

MICROBIOLOGICAL LEACHING OF A ZINC SULFIDE CONCENTRATE

by

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in the Department

of

CHEMICAL ENGINEERING

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

May, 1970

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The applicability of microbiological oxidation for the recovery of zinc from a high-grade zinc sulfide concentrate has been investigated using a pure strain of Thiobacillus ferrooxidans. Factors affecting the bacterial activity and consequently the rate and extent of zinc extraction were studied. These factors were: temperature, pH, nutrient and substrate concentrations, solid particle size and surface area. The effect of carbon dioxide concentration in the air supplied to the oxidation was also studied. Larger scale experiments were carried out to simulate more closely possible industrial conditions.

The optimum temperature was found to be 35°C, the optimum pH 2.3. Nutrient levels of 89 mg phosphate P/l and 636 mg ammonia N/l were sufficient to avoid rate limitation and provide for maximum extraction, respectively. Increasing the particle surface area, the pulp density, or the total surface per unit volume of leach liquor increased the rate of zinc extraction up to a point beyond which further increases were not effective. Increasing the carbon dioxide content of the air had a similar effect.

The larger scale experiments gave similar extraction rates to those observed in shake flasks but the extent of zinc extraction was significantly higher. The final concentration of zinc in leach solutions reached levels currently employed in commercial electrowinning procedures. A form of the generalized logistic equation was shown to be capable of representing the complete extraction curve under a variety of experimental conditions.

This dissertation is dedicated
to my wife, Katalin, to whom
special gratitude is expressed
for her endless patience, understanding and encouragement.

The author wishes to express sincere appreciation to Dr. C. Craig Walden and Dr. Richard M. R. Branion for their tireless interest, guidance and encouragement throughout this study.

Also, the author wishes to thank Dr. Douglas W. Duncan, B. C. Research, for his advice and suggestions in the field of micro-biological leaching.

Thanks are due to Mr. Ron Orr for the use of the "Dynamic Nitrogen Adsorption Apparatus"; to the British Columbia Institute of Technology for the use of some of their equipment, and to B. C. Research for providing the use of all of their facilities necessitated by this investigation.

The author is indebted to his employer, the Quebec Department of Natural Resources, for providing him with a leave of absence for the duration of this study.

The work reported in this dissertation was supported by a B. C. Research Fellowship.

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|------------------------|--|
| a_0, a_s, \dots, a_5 | = polynomial constants (equation 22) |
| a, b, c, d | = polynomial constants (equation 16) |
| a, b | = slope and intercept (equation 18) |
| d | = particle diameter (equation 29) |
| B | = constant (equation 14) |
| E_0 | = initial enzyme concentration, g/l |
| E | = enzyme concentration, g/l |
| ES | = enzyme -substrate complex concentration, g/l |
| E_r | = energy required for carbon dioxide fixation, calories/g |
| E_p | = energy produced by substrate oxidation, calories /g |
| FEE | = free energy efficiency, % |
| f_1 | = function depends on cell concentration (equation 9) |
| f_2 | = function depends on substrate consumption (equation 10) |
| f_3 | = function depends on product formation (equation 11) |
| G | = glucose concentration (equation 20), g/l |
| ΔH_a | = activation energy, Kcal/mole |
| K | = proportionality constant (equation 29) |
| k_1, k_2, k_3 | = rate constants (equation 12, 19 and 20) |
| K_1, K_2 | = proportionality constants (equation 15) |
| K_m | = Michaelis-Menten constant |
| N | = neomycin concentration (equation 20), g/l |
| P | = product concentration, g/l |
| PD | = pulp density, g x 100/ml |
| P_m | = maximum value of product concentration, g/l |

| | |
|---------------|---|
| Q_{10} | = temperature coefficient |
| R | = gas constant, calories/°K mole |
| S, S_1, S_2 | = substrate concentrations, g/l |
| SSA | = specific surface area, m^2/g |
| t | = time, hr |
| T_1, T_2 | = absolute temperatures, °K |
| TSA | = total surface area per unit volume of liquid medium, m^2/ml |
| V | = specific growth rate, hr^{-1} or zinc extraction rate, mg/l hr |

V_m = maximum value of above

X = cell (mass or number) concentration

Appendix 3

c = constant

P = partial pressure of nitrogen in the He - N_2 gas mixture, mm Hg

P_o = saturation pressure of nitrogen at temperature of liquid nitrogen, mm Hg

V_{ads} = volume of nitrogen adsorbed on sample (STP), μl

V_m = volume of adsorbed nitrogen due to monolayer coverage, μl

V_{mspc} = volume of adsorbed nitrogen due to specific monolayer coverage, $\mu l/g$

1. Nature of the problem

The discovery of the obligate chemoautotrophic bacterium, Thiobacillus ferrooxidans, opened up an area of research which has had and will continue to have considerable economic significance. This microorganism can tolerate exceptionally high concentrations of most cations and is involved in the leaching of sulfide ores and wastes.

The possibility of using this microorganism in hydrometallurgical metal extraction processes was recognized early by all investigators. It represents a potential solution to the problem faced in many countries where continuing depletion of high-grade ore deposits has created a need to develop effective methods for recovering metal values from low-grade sulfide ores.

The microbiological leaching process involves complex interactions between the microorganism, substrate and the trace nutrient concentrations, which are not yet completely understood. Altogether, a more economic use of this leaching process requires a better understanding of the various factors influencing bacterial growth and the microbiological metal dissolution processes.

2. Objectives

The present work investigates the microbiological extraction of zinc from a high-grade zinc sulfide concentrate, using a pure strain of T. ferrooxidans. Conditions such as temperature, pH, pulp density, nutrient concentrations, and specific surface area of solid substrate are studied in terms of their effects on zinc extraction rate and, in some instances, on the final zinc concentration in solution. Where appropriate, optimum conditions for leaching are specified. In addition,

factors limiting the rate of zinc extraction are delineated as well as those conditions under which they become limiting. Further, an effort is made to describe the form of an equation suitable for curve fitting the data obtained in these microbiological leaching studies.

Most bacterial species utilize complex organic compounds for energy. Such organisms are classified as the heterotrophs. Only a few species, called autotrophic bacteria, are able to synthesize their carbohydrates, fats and proteins from carbon dioxide and inorganic sources of nitrogen. The autotrophic capabilities of bacteria were established by Winogradsky^(1, 2) in 1887 and 1888. He concluded that bacteria exist which were able to grow by utilizing the energy liberated by oxidation of reduced forms of sulfur and ferrous iron. The bacteria may be distinguished as obligate or facultative autotrophs. The obligate forms obtain their energy solely from oxidation of inorganic compounds, whereas the facultative forms also may utilize organic compounds, when inorganic compounds are not available.

T. ferrooxidans, which is responsible for microbiological leaching, has been placed in the fifth genus, Thiobacillus, of the family Thiobacteriaceae⁽³⁾. This organism possesses the following morphological characteristics^(3, 4, 5):

cell: short rod; 0.5 by 1.5 microns; motile; cells occur singly or as diplobacilli; Gram stain-negative.

colony: (form when cultured on solid media) minute; irregular edge; flat; granular surface; opaque.

1. Description and physiology of *T. ferrooxidans*

T. ferrooxidans was discovered by Colmer and Hinkle⁽⁶⁾ in the acid, iron-containing drainage water of some bituminous coal mines, and described later by Colmer et al⁽⁴⁾ and Temple and Colmer⁽⁵⁾ as an obligate, chemoautotrophic, acidophilic, iron oxidizing bacterium. It obtains carbon (in form of carbon dioxide) and oxygen from the atmosphere and derives its metabolic energy from the oxidation of reduced iron and sulfur compounds.

This organism is morphologically similar to Thiobacillus thiooxidans. The fundamental difference between the two species is generally recognized to be the inability of T. thiooxidans to oxidize ferrous iron and insoluble sulfides^(4,5,7).

Leathen and Braley⁽⁸⁾ and Leathen et al⁽⁹⁾ studied an organism which oxidized ferrous iron but not elemental sulfur or thiosulfate. Because of its inability to utilize these reduced sulfur substrates, it was considered to be a new genus and assigned the name Ferrobacillus ferrooxidans. Similarly, Kinsel⁽¹⁰⁾ assigned the name Ferrobacillus sulfooxidans to an organism she isolated, which utilized ferrous iron and elemental sulfur but not thiosulfate.

Subsequent investigations by Unz and Lundgren⁽¹¹⁾, Ivanov and Lyalikova⁽¹²⁾, Beck and Shafia⁽¹³⁾ and Hutchinson et al⁽¹⁴⁾ indicated that these organisms (T. ferrooxidans, F. ferrooxidans and F. sulfooxidans) were identical and should be called T. ferrooxidans. All these organisms were capable of oxidizing elemental sulfur and thiosulfate in addition to ferrous iron⁽¹⁴⁾. In spite of these conclusive data, some authors continue to use the name F. ferrooxidans.

2. Occurrence of *T. ferrooxidans*

5.

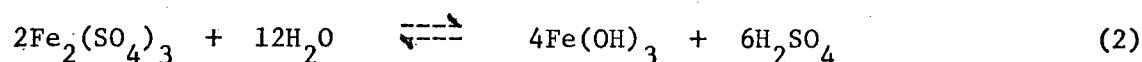
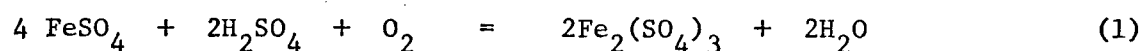
The organism, *T. ferrooxidans*, is virtually ubiquitous in nature. Since its original isolation^(4,5,6), it has been isolated in Australia⁽¹⁵⁾, Canada^(16,17), Congo⁽¹⁸⁾, Denmark⁽¹⁹⁾, England⁽²⁰⁾, Germany⁽²¹⁾, Japan⁽²²⁾, Mexico⁽²³⁾, Scotland⁽²¹⁾, South Africa⁽²⁴⁾, Spain⁽¹⁶⁾, Sweden⁽²¹⁾, U.S.A.^(7,8,10,25-31) and in the U.S.S.R.⁽³²⁻³⁶⁾.

3. Microbiology of *T. ferrooxidans*.

The activity of these bacteria is influenced by the nutrients available for its growth and reproduction. The liquid media most frequently used for *T. ferrooxidans* are those of Leathen *et al*⁽⁹⁾ and Silverman and Lundgren⁽³⁷⁾. These media are compared in Table 1.

Silverman and Lundgren⁽³⁷⁾ designated their medium 9K. It will support 2×10^8 to 4×10^8 cells per ml compared to 7×10^6 cells per ml for the medium of Leathen *et al*⁽⁹⁾.

During bacterial growth, the ferrous iron is oxidized to ferric iron (equation 1), which has been considered to hydrolyze to ferric hydroxide and sulfuric acid (equation 2)⁽³⁷⁾.



Reaction 1 is a metabolic reaction of the bacteria. Reaction 2 is a chemical reaction, which results in an increase in the acid content of the medium.

Leathen *et al*⁽³⁸⁾ have indicated that the hydrolysis of ferric sulfate is incomplete in acid medium and basic ferric sulfates are produced; the relative amounts of iron, hydroxyl and sulfate will depend upon the

Table 1

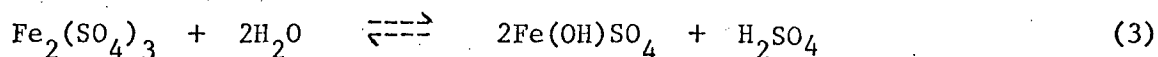
6.

Liquid Media for T. ferrooxidans

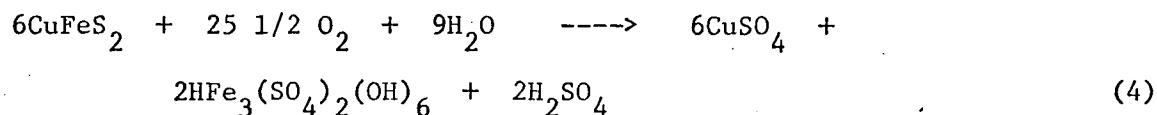
| Components | Leathen <u>et al</u> ⁽⁹⁾ in g | Silverman and Lundgren ⁽³⁷⁾ in g |
|--|---|---|
| <u>Basal salts:</u> | | |
| $(\text{NH}_4)_2\text{SO}_4$ | 0.05 | 3.00 |
| KCl | 0.05 | 0.10 |
| K_2HPO_4 | 0.05 | 0.50 |
| $\text{MgSO}_4 \times 7\text{H}_2\text{O}$ | 0.50 | 0.50 |
| $\text{Ca}(\text{NO}_3)_2$ | 0.01 | 0.01 |
| Dist. H_2O | 1000 ml | to 700 ml |
| 10N H_2SO_4 | pH = 3.5 | 1.00 ml |
| <u>Energy source:</u> | | |
| $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ | 10 ml of a 10% W/V solution | 300 ml of a 14.74% W/V solution |

Where W/V = weight per volume

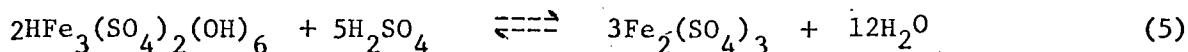
dilution and the acidity during hydrolysis. They represented the hydrolysis by the reaction of equation 3.



The iron chemistry involved is certainly more complex than is indicated by the foregoing equations. Observations on microbiological chalcopryrite leaching⁽³⁹⁾ indicate the following overall reaction for the formation of insoluble ferric sulfate:



Reaction 4 results in a reduction of pH and of ferric and sulfate ion concentrations. The acidity of the solution is stabilized near pH 2, according to the equilibrium equation:



The early literature concerning the capability of this microorganism to utilize different energy sources is somewhat confused. The ability of T. ferrooxidans to oxidize ferrous iron has been demonstrated by numerous authors^(4,5,14,37). Similar agreement has not been obtained concerning the utilization of different sulfur compounds as substrates, because some authors have failed to demonstrate the oxidation of elemental sulfur^(4,5,8,9) or thiosulfate^(8,9). A possible explanation of this lack of success by certain authors is given by Hutchinson et al⁽¹⁴⁾, who pointed out the importance of initiating growth at the correct pH.

However, the majority of investigators have shown that T. ferrooxidans is able to derive its energy from the oxidation of elemental sulfur and thiosulfate^(3,10,11,14,16,21,40,41). The pH optimum for the oxidation of elemental sulfur ranges from 1.75 to 5^(42,121) and for thiosulfate between 4 and 5.5^(11,14,42,43).

These pH optima are higher than those found for bacterial activity on ferrous sulfate media. It should be noted that the internal cellular pH of these organisms normally is higher than that of their external environment⁽⁴⁴⁾. Recently, workers at B. C. Research have published a series of communications^(42,45-48) concerning substrate utilization by T. ferrooxidans. They have found that these organisms oxidize soluble and insoluble ferrous iron, sulfur, insoluble and soluble sulfide, thiosulfate, trithionate and tetrathionate. The oxidation rate of sulfur was always slower than the rate of iron oxidation⁽⁴¹⁾.

Although the literature concerning the energy transfer mechanisms of thiobacilli is growing rapidly, only limited information is available concerning electron transfer from ferrous iron and sulfur compounds to molecular oxygen. Various theories exist involving enzymes and proteins present in the organisms^(44, 49-63). Trudinger⁽⁶⁴⁾ has published a review of the metabolism of inorganic sulfur compounds and Peck⁽⁶⁵⁾ one on energy coupling mechanisms. Nonetheless, no overall understanding of the energy transfer reactions in T. ferrooxidans has yet been achieved.

Biological cells tend to lose energy at all sites of energy transfer⁽⁶⁶⁾; a measure of their efficiency in retaining the energy available to them is the free energy efficiency (FEE). The FEE of carbon dioxide fixation by T. ferrooxidans may be evaluated using a relationship

proposed by Baas-Becking and Parks⁽⁶⁷⁾:

$$\text{FEE (\%)} = 100 \frac{E_r}{E_p} \quad (6)$$

where E_r = energy used for carbon dioxide fixation;

E_p = energy produced by substrate oxidation.

Using ferrous iron as substrate, Temple and Colmer⁽⁵⁾ found that the free energy efficiency of carbon dioxide fixation for T. ferrooxidans was about 3.2%. Lyalikova⁽⁶⁸⁾ observed that this efficiency decreases with the age of the culture. An average value of 30% was obtained with a two-day old culture. Silverman⁽⁶⁹⁾ reported values ranging from 13.8 to 28.6% with an average value of free energy efficiency of 20.5% for carbon dioxide fixation.

Certain compounds synthesized by autotrophic organisms from carbon dioxide are secreted into the medium to a significant extent⁽⁶³⁾. For example, T. thiooxidans releases amino acids and phosphatidyl compounds^(209, 210) and T. ferrooxidans pyruvate⁽⁷⁰⁾. Amino acids in solution may act as chelating agents and phosphatidyl compounds as a wetting agent, possibly a selective advantage for these microorganisms in attaching themselves to solid surfaces.

Under completely anaerobic conditions, Pugh and Umbreit⁽⁶¹⁾ were able to demonstrate carbon dioxide fixation that was associated with oxidation of a specific substrate. For example, these authors using T. ferrooxidans (F. sulfooxidans) showed that carbon dioxide was fixed when ferrous iron was oxidized to ferric iron. Further, these authors support the concept that an electron transport system is interposed between

the inorganic substrate oxidized and the actual oxygen utilized. No mechanism was given to explain this phenomenon.

4. Biochemical activity of *T. ferrooxidans*

Bacteria are influenced markedly by their environment⁽⁷¹⁾.

Factors such as temperature, pH, energy source, pulp density, particle size, oxygen, carbon dioxide, nutrient concentrations and agitation may be expected either to stimulate or suppress the microbial activity of *T. ferrooxidans*.

For leaching of mineral sulfides by *T. ferrooxidans*, the following conditions are reported in the literature:

4.1 Temperature

The optimum temperature has been found to be 35°C^(16,72); the bacteria are inhibited at 40°C^(46,73,74); no minimum temperature limit for growth has been established.

4.2 pH

The following pH-values were reported to be the limits for growth of *T. ferrooxidans*: 2 and 4 by Razzell⁽⁷⁵⁾ and 1 and 5 by Silverman and Ehrlich⁽⁷⁶⁾. The optimum pH is below 3⁽⁷⁷⁾; more exactly it is at 2.5^(16,46,72). Above pH 6.0 bacterial action is almost completely inhibited and above pH 9.0, the bacteria are destroyed⁽⁷²⁾.

4.3 Energy source

Substrate oxidation rates are said to be much higher on ferrous iron than on inorganic sulfide substrates. This organism often requires a period of adaptation to the new energy source⁽⁷⁸⁾. Sulfide minerals are more rapidly leached as fine particles than as coarse ones^(7,26,46,74,77); no optimum particle size data have been reported.

4.4 Surface active agents

Some surfactants exert a beneficial effect on metal extraction

rates⁷⁹⁻⁸¹⁾ and reduce the lag time⁽⁸²⁾; but the presence of surfactants diminishes the level of final metal extraction⁽⁸³⁾, possibly through limitation of oxygen transfer⁽⁸⁴⁾.

4.5 Carbon dioxide

Normal air concentrations are adequate⁽⁷⁸⁾; up to 2% carbon dioxide concentration in the gas phase may be desirable⁽¹³⁾.

4.6 Oxygen

Oxygen is required in large quantities (every pound of sulfur as sulfide, requires two pounds of oxygen for complete conversion to sulfate). The supply of this oxygen is the key problem in the leaching process^(46,78). The low solubility of oxygen and carbon dioxide in the leaching medium means that high rates of gas transfer are necessary. This necessitates the use of some kind of agitation.

4.7 Nutrients

The nutrient requirements of T. ferrooxidans are normal for a chemosynthetic autotroph. Early reports indicated a requirement for such inorganic compounds as carbon dioxide (for cell growth), ammonium sulfate and dipotassium hydrogen phosphate (as nitrogen and phosphate sources), ferrous iron and sulfur compounds (as energy sources), and magnesium sulfate, potassium chloride and calcium nitrate (as growth factors)⁽⁷⁴⁾. However, experiments carried out at B. C. Research⁽³⁹⁾ have demonstrated that T. ferrooxidans has no requirement for magnesium, calcium and potassium ions beyond those levels contained in reagent grade ammonium sulfate, dipotassium hydrogen phosphate and sulfide minerals.

Of these factors influencing microbiological leaching, the most important probably are temperature and pH. These directly affect activity (metabolism) and growth of the bacteria. Another requirement for the oxidation of sulfides by the bacteria is the availability of the substrate.

The most ideal condition exists when the substrate is soluble such as are ferrous iron salts. For insoluble substrates, the sulfide minerals must have an adequate amount of exposed surface area.

Although the surface phenomena have been observed by many authors^(7,26,46,77,78), no investigations have been undertaken to establish the relationship between the specific surface area and bacterial growth and the effect on the metal extraction rate.

However, experiments on microbiological chalcopyrite leaching⁽³⁹⁾ have indicated that, below a certain particle size, no benefit in extraction rate is achieved and, in this instance, only the total extraction is enhanced.

5. Microbiological leach techniques

Prior to 1964⁽⁷⁹⁾, laboratory studies on the microbiological leaching of sulfide ores were carried out with airlift percolators, described by Bryner et al⁽²⁵⁾, the Warburg respirometer⁽⁴⁰⁾ or with stationary leach bottles⁽⁷⁷⁾. The oxygen supply is poor in both the percolator and the stationary leach bottle techniques; whereas the size and the principle of the Warburg apparatus render it unsuitable for practical leaching.

Using percolators for the bacterial leaching of chalcopyrite, Bryner et al⁽²⁵⁾ found 2.7% of copper extracted from one sample and 6.1% of copper from another sample in 70 days; Malouf and Prater⁽²⁹⁾ reported about 40% after 70 days and 60% extraction after 470 days.

Duncan, Trussell and Walden⁽⁷⁹⁾ described a practical method, gyratory shaking, which produces rapid aeration and an accelerated rate of leaching. Using the shake-flask technique, Duncan and Trussell⁽⁸²⁾ reported that T. ferrooxidans leached 72% of the copper from museum grade chalcopyrite in 12 days and 100% in 26 days. This comparison shows the

However, besides the gyratory shaking there are many other types of mixers available for use in laboratory leaching experiments, e.g., air spargers, magnetic stirrers and reciprocating shakers. The effects of these techniques on microbiological copper extraction are compared by Duncan et al⁽⁸⁵⁾. They found that magnetic stirring and reciprocating shaking gave results comparable with those for gyratory shaking.

Laboratory column leaching techniques^(78,85) may simulate the commercial procedures for heap or dump leaching. A sample of ore is placed in a column and the liquid medium is circulated through it continuously by an air lift. One concurrent effect of this technique is to provide the column with oxygen and CO₂ saturated medium. Although, because of the high oxygen requirement of the process, oxygen still may be a limiting factor.

Another leach technique which may be used for laboratory microbiological metal extraction is the tank leaching technique. This method is particularly useful for evaluating high-grade materials and provides for easy control of all the important parameters influencing this type of leaching. The interpretation of the results of tank leaching experiments also may contribute to a future acceptance of the bioleaching technique for recovery of metals from certain ore concentrates, which are presently recovered by conventional hydro- or pyrometallurgy.

So far, only two microbiological leach techniques have been applied in the commercial recovery of metals from sulfide materials. These are dump or heap leaching and in situ leaching. The first technique is used mainly for copper recovery^(86-94,211) in the western

states of U.S.A., where now more than 100,000 tons/year of copper are produced in this manner⁽⁷⁸⁾. The only other metal which is being leached commercially is uranium⁽⁸⁵⁾. It is recovered by in situ leaching in the Elliot Lake area of Ontario^(95,96) in amounts of 10,000 lbs of U_3O_8 per month, and in South Africa⁽²⁴⁾.

6. Microbiological leaching of mineral sulfides

All living organisms require small quantities of trace elements for protoplasm synthesis and for action of their enzyme systems. However, transformation of appreciable quantities of minerals is restricted to certain groups of microorganisms⁽⁷⁶⁾.

