A STUDY OF THE SIMULTANEOUS LEACHING AND SOLVENT EXTRACTION OF COPPER FROM MALACHITE.

A thesis submitted for the degree of
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by

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CONTENTS.

ABSTRACT

1.

A process is suggested whereby a non-sulphide ore or low-grade concentrate is leached with a small amount of an aqueous acid, and the valuable constituents extracted into an organic solvent which is simultaneously contacted with the wetted solid. The objects of the investigation were to determine the rate-controlling stage, to produce an optimum set of conditions for the operation of the process on a large scale, and to obtain an estimate of the solvent loss occurring in the process.

Using statistical methods, the extraction of copper by this process from a synthetic malachite ore (1% copper by weight) was studied in detail, using leaching solutions of 10^{-3} and 10^{-5}M sulphuric acid and 0.1-1.7M solutions of naphthenic acid in paraffin as the organic solvent. Utilizing the results of this investigation it was found that it would take 2.1/2 weeks to leach 100 tons of ore initially containing 5% copper by weight, and the solvent loss would be 1.5 tons of solvent per ton of copper extracted.

The rate of extraction was found to be controlled by the transfer of copper and acid across the aqueous-organic interface. The malachite was found to contain a considerable quantity of chrysocolla, present as find grains, which caused the rate of extraction to be severely reduced when the malachite had been exhausted. The selectivity of the process for copper over calcium was investigated and found to be low.

The investigation showed that the process, in the form studied, was too slow and unselective to be considered as an alternative to the existing processes for the chemical treatment of non-sulphide ores, and the excessive loss of the organic solvent would have to be drastically reduced to make the process economic.

2. INTRODUCTION

2.1 General Description of Project.

The chemical treatment and concentration of ores usually involves a long series of unit operations, such as leaching, filtration, precipitation, etc., many of which tend to be inefficient and costly and often involve a large capital expenditure on pieces of plant. The possible elimination of some of these operations in a chemical processing plant could result in reduced operating and capital costs and possibly a reduced loss of the valuable material in the waste solutions.

A process has been investigated whereby a non-sulphide ore or low-grade concentrate is leached with a small amount of an aqueous acid, and the valuable constituents extracted into an organic solvent which is simultaneously contacted with the wetted solid. This process is feasible with the oxide or oxysalt minerals of several metals, e.g. zinc, lead, copper, cobalt and uranium. Copper was considered one of the base metals which was most likely to be successfully and economically extracted by this method, and the application of the process to the extraction of copper from one of its oxysalt minerals, malachite, was studied in detail. Measurements were made of the rate of extraction and of the amount of extraction possible under various conditions, and the results used to indicate the rate controlling stage in the process. The selectivity of the process was also investigated and a study was made of the ease of separating the organic solvent from the spent ore at the end of the extraction process.

2.2. Metal Production.

The process of obtaining a metal from the earth's crust consists of four main stages, viz. (i) mining, to remove the selected ore from the earth, (ii) concentration, to separate the valuable mineral from the ore and to convert it to a suitable physical and chemical state, (iii) extraction, to obtain the metal from the concentrated mineral and (iv) refining, where the extracted metal is purified and treated prior to fabrication. A variety of methods is used in these four stages, and is illustrated by a brief summary of the production of tin, aluminium, zinc and uranium. The concentration and extraction of copper from its non-sulphide minerals is described in more detail in section 2.3.2.

2.2.1. Tin Production. The only mineral of tin which is of any economic importance is cassiterite, SnO_2, which is mined from underground vein deposits or from alluvial deposits by dredging. The vein rock is ground to liberate the cassiterite particles from the gangue (other minerals); the alluvial deposits are naturally liberated. The cassiterite is concentrated by gravity methods on account of the large density difference between it and the gangue (cassiterite 6.9g/cc; gangue 2.7g/cc), and a variety of historic and ingenious machines is used. The metal is extracted from the cassiterite concentrate by smelting with coke at temperatures up to 1300°C and several designs of furnace are used(1). The crude tin is refined by liquation (a process of partial melting); by poling (stirring the smelt with green wood poles) or by oxidizing the impurities by blowing air through the melt. Electrolytic refining from fluorosilicic acid has also been used.

2.2.2. Aluminium Production. Aluminium is mined as the hydrated oxide, bauxite ($Al_2O_3.H_2O$), which as it usually occurs near the earth's surface, is mined from open-cast pits. No satisfactory physical methods of concentrating the mineral have yet been devised, and so the ore is processed chemically. The bauxite is first freed from siliceous and ferrous impurities by the Bayer process(2), in which the ground ore is heated with caustic soda solution to convert the aluminium oxide into the soluble sodium aluminate, leaving a residue of insoluble impurities. The resulting solution is then stirred with a seed of finely crystalline aluminium hydroxide. The precipitated hydroxide is washed and calcined to the oxide, which is then dissolved in molten cryolite (Na_3AlF_6) and electrolysed at 920-990°C using carbon electrodes. The crude metal sinks to the bottom of the cell and is tapped off periodically and kept in 'holding furnaces' (to allow any suspended impurities to settle) before being cast(3). The metal is refined by further electrolysis, usually by the three-layer process, in which the crude aluminium is fed to a molten copper-aluminium alloy, made the anode, on top of which is a molten mixture of cryolite, aluminium, barium and calcium fluorides. Pure aluminium forms the top layer which is made the cathode. Aqueous electrolysis of aluminium is not possible on account of its position in the electrochemical series.

2.2.3 Zinc Production. The most important mineral of zinc is the sulphide (sphalerite), which often occurs with veins of the carbonate (smithsonite) or other valuable sulphide minerals, such as galena (PbS). The ground sulphide ores are separated from the gangue by flotation, a highly selective process, based on the ability of certain species of mineral particles to adhere to air bubbles, which can also be used to separate and concentrate other valuable constituents (such as galena) from the ore, by suitably adjusting the conditions. The concentrated zinc sulphide is roasted to form the oxide, which together with the carbonate is leached with dilute sulphuric acid. After clarification and the separation of any valuable impurities(4), the leach liquor is electrolysed, and the zinc cathodes produced can be further refined by smelting or distillation(5).

2.2.4. Uranium Production. The demand for uranium as a nuclear fuel has led to a situation where it is necessary to extract the metal from low-grade ores such as pitchblende (which may contain as little as 0.1% U_3O_8 and still be economical to process). As the demand is for high purity uranium, and the cost of extracting the metal from the ore is minute in comparison with the cost of the power producing plant, fuel processing, etc., an elaborate series of hydrometallurgical operations has resulted(6)(7)(8)(9).

The ground ore is dissolved in sulphuric acid and digested with air and manganese dioxide for about 3 hours at 90°C, to convert the uranium to the more soluble hexavalent form. The mixture is filtered and the uranium bearing filtrate is passed to an anion exchange column where the uranium is adsorbed. The column is eluted with a mixture of ammonium nitrate and nitric acid, and any iron present precipitated by the addition of calcium hydroxide. If necessary the uranium bearing solution can be further purified and concentrated by extracting the uranium into a solution of tri-butyl phosphate in kerosene. The uranium is back-extracted into water and precipitated as uranium diuranate by the addition of ammonium hydroxide. The ammonium diuranate is calcined to the orange oxide UO_3, which is then reduced with hydrogen to UO_2. This oxide is heated to 450°C with hydrogen fluoride to produce green uranium tetrafluoride which is pelletized with calcium or magnesium and reduced to uranium metal in a graphite lined electric furnace.

2.3 The Extraction of Copper from its Oxide Minerals.

When applied to copper, the term 'oxide mineral' is used loosely to describe those copper minerals which are not obviously chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), chalcocite (Cu_2S) other sulphides or native copper. These so-called oxide minerals include a large number of copper phosphate, carbonates and silicates whose only common properties are that they are usually green in colour and dissolve to some extent in dilute sulphuric acid. They usually occur in the zone of weathering of copper sulphide deposits. A brief description of the more important oxide minerals is given in the following section.

2.3.1. Description of Oxide Copper Minerals(10).

2.3.1.1. Malachite. Malachite corresponds to the formula $CuCO_3Cu(OH)_2$, and contains 57.3% copper by weight. It is bright green in colour, and different shades of the colour often follow a concentrically banded arrangement. Malachite often occurs massive, and is found in the zone of weathering or oxidation of copper deposits, especially in France, Siberia, South Australia, Zambia and the Congo.

2.3.1.2. Azurite. Azurite is another basic carbonate of copper, corresponding to the formula $2CuCO_3Cu(OH)_2$, and contains 55.1% copper by weight. The colour is deep blue, and the crystals are monoclinic in form, occurring as modified prisms. Azurite occurs with other oxidised copper minerals, such as malachite.

2.3.1.3. Atacamite. This is a hydrated oxychloride of copper $CuCl_2.3Cu(OH)_2$ containing 59.4% copper by weight; it is deep green in colour and has an orthorhombic crystal structure. Atacamite is found in the weathering zone of copper minerals, especially where the weathering has occurred under desert conditions, such as in the Atacama Desert in South America and the Burra Mine in South Australia.

2.3.1.4. Cuprite. Cuprite, or the red oxide of copper, Cu_2O contains 88.8% copper and has a cubic crystal system. It is red in colour and occurs with the other oxidised copper minerals such as malachite and azurite.

2.3.1.5. Chrysocolla. Chrysocolla approximates to the formula $CuSiO_3xH_2O$; it is blue-green to sky-blue in colour, and is of an amorphous nature. Chrysocolla can absorb a considerable amount of moisture, owing to the porous nature of its structure. It occurs in the same region as the other oxidised copper minerals.

2.3.2 Description of an Oxide Copper Extraction Process.

A typical process for the leaching of an oxide copper concentrate is given by Page (11), (12) and (13), and a summary is given here. The flowsheet for the process is given in fig. (1).

The ore from the mine, after initial crushing and grinding is separated by differential flotation to produce a sulphide concentrate and a non-sulphide (or oxide) concentrate. The sulphide concentrate is smelted directly in a reverberatory furnace to produce an impure copper product which is then refined electrolytically.

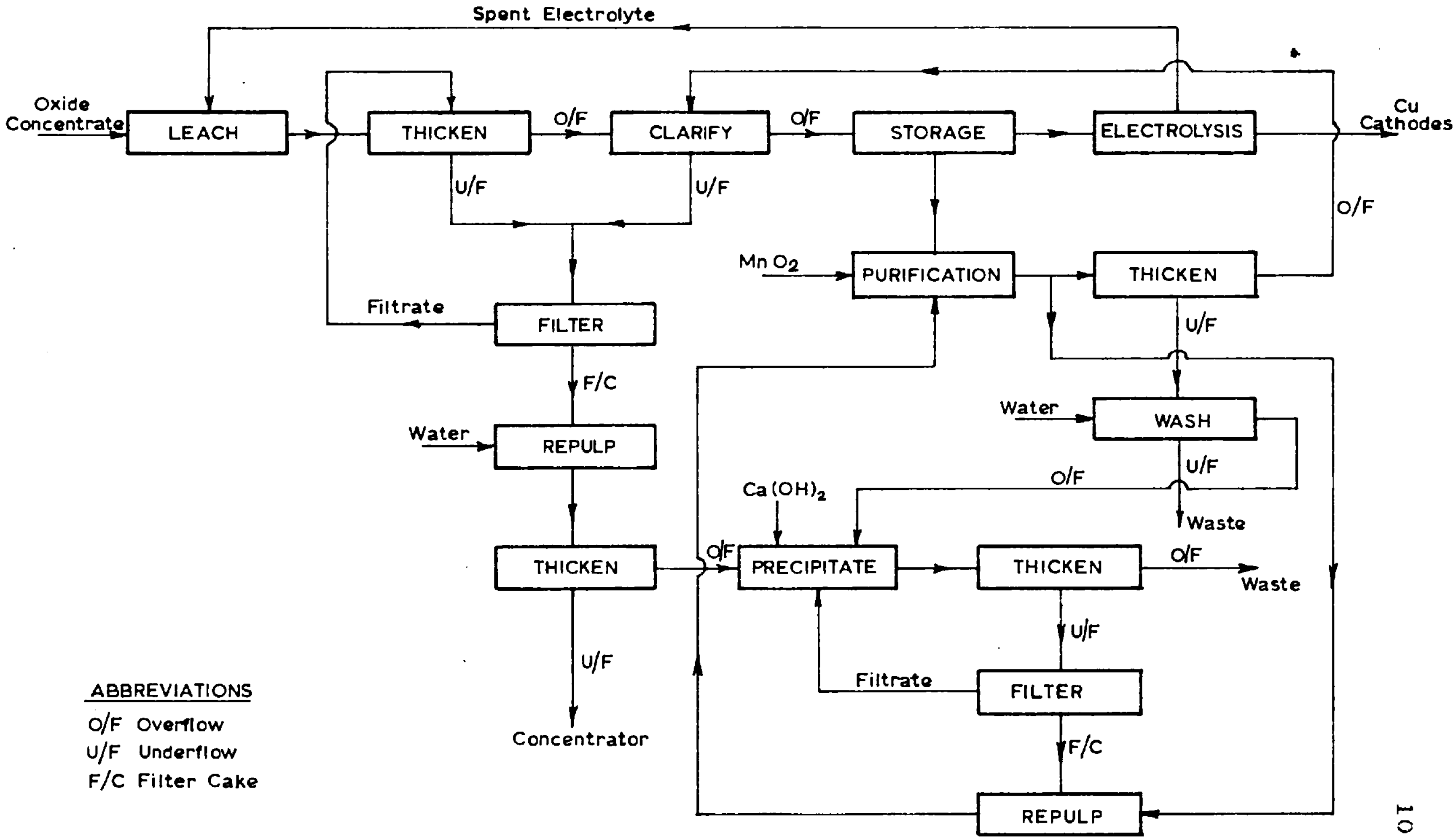


Fig. 1 FLOWSHEET FOR A TYPICAL OXIDE COPPER PRODUCING PLANT

The oxide concentrate, containing about 12% total copper is mixed with spent electrolyte (i.e. sulphuric acid from the electrolytic tank house) and leached in mechanically agitated, lead-lined, mild steel tanks for about 4.1/2 to 5 hours. By careful control of the acid concentration, it is possible to prevent excessive dissolution of the iron in the concentrate. After leaching, the pulp is thickened, the thickening being enhanced by the addition of flocculants. The thickener overflow, containing about 22 g/l of copper is clarified and passed to the tank house for electrolysis. The underflow from the thickener is filtered and the filtrate returned to the primary thickeners after the leaching stage. The filter cake is repulped and thickened, and the residue returned to the concentrator. The copper in the washing water is recovered by precipitation with milk of lime, the precipitate being thickened and the overflow pumped to waste. The underflow is filtered and the cake, containing about 20% copper on a dry basis, is repulped with the leach liquor from the purification section and passed to the purification plant for iron removal. The filtrate is returned to the precipitation section.

The iron in the solution is oxidised by the addition of finely ground manganese dioxide to the solution which is maintained at a pH between 1.9 and 2.2 by the addition of primary leach liquor. Some of the purified solution containing about 0.1 g/l of iron is used to repulp the hydroxide, and the remainder passed to a thickener before joining the primary leach liquor in the clarification thickener. The underflow from the purification thickener is washed with water and the residue pumped to waste. The washings are returned to the precipitation section for copper recovery.

In the tank house, the solutions are electrolysed in lead-lined concrete cells using thin starting-sheets of pure copper as the cathodes and antimonial-lead anodes. The spent solutions from the tank house are returned to the leaching plant.

This process is basically the same for all oxide copper minerals, although variations are found according to the nature of the gangue materials and to the economic availability of reagents. For example, in Chile. it is found preferable to extract the copper from the leach solution by precipitating it on to iron(14).

Reference to Fig.(1) will show that the process described for the leaching of an oxide copper concentrate involves a large number of operations, many of which must be duplicated on account of their inherent inefficiency when treating materials of the type encountered in such a process. Acid-consuming gangue causes large losses of reagent in the leaching stage. Several other subsidiary operations are also necessary for the recovery of the copper from washing solutions, filtrates, etc. Many of the copper bearing solutions are extremely dilute, and hence large volumes must be handled in order to recover relatively small quantities of copper.

2.4 The Use of Solvent Extraction.

One method of separating the copper (or other metals) from the iron in the leach solutions, and at the same time effecting the concentration necessary before the electrolysis, is solvent extraction. As yet, solvent extraction has not been widely used for metal extraction, the exceptions being uranium(6) (7) (8) (9), thorium(15) and other nuclear metals, and the rare earth elements(16) (17) (18). The main objections to the use of solvent extraction have been (a) the cost of the solvent, which has limited its use to the more costly metals such as uranium, (b) difficulty in finding solvents which were non-toxic, non-inflammable, non-volatile, non-corrosive, had a low mutual solubility with the aqueous phases with which they were brought into contact, as well as being sufficiently different in density from the aqueous phases to prevent emulsion formation and were sufficiently selective towards the valuable metal. Other important considerations are the distribution coefficient for the metal between the aqueous and organic phases, the ability to strip the metal from the loaded solvent and the ease of separating the aqueous and organic phases before the solvent is re-used.

Several solvents have been used for the extraction of metals, uranium is extracted into tri-butyl phosphate from nitric solutions, and this solvent is also used for the extraction of thorium. Zirconium and hafnium are separated by the use of methyl-iso-butyl ketone (MIBK)(19). More recently, considerable attention has been directed towards the search for solvent extraction reagents for use with the more common metals, and it has been found that certain long-chain carboxylic acids possess suitable solvent extraction properties. One of these acids is naphthenic acid, and a considerable amount of work has been done on the use of naphthenic acid for the separation and extraction of metals(20)(21)(22). Synthetic carboxylic acids, with similar solvent extraction properties have also been investigated(23).

2.4.1. Naphthenic Acid as a Solvent Extraction Reagent.
Naphthenic acid is a mixture of mono-carboxylic acids of mean molecular weight approximately 200: The hydrocarbon groups are basically cyclo-pentane, with saturated ali-

phatic groups attached. The carboxylic group is bound to the hydrocarbon ring or to one of the alkyl side-chains. Several grades are available, all derived from crude petroleum, differing slightly in composition and molecular weight, according to the origin of the crude oil from which the naphthenic acids are derived(24). Naphthenic acids have a low mutual solubility with water, but are soluble in most organic solvents, such as paraffin, acetone, carbon tetrachloride, etc. Fletcher and Wilson(22) have shown that the extraction of metals from aqueous sulphate solutions depended largely on the pH of the solution, the pH dependence being of the form shown in Fig.(2). The metals can be stripped from the naphthenic acid solutions by a strong solution of a mineral acid.

The reaction involved in the extraction and stripping processes have been found to be stoichiometric, thus for divalent metals, two moles of naphthenic acid are required to extract one mole of the metal, but in certain cases, the metal naphthenate appears to be solvated with one molecule of naphthenic acid(25).

By virtue of the pH dependence of the extraction process, it is possible to separate certain metal mixtures, by the use of naphthenic acid, and Fletcher and Wilson have demonstrated the separation of copper and nickel by this method.

Comparisons of different grades of naphthenic acid of molecular weights in the range 244 to 311 showed that there was only a small difference in the behaviour of various grades of acid.

Measurements of reagent loss by solubility in the aqeuous phase indicated that the loss was not excessive,

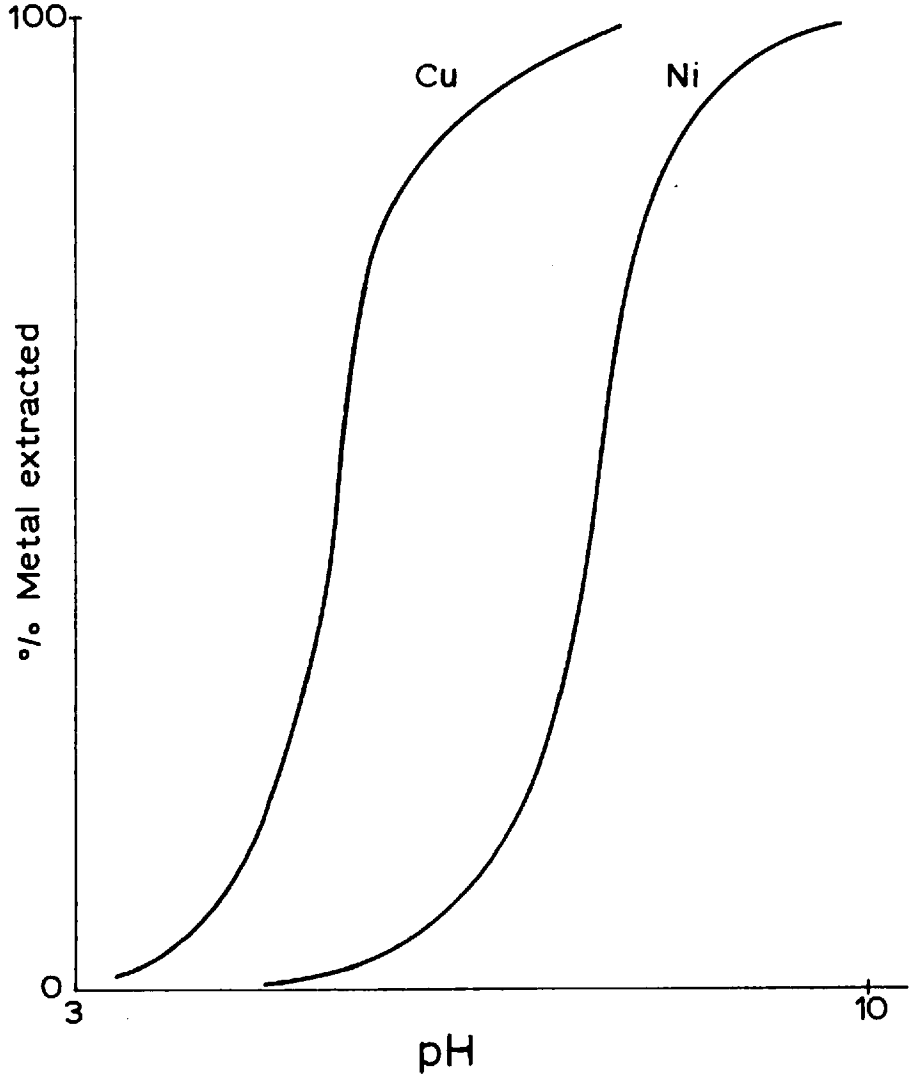


Fig. 2 pH DEPENDANCE OF EXTRACTION OF METALS FROM SULPHATE SOLUTIONS BY NAPHTHENIC ACID but tended to increase with increasing pH of the aqueous phase, especially in the presence of ammonium sulphate.

2.5 The Use of a Combined Leaching and Solvent Extraction Process.

The use of solvent extraction as a means of separating the copper from the iron in a process such as that described in section 2.3.2. could possibly result in a saving of capital cost and reduction of operating costs by elimination of the precipitation stage and subsequent thickening and filtration operations. However, a much greater saving would be possible if the thickening and filtration stages after the leaching operation could also be eliminated and any reduction of acid consumption by the gangue materials could also result in reduced operating costs. By the use of a combined leaching and solvent extraction process, it is possible to eliminate some of these intermediate stages.

In a combined leaching and solvent extraction process, the mineral is moistened with a small amount of an aqueous leaching solution, to convert the valuable metal into a form which can be extracted into an organic solution which is simultaneously contacted with the wetted mineral. By a suitable choice of reagents, the leaching solution can be regenerated by the organic solvent during the extraction process. Suppose malachite is used as the mineral and sulphuric acid is used as the leaching agent. If a particle of malachite is coated with a thin layer of sulphuric acid, a small amount of the malachite will dissolve, according to the equation:

$$CuCO_3\ Cu(OH)_2 + 2H_2SO_{4(aq)} \longrightarrow 2CuSO_{4(aq)} + 3H_2O + CO_2 \quad (1)$$

The copper ions will diffuse across the aqueous layer, and, on arriving at the aqeuous-organic interface, will be extracted into the organic phase, according to the equation:

$$2CuSO_{4(aq)} + 4HR_{(org)} \longrightarrow 2CuR_{2(org)} + 2H_2SO_{4(aq)} \qquad (2)$$

The sulphuric acid will be regenerated by the reaction corresponding to equation (2) and diffuses back to the mineral surface under the influence of a concentration gradient (set up due to the depletion of acid by reaction (1)) to continue the process. This process is shown diagramatically in Fig.(3) with naphthenic acid as the organic solvent. When the mineral has been exhausted, the organic solution must be removed from the spent ore, which can be done by 'floating' it off by mixing the spent ore with water, and the organic solvent will rise to the surface and can be skimmed off. The valuable metal can be stripped from the loaded organic solvent and the metal recovered from the resulting aqueous solution by precipitation, electrolysis, or other methods. The stripped organic solvent can then be re-used. The flow-sheet for the proposed process is illustrated in Fig.(4), and comparison with Fig.(1) shows that many of the operations have been eliminated.

Such a process has the possible advantages of a better overall selectivity than the conventional process on account of the extraction characteristics of the organic solvent.

This type of process has been successfully operated on a pilot-plant scale using several Colorado Plateau uranium ores(26).

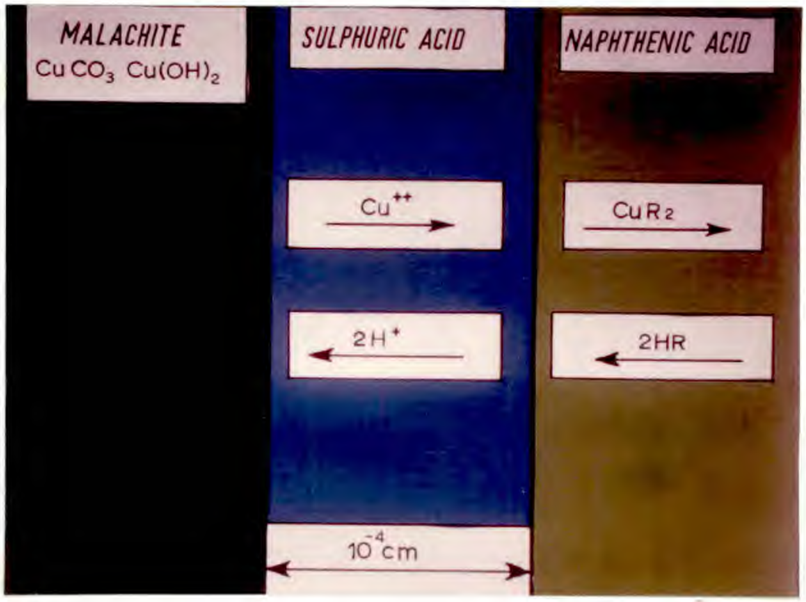


Fig.3. Diagramatic Representation of Combined Leaching and Solvent Extraction Process.

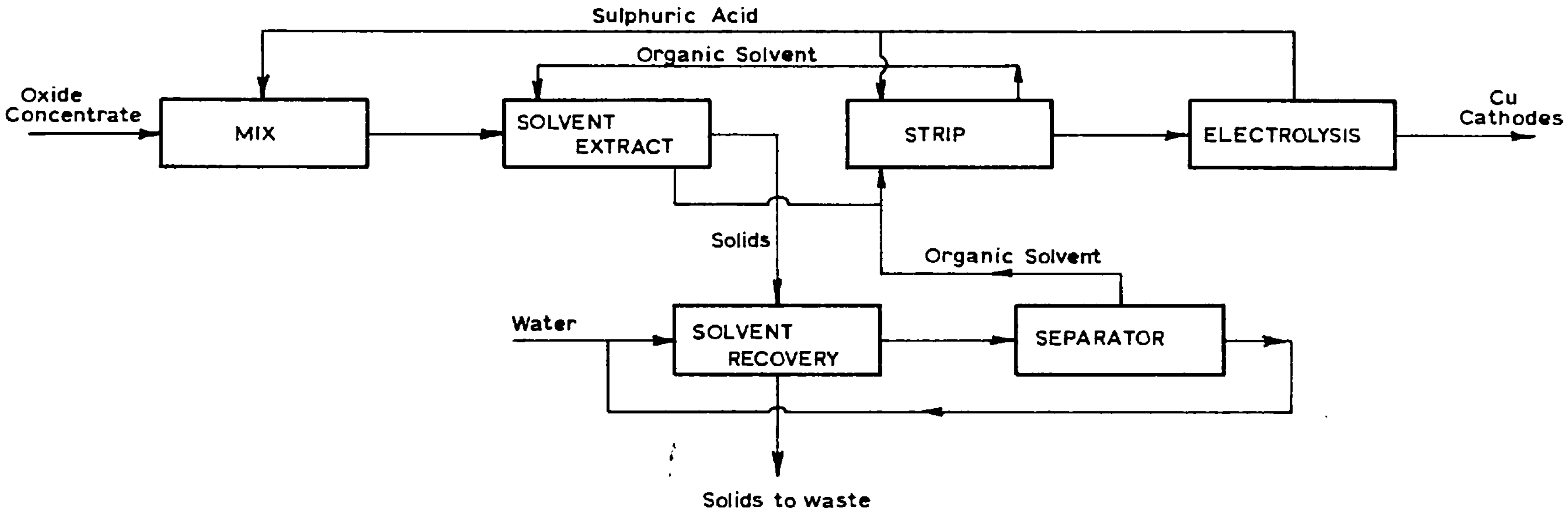


Fig. 4 SUGGESTED FLOWSHEET FOR A SIMULTANEOUS LEACHING AND SOLVENT EXTRACTION PROCESS APPLIED TO AN OXIDE COPPER CONCENTRATE

3. STATISTICAL THEORY

3.1. Introduction.

When a new process is being investigated there is often a large number of variables which could conceivably have some influence on the process. Usually the process is of too complex a nature, or insufficient is known about the underlying mechanisms for the effects of these variables to be predicted analytically, and hence an empirical approach must be employed. In order to do this efficiently, as much information as can be deduced about the process from other sources must be incorporated into the planning of the investigation.

By the use of statistical techniques, it is possible to plan in advance a programme of tests which will enable all the desired information to be produced with the minimum amount of effort and with a known precision. Such a programme of tests can be used as a starting point to find an optimum set of conditions for the process. Such techniques are particularly valuable when dealing with process variables that are liable to be of low reproducibility.

The simultaneous leaching and solvent extraction process under consideration is one for which only a tentative analytical approach is possible. Although the possible variables can be listed, their influence cannot be deduced, and some of them, particularly those related to the aqueous phase on the mineral surface, will be difficult to control. An investigation into the feasibility of the process appeared to require statistical planning and interpretation to obtain satisfactory information in a reasonable time. The remaining part of this section is concerned with the details of the statistical methods used in the research.

3.2 Definitions.

3.2.1. Factor. Any feature of an experiment which can be controlled at will is termed a factor, and these may be quantitative or qualitative. Quantitative factors are those for which the values can be represented by points in a specific order on a numerical scale, e.g. particle size, flow-rate, pH, etc. Qualitative factors are those for which it is not possible to arrange the values in any particular order. Examples of qualitative factors would be the use of different extraction reagents or the use of different pieces of plant to carry out the process.

3.2.2. Levels of Factors. The various values of a factor used in an experiment are termed the levels of the factor. In 'two-level experiments', where factors are investigated at two levels only, these are called the 'high' and 'low' levels of particular factor, and are denoted by the subscripts '$_1$' and '$_o$' respectively. For example, if M represents the factor of particle size, and its effect is to be investigated at mean diameters 60μ and 120μ, then M_o represents the low level of particle size (60μ) and M_1 represents the high level of particle size (120μ).

3.2.3. Treatment Combination. The set of levels of all the factors used in a particular test is termed the treatment combination. (The name derives from the days when statistical experiments were used solely for agricultural purposes.) Thus if particle size (M), flow-rate (F) and reagent concentration (C) were investigated in a particular experiment, the treatment combination denoted by $M_oF_1C_1$

would imply that the test was carried out at the low level of particle size and at the high levels of both flow-rate and reagent concentration. An alternative notation is to write the treatment combination in terms of the subscripts in a specified order, thus $M_cF_1C_1$ would be written as 011. Another method of specifying the treatment combination (and also of representing algebraically the result of the test performed at that particular treatment combination) is to denote the factor by its small letter if it appears at the high level, and to omit it if it appears at the low level, hence $M_oF_1C_1$ would appear as fc. If all the factors appear at the low level, this treatment combination known as the 'control experiment' is denoted by the symbol "(1)".

All the above systems of notation are useful in certain circumstances and will all be used in this thesis.

3.2.4. Response. This is the numerical result of a paricular test.

3.2.5. Factorial Experiment.

In a factorial experiment, tests are carried out at all the combinations of all the levels of all the factors. Thus if three factors, each at two levels, are being investigated, 2^3(=8) tests must be performed and the factorial experiment is termed a 2^3 experiment.

The basic fact which underlies factorial experiments is that no test is repeated, but that the effect of a given factor is repeated over different experimental conditions. Thus in a 2^3 experiment, the effect of each factor is repeated four times. This uses all the combinations of all the levels of all the factors and enables interactions between factors as well as main effects to be estimated.

3.2.6. Main Effect of a Factor. The main effect of a factor is defined as the difference between the mean result of all tests at the high level of that factor, and the mean result of all tests at the low level of that factor.

3.2.7. Interaction Between Factors. Consider two factors B and D. If the effect of B is independent of the level of factor D, then there is no interaction and the lines of constant D in Fig.(5) are parallel.

When the factors interact the lines are not parallel, as shown in Fig.(6). An interaction is thus defined as the change in effect of one factor due to the change in level of another factor. Numerically, the interaction between B and D is given by the difference between the effect of B at the high level of D and the effect of B at the low level of D, divided by 2^{n-1}, where n is the total number of factors in the experiment. Thus for the two factors B and D the interaction BD is given by:-

$$BD = 1/2[(bd-d) - (b-(1))] \qquad (3)$$

3.2.8. Tests for Significance.

3.2.8.1. The Null Hypothesis. Statistical experimentation is always performed in an attempt to disprove the Null Hypothesis, which postulates that the difference between an observed result and an expected result is due to error only. This hypothesis cannot be proved, but can be disproved where the differences are due to assignable causes. For example, a result is said to be significant at the 5% level if the probability that the Null Hypothesis is true is less than 0.05. That is, if 95 out of every

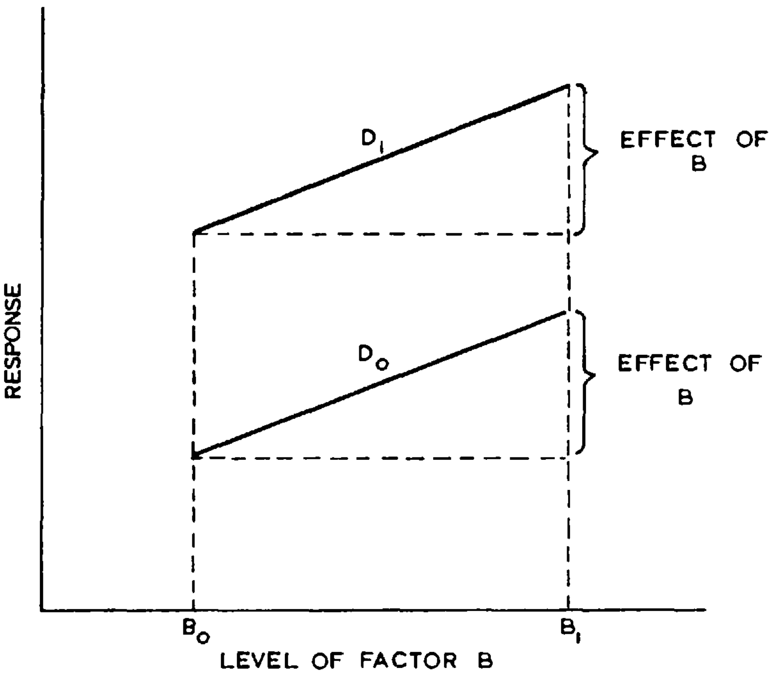

RESPONSE
D₁
D₀
EFFECT OF B
EFFECT OF B
B₀
B₁
LEVEL OF FACTOR B

Fig. 5

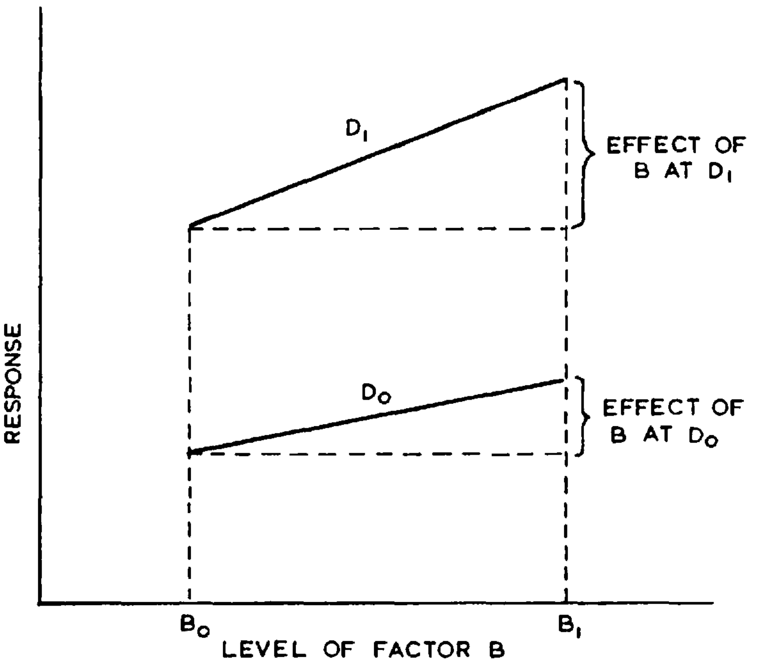

RESPONSE
D₁
D₀
EFFECT OF B AT D₁
EFFECT OF B AT D₀
B₀
B₁
LEVEL OF FACTOR B

Fig. 6

100 tests gave differences between the observed and expected values greater than those due to chance alone, then such a result would be significant at the 5% level. It is universally accepted that a 5% (or lower) significance level corresponds to a real cause, although the actual choice of significance levels depends on the purpose of the experiment.

3.2.8.2. Variance. The variance, V, is a measure of the scatter of a set of observations about the mean of the set. Numerically it is defined as

$$V(x) = \frac{\sum(x - \bar{x})^2}{\nu} = \sigma^2 \qquad (4)$$

where ν is the number of degrees of freedom, i.e. the difference between the number of observations and the number of relationships between the observations, and is the standard deviation.

3.2,8.3. The F-test. The object of this test is to determine whether the variances σ_A^2 and σ_B^2 of two sets of observations A and B are significantly different. The ratio, F, is computed such that

$$F = \frac{\sigma_A^2}{\sigma_B^2} > 1 \qquad (5)$$

Values of F are tabulated in most statistical works for various significance levels and for the different degrees of freedom of σ_A^2 and σ_B^2. If the value of F, as obtained from the ratio in eqn. (5), is greater than the tabulated value for the particular significance level chosen, then the variances σ_A^2 and σ_B^2 are significantly different.

3.2.8.3. The t-test. The t-test is used to determine whether two means are significantly different, and is defined by:-

$$t = \frac{\text{Difference of means}}{\text{Standard deviation of difference of means}} \qquad (6)$$

$$= \frac{\bar{x}_A - \bar{x}_B}{\sqrt{\sigma^2_p/n_A + \sigma^2_p/n_B}}$$

$$= \frac{\bar{x}_A - \bar{x}_B}{\sigma_p \sqrt{\frac{n_A n_B}{n_A + n_B}}} \qquad (7)$$

where n_A and n_B are the numbers of observations in sets A and B respectively and ν_p is the pooled variance defined by

$$\sigma^2_p = \frac{\sigma^2_A \nu_A + \sigma^2_B \nu_B}{\nu_A + \nu_B} \qquad (8)$$

ν_A and ν_B are the number of degrees of freedom of σ^2_A and σ^2_B respectively.

The value of t chosen for significance is based on the degree of freedom ν_p of the pooled variance, where

$$\nu_p = \nu_A + \nu_B \qquad (9)$$

Values of t are tabulated in most statistical works for various significance values and different degrees of freedom. The t-test can only be used if the two means come from the same population, i.e. the variances must be homogeneous before they can be pooled - this can be tested by means of the F-test (Section 3.2.8.3.)

For the case in which $\nu_A = 1$ and for all values of ν_B

$$t^2 = F \qquad (10)$$

3.2.9. The L_1 Test. This test is used to determine whether or not several variances are homogeneous, i.e. whether they all come from the same population. L_1 is defined by:-

$$L_1 = \frac{\text{Geometric mean of variances}}{\text{Arithmetic mean of variances}} \qquad (11)$$

Significance is suggested by low values of L_1 (i.e. the Null Hypothesis is disproved). The L_1 test can only be used when all the variances are based on the same number of degrees of freedom. If one variance is very much smaller than the rest, this will make the geometric mean very small, giving a low value of L_1 and possibly an incorrect conclusion. In this case the low variance is usually neglected. Tables of L_1 for various levels of significance are available, giving values of L_1 for k variances each based on n degrees of freedom(27)(28).

3.2.10. Confidence Limits. When an estimate of some quantity has been made, it is desirable to know how precise the estimate is, and a convenient way of doing this is to state the limits, which with a given probability, include the true value of the estimated quantity. It can then be said that the true value is unlikely to lie outside a pair of limits. These limits are called confidence limits. For a mean value, $\bar{x}$, the confidence limits are given by

$$\bar{x} \pm t_{\alpha}\delta/\sqrt{n} \qquad (12)$$

where δ is the standard deviation of the mean, calculated from eqn. (4), n is the number of observations, and t is the value of t (Section 3.2.8.3.) for significance at the α% level, based on the appropriate number of degrees of freedom.

These limits are said to be the $100(1-2\alpha)$% confidence limits. Thus if $\alpha = 0.05$, it is possible to say that in

90 cases out of 100, the value of $\bar{x}$ will lie in the range $\bar{x} \pm t_{0.05}\sigma/\sqrt{n}$, and these are the 90% confidence limits.

3.3. Confounding in Factorial Experiments.

In experiments which last a long time (either by virtue of the nature of each test or by the size of the experiment), uncontrolled variables may be introduced, e.g. the plant may break down and have to be replaced by another, or the temperature gradually changes, thus introducing a bias to the results. It is possible, by suitably designing the experiment, to reduce the number of tests which have to be performed under constant conditions. The experiment is split up into a number of blocks and certain (unimportant) effects are combined (or confounded) with differences between these blocks.

Consider a 2^2 factorial experiment, using the factors A and B, and suppose it is done in two blocks of two tests each, as shown below:-

Block I	Block II
(1)	a
ab	b

Suppose the responses in block II are each increased by an amount x for some unknown reason.

