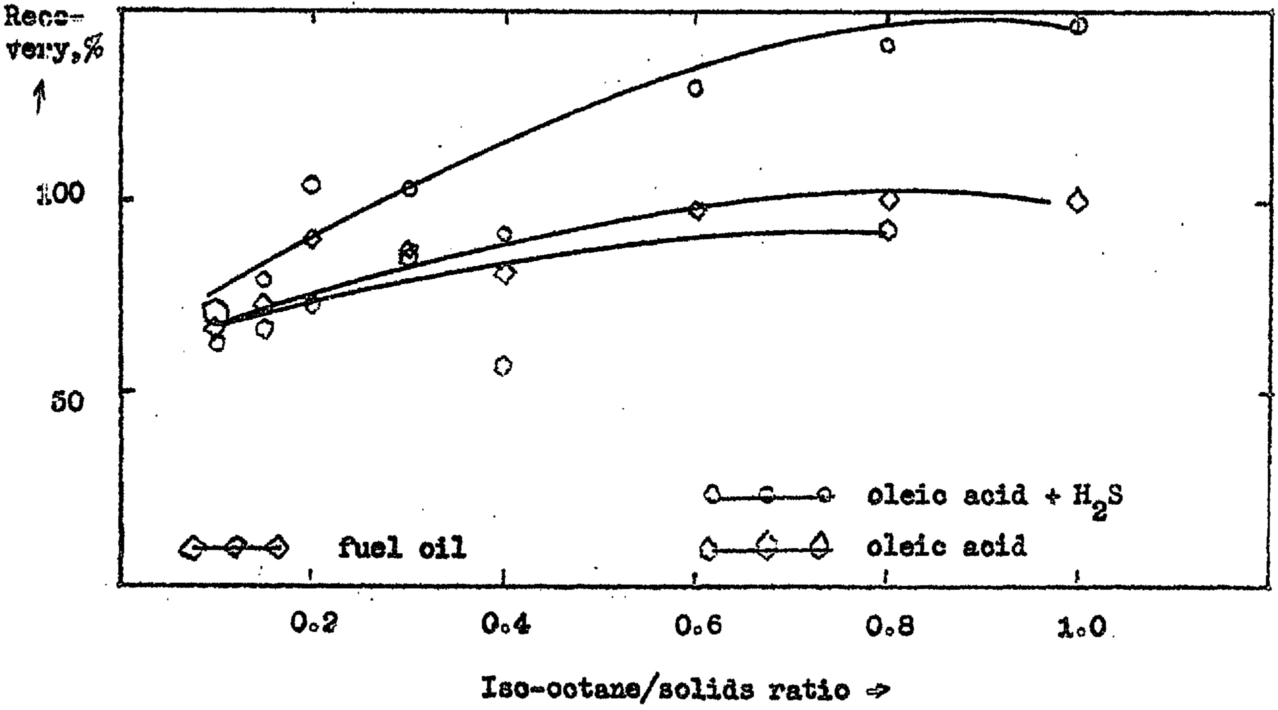


FIGURE 1.15

RECOVERIES OF OLEIC ACID AND FUEL OIL AS A FUNCTION OF THE ISO-OCTANE/SOLIDS RATIO AT THE OPTIMAL NORMALITY OF 2.5N.



these errors was considered in the following tests.

In the third series of tests the reagents were desorbed at iso-octane/solids ratios varying over the range 1:10 to 1:1. In some of these tests fuel oil only was added to the ilmenite in order to eliminate any possible effect of oleic acid. The other parameters were: 50g ilmenite, 25g water, 1.86-2.51g/kg oleic acid, 1.24-5.47 g/kg fuel oil, and 2.5N H_2SO_4 concentration.

The results are presented in fig. 1.15 and the related data in table 1.19 for fuel oil contents and in table 1.21 for oleic acid contents.

The results presented in table 1.19 show that the complete extraction of fuel oil into the iso-octane was possible when the fuel oil concentration in the iso-octane extract did not exceed 2g/l. This was the case in the absence as well as in the presence of oleic acid. At concentrations $<$4g/l in the iso-octane extract only 90% of the fuel oil was recovered, and at concentrations of fuel oil $<$8g/l less than 90% was extracted. These results explain the low fuel oil recoveries observed in the preceding two series of tests, since the fuel oil concentration was close to 4g/l in the respective iso-octane extracts.

An attempt was made in this series of tests to connect the excessive oleic acid recoveries observed in the preceding series, with the potentiometric titration. This was accomplished by conducting the potentiometric titration in the following manner: the alkaline layers were first titrated as described (1.4.2.) with

TABLE 1.19

Results of the desorption of fuel oil from simulated flotation concentrates as a function of the iso-octane/solids ratio at 2.5N.

Test No.	Iso-octane /solids ratio	Initial fuel oil mg.	Max. f.o. concentration, g/l	Fuel oil found, mg.	% recovery of f.o.	Initial o.a. mg.
1	4:10	79	3.95	71	90	0.0
2	8:10	80	2.0	80	100	0.0
3	4:10	170.5	8.5	148	87	0.0
4	8:10	173.5	4.35	155	89.5	0.0
5	10:10	66.5	1.55	66.5	100	99.5
6	8:10	73.5	1.89	72	99.5	115.2
7	6:10	62	2.07	60	99	95
8	4:10	65.5	3.27	60.5	92.5	98.5
9	3:10	83.5	5.56	79	94.5	125.5
10	2:10	66	6.6	63.5	96	99.0
11	1.5:10	69	9.2	61.5	89	105.5
12	1:10	74	14.8	63.5	86	111.0

Note : f.o. - fuel oil, o.a. - oleic acid.

HCl solution until pH 3.3 was reached, and the resulting acidified solutions were agitated strongly and were then back titrated with aqueous NaOH. The end-point results of the titrations and back titrations are presented in table 1.20 and the potentiometric titration curves in one test are presented in Fig. 1.16.

Fig. 1.16 shows that the curves corresponding to the titration and back titration do not coincide. The alkaline solution was retitrated with HCl solution and the resulting potentiometric titration curve coincides with the back titration potentiometric curve. This indicated that the impurity causing the erroneous determination has disappeared.

The results presented in table 1.20 show that the difference between the end-points in the case of the titration with HCl and the back titration with NaOH was equivalent to the errors obtained in the oleic acid determinations. The uncorrected as well as the corrected values for the oleic acid recoveries were presented in table 1.21. When using the corrected values the recoveries of oleic acid and fuel oil were found equal, and the respective ratio between these recoveries was close to 1. These results also show that the difference between the end-point results diminished with decreasing iso-octane/solids ratios, which explains the low ratios between the oleic acid and fuel oil recoveries observed in the preceding series of tests at the low iso-octane/solids ratio of 1:4.

In order to establish the nature of the impurity the following tests were performed:

TABLE 1.20

End-point results of the potentiometric titrations with HCl of saponification mediums after extraction of oleic acid from iso-octane extracts and end point results of the potentiometric back titration with NaOH of the same solutions after agitation at pH 3.5 for removal of impurity.

	Titration with HCl				Back titration with NaOH		
Test No.	N/10 NaOH total, ml.	N/10 NaOH excess, ml.	N/10 CO_3^{--} ml.	o.a. found, mg.	N/10 oleate+ N/10 carbonate	N/10 oleate ml.	o.a. mg.
5	5.05	3.15	0.25	47			
6	5.05	2.50	0.25	66	2.07	1.82	52
7	5.05	2.39	0.25	69			
8	5.05	1.66	0.25	90	2.95	2.70	77.2
9	5.05	1.82	0.25	85	2.96	2.71	77.5
10	5.05	3.48	0.25	38	1.41	1.16	33
11	5.05	2.60	0.25	63	2.34	2.09	59.7
12	5.05	2.82	0.25	56.5	2.22	1.97	56.4
	Same after preliminary outgassing of the iso-octane extracts by vacuum						
2	5.05	4.8	0.25	0	0.25	0	0
4	5.05	4.8	0.25	0	0.25	0	0
5	5.05	3.7	0.25	31	1.35	1.1	31
6	5.05	3.05	0.25	54	1.95	1.7	53

Note: oleic acid = o.a.

FIGURE 1.16

DISCREPANCY IN POTENTIOMETRIC TITRATION CURVES OF SAPONIFICATION MEDIA BEFORE AND AFTER EXPULSION OF THE H_2S ORIGINATING IN THE ORE.

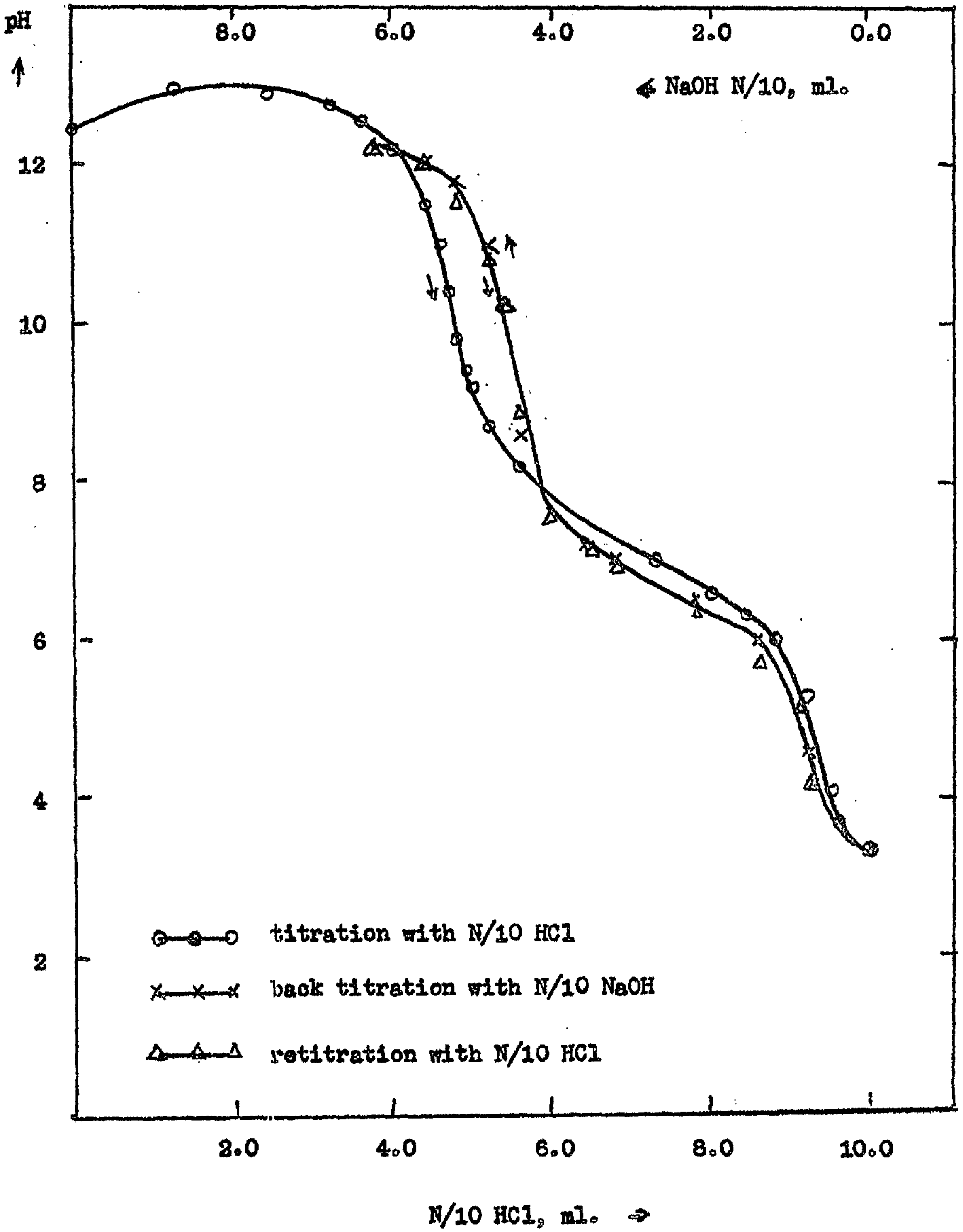


TABLE 1.21

Results of the desorption of oleic acid from simulated flotation concentrates in the presence of fuel oil (before and after H_2S elimination)

Test No.	Initial o.a. mg.	Oleic acid found, mg.		% recovery o.a.			% recovery ratios		Iso-octane /solids ratio
		corr.	uncor.	corr.	uncor.	f.o	corrected	uncorrected	
5	99.5		117.5		118.5	100		1.185	10:10
6	115.2	104	132	97	116.5	99.5	0.98	1.17	8:10
7	95		104		112	99		1.13	6:10
8	98.5	81.2	95	82	96	92	0.89	1.04	4:10
9	125.5	115.5	127	94	101.5	94	0.99	1.085	3:10
10	99	88	101	89	101.5	96	0.92	1.06	2:10
11	103.5	89.5	94.5	86	91	89	0.97	1.03	1.5:10
12	111	97.5	94.5	88	85	86	1.02	0.99	1:10

Note: o.a. - oleic acid, f.o. - fuel oil, corr. - corrected

The iso-octane extracts from tests No. 2, 4, 5, and 6 (see table 1.19) were sampled and vacuum was applied to these solutions, before saponification. Bubble formation was observed on the container walls, which ceased after several minutes if a light vacuum only was applied. When a high vacuum was applied to the iso-octane or to the iso-octane extracts they immediately boiled at room temperature.

The outgassed iso-octane extracts were saponified and the ethanol-water solutions were titrated with HCl and then back titrated with NaOH solution. The end-point results of the titrations and back titrations are presented last in table 1.20. In these tests no practical difference was observed between the respective end-point results, indicating that the impurity had been eliminated by the vacuum applied before saponification.

The excessive oleic acid recoveries can now be explained by assuming that H_2S was evolved by the action of the H_2SO_4 on the sulfide traces in the ilmenite. A faint H_2S smell accompanied all iso-octane extracts while still in contact with the acidified pulp. The H_2S was dissolved in the iso-octane phase at normal pressure but it could be eliminated by applying a vacuum. If the H_2S was not eliminated in this manner, it was extracted by the alkaline saponification medium, and it registered as a weak acid together with the oleic acid and the CO_3^{--} when this solution was titrated with HCl. A strong agitation at pH 3.3 in the presence of air bubbles expelled the H_2S from the acidified saponification medium and the H_2S did not report when back titrating with NaOH solution or when retitrating with HCl solution.

It was concluded that the analysis of iso-octane extracts for oleic acid must include back titration with NaOH solution in order to eliminate errors due to H_2S. Vacuum outgassing of the iso-octane extracts before the saponification was considered unreliable because of possible changes in the iso-octane volume.

Since the oleic acid content of the iso-octane extracts could be determined by the back titration only, it was possible to add at once the amount of HCl solution necessary for lowering the pH to 5.5 before the back titration was performed. This was an advantage as it reduced the time during which the saponification medium was exposed to air, thus minimising the CO_2 absorption (1.5.5.). This procedure was adopted in all following desorption tests.

1.7. DESORPTION OF TALL OIL AND FUEL OIL FROM ILMENITE.

1.7.1. Effects of the H_2SO_4 concentration and the iso-octane/solids ratio.

The method developed for quantitative desorption of oleic acid and fuel oil from "simulated flotation concentrates" had been applied in some preliminary experiments to industrial flotation circuit products containing tall oil and fuel oil (for details see Appendix section 1.11.1.). It was established in these tests that the desorption medium must be modified by addition of ethanol.

The modified method was applied to the desorption of tall oil and fuel oil from "simulated flotation concentrates" in order to investigate the effects of the following factors: the iso-octane/solids ratio, the H_2SO_4 concentration, the ethanol/water ratio, the reagent concentration, and the tall oil/fuel oil ratio.

The parameters in the first series of tests were: 20g ilmenite, 10g water, 1.8-2.4g/kg tall oil, 1.2-1.6g/kg fuel oil, 1:2 ethanol/water ratio, 0.5-5.0N H_2SO_4 concentration, and iso-octane/

solids ratios of 1.1:2 and 1.1:1.

The results presented in table 1.22 show that the desorption of tall oil and fuel oil from "simulated flotation concentrates" was not quantitative at an iso-octane/solids ratio 1:2 (vol./wt.) at 0.5–3.0N H_2SO_4 concentration in contrast to the case of oleic acid and fuel oil (see section 1.6.3.). The iso-octane/solids ratio of 1:1 was the minimum necessary for quantitative desorption of the tall oil and the fuel oil. The necessary H_2SO_4 concentration was 1N and concentrations up to 3N had no detrimental effect on the desorption.

Examination of the potentiometric end-point results show that the H_2S concentration in the iso-octane extracts was nearly constant. It was therefore necessary to eliminate the H_2S in this case too by the method employed in the case of oleic acid and fuel oil (see section 1.6.3.).

A second series of tests was carried out, the parameters being: 20g ilmenite, 10g water, 1.6–2.4g/kg tall oil, 1.1–1.6g/kg fuel oil, 1:1.6 ethanol/water ratio, 0.0–1.24N H_2SO_4 concentration, and iso-octane/solids ratios of 0.625:1 and 1.25:1.

The results presented in table 1.23 confirm the earlier conclusion that iso-octane/solids ratios < 1:1 do not result in a complete desorption of the reagents. At an iso-octane/solids ratio of 1.25:1 the H_2SO_4 concentration of 0.5N was sufficient for quantitative desorption of both the tall oil and the fuel oil. Since the quantity of acid consumed by crude ilmenite exceeded that consumed by pure ilmenite, H_2SO_4 concentrations in the range 2–3N should be applied

TABLE 1.22

Results of the desorption of tall oil and fuel oil from simulated flotation concentrates as a function of the H_2SO_4 concentration.

Normality N	Initial reagents t.o. mg.	Initial reagents f.o. mg.	Reagents found t.o. mg.	Reagents found f.o. mg.	Error t.o. %	Error f.o. %	H_2S meq	Iso-octane/solids.
0.5	35.8	23.8	32.0	21	-10.5	-11.7	0.03	1.1:2
1.0	38.1	25.5	31.8	21.4	-16.5	-15.0	0.05	1.1:2
1.5	47.8	31.8	37.3	26.6	-22.0	-16.5	0.04	1.1:2
2.0	37.0	24.8	35.8	22.0	- 3.2	-10.9	0.05	1.1:2
2.5	39.5	26.3	33.9	24.0	-16.2	- 8.3	0.04	1.1:2
3.0	38.8	25.8	32.7	22.2	-15.2	-13.7	0.04	1.1:2
0.5	38.1	25.5	34.8	24.0	- 8.6	-5.5	0.03	1.1:1
1.0	39.7	26.5	39.0	25.6	- 1.7	- 3.0	0.03	1.1:1
1.5	37.6	25.1	35.8	24.4	- 4.8	- 2.5	0.03	1.1:1
2.0	44.4	29.5	45.5	28.9	-.2.0	- 2.0	0.03	1.1:1
2.5	37.4	24.9	38.2	24.4	+ 2.1	- 1.6	0.03	1.1:1
3.0	38.0	25.3	40.0	25.2	+ 5.2	0	0.03	1,1:1

Note: t.o. - tall oil, f.o. - fuel oil.

TABLE 1.23

Results of the desorption of tall oil and fuel oil from simulated flotation concentrates as a function of the H_2SO_4 concentration.

Normality	Initial reagents mg t.o.	f.o.	Reagents found mg t.o.	f.o.	Error % t.o.	f.o.	Iso-octane/ solids
0.0	16.6	11.1	8.5	14.8	-49.5	+10.2	0.625:1
0.25	18.4	12.3	19.1	11.0	+ 3.8	- 9.8	0.625:1
0.5	20.3	13.5	22.0	14.4	+ 8.4	+ 6.6	0.625:1
0.65	17.8	11.8	15.5	10.0	-12.9	-15.3	0.625:1
0.85	17.7	11.8	13.1	9.8	-26	-19	0.625:1
1.05	17.5	11.7	16.7	11.7	- 4.5	+ 5.6	0.625:1
1.24	17.8	11.8	14.3	9.6	-19.6	-19	0.625:1
0.0	20.6	13.8	7.5	13.0	-65	- 5.5	1.25:1
0.25	21.1	14.1	22.6	12.7	+ 7.5	- 9.6	1.25:1
0.5	22.7	15.1	23.5	17.0	+ 3.5	+12.6	1.25:1
0.65	23.6	15.7	23.8	15.4	+ 0.9	- 1.2	1.25:1
0.85	21.7	14.4	22.3	14.6	+ 2.8	+ 1.2	1.25:1
1.05	20.8	13.9	20.2	15.0	- 2.6	+ 8.2	1.25:1
1.24	16.6	11.1	15.8	11.2	- 4.8	+ 0.6	1.25:1

Note: t.o. - tall oil, f.o. - fuel oil

in the desorption of tall oil and fuel oil from actual flotation products.

1.7.2. Effects of the ethanol/water ratio on the desorption of tall oil and fuel oil.

In the following tests the ratio ethanol/water in the stripping solution was varied from 0 to 1:2 while keeping the total volume of this solution at a constant value. The other parameters were : 20g ilmenite, 15ml stripping solution, 1.7-2.0g/kg tall oil, 1.15-1.54g/kg fuel oil, 2.5N H_2SO_4 concentration, and 1.25:1 iso-octane/solids ratio. The results are presented in table 1.24 (first 6 tests).

The results of these tests show that an ethanol/water ratio of 1:2 is a minimal requirement for quantitative desorption of tall oil and fuel oil from "simulated flotation concentrates". The corresponding ethanol/solids ratio was 1:4 (vol./wt.).

1.7.5. Effects of the reagent concentration on the desorption.

Various reagent concentrations could be expected in flotation products. The desorption procedure was therefore examined at different reagent concentrations, employing optimal values for the other parameters: 20g ilmenite, 15ml stripping solution, 1:2 ethanol/water ratio, 2.5N H_2SO_4 concentration, and 1.25:1 iso-octane/solids ratio.

The results presented in table 1.24 (last 8 tests) show that the reagent desorption was quantitative over the entire range

TABLE 1.24

Results of the desorption of tall oil and fuel oil from simulated flotation concentrates as a function of the ethanol/water ratio (first 6 tests) and of the reagent concentration (last 8 tests).

Water ml.	Ethanol ml.	Initial reagents t.o. mg.	Initial reagents f.o. mg.	Reagents found t.o. mg.	Reagents found f.o. mg.	Error % t.o.	Error % f.o.
15	0	34.0	22.7	32.6	21.2	- 4.1	- 6.6
14	1	35.3	23.5	33.6	22.0	- 4.7	- 6.4
13	2	40.2	26.8	37.0	23.8	- 7.8	-11.2
12	3	37.4	24.8	32.6	20.8	-12.8	-16.1
11	4	36,5	24.4	33.6	24.0	- 8.0	- 1.6
10	5	36.8	24.6	38.2	24.0	+ 3.8	- 2.5
10	5	4.3	2.9	4.6	3.8	+ 7	+ 6.2
10	5	8.6	5.7	8.15	5.5	- 5.2	- 3.1
10	5	13.0	8.6	14.0	8.6	+ 7.7	0
10	5	17.5	11.7	18.7	11.5	+ 6.9	- 1.7
10	5	22.0	14.6	24.2	13.4	+10.0	- 9
10	5	26.6	17.8	27.9	17.4	+ 4.9	- 2
10	5	31.5	21.0	32.6	21.4	+ 3.5	+ 1.7
10	5	53.5	35.9	55.2	35.8	+ 3.2	- 0.5

Note: t.o. - tall oil, f.o. - fuel oil.

of concentrations examined - 0.215-2.67g/kg tall oil and 0.145-1.8g/kg fuel oil.

1.7.4. Effects of the tall oil/fuel oil ratio on the desorption.

Since different tall oil/fuel oil ratios were expected on ilmenite flotation products it was necessary to investigate the effect of this ratio on the desorption. The parameters in the following tests were: 20g ilmenite, 15ml stripping solution, 1:1.6 ethanol/water ratio, 2.5N H_2SO_4 concentration, 1.25:1 iso-octane/solids ratio, 0.0-4.32g/kg tall oil and 4.14-0.0g/kg fuel oil. The total reagent concentration was kept constant while the ratio tall oil/fuel oil was varied.

The results are presented in table 1.25. The results for the tall oil determination show that it was not affected by the changing tall oil/fuel oil ratio. The results for the fuel oil determination, which were corrected by subtracting a value proportional to the tall oil concentration, show that errors were obtained at low tall oil/fuel oil ratios. The error was attributable to the fuel oil concentration in the iso-octane extract which exceeded in these cases the limitting value of 2g/l (1.6.5.)

TABLE 1.25

Results of the desorption of tall oil and fuel oil from simulated flotation concentrates as a function of the tall oil/fuel oil ratio.

Tall oil/ fuel oil ratio	Initial reagents total mg.	t.o. mg.	f.o. mg.	Reagents found t.o. mg.	f.o. mg.	Error % t.o.	f.o.
0.0:	82.8	0.0	82.8	0.0	77.2		- 7.25
1.0:15.8	74.1	4.4	69.7	5.65	65.6	+2.8	- 5.75
1.0: 7.1	70.6	8.6	61.9	9.35	55.8	+8.2	-10.6
1.0: 3.8	81.6	17.1	64.5	16.0	58.2	-6.4	- 9.65
1.0: 2.5	91.9	26.1	65.8	26.4	58	+1.1	-11.8
1.0: 2.0	68.3	22.7	45.6	24.3	42.8	+7.0	- 6.15
1.0: 1.0	69.3	35.2	34.1	37.1	34.3	+5.4	+ 0.9
1.5: 1.0	64.6	38.8	25.8	39.8	26.2	+2.6	+ 1.5
3.3: 1.0	71.7	55.1	16.6	53.5	17.0	-2.9	+ 2.4
6.4: 1.0	63.0	54.5	8.5	54.4	9.0	-0.2	+ 6.5
6.7: 1.0	85.3	74.2	11.1	74.2	10.5	0	- 5.5
: 0.0	86.4	86.4	0.0	85.5	0.0	-1.0	

Note: t.o. - tall oil, f.o. - fuel oil

1.8. DESORPTION OF TALL OIL AND FUEL OIL FROM FLOTATION PRODUCTS.

1.8.1. Desorption of reagents from properly conditioned feeds.

Having shown in section 1.7. that tall oil and fuel can be desorbed from "simulated flotation concentrates" it is necessary to show that the method can be applied to properly conditioned flotation products, and this was first examined in the case of flotation feeds. The material used for preparing feeds was a crude ilmenite described in section 2.2.1. The conditioning procedure was that normally applied in flotation tests and is described in section 2.2.3.

In the first series of tests the entire contents of the conditioning tank were transferred into suitable ground-glass stoppered flasks and the necessary proportions of H_2SO_4, ethanol, and iso-octane were added according to the optimal parameters established in 1.7.2. The flasks were vigorously shaken for several minutes, left to stand, and samples were then withdrawn from the liquids for phase separation by centrifugation. The iso-octane extracts were then analysed for tall oil and fuel oil.

In this series of tests 150mg ilmenite samples were conditioned at 70% solids with various quantities of tall oil and fuel oil at 1200 r.p.m. and for a sufficiently long duration (30min.) to ascertain adequate adsorption of the reagents on the mineral surface. in each case four samples of the iso-octane extracts were saponified individually in order to assess the reproducibility. The results for the tall oil assays are presented in table 1.26 and those for the fuel oil assays in table 1.27.

TABLE 1.26

Results of the desorption of tall oil from properly conditioned feeds

Tall oil, mg. Initial	found	Error %	Fuel oil, mg initial	found
179.0	170.0	-5.0	0.0	20
179.0	174.0	-2.8	0.0	20
179.0	174.0	-2.8	0.0	19.8
179.0	178.0	-0.5	0.0	19.9
52.5	50.9	-3.0	0.0	9.6
52.5	54.5	+3.8	0.0	9.6
52.5	52.6	+0.2	0.0	8.5
52.5	50.9	-3.0	0.0	9.4
22.5	21.8	-3.1	0.0	7.5
22.5	23.6	+4.9	0.0	7.4
22.5	21.8	-3.1	0.0	7.7
22.5	23.6	+4.9	0.0	7.4

TABLE 1.27

Results of the desorption of fuel oil from properly conditioned feeds

Fuel oil, mg. initial	found	Error %
108.6	100	- 8.0
108.6	101.6	- 6.5
108.6	101.6	- 6.5
108.6	101.6	- 6.5
45.9	46.6	+ 1.5
45.9	46.0	+ 0.2
45.9	46.4	+ 1.1
45.9	46.4	+ 1.1
21.9	25.0	+14.1
21.9	24.6	+12.3
21.9	24.5	+11.9
21.9	24.8	+13.2

The results in table 1.26 show that a considerable amount of the tall oil impurity was left in the iso-octane extract after the saponification when fuel oil was absent. The fuel oil concentration corresponding to the optical density of this impurity was equivalent to 8% by wt. of the tall oil concentration.

The results in table 1.27 indicate the presence of an impurity due to the ilmenite, which contributed to the optical density of the iso-octane extract. This contribution was equivalent to 0.02g/kg fuel oil and must therefore be taken into account when the fuel oil concentration on the rock specimen is low.

The results in both tables show that the entire amount of reagents was desorbed from the conditioned samples and that the assaying reproducibility was satisfactory in the case of both reagents.

1.8.2. Desorption of the reagents from filtered and dried conditioned feeds.

Wet sampling of the pulp of conditioned or floated material aimed at desorption of the reagents by the procedure adopted in 1.8.1. for slurries was considered impractical. It was therefore necessary to determine whether filtration of the pulps and drying of the filter cake were permissible for the purpose of the reagent assays.

A 500g crude ilmenite sample was conditioned at 70% solids with 334mg tall oil and 222mg fuel oil. After conditioning for 30 min. at 1500 r.p.m. the pulp was filtered. The filter cake containing 8%

moisture was blended by shaking for 1 minute in a hemispherical bowl, so as to produce a continuous mixing of the moist material without any pelletising. This simple procedure was found satisfactory from the view point of sample reproducibility.

Six samples were withdrawn and the reagents were desorbed and determined by the methods developed. The results are presented in table 1.28. The filtered sample was left to dry in air until of constant weight and six further samples were analysed for tall oil and fuel oil. These results are also presented in table 1.28 (last 6 tests).

The results obtained show that filtration of the pulp was permissible before assaying for reagent content, but drying of the filter cake at room temperature was detrimental. The reproducibility of the samples was satisfactory in both cases.

In an attempt to check the analytical method of Runollina et al (1) samples of the air dried material were extracted several times with ether, the ether extracts were collected, and after centrifugation the clear solution was titrated potentiometrically with NaOH solution. No organic acid was detected in the extracts by this method.

In order to establish a proper sampling procedure the following test was performed. A 500g crude ilmenite sample was conditioned with 578mg tall oil and 252mg fuel oil. After 30 minutes' conditioning the pulp was filtered and the filter cake was blended by the above mentioned procedure. The sampling procedure adopted comprised: collection of small amounts of material from various parts of the bulk, close packing into 10ml cylindrical containers, and covering with tight lids. These contai-

TABLE 1.28

Results of the desorption of tall oil and fuel oil from conditioned pulps after filtration and after drying in air at room temperature.

Sample weight, mg	Initial reagents		Reagents found		Error in %	
	tall oil mg	fuel oil mg	tall oil mg	fuel oil mg	tall oil	fuel oil
16.6	11.1	7.4	10.8	7.3	-2.7	-1.4
16.55	11.05	7.35	10.8	7.3	-2.2	-0.7
16.25	10.85	7.25	11.4	6.95	-5.0	-4.1
15.85	10.6	7.05	10.0	6.75	-5.7	-4.25
15.65	10.45	6.95	10.8	6.55	+3.3	-5.7
16.2	10.8	7.2	10.8	6.85	0.0	-4.9
Air dried samples						
17.5	11.7	7.8	8.65	5.05	-26.0	-35.0
16.4	10.95	7.3	9.15	4.9	-21.0	-33.0
18.5	12.2	8.15	10.5	5.75	-14.0	-29.5
18.6	12.4	8.27	10.5	5.8	-15.4	-30.0
18.4	12.3	8.2	10.5	5.85	-14.7	-28.7
16.5	10.9	7.25	8.65	5.275	-20.6	-27.4

ners had the double purpose of ascertaining a standard volume of the sample and of enabling storage in the moist state. The samples were directly transferred into 50ml centrifuge test tubes and the necessary amounts of ethanol, H_2SO_4, and iso-octane were added to permit immediate desorption. The test tubes were closed tightly with polythene lids so that there was no contamination of the iso-octane and no losses by evaporation. The moisture content of the samples was calibrated by means of parallel samples, collected in the same manner, and dried within the containers to constant weight.

Such samples were collected immediately after filtration, after 90 minutes' standing in the bowl, after 90 minutes' drying on the table, after 270 minutes drying on the table, and after 15 minutes drying at 105°C. The correlation between the moisture content of the sample and the tall oil and fuel oil concentration determined was presented in table 1.29

The results show that a small amount of tall oil and fuel oil was not accounted for in the samples taken immediately after the filtration. The cause for this apparent loss is found at a later stage of this study (see section 2.5.2.).Table 1.29 shows that the tall oil content of the sample that can be determined by the desorption method reduced once the moisture content approaches nil. The fuel oil content decreased in proportion to the decrease in the moisture content. Drying at 105°C caused very high losses of fuel oil.

Separate experiments have shown that the evaporation of fuel oil results in a proportional lowering of the optical density,

TABLE 1.29

Moisture and reagents contents of filtered samples, partially or totally dried at room temperature

Moisture content,%	Reagent content in % of initial Tall oil	Fuel oil	Drying duration hours	Remarks
7.0	98.8±2.1	91.0±1.5	0	In bowl
6.4	96.9±2.4	86.1±0.8	1½	"
2.2	87.7±0.7	65.1±2.5	3	On table
0.0	64.0±2.0	50.7±0.7	6	"
0.0	55.4±1.4	36.5±1.1	1/4	At 105°C

TABLE 1.30

Tall oil and fuel oil contents of flotation feed, concentrate, and tailings

	Feed	Concentrate	Tailings
Tall oil,g/kg	0.852±0.017	2.25±0.000	0.240±0.024
Fuel oil,g/kg	0.550±0.008	1.625±0.010	0.075±0.005

Reagent material balance

	Feed	(Feed)*	Concentrate	Tailings	Total
Tall oil,mg	852	(690)*	528	135	661
Fuel oil,mg	550	(460)*	382	42	424

(*) Reagents left in 890g feed which were actually floated.

indicating that the light absorbing component evaporated at the same rate as the entire fuel oil quantity. These experiments suggest that the decreasing fuel oil contents as a function of the moisture content were caused by evaporation of the fuel oil. The desorption must therefore be carried out immediately after the filtration, and samples should be stored either as a slurry or as moist solids soaked in ethanol within the centrifuge test tubes.

1.8.5. Desorption of the reagents from actual flotation products.

The possibility of obtaining a reagent material balance when assaying flotation feed, concentrate, and tailings, was the final proof necessary before adopting the desorption and assaying methods in a detailed study of fatty acids and fuel oil adsorption on ilmenite flotation products.

A deslimed 990g crude ilmenite sample was conditioned with 865mg tall oil and 575mg fuel oil . Part of the pulp was filtered and sampled for determination of the reagent content of the feed. The remainder was floated at 50% solids to produce 255g concentrate and 555g tailings, containing theoretically 690mg tall oil and 459mg fuel oil. The concentrate and tailings were collected, filtered, blended and sampled. The results of the assays are presented in table 1.30. It was concluded from the reagent material balance that the desorption of the reagents from both flotation concentrate and tailings was complete, and that the amount of reagents found on these two products was equal to the amount of reagents found on the conditioned feed.

Additional tests show that the same method can be applied to determine the reagent content of industrial flotation products (see Appendix, section 1.11.1).

1.9. SUMMARY AND CONCLUSIONS.

The analytical method developed permits accurate determination of the fatty acid and the fuel oil adsorbed on ilmenite flo-flotation products. This method was characterised by the following points:

a. Fatty acid and fuel oil adsorbed on ilmenite or gangue minerals can be desorbed by applying a strongly acidic solution containing 40% ethanol, and the desorbed reagents can be extracted by a hydrocarbon solvent such as iso-octane.

b. In order to prevent loss of reagents from the mineral surface by evaporation or insolubilisation, the flotation products must be sampled in the moist state and must be treated with the desorption medium as soon as possible.

c. In order to prevent contamination and evaporation of the highly volatile solvent all operations must be carried out in closed containers which are suitable for centrifuges.

The two reagents in the iso-octane extract can be separated by saponifying with N/20 NaOH solutions in 0.6:1 ethanol/water; the organic acids are extracted by the alkaline phase, which is separated from the iso-octane phase by centrifugation.

e. The fuel oil is determined by measuring the optical density at 224mμ in the iso-octane solution; suitable corrections for the errors introduced by impurities from the solids and from the fatty acids are necessary.

The fatty acids are determined by acidimetric titration, preferably using indicators (see Appendix, section 1.11.5); before the titration with NaOH the saponification medium must be diluted with further ethanol and acidified with HCl solution to pH 5.5, when the H_2S contamination, originating in the ore, can be expelled by strong agitation.

The experiments performed have enabled determination of requirements which must be rigorously maintained in order to prevent considerable errors. These requirements have been incorporated in the actual procedure which is outlined in the following section.