Mineral transformations can be effected not only by direct enzymatic interaction but also by interaction with the end product(s) of metabolism⁽⁷⁶⁾. This statement pertains also to the autotrophic acidophilic organism, T. ferrooxidans. For example, Temple et al^(4,5,6, 97,98) reported that T. ferrooxidans and T. thiooxidans were present in the acid mine waters and were involved in acid formation in the coal mines.

The process of the microbiological leaching of metal sulfides may be defined as a biochemical (biogeochemical) oxidation process, catalyzed by a living organism⁽¹²³⁾. However, in nature, only the insoluble sulfides are of consequence, and unless the oxidation product is soluble, such an oxidation would be of little commercial consequence.

T. ferrooxidans oxidizes different mineral sulfides at different rates, the rate of oxidation of the mixture being the sum of the rates of the individual components of the mixture⁽⁸³⁾.

T. ferrooxidans has been found able to oxidize antimony sulfides^(25,8,3,99), arsenic sulfides⁽⁹⁹⁻¹⁰¹⁾, cobalt sulfides^(18,99), copper sulfides^(16,25,26,28-32,36,74,75,77-83,85-94,102-106), iron sulfides^(7,17,24-27,29,30,32,48,99,103-112), molybdenum sulfide^(26,28,29,85;113,114), nickel

sulfides^(77,82,83,85) and tin sulfide^(83,85). Uranium is also leached^{15.} in the presence of these microorganisms^(95,96,115-119), but the mechanism of uranium extraction is due to a secondary chemical effect not by direct attack on the crystal structure by the bacteria as is the case for sulfide minerals^(48,120).

For the biooxidation of zinc sulfide, the overall equation can be written as follows:



Where E_p is the free energy of the reaction described by equation 7, corresponding to the removal of eight electrons from the sulfide as indicated by equation 8.



Some investigators^(30,122) attribute the oxidation of zinc sulfide solely to the chemical action of acidic ferric iron solutions. According to this hypothesis, the organism oxidizes to ferric iron, the ferrous iron contained in most sulfide mineralizations. The subsequent oxidation of sulfide to sulfate, in turn, reduces the iron to the ferrous form, which is then reoxidized by the bacterium. However, Duncan et al⁽⁴⁸⁾, by selective inhibition of enzymes in the organism, segregated ferrous ion and sulfide ion oxidations and showed that the sulfide ion oxidation was the rate-controlling step. Support of the hypothesis that the bacterium itself oxidizes sulfide directly is available^(120,121).

Information on the microbiological leaching of zinc sulfide is limited. The earliest report was embodied in a patent issued to Zimmerly et al⁽³⁰⁾ in 1958. These inventors found that T. ferrooxidans could adapt to zinc concentrations as high as 17 grams per liter. Marchlenitz et al⁽¹⁰⁷⁾ noted that after adaptation these organisms grew well in solutions having zinc concentrations of 25 grams per liter. Silverman and Ehrlich⁽⁷⁶⁾ reported that the organisms can adapt to zinc concentrations up to 40 grams per liter. On the other hand, Moss and Anderson⁽⁷⁸⁾ reported that zinc concentrations in the range 30 to 50 grams per liter are toxic to T. ferrooxidans. They found also that the zinc concentration toxicity level was dependent on the procedure used for adaptation of these bacteria. Recently in the laboratories of B. C. Research⁽³⁹⁾, growth of T. ferrooxidans has been observed in zinc concentrations as high as 56.5 grams per liter, indicating the adaptability of this organism.

Ivanov et al⁽³²⁾ reported that T. ferrooxidans increased the rate of sphalerite (ZnS) leaching, and that the rate was further accelerated by the addition of soluble iron. Using percolators, Malouf and Prater⁽²⁹⁾ increased the extraction of zinc from sphalerite about five fold by mixing it with pyrite. After 340 days of leaching, the solution of sphalerite contained about 0.6 grams of zinc per liter and that of sphalerite plus pyrite about 3 grams of zinc per liter. Szolnoki and Bognar⁽¹⁰⁶⁾ also reported that T. ferrooxidans had a positive effect on the rate of sphalerite oxidation. Lyalikova⁽⁹⁹⁾ demonstrated that this microorganism could accelerate the oxidation of chemically prepared zinc sulfide. The possibility of utilizing this

organism in the recovery of small quantities of metals (copper, zinc)^{17.}
from rougher tailings has been considered by Duncan, Walden and
Trussell⁽⁴⁶⁾. Using a tank leaching technique and a zinc sulfide ore
containing 1.5 to 2.8% zinc, Duncan et al⁽⁸⁵⁾ obtained a zinc extraction
rate of 14 mg per liter per hour and, after 30 days of leaching, a
final zinc concentration of about 6 grams per liter.

All of the foregoing data which are available in references 29,
30, 32, 39, 46, 76, 78, 85, 99 and 106, have been derived from pre-
liminary experiments. Altogether, these studies indicate that zinc
concentrations are nontoxic to the leaching organism, T. ferrooxidans,
at relatively high concentrations and that the bioleaching of zinc
sulfide ores is technically feasible. However, these references con-
tain limited or no information on specific values for the important
factors such as temperature, pH, pulp density, specific surface area of
solid and nutrient concentrations which will lead to maximum rates of
zinc extraction.

1. Introduction

Use of mathematical models in the description of the microbiological leach phenomena is of great interest. For example, the models based on the variables influencing the metal sulfide leaching could permit one to study the effect of a variable without performing experimental work. Such theoretical study could predict results and save material and time, which are of economic significance, provided of course that the model had been adequately tested with experimental data.

2. Difficulties in biokinetic modeling

Biokinetic modeling is especially difficult because of the many different metabolic pathways and side reactions involved. Major complications arise because many of the reaction mechanisms of the cell's metabolic reactions are not completely understood. Factors influencing bacterial growth are numerous and the biological knowledge and mathematical tools necessary for the formulation and study of a completely general model do not exist⁽¹²⁴⁾. An exact kinetic model for bacterial metabolism is beyond the scope of the present study. Rather with respect to microbiological leaching of zinc sulfides, those variables which have the greatest economic interest have been investigated while holding other variables constant.

The most commonly used variables in fermentation kinetics are the concentrations of cells, substrates and products. Recently, the cell composition and the cell size distribution in a given population have been recognized as important for this purpose.

3. Classification of fermentation processes

The kinetic character of individual fermentation processes

differs widely. However, certain characteristics permit classification in three different ways: phenomenologic^(125,126), thermodynamic⁽¹²⁷⁾ and kinetic^(128,129). The phenomenological approach is based on a comparison of specific product formation rate with associated growth phenomena. In the thermodynamic approach the activation energies of growth, respiration and biosynthesis are measured, whereas in the kinetic analysis the rate of product formation is studied in respect to the fermentation parameters.

Another basis for the classification of models of bacterial population has been given by Tsuchiya et al⁽¹²⁴⁾. In their system, the population model is described as either "distributed" or "segregated". The segregated model recognizes the distribution of different physiological states among the cells in the population, while the distributed model does not. In this latter model, it is assumed that all the cells have the same properties. The distributed model is the simpler, since the process of reproduction is not involved in the model. Further, it may be assumed that the cell is either structured or unstructured. The structured model recognizes the different compounds present in the cell while the unstructured model does not.

4. Development of bacterial kinetics

Rather than summarize existing reviews of bacterial kinetics,^(124-126,130-133) this section emphasizes the steps leading to the evolution of fermentation kinetics.

4.1 Orders of biological (enzymatic) reactions

If the substrate level is high the biological reaction rate follows a zero-order course (reaction rate is constant). If this level falls, either because substrate is used up or is inadequately replaced, the rate more closely approximates a first-order reaction (the reaction

rate is proportional to the concentration of substrate). Therefore, it is difficult to classify the overall bacterial (enzymatic) reaction as being of a specific order or reaction⁽¹³⁴⁾.

Most kinetic models deal with cell growth and product formation involving limitation of nutrients and products. These models do not take in account the difference between individual cells, and the following may be written:

$$\frac{dX}{dt} = f_1(X, S, P) \quad (9)$$

$$\frac{dS}{dt} = -f_2(X, S, P) \quad (10)$$

$$\frac{dP}{dt} = f_3(X, S, P) \quad (11)$$

where X = cell (mass or number) concentration;

S = substrate concentration;

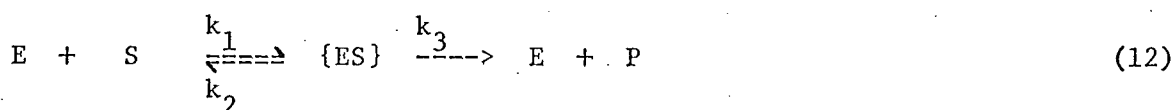
P = product concentration;

f_1 , f_2 and f_3 are functions which depend on cell concentration, substrate consumption and product concentration respectively.

If these equations 9, 10 and 11 are divided by the cell concentration (X) expressions for specific growth rate, specific substrate consumption and specific product formation are attained⁽¹³⁵⁾.

Constant specific growth rate is the simplest form of the rate equations. This should apply explicitly to exponential growth of a culture and may not be applicable to other phases of the growth curve of a culture.

The hypothesis that the enzyme (E) and the substrate form a complex (ES) in enzyme catalyzed reactions, was derived originally by Michaelis and Menten⁽¹³⁶⁾ in 1913:



Where k_1 = rate constant of the forward reaction for enzyme-substrate complex formation;

k_2 = rate constant of the backward reaction;

k_3 = reaction rate constant for dissociation of the enzyme-substrate complex.

The specific growth rate (V) of the reaction of equation 12 may be written as follows⁽¹³⁷⁾:

$$V = \frac{V_m [S]}{K_m + [S]} \quad (13)$$

Where V_m = maximum specific growth rate;

K_m = Michaelis-Menten constant.

The value of K_m is equal to the substrate concentration when the reaction proceeds at one half the maximum reaction rate. This K_m value represents a fundamental constant in enzyme kinetics.

The Michaelis-Menten equation 13 can also be derived from Langmuir's adsorption isotherm theory^(138,139).

An equation analogous to equation 13 has been proposed by Monod^(131,140) for microbial growth. In his equation V is replaced by μ and V_m by μ_{max} respectively.

Lineweaver and Burk⁽¹⁴¹⁾ showed that equation 13 could be linearized; if one plots $1/V$ versus $1/[S]$. Then the intercept of this straight line with the ordinate represents $1/V_m$, while that with the abscissa is equal to $-1/K_m$ and the slope of this line is K_m/V_m . There exist many alternate forms of the Lineweaver-Burk plot, claiming additional advantages⁽¹⁴²⁻¹⁴⁴⁾.

Many workers^(145,146) have proposed alternate models for the specific growth rate of microorganisms. Under certain limiting conditions these reduce to the Monod or Michaelis-Menten type equations. Other workers such as Contois⁽¹⁴⁷⁾ and Fujimoto⁽¹⁴⁸⁾ have incorporated the cell concentration into the growth rate equation, e.g.:

$$V = \frac{V_m [S]}{BX + [S]} \quad (14)$$

Monod's equation (hyperbolic rate equation) is supposed to describe the effect of a single limiting substrate on the specific growth rate. However, in many important fermentation processes this condition is not maintained and more than one substrate is used. For these cases equation 13 has to be modified. Laidler and Socquet⁽¹⁴⁹⁾ derived a rate equation for a two-substrate reaction in which each substrate independently forms a complex with adjacent sites on the enzyme:

$$V = \frac{V_m [S_1][S_2]}{(1 + K_1[S_1])(1 + K_2[S_2])} \quad (15)$$

Equation 15 reduces to the hyperbolic form when one of the substrate concentrations is constant or its equivalent, i.e., when the concentration of one substrate greatly exceeds that of the other. Similarly, an equation for ternary complex formation was derived by Segal et al⁽¹⁵⁰⁾.

Despite the fact that most workers^(131,140,145,146,151-155) have regarded the specific growth rate of a microbial population as a single function of the concentration of the limiting substrate, Contois⁽¹⁴⁷⁾ and Fujimoto⁽¹⁴⁸⁾ were able to show that it is also a function of the population density (X). More recent work⁽²¹²⁾ suggests density effects are due to limitations of a number of other factors.

4.3 Product limited models

Inhibitory metabolic products normally are formed and accumulated during any growth processes. These may compete with substrates for active sites on the enzyme molecules and can thus result in a diminution in the rate of product formation and in the number of viable organisms. Several models have been proposed in the literature to describe this relationship.

In the area of population growth Pritchett⁽¹⁵⁶⁾ used a third order polynomial to describe the growth as a function of time. The same order of polynomial has been applied by McDonald⁽¹²²⁾ to describe the bacterial ferrous iron oxidation curve. Pearl⁽¹⁵⁷⁾ demonstrated the applicability of a logarithmic form to growth curve representation.

Numerous models have been proposed in describing sigmoid-shape growth curves⁽¹⁵⁸⁻¹⁷²⁾ which were found useful in studies of growth phenomena. The logistic type equation, for example⁽¹⁶¹⁾:

$$X = X_m / (1 + \exp(a + bt + ct^2 + dt^3)) \quad (16)$$

where a, b, c and d are constants and t the time, may be written in a linearized form which is more adaptable to certain computational techniques⁽¹⁷³⁻¹⁸⁰⁾.

A generalized logistic equation which can fit many types of growth curves has been proposed by Edwards⁽¹³⁵⁾ and Edwards and Wilke⁽¹⁸¹⁾:

$$X = X_m / (1 + \exp(f(t))) \quad (17)$$

where $f(t)$ is a fifth order polynomial.

Leudeking and Piret⁽¹⁸²⁾ have described a model for product formation in product limited cultures:

$$\frac{1}{X} \frac{dP}{dt} = a \frac{1}{X} \frac{dX}{dt} + b \quad (18)$$

In equation 18 the first term on the right hand side is an expression for specific growth-associated product formation and the second term is a constant. Based on equation 18, a plot of the specific rate of product formation, $\frac{1}{X} \frac{dP}{dt}$, versus the specific growth rate, $\frac{1}{X} \frac{dX}{dt}$, should give a straight line, where b is the intercept and a the slope of the regression line.

4.4 Substrate and product limited models

The simultaneous effect of product and substrate on the rate of product formation has been demonstrated by Chen et al⁽¹⁸³⁾.

$$-\frac{dS}{dt} = \frac{k_1 k_2 E_0 S}{1 + k_2 S + k_3 P} \quad (19)$$

where k_1 = reaction rate constant for enzyme-substrate complex formation;
 k_2 = inverse of Michaelis-Menten constant;
 k_3 = desorption constant;
 E_0 = initial enzyme concentration.

The authors⁽¹⁸³⁾ claim that equation 19 fit their data better than the simple substrate limited model.

Using enzyme kinetic models, Maxon and Chen⁽¹⁸⁴⁾ have been able to solve complicated fermentation processes, such as semicontinuous substrate addition. Their models are oriented towards description of industrial fermentation processes (e.g., the production of neomycin) as shown by equation 20.

$$\frac{dX}{dt} = \frac{k_1 \times G}{1 + k_2 G + k_3 N} \quad (20)$$

Where the growth rate is based on glucose (G) concentration and inhibition is due to neomycin (N) concentration.

5. Proposed models

The current literature of biological kinetics contains many examples of mathematical models derived for homogeneous systems. In general, in the choice of a model which quantitatively describes the biological phenomena, one has to be certain that it has validity, generality and prediction ability⁽¹⁸⁵⁾. Further, the choice or design of a valid mathematical model should depend on what is already known about the system and on what type of results one expects to obtain.

A complete description of the bacterial kinetic processes will not be possible until an exact and complete description of the metabolism of the organism is available. This could also require new biological principles which should be consistent with the physical principles but perhaps not derivable from them⁽¹⁸⁵⁾.

In the case of the heterogeneous system of microbiological leaching of zinc sulfide, there are problems which are not evident in homogeneous systems. The availability of substrate in the sulfide is not

only a function of the mass but also of the specific surface area. 26.

Further, the surface area of the zinc sulfide ore is inhomogeneous in its energy characteristics and thus only certain sites should be considered available for bacterial action.

The microbiological oxidation of zinc sulfide ores may be considered as a multisubstrate system, in which oxidation of sulfide to sulfate and of ferrous iron to ferric iron take place. Commercial zinc sulfide ores always contain a certain quantity of ferrous iron.

Another major problem involved in this system is the availability of the number of organisms. Unfortunately there exists no method of estimating the number of organisms in systems where solid particles are involved.

From this introduction it is obvious that the mathematical expressions derived so far for bacterial kinetics are not applicable to this heterogeneous system of microbiological zinc sulfide oxidation. Therefore, all kinetic data throughout this present work will be expressed in terms of product formation (zinc extraction).

1. General

Because the number of variables under consideration is large (8 variables), and because of the limited availability of some subsieve fractions of the substrate, statistically designed experiments were not used. The procedure was to study one variable at a time. When the value of the variable which gave maximum leaching rate was determined, it was held constant in subsequent experiments while other variables were examined.

2. Organisms

An inoculum of Thiobacillus ferrooxidans (N.C.I.B. No. 9490), isolated by Razzell and Trussell⁽¹⁶⁾ was adapted to a medium containing the basal salts of the medium described by Silverman and Lundgren⁽³⁷⁾ but with zinc sulfide concentrate replacing ferrous sulfate as the energy source. When growth in batch culture reached the stationary phase the bacteria were maintained by transfer or were used as an experimental inoculum.

3. Substrate

All work has been carried out with a single lot of high-grade zinc sulfide concentrate. This material was supplied by Cominco Ltd., Trail, B. C. after special flotation to remove excess pyrite. This marmatic preparation was wet ball-milled to pass a 400 mesh sieve. After drying at 45°C, a chemical analysis gave the following composition: 60.78% zinc, 33.23% sulfur, 2.50% iron, 1.79% lead, 1.29% calcium oxide and some impurities (Cd, Cu, Mg,...). Corresponding to this analysis, the zinc sulfide concentrate is 90.6% pure, as zinc sulfide.

The density of the subsieve material has been determined pycnometrically to be 3.7990 gram per ml (186).

3.1 Substrate fractionation

In order to study the effect of particle size of substrate on the microbiological zinc extraction, the subsieve zinc sulfide concentrate (-400 mesh) was fractionated into definite size fractions using both a wet and a dry technique.

Wet subsieve fractionation consisted of collecting six subsieve fractions, using a Warman Cyclosizer Apparatus⁽¹⁸⁷⁾. This is a hydraulic cyclone elutriator whose operating principles have been described by Kelsall and McAdam⁽¹⁸⁸⁾.

The dry technique consisted of collecting eight subsieve fractions using a Bahco No. 6000 Microparticle Classifier⁽¹⁸⁹⁾. This device is a combination of an air elutriator and a centrifuge.

3.2 Determination of particle size

The main particle diameters (Stokesian diameters) of the Cyclosizer fractions were obtained from the operating curves of the Cyclosizer Manual⁽¹⁹⁰⁾ and by microscopic measurements, which consisted of comparison of the particle images with a graticule. The Bahco-sizer fractions were investigated by microscopic measurements only.

In these microscopic measurements, the particle diameter was determined as the average of the two dimensions exhibited by the particle. For each fraction thirty individual particles were observed and the average value of these measurements registered.

3.3 Determination of specific surface area

Specific surface area, which is the surface area per unit mass of solids, of the unfractionated zinc sulfide concentrate (-400 mesh)

and of the various subsieve fractions mentioned above, was determined by the B.E.T.-technique⁽¹⁹¹⁾ using a dynamic nitrogen adsorption apparatus. This apparatus was built by Orr⁽¹⁹²⁾ for surface area measurements of paper samples, and was made available for this study.

The dynamic nitrogen adsorption method⁽¹⁹³⁻¹⁹⁹⁾ is essentially a gas chromatographic technique in which the sample powder replaces the solid in the normal chromatographic column. Nitrogen is adsorbed by the sample at the temperature of liquid nitrogen from a continuous gas stream of nitrogen and helium, and desorbed upon warming the sample. The difference in nitrogen concentration of the gas mixture is measured by a calibrated thermal conductivity cell. The surface area of the solid is evaluated by application of the B.E.T.-equation. Details are given in Appendix 3.

4. Culture techniques

4.1 Shake technique

The microbiological leaching experiments were carried out on a gyratory shaker⁽²⁰⁰⁾, using a batch technique developed by Duncan et al⁽⁷⁹⁾. The desired quantity of zinc sulfide concentrate and 70 ml of iron free medium⁽³⁷⁾ were placed in baffled, 250 ml Erlenmeyer flasks. Then these flasks were inoculated with 5 ml of an active culture of Thiobacillus ferrooxidans previously adapted to the zinc sulfide concentrate. In the sterile control flasks instead of the inoculum, 5 ml of a solution containing two per cent of thymol in alcohol, were added.

The flasks were incubated at constant temperature on a thermostated gyratory shaker. Periodically any water lost through evaporation was replaced with distilled water and the pH adjusted with sulfuric acid (1N) or sodium hydroxide (1N) if necessary. The flasks were not stoppered in any manner.

Constant pH experiments were carried out in shake flasks equipped with a pH-stat⁽²⁰¹⁾.

4.2 Tank leaching

Large scale experiments were carried out at increased carbon dioxide partial pressure in a temperature controlled room:

- a) in an unbaffled stainless steel tank (12 inches inside diameter and 24 inches deep length) equipped with a marine-impeller, air containing 1% carbon dioxide was introduced into the medium under the impellers at a flow rate of 10,000 ml per minute;
- b) in a baffled (three baffles 120° apart) plexiglass tank (with the same dimensions as the unbaffled one) equipped with pH-stat⁽²⁰¹⁾ and a turbine impeller, air supply was the same as in the unbaffled tank.

5. Chemical analysis

5.1 Substrate

Metal contents (Zn, Fe, Pb, CaO, and so on) of the zinc sulfide concentrate were determined on the solutions obtained by acidic digestion⁽²⁰²⁾ using a Perkin Elmer Model 303 atomic absorption spectrophotometer.

The sulfur content of the zinc sulfide concentrate was determined gravimetrically⁽²⁰²⁾.

5.2 Leach solutions

The extracted zinc concentrations were determined periodically during the individual leaches by removing one ml samples and measuring their zinc contents by atomic absorption spectrophotometry. The volume removed for zinc determination was replaced with an equivalent volume of iron-free medium⁽³⁷⁾.

In the work described later in this thesis a rate of zinc extraction is related to a variety of parameters. Figure 1 is a plot of zinc concentration versus time and is typical of the leach curves obtained. The slope of such a curve is the rate of leaching or rate of extraction. Obviously there is a range of extraction rates obtainable from such a curve. The one used later for correlative purposes is the slope of the linear region of the curve of Figure 1, that is the region between a and b. The slope of this linear portion was determined by a least squares (203) computer program.