The main effect of A, as defined in section 3.2.6., is given by:-

$$A = 1/2[(a + x) + ab - (1) - (b + x)]$$

$$A = 1/2[a + ab - (1) - b] \qquad (13)$$

Thus the main effect of A is free from the difference between the blocks. The interaction AB, defined as in section 3.2.7., eqn. (3), is given by:-

$$AB = 1/2[ab - (b + x) + (1) - (a + x)]$$

$$= 1/2[ab - b + (1) - a - 2x] \qquad (14)$$

and is not free from the difference between the blocks and is described as being 'confounded with the difference between blocks'. The experiment must be carefully designed so as not to confound differences between blocks with important effects.

3.3.1. <u>Design of Confounded Experiments</u>. The technique of confounding is based on two axioms:-

(i) Symbols of either a test or effect group can be multiplied together according to the usual laws of algebra with the additional condition that

$$a^2 = b^2 = c^2 = \ldots\ldots = 1 \qquad (15)$$

e.g. $(abc)(acd) = (bd)$

$(abd)(abd) = (1)$

(ii) Two symbols of either test or effect group are described as being orthogonal if the number of letters they have in common is even (or zero) e.g.

abc , acd orthogonal, a and c are common
ab , cd orthogonal, no letters in common
abc , cd not orthogonal, one letter in common.

When choosing an effect with which to confound a block difference it is essential that the effect should not be important, thus it should not be a main effect or two-factor interaction, unless these are known from previous work to be small or zero.

3.3.2. <u>Rules of Confounding</u>. Suppose it is required to confound a 2^4 factorial experiment (consisting of 16 tests) into four blocks of four tests each. Let the factors be denoted by A, B, C and D, and suppose it is known that the interactions ABC and AD are not important. When two effects are confounded, their product is also confounded, yielding what is known as the confounded sub-group. Thus in this experiment the confounded sub-group is:-

$$ABC = AD = BCD = I$$

The identity, I, (i.e. the mean result of all the tests performed in the experiment) is always confounded.

The tests in each block can be chosen by applying the following rules:-

i) The tests in the first block must include the control experiment.

ii) The tests in the first block must be orthogonal to the confounded sub-group.

iii) The product of the symbols of two tests in a block is also a test in the same block.

iv) The test in the other blocks are obtained from the first block by multiplying it by any test not yet included.

Thus applying these rules to the design of a 2^4 experiment, the tests are:-

Block 1	(1)	bc	acd	abd	
Block 2	a	abc	cd	bd	(multiply Block 1 by a)
Block 3	b	c	abcd	ad	(multiply Block 1 by b)
Block 4	d	bcd	ac	ab	(multiply Block 1 by d)

When executing the experiment, the blocks must be performed in a random order, and the tests within a block must also be performed in a random order, to eliminate the possibility of a time trend in the experiment. The randomisation process is carried out by using the tables of random numbers which are found in most statistical works. Basically the procedure is to work along one of of the rows (or down one of the columns) of numbers and, for this particular example, to do the blocks in the order in which the numbers 1, 2, 3 and 4 appear in the table. Similarly for the tests within each block.

3.4. Analysis of Factorial Experiments by Yates' Method.

A full description of this method of analysis is given by Yates(29). The analysis may be checked by using a method devised by Eisenklam(30). The application to two-level factorial experiments is now given (as only two-level factorial experiments were used in the actual experimental investigation). The complete analysis for a 2^3 factorial experiment is set out in table 1, which is constructed as described below.

The treatment combinations are first arranged in columns in standard order. For the factors (say) P, Q, R ...... the standard order is derived by writing down factor P at the low and high level, with all other factors at the low level, i.e. (1) and p; the next factor, Q, is added by multiplying the existing order by q and adding it on, viz. (1) p q pq. For three factors, the standard order for two factors is multiplied by the third factor (r), and the result added on to the existing order for two factors, viz: (1) p q pq r pr qr pqr. The process is continued until all the factors have been used. It is usual, in this method of analysis, to denote the standard order in terms of the 0 and 1 notation, as described in section 3.2.3.

Alongside the column containing the treatment combination in standard order is written a column containing the response corresponding to that particular treatment combination. The next column (Column (I)) is

Table 1.

Example of the Use of Yates' Method of Analysis for a 2^3 Experiment.

Factor P Q R	Response	Column (I)	Column (II)	Column (III) (Total effect)	Mean Effect	Mean Square
(1) (000)	a	a + b	a+b+c+d	a+b+c+d+e+f+g+h	(a+b+c+d+e+f+g+h)/8	$(a+b+c+d+e+f+g+h)^2/8$
p (100)	b	c + d	e+f+g+h	-a+b-c+d-e+f-g+h	(-a+b-c+d-e+f-g+h)/4	$(-a+b-c+d-e-f-g+h)^2/8$
q (010)	c	e + f	-a+b-c+d	-a-b+c+d-e-f+g+h	(-a-b+c+d-e-f+g+h)/4	$(-a-b+c+d-e-f+g+h)^2/8$
pq (110)	d	g + h	-e+f-g+h	a-b-c+d+e-f-g+h	(a-b-c+d+e-f-g+h)/4	$(a-b-c+d+e-f-y+h)^2/8$
r (001)	e	-a + b	-a-b+c+d	-a-b-c-d+e+f+g+h	(-a-b-c-d+e+f+g+h)/4	$(-a-b-c-d+e+f+y+h)^2/8$
pr (101)	f	-c + d	-e-f+g+h	a-b+c-d-e+f-g+h	(a-b+c-d-e+f-g+h)/4	$(a-b+c-d-e+f-g+h)^2/8$
qr (011)	g	-e + f	a-b-c+d	a+b-c-d-e-f+g+h	(a+b-c-d-e-f+g+h)/4	$(a+b-c-d-e-f+g+h)^2/8$
pqr (111)	h	-g + h	e-f-g+h	-a+b+c-d+e-f-g+h	(-a+b+c-d+e-f-g+h)/4	$(-a+b+c-d+e-f-g+h)^2/8$
TOTAL	a+b+c+d+e+f+g+h	2(b+d+f+h)	4(d+h)	8h		$a^2+b^2+c^2+d^2+e^2+f^2+g^2+h^2$
CHECK TOTAL	2(b+d+f+h)	4(d+h)	8h			
SUM OF SQUARES	$a^2+b^2+c^2+d^2+e^2+f^2+g^2+h^2$					

N.B. On squaring the entries in the Total Effect column, the cross-product terms vanish on summing the entries.

derived from the response column by adding the entries in the response column in pairs. Thus the first entry in Column (I) corresponds to the sum of the first two entries in the response column, and the second entry in the column is the sum of the third and fourth entries in the response column, etc. This therefore completes the top half of column (I). The bottom half is derived by subtracting the first entry in the response column from the second entry in the response column, giving the first entry in the second half of column (I). The second entry in the bottom half of column (I) is the fourth entry in the response column minus the third entry in the response column, etc. Column (II) is derived from column (I) in exactly the same way as column (I) was derived from the response column. This procedure is repeated until the total number of columns (excluding the response column) is the same as the number of factors. The final column contains the total effects, and the mean effects are derived from the total effect column by dividing each entry by 2^{n-1} (where n is the number of factors), with the exception of the first entry, corresponding to the control experiment, which is divided by 2^n, as this represents the mean result of all the tests. The mean squares are derived from the total effect column by squaring each entry and then dividing by 2^n.

3.4.1. Checks on the Analysis. Each column may be checked in turn before proceeding to compute the following column by means of the method due to Eisenklam,(30) which consists essentially of performing the sum and difference operations together.

Consider a pair of entries in any column j; let entry 2k-1 be x and entry 2k be y, $(2 \leqslant 2k \leqslant 2^n)$.

The summing operation produces: $x + y$
The differencing operation produces: $-x + y$
The sum of these two is: $2y$

Hence the sum of all the entries in column $j + 1$ must be equal to twice the sum of all the entries in the even position of column j. As compensating errors are unlikely, this check is virtually infallible.

An overall check on the analysis is supplied by summing the squares of the entries in the response column, and comparing the total with that of the mean squares column. These two totals should agree to within the limits of any rounding-off errors.

3.4.2. Testing the Mean Squares for Significance. When all the main effects and interactions have been evaluated, they must be tested for significance (i.e. to see if they represent genuine effects or are only random error fluctuations) by means of the F-test.

$$F = \frac{\text{Mean Square of Effect}}{\text{Mean Square of Error}}$$

Now each effect can be considered as consisting of two parts, one due to an assignable cause and the other due to error. The Null Hypothesis is then used to postulate that each effect consists of error only and this assertion tested by means of the F-test. As each effect is assumed to consist of error only, and error has a mean of zero, the variance of any effect is simply the square of the effect itself.

3.4.3. Estimation of Experimental Error. As yet, there is no estimate of the experimental error of the factorial experiment, and without this estimate it is not possible to test for significance. A valid estimate of the experimental error can be obtained by repeating the whole factorial experiment. However, this usually involves a lot of work and often the error is not required to such a high degree of precision as to warrant repeating the experiment. In normal physical and chemical situations it is very rare to find interactionsbetween three or more factors which have any importance, and hence in the analysis of experiments these interactions should be zero; any deviation from zero will thus be entirely due to experimental error, and hence these values can be combined to give an estimate of the mean square of the error. Before these interactions can be combined, it must be ascertained that they all come from the sameerror population, and this can be done by means of the L_1 test. Another conditon is that in order to obtain a valid estimate of error, it should be based on at least eight degrees of freedom. This is because the level at which the variance ratio is significant is very sensitive to the number of degrees of freedom of the variance estimate in the denominator, when this number is small.

3.4.4. Variance of Effects in Factorial Experiments. In a 2^n factorial experiment the effect of a factor or interaction between factors is given by the difference between two sums each of $(1/2) \times 2^n$ quantities, (see sections 3.2.6. and 3.2.7).

Now for a function of several variables

$$f = f(x_1, x_2, x_3 \ldots\ldots)$$

The variance of the function is given by:-

$$V(f) = \left(\frac{\partial f}{\partial x_1}\right)^2 V(x_1) + \left(\frac{\partial f}{\partial x_2}\right)^2 V(x_2) + \left(\frac{\partial f}{\partial x_3}\right)^2 V(x_3) + \ldots \quad (16)$$

Now a main effect E of a factor is given by:-

$$E = \frac{\sum_{i=1}^{2^{n-1}} y_{hi} - \sum_{i=1}^{2^{n-1}} y_{li}}{2^{n-1}} \qquad (17)$$

where y_h and y_l correspond to the response at the high and low levels of the factor respectively.

$$\therefore V(E) = \frac{\sum_{i=1}^{2^{n-1}} [\frac{\partial}{\partial y_{hi}}(y_{hi})]^2 + \sum_{i=1}^{2^{n-1}} [\frac{\partial}{\partial y_{li}}(y_{li})]}{2^{2n-2}} \qquad (18)$$

If the variances of each term are equal to δ^2:-

$$V(E) = \frac{2^{n-1}\delta^2 + 2^{n-1}\delta^2}{2^{2n-2}} = \frac{\delta^2}{2^{n-2}} \qquad (19)$$

Thus in a factorial experiment, the main effects and interactions can be estimated with a high degree of precision, even if the variance of the initial response is high.

3.5 Fractional Factorial Experiments.

When a large number of factors has to be investigated, a full factorial experiment becomes large and cumbersome, (e.g. with six factors, each at two levels, the experiment would involve 64 separate tests). Large experiments produce much unwanted information as well as producing an estimate of error (from high-order interactions) of unnecessarily high precision. In such cases it is possible to design the experiment in such a way that only a fraction of the total number of tests need be performed, and the results analysed before proceeding to the next fraction, or revising the plan of experimentation in the light of the results of the preceeding fraction. This technique is called fractional replication.

3.5.1. Example of a Fractional Factorial Experiment.

Consider the first two blocks of the 2^4 experiment discussed in section 3.5.2. The tests involved were:-
(1), bc, acd, abd, a, abc, cd, bd.
It can be easily verified that these tests would form the first block of a 2^4 factorial experiment, confounded into two blocks of eight tests each, with the interaction BCD confounded between blocks.

Using the definition of the main effect of a factor as in section 3.2.6., it is possible to obtain expressions for the main effects of the four factors A, B, C and D, viz:

$$A = 1/4[acd + abd + a + abc - (1) - bc - cd - bd] \tag{20}$$

$$B = 1/4[bc + abd + abc + bd - (1) - acd - a - cd] \tag{21}$$

similarly for the factors C and D.

From these eight tests it is thus possible to obtain estimates of the main effects of each factor, whereas the full factorial experiment would have required 16 tests to produce this information.

3.5.2. Combination of Effects in Fractional Factorial Experiments.

It is also possible to estimate interactions from the same eight tests used in section 3.5.1. to estimate the main effects. Applying the definition of section 3.2.7. for the two-factor interaction CD:-

$$CD = 1/4[(acd + cd - abc - bd) - (abc + bc - a - (1))] \tag{22}$$

rearranging:-

$$CD = -1/4[bc + abd + abc + bd - (1) - acd - a - cd] \tag{23}$$

On comparing this with the expression for the main effect of B, equation (21), it is seen that the terms inside the bracket are identical in both cases. Thus equation (21) not only gives an estimate of B, but also of -CD, and hence both the main effect B and the interaction CD contribute to the numerical value of the comparison denoted by equation (21). Now if CD is known to be small or zero, the comparison can be taken solely as a measure of the main effect of A. In a similar way the comparison for A measures A and -ABCD, that for C measures C and -BD, and that for D measures D and -BC. The pairs of effects A, -ABCD; B, -CD; C, -BD; and D, -BC are known as aliases, and the two effects in each group are said to be "equated" to each other. If an experiment were designed in which the main effects were "equated" to high order interactions, it could be safely assumed that the effects estimated by the experiment were entirely due to the main effects of the factors themselves, as the contributions from the high order interactions would be negligible in comparison.

3.5.3. Design of Fractional Factorial Experiments. A fractional factorial experiment can be constructed in a similar way to that used for forming a block in a confounded factorial experiment.

Suppose it is required to investigate four factors, A, B, C and D in eight tests. The full factorial experiment would require 2^4 (i.e. 16) tests and so this design will constitute a half-replicate. Now in the 2^3 experiment involving only the factors A, B and C it is usually reasonable to assume that the interaction ABC would be small, and hence the additional factor D and be "equated" to this interaction, i.e.

$$D = ABC$$

Multiplying both sides of this equation by D, according to the rules of section 3.3.1, will yield

$$D^2 = I = ABCD$$

ABCD is termed the alias sub-group (c.f. the confounded sub-group of section 3.5.2.). The tests to be performed in this particular fraction are obtained by applying the following rules:-

1) The first fraction must contain the control experiment.
2) The tests in the first fraction must be orthogonal to the alias sub-group.
3) The product of any two tests in a fraction is also a test in the same fraction.
4) The tests in any complementary fraction can be obtained by multiplying the tests in the first fraction by any test not yet performed.

By comparison with section 3.3.2. it will be seen that these rules are identical to those for confounding but with the confounded sub-group replaced by.the alias sub-group.

Applying these rules to obtain the half replicate of the 2^4 experiment, the tests to be performed are:-

(1), ab, cd, abcd, ad, bd, ac, bc.

The complementaryfraction may be obtained by multiplying this fraction by a test not yet performed, e.g. 'a' yielding

a, b, acd, bcd, d, abd, c, abc.

These two fractions together form the complete 2^4 factorial experiment, confounded into two blocks of eight tests each, with ABCD confounded between blocks.

3.5.4. <u>Analysis of Fractional Factorial Experiments</u>. Fractional factorial experiments are analysed in the same way as full factorial experiments - i.e. using Yates,' method as described in section 3.6, but with certain slight differences. The tests are arranged in standard order with respect to the number of factors required for the full factorial experiment which would have the same number of tests as the fractional replicate under consideration. Thus for the half replicate of the 2^4 experiment considered, three factors would be required for a full factorial experiment of eight tests, and so the tests are arranged in standard order with respect to any three of the four factors. e.g. A, B and C. The levels of factor D are then inserted to correspond with the levels of A, B and C as used in the tests in the experiment. The responses from each test are then analysed as for a 2^3 factorial experiment, and the total effects, mean effects and mean squares computed. Now in a fractional factorial experiment, each result measures more than one main effect or interaction, and it is necessary to find out which effects are measured by each result.. This is done by multiplying the effect or interaction for the equivalent full factorial experiment by the alias sub-group for the corresponding fractional replicate, the rules of section 3.5.1. being applied. The analysis procedure is illustrated in table 2.

Table 2.

Factors A B C D	Treatment Combination		Effect for 2^3 Expt.	Effects in $1/2 \times 2^4$ Expt
0 0 0 0	(1)	Analysis as for a 2^3 Factorial Experiment	Total (I)	I, ABCD
1 0 0 1	ad		A	A, BCD
0 1 0 1	bd		B	B, ACD
1 1 0 0	ab		AB	AB, CD
0 0 1 1	cd		C	C, ABD
1 0 1 0	ac		AC	AC, BD
0 1 1 0	bc		BC	BC, AD
1 1 1 1	abcd		ABC	ABC, D

Before deciding which effect is actually measured by the results of a fractional factorial experiment, additional information is usually necessary. In the above example, it would be reasonable to assume that the pairs A, BCD; B, ACD; C, ABD; D, ABC; were estimates of the main effects A, B, C and D only, as the three factor interactions are usually negligible. However, it is not so easy to make a decision with the pairs of two-factor interactions AB, CD; AC, BD; BC, AD as in the absence of any other information either, or both, of the interactions could be significant, or alternatively if the estimate of the combined effect was small, the two interactions could be of comparable magnitude but of opposite sign. It must therefore be concluded that, in the absence of any other information, this particular fractional factorial experiment provides estimates of the main effects only, and nothing can be said about the two-factor interactions.

As information regarding the two-factor interactions is lost, no harm would be done by confounding this half replicate into (say) two blocks of four tests each, and using one of the pairs of two-factor interactions to estimate the block difference.

3.5.5. Estimate of Experimental Error in Fractional Factorial Experiments. The object of using fractional factorial experiments is to reduce the number of tests necessary to produce the required information, and one of the consequences of reducing the number of tests in an experiment is that often insufficient high order interactions are available to provide a reliable estimate of the experimental error for the reason outlined in section 3.6.3. This can be overcome by repeating the experiment (which may defeat the object of fractional replication as it may involve the same number of tests as a full factorial experiment) or by using an estimate available from previous work on the system.

3.6. Regression Analysis.

On several occasions during the course of the project it was required to fit a straight line or curve to a series of experimental points. By the use of regression analysis it is possible to fit such a straight line or curve in such a way that it corresponds to the 'best' line through the points. This is done by minimising the squares of the deviations of the points from the line.

3.6.1. Linear Regression. If it is known, or suspected, that a set of experimental points obeys a linear law, then the line of 'best fit' through the points will be given by:-

$$Y = b_o + b_1(x - \bar{x}) \qquad (24)$$

where Y is the dependant variable and x is the independent variable which is assumed to be free from error.

b_o and b_1 are calculated to make the sum of squares of y_i a minimum, where

$$y_i = b_o + b_1(x_i - \bar{x})$$

i.e. $$\sum_{i=1}^{n} (y_i - Y_i)^2 \longrightarrow \text{minimum}$$

For this to be so:-

$$b_o = \frac{\sum y}{n} = \bar{y} \qquad (25)$$

$$b_1 = \frac{\sum xy - \frac{1}{n}\sum x \sum y}{\sum x^2 - {}^1/_n(\sum x)^2} \qquad (26)$$

The derivation of these equations is given in reference(31).

Having obtained values of b_o and b_1 by means of equation (25) and (26) it is necessary to test whether or not they are significantly different from zero, and this is done by means of a t-test.

Now a measure of the 'goodness of fit' of the best straight line is provided by the residual sum of squares, $(^{s}/s)yx$, of y about the regression line.

i.e. $$(^{s}/s)yx = \sum (y - Y)^2 = \sum (y - \bar{y})^2 - \sum (Y - \bar{y})^2 \qquad (27)$$

$$\therefore \begin{Bmatrix}\text{sum of squares of y}\\ \text{about regression line}\end{Bmatrix} = \begin{Bmatrix}\text{sum of squares of y}\\ \text{about mean}\end{Bmatrix} - \begin{Bmatrix}\text{sum of squares}\\ \text{due to regression}\end{Bmatrix}$$

Substituting (25) into (24)

$$Y = \bar{y} + b_1(x - \bar{x}) \qquad (28)$$

$$\therefore \sum (Y - \bar{y})^2 = b_1{}^2 \sum (x - \bar{x})^2$$

and substituting this into (27)

$$\sum (y - Y)^2 = \sum (y - \bar{y})^2 - b_1^2 \sum (x - \bar{x})^2 \qquad (29)$$

Thus the variance about the regression line (s^2_{yx}) is given by

$$s^2_{yx} = \frac{\sum (y - \bar{y})^2 - b_1^2 \sum (x - \bar{x})^2}{n - 2} \qquad (30)$$

(There are n - 2 degrees of freedom as b_o and b_1 represent two relations between the n experimental points, see section 3.2.8.2.)

The variance of b_o is given by

$$s^2_{b_o} = \frac{s^2_{yx}}{n} \qquad (31)$$

Thus $$t_{b_o} = \frac{b_o}{(s_{yx}/\sqrt{n})} \qquad (32)$$

The variance of b_1 is given by

$$s^2_{b_1} = \frac{s^2_{yx}}{\sum(x - \bar{x})^2} \qquad (33)$$

$$\therefore \quad t_{b_1} = \frac{b_1}{s_{yx}/\sqrt{\sum(x - \bar{x})^2}} \qquad (34)$$

3.6.2. Multiple and Polynomial Regression. It is often required to fit a relationship of the form

$$y = a + bx_1 + cx_2 + dx_3 + \ldots \qquad (35)$$

to a set of experimental points. Several situations arise where such a relation can be used, a typical example being the expression for the equilibrium constant, viz:

$$K = \frac{[A]^w \; [B]^x}{[C]^y \; [D]^z} \qquad (36)$$

By taking logs and re-arranging:-

$$y \log [C] + z \log [D] + \log [K] = w \log [A] + x \log [B]$$

or

$$\log [C] = -\frac{1}{y} \log [K] + \frac{w}{y} \log [A] + \frac{x}{y} \log [B] - \frac{z}{y} \log [D] \quad (37$$

This is of the same form as equation (35), with x_1, x_2 and x_3, represented by log [A], log [B] and log [D].

If x_1, x_2, x_3 ... represent different independent variables then the process of fitting the curve is called multiple regression. However, it is also possible for x_1, x_2, x_3 ... to represent a power series of the same independent variable, e.g. the equation (35) would now become

$$Y = a + bx + cx^2 + dx^3 + \ldots \qquad (38)$$

and the curve fitting process is known as polynomial regression.

The method of least squares, outlined in the previous section for the case of a straight line, can be extended to deal with these problems.

Taking equation (35) the least square equations are:

$$\left.\begin{aligned} & b\sum(x_1-\bar{x}_1)^2 + c\sum(x_1-\bar{x}_1)(x_2-\bar{x}_2) + d\sum(x_1-\bar{x}_1)(x_3-\bar{x}_3) + \ldots \\ & \qquad = \sum(x_1-\bar{x}_1)(y-\bar{y}) \\ & b\sum(x_1-\bar{x}_1)(x_2-\bar{x}_2) + c\sum(x_2-\bar{x}_2)^2 + d\sum(x_2-\bar{x}_2)(x_3-\bar{x}_3) + \ldots \\ & \qquad = \sum(x_2-\bar{x}_2)(y-\bar{y}) \\ & b\sum(x_1-\bar{x}_1)(x_3-\bar{x}_3) + c\sum(x_2-\bar{x}_2)(x_3-\bar{x}_3) + d\sum(x_3-\bar{x}_3)^2 + \ldots \\ & \qquad = \sum(x_3-\bar{x}_3)(y-\bar{y}) \end{aligned}\right\} \quad (39)$$

etc.

$$a = \bar{y} - b\bar{x}_1 - c\bar{x}_2 - d\bar{x}_3 \ \ldots \qquad (40)$$

Values of a, b, c, d etc., are obtained by solving these equations.

The derivation of these equations is given in full in reference (32). [The solution of these equations is simplified by using the relation:-

$$\begin{aligned} \sum(x-\bar{x})(y-\bar{y}) &= \sum(xy - \bar{x}y - \bar{y}x + \bar{x}\bar{y}) \\ &= \sum xy - \bar{x}\sum y \qquad (41)] \end{aligned}$$

As for linear regression, the residual sum of squares is given by

(Sum of squares about mean) - (Sum of squares due to regression)

$$= \sum(y-\bar{y})^2 - [b^2\sum(x_1-\bar{x}_1)^2 + c^2\sum(x_2-\bar{x}_2)^2 + d^2\sum(x_3-\bar{x}_3)^2 + \ldots] \quad (42)$$

Now $b = \dfrac{\sum(x_1-\bar{x}_1)(y-\bar{y})}{\sum(x_1-\bar{x}_1)^2}$ for one independent variable (cf eqn.(26)) (43)

$$\therefore \quad b^2\sum(x_1-\bar{x}_1)^2 = b\sum(x_1-\bar{x}_1)(y-\bar{y}) \qquad (44)$$

and similarly for the other terms.

Substituting equation (44) into (42)

$$({}^{s}/{}_{s})_{yx} = \sum(y-\bar{y})^2 - [b\sum(x_1-\bar{x}_1)(y-\bar{y}) + c\sum(x_2-\bar{x}_2)(y-\bar{y}) + ..] \qquad (45)$$

Also, by definition,

$$s^2_{yx} = \frac{({}^{s}/{}_{s})_{yx}}{n - k}$$

where k is the number of coefficients which have been fitted to the data.

The variance of each coefficient, by analogy with linear regression, is given by:-

$$s^2_b = \frac{s^2_{yx}}{\sum(x_1-\bar{x}_1)^2} \qquad (46)$$

$$s^2_c = \frac{s^2_{yx}}{\sum(x_2-\bar{x}_2)^2} \quad \text{etc.} \qquad (47)$$

Each coefficient can then be tested for significance by the t-test.

3.6.3. Polynomial Regression using Orthogonal Polynomials.

Although the method of polynomial regression outlined in section 3.8.2. is useful for comparison with linear regression, the actual computation is simplified by using orthogonal polynomials. This latter method can only be used if the values of the independent variable, x, have equal spacing.

Suppose that there are n points, and the fitted curve is of the form of equation (38) in section 3.8.2., i.e.

$$Y = a + bx + cx^2 + dx^3 + \ldots. \qquad (38)$$

$$\begin{aligned} \text{Let } \phi_o &= 1 & \therefore \sum\phi_o &= n \\ \phi_1 &= x-\bar{x} & \sum\phi_1 &= o \\ \phi_2 &= \phi_1^2-\bar{\phi}_1^2 & \sum\phi_2 &= o \\ \phi_3 &= \phi_1^3-\bar{\phi}_1^3 & \sum\phi_3 &= o \end{aligned}$$

Equation (38) becomes on substitution:

$$Y = b_o + b_1\phi_1 + b_2\phi_2 + b_3\phi_3 + \ldots. \qquad (48)$$

where b_o, b_1, b_2 etc are related to the coefficients a, b, c etc. in equation (38). The equations for b_o, b_1, b_2, etc., obtained by minimising the sum of squares of Y about the fitted line are:-

$$\left.\begin{aligned} b_o\sum\phi_o + b_1\sum\phi_1 + b_2\sum\phi_2 + \ldots. &= \sum\phi_o y \\ b_o\sum\phi_1 + b_1\sum\phi_1^2 + b_2\sum\phi_1\phi_2 + \ldots &= \sum\phi_1 y \\ b_o\sum\phi_2 + b_1\sum\phi_1\phi_2 + b_2\sum\phi_2^2 + \ldots &= \sum\phi_2 y \\ b_o\sum\phi_3 + b_1\sum\phi_1\phi_3 + b_2\sum\phi_2\phi_3 +. &= \sum\phi_3 y \end{aligned}\right\} \qquad (49)$$

Now by adjusting the values of the ϕ's it is possible to make all the cross-products in the above set of equations equal to zero, hence

$$b_o = \frac{\sum\phi_o y}{n} \quad \left(\text{as } \sum\phi_o = n \text{ and } \sum\phi_i = o \text{ for } i \neq o\right)$$

$$b_1 = \frac{\sum\phi_1 y}{\sum\phi_1{}^2}$$

$$b_2 \quad \frac{\sum\phi_2 y}{\sum\phi_2{}^2}$$

etc.

The new values of the ϕ's are given by:-

$$\phi_o = 1$$

$$\phi_1 = \frac{(x-\bar{x})}{(x_{i+1}-x_i)}$$

$$\phi_2 = \phi_1^2 - \phi_1^2$$

$$\phi_{r+1} = \phi_1\phi_r - \frac{r^2(n^2-r^2)\ \phi_{r-1}}{4(4r^2 - 1)} \qquad r \geqslant 2$$

Where n is the number of points for with the orthogonal polynomials are required.

Values of ϕ_r, as whole numbers for convenience, with the appropriate multipliers to convert them to the appropriate values, are tabulated (33). The residual mean squares, and significance of the coefficients are calculated as in section 3.6.2.

4. EXPERIMENTAL INVESTIGATION OF THE RATE OF EXTRACTION OF COPPER FROM MALACHITE

4.1. Introduction.

The aim of the investigation was to determine which variables controlled the rate of extraction of copper from malachite by the combined leaching and solvent extraction process, described in section 2.5; also, if possible to obtain some indication of the mechanism of the process. It was decided to study the effect of varying the quantities which could be most easily and economically controlled on a large scale and to see how they affected the amount of copper which could be extracted from a mineral bed by a given quantity of the organic solvent, and also the rate at which this extraction occurred.

4.2. Model of Extraction Process.

By postulating that the combined leaching and solvent extraction process occurs as illustrated in fig.(3), it is possible to identify seven separate stages, each of which could control the rate of the overall extraction process. These stages are:-

(i) Transport of the naphthenic acid to the aqueous-organic interface.

(ii) Transfer of acid across the aqueous-organic interface.

(iii) Transport of hydrogen ions to the mineral surface.

(iv) Leaching reaction at the mineral surface.

(v) Transport of copper ions to the aqueous-organic interface.

(vi) Transfer of copper ions across the aqueous-organic interface.

(vii) Transport of copper to the bulk of the organic phase.

4.2.1. *Analysis of Rate-Controlling Stages.* By considering in turn the effect on the process if each of the seven stages listed in section 4.2. were rate-controlling, it is possible to determine which are the variables that ought to be studied.

4.2.1.1. *Transport in the Organic Phase is Rate Controlling.* It is possible that if the process is controlled by the rate of transfer of naphthenic acid to the aqueous-organic interface, the rate of transfer of copper naphthenate from the interface to the bulk of the organic phase will also tend to be slow. Hence stages (i) and (vii) of section 4.2. could both be rate-controlling. In this case, the concentration profiles would appear as in fig.(7). If these stages are rate-controlling, they will be affected by the movement of the organic phase relative to the aqueous phase, and also by the naphthenic acid concentration in the organic phase. Equilibrium will exist between the malachite and aqueous leaching solution, and also between the layers of organic and aqueous solutions immediately adjacent to the organic-aqueous interface.

4.2.1.2. *Transfer across the Aqueous-Organic Interface is Rate Controlling.* The transfer of ions across the aqueous-organic interface occurs according to equation (2) in section 2.5:-

$$CuSO_{4(aq)} + 2HR_{(org)} \longrightarrow CuR_{2(aq)} + H_2SO_{4(org)} \qquad (2)$$

For the case of copper being extracted into naphthenic acid, it has been shown(23) that the actual reaction is:

$$2Cu^{++}_{(aq)} + 3(HR)_{2(org)} \longrightarrow 2CuR_2.HR_{(org)} + 4H^{+}_{(aq)} \qquad (50)$$

Reaction (50) controls the transfer of copper across the aqueous-organic interface and also the regeneration of hydrogen ions. Stages (ii) and (vi) in section 4.2. are thus represented by this reaction, and the case where this is the rate-controlling stage is illustrated in terms of the relavent concentration profiles in fig. (8). Equilibrium exists at the mineral-aqueous boundary, but not at the aqueous-organic interface. Such a situation would be revealed by a high copper concentration and by a low acid concentration in the aqueous layer on the mineral; hence it would be desirable to have an estimate of these quantities and their variation during the course of a leaching experiment. Increasing the rate of removal of the extracted copper by increasing the movement of the organic phase relative to the aqueous phase might speed up the reaction and increasing the naphthenic acid concentration might also increase the rate of reaction. By increasing the pH of the aqueous phase, the transfer of acid from the organic phase is favoured, by consideration of equation (50) and also for the reasons given in section 2.4.1.

4.2.1.3. Transfer Across Aqueous Layer is Rate-Controlling. As the diffusion coefficients of hydrogen and copper ions are approximately the same, both stages (iii) and (iv) of section 4.2. are liable to control the process, and the concentration profiles will be as in fig. (9). By varying the thickness of the aqueous layer, it would be possible to determine whether these stages are rate controlling. Equilibrium exists at the solid-aqueous boundary and also between the organic and aqueous layers immediately adjacent to the organic-aqueous interface.

CONCENTRATION PROFILES

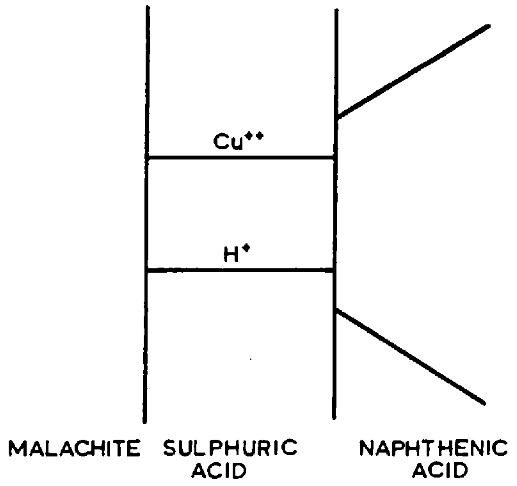


Fig. 7 TRANSPORT IN ORGANIC PHASE RATE-CONTROLLING

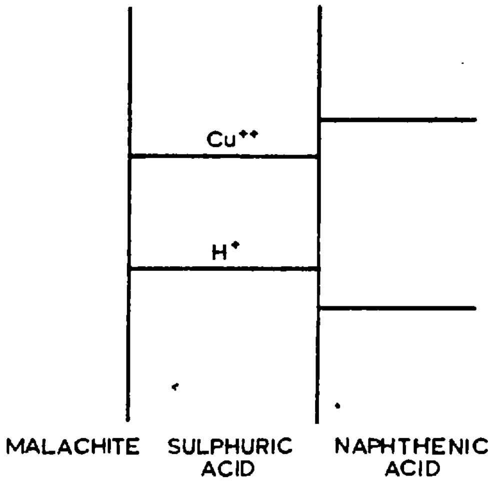


Fig. 8 TRANSFER ACROSS AQUEOUS–ORGANIC INTERFACE RATE-CONTROLLING

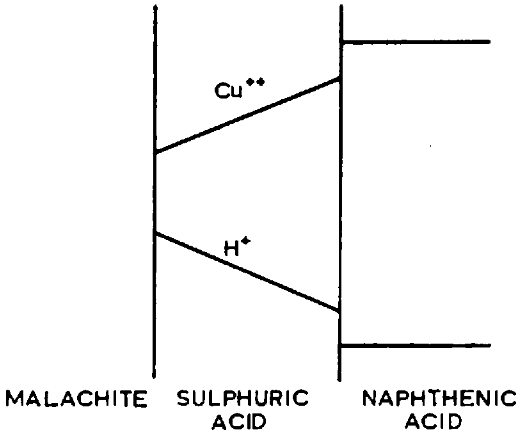


Fig. 9 TRANSPORT ACROSS AQUEOUS LAYER RATE-CONTROLLING

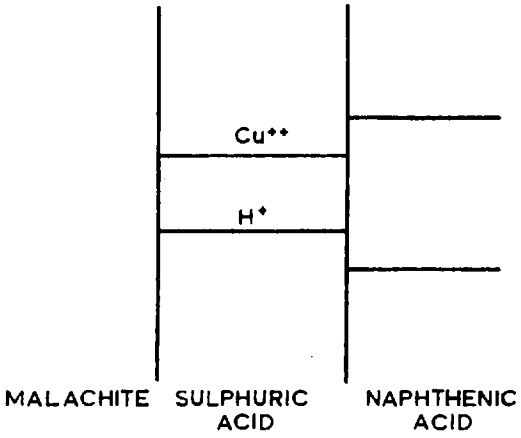


Fig. 10 DISSOLUTION OF MALACHITE RATE-CONTROLLING

4.2.1.4. Leaching Reaction is Rate-Controlling. If the leaching reaction at the malachite surface is controlling the rate of extraction, the rate might vary with the acid concentration of the leaching solution. The concentration profiles for this situation are shown in fig.(10). Equilibrium exists between the aqueous and organic solutions, but not between the aqueous solution and the solid.

4.3. Variables Investigated.

From the preceding section, the most important variables which are liable to have any influence on the process are (i) the acid concentration of the aqueous phase, (ii) the thickness of the aqueous layer on the mineral particles, (iii) the movement of the organic phase relative to the mineral and (iv) the naphthenic acid concentration of the organic phase. The rates of all the seven stages listed in section 4.2 are all dependent on surface area, and as the total surface area depends on the particle size of the mineral, this variable should also be included. It was considered that these variables could best be investigated by packing the mineral into a column, and allowing the naphthenic acid solution to percolate through the mineral bed. The five variables (or factors), each investigated at two levels would constitute a 2^5 factorial experiment involving 32 separate tests.

4.4. Design of Experiment.

4.4.1. Notation.

The five factors involved in the investigation were denoted by the following letters:-

M, particle size of mineral.
P, sulphuric acid concentration of aqueous leaching phase.
A, thickness of aqueous leaching layer.

F, flow-rate of organic phase through mineral bed.

C, naphthenic acid concentration of organic phase.

4.4.2. Levels of Factors. The levels at which the factors were investigated are given in table 3.

Table 3.

FACTOR	LOW LEVEL	HIGH LEVEL
Particle size (Tyler mesh)	-200+270	-100+150
$[H_2SO_4]_{aq}$ (moles/l)	10^{-5}	10^{-3}
Aqueous layer thickness (μ)	2.0	6.0
Flow rate (ml/min)	1.0	5.0
Naphthenic acid conc. (moles/l)	0.1	0.5

The lower level of particle size was fixed by the size fraction which could be reliably sectioned by screening, and -200+270# corresponded to a mean particle diameter of 63μ. The -100+150# fraction corresponds to a mean particle diameter of 126μ. The sulphuric acid concentrations are at each end of the pH range where it may be expected that the mineral will be leached and the copper extracted into the organic phase.

The thickness of the aqueous layer is determined to a certain extent by the amount of moisture which can be accommodated on the mineral bed before it is displaced by the motion of the organic phase, and also by the smallest amount of moisture which can be employed to guarantee that all of the particles are moistened by the solution. Preliminary experiments had shown that aqueous layers of thickness 2.0μ and 6.0μ fulfilled these conditions. The actual quantity of leach solution used for each level of both particle size and aqueous layer thickness is calculated as in Appendix B1 and the results are summarised in table 4.

Table 4.

LEVEL OF FACTOR M	LEVEL OF FACTOR A	WT.% LEACH SOLUTION REQUIRED
0	0	7.74
1	0	3.75
0	1	26.04
1	1	11.95

The levels of the flow-rate of the organic phase were determined by both the lowest flow-rate through a bed of large particles and the highest flow-rate through a bed of small particles which could be controlled within the confines of the apparatus.

The naphthenic acid concentrations were chosen to give reasonable rates of extraction (over a period of 50 - 100 hours) and low solvent loadings, to prevent the possibility of a change in the rate-controlling stage of the process during the course of a test.

4.4.3. Design Procedure. The five factors, each investigated at two levels, constituted a 2^5 experiment, i.e. 32 tests in the full factorial experiment. The tests were performed eight at a time, and so the experiment was confounded into four blocks of eight tests each. In this case, it was not considered satisfactory to perform a half-replicate, as it would not have been possible to obtain a valid estimate of the experimental error from the sixteen tests, and also because some information would have been lost through confusion of two- and three-factor interactions.

4.4.3.1. Choice of the Confounded Sub-Group. A preliminary small scale factorial experiment had shown that the interaction AP (thickness and sulphuric acid concentration of the aqueous layer) was zero, and so this was an obvious choice as one member of the confounded sub-group. Another interaction which was liable to have no physical significance was the five-factor interaction MPAFC; thus if AP and MPAFC are confounded their product, MFC, is also confounded (see section 3.3.2.). Hence the confounded sub-group is

$$I = AP = MFC = MPAFC.$$

This arrangement yields all the main effects and two-factor interactions (which the exception of AP) clear of block effects, and allows an estimate of the experimental error to be obtained from the nine remaining 3-factor interactions and the five 4-factor interactions.