1.10. SPECIFICATIONS FOR DETERMINATION OF FATTY ACID AND FUEL OIL CONTENT OF ILMENITE FLOTATION PRODUCTS.

1.10.1. Desorption of the reagents from the flotation products.

Collect the sample as a slurry and if necessary store in this form. Filter the sample and transfer the filter cake immediately into hemispherical bowls. Blend quickly by abrupt jerks, taking care that no polletising occurs.

Spot sample the moist material and collect four samples in 10ml cylindrical containers (diam. = height = 1.5cm, to enable quick removal of the moist material) with close fitting lids to prevent evaporation. Dry two samples at 105°C to calibrate the moisture content.

Transfer two samples, as soon as possible after filtration, into 50ml centrifuge test tubes. The close-packed moist cylindrical sample slides easily into the test tubes, permitting quick transfer. The volume of these test tubes is sufficient for the liquids required in the desorption operation.

Weigh the sample container when full and empty and compute the dry weight of the sample by correcting for the moisture content determined on parallel samples.

Submerge the sample in 6-7ml ethanol and remove air pockets to permit proper soaking for 15 minutes. The samples can be stored in this way for several days if the centrifuge test tubes are tightly closed with the lids.

Start desorption by adding 3ml of 12N H_2SO_4 and by pipetting 25 ml iso-octane. Fit the tight lids and shake by hands for 3-5 min. to permit extensive mixing of the three phases. Follow by centrifuging for 3-5 minutes at 3000 r.p.m. to permit good separation of the iso-octane extract from the other two phases. Pipette immediately 20 ml of the iso-octane extract into similar 50ml centrifuge test tubes and close the latter immediately with tight lids.

Before use clean the centrifuge test tubes by rinsing twice with ethanol and clean the pipettes by rinsing with ethanol and iso-octane. A very high degree of cleanliness is imperative.

1.10.2. Separation of the fatty acids from the fuel oil.

To the 20ml aliquots of iso-octane extract pipette quickly 2ml ethanol and 4ml N/20 NaOH (the volumes and concentrations should be increased in proportion to the fatty acid concentration), and close immediately. Shake by hand for 2-5 minutes until thoroughly dispersed and centrifuge at 5000 r.p.m.

The two layers may be left in contact with each other for 24 hours before assaying for reagent content, provided the test tubes are tightly closed.

1.10.3. Determination of the fuel oil content in the saponified iso-octane extract.

Pipette 2ml of the iso-octane extract into 10ml volumetric flasks and complete with iso-octane to the mark, using a pipettte. If greater dilution is necessary redilute the solution obtained . For the sake of accuracy dilute to an expected optical density below 1.0. Iso-octane extracts from flotation tailings rarely need dilution.

Measure the optical density of the iso-octane solutions at the wavelength corresponding to maximum optical density. Use 2mm fused silica cells because of the high optical density of fuel oil solutions.

Rinse carefully before each measurement with the sample solution, and keep the external walls dry and the cells closed, because of the very high volatility of the iso-octane. Use iso-octane as the reference liquid and change it frequently when measuring a long series of iso-octane extracts.

Calibrate beforehand the dependence of the optical density on the fuel oil concentration at the wavelength corresponding to maximum optical density.

Correct for the errors due to impurities from the fatty acids and the ore by measuring the optical density of iso-octane extracts from ore samples conditioned at various concentrations of fatty acids and fuel oil.

1.10.4. Determination of the fatty acids in the saponification medium.

Transfer the alkaline layer, by means of a graduated pipette, into a beaker containing 25 ml ethanol and 5 ml N/20 HCl (increase the volume and concentration according to the alkaline content).

Agitate at maximum possible speed (use magnetic stirrer covered with perfectly inert material) for several minutes until all the H_2S has been expelled. Calibrate the exact duration of the agitation with a solution originating from the particular ore studied.

Reduce the speed of rotation to prevent entrainment of air bubbles, add 8 drops tetra-iodo-phenol-sulphone-phthalein, and titrate with NaOH (choose concentration according to fatty acid content) until colour change from pale green to pale blue, on addition of one drop of

NaOH solution.

Add 8 drops of di-phenol-purple solution (blue changes back to green) and continue titration until colour turns to violet, and persists for 1 minute. Determine the fatty acid content by subtracting the volumes of NaOH required to reach the two end-points.

When using tall oil, calibrate its equivalent content of organic acids by titrating solutions in the same ethanol-water medium with the NaOH solution used, in the presence of the two indicators. Titrate the ethanol-water medium in the absence of fatty acids in order to calibrate its CO_2 content.

Calibrate the error due to the particular ore by titrating solutions obtained when applying the desorption and saponification procedures to untreated ore samples. Check also for reproducibility of the saponification method by treating iso-octane solutions of known fatty acid and fuel oil content.

Check for the reproducibility of the desorption method by applying it to ore samples treated with known amounts of fatty acids and fuel oil.

The same procedure can be applied to pure fatty acids, such as oleic acid, and to mixtures of fatty and resin acids, such as tall oil.

Before using the above mentioned indicators it is imperative to determine the coincidence of the potentiometric curve inflections with the colour changes of the two indicators. The potentiometric titration must be carried out very slowly, as the response of the glass electrode is slow in the ethanol-water medium. Check this in the case of a pure fatty acid, in the case of a mixture, and in the case of fatty acids desorbed from ores samples.

The saponification number of 0.01 meq. organic acid can be determined at an accuracy of ±10% when N/50 NaOH solution is used in this method.

1.11. APPENDIX.

1.11.1. Desorption of the reagents from industrial flotation products.

The methods developed for determination of tall oil and fuel oil adsorbed on "simulated flotation concentrates" were applied for the determination of the reagents adsorbed on industrial flotation products, which may differ from the former in certain respects.

When desorption solutions lacking ethanol were applied to such samples it was impossible to extract quantitatively the adsorbed reagents, even at an H_2SO_4 concentration of 12N. It was found in addition when sampling the filtered products, stored in closed containers, at weekly intervals, that the reagent content decreased considerably.

The optimal desorption conditions established in 1.8.5. were employed in the case of the following 5 samples:

A - the feed of the ilmenite flotation circuit;

B - the tailings of the rougher flotation stage;

C - the combined tailings of the cleaner flotation stages;

D - the cleaner flotation concentrate;

E - the final flotation concentrate after removal of part of the reagents at pH 1.

The results obtained by analysing the iso-octane extracts obtained for the tall oil and fuel oil are presented in table 1.31. The reagent material balance is presented ay the end of this table.

TABLE 1.31

Tall oil and fuel oil content of inductrial flotation products.

Sample	Weight%	Tall oil g/kg	Fuel oil g/kg
A (Feed)	100	0.98	0.465
B (Tailings)	44.5	0.15	0.08
C (Tailings)	8.6	0.91	0.49
D (Concentrate)	46.9	1.71	0.87
E (Leached concentrate)		0.35	0.07

Material balance of reagents (*)

	A (Feed)	B (Tailings)	C (Tailings)	D (Concentrate)	Total
Tall oil, g	98	6.7	7.8	80	94.5
Fuel oil, g	46.5	3.5	4.2	40.7	48.4

(*) The results were based on 1000kg feed.

The results presented in this table demonstrate that the desorption method and the analytical methods established can be applied successfully to industrial flotation products.

It was desirable to adapt these methods to the assay of the flotation reagent content of the floated pulp of the last stage of the industrial flotation circuit. This was examined next.

The floated pulp of the last stage of the industrial Tellnes ilmenite flotation circuit consisted of pyrites, some ilmenite, and a great proportion of reagents, floating on the surface of the accompanying aqueous phase. This slurry was obtained when the cleaner flotation concentrate - D - was leached and depressed at pH 1 in order to produce the final ilmenite concentrate - E.

Tests performed on such a slurry have shown that the following procedure was most suitable for extraction of the reagents and for the determination of their concentration:

a. collect the pulp directly in the bottle in which the extraction is to be carried out;

b. extract the unadsorbed reagents by treating four times with fresh iso-octane at a 1:1 iso-octane/solids ratio in the presence of 1:4 ethanol/solids, decant the extracts and combine them;

c. dilute a small sample of the combined extract with pure iso-octane and saponify according to the procedure described in 1.10.2. and determine the reagent content;

d. filter the pulp, and analyse the reagent content of the filter cake by the procedure outlined in 1.10.

Application of this procedure to a sample from the industrial flotation circuit showed that 59g tall oil and 26g fuel oil were present in 1 l. slurry containing 550g solids. Steps b and c accounted for 99% of the reagents while the solids contained only 0.7g/kg tall oil and 0.46g/kg fuel oil.

1.11.2. Potentiometric titration of organic acids with N/50 NaOH.

It was desirable to use N/50 NaOH solutions for the titration of ethanol-water solutions containing very small amounts of organic acids, in order to increase the accuracy in the determination of the reagent content in tailings. The procedure used in these titrations was the same as that used with N/20 NaOH solutions. Both oleic acid and tall oil containing solutions were examined. The results are presented in tables 1.32 and 1.33 and some potentiometric titration curves are presented in figures 1.17 and 1.18 respectively.

Comparison of the curves obtained in fig. 1.17 and fig. 1.18 with the curves obtained in fig. 1.10 and fig. 1.11 respectively, shows that despite the less steep inflections the end-points were clear enough for determination of the reagent content. The end-point results show that the use of N/50 NaOH solutions enables accurate determination of several miligrams of oleic acid or tall oil at an error of ±1%. Tests with organic acids extracted from ore samples have indicated that such dilute titrants were useful at organic acid contents below 0.1 meq. per sample (i.e. below 5ml N/50 NaOH).

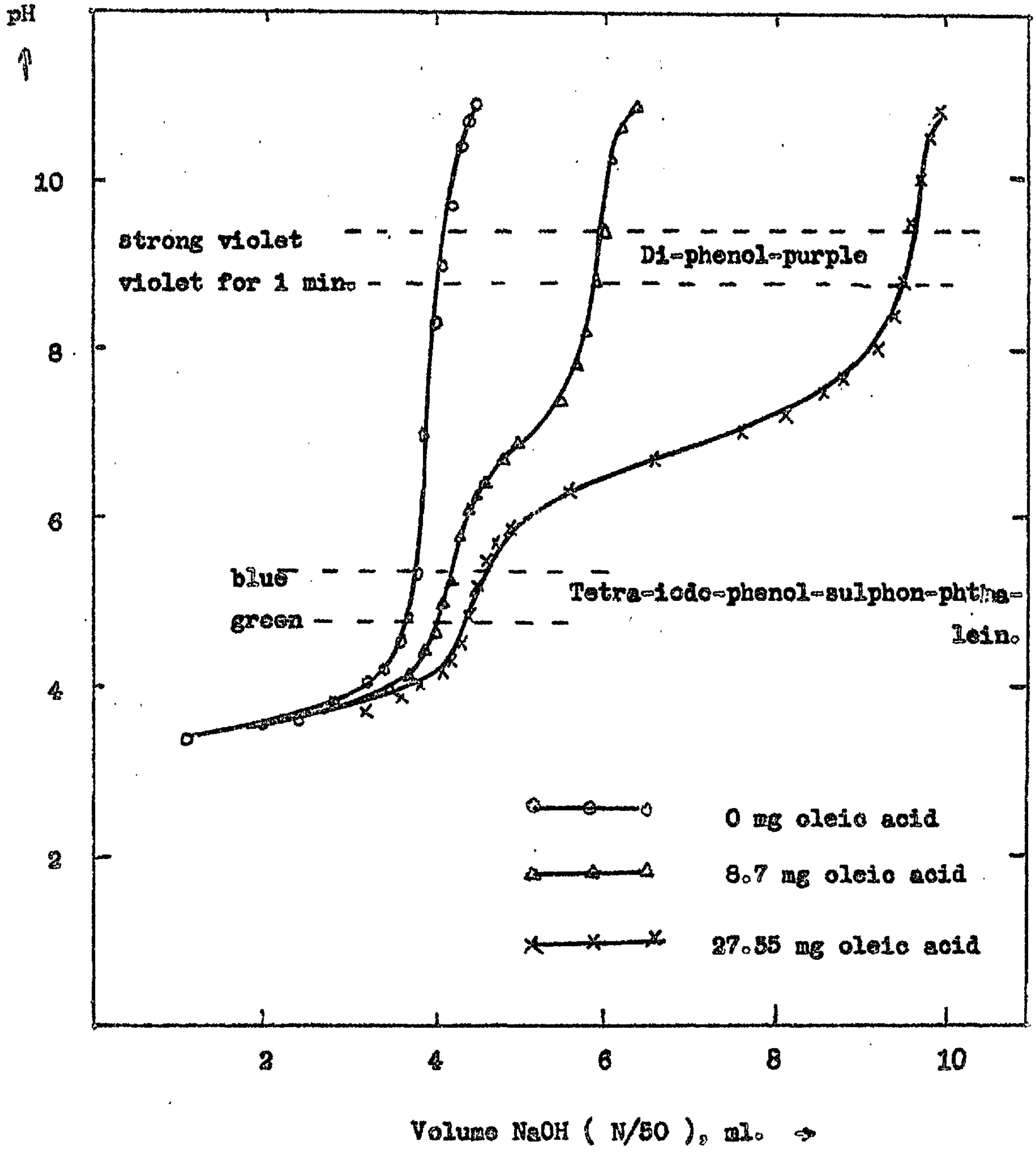
1.11.3. Acidimetric titration of fatty acids using indicators.

The potentiometric titration method used was found to be very slow when applied to tall oil desorbed from ilmenite because of very slow response of the electrodes to the pH changes in the ethanol water medium. When using N/50 NaOH solutions (1.11.2.) the normal duration of each titration was 20-30 minutes.

An attempt was made to shorten this duration by using

FIGURE 1.17

POTENTIOMETRIC TITRATION CURVES OF OLEIC ACID WITH N/50 NaOH IN ETHANOL-WATER 1.6:1 MEDIUM IN THE PRESENCE OF INDICATORS



F I G U R E 1.18

POTENTIOMETRIC TITRATION CURVES OF TALL OIL WITH N/50 NaOH IN ETHANOL-WATER 1.6:1 MEDIUM IN THE PRESENCE OF INDICATORS.

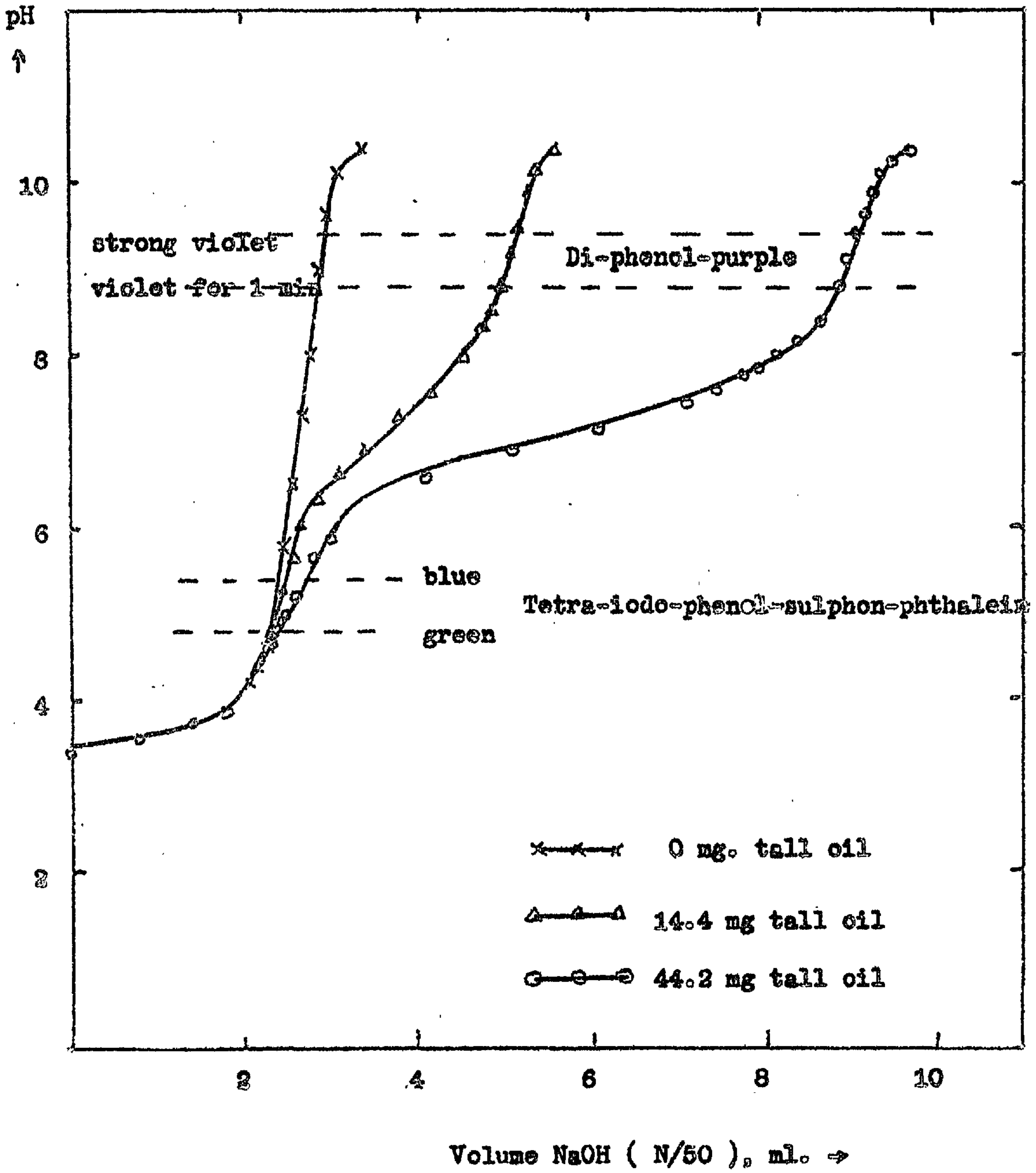


TABLE 1.52

End-point results of the potentiometric titration of oleic acid in 1.6:1 ethanol-water with N/50 NaOH.

Oleic acid mg.	N/50 NaOH ml	N/50 $CO_3^{=}$ ml.	Oleate meq.	Oleic acid mg.
4.55	1.2	0.4	0.016	4.6
8.7	1.9	0.4	0.03	8.7
12.5	2.5	0.4	0.042	12.4
17.0	3.3	0.4	0.058	16.8
27.4	5.1	0.4	0.094	27.2

Error - ±1%

TABLE 1.53

End-point results of the potentiometric titration of tall oil in 1.6:1 ethanol-water with N/50 NaOH.

Tall oil, mg.	N/50 NaOH ml.	N/50 $CO_3^{=}$ ml.	Salt meq.	Tall oil, mg.
0.0	0.4	0.4		
14.4	2.4	0.4	0.04	14.5
28.0	4.25	0.4	0.077	27.9
41.8	6.1	0.4	0.114	41.3
44.2	6.5	0.4	0.122	44.3

Error - ±1%

TABLE 1.54

End-point results of the acidimetric titration of oleic acid in 1.6:1 ethanol-water using indicators.

Oleic acid initial, mg.	N/50 NaOH ml.	Oleic acid found, mg.(*)
0.0	(0.5)	0.0
4.9	0.85	4.95
10.4	1.8	10.5
13.8	2.4	13.9
19.0	3.3	19.2
24.7	4.3	24.9

Error - ±1%

TABLE 1.55

End-point results of the acidimetric titration of tall oil in 1.6:1 ethanol-water using indicators.

Tall oil, initial, mg.	N/50 NaOH ml.	Tall oil found, mg.(*)
5.85	0.8	5.8
14.8	2.05	14.85
20.4	2.85	20.6
34.2	4.75	34.3
31.0	4.25	30.7
40.8	5.65	40.9

Error - ±1%

(*) These values were calculated using the equivalents of N/50 NaOH which were established by the potentiometric titration.

indicators instead of the glass-calomel electrode assembly. Of the many indicators with colour changes in the required pH intervals only two pairs were found applicable: bromo-phenol-blue + cresol-red and tetra-iodo-phenol-sulphone-phthalein + diphenol-purple. In both cases the first end-point of the titration (pH 4.6-5.5) was indicated by a colour change of the first component of each pair, and the second end-point (pH 8.6-9.4) by a colour change of the second component. In both cases the first component did not interfere with the second component but the second component could be added only after reaching the first end-point since it interfered with the determination of the first end-point.

Of the two couples the combination tetra-iodo-phenol-sulphone-phthalein + diphenol-purple gave more reproducible results with both oleic acid and tall oil, and the great accuracy obtained was demonstrated by the results presented in tables 1.54 and 1.55. Comparison of the errors in these tables with the errors in tables 1.52 and 1.53 respectively shows that they are in the same range, but the duration of the titration was only 2-5 minutes.

The optimal titration procedure consisted of:

a. titration of the solution in the presence of 8 drops tetra-iodo-phenol-sulphone-phthalein until colour changed from yellow-green to light blue (see figures 1.17 and 1.18), and

b. continued titration after 8 drops diphenol-purple were added (colour turned green) until colour changed from green to blue and finally to violet which persisted for one minute.

1.11.4. Conductimetric titration of fatty acids.

Conductimetric titration of weak acids is often superior to potentiometric titration. This possibility was examined in the case of the ethanol-water saponification medium containing oleic acid or tall oil. The equipment used was a Pye Conductance bridge Cat. No. 11700 and a Mullard Conductivity cell. The range used was 10^{-4}-10^{-5} Mho.

The standard ethanol-water titration medium was acidified and small aliquots of N/20 NaOH solution were added and the conductivity was measured 30-90 seconds after each addition. The results of some of these measurements in the absence or presence of fatty acids were presented in tables 1.56 and 1.57. The actual conductivity values are plotted as a function of the titrant volume in figures 1.19 and 1.20.

The resulting plots were composed of three straight lines. The lines corresponding to all weak acids present had the same slope. Attempts to correlate the fatty acids contents with the differences between the titration end-points were not successful, especially in the case of reagents which had been desorbed from ore samples. This was attributed to the presence of varying concentrations of metal ions which affected the conductivity.

It was concluded from these results that the conductimetric titration could not be used for the determination of fatty acids adsorbed on ilmenite flotation products.

F I G U R E 1.19

CONDUCTIMETRIC TITRATION OF SAPONIFIED OLEIC ACID IN ETHANOL-WATER 1.6:1 MEDIUM (WITH N/20 HCl).

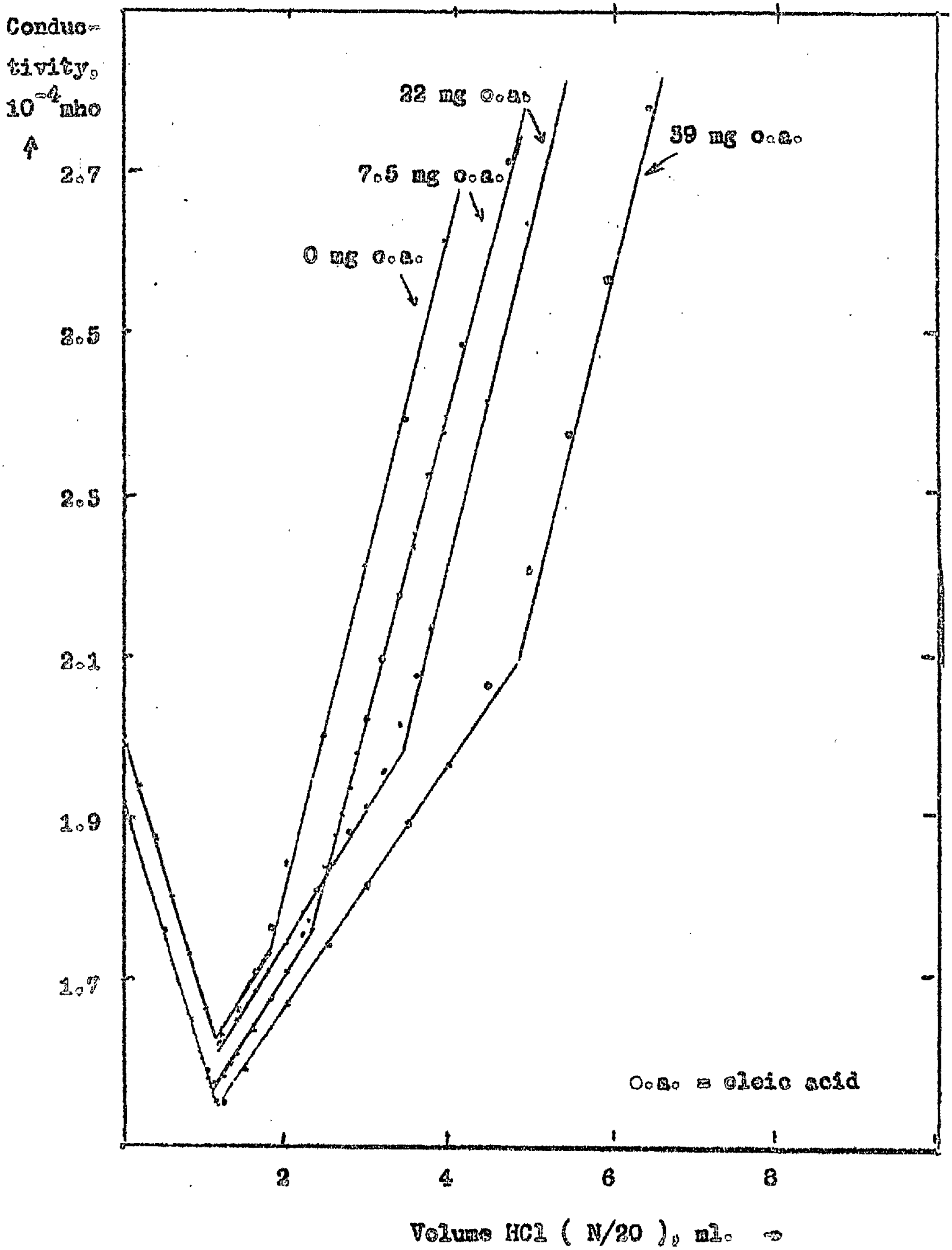


FIGURE 1.20

CONDUCTIMETRIC TITRATION OF SAPONIFIED TALL OIL IN ETHANOL-WATER 1.6:1 MEDIUM (WITH N/20 HCl).

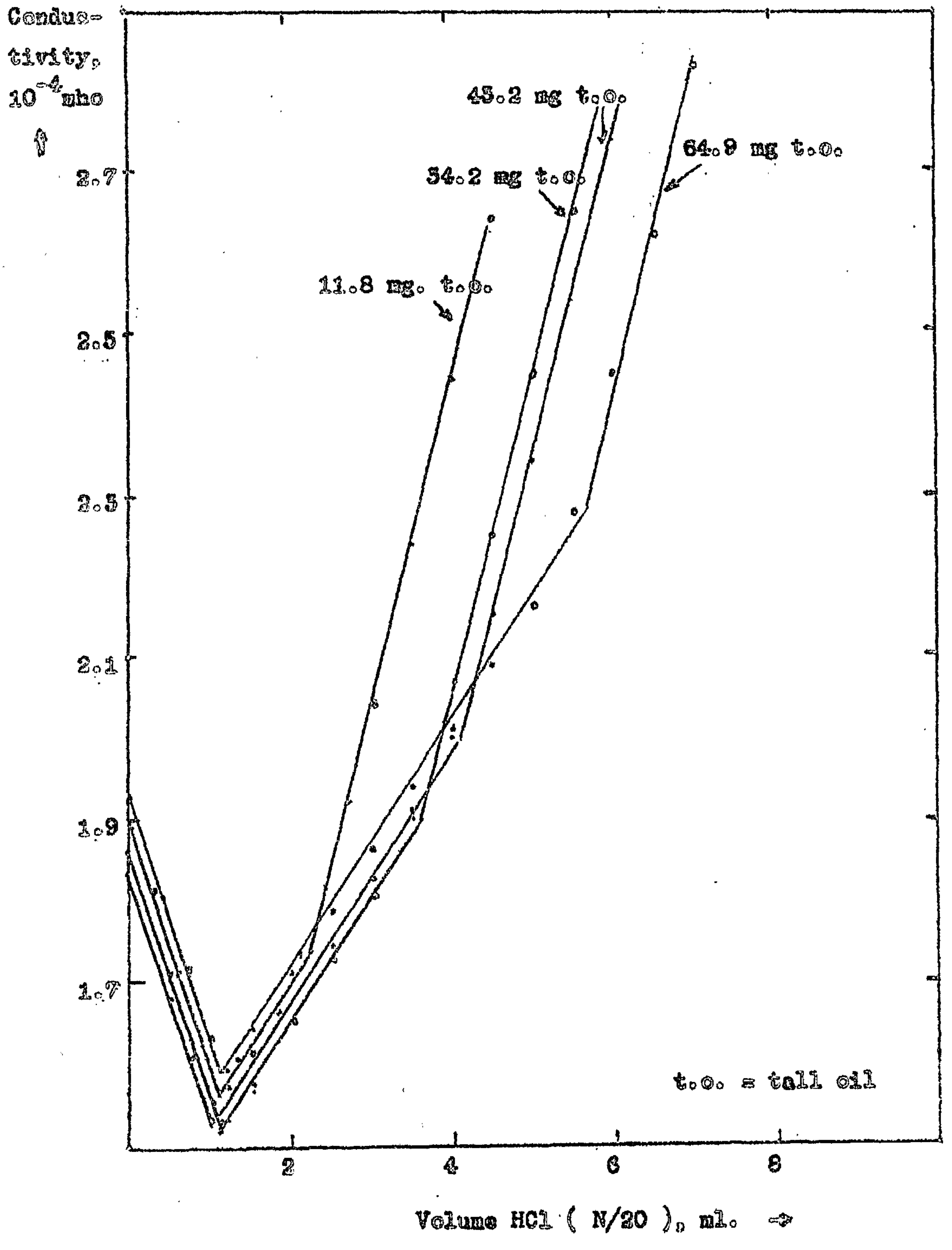


TABLE 1.36

End-point results of the conductimetric titration of oleic acid in 1.6:1 ethanol-water solution.

Oleic acid mg.	N/20 NaOH total, ml	N/20 CO$_3^{--}$ ml.	N/20 oleate meq.	Conversion factor, mg/meq.
0.0	0.65	0.65	0.0225	
7.5	1.1	0.65	0.0225	334
22.0	2.25	0.65	0.08	276
39.0	3.65	0.65	0.15	260

TABLE 1.37

End point results of the conductimetric titration of tall oil in 1.6:1 ethanol-water solution.

Tall oil mg.	N/20 NaOH total, ml.	N/20 CO$_3^{--}$ ml.	N/20 organic salt meq.	Conversion factor, mg./meq.
11.8	1.15	0.65	0.025	472
34.2	2.5	0.65	0.0925	370
43.2	3.0	0.65	0.1175	368
64.9	4.55	0.65	0.195	332

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PART II

2. CONDITIONING AND FLOTATION OF ILMENITE ORE.

2.1. INTRODUCTION.

The conditioning of ilmenite ore at pulp densities of about 70% solids consumes considerable amounts of energy. Several authors have shown that the integral energy consumption during conditioning of metal oxides with fatty acids and neutral oils (1,25) or the power consumption (24) were factors which influenced the flotation results. In order to study the effects of these factors on the flotation of ilmenite, it was necessary to design a test assembly for determining the nett power consumption in the conditioning tank. It was also required that this test assembly should permit sensitive and accurate control of the impeller speed.

The d.c. shunt wound motor with separate excitation was especially suited for this purpose, as its speed could be varied or kept constant at any desired value by controlling the field voltage or the armature voltage (25,26). The characteristics of such a motor and the different methods of excitation are presented in the Appendix, sections 2.6.1.-2.6.5. Preliminary tests based on theoretical considerations have enabled a test assembly with the required properties to be constructed (see fig. 2.27 in the Appendix, section 2.6.4.). The test assembly was operated at different speeds, while idling or under load, as described in the Appendix, sections 2.6.4. and 2.6.5.. It was established in these tests that both the impeller speed control and the nett power consumption were reproducible within ±2%.

This test assembly was used for the conditioning of samples of Tellnes ilmenite ore, and the subsequent results were correlated with the measured nett power consumption as well as with the analytical results for the reagent contents of the flotation products, in order to elucidate some aspects of fatty acid and fuel oil adsorption on iron-titanium minerals.

2.2. EXPERIMENTAL DETAILS.

2.2.1. Experimental materials.

The Tellnes ilmenite batch contained approximately 20% TiO_2 or 45% ilmenite and 2% magnetite (2). The magnetite was not removed in these tests, and probably accompanied the ilmenite in flotation. The ore could be classified as an "ilmenorite", with ilmenite and magnetite as the valuable minerals. The gangue consisted of feldspar, hypersthene, and biotite, with secondary minerals such as olivine, hornblende, diopside, apatite and spinels. Pyrite, pyrrhotite, and chalcopyrite were present in small quantities corresponding to 0.2% S. The phosphate content varied from 0.2 to 0.4% P_2O_5. The Tellnes orebody is rather finely crystalline, with very few grains larger than about 0.6 mm.

The tall oil, the fuel oil, and the kerosene used were of technical grade, and were supplied by Titania A/S. These were samples of the actual reagents used in the industrial flotation circuit of Tellnes ilmenite. The oleic acid and the iso-octane were analytical grade reagents.

2.2.2. Experimental apparatus.

The test assembly for conditioning of the ore comprised:

a. a 150x110mm diameter stainless steel conditioning tank;

b. a 1/25 h.p. d.c. shunt wound motor coupled to a shaft with three interchangeable impellers, in the form of three-bladed brass propellors, of 48, 66, and 84mm diameter respectively, with the blades at 20° inclination, and with total blade areas of 4.5, 9, and 18 cm^2 respectively;

c. a d.c. test assembly, described in the Appendix, section 2.6.4.

The flotation assembly comprised a standard laboratory Fagergren unit, operated at 2200 r.p.m.

The apparatus for reagent assaying comprised:

a. 10x10mm diameter plastic containers with close fitting lids for the collection of samples;

b. 50ml centrifuge test tubes with close fitting lids for reagent desorption and for fatty acid saponification;

c. miscellaneous glassware for titrations and optical density measurements

2.2.3. Experimental procedure.

The crushed ilmenite ore (-10#) was wet ground in laboratory batch mild steel rod mills to 99% below 65# BSS. Individually ground batches, each of 1.1 kg, were deslimed by settling and decantation. The desliming was controlled in such a way that 10% of the feed was removed as slimes. The deslimed batches were stored under water until required. Distilled water was used in all operations in order to eliminate the effect of tap water ions. A standardised procedure was adopted for both the grinding and the desliming, so that the grain size distribution of the individual batches was nearly constant.

After thermal equilibrium in the electrical circuits of the test assembly had been reached (see section 2.6.4. in the Appendix) the wet feed was transferred to the conditioning tank at 70% solids. After thermal equilibrium was regained at the impeller speed used, the reagents were added by means of a syringe, which was accurately weighed before and after reagent addition. The variable resistance controlling the voltage applied across the armature permitted a constant impeller speed or a constant agitation throughout the conditioning period to be maintained. Power consumption values were recorded at regular intervals using the procedure outlined in section 2.6.4. of the Appendix.

After the desired conditioning time the pulp was transferred to the flotation cell, diluted to 30% solids, agitated for half a minute with the air inlet valve closed, and then floated. This initial agitation time over the range ½-5 minutes had no effect on the flotation results. The amount of air introduced did not affect the flotation results when flotation was carried out to the visual end-point, as judged by the appearance of a white, barren froth.

Each flotation product was filtered, blended, sampled, and assayed for reagent content according to the procedure outlined in section 1.10. The ilmenite content of the flotation products was determined at Titania A/S.

The parameters to be varied in the tests described in the following sections, 2.5.1.-2.5.12., were: the initial reagent addition, the impeller speed, the conditioning time, the mode of addition of the reagents, the tall oil/fuel oil ratio, reagent mixtures other than tall oil-fuel oil, the ferric chloride addition, the sulphuric acid addition, and the addition of the fine fraction of the batches.

In all tests the conditions in the flotation cell were practically constant, and since flotation was carried out to the visual end-point the flotation results were always a direct function of the conditioning parameters. The flotation results at any particular combination of these parameters were reproducible within ±5% and because of this the results of one test only were reported for each combination.

The following terms were used when presenting the flotation results:

"Initial reagent addition" - the quantity of the respective reagent added to the conditioning tank, expressed as grams of reagent per kilogram of dry ilmenite ore;

"Per cent weight rougher concentrate" - the per cent weight of the rougher concentrate expressed in terms of the initial ilmenite ore feed;

"Rougher concentrate grade" - the per cent ilmenite content by weight of the rougher concentrate;

"Ilmenite recovery" - the per cent weight of ilmenite in the feed which is found in the rougher concentrate;

"Gangue recovery" - the per cent weight of gangue in the feed which is found in the rougher concentrate;

"Reagent recovery" - the per cent weight of each initial reagent addition which is found in each flotation product;

"Reagent concentration" - the reagent content of each flotation product expressed in terms of grams of reagent per kilogram of dry flotation product;

"Power consumption" - the nett power consumed at any particular instant during conditioning in agitating the pulp (see sections 2.6.4.-2.6.5. in the Appendix).

The effects of the parameters mentioned above on these flotation results are presented in the sections which follow. The data relating to the individual tests are tabulated in section 2.6.6. of the Appendix, and these tests are referred to by a series of consecutive numbers.