Attempts were made for some of the experimental runs, to fit a mathematical expression to the complete leaching curve. The expression chosen was the generalized logistic equation employed by Edwards⁽¹³⁵⁾ and Edwards and Wilke⁽¹⁸¹⁾ which is written

$$P = P_m / (1 + \exp(f(t))) \quad (21)$$

$$f(t) = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + a_5 t^5 \quad (22)$$

where P = product (zinc) concentration;

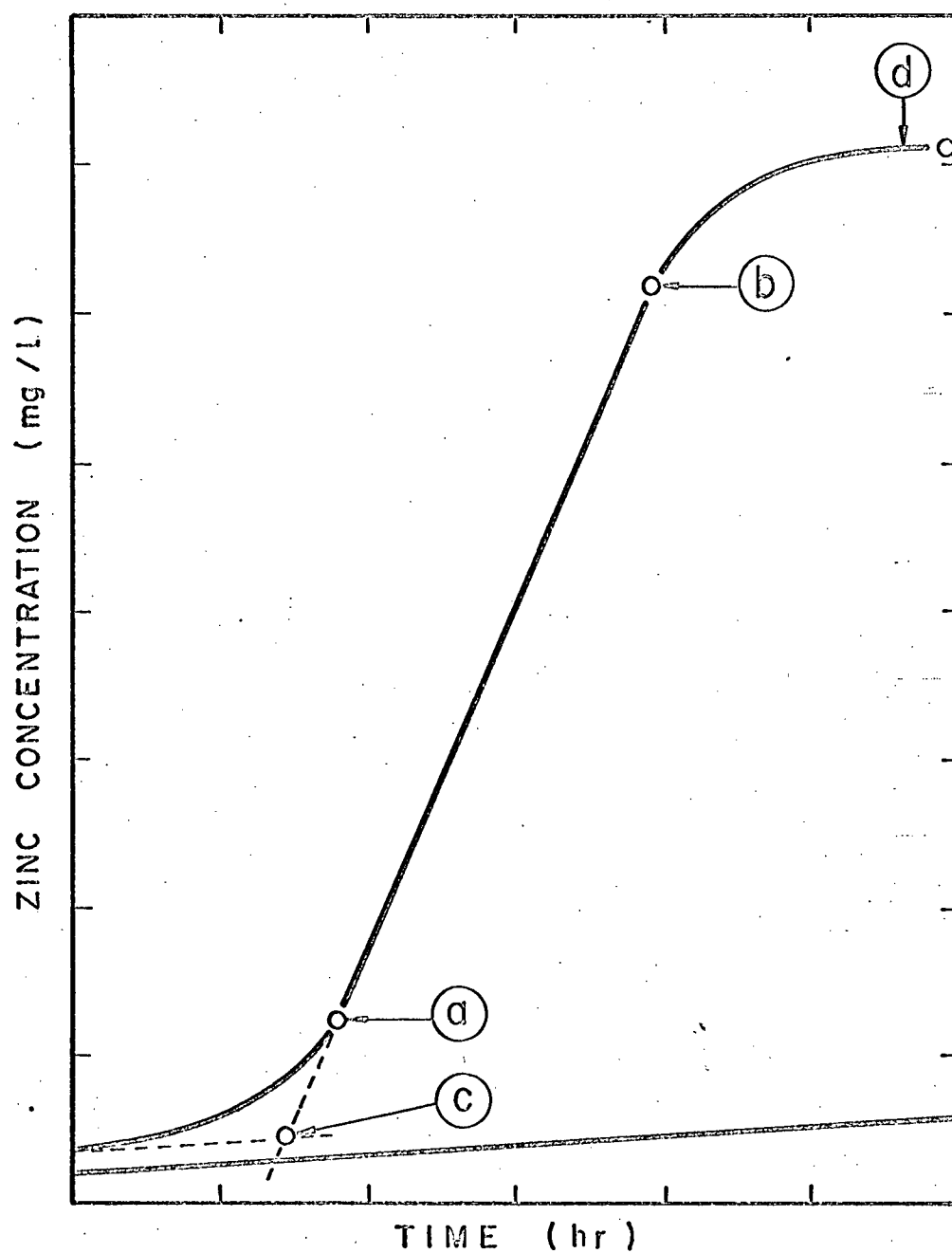
P_m = maximum product concentration;

t = time;

$a_0, a_1, a_2, a_3, a_4, a_5$ are constants for a particular leach.

Equation 21 is very flexible, having 7 constants, two obtainable from the leach curve and five of them adjustable. Thus it is able to reproduce a variety of sigmoid (S-shaped) curves⁽²⁰⁴⁾. It is stated to be especially useful for systems displaying product inhibition⁽¹⁸¹⁾.

Figure 1
TYPICAL ZINC SULFIDE LEACH CURVE



P_m the maximum product concentration is obtainable directly from the 33
leach curve (e.g., it is the zinc concentration at point d on Figure 1).

At the start of the leach (time zero) there is a small but finite concentration of zinc (P_o) which was introduced with the inoculum. When $t = 0$, equation 21 reduces to:

$$P_o = \frac{P_m}{1 + \exp(a_o)} \quad (23)$$

which allows estimation of a_o from knowledge of P_o and P_m . However, due to the experimental difficulties involved in the initial part of the leach curve a_o was not measured in this work but was determined using a least squares technique described below.

Having fitted an equation of the form of equation 21, one could differentiate it to get the extraction rate thus

$$\frac{dP}{dt} = -P(1 - \frac{P}{P_m}) f'(t) \quad (24)$$

$$\text{where } f'(t) = a_1 + 2a_2t + 3a_3t^2 + 4a_4t^3 + 5a_5t^4 \quad (25)$$

The generalized logistic equation, equation 21, may be converted to a polynomial expression⁽¹⁸¹⁾ by taking logarithms. Thus,

$$y = \ln\left(\frac{P_m - P}{P}\right) = a_o + a_1t + \dots + a_5t^5 \quad (26)$$

In the curve fitting procedure used P_m was obtained from the leach curve and the remaining six constants (a_o, a_1, \dots, a_5) were determined by a

least squares fitting technique using a multiple regression analysis 34

program written for the I.B.M. 360 digital computer^(205, 206) .

Another program reproduced in Table 1 of Appendix 2 was used to calculate the fitted values for the data and to tabulate them alongside of the measured values for comparison.

1. Effects of temperature

The effect of temperature variation on zinc extraction was studied over a range of 25°C to 45°C. The leach suspensions contained 5.3% pulp density $\left(\frac{\text{mass solids} \times 100}{\text{volume of liquid medium}} \right)$ with the initial pH adjusted to 2.5. All experiments were done in duplicate and with sterile controls. The experimental data are given in Table 1 (A and B) of Appendix 1.

The sterile controls show the extent of chemical dissolution of zinc from the zinc sulfide concentrate. The zinc concentrations in these sterile controls can be seen from Table 1 (A and B) of Appendix 1 to be much lower than those obtained in the presence of T. ferrooxidans, thus establishing the role of the bacteria in such leaching.

The effect of temperature on the microbiological zinc extraction is presented graphically in Figure 2. Each point on this graph is the average of the duplicate runs reported in Table 1 (A and B) of Appendix 1. From Figure 2 it is easily seen that the fastest zinc extraction rate was achieved at 35°C.

The zinc extraction rates in mg/l hr are plotted against temperature in Figure 3. A maximum in this extraction rate curve is discernible at around 35°C. Subsequent experimentation was done at 35°C. This value is in agreement with values reported by other workers for oxidation of ferrous iron in solution and metallic sulfide ores (16,72,74,77,207). These workers have quoted optimum temperatures in the range 28°C to 40°C. Figure 3 indicates extremely limited microbiological leaching activity at temperatures above 45°C. Bryner et al (207) found that biological

Figure 2

EFFECT OF TEMPERATURE

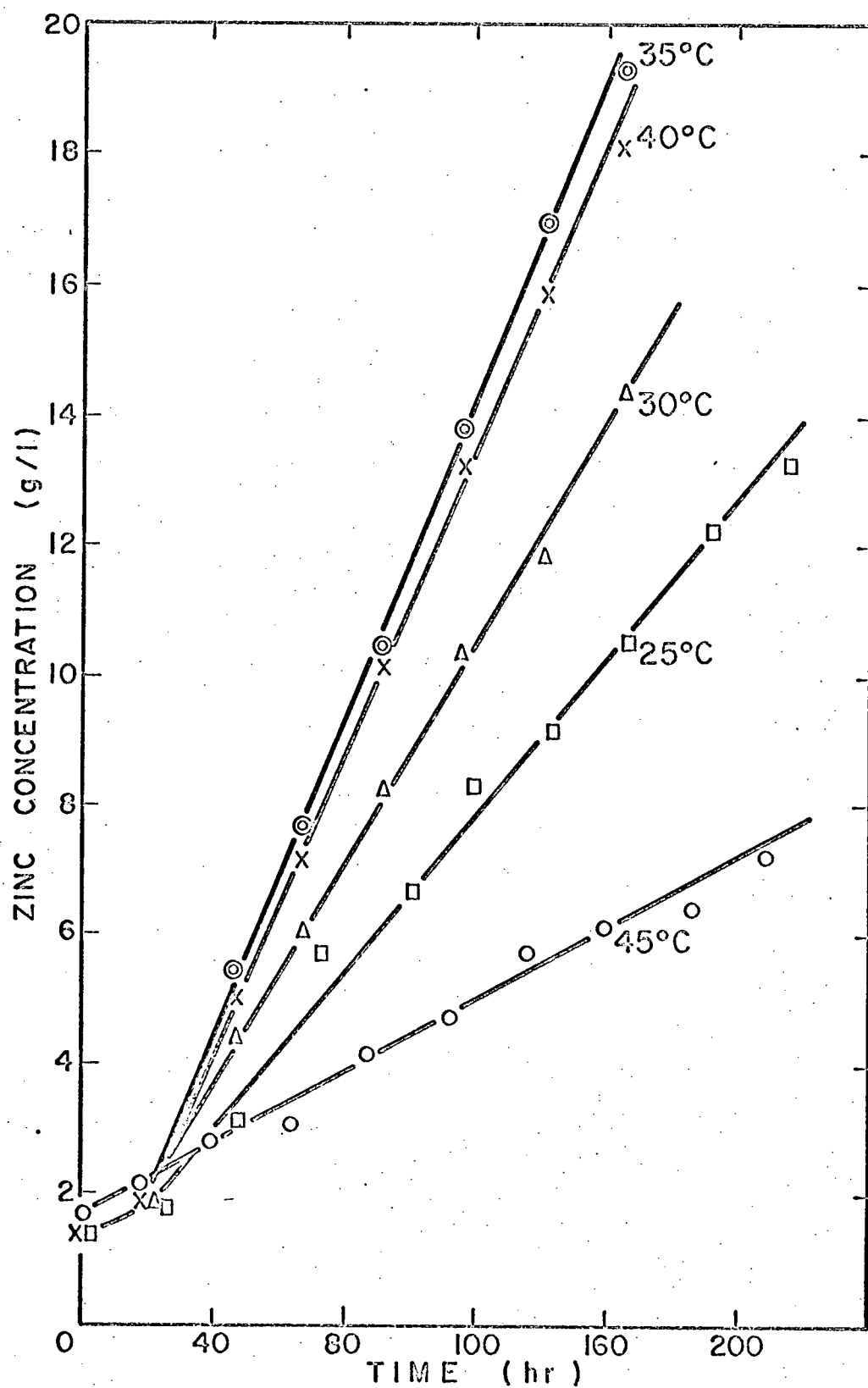
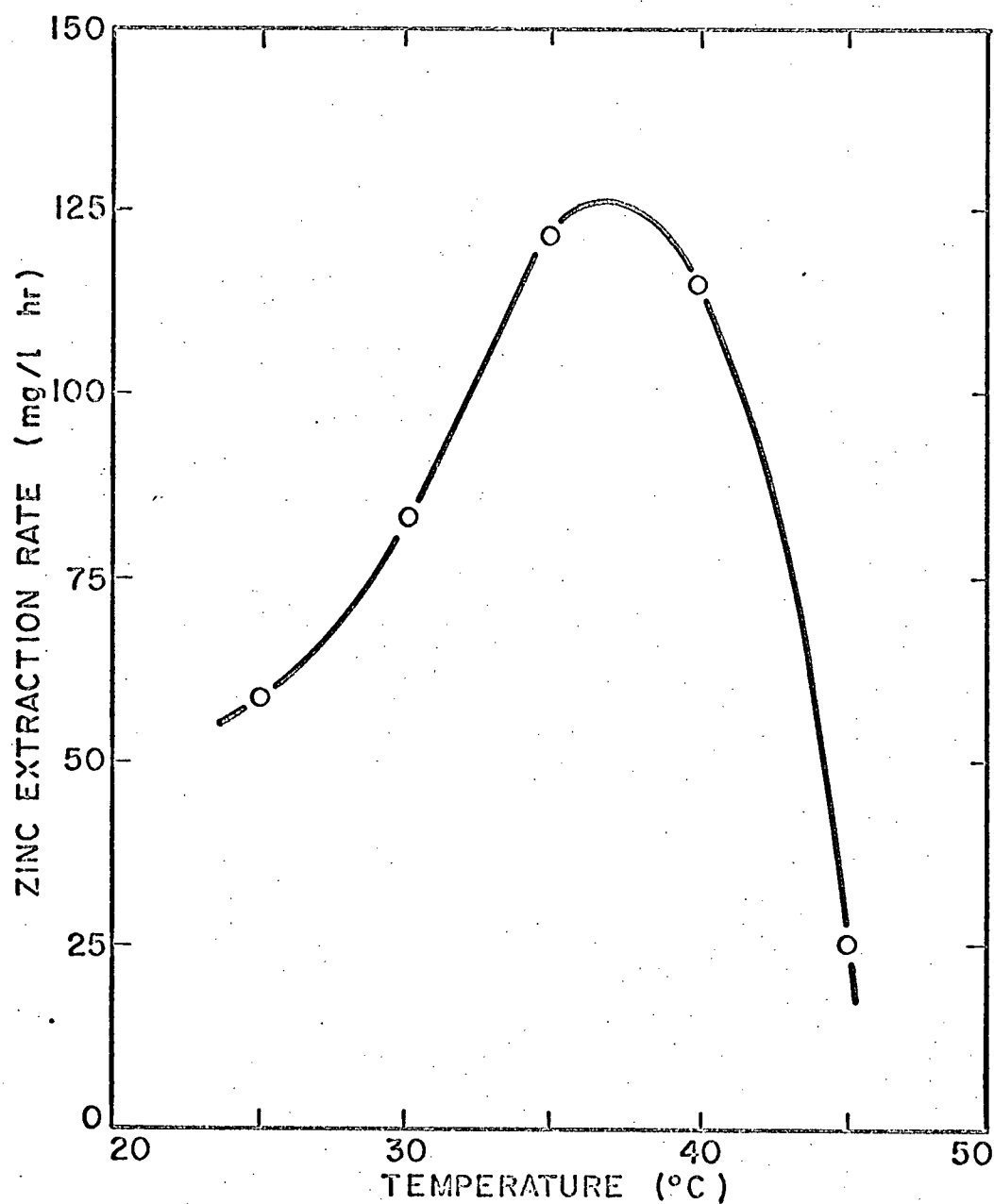


Figure 3
EFFECT OF TEMPERATURE
ON THE MICROBIOLOGICAL ZINC EXTRACTION RATE



oxidation of chalcopyrite ceased at around 55°C and that at higher 38 temperatures only chemical oxidation occurred. The value obtained for the optimum temperature (35°C) would place T. ferrooxidans in that class of organisms called mesophiles. This temperature optimum is greater than the values usually found for soil microorganisms, which generally are psychrophilic.

The shape of the zinc extraction rate versus temperature plot is typical of biological reactions. There are two competing rate processes to be considered, the usual kinetic rise in reaction rate with increasing temperature and at the same time an increase in the rate of thermal death of the microorganisms. Thus, as temperature increases the rate of thermal death of the microorganisms increases more rapidly than does the increase in extraction rate. The net result is a maximum in the extraction rate versus temperature plot.

Using the data summarized in Figure 3 values for the temperature coefficient (Q_{10}) of the zinc extraction rate process were calculated from equation 27:

$$Q_{10} = \left(\frac{V_2}{V_1} \right)^{\frac{10}{T_2 - T_1}} \quad (27)$$

where T_1 and T_2 are temperatures in absolute units;

V_1 and V_2 are the extraction rates corresponding to temperatures T_1 and T_2 .

Also, values for the activation energy defined by:

$$A_{H_a} = \frac{T_1 T_2 R}{T_2 - T_1} \ln\left(\frac{V_2}{V_1}\right) \quad (28)$$

were calculated, where R is the gas constant.

The results of these calculations over four temperature ranges are presented in Table 2. For temperatures of up to 35°C, the Q_{10} values are of the order of 2 which is a typical value for many chemical reactions and is the basis for the rule of thumb that typically reaction rates double for a 10°C increase in temperature. So the values obtained for Q_{10} over the range 25°C to 35°C are typical for both biological and nonbiological reactions. The activation energies found for the temperature range 25 to 35°C (12.8 Kcal/mole) are also typical of a wide variety of biological and nonbiological reactions. The activation energy obtained for the 40 to 45°C range is much larger and opposite in sign. This value is typical of the values found for the denaturation of proteins. It is also the reason for the low value of Q_{10} because the rule of doubling this reaction rate for a 10°C temperature increase is only valid if the activation energy is between 10 and 20 Kcal/mole. The sign is negative because the rate in this region of Figure 3 decreases with increased temperature.

2. Effects of pH

After initial pH adjustment and inoculation with T. ferrooxidans the pH of the leach solutions, unless controlled, tends to rise. This may be due to the buffering nature of the alkaline concentrate or to the inherent pH of zinc sulfate. However, during the

Table 2

Temperature coefficients and activation energies
for zinc extraction from the zinc sulfide concentrate by T. ferrooxidans

| Temperature range (°C) | Q_{10} | ΔH_a Kcal/mole |
|------------------------------|----------|---------------------------|
| 25 - 30 | 2.05 | 12.8 |
| 25 - 35 | 2.02 | 12.8 |
| 30 - 35 | 2.00 | 12.8 |
| 40 - 45 | 0.05 | -57.6 |

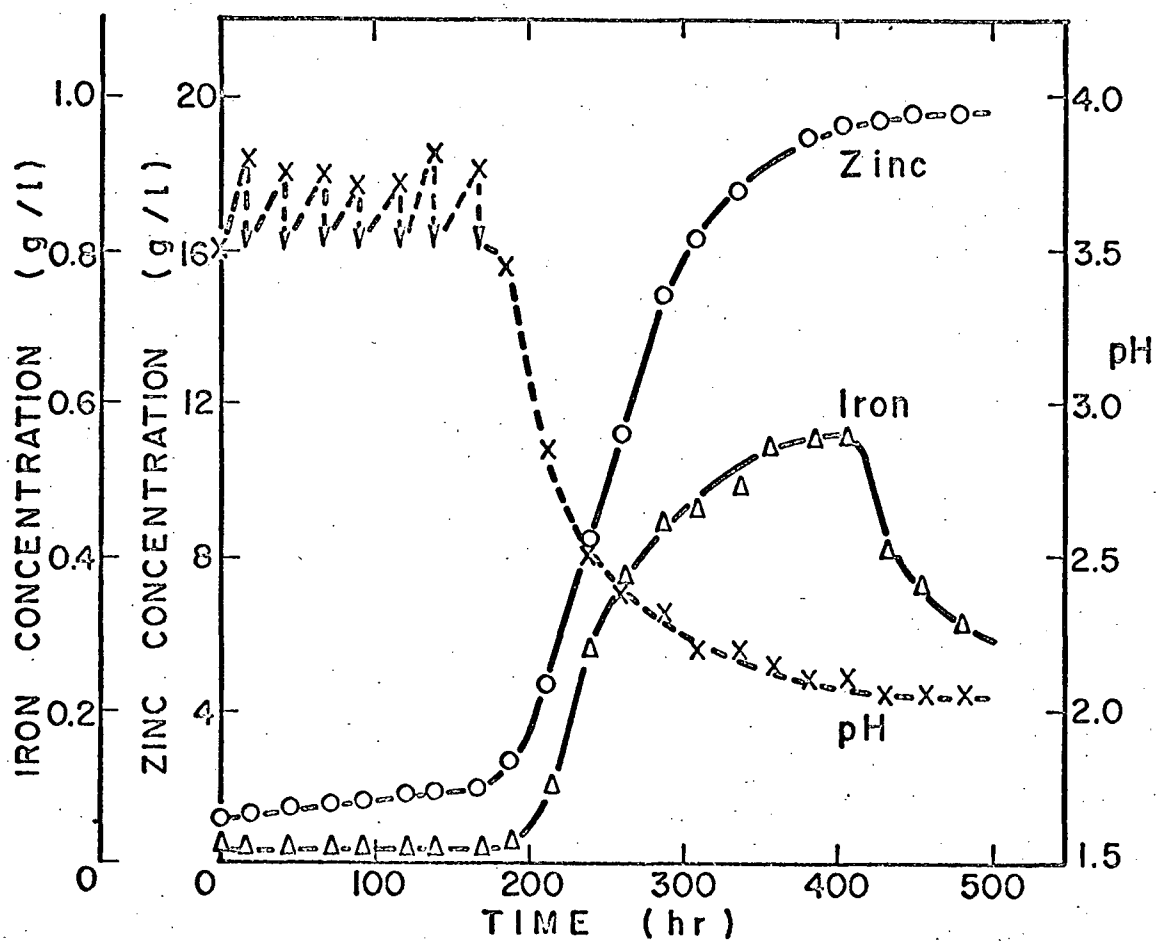
period of rapid metal release the pH, unless controlled, tends to 41
become more acidic.

2.1 Effect of initial pH

The effects of initial pH (varying from 1.5 to 4.0) on microbiological zinc extraction were studied on leach suspensions containing 5.3% solids incubated at 35°C. The initial pH of these solutions was controlled manually adjusting the pH back to the initial value as necessary, until the reaction started. Subsequently the pH was not adjusted but left to seek its own level, the final pH value representing chemical stabilization of the system. During the leaching process, hydrogen ion, zinc and iron concentrations were measured at various times. These results are presented in Table 2A to 2F of Appendix 1. A typical plot of pH and zinc and iron concentration as functions of time is provided by Figure 4. In this Figure 4 it can be seen that the initially established pH tends to rise unless acid was added. When the leaching started the pH dropped and the zinc concentration rose to reach a final, stable level. The iron concentration, which was very low, rose initially and then decreased. Iron may have precipitated partially in the form of basic iron sulfates as has been suggested by Leathen et al⁽³⁸⁾ and Duncan⁽³⁹⁾. This precipitation of iron may have contributed to the drop in pH. However, at lower values of initial pH (1.5, 2.0, and 2.5) iron precipitation probably was not significant.

In the pH 1.5 run, the pH tended to be higher than the initial pH throughout the leach. However, in all the remainder of this series of experiments (pH uncontrolled after reaction started) the pH ultimately stabilized at about 2.1. This may be

Figure 4
EFFECT OF INITIAL pH
(pH = 3.5)
5.3% Pulp Density



characteristic to a degree of this particular medium and strain of T. ferrooxidans for in other environments such as acid mine waters the pH has been reported to be maintained at various values ranging from 1.5 to 3.5 .

Figure 5 presents plots of zinc concentration versus time for various values of initial pH. It shows that the most significant effect of initial pH is on the lag (initiation) time. The zinc extraction rates are more or less constant. This lag time (defined in point c of Figure 1) is the time it takes for the reaction to reach the rapid, constant zinc extraction rate. It is a period in the microbiological growth cycle wherein the organisms adapt themselves to their environment at the end of the lag period or phase and rapid cell division of the organisms begins. Although in this work cell reproduction rates were not measured, the curves of Figure 4 would suggest that the lag phase ended at the time that significant amounts of zinc begin to be released. Table 3 summarizes the data given in Figure 4 and in Tables 2A to 2F of Appendix 1. The shortest lag times were observed in leach solutions which were initially at pH 2.0. The calculated extraction rates were only slightly dependent on initial pH. The fastest extraction rate (119.5 mg/l hr) in this series of experiments was observed with an initial pH of 2.5 .