Applying the rules of confounding, as in section 3.3.2., the tests in each block are:-

Block (1)	(1)	pa	mf	mc	mpaf	mpac	fc	pafc
Block (2)	ac	pc	mafc	ma	mpfc	mp	af	pf
Block (3)	a	p	maf	mac	mpf	mpc	afc	pfc
Block (4)	m	mpa	f	c	paf	pac	mfc	mpafc

4.5. Analysis of the Organic Samples for Copper.

The green colour of copper naphthenate is ideally suited to colorimetric analysis, and use was made of this fact in analysing the organic solutions for copper. The optical density was determined by means of a Unicam SP500 Spectrophotometer, using 1 cm.cells, and a blank of 0.3M naphthenic acid in paraffin. Fig.(11) shows the variation of optical density with wavelength, from which it is seen that the optical density is virtually constant in the range 675-685 mμ. This value of the wavelength for the maximum optical density is in good agreement with that obtained by Flett(22). All samples were subsequently analysed at 680mμ. To obtain the variation of optical

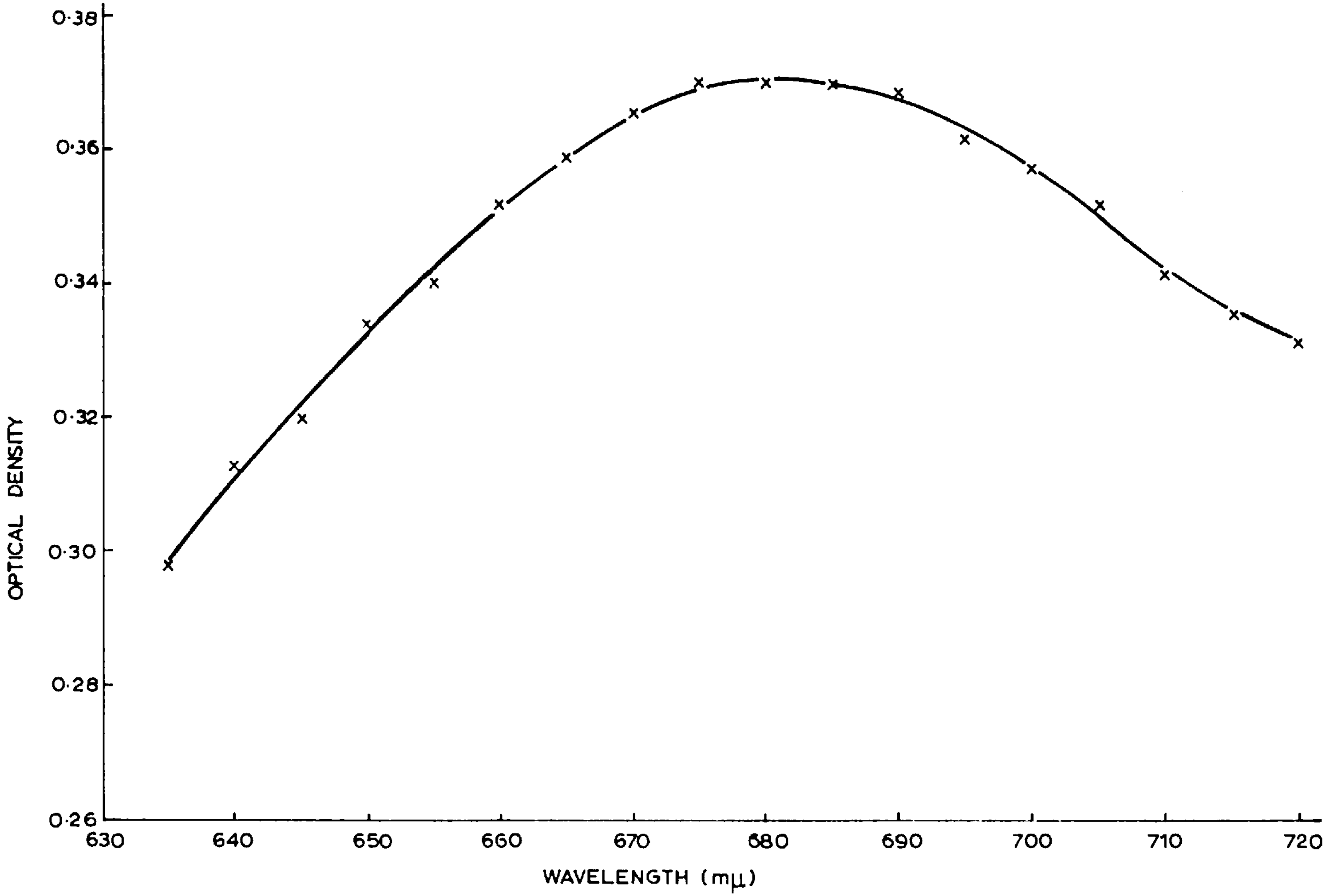


Fig 11 VARIATION OF OPTICAL DENSITY OF COPPER NAPHTHENATE WITH WAVELENGTH

density with copper concentration, aqueous solutions of known concentrations of copper sulphate were prepared, and the pH raised to about 9.0 by the addition of ammonium hydroxide, the copper was then extracted into naphthenic acid solutions (virtually 100% extraction is achieved at this pH)(20) and the resulting solutions analysed spectrophotometrically. Fig.(12) shows the variation of optical density with copper concentration, and the best straight line through these points was found by the method of least squares (section 3.6.1.) to be:-

$$Y = 6.20 \times O.D. - 0.108 \qquad (51)$$

where Y is the copper concentration in m.moles/l of the naphthenic acid. Details of the calculation are given in Appendix B2.

When using this method of analysis, some difficulty was initially experienced in obtaining reproducibe results. This was found to be due to the liquid creeping over the top of the cell and running down the sides, thus causing reflections within the cell giving false readings for the optical density. This was eventually overcome by keeping the cells well stoppered and automatically filling and emptying the sample cell by means of the 'Autocell' attachment for the SP500, which also obviated any need to handle the cells during the analysis. During the investigation into the poor reproducibility of the optical density measurements, the following variables were investigated but found to be without effect: moisture content of organic solution, temperature, carbon dioxide content of organic solution and the type of solvent used for naphthenic acid. As the naphthenic acid solutions were stored over water, it was found necessary to clarify the naphthenic acid solution (used for diluting the more

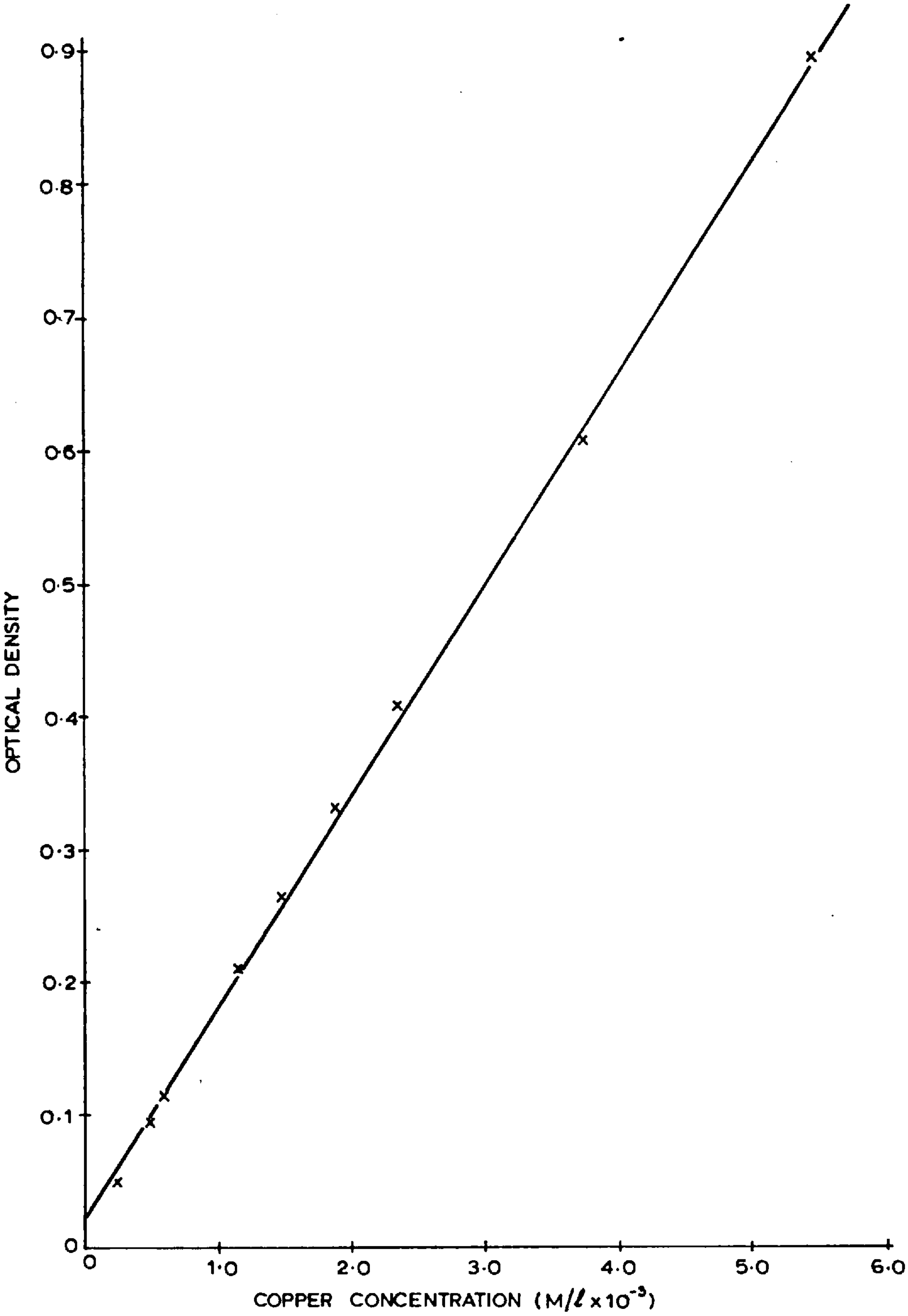


Fig. 12 VARIATION OF OPTICAL DENSITY WITH COPPER CONCENTRATION

concentrated copper solutions) from small particles of suspended matter which originated at the aqueous-organic interface in the storage vessels.

4.6. Measurements of pH and Copper Concentration of Aqueous Phase.

Examination of the model of the simultaneous leaching and solvent extraction process, as in section 4.2., indicates that it is desirable to have some information about the pH and copper content of the aqueous phase, in order to help the prediction of a rate controlling stage. As only small quantities of the aqueous phase were present and in the form of a thin layer it was decided to attempt to determine pH and copper concentration electrochemically.

4.6.1. pH Measurement of the Aquoous Phase. As it is possible to measure the pH of moist soils by inserting a glass electrode and a reference electrode into the soil, and measuring the resulting E.M.F. on a valve voltmeter, it was decided to attempt to use this technique for measuring the pH of the aqueous layer on the mineral bed. Experiments using a spear-type glass electrode and a saturated calomel electrode, inserted into a bed of silver sand covered with a buffer solution of mean thickness 2.0µ (the lowest lever of factor A (section 4.4.2.)) indicated that steady, reproducible readings could be obtained, within ± 0.1 pH units of the nominal pH of the buffer solution. These readings were unchanged when naphthenic acid in paraffin was percolated through the bed.

In practice it was found that the organic solution tended to work its way into the interior of the calomel electrode, giving unsteady readings. This was overcome by replacing the saturated calomel electrode by a silver-silver chloride electrode, and adding a small quantity of chloride ions to the aqueous solution used.

4.6.2. Measurement of the Copper Concentration of the Aqueous Phase. It was found possible to obtain an estimate of the copper concentration of the aqueous phase on the mineral bed by using a copper electrode in conjunction with a silver-silver chloride electrode and measuring the resultant E.M.F. on a valve voltmeter. This system made it necessary to add some chloride ions to the aqueous phase, in order that the silver-silver chloride electrode could function. The electrode system was calibrated by measuring the E.M.F. of the cell with several solutions of different concentrations of copper sulphate, but each 10^{-2}M in potassium chloride. The relation between the E.M.F. of the cell (E) in mV, and copper concentration is given by:-

$$E = 48.41 - 11.01 \log_{10} [Cu^{++}] \qquad (52)$$

The copper electrode was of positive polarity. The comparison between the experimental points and those predicted by theory (as calculated in Appendix B3) is given in Fig.(13) and in view of the approximations in the calculated values the agreement is regarded as satisfactory.

4.6.3. Preparation of Silver-Silver Chloride Electrodes. The silver-silver chloride electrodes, consisting of pieces of 1/16" diameter silver rod sealed into pieces of glass tube, were cleaned by allowing them to stand overnight in 0.880 ammonia. They were then anodised in a solution of 0.1M hydrochloric acid for 30 minutes, using a current of 1 to 2 mA and a platinum electrode as the cathode. After anodising they were rinsed with distilled water, washed with acetone and allowed to dry in air and were used without further storage.

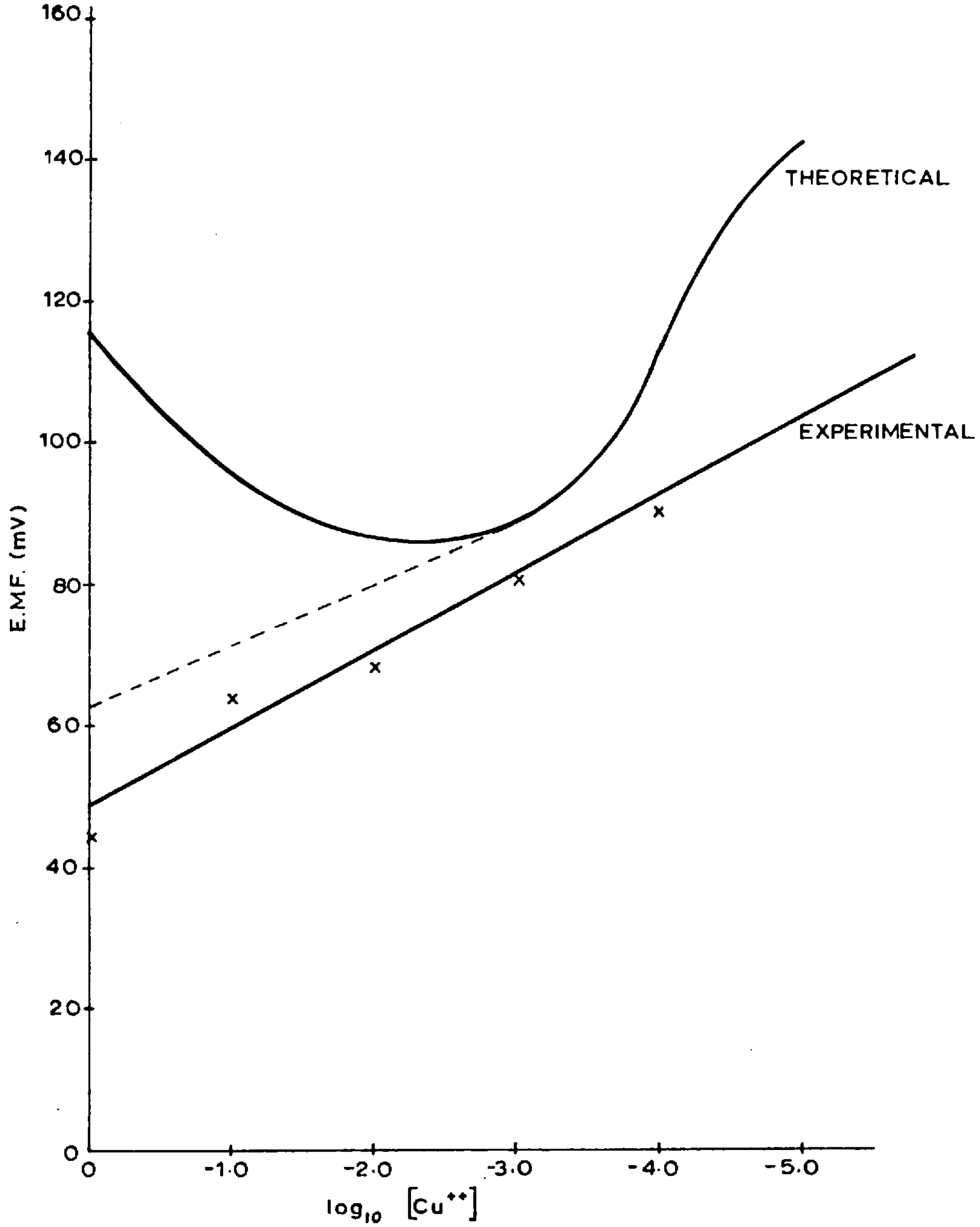


Fig. 13 VARIATION OF E.M.F. WITH COPPER CONCENTRATION FOR COPPER/SILVER-SILVER CHLORIDE ELECTRODE SYSTEM

4.6.4. Preparation of Copper Electrodes. The copper electrodes, consisting of pieces of 1/16" diameter copper wire, were prepared by making them the cathode in an electrolysis bath containing dilute sulphuric acid, using a platinum electrode as the anode. A current of about 1 mA was passed until the surface of the copper became pink in colour. The electrodes were stored in dilute sulphuric acid until they were required.

4.6.5. Behaviour of Electrodes in Practice. When the electrode systems described in sections 4.6.1. and 4.6.2. were used in a leaching test, it was found that the readings became unsteady, with violent fluctuations, after about 30 - 36 hours. This was eventually traced to the fact that the moisture on the mineral bed had disappeared and a conducting path between the electrodes no longer existed. This was discovered by inserting two small grids, about 1/4" sq. of 100# stainless steel gauze, into the mineral bed, one near the top and the other near the bottom. A potential of about 50 V was applied between these two grids for an instant, and the current passing measured on a micro-ammeter. It was found that no current passed when the electrodes began to give fluctuating readings, thus indicating that a conducting path no longer existed and that the mineral bed had dried out. This was overcome by the methods described in the following section.

4.7. Description of Apparatus Used in Leaching Tests.

The apparatus used for measuring the rate of extraction of copper from the synthetic malachite ore is illustrated in Figs.(14) and (15). Basically it consisted of a cylindrical glass column, 2' tall and 3/4" I.D.. At a distance 1.1/2" from the base of the column were three side-arms on a 120° pitch, two inclined upwards at 45° and the third

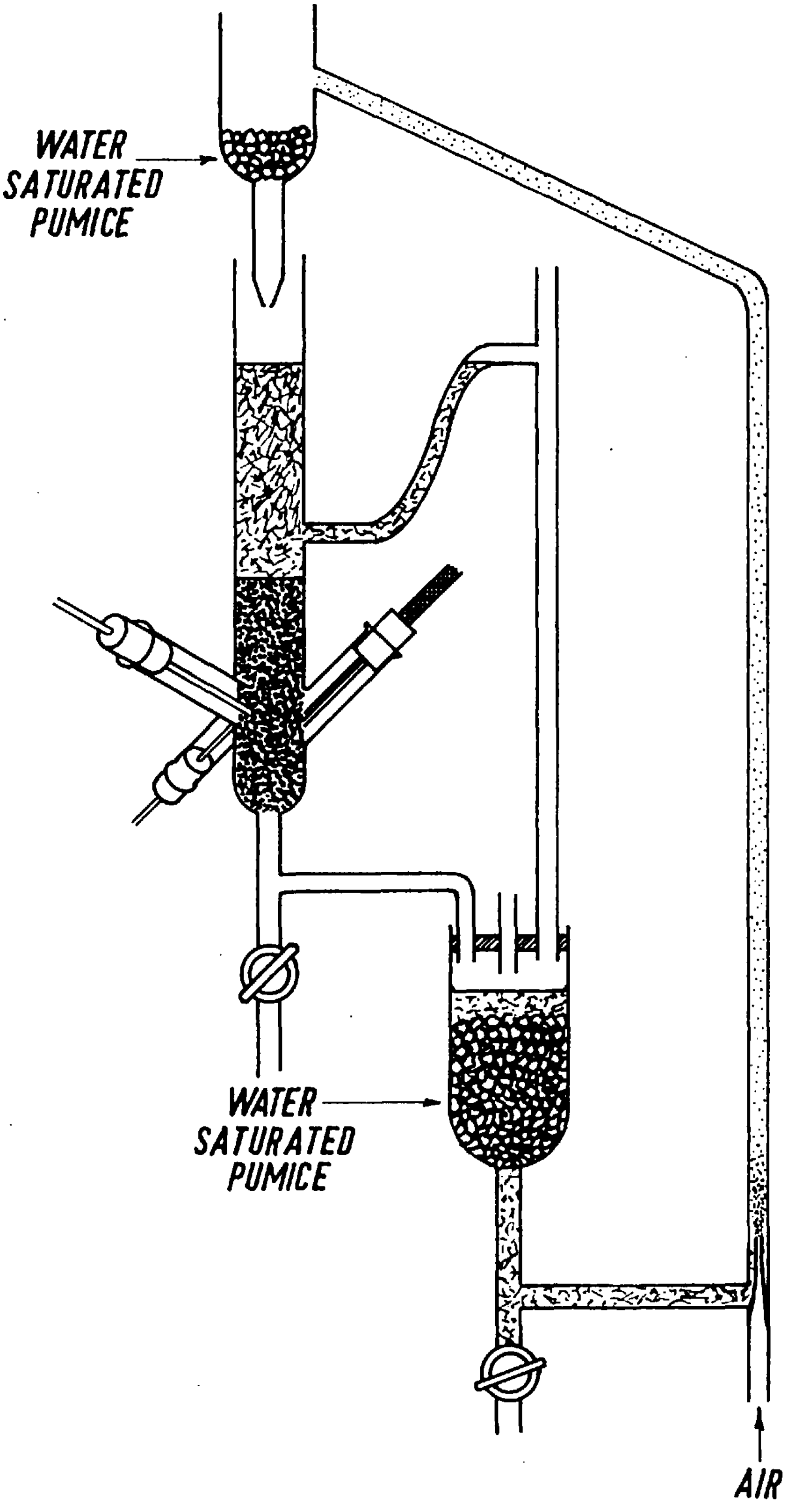


Fig.14 APPARATUS USED FOR EXTRACTION EXPERIMENTS

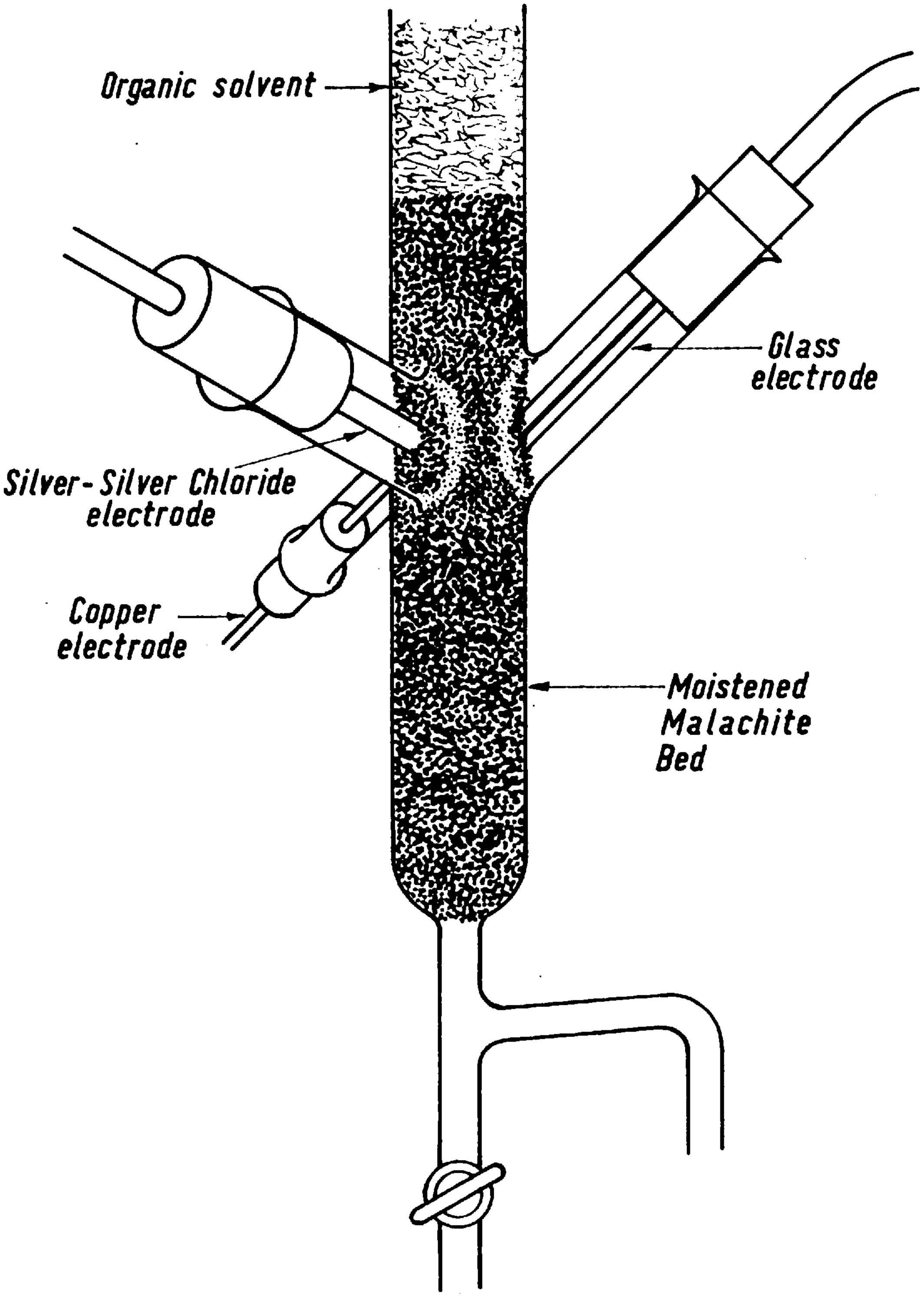


Fig. 15 DETAILS OF ELECTRODE ARRANGEMENT ON EXTRACTION APPARATUS

inclined downwards at 45°, carrying the three monitoring electrodes (see section 4,6.). The head of solvent above the bed was controlled by means of a 'jack-leg' arrangement and the overflow outlet placed 6" from the base of the column. At the base of the column was a tap, which enabled the flow-rate of solvent through the bed to be measured.

The solvent, after passing either through the bed or the overflow, passed to a capacity vessel 12" high and 1" I.D., packed with water-saturated pumice, (to keep the organic solvent saturated with water and thus prevent it absorbing moisture from the mineral bed). From the capacity vessel, the solvent was circulated by means of an air-lift to the top of the column. The air used in the air-lift was supplied by a small reciprocating compressor and was first passed through two large vessels, one containing water and the other containing paraffin, in order to reduce the evaporation losses of the solvent from the column. Evaporation losses from the column were minimised by plugging all openings to the atmosphere with paper tissue.

Eight of these columns were operated simultaneously, the air for each air-lift being obtained from a common line supplied by the compressor. The silver-silver chloride electrodes were connected to a common unshielded line which was in turn connected to the reference terminal (for pH) or negative terminal (for the aqueous copper concentration) of a Pye Universal pH meter. The glass electrodes were connected singly to the pH meter by means of a co-axial wander lead. The copper electrodes were singly connected to the positive terminal of the pH meter, via an unshielded line.

4.8. Description of Malachite Used in Leaching Tests.

The malachite used in the leaching tests originated from Northern Rhodesia, and was obtained as a 2 lb. lump. The lump contained regions of brown and black material intermixed with the predominating green area of malachite. Several preliminary tests were carried out, as described in the following sections.

4.8.1. Acid Soluble Copper-Content. This was measured by dissolving samples (obtained by riffling) of the ground mineral in sulphuric acid. The copper content of the solution was determined volumetrically by titrating the iodine liberated by the copper from potassium iodide with sodium thiosulphate. By this method, the acid soluble copper content was found to be 42.6% corresponding to a malachite content of 76.9% based on the formula $CuCO_3Cu(OH)_2$. Details of the calculation are given in Appendix B4.

4.8.2. Carbon Dioxide Content. An estimate of the malachite content can be made by determining the carbon dioxide content of the mineral. This was done by dissolving a sample of the mineral in sulphuric acid, and passing the gases evolved through a standardised solution of caustic potash, which was then back-titrated to yield results which corresponded to a malachite content, (between 25% and 30%) based on the formula $CuCO_3Cu(OH)_2$. (Appendix B5).

4.8.3. Examination of the Mineral by Electron Probe Micro-Analysis. A polished section from the original lump of malachite was examined by electron probe micro-analysis by Dr. J. Gravilovic of the Mineral Technology Department, Imperial College. The sample was shown to consist mainly of malachite, but interspersed with grains (approximately 2µ across) of silica and a copper silicate, which was thought to be chrysocolla, $CuSiO_3.xH_2O$. An electron micrograph of the sample is shown in fig.(16).

4.9. Preparation of Samples.

Mixtures of 97.5% silver sand and 2.5% malachite were used in the leaching experiments. Each component of the mixture was wet-ground in a rod mill and the iron removed from the malachite by washing well with water, and from the silver sand by dissolving it in concentrated hydrochloric acid. After washing well with water, each component was wet-screened to obtain the required size fractions and the fractions dried in an oven. Appropriate proportions of silver sand and malachite were mixed by the method of rolling, described by Taggart(34).

4.10. Preparation of Solutions.

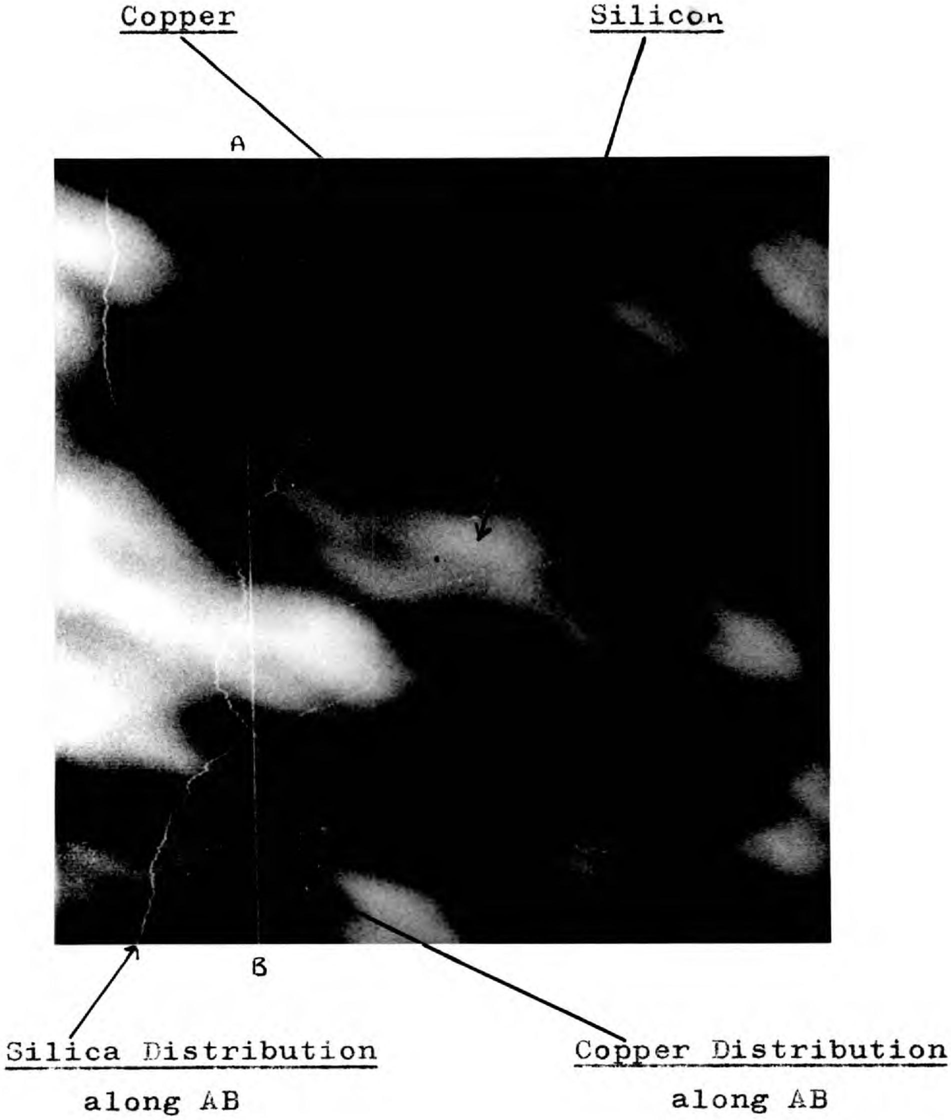
4.10.1. Aqueous Leaching Solutions.

Solutions of 10^{-3}M and 10^{-5}M sulphuric acid were prepared by dilution from a stock solution of sulphuric acid, standardised by titration against potassium hydroxide solution. The pH of the diluted sulphuric acid solutions were recorded. The leaching solutions were made 10^{-2}M with respect to potassium chloride to enable the silver-silver chloride electrodes to be used.

4.10.2. Naphthenic Acid Solutions.

The naphthenic acid solutions used in the leaching experiments were prepared by diluting the naphthenic acid with paraffin. Commercial paraffin was used and was freed from surface-active impurities by allowing it to percolate through a column of chromatograph-grade aluminium oxide. The purified paraffin was then saturated with water by percolation through a bed of aluminium oxide soaked with distilled water. It was stored over water.

The naphthenic acid used in the experiments had a mean molecular weight of 288 and was of approximately unit



Magnification 4400X

Fig.16. Electron Micrograph of Malachite Sample.

density. The solutions were prepared by diluting the required volume with the water saturated paraffin. All the naphthenic acid solutions were stored over water. This was necessary to prevent the organic solutions from absorbing water from the mineral bed and causing the extraction process to stop, as well as having an adverse effect on the behaviour of the electrodes inserted into the bed (section 4.6.5.).

4.11. Procedure for a Leaching Test.

About 30g. of the mixed ore of the appropriate size fraction were carefully weighed out, and mixed with the amount of the leach solution required by that particular test (see Table 4); the ore being moistened by stirring the leach solution into the ore in a beaker. The moistened ore was then packed into the column (described in section 4.7.) on top of a glass-wool plug and gently tamped down to from a firm bed. The electrodes were inserted into their respective side-arms and the column connected into the remainder of the circulating apparatus.

Paraffin, saturated with water, was circulated round the apparatus for approximately 24 hours to enable the bed to settle to its most stable arrangement, while the flow-rate was maintained some 50% higher than that to be used in the test. When the paraffin had been circulated for a sufficient length of time, the apparatus was drained and 250 ml of naphthenic acid in paraffin of the required strength poured into the column and the flow-rate reduced to the required value by adjusting the head of liquid above the bed. Approximately 20 samples of the organic phase were withdrawn from the apparatus over a period of 100 hours (50 hours when the more concentrated naphthenic acid solutions were used) and analysed spectrophotometrically for copper (see section 4.5.). After analysis, the organic solutions were returned to the column. At the same time as the organic samples were withdrawn, the flow-rate of the organic phase through the bed was checked, and the readings of the glass/silver-silver chloride and copper/silver-silver chloride electrode systems were noted.

4.12. Results of Leaching Experiments.

The variation with time of the organic phase copper concentration, pH and aqueous copper concentration of a typical experiment are plotted in figs.(17) and (18). The readings from the experiments are tabulated in Appendix A1.

4.13. Interpretation of the Results.

4.13.1. Copper Concentration of the Organic Phase as a Function of Time.

It was considered likely that the overall rate of extraction of copper from the ore would obey first-order kinetics, and hence the copper concentration, C, of the organic phase after a time of extraction, t, could be expressed by the equation

$$dC/dt = k(C_f - C) \qquad (52)$$

where C_f is the organic phase copper concentration at infinite time and k is the first-order rate constant.

On integration, and inserting the boundary condition that C=0 at t=0, equation (52) becomes:-

$$C = C_f\ [1 - \exp(-kt)] \qquad (53)$$

It is not possible to convert equation (53) to a straight-line form to estimate the values of C_f and k, and hence the equation was fitted to the experimental points by computer. The 'best' values of C_f and k were determined by minimizing the function

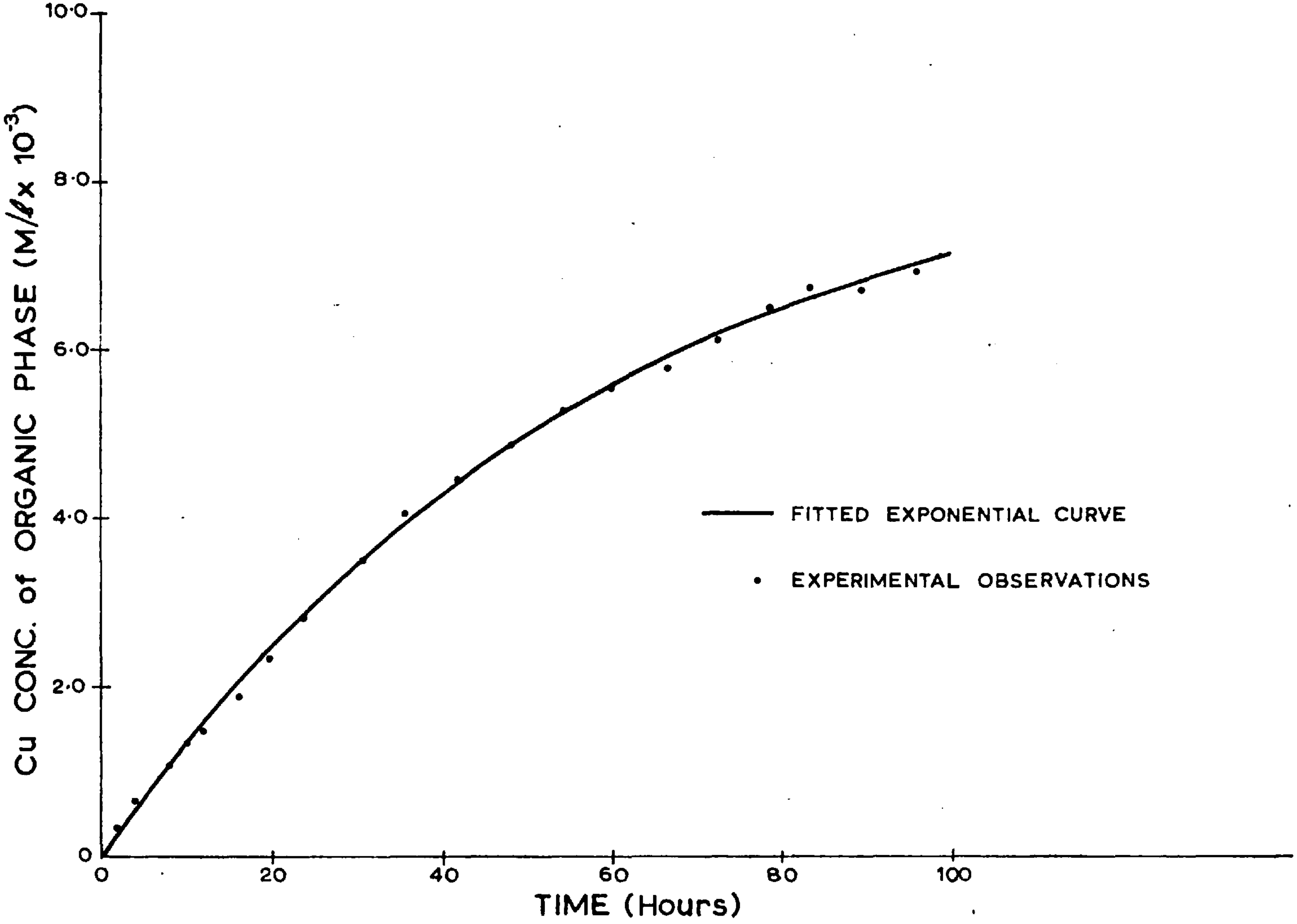


Fig. 17 VARIATION OF ORGANIC PHASE COPPER CONCENTRATION WITH TIME IN A TYPICAL EXTRACTION EXPERIMENT

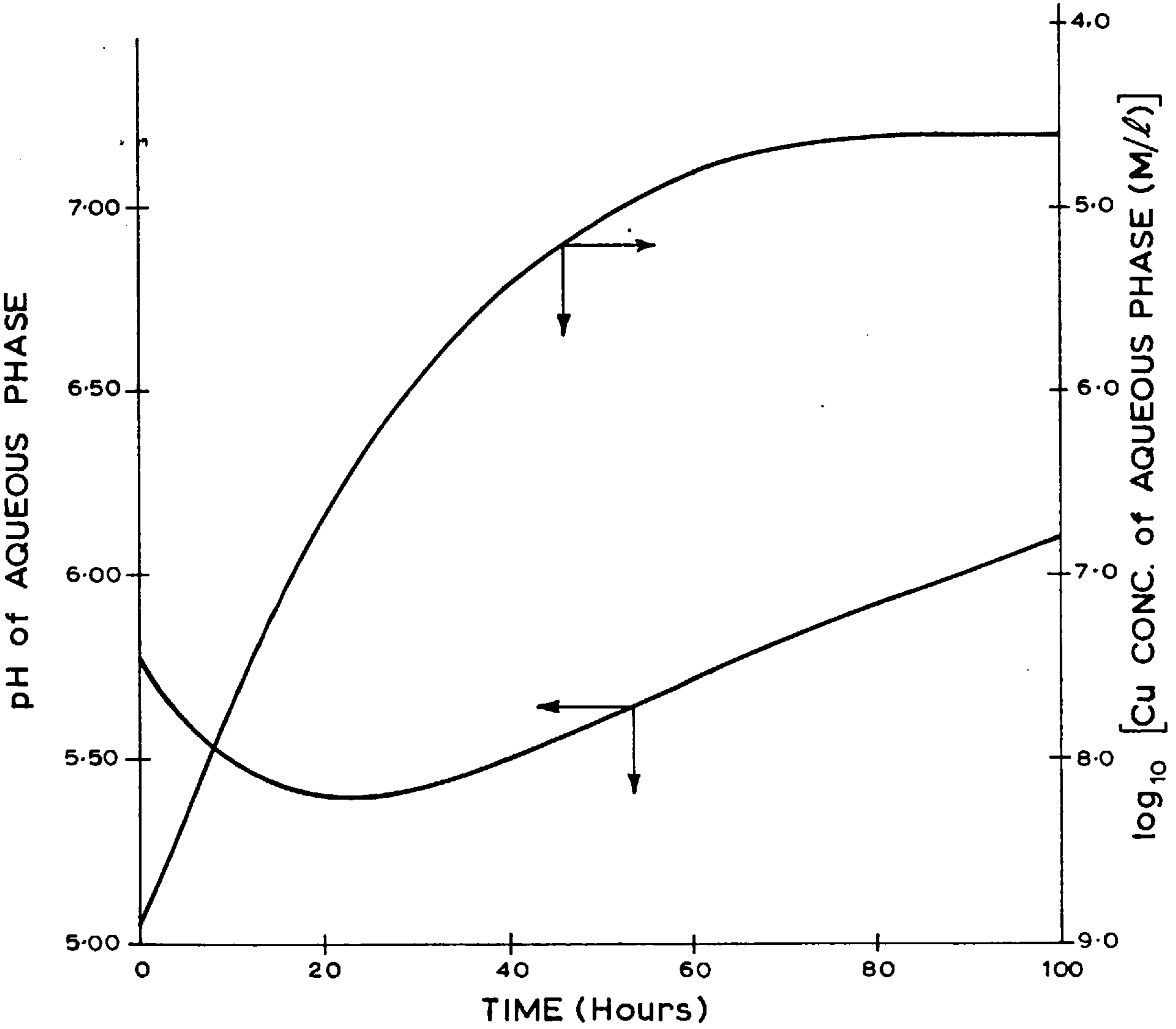


Fig. 18 VARIATION OF pH AND COPPER CONCENTRATION OF AN AQUEOUS PHASE IN A TYPICAL EXTRACTION EXPERIMENT

$$f(C) = \sum_{i=1}^{n} \left\{ C_i - C_f[1-\exp(-kt_i)] \right\}^2 \qquad (54)$$

where n is the number of corresponding values of C_i and t_i, C_i is the organic phase copper concentration at time t_i.

This was done on the University of London computer 'Mercury' (which was later superseded by 'Atlas'), making use of the Library Routine R970 for the minimisation of a function of n variables by a method of steepest descent. The values of each of the n variables which make the function a minimum, together with the minimum value of the function can be determined by this routine. The programme was written in such a way that it would stop if (a) successive values of f(C) differed by less than a factor of 10^{-4} times the current value of f(C), or (b) after twelve successive improvements of the values of C_f and k. This latter precaution was necessary, as in a few cases an exponential curve of the form shown in equation (53) did not accurately represent the data.

Fig.(17) shows the comparison between a typical set of experimental points, and the exponential curve, fitted as outlined above.

4.13.2. <u>Statistical Analysis of the Experimental Values Values of C_f and k.</u> The values of C_f and k, obtained by the method described in section 4.13.1. and tabulated in Appendix A2 were analysed statistically as the responses of a 2^5 factorial experiment, using the method illustrated in section 3.4. The results are summarised in tables 5 and 6, with the values for the limiting organic phase copper concentration being expressed in terms of the optical densities of the solutions. (They can be converted to copper concentrations by means of equation (51).)