2.5. EXPERIMENTAL RESULTS.

2.5.1. The relation between the initial reagent addition and the flotation results.

The initial reagent addition was varied in a series of preliminary tests (Nos. 1-15) in which the ilmenite ore was conditioned for 15 minutes at 1100 r.p.m. using the 84mm diameter impeller. No change in the pH was observed during conditioning (6.5±0.2). The pulp became viscous several minutes after reagent addition. Therefore the impeller speed was raised to 1400 r.p.m. in order to maintain proper movement of the pulp. The apparent viscosity of the pulp decreased gradually, so that the impeller speed could again be lowered to the initial value of 1100 r.p.m. towards the end of the conditioning period.

The ilmenite recovery, the gangue recovery, and the rougher concentrate grade were plotted as functions of the initial reagent addition in fig. 2.1. The per cent weight rougher concentrate, the reagent recoveries in the rougher concentrate, and the reagent recoveries in the rougher tailings were plotted as functions of the same parameter in fig. 2.2.

Fig. 2.1 shows that the ilmenite recovery increased from 17.5 to 94%, while the gangue recovery increased from 15 to 58% when the initial reagent addition was increased from 0.76 to 1.04 g/kg of a 1:1 (by weight) tall oil/fuel oil mixture. The ilmenite recovery increased very little while the gangue recovery increased

FIGURE 2.1

ILMENITE RECOVERY, GANGUE RECOVERY, AND ROUGHER CONCENTRATE GRADE AS FUNCTIONS OF THE INITIAL REAGENT ADDITION.

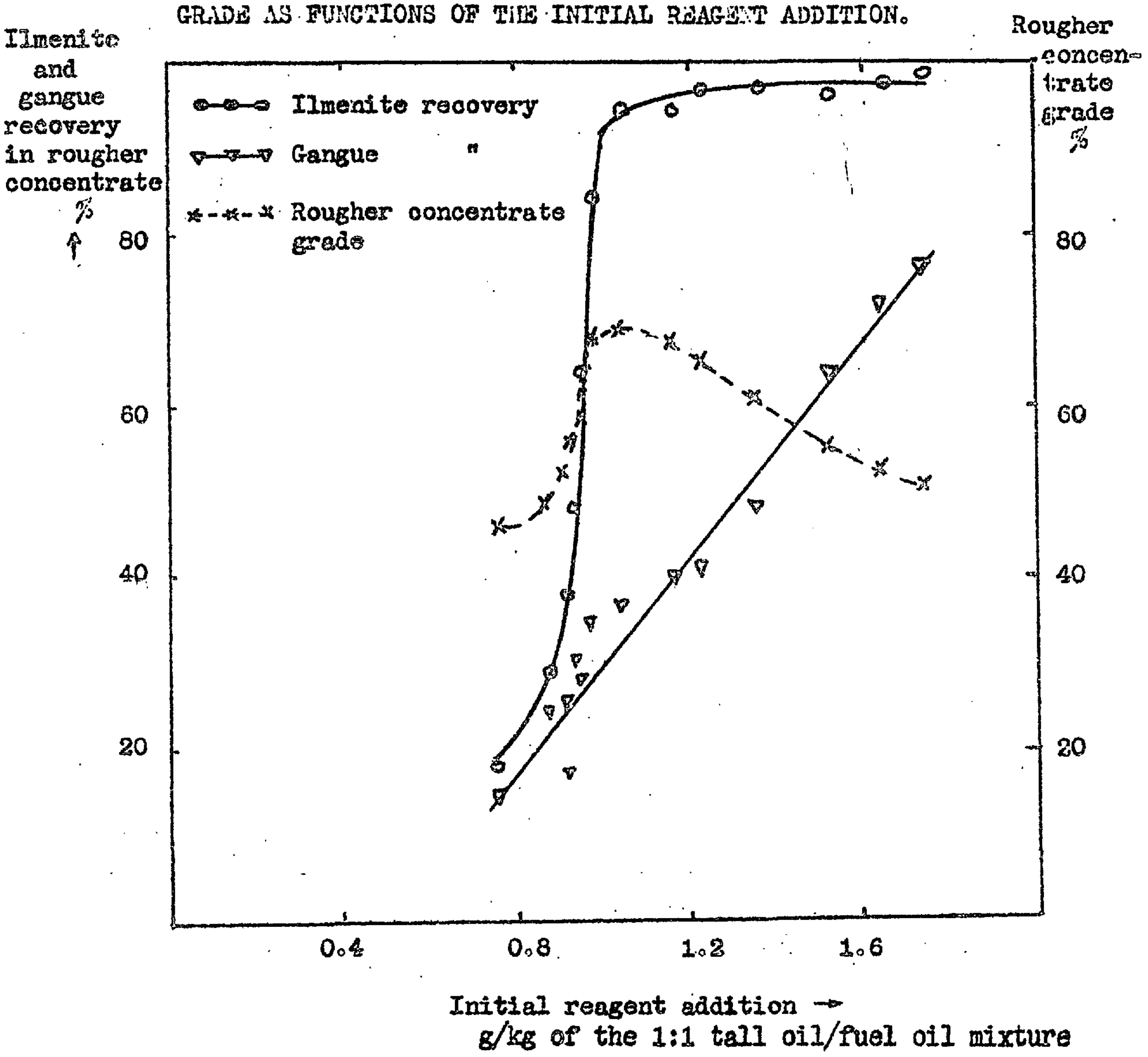
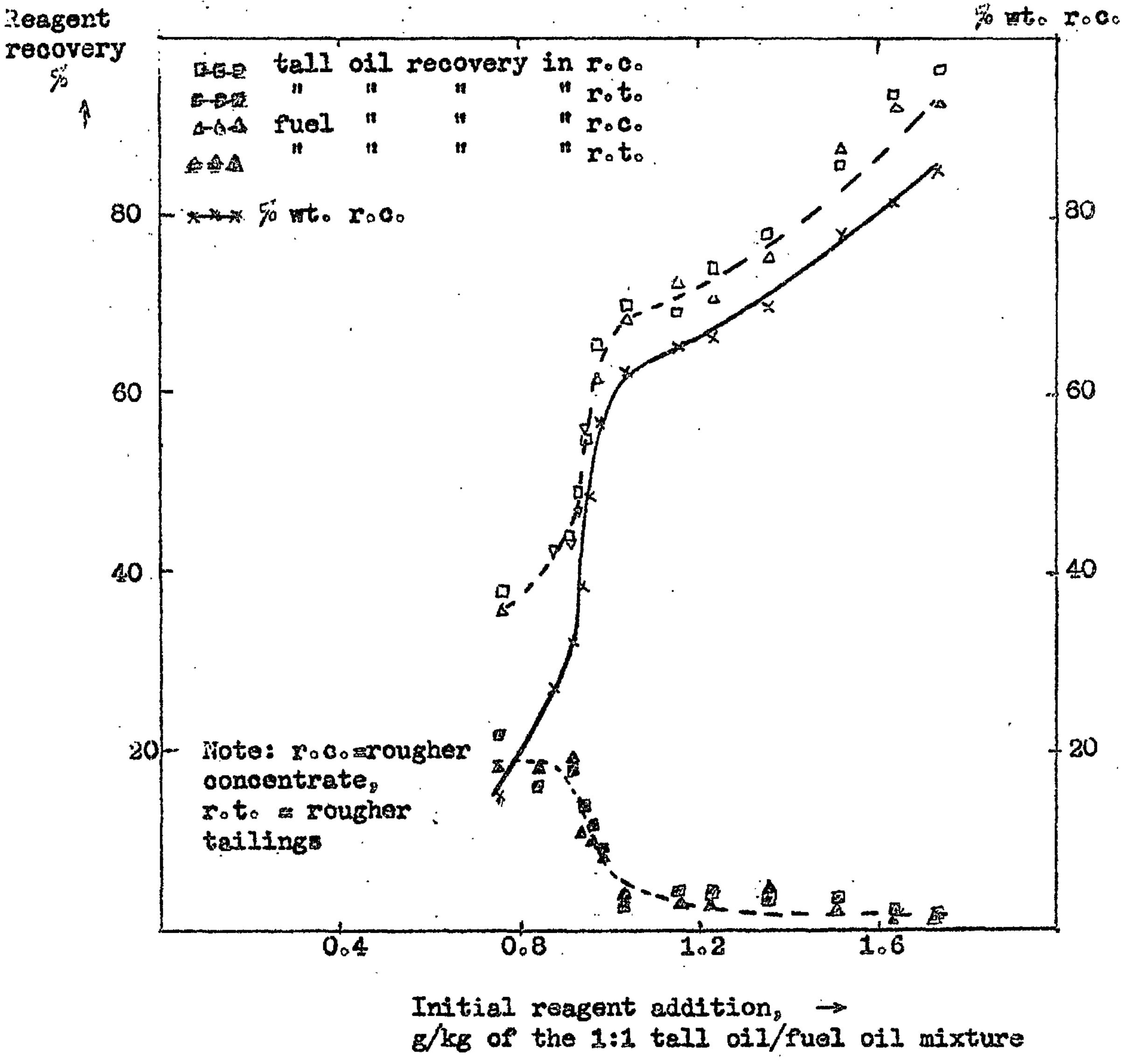


FIGURE 2.2

TALL OIL AND FUEL OIL RECOVERIES IN ROUGHER CONCENTRATE AND IN ROUGHER TAILINGS, AND PER CENT WEIGHT ROUGHER CONCENTRATE AS FUNCTIONS OF THE INITIAL REAGENT ADDITION.



steadily to 76% when the initial reagent addition was further increased from 1.04 to 1.74 g/kg of the 1:1 tall oil/fuel oil mixture. Fig. 2.1 also shows that the rougher concentrate grade was a maximum at an initial reagent addition of 1.04 g/kg of the reagent mixture.

Fig. 2.2 shows that the tall oil and fuel oil recoveries in the rougher concentrate increased with the initial reagent addition in proportion to the increase in the per cent weight rougher concentrate. It also shows that the tall oil/fuel oil ratio in the rougher concentrate was the same as in the feed. The reagent recoveries in the tailings were negligible - except in tests where the per cent rougher concentrate was low. Analysis of the feed immediately after conditioning showed however that all the initial reagent addition was present in the bulk solids.

The reagents unaccounted for in the flotation products were found in the flotation liquor, and were probably present as a slow-settling colloidal suspension, which could be flocculated by addition of ferric chloride. Having been loosened during conditioning they were removed from the mineral surface by dispersion in the greater water volume. This phenomenon was confirmed in all tests performed.

The viscosity changes mentioned above which occur in the pulp during conditioning were reflected in changes in the power consumption. The relationship between this factor and the flotation results is therfore considered in the section which follows.

2.3.2. The relationship between the pattern of the power consumption curve during conditioning and the flotation results.

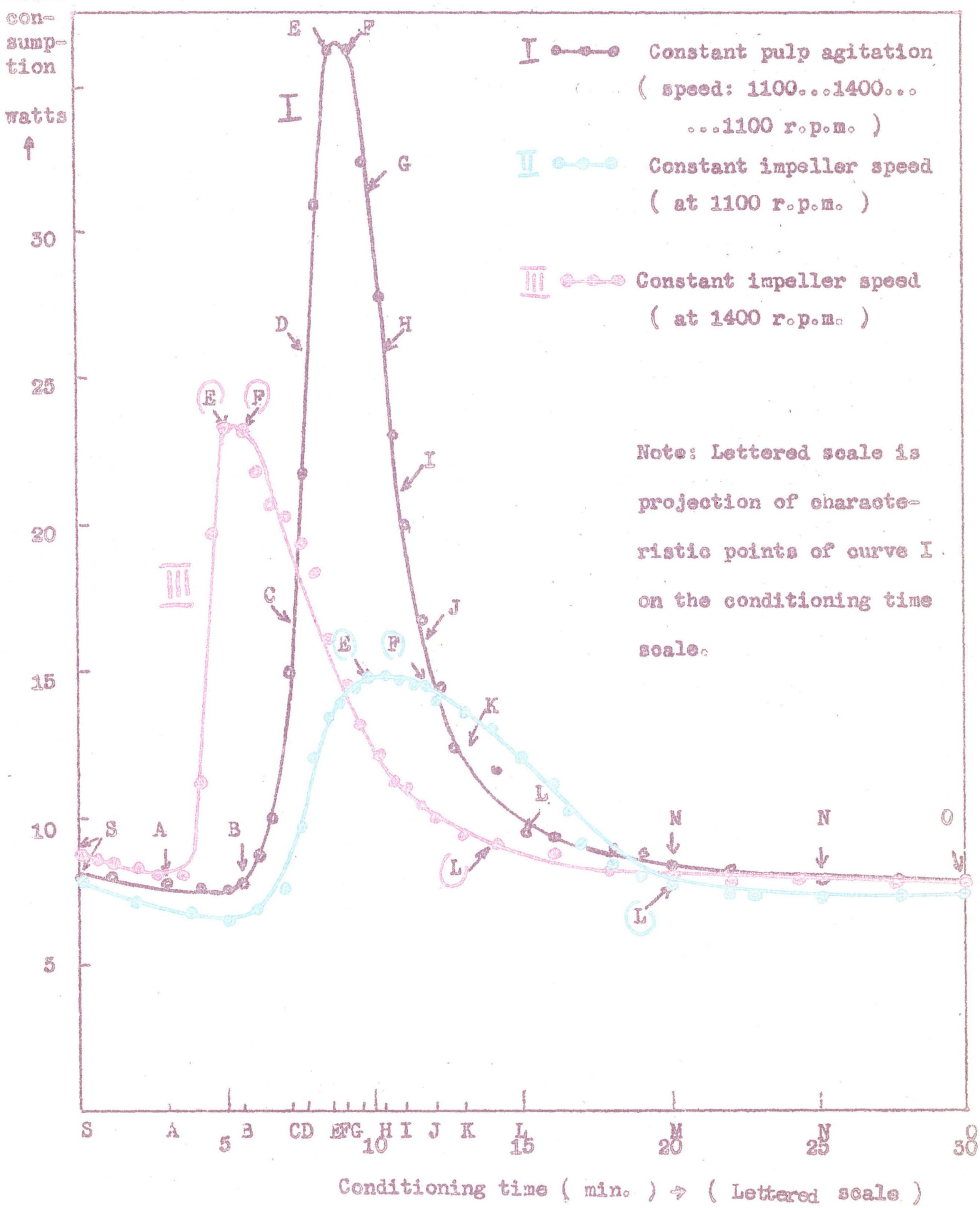
To establish a relation between the pattern of the power consumption during conditioning and the flotation results, the initial reagent addition was kept essentially constant at 1.08±0.02 g/kg of the 1:1 tall oil/fuel oil mixture. This initial reagent addition was slightly higher than that which gave maximum ilmenite recovery and maximum rougher concentrate grade in the tests of the preceding section (2.3.1.).

The power consumption was measured at regular intervals during conditioning and the values obtained (see tables 2.4-2.6 in section 2.6.6. of the Appendix) were plotted as a function of the conditioning time in fig. 2.3. The power consumption curves obtained in all these tests corresponded closely to one of the three curves presented in this figure, which were typical of the three different modes of control of the impeller speed during conditioning, as described below.

Curve I was obtained when the impeller speed was raised from 1100 to 1400 r.p.m. in relation to the increasing viscosity (see tests Nos. 14-17 in table 2.4, section 2.6.6. in the Appendix), as mentioned in the preceding section. As a result the nett power consumption reached a peak of about 36 watts. The impeller speed was then lowered to the initial value as the viscosity decreased again and was maintained at this level. The increased impeller speed was necessary in order to keep the pulp in nearly constant movement

FIGURE 2.5

TYPICAL CURVES OF POWER CONSUMPTION V. CONDITIONING TIME AT CONSTANT IMPELLER SPEED AND AT CONSTANT PULP AGITATION.



throughout the entire conditioning period, as judged by visual observation of the vortex.

Curve II was obtained when the impeller speed was kept constant at the low level of 1100 r.p.m. by varying the power input during the period of increased viscosity (see tests Nos. 18-28 in table 2.5, section 2.6.6. in the Appendix). As a result the nett power consumption reached a peak of about 15 watts. The pulp moved slowly during the period of increased viscosity.

Curve III was obtained when the impeller speed was kept constant at 1400 r.p.m. by varying the power input during the increased viscosity period (see tests Nos. 29-38 in table 2.6, section 2.6.6. of the Appendix). As a result the nett power consumption reached a peak of about 24 watts. The high impeller speed kept the pulp in satisfactory movement throughout the entire conditioning period, as judged by visual observation of the vortex.

These three typical curves represented two extreme- II and III - and one intermediate case - I - of conditioning intensity. In the case of curve II the pulp movement was at the lowest limit (see section 2.6.5. in the Appendix) during the increased viscosity period, and in the case of curve III it was at the top limit (see section 2.6.5.) during the normal viscosity periods. Only in the case of curve I was the pulp movement uniform during the entire conditioning period.

It was mentioned in the preceding section (2.5.1.) that the variation of the net power consumption in the conditioning tank reflected the viscosity changes during conditioning. A considerable flocculation of the pulp was observed during the conditioning and it was therefore assumed that the increased pulp viscosity was a result of this bulk flocculation, while the decreasing viscosity was a result of the subsequent deflocculation of the bulk. On the basis of this assumption the five distinct sections on the three typical power consumption curves were identified by referring to the observed flocculation-deflocculation phenomenon in the pulp.

Fig. 2.5 shows a series of characteristic points (S - O) which were assigned to the typical power consumption curves in order to permit correlation with the flotation results obtained when pulps were conditioned to these particular points. These characteristic points were placed at the extremities of the five sections, and at equi-distant positions along the sections, as shown in fig. 2.5. These five sections of the power consumption curves corresponded to the following five periods of the conditioning process:

a. the "induction period" - between the characteristic points S (for start) and B, during which the viscosity and the power consumption changed very little;

b. the "flocculation period" - between points B and E, during which the viscosity increased rapidly to a maximum;

c. the "flocculation peak" - between points E and F, occuring at the highest values of power consumption during conditioning, which mark the end of the flocculation process;

d. the "deflocculation period" - between points F and L, during which the viscosity decreased rapidly to the initial level;

e. the "dispersion period" - starting at the characteristic point L, during which the original values of the power consumption were maintained to the end of the conditioning process.

Fig. 2.5 (see also table 2.1) shows that the high impeller speed in the case of curve I reduced the duration of the flocculation period, of the flocculation peak, and of the deflocculation period, in contrast with the case of curve II. The high impeller speed during the induction period in the case of curve III also reduced the duration of the induction period compared with the cases of curves I and II. These comparisons showed that the increased impeller speed accelerated the flocculation-deflocculation phenomenon during conditioning.

In every group of tests corresponding to one of the three typical cases of impeller speed control, the actual power consumption curves were slightly displaced in relation to each other, both along the time scale and along the power consumption scale (see tables 2.4, 2.5, and 2.6 in section 2.6.6. of the Appendix). The small displacements observed were a result of experimental errors such as slight variations in the initial power consumption value, which was a function of the pulp density, of the particles size distribution, and of the weight of the sample, as well as slight variations in the manual control of the impeller speed during the periods of rapidly increasing or decreasing viscosity (measurements of the power consumption and adjustments of the impeller speed were carried out at 30 seconds intervals). These experimental errors were within ±5% and had no effect on the position of the characteristic points. They also had little effect on the flotation results, as shown later in this section.

The time values corresponding to the characteristic points on curve I were chosen as the reference scale for graphical presentation, since these characteristic points appeared to be important in the study of the conditioning and flotation behaviour. This means that a particular characteristic point such as E, on the three different curves shown in fig. 2.3, would appear to have the same effective conditioning time of 8½ minutes as in the case of curve I, even if the actual conditioning time were 5 minutes in the case of curve III or 10 minutes as in the case of curve II.

A lettered scale S, A, B, ... Q, was used in all these tests (Nos. 14-38) as abscissa, and the position of these characteristic points was determined from the projection of the respective points on curve I onto the time scale, as shown in fig. 2.3. For the purpose of comparison the actual time values corresponding to the projections of the characteristic points of curves I, II, and III were presented in table 2.1.

The pulps in tests Nos. 14-38 were conditioned to the different characteristic points along the individual power consumption curves (see tables 2.4, 2.5, and 2.6, section 2.6.6. of the Appendix) and the flotation results (see tables 2.7, 2.8, and 2.9, section 2.6.6. of the Appendix) are presented as a function of the

TABLE 2.1

The values, in minutes, corresponding to the projection of the characteristic points of the three power consumption curves on the time scale.

Point / Curve	S	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
I	0	3	5½	7	8	8½	9	9½	10	11	12	13	15	20	25	30	35	40
II	0	4	6	7½	8½	9½	11	12	13	15	16	17	19	24	29	34	39	44
III	0	1½	3½	4	4½	5	5½	6½	7½	8½	9	10	12	16	20	24	28	32

Durations of the periods on the three power consumption curves (in minutes)

Period / Curve	Induction	Flocculation	Peak	Deflocculation
I	5½	3	½	6
II	6	5½	1½	8
III	3½	1½	½	6½

characteristic point in figures 2.4 and 2.5, using the lettered scale defined above. The ilmenite recovery and the gangue recovery are presented as function of this parameter in fig. 2.4. The percent weight rougher concentrate, the reagent recoveries and the reagent concentrations in the rougher concentrate are shown in fig. 2.5.

FIGURE 2.4 ILMENITE RECOVERY AND GANGUE RECOVERY AS FUNCTIONS OF THE CHARACTERISTIC POINT ON THE POWER CONSUMPTION CURVE.

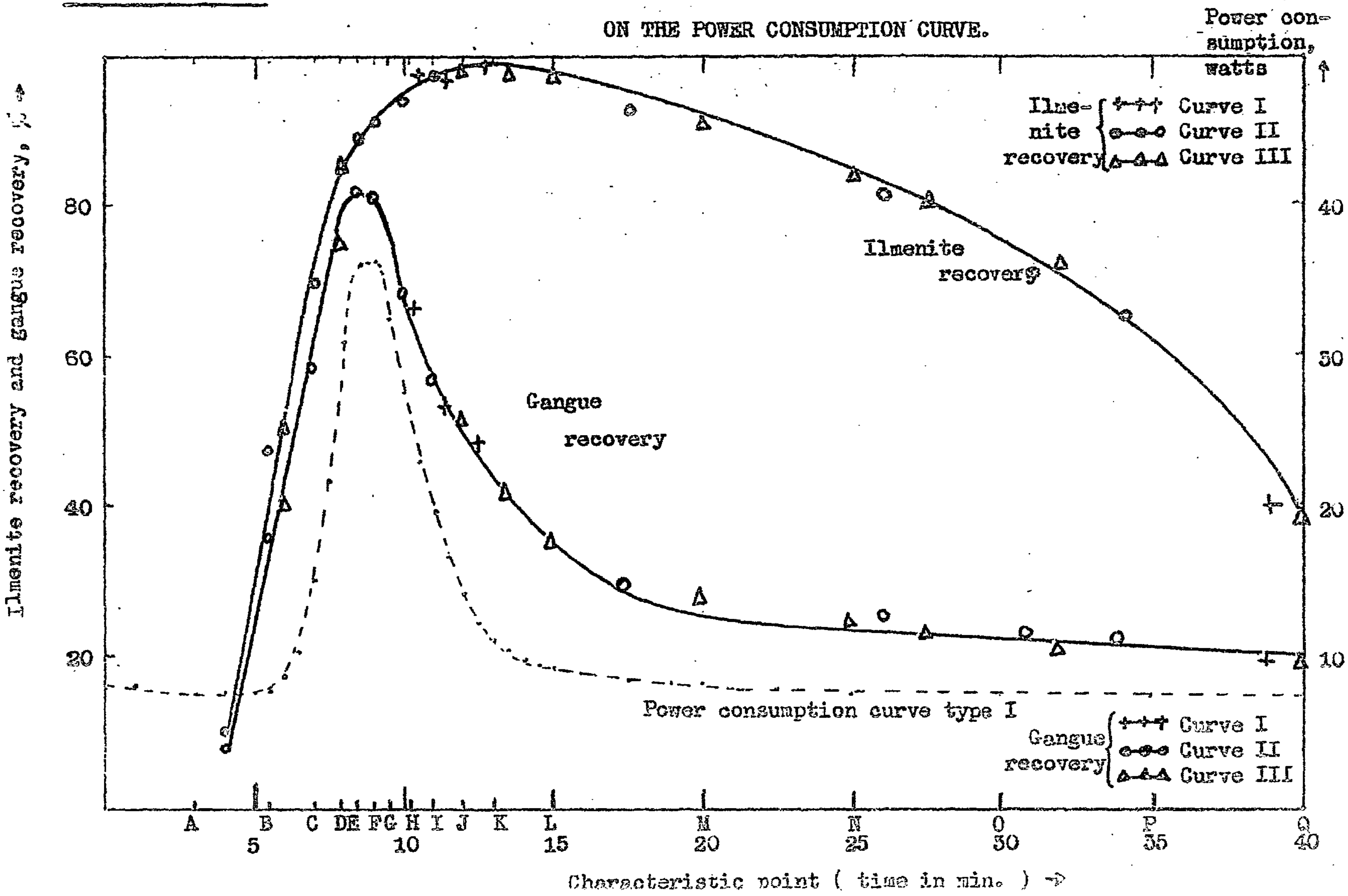
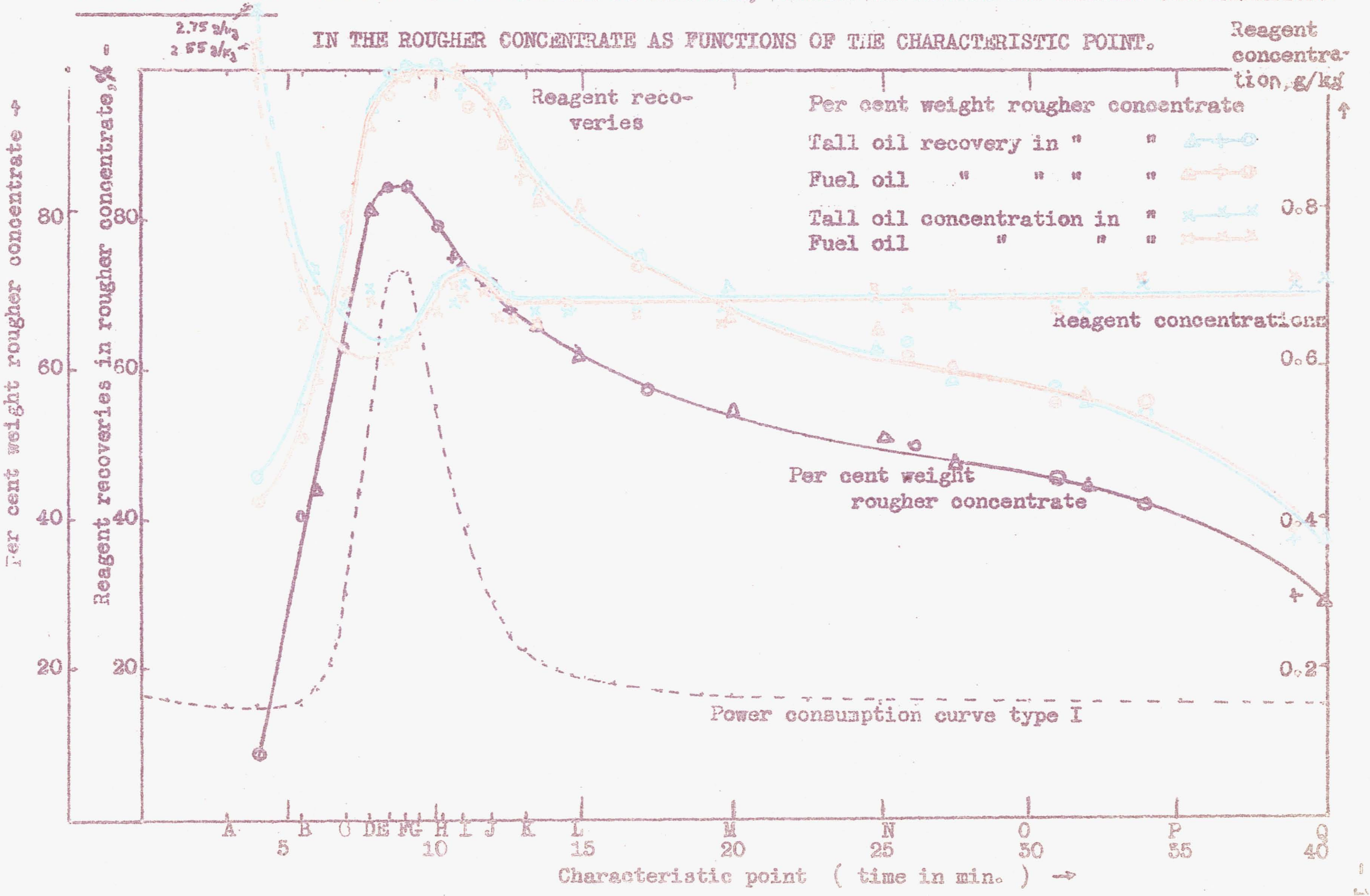


FIGURE 2.5 PER CENT WEIGHT ROUGHER CONCENTRATE, REAGENT RECOVERIES AND REAGENT CONCENTRATIONS IN THE ROUGHER CONCENTRATE AS FUNCTIONS OF THE CHARACTERISTIC POINT.



The power consumption curve I is shown as a dotted line in both fig. 2.4 and fig. 2.5 for reasons of comparison.

Examination of the curves in figures 2.4 and 2.5 shows that the following results were obtained by conditioning up to and during the particular periods:

a. Conditioning during the "induction period" gave very low per cent weights of rougher concentrate, consisting mainly of fines, and only part of the reagents was found in the rougher concentrate at very high concentrations of the reagents; this indicated that only part of the reagents were adsorbed during this period.

b. Conditioning during the "flocculation period" gave a gradual and non-selective increase of ilmenite and gangue recoveries, and a corresponding increase of the reagent recoveries in the rougher concentrate, both being proportional to the increase in the power consumption; in addition the concentration of the reagents in the rougher concentrate decreased rapidly. This indicated that more reagents were quickly adsorbed during this period and were randomly distributed between an increasing number of particles. The increasing bulk flocculation in the conditioning tank and the increasing per cent weight rougher concentrate were both a result of the increasing number of reagent-coated particles.

c. Conditioning during the "flocculation peak" gave maximum per cent weight rougher concentrate and maximum reagent recoveries in the rougher concentrate, while the reagent concentration in the rougher concentrate was at a minimum and the selectivity was still negligible. This indicated that nearly all of the initial reagents were adsorbed on a maximum number of particles of all species, and as a result bulk flocculation and per cent weight of rougher concentrate were at a maximum.

d. Conditioning during the "deflocculation period" gave a rapid depression of the gangue while the ilmenite recovery increased further and levelled off at a maximum value near 100%; at the same time the reagent recoveries in the rougher concentrate started to decrease while the reagent concentration first increased and then levelled off at a constant value. These results suggest that a rapid transfer of reagents from the gangue to the ilmenite particles took place during the period when almost all particles were flocculated and hence in intimate contact. Subsequent to this transfer, the reagents were removed from the now poorly coated gangue particles by the attrition in the highly dense pulp, to be dispersed in the flotation liquor as colloids. As a result of the decreasing number of reagent-coated particles the pulp deflocculated and the viscosity decreased rapidly.

e. Conditioning during the "dispersion period" gave a gradual depression of the ilmenite and a much slower depression of the gangue, with decreasing reagent recoveries in the rougher concentrate proportional to the decreasing per cent weight of rougher concentrate, the reagent concentration in the rougher concentrate being nearly constant. This indicated that the reagents were removed from the ilmenite particles in a manner similar to that suggested for the gangue particles during the deflocculation period. The reagent concentration in the rougher tailings was negligible at all characteristic points, which supports the suggested explanation of reagent removal from the poorly coated particles. Since the depression of ilmenite was accelerated at higher speeds during the dispersion interval, the suggested attrition of the reagents received further support.

The correlation described above showed that under circumstances of sufficiently high pulp density for example, which permit bulk flocculation to take place, the flotation results of an ilmenite pulp conditioned with tall oil and fuel oil were a direct function of the conditioning process, as represented by the power consumption curve. Since the flotation results obtained according to the three different power consumption curves gave continuous curves when presented as a function of the characteristic point in figures 2.4 and 2.5, it was evident that the characteristic point on the power consumption curve was an appropriate indicator for the conditioning process and for the phenomena taking place during conditioning. This was equally valid for tests in which the impeller speed was kept constant at low or high levels during conditioning, as well as for tests in which the pulp movement was kept nearly constant.

These considerations show that the effects of different factors such as initial reagent addition, reagent ratio, and type of reagent on the flotation results, must always be examined whilst referring to characteristic points on the power consumption curve which denote a particular stage of the conditioning process. The points of major importance were firstly the "flocculation peak" (E - F), characterised by maximum per cent weight of rougher concentrate and maximum reagent recoveries, that is at the end of the reagent adsorption process, and secondly the end of the "deflocculation period" (L), characterised by maximum ilmenite recovery and by maximum selectivity, that is the highest rougher concentrate grade.

It was important to examine the net energy inputs required on all three power consumption curves to reach the two characteristic points mentioned above. The net energy inputs were calculated by integration of the respective areas below the power consumption curves in fig. 2.3, and are presented in table 2.2.

TABLE 2.2

Net energy inputs required to reach the flocculation peak (E) and the end of the deflocculation period (on the three typical power consumption curves).

Curve	Start of flocculation peak			End of flocculation period		
	Time, min.	Energy consumption, J/kg	kWh/ton	Time, min.	Energy consumption, J/kg	kWh/ton
I	6½	5700	1.57	15	14500	4.03
II	9½	5250	1.26	19	12000	3.34
III	5	3150	0.75	12	11000	3.06

Examination of table 2.2 shows that the integral energy input required to reach the given characteristic points on the three curves differed, allthough the flotation results were the same, as shown earlier in this section. The lowest net energy input was obtained when the agitation intensity was highest throughout the entire conditioning period. It is significant that the energy consumption during the deflocculation period of curve III was 75% of the total energy input required to reach this point.

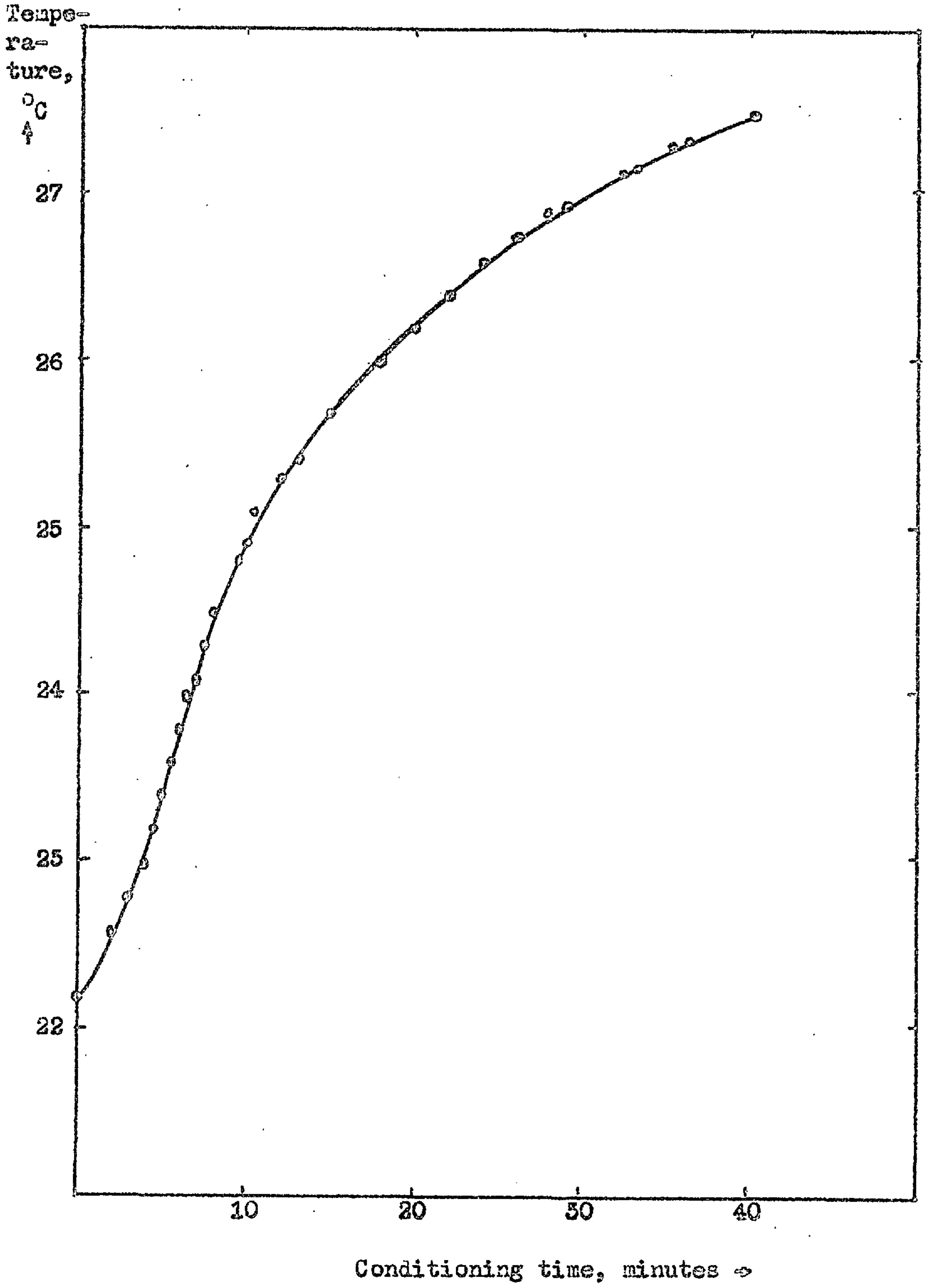
The temperature of the pulp was measured during conditioning and a typical curve presented in fig. 2.6 shows the temperature as a function of conditioning time. Starting temperatures of 20-25°C had no effect on the correlation between the flotation results and the characteristic points (shown earlier in this section).