2.2 Effect of constant pH

The effects of controlled, constant pH on microbial zinc extraction were studied on leach suspensions containing 16% of solid substrate. These suspensions were maintained at 35°C in shake flasks. The 16% pulp density (solids concentration) is, as will be shown in Section 4, an optimum value for substrate concentration. The pH values

Figure 5
EFFECT OF INITIAL pH ON ZINC EXTRACTION
5.3% Pulp Density

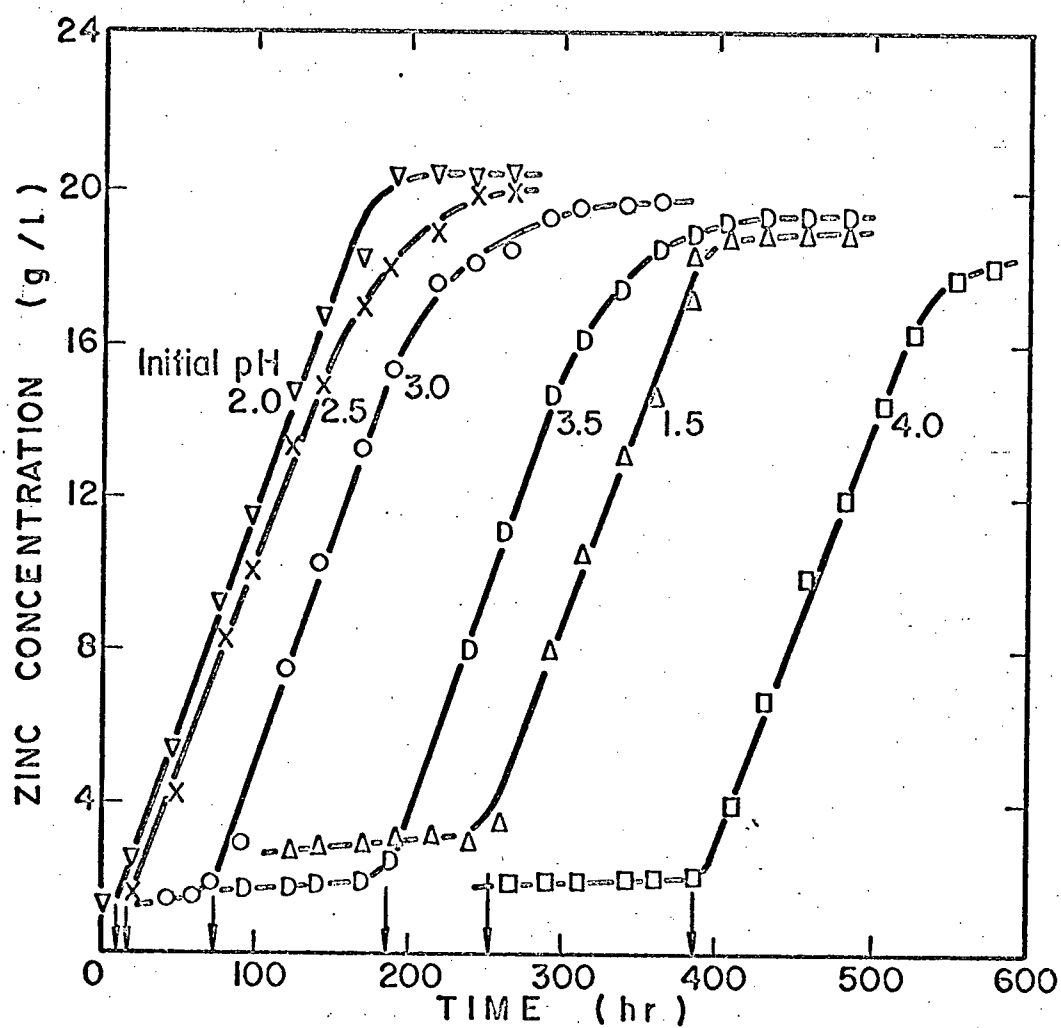


Table 3
Effect of initial pH

| Initial pH | Final pH | Lag time (hr) | Zinc extraction rate (mg/l hr) |
|---------------|-------------|------------------|--------------------------------------|
| 1.5 | 1.75 | 252 | 99.7 |
| 2.0 | 2.05 | 10 | 106.4 |
| 2.5 | 2.2 | 18 | 119.5 |
| 3.0 | 2.1 | 74 | 116.3 |
| 3.5 | 2.05 | 192 | 108.4 |
| 4.0 | 2.2 | 390 | 96.9 |

of these solutions were initially adjusted to values between 1.5 and 4.0 at 0.5 pH unit intervals and maintained to within ± 0.1 pH units of these values automatically using a pH stat⁽²⁰¹⁾. This series of experiments was carried out with single samples only except for the run at pH 1.5 which was duplicated. No sterile control was made. The experimental results are summarized in Table 3 (A and B) of Appendix 1, and are presented in Figure 6. This figure shows that the extraction rate was significantly affected only at the extreme values of the pH range studied (i.e. 1.5 to 4.0). The shortest lag time and maximum zinc concentrations were obtained when the pH was controlled at 2.0 and 2.5.

Maximum zinc concentrations differed considerably in those experiments where pH was or was not controlled (Figures 5 and 6). These differences, i.e. 20 to 70 g/l, were attributed almost entirely to the different pulp densities employed and not to the difference in pH control. However, when pH was controlled, the final zinc concentration and maximum extraction dropped off sharply at pH values above and below the 2.0 to 2.5 range. No attempt was made to assess whether this effect was on the organism or was due to substrate modification or both.

The relations between pH and lag time for both the initial pH runs and the constant pH runs are shown in Figure 7. A definite minimum lag time occurs at around pH 2.3 for both sets of data. This minimum is somewhat sharper for the initial pH data than for the controlled pH data. This value (pH = 2.3) is in good agreement with the optimum

Figure 6
EFFECT OF CONSTANT pH ON ZINC EXTRACTION
16% Pulp Density

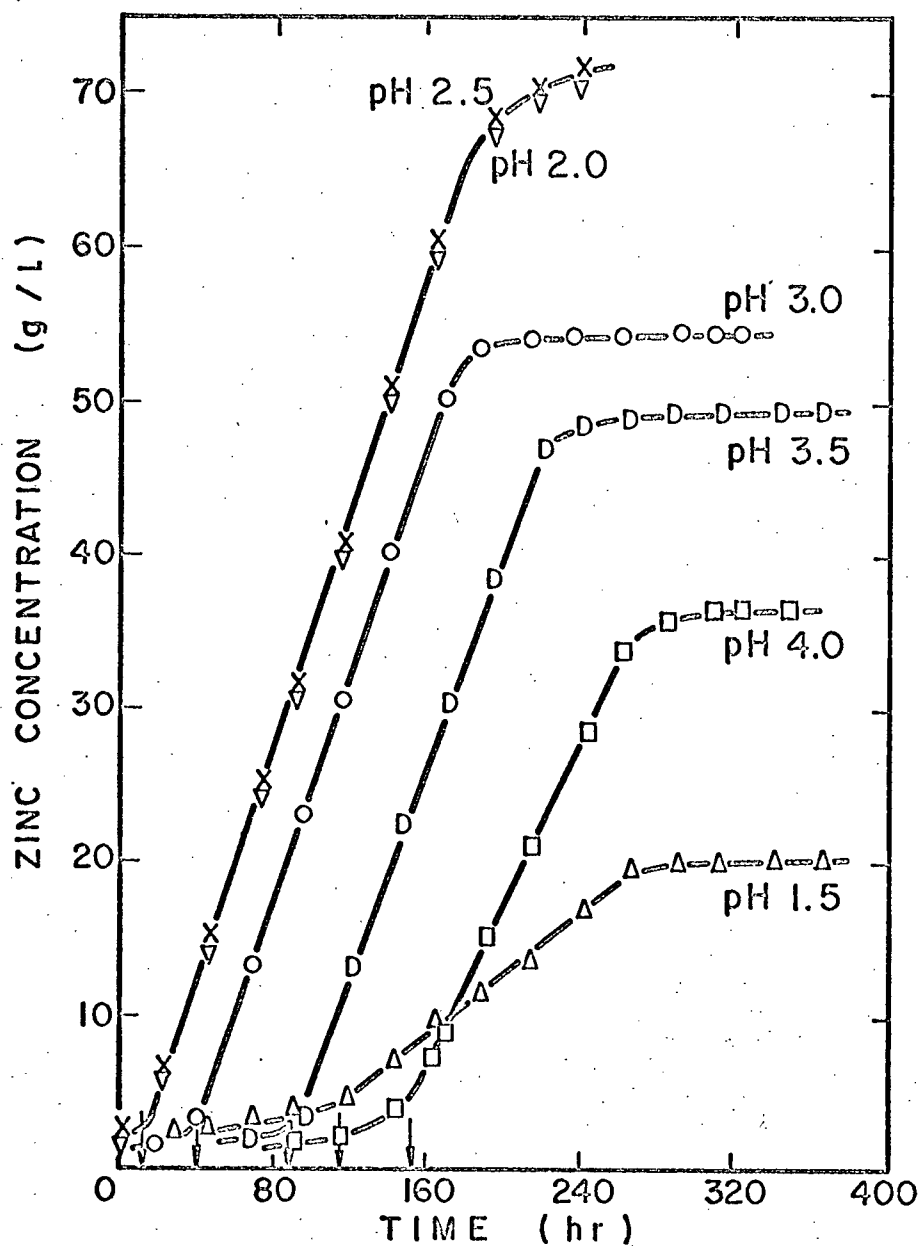


Figure 7
EFFECT OF pH ON LAG TIME

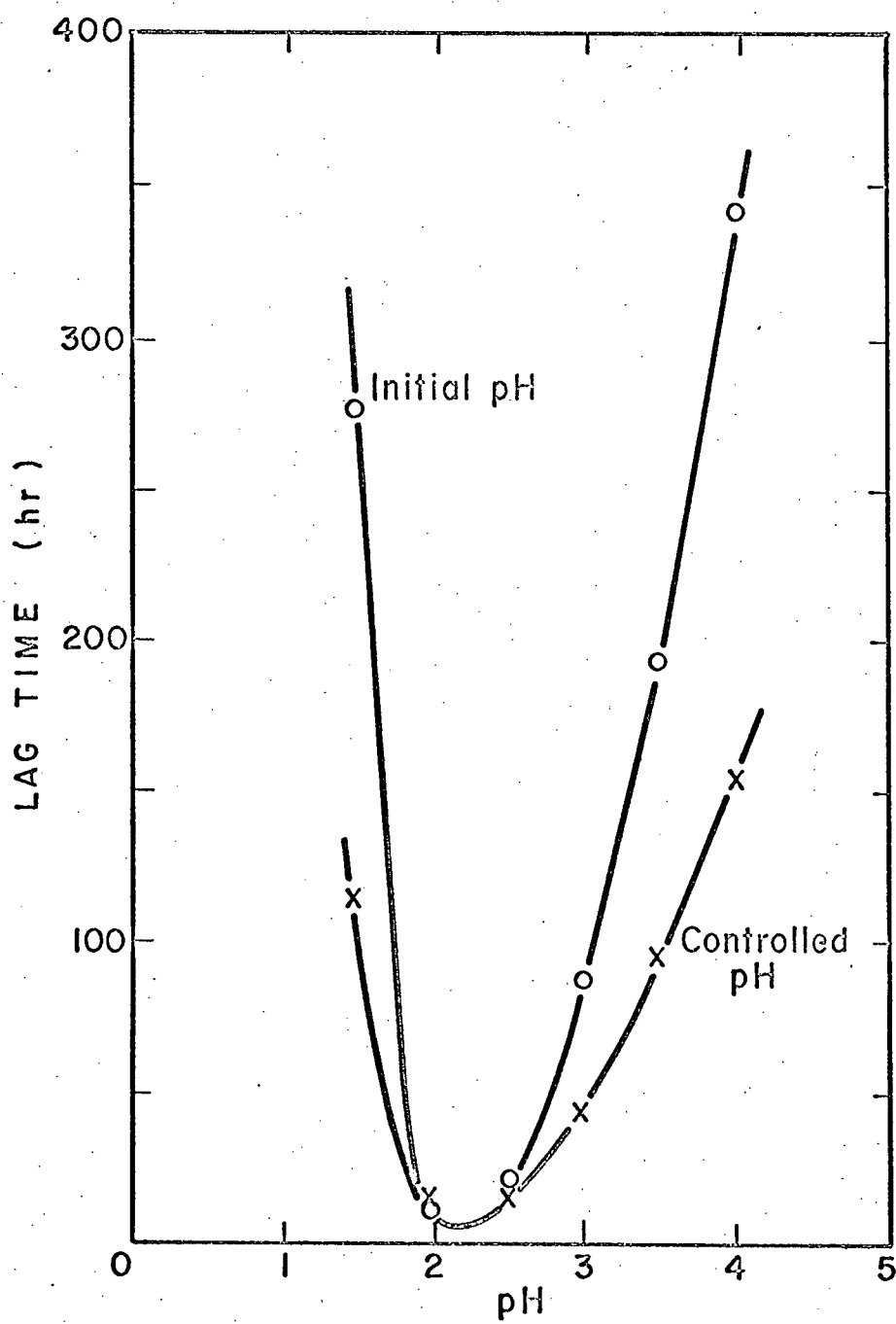


Table 4
Effects of constant pH

| pH | Lag time (hr) | Zinc extraction rate (mg/l hr) | Final zinc extraction (g/l) |
|-----|------------------|--------------------------------------|-----------------------------------|
| 1.5 | 116 | 99.2 | 19.8 |
| 2.0 | 12 | 369.6 | 70.3 |
| 2.5 | 12 | 375.9 | 71.4 |
| 3.0 | 42 | 373.7 | 54.1 |
| 3.5 | 93 | 326.8 | 49.3 |
| 4.0 | 154 | 255.1 | 36.4 |

pH's reported by other workers^(16, 72, 77, 122, 207) for the oxidation of metallic sulfides and ferrous iron by T. ferrooxidans.

This minimum lag time is of some practical significance since in a commercial batch, microbiological leaching of zinc sulfide the lag time, which is unproductive time, would be minimized.

At constant pH measurements, the final zinc concentrations and the zinc extraction rates were much higher than those derived in the initial pH measurements. The improvements can be attributed to the increase in substrate concentration from 5.3 to 16% pulp densities.

The above data and those of others have shown the importance of pH on T. ferrooxidans. This organism is relatively unique in being able to survive at such low pH's. This fact is of considerable economic significance because, unlike many other fermentations, this one does not require an expensive sterilization of the medium prior to inoculation.

3. Effects of nutrient concentrations

A study of the effects of various concentrations of nutrients in the basal medium⁽³⁷⁾ on zinc extraction rates and final zinc concentrations was performed using zinc sulfide concentrate suspensions maintained at pH 2.3 and 35°C. The pulp density was 16%. All experiments were carried out in duplicate.

The first group of these experiments demonstrates the effects on the leaching activity of T. ferrooxidans of the absence of certain nutrients from the basal medium, which has been described in Table 1. These experiments were carried out by withdrawing ammonium sulfate, dipotassium hydrogen phosphate, and the rest of the nutrient components

(potassium chloride, magnesium sulfate, and calcium nitrate) from the liquid medium⁽³⁷⁾ one at a time. The resulting data are recorded in Table 4 of Appendix 1.

In the absence of potassium chloride, magnesium sulfate and calcium nitrate the final zinc concentration (69.5 g/l) and the zinc extraction rate (351.7 mg/l hr) are comparable to those achieved when these salts were present; e.g., the data typified by Table 7E of Appendix 1.

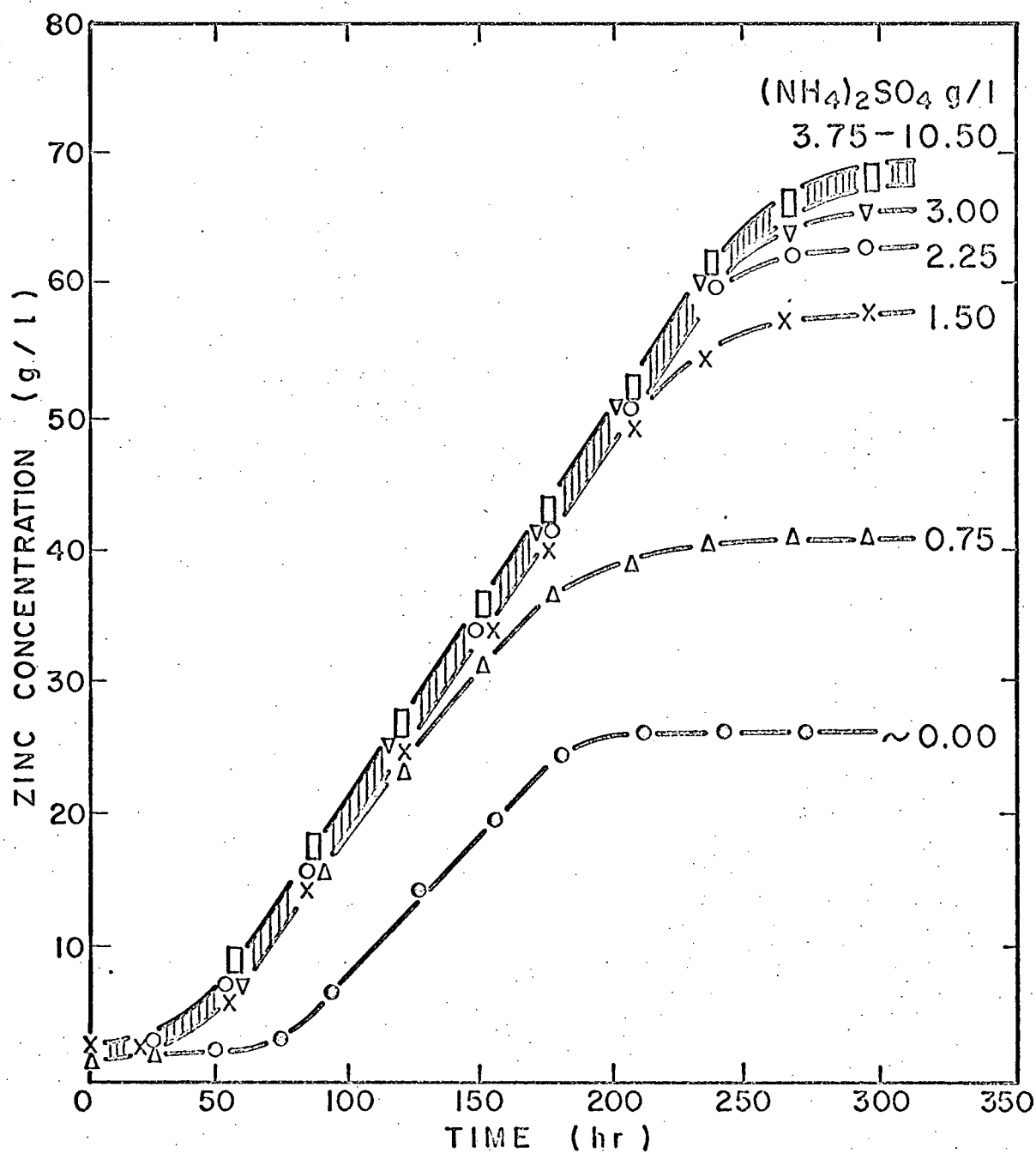
However, the absence of either ammonium sulfate or dipotassium hydrogen phosphate from the basal medium had a considerable, deleterious effect on the activity of the organism. In both cases the measured zinc concentration and the zinc extraction rate were reduced. The limited bacterial activity that did occur indicates that small quantities of nitrogen and phosphorus must have been available to the organism. These small quantities of nutrients probably were supplied with the inoculum which constituted approximately 7% of the suspension volume.

The effects of the concentrations of the nitrogen and phosphorus sources were investigated further over a range encompassing 0 to 3.5 times the amounts contained in the basal medium⁽³⁷⁾.

The data on the variation of ammonium sulfate concentration are given in Table 5 (A to C) of Appendix 1 and are graphed in Figure 8. Ammonium sulfate concentration had its principal effect on the final zinc concentration. Its effect on the zinc extraction rate was virtually negligible.

In studying the effects of variations in phosphate concentration, the inoculum was grown on reduced phosphate level media

Figure 8
EFFECT OF AMMONIUM CONCENTRATION



and was transferred twice before inoculation into the leach suspension. This series of investigations indicated that dipotassium hydrogen phosphate concentration had little effect on the final zinc concentration but did influence the zinc extraction rate. These statements are supported by the data of Table 6 (A to C) of Appendix 1 and Figure 9.

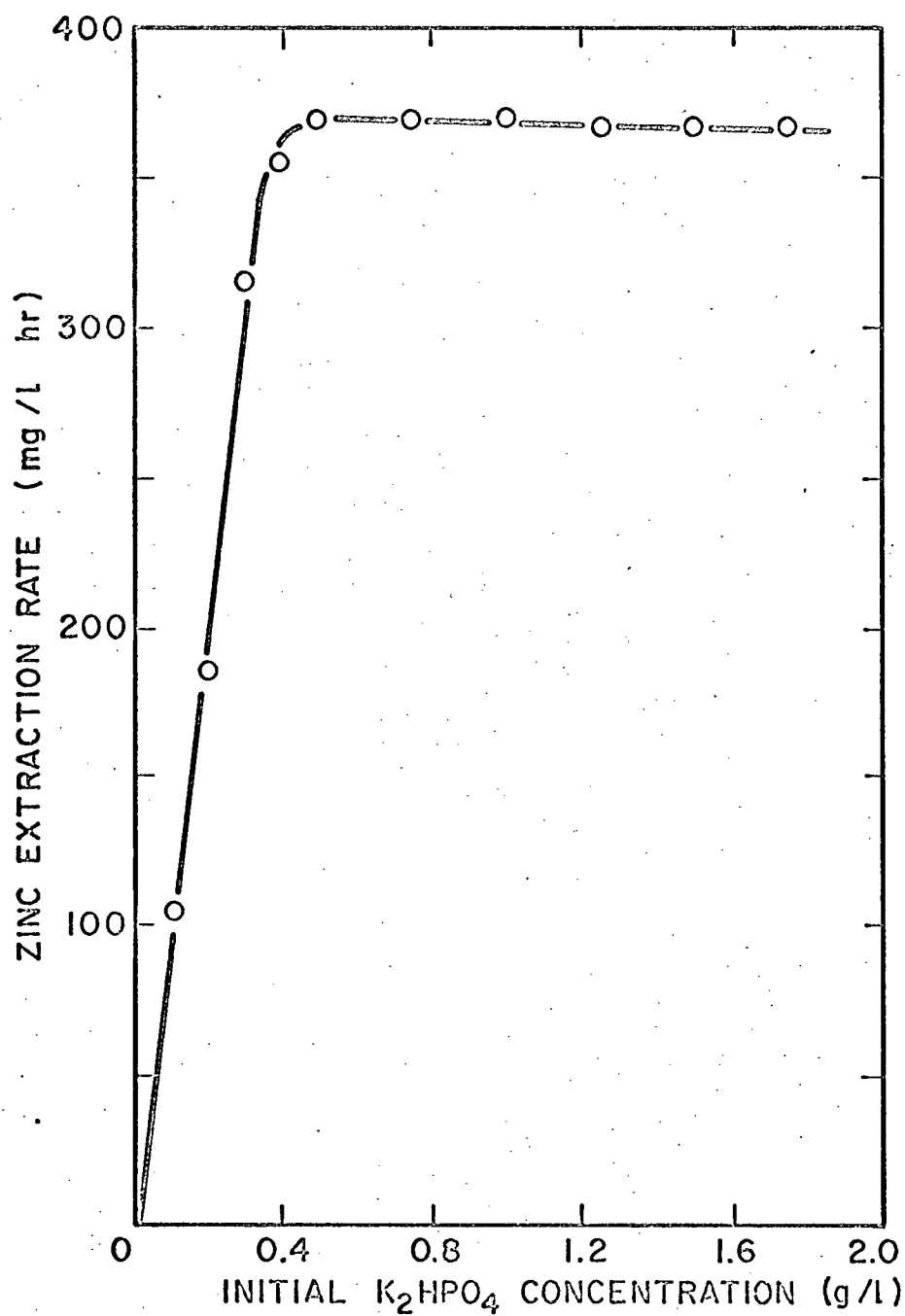
Since the make up of the basal medium was presented in 1959⁽³⁷⁾ only limited information has been published concerning the nutritional requirements of T. ferrooxidans. Studies have not been undertaken on the nutritional requirements of this organism while leaching zinc sulfide minerals. The data summarized in Figures 8 and 9 indicate that the nutrient levels called for in the basal medium (3 g/l of ammonium sulfate and 0.5 g/l of dipotassium hydrogen phosphate) are adequate. The minor nutrients (potassium chloride, magnesium sulfate, calcium nitrate) were required by the organism in such small quantities that any requirement beyond the amounts contained as impurities in the ammonium and phosphate salts or in the zinc concentrate could not be demonstrated.

Similar evidence for the effects of ammonium sulfate and dipotassium hydrogen phosphate has been found for the oxidation of chalcopyrite by T. ferrooxidans in the laboratories of B. C. Research⁽²⁰⁸⁾.