From table 5 it can be seen that only two of the factors investigated, i.e. the particle size of the mineral and the naphthenic acid concentration, have any effect on the limiting copper concentration in the organic phase which increases with decreasing particle size and increasing naphthenic acid concentration.

Table 5.

Summary of Analysis of Variance of C_f

Source of Variance	Degrees of Freedom	Mean Effect	Mean Square Effect	F-Ratio
Particle size om mineral (M)	1	-0.4189	1.4039	5.83
Sulphuric acid concentration of aquaous phase (P)	1	0.1451	0.1684	0.702
Thickness of aqueous layer (A)	1	0.2510	0.5039	2.09
Flow-rate of organic phase (F)	1	-0.0036	0.0001	0.00
Naphthenic acid concentration (C)	1	1.0132	8.2128	34.2
Error (from 3- and 4-factor interactions)	14	-	0.2403	1.00

For significance at the 10% level F = 3.10; at the 5% level F = 4.60 at the 1% level F = 8.86.

Table 6 shows that the rate constant is also influenced by the particle size of the mineral and the naphthenic acid concentration, in the same way as the limiting organic phase copper concentration.

The detailed calculation of tables 5 and 6 is given in Appendices B7 and B8.

Table 6.

Summary of Analysis of Variance of the Rate Constant k.

Source of Variance	Degrees of Freedom	Mean Effect	Mean Square Effect	F-Ratio
Particle size of mineral (M)	1	-1.0014	8.0231	4.38
Sulphuric acid concentration of aqueous phase (P)	1	-0.1362	0.1485	0.081
Thickness of aqueous layer (A)	1	-0.4989	1.9915	1.09
Flow-rate of organic phase (F)	1	-0.2085	0.3478	0.186
Naphthenic acid concentration (C)	1	1.8984	28.8327	15.3
Error (from 3- and 4-factor interactions)	14	-	1.8580	1.00

For significance at the 10% level, F = 3.10; at the 5% level F = 4.60; at the 1% level F = 8.86.

As only two effects are significant, in each case the 2^5 factorial experiment reduces to a 2^2 factorial experiment in the factors M and C, replicated eight times. The mean values of C_f and k obtained from the experiment, together with their 95% confidence limits as calculated in Appendix B9, are shown in table 7.

Table 7.

Naphthenic Acid Conc. (M/l)	Limiting Organic Phase Cu Conc ($M/l \times 10^{-3}$)		Rate Constant ($hr^{-1} \times 10^{-2}$)	
	Particle Size		Particle Size	
	-200+270#	-100+150#	-200+270#	-100+150#
0.1	10.76±1.31	8.60±2.56	2.03±0.691	1.27±0.292
0.5	17.13±2.46	14.45±3.91	4.25±1.81	2.93±0.884

4.13.3 Correlation Between the Copper Concentration in the Aqueous and Organic Phases and pH at the End of an Extraction Test. One stage of the model of the extraction process, postulated in section 4.2, consists of the exchange of hydrogen and copper ions between the aqueous and organic phases, as represented by equation (50).

$$2Cu^{++}_{(aq)} + 3(HR)_{2(org)} \longrightarrow 2Cu\ R_2\ HR_{(org)} + 4H^{+}_{(aq)} \qquad (50)$$

If the end of the extraction process corresponds to an equilibrium state between the aqueous and organic phases, then a correlation will exist between the copper concentration in the aqueous phase, the copper concentration in the organic phase and the pH of the aqueous phase. If this is the case, then these quantities could be correlated by an equation of the form:-

$$K' = \frac{[CuR_2.HR]^p[H^+]^q}{[Cu^{++}_{(aq)}]^r} \qquad (55)$$

K' will depend on the naphthenic acid concentration (which remained virtually constant over the course of a test). Equation (55) can be rewritten in the form:-

$$\log[CuR_2.HR] = \log K + b \log[H^+] + c \log[Cu^{++}_{(aq)}] \qquad (56)$$

where $K = (K')^{1/p}$, $b = q/p$, $c = t/p$
$[Cu\ R_2.HR]$, $[H^+]$ and $[Cu^{++}_{(aq)}]$ can be obtained from the optical density, pH and copper/silver-silver chloride electrode readings respectively for a given test.

Equation (56) is of the form of equation (35) in section 3.6.2. and values of K, y and z were found for equation (56) by the use of the multiple regression method described in that section. On inspection of the experimental results, it was found that the values of the optical density, pH and aqueous phase copper concentration were approximately stationary for the last three sets of readings of each test, and so the mean result of each of these quantities was used in the calculation of K, b and c. The details of the calculation are set out in Appendix B.10, and the results of the analysis with the 95% confidence limits are given in table 8 .

Table 8.

	Naphthenic Acid Concentration	
	0.1M	0.5M
K	2.15 ± 1.12	8.19 ± 2.97
b	-0.059 ± 0.90	-0.153 ± 0.605
c	0.0046 ± 3.53	-0.0054 ± 1.75

The results of the analysis, shown in table 8 indicate that there is no relation of the form postulated in equation (55) between the aqueous and organic phase copper concentrations and the pH of the aqueous phase at the end of an extraction test.

4.14. Effect of Naphthenic Acid Concentration on the Extraction Process.

The results of the factorial experiment, summarised in tables 5 and 6 indicated that improved values of the limiting organic phase copper concentration and rate constant could be obtained by reducing the size of the mineral particles and by increasing the naphthenic acid concentration. However, as the smallest size fraction of the mineral used in the original experiment was -200+270# (Tyler) - corresponding to a mean particle size of 63µ - it was considered that it would be of no practical interest to reduce the particle size further, and hence a set of experiments was run at this particle size to investigate the effect of naphthenic acid concentration in the range 0.1 - 1.7M. The results of these experiments are plotted in figs. (19) and (20). Fig.(19) shows that the limiting organic phase copper concentration increases with increasing naphthenic acid concentration, although the results for this particular set of experiments were much lower than those obtained in the factorial experiment.

The rate constant, plotted in fig.(20) increases with increasing naphthenic acid concentration, and reaches an approximately constant value at a naphthenic acid concentration corresponding to 1.0M.

4.15. Investigation of the Selectivity of the Process.

The pH measurements taken during the course of the factorial experiment showed that the extraction process occurred at pH values between 3.3 and 6.0. Now it has been shown by Fletcher and Wilson(22) that at these pH values, calcium is not extracted by naphthenic acid. This being so, the process should be useful for extracting copper from gangue containing calcite. In order to test this, a mixture in the size fraction -200+270# (Tyler), of 97.5% calcite and 2.5% malachite was prepared and leached by the usual method, as described in section 4.11. The resulting organic solution was stripped with a known volume

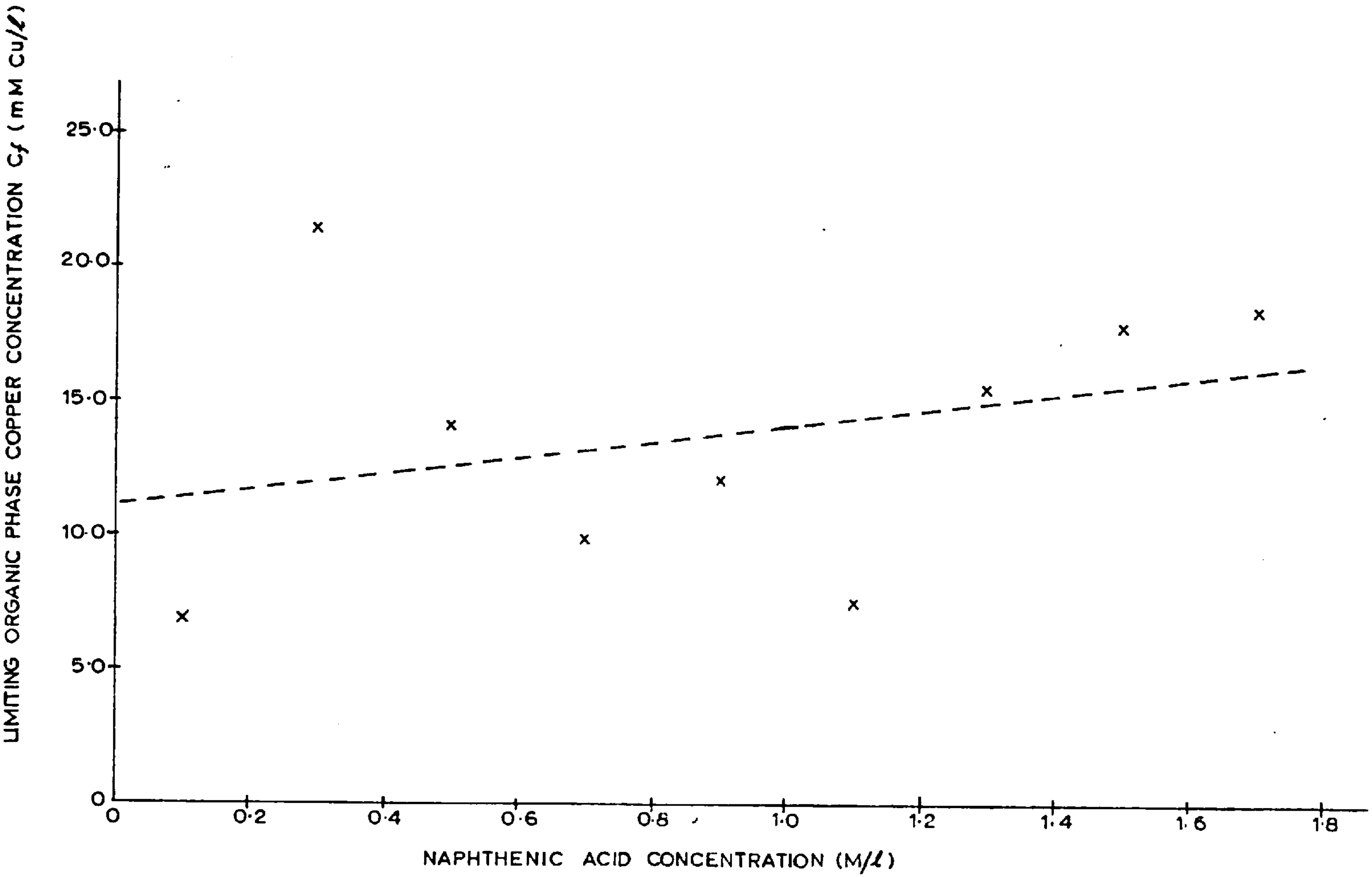


Fig. 19 VARIATION OF C_f WITH NAPHTHENIC ACID CONCENTRATION

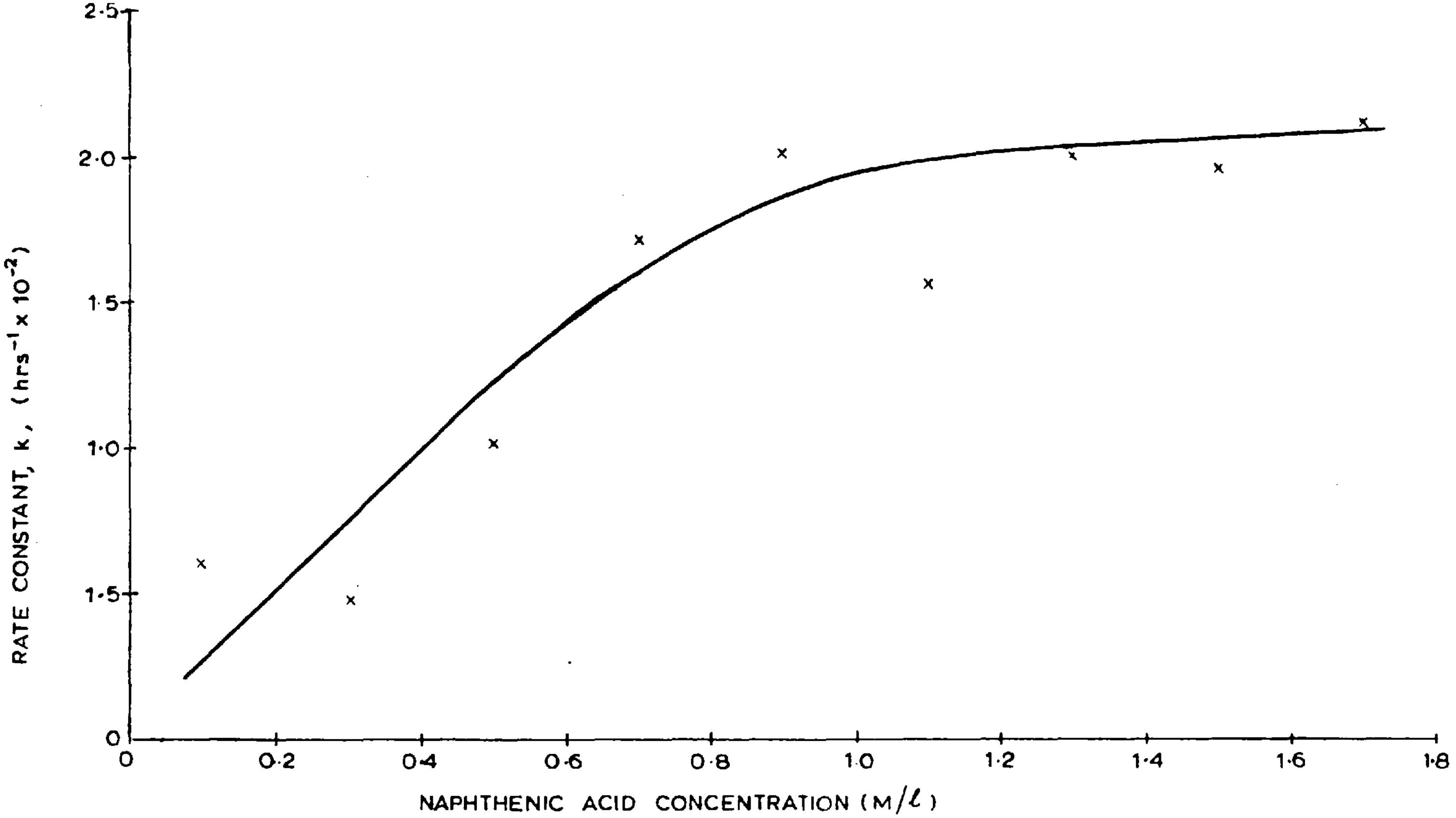


Fig. 20 VARIATION OF RATE CONSTANT WITH NAPHTHENIC ACID CONCENTRATION

of standardised hydrochloric acid, which was then titrated against potassium hydroxide to an end point at pH 5. The copper concentration of the original organic solution was deduced from the optical density. As the stripping process is stoichiometric, two moles of hydrochloric acid were required to remove one mole of calcium or copper from the naphthenic acid, hence the amount of calcium which had been extracted from the mixture by the naphthenic acid can be obtained by difference. The results of the calcium determination were checked by precipitating the calcium with ammonium oxalate and then weighing the dried precipitate. From these results it is possible to calculate the selectivity of the process, defined by the ratio:-

$$\frac{\text{Moles of copper: Moles of calcium in organic phase}}{\text{Moles of copper: Moles of calcium in solid}} \tag{57}$$

These calculations are presented in detail in Appendix B.11 together with a theoretical prediction of the selectivity and the results are summarised in table 9 .

Table 9.

	Test 1	Test 2
Moles of calcium in solid	0.300	0.289
Moles of copper in solid	0.00517	0.00589
Moles of calcium extracted	0.0216	0.0248
Moles of copper extracted	0.00033	0.00067
Selectivity for copper	0.89	1.37

The results show that on average there is a certain degree of selectivity towards copper, but is too low for the process to be of any practical application on a large scale. When the organic solution of copper and calcium naphthenate is stripped with sulphuric acid, the calcium will be precipitated as calcium sulphate and the sulphuric acid lost; the copper can be electrolysed to produce metallic copper and regenerate the sulphuric acid, as in section 2.5, fig.(4).

4.16. Effect of Extent of Leaching of Solid on Process.

It was decided to investigate whether the rate of extraction was influenced by the amount of copper which had been extracted from the malachite sample.

Four tests were run as described in section 4.11, using 250 ml of 0.5M naphthenic acid, three columns containing -200+270# particles, and one containing -100+150# particles. When the naphthenic acid had reached a near-steady copper concentration, it was drained from the apparatus, which was then flushed with water-saturated paraffin and drained. 250 ml of fresh naphthenic acid solution were added to the apparatus.and allowed to circulate until the copper concentration in the organic phase again reached a near steady value, when the apparatus was drained, flushed and refilled as before.

The values of C_f and k, obtained as in section 4.13, are plotted against the weight fraction of copper remaining in the bed (obtained by a material balance) in figs.(21) and (22). It is seen that the results from each column show the same trend, i.e. a decrease in C_f and k with the decrease of the weight fraction of copper in the bed, although there is a large variation between columns, due to some uncontrolled factor. The details of the calculations are given in Appendix E.12.

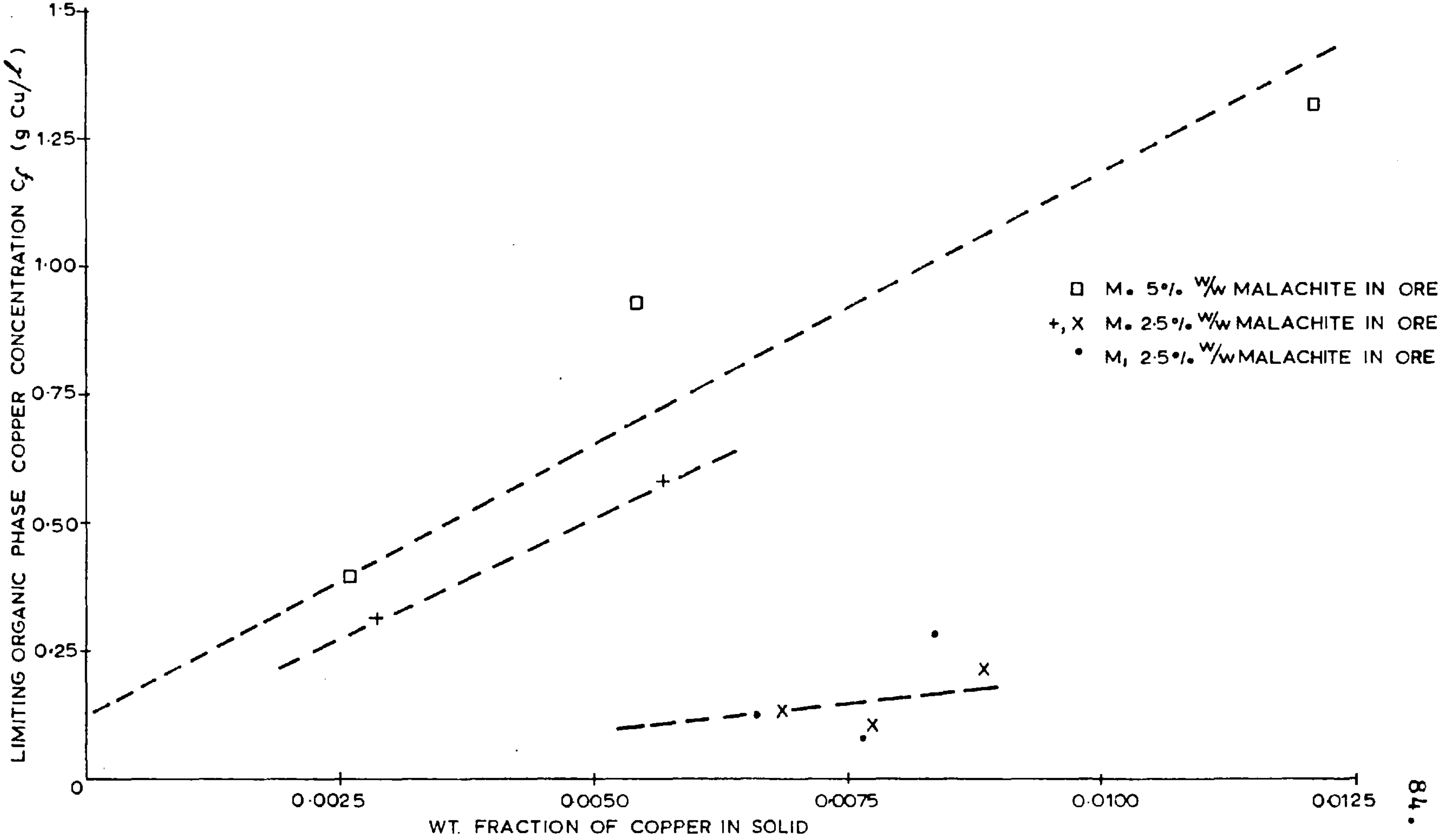


Fig. 21 VARIATION OF C_f WITH WEIGHT FRACTION OF COPPER IN SOLID

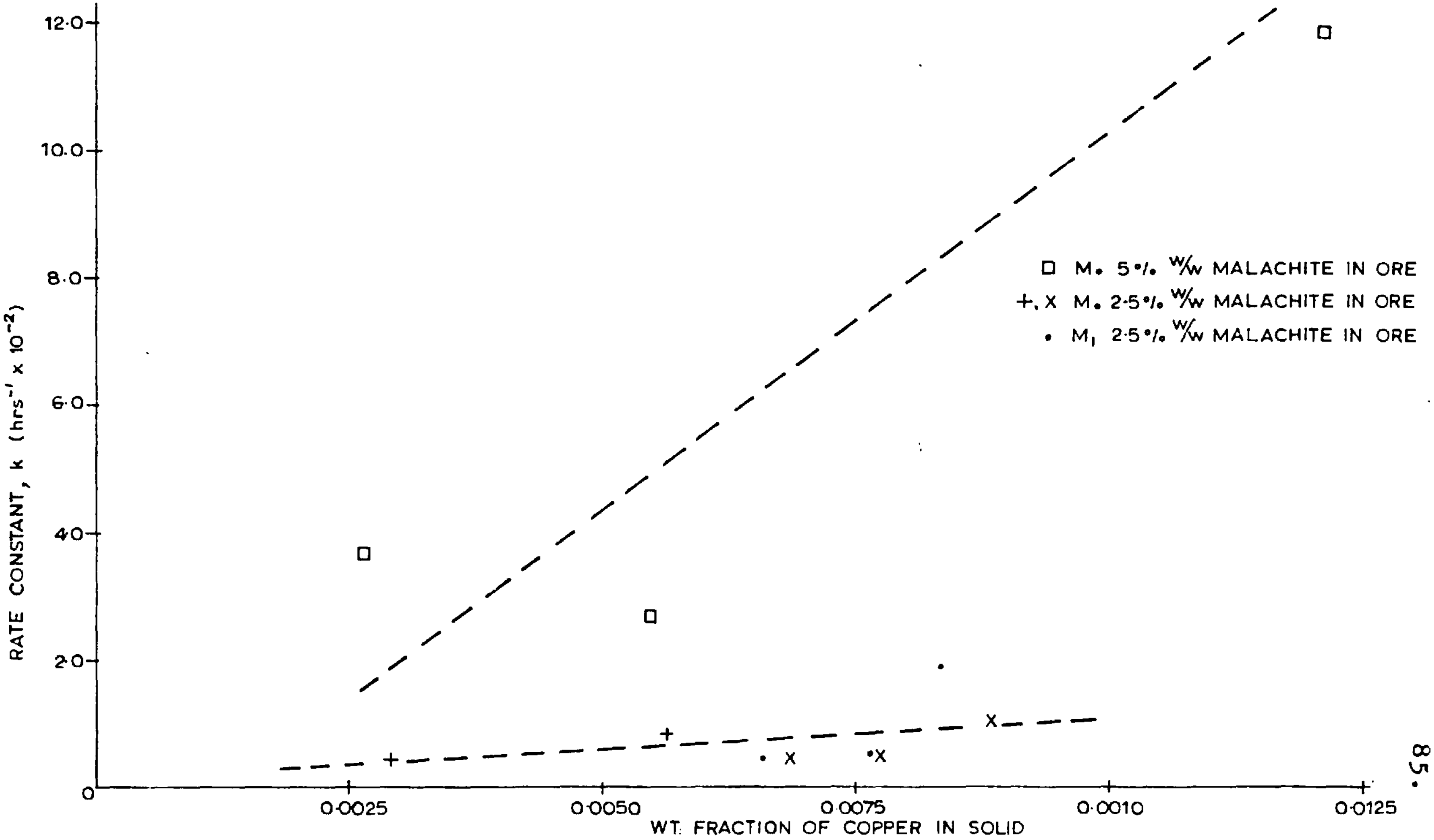


Fig. 22 VARIATION OF RATE CONSTANT WITH WEIGHT FRACTION OF COPPER IN SOLID

5. EXPERIMENTAL INVESTIGATION OF THE RECOVERY OF ORGANIC SOLVENT FROM THE MINERAL BED.

5.1. Introduction.

When all the valuable metal has been extracted from the mineral it is necessary, before discarding the residual solids, to recover as much of the organic solvent as possible in order to reduce the cost of the operation. In practice it has been found difficult to separate the solid from the organic solvent, and this has resulted in a high wastage of solvent(26). In view of this difficulty, it was decided to investigate whether any of the process variables of the extraction stage had any effect on the solvent loss, as this would be an important factor in the economic assessment of the process, and if possible to suggest methods of obtaining an efficient separation between the organic solvent and solid material.

The loss of the organic solvent on the spent mineral bed could be due to two causes, (a) occlusion of drops of the solvent in the interstices of the bed or (b) by physical or chemical attachment to the solid particles forming the bed. This latter cause bears a strong resemblance to the process of flotation, and is discussed more fully in the following section. A similar comparison has been made by Wilson(35), who also performed some preliminary tests on the attachment of drops of naphthenic acid solution to particles of calcite, malachite and quartz, in the presence of an aqueous phase.

5.2. Analogy with Flotation.

Flotation is an important and widely used operation in mineral processing, which depends for its success on the ability of mineral particles to attach themselves to air bubbles. For this to occur, the surface of the mineral must be hydrophobic (i.e. not wetted by water), and this condition must also exist if an organic phase is to wet a mineral surface in the presence of an aqueous phase. In flotation, the particles are conditioned by coating them with a small amount of a 'collector', such as a carboxylic acid (naphthenic acid is a carboxylic acid (section 2.41)) which forms a hydrophobic coating on selected minerals assisting the attachment to air bubbles. The attachment of undesired mineral species to air bubbles can be prevented by the use of 'depressants', which act by affecting either the collector or the mineral. The pH of the mineral suspension has an important effect on flotation, and is commonly used to improve the selectivity. By virtue of the common-ion effect, the presence of certain ions in the suspension can also affect the floatability of a mineral.

The attachment of a mineral particle to an organic droplet in an aqueous medium has several factors in common with the operation of flotation. The preferential wetting of the mineral surface by the aqueous or organic phase could depend on pH, the presence of other ions and the concentration of organic reagent, as well as the particle size of the mineral and contact time between the solid and the organic solution.

5.3. Variables Investigated.

From the preceding section, the variables which are liable to have an effect on the loss of solvent on the spent mineral bed were (a) particle size of solid, (b) pH of the aqueous phase, (c) naphthenic acid concentration of the organic phase, (d) copper concentration of the organic phase and (e) the contact time between the phases. The thickness of the aqueous leaching layer was also considered to have a possible effect on the solvent loss. On a process scale, the spent mineral bed would consist mainly of quartz, and the effect of these variables on quartz alone was investigated. The possible effects of each of these variables are discussed in the following sections.

5.3.1. Particle Size of Gangue. If solvent is lost on the bed by inclusion, the particle size of the solid will affect the volume of the individual voids and hence the size of drop which can be accommodated; it may be easier to dislodge large drops of solvent (by virtue of their greater ability to deform) from the bed than small drops. If the solvent is lost by attachment to the solid particles, then the specific surface (i.e. surface per unit mass or volume) of the bed will be of great importance, as the larger the specific surface (i.e. the smaller the particles) the greater will be the area available for attachment.

5.3.2. Sulphuric Acid Concentration of Aqueous Phase. By analogy with flotation it is conceivable that the pH of the aqueous leaching phase could affect the ability of the naphthenic acid solution to wet the surface of the solid by breaking the aqueous film around the solid particle.

5.3.3. Thickness of Aqueous Leaching Layer. When the mineral mixture is initially moistened with the sulphuric acid leaching solution, it is possible that, on account of the very small amounts of solution used, not all of the solid surface is covered with the aqueous film. Hence there may be places where the organic solvent has direct access to the solid, possibly forming a strong bond. The possibility of this happening would be reduced by increasing the amount of aqueous phase used.

5.3.4. Contact Time Between Organic Solution and Solid. If the process of attachment of the organic phase to the solid is slow, the longer the extraction stage of the leaching process continues, the higher will be the loss of solvent by attachment to the gangue. Hence this factor would have to be considered when assessing the optimum time for the extraction stage to be run.

5.3.5. Naphthenic Acid Concentration. If the naphthenic acid concentration is increased to give an increase in the rate and extent of extraction of copper from the mineral (in accordance with the results in section 4.13.2.), these advantages may be outweighed by an increase in the loss of solvent on the residual gangue. It has been shown by Wilson(35) that naphthenic acid is most readily attached to quartz particles at the higher naphthenic acid concentration in the range 0.07M - 0.35M.

5.3.6. Copper Concentration of Organic Phase. In flotation practice, the presence of certain ions (particularly cations in conjunction with carboxylic acid collectors) can increase the probability of a mineral particle attaching itself to an air bubble. Similar considerations could well apply to the presence of copper in the organic phase affecting its attachment to gangue particles. If this is the case, knowledge of this fact would be an important factor in assessing the optimum organic phase copper concentration in the extraction stage of the process.

5.4. Method of Investigation.

Preliminary experiments indicated that large quantities of the organic solvent were released from the spent mineral bed by passing water upwards through the bed. The organic solvent, being less dense than the water, rose to the surface and was carried away with the overflow, from which it could be separated. It was decided to use this method of solvent removal to investigate the effects of the six variables described under section 5.3, and to estimate the amount of solvent remaining on beds of quartz particles by the method described in section 5.6.

As six variables were involved in the investigation, it was decided to use statistical methods to estimate the effects of each variable and the interactions between the variables.

5.5. Design of Experiment.

5.5.1. Notation. The six factors involved in the investigation were denoted by the following letters;-

M, particle size of quartz particles
P, sulphuric acid concentration of aqueous leaching phase
A, thickness of aqueous leaching phase
T, contact time between organic phase and solid
C, naphthenic acid concentration of organic phase
R, copper concentration or organic phase.

5.5.2. Levels of Factors. The levels at which the factors were investigated are given in table 10 .

Table 10.

Factor	Low Level	High Level
Particle size (Tyler mesh)	-200+270	-100+150
$[H_2SO_4]_{aq}$ (moles/l)	10^{-5}	10^{-3}
Aqueous layer thickness (μ)	2.0	6.0
Contact time (hrs)	50	150
Naphthenic acid conc. (moles/l)	0.5	1.0
Organic copper conc.(opt.dens)	0.5	1.5

The levels of factors M, P and A are the same as those used in the extraction tests, as it was decided to investigate the possible effect of these operating variables on the solvent loss, although the extraction tests had shown that P and A were without influence on the process (section 4.13.2.).

The lower level of the time of contact corresponded to the average duration of the shorter runs in the extraction tests, and the higher level to just under twice the length of the longer runs.

The results of the experiments on the effect of the naphthenic acid concentration on the extraction stage (section 4.14) had shown that the rate constant became virtually constant at a naphthenic acid concentration of 1.0M, and hence no advantage would be gained by increasing the naphthenic acid concentration above this value. 1.0M was therefore used as the high level of factor C, the lower limit (0.5M), being one which could conceivably be used in practice, as it gave a reasonable rate of extraction.

The levels of the organic phase copper concentration were slightly lower than the mean values of C_f for naphthenic acid strengths of 0.1 and 0.5M, as obtained from the extraction experiments. (Table 7).

5.5.3. Design of Experiments. Six factors, each investigated at two levels constitutes a 2^6 factorial experiment, involving 64 tests. The 63 measured effects (in addition to the mean response) would consist of:-

6	main effects
15	two-factor interactions
20	three-factor interactions
15	four-factor interactions
6	five-factor interactions
1	six-factor interaction

Of these effects, only the main effects and the two-factor interactions associated with factor C (i.e. naphthenic acid concentration) were of any interest. (It has been shown in section 4.13.2. that the effect of the naphthenic acid concentration on the extraction process was very pronounced, and any influence on the solvent recovery from the spent mineral bed by interaction with other factors could be an important consideration in the choice of operating conditions, hence it was decided to investigate these interactions). Now a full 2^6 factorial experiment would give an estimate of the experimental error based on 42 degrees of freedom, which would be unnecessarily precise; also 64 tests was considered an excessive number to perform in order to obtain the necessary information. In view of these considerations, it was decided to perform a half replicate of the experiment, consisting of 32 tests, designed in such a way that (i) all main effects were confused with three- (or more) factor interactions, (ii) all the two-factor interactions of C were clear of other two-factor interactions and (iii) to leave as many degrees of freedom as possible for the estimate of the experimental error.

5.5.4. Choice of Alias Sub-Group. In order to fulfil the conditions of the previous section, it was found necessary to 'equate' factor R to the three-factor interaction MPA of the corresponding 2^5 factorial experiment (see section 3.5.2.). Hence the alias sub-group was:-

$$I = MPAR$$

Applying the rules of section 3.5.3., the tests to be performed in this fraction were:-

(1)	mr	pr	mp	ar	ma	pa	mpar
t	mtr	ptr	mpt	atr	mat	pat	mpatr
c	mcr	pcr	mpc	acr	mac	pac	mpacr
tc	mtcr	ptcr	mptc	atcr	matc	patc	mpatcr

5.5.5. Effects Measured by the Experiment. In section 3.5.4. it was shown how it is determined which effects are measured by a half replicate of a factorial experiment. Applying these rules to the present case, the information obtained from this particular experiment is given in table 11

from which it is seen that three pairs of two-factor interactions are lost, but this is unavoidable in this particular design. 13 degrees of freedom are available for the error estimate.

5.6. Description of Apparatus Used for Removal of Organic Solvent from the Spent Mineral Bed.

The apparatus used to remove the organic solvent from the spent mineral bed is illustrated in fig.(23). Basically it consisted of a vertical glass column 6" high and 1/2" I.D., fitted with a sintered glass disc at the base. At the top of the column was a conical section, 9" high having a maximum diameter of 6", with an overflow outlet 1/2" from the top surface. Water could be passed upwards through the apparatus and its flow-rate measured by a rotameter.

The mixture of solids and organic solution to be separated was poured into the apparatus and, on passing water up through the bed of solids formed, the bed was expanded, the released solvent rose to the surface of the water and was carried out of the overflow. The conical section, by reducing the water velocity, prevented any solid particles from being washed out of the apparatus by the water.

5.7. Estimation of Residual Solvent on the Bed.

An estimate of the quantity of naphthenic acid remaining on the bed was obtained by using the copper content of the organic solution as a tracer. By pouring a solution of sulphuric acid through the bed, the copper in the residual

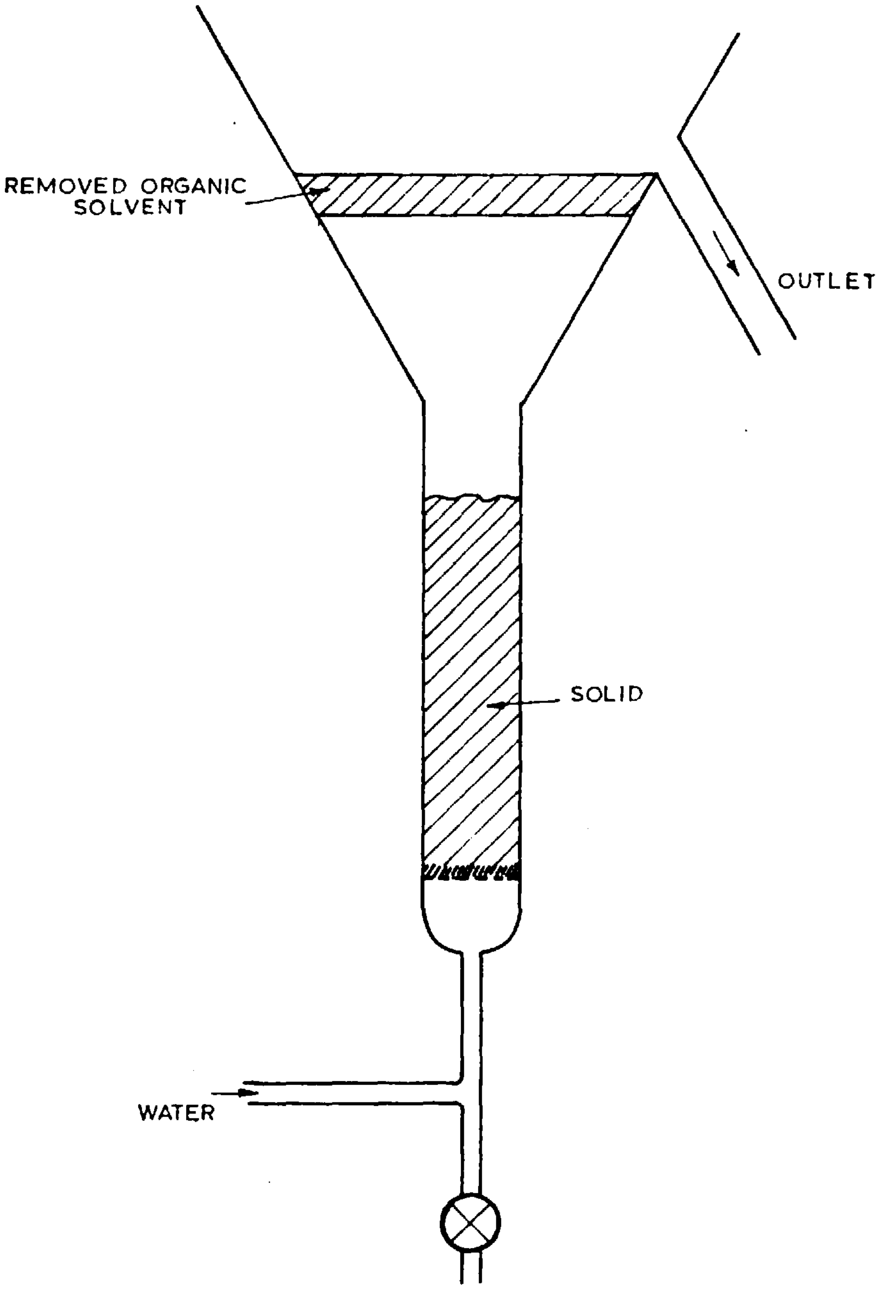


Fig. 23 DIAGRAM OF APPARATUS USED FOR INVESTIGATING LOSS OF SOLVENT ON MINERAL

Table 11.

Treatment Comb. M P A T C R	Effect for 2^5 Expt.	Effects for 2^6 Expt.	Information Obtainable
0 0 0 0 0 0	I	I, MPAR	-
1 0 0 0 0 1	M	M, PAR	M
0 1 0 0 0 1	P	P, MAR	P
1 1 0 0 0 0	MP	MP, AR	lost
0 0 1 0 0 1	A	A, MPR	A
1 0 1 0 0 0	MA	MA, PR	lost
0 1 1 0 0 0	PA	PA, MR	lost
1 1 1 0 0 1	MPA	MPA, R	R
0 0 0 1 0 0	T	T, MPATR	T
1 0 0 1 0 1	MT	MT, PATR	MT
0 1 0 1 0 1	PT	PT, MATR	PT
1 1 0 1 0 0	MPT	MPT, ATR	error
0 0 1 1 0 1	AT	AT, MPTR	AT
1 0 1 1 0 0	MAT	MAT, PTR	error
0 1 1 1 0 0	PAT	PAT, MTR	error
1 1 1 1 0 1	MPAT	MPAT, TR	TR
0 0 0 0 1 0	C	C, MPACR	C
1 0 0 0 1 1	MC	MC, PACR	MC
0 1 0 0 1 1	PC	PC, MACR	PC
1 1 0 0 1 0	MPC	MPC, ACR	error
0 0 1 0 1 1	AC	AC, MPCR	AC
1 0 1 0 1 0	MAC	MAC, PCR	error
0 1 1 0 1 0	PAC	PAC, MCR	error
1 1 1 0 1 1	MPAC	MPAC, CR	CR
0 0 0 1 1 0	TC	TC, MPATCR	TC
1 0 0 1 1 1	MTC	MTC, PATCR	error
0 1 0 1 1 1	PTC	PTC, MATCR	error
1 1 0 1 1 0	MPTC	MPTC, ATCR	error
0 0 1 1 1 1	ATC	ATC, MPTCR	error
1 0 1 1 1 0	MATC	MATC, PTCR	error
0 1 1 1 1 0	PATC	PATC, MTCR	error
1 1 1 1 1 1	MPATC	MPATC, TCR	error

organic solution was extracted into the sulphuric acid solution. The resulting aqueous effluent was analysed spectrophotometrically for copper using the sodium diethyldithiocarbamate method(36). From a knowledge of the volume of the aqueous effluent and the copper concentration of the aqueous and original organic solutions, the amount of naphthenic acid remaining on the bed was extimated. This calculation is presented in detail in Appendix B.14.

5.7.1. <u>Analysis of Aqueous Effluent for Copper</u>. The copper concentration of the aqueous effluent from the column was determined by the sodium diethyldithiocarbamate method(36), as described below.

A 10 ml sample of the aqueous effluent was added to 5 ml of an ammonium citrate buffer solution (made by adding 0.880 ammonia to a 5% solution of citric acid until the pH reached 9.0 - 9.2). 20 ml of A.R. carbon tetrachloride and 1 ml of a 0.1% solution of sodium diethyldithiocarbamate were added to the solution which was then shaken for 2 minutes in a separating funnel. After allowing the phases to separate, the carbon tetrachloride was run out slowly over a strip of filter paper pushed up the stem of the separating funnel into a suitable cell, and analysed spectrophotometrically at 440 mμ using a blank of carbon tetrachloride.

The variation of the optical density of the carbon tetrachloride solution with copper concentration is given in fig.(24) By linear regression, the best straight line representing this variation was found to be

$$Y = 46.6 \times \text{O.D.} - 0.5 \qquad (59)$$

where Y is the copper concentration of the carbon tetrachloride solution in g/l x 10^{-4}.