2.5.3. - 2.5.12. Effects of various parameters on the flotation results in relation to the characteristic points on the power consumption curve.

The effects of a series of parameters on the flotation results are examined in these sections, in correlation with the characteristic points on the power consumption curve mentioned in section 2.5.2., namely the flocculation peak and the end of the deflocculation period, that is the pulps were always conditioned to one of these points and then floated. In this manner the conditioning process had always progressed to the same stage.

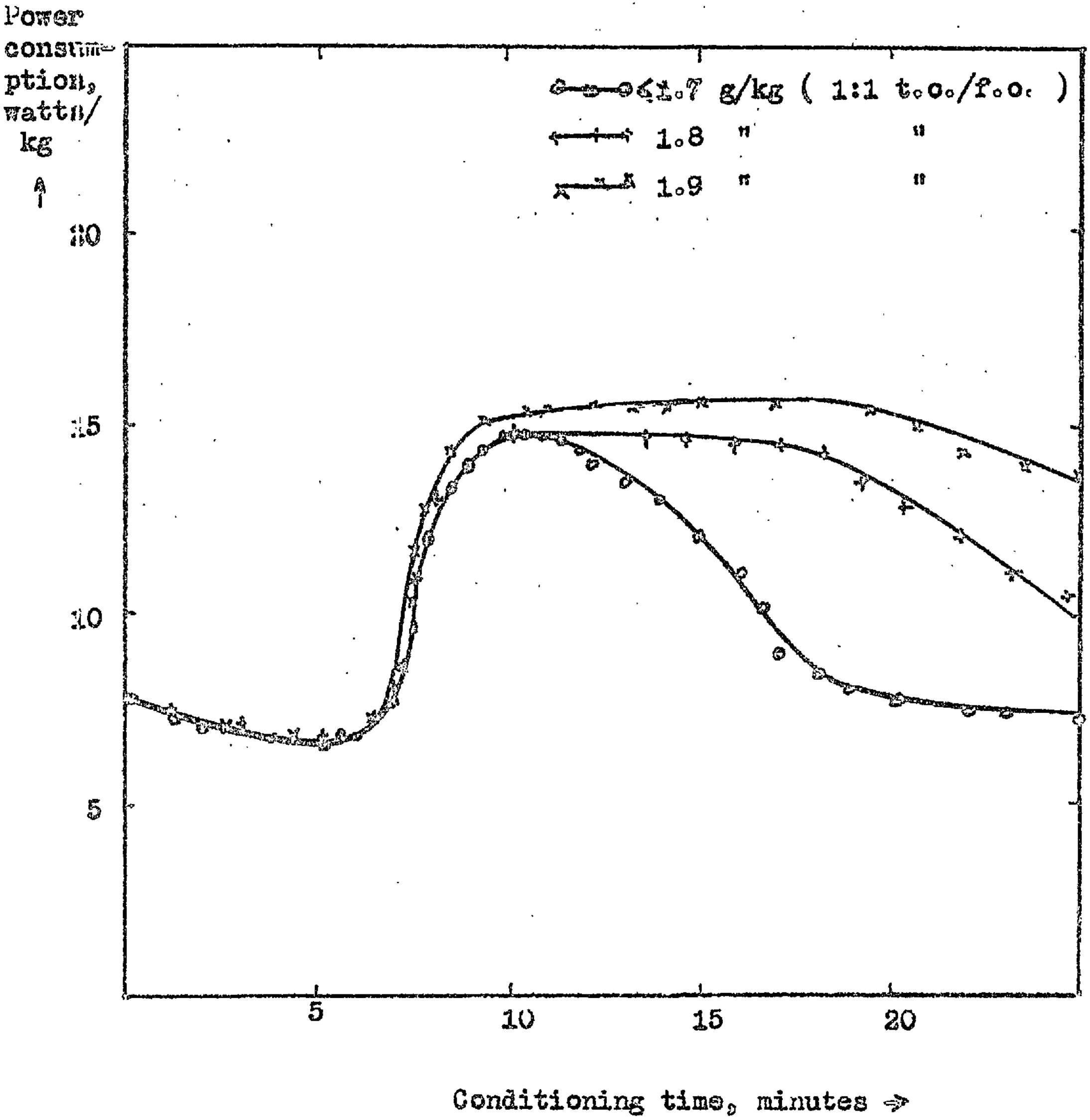
FIGURE 2.6

CONDITIONING TEMPERATURE V. CONDITIONING TIME



F I G U R E 2.7

POWER CONSUMPTION V. CONDITIONING TIME CURVES AT DIFFERENT INITIAL REAGENT ADDITIONS.



2.3.3. Initial reagent addition.

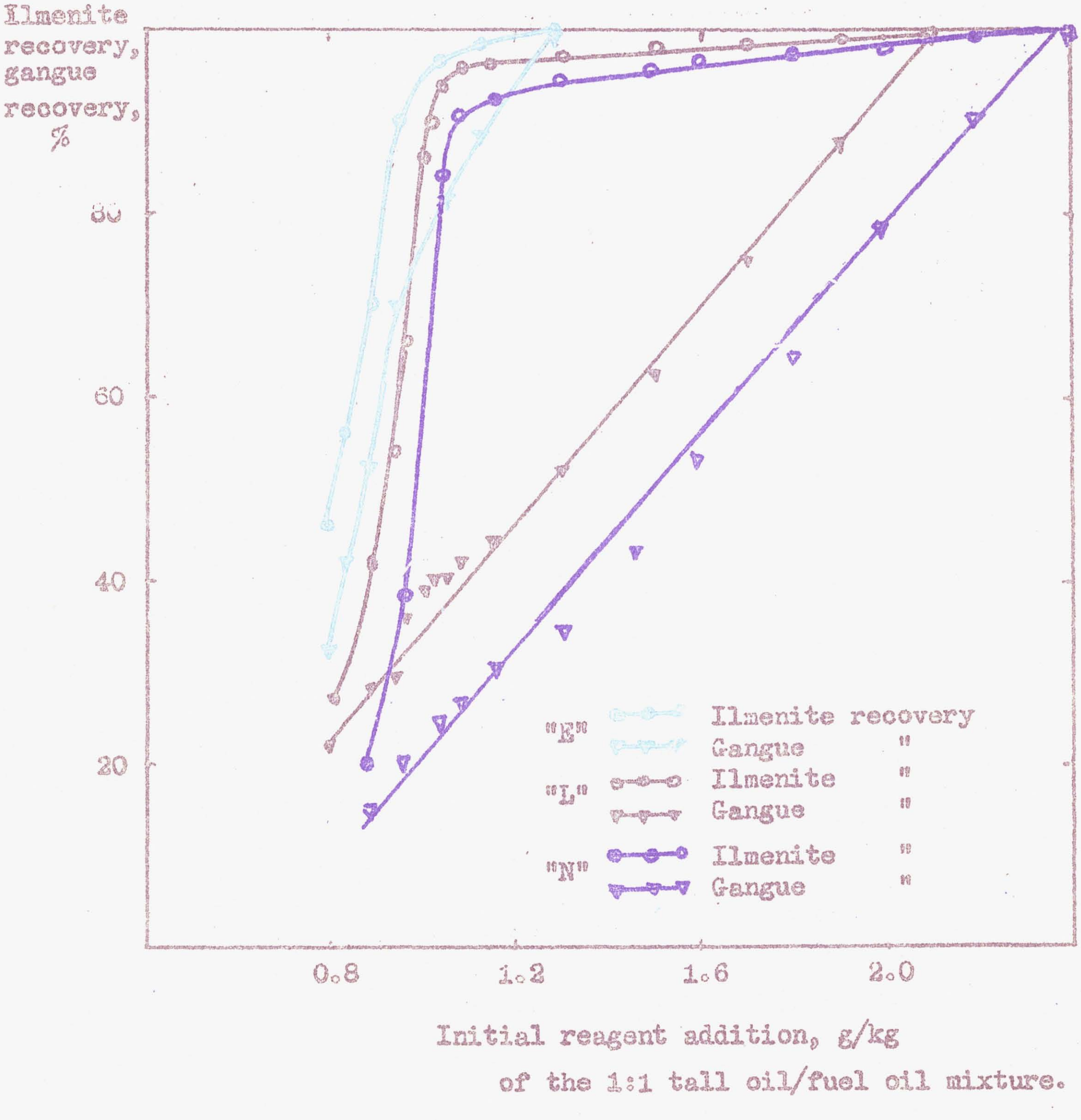
The initial reagent addition was varied from 0.76 to 2.1 g/kg of the 1:1 tall oil/fuel oil mixture. The conditioning was stopped at the start of the flocculation peak, "E", in tests Nos. 54-57, at the end of the deflocculation period, "L", in tests Nos. 53-55, and at point "N" in the dispersion period, in tests Nos. 58-69. Power consumption measurements showed that curves of type II were obtained in all cases when the initial reagent addition was not greater than 1.7 g/kg of the reagent mixture. Above this initial reagent addition the deflocculation was incomplete as shown in fig. 2.7.

The ilmenite and gangue recoveries at different characteristic points are presented as functions of the initial reagent addition in fig. 2.8. The correlation between the ilmenite and gangue recoveries and the initial reagent addition which was obtained at the characteristic point "L" was the same as that obtained in tests Nos. 1-15 and shown in fig. 2.1. This was attributed to the fact that the conditioning was stopped in both series of tests at the end of the deflocculation period, when the initial pulp viscosity was regained as mentioned in section. 2.3.1.

The correlations between the ilmenite and gangue recoveries and the initial reagent addition which were obtained at the characteristic point "N" were the same as those obtained at point "L", but the respective curves were shifted towards lower recoveries because of the further depression of particles in the period between points "L" and "N". The respective characteristic correlations obtained at point "E" were also similar, but the curves were shifted towards

FIGURE 2.8

ILMENITE AND GANGUE RECOVERIES AT SELECTED CHARACTERISTIC POINTS ("E", "L", "N") ON THE POWER CONSUMPTION CURVE AS FUNCTIONS OF THE INITIAL REAGENT ADDITION.



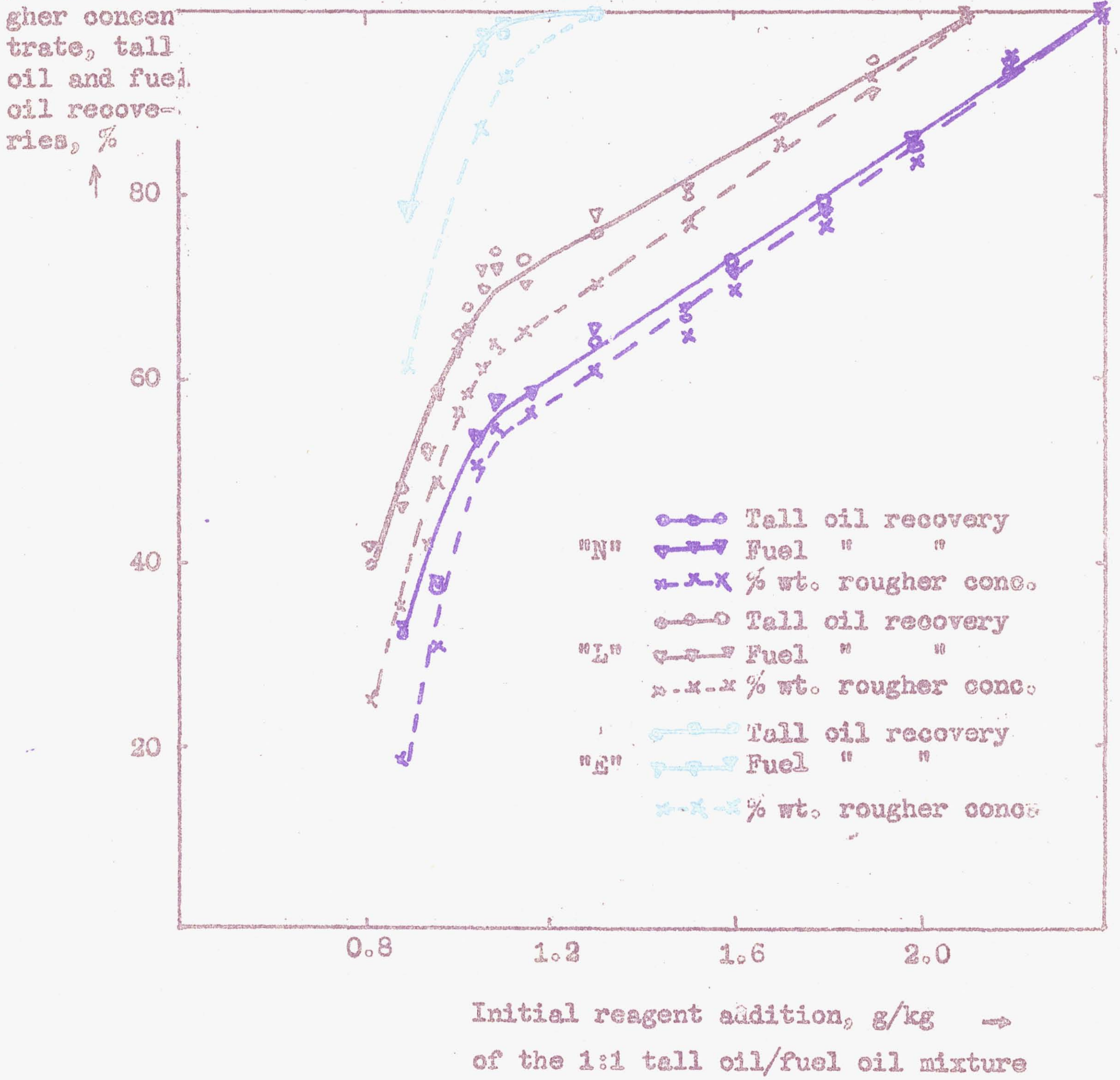
high recoveries at even low initial reagent addition, and showed little selectivity of flotation, in good agreement with the characteristic of this point.

The curves in fig. 2.8 also show that all the solids were floated at particular initial reagent additions which were determined by the position of the characteristic point. Maximum selectivity of flotation was observed at an initial reagent addition of 1.1 g/kg of the 1:1 tall oil/fuel oil mixture at the characteristic points "L" and "N", in good agreement with the value obtained in section 2.5.1.

The per cent weight rougher concentrate and the reagent recoveries in the rougher concentrate, corresponding to the data presented in fig. 2.8, are plotted as a function of the initial reagent addition in fig. 2.9. The correlation observed at the characteristic point "L" was the same as that shown in fig. 2.2, analogous to the similarity between the corresponding curves in figures 2.8 and 2.1 mentioned above. The curves obtained at the characteristic points "E" and "N" showed a similar correlation, but they were shifted to higher or lower recoveries, respectively, depending on whether the desorption process had not yet started or had already proceeded beyond the end of the deflocculation period, "L". In all cases the reagent recoveries increased with increasing per cent weight rougher concentrate, and the recoveries of both reagents were nearly equal at all points, thus maintaining the initial 1:1 tall oil/fuel oil ratio.

FIGURE 2.9

PER CENT WEIGHT ROUGHER CONCENTRATE, TALL OIL RECOVERY AND FUEL OIL RECOVERY IN ROUGHER CONCENTRATE AT SELECTED CHARACTERISTIC POINTS ("E", "L", "N") ON THE POWER CONSUMPTION CURVE AS FUNCTIONS OF THE INITIAL REAGENT ADDITION.



The reagent concentrations in the rougher concentrate were presented as a function of the initial reagent addition in fig. 2.10. The curves obtained show that this reagent concentration was at a minimum for an initial reagent addition of 1.1 g/kg of the reagent mixture, which was the same as the optimal initial reagent addition giving maximum ilmenite recovery and maximum flotation selectivity at the characteristic point "L", as shown in fig. 2.8.

The data presented in fig. 2.8 were used for the construction of a set of curves shown in fig. 2.11, each representing a constant initial reagent addition and each showing the relationship between ilmenite and gangue recoveries and the position of the characteristic point. The corresponding curves from fig. 2.4 are also presented, as they were used for the construction of the other curves in the interval between points "E" and "N". The curves obtained showed that the depression of ilmenite was delayed at high initial reagent addition, and that it started even in the deflocculation period when the initial reagent addition was 10% below the optimal value mentioned above. The gangue recovery was shifted towards lower or higher values, depending whether the initial reagent addition was below or above the optimal value, respectively.

These correlations show that the flotation results were a function of the initial reagent addition at any given characteristic point over this range, and that accordingly, the desorption of the reagents during the deflocculation and dispersion periods was a function of the reagent concentration on the particles.

F I G U R E 2.10

TALL OIL AND FUEL OIL CONCENTRATION IN ROUGHER CONCENTRATE AT SELECTED CHARACTERISTIC POINTS ("E", "L", "N") ON THE POWER CONSUMPTION CURVE AS FUNCTION OF THE INITIAL REAGENT ADDITION.

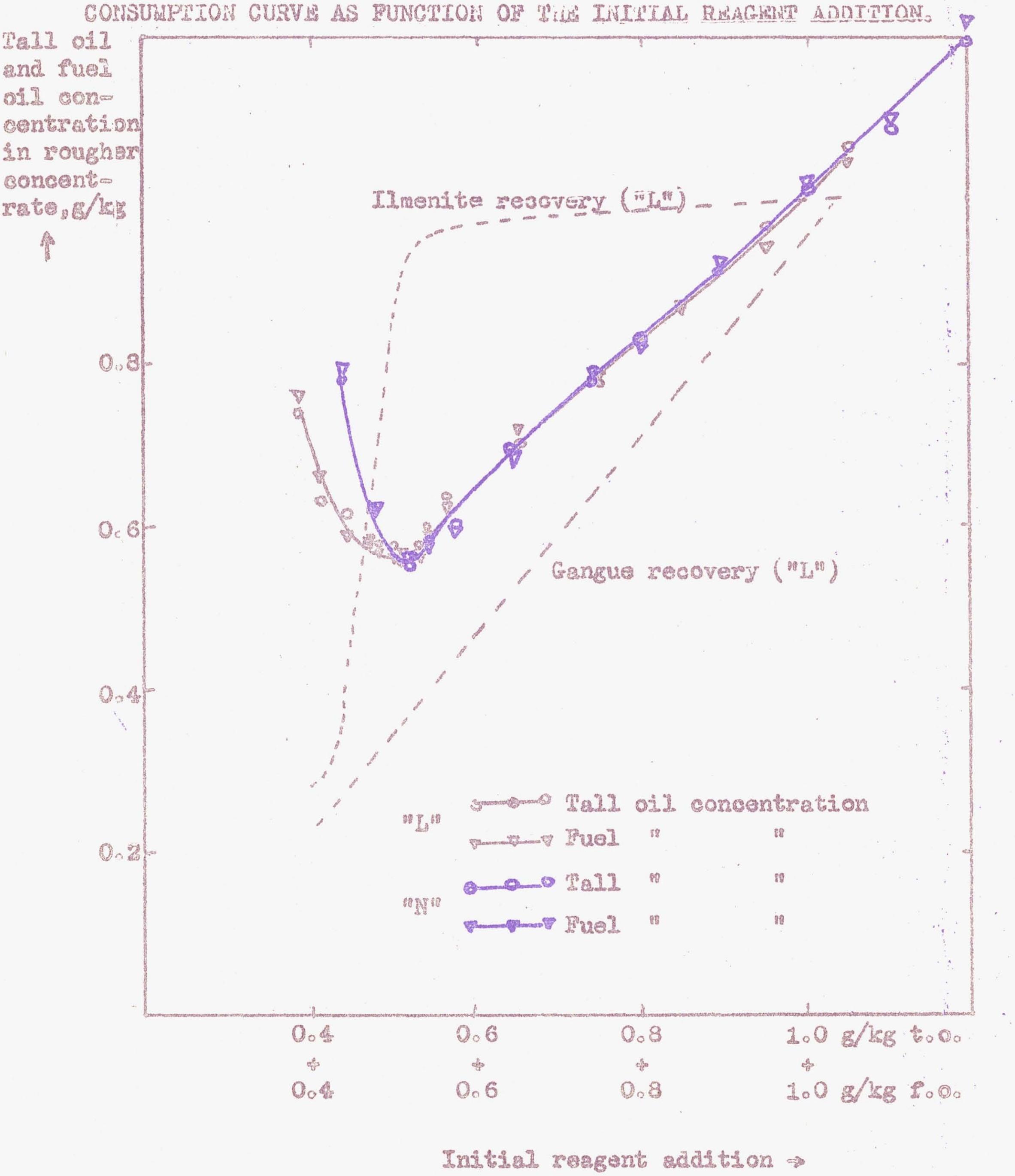
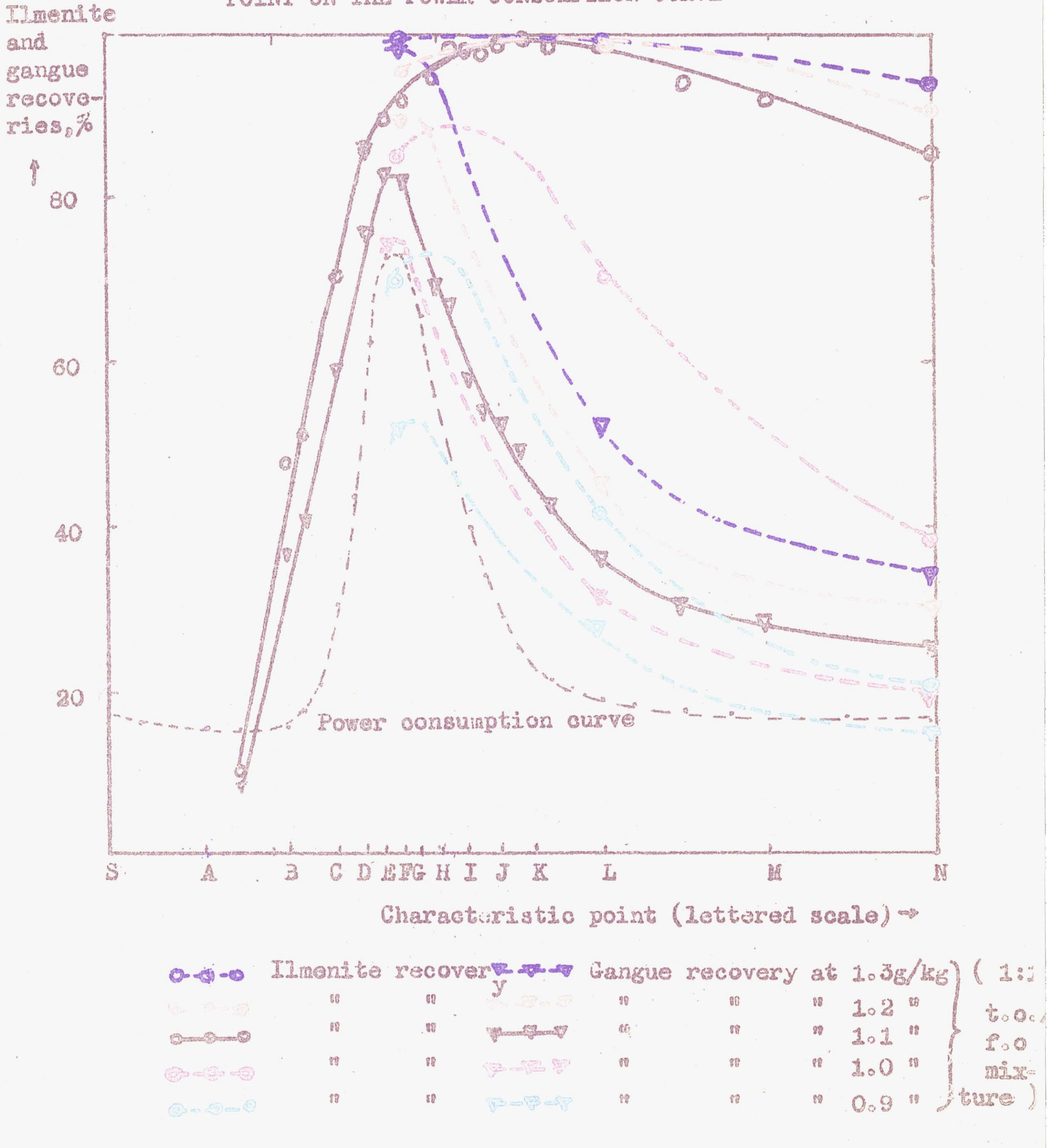


FIGURE 2.11

ILMENITE AND GANGUE RECOVERIES AT DIFFERENT INITIAL REAGENT ADDITIONS AS FUNCTIONS OF THE CHARACTERISTIC POINT ON THE POWER CONSUMPTION CURVE



These correlations also show that the optimal initial reagent addition made it possible to obtain nearly 100% ilmenite recovery at maximum flotation selectivity at the expense of the smallest energy consumption, required to reach the characteristic point "L". The same flotation results were obtained at higher reagent additions after longer conditioning time to the characteristic points "M" or "N", at the expense of higher energy consumptions. The power consumption curves were however the same at all initial reagent additions below 1.7 g/kg of the reagent mixture, showing that the same energy input was required to reach a given characteristic point at different initial reagent contents over this range.

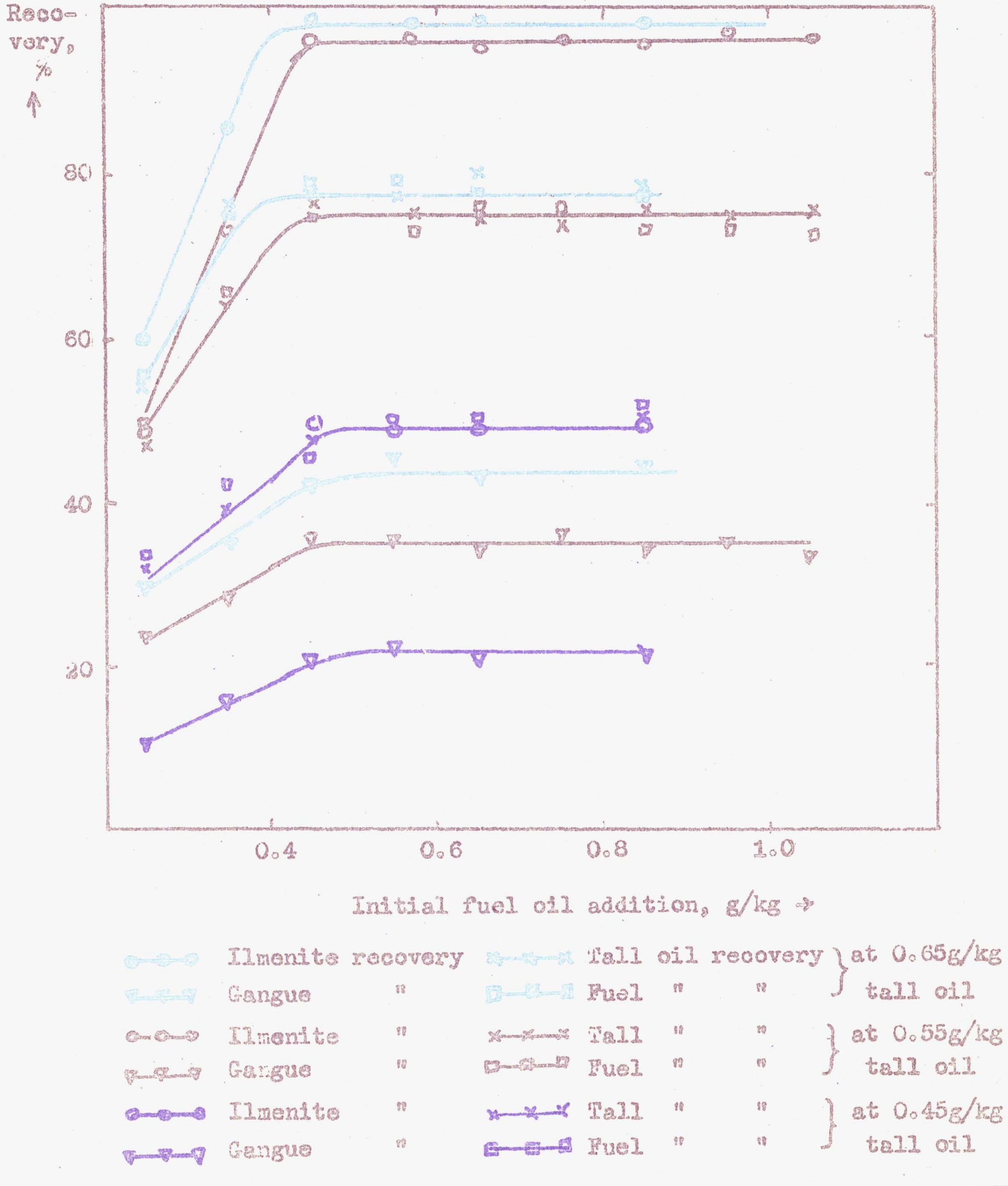
2.5.4. Tall oil/fuel oil ratio.

The tall oil/fuel oil ratio was varied in a series of tests (Nos. 70-90) over the range 2:1 to 1:2. This was accomplished by keeping the initial tall oil addition constant at 0.45, 0.55, and 0.65 g/kg, and varying the fuel oil addition over the range 0.25 to 1.05 g/kg. The pulps were conditioned to the end of the deflocculation period, "L", and a power consumption curve of type I was obtained in all cases. This showed that the variation of the fuel oil addition did not affect the total energy consumed up to this characteristic point.

The ilmenite, gangue and reagent recoveries in the rougher concentrate at different initial tall oil additions are presented as functions of the initial fuel oil addition in fig. 2.12. The curves obtained show that the ilmenite and gangue recoveries were constant

FIGURE 2.12

ILMENITE, GANGUE, TALL OIL AND FUEL OIL RECOVERIES IN THE ROUGHER CONCENTRATE AT DIFFERENT INITIAL TALL OIL ADDITIONS AS FUNCTIONS OF THE INITIAL FUEL OIL ADDITION (POINT "L").



at an initial fuel oil addition exceeding 0.45 g/kg, but fell off when the fuel oil addition was decreased below this value. It was concluded from this that the optimal flotation results obtained at 1.1 g/kg of the 1:1 tall oil/fuel oil mixture in section 2.5.5. corresponded actually to an optimal initial tall oil addition of 0.55 g/kg in conjunction with an optimal initial fuel oil addition of 0.45 g/kg.

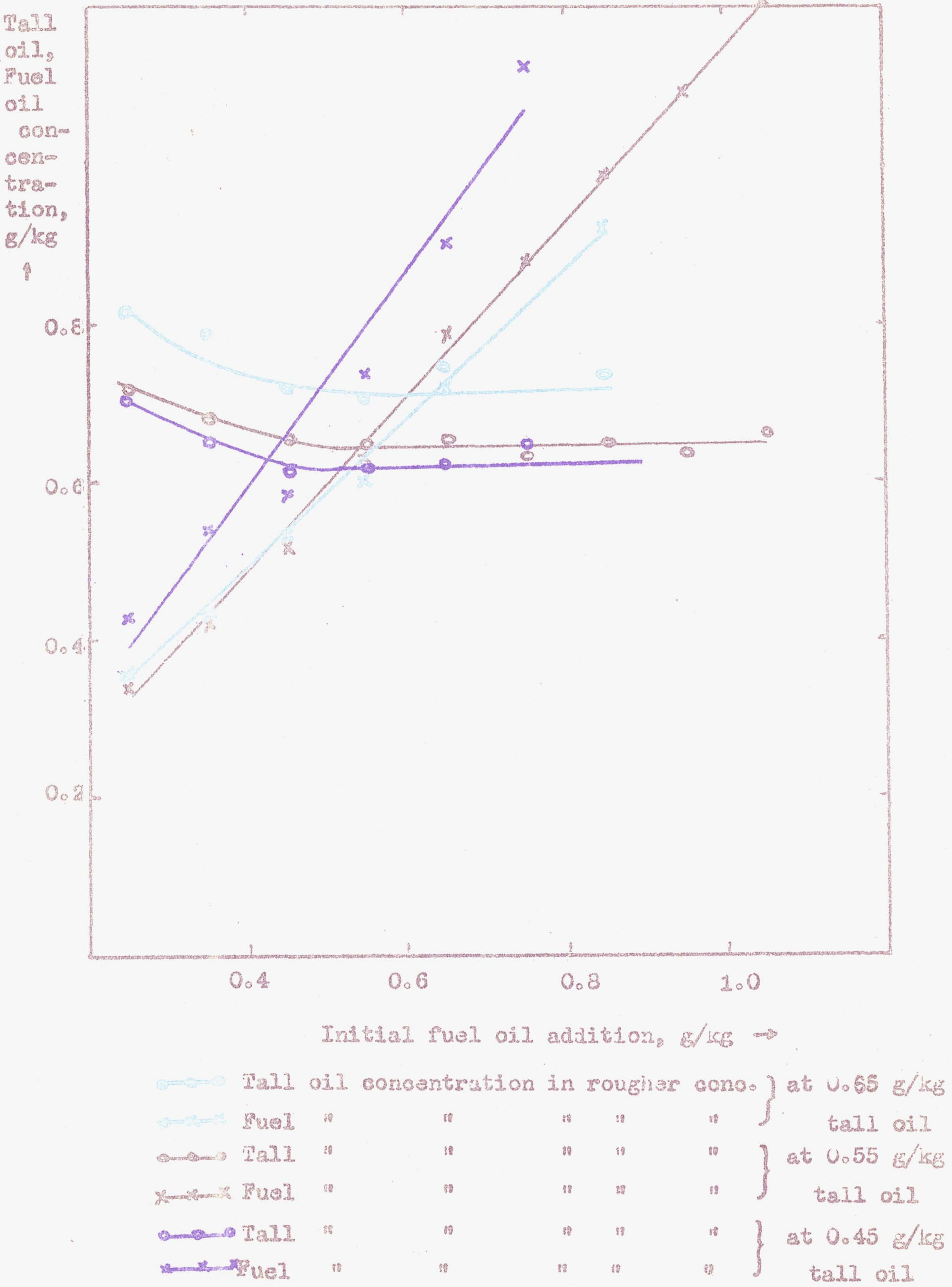
The tall oil and fuel oil recoveries in each rougher concentrate were equal to each other at any tall oil/fuel oil ratio applied, showing that the distribution of these two reagents on the surface was always the same as in the feed. This was confirmed from the values of the reagent concentrations in the rougher concentrate, presented as a function of the fuel oil addition in fig. 2.15. The curve corresponding to 0.45 g/kg initial tall oil addition was most significant, showing that despite the low per cent weight rougher concentrate, the tall oil concentration of about 0.65g per kg rougher concentrate was almost the same as that obtained at 0.55 g/kg initial tall oil content with nearly 100% ilmenite recovery. This was evidently the minimum average surface coating of floatable particles at this size distribution.

2.5.5. Addition of sulphuric acid.

Addition of sulphuric acid to the conditioning tank, at the point corresponding to the end of the flocculation peak, resulted in an immediate deflocculation. The duration of the

FIGURE 2.15

REAGENT CONCENTRATIONS IN ROUGHER CONCENTRATE AT DIFFERENT TALL OIL ADDITIONS AS FUNCTIONS OF THE INITIAL FUEL OIL ADDITION (POINT "L")



deflocculation period was reduced from the usual 8-9 minutes to half a minute, when the pH of the pulp was reduced from 6.5 to 4.5 by the addition of 4 mequiv. sulphuric acid per kg. solids, as shown by the power consumption curve of test No. 100 in fig. 2.14. The power consumption level reached during this accelerated deflocculation was a function of the pH, as shown by comparison of the curves of tests Nos. 92, 96, 100 and 104 in fig. 2.14.

The resulting saving in the energy consumption, determined by integration of the areas below the respective four curves, were 50, 60, and 70% of the nett energy consumption required to reach point "L" at constant pH (6.5), when the sulphuric acid added at the end of the flocculation peak reduced the pH to 5.5, 4.5, and 3.5 respectively (see also end of section 2.3.2 and table 2.2).

The ilmenite and gangue recoveries at different initial reagent additions are presented as functions of the pH value reached during deflocculation in fig. 2.15 (tests Nos. 91-108). The curves obtained show that the gangue was already depressed by the small addition of 2 mequiv. sulphuric acid, which corresponds to the lowering of the pH from 6.5 to 5.5. Further lowering of the pH resulted in less pronounced gangue depression. The ilmenite was also depressed, especially at low initial reagent addition, at values below or equal to the optimal addition of 1.1g/kg of the 1:1 tall oil/fuel oil mixture, determined for deflocculation at constant pH (6.5) in section 2.3.3. The depression of ilmenite however, increased progressively with increasing sulphuric acid addition. Both ilmenite and

FIGURE 2.14

INFLUENCE OF THE SULPHURIC ACID ADDITION ON THE DEFLOCCULATION PERIOD OF THE POWER CONSUMPTION CURVE.