4. Effects of pulp density (solid concentration)

The influence of the initial pulp density or solids concentration on the rate of zinc extraction has been studied over a range of 1 to 26.6%. All experiments were duplicated and sterile controls were maintained in almost all cases. No effort was made in this series of experiments to determine the change in pulp density during the course

Figure 9
EFFECT OF PHOSPHATE CONCENTRATION



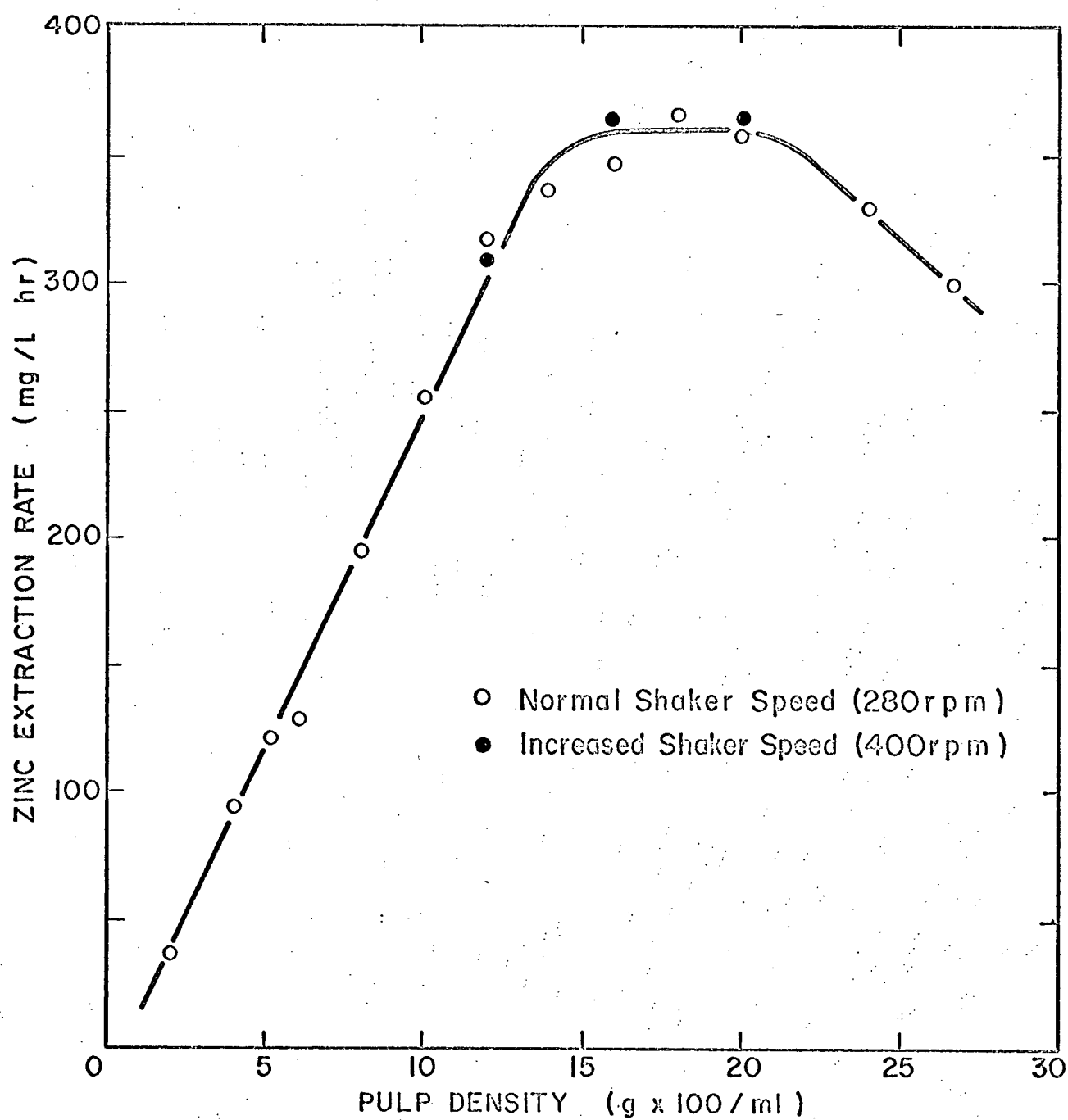
of a leach. The results of these experiments which were run at 35°C and pH 2.3 are presented in Table 7 (A to G) of Appendix 1. Table 7H of Appendix 1 provides some data on a series of leaches done by increasing the speed of the gyratory incubator from the standard 280 to 400 rpm. No sterile controls were run with the latter set.

The rates of zinc extraction calculated from the averaged data from the duplicate runs are plotted versus pulp densities in Figure 10. As can be seen zinc extraction rates increase with increasing pulp density up to about 16%. The improvement in rate above pulp densities of 13% is marginal. At low pulp densities the zinc extraction rate is directly proportional to the pulp density but tends to taper off at higher pulp densities. At still higher values the extraction rate decreases.

At low solids concentration the extraction rate of zinc is no doubt limited by the amount of substrate (ZnS) available. That is, the rate of growth of the organism is limited by the availability of its energy source. At higher pulp densities there is a surfeit of energy source and the rate of organism growth and hence the zinc extraction rate, which we are assuming is proportional to growth, becomes limited by some other factor.

If this other limiting factor were the mass transfer rates from air to the leach solution of the gases(carbon dioxide and oxygen) which the organism requires one would anticipate that increasing the shakerspeed would increase the mass transfer rate due to an increased degree of agitation. However, this did not produce markedly different results and the tentative conclusion was reached that such mass

Figure 10
EFFECT OF PULP DENSITY



transfer was not limiting. It should be noted that these experiments were done before those reported in the previous section on nutrient requirements. When it became evident that under these conditions nutrient concentrations were not limiting, further work on carbon dioxide requirements was begun. This is reported in section 6 of this work.

The decline in extraction rate at high pulp densities probably can be attributed to the interference of the solids with the mass transfer of oxygen or carbon dioxide to the organism.

At 16 - 20% solids the zinc extraction rates were highest (ca 350 mg/l hr) implying that if the initial pulp density were 16% or greater that pulp density would not be rate limiting. The final zinc concentrations achieved were of the order of 50 to 70 g/l for pulp densities ranging from 16 to 26.6%.

Behaviour of the organism at high initial zinc concentrations was studied by adding fresh quantities of the solid substrate (ZnS concentrate) to liquors decanted from the leaches already carried out at 18 and 20% pulp density. In other words leaches were done at initial pulp densities of 18 and 20%. When extraction ceased the liquors were separated from the leached solids and new solids added. The zinc concentrations after the first leach were 70.1 g/l for the 18% suspension and 70.6 g/l for the 20% one. The data given in Table 5 show that these concentrations increased to 91.9 g/l and 90.8 g/l respectively during the second extraction. These concentrations, as will subsequently be shown, do not represent the maximum tolerance toward zinc of this organism. These high zinc concentrations approach those used in direct recovery of zinc from solution by electrowinning. Thus a new possibility for

Table 5Effect of pulp density and zinc concentration

| Time (hr) | ZINC EXTRACTIONS (g/l) | |
|--------------|------------------------|---------------------|
| | Pulp density 18% | Pulp density 20% |
| 0 | 66.1 | 64.2 |
| 22 | 66.4 | 64.8 |
| 45 | 67.6 | 73.6 |
| 68 | 78.2 | 80.3 |
| 92 | 89.5 | 84.5 |
| 102 | 91.6 | 89.3 |
| 117 | 91.7 | 90.3 |
| 127 | 91.9 | 90.8 |

hydrometallurgical extraction has been demonstrated which involves a microbiological treatment in the recovery of zinc from a high-grade zinc sulfide concentrate.

5. Effects of initial particle diameter and specific surface area

In this section of this work we consider the effects on leaching of the particle size and specific surface area of the solid zinc sulfide concentrate. Particles of a variety of sizes and specific surface areas were obtained from the unfractionated subsieve concentrate by wet (Cyclosizer) and dry (Bahco-sizer) separation techniques. See section V. 3.1 . All experiments were carried out in duplicate with sterile controls. The leach suspensions were maintained at pH 2.3, 35°C and had a pulp density of 16%. The leaching data obtained with the Cyclosizer fractions are given in Table 8 (A to C) of Appendix 1 and those obtained with the Bahco-sizer fractions in Table 9 (A to D) of that Appendix. Note that with the Cyclosizer fractions and with the first four Bahco-sizer fractions the lag time was abnormally long. This can be attributed to the use of an old inoculum which required a prolonged period of time for adaptation.

Table 6 summarizes the effects of the subsieve fractions on the microbiological zinc extractions using normal air for aeration. The final zinc concentrations of both the inoculated samples and the sterile controls as well as the zinc extraction rates were strongly dependent on the specific surface area or the particle size. Table 6 also includes data taken from Table 7E of Appendix 1 which were obtained using the unfractionated -400 mesh zinc sulfide concentrate also having a pulp density of 16%.

As particle size decreased and specific surface area increased the amount of zinc solubilized in the sterile controls increased. The surface area of these particles may have been partially oxidized and thus the finer fractions may have contained larger quantities of zinc oxide which dissolved due to the action of sulfuric acid. Therefore, the relatively high zinc concentrations in the sterile controls (e.g., 2.49 and 10.9 g/l for the finest Cyclosizer size fraction and Bahco-sizer size fraction respectively) may be attributed not only to the size effect but possibly also to an increased amount of air oxidation of the finer particles.

Figure 11 and 12 are photographs showing the relative size and uniformity of the Cyclosizer and Bahco-sizer fractions respectively. The coarsest size fraction (C.S. No. 6) from the Cyclosizer was obtained in such small quantities that it was not used in bacterial leaching experiments.

Despite the different techniques used in determining the particle diameters of the Cyclosizer fractions, Table 6 indicates good agreement between the two techniques. These techniques were microscopic measurement and the method described in the Cyclosizer Manual⁽²⁰⁹⁾. The particle sizes of the Bahco-sizer fractions were measured by microscope. The microscopic measurements for both sets of particles are the ones used subsequently.

Figure 13 demonstrates the effect of particle size on the microbiological zinc extraction rate. Figure 13A is a plot of the data which suggests a logarithmic relationship. Figure 13B shows this logarithmic relation which is of the form

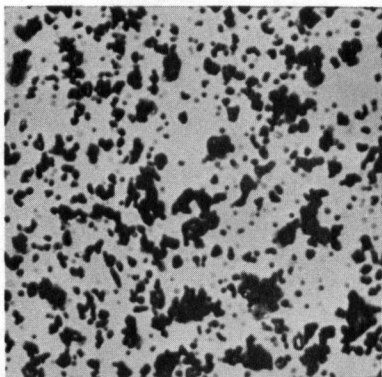
Table 6

Effect of subsieve fractions

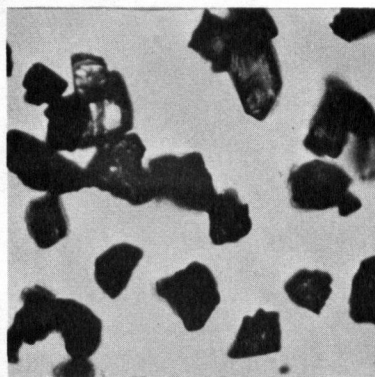
| Sample | FINAL ZINC CONCENTRATION (g/l) | | Zinc extraction rate (mg/l hr) | Specific surface area (m ² /g) | MEAN PARTICLE DIAMETER (micron) | |
|-------------|-----------------------------------|------------|---|--|------------------------------------|----------------------|
| | In presence of bacteria | In Sterile | | | Microscopic Measur. | Cyclosizer Manual |
| C.S.* No. 1 | 70.1 | 2.49 | 496.2 | 6.04 | 3.5 | |
| 2 | 63.1 | 1.32 | 359.8 | 1.20 | 8.8 | 8.9 |
| 3 | 51.8 | 1.16 | 263.6 | 0.66 | 12.6 | 12.2 |
| 4 | 37.4 | 0.97 | 204.3 | 0.55 | 19.1 | 18.6 |
| 5 | 33.0 | 0.86 | 158.0 | 0.45 | 25.6 | 26.7 |
| B.S.* No. 1 | 72.8 | 10.9 | 516.8 | 6.90 | 2.2 | |
| 2 | 70.0 | 8.9 | 484.2 | 4.11 | 3.6 | |
| 3 | 65.4 | 4.24 | 446.2 | 2.85 | 5.4 | |
| 4 | 61.3 | 3.21 | 349.3 | 1.25 | 9.0 | |
| 5 | 53.0 | 2.74 | 274.3 | 0.73 | 13.6 | |
| 6 | 46.0 | 0.84 | 173.1 | 0.47 | 21.7 | |
| 7 | 38.9 | 1.02 | 132.7 | 0.39 | 27.8 | |
| 8 | 27.7 | 1.27 | 73.4 | 0.29 | 39.9 | |
| -400 mesh | 63.7 | 1.20 | 343.3 | 1.37 | | |

* C.S. = Cyclosizer fraction; B.S. = Bahco-sizer fraction

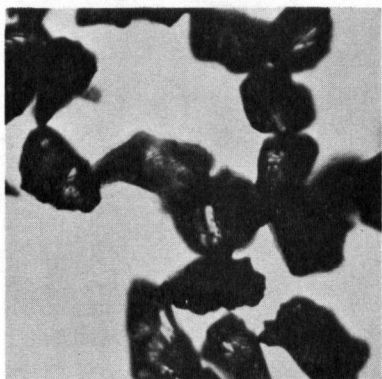
CYCLOSIZER FRACTIONS



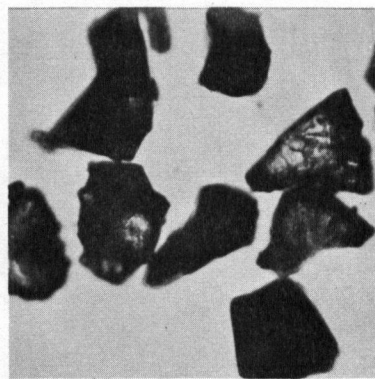
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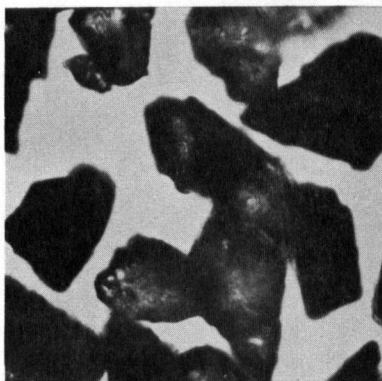
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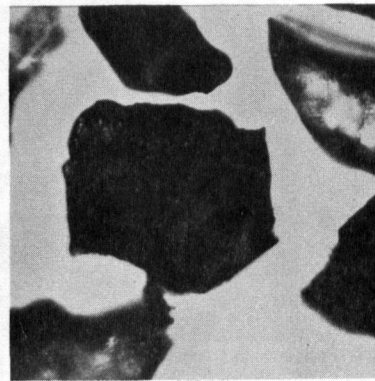
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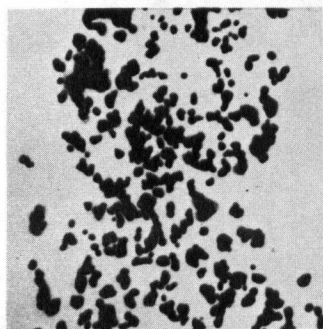


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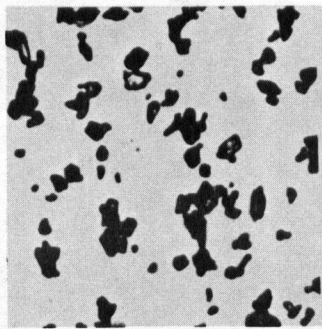


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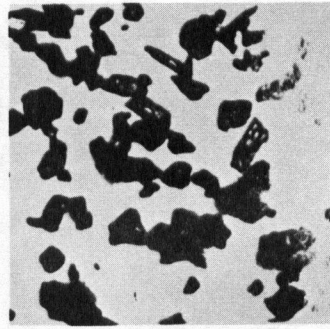
BAHCO-SIZER FRACTIONS



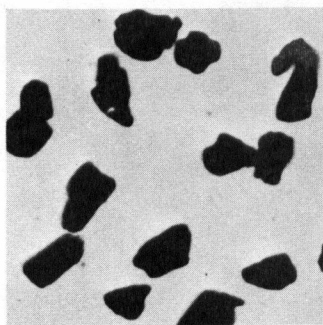
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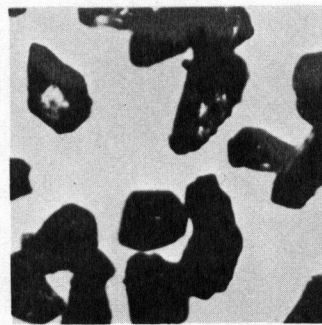
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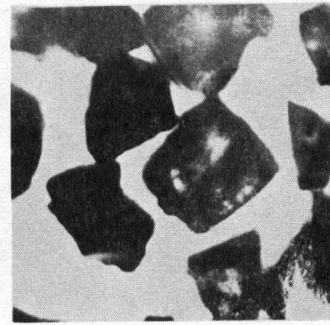
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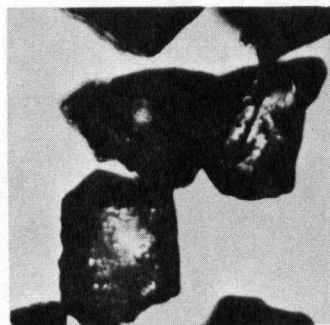
No. 4.



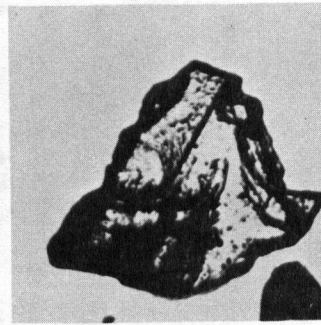
No. 5.



No. 6.



No. 7.



No. 8.

$$V = V_m \times \exp (K \times d) \quad (29)$$

where V = zinc extraction rate (mg/l hr);

V_m = maximum zinc extraction rate (mg/l hr);

K = constant;

d = particle diameter (micron).

Least squares fitting of the data pairs resulted in

$$\ln V = 6.34 - 5.24 \times 10^{-2} \times d \quad (30)$$

As the particle diameter tends to zero the solid substrate would become so finely divided that it would approach molecular dimensions which could be considered to be in solution. If this were so one would expect then that as d goes to zero the maximum extraction rate would be obtained. Following this line of reasoning the maximum extraction rate was found from equation 30 to be 569 mg/l hr. Thus, whereas for maximum extraction rates the ore should be ground as finely as possible, commercially this would have to be balanced against the increased costs of grinding.

The zinc extraction rate data of Table 6 are replotted in Figure 14 this time using the initial specific surface area of the different size fractions as the dependent variable. Also plotted is a point representing the unfractionated subsieve material. The curve of Figure 14 suggests that where specific surface is low (with large particles) the extraction rate is limited by the availability of surface. The bacteria must contact the surface of the solid mineral particle to effect the solubilization of zinc and if only so much surface is available

it can be the rate limiting factor. At higher values of specific surface the rate tends toward a constant value, suggesting that some other factor has become rate limiting. Thus these experiments carried out on the sized fractions of the subsieve zinc sulfide concentrate have been able to demonstrate the effects of particle diameter and specific surface area on microbiological leaching rates which were predicted by a number of investigators (7, 16, 27,46).

These data relating particle specific surface to leaching rate complement those obtained in the pulp density experiments. If zinc extraction rate (V) is plotted against initial total surface area of solids per unit volume of liquid medium (TSA) the curves from the pulp density variation experiments and from the particle size variation experiments coincide in the region of low area per unit volume. That is at low pulp densities or for particles having low values of specific surface the curves overlap as evidenced by Figure 15. Thus it appears that the true rate limiting factor associated with the energy source (zinc sulfide) is the amount of surface area available per unit volume of leach solution. The organisms cannot attack the substrate in the interior of the concentrate particle until the outer material is dissolved. Increasing the pulp density puts more particle mass of fixed specific surface (surface area per unit mass) into a unit volume thus increasing the total available surface. Increasing the particle specific surface puts the same particle mass with increasing specific surface into a unit volume, again increasing the total available surface. At higher values of pulp density other factors become rate limiting as previously mentioned in section 4.