When using this method of analysis, the following precautions were taken:

(a) The carbon tetrachloride was run slowly into the analysis cell to prevent any water droplets from entering the cell. If water got into the cell it attached to the

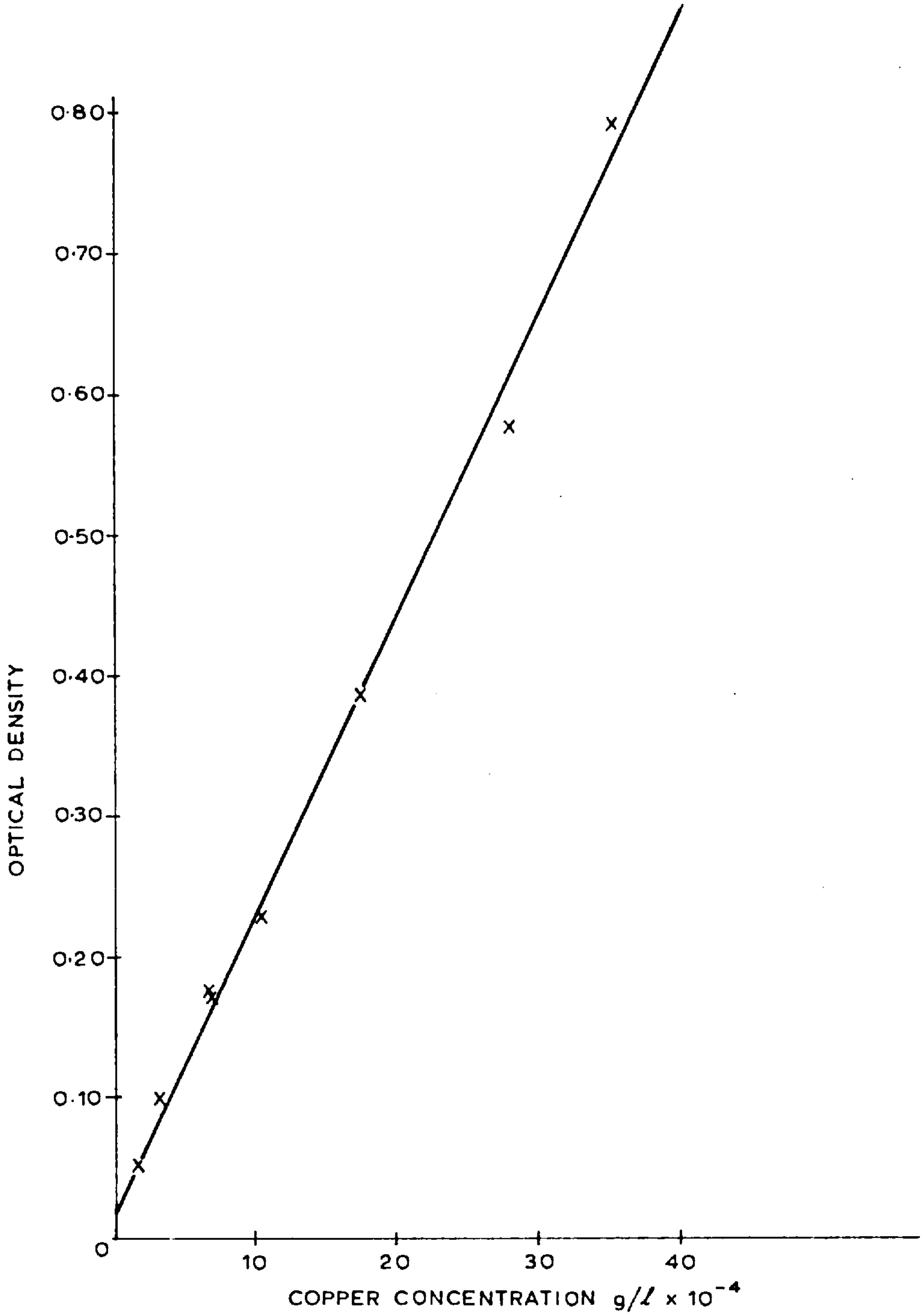


Fig. 24 VARIATION OF OPTICAL DENSITY OF CARBON TETRACHLORIDE SOLUTION WITH COPPER CONC. AT 440 mμ

cell walls and gave false readings for the optical density.

(b) The copper complex was light-sensitive and was analysed within ten minutes of being formed.

(c) The sodium diethyldithiocarbamate solution was kept in a dark glass bottle.

5.8. Preparation of Materials.

5.8.1. Quartz Samples. The quartz used in the tests was silver sand, ground and screened and dried as described in section 4.9.

5.8.2. Aqueous Leaching Solutions. These were prepared as described in section 4.10.1., but no chloride ions were added.

5.8.3. Organic Solutions. The organic solutions used in the investigation were obtained from the copper bearing solutions produced during the extraction tests. The copper and naphthenic acid concentrations were adjusted to the required values by the addition of naphthenic acid. The optical densities of the solutions were checked before use.

5.9. Experimental Procedure.

A weighed amount of silver sand of the appropriate size fraction was moistened with the required amount of the aqueous leach solution demanded by the test, by the same procedure as was used in the extraction tests (section 4.11.). 50 ml of the appropriate solution of copper naphthenate in paraffin were added to the mixture in a beaker, which was then covered with a piece of polythene sheet and allowed to stand for 50 or 150 hours, as required by the test. After standing, the mixture was transferred to the removal apparatus, and tap water passed upwards through it at 25 ml/min for 15 mins. (This flow-rate was sufficient to gently agitate the particles of the bed without causing violent fluidisation, and 15 mins was found to be a sufficient length of time to remove all of the solvent which could be removed by this method). At the end of this time, the column was allowed to drain, and then 50 ml of 10^{-2}M sulphuric acid poured through the bed. The effluent was collected and analysed for copper as in section 5.7. It was found that all of the copper remaining on the bed was extracted into the 50 ml aliquot of sulphuric acid used. The draining time of the column and percolation time of the sulphuric acid was reduced by applying a slight suction to the outlet at the base of the column.

5.10. Interpretation of Results.

The results of each test, expressed as the weight of naphthenic acid remaining on unit weight of dry quartz, calculated as described in Appendix B14.3 were analysed statistically as the responses of a half replicate of a 2^6 factorial experiment, according to the method described in section 3.5.4. The details of the tabular analysis are given in Appendix B14.3 and the results are summarised in table 12 .

The results show that the solvent lost per unit weight of dry quartz increases with increasing particle size and naphthenic acid concentration and decreases with increasing organic phase copper concentration.

The mean results of the tests, at the high and low levels of particle size, naphthenic acid concentration and organic phase copper concentration are given in table 13), togther with their 95% confidence limits.

Table 12.

Summary of Analysis of Variance for Solvent Loss

Source of Variance	Degrees of Freedom	Mean Effect	Mean Square Effect	F-Ratio
Particle size of solid (M,PAR)	1	7.823	489.6	32.10
Naphthenic acid concentration (C,MPACR)	1	3.159	79.85	5.23
Organic phase copper concentration (R,MPA)	1	-8.782	617.0	40.44
Interaction MC,PACR	1	-5.942	282.5	18.51
Interaction TR,MPAT	1	3.887	120.9	7.92
Interaction TC, MPATCR	1	4.381	153.5	10.06
Interaction PC, MACR	1	3.304	87.40	5.73
Interaction CR, MPAC	1	-4.274	146.2	9.58
Error (from high order interactions)	11	-	15.26	1.00

For significance at the 5% level, F = 4.84, and at the 1% level F = 9.65.

Table 13.

Summary of Results of Solvent loss/Unit weight of Quartz.

Naphthenic Acid Conc. (M/1)	Organic Phase Copper Conc. (Optical Density)	Solvent Loss (g Naphthenic Acid/g ore x 10^{-3})	
		Particle Size (Tyler mesh)	
		-200+270#	-100+150#
0.5	0.5	7.9 ± 4.2	25.6 ± 32.2
	1.5	7.3 ± 4.9	17.1 ± 22.8
1.0	0.5	21.2 ± 8.1	26.3 ± 21.2
	1.5	11.3 ± 17.1	10.9 ± 12.0

From these figures the mean loss of solvent was calculated to be 1.50 tons of naphthenic acid per ton of copper extracted.

5.11. Investigation of Distribution of Residual Solvent on Bed.

During the process of removing the solvent from the quartz it was observed that the organic solvent tended to rise to the surface in small drops, with particles of quartz attached, as in flotation. When the water flow was stopped, these drops returned to the surface of the bed as it settled, and it was decided to investigate what fraction of the residual solvent was retained on the top portion of the settled bed.

Two experiments were performed, under the same conditions according to the procedure described in section 5.9. When the column was drained after the water had been passed up through the bed, the top portion of the bed was removed to a sintered glass funnel and the residual solvent on both portions of the bed determined by the method described in section 5.7. The top portion of the bed, which had been removed was washed with acetone to remove the water and residual naphthenic acid solution, dried in an oven and weighed. From these figures, and a knowledge of the total weight of the bed, it was found that 35-40% of the residual solvent was recovered from the top 20% of the extracted bed. Hence in practice the need for treating all of the extracted bed to recover the organic solvent may be obviated

6. DISCUSSION OF RESULTS

6.1. Extraction Experiments.

6.1.1. Acceptability of Results of Extraction Experiments.

Inspection of the results obtained from the many extraction experiments (Table 7, Figs.(19), (20), (21), (22)) reveals that there is a considerable scatter. This scatter can only arise from some factor which was not adequately controlled during the course of the experiments. An example of this is found by comparing the results obtained for C_f and k in the factorial experiment (Appendix A.2) with those obtained in the investigation of the effect of naphthenic acid concentration on the process (Appendix A.4). This latter set of values is considerably lower than those obtained in the factorial experiment. Although no direct evidence could be obtained regarding the factor causing the scatter, the most likely origin is thought to be the aqueous leaching layer on the mineral surface. This is not easily controlled, and the method used for moistening the mineral (i.e. by stirring the aqueous solution into the solid in a beaker)might have failed to produce a uniform aqueous layer over all the particles. It is suggested that in any future work on this subject more attention should be paid to the formation of a uniform aqueous layer on the mineral surface. During the experiments, every effort was made to reproduce the conditions from one group of tests to the next. However, despite the scatter, it is still possible to identify certain distinct trends in the results, particularly in those obtained from the factorial experiment. The results from the other sets of experiments are based on fewer data and hence less definite conclusions can be drawn.

The original objectives of the extraction experiments were to determine the rate of extraction and the amount of extraction possible under various conditions, and to indicate the rate controlling stage of the process. The results will now be discussed in these terms.

6.1.2. Mechanism of the Extraction Process. It was originally expected that the overall rate of extraction of copper from the ore by the simultaneous leaching and solvent extraction process would be proportional to the displacement from an equilibrium state, i.e.

$$\frac{dC}{dt} = k\,(C_f - C) \qquad (52)$$

where C_f is the equilibrium concentration.
On integration this leads to the first-order rate equation:-

$$C = C_f[1 - \exp(-kt)] \qquad (53)$$

It was expected that an indication of the mechanism of the process could be obtained from the dependence of the rate constant, k, on the five variables investigated in the factorial experiment. This proposal was discussed in section 4.2. The results of the factorial experiment show clearly that C_f and k are both functions of particle size and naphthenic acid concentration. The dependence of C_f on particle size indicates that it is not an equilibrium value, and hence the simple mechanism proposed is not acceptable. In view of this, there is some doubt about the physical significance of C_f and hence k.

One possible explanation of the dependence of C_f on particle size lies in the nature of the malachite used in the ore for the leaching tests. The examination of the mineral by the electron probe micro-analyser (section 4.8.3) revealed that the malachite sample contains fine grains of a copper silicate, which could quite possibly be chrysocolla $CuSiO_3\ x\ H_2O$, a mineral often found in conjunction with malachite. Chrysocolla dissolves in acids much more slowly than does malachite, hence the malachite will be exhausted in the early part of a test, and the dissolution of the chrysocolla may then continue either to exhaustion or equilibrium. It is shown in Appendix B.6 that for total dissolution of all the copper in the ore sample, the organic phase copper concentration would be approximately 20 mM/1, corresponding to an optical density of 3.26. In Appendix B.5, the malachite content of the ore, obtained by a carbon dioxide assay, was found to be 25 - 30%, and for total dissolution of all the malachite, the corresponding optical density of the organic phase would be about 0.8 - 1.1. Inspection of the values of C_f in Appendix A.2 reveals that in all but eight cases the optical density value of C_f lies between 1.4 and 3.1, indicating that C_f corresponds to the dissolution of more copper than that represented by the malachite but not to the total dissolution of all the copper. Fig.(25) shows how an exponential curve of the type

$$C = C_f[1 - \exp(-kt)] \qquad (53)$$

could easily be approximated to the sum of the two curves representing the leaching of the malachite and the leaching of the chrysocolla. The diagram also shows how a higher value of C_f would be obtained with the smaller particles than with the larger ones, owing to the higher rates of leaching of both malachite and chrysocolla particles.

In view of the uncertainty over the physical significance of C_f and k, it is unreasonable to discuss the results in these terms. The experimental concentration-time plots are well represented by equations of the form of (53), and from these, the initial rate of extraction (C_f x k) can be deduced, as this is an experimentally determined quantity. The inital rate of extraction is thus a function only of particle size and naphthenic acid concentration.

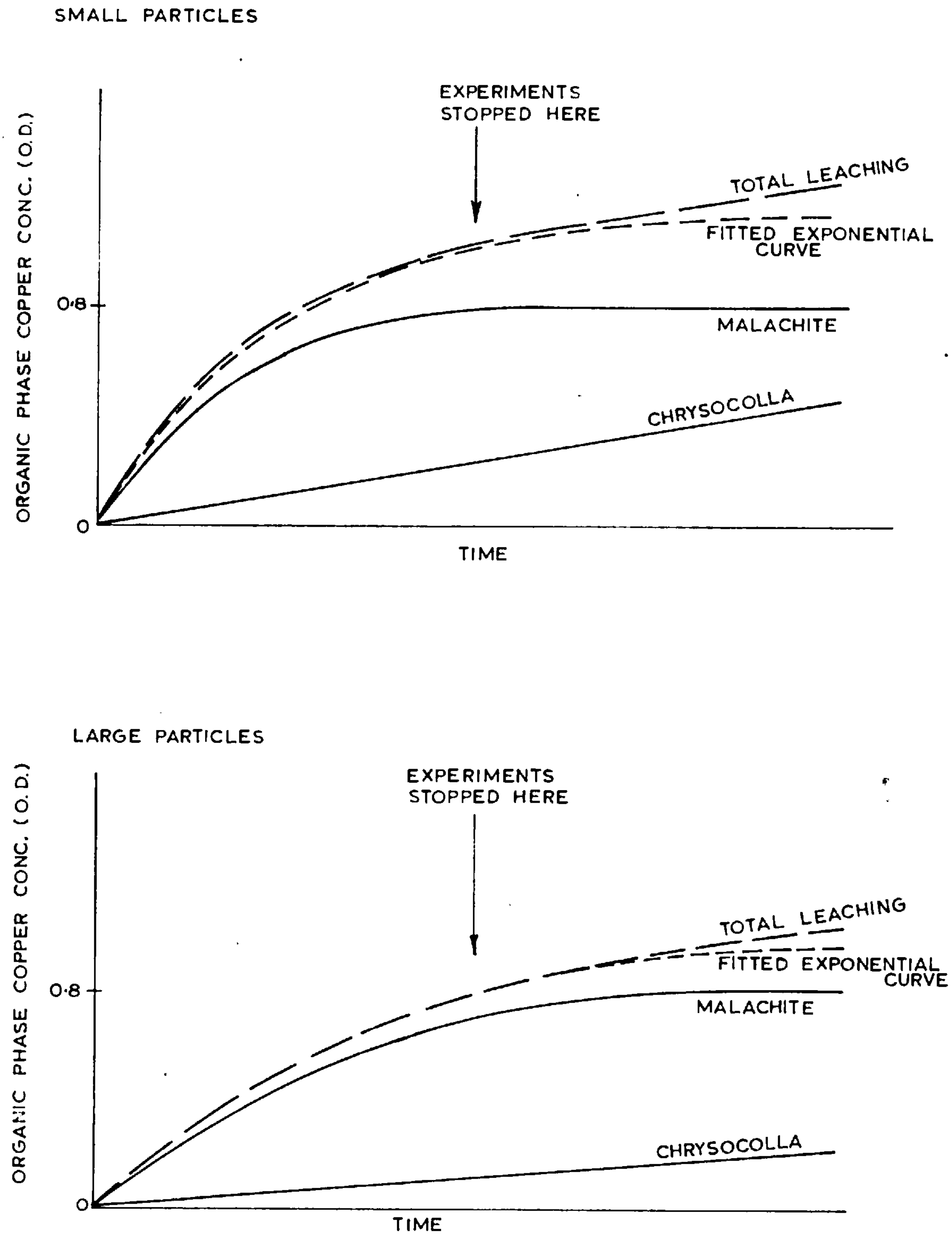


Fig. 25 POSSIBLE CAUSE OF VARIATION OF C_f WITH PARTICLE SIZE.

6.1.2.1. Factors Affecting the Initial Rate of Extraction. Rewriting Table 7 in terms of the initial rate, it is seen that the initial rate is approximately inversely proportional to the mean particle diameter, hence it is proportional to the specific interfacial area of the solid.

Table 14.

Naphthenic Acid Conc. (M/1)	Initial Rate of Extraction (M/1/hr)	
	Particle Size	
	-200+270# (63µ)	-100+150# (126µ)
0.1	0.218	0.109
0.5	0.730	0.424

In the model of the process postulated in section 4.2. all the stages are dependent on the interfacial area, thus this is the expected result.

The initial rate of extraction increases with increasing naphthenic acid concentration as is shown in Table 14 and also in Fig.(26). The results of the experiment investigating the effect of naphthenic acid concentration fitted a linear relation between the initial rate and naphthenic acid concentration. This dependence implies that the rate controlling stage is in some way connected with the organic phase, and, according to the model of the process described in section 4.2., is either the transport of copper or acid in the organic phase, or the transfer of these species across the aqueous-organic interface. If transfer across the interface is the rate-controlling stage, the influence of flow-rate is expected to be negligible, whereas if transport within the organic phase is rate-controlling, the flow-rate of the organic

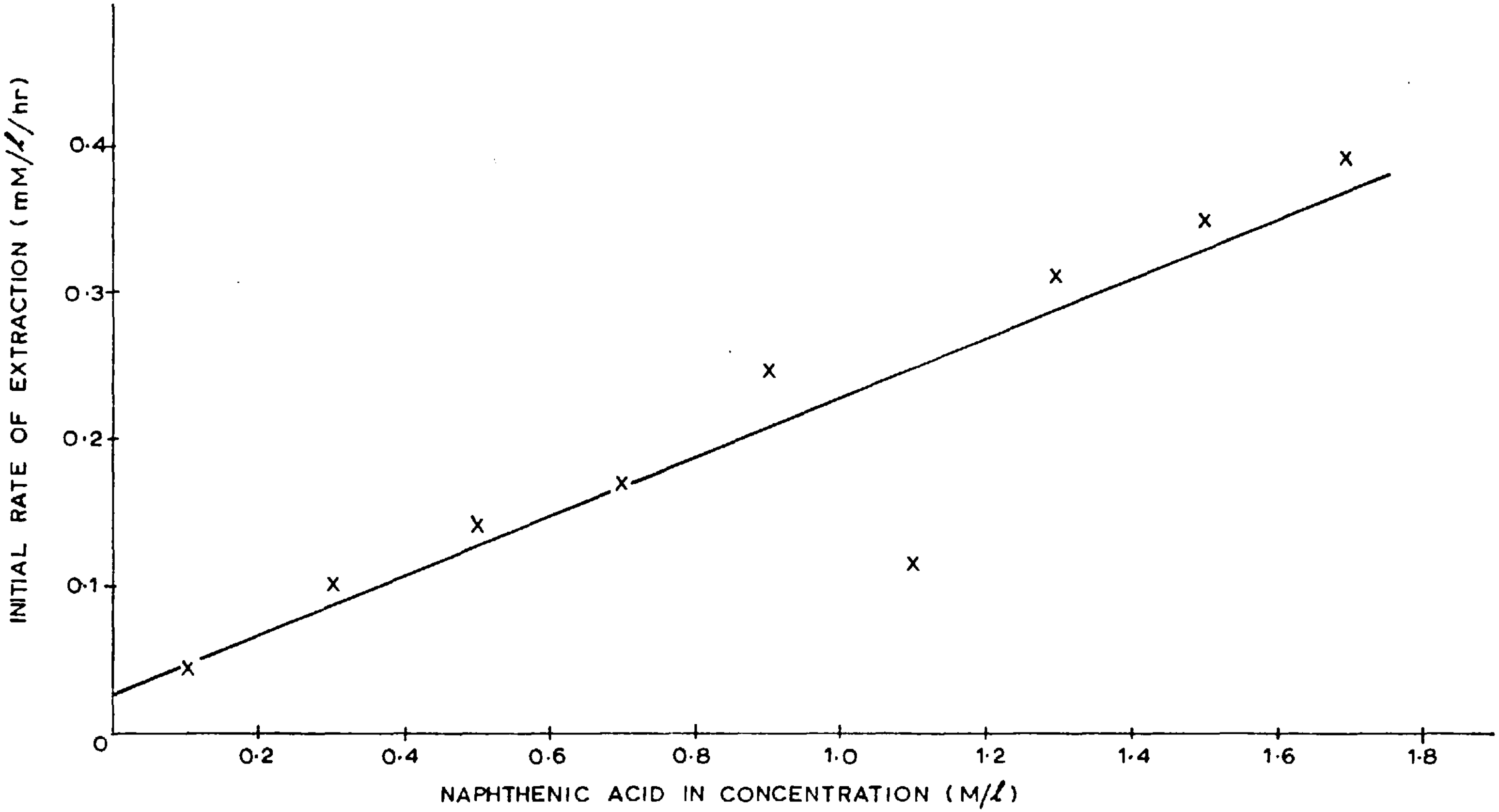


Fig. 26 VARIATION OF INITIAL RATE OF EXTRACTION WITH NAPHTHENIC ACID CONCENTRATION

phase is expected to have an effect on the rate of extraction.

The rate is also independent of the thickness of the aqueous leaching layer and this suggests that diffusion of hydrogen and copper ions across this layer is not rate-controlling. The calculated mean thickness of this layer is 2μ or 6μ which is considerably less than the diffusion boundary layer of 100μ usually associated with mass transfer across solid-liquid and liquid-liquid interfaces. Thus this result is as expected.

The Reynolds numbers for the flow of the organic solvent through the bed were found to lie in the range 8×10^{-4} to 8×10^{-3}, i.e. the flow was well within the laminar regime. This implies that there is no mass transfer by eddies due to the flow. Eddies could, however, arise from spurious occurrences within the bed, e.g. the release of a bubble of carbon dioxide, which would affect the hydrodynamic conditions at the interface. The absence of eddy diffusion implies that all the resistance to mass transfer should be in the bulk of the phase, as predicted from the work of Lewis(41). This is inconsistent with the results of the present investigation, which have indicated that mass transfer is controlled by the rate of transfer across the aqueous-organic interface. However,as Lewis worked at much higher Reynolds numbers (in the range 1000-4000) than in the present case, and with mass transfer in stirred cells, not packed beds, the comparison with the present work might be unjustified.

The rate of extraction has also been shown to be independent of the pH of the aqueous leaching phase, and this implies that the leaching reaction at the solid-liquid boundary is not rate-controlling, according to the model of the process described in section 4.2.

All the evidence so far obtained points to the initial rate of extraction, corresponding to the dissolution of malachite, being controlled by the reaction at the aqueous-organic interface.

The apparent lack of influence of the flow-rate of the organic phase, the sulphuric acid concentration and pH of the aqueous leaching layer does not necessarily mean that these factors are entirely without influence. It may be that the levels at which the factors were investigated were too close together, and possibly some influence may be revealed by increasing the interval between the factor levels, or by investigating the effects of the factors at a different set of levels considerably removed from those used in the experiment. For example, the thickness of the aqueous leaching layer did not appear to affect the process, but if the mineral bed dried out during an extraction test, the extraction stopped. Thus some influence of the aqueous layer thickness can be expected at a lower level of this factor.

The results of the test for correlation between the pH and copper concentration of the aqueous phase and the organic phase copper concentration, shown in table 7, indicate that there is no correlation of the form postulated in equation (55) between these quantities at the end of an extraction test. This in turn implies that at the end of an extraction test, the organic phase copper concentration is independent of the pH and copper concentration of the aqueous phase, and thus does not correspond to an equilibrium value as suggested by equation (55). As equilibrium does not exist between the bulk concentration of the aqueous and organic phases, it again indicates that the aqueous-organic boundary reaction could be rate-controlling.

6.1.2.2. Effect of Extent of Leaching of the Solid. The results of the experiments performed to investigate the effect of the extent of leaching of the solid on the extraction process, plotted in terms of the initial rate of extraction in Fig.(27), show that after the first stage, the initial rate drops to a virtually constant value. The fall in the rate is due partly to the reduction of the interfacial area available for extraction, and is also consistent with the presence of chrysocolla in the sample. The malachite will have been exhausted in the first stage, leaving only the chrysocolla to be leached; the rate of extraction in the later stages might be determined by the rate of leaching of the solid and not by transfer across the aqueous-organic interface. The evidence in Fig. (27) for the fall in the initial rate of extraction is consistent with the possible explanation of the variation of C_f with particle size given in section 6.1.2.

6.1.2.3. Selectivity of the Process. The calculation of the ratio of the organic phase copper and calcium concentration (Appendix B.11) suggested that at equilibrium, the naphthenic acid solution should contain approximately times as much copper as calcium. In practice it was found that copper and calcium were extracted into the organic solvent in approximately the same ratio as these two metals were present in the solid. This indicates that there is only a slight preferential selectivity for copper over calcium. (Table 9).

A possible explanation of the discrepancy between the observed and predicted results lies in the fact that the experimental system did not correspond to an equilibrium state, whereas the calculated prediction was based on the assumption of equilibrium. The predicted result was obtained by combining the

Other values obtained:-	wt. fraction of Cu	Initial rate (g/ℓ/hr)
M_1, 5% MALACHITE IN ORE	0·0121	0·155
	0·00543	0·0248
	0·00260	0·0142

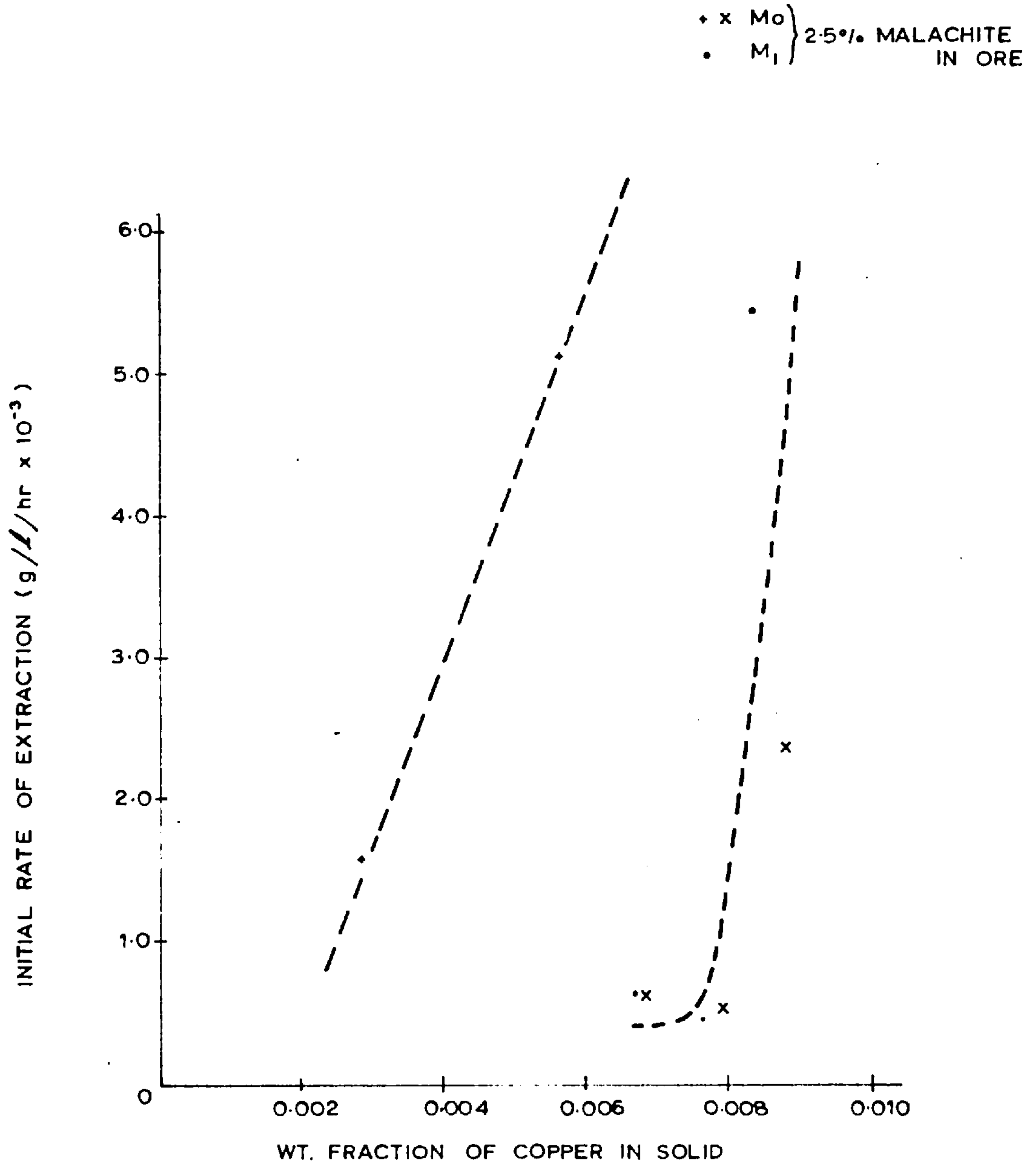


Fig. 27 VARIATION OF INITIAL RATE WITH COPPER CONTENT OF SOLID

relevant stability constants, which could lead to errors of up to a factor of 100.

6.1.3. **Application of Results of Extraction Experiments to a Large Scale Process.** By using the method described in reference$^{(37)}$, it is possible to use the results of the extraction experiments to investigate the feasibility of the simultaneous leaching and solvent extraction process on a large scale. The physical significance of C_f and k is now not a problem, as the data for the extraction experiments is well represented by equation (53). An analogy can be drawn between the experimental investigation of the extraction process, and a batch process in a stirred reactor. This provides the relation between the rate constant as measured by k in the experiments and the overall mass transfer coefficient for the process. The relation is used in the evaluation of the large-scale operation in a tower.

6.1.3.1. **Batch Process in a Stirred Reactor.** Consider a solid infinite diffusivity, (so that no appreciable concentration gradients occur inside the solid) containing copper, immersed in a liquid which is well stirred (Fig.(28)).

Let C be the copper concentration in the liquid at time t,

C_f be the limiting copper concentration in the liquid

K_{OL} be the overall mass transfer coefficient based on the copper concentration driving force in the liquid phase

a' be the area of transfer per unit mass of solid

M be the mass of solid

V be the volume of liquid

x_o be the original weight fraction of copper in the solid.

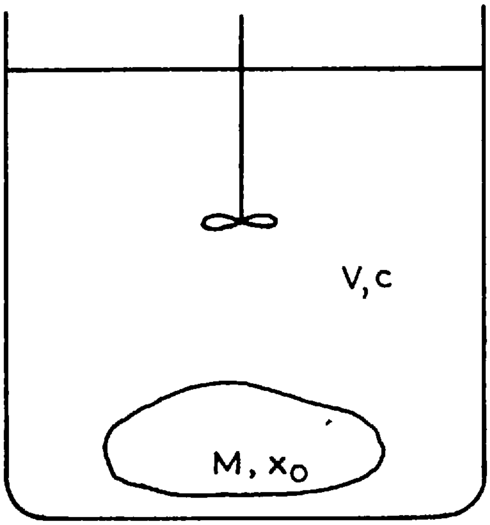


Fig. 28

assuming that $M_{x_o} > VC_f$

By a material balance on the copper:-

$$Vdc = K_{OL}\, a'\, M(C_f - C)dt \tag{59}$$

Integrating:- $\displaystyle\int_0^C \frac{VdC}{C_f - C} = K_{OL}a'Mt$

$$\therefore \quad \ln\left[\frac{C_f}{C_f - C}\right] = K_{OL}a'Mt \tag{60}$$

$$\therefore \quad C_f - C = C_f \exp\left\{-\frac{K_{OL}a'Mt}{V}\right\} \tag{61}$$

$$\therefore \quad C = C_f\left[1 - \exp\left\{\frac{-K_{OL}a'Mt}{V}\right\}\right] \tag{62}$$

Equation (62) is of the same form as equation (53) section 4.13.1., which was fitted to the experimental results of the leaching experiments, but with k replaced by $K_{OL}a'M/V$. This confirms the analogy. From the leaching experiments, values of C_f and $K_{OL}a'M/V$ can be obtained.

6.1.3.2. Large Scale Process in a Packed Tower. Consider a tower packed with the ore to be leached by the simultaneous leaching and solvent extraction process.

Let G be the volumetric flow-rate of liquid/unit tower area

C be the copper concentration in the liquid

a be the mass transfer area per unit tower volume.

H be the mass of ore per unit tower volume

h be the mass of liquid per unit tower volume

z be the vertical distance from the point of entry of the liquid

C_f be the limiting copper concentration in the liquid

x be the weight fraction of copper in solids

A be the cross-sectional area of tower

K_{OL} be the overall mass transfer coefficient, based on the liquid phase/copper concentration driving force

N_{Cu} be the diffusional mass flux of copper

ρ be the density of the liquid.

Consider a mass balance on the copper in an element of the liquid phase (Fig.(29)).

$$GAC + N_{Cu}A - GA(C + dC) = \frac{\partial}{\partial t}(h.A.C.dz) \tag{63}$$

$$N_{Cu} = K_{OL}.a.dz\ (C_f - C) \tag{64}$$

Subs. (64) in (63):-

$$K_{OL}.a.dz.(C_f - C) - GdC = hdz\ \frac{\partial C}{\partial t}$$

$$\therefore\ - G\ \frac{\partial C}{\partial z} + K_{OL}.a.(C_f - C) = h\ \frac{\partial C}{\partial t} \tag{65}$$

By a mass balance on the copper contained in the solid in the element:-

$$K_{OL}.a.A.dz(C_f - C) = -H\frac{\partial x}{\partial t}\ .Adz \tag{66}$$

$$K_{OL}.a.(C_f - C) = -H\frac{\partial x}{\partial t} \tag{67}$$

The relationship between C_f and x must be known before a solution is possible. This relationship can be obtained from the experiments on the extent of leaching of the ore (section 4.16) and in Appendix B.12. it was shown that the relation could be approximately represented by an equation of the form:-

$$C_f = mx + b \tag{68}$$

Let $$C_f = mx + b = w \tag{69}$$

$$N = \frac{K_{OL}\ az}{G} \tag{70}$$

$$\theta = \frac{K_{OL}\,am}{H}\left(t - \frac{hz}{G\rho}\right) \tag{71}$$

N and θ are now both dimensionless. N represents the number of transfer units contained in the tower to a depth z, and θ represents the time that an element of solid, at a depth z in the tower, has been in contact with liquid, other than that originally present in the column.

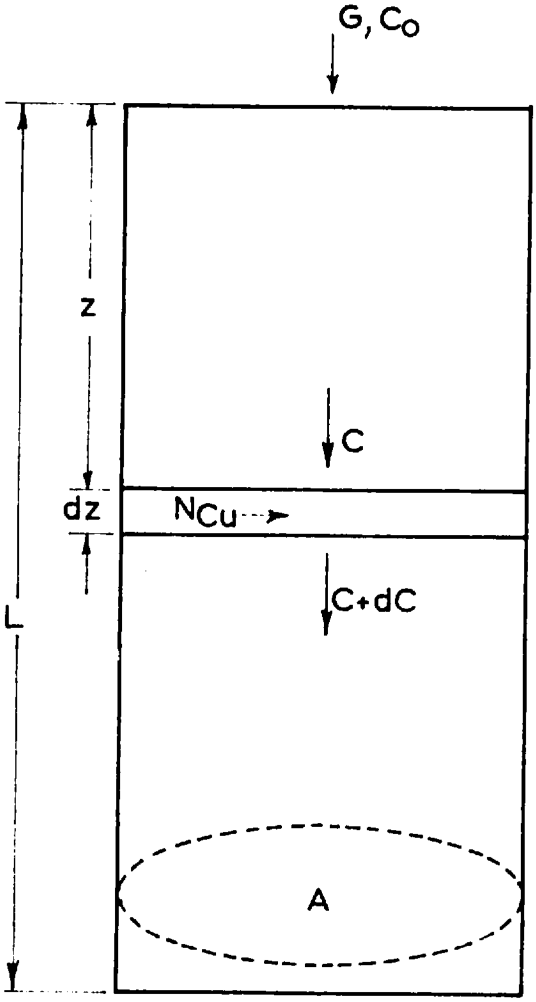


Fig. 29

Now $C = f(z,t) = f(N,\theta)$

$$\therefore\ dC = \left.\frac{\partial C}{\partial z}\right|_t dz + \left.\frac{\partial C}{\partial t}\right|_z dt = \left.\frac{\partial C}{\partial N}\right|_\theta dN + \left.\frac{\partial C}{\partial \theta}\right|_N d\theta$$

$$\therefore\ \left.\frac{\partial C}{\partial z}\right|_t = \left.\frac{\partial C}{\partial N}\right|_\theta \cdot \left.\frac{\partial N}{\partial z}\right|_t + \left.\frac{\partial C}{\partial \theta}\right|_N \cdot \left.\frac{\partial \theta}{\partial z}\right|_t$$

Substituting for N and θ from equations (70) and (71)

$$\left.\frac{\partial C}{\partial z}\right|_t = \left.\frac{\partial C}{\partial N}\right|_\theta \cdot \frac{K_{OL}a}{G} - \left.\frac{\partial C}{\partial \theta}\right|_N \frac{K_{OL}amh}{HG} \qquad (72)$$

Similarly:-

$$\left.\frac{\partial C}{\partial t}\right|_z = \left.\frac{\partial C}{\partial N}\right|_\theta \cdot \frac{\partial N}{\partial t}\ z + \left.\frac{\partial C}{\partial \theta}\right|_N \cdot \left.\frac{\partial \theta}{\partial t}\right|_z$$

Substituting for θ from equation (71)

$$\left.\frac{\partial C}{\partial t}\right|_z = \left.\frac{\partial C}{\partial \theta}\right|_N \cdot \frac{K_{OL}am}{H} \qquad (73)$$

(as ${}^{\partial N}/\partial t = 0$).

Substituting (72) and (73) in equation (65)

$$-G \left.\frac{\partial C}{\partial N}\right|_\theta \cdot \frac{K_{OL}a}{G} - \left.\frac{\partial C}{\partial \theta}\right|_N \cdot \frac{K_{OL}amh}{HG} + K_{OL}a(w-C) = h\,\frac{K_{OL}am}{H} \left.\frac{\partial C}{\partial \theta}\right|_N$$

$$\therefore\ -\left.\frac{\partial C}{\partial N}\right|_\theta = C - w \qquad (74)$$

Now $x = f(z,t) = f(N,\theta)$

$$\therefore\ dx = \left.\frac{\partial x}{\partial t}\right|_z dt + \left.\frac{\partial x}{\partial z}\right|_t dz = \left.\frac{\partial x}{\partial \theta}\right|_N d\theta + \left.\frac{\partial x}{\partial N}\right|_\theta dN.$$

$$\therefore\ \left.\frac{\partial x}{\partial t}\right|_z = \left.\frac{\partial x}{\partial \theta}\right|_N \cdot \left.\frac{\partial \theta}{\partial t}\right|_z + \left.\frac{\partial x}{\partial N}\right|_\theta \cdot \left.\frac{\partial N}{\partial t}\right|_z$$

Subs. for θ from equation (71)

$$\left.\frac{\partial x}{\partial t}\right|_z = \left.\frac{\partial x}{\partial \theta}\right|_N \cdot \frac{K_{OL}am}{H} \qquad (75)$$

Also, from equation (68)

$$x = \frac{w}{m} - \frac{b}{m}$$

$$\therefore \quad dx = \frac{1}{m}\,dw$$

Subs. in equation (67)

$$K_{OL}am(w - C) = -H \frac{\partial w}{\partial \theta}_N \, \frac{K_{OL}am}{H} \cdot \frac{1}{m}$$

$$\therefore \frac{\partial w}{\partial \theta}_N = C - w \tag{76}$$

The boundary conditions are:-

$$\text{at } t = 0, \quad x = x_o \qquad 0 < z < L$$

$$\therefore \text{at } \theta = 0 \quad w = w_o \qquad 0 < N < N_L$$

$$\text{at } z = 0 \quad C = C_o \qquad 0 < t < \infty$$

$$\therefore \text{at } N = 0 \quad C = C_o \qquad 0 < \theta < \infty$$

L = total depth of tower.

Equations (74) and (76) can be solved by using the Laplace Transform method. Taking the Laplace Transform of equation (76) with respect to θ:-

$$p\bar{w} - w_o = \bar{C} - \bar{w}$$

$$\therefore \bar{w}\,(p + 1) = \bar{C} + w_o$$

$$\therefore \quad \bar{w} = \frac{\bar{C} + w_o}{p + 1} \tag{77}$$

From equation (74):-

$$-\frac{d\bar{C}}{dN} = \bar{C} - \bar{w}$$

Substituting for $\bar{w}$ from equation (77)

$$-\frac{d\bar{C}}{dN} = \bar{C} - \frac{\bar{C} + w_o}{p + 1} = \frac{\bar{C}p - w_o}{p + 1}$$

$$\therefore \quad -\int \frac{d\bar{C}}{\bar{C}p - w_o} = \frac{\& \ N}{p + 1} + \text{const.}$$

$$\therefore \quad \frac{1}{p}\ln(\bar{C}p - w_o) = \frac{-N}{p + 1} + \text{const.}$$

$$\therefore \quad \bar{C}p - w_o = A' \exp[-Np/(p + 1)]$$

$$\bar{C} = \frac{w_o + A' \exp[-Np/(p + 1)]}{p} \qquad (78)$$

Now at $N = 0$, $C = C_c$ $\therefore$ $\bar{C} = C_{o/p}$

Subs. in (78):-

$$\therefore \quad \frac{C_o}{p} = \frac{w_o + A'}{p}$$

$$\therefore \quad A' = C_o = w_o \qquad (79)$$

Subs. for A' in eqn. (78)

$$\bar{C} = \frac{w_o + (C_o - w_o) \exp[-N.p/(p + 1)]}{p} \qquad (80)$$

Now $\dfrac{p}{p+1} = 1 - \dfrac{1}{p+1}$

$$\therefore \quad \bar{C} = \frac{w_o + (C_o - w_o) \exp(-N) \ . \ \exp[N/(p + 1)]}{p} \qquad (81)$$

From equation (77)

$$\bar{C} = \bar{w} \ (p + 1) - w_o$$

Subs in (81)

$$\bar{w} \ (p + 1) - w_o = \frac{w_o + (C_o - w_o) \exp(-N) \exp[N/(p + 1)]}{p}$$

$$\therefore \quad \bar{w} = \frac{w_o}{p} + \frac{(C_o - w_o) \exp(-N) \exp[N/(p + 1)]}{p(p + 1)} \qquad (82)$$

Now $\mathcal{L}[J_o 2\sqrt{\alpha t}] = \dfrac{\exp(-\alpha/p)}{p}$

By the use of the Shift Theorem:-

$$\mathcal{L}\left\{[J_0\, 2\sqrt{\alpha t}\,]\exp(-\beta t)\right\} = \frac{\exp[-\alpha/(p+\beta)]}{p+\beta}$$

also $\mathcal{L}(C_o - w_o) = \dfrac{(C_o - w_o)}{p}$

By convolution:-

if $f(p) = \bar{g}(p)\,\bar{h}(p)$

then $f(t) = \int_0^t g(\tau).h(t-\tau)\,d\tau$

Hence equation (82) can be inverted by convolution to yield.

$$\frac{w - w_o}{c_o - w_o} = \int_0^{\theta} J_0(2i\sqrt{Ns}).\exp(-N).\exp(-s)\,ds \qquad (83)$$

(s being an integration variable).