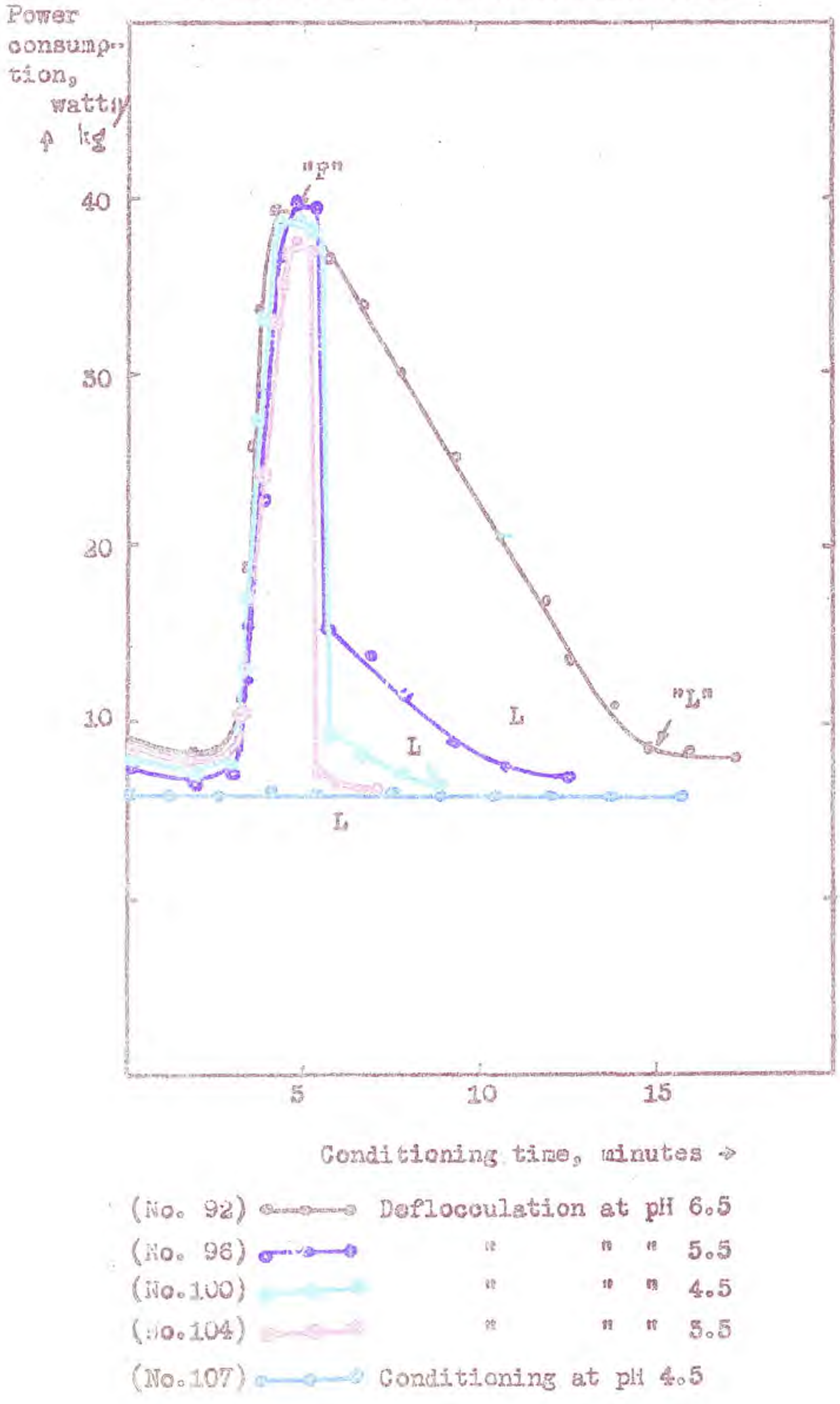
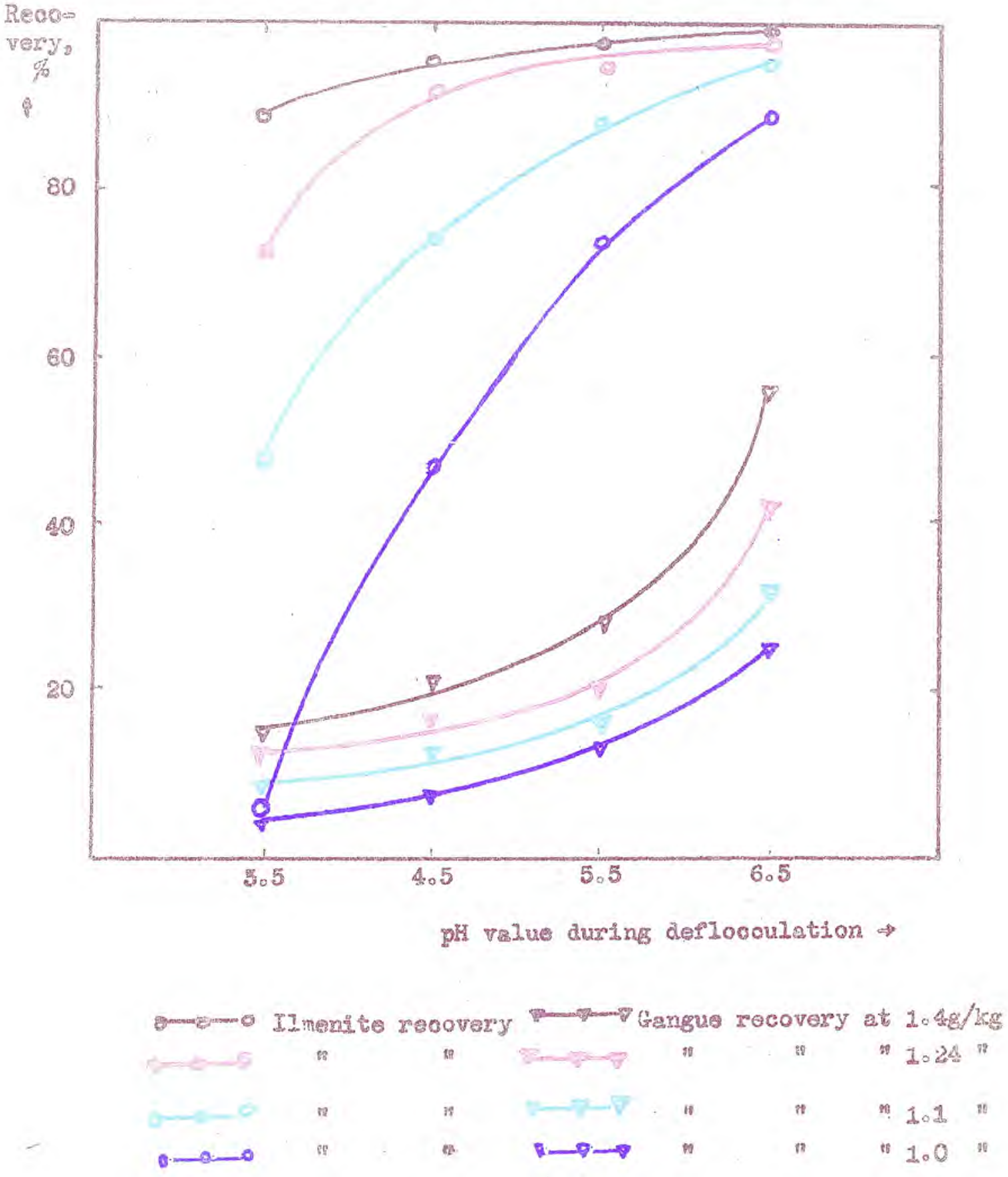


FIGURE 2.15

ILMENITE AND GANGUE RECOVERIES AT DIFFERENT INITIAL REAGENT ADDITIONS AS FUNCTIONS OF THE PH DURING THE DEFLOCCULATION.



(The 1:1 tall oil/fuel oil mixture was used) gangue recoveries were higher at higher initial reagent additions when the pH was lowered to a given value. Fig. 2.15 shows that the ilmenite recovery at 1.24 g/kg reagent mixture and at pH 4.5 was equal to that at 1.1 g/kg reagent mixture at pH 6.5, whereas the gangue recovery in the former case was half of that in the latter case. These improved results were obtained with the additional advantage of a 60% reduction in the energy consumption, as shown above.

The reagent recoveries in the rougher concentrate and the per cent weight rougher concentrate at different initial reagent additions are shown as functions of the lowered pH in fig. 2.16. The curves obtained showed that the reagent recoveries were proportional to the per cent weight rougher concentrate at all pH values. This suggested that the desorption of the reagents by means of sulphuric acid was not basically different from the normal desorption of the reagents by attrition, but the rate of the desorption was much higher.

The reagent concentrations in the rougher concentrates at different initial reagent additions are shown as functions of the pH in fig. 2.17. The curves obtained show that the reagent concentration was nearly constant at any given initial reagent addition, with the initial tall oil/fuel oil ratio being maintained. A line marking the points of 95% ilmenite recovery drawn in fig. 2.17 intersects the reagent concentration curves at the points corresponding to the minimum surface coverage at different pH values. This minimum reagent concentration increased in inverse proportion to the pH.

FIGURE 2.16

PER CENT WEIGHT ROUGHER CONCENTRATE AND REAGENT RECOVERIES IN THE ROUGHER CONCENTRATE AT DIFFERENT INITIAL REAGENT ADDITIONS AS FUNCTIONS OF THE PH DURING THE DEFLOCCULATION PERIOD.

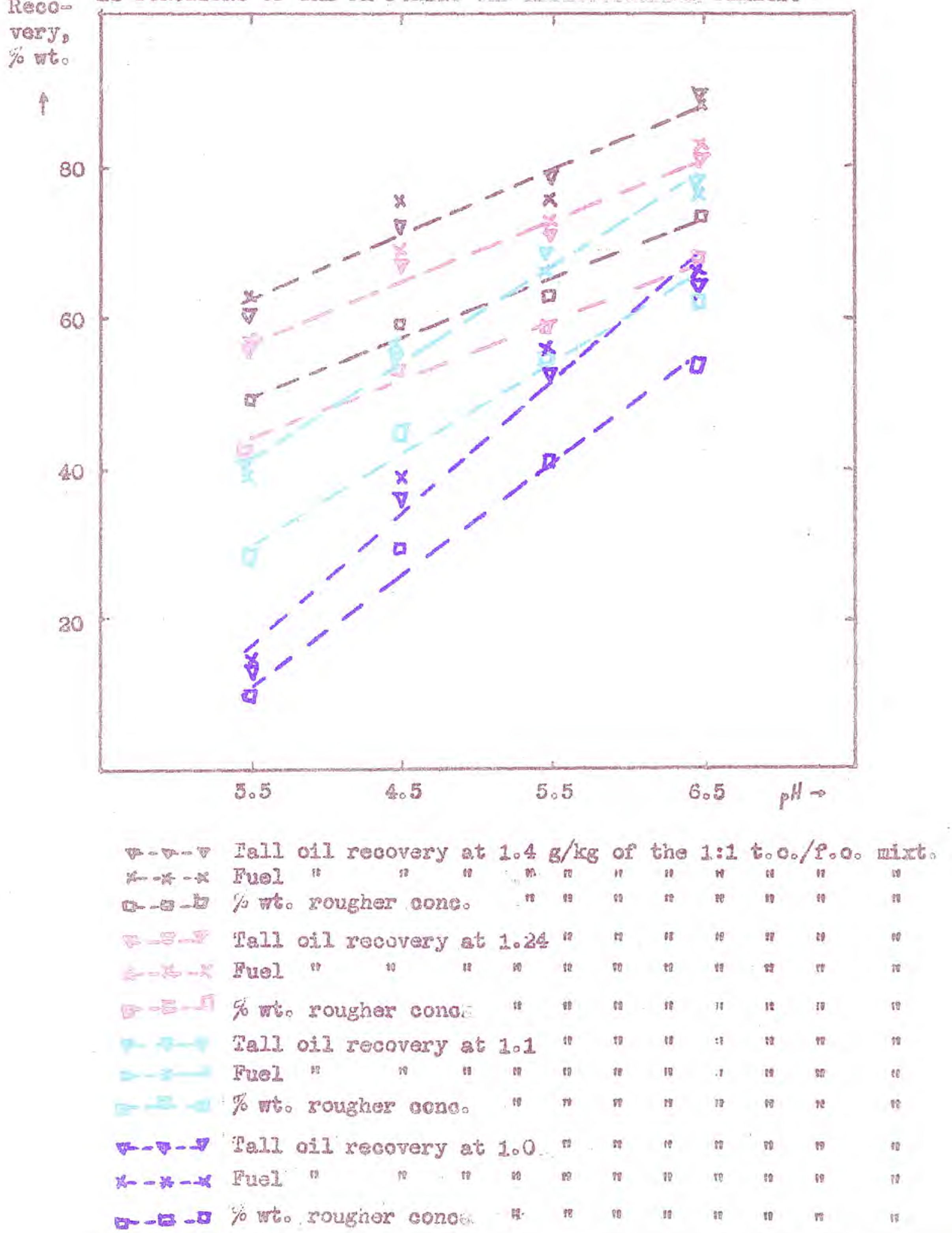
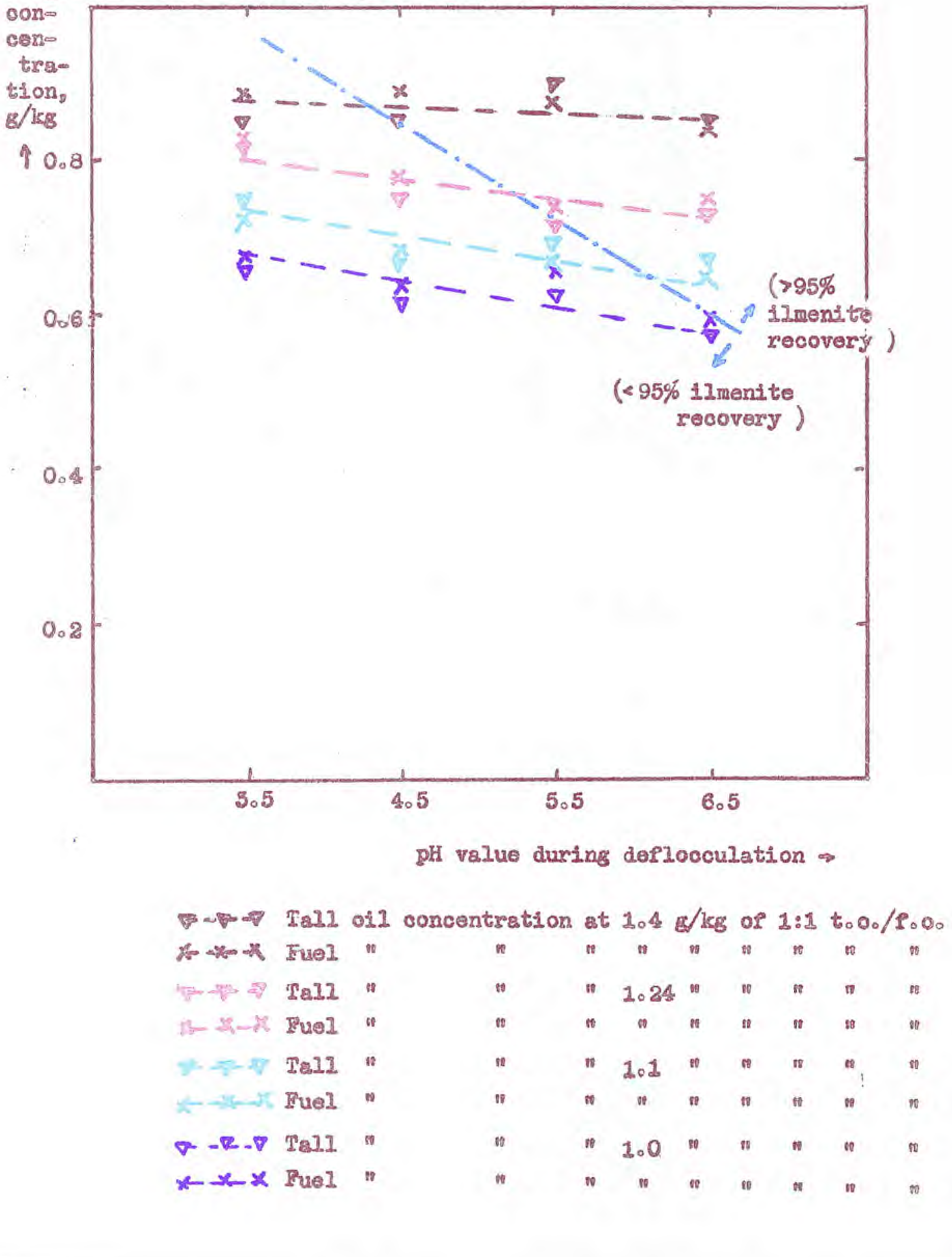


FIGURE 2.17

REAGENT CONCENTRATIONS IN THE ROUGHER CONCENTRATE AT DIFFERENT INITIAL REAGENT ADDITIONS AS FUNCTIONS OF THE PH DURING THE DEFLOCCULATION PERIOD.



Addition of sulphuric acid prior to reagent addition prevented bulk flocculation, as shown by the power consumption curve of test No. 107 in fig. 2.14, in which the initial pH was lowered from 6.5 to 4.5, in comparison with the curve of test No. 100. The pulp in test No. 107 was conditioned for the same length of time which corresponded to point "L" in test No. 92, at a constant pH (6.5), as shown in fig. 2.14. The resultant ilmenite and gangue recoveries in test No. 107 were 95.5% and 56% respectively, compared with 98% and 42% respectively in test No. 95, in which the same initial reagent addition of 1.24 g/kg was used at pH 6.5. The recoveries in the corresponding test No. 101, in which the same initial reagent addition was used and with the pH lowered to 4.5 after the flocculation had taken place, were 92.5 and 17% respectively. This comparison showed that addition of the sulphuric acid before the reagents were added did not prevent their adsorption. The addition of the sulphuric acid prior to the reagent addition, however, was not as effective in the subsequent desorption of the reagents from the gangue particles, as was the addition of the same amount of sulphuric acid after the flocculation peak was attained.

It was concluded that sulphuric acid was effective as a depressant when introduced after the flocculation peak was reached, when it induced a stronger depression of the gangue with a considerable saving in energy consumption.

2.5.6. Rougher flotation and reconditioning at high pulp density.

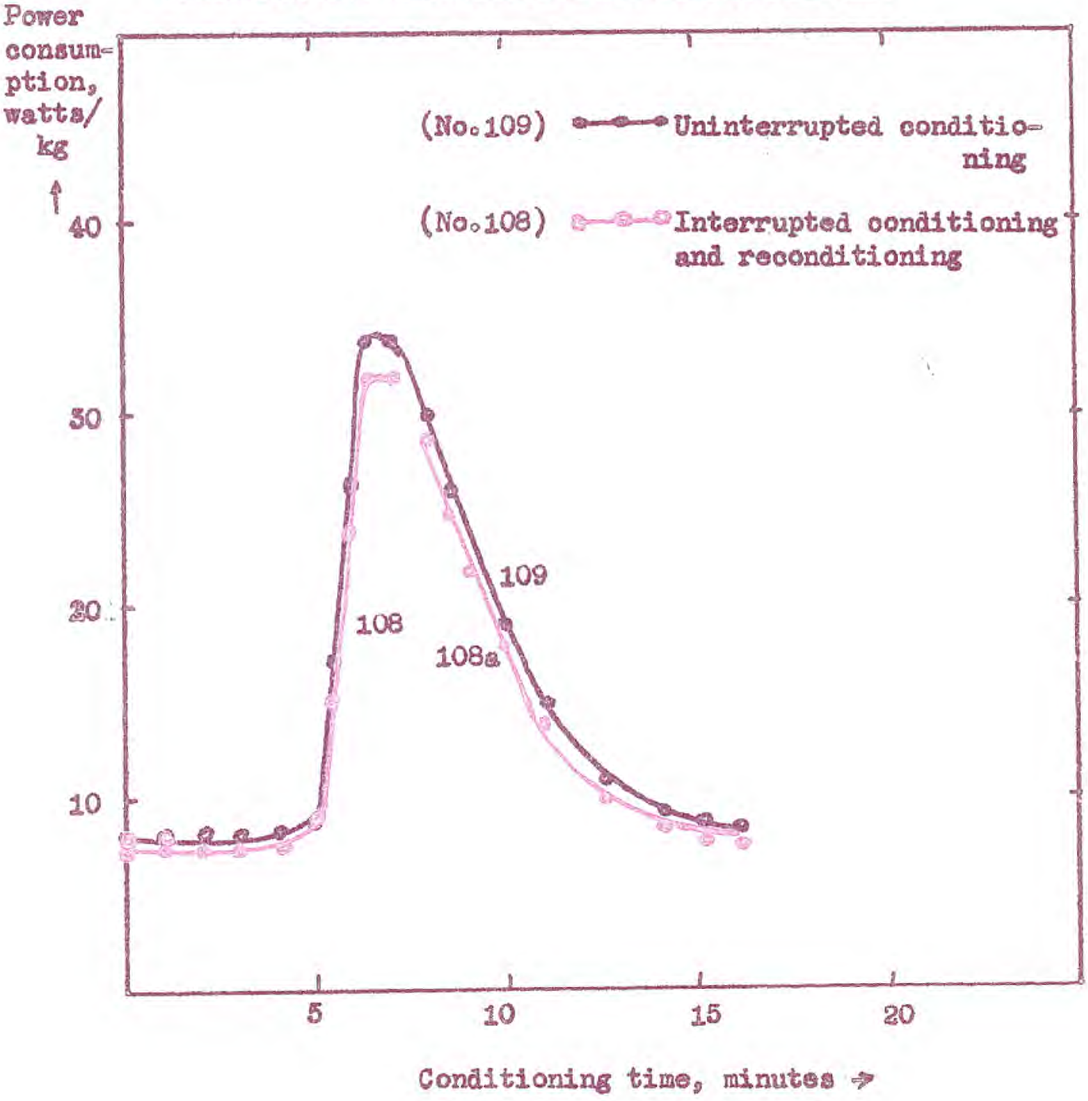
The pulp in test No. 108 was first conditioned until the flocculation peak was reached, as shown by the power consumption curve in fig. 2.18. The ilmenite and gangue recoveries were 97 and 84.5% respectively in correspondence to the initial reagent addition of 1.15 g/kg of the 1:1 tall oil/fuel oil mixture and to the characteristic point "F". The rougher concentrate and tailings were thickened and returned to the conditioning tank, followed by reconditioning at the original pulp density of 70% solids. The power consumption curve obtained was a continuation of the original power consumption curve, as shown for test No. 108a in fig. 2.18. The pulp was conditioned to the end of the deflocculation period, and the ilmenite and gangue recoveries were 96 and 40% respectively, in comparison with 95 and 41% respectively in test No. 109, which was carried out by uninterrupted conditioning to the same characteristic point "L", as shown in fig. 2.18.

This phenomenon was observed when the rougher concentrate only was reconditioned, or when reconditioning at constant pH (6.5) or at successively lowered pH was interrupted several times by intermediate flotation cleaner stages. In each case the flotation results corresponded to the characteristic point reached during the reconditioning, and the preceding flotation had no effect.

These results have shown that the process of desorption of the reagents during the deflocculation period can be carried out in the presence as well as in the absence of the gangue particles which are depressed during the rougher or cleaner flotations, provided the original high pulp density is applied during reconditioning. The advantages

F I G U R E 1.18

POWER CONSUMPTION V. CONDITIONING TIME CURVES WHEN THE CONDITIONING WAS INTERRUPTED AT POINT "F" BY ROUGHER FLOTATION AND THE PRODUCTS WERE RECONDITIONED.



of reconditioning after the flocculation peak were, therefore, a direct result of the removal of part of the gangue during rougher or cleaner flotation, so that both energy consumption and acid consumption were reduced during the deflocculation period.

2.3.7. Repeated cleaner flotation at constant pH and at successively reduced pH values.

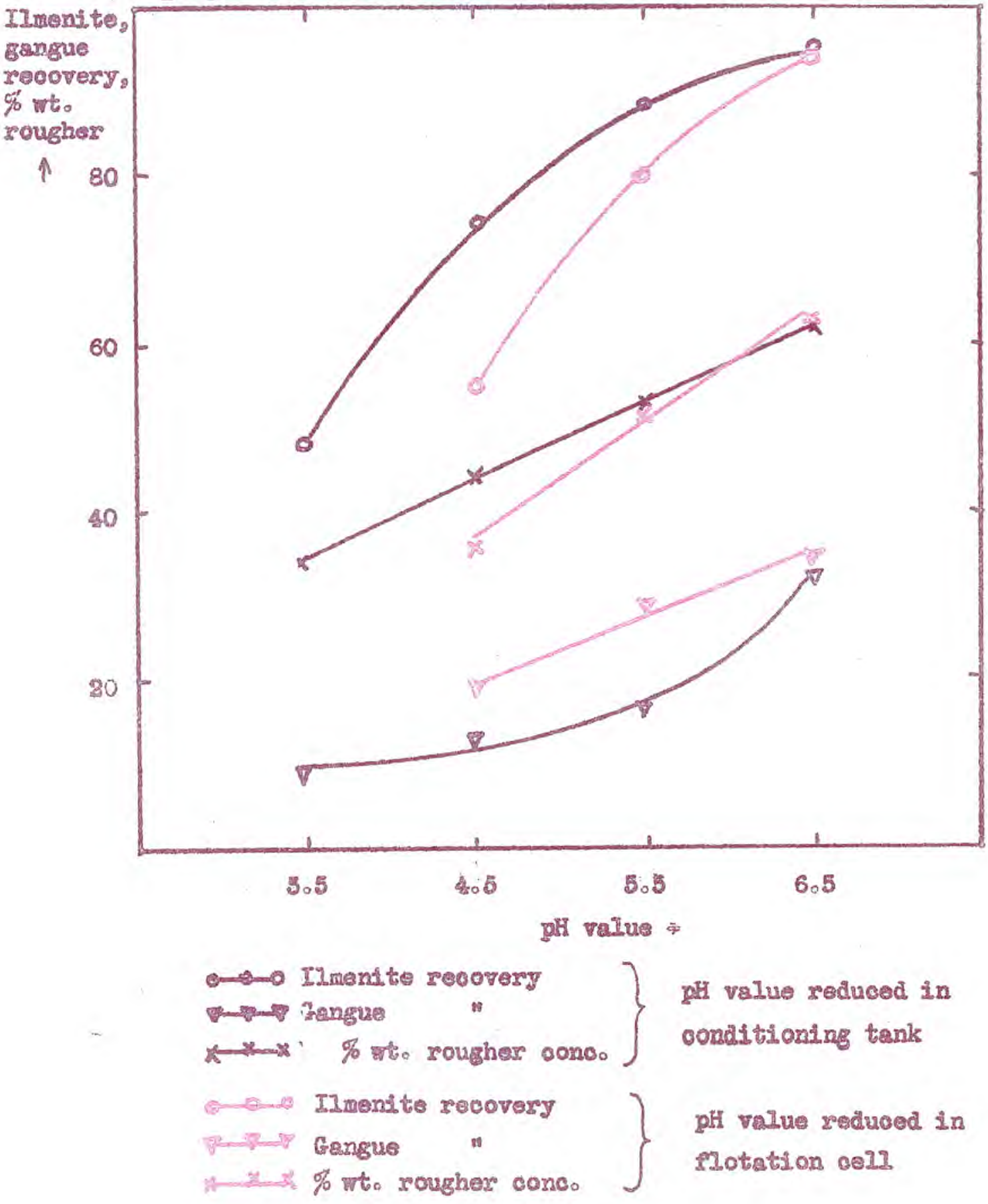
An ilmenite ore pulp was conditioned until the end of the deflocculation period was reached and was floated (test No. 110). The rougher concentrate was returned 15 times, successively, to the flotation cell, and was refloated. The final ilmenite and gangue recoveries were 94 and 35% , respectively, compared with 95 and 38% obtained for the rougher concentrate in test No. 111, using the same initial reagent addition of 1.1 g/kg of the reagent mixture, and conditioning to the same characteristic point "L".

These results showed that the reagent desorption process did not take place in the flotation cell, where the pulp density was only 30% solids. This also explained the phenomenon observed in the preceding section, whereby the conditioning process at high pulp density could be continued after the rougher flotation.

The rougher concentrate of test No. 111 was returned to the flotation cell, and was refloated at pH 5.5. The quantity of acid used for reduction of the pH value from 6.5 was 8 mequiv. sulphuric acid, compared with only 2 mequiv. sulphuric acid needed to produce the same lowering of the pH in the conditioning tank, which contains only 1/6 of the water volume used in the flotation cell. The cleaner

FIGURE 2.19

ILMENITE RECOVERY, GANGUE RECOVERY, AND PER CENT WEIGHT ROUGHER CONCENTRATE V. PH VALUE PRODUCED BY ADDITION OF H_2SO_4 TO CONDITIONING TANK OR TO FLOTATION CELL.



flotation was repeated at pH 4.5, and the flotation results are presented in fig. 2.19, to compare with the results obtained when similar reductions of the pH value were effected in the conditioning tank, during deflocculation. Fig. 2.19 shows that the depression of the minerals was less selective when pH reduction was effected in the flotation cell, than when carried out in the conditioning tank, and in addition the sulphuric acid consumption was much greater.

2.5.8. Addition of fines.

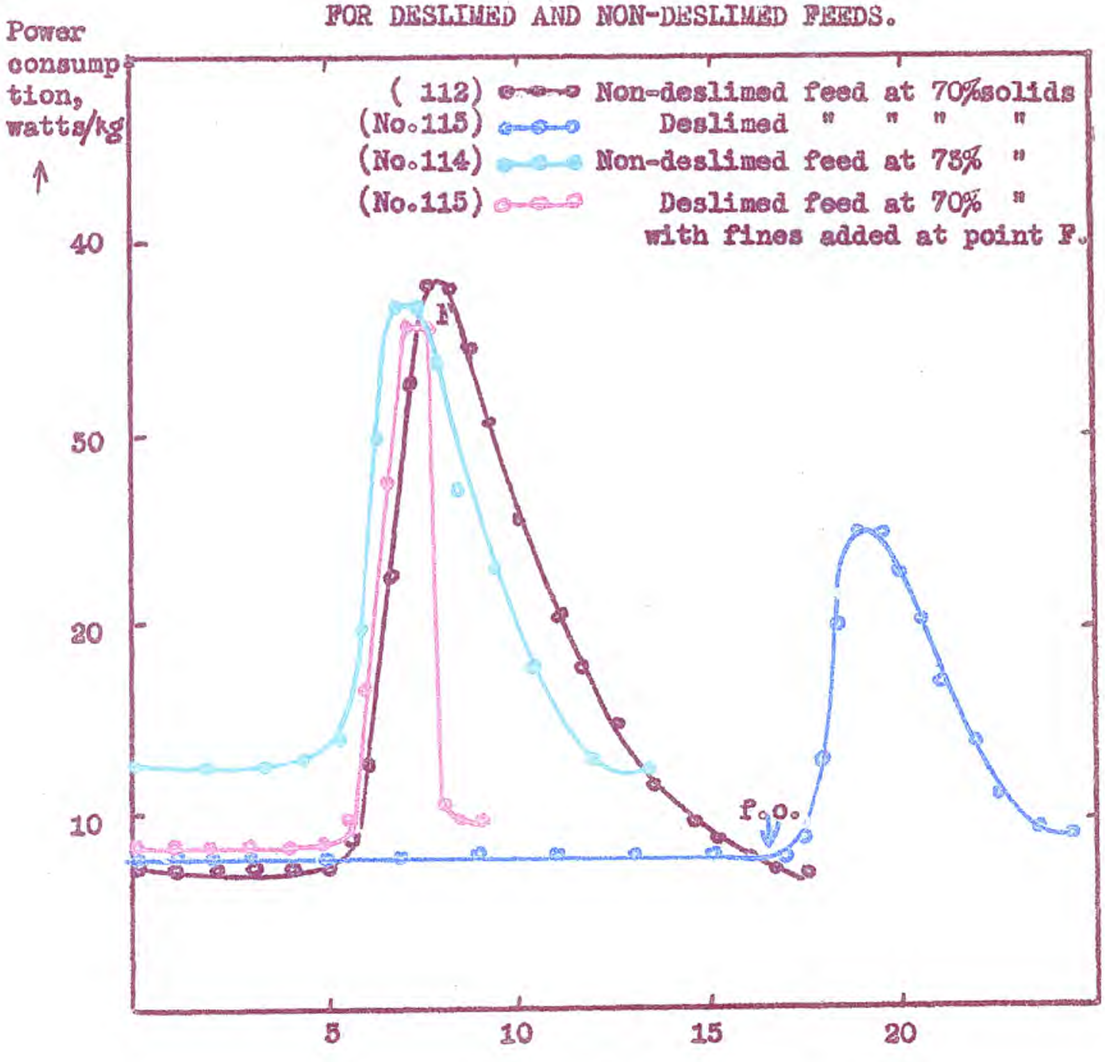
It was mentioned in section 2.2.5., on the experimental procedure, that the ground ilmenite ore feed was 10% deslimed. The flotation behaviour of feeds which were not deslimed was studied in the following tests.

A non-deslimed feed was conditioned with 2.8 g/kg of the 1:1 tall oil/fuel oil mixture, and the power consumption curve obtained in this test (No. 112) is presented in fig. 2.20. This curve shows that no flocculation occured during 15 minutes conditioning, despite the very high reagent addition. Addition of further fuel oil only, at the point indicated on the curve, caused a rapid flocculation of the pulp. The flotation at the characteristic point "L" gave 95.5% ilmenite recovery and 57% gangue recovery, in comparison with 96% and 55% respectively, in test 115, where a 10% deslimed feed was conditioned to the same characteristic point, as shown by the curve (test No. 115) in fig. 2.20, using only 1.1 g/kg of the reagent mixture. The concentrations of the reagents in the respective

F I G U R E 2.20

POWER CONSUMPTION V. CONDITIONING TIME

FOR DESLIMED AND NON-DESLIMED FEEDS.



Conditioning time, minutes →

rougher concentrates were of course correspondingly higher when the feeds were not deslimed, but the reagent recoveries were, however, the same in both cases, at values around 75% of the initial reagent addition.

A similar non-deslimed feed was conditioned with the same initial reagent addition of 2.8 g/kg, but the pulp density was increased to 75% (test No. 114). As a result, normal bulk flocculation was obtained as shown by the power consumption curve of this test in fig. 2.20. Flotation after conditioning to the same characteristic point "L" as above, also gave 97% ilmenite and 36.5% gangue recoveries. The reagent recoveries and reagent concentrations in the rougher concentrate were also the same as in test No. 112.

A standard 10% deslimed feed sample was conditioned with 2.1 g/kg of the reagent mixture, at the normal pulp density of 70% solids, The usual bulk flocculation was produced, as shown by the power consumption curve for this test, No. 115, in fig. 2.20. At the flocculation peak the dried slime fraction of this feed was added to the conditioning tank, resulting in an immediate deflocculation, as shown by this power consumption curve. This phenomenon was very similar to the sudden deflocculation observed when sulphuric acid was added at the same characteristic point "F" (see fig. 2.14). Flotation at the point "L" resulted in 95.5% ilmenite recovery and 35.5% gangue recovery, these values being equal to those obtained in the previous two tests where a greater initial reagent addition was applied. In this test however, the reagent recoveries in the rougher concentrate were nearly 100% compared with only 75% in the earlier two tests. This indicated that the reagents were transferred from the coarser gangue particles to the ilmenite fines, which were added, during the very brief deflocculation period. This was confirmed by the reagent concentrations in the rougher concentrate, which were the same in this as well as in the earlier tests.

The results of these tests showed that the presence of fines in the conditioning tank prevented bulk flocculation at normal pulp densities of 70% solids, but an increase of pulp density permitted larger proportions of fines to be present so that bulk flocculation could then take place. The fines consumed large amounts of reagents because of their great specific surface, and this property was exploited when the fines were added to the conditioning tank before deflocculation started. As a result, the reagents which were otherwise desorbed and lost in the flotation liquor, were consumed by the fine ilmenite particles. It must be noted that prolongued agitation of deslimed feeds before the reagents were added had no effect on the flotation results, so that the fines produced during such attrition could not be considered as having the same role as fines added after flocculation.

The nett energy inputs required to reach the characteristic point "L" in tests No. 115 and No. 113 were compared by integration of the areas below the corresponding power consumption curves. This showed a reduction of 70% in the total energy consumption when fines were added beyond the flocculation peak, similar to that obtained when the pH was reduced to 5.5 during deflocculation (see section 2.5.5. and also end of section 2.5.2.).

2.5.9. Addition of the flotation reagents in stages.

Addition of the flotation reagents in stages during the induction period, the flocculation period, or the flocculation peak did not affect the flotation results, which were always a function of the total reagent addition and of the characteristic point reached during the conditioning. The same applied to separate additions of tall oil and fuel oil, irrespective of the order of addition. In the case of tall oil addition after the fuel oil, however, the bulk flocculation did not start until tall oil was added.

To illustrate these points, the power consumption curves corresponding to tests Nos. 116-119 are presented in fig. 2.21, with the points of addition of the reagents marked on these curves. The conditioning was stopped in all tests at the characteristic point "L" and the flotation resulted in the same ilmenite recoveries around 96% and gangue recoveries of about 35%. The reagent recoveries in the rougher concentrate were about 75%. As the flocculation period and flocculation peak were very brief, the reagents added during these periods were obviously distributed very quickly among the reagents already present on the surface of the particles and gave the same flotation results for this reason.