Figure 13
EFFECT OF PARTICLE SIZE
(UNDER NORMAL AERATION) CONDITIONS

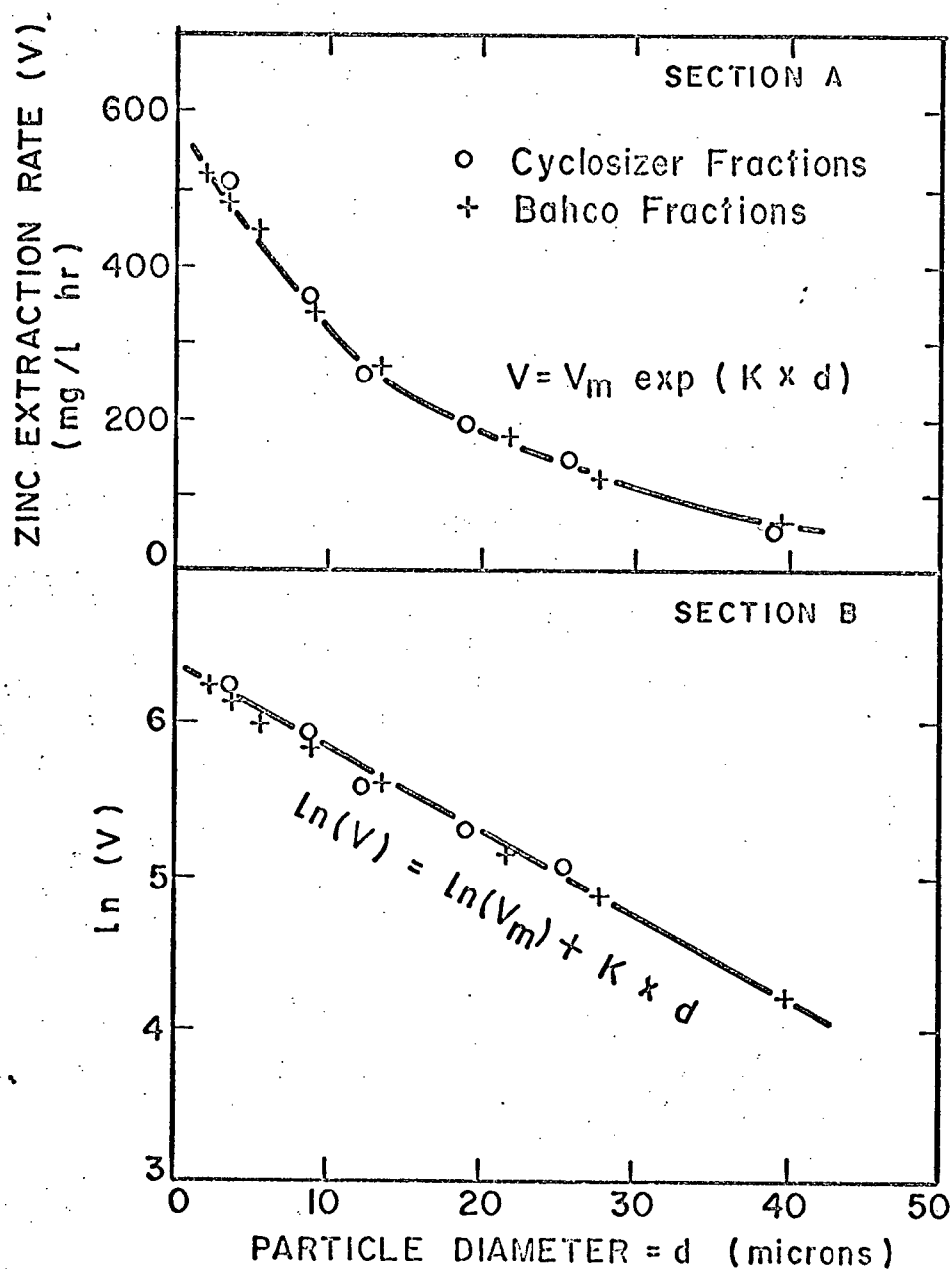


Figure 14
EFFECT OF SPECIFIC SURFACE AREA

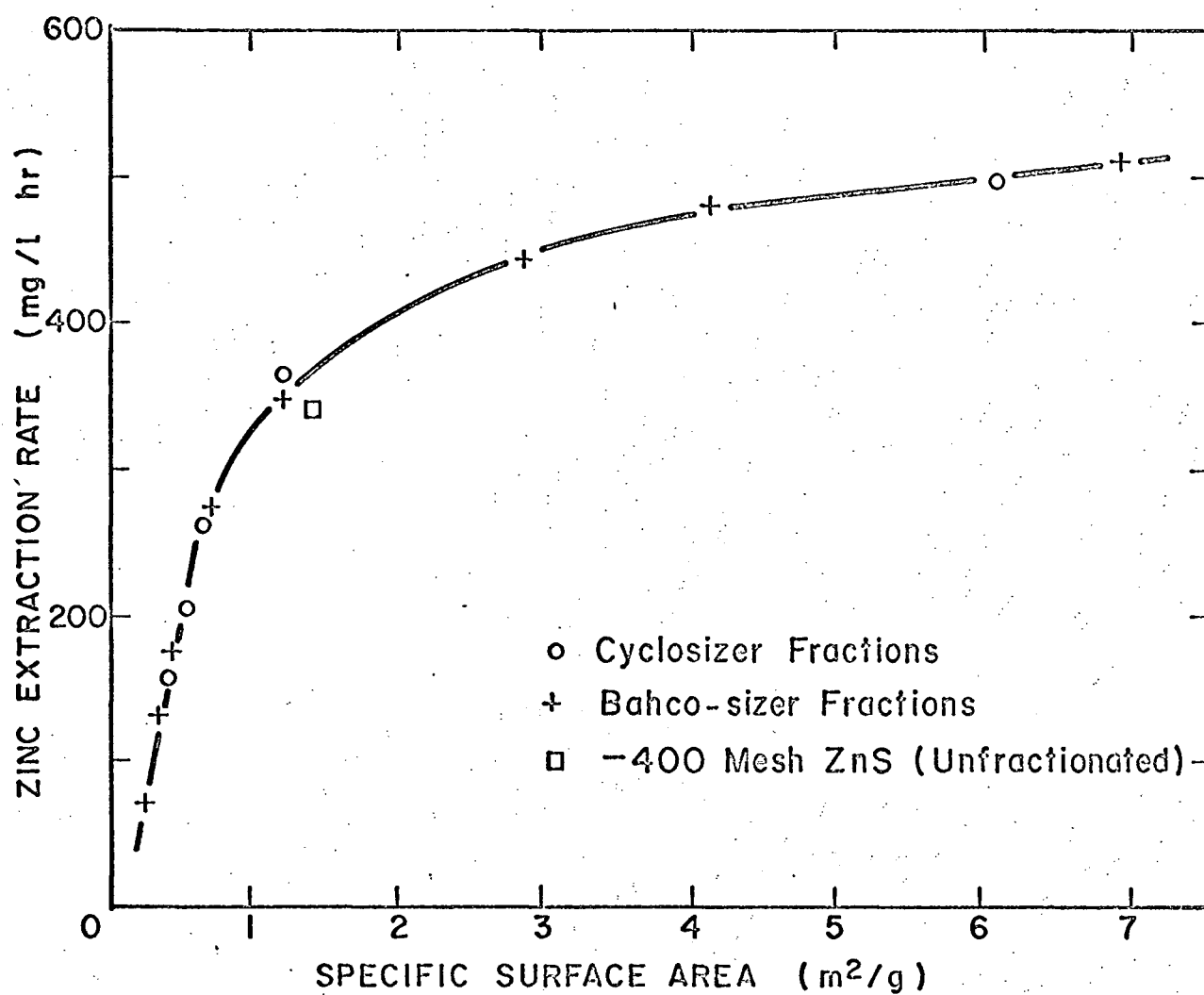
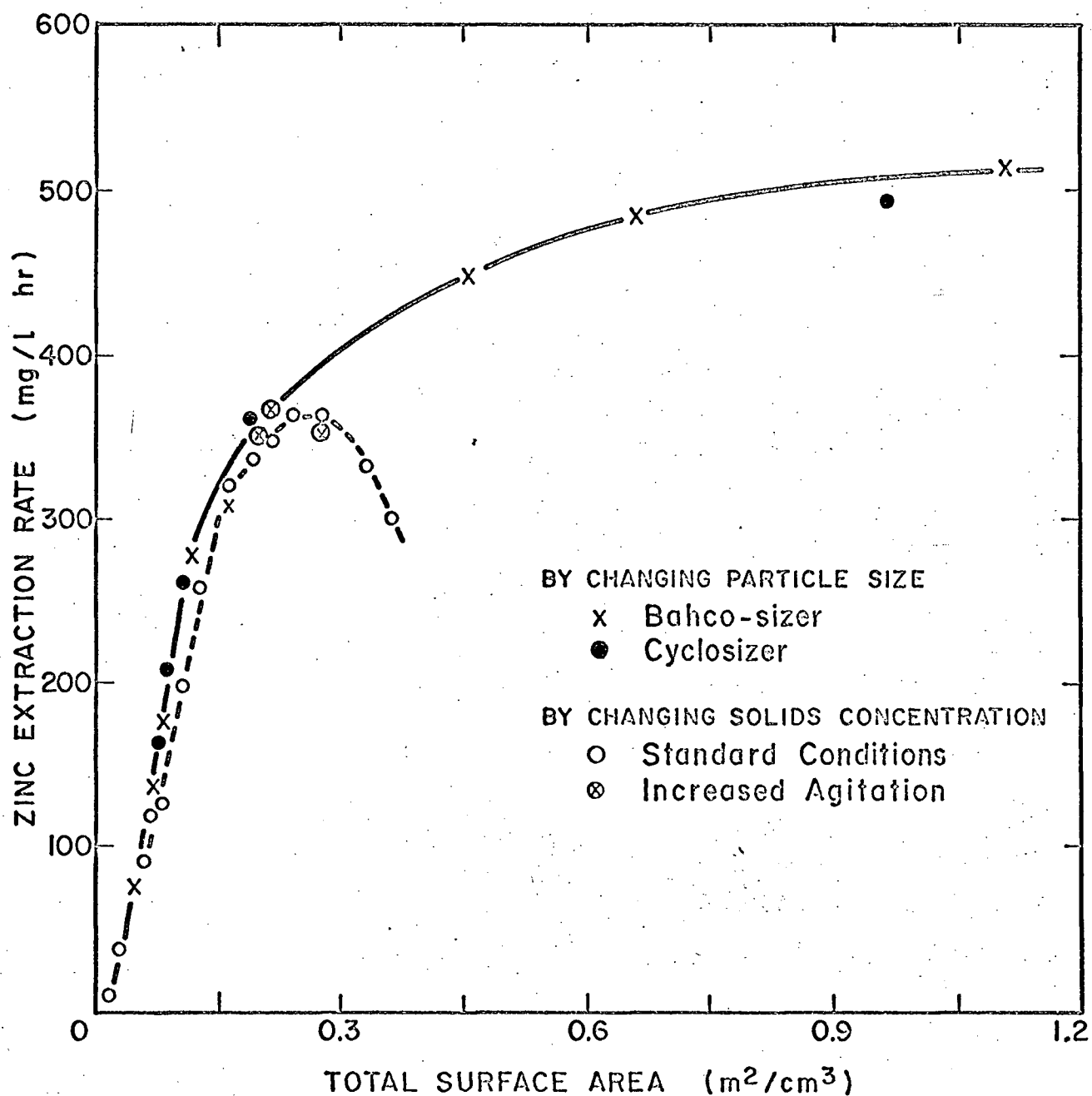


Figure 15
EFFECT OF TOTAL SURFACE AREA OF SOLID



No significant differences were observed between the effects of the wet and dry classified subsieve fractions on the zinc extraction rate. Also the unfractionated material showed similar behaviour to the sized fractions when compared on a specific surface or total surface per unit volume basis. The maximum zinc extraction rates observed were about 517 mg/l hr which was obtained with the fraction having the largest specific surface. Extrapolation of the rate-particle diameter curve suggested a maximum rate of about 570 mg/l hr.

6. Effects of carbon dioxide concentration

In order to further delineate the rate limiting factors in zinc extraction a series of experiments was carried out aerating the leach suspensions with air containing a variety of concentrations of carbon dioxide; the sole carbon source for T. ferrooxidans. These experiments were duplicated and were done at 35°C and pH 2.3 on leach suspensions with various pulp densities in the range 5.3 to 26.6%. The carbon dioxide concentrations in the air supplied to the enclosed, thermostated, gyratory shaker were controlled at between 0.13 and 7.92 volume per cent.

The experimental data obtained at 7.92% carbon dioxide are given in Table 10 (A and B) of Appendix 1. The 16, 18, 20 and 24% pulp density experiments were done in duplicate with sterile controls. The results obtained with the sterile controls showed no significant effect of increased carbon dioxide level (7.92%) on the zinc extraction in the controls, as can be seen by comparison of results to those obtained with normal air (0.03% carbon dioxide), i.e., in Table 7 (A to G) of Appendix 1.

The effects of pulp density on zinc extraction rate at the

different carbon dioxide levels [Table 10 to 13 (A and B) of Appendix 1] are summarized in Table 7. This table also includes the pulp density study results under normal aeration conditions; transposed from Figure 10. At carbon dioxide levels of 7.92%, 1.03% and 0.23% the zinc extraction rates are virtually identical, indicating that a carbon dioxide concentration of 0.23% in air is sufficient to insure a maximum extraction rate. The highest extraction rate (about 640 mg/l hr) was obtained with leach suspensions of 24 and 26.6% pulp densities. This value is about 280 mg/l hr higher than obtained under normal aeration conditions (360 mg/l hr). At 0.13% carbon dioxide the maximum zinc extraction rates were slightly inferior to those maxima obtained at higher carbon dioxide concentrations. For this experiment the maximum rate was 570 mg/l hr obtained with pulp densities of 24 and 26.6%.

These data are presented graphically in Figure 16. The zinc extraction rate versus pulp density curve increases linearly up to pulp densities of about 22%. At higher pulp densities this rate levels out suggesting that pulp density is no longer limiting. Note that with carbon dioxide enriched air the linear portion of the plot extends past the linear portion of the zinc extraction rate versus pulp density which was obtained with normal air (Figure 10). This suggests that in Figure 10 the carbon dioxide concentration was the limiting factor for pulp densities above 12%.

A least squares fit of the linear part of Figure 16 (pulp densities up to 20%) gave

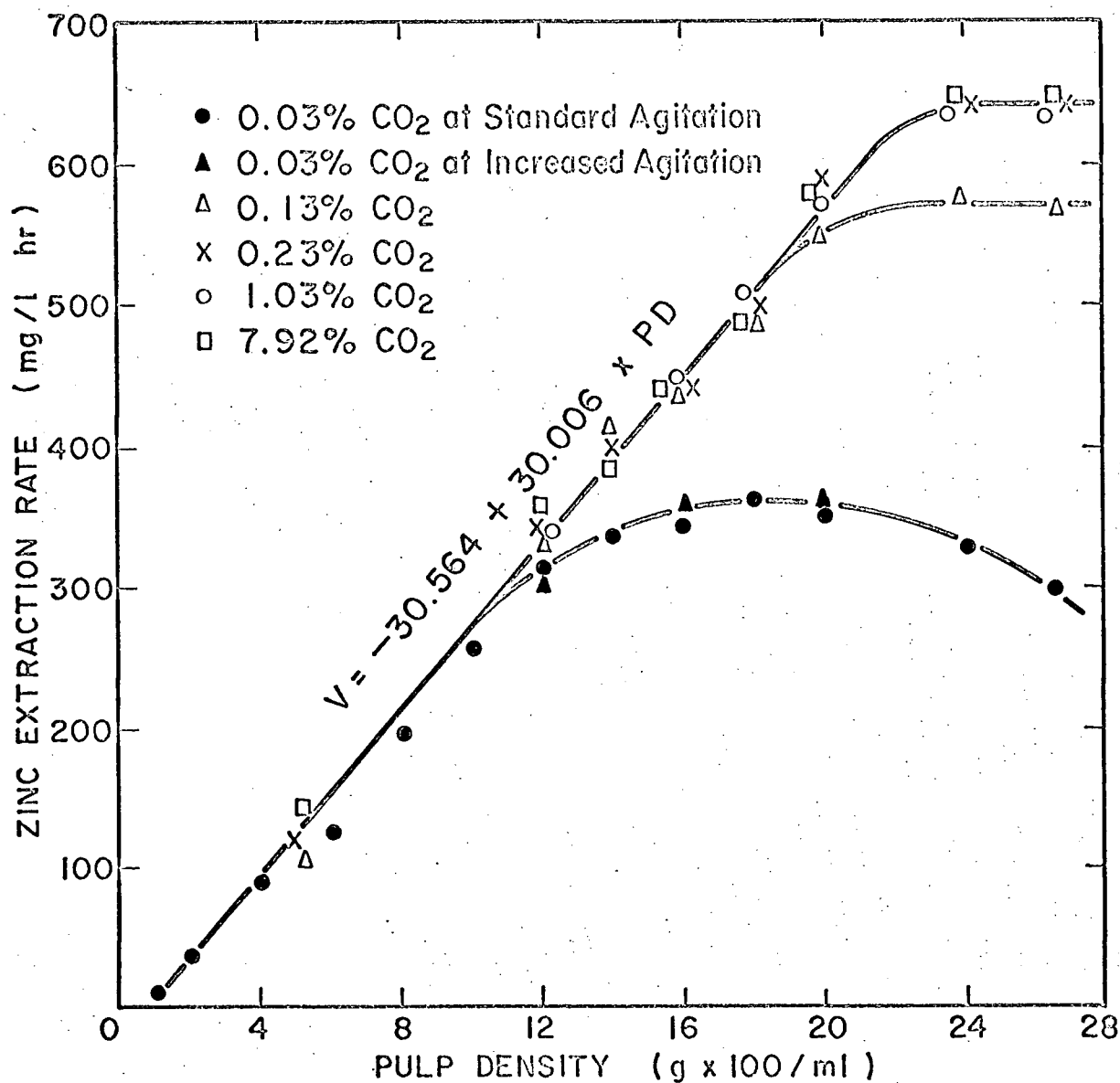
$$Y = 30.0 \times PD - 30.6 \quad (31)$$

Table 7

Effect of pulp density at different carbon dioxide partial pressures

| Pulp Density (%) | ZINC EXTRACTION RATE (mg/1 hr) | | | | |
|------------------------|--------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| | 7.92% CO ₂ | 1.03% CO ₂ | 0.23% CO ₂ | 0.13% CO ₂ | 0.03% CO ₂ |
| 5.3 | 141.3 | 133.9 | 118.5 | 107.6 | 121.0 |
| 12 | 355.1 | 339.8 | 339.4 | 331.3 | 312.5 |
| 14 | 383.0 | 405.2 | 399.7 | 414.3 | 335.4 |
| 16 | 438.8 | 438.5 | 439.8 | 444.2 | 343.3 |
| 18 | 488.1 | 513.3 | 496.5 | 490.7 | 364.3 |
| 20 | 577.8 | 574.6 | 589.0 | 549.0 | 353.4 |
| 24 | 640.8 | 644.4 | 636.0 | 576.2 | 327.5 |
| 26.6 | 640.6 | 636.9 | 636.5 | 563.6 | 297.1 |

Figure 16
EFFECT OF PULP DENSITY
AT DIFFERENT CARBON DIOXIDE PARTIAL PRESSURES



where V = zinc extraction rate (mg/l hr);

73

PD = pulp density in %.

The negative extraction rate obtained at very low pulp densities is not real, is of doubtful significance and probably is due to experimental error.

At the highest values of pulp density the intrinsic rate of the reaction expressed by equation 7 may be limiting or the solids may interfere with the rate of mass transfer of carbon dioxide or even oxygen. The carbon dioxide content was measured only in the gas phase, not in the liquid phase. However, it is reasonable to assume that if the gas phase concentration is raised, other things being equal, the liquid phase concentration also will be increased. Mass transfer rates were not measured.

Figure 17 is a cross plot of the data given in Table 7 where zinc extraction rate is plotted against carbon dioxide concentration with pulp density as a parameter. The pulp density or substrate concentration affects the level at which slope of the extraction rate curve approaches zero. The latter level rises as the pulp density increased, up to pulp densities of 24%.

7. Effects of initial particle diameter and surface area at 1.0% carbon dioxide

In view of the data observed for leaching rates with increased carbon dioxide levels the effects of particle size and specific surface area on leaching rates were reexamined at an increased concentration (1.0%) of carbon dioxide in air. All of these experiments were done in single runs in 16% pulp density leach suspensions using the various subsieve concentrate fractions described in section 5. Again the pH was 2.3 and the temperature 35°C. The results are presented in Tables 14

Figure 17
EFFECT OF CARBON DIOXIDE PARTIAL PRESSURES
AT DIFFERENT PULP DENSITIES

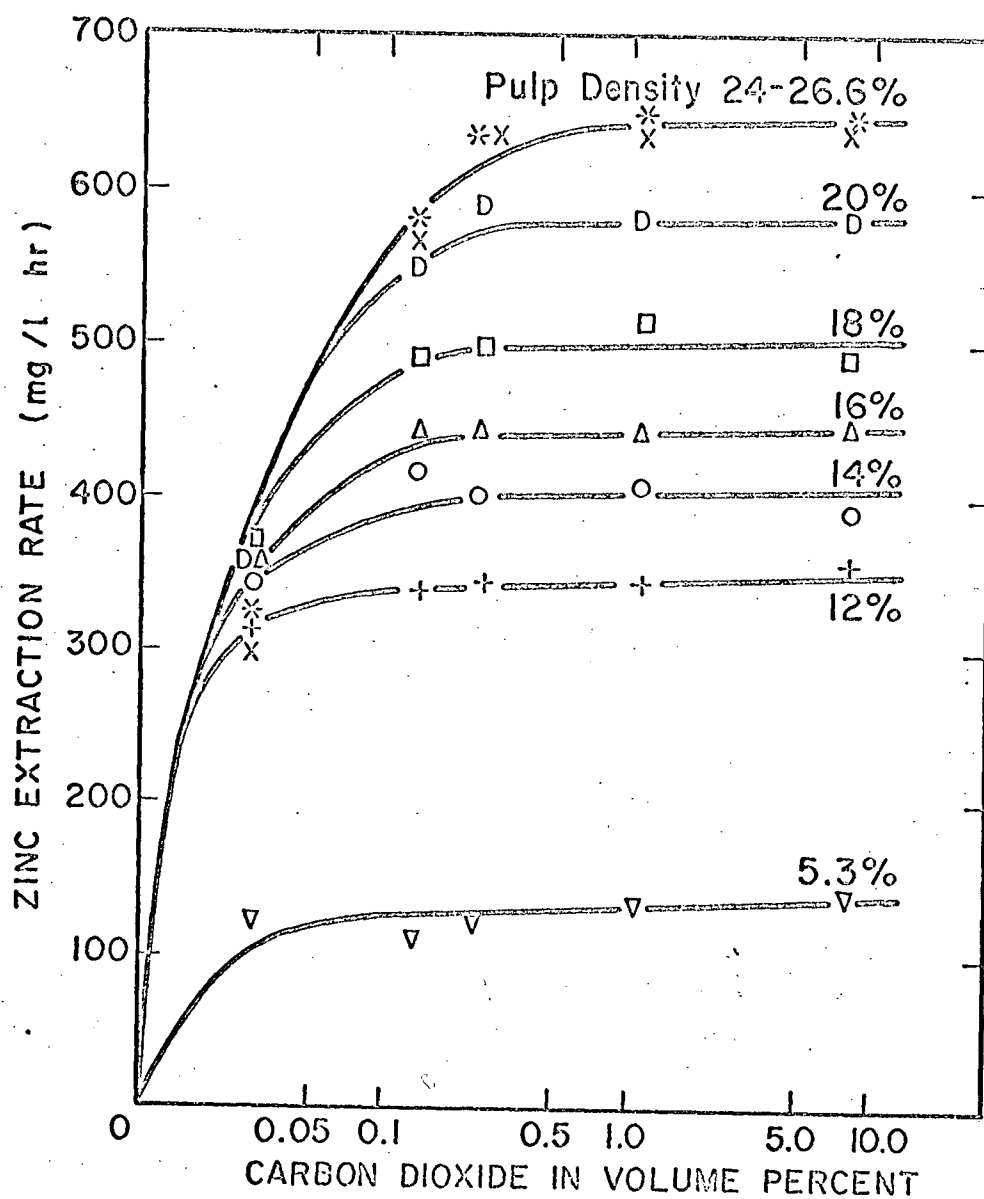


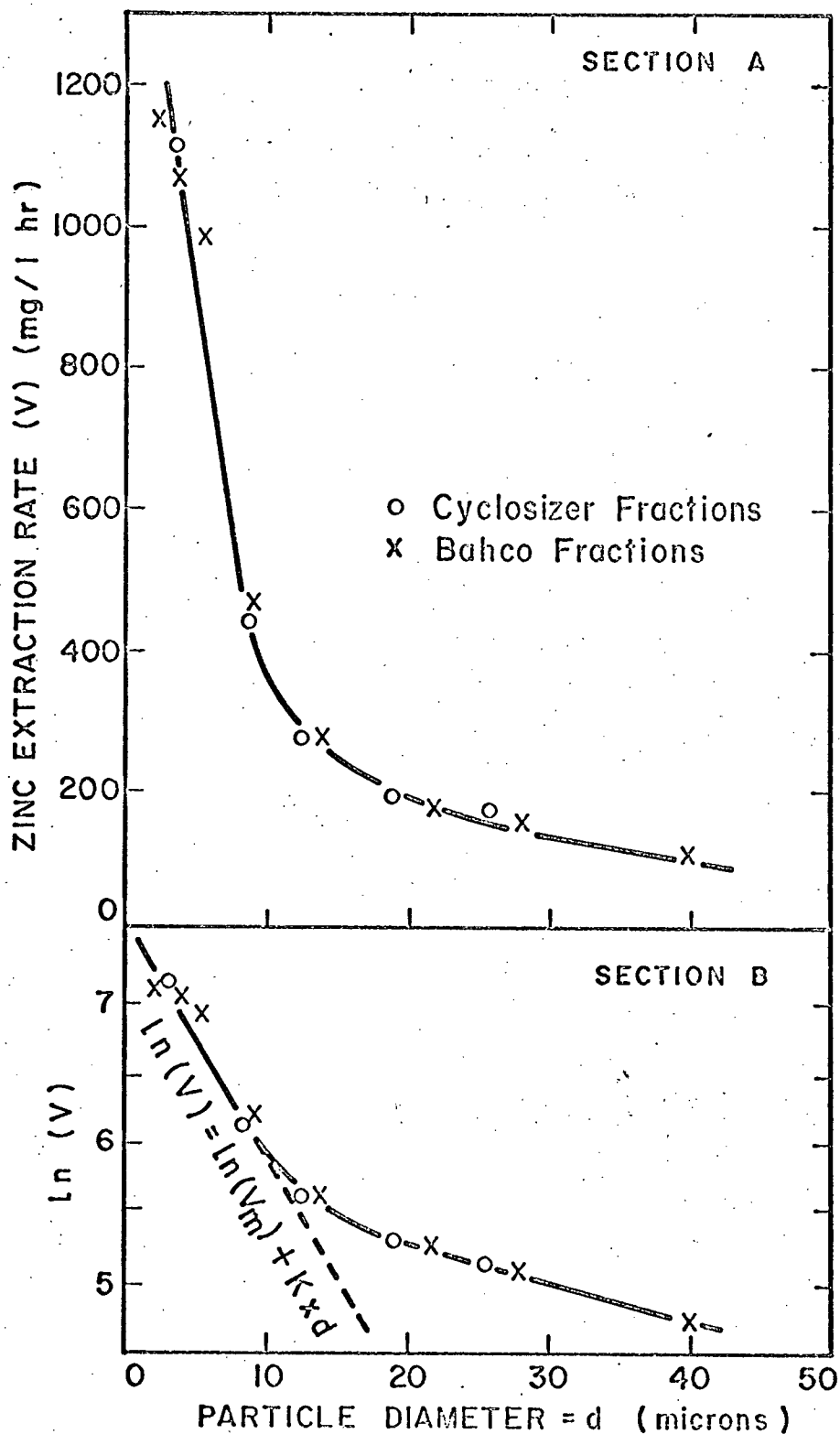
Table 8 summarizes the effects of the various fractions and unfractionated ore concentrate on the microbiological zinc extraction rate; both under normal aeration and under aeration with carbon dioxide enriched air. The results presented in Table 8 indicate that for the smallest size particles the zinc extraction rates obtained with carbon dioxide enriched air were more than double those obtained using normal air. Thus for example, the highest zinc extraction rate under normal aeration was 516.8 mg/1 hr obtained with the fraction having the highest specific surface area ($6.90 \text{ m}^2/\text{g}$) whereas when the air used for aeration contained 1% carbon dioxide this same size fraction gave rise to an extraction rate of 1,152.3 mg/1 hr. With the particle sizes having lower specific surface areas the increases in extraction rate attributable to increased availability of carbon dioxide became marginal. Under these conditions the availability of surface is rate limiting rather than the availability of carbon dioxide.