This equation provides, in dimensionless form, the relation between the solid phase copper content at any depth in the tower, the extraction time, and the copper concentration in the solvent.

Equation (83) can be solved to give the time taken for the copper concentration at a given depth in the column to reach a given level. The solution is obtained by evaluating the integrand numerically over the range from zero to an estimated value of θ. The integral is evaluated by Simpsons rule, and plotted as a function of θ, from which the required value of θ can be obtained from a knowledge of the value of $(w - w_o)/(C_o - w_o)$ from the conditions stated.

For values of $Ns > 4$ it is possible to simplify equation (83).

Now for an imaginary argument:-

$$J_n(iy) = i^{-n} I_n(y)$$

If $n = o$ then $J_o(iy) = I_o(y)$

and for large values of y

$$I_o(y) \simeq \frac{\exp(y)}{\sqrt{2\pi y}}$$

Substituting this equation (83)

$$\frac{w - w_o}{C_o - w_o} = \int_o^{\theta} I_o(2\sqrt{N\theta}) \exp(-N) \exp(-\theta)\, d\theta$$

$$= \int_o^{\theta} \frac{\exp(-N) \exp(-\theta) \exp(2\sqrt{N\theta})}{\sqrt{2\pi . 2\sqrt{N\theta}}}\, d\theta$$

$$\therefore \quad \frac{w - w_o}{C_o - w_o} = \int_o^{\theta} \frac{\exp(-N) \exp(2\sqrt{N\theta} - \theta)}{2\sqrt{\pi\sqrt{N\theta}}}\, d\theta \qquad (84)$$

An example of the numerical solution of equation (84) is given in Appendix B.13, from which it is shown that it would take 446 hours (approximately 2.1/2 weeks) to leach 100 tons of ore initially containing 5% copper by weight, until the ore at the base of the tower contained less than 0.1% copper. This is very much slower than the rates obtained in acid leaching plants, where all of the acid-soluble copper is extracted in about 5 hours$^{(11)}$.

6.13.3. Optimum Operating Conditions.

The results of the factorial experiment (Table 14) indicate that higher initial rates of extraction can be obtained by reducing the particle size of the solid, and by increasing the naphthenic acid concentration. The initial rate of extraction was found to increase linearly with naphthenic acid concentration (fig.(26)). This implies that the conditions for a maximum rate of extraction are obtained by using as high a naphthenic acid concentration and as small a particle size as possible. Against these considerations must be placed the cost of grinding the particles to smaller sizes, the increased resistance to flow through beds of small particles compared with beds of large particles, the fact that the organic solution becomes viscous at high copper naphthenic concentrations, and the increased loss of naphthenic acid per unit weight of bed at higher napthenic acid concentrations (Table 12).

In the absence of any specific costing data, it is not possible to specify a set of operating conditions for the optimum performance of the process, but the experimental investigation has shown the trends to be expected on a large scale.

6.2. Solvent Loss Experiments.

6.2.1. Acceptability of Results of Solvent Loss Experiments. Inspection of the results of the solvent loss experiments (summarised in Table 13) reveals that, as with the extraction experiments, there is a considerable scatter. This set of experiments required the use of a moistened solid, as did the extraction experiments, and this could well be the cause of the scatter, for reasons similar to those set out in 6.1.1. for the extraction experiments. However, the factorial experiment showed that, despite the scatter, definite conclusions could be drawn from the results concerning the loss of solvent on the solid bed.

6.2.2. Factors Influencing Solvent Loss. The results of the variance analysis for the solvent loss experiments (summarised in Table 12) show that the solvent loss increas s with increasing particle size, naphthenic acid concentration and with decreasing organic phase copper concentration.

The effect of particle size can be attributed to the fact that in the removal of the solvent by water displacement (as described in section 5.9), the same water velocity was used throughout the experiment. This means that the smaller particles would be agitated much more violently than the larger particles, and hence the chance of rupturing any bond between the organic solvent and the solid would be increased.

The results for the effect of naphthenic acid concentration on the solvent loss are in agreement with those of Wilson(35), who found that drops of naphthenic acid solutions would attach themselves to quartz particles more readily at high napthenic acid concentrations than at low concentrations.

Although no copper ions were introduced directly into the aqueous phase, the moistened quartz remained in contact with the organic copper naphthenate solution for 50 or 150 hours, which was ample time for equilibrium to be attained between the two phases, and hence the quartz would be in contact with a dilute copper solution. According to Wilson(35) the presence of copper ions did not affect the ability of naphthenic acid solution to attach to quartz particles, and this is oontradictory to the results obtained in the present investigation of solvent loss.

During the investigation, drops of naphthenic acid were observed with particles of quartz attached. This would appear to indicate that the solvent is not lost by physical occlusion within the interstices. In view of this fact, consideration should be given to other methods of separating the organic solvent from the solid, either physically or chemically. The bond between the solvent and the solid might be broken by violent pulsing or vibration of the bed, or by the use of ultra-sonics.

The organic solution loss per ton of leached ore residue after water displacement was 12-25 gallons, which is lower than the figure of 15-50 galls/ton of residue quoted by Galvanek(26) for a similar process using a uranium ore and an organic solvent of tri-butyl phosphate. Galvanek has advocated the use of continuous centrifuging as a means of solvent removal(26).

7. CONCLUSIONS.

The results of the investigation into the extraction of copper from malachite by the simultaneous leaching and solvent extraction process show that:-

a) the initial rate of extraction is controlled by the transfer of copper and acid across the aqueous-organic interface, and is independant of the flow-rate of the organic phase and pH and thickness of the aqueous leaching layer,

b) the selectivity of the process for copper over calcium is low,

c) the presence of chrysocolla in the malachite causes a severe reduction in the rate of extraction,

d) the maximum rate of extraction is obtained by using the smallest particle size and highest naphthenic acid concentration compatible with the economics of the process,

e) the mean solvent loss amounted to 1.5 tons of naphthenic acid per ton of copper extracted, the loss occurring by the direct attachment of solid particles to the organic phase.

It is concluded that, in its present form, the process is too slow and unselective to be considered as an alternative to the existing processes for the chemical treatment of non-sulphide ores, and the excessive loss of the organic solvent would have to be drastically reduced to make the process economical.

Appendix A.

Experimental Readings for Leaching Experiments and Solvent Loss Experiments.

A.1. Experimental Readings for Leaching Experiments.

In all these experiments, except where otherwise stated, the ore contained 2.5% $^{w}/w$ malachite, and the copper was extracted into 250 ml of naphthenic acid solution. The weight % of leach solution used was the quantity calculated as in appendix B.1.

A.1.1. Block 1.

Treatment Combination $M_0P_0A_0F_0C_0$

Wt. of ore used 29.8954 g

Wt. % Leach solution used 7.74%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	3.60	120
2.33	0.078	3.60	118
4.42	0.124	3.60	115
8.33	0.230	3.53	81
12.58	0.350	3.59	71
16.92	0.466	3.64	61
20.33	0.560	3.72	60
24.42	0.635	3.82	61
30.58	0.770	3.90	59
35.16	0.905	3.91	54
42.33	0.965	4.08	42
48.50	1.05	4.19	42
54.58	1.15	4.35	50
59.42	1.25	4.42	58
66.58	1.34	4.72	40
72.42	1.39	5.01	34
78.83	1.48	5.21	59
83.25	1.51	5.01	71
90.92	1.60	5.01	51
96.25	1.68	5.05	41

Treatment Combination	$M_0P_1A_1F_0C_0$
Wt. of ore used	30.7901 g
Wt % Leach solution used	26.04%

Extraction time (hrs)	Optical Density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	4.20	90
2.33	0.115	4.15	69
4.42	0.186	4.20	75
8.33	0.289	4.26	90
12.58	0.418	4.30	91
16.83	0.521	4.32	87
20.25	0.602	4.35	63
24.42	0.660	4.25	100
30.58	0.775	4.40	74
35.08	0.845	4.41	85
42.25	0.950	4.42	63
48.50	1.04	4.60	59
54.58	1.12	4.71	70
59.33	1.20	4.85	-
66.50	1.29	5.02	50
72.42	1.29	5.22	60
78.75	1.37	5.60	68
83.25	1.46	5.50	59
90.83	1.50	5.70	60
96.17	1.56	5.79	48

Treatment Combination $M_1P_0A_0F_1C_0$

Wt. of ore used 30.6507 g.

Wt. % Leach solution used 3.75%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.64	290
1.67	0.082	5.55	130
2.75	0.065	5.65	265
6.25	0.104	5.60	130
8.58	0.124	5.95	120
11.67	0.169	5.85	105
14.75	0.200	5.85	110
17.75	0.230	5.76	111
20.75	0.264	5.74	110
24.25	0.295	5.66	100
26.75	0.322	5.73	100
29.42	0.332	5.80	98
35.25	0.389	5.95	98
48.00	0.501	6.05	62
52.17	0.535	6.28	70
55.92	0.575	6.23	60
73.75	0.662	5.35	70
101.33	0.810	5.40	71

Treatment Combination $M_1P_1A_1F_1C_0$

Wt, of ore used 29.7638 g

Wt. % Leach solution used 11.95%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.29	109
1.92	0.062	5.18	122
4.00	0.114	5.09	130
7.92	0.206	4.67	110
12.25	0.300	4.99	119
16.33	0.392	4.46	100
19.67	0.488	4.90	98
24.17	0.540	4.54	90
30.33	0.630	4.71	90
34.58	0.710	4.90	90
41.67	0.825	5.20	92
48.00	0.925	5.29	88
54.17	1.01	4.29	81
58.75	1.06	5.09	82
65.92	1.16	5.10	85
71.92	1.22	4.71	89
78.16	1.29	4.51	88
82.67	1.29	4.69	89
90.25	1.44	5.03	73
95.58	1.48	4.29	71

Treatment Combination $M_1P_0A_0F_0C_1$

Wt. of ore used 29.9370 g

Wt. % Leach solution used 3.75%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	4.60	120
1.00	0.126	4.50	122
1.92	0.195	4.42	121
4.00	0.360	4.29	110
6.00	0.499	4.00	90
7.92	0.622	4.00	89
10.00	0.810	5.20	130
12.25	0.910	5.20	101
16.42	1.32	5.30	89
19.75	1.34	5.70	115
24.17	1.50	5.05	150
26.50	1.58	4.80	170
30.25	1.68	-	-
33.17	1.75	-	-
34.58	1.75	-	-
40.08	1.85	-	-
41.67	1.95	-	-
44.67	2.15	-	-
48.00	2.04	-	-
54.17	2.19	-	-

Treatment Combination	$M_0P_0A_0F_1C_1$
Wt. of ore used	30.3041 g
Wt. % Leach solution used	7.74%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	2.98	98
1.08	0.308	3.39	95
2.08	0.540	3.39	90
4.08	0.970	3.28	79
5.00	1.06	3.29	80
9.83	1.75	3.02	74
11.50	1.64	3.04	62
14.50	1.95	2.92	65
17.92	2.09	2.84	60
20.00	2.15	-	-
24.08	2.44	2.78	59
27.17	2.56	2.79	59
28.67	2.50	2.78	58
34.33	2.84	2.80	55
35.75	2.84	2.80	53
38.25	3.10	2.79	50
41.83	3.01	2.79	51
45.00	3.20	2.74	48
48.00	3.28	2.69	48
52.50	3.28	2.80	48

Treatment Combination $M_1P_1A_1F_0C_1$

Wt. of ore used 28.9772 g

Wt. % Leach solution used 11.95%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	4.75	145
1.25	0.109	4.72	-
2.25	0.146	4.59	112
4.33	0.312	4.54	105
6.17	0.458	4.39	92
8.25	0.605	4.30	88
10.25	0.775	4.32	82
12.58	0.910	4.35	88
16.58	1.23	4.32	81
19.92	1.40	4.32	62
24.50	1.50	4.38	54
26.67	1.58	4.28	60
30.58	1.64	4.21	90
33.33	1.73	4.31	81
34.83	1.72	4.30	180
40.25	1.91	4.44	68
41.92	1.96	4.50	59
44.92	1.76	4.50	72
48.25	2.15	4.50	71
54.50	2.20	4.72	200

Treatment Combination	$M_0P_1A_1F_1C_1$
Wt. of ore used	30.1507 g
Wt. % Leach solution used	26.04%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	3.39	87
1.00	0.215	3.49	99
2.00	0.370	3.40	92
4.08	0.655	3.39	88
6.00	0.860	3.39	80
8.00	1.01	3.41	84
10.00	1.13	3.39	79
12.25	1.25	3.39	80
16.42	1.48	3.36	79
19.83	1.67	3.37	73
24.25	1.95	3.31	71
26.50	1.90	3.37	78
30.25	2.05	3.37	72
33.17	2.10	3.38	78
34.67	2.04	3.35	72
40.17	2.17	3.37	78
41.83	2.25	3.42	70
44.83	2.36	3.35	70
48.08	2.41	3.29	65
54.25	2.61	-	68

A.1.2. Block 2.

Treatment Combination $M_0P_0A_1F_0C_1$

Wt. of ore used 30.2195 g

Wt. % Leach solution used 26.04%

Extraction time (hrs)	Optical denisty of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	3.82	-
1.08	0.330	4.10	-
2.25	0.394	4.10	-
4.00	0.565	4.10	-
6.08	0.763	4.07	100
7.42	0.905	4.10	110
9.25	1.09	4.04	100
12.08	1.31	4.04	101
15.08	1.43	4.04	90
18.33	1.58	4.00	90
21.33	1.74	4.12	90
24.08	1.97	4.15	103
27.08	2.18	4.20	90
30.33	2.17	4.17	88
32.92	2.35	4.20	130
36.33	2.45	-	-
39.17	2.78	4.12	80
42.58	2.49	-	-
48.00	2.66	4.26	60

Treatment Combination $M_0P_1A_0F_0C_1$

Wt. of ore used 29.5270 g

Wt. % Leach solution used 7.74%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	3.11	-
1.33	0.384	3.14	-
2.42	0.580	3.25	-
4.33	0.870	3.21	-
6.33	1.05	3.09	90
7.58	1.20	3.29	70
9.50	1.32	3.29	89
12.33	1.58	3.40	86
15.33	1.70	3.49	92
18.58	1.88	3.51	82
21.58	2.02	3.50	82
24.33	2.38	3.53	70
27.25	2.40	3.45	40
30.50	2.38	3.49	42
33.17	2.45	3.50	52
36.58	2.67	-	-
39.42	2.95	3.48	80
42.75	2.62	-	-
48.17	2.76	3.55	-

Treatment Combination $M_1P_0A_1F_1C_1$

Wt. of ore used 30.0150 g

Wt. % Leach solution used 11.95%

Extraction time (hrs)	Optical density of original phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.05	50
1.33	0.054	5.68	120
2.42	0.096	3.65	40
4.33	0.147	3.55	138
6.50	0.199	3.25	89
7.58	0.232	3.75	190
9.42	0.302	3.44	92
12.33	0.418	3.35	85
15.33	0.520	3.35	50
18.58	0.750	3.25	70
21.50	0.850	3.05	60
24.25	1.50	2.95	59
27.17	1.58	3.25	30
30.42	1.48	3.25	22
33.08	1.57	3.25	60
36.58	1.57	3.27	50
39.42	1.75	3.06	70
42.67	1.59	-	-
48.08	1.84	3.65	73

Treatment Combination	$M_1P_0A_1F_0C_0$
Wt. of ore used	30.0945 g
Wt. % Leach solution used	11.95%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.08	25
2.25	0.026	5.10	149
4.17	0.053	5.08	141
7.33	0.120	5.08	130
12.17	0.172	5.04	160
16.42	0.228	5.10	232
21.33	0.308	5.13	137
24.00	0.350	5.08	80
30.25	0.468	5.02	120
36.42	0.530	5.10	190
42.42	0.620	-	-
47.83	0.675	5.14	117
53.92	0.890	5.14	110
60.08	0.950	5.20	155
65.75	0.900	5.18	170
72.17	0.950	5.08	119
78.08	1.01	4.92	170
84.92	1.05	4.98	230
89.83	1.10	5.00	118

Treatment Combination $M_1P_1A_0F_1C_1$

Wt. of ore used 30.3309 g

Wt. % Leach solution used 3.75%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	-	20
0.92	0.089	4.31	178
2.08	0.142	4.88	146
4.00	0.219	5.00	180
5.92	0.285	4.59	142
7.17	0.340	4.80	139
9.00	0.432	4.90	110
11.92	0.605	4.89	149
14.92	0.760	5.59	139
18.17	0.910	-	130
21.17	1.08	4.14	180
23.75	1.45	4.71	124
26.67	1.55	4.78	92
30.00	1.69	4.80	111
32.67	1.73	4.80	-
36.17	1.68	4.81	119
38.92	1.85	4.70	120
42.17	1.63	-	-
47.67	1.77	4.99	130

Treatment Combination	$M_1P_1A_0F_0C_0$
Wt. of ore used	29.5700 g
Wt. % Leach solution used	3.75%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.21	130
2.00	0.087	4.86	127
3.92	0.073	5.01	140
7.00	0.124	4.90	129
11.83	0.201	4.89	129
16.00	0.269	4.89	125
21.08	0.330	4.76	119
23.58	0.354	4.71	117
29.83	0.428	4.70	110
36.08	0.482	4.71	214
42.08	0.540	-	-
47.50	0.598	4.61	105
53.58	0.680	4.60	104
59.75	0.670	4.61	102
65.42	0.730	4.55	100
71.75	0.780	4.58	100
77.67	0.805	4.59	100
84.50	0.850	4.63	110
89.42	0.850	4.79	109

Treatment Combination $M_0P_0A_1F_1C_0$

Wt. of ore used 29.9672 g

Wt. % Leach solution used 26.04%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	-	-
2.08	0.181	-	-
3.92	0.300	-	-
7.00	0.449	-	-
11.92	0.600	-	-
16.00	0.702	-	-
21.08	0.807	-	-
23.58	0.855	-	-
29.83	0.960	-	-
36.17	1.07	-	-
42.08	1.16	-	-
47.50	1.22	-	-
53.58	1.30	-	-
59.83	1.35	-	-
65.42	1.39	-	-
71.75	1.45	-	-
77.75	1.48	-	-
84.50	1.55	-	-
89.42	1.58	-	-

Treatment Combination	$M_0P_1A_0F_1C_0$
Wt. of ore used	30.2619 g
Wt. % Leach solution used	7.74%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	3.40	10
2.00	0.184	4.84	2
3.92	0.305	3.35	40
6.92	0.440	3.41	14
11.92	0.630	3.40	19
15.92	0.720	3.36	32
21.08	0.780	3.39	32
23.58	0.825	3.38	49
29.75	0.920	3.45	49
36.08	1.01	3.52	60
42.00	1.09	-	-
47.42	1.17	3.63	59
53.58	1.25	3.60	60
59.75	1.31	3.71	49
65.33	1.37	3.64	60
71.67	1.44	3.64	57
77.67	1.48	3.52	60
84.42	1.55	3.70	72
89.42	1.59	3.80	70

A.1.3. Block 3.

Treatment Combination	$M_0P_0A_1F_0C_0$
Wt. of ore used	29.8604 g
Wt. % Leach solution used	26.04%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.02	91
1.42	0.080	4.75	81
3.92	0.156	4.61	81
8.00	0.251	4.80	81
12.08	0.330	5.41	91
15.92	0.393	5.32	98
19.75	0.444	5.40	100
23.83	0.500	-	93
30.00	0.582	5.30	90
36.25	0.700	-	89
41.75	0.760	5.38	89
47.83	0.855	5.17	81
53.83	0.940	5.19	62
59.92	1.04	5.60	90
65.67	1.11	5.70	94
71.75	1.15	5.70	91
78.25	1.25	5.89	90
83.83	1.31	6.05	100
89.33	1.35	6.11	91

Treatment Combination	$M_0P_1A_0F_0C_0$
Wt. of ore used	29.8524 g
Wt. % Leach solution used	7.74%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.09	100
1.25	0.095	4.88	91
3.83	0.156	4.79	88
7.83	0.283	4.89	92
12.00	0.376	5.00	100
15.75	0.450	5.10	99
19.50	0.492	4.96	85
23.58	0.555	5.11	88
29.83	0.650	5.30	88
36.17	0.722	5.40	81
41.50	0.805	5.50	75
47.58	0.840	5.37	70
53.67	0.925	5.62	75
59.75	0.990	5.69	71
65.50	1.05	5.88	80
71.50	1.09	5.80	78
78.08	1.16	5.80	82
83.67	1.20	5.92	78
89.08	1.25	6.00	80

Treatment Combination $M_1P_0A_1F_1C_0$

Wt. of ore used 30.4034 g

Wt. % Leach solution used 11.95%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.30	29
1.25	0.018	5.15	22
3.75	0.036	4.70	25
7.83	0.067	4.80	20
12.00	0.095	5.00	30
15.75	0.119	5.10	32
19.42	0.134	5.11	32
23.50	0.150	4.76	22
29.83	0.190	4.88	30
36.08	0.228	4.78	38
41.42	0.240	5.06	50
47.50	0.284	4.80	39
53.58	0.331	5.06	72
59.75	0.380	5.30	61
65.42	0.410	5.08	52
71.42	0.448	4.94	51
78.00	0.506	5.10	69
83.67	0.548	5.26	60
89.50	0.599	5.31	60

Treatment Combination	$M_1P_0A_1F_0C_1$
Wt. of ore used	30.1662 g.
Wt. % Leach solution used	11.95%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	-	-
1.00	0.046	-	-
2.00	0.094	-	-
4.08	0.157	-	-
6.08	0.219	-	-
7.75	0.261	-	-
9.83	0.321	-	-
11.75	0.370	-	-
14.75	0.468	-	-
18.25	0.550	-	-
19.58	0.600	-	-
24.50	0.790	-	-
27.08	0.860	-	-
29.75	0.950	-	-
33.75	0.985	-	-
35.83	1.045	-	-
38.58	1.10	-	-
42.00	1.24	-	-
48.08	1.35	-	-

Treatment Combination	$M_1P_1A_0F_1C_0$
Wt. of ore used	30.1981 g
Wt. % Leach solution used	3.75%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.52	19
1.75	0.080	5.20	20
4.25	0.083	5.71	29
8.25	0.130	5.02	41
12.33	0.201	5.11	60
16.25	0.226	5.10	65
20.08	0.275	5.10	69
24.25	0.295	4.98	68
30.33	0.350	4.80	69
36.50	0.410	5.02	72
42.08	0.446	5.09	70
48.33	0.487	4.85	79
54.17	0.538	4.88	61
60.25	0.585	5.21	70
66.08	0.645	5.29	67
72.17	0.655	5.21	62
78.58	0.690	5.39	61
84.17	0.725	5.50	61
89.75	0.765	5.60	60

Treatment Combination $M_1P_1A_0F_0C_1$

Wt. of ore used 30.2709 g

Wt. % Leach solution used 3.75%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.49	62
1.17	0.050	5.37	89
2.00	0.082	5.29	100
4.17	0.123	4.88	100
6.42	0.180	4.70	90
8.25	0.240	4.81	92
11.50	0.370	4.99	91
12.33	0.390	5.07	91
15.50	0.460	4.89	86
18.33	0.521	4.94	96
22.25	0.615	5.00	95
24.17	0.700	4.88	91
27.08	0.760	4.89	45
30.25	0.825	4.79	39
31.83	0.855	4.88	81
36.50	0.870	5.08	82
39.25	0.975	5.14	81
42.00	1.11	5.11	80
48.25	1.14	4.93	94

Treatment Combination $M_0P_0A_1F_1C_1$

Wt. of ore used 30.3602 g

Wt. % Leach solution used 26.04%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.19	92
1.00	0.044	5.41	118
1.92	0.063	5.60	129
4.17	0.115	5.18	115
6.33	0.161	5.20	110
8.25	0.210	5.40	120
11.33	0.300	5.57	128
12.33	0.318	5.52	122
15.42	0.347	5.60	125
18.25	0.426	5.68	130
22.08	0.512	5.63	122
24.00	0.605	5.43	119
26.92	0.690	5.60	129
30.25	0.760	5.49	120
31.75	0.810	5.40	129
36.50	0.905	5.60	121
39.17	0.975	5.70	122
41.92	1.04	5.71	128
48.00	1.20	5.46	118

Treatment Combination	$M_0P_1A_0F_1C_1$
Wt. of ore used	30.2943 g
Wt. % Leach solution used	7.74%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.50	11
1.33	0.085	5.55	14
2.25	0.097	5.39	35
4.33	0.156	5.00	29
6.58	0.233	4.99	24
8.33	0.294	5.07	29
11.67	0.432	5.12	30
12.42	0.460	5.15	30
15.50	0.540	4.94	25
18.42	0.676	4.98	20
22.50	0.855	5.02	18
24.42	0.925	4.77	16
27.33	1.045	4.65	18
30.42	1.11	4.50	15
32.08	1.15	4.69	20
36.67	1.25	4.50	21
39.42	1.32	4.82	12
42.25	1.41	4.80	20
48.50	1.54	4.46	16

A.1.4. Block 4.

Treatment Combination	$M_1P_0A_0F_0C_0$
Wt. of ore used	30.1592 g
Wt. % Leach solution used	3.75%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	4.96	110
1.92	0.064	4.76	98
3.83	0.090	4.75	122
8.17	0.153	5.03	129
12.25	0.197	5.00	122
16.00	0.244	5.09	124
20.33	0.299	5.13	108
25.33	0.351	5.06	110
30.08	0.388	5.04	107
36.50	0.440	5.08	100
42.17	0.490	5.24	99
49.08	0.542	5.02	90
54.00	0.580	4.88	88
60.00	0.600	4.66	82
73.00	0.675	5.29	80
78.00	0.720	5.34	80
84.00	0.750	4.79	77
90.00	0.795	4.75	78

Treatment Combination	$M_1P_1A_1F_0C_0$
Wt. of ore used	30.0177g
Wt. % Leach solution used	11.95%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	-	-
1.83	0.037	-	-
3.75	0.061	-	-
8.00	0.112	-	-
11.67	0.136	-	-
15.50	0.196	-	-
20.00	0.250	-	-
25.17	0.302	-	-
29.92	0.331	-	-
35.92	0.392	-	-
41.58	0.460	-	-
48.92	0.535	-	-
53.58	0.580	-	-
59.42	0.612	-	-
72.58	0.745	-	-
77.50	0.780	-	-
83.50	0.840	-	-
89.50	0.905	-	-

Treatment Combination $M_0P_0A_0F_1C_0$

Wt. of ore used 29.8354 g

Wt. % Leach solution used 7.74%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	4.89	108
1.75	0.080	4.75	110
3.67	0.118	4.99	119
7.92	0.194	5.38	138
11.50	0.228	5.35	130
15.25	0.283	5.31	126
19.83	0.360	-	118
25.00	0.439	5.00	110
29.83	0.490	4.88	101
35.75	0.580	4.83	93
41.42	0.680	4.73	87
48.83	0.780	4.47	80
53.42	0.867	4.50	81
59.25	0.900	4.43	76
72.50	1.04	4.48	70
77.75	1.04	4.28	82
83.67	1.11	4.32	73
89.67	1.15	4.28	74

Treatment Combination $M_0P_0A_0F_0C_1$

Wt. of ore used 30.5526 g

Wt. % Leach solution used 7.74%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	-	-
0.75	0.146	4.54	80
1.75	0.223	4.65	102
3.67	0.355	4.55	109
5.58	0.552	4.47	100
7.92	0.805	4.25	86
9.25	0.870	4.14	80
11.42	0.975	4.15	80
14.33	1.19	4.12	71
17.83	1.35	4.15	71
20.67	1.44	4.22	70
25.08	1.58	4.05	69
26.58	1.70	3.90	70
29.83	1.69	3.88	69
32.33	1.75	3.97	67
35.67	1.85	4.04	68
38.33	1.90	4.05	56
41.42	2.00	4.04	55
48.83	2.11	3.93	58

Treatment Combination	$M_0P_1A_0F_1C_0$
Wt. of ore used	30.1350 g
Wt. % Leach solution used	26.04%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	4.73	51
2.42	0.141	4.82	60
4.33	0.190	4.98	66
8.67	0.280	4.78	88
12.58	0.363	4.72	103
16.33	0.437	4.70	106
20.75	0.545	4.71	99
25.83	0.675	4.50	86
30.58	0.750	4.25	80
36.83	0.895	4.38	70
42.42	0.955	4.38	61
49.58	1.05	4.19	68
54.33	1.09	-	60
60.25	1.16	4.29	49
73.42	1.30	4.42	49
78.33	1.31	4.40	58
84.33	1.37	4.44	50
90.33	1.45	4.47	37

Treatment Combination	$M_0P_1A_1F_0C_1$
Wt. of ore used	29.8880 g
Wt. % Leach solution used.	26.04%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	4.26	82
1.17	0.136	4.41	58
2.08	0.204	4.50	73
4.00	0.288	4.45	97
6.17	0.412	4.39	118
8.25	0.537	4.33	112
9.92	0.760	4.18	125
12.17	0.730	4.44	100
15.00	0.900	4.14	102
18.50	1.15	4.34	95
21.25	1.28	4.37	94
25.42	1.50	4.17	102
27.08	1.65	4.03	93
30.25	1.69	4.35	-
33.00	1.76	4.20	88
36.42	1.89	4.54	85
39.08	1.95	4.64	87
42.00	2.05	4.88	94
49.25	2.25	4.55	82

Treatment Combination	$M_1P_0A_0F_1C_1$
Wt. of ore used	30.2247 g
Wt. % Leach solution usedc	3.75%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.04	78
1.08	0.045	5.04	90
2.00	0.106	5.62	-
3.92	0.134	4.76	109
6.00	0.208	4.46	110
8.17	0.282	4.50	110
9.75	0.311	4.58	109
11.92	0.380	-	-
14.83	0.480	-	-
18.33	0.655	-	-
21.08	0.720	-	-
25.33	0.825	-	98
27.00	0.970	-	105
30.17	0.950	-	-
32.83	1.00	-	110
36.17	1.06	-	-
38.92	1.11	-	-
41.83	1.19	-	-
49.08	1.26	-	-

Treatment Combination $E_1P_1A_1F_1C_1$

Wt. of ore used 29.4218 g

Wt. % Leach solution used 11.95%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	3.92	110
1.08	0.104	3.85	119
1.92	0.141	4.89	121
3.83	0.214	4.75	120
6.08	0.307	3.72	119
8.17	0.400	3.62	112
9.92	0.458	3.81	-
12.17	0.555	3.67	101
15.00	0.725	3.55	98
18.50	0.905	3.60	90
21.17	1.04	3.56	88
25.33	1.34	3.32	80
27.00	1.36	3.10	79
30.08	1.34	3.42	80
33.00	1.44	3.15	78
36.42	1.51	-	77
39.08	1.56	-	74
42.00	1.70	-	71
49.08	1.80	-	70

A.2. Summary of Results of Curve Fitting for Tests in Factorial Experiment.

Treatment Combination M P A F C	C_r (Optical density)	k (hrs^{-1})	Residual sum of squares
0 0 0 0 0	2.2439	0.013628	0.007654
1 0 0 0 0	0.9751	0.017040	0.005469
0 1 0 0 0	1.4281	0.020726	0.02655
1 1 0 0 0	1.1200	0.016250	0.005179
0 0 1 0 0	1.9339	0.012872	0.021847
1 0 1 0 0	1.9995	0.009081	0.037031
0 1 1 0 0	1.8375	0.018052	0.019723
1 1 1 0 0	1.6731	0.008043	0.005641
0 0 0 1 0	1.6798	0.012733	0.010844
1 0 0 1 0	1.0840	0.013178	0.005716
0 1 0 1 0	1.5914	0.031762	0.10038
1 1 0 1 0	0.9669	0.015746	0.008578
0 0 1 1 0	1.5876	0.033732	0.055405
1 0 1 1 0	0.8856	0.009713	0.020800
0 1 1 1 0	1.7254	0.018941	0.011411
1 1 1 1 0	2.0858	0.012327	0.008091

Treatment Combination M P A N C	C_f (Optical density)	k (hrs^{-1})	Residual sum of squares
0 0 0 0 1	2.2271	0.051520	0.026809
1 0 0 0 1	2.4208	0.040193	0.061019
0 1 0 0 1	2.8781	0.065110	0.026624
1 1 0 0 1	2.0295	0.016966	0.014289
0 0 1 0 1	3.0484	0.044396	0.18630
1 0 1 0 1	1.3665	0.037545	0.15143
0 1 1 0 1	3.3402	0.022902	0.038851
1 1 1 0 1	2.4311	0.038021	0.10973
0 0 0 1 1	3.3051	0.060779	0.38750
1 0 0 1 1	1.3434	0.039370	0.099317
0 1 0 1 1	2.8093	0.015755	0.039523
1 1 0 1 1	2.8132	0.024858	0.31723
0 0 1 1 1	2.1293	0.014801	0.044844
1 0 1 1 1	3.5333	0.015981	0.57324
0 1 1 1 1	2.5095	0.058106	0.14519
1 1 1 1 1	2.8449	0.021236	0.068265

A.3. Experimental Readings for the Investigation of the Effect of Naphthenic Acid Concentration on the Extraction Process.

In this set of experiments, the factors M, P, and F were all maintained at their low level. Factor A (thickness of aqueous leaching layer) was maintained at its high level. The ore contained 2.1/2% malachite by weight, and was contacted with 250 ml of naphthenic acid solution.

Naphthenic acid concentration	0.1M
Wt. of ore used	30.04 g

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	6.85	152
1.67	0.003	6.78	165
3.83	0.014	6.72	169
7.00	0.031	6.72	163
9.92	0.048	6.70	178
13.17	0.066	6.59	170
23.67	0.119	6.68	165
28.00	0.145	6.82	172
32.17	0.172	6.80	163
37.00	0.211	-	162
48.33	0.260	-	150
53.75	0.334	6.90	140
73.33	0.436	7.10	137
79.33	0.470	-	150
99.08	0.525	4.68	159
121.58	0.602	-	140
149.00	0.645	6.90	139

Naphthenic acid concentration 0.3M

Wt. of ore used 30.01 g

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	7.18	165
1.67	0.020	6.61	195
3.75	0.048	6.50	189
7.00	0.093	6.49	182
9.92	0.133	6.64	160
13.17	0.179	6.39	180
23.67	0.316	6.37	158
27.92	0.370	6.57	184
32.17	0.433	6.50	148
37.00	0.505	6.79	160
48.33	0.695	6.91	148
53.75	0.755	7.22	192
73.33	1.005	7.19	140
79.33	1.11	-	165
99.00	1.40	7.24	125
121.50	1.60	7.19	120
149.00	1.81	7.67	140

Naphthenic acid concentration 0.5M

Wt. of ore used 30.02 g

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	6.11	100
1.67	0.032	5.93	100
3.75	0.078	6.00	110
7.00	0.139	5.80	150
9.92	0.207	5.64	130
13.08	0.269	5.63	100
23.67	0.473	5.51	142
27.92	0.545	5.59	147
32.17	0.715	5.56	119
36.92	0.780	5.91	127
48.33	0.910	5.71	108
53.67	0.940	5.61	100
73.33	1.22	5.71	82
79.33	1.27	5.73	72
99.00	1.41	5.71	40
121.50	1.56	3.51	96
145.17	1.85	3.21	54

Naphthenic acid concentration 0.7M

Wt. of ore used 30.01 g

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	-	-
1.50	0.048	-	-
3.58	0.110	-	-
6.75	0.184	-	-
9.75	0.251	-	-
12.92	0.330	-	-
23.50	0.522	-	-
27.75	0.675	-	-
31.92	0.720	-	-
36.75	0.775	-	-
48.17	0.825	-	-
53.50	0.995	-	-
73.17	1.15	-	-
79.08	1.19	-	-
98.75	1.31	-	-
121.25	1.40	-	-
148.75	1.54	-	-

Naphthenic acid concentration 0.9M

Wt. of ore used 30.02 g

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	4.31	52
1.42	0.072	4.13	92
3.50	0.139	4.36	110
6.75	0.247	4.13	111
9.67	0.341	4.31	109
12.83	0.449	4.44	111
23.50	0.770	4.15	108
27.67	0.865	4.68	108
31.92	0.960	4.62	100
36.67	1.05	4.56	106
48.08	1.21	4.41	105
53.42	1.27	4.23	108
73.08	1.49	4.60	110
79.00	1.58	4.74	109
98.75	1.63	4.55	120
121.17	1.79	3.53	117
148.67	1.95	3.51	115

Naphthenic acid concentration 1.1M

Wt. of ore used 29.99 g

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	-	-
1.42	0.040	-	-
3.50	0.061	4.95	150
6.75	0.102	4.98	159
9.67	0.141	4.93	152
12.75	0.180	4.92	149
23.42	0.303	4.93	139
27.67	0.352	4.94	140
31.83	0.416	4.94	135
36.58	0.457	4.93	139
48.08	0.550	4.93	137
53.33	0.600	4.87	132
73.08	0.820	4.83	129
79.00	0.885	4.85	132
98.67	1.03	4.93	130
121.17	1.18	4.93	110
148.67	1.45	4.83	110

Naphthenic acid concentration	1.3M
Wt. of ore used	30.10 g

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	4.56	-
1.33	0.077	4.50	123
3.58	0.185	4.39	170
6.67	0.324	4.40	170
9.67	0.453	4.32	160
12.75	0.587	4.48	160
23.42	1.08	4.26	158
27.67	1.10	4.25	155
31.83	1.18	4.18	142
36.58	1.33	4.19	155
48.08	1.52	3.98	164
53.33	1.64	3.88	154
73.08	1.88	3.66	152
78.92	1.92	3.53	140
98.67	2.16	3.26	154
121.08	2.34	2.88	140
148.58	2.46	2.50	138

Naphthenic acid concentration 1.5M

Wt. of ore used 30.02 g

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	-	-
1.33	0.109	-	-
3.42	0.231	-	-
6.67	0.390	-	-
9.58	0.545	-	-
12.67	0.865	-	-
23.42	1.13	-	-
27.58	1.28	-	-
31.83	1.36	-	-
36.50	1.47	-	-
48.00	1.75	-	-
53.33	1.75	-	-
73.00	2.08	-	-
78.92	2.15	-	-
98.58	2.50	-	-
121.08	2.59	-	-
148.58	2.91	-	-

Naphthenic acid concentration	1.7M
Wt. of ore used	30.02 g

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	-	-
1.42	0.160	-	-
3.42	0.260	-	-
6.67	0.441	-	-
9.67	0.605	-	-
12.67	0.950	-	-
23.42	1.29	-	-
27.67	1.37	-	-
31.83	1.48	-	-
36.50	1.60	-	-
48.08	1.83	-	-
53.33	1.92	-	-
73.08	2.20	-	-
78.92	2.33	-	-
98.58	2.61	-	-
121.08	2.82	-	-
148.58	3.00	-	-

A.4. Summary of Results of Curve Fitting.

Naphthenic acid concentration (M/1)	C_f (optical density)	k (hrs^{-1})	Residual sum of squares
0.1	1.1338	0.006028	0.008919
0.3	3.4734	0.004821	0.033223
0.5	2.2957	0.010199	0.025292
0.7	1.6235	0.017132	0.016705
0.9	1.9769	0.020009	0.015814
1.1	1.2087	0.015417	0.196280
1.3	2.5250	0.020055	0.039232
1.5	2.8988	0.019503	0.147930
1.7	2.9914	0.021171	0.163360

A.5. Experimental Readings for Selectivity Investigation.

Treatment combination	$M_0P_0A_1F_0C_1$
Wt. of calcite/malachite mixture	30.7886 g
% malachite in mixture	2.5%
Wt. % leach solution used	26.04%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.60	145
1.83	0.040	5.50	134
3.92	0.050	5.85	158
8.50	0.086	5.90	160
13.50	0.111	5.90	160
26.00	0.152	5.91	180
32.25	0.161	5.98	178
37.83	0.186	5.85	182
50.17	0.208	6.02	180
56.74	0.212	5.90	153

Treatment combination	$M_0P_0A_1F_0C_1$
Wt. of calcite/malachite mixture	29.8596%
% malachite in mixture	2.94%
Wt. % leach solution used	26.04%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
0.00	0.000	5.95	120
0.92	0.016	5.72	125
2.92	0.041	5.80	139
6.83	0.071	6.02	143
9.00	0.101	6.20	152
12.92	0.116	5.97	147
25.42	0.193	6.02	150
31.75	0.239	6.08	153
37.42	0.266	6.09	158
49.17	0.310	5.85	150
56.08	0.317	6.08	158
60.92	0.340	5.95	160
74.33	0.378	6.20	160
85.08	0.387	6.20	160
98.00	0.418	6.20	160
107.67	0.425	6.22	160
121.92	0.451	6.22	160

A.6. Experimental Readings for Investigation into Extent of Leaching.