Stage-wise addition of the reagents during or at the end of the deflocculation period caused a renewed flocculation-deflocculation cycle of the pulp, as shown by the power consumption

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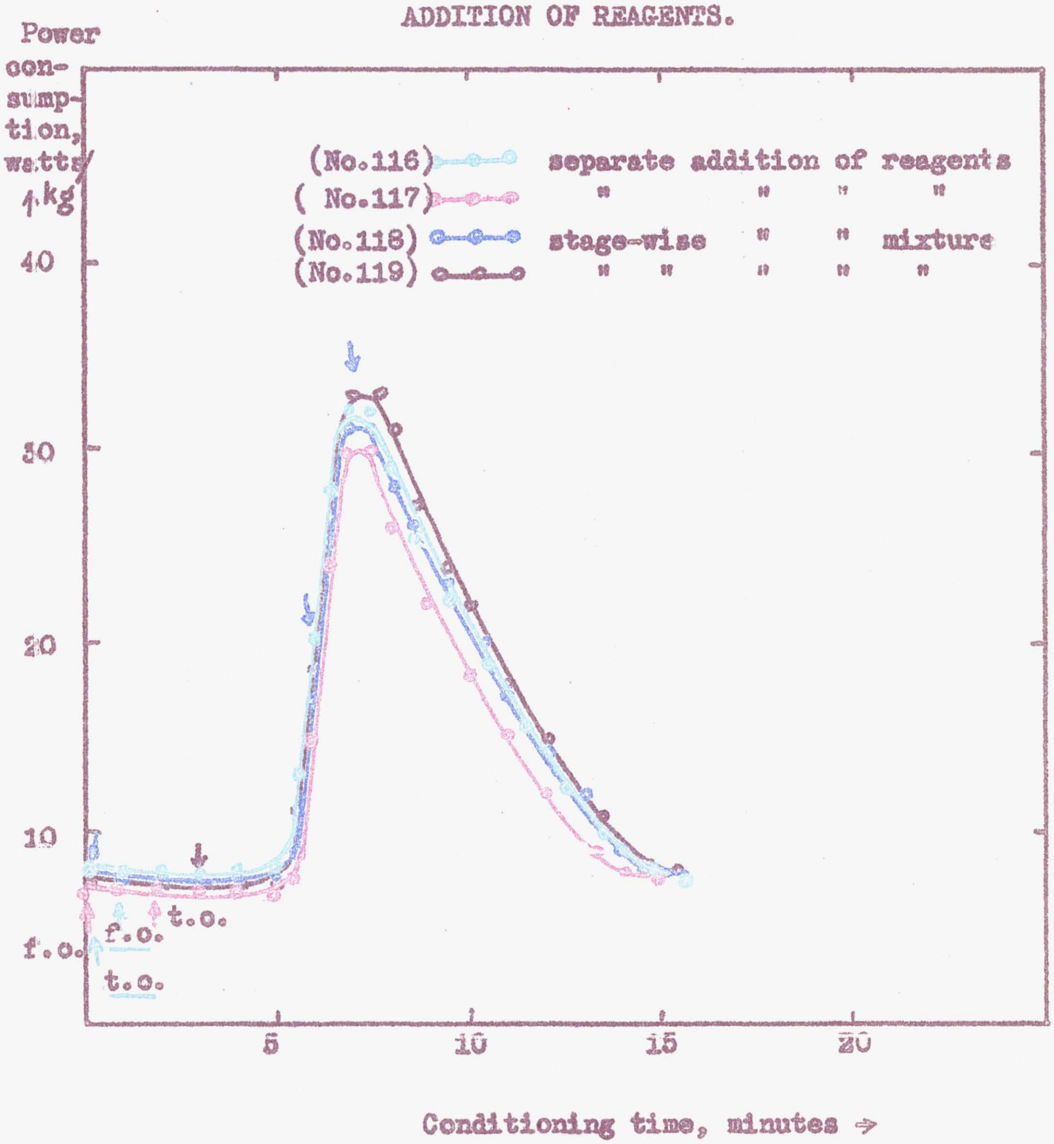
FIGURE 2.21

POWER CONSUMPTION V. CONDITIONING TIME FOR STAGE-WISE ADDITION OF REAGENTS.



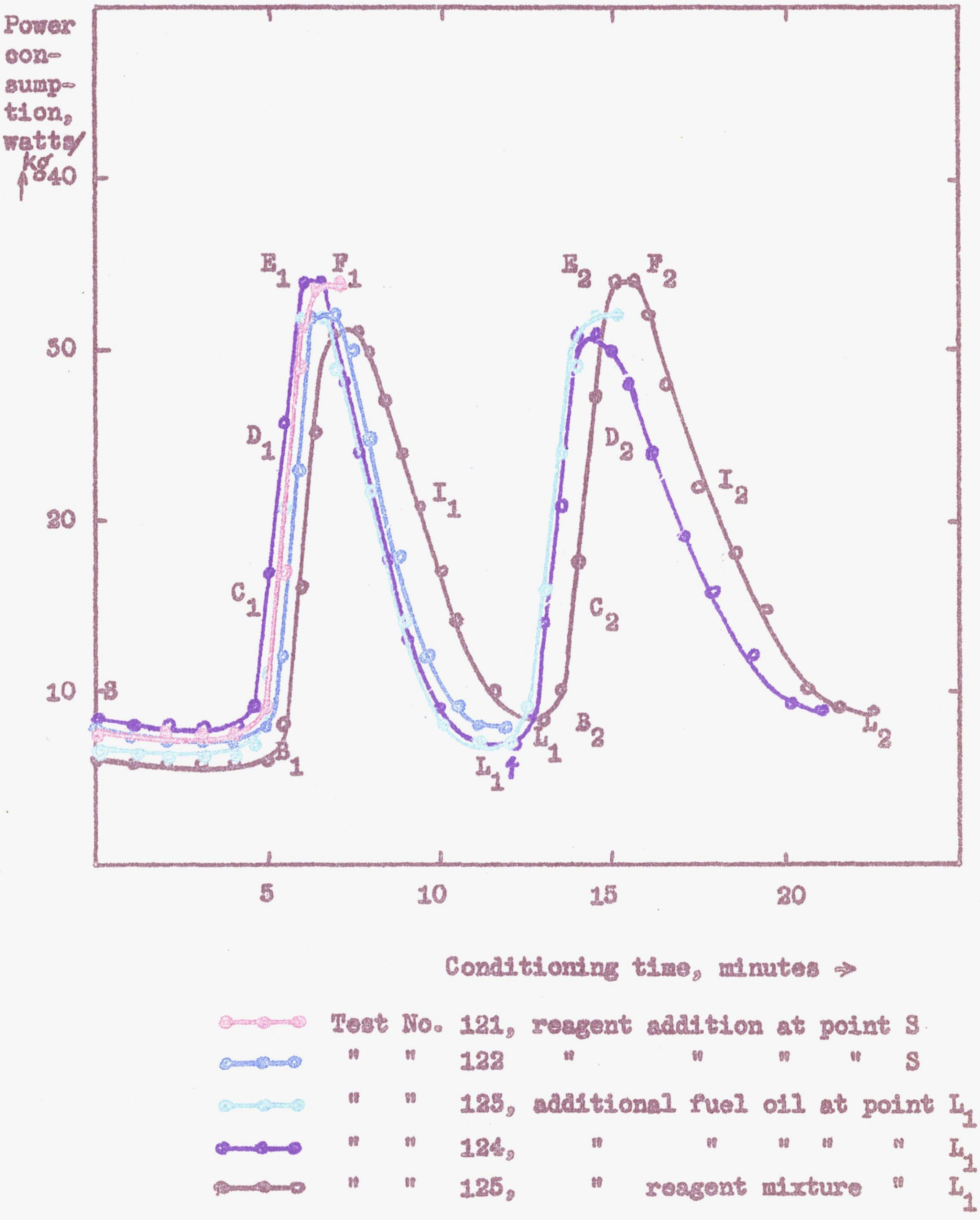
curves for tests Nos. 123-125 in fig. 2.22. In tests Nos. 123 and 124 the first flocculation-deflocculation cycle was obtained by using an initial reagent addition of 1.2 g/kg of the 1:1 tall oil/fuel oil mixture, and a further 0.3 g/kg fuel oil was added at the end of the first deflocculation period, "L_1". In test No. 125 the first cycle was obtained at an initial reagent addition of 1.0 g/kg of the reagent mixture, while a further 0.2 g/kg of the mixture was added at the characteristic point "L_1" to produce the second cycle.

In tests Nos. 123 and 125 conditioning was continued to the characteristic point "L_2" at the end of the second deflocculation, where the ilmenite and gangue recoveries were about 97-89% and 41-42% respectively. Similar results were obtained in test No. 122, at the same initial reagent addition, when conditioning was stopped at the end of the first deflocculation period as shown by the corresponding power consumption curve in 2.22. The reagent recoveries were around 85% in all three tests.

In test No. 124 conditioning was stopped at the characteristic point "F_2", at the end of the second flocculation peak, resulting in 97% ilmenite and 89% gangue recoveries. The same results were obtained in test No. 121, by conditioning to point "F_1", at the end of the first flocculation peak, as shown by the corresponding power consumption curve. The reagent recoveries were nearly 100% in both these tests. This demonstrated that the reagents desorbed during the first deflocculation period were readsorbed and redistributed during during the second flocculation period, this being followed by normal

FIGURE 2.22

POWER CONSUMPTION V. CONDITIONING TIME FOR STAGE-WISE ADDITION OF REAGENT AT THE END OF THE DEFLOCCULATION PERIOD.



desorption during the second deflocculation period. Each characteristic point on the second section of the curve corresponded therefore to the equivalent characteristic point on the first section.

2.5.10. Addition of the reagents as an emulsion.

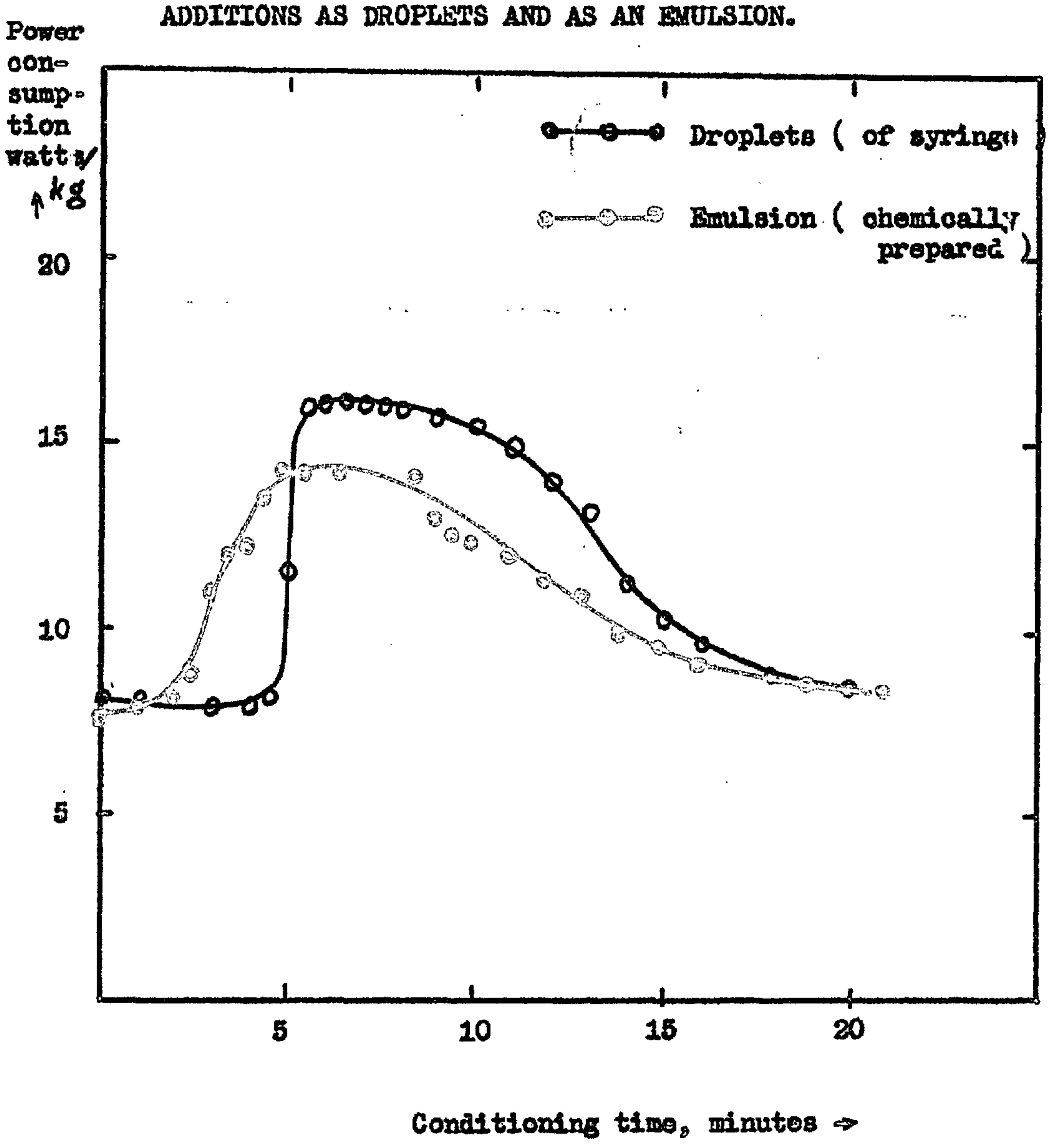
In a set of three tests (Nos. 126-128) the reagents were added to the conditioning tank by means of a syringe, which was the usual method in this study (see section 2.2.5.) and the pulps were conditioned to the characteristic points "F", "L", and "N" respectively. In a set of three parallel tests (Nos. 129-131) the same initial reagent addition, of 1.1 g/kg of the 1:1 tall oil/fuel oil mixture, was applied in the form of an emulsion. This emulsion was prepared by saponification of the reagent mixture in aqeous NaOH followed by neutralisation with an equivalent amount of HCl. This resulted in a very finely divided emulsion of the oil in the water. The conditioning was carried out to the same three characteristic points, respectively.

Comparison of the characteristic power consumption curves (fig. 2.25) showed that addition of the reagents in the form of an emulsion reduced the induction period, which was thus merged with the flocculation period, the slope of which was decreased correspondingly. Allthough the peak power consumption was lower when an emulsion was used, there was little saving in conditioning energy required to reach point "L" because of the prolongued flocculation period.

The ilmenite and gangue recoveries were the same at each of the three characteristic points, irrespective of the mode of reagent

FIGURE 2.25

POWER CONSUMPTION V. CONDITIONING TIME FOR REAGENT ADDITIONS AS DROPLETS AND AS AN EMULSION.



addition, being around 97 and 82% respectively at point "F", 97 and 55% respectively at point "L", and 96 and 29% respectively at point "N".

2.5.11. Reagent mixtures other than tall oil-fuel oil.

In the following tests (Nos. 152-159) initial reagent additions around 1.1g/kg fatty acid/neutral oil were used, the fatty acid being tall oil (No. 152 and 154) or oleic acid (Nos. 153, 155, and 156-159), and the neutral oil being fuel oil (Nos. 152-155), kerosene (Nos. 156-157) or iso-octane (Nos. 158-159). When using iso-octane the double proportion of neutral hydrocarbon was used because of its high volatility.

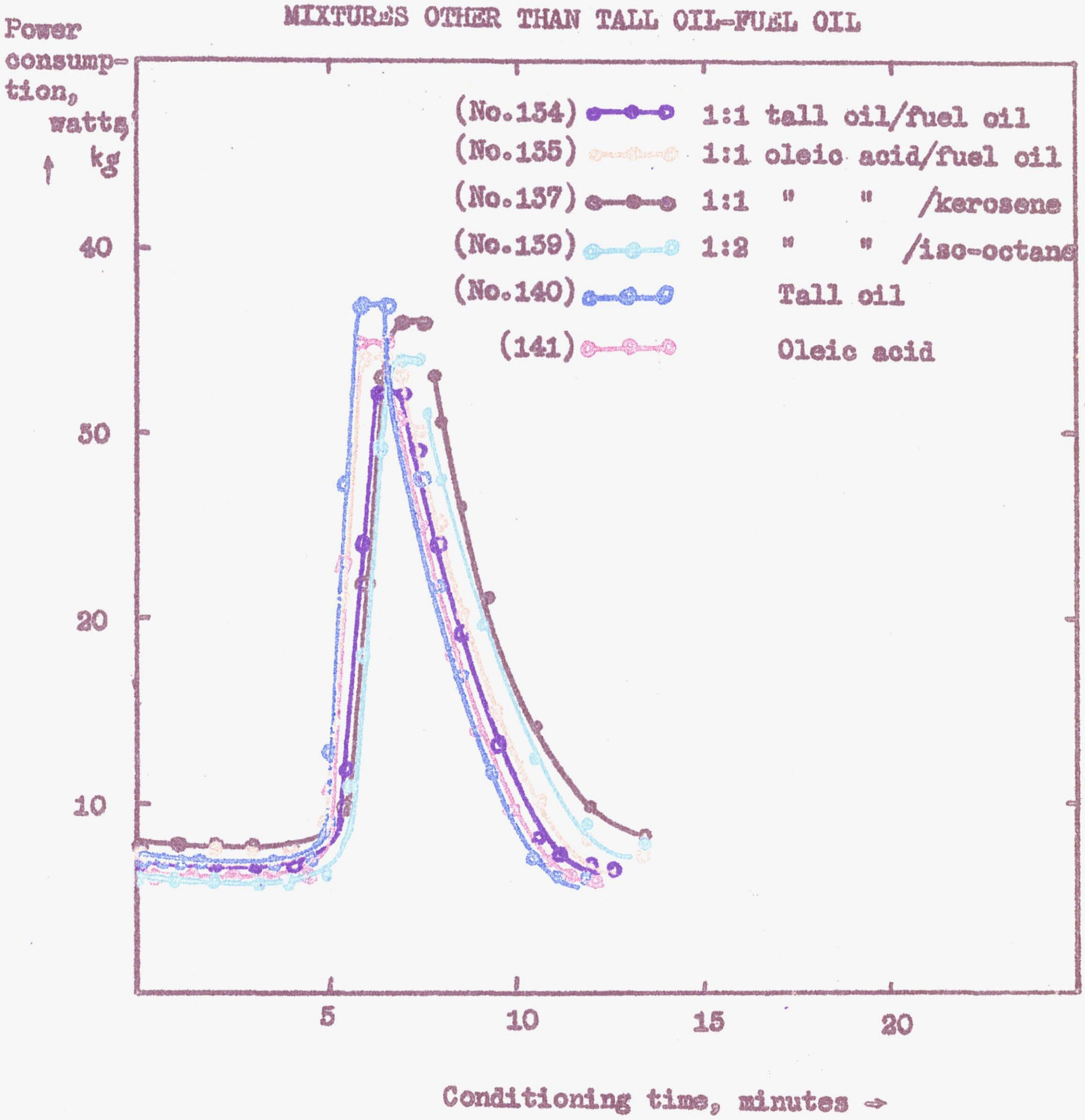
Virtually the same power consumption curves were obtained in all these tests as shown in fig. 2.24. The ilmenite and gangue recoveries at point "F" were in all cases around 96 and 82% respectively, and the reagent recoveries (iso-octane recovery could not be determined) were nearly 100%. The ilmenite and gangue recoveries at point "L" were in all cases about 95 and 55% respectively, and the reagent recoveries in the rougher concentrate were about 77%.

These results showed that oleic acid and tall oil were interchangeable as fatty acids, while fuel oil, kerosene and iso-octane were interchangeable as neutral hydrocarbons, when used as flotation reagents for ilmenite.

In two tests the rougher concentrates , obtained at the characteristic point "F" with equal tall oil/fuel oil and oleic acid/

FIGURE 2.24

POWER CONSUMPTION V. CONDITIONING TIME FOR REAGENT MIXTURES OTHER THAN TALL OIL-FUEL OIL



fuel oil mixtures (in tests Nos. 152 and 155) were reconditioned at pH 5.5 to the characteristic point "L". As a result the ilmenite and gangue recoveries were 85.5 and 25% with the tall oil (Test No. 152a) and 93 and 52% respectively with the fuel oil (No. 155a). This demonstrated that oleic acid gave better resistance to the depressive action of sulphuric acid, very likely because it does not contain resin acids.

In some paralle tests (Nos. 140-141) the tall oil or the oleic acid were applied as sole flotation reagents. It was necessary to add a greater amount of fatty acid in these tests, than that applied when fuel oil was added, in order to induce flocculation. The power consumption curves obtained at such high fatty acid additions of 1.5 g/kg were identical with those obtained in the tests described above, at an initial reagent addition of only 1.1 g/kg of the 1:1 fatty acid/fuel oil mixtures, as shown in fig. 2.24.

The ilmenite and gangue recoveries at the characteristic point "F" were around 98 and 80% respectively, when 1.5 g/kg tall oil (No. 140) or oleic acid (No. 141) was applied, in comparison with the same recoveries when the lower amount of the 1:1 fatty acid/fuel oil mixture was applied. The reagent recoveries were in both cases nearly 100%. Reconditioning of the rougher concentrates to the characteristic point "L" gave 97% ilmenite and 35% gangue recovery, which are in perfect agreement with the results obtained when reagent mixtures were applied.

It was concluded from these results that a fatty acid alone can be used for flotation conditioning of ilmenite but 40% more reagent is needed than that required in the case of the 1:1 fatty acid/fuel oil mixture.

2.3.12. Addition of ferric chloride.

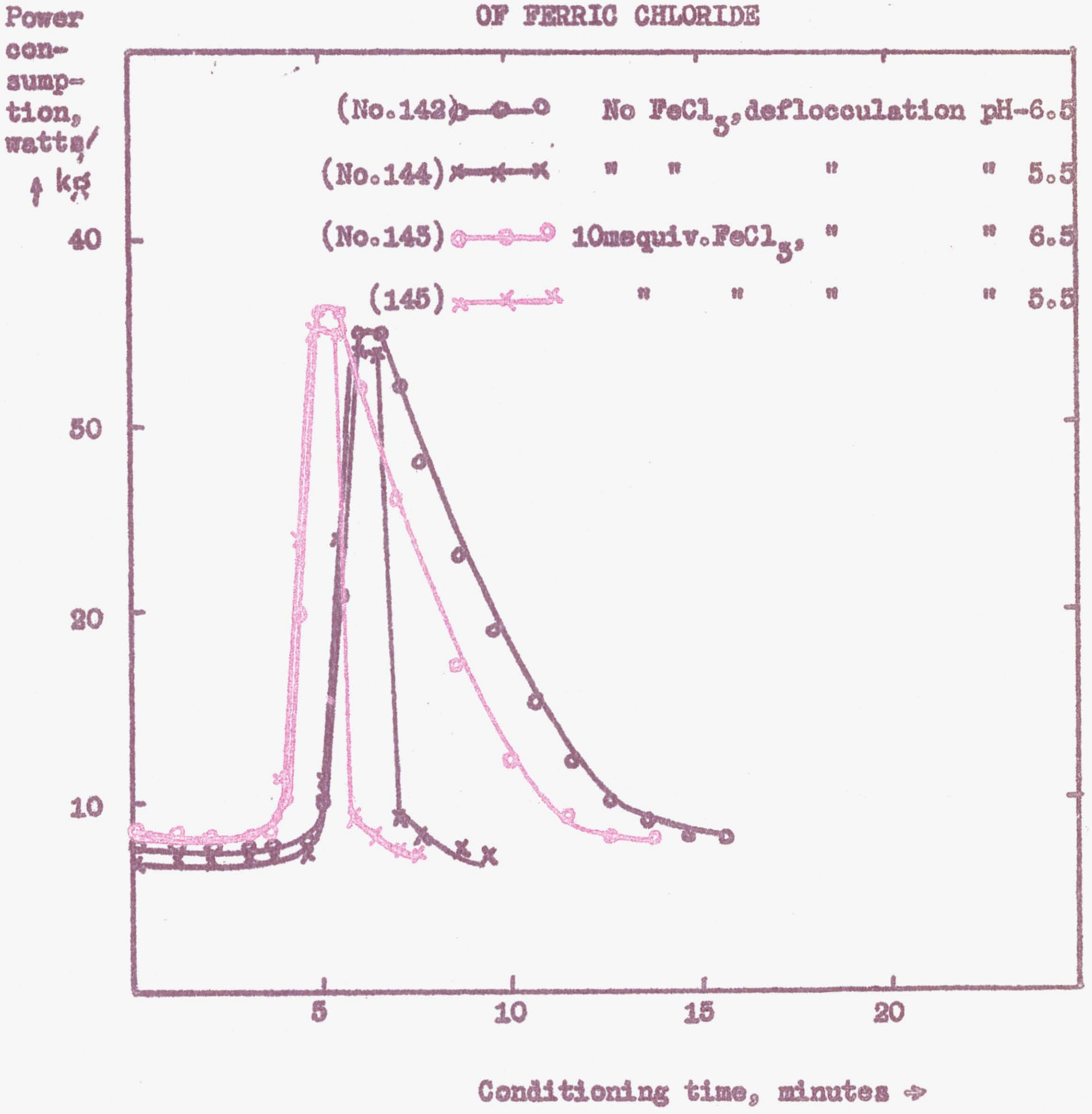
The addition of 2-10 mequiv. ferric chloride per kg solids to the conditioning tank, before or after the reagent addition (of 1.1 g/kg of the 1:1 tall oil/fuel oil mixture) did not affect the flocculation-deflocculation pattern, except for a small reduction in the time of the induction period. This was shown by a comparison of the power consumption curves for tests 142 and 143, where the pH was constant, and for tests Nos. 144 and 145, where sulphuric acid was added at the characteristic point "F" to reduce the pH to 5.5 (the curves are presented in fig. 2.25). No ferric chloride was added in tests Nos. 142 and 144.

The ilmenite and gangue recoveries at point "L" were the same in tests Nos 142-143, namely about 95 and 37% respectively. These recoveries were also the same at point "L" in tests 144-145, being 92.5 and 22% respectively. These similar results were obtained despite the fact that the initial pH of the pulp was reduced by the HCl formed on hydrolysis of the ferric chloride, and despite the fact that the fatty acid content was only 1.5 mequiv (1 mequiv. tall oil = 350 mg) as compared to 2-10 mequiv. ferric chloride.

The addition of 2-10 mequiv. ferric chloride per kg solids

FIGURE 2.25

POWER CONSUMPTION V. CONDITIONING TIME IN THE PRESENCE OF FERRIC CHLORIDE



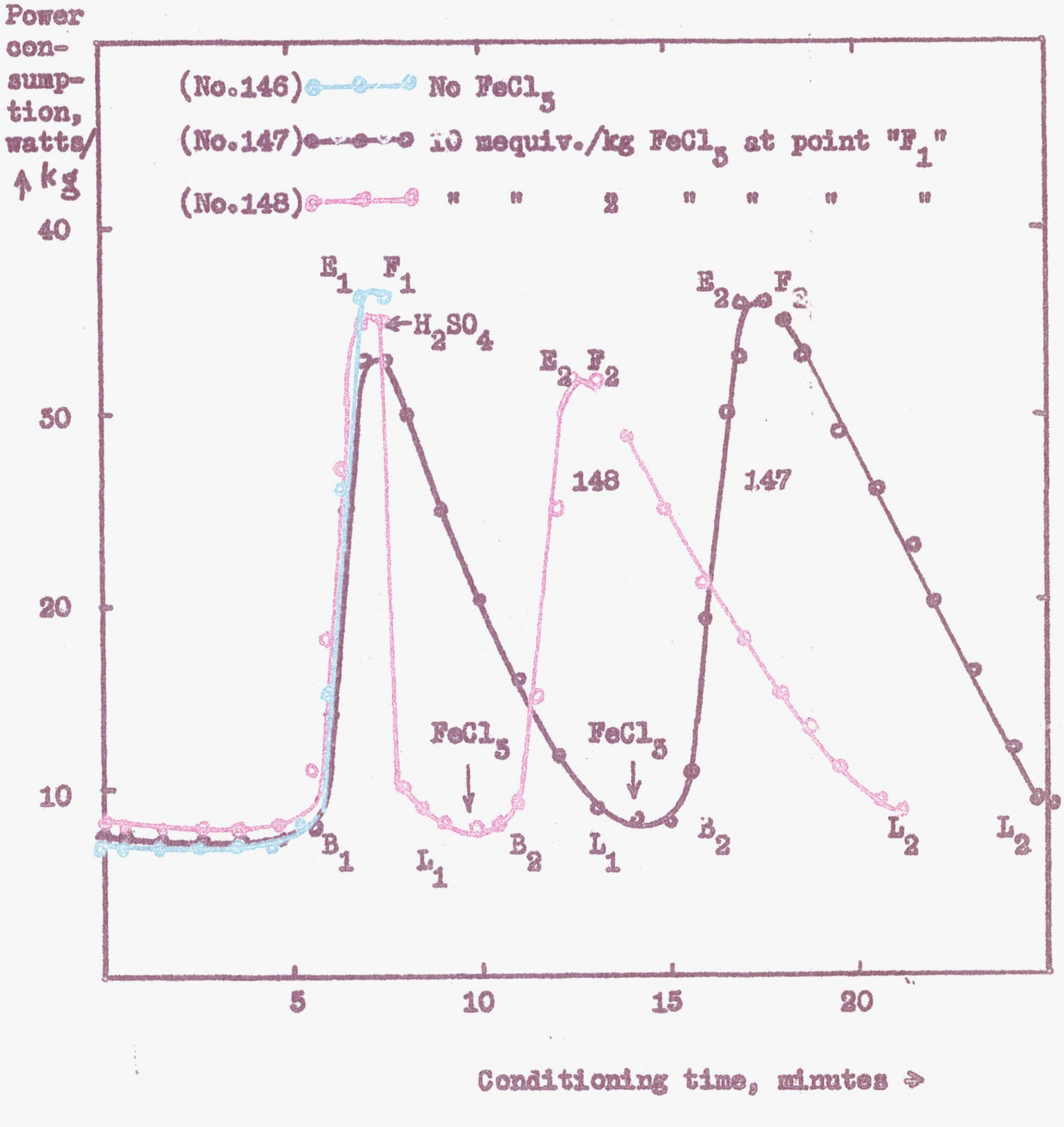
after the deflocculation period resulted in a reflocculation as shown by the power consumption curves for tests Nos. 147 (first deflocculation at pH 6.5) and 148 (first deflocculation at pH 5.5) in fig. 2.26. This phenomenon was similar to that observed when additional reagents were added at the same point "L", as shown in fig. 2.22 (section 2.3.9.).

The ilmenite and gangue recoveries in both these tests were 95 and 85% respectively at the characteristic point "F_3", being equal to the respective recoveries in test No. 146, at the same initial reagent addition of 1.1 g/kg of the reagent mixture, but at the characteristic point "F_1". The reagent recoveries were nearly 100% in all three tests. The rougher concentrates of these tests were reconditioned, resulting in the three tests in 95% ilmenite and 36% gangue recovery.

Similar effects were observed when oleic acid/fuel oil mixtures were used. It was therefore concluded that the Fe^{+++} ions strongly activated the mineral surface, so that the depressive action of the HCl set free could not take effect. This activation was strong enough to permit adsorption of the desorbed reagents, but could not prevent the normal desorption of the reagents during the deflocculation period.

FIGURE 2.26

POWER CONSUMPTION CURVES V. CONDITIONING TIME WHEN FERRIC CHLORIDE WAS ADDED AFTER THE DEFLOCCULATION.



2.4. DISCUSSION OF THE RESULTS.

The results presented in the preceding sections 2.5.1.-2.5.12 can be summarised as follows:

When ilmenite ore was conditioned with fatty acids, such as tall oil or oleic acid, and neutral oils, such as fuel oil or kerosene, at pulp densities of 70% solids, a bulk flocculation-deflocculation process was observed in the pulp (2.5.2.). This process took place when the impeller speed was sufficient to maintain satisfactory movement of the pulp (2.6.5.) and when the initial reagent addition exceeded a minimal limit which was related to the particle size distribution of the solids (2.5.8.).

This bulk flocculatio-deflocculation process could be studied by following the nett power consumption as a function of conditioning time for constant impeller speed or for constant agitation of the pulp, since the flocculation gave rise to an increased apparent viscosity (2.5.2.). The power consumption curve, obtained by the aid of a sensitive electrical test assembly, brought out five distinct periods in the conditioning process, namely - the "induction period", the "flocculation period", the "flocculation peak", the "deflocculation period", and the "dispersion period".

The effects of conditioning during these periods on the flotation results were as follows:

During the "induction period" no selectivity was observed and the quantities floated were small. During the "flocculation period" a gradual non-selective increase in the ilmenite and gangue recoveries took place, approaching a maximum at the "flocculation peak". In the "deflocculation period" the ilmenite recovery continued to increase while the gangue recovery decreased, so that at the end of this period maximum ilmenite recovery with maximum flotation selectivity was obtained, that is maximum grade of the rougher concentrate. The "dispersion period" that followed marked a gradual decrease in both the ilmenite and gangue recoveries.

These periods made it possible to assign characteristic points along the power consumption curve which revealed the following properties (2.3.2.):

The flotation results obtained at constant initial reagent addition at a given characteristic point (beyond the induction period) were the same, irrespective of impeller speed, impeller size, total nett energy input, and conditioning time required to reach the characteristic point. The flotation results obtained at a given characteristic point were, however, dependent on the reagent addition.

Thus, the ilmenite and gangue recoveries at a given characteristic point increased with increasing initial reagent addition. The ilmenite recovery was nearly 100% and the selectivity was a maximum at the end of the deflocculation period, when an initial reagent addition of 0.55g tall oil and 0.45g fuel oil per kg solids was used (2.3.4.). An increase in the tall oil addition above this optimal value resulted in increasing gangue recoveries, while an increase in the fuel oil addition did not affect the recoveries. Higher initial tall oil additions required longer conditioning time to reach a characteristic point in the dispersion period to give the same flotation results (2.3.5.).

The reagent concentrations in the rougher concentrate were roughly constant at constant initial reagent addition in the deflocculation and dispersion periods. A slight minimum was observed at the flocculation peak, followed by a small increase in the reagent concentration. This showed that some reagents were transferred from gangue particles to ilmenite particles (2.3.2.). The original tall oil/fuel oil ratio, which varied over the range 2:1 to 1:2, was always maintained by the reagents adsorbed on the rougher concentrates (2.3.4.). The reagent concentration in the tailings was negligible in all tests, and the reagents not accounted for in the flotation products were found as colloidal suspensions in the flotation liquor, in quantities proportional to the per cent weight of the tailings (2.3.1.).

The variation of the reagent concentrations in the rougher concentrate obtained at the end of the deflocculation period, in dependence of the initial reagent addition, showed a minimum at the optimal initial reagent addition mentioned above (2.3.3.). This minimum reagent concentration gave minimum average surface coverage effective for flotation.

The flotation results were not affected when the reagents were added separately, as a mixture (2.3.9.), as an emulsion (2.3.10.)

or even stage-wise during the induction period, flocculation period and flocculation peak (2.5.9.). When a portion of the reagents was added during or even at the end of the deflocculation period, the pulp re-flocculated. The flotation results in this case were determined by the total amount of reagents added and by the new characteristic point on the second flocculation-deflocculation cycle (2.5.9.). Such a re-flocculation was obtained by addition of fatty acid only, of fuel oil only or of a mixture of both.

A similar re-flocculation was obtained when 2-10 mequiv. ferric chloride was added during or at the end of the deflocculation period (2.5.12). Addition of ferric chloride before or during the flocculation period had no effect on the flotation results, in spite of the hydrochloric acid produced by hydrolysis and the low fatty acid addition of only 1.5 mequiv.

Tall oil and oleic acid were interchangeable as flotation reagents, and so were fuel oil, kerosene, and iso-octane (2.5.11.). Tall oil or oleic acid only were effective as flotation reagents, but the reagent consumption was greater than the sum of fatty acid plus neutral oil needed to obtain the same ilmenite and gangue recoveries. The dependence of the flotation results on the characteristic points of the power consumption curve was the same whether the flotation reagents were fatty acid alone or fatty acid/neutral oil mixtures.

Addition of sulphuric acid at the end of the flocculation peak accelerated deflocculation and caused a more efficient depression of the gangue (2.5.5.). Separate addition of the original slime fraction at the end of flocculation peak resulted in a similar acceleration of the deflocculation process (2.3.8.). In this case the reagents normally unaccounted for at the end of the deflocculation period reported now in the rougher concentrate which contained the ilmenite fines added. The assays showed that the reagent consumption of the fines was greater than that of the coarse particles. When non-deslimed feeds were conditioned at normal pulp densities of 70% solids, bulk flocculation did not occur. It could be induced, however, by increasing the pulp density from 70 to 73-75% solids.

The conditioning process could be interrupted once or several times by cleaner flotations at any point beyond the flocculation peak, and could then be continued on the rougher concentrate only, or on the combined concentrate and tailings, without affecting the final flotation results (2.5.6.). The final ilmenite and gangue recoveries were always a function of the final characteristic point, irrespective of the number of conditioning steps. The rougher concentrate could be refloated many times in the same flotation liquor without any observed effect on the ilmenite, gangue, or reagent recoveries (2.3.7.). Lowering of the pH during reflotation caused a depression of the gangue and of the ilmenite, which was however less selective than that obtained by lowering of the pH during conditioning.

The normal nett energy consumed up to the flocculation peak at intensive agitation of the pulp was 0.75 kWh/ton, and the nett energy consumed further until the end of the deflocculation period was 2.25 kWh/ton (2.3.2.). The latter could be minimised to a negligible value by accelerating the deflocculation, using either sulphuric acid or the originally removed fines (2.3.5. and 2.3.8.). The former value could be reduced by using the highest practical impeller speed and the highest practical pulp density. When the bulk flocculation-deflocculation process took place at slow agitation intensity, the energy consumed up to any particular characteristic point was greater than when intensive agitation was applied.