The plot of zinc extraction rate against particle diameter, with carbon dioxide enriched air, is given in Figure 18. Figure 18A shows that initially the zinc extraction rate decreases rapidly with an increase in particle diameter and subsequently more slowly. Unlike Figure 13B a semilog plot of these data, as can be seen from Figure 18B, does not produce a straight line. In an attempt to predict a maximum obtainable extraction rate by extrapolating the extraction rate versus particle size plot to zero particle diameter only those data for particle diameters less than 10 microns were used. This part of the curve could be described by the following equation.

Table 8
Effect of subsieve fractions

| Sample | Particle Diameter (micron) | Specific Surface area (m ² /g) | ZINC EXTRACTION RATE (mg/l hr) | |
|------------|-------------------------------|--|-----------------------------------|----------------------|
| | | | 0.03% CO ₂ | 1.0% CO ₂ |
| C.S. No. 1 | 3.5 | 6.04 | 496.2 | 1,115.5 |
| 2 | 8.8 | 1.20 | 359.8 | 441.9 |
| 3 | 12.6 | 0.66 | 263.6 | 268.7 |
| 4 | 19.1 | 0.55 | 204.3 | 198.6 |
| 5 | 25.6 | 0.45 | 158.0 | 170.2 |
| B.S. No. 1 | 2.2 | 6.90 | 516.8 | 1,152.3 |
| 2 | 3.6 | 4.11 | 484.2 | 1,068.3 |
| 3 | 5.4 | 2.85 | 446.2 | 989.8 |
| 4 | 9.0 | 1.25 | 439.3 | 460.9 |
| 5 | 13.6 | 0.73 | 274.3 | 271.6 |
| 6 | 21.7 | 0.47 | 173.1 | 184.1 |
| 7 | 27.8 | 0.39 | 132.7 | 157.6 |
| 8 | 39.9 | 0.29 | 73.4 | 107.0 |
| -400 mesh | | 1.37 | 343.3 | 438.5 |

Figure 18
EFFECT OF PARTICLE SIZE
AT 1.0% CARBON DIOXIDE PARTIAL PRESSURE



$$\ln V = 7.52 - 0.152 \times d \quad (32)$$

This leads to a maximum extraction rate of $V_m = 1,840 \text{ mg/l hr.}$

Because of the limitations imposed on the extrapolation this figure is only to be considered as a very rough estimate. Note that it is approximately three times the estimate made previously (section 5) for normal air conditions.

Figure 19 presents zinc extraction rate as a function of specific surface area of the ore concentrate particles under normal and carbon dioxide enriched air conditions. Where carbon dioxide enriched air has been used the zinc extraction rate is proportional to the specific surface, for values below $2.5 \text{ m}^2/\text{g}$. Further increases in surface area become less and less effective in increasing the extraction rate. For normal aeration the proportionality holds only up to specific surfaces of around $0.75 \text{ m}^2/\text{g}$. Also Figure 19 shows clearly that in the high specific surface range the rates in enriched air are more than double those observed in normal air.

Figure 20 is the curve of zinc extraction rate versus total surface area per unit volume of liquid medium. This plot indicates all the data obtained with 1.03% carbon dioxide enriched air by variation of pulp density and by using particles having a variety of specific surface areas. The various data points fit well onto a single curve save for those points obtained at high pulp densities where some interference with mass transfer has been postulated.

8. Larger scale experiments

All of the previously discussed experiments were carried out

Figure 19
EFFECT OF SPECIFIC SURFACE AREA
AT 1.0% CARBON DIOXIDE

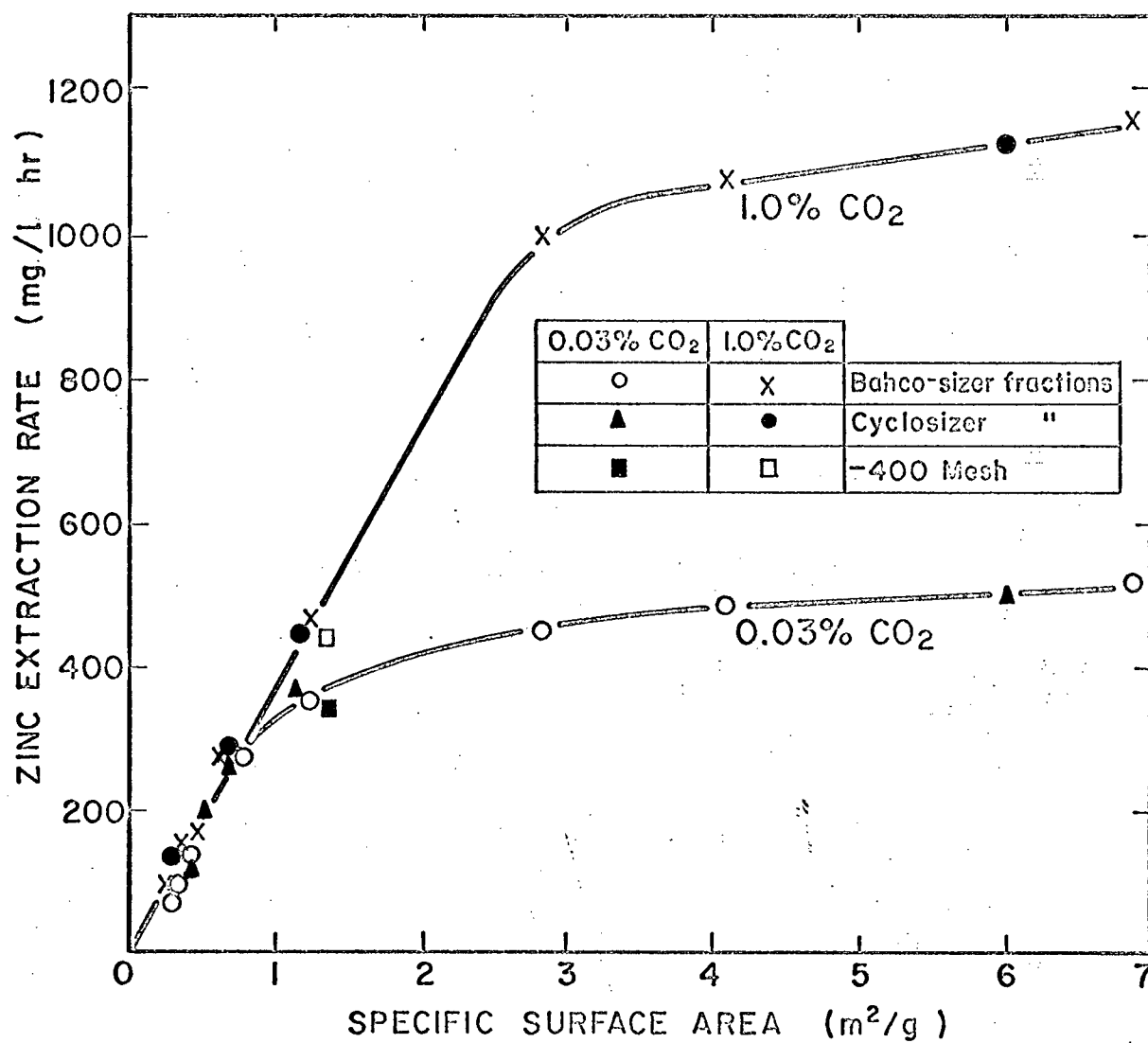
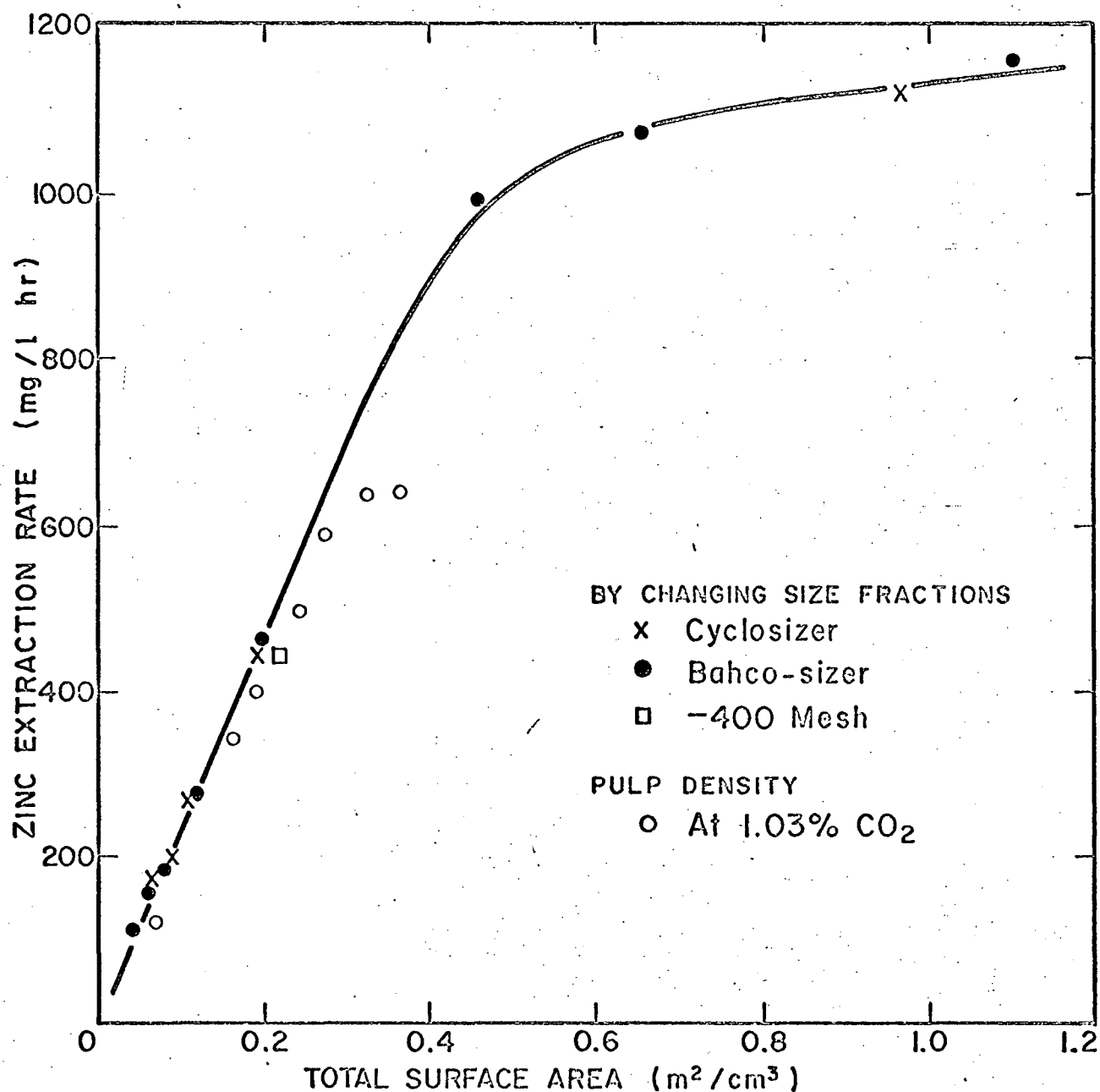


Figure 20
EFFECT OF TOTAL SURFACE AREA
OF SIZE FRACTIONS AT 1.0% CO₂



in Erlenmeyer flasks on a gyratory shaker. As a preliminary scale-up procedure to a potentially commercial-sized installation some experiments were undertaken in stirred tanks, with much larger volumes of suspension. These were undertaken to ascertain the relevance of data obtained in shake flasks for scale-up purposes. These large scale leaches were done at a pulp density of 24% using unfractionated -400 mesh concentrate at pH 2.3, 35°C and with carbon dioxide enriched air (1%).

The first experiment was done with 30 liters of leach suspension in an unbaffled tank. The pH was controlled manually. The data obtained are presented in Table 2 of Appendix 2. The zinc extraction rate was calculated to be 635.3 mg/l hr in good agreement with the 636.9 mg/l hr found for similar conditions in the shake flask. However, the final zinc concentration observed in the stirred tank (112.2 g/l) was significantly greater than that observed in the shake flask (70.4 g/l).

Another experiment was done in a baffled, stirred tank using 12 liters of ore suspension (24% pulp density, pH 2.3, 35°C, 1% CO₂) with automatic pH control. The results are noted in Table 3 of Appendix 2. The zinc extraction rate observed (651.4 mg/l hr) again agreed well with the shake flask result (636.9 mg/l hr). The final zinc concentration was measured as 119.8 g/l slightly superior to that observed in the unbaffled tank. The differences between baffled and unbaffled tanks are minimal. Agitator power consumption might be different but this was not measured.

These final zinc concentrations are the highest observed in this work and are in the range of zinc concentrations (80 - 160 g/l) currently used in the commercial electrowinning of zinc from solution.

Samples of the leach liquors have been sent to Cominco Ltd. for 82
evaluation of their suitability for electrowinning. The zinc recoveries
or yields in the unbaffled and baffled stirred tank leaches were 76.9
and 82.1% respectively. Results obtained by Cominco Ltd. indicated a
satisfactory quality of cathode zinc, produced after pretreatment to
remove iron by precipitation of the ferric form at pH 5 and cementation
of other minor impurities with zinc dust. Current efficiencies of 79 -
83% were lower than acceptable commercial levels (90%). It was con-
sidered that this deficiency could be overcome by minor modification of
purification procedures, prior to electrowinning.

The reason for the difference in the final zinc concentrations
in the shake flask and stirred tank leaches is not readily evident.
Periodic stopping of the shaker for sampling may have interfered with
the extraction process or perhaps the different type of mixing in the
stirred tanks resulted in some self-grinding of the concentrate,
producing more surface. However, no definitive explanation is avail-
able.

During these large scale experiments alterations which occurred
as time progressed in the size distribution and chemical composition
of the substrate ore particles were investigated. After removal of
400 ml samples from the leach suspension, the solids were filtered out
and were washed three times with one liter of distilled water. After
drying at 45°C these solids were fractionated on the Bahco-sizer
apparatus and the zinc contents of fractions 1, 3, 5 and 8 determined.
The results are in Table 9. These were obtained from the leach done
in the baffled tank.

From Table 9, most of the zinc is leached from the smaller particles because their zinc concentration drops most rapidly with time. Also there is a smaller percentage of the smallest particles remaining after 338 hours of leaching. The relative proportion of the large particles increases and the composition remains more or less constant. These facts are consistent with having an initial particle distribution the smallest fractions of which are leached faster than the largest fraction while those particles in the large fraction diminish in size to become part of the smaller fractions. The smallest fraction particles will not completely disappear due to the inert material initially present in the ore concentrate.

9. Modelling

9.1 General

The shapes of the plots of zinc extraction rates versus pulp density, specific surface, and total surface area per unit volume of leach liquor are similar both under normal and carbon dioxide enriched air conditions. At relatively low values of the various dependent variables the zinc extraction rates are directly proportional to the dependent variables. At higher values of the dependent variables the zinc extraction rates level off and tend to become independent. One of the simplest equations which can be used to describe this kind of behaviour is the hyperbolic equation (equation 13) suggested by Monod (131,140). This is also known as the Michaelis-Menten⁽¹³⁶⁾ equation (see section IV.4.2).

Equation 13 has been adapted in this work to describe the effects of various factors on the kinetics of microbial zinc extraction.

Table 9

Alterations in substrate during leaching

| Time | 0 hr | | | 212 hr | | | 338 hr | | |
|------------------------|-------------|----------------------|------------------|-------------|----------------------|------------------|-------------|----------------------|------------------|
| Yield of Zn - extr. | 0% | | | 47.0% | | | 82.1% | | |
| Bahco- fractions | Weight % | Zinc content % | Weight * g | Weight % | Zinc content % | Weight * g | Weight % | Zinc content % | Weight * g |
| 1 | 5.3 | 60.85 | 5.3 | 1.3 | 18.79 | 0.7 | 0.8 | 14.73 | 0.1 |
| 2 | 2.7 | | 2.7 | 2.0 | | 1.0 | 1.9 | | 0.3 |
| 3 | 11.3 | 60.63 | 11.3 | 8.0 | 41.51 | 4.2 | 6.7 | 38.74 | 1.2 |
| 4 | 14.7 | | 14.7 | 11.0 | | 5.8 | 9.7 | | 1.7 |
| 5 | 19.0 | 60.89 | 19.0 | 19.3 | 58.96 | 10.2 | 22.7 | 53.20 | 4.1 |
| 6 | 19.3 | | 19.3 | 21.7 | | 11.5 | 16.7 | | 3.0 |
| 7 | 6.3 | | 6.3 | 8.0 | | 4.2 | 10.3 | | 1.8 |
| 8 | 21.3 | 60.92 | 21.3 | 28.7 | 60.21 | 15.2 | 21.3 | 60.45 | 5.6 |
| TOTAL | 99.9 | | 99.9 | 100.0 | | 52.9 | 100.1 | | 17.8 |

* Calculated from average yield

Thus the substrate concentration (S) is replaced by pulp density (PD), specific surface area (SSA), or total surface area per unit volume (TSA). Equation 13 is used in this work to estimate values for K_m and V_m , particularly the latter which is an indication of the maximum rate attainable. This maximum rate would be of considerable importance in an industrial scale operation.

Monod^(131, 140) specified a number of conditions which must be met when using equation 13 to characterize bacterial growth curves. Not all of these are met in the present work which renders treatment thereof more empirical in nature. In this work we were concerned with a product (zinc) formation rate rather than a bacterial cell growth rate. In Monod's work the growth rate was the growth rate observed in the logarithmic phase of the cell population growth. In this work the product rate used was the product rate which appeared as the linear portion of a plot of zinc concentration versus time.

Monod assumed that all nutrients and/or substrates were present in excess save one which was said to be the limiting substrate. The limiting substrate concentration is the one represented in equation 13 by S. In the present study both the availability of energy source and carbon dioxide can be limiting. As has been shown in section 4 there can be a transition from one limiting factor to another. In this study equation 13 was applied without regard to this limitation as will be shown below. Thus the V_m and K_m values observed may not represent solely the effects of a limiting substrate. However, under conditions where carbon dioxide was in excess the Monod condition of a single limiting substrate probably is met. In this case the limiting substrate is insoluble zinc sulfide.

In this heterogeneous system the substrate concentration should be expressed as a surface because the energy source for the organism is only available through this surface. Hence as suggested by Moss and Andersen⁽⁷⁸⁾ specific surface or total surface areas have been used as well as zinc sulfide concentrations expressed as pulp densities.

Due to the complicating factors listed above this modelling work should be regarded as preliminary. Further work should be undertaken to provide a more accurate simulation of the leaching curves.

In the following the values of the constants V_m and K_m were estimated through least squares fitting of the data using the Lineweaver and Burk technique⁽¹⁴¹⁾ to linearize equation 13.

9.2 Determination of V_m and K_m values under normal air conditions

The relation between zinc extraction rate (V) and pulp density (PD) was written as

$$V = \frac{V_m \times (PD)}{K_m + (PD)} \quad (33)$$

V_m = maximum zinc extraction rate (mg/l hr);

K_m = Michaelis-Menten constant (% pulp density).

When the data of Figure 10 were plotted in the linearized form ($\frac{1}{V}$ vs $\frac{1}{PD}$) a straight line was not observed save in the relatively narrow region between pulp densities of 12 to 18%. From the Lineweaver-Burk plot the value of V_m is derived from the intercept of the straight line on the $1/V$ axis. It was felt that the data points from pulp densities between 12% and 18% could be used to get a reasonable estimate of V_m . Data points for higher pulp densities which lay

closer to the $1/V$ axis were not useful because the high solids concentration apparently reduced the rate. The values found were $V_m = 574 \text{ mg/l hr}$ and $K_m = 10.1\%$ pulp density; see Figure 21.

The K_m value represents the pulp density which is half the pulp density required to achieve maximum rate. Thus if this were the correct model, the maximum rate should be achieved at a pulp density of 20.2%. The fact that at this pulp density the rate was lower than 574 mg/l hr means that some unaccounted for factor has interfered. This has already been commented upon when discussing Figure 10.

The extraction rate data from Figure 14 were studied using specific surface area (SSA) to represent substrate concentration in equation 13. Thus

$$V = \frac{V_m \times (\text{SSA})}{K_m + (\text{SSA})} \quad (34)$$

From the plot of Figure 22 the maximum zinc extraction rate and Michaelis-Menten constant were determined to be $V_m = 566 \text{ mg/l hr}$ and $K_m = 0.77 \text{ m}^2/\text{g}$. The data corresponding to particles having low surface areas deviated from the straight line and were not used in drawing the straight line. In Figure 22, similar extrapolation of the tangent to the dotted line, suggests a difference in reactivity of large particle size substrates.