Test 1.	Treatment combination	$M_0P_0A_1F_0C_1$
	Wt. of ore used	29.6987 g
	Wt. % leach solution used	26.04%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
Stage 1.			
0.00	0.000	6.78	109
1.17	0.007	6.51	108
3.17	0.008	6.50	120
7.00	0.025	6.24	137
9.08	0.037	5.78	98
13.33	0.070	5.90	160
25.67	0.112	5.90	148
32.00	0.166	5.80	130
37.75	0.207	5.79	152
49.42	0.246	5.55	142
56.33	0.260	5.63	136
61.25	0.285	5.60	145
74.67	0.330	5.50	110
85.42	0.339	5.54	134
98.33	0.374	5.45	141
Stage 2.			
0.00	0.000	5.60	150
1.25	0.003	5.40	130
8.67	0.020	5.38	157
22.83	0.041	5.30	130
34.67	0.047	5.25	142
46.75	0.067	5.20	135
72.25	0.073	5.20	120
95.25	0.107	5.10	120
119.33	0.122	5.03	120
189.75	0.190	4.89	121
Stage 3.			
0.00	0.000	5.09	130
7.08	0.005	5.20	130
20.92	0.013	4.92	137
31.42	0.020	4.94	123
44.17	0.034	4.95	150
68.00	0.060	4.92	132
91.50	0.089	4.91	98
121.58	0.137	4.97	90
174.33	0.215	4.90	110
188.08	0.220	4.85	100
211.42	0.240	4.85	118

Test 2. Treatment combination $M_0P_0A_1F_0C_1$

Wt. of ore used 29.0684 g

Wt. % leach solution used 26.04%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
Stage 1.			
0.00	0.000	5.65	100
1.17	0.007	5.56	120
3.08	0.015	5.58	147
7.00	0.043	5.70	174
9.25	0.065	5.59	182
13.25	0.099	5.10	180
25.67	0.211	5.32	174
32.00	0.311	5.25	170
37.67	0.390	5.14	162
49.42	0.529	5.13	159
56.33	0.591	5.12	155
61.17	0.620	5.06	152
74.58	0.755	5.04	149
85.33	0.770	4.95	145
98.33	0.920	5.02	143
108.50	0.995	5.09	150
Stage 2.			
0.00	0.000	5.00	160
14.00	0.043	4.92	150
27.75	0.088	4.88	152
37.92	0.136	4.98	145
63.42	0.220	4.78	140
86.42	0.286	4.70	141
110.42	0.341	4.60	128
180.83	0.493	4.95	138

Test 3. Treatment combination $M_1P_0A_1F_0C_1$

Wt. of ore used 29.5933 g

Wt. % leach solution used 11.95%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
Stage 1.			
0.00	0.000	5.25	102
1.08	0.003	5.40	120
6.92	0.070	5.50	92
9.08	0.104	5.62	101
13.08	0.147	5.89	120
25.50	0.304	5.95	120
31.92	0.347	6.05	131
37.58	0.394	6.20	135
49.33	0.430	5.82	139
56.17	0.469	6.00	110
60.08	0.520	6.21	110
74.50	0.578	6.04	110
85.17	0.605	6.38	130
98.17	0.610	6.20	115
Stage 2.			
0.00	0.000	6.53	120
1.17	0.001	6.10	100
8.58	0.011	6.56	123
22.83	0.031	6.24	128
34.67	0.043	6.25	-
46.83	0.055	5.89	110
72.33	0.075	5.85	112
95.25	0.092	6.10	107
119.33	0.107	5.69	100
189.67	0.155	6.89	90
Stage 3.			
0.00	0.000	6.26	105
7.25	0.003	6.00	110
21.00	0.012	5.66	100
31.58	0.024	6.11	85
44.25	0.037	5.90	85
68.17	0.067	5.91	93
91.75	0.097	5.50	94
121.67	0.139	5.96	98
174.42	0.218	6.10	100
188.25	0.230	5.50	89
211.50	0.253	5.72	99

Test 4. Treatment combination $M_0P_0A_1F_0C_1$

Wt. of ore used 33.5897 g

Wt. % malachite in ore 5%

Wt. % leach solution used 26.04%

Extraction time (hrs)	Optical density of organic phase	pH	Cu/Ag-AgCl Electrode (mV)
Stage 1.			
0.00	0.000	-	-30
1.00	0.674	3.35	-10
1.92	0.920	-	9
3.67	1.35	-	20
5.33	1.68	-	31
8.67	2.00	-	39
12.17	2.27	-	41
22.17	2.96	-	49
27.75	3.19	-	49
36.83	3.35	-	50
47.25	3.30	-	50
47.75	3.50	-	48
Stage 2.			
0.00	0.000	-	48
1.75	0.344	-	42
4.92	0.487	-	20
8.58	0.655	-	10
23.58	0.970	-	20
28.42	1.25	-	20
53.75	1.76	-	25
94.75	2.26	-	25
Stage 3.			
0.00	0.000	-	20
2.25	0.188	-	-40
6.00	0.235	-	-20
9.50	0.295	-	-15
21.42	0.507	-	0
33.08	0.670	-	2
44.92	0.850	-	2

A.7. Summary of Results of Curve Fitting.

Test	Stage	C_f (Optical density)	k (hrs^{-1})	Residual sum of squares
1	1	0.5695	0.010926	0.002030
	2	0.2797	0.005251	0.000680
	3	0.3403	0.004601	0.005183
2	1	1.4949	0.008830	0.032609
	2	0.8309	0.004847	0.000312
3	1	0.7409	0.01908	0.003394
	2	0.2304	0.00574	0.000079
	3	0.3375	0.00496	0.006200
4	1	3.3412	0.11802	0.34672
	2	2.3975	0.02648	0.14905
	3	1.0098	0.03631	0.01747

A.8. Experimental Readings for Solvent Loss Experiments.

Test M P A T C R	Wt. of quartz (g)	% Leach Soln. (by weight) used	Vol. of aqueous effluent collected (ml)	Dilution of sample	O.D. of diluted sample.
0 0 0 0 0 0	35.9577	7.74	50.0	6.25	0.105
1 0 0 0 0 1	32.7390	3.75	50.0	12.5	0.255
0 1 0 0 1 1	32.5063	7.74	50.0	4.17	0.061
1 1 0 0 1 0	32.7984	3.75	50.0	12.5	0.071
0 0 1 0 1 1	33.6456	26.04	50.0	6.25	0.137
1 0 1 0 1 0	32.8294	11.95	50.0	6.25	0.136
0 1 1 0 0 0	32.8268	26.04	50.0	6.25	0.113
1 1 1 0 0 1	32.3940	11.95	50.0	6.25	0.128
0 0 0 1 1 0	32.9852	7.74	50.0	6.25	0.134
1 0 0 1 1 1	32.4206	3.75	50.0	6.25	0.131
0 1 0 1 0 1	32.0418	7.74	50.0	6.25	0.254
1 1 0 1 0 0	31.3883	3.75	50.0	6.25	0.157
0 0 1 1 0 1	32.3321	26.04	50.0	6.25	0.193
1 0 1 1 0 0	32.4663	11.95	50.0	6.25	0.163
0 1 1 1 1 0	32.0448	26.04	46.0	25	0.090
1 1 1 1 1 1	32.7493	11.95	50.0	6.25	0.110

Test						Wt. of quartz (g)	% Leach Soln. (by weight) used	Vol. of aqueous effluent collected (ml)	Dilution of sample	O.D. of diluted sample.
M	P	A	T	C	R					
0	1	0	0	0	1	33.2294	7.74	50.0	5	0.601
1	1	0	0	0	0	32.7692	3.75	50.0	5	0.625
0	0	1	0	0	1	32.6240	26.04	50.0	5	0.557
1	0	1	0	0	0	33.0632	11.95	50.0	5	0.965
0	0	0	1	0	0	32.5998	7.74	50.0	5	0.224
1	0	0	1	0	1	32.5565	3.75	50.0	12	0.801
0	1	1	1	0	0	32.5420	26.04	50.0	5	0.148
1	1	1	1	0	1	33.4033	11.95	50.0	10	0.573
1	0	0	0	1	1	32.1617	3.75	50.0	5	0.531
0	1	1	0	1	0	32.6002	26.04	60.0	5	0.203
1	1	1	0	1	1	31.9508	11.95	50.0	5	0.376
0	1	0	1	1	1	32.9152	7.74	50.0	5	0.698
1	1	0	1	1	0	33.1477	3.75	50.0	5	0.412
0	0	1	1	1	1	32.6246	26.04	50.0	5	0.347
1	0	1	1	1	0	32.4504	11.95	50.0	5	0.392
0	0	0	0	1	0	33.0167	7.75	50.0	5	0.289

Appendix B.

Sample Calculations.

B.1. Calculation of the Amount of Aqueous Leaching Solution Required.

Let r be the radius of the mineral particle, (assumed spherical)

t be the thickness of the aqueous layer required

x be the wt.% of aqueous solution required to give an aqueous layer of thickness t.

ρ be the density of the particle.

Now, mass of particle $= 4/3.\pi\, r^3\rho = m.$ (85)

Wt. of leach solution required $= \dfrac{xm}{100}$

Assuming unit density of the leach solution:-

$$\frac{mx}{100} = \frac{4\pi}{3}\left\{(r+t)^3 - r^3\right\} \qquad (86)$$

$$= {}^{4\pi}/_{3}.(r^3 + 3r^2t + 3rt^2 + t^3 - r^3)$$

as $r \quad t$, t^3 can be neglected

$$\therefore \frac{mx}{100} = 4\pi\,(r^2t + t^2r)$$

Now $m = \dfrac{4\pi r^3\rho}{3}$ from eqn. (85)

$\therefore$ subs. in (86) and re-arranging:-

$$3t^2 + 3rt - \frac{r^2\rho\, x}{100} = 0$$

$$x = \frac{100}{r^2\rho}.\left\{3t^2 + 3rt\right\}$$

$$x = \frac{300}{\rho r}\, t\left\{\frac{t}{r} + 1\right\} \qquad (87)$$

Now, the mean density of the mineral mixture = 2.62 g/cc.

$$\therefore \frac{300}{\rho} = \frac{300}{2.62} = 114.6.$$

For -200+270# particles (i.e. M_0) $\bar{d} = 1/2(0.074+0.052)$mm
$= 0.063$mm

$$\therefore \bar{r} = 0.0315 \text{ mm.}$$

and for $t = 2\mu$:- (A_0)
subs. in (87)

$$x = 114.6 \times \frac{0.002}{0.0315} \left\{ \frac{0.002}{0.0315} + 1 \right\}$$

$$\underline{\underline{x = 7.74\%}}$$

By a similar calculation for the other values of M and A, the corresponding values of x were obtained, and are summarised in table 4 (section 4.4.2.).

B.2. Calculation of Calibration Curve for Variation of of Optical Density of Copper Naphthenate Solution with Copper Concentration.

The experimental results are summarised in Table 15.

Table 15.

Copper Conc^{n}. (M/l x 10^{-3})(=x)	Optical Density (=y)
0.000	0.000
0.245	0.050
0.490	0.095
0.590	0.114
1.17	0.210
1.47	0.265
1.87	0.331
2.33	0.410
3.75	0.610
5.48	0.895

The calibration curve was expected to be of the form

$$Y = a + bX$$

and linear regression was used to find the values of a and b, as outlined in section 3.6.1. .

Now from these figures:-

$$\sum x = 17.405, \quad n=10, \quad \therefore \bar{x} = 1.7405$$

$$\sum x^2 = 57.2434 \qquad (\sum x)^2 = 302.9430$$

$$\sum xy = 9.5318 \qquad \sum y = 2.980$$

$$b = \frac{\sum xy - {}^1/_n \sum x \sum y}{\sum x^2 - {}^1/_n (\sum x)^2} = \frac{9.5318 - 2.980 \times 17.405/10}{57.2434 - 302.9430/10}$$

$$= \frac{4.3451}{26.95}$$

$$= \underline{\underline{0.1612}}$$

$$a = \bar{y} - b\bar{x} = 0.2980 - 0.1612 \times 1.7405 = 0.0174$$

$$\therefore \quad \underline{\underline{Y = 0.0174 + 0.1612X}} \qquad (88)$$

The variance about the regression line of equation (88) is calculated according to the procedure in section 3.6.1. .

$$s_{yx}^2 = \frac{1}{n-2} \quad \sum (y-\bar{y})^2 - b^2 \sum (x-\bar{x})^2$$

Now $\sum y = 2.980$, $\sum y^2 = 1.58963$

$$\therefore s_{yx}^2 = \frac{1}{8} [1.58963 - \frac{1}{10} \times (2.980)^2$$

$$- 0.1612^2 (57.2434 - 302.9430^2/10)]$$

$$= \frac{1}{8} [0.70159 - 0.1612^2 \times 26.95]$$

$$= 0.00016$$

$$\therefore s_{yx} = 0.01265.$$

Variance of b $= V(b) = \dfrac{0.00016}{26.95} = 5.936 \times 10^{-6}$

$$t_b = \frac{b\sqrt{\sum(x-\bar{x})^2}}{s_{yx}} = \frac{0.1612 \times \sqrt{26.95}}{0.01265} = 66.2$$

For 8 degrees of freedom, at the 5% significance level $t_5 = 1.86$, hence b is significant.

Now variance of a $= V(a) = V(\bar{y} - b\bar{x})$

By equation (16):-

$$V(a) = V(\bar{y}) + \bar{x}^2\ V(b) \quad \text{(as } V(\bar{x}) = 0 \text{ by definition)}$$

$$\therefore\ V(a) = \frac{s_{yx}^2}{n} + \frac{\bar{x}^2\ s_{yx}^2}{\sum(x-\bar{x})^2}$$

$$= \frac{0.00016}{10} + \frac{1.7405^2 \times 0.00016}{26.95}$$

$$= 0.000034$$

$$\therefore s_a = \sqrt{0.000034} = 0.00583$$

$$\therefore t_a = \frac{0.0174}{0.00583\sqrt{\left\{\frac{1}{10} + \frac{1}{10}\right\}}} = 6.68$$

t_a is based on 18 degrees of freedom, and at the 5% significance level $t_5 = 1.73$, hence a is significant.

Now, in equation (51) 1/b appears as the slope of fig.(12), and by equation (16)

$$V(^1/b) = (^1/b)^4\ V(b)$$

$$= \frac{5.936 \times 10^{-6}}{0.1612^4}$$

$$= 8.788 \times 10^{-3}.$$

$$\therefore 95\%\ \text{confidence limits} = \pm\ t_{2.5}\ \frac{V(^1/b)}{\sum(x-\bar{x})^2}$$

$$= \pm\ 2.31\ \sqrt{\frac{8.788 \times 10^{-3}}{26.95}}$$

$$= \pm\ 0.0417.$$

Equation (88) was required to convert optical densities to copper concentrations and was thus rewritten as

$$\underline{\underline{X = 6.20\ Y - 0.108}} \qquad (51)$$

The slope is 6.20 ± 0.04.

B.3. Calculation of Calibration Curve for Copper/Silver-Silver Chloride Electrode System.

The experimental readings are summarised in Table 16.

Table 16

Copper Conc. (M/1)	Chloride ion conc. (M/1)	1/2 log[Cu^{++}] + log [Cl$^-$]	E.M.F. (E) (mV)
1.025	0.0100	-1.9948	44.5
0.1025	0.0110	-2.4528	64.0
0.01025	0.0111	-2.9489	68.3
0.001025	0.0111	-3.4485	80.5
0.0001025	0.0111	-3.9485	90.5

The best straight line through these points, found by linear regression is

$$E = 4.37 - 22.02\left(\frac{1}{2}\log[Cu^{++}] + \log[Cl^-]\right) \qquad (89)$$

Now in all the leaching experiments, the chloride ion concentration was maintained at 10^{-2}M

$$\therefore \quad \log[Cl^-] = -2.000$$

Substituting this value into equation (89):-

$$\underline{\underline{E = 48.41 - 11.01 \log[Cu^{++}]}} \qquad (52)$$

The copper electrode was of positive polarity, and the electrolyte temperature was 15°C.

Comparison with Theoretical Prediction.

The two relevant half-cell reactions are given by equations (90) and (91).

$$Cu^{++} + 2e \longrightarrow Cu \qquad (90)$$

$$\underline{2Ag + 2Cl^- \longrightarrow 2AgCl + 2e} \qquad (91)$$

$$2Ag + 2Cl^- + Cu^{++} \longrightarrow 2AgCl + Cu \qquad (92)$$

Equation (92) represents the overall reaction.

Thus for the cell:-

$$E = E_o + \frac{RT}{2F} \ln (a_{Cu^{++}}) (a_{Cl^-})^2 \qquad (93)$$

where a_i is the activity of the ionic species i.

$a_{Cu} = a_{Ag} = a_{AgCl} = 1$ by definition.

E = e.m.f. of cell.

E_o = e.m.f. at standard conditions

Now if $f_{\pm}$ is the mean activity coefficient of the ions, and c is the molar concentration of the ion, then

$a_{Cu^{++}} = f_{\pm}\, c_{Cu^{++}}$

$a_{Cl^-} = f_{\pm}\, c_{Cl^-}$

Now the value of $f_{\pm}$ depends on the ionic strength of the electrolyte, and when $[Cu^{++}] > [Cl^-]$, $f_{\pm}$ will be determined by the copper and sulphate ions, and when $[Cu^{++}] < [Cl^-]$ $f_{\pm}$ will be determined by the potassium and chloride ions.

Substituting the values for $a_{Cu^{++}}$ and a_{Cl^-} in equation (93):-

$$E = E_o + \frac{RT}{2F} \ln(f_{\pm}^3 \; c_{Cu^{++}} \cdot c_{Cl^-}^{\;2}) \qquad (94)$$

$E_o = (E_o)_{Cu} - (E_o)_{Ag/AgCl} = 0.340 - 0.222 = 0.118$ V

At 15°C, $2.303RT/F = 0.05718$.

Also $c_{Cl^-} = 10^{-2}$M.

Substituting these values in equation (94), and expressing E in mV.

$$E = 4 + 28.59 \log(f_{\pm}^3 \; c_{Cu^{++}}) \qquad (95)$$

Values of $f_{\pm}$ are tabulated in reference (38).

The values of E, calculated from equation (95) for copper ion concentrations in the range 1.0 -10^{-5}M, are summarised in Table 17.

Table 17.

Copper Conc. (M/l)	log$[Cu^{++}]$	$f_{\pm}$	log$(f_{\pm}^{3}\ Cu^{++})$	E.M.F. (mV)
1.0	0.000	0.04	-4.1938	116
0.1	-1.000	0.15	-3.4718	95
10^{-2}	-2.000	0.41	-3.1617	86
10^{-3}	-3.000	0.821	-3.2570	89
10^{-4}	-4.000	0.902	-4.1344	114
10^{-5}	-5.000	0.902	-5.1344	143

The calculated activity goes through a maximum, implying a range of conditions where two solutions have the same activity of Cu^{++}. Such a situation only occurs when the two solutions are immiscible. In reality, $a_{Cu^{++}}$ does not go through a maximum, but continues to increase with increasing concentration, and this implies that the estimated values of $f_{\pm}$ at high concentrations are incorrect. The expected form of the e.m.f. versus concentration curve is that shown by the dashed line in fig.(13).

B.4. Calculation of Copper Content of Ore by Iodine Titration.

This method of determining the acid-soluble copper content of an ore is described in detail in reference(39).

Briefly the weighed ore sample was dissolved in sulphuric acid, and 0.880 ammonia added until a faint permanent white precipitate appeared. The precipitate was redissolved by adding acetic acid, and the solution diluted to 250 ml. To a 50 ml aliquot was added a solution of potassium iodide, the copper was precipitated as cuprous iodide and one atom of iodine liberated for each atom of copper precipitated. The liberated iodine was titrated with sodium thiosulphate using a starch indicator.

The relevant equations are:-

$$2Cu^{++} + 4I^{-} \longrightarrow Cu_2I_2 + I_2 \qquad (96)$$

$$\underline{2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI} \qquad (97)$$

$$2Cu^{++} + Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI + Cu_2I_2 \qquad (98)$$

Hence the equivalent weight of copper is its molecular weight.

The experimental results are summarised in table 18.

Table 18

Sample No.	1	2	3	4	5
Size fraction (#)	-65+100	-100+150	-100+150	-150+200	-150+200
Wt. of sample (g)	1.416	1.387	1.691	0.800	0.807
Vol.of soln. titrated (ml)	50	50	50	50	50
Vol.of $Na_2S_2O_3$ used (ml)	18.07	17.67	21.77	10.23	10.33

Normality of sodium thiosulphate used = 0.1048N.

Taking sample 1 as an example of the method of calculation:- 50 ml of copper solution require 18.07 ml of sodium thiosulphate solution.

$$\therefore \text{ Normality of copper solution} = \frac{18.07 \times 0.1048}{50} \text{ N.}$$

$\therefore$ Wt. of copper in 250 ml of solution =

$$\frac{18.07 \times 0.1048 \times 63.54 \times 250}{50 \times 1000} \text{ g}$$

This weight of copper was obtained from 1.416 g ore.

$\therefore$ Copper content of ore $\frac{18.07 \times 0.1048 \times 63.54 \times 250 \times 100}{50 \times 1000 \times 1.416}$ %

Copper content of ore = 42.49%

By a similar procedure, the copper content of the other samples was determined and the results are summarised in Table 19.

Table 19.

Sample No	% Copper
1	42.49
2	42.46
3	42.87
4	42.72
5	42.63
Mean	42.64

Now if all the acid-soluble copper, as determined by the iodine titration method, is derived from malachite, the malachite content of the ore can be deduced as shown below.

Molecular weight of malachite, $CuCO_3Cu(OH)_2$ = 221.11

$\therefore$ Wt. % copper in malachite = $\frac{2 \times 63.54}{221.11} \times 100\%$

= 57.47%

$\therefore$ % Malachite in ore = $\frac{42.64}{57.47} \times 100\%$

$\therefore$ % Malachite in ore = 76.87%

B.5. Determination of Carbon Dioxide Content of Ore.

The carbon dioxide content of the ore was determined by dissolving a weighed amount of the ore in sulphuric acid, and passing the gases evolved through a standardised solution of potassium hydroxide. The potassium hydroxide was then titrated to determine the amount of carbon dioxide absorbed. A 'blank' determination was necessary to measure the amount of atmosphere carbon dioxide absorbed during the test. The amount of carbon dioxide absorbed was checked by adding excess barium chloride to the solution, and weighing the precipitate of barium carbonate obtained.

Normality of potassium hydroxide solution used	= 2.713N
Normality of hydrochloric acid solution used	= 1.37N
Wt. of ore sample	= 1.279g
Vol. of KOH used to absorb CO_2	= 25.0 ml
Vol. of HCl required to neutralise excess KOH	= 46.5 ml
Duration of test	= 60 mins

In the determination of the absorption of atmospheric carbon dioxide, 25 ml of potassium hydroxide solution were allowed to stand in the apparatus for 60 minutes, and then titrated with hydrochloric acid. 49.4 mls of acid were required to neutralise the solution.

Now 49.4 ml of 1.37N HCl $\equiv \frac{49.4 \times 1.37}{2.713} \equiv$ 24.95ml of 2.713 N KOH

$\therefore$ 25.00 - 24.95 = 0.05 ml of KOH ore used up by atmospheric CO_2.

Now in the test on the ore:-

46.5 ml of 1.37N HCl $\equiv \frac{46.5 \times 1.37}{2.713} \equiv$ 23.51 ml of 2.713N KOH

$\therefore$ 25.00 - 23.51 = 1.49 ml KOH used up by CO_2.

KOH used up by CO_2 from ore = 1.49 - 0.05 = 1.44 ml.

Now

$$2KOH + CO_2 \longrightarrow K_2CO_3 + 2H_2O \qquad (99)$$

$\therefore$ 2 moles KOH $\equiv$ 1 mole CO_2

$\therefore$ 1.44 ml KOH $\equiv \dfrac{1.44 \times 2.713}{1000 \times 2}$ moles CO_2

Also $CuCO_3.Cu(OH)_2 + 2H_2SO_4 \longrightarrow 2CuSO_4 + CO_2 + 3H_2O$ (100)

$\therefore$ 1 mole malachite $\equiv$ 1 mole CO_2

$\therefore$ % malachite in ore sample $= \dfrac{1.44 \times 2.713 \times 22.1}{1000 \times 2 \times 1.2792} \times 100\%$

$= \underline{\underline{33.7\%}}$

A check on this figure was obtained by adding excess barium chloride solution, and weighing the dried precipitate of barium carbonate.

Weight of $BaCO_3$ precipitate = 0.2711g = $\dfrac{0.2711}{197.4}$ g moles

Now in 25.00 ml of KOH, 0.05 ml are used up by atmospheric CO_2.

$\therefore$ 0.05 ml of 2.713N KOH $\equiv \dfrac{0.05 \times 2.713}{1000 \times 2}$ moles CO_2

$= 0.6775 \times 10^{-4}$ moles.

$\therefore$ Moles CO_2 from ore $= \dfrac{0.2711}{197.4} - 0.6775 \times 10^{-4}$ g moles

$= 1.304 \times 10^{-3}$ g moles.

$\therefore$ % malachite in sample $= \dfrac{1.304 \times 10^{-3} \times 221 \times 100}{1.2792}$ %

$= \underline{\underline{22.6\%}}$

(cf 33.7% obtained by titration).

The higher figure obtained from the titration method is possibly due to sulphuric acid droplets being carried over into the potassium hydroxide solution during the dissolution of the ore sample, despite the use of a glass wool plug, in an attempt to prevent this entrainment. In view of this, the agreement between the two figures is considered to be satisfactory.

B.6. Calculation of Maximum Optical Density in an Extraction Test.

The maximum optical density of the organic solution, corresponding to the total dissolution of all the copper in the ore sample used in an extraction test can be calculated as follows:

Wt. of ore sample = 30.0g
Malachite content of ore = 2.5%
Copper content of malachite = 42.64%
Volume of naphthenic acid solution used = 250 ml.

Now, moles of copper in ore sample $= \dfrac{30 \times 0.025 \times 0.4264}{63.54}$

$= 5.033 \times 10^{-3}$ moles

.˙. Copper concentration of organic solution if all the copper were extracted

$$= \frac{5.033 \times 10^{-3} \times 1000}{250} \times 1000 \text{mM/1}$$

$$= 20.13 \text{ mM/1}$$

Thus from equation (88) maximum optical density

$$= 0.1612 \times 20.13 + 0.0174$$
$$= 3.262$$

.˙. Calculated maximum optical density = 3.262

B.7. Tabular Analysis of Limiting Organic Phase Copper Concentration.

The values of C_f for the factorial experiment described in section 4 and obtained by the method outlined in section 4.13.1 are tabulated in Appendix A2. The statistical analysis by Yates' method, as described in section 3.4 is presented in Table 20.

The symbol (E) in the 'effects' column denotes that this particular effect was used in the estimate of the experimental error.

The symbol (B) in the 'effects' column denotes that this particular effect was confounded with differences between blocks.

Now, the sum of 'error mean squares' = 3.3648 = error sum of squares based on 14 degrees of freedom.

$$\therefore \quad \text{Error mean square} = \frac{3.3648}{14} = 0.2403$$

Product of error mean squares = 3.810×10^{-15}

$\therefore$ Geometric mean of error mean squares = 0.09335.

Applying the L_1 test for homogeneity of variance:-

$$L_1 = \frac{0.09335}{0.2403} = 0.3885$$

From tables(27) for 14 variances, each based on 1 degree of freedom $L_1 = 0.130$, hence the variances are homogeneous and can be combined for use as an estimate of the experimental error.

Now, from tables, the values of the F-ratio for two variances based on 14 and 1 degrees of freedom are:-
at 1% F = 8.36, at 5% F = 4.60, at 10% F= 3.10.

Hence, mean squares greater than 8.36 x 0.2403 (= 2.13) are significant at the 1% level, those greater than 1.11 are significant at the 5% level and those greater than 0.745 are significant at the 10% level.

Table 20

Tabular Analysis of Limiting Copper Concentration in Organic Phase

Factor Levels MPAFC	Response	(I)	(II)	(III)	(IV)	Total Effect	Mean Effect	Mean Square Effect	Effect
00000	2.2439	3.2190	5.7671	13.2111	24.8183	65.8480	2.0578	135.4987	Total
10000	0.9751	2.5481	7.4441	11.0672	41.0297	-6.7026	-0.4189	1.4039	M
01000	1.4821	3.9334	5.3228	19.7417	-3.2383	2.3214	0.1451	0.1683	P
11000	1.1200	3.5106	6.2844	21.2880	-3.4643	3.2912	0.1495	0.1787	MP
00100	1.9339	2.7638	9.5555	-1.6757	0.0395	4.0152	0.2510	0.5038	A
10100	1.9995	2.5590	10.1862	-15626	2.2819	4.1186	0.2574	0.5301	MA
01100	1.8375	2.4732	10.2710	-3.2459	1.7637	1.6054	0.1003	0.0805	PA (B)
11100	1.6731	3.8112	11.0170	-0.2184	0.6275	-1.3180	-0.0824	0.0543	MPA (E)
00010	1.6798	4.6479	-1.5769	-1.0937	2.6385	-0.0576	-0.0036	0.0001	F
10010	1.0840	4.9076	-0.0988	1.1332	1.3767	3.1406	0.1963	0.3082	MF
01010	1.5921	4.4149	-1.2210	1.6161	2.3575	1.2766	0.0798	0.0509	PF
11010	0.9669	5.7713	-0.3416	0.6658	1.7611	1.4688	0.0918	0.0674	MPF (E)
00110	1.5876	4.6485	-0.6549	0.7307	1.7909	-0.6000	-0.0375	0.0113	AF
10110	0.8856	5.6225	-2.5910	1.0330	-0.1855	5.0346	0.3147	0.7921	MAF (E)
01110	1.7254	5.6626	-1.9578	-0.2695	-0.0989	-1.0842	-0.0678	0.0367	PAF (E)
11110	2.0858	5.3544	-1.7394	0.8970	-1.2191	-2.5668	-0.1604	0.2059	MPAF (E)
00001	2.2271	-1.2688	-0.6709	1.6769	-1.6039	16.2114	1.0132	8.2128	C
10001	2.4208	-0.3081	-0.4228	0.9616	1.5463	-0.2260	-0.0141	0.0016	MC
01001	2.8781	0.0656	-0.2048	0.6307	0.1131	2.2424	0.1402	0.1571	PC
11001	2.0295	-0.1644	1.3380	0.7460	3.0275	-1.1362	-0.0710	0.0403	MPC (E)
00101	3.0484	-0.5958	0.2597	1.4781	2.2269	-1.2618	-0.0789	0.0498	AC
10101	1.3665	-0.6252	1.3564	0.8794	-0.9503	-0.5964	-0.0373	0.0111	MAC (E)
01101	3.3402	-0.7020	0.9740	-1.9361	0.3023	-1.9764	-0.1235	0.1221	PAC (E)
11101	2.4311	0.3604	-0.3082	3.6972	1.1665	-1.1202	-0.0700	0.0392	MPAC (E)
00011	3.3051	0.1937	0.9607	0.2481	-0.7153	3.1502	0.1969	0.3101	FC
10011	1.3434	-0.8486	-0.2300	1.5428	0.1153	2.9144	0.1822	0.2654	MFC (B)
01011	2.8093	-1.6819	-0.0294	1.0967	-0.5987	-3.1772	-0.1986	0.3154	PFC (E)
11011	2.8132	-0.9091	1.0624	-1.2822	5.6333	0.8642	0.0540	0.0233	MPFC (E)
00111	2.1293	-1.9617	-1.0423	-1.1907	1.2947	0.8306	0.0519	0.0216	AFC (E)
10111	3.5333	0.0039	0.7728	1.0918	-2.3789	6.2302	0.3895	1.2137	MAFC (E)
01111	2.5095	1.4040	1.9656	1.8151	2.2825	-3.6736	-0.2296	0.4217	PAFC (E)
11111	2.8449	0.2254	-1.0686	-3.0342	-4.8493	-7.1318	-0.4457	1.5895	MPAFC (B)
TOTAL	65.8480	59.1454	63.8580	72.2792	78.8912	91.0368		152.6857	
CHECK TOTAL	59.1454	63.8580	72.2792	78.8912	91.0368				
SUM OF SQUARES	152.6859								

From Table 20 it is seen that the effect of factor C is significant at the 1% level, and factor M at the 5% level and also the five-factor interaction MPAFC. This interaction is unlikely to have any physical significance, and is more than likely due to some difference between the results from two of the four blocks into which the experiment was confounded.

B.8. Tabular Analysis of Rate Constant.

The values obtained for the rate constant for the extraction process (presented in Appendix A2) were analysed statistically by the same procedure as that used for the analysis of the limiting organic phase copper concentration. The analysis is presented in Table 21, and the significance testing was carried out as previously.

The results of the analysis for both C_f and k have been summarised in Tables 5 and 6 in section 4.13.2.

The symbol (E) in the 'effects' column denotes that this particular effect was used in the estimate of the experimental error.

The symbol (B) in the 'effects' column denotes that this particular effect was confounded with differences between blocks.

Table 21.

Tabular Analysis of Rate Constant k.

Factor Levels MPAFC	Response (x100)	(I)	(II)	(III)	(IV)	Total Effect	Mean Effect	Mean Square Effect	Effect
00000	1.3628	3.0668	6.7644	11.5692	26.3788	83.1327	2.5979	215.9702	Total
10000	1.7040	3.6976	4.8048	14.8096	56.7539	-16.0231	-1.0014	8.0231	M
01000	2.0726	2.1953	7.3383	31.6653	-6.1032	-2.1797	-0.1362	0.1485	P
11000	1.6250	2.6095	7.4713	25.0886	-9.9199	-3.5511	-0.2219	0.3941	MP
00100	1.2872	2.5911	17.3789	-1.4864	1.9834	-7.9829	-0.4989	1.9915	A
10100	0.9081	4.7472	14.2864	-4.6168	4.1631	1.6521	0.1033	0.0853	MA
01100	1.8052	4.3445	14.0762	-5.1203	-1.3126	6.0811	0.3801	1.1556	PA (B)
11100	0.8043	3.1268	11.0.24	-4.7992	-2.2385	2.5725	0.1608	0.2068	MPA (E)
00010	1.2733	9.1713	-0.1064	1.0450	-1.8266	-3.3363	-0.2085	0.3473	F
10010	1.3178	8.2076	-1.3800	0.9384	-6.1563	-2.8097	-0.1756	0.2467	MF
01010	3.1726	8.1941	-1.5535	-3.0655	-2.7834	1.8613	0.1163	0.1083	PF
11010	1.5746	6.0923	-3.0633	-1.0976	4.4355	2.2395	0.1400	0.1567	MPF (E)
00110	3.3732	10.0149	-5.9471	-1.4106	-3.5904	2.1213	0.1326	0.1406	AF
10110	0.9713	4.0613	0.8268	0.0980	9.6715	-9.3485	-0.5843	2.7311	MAF (E)
01110	1.8941	3.0782	-1.2306	-1.4847	3.5500	8.7905	0.5494	2.4148	PAF (E)
11110	1.2327	7.9342	-3.5690	-0.7538	-0.9775	-9.5189	-0.5949	2.8315	MPAF (E)
00001	5.1520	0.3412	0.6308	-1.9596	3.2404	30.3751	1.8984	28.8327	C
10001	4.0193	-0.4476	0.4142	0.1330	-6.5767	-3.8167	-0.2385	0.4552	MC
01001	6.5110	-0.3701	2.1561	-3.0925	-3.1304	-6.1465	-0.3842	1.1806	PC
11001	1.6966	-1.0009	-1.2177	-3.0638	0.3207	-0.9259	-0.0579	0.0268	MPC (E)
00101	4.4396	0.0445	-0.9637	-1.2736	-0.1066	-4.3297	-0.2706	0.5858	AC
10101	3.7545	-15980	-2.1018	-1.5098	1.9679	7.2189	0.4512	1.6285	MAC (E)
01101	2.2902	-2.4019	-5.9536	6.7739	1.5086	13.2619	0.8289	5.4962	PAC (E)
11101	3.8021	-0.6614	4.8560	-2.3384	0.7309	-4.5275	-0.2830	0.6406	MPAC (E)
00011	6.0779	-1.1327	-0.7888	-0.2166	2.0926	-9.8171	-0.6136	3.0117	FC
10011	3.9370	-4.8144	-0.6218	-3.3738	0.0287	3.4511	0.8157	0.2722	MFC (B)
01011	1.5755	-0.6851	-1.6425	-1.1381	-0.2362	2.0745	0.1297	0.1345	PFC (E)
11011	2.4858	1.5119	1.7405	10.8096	-9.1123	-0.7777	-0.0486	0.0189	MPFC (E)
00111	1.4801	-2.1409	-3.6817	0.1670	-3.1572	-2.0639	-0.1290	0.1331	AFC (E)
10111	1.5981	0.9103	2.1970	3.3830	11.9477	-8.8761	-0.5548	2.4620	MAFC (E)
01111	5.8106	0.1180	3.0512	5.8787	3.2160	15.1049	0.9441	7.1299	PAFC (E)
11111	2.1236	-3.8670	-3.8050	-6.8562	-12.7349	-15.9509	-0.9969	7.9510	MPAFC (B)
TOTAL	83.1327	67.1096	61.3788	63.7016	53.7008	67.9552		297.0123	
CHECK TOTAL	67.1096	61.3788	63.7016	53.7008	67.9552				
SUM OF SQUARES	297.0124								

B.9. Calculation of Mean Responses from the Factorial Experiment.

As only two effects were significant in the factorial experiment, (i.e. the particle size of the mineral (M) and the naphthenic acid concentration (C)) in each case the 2^5 experiment reduced to a 2^2 experiment in the factors M and C, repeated eight times. Hence it is possible to evaluate the mean responses at the four combinations of the factors used, i.e. M_0C_0, M_1C_0, M_0C_1, M_1C_1.

Consider the limiting organic phase copper concentration results as an example.

The values of C_f given in Appendix A2 can be regrouped according to the levels of factors M and C, as in Table 21, and the mean responses calculated. The confidence limits can also be deduced. The mean responses were converted to copper concentration in mM/l by equation (51), and in estimating the variance of mean responses (in terms of copper concentrations), equation (51) was assumed to be free from error. Reference to section B2 will show that this approximation is justified as the error of the equation is small compared with that of the experimental values of C_f.

Each variance is based on 7 degrees of freedom, and thus for the 95% confidence limits, $t_{2.5,7} = 2.37$

Thus the confidence limits are $\pm\ 2.37 \sqrt{\frac{V(\bar{C}_f)}{8}}$

For the results for M_0C_0, $V(\bar{C}_f) = 2.4492$

$\therefore$ Confidence limits are $\pm\ 2.37 \sqrt{\frac{2.4492}{8}}$

$\underline{\pm\ 1.31.}$

Hence the mean value of C_f for the tests M_0C_0 is

$$\underline{\underline{10.76 \pm 1.31 \text{ mM/l}}}$$

Table 22

	Limiting Organic Phase Copper Concentration (C_f)			
	M_0C_0	M_1C_0	M_0C_1	M_1C_1
	2.2439	0.9751	2.2271	2.2408
	1.4281	1.1200	2.8781	2.0295
	1.9339	1.9995	3.0484	1.3665
	1.8375	1.6731	3.3402	2.4311
	1.6798	1.0840	3.3051	1.3434
	1.5914	0.9669	2.8093	2.8132
	1.5876	0.8856	2.1293	3.5333
	1.7254	2.0858	2.5095	2.8449
$\sum C_f$ (A)	14.0270	10.7900	22.2470	18.7827
$\sum C_f^2$ (B)	25.04269	16.24728	63.44125	48.05320
${}^{s}/_{s} = B - A^2/8$	0.44600	1.69427	1.57513	3.95448
$V(\bar{C}_f) = ({}^{s}/_{s})/7$	0.063714	0.24204	0.22502	0.56492
$\bar{C}_f = A/8$	1.7535	1.3494	2.7809	2.3488
$\bar{C}_f'$ (mM/1) $= 6.20\ \bar{C}_f - 0.108$	10.763	8.603	17.133	14.450
$V(\bar{C}_f') = 6.20^2 V(\bar{C}_f)$	2.4492	9.3040	8.6499	21.7155

Similarly for the other levels of M and C.

The results of these calculations, together with those for the rate constant k, have been summarised in table 7, (section 4.13.2.).

B.10. Calculation of Correlation Between Aqueous and Organic Phase Copper Concentration and pH at the end of an Extraction Test.

In section 4.13.3. it was suggested that the aqueous and organic phase copper concentration and pH at the end of an extraction test could be correlated by an equation of the form

$$K' = \frac{[CuR_2.HR]^p\ [H^+]^q}{[Cu^{++}_{aq}]^r} \qquad (55)$$

Equation (55) can be rewritten in the form:-

$$\log[CuR_2.HR] = \log K + b \log[H^+] + c \log[Cu^{++}_{aq}] \qquad (56)$$

and the values of K, b and c found by multiple regression as described in section (3.6.2.).

Now $[CuR_2.HR]$ is proportional to the optical density of the organic solution, $[H^+]$ is represented by the pH measurements and $[Cu^{++}_{aq}]$ by the copper/silver-silver chloride electrode readings. These quantities were found to be approximately stationary for the last three sets of readings in each test and the mean values were thus used in the calculation. These figures, obtained from the experimental results tabulated in Appendix A.1., are given in Table 23. Where no values for pH or mV are quoted, it was because no reliable readings could be obtained.

The logarithm of the mean aqueous phase copper concentration was calculated from equation (52), with E being represented by the mean value of the e.m.f. over the last three readings of an extraction test.

As the value of K depended on the naphthenic acid concentration, the calculation of K, b and c was performed separately for the testsusing 0.1M naphthenic acid and those using 0.5M naphthenic acid. The calculation for the 0.1M acid is given in detail, and the same method was used for the 0.5M acid.

Now, from table 23, denoting $\log(\overline{O.D.})$, $\overline{pH}$ and $\log[Cu^{++}_{aq}]$ respectively by y, x_1 and x_2 for convenience:-

Table 23.