The correlation established between the ilmenite, gangue, and reagent recoveries and the pattern of the power consumption during conditioning, and the effects of the variables mentioned above on the conditioning and flotation results, permitted the postulation of the following mechanism for the successive sorption processes of the reagents during conditioning and flotation of ilmenite:

a. dispersion of the reagents in the pulp;

b. random adsorption by the different mineral species;

c. formation of a "quasi-continuous" reagent film on the surface of the particles;

d. rapid redistribution of the reagents in this film according to the specific adsorptive capacity of the mineral species;

e. break-up of this film by decreasing number of reagent coated particles;

f. desorption of the reagents from the gangue particles by attrition or by deliberate lowering of the pH;

g. similar desorption of the reagents from the ilmenite particles.

This mechanism implied that the conditioning process proceeded from a state of all particles being non-floatable through successive stages of all particles being floatable, of ilmenite particles being floatable and gangue particles non-floatable, to the final state of all particles being non-floatable, after prolongued conditioning.

The above mechanism was correlated with the power consumption curve, which reflected the degree of bulk flocculation (2.3.2.). It was therefore examined in detail according to the five characteristic sections of this curve, while interpreting the effects of the different factors on the conditioning and flotation results.

1. In the course of the "induction period" the reagents were dispersed in the pulp by shearing forces and were gradually captured by the particles through random collisions. This random sorption of the reagents was favoured by high pulp densities, high reagent contents, high impeller speeds, absence of fines, use of emulsions, and presence of activators such as Fe^{+++}, with the result that the duration of this period was reduced. The random sorption of the reagents was indicated by the absence of selectivity in the flotation results. The small number of particles coated with sufficient reagents during this period was proven by the very low ilmenite, gangue and reagent recoveries. The rougher concentrate in such cases contained only fines.

2. In the course of the "flocculation period" a progressively increasing number of particles was coated with the reagents

through further random collisions with oil droplets and with richly coated particles. The hydrophobic coated particles adhered to each other, and cohesive forces appeared in the pulp, as reflected in an increasing power consumption for maintaining the same impeller speed, and in increasing impeller speeds required for maintaining the same pulp agitation (as judged by observation of the vortex). The cohesive forces in the pulp increased obviously with the increasing number of reagent coated particles.

This random increase of reagent-coated particles was evidenced by the progressively and equally increasing ilmenite and gangue recoveries, and by the corresponding increase of the reagent recoveries in the rougher concentrate. The increasing ilmenite and gangue recoveries were directly proportional to the increasing power consumption during this period.

Since the particles were continuously moving as a result of the agitation, but the cohesive forces continued to increase, the reagent had been spread quickly on the surface of the reagent coated particles, so that the particles were at all instances "bound" by small oil "patches". The rapidity of the bulk flocculation process suggested that near its end the quickly spreading reagents had formed a "quasi-continuous" oil film over the surface of the mineral particles, thorugh the small oil patches which bridged the particles that were perpetually in contact with one another at any instant. This film is considered to be analogous to the continuous oil film in "water-in-oil" emulsions, in which the continuity of the oil phase is static, whereas in the present case, the continuity of the oil phase was a dynamic phenomenon, since the points of contact between the moving particles were constantly changing. The particular system formed was, in fact, analogous to a "water-in-oil" suspension, in which the mineral particles played the part of filler of the oil phase while the water was dispersed within the interstices formed by the adhering particles.

Thus, the stability of the system was dependent on the water content, the oil content, and the particle size distribution of the ground ore. This system occured therefore at sufficiently high pulp densities, which allowed the swirling particles under conditions of constant agitation to be in contact with each other at any instant, and at sufficient initial reagent addition, which allowed the coating of a great number of particles with the hydrophobic reagents. Indeed in the case when the reagent addition was low or when the proportion of water was too high the bulk flocculation, as reflected in an increased apparent viscosity, did not occur, and as a result the process of reagent transfer was considerably retarded since it proceeded through random collisions of particles, and not through a "quasi-continuous" oil phase.

The use of reagent emulsions accelerated the adsorption of the reagents on a large number of particles, but because of the small size of the oil droplets formed by chemical dispersion, the formation of the "quasi-continuous" oil phase proceeded at a slower rate, through coalescence of the tiny reagent patches on the surface of the particles. This was reflected by the disappearance of the "induction period" in the power consumption curve, and by the small slope of the prolongued "flocculation period".

3. At the "flocculation peak" the adsorption and random transfer of the entire initial reagent content had been completed, and the "quasi-continuous" oil film was fully formed. As a result bulk flocculation was at a maximum, and maximum power was therefore consumed by the pulp when the initial vortex was maintained. The quasi-continuous oil phase permitted very rapid redistribution of the reagents according to the specific adsorptive capacity of the diverse mineral species. As a result, reagents were transferred from the gangue to the ilmenite particles. These processes were evidenced by an increasing ilmenite recovery and by a maximum gangue recovery, as well as by a maximum or complete reagent recovery in the rougher concentrate.

Addition of reagents at this stage resulted in their immediate incorporation in the quasi-continuous oil phase, and their immediate distribution along the mineral surface, as evidenced by the reagent concentrations in the rougher concentrate samples, which were the same as if all the reagents were added before flocculation.

4. In the course of the "deflocculation period" the process of reagent redistribution was completed, resulting in richly coated ilmenite particles and poorly coated gangue particles. The attrition in the highly dense pulp scoured the reagents from the poorly coated gangue particles, on which they were now weakly held. The scoured reagents appeared very likely as colloidal metal soaps, which adhered to the mineral particles in the highly dense pulp of the conditioning tank. In the dilute pulp of the flotation cell, however, these colloids

were dispersed as a slow settling suspension, and were therefore not accounted for in the reagent assays of the tailings. The resulting depression of the particles was dependent on the initial reagent addition indicating that the particles coated with the least reagents were depressed first.

At the end of the "deflocculation period" the gangue recovery levelled off at a value related to the initial reagent addition, while the ilmenite recovery retained the maximal value, which was also related to the initial reagent addition. The reagent recoveries in the rougher concentrate were roughly proportional to the per cent weight of rougher concentrate. The concentration of the reagents in the rougher concentrate increased however by a small degree, because of the reagent transfer to the ilmenite particles at the beginning of this period.

As a result of the decreasing number of oil-coated particles, the viscosity reduced gradually and the quasi-continuous oil phases broke up (it should be noted that the volume ratio ilmenite/gangue in the ilmenite ore was about 1:2). The decreasing apparent viscosity and the diminishing bulk flocculation were of course reflected in the decreasing power consumption of the pulp. At the end of this period the original power consumption value was reached, and the "water-in-oil" system returned to the initial state of an "oil-in-water" dispersion, analogous to the break up of ta "water-in-oil" emulsion by coalescence of the oil film to small droplets. The transfer of the reagents from the gangue particles to the ilmenite particles, at the beginning of this period, was in fact very likely analogous to such a coalescence.

Addition of sulphuric acid at the start of the deflocculation period greatly accelerated the desorption process since the acid, which was immediately dispersed, was in direct contact with the entire mineral surface. As a result, the reagents were immediately desorbed from the poorly coated gangue particles, possibly in the form of the same metal soap colloids obtained by attrition at constant pH. The swiftly decreasing number of reagent coated particles was reflected in a swiftly decreasing power consumption during this period. The number of gangue particles depressed was a function of the amount of sulphuric acid added and also a function of the initial reagent addition which supports the suggestion of desorption from the poorly-coated particles first.

Addition of fines at the start of the deflocculation period resulted in a fast redistribution of the reagents on to the fresh - and extensive - ilmenite area, which caused immediate deflocculation, similar to that observed on addition of sulphuric acid. In this case, however, the reagents desorbed from the gangue particles were transferred to the ilmenite fines, so that almost all the initial reagent addition reported in the rougher concentrate at the end of the deflocculation period.

Addition of activators such as Fe^{+++} or of additional reagents during or at the end of the deflocculation period resulted in a re-flocculation, indicating the renewed formation of a "quasi-continuous" oil phase. This phase was formed in the first case by re-adsorption of the desorbed reagents (during this period) on to the freshly activated sites on the gangue particles, and in the second case by the adsorption of fresh reagent on the gangue particles. As a result of the newly formed "water-in-oil" system the entire reagent content of the pulp was readsorbed, and was redistributed after the flocculation peak was reached again, according to the specific adsorptive capacity of the mineral species. The flotation results were therefore a function of the new characteristic point on the power consumption curve, and of the total reagent addition, as if added before a normal bulk flocculation. The re-flocculation took place irrespective of whether the preceding deflocculation occured through attrition at constant pH or through lowering of the pH by sulphuric acid addition, indicating that the desorbed reagents were present in both cases in a similar form. It was established that the second flocculation-deflocculation cycle completely obliterated the previous conditioning "history".

5. In the course of the "dispersion period" further reagents were desorbed from the remaining reagent coated gangue particles as well as from the ilmenite particles through attrition in the highly dense pulp. This was revealed by progressively decreasing ilmenite recovery, and in some cases also gangue recovery. It was very likely that reagent desorption subsequent to the flocculation peak proceeded at a roughly constant rate, so that all particles approached gradually the threshold of minimum surface coverage, below which they were rendered non-floatable. This was supported by the fact that increase of the impeller speed during this period accelerated the depression of ilmenite, as shown by the closeness of the characteristic points L-Q in the case of curve III (see table 2.1). The reagent recoveries

in the rougher concentrate continued to decrease in proportion to the decreasing per cent weight rougher concentrate, while the reagent concentration was nearly constant. The power consumption remained at a value equal to the original value at the start of conditioning, unless excessive amounts of sulphuric acid were added during deflocculation.

This postulated mechanism permitted interpretation of other observed phenomena, such as repeated reflotation and reconditioning. Repeated reflotations of a particular rougher concentrate was made possible by the fact that the reagents which had been adsorbed during conditioning at high pulp density were not desorbed at the low pulp density in the flotation cell, unless the pH was reduced. Reduction of the pH had the same desorptive effect as in the conditioning cell, but it was less selective and the acid consumption was greater because of the large volume of water.

The conditioning process could be continued after an intermediate flotation stage since the reagents adsorbed during the conditioning were not affected in the course of the flotation at low pulp density. Naturally this was the case when the initial conditioning had progressed at least to the flocculation peak, so that all the initial reagent addition had been adsorbed. Reconditioning of the rougher concentrate only rendered the acid desorption process more economical as a major part of the acid consuming gangue had been removed during flotation.

The role of fatty acid and fuel oil in the flotation of ilmenite can be understood when it is noted that the phenomena described above occured when using different fatty acid/neutral oil mixtures, and also in the absence of neutral oil, though in the latter case the necessary initial fatty acid addition was three times greater. It should also be noted that there was an optimal initial fatty acid addition giving best flotation results, and a minimumm neutral oil addition, which when exceeded did not affect the flotation results. There were the additional facts that the initial fatty acid/neutral oil ratio was always maintained in the rougher concentrate and that reflocculation could be induced by fuel oil only.

These findings can be explained by assuming that the fatty acid was adsorbed directly on to the mineral surface at the active sites, while the fuel oil was adsorbed on the non-polar ends of the fatty acid molecules, always at the original fatty acid/fuel oil ratio, and always accompanied the fatty acid in the course of reagent redistribution, adsorption, or desorption at the same ratio. The minimum proportion of fuel oil was needed to give either minimum surface coverage with a minimum amount of fatty acid or, alternately, to render the surface covered by the fatty acid completely hydrophobic. When an equal amount of fatty acid replaced this minimum proportion of fuel oil, it was attracted to the free active sites on the already sufficiently coated mineral particles, so that a much larger amount was needed to give sufficient surface coverage to the reagent-deficient particles, or alternately, more fatty acid was required to give the same degree of hydrophobicity as that of a smaller proportion of fuel oil, which is completely non-polar.

The complex flotation circuit of the Tellnes ilmenite (4) involving conditioning at 70% solids and at pH 6.5, followed by three reconditioning steps at the same pulp density and at the respective pH values 5.5, 4.5 and 3.5, can be explained when it is assumed that the first conditioning step corresponds to the "induction period", "flocculation period" and "flocculation peak". Indeed, practically all the ilmenite and a small part of the gangue were recovered during the rougher flotation stage in the industrial flotation circuit. The three subsequent reconditioning stages, at successively lowered pH values, before the three flotation cleaner stages, corresponded to three steps along the "deflocculation period", the gangue being gradually depressed, while the ilmenite was little affected.

The mechanism postulated and the phenomena described above were examined next in connection with conclusions reached in studies of similar metal oxide flotation conditioning processes with fatty acids and hydrocarbons.

Chi and Young, studying the kinetics of flotation conditioning of a hematite ore, using a fatty acid reagent (27), observed that the characteristic recovery v. conditioning time curves for iron oxide and silica showed a maximum recovery at roughly the same time point, followed by a decrease and a levelling off of the two recoveries at two different values; the values of these recoveries increased with collector concentration. These findings parallel the behaviour of the ilmenite ore as discussed earlier in this section.

Kun Li et al (5), studying flotation conditioning of iron ore with petroleum sulphonate and fuel oil, has observed that the process begins with all solids completely floatable and ends up with only iron ore particles floatable and silica particles non-floatable. They have also observed a decrease in the iron recovery with conditioning time at the high impeller speeds.

A mechanism involving reagent transfer from the silica particles to the iron particles was postulated to explain the decreasing silica recovery with conditioning time. Since no reagent assays were made, and since the iron ore recovery was constant, it was just as likely that the reagents were desorbed from the poorly coated silica particles by attrition, as is assumed in the present study. Indeed, the characteristic curves of iron ore and silica recovery v. conditioning time bore a remarkable resemblance to the corresponding curves in this study, in the "deflocculation period". This indicated that the adsorption of the reagents on the iron oxide and silica was practically instantaneous, so that the increase in recovery characteristic to the induction and flocculation periods was not oserved.

The suggestion that the decreasing iron ore recovery at high impeller speeds was due to degradation of iron ore particles and increasing surface area was, however, unlikely. The present study has shown that prolongued agitation of the pulp prior to reagent addition had no effect on the flotation results at all characteristic points, including the gradually decreasing ilmenite recovery during the dispersion period. It is, however, likely that the fines serving as carriers scavenge the already desorbed soap particles in the flotation liquor.

Collins and Moir (28) suggested in the discussion of Kun Li's paper that the collector was only physically adsorbed on the silica particles, therefore reacted with the various cations in the solution and was thus desorbed. This seemed unlikely since the present study suggested that the collector was present as metal soap particles on the gangue surface, through reaction of the collector with the cations adsorbed on the silica, which formed the actives sites. These soap particles were probably scoured from the gangue surface by attrition or by acid attack. Indeed, even the presence of 2-10 mequiv. ferric chloride did not prevent the adsorption of only 1.5 mequiv. fatty acid, and furthermore, accelerated it by formation of a great number of active sites on the gangue particles.

Runolinna et al (1), studying the agglomeration flotation of Otanmaki ilmenite ore, have suggested that the unselective flocculation of the ilmenite particles at the beginning of the conditioning process was caused by the adsorption of a hydrophobic film on to all solid/liquid interfaces. When conditioning continued for some time the film was supposedly removed from the silicate minerals by oil droplets which had a stronger adhesion to it than the silicates. The adhesion of the film to the ilmenite surface was considered strong enough to permit agglomeration of the ilmenite particles by the oil.

The results of the present study indicate that this postulated mechanism of selective flocculation of ilmenite particles was not a cause of the selective flotation, but rather an equal result of a common cause which was proper hydrophobic surface coverage. The flocculation of the ilmenite particles was in fact another manifestation of the conditioning pattern, which resulted either in non-selective or in selective flocculation and flotation. The increasing non-selective flocculation of the pulp followed by selective deflocculation which was observed in the present study was, in fact, a dynamic parallel to the static observation of non-selective flocculation followed by selective flocculation on increase of the conditioning time, which was observed by Runolinna et al. Obviously, the particles retaining sufficient reagents to float, flocculated under the static conditions of the tests described by these investigators (1).

The mechanism postulated for removal of the reagents from the silicate grains by a detergent action of the fuel oil droplets (1) was equally unlikely. The present study showed that desorption of reagents from the gangue particles, in the course of the "deflocculation period" occurred both in the presence and absence of fuel oil, kerosene or iso-octane. It also showed that desorption and depression of the gangue started only after all reagents had been adsorbed on the mineral particles.

The suggestion (1) that reconditioning between cleaner stages in the case of Tellnes ilmenite might be needed because of its weaker adhesion to the collector was unlikely. The present study showed that once conditioned to a certain characteristic point, the rougher concentrate could be refloated a great number of times, without loosing any of its reagents by "peeling off" through contact with the air bubbles in the flotation liquer.

The differences between the spreading coefficients of tall oil and of tall oil/fuel oil mixtures on ilmenite particles, and of fuel oil alone on tall oil coated particles, determined from measurements carried out under static conditions (1), were not responsible for the differences in flotation results under dynamic conditions. The flotation results were the same irrespective of the order of the reagent addition as long as the same characteristic point on the power consumption was reached. Indeed, the flocculation-deflocculation process occurred equally well in the presence as in the absence of the fuel oil. The high spreading coefficient of fuel oil on tall oil-coated particles explained, however, the very rapid re-flocculation obtained by addition of fuel oil at the end of the "deflocculation period".

It was mentioned in the course of the discussion of Runolinna's paper that agglomeration and flocculation were observed in other systems as well, such as cassiterite-wolframite and sulfide minerals, when oleic acid and neutral oils were used as reagents, thus implying that the phenomenon was perhaps a a more general occurence.

More detailed examinations of a different system were presented by Fahrenwald (24) and Gates (25). Fahrenwald described "emulsion flotation" of a manganese ore, with the necessary reagents being a primary activating agent and the emulsion consisting of a neutral oil, soap and a wetting agent. He suggested a mechanism very similar to that postulated in the present study. It was assumed that activators like Fe^{++} and Mn^{++} ions gave anchoring points to the polar groups of the soap used as collector, while the neutral petroleum oil which was added covered the particles with a water-repelling surface. The further suggestion, that the neutral oil itself may act as collector was shown to be unlikely in the case of the ilmenite ore. The present study showed that increase of the tall oil addition always increased ilmenite and gangue recovery, while increase of the fuel oil proportion, over a certain minimum, did not increase the recoveries.

Fahrenwald also found that the flotation results were highest at an optimum impeller speed and optimum conditioning time, indicating clearly that excessive conditioning had resulted in depression of the mineral, analogous to that occurring in the "dispersion period". The assumption of Fahrenwald that the flocculation was a result of conditioning and that flotation was a result of the flocculation, seems however, unlikely, since both flocculation and floatability were manifestations of the hydrophobicity of the mineral surfaces.

Gates has reached similar conclusions, using a mixture of tall oil soap skimmings, petroleum oil, and a petroleum sulphonate wetting agent, for "agglomeration flotation" of a similar manganese ore.

The similarity in the phenomena observed during flotation conditioning of different metal oxides with different organic acids as collectors in mixture with neutral hydrocarbons, suggests that the "power consumption curve" applied to cases where the pulp density permitted bulk flocculation, and the method for determination of organic acid and fuel oil content of flotation products were important tools for the elucidation of these phenomena. The lack of these tools has resulted in conclusions which seem to be incorrect, if an extrapolation of the present system to other systems already discussed is permissible. The accumulated evidence indicates that it is. It is therefore advisable to apply these tools to a re-examination of the other systems, especially since there seems to be a critical pulp density which permits flocculation to take place in the agitated pulps, giving rise to "quasi-continuous" oil phases in which rapid re-distribution of the reagents can occur.

2.5. SUMMARY AND CONCLUSIONS.

1. An analytical method has been developed for the determination of the fatty acid and fuel oil contents of ilmenite flotation products. It was necessary to sample the flotation products while moist in order to prevent reagent losses by drying of the unsaturated fatty acids or by evaporation of the fuel oil. The reagents were desorbed from the moist samples by means of a 5N sulphuric acid solution in 40% ethanol, and were extracted into pure iso-octane. The organic acids were saponified by N/50 NaOH in 40% ethanol, and the accompanying H_2S from the mineral samples was removed by agitation of the acidified solution (pH = 5.5). The organic acid content was then determined by titration with N/10-N/50 NaOH solution, after adding further ethanol to 60%, using tetra-iodo-

phenol-sulphone-phthalein as indicator for the end-point of mineral acid (pH 4.8-5.2) and diphenol-purple as indicator for the end-point of weak acids (pH 9.2-9.6). The fuel oil was determined in the saponified iso-octane extract by optical density measurements at 224mμ. The method was accurate and reproducible within ±2.5%, and was applicable to quantities as low as 1mg fatty acid or fuel oil per 20g flotation product, that is 0.05 g/kg.

2. An electrical test assembly was designed for control of the conditioning process and for accurate determination of the power consumption during the conditioning of ilmenite ore with fatty acid and fuel oil. It comprised a 0.04 h.p., d.c. shunt wound motor with separate excitation, a control unit containing sensitive current and voltage meters, and a constant d.c. power supply. This test assembly permitted maintenance of constant impeller speed or approximately constant pulp agitation during conditioning, by variation of the voltage across the armature coil of the motor. The sensitivity of the measuring and controlling unit was ±0.1 watt nett power consumption. When no reagents were added the impeller speed remained constant for long periods. This was made possible by the constant voltage across both the field and the armature coils.

3. Addition of the reagents to an agitated pulp caused little change in the power consumption during several minutes, termed the "induction period". The power consumption increased very rapidly from an initial value of about 8 watts to a maximum value of up to 55 watts in the following 1-3 minutes, termed the "flocculation

period" , as a result of an appreciable bulk flocculation of the pulp. The value of the power consumption at the "flocculation peak" was dependent on the impeller speed. The power consumption decreased in the following 8-9 minutes, termed the "deflocculation period", as a result of a bulk deflocculation. At the end of this period the initial power consumption value was regained, and was constant on further conditioning during the "dispersion period".

4. This pattern of the power consumption v. conditioning time was examined in relation to the flotation results and to the reagent contents of the flotation products. These factors were found to be closely related and made it possible to postulate a mechanism to explain the adsorption-desorption phenomena taking place during conditioning and flotation:

a. The reagents were first dispersed in the pulp and adsorbed on a small number of particles of both ilmenite and gangue during the "induction period".

b. The reagents were rapidly distributed at random over a greater number of particles during the "flocculation period" resulting in the formation of a "quasi-continuous" oil film along the mineral surface, analogous to the oil film in "water-in-oil" emulsions; as a result of the cohesive forces between the reagent coated particles the power consumption of the pulp increased rapidly.

c. The reagents were rapidly transferred from gangue particles to ilmenite particles when this "quasi-continuous" oil film was complete, all the reagents having been adsorbed and distributed on a maximum number of particles at the "flocculation peak", which were thus rendered floatable.

d. As a result of the now poorly coated gangue particles the cohesive forces decreased, and the power consumption decreased during the "deflocculation period", while the reagents were desorbed from these particles so that at the end of this period all the ilmenite and only a small proportion of the gangue were floatable.

e. The reagents were further desorbed from the ilmenite particles as well during the "dispersion period" resulting in decreasing selectivity.

5. The flotation results were always the same at a given characteristic point on the power consumption curve at which conditioning was stopped, irrespective of the energy input, impeller speed or conditioning time required to reach this point. The flotation results at any given point on the power consumption curve were, however, functions of the initial reagent additions in the pulp. The optimum initial reagent addition giving nearly 100% ilmenite recovery at maximum flotation selectivity was 0.55 g tall oil and 0.45g fuel oil per kg solids. Any increase in the fuel oil addition did not improve the recoveries, while any increase in the tall oil addition increased the gangue recovery.

The original tall oil/fuel oil ratio was always maintained in the rougher concentrate. When fatty acids alone were used as flotation reagents the reagent consumption was 1.4g/kg as compared to 1.0 g/kg of the fatty acid/fuel oil mixture. This showed that the fatty acid was the actual collector while fuel oil was needed at a minimum proportion to render the surface completely hydrophobic and was therefore only a promoter. Oleic acid and tall oil were interchangeable as collectors, while fuel oil and light hydrocarbons, such as kerosene or iso-octane, were interchangeable as promoters for surface hydrophobicity.

6. Repeated reflotations did not affect the flotation results as no further reagents were desorbed at the low pulp density. When the rougher concentrate was reconditioned at high pulp density the process of reagent desorption proceeded as in the presence of the gangue, and the flotation results were again a function of the final point on the power consumption curve.

7. The adsorption of the reagents could be accelerated by high impeller speeds and high pulp densities, so that the induction period in particular and the flocculation period were shortened. The desorption of the reagents could be accelerated by addition of sulphuric acid or fines just beyond the flocculation peak, so that the deflocculation period was shortened from 9 to 1 minute. The desorbed reagents did not report in the flotation products but were found as a colloidal suspension in the flotation liquor. When fines were used to accelerate the deflocculation the desorbed reagents were adsorbed by the ilmenite fines added. The desorbed reagents in the conditioning tank could be re-adsorbed and redistributed on the solids when reagents or activators such as ferric chloride were added at the end of the deflocculation period. The new flocculation-deflocculation cycle was equivalent to the first

cycle from the view point of the flotation results.

8. The nett energy input required to reach a given point on the power consumption curve decreased with increasing impeller speed. The optimal values required to reach the flocculation peak and the end of the deflocculation period, at normal reagent adsorption-desorption at constant pH of 6.5, were 0.75 kWh/ton and 5 kWh/ton respectively. These values could be reduced by accelerating the reagent adsorption process and by eliminating the lengthy deflocculation period through addition of sulphuric acid or fines, as mentioned above.

9. It was concluded that the correlation of the flotation results with the pattern of the power consumption curve and with the reagent contents of the flotation products revealed the adsorption--desorption phenomena of fatty acids and neutral hydrocarbons on ilmenite. The same correlations may be applicable to other systems of metal oxides floated with similar reagents (and possibly to all systems where flocculation was observed) as somewhat analogous results were reported in the literature but were not supported by sufficient evidence.

The possibility of establishing a power consumption curve for different systems by means of a relatively simple and cheap electrical test assembly has the following advantages:

a. determination of the optimal pulp density for bulk flocculation - and hence formation of the "quasi-continuous" oil phase - to occur,

b. determination of the optimal initial reagent addition from the flotation results at the flocculation peak and at the end of the deflocculation period,

c. determination of the optimal energy consumption, and

d. determination of the effects of various activators and depressants on the reagent adsorption-desorption, and of the point of their optimal application to the pulps being conditioned.

Since the adsorption-desorption kinetics of flotation reagents on different mineral species can be determined by application of these methods, the use of analogue computers (27) would become practical for the design of conditioning equipment.

2.6. APPENDIX. (PART II)

2.6.1. Characteristics of the d.c. motor. (25,26,29)

The current passing through the armature of the d.c. motor, when its field coils are excited, establishes a torque as a result of which action the armature rotates. Rotation of the armature induces an e.m.f. which, according to Lenz's law, opposes the flow of current, and is referred to as the back e.m.f.

The power consumed by the armature of such a motor is represented by

$$(1) \qquad V_a \cdot I_a = E \cdot I_a + I_a^2 \cdot R_a$$

where: V_a = the voltage applied across the armature, E - the back e.m.f., I_a - the armature current, and R_a - the ohmic resistance of the armature. In equation (1) the product $I_a^2 \cdot R_a$ represents the power lost in the resistance and the product $E \cdot I_a$ represents the power available for performing mechanical work, including that lost by friction at the bearings and brushes, and by hysteresis and circulating eddy currents within the iron core.

Division of equation (1) by I_a gives

$$(2) \qquad V_a = E + I_a \cdot R_a \quad \text{or} \quad E = V_a - I_a R_a$$

The back e.m.f. can also be determined from ordinary considerations of flux, number of conductors, and speed by the relation

$$(5) \qquad E = 2 \cdot \frac{Z}{c} \cdot \frac{Np}{60} \cdot \phi \cdot V_a$$

where: ϕ - the total flux per pole in webers, p - the number of pairs of poles, N - the speed in r.p.m., Z - the total number of armature conductors, and c - the number of parallel paths through winding between positive and negative brushes.

Combination of equations (2) and (3) results in

$$(4) \qquad N = \frac{c.60}{Z.2p\phi}.(V_a - I_a R_a)$$

For any given motor Z, c, and p, are fixed and thus

$$(5) \qquad \frac{2Zp}{60c} = k$$

When (5) is introduced in (4) the simplified relation

$$(6) \qquad N = \frac{V_a - I_a R_a}{k\phi}$$

resulted. As the value of $I_a R_a$ is usually less than 5% of V_a, the speed of a given d.c. motor may well be assumed to vary in direct proportion to the applied voltage and in inverse proportion to the field strength.

The mechanical power developed by a motor - EI_a - is a function of the torque T (lb/ft) exerted on the armature, according to the relation

$$(7) \qquad EI_a = \frac{2\pi NT}{33000}\ \text{h.p.} = \frac{2\pi NT.746}{33000}\ \text{watts}$$

Combination of (7), (6) and (2) results in

$$(8) \qquad T = 33000\ k\phi I_a$$

showing that the torque of a given d.c. motor is proportional to the product of the flux per pole and the armature current.

2.6.2. Characteristics of the d.c. shunt wound motor.

Relations (6) and (8) show that both the impeller speed and the torque developed can be kept constant by keeping ϕ and V_a (and hence I_a) constant. Constant ϕ is obtained by applying a constant voltage across the field resistance. Relation (8) shows that maximum torque is developed when this voltage is kept at a maximum value.

As a result of keeping ϕ constant, both N and T can be kept constant or can be varied in proportion to the variation of the voltage across the armature. At constant ϕ the mechanical losses mentioned before were constant, and were proportional to N, and hence to V_a or I_a. The electrical and magnetic losses were proportional to I_a or I_a^2. All these losses can be calibrated by determining the power consumption when no load was applied ($V'_a I'_a$) as a function of the impeller speed N. The nett power available at any particular speed can then be determined by subtracting this value from the power consumption in the armature circuit when a load was applied ($V''_a I''_a$). Both the idling and load power consumptions are first corrected by subtracting the respective ohmic losses in the armature ($I'^2_a R_a$ and $I''^2_a R_a$) at the two different current values. The difference in the armature resistance can be neglected. The power consumption in the field circuit is roughly the same at idling and under load ($V_f I_f$) and is cancelled by the subtraction

$$(9) \qquad (V_f I_f + V''_a I''_a - I''^2_a R_a) - (V_f I_f + V'_a I'_a - I'^2_a R_a)$$

which gives the nett power consumption, W_0.

2.6.5. Methods of excitation of the shunt wound motor.

The characteristics of the d.c. shunt wound motor presented above show that separate excitation is imperative when it is necessary to drive the load at various speeds, any one speed being maintained constant for a relatively long period, and when it is desired to keep the exciting current in the field circuit entirely independent of the load current in the armature.

There are two alternative methods for controlling the voltages across the two parts of the motor circuit: by connection in series to or potentiometrically across the two coils. The flux variation can be controlled by a variable resistance termed a field regulator, and the armature voltage variation may be attained by means of a variable resistance termed a controller.

The main advantage of the potentiometric connection of the field regulator is that the field circuit of the motor is never actually opened whilst carrying current and that quite low values of exciting currents are available without the need of a relatively high value for the resistance. In the case under consideration the latter is of little value since the flux must be kept at the highest possible level. The main advantage of the connection in series is economy in power consumption, whilst a suitable sequence of switching (field on first, armature on second, and armature off first, field off last) prevents effectively the opening of the field circuit when current is carried by the motor. The latter method was adopted for the design of the test assembly.

Series connection of the controller to the armature circuit is not desirable as it reduces the speed of the motor with the load and as quite high resistances are necessary if very low speeds are desired. Potentiometric control is very convenient for obtaining reduced speed from small motors. Allthough the reduced voltage will

will vary somewhat with the load on the motor, the larger the current in the controller relative to that in the armature, the more constant will be the voltage across the armature. This evidently requires a low resistance in parallel to the armature. Potentiometric control of the armature circuit was adopted for the design of the test assembly circuit.

2.6.4. The test assembly and performance of the d.c. shunt wound motor.

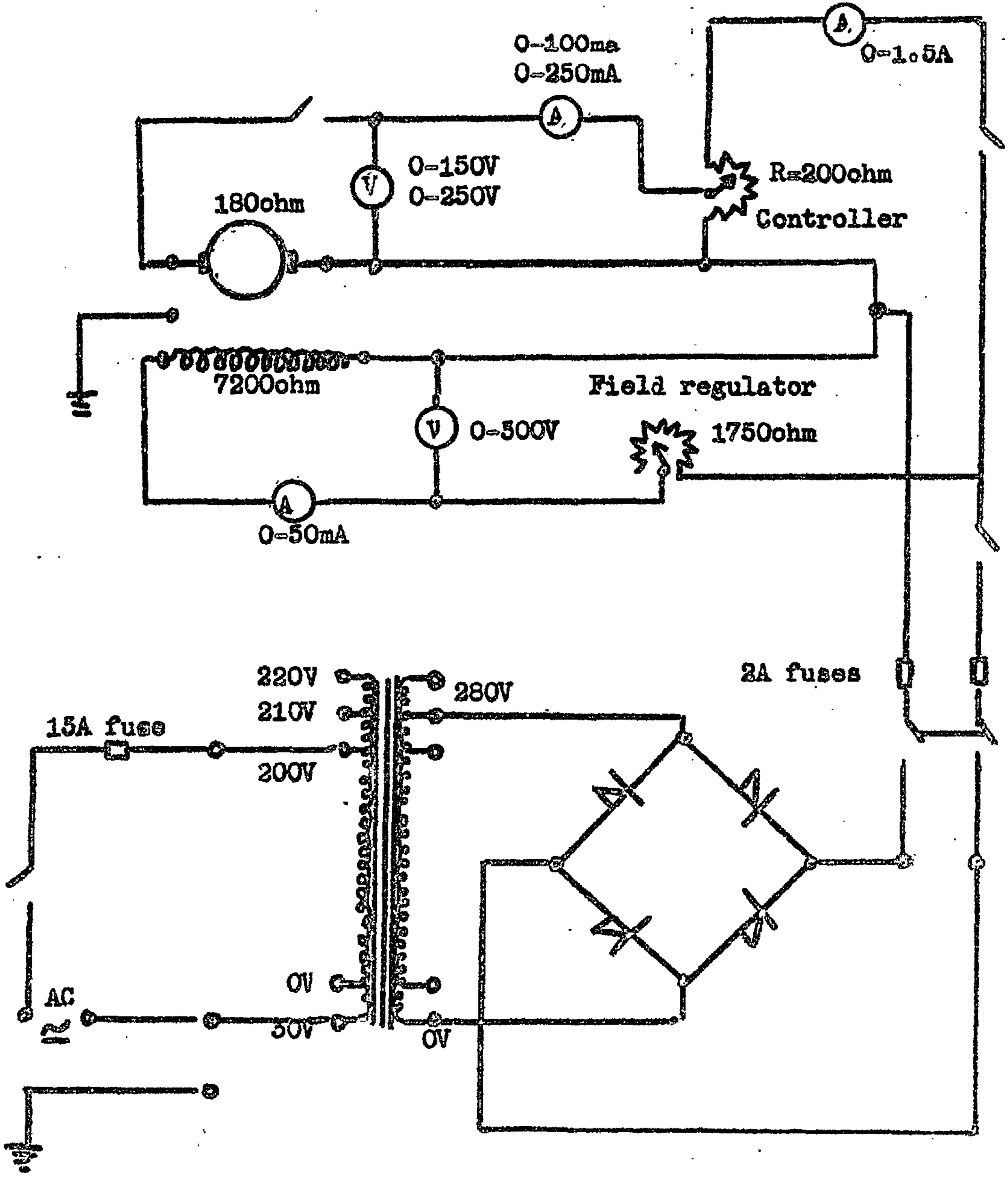
Preliminary experiments with a 0.25 h.p., d.c. motor have indicated that the nett power consumption of 1kg batches of ilmenite ore, -65#, at 70% solids, was about 10 watts in the conditioning tank used. The motor finally chosen on the basis of these preliminary tests was a Parvalux type SD1, 0.04 h.p., d.c. shunt wound motor, with a field resistance of 7200 ohm and an armature coil resistance of 180 ohm. A Westalite rectifier style DRT 288/2 with a d.c. output of 2.5A was used as a satisfactory constant d.c. power supply. Highly sensitive (10000 ohm/V) voltmeters and ammeters were used for the measurements.

The field coil of the motor was connected in series to a 1750 ohm field regulator, as shown in fig. 2.27, and the armature coil was connected potentiometrically across a 200 ohm controller (1.5A), as shown in the same figure. Under thermal equilibrium conditions in the circuit resistances, obtained after 30 minutes operation, the field regulator was reduced to minimum resistance so as to permit a maximum constant current of 0.033A through the field coil, which corresponded to a constant power loss of 8 watts.

FIGURE 2.27

ELECTRICAL CIRCUIT OF THE TEST ASSEMBLY

FOR THE CONDITIONING OF ILMENITE ORE.



Potentiometric control of the field coil was not necessary in this case, as a suitable "on" and "off" switching sequence prevented the actual opening of the field circuit while carrying current. Potentiometric control of the armature was of great advantage as it permitted proportional variation of the voltage applied across the armature from 0 to 230V, the current in the 200 ohm controller being about 1A compared with 0.02-0.25A in the armature coil (see preceding section 2.6.3.).

The motor was run with no load at a series of speeds over the range 400-2800 r.p.m., by increasing or decreasing the voltage applied to the armature circuit. Fig. 2.28 shows that the speed of the motor was directly proportional to this voltage when no load was applied to the motor. This relation was obtained after 30 minutes from the start of the operation of the motor and 3-5 minutes after any change from one value of the voltage to another. These durations were necessary to permit thermal equilibrium of the resistances. Fig. 2.28 also shows that the current through the armature coil was also directly proportional to the voltage applied across it.

The idling power losses were determined by subtracting the ohmic losses from the total power consumed during idling in the armature coil. The values obtained at different speeds were plotted in fig. 2.29. The curve obtained satisfied the empirical formula

$$(10)\ w_0 = 0.51N^2 + 1.88N + 0.02$$

where: w_0 - the idling power losses in watts, and N - the speed in 10^3 r.p.m. The idling power losses were roughly constant at any given speed, and varied only slightly with the load applied. The nett power consumption at any given speed was obtained by subtracting the idling

FIGURE 2.28

MOTOR SPEED AND ARMATURE CURRENT AS FUNCTIONS OF THE VOLTAGE APPLIED ACROSS THE ARMATURE.

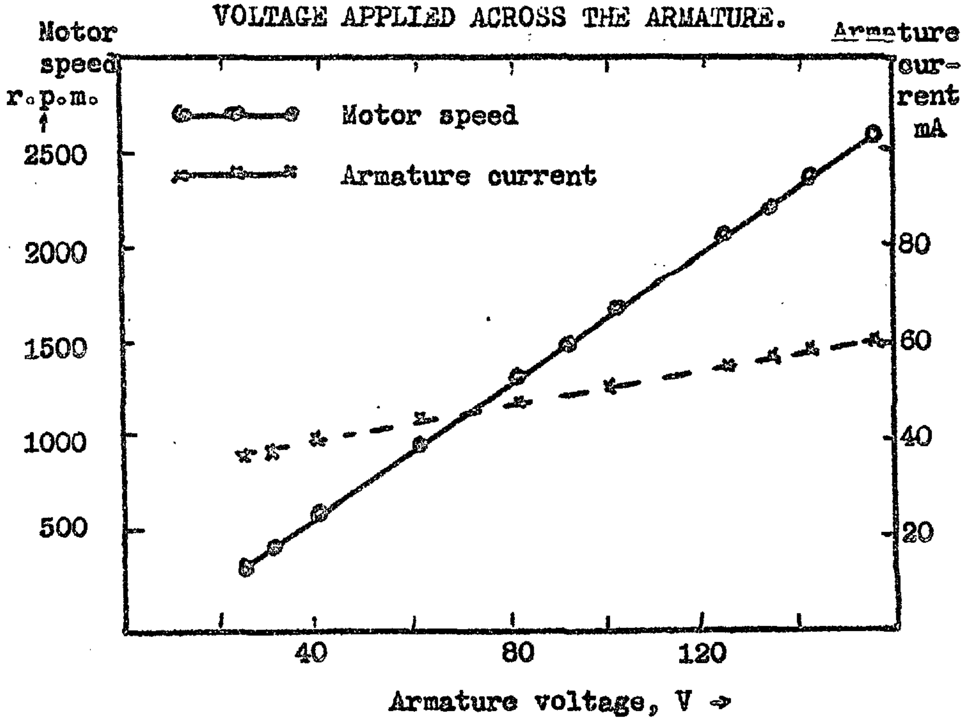
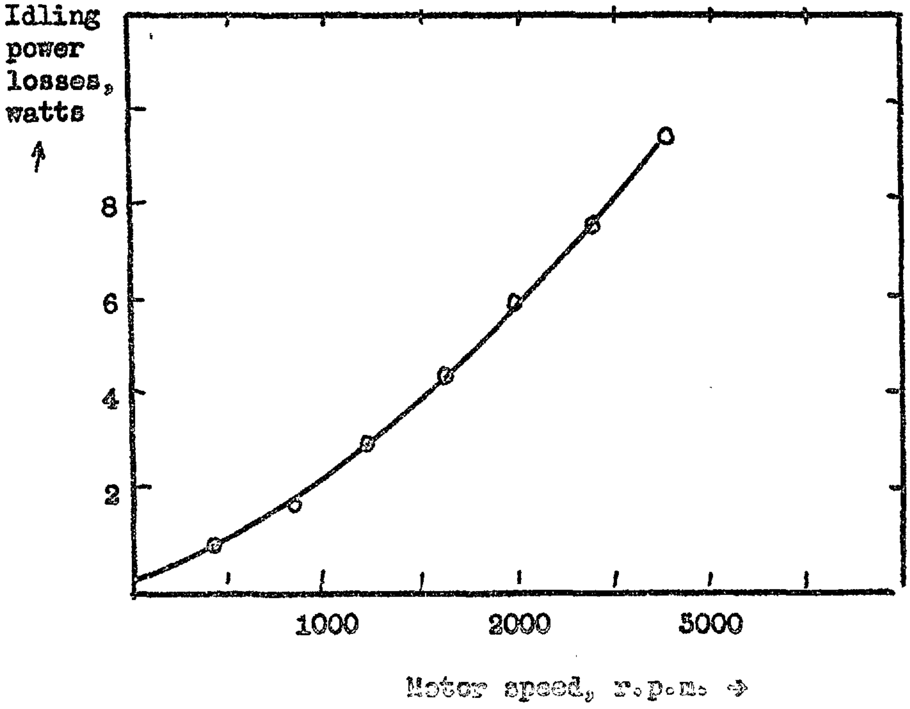


FIGURE 2.29

IDLING POWER LOSSES AS A FUNCTION OF THE MOTOR SPEED.



losses at this speed and the ohmic losses under the load from the gross power consumption in the armature coil (relation (9)).

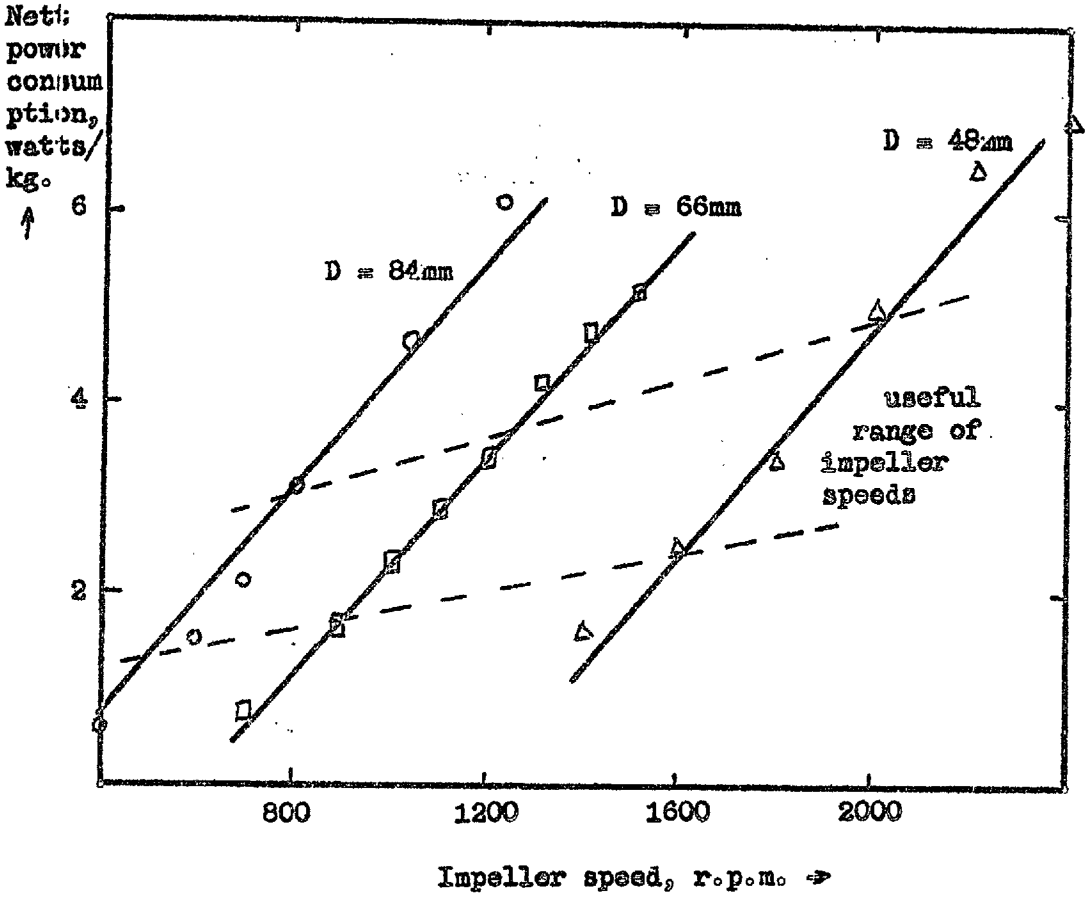
2.6.5. Parameters affecting the nett power consumption.

In these tests the load was a 1kg batch of crude ilmenite at 70% solids, contained in a 150.110mm diameter glass conditioning tank, and was applied to the motor by means of three-bladed propellors. Three propellors were used, with diameters 48, 66, and 84mm respectively, at an inclination of 20°, and with total blade areas of 4.5, 9, and 18 cm^2 respectively.

The values of the nett power consumption at different impeller sizes were presented in fig. 2.50 as a function of the impeller speed. Fig. 2.50 shows that the nett power consumption was proportional to the impeller speed, the proportionality factor being the same for all three impellers. In each case a lower speed limit was observed, at which the pulp was barely moving, and a top speed limit, at which the vortex descended too low, allowing air intake at the blade plane, with resulting strong fluctuations of both impeller speed and power consumption. These thresholds were shifted towards higher speeds as well as higher nett power consumptions when the impeller size decreased. The "iso-effectivity" curves, giving the same agitation of the pulp, were approximately straight lines. The extent of the range of useful speeds was therefore almost the same in all three cases. When temperature equilibrium was established, the speed and power consumption were constant and reproducible within ±2% for the same weight of ilmenite ore, at the same size distribution and at the same pulp density.

FIGURE 2.50

NETT POWER CONSUMPTION AT DIFFERENT IMPELLER SIZES AT 70% SOLIDS AS A FUNCTION OF THE IMPELLER SPEED.



In some of the tests the pulp density was varied over the range 67.5-77.5% solids, while using the large impeller. The nett power consumption values at the different pulp densities were plotted as a function of the impeller speed in fig. 2.31, and the same values at different impeller speeds are presented as a function of the pulp density in fig. 2.32. Fig. 2.31 shows that the proportionality factor between the nett power consumption and the impeller speed increased with increasing pulp density. Fig. 2.32 shows that the nett power consumption increased slowly at first with increasing pulp density up to about 70% solids. Above this value a point of inflection was observed at all speeds, and the nett power consumption increased very rapidly with increasing pulp density. These curves also show that the test assembly was sensitive to power consumption variations of ±0.1 watts at constant impeller speed. They also show that under normal conditions 70% solids was the optimal pulp density, since the nett power consumption at this value was still comparatively low.

In some of the tests the distance between the impeller blade plane and the tank bottom was varied from 10 to 60mm. This variation had no effect on the nett power consumption, so that the impeller was always kept as low as possible, in order to produce good agitation at even low speeds and in order to minimise air intake at the higher speeds.

In some of the tests a smaller conditioning tank (75mm diameter) was used for conditioning of 400g batches of ilmenite ore at 70% solids. The variation of nett power consumption with impeller speed, impeller size, and pulp density was the same as in the larger

FIGURE 2.31

NETT POWER CONSUMPTION AT DIFFERENT PULP DENSITIES AS A FUNCTION OF THE IMPELLER SPEED.

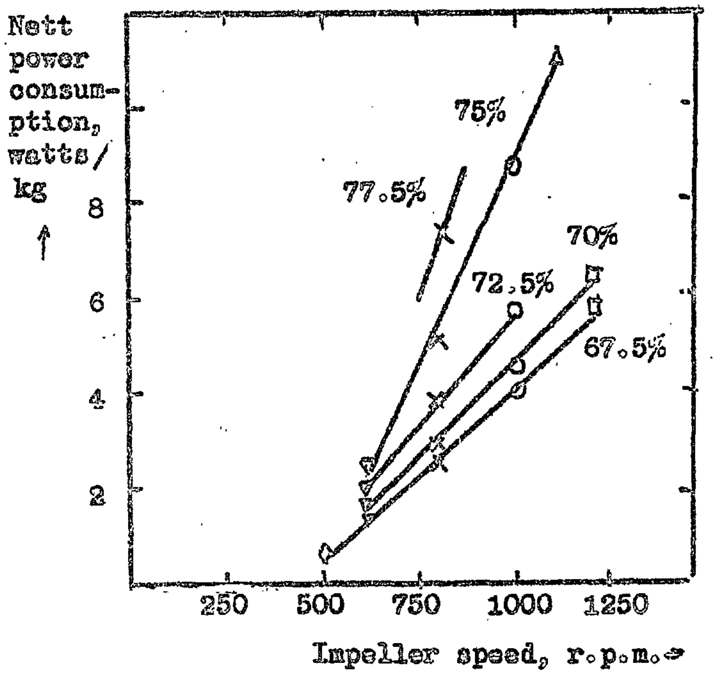
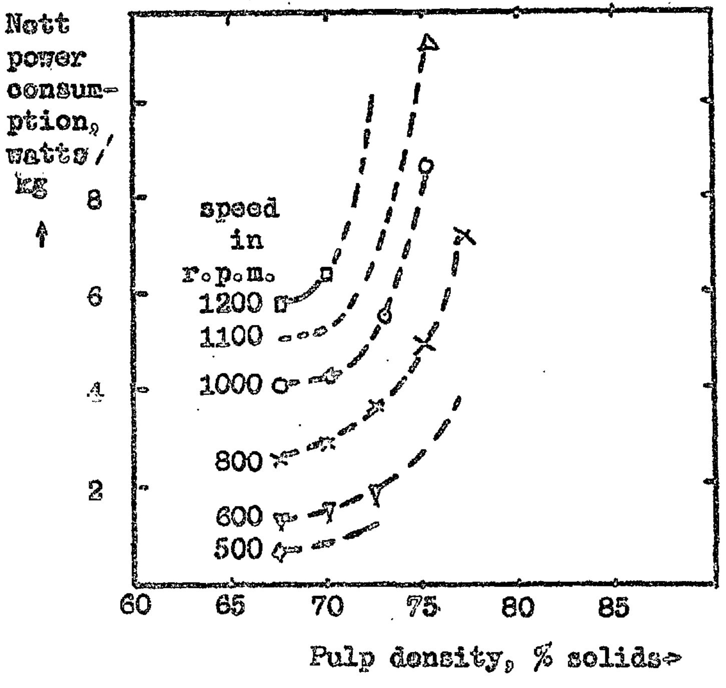


FIGURE 2.32

NETT POWER CONSUMPTION AT DIFFERENT IMPELLER SPEEDS AS A FUNCTION OF THE PULP DENSITY.



tank. The nett power consumption was approximately the same for each speed in both the large and small tanks, but owing to the smaller amount of material the specific nett power consumption per kg solids was 2.5 times greater in the smaller tank. This indicated that the resistance of the pulp to movement was practically the same in both cases and was due to geometrical factors.

The ratio between the nett power consumption and the gross power consumption in the armarture circuit was nearly 1:2 in all cases of impeller speed, impeller size, and pulp density.

This test assembly was employed in the conditioning of ilmenite ore with fatty acid and fuel oil as described in part II.

2.6.6. Experimental data of conditioning and flotation tests.

The experimental data obtained in the conditioning and flotation tests described in sections 2.5.1.-2.5.12. are presented in the following tables, using the consecutive test numbers for reference.

The following abbreviations were employed for convenience:

t.o. - tall oil,

f.o. - fuel oil,

r.c. - rougher concentrate,

f.a. - fatty acid,

n.o. - neutral oil.

TABLE 2.3

Variation of the initial reagent addition. Conditioning until the initial apparent viscosity was regained.

Test No.	Initial reagent addition, g/kg		% wt. r.c.	R.c. grade %	Recovery, %		Reagent recovery in r.c., %	
	t.o.	f.o.			ilmenite	gangue	t.o.	f.o.
1	0.87	0.87	85.5	50.5	98	76	91	93
2	0.82	0.82	82	52.5	97	72	88	87
3	0.76	0.76	78	54.5	96	65.5	82	83
4	0.68	0.68	70	61.5	97.5	48	78	75.5
5	0.615	0.615	66.5	65	98.5	41	74	70.5
6	0.58	0.58	65.5	67	94	40	69.5	72.5
7	0.52	0.52	62.5	68.5	94	38	70	68.5
8	0.49	0.49	57.5	66	83.5	36.5	66	62
9	0.48	0.48	48.5	58.6	65	35.5	57.5	55.5
10	0.47	0.47	38.5	56	49	30	49	47.5
11	0.46	0.46	32	52	37.5	27	43.5	44.5
12	0.44	0.44	27	48	29	25.5	41	41.5
13	0.38	0.38	15	46	17.5	15	38	36

Note: t.o. - tall oil, f.o. - fuel oil,

r.c. - rougher concentrate

TABLE 2.4

Power consumption (in watts/kg) v. conditioning time, when the impeller speed was increased during the period of high viscosity

Time min.	No. 14	No. 15	No. 16	No. 17	Time min.	No.17 continued
0	8.2	7.8	8.3	8.1		
1	8.1	7.8	8.5	8.1	19	8.7
2	8.1	7.5	8.1	8.0	20	8.4
3	7.9	7.3	7.9	7.8	22	8.1
4	7.8	7.5	7.8	7.6	24	7.8
5	7.8	7.5	7.8	7.5	26	7.9
5½	7.8	7.5	8.9	7.8	28	7.8
6	9.1	8.2	11.0	8.7	30	7.9
6½	11.2	9.5	25.0	10.0	40	7.9
7	17.0	13.1	55.0	15.0		
7½	26.0	20.2	57.5	21.8		
8	37.1	30.5	57.5	31.0		
8½	37.1	35.8	55.0	36.2		
9	36.2	35.8	50.0	36.2		
9½	35.4	30.6	26.5	32.5		
10	28.2	26.5	20.0	27.8		
10½	24.0	21.3	19.1	25.0		
11		19.5	17.5	20.0		
11½		16.0	15.2	16.7		
12			13.1	14.5		
12½			11.9	12.5		
13				11.9		
14				11.5		
15				9.4		
16				9.5		
17				9.1		
18				8.9		

TABLE 2.5

Power consumption (in watts/kg) v. conditioning time, when the impeller speed was kept constant at 1100 r.p.m. (Curve II)

Time min	No.28	No.27	No.26	No.25	No.24	No.23	No.22	No.21	No.20	No.19	No.18
0	7.8	7.8	7.7	7.9	8.0	7.9	7.5	7.8	7.7	7.8	7.7
2	7.1	7.8		7.8	7.9	7.8	7.5	7.6	7.7	7.6	7.5
4	6.7	7.2	7.5	7.5	7.8	7.6	7.2	7.5	7.7	7.5	7.4
5	6.5	7.2	7.5	7.5	7.8	7.4	7.2	7.3	7.7	7.5	
6.	6.8	7.3	7.7	7.5	7.8	7.4	7.2	7.3	7.7	7.5	
7	7.5	7.2	7.7	8.9	7.8	7.9	7.5	7.3	7.9		
7½	9.6	10.1	9.3	9.9	10.0	9.0	9.2	7.3	10.5		
8	12.0	13.2	11.9	13.5	13.5	11.5	12.3	8.5			
8½	13.4	14.1	13.5	14.0	14.2	12.6	13.5	12.4			
9	13.9	14.5	13.1	14.7	14.7	13.9	14.4	13.3			
9½	14.4	14.9	13.9	15.3	15.3	14.6	14.6	13.9			
10	14.9	15.1	14.1	15.6	15.3	15.5	14.8	14.4			
10½	14.9	15.1	14.5	15.6	15.3	15.3	14.8				
11	14.8	14.9	14.9	15.6	14.8	15.3	14.8				
11½	14.6	14.8	14.9	15.1	14.5	14.8					
12	14.4	14.7	14.9	14.9	14.2	14.3					
13	14.0	14.5	14.6	14.4	13.9	14.1					
14	13.2	13.8	14.0	13.6	13.6						
15	12.3	12.7	13.6	12.8	12.9						
16	11.3	11.5	12.5	11.5							
17	9.3	9.1	10.5	9.6							

continued on page 234

TABLE 2.6

Power consumption (in watts/kg) v. conditioning time, when the impeller speed was kept constant at 1400 r.p.m.(Curve III)

No.38	No.37	No.36	No.35	No.34	No.33	No.32	No.31	No.30	No.29	Time min.
8.5	8.6	7.9	8.6	8.5	8.7	8.4	8.2	8.6	8.5	0
8.1	8.4	7.9	8.4	8.1	8.4	8.3	8.0	8.6	8.5	2
7.9	8.4	7.9	8.3	8.1	8.7	8.2	8.0	8.6	8.3	3
7.8	8.9	7.9	8.2	8.1	8.7	8.2	7.9	8.6	8.3	3½
11.0	11.5	8.5	10.9	11.2	11.7	12.0	7.9	11.9		4
18.9	22.0	12.0	25.0	19.8	19.8	20.1	12.0	19.9		4½
23.1	25.0	17.9	24.1	23.5	24.3	24.9	20.1			5
23.0	25.0	22.2	24.1	23.5	24.3	24.9	24.4			5½
21.7	22.0	22.2	21.0	22.0	22.1	22.0	24.5			6
20.5	19.8	20.2	20.2	21.2	20.1	21.0	20.2			6½
20.0	18.9	19.5	19.3	20.5	19.2	20.1	19.1			7
19.1	18.4	18.7	18.9	20.0	18.3	19.2	18.4			7½
18.2	17.1	17.9	18.0	19.1	16.9	18.1	16.9			8
15.9	15.1	15.5	16.2	18.3	15.5	16.0	15.9			8½
14.4	14.1	13.8	15.3	15.8	14.9	15.0	14.9			9
13.0	12.9	12.8	14.3	14.6	13.8	13.5				9½
12.0	11.5	11.7	12.1	13.5	12.9	12.0				10
11.2	11.0	11.1	11.5	12.2	12.0	11.0				10½
10.9	10.7	10.3	10.9	11.3	11.2					11
9.9	9.5	9.5	10.0	9.5	9.9					12
9.2	9.0	8.9	9.5	8.9						13

(continued page 254)

TABLE 2.5 (continued)

Time min.	No.28	No.27	No.26	No.25
18	8.4	8.1	9.1	8.9
19	8.0	7.8	8.5	8.5
20	7.7	7.7	8.0	7.9
22	7.5	7.6	7.8	7.7
24	7.4	7.6	7.7	
26	7.3	7.6	7.7	
30	7.3	7.5	7.7	
35	7.2	7.5		
38	7.2			

TABLE 2.6 (continued)

Time min	No.38	No.37	No.36	No.35	No.34
14	9.0	8.9	8.5	8.9	8.7
16	8.5	8.8	8.2	8.6	8.5
18	8.1	8.8	8.0	8.6	
20	8.0	8.7	7.9		
22	7.9	8.7	7.9		
24	7.8	8.6			
28	7.8				
30	7.8				
32	7.8				

TABLE 2.7

Flotation results of ilmenite ore conditioned to different characteristic points on the power consumption curve type I when the impeller speed was increased during the period of increased viscosity (flocculation and deflocculation)

Test No.	Time min	Initial reagent addition, g/kg t.o.	f.o.	% wt. r.c.	R.c. grade	Recovery, % ilmenite	gangue	Reagent recovery in r.c., % t.o.	f.o.
14	10½	0.55	0.53	75.5	57	97	66	97	101
15	11½	0.54	0.54	72	56.5	96	55.5	97	98
16	12½	0.55	0.55	68	61.5	97	45	85	83
17	40	0.55	0.55	28.5	60.5	40	19.5	56	55.5

TABLE 2.8

Flotation results of ilmenite ore conditioned to different characteristic points on the power consumption curve type II when the impeller speed was kept constant at 1100 r.p.m.

Test No.	Time min.	Initial reagent addition, g/kg t.o.	Initial reagent addition, g/kg f.o.	% wt. r.c.	R.c. grade %	Recovery, % ilmenite	Recovery, % gangue	Reagent recovery in r.c., % t.o.	Reagent recovery in r.c., % f.c.
18	4	0.55	0.55	9	45	9.1	8.3	45	42
19	6	0.54	0.54	41	50.5	47.5	56	54	50
20	$7\frac{1}{2}$	0.55	0.55	65	49.5	69.5	58	78	80
21	10	0.54	0.54	85	48	89	82	99	97
22	11	0.54	0.54	84	49	91	81	101	99
23	13	0.55	0.55	79	53	93.5	67.5	102	97
24	15	0.54	0.54	74.5	59	97.5	56	98	95
25	22	0.55	0.55	57.5	70.5	92	29.5	76.5	72
26	30	0.54	0.54	50	75	81.5	25.5	65	63
27	35	0.54	0.54	45.5	67	71	25	58	60
28	38	0.54	0.54	42.5	70	66	22	55	57

TABLE 2.9

Flotation results of ilmenite ore conditioned to different characteristic points on the power consumption curve type III when the impeller speed was kept constant at 1400 r.p.m.

Test No.	Time min.	Initial reagent addition, g/kg		% wt. r.c.	R.c. grade %	Recovery, %		Reagent recovery in r.c., %	
		t.o.	f.o.			ilmenite	gangue	t.o.	f.o.
29	3½	0.545	0.545	44.5	49.5	50	40	60	58
30	4½	0.55	0.55	85	46	86	75.5	95	95
31	9	0.54	0.54	74	60.5	97.5	51.5	95	90
32	10½	0.55	0.55	66	65.5	87	41.5	81	82
33	12	0.55	0.55	62	64	96	55.5	79	78
34	16	0.54	0.54	57	70	91	28.5	71	71
35	18	0.54	0.54	51	75	84.5	24	65	64
36	22	0.55	0.55	47	75	81	22	60	58
37	24	0.55	0.55	44.5	72.5	75	21	56	56
38	32	0.55	0.55	28.6	62.5	59.5	19.5	57	56

TABLE 2.10

Flotation results of ilmenite conditioned to the characteristic point "L" on the power consumption curve type II at different initial reagent additions over the range 0.76-2.1g/kg (1:1)

Test No.	Initial reagent addition, g/kg		% wt. r.c.	R.c. grade %	Recovery, %		Reagent recovery in r.c., %	
	t.c.	f.c			ilmenite	gangue	t.c.	f.c
39	0.38	0.38	16	46	18.5	16	34	32
40	0.405	0.405	25.5	47	27	22	40	42
41	0.445	0.445	35.5	55	42	28	48	46
42	0.47	0.47	42	57	54	29	52	52
43	0.48	0.48	49	59	66	36	59	58
44	0.50	0.50	56.5	67	86	39	65	63
45	0.51	0.51	58.5	68	90	40	64.5	65
46	0.525	0.525	61.5	67.5	94	40	68	67
47	0.54	0.54	64	66	96	42	72	72
48	0.575	0.575	65	65	96	44	75	70
49	0.65	0.65	70	61	97	52	76	78
50	0.75	0.75	77	56	98	62	80	81
51	0.85	0.85	86	55	98.5	75	88	88
52	0.95	0.95	95	48	99	87	95	92
53	1.05	1.05	99.5	45	100	99	101	99

TABLE 2.11

Flotation results of ilmenite ore conditioned to the characteristic point "E" or "N" on the power consumption curve type II at different initial reagent addition over the range 0.9-2.4g/kg (1:1).

Test No.	Initial reagent addition, g/kg		% wt. r.c.	R.c. grade %	Recovery,%		Reagent recovery in r.c.,%	
	t.c.	f.c.			ilmenite	gangue	t.c.	f.c.
	Characteristic point "E"							
54	0.45	0.45	61.5	50	70	52	78	78
55	0.55	0.55	87.5	48.5	96	81	98	96
56	0.57	0.57	93	47	98	88	98	99
57	0.65	0.65	100	44	100	100	100	101
	Characteristic point "N"							
58	0.44	0.44	18.5	47	20	15	52.5	55
59	0.48	0.48	29	58	58	20	37.5	57.5
60	0.52	0.52	50.5	73	84	24	55.5	54.5
61	0.54	0.54	54.5	73	90	26.5	57.5	58
62	0.58	0.58	56	72.5	92	30	58	58
63	0.65	0.65	61	68	94	34	65.5	65.5
64	0.75	0.75	64.5	65	95	45	66.5	67.5
65	0.80	0.80	70	60.5	96	53	71.5	72
66	0.90	0.90	77	55	96.5	64	77.5	79
67	1.0	1.0	83.5	51	97	78	85.5	85.5
68	1.1	1.1	95	46	99	90	94	95
69	1.2	1.2	99.5	44	100	99	100	99

TABLE 2.12

Flotation results of ilmenite ore conditioned to point "L" at different tall oil additions and at different tall oil/fuel oil ratios.

Test No.	Initial reagent addition, g/kg		% wt. r.c.	R.c. grade %	Recovery, %		Reagent recovery in r.c., %	
	t.o.	f.o.			ilmenite	gangue	t.o.	f.o
70	0.55	0.25	37	58	49	24	48	50
71	0.55	0.35	52	61.5	79.5	28.5	64	62
72	0.55	0.45	65	62	97	36	77	75.5
73	0.55	0.55	64	62.5	96	35	75.5	75.5
74	0.55	0.65	63	63	95	34	75	76.5
75	0.55	0.75	64.5	62	96.5	36.5	74	77
76	0.55	0.85	64	63	95.5	34.5	76	74.5
77	0.55	0.95	65	64	97.5	35.5	75	75
78	0.55	1.05	63.5	63	96.5	35.5	76	75
79	0.45	0.25	19	55	25.5	10	30.5	35
80	0.45	0.35	27	57	36	15.5	39.5	42
81	0.45	0.45	36	58.5	49.5	20	47	45
82	0.45	0.55	37	58	48	22	49.5	48
83	0.45	0.65	36.5	58.5	48.5	21	50	50
84	0.45	0.85	37.5	57.5	49.5	21	52	48
85	0.65	0.25	43.5	56	59.5	30	54	55.5
86	0.65	0.35	62	61	85.5	35.5	76	76
87	0.65	0.45	70	62	99	42.5	77	79
88	0.65	0.55	71	61	97.5	45	77	79
89	0.65	0.65	69.5	62	98	43.5	80	77.5
90	0.65	0.85	70	61	97.5	44	78.5	76.5

Note: t.o. - tall oil, f.o. - fuel oil,

r.c. - rougher concentrate

TABLE 2.15

Flotation results of ilmenite ore conditioned to point "L" at different reagent additions, when the pH was lowered at point "F".

Test No.	H_2SO_4 m.equiv	pH	Initial reagent addition, g/kg		% wt. r.c.	R.c. grade %	Recovery, %		Reagent recovery in r.c., %	
			t.o.	f.o.			ilmenite	gangue	t.o.	f.o.
91	0	6.5	0.49	0.49	54	71.5	88	25	65	65
92	0	6.5	0.54	0.54	62	67.5	95	32	75	77
93	0	6.5	0.62	0.62	67.5	64	98	42	82	80
94	0	6.5	0.70	0.70	74.5	58.6	99	56	88	89.5
95	2	5.5	0.495	0.495	40	80.5	73	13	55	52
96	2	5.5	0.545	0.545	55	76.5	92	16	65	68
97	2	5.5	0.59	0.59	58	73	95	20	72	70
98	2	5.5	0.71	0.71	62	69	97	28	75.5	78
99	4	4.5	0.49	0.49	29	70	46	7	58	55
100	4	4.5	0.54	0.54	44	74	74	13	56	54
101	4	4.5	0.61	0.61	53.5	77	92.5	17	72	70
102	4	4.5	0.70	0.70	59	72	95.5	21	75	72
103	8	3.5	0.485	0.485	5	55	6	4	14	13
104	8	3.5	0.54	0.54	28	75.5	48	8	38	40
105	8	3.5	0.62	0.62	42	75	72	13	56	56
106	8	3.5	0.70	0.70	49	80	89	15	62	60
	Lowering of the pH at point "S"									
107	4	4.5	0.60	0.60	73.5	57	95.5	56	85	84

TABLE 2.14

Flotation results of the tests described in sections 2.3.6.-2.3.9.

(Repeated flotations, reconditioning, addition of fines)

Test No.	Initial reagent addition, g/kg		% wt. r.c.	R.c. grade %	Recovery, %		Reagent recovery in r.c., %	
	t.o.	f.o.			ilmenite	gangue	t.o.	f.o.
108	0.575	0.575	90.5	47.5	97.5	84.5	99.5	98
108a			65	65.5	96	40	74	72
109	0.56	0.56	65	64.5	95	41.5	73	75.5
110	0.54	0.54	61.5	67	94	35	71	73.5
111	0.56	0.56	62.5	65	95	37	74	72.5
111a			51.5	68	80	29	65	63
111b			35.4	69	55.5	19.5	48	46
112	1.4	2.0	63	67	95.5	37	75	74
113	0.55	0.55	61.5	70	96	35.5	75.5	75.5
114	1.4	1.4	62.5	70	97	36.5	77	75.5
115	1.0	1.0	61	69	95.5	35.5	99	97.5

Note: t.o. - tall oil, f.o. - fuel oil

r.c. - rougher concentrate

TABLE 2.15

Flotation results of the tests described in sections 2.3.9.-2.3.10.

(Stage-wise addition of the reagents and addition as an emulsion)

Test No.	Initial reagent addition, g/kg		% wt. r.c.	R.c. grade %	Recovery, %		Reagent recovery in r.c., %	
	t.o.	f.o.			ilmenite	gangue	t.o.	f.o.
116	0.555	0.555	62	67	96.5	34	74	76.5
117	0.55	0.55	62.5	68	97	33.5	77	77
118	0.56	0.56	61.5	69	97	34	75.5	76.5
119	0.54	0.54	60.5	69.5	95.5	34	75	73.5
120	0.61	0.61	66	65.5	98	41	84	82
121	0.615	0.915	91.5	47.5	97	87	100	99
122	0.60	0.90	67.5	64.5	98.5	42.5	83	84
123	0.61	0.91	66	65	97	41.5	81	83.5
124	0.61	0.91	93	46	97	89	101	98
125	0.6	0.6	67	68	98	41	82	84
126	0.56	0.56	89	48.5	97	81	99	101
127	0.565	0.565	61	70	96.5	36	74	76
128	0.555	0.555	59	71.5	95	28	71	73
129	0.555	0.555	90	49	98	82	100	98.5
130	0.57	0.57	63	68	97	35	75	75.5
131	0.56	0.56	58	73	96.5	29	71	72

Note: t.o. - tall oil, f.o. - fuel oil

r.c. - rougher concentrate

TABLE 2.16

Flotation results of the test described in section 2.3.11.

(reagent mixtures other than tall oil/fuel oil)

Test No.	Initial reagent addition, g/kg f.a.	Initial reagent addition, g/kg n.c.	% wt. r.c.	R.c. grade %	Recovery, % ilmenite	Recovery, % gangue	Reagent recovery in r.c., % f.a.	Reagent recovery in r.c., % n.c.
				tall oil - fuel oil				
132	0.545	0.545	90	47	96	82	97	99
132a			50	75.5	85.5	23	62	60.5
				oleic acid - fuel oil				
133	0.555	0.555	88.5	48	95	80	98	97
133a			57.5	71	92.5	32	70	68
				tall oil - fuel oil				
134	0.56	0.56	61	69.5	95	37.5	78	75
				oleic acid - fuel oil				
135	0.54	0.54	61.5	70	96.5	33	76	77.5
				oleic acid - kerosene				
136	0.55	0.55	91	47.5	96	85	99.5	
137	0.56	0.56	60.5	69.5	94.5	33.5	77.5	
				oleic acid - iso-octane				
138	0.56	1.12	92	48	97	84	101	
139	0.55	1.1	61.5	70.5	95.5	36	79	
				tall oil only				
140	1.55		89	49	98	81.5	100	
140a			62	69	96.5	35	75.5	
				oleic acid only				
141	1.56		87	50	97	79.5	99	
141a			62.5	69	97	36	76	

TABLE 2.17

Flotation results of the tests described in section 2.3.12.

(ferric chloride addition)

Test No.	Initial reagent addition, g/kg		% wt. r.c.	R.c. grade %	Recovery, %		Reagent recovery in r.c., %	
	t.o.	f.o.			ilmenite	gangue	t.o.	f.o.
142	0.56	0.56	61	70.5	95	37.5	74.5	76
143	0.55	0.55	61.5	69.5	95.5	36.5	76.5	77
144	0.54	0.54	51.5	79	95.5	22	68	68
145	0.55	0.55	50.5	78	91.5	23	65	67.5
146	0.555	0.555	92	47	96	84	99	96
146a			61.5	70	95	36	77	75.5
147	0.545	0.545	91	46	95	85	95	98
147a			60.5	69	94	35	74	76
148	0.55	0.55	91	47.5	95.5	84.5	98	99
148a			62	70.5	95	37	75	73.5

Note: tao. - tall oil, f.o. - fuel oil,

r.c. - rougher concentrate

Note to table 2.16:

f.a. - fatty acid, n.o. - neutral oil

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