Test MPAFC	$\overline{\text{O.D.}}$	$\overline{\text{pH}}$ (x_1)	Mean Cu/Ag-AgCl Electrode E.M.F. (mV)	$\log(\overline{\text{O.D.}})$ (y)	$\log[\overline{\text{Cu}^{++}_{aq}}]$ (x_2)
00000	1.60	5.02	54.3	0.204	-0.536
10000	0.755	4.96	78.3	-0.122	-2.718
01000	1.20	5.91	80.0	0.079	-2.870
11000	0.835	4.67	106.3	-0.078	-5.259
00100	1.30	6.02	93.7	0.114	-4.114
10100	1.05	4.97	172.3	0.021	-11.253
01100	1.51	5.66	55.7	0.179	-0.663
11100	0.842	-	-	-	-
00010	1.10	4.29	76.3	0.041	-2.534
10010	0.682	5.66	67.0	-0.166	-1.689
01010	1.54	3.67	66.7	0.188	-1.662
11010	0.727	5.49	60.7	-0.142	-1.117
00110	1.54	-	-	-	-
10110	0.551	5.22	63.0	-0.259	-1.326
01110	1.38	4.43	48.3	0.140	+0.009
11110	1.40	4.67	77.7	0.146	-2.661
00001	2.00	3.99	56.3	0.301	-0.718
10001	2.13	-	-	-	-
01001	2.78	3.51	80.0	0.444	-2.870
11001	1.07	5.06	85.0	0.029	-3.324
00101	2.64	4.19	70.0	0.422	-1.962
10101	1.23	-	-	-	-
01101	2.08	4.69	87.7	0.318	-3.569
11101	2.04	4.59	71.5	0.310	-2.098
00011	3.25	2.74	48.0	0.512	+0.036
10011	1.18	-	-	-	-
01011	1.42	4.69	32.0	0.152	+1.490
11011	1.75	4.85	125.0	0.243	-6.957
00111	1.07	5.62	123.0	0.029	-6.776
10111	1.72	3.25	71.5	0.236	-2.098
01111	2.45	3.32	67.7	0.389	-1.753
11111	1.69	-	72.3	0.228	-2.171

$$\sum y = 0.345$$
$$\sum y^2 = 0.3070$$
$$\sum x_1 = 69.96$$
$$\sum x_1^{\,2} = 356.3580$$
$$\sum x_2 = -38.393$$
$$\sum x_2^{\,2} = 209.686463$$
$$\sum x_1 y = 1.32285$$
$$\sum x_2 y = -0.439436$$
$$\sum x_1 x_2 = -192.30121$$
$$n = 14$$

By equation (39)

$$\left.\begin{aligned} b\sum(x_1-\bar{x}_1)^2 + c\sum(x_1-\bar{x}_1)(x_2-\bar{x}_2) &= \sum(x_1-\bar{x}_1)(y-\bar{y}) \\ b\sum(x_1-\bar{x}_1)(x_2-\bar{x}_2) + c\sum(x_2-\bar{x}_2)^2 &= \sum(x_2-\bar{x}_2)(y-\bar{y}) \end{aligned}\right\} \qquad (39)$$

$$\therefore \sum(x_1-\bar{x}_1)^2 = \sum x_1^{\,2} - {}^1/n\left(\sum x_1\right)^2$$
$$= 356.3580 - \frac{69.96^2}{14} = 6.7579$$

$$\sum(x_2-\bar{x}_2)^2 = \sum x_2^{\,2} - {}^1/n\left(\sum x_2\right)^2$$
$$= 209.686463 - \frac{38.393^2}{14} = 104.39915$$

$$\sum(x_1-\bar{x}_1)(y-\bar{y}) = \sum x_1 y - \bar{x}_1\sum y$$
$$= 1.32285 - \frac{69.96 \times 0.345}{14} = -0.40116$$

$$\sum(x_2-\bar{x}_2)(y-\bar{y}) = \sum x_2 y - \bar{x}_2\sum y$$
$$= -0.439436 + \frac{38.393 \times 0.345}{14} = 0.506677$$

$$\sum(x_1-\bar{x}_1)(x_2-\bar{x}_2) = \sum x_1 x_2 - \bar{x}_1\sum x_2$$
$$= -192.30121 + \frac{69.96 \times 38.393}{14} = -0.44591.$$

Substituting in equation (39):-

$$6.75796b - 0.4459c = -0.4012 \tag{101}$$

$$-0.44596b + 104.3992c = 0.5067 \tag{102}$$

Multiplying equation (101) by 0.4459 and equation (102) by 6.7579:-

$$\begin{array}{lrcr} & 3.01335b - 0.1988c & = & -0.1789 \\ & \underline{-3.01335b + 705.5194c} & \underline{=} & \underline{3.4242} \\ \text{adding:-} & 705.3206c & = & 3.2453 \end{array}$$

$$\therefore c = \frac{3.2453}{705.3206} = \underline{\underline{0.0046}}$$

Subs. in (101)

$$\therefore b = \frac{-0.4012 + 0.4459 \times 0.0046}{6.7579} = \underline{\underline{-0.0591}}$$

The values obtained for b and c must now be tested for significance.

Sum of squares due to regression =

$$b\sum(x_1-\bar{x}_1)(y-\bar{y}) + c\ (x_2-\bar{x}_2)(y-\bar{y}) \text{ from eqns.(42)\&(44)}$$

$$= -0.0591 \times (-0.4012) + 0.0046 \times 0.5067$$

$$= 0.02602$$

$$\therefore \text{Residual sum of squares} = \sum(y-\bar{y})^2 - 0.02602$$

$$= 0.3070 - \frac{0.345^2}{14} - 0.02602$$

$$= 0.2725.$$

$$\text{Residual variance} = s_{xy}^2 = \frac{0.2725}{11} = 0.02478$$

Hence for b,

$$t_b = \frac{b}{s_{xy}\sqrt{\sum(x_1-\bar{x}_1)^2}} = \frac{-0.059}{\sqrt{0.02478 \times 6.758}} = 0.144$$

At the 5% level, for 11 degrees of freedom, t = 1.80.

Thus b is not significant.

Similarly for c.

$$t_c = \frac{c}{s_{xy}\sqrt{(x_2-\bar{x}_2)^2}} = \frac{0.0046}{\sqrt{0.02478 \times 104.4}} = 0.00286$$

Thus c is not significant.

The 95% confidence limits of b are given by

$$\pm\, t_{2.5}\, s_{xy}\sqrt{\sum(x_1-\bar{x}_1)^2}$$

and at the 2.5% level, for 11 degrees of freedom t = 2.20

$$\therefore \text{ Confidence limits are } \pm\, 2.20 \times \sqrt{0.02478 \times 6.758}$$

$$\text{i.e. } \pm\, 0.901$$

$$\therefore \quad \underline{\underline{b = -0.0591 \pm 0.901}}$$

Similarly for c, the confidence limits are

$$\pm\, t_{2.5}\, s_{xy}\sqrt{\sum(x_2-\bar{x}_2)^2}$$

$$\text{i.e. } \pm\, 2.20 \times \sqrt{0.02478 \times 104.4}$$

$$\pm\, 3.53$$

$$\therefore \quad \underline{\underline{c = 0.0046 \pm 3.53}}$$

From equations (40) and (56)

$$\log K = a = \bar{y} - b\bar{x}_1 - c\bar{x}_2$$

$$= \frac{0.345 + 0.0591 \times 69.96 + 0.0046 \times 38.393}{14}$$

$$\log K = 0.3323$$

$$\therefore \quad \underline{\underline{K = 2.15}}$$

From equation (16)

$$V(a) = V(\bar{y}) + b(\bar{x}_1)^2\, V(b) + (\bar{x}_2)^2\, V(c) \qquad (103)$$

as in multiple regression it is assumed that $V(x_i) = 0$.

Now $V(\bar{y}) = \dfrac{\sum(y-\bar{y})^2}{n-1}$ $\quad V(b) = \dfrac{s_{xy}^2}{\sum(x_1-\bar{x}_1)^2}$ $\quad V(c) = \dfrac{s_{xy}^2}{\sum(x_2-\bar{x}_2)^2}$

$$\therefore\ V(a) = \frac{0.3070 - 0.345^2/14}{13} + \frac{69.96^2}{14^2} \times \frac{0.02478}{6.758}$$

$$+ \frac{38.393^2}{14^2} \times \frac{0.02478}{104.4}$$

$$= 0.022965 + 0.091564 + 0.001785$$

$$= 0.1163$$

Now $a = \log K$

Thus by equation (16)

$$V(a) = \left(\frac{0.4343}{K}\right)^2 V(K)$$

$$\therefore\ V(K) = \left(\frac{K}{0.4343}\right)^2 V(a)$$

$$= \left(\frac{2.15}{0.4343}\right)^2 \times 0.1163$$

$$\therefore\ V(K) = 2.850$$

$$\therefore\ s_K = \sqrt{V(K)} = 1.688$$

Thus the 95% confidence limits for K are given by:-

$$\pm\ t_{2.5}\ s_K/\sqrt{11}$$

$$\pm\ \frac{2.2 \times 1.688}{\sqrt{11}}$$

$$\pm\ 1.12.$$

$$\therefore\qquad \underline{\underline{K = 2.15 \pm 1.12}}$$

The results of these calculations, and those for the case of the 0.5M naphthenic acid, which were performed in the same way, are summarised in Table 8.

B.11. Calculation of the Selectivity of the Process.

B.11.1. Prediction of Selectivity at Equilibrium. Consider a mixture of calcite ($CaCO_3$) and malachite being leached by the simultaneous leaching and solvent extraction process, as described in section 2.5.

For the dissolution of the calcite:-

$$CaCO_3 + 2H^+ \rightleftharpoons Ca^{++} + CO_2 + H_2O \qquad (104)$$

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \qquad (105)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--} \qquad (106)$$

Let

$$K_{a_I} = \frac{[H^+][HCO_3^-]}{[CO_2]} \qquad (107)$$

$$K_{a_2} = \frac{[H^+][CO_3^{--}]}{[HCO_3^-]} \qquad (108)$$

Multiplying (107) and (108)

$$K_a = K_{a_1}K_{a_2} = \frac{[H^+]^2[CO_3^{--}]}{[CO_2]} \qquad (109)$$

Now is S_{Ca} represents the solubility product of calcite, then

$$S_{Ca} = [Ca^{++}][CO_3^{--}] \qquad (110)$$

$$\therefore [CO_3^{--}] = \frac{S_{Ca}}{[Ca^{++}]} \qquad (111)$$

Substituting into (109)

$$K_a = \frac{S_{Ca}[H^+]^2}{[Ca^{++}][CO_2]} \qquad (112)$$

For the extraction of calcium into naphthenic acid:-

$$Ca^{++} + 2HR \rightleftharpoons CaR_2 + 2H^+ \qquad (113)$$

Let $$K_{Ca} = \frac{[CaR_2][H^+]^2}{[Ca^{++}][HR]^2} \qquad (114)$$

Substituting for $[Ca^{++}]$ from (112):-

$$K_{Ca} = \frac{K_a[CO_2][CaR_2]}{S_{Ca}[HR]^2}$$

$$\therefore [CaR_2] = \frac{K_{Ca}S_{Ca}}{K_a} \cdot \frac{[HR]^2}{[CO_2]} \qquad (115)$$

For the dissolution of malachite:-

$$CuCO_3Cu(OH)_2 \rightleftharpoons 2Cu^{++} + CO_3^{--} + 2OH^- \qquad (116)$$

The solubility product of malachite, S_{Cu}, is given by:-

$$S_{Cu} = [Cu^{++}]^2[CO_3^{--}][OH^-]^2 \qquad (117)$$

For the extraction of copper into naphthenic acid:-

$$Cu^{++} + 2HR \rightleftharpoons CuR_2 + 2H^+ \qquad (118)$$

Let $$K_{Cu} = \frac{[CuR_2][H^+]^2}{[Cu^{++}][HR]^2} \qquad (119)$$

Now from (117) $$[Cu^{++}] = \frac{\sqrt{S_{Cu}}}{[OH^-]\sqrt{[CO_3^{--}]}}$$

and from (109) $$[CO_3^{--}] = \frac{K_a.[CO_2]}{[H^+]^2}$$

also $[H^+][OH^-] = K_w$

Substituting in (119)

$$K_{Cu} = \frac{[CuR_2] \cdot K_w\sqrt{K_a[CO_2]}}{\sqrt{S_{Cu}} \cdot [HR]^2}$$

$$\therefore [CuR_2] = \frac{K_{Cu}}{K_w}\sqrt{\frac{S_{Cu}}{K_a}} \cdot \frac{[HR]^2}{\sqrt{[CO_2]}} \qquad (120)$$

The ratio of copper and calcium in the organic phase is obtained from equations (115) and (120)

$$\frac{[CuR_2]}{[CaR_2]} = \frac{K_{Cu}\sqrt{K_a S_{Cu}}}{K_{Ca}\ K_w\ S_{Ca}} \cdot \sqrt{[CO_2]} \qquad (121)$$

Now, from reference$^{(40)}$ $S_w = 10^{-33.8}$, $S_{Ca} = 10^{-8.1}$
$K_w = 10^{-14}$, $K_a = 10^{-18.3}$

also, in the extraction column, the pressure of CO_2 is 1 atmos, hence $[CO_2] = 1$.

∴ Substituting in equation (121)

$$\frac{[CuR_2]}{[CaR_2]} = \frac{K_{Cu} \cdot \sqrt{10^{-18.3} \times 10^{-33.8}}}{K_{Ca} \times 10^{-14} \times 10^{-8.1}}$$

$$= 10^{-3.95}\ \frac{K_{Cu}}{K_{Ca}} \qquad (122)$$

Now, the distribution constant for copper, D_{Cu}, is defined by:-

$$D_{Cu} = \frac{[CuR_2]}{[Cu^{++}]} \qquad (123)$$

and from equation (119)

$$K_{Cu} = D_{Cu}\ \frac{[H^+]^2}{[HR]^2} \qquad (124)$$

Similarly for calcium:-

$$K_{Ca} = D_{Ca}\ \frac{[H^+]^2}{[HR]^2} \qquad (125)$$

Thus under identical conditions of pH and naphthenic acid concentration

$$\frac{K_{Cu}}{K_{Ca}} = \frac{D_{Cu}}{D_{Ca}} \qquad (126)$$

Now from reference (25), at a pH of 6 (corresponding to that used in the leaching test) and a naphthenic acid concentraction of 0.643M, $D_{Cu} = 10^{5.5}$. Thus from equation (124), for 0.5M naphthenic acid

$$D_{Cu} = \frac{10^{5.5} \times [0.5]^2}{[0.643]^2}$$

$$\therefore D_{Cu} = 10^{5.3}$$

Now, the pH for 50% extraction of calcium into 1.01M naphthenic acid is known from Flett(42) to be 5.95.

Thus from equation (124), for 0.5M naphthenic acid and an equilibrium pH of 6:-

$$D_{Ca} = 1.0 \times \frac{[0.5]^2}{[1.01]^2} \times \frac{[10^{-5.95}]^2}{[10^{-6}]^2}$$

$$\therefore D_{Ca} = 10^{-0.5}.$$

Thus, substituting in equation (122) and using equation (126) for K_{Cu}/K_{Ca}

$$\frac{[CuR_2]}{[CaR_2]} = \frac{10^{-3.95} \times 10^{5.3}}{10^{-0.5}} = 10^{1.85}$$

$$\therefore \underline{\underline{\frac{[CuR_2]}{[CaR_2]} \simeq 70}}$$

Thus at equilibrium, at pH 6, it can be expected that the organic phase copper concentration is about 70 times higher than the calcium concentration.

B.11.2. Calculation from Experimental Results.

The calcium content of the naphthenic acid solution at the end of the test was determined by stripping the solution with a known volume of standardised hydrochloric acid. The acid was then titrated to pH 5 with potassium hydroxide, and the amount of acid used in the stripping process calculated. As the stripping process is stoichiometric, and the copper content of the naphthenic acid is known from the optical density measurements, the calcium content can be determined by difference. A blank test had shown that negligible hydrochloric acid was extracted by the naphthenic acid. The calcium content was checked by stripping a known volume of the organic solution with hydrochloric acid, precipitating the copper by the addition of sodium sulphide, and then adding excess ammonium oxalate to the filtrate. The precipitate of calcium oxalate was dried in an oven and weighed. The experimental readings are presented in Table 24.

Table 24.

	Test 1	Test 2
Volume of organic soln. stripped	100 ml	100 ml
Original HCl normality	1.462 N	1.394 N
HCl normality after stripping	0.769 N	0.667 N
Vol. of HCl used for stripping	30 ml	30 ml
O.D. of organic soln.	0.212	0.451
Wt. of ore used	30.7886 g	29.8596 g
% $^{w}/w$ malachite in ore	2.50%	2.94%
Vol. of naphthenic acid used	250 ml	250 ml
OXALATE Ca^{++} DETERMINATION		
Volume of organic soln. stripped	20 ml	25 ml
Wt. of $CaC_2O_4.H_2O$ ppt	0.2047 g	0.3381 g

Consider test 1 as an example, assuming the process to have reached an equilibrium state.

Moles of acid used in stripping $= \frac{30 \times (1.426 - 0.769)}{1000}$

$= 0.02079$

Copper concentration of naphthenic acid solution (from eqn.(51))

$$= (6.20 \times 0.212 - 0.108) \times 10^{-3} \text{ M/l}$$

$$= \underline{\underline{1.325 \times 10^{-3}}} \text{ M/l.}$$

$\therefore$ Moles of HCl required to liberate copper from 100 ml organic solution

$$= \frac{1.325 \times 10^{-3} \times 2 \times 100}{1000}$$

$$= 2.65 \times 10^{-9}$$

$\therefore$ Moles HCl used in liberating calcium = 0.02079 - 0.00027
= 0.02052.

$\therefore$ Calcium concentration of naphthenic acid solution

$$= \frac{0.02052 \times 1000}{2 \times 100} \text{ M/l}$$

$$= \underline{\underline{102.6 \times 10^{-3} \text{ M/l}}}$$

Now, from the oxalate precipitation:-

0.2047 g $CaC_2O_4.H_2O$ were obtained from 20 ml naphthenic acid.

Molecular weight of $CaC_2O_4.H_2O$ = 146.12

$\therefore$ Moles of calcium in 20 ml naphthenic acid = $\frac{0.2047}{146.12}$

= 1.405×10^{-3}.

$\therefore$ Calcium concentration of naphthenic acid solution

$$= \frac{1.405 \times 10^{-3} \times 1000}{20}$$

$$= \underline{\underline{70.25 \times 10^{-3} \text{ M/l.}}}$$

(cf. 102.6×10^{-3} M/l from titration).

$\therefore$ Mean calcium concentration = $\left(\frac{102.6 + 70.25}{2}\right) \times 10^{-3}$

= 86.4×10^{-3} M/l.

Now, moles of copper extracted $= \dfrac{1.325 \times 10^{-3} \times 250}{1000}$

$= 3.31 \times 10^{-4}$

moles of calcium extracted $= \dfrac{86.4 \times 10^{-3} \times 250}{1000} = 216 \times 10^{-4}$

$\therefore$ Ratio or organic phase copper and calcium concentration

$$= \frac{3.31 \times 10^{-4}}{216 \times 10^{-4}} = 1.53 \times 10^{-2}$$

The predicted value at equilibrium (section B.11.1.) was 70.

Moles of copper originally present in solid

$$= \frac{30.7886 \times 2.5 \times 42.64}{100 \times 100 \times 63.54} = 0.005165$$

Moles of calcium originally present in solid

$$= \frac{30.7886 \times 97.5}{100 \times 100.13} = 0.2998$$

Thus, moles of copper present in solid at equilibrium

$= 0.005165 - 0.000331$

$= 0.004834$

Moles of calcium present in solid at equilibrium

$= 0.2998 - 0.0216$

$= 0.2782$

Thus selectivity for copper, as defined in equation (57)

$$= \frac{\text{Moles of copper : Moles of calcium in organic phase}}{\text{Moles of copper : Moles of calcium in solid}}$$

$$= \frac{3.13 \times 10^{-4}/216 \times 10^{-4}}{4.834 \times 10^{-3}/278.2 \times 10^{-3}} = 0.889.$$

$\therefore$ $\underline{\underline{\text{Selectivity for copper} = 0.889.}}$

Test 2 was calculated in the same way, and the results have been summarised in Table 9 (section 4.15).

B.12. Extent of Leaching of Solid.

The values of the limiting organic phase copper concentration, obtained as described in section 4.13., in the experiments performed to investigate the effect of the extent of leaching the solid on the process, as summarised in Table 25.

Table 25.

Test MPAFC	Wt. of ore (g)	Original Malachite Content %	Stage	C_f (Optical Density)
00101	29.6987	2.5	1	0.5695
			2	0.2797
			3	0.3403
00101	29.0684	2.5	1	1.4950
			2	0.8309
10101	30.6402	2.5	1	0.7409
			2	0.2304
			3	0.3375
00101	35.1551	5.0	1	3.341
			2	2.398
			3	1.010

Now from equation (51):-

$$\text{Copper concentration of organic phase} = 6.20\ (\text{O.D.}) - 0.108\ \text{mM/l}$$
$$= [6.20\ (\text{O.D.} - 0.108] \times 63.54 \times 10^{-3}\ \text{g Cu/l}$$

$\therefore$ Wt. of copper extracted by 250 ml of solution

$$= \frac{[6.20\ (\text{O.D.}) - 0.108] \times 63.54 \times 250 \times 10^{-3}}{1000}\ \text{g}$$

Consider the first stage of test 1 in table 25.

The malachite contains 42.64% copper (Table 19).

$\therefore$ Wt. of copper in column = $\dfrac{29.6987 \times 2.5 \times 42.64}{100 \times 100} = 0.31658\text{g}$

Wt. of copper extracted in stage 1

$= [6.20 \times 0.5695 - 0.108] \times 250 \times 63.54 \times 10^{-6}\text{g}$

$= 0.05438\text{g}.$

$\therefore$ Wt. fraction of copper at end of stage 1

$$= \frac{0.31658 - 0.05438}{29.6987 - 0.05438} = \frac{0.26220}{29.6443}$$

$$= \underline{\underline{0.008845}}$$

Similarly, weight of copper extracted in stage 2

$= [6.20 \times 0.2797 - 0.108] \times 250 \times 63.54 \times 10^{-6}\text{g}$

$= 0.02583.$

$\therefore$ Wt. fraction of copper at end of stage 2

$$= \frac{0.26220 - 0.02583}{29.6443 - 0.02583} = \frac{0.23637}{29.6185}$$

$$= \underline{\underline{0.007980}}$$

Similarly for stage 3 and the other tests.

The results of these calculations, together with the rate constants (obtained as in section 4.13) and the limiting organic phase copper concentrations expressed g/l (by means of equation (51)) are summarised in table 26, and presented graphically in Figs.(21) and (22).

The analytical treatment of the large scale operation of the simultaneous leaching and solvent extraction process, derived in section 6.1.3, requires a relation between the limiting organic phase copper concentration and the solid phase copper concentration. Inspection of figs. (21) and (22) shows that the reproducibility between the tests is

Table 26.

Test MPAFC	Stage	C_f (g Cu/l)	k hrs^{-1}	Wt. Fraction of Cu in Solid
00101	1	0.2175	0.010926	0.008845
	2	0.1033	0.005251	0.007980
	3	0.1334	0.004601	0.006862
00101	1	0.5821	0.008830	0.005681
	2	0.3205	0.004848	0.002919
10101	1	0.2850	0.019080	0.008354
	2	0.0839	0.005574	0.007673
	3	0.1261	0.004956	0.006647
10101	1	1.3093	0.118020	0.01212
	2	0.9378	0.026476	0.005426
	3	0.3918	0.036172	0.002600

poor, but the tests indicate that a straight line of variable slope will represent the data moderately well.

The calculation for a large scale process (section 6.1.3.) is simplified if the relation between C_f and the weight fraction of copper in the solid is linear, and for this reason, the data for the ore sample initially containing 5% malachite by weight (being nearest to the conditions of the hypothetical problem in section B.13) were found by linear regression to be represented by the equation

$$C_f = 8.41x + 0.0117 \qquad (123)$$

Where C_f is the limiting organic phase copper concentration in lb Cu/ft^3

x is the weight fraction of copper in solid.

The origin was used as an experimental point in the calculation of equation (123).

B.13. Calculation of the Large Scale Operation of the Process.

In section 6.1.3, an analytical treatment of the simultaneous leaching and solvent extraction process on a large scale was developed. This theory was applied to evaluate the following hypothetical problem.

'100 tons of ore, containing 5% copper by weight, ground to -200+270# (Tyler), is packed into a tower, and, after moistening with dilute sulphuric acid is contacted with fresh 0.5M naphthenic acid, at a flow-rate of 10 gall/ft^2 hr. How long will it be before the ore at the base of the tower contains $<$0.1% copper?'

The following assumptions were made:-

(a) All copper is present as malachite ($CuCO_3Cu(OH)_2$).
(b) The gangue consists of quartz.
(c) Voidage = 0.45.
(d) Particles are spherical.
(e) Mean particle diameter = 0.0063 cm.
(f) (Tower height) $\simeq$ 4x(tower diameter).
(g) Density of malachite = 3.9 g/cc.
(h) Density of quartz = 2.65 g/cc.
(i) Density of naphthenic acid solution = 0.8 g/cc.
(j) Rate constant for extraction = 0.0425 hrs^{-1} (see table 7).
(k) The relation between C_f and the weight fraction of. copper in the ore is given by

$$C_f = 8.41x + 0.0117 \text{ lb Cu/ft}^3 \qquad (123)$$

where x is the weight of copper in the mineral.

Now, by weight, malachite is 57.5% copper

$$\therefore \ \% \text{ malachite in ore} = \frac{5 \times 100}{57.5} \% = 8.7\%$$

$$\therefore \ \% \text{ quartz in ore} = 100 - 8.7\% = 91.3\%$$

$$\therefore \ \text{Mean density of ore} = 0.913 \times 2.65 + 0.087 \times 3.9$$
$$= 2.75 \text{ g/cc}$$

$$\text{Bulk volume of ore} = \frac{100 \times 2240}{(1.00 - 0.45) \times 2.75 \times 62.4} = 2380 \text{ ft}^3$$

Let d be the tower diameter in feet.

$$\therefore \ \pi . \frac{d^2}{4} . 4d = 2380$$

$$\therefore \ d = \sqrt[3]{2380/\pi} = 9.1 \text{ ft.}$$

Take tower diameter as 10 ft.

$$\therefore \ \text{Tower height} = \frac{2380 \times 4}{10^2 \times \pi} = 30.3 \text{ ft.}$$

$$\text{Solid hold-up per unit tower volume} = \frac{100}{2380} \text{ ton/ft}^3$$
$$= 0.042 \text{ ton/ft}^3$$

Liquid hold-up per unit tower volume

$$= \frac{0.45 \times 2380 \times 62.4 \times 0.8}{2240 \times 2380} \text{ ton/ft}^3$$

$$= 0.010 \text{ ton/ft}^3.$$

Now from equation (62):-

$$\frac{K_{OL} a'M}{V} = k = 0.0425 \text{ hrs}^{-1}$$

This value of k was obtained from the results of the factorial experiment in section 4, in which 30g ore mixtures containing 2.5% malachite by weight were contacted with 250 ml 0.5M naphthenic acid.

Thus mean density of ore mixture

$$= 0.975 \times 2.65 + 0.025 \times 3.9$$

$$= 2.68 \text{ g/cc.}$$

Specific surface $= a' = \frac{6}{d\rho} = \frac{6}{0.0063 \times 2.68}$ cm^2/g.

M = mass of mixture = 30g.

V = volume of solvent used to extract copper from mixture

= 250 ml.

$$\therefore \quad K_{OL} = \frac{0.0425 \times 250 \times 0.0063 \times 2.68}{6 \times 30 \times 2.54 \times 12} = 3.21 \times 10^{-5} \text{ ft/hr.}$$

Now from equation (70):-

$$N = \frac{K_{OL} a z}{G} \tag{70}$$

a = contact area/unit tower volume

$$= \frac{6 \times 454 \times 100 \times 2240}{0.0063 \times 2.75 \times 2.54^2 \times 144 \times 2380}$$

$$= 1.593 \times 10^4 \text{ ft}^2/\text{ft}^3$$

Also, from equation (71):-

$$\theta = \frac{K_{OL} a m}{H} \left\{ t - \frac{hz}{G\rho} \right) \tag{71}$$

$$\therefore \theta = \frac{3.21 \times 10^{-5} \times 1.593 \times 10^4 \times 8.41}{0.042 \times 2240} \left(t - \frac{0.01 \times 2240 \times 30.3}{10 \times 0.8 \times 10} \right)$$

$$= 4.57 \times 10^{-2} (t - 8.48 \qquad \text{(t expressed in hours)}$$

$$N = \frac{3.21 \times 10^{-5} \times 1.593 \times 10^4 \times 30.3 \times 6.24}{10} = 9.67.$$

$$\therefore \quad \exp(-N) = 6.325 \times 10^{-5}$$

Now, when the ore at the base of the tower contains 0.1% copper

$$\frac{w - w_o}{C_o - w_o} = \frac{(8.41 \times 0.001 + 0.0117) - (8.41 \times 0.05 + 0.117)}{0 - (8.41 \times 0.05 + 0.0117)}$$

$$= 0.953.$$

Thus substituting in eqn. (83):-

$$0.953 = \int_0^\theta J_0(2i\sqrt{9.67\theta})\ \exp(-9.67)\ \exp(s).ds.$$

Making use of the approximation for $J_0(2i\sqrt{9.67\theta})$, (eqn. (84))

$$0.953 = \int_0^\theta \frac{\exp(-9.67)\ \exp(2\sqrt{9.67\theta} - \theta)}{2\sqrt{\pi\sqrt{N\theta}}}\ d\theta$$

This equation may be solved for θ by a numerical method.

The integrand is evaluated for various values of θ, and integrated by Simpson's Rule. The integral is plotted as a function of θ, and the solution corresponds to the value of θ which gives an integral of 0.953. The solution is presented in tabular form in Table 27, and the graph of the integral as a function of θ is plotted in Fig.(30).

From Fig.(30)

$$\frac{w - w_o}{C - C_o} = 0.953 \quad \text{when } \theta = 20.$$

Now $\theta = 4.57 \times 10^{-2}\ (t - 8.48)$

$$\therefore \quad t = \frac{20}{4.57 \times 10^{-2}} + 8.48$$

$$\therefore \quad \underline{\underline{t = 446 \text{ hours}}} \qquad \text{(approx. 2.1/2 weeks)}$$

Thus after 2.1/2 weeks, the ore at the base of the column would contain less than 0.1% copper.

Table 27.

θ	$N\theta$	$2\sqrt{N\theta}-\theta$	$\exp(2\sqrt{N\theta}-\theta)$ $= A$	$\pi\sqrt{N\theta}$	$2\sqrt{\pi\sqrt{N\theta}}$ $= B$	$\frac{A}{B} = y_i$	$y_{i-1}+4y_i+y_{i+1}$ $= z$	$\sum z$	$\frac{h}{3}\sum z$	$\frac{h}{3}\sum z.\exp(-N)$
0	0	0	1.000	0	0	-	0	0	0	0
2.5	24.18	7.33	1525.4	15.45	7.860	194.07	-	-	-	-
5.0	48.35	8.91	7404.8	21.85	9.348	792.13	1568.41	1568.41	1307.01	0.0825
7.5	72.53	9.53	13766.4	26.76	10.54	1306.11	-	-	-	-
10.0	96.70	9.67	15835.1	30.90	11.12	1424.02	7440.59	9009.00	7507.50	0.4748
12.5	120.9	9.48	13095.4	34.53	11.75	1114.50	-	-	-	-
15.0	145.1	9.08	8778.1	37.83	12.30	713.67	6595.69	15604.69	13003.91	0.8225
17.5	169.2	8.52	5014.1	40.88	12.79	392.03	-	-	-	-
20.0	193.4	7.80	2440.6	43.67	13.22	184.61	2466.40	18071.09	15059.24	0.9525
22.5	217.6	7.00	1096.6	46.34	13.61	80.57	-	--	-	-
25.0	241.8	6.10	445.86	48.86	13.98	32.61	539.50	18610.59	15508.82	0.9809
27.5	265.9	5.12	167.34	51.25	14.32	11.69	-	-	-	-
30.0	290.1	4.06	57.924	53.51	14.63	3.96	83.33	18693.92	15578.27	0.9853
32.5	314.3	2.96	19.298	55.71	14.93	1.29	-	-	-	-
35.0	338.5	1.78	5.930	57.78	15.20	0.39	9.51	18703.43	15586.19	0.9858

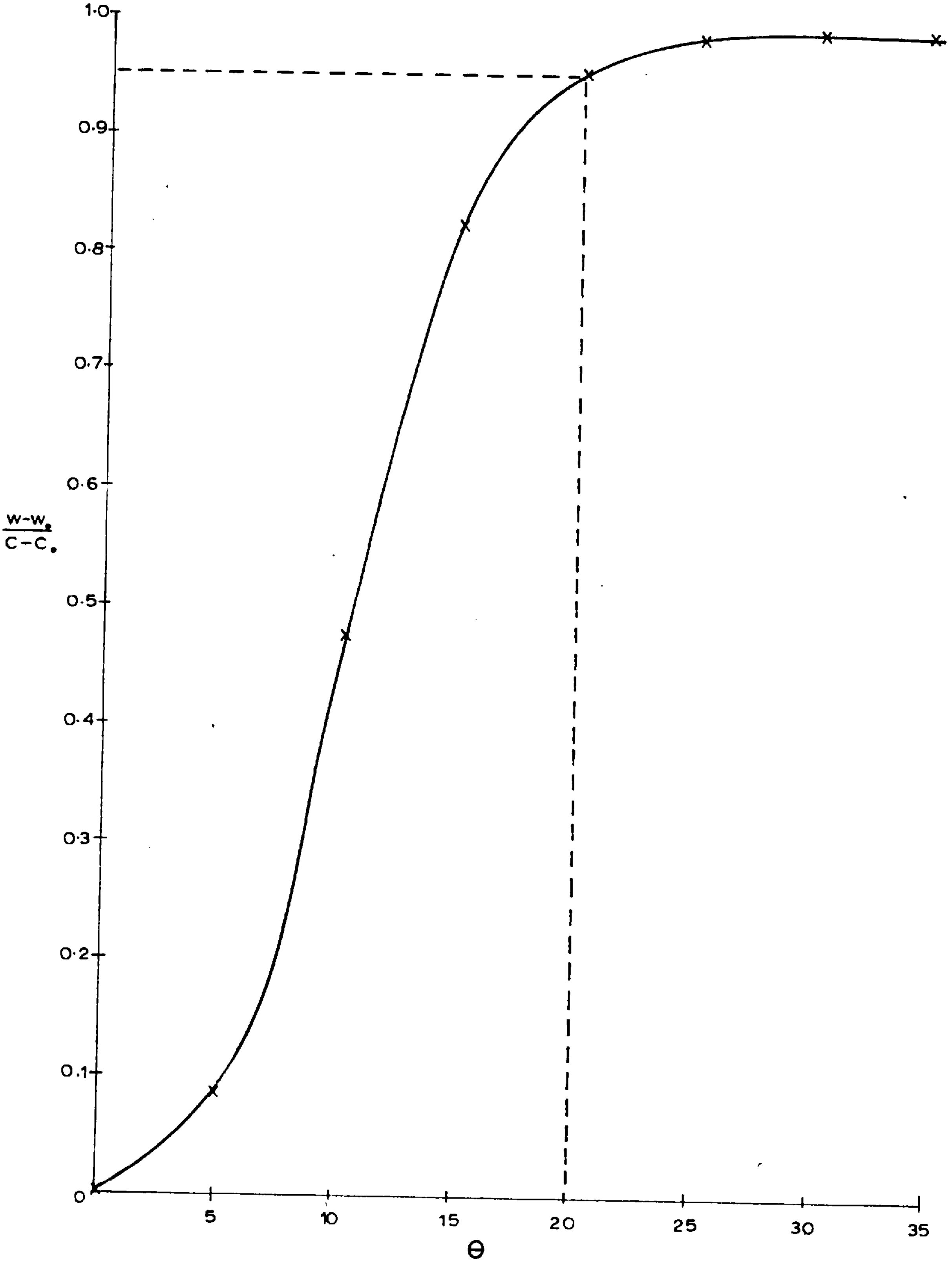


Fig. 30

B.14. Calculation of Residual Solvent on Bed.

B.14.1. Calculation of Calibration Curve for the Variation of Optical Density of Copper Complex with Copper Concentration.

The experimental results are summarised in Table 28.

Table 28.

Cu Conc.of CCl_4 Solution, g/1 x 10^{-4}	Optical Density
0.00	0.000
1.75	0.051
3.50	0.100
7.01	0.170
7.01	0.173
10.50	0.229
17.50	0.388
28.04	0.578
35.00	0.791

By linear regression, as in section (3.6.1.) the best straight line through these points was found to be

$$Y = 46.6 \text{ O.D.} - 0.5 \qquad (59)$$

where Y is the copper concentration of the carbon tetrachloride solution in g/1 x 10^{-4}.

B.14.2. Solvent Loss Calculations. Consider, as an example of the calculation method, the test corresponding to the treatment combination $M_0P_CA_CT_CC_CR_C$. From the table of experimental readings (Appendix A.8):-

Wt. of sand used = 32.7949g.
Volume of aqueous effluent collected = 50.0 ml.
Dilution of aqueous effluent prior to analysis = 6.25
Optical density of copper complex = 0.105.

Now, from equation (59)

Copper concentration of carbon tetrachloride solution in analysis $= [46.6 \times 0.105 - 0.5] \times 10^{-4}$ g Cu/l

∴ Copper concentration of diluted effluent

$$= 2 \times [46.6 \times 0.105 - 0.5] \times 10^{-4} \text{ g Cu/l.}$$
$$= 9.744 \times 10^{-4} \text{ g Cu/l.}$$

(as 10 ml of copper solution were contacted with 20 ml of carbon tetrachloride in the analytical procedure (section 7.1))

∴ Wt. of copper removed from bed

$$= \frac{9.744 \times 10^{-3} \times 6.25 \times 50}{1000} \text{ g}$$
$$= 3.045 \times 10^{-4} \text{g.}$$

Now, copper concentration of organic solution (from equation (51))

$$= (6.20 \times 0.5 - 0.108) \times 63.54 \times 10^{-3} \text{ g/l}$$
$$= 1.970 \times 10^{-1} \text{ g/l.}$$

∴ Volume of organic solution left on bed

$$= \frac{3.045 \times 10^{-4}}{1.970 \times 10^{-4}} \text{ ml}$$
$$= 1.546 \text{ ml.}$$

Now 0.5M napthenic acid (C_o) was used in this test, and the molecular weight of the acid was 288.

$\therefore$ Wt, of napthenic acid left of bed

$$= \frac{1.546 \times 0.5 \times 288}{1000}\ g$$

$$= 0.2226g.$$

$\therefore$ Wt. of naphthenic acid left on unit weight of bed

$$= \frac{0.2226}{35.9577}\ g/g$$

$$= \underline{\underline{0.00619\ g/g}}$$

The solvent losses for the remaining 31 tests were calculated in the same way, and analysed statistically as the responses of a half replicate of a 2^6 factorial experiment, by the method outlined in section 3.5.4. The solvent losses per unit weight of bed for each test are in the 'response' column of table 29.

B.14.3. Statistical Analysis of Responses. Table 29 contains the detailed statistical analysis of the solvent loss experiments, by the method described in section 3.5.4.

The symbol (E) in the 'effects' column denotes that this particular effect was used in the estimates of experimental error.

Inspection of the 'mean square effect' column revealed that the effects corresponding to PATC, MTCR and MPATC, TCR were exceptionally large, and to include these in the error estimate would completely invalidate the experiment, as the error estimate would then be so large that no effects would appear significant. These effects were therefore ignored when computing the estimate of experimental error by the procadure outlined in calculation B.7.

Table 29.

Tabular Analysis of Solvent Loss/Unit Weight of Quartz.

Factor Levels MPATCR	Response (x1000)	(I)	(II)	(III)	(IV)	Total Effect	Mean Effect	Mean Square Effect	Effect
000000	6.19	16.79	60.30	129.29	231.36	513.27	16.0397	8232.6904	I,LPAR
100001	10.60	43.51	68.99	102.07	281.91	125.17	7.8231	489.6102	M,PAR
010001	10.10	60.35	62.10	119.52	110.12	-36.05	-2.2531	40.6185	P,MAR
110000	33.41	8.64	39.97	162.39	15.05	-60.51	-3.7819	114.4206	MP,AR
001001	9.69	47.64	62.57	65.19	-44.46	-24.73	-1.5456	19.1116	A,MPR
101000	50.66	14.46	56.95	44.93	8.41	-4.87	-0.3044	0.7411	MA,PR
011000	6.07	13.13	84.03	7.54	-39.54	-50.09	-3.1306	78.4065	PA,MR
111001	2.57	24.68	78.36	7.51	-20.97	-140.51	-8.7819	616.9706	MPA,R
000100	11.66	46.71	27.72	-24.99	-13.44	15.65	0.9781	7.6538	T,MPATR
100101	35.98	15.68	27.47	-19.47	-11.29	-20.29	-1.2681	12.8751	MT,PATR
010101	5.39	20.22	28.00	-14.34	-1.32	42.61	2.6631	56.7378	PT,MATR
110100	9.07	36.73	16.93	22.75	-3.55	-12.17	-0.7606	4.6284	MPT,ATR (E)
001101	4.00	19.85	6.31	-25.57	-31.54	-30.87	-1.9294	29.7799	AT,MPTR
101100	9.13	64.18	1.23	-13.97	-13.55	-14.21	-0.8881	6.3101	MAT,PTR (E)
011100	7.52	49.97	2.99	1.40	-36.06	12.05	0.7531	4.5375	PAT,MTR (E)
111101	19.32	28.39	4.52	-22.37	-104.45	62.19	3.8869	120.8623	MPAT,TR
000010	26.70	4.41	26.72	8.69	-27.22	50.55	3.1594	79.8532	C,MPACR
100011	20.01	23.31	-51.71	-22.13	42.87	-95.07	-5.9419	282.4570	MC,PACR
010011	1.43	40.97	-33.18	-5.62	-20.26	52.87	3.3044	87.3511	PC,MACR
110010	14.43	-3.50	13.71	-5.67	-0.03	18.57	1.1606	10.7764	MPC,ACR (E)
001011	5.23	24.32	-30.85	9.75	5.52	2.15	0.1344	0.1444	AC,MPCR
101010	14.99	3.68	16.51	-11.07	37.09	-2.23	-0.1394	0.1554	MAC,PCR (E)
011010	22.63	5.13	44.33	-5.08	11.60	12.99	0.8119	5.2731	PAC,MCR (E)
111011	14.10	11.80	-21.58	1.53	-23.77	-68.39	-4.2744	146.1622	MPAC,CR
000110	14.69	-6.67	18.90	-78.43	-30.82	70.09	4.3806	153.5190	TC,MPATCR
100111	5.16	13.00	-44.47	46.89	-0.05	20.23	1.2644	12.7891	MTC,PATCR (E)
010111	25.83	9.76	-20.64	47.36	-20.82	21.57	1.9731	31.1457	PTC,MATCR (E)
110110	38.35	-8.53	6.67	-65.91	6.61	-35.37	-2.2106	39.0949	MPTC,ATCR (E)
001111	12.75	-9.53	19.69	-63.37	125.32	30.77	1.9231	29.5872	ATC,MPTCR (E)
101110	37.22	12.52	-18.29	27.31	-113.27	27.43	1.7144	23.5126	MATC,PTCR (E)
011110	24.17	24.47	22.05	-37.98	90.68	-238.59	-14.9119	1178.9121	PATC,MTCR (E)
111111	4.22	-19.95	-44.42	-66.47	-28.49	-119.17	-7.4481	443.7965	MPATC,TCR (E)
TOTAL	513.27	638.44	541.88	321.68	376.64	135.04		12960.4583	
CHECK TOTAL	638.44	541.88	321.68	376.64	135.04				
SUM OF SQUARES	1290.4695								

The results of the analysis have been summarised in Table 12, section 5.10.

B.14.4. Calculation of Mean Loss of Solvent. From Table 29 the mean loss of solvent per unit weight of quartz is given by the result in the 'mean effect' corresponding to the control experiment.

$\therefore$ Mean loss = 16.04×10^{-3} g/g ore.

Now the original ore contained 2.5% malachite of copper content 42.64%.

$\therefore$ Loss of solvent/ton of copper extracted

$$= \frac{16.04 \times 10^{-3}}{0.025 \times 0.4264} \text{ tons}$$

$$= \underline{\underline{1.50 \text{ tons.}}}$$

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