Similarly total surface area per unit volume (TSA) can represent substrate concentration and

$$V = \frac{V_m \times (\text{TSA})}{K_m + (\text{TSA})} \quad (35)$$

The linearized plot of equation 35 is given in Figure 23 which includes points from the various pulp density experiments and points from the

Figure 21
EFFECT OF PULP DENSITY
LINEWEAVER - BURK PLOT

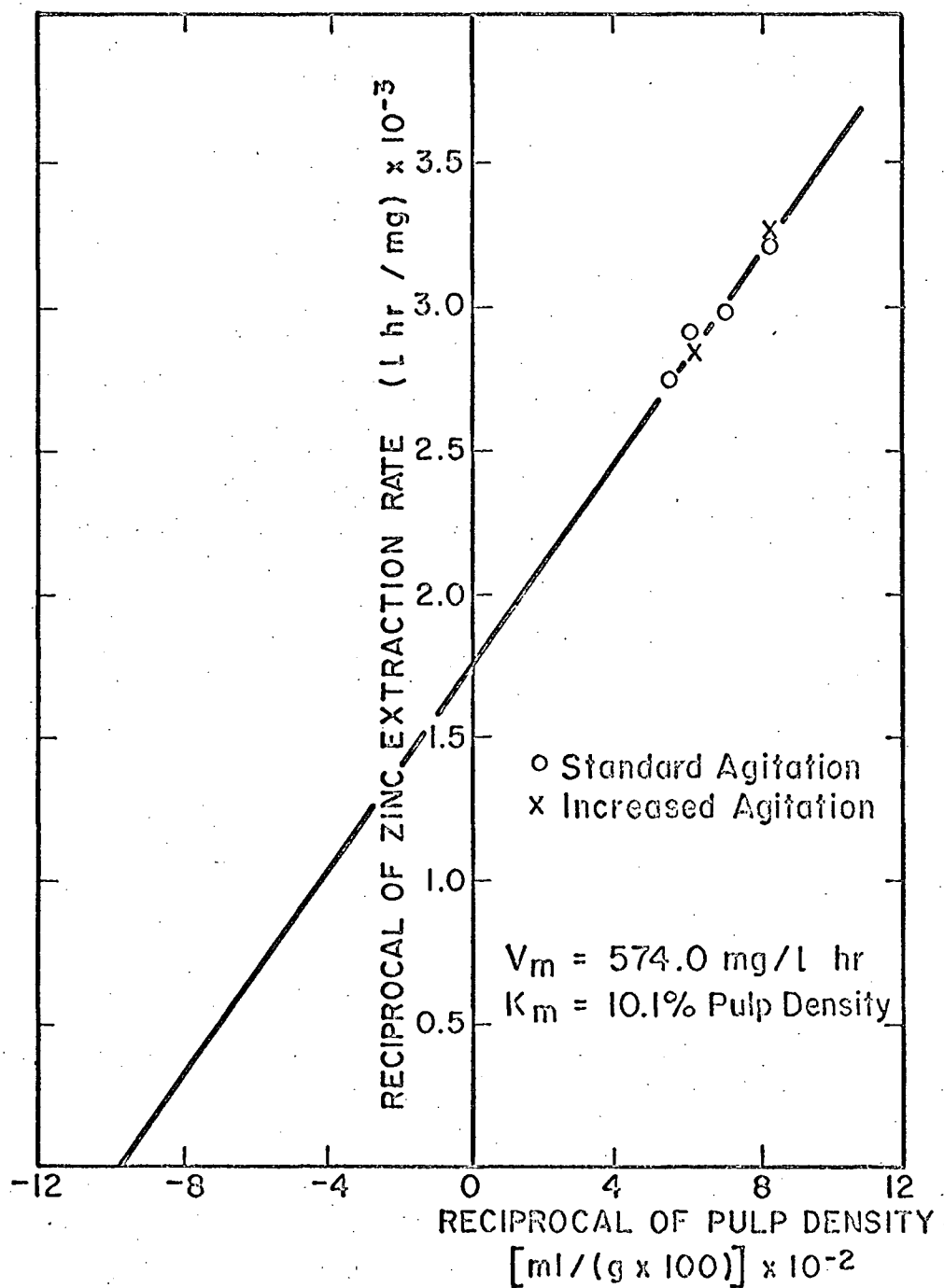
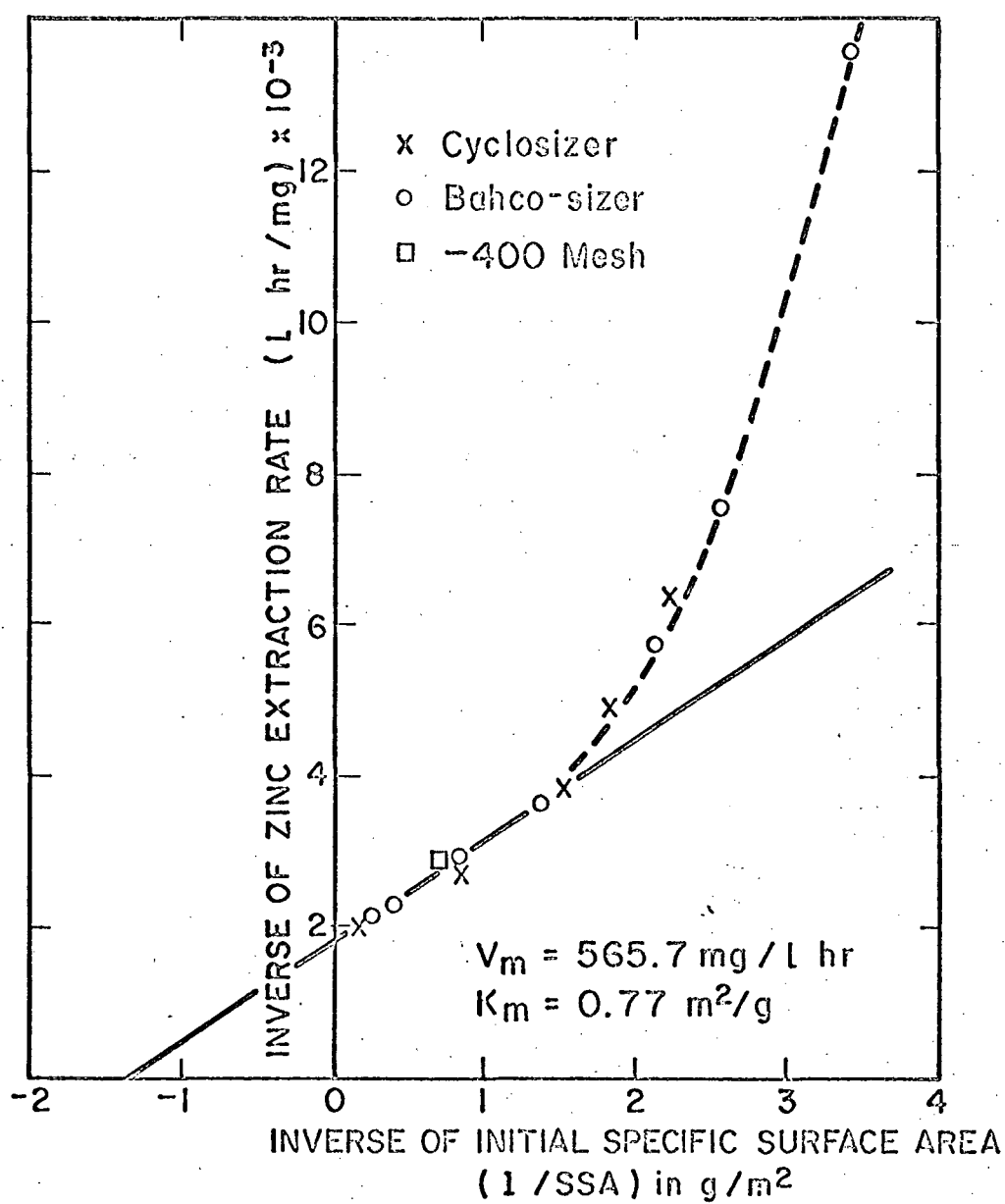


Figure 22
EFFECT OF SPECIFIC SURFACE AREA
LINEWEAVER - BURK PLOT



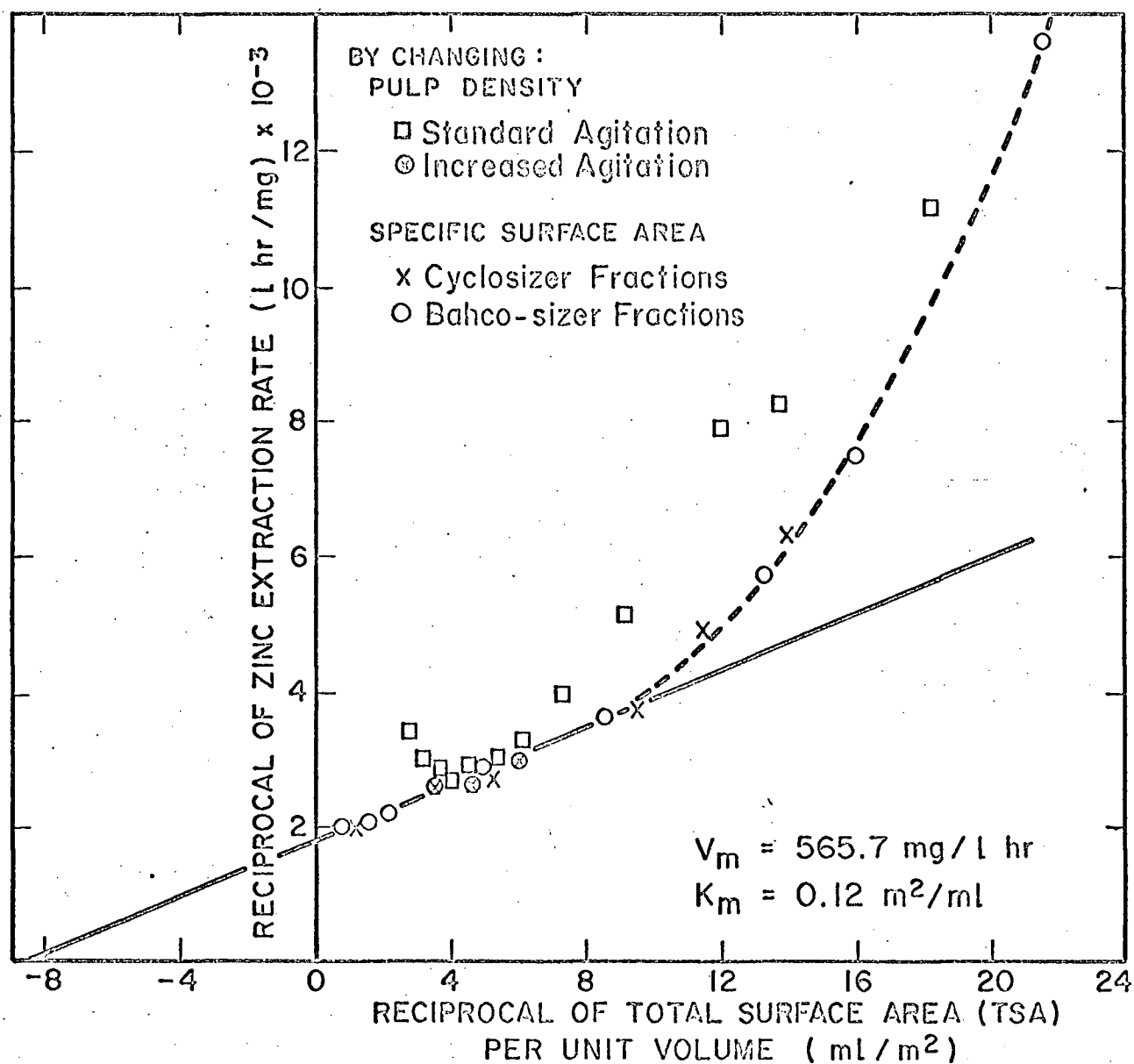
various subsieve fraction experiments. In the 12 to 18% pulp density range the data from the pulp density experiments agree well with those from the subsieve fraction experiments. The values found for V_m and K_m were 566 mg/l hr and $0.12 \text{ m}^2/\text{ml}$ respectively. Again the data which deviated markedly from the straight line were not used in the computation of V_m and K_m . This V_m value is the same as the one obtained for the zinc extraction rate as a function of specific surface area equation (equation 34). However, this is not unexpected since much of the same data were used. The differences in the values of K_m are due to the different units used.

The values obtained for the maximum extraction rate, 574 mg/l hr from the pulp density experiments and 566 mg/l hr from the specific surface area and total surface area experiments, are in good agreement with the maximum extraction rate (569 mg/l hr) obtained by extrapolating the particle diameter versus extraction rate curve to zero diameter. All of these values were obtained from experiments done under normal air condition. No literature data are available for comparison.

9.3 Determination of V_m and K_m values under carbon dioxide enriched air conditions

The effects of pulp density on zinc extraction rates under carbon dioxide enriched air conditions have been demonstrated in Figure 16. The rates obtained at carbon dioxide levels of 0.23, 1.03, and 7.92% are similar. Thus these data are plotted in Figure 24 for the determination of the V_m and K_m constants of equation 33. Figure 25 is a similar plot based on the data obtained at a carbon dioxide level of 0.13%.

Figure 23
EFFECT OF TOTAL SURFACE AREA
LINEWEAVER - BURK PLOT



For the 0.13% carbon dioxide experiments V_m was estimated to be 2,796 mg/l hr and K_m to be 85.4% pulp density. The values obtained for the higher carbon dioxide levels were 3,457 mg/l hr and 107.8% pulp density. As expected the V_m and K_m values were lower at the lower carbon dioxide level. These high maximum extraction rates can probably only be approximated in practice. Equation 33 predicts that the pulp densities required to achieve these maximum rates will be about 170 and 216%. These values are so high that they will lead inevitably to limitations. The relative limitation free situation existed at normal air conditions in a narrow pulp density range of 12 to 18% only. This range was expanded to 20% at increased carbon dioxide partial pressures. At higher pulp densities (as at these extreme pulp densities), the solid concentrations probably will impose limitations on the mass transfer rate of oxygen and carbon dioxide to the organisms.

The effects of specific surface area and total surface area on the microbiological zinc extraction rates were demonstrated in Figures 19 and 20 at carbon dioxide concentrations of 1%. Application of the linearized forms of equations 34 and 35 to these data resulted in the following values (see Figures 26 and 27): for specific surface area $V_m = 3,586$ mg/l hr and $K_m = 8.98 \text{ m}^2/\text{g}$, and for total surface area per unit volume $V_m = 3,586$ mg/l hr and $K_m = 1.44 \text{ m}^2/\text{ml}$. These maximum rates agree with that observed in the pulp density experiments (3,457 mg/l hr) at carbon dioxide levels of 0.23, 1.03, and 7.92%. However, these values are almost double the rough value (1,840 mg/l hr) obtained by extrapolating the zinc extraction rate-particle diameter curve.

Figure 24

EFFECT OF PULP DENSITY
AT INCREASED CARBON DIOXIDE PARTIAL PRESSURES
LINEWEAVER - BURK PLOT

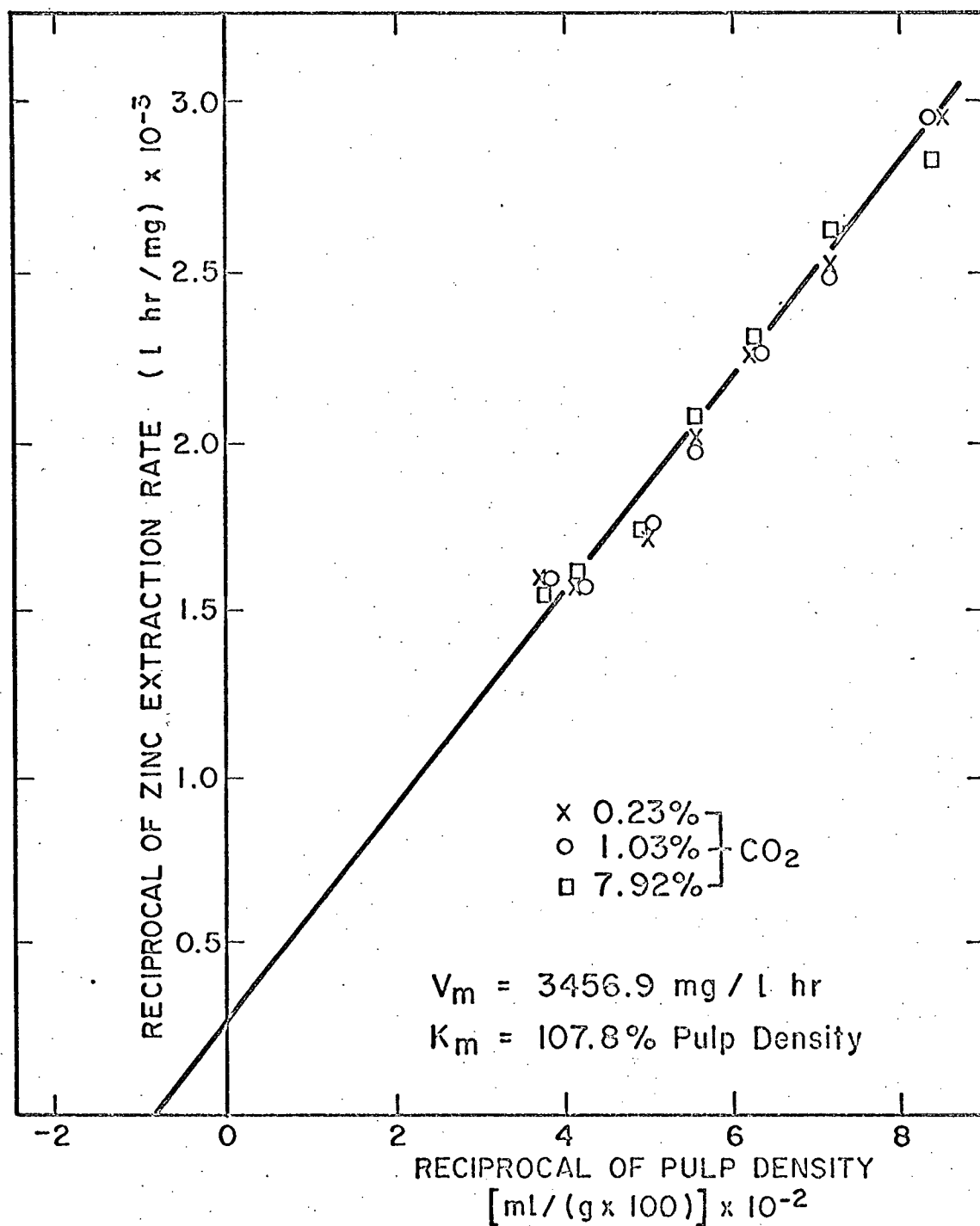


Figure 25
EFFECT OF PULP DENSITY AT 0.13% CO₂
LINEWEAVER - BURK PLOT

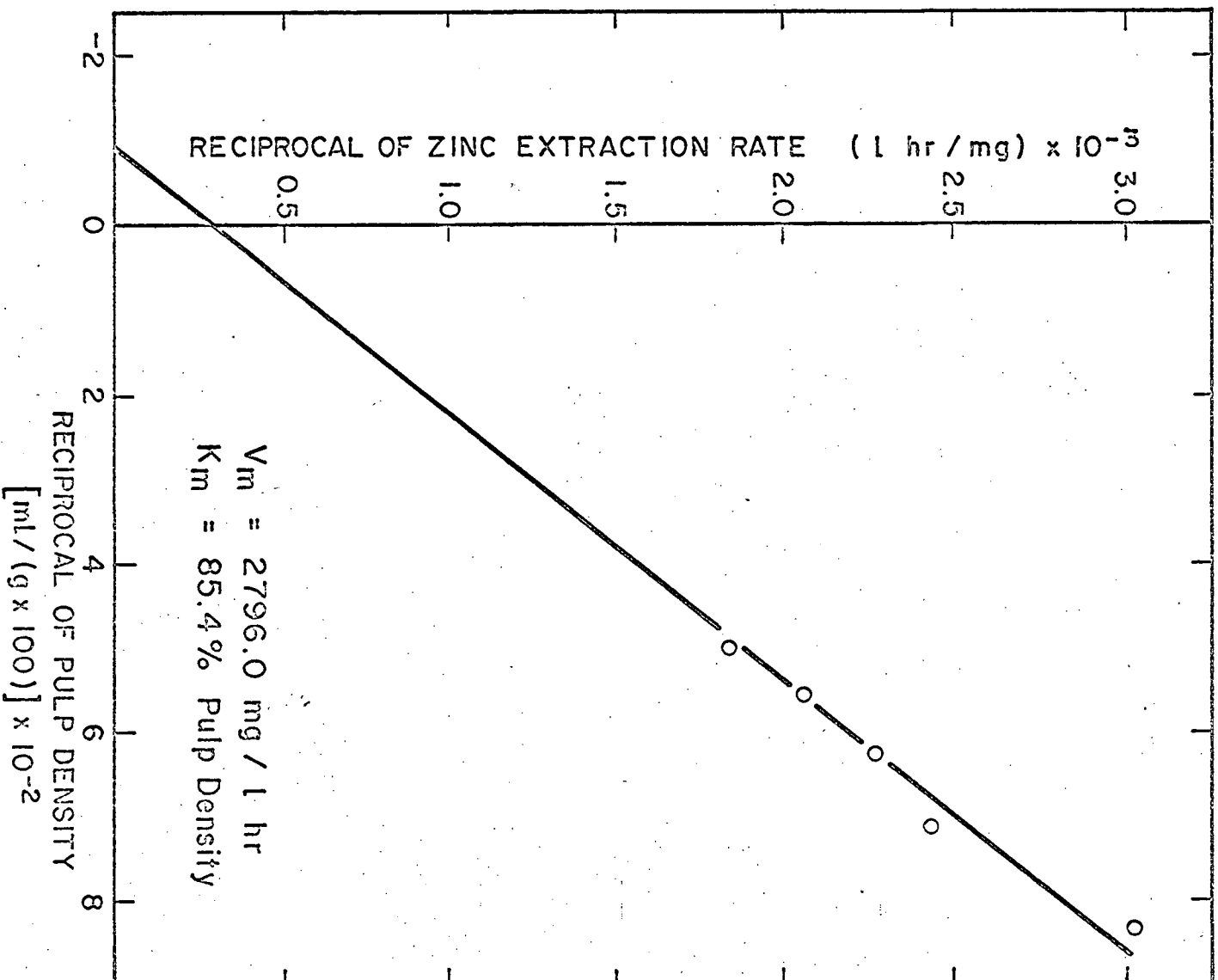
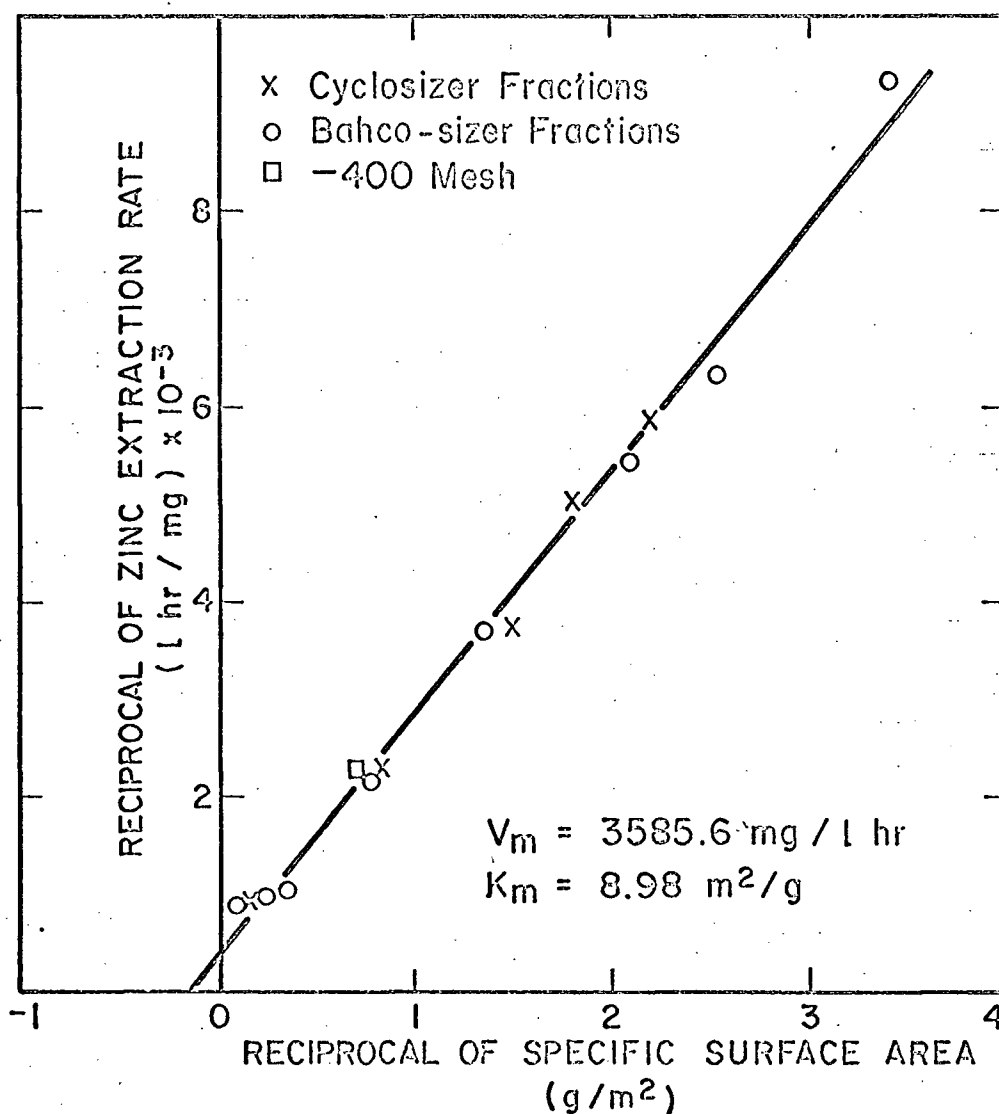


Figure 26
EFFECT OF SPECIFIC SURFACE AREA AT 1.0% CO₂
LINEWEAVER-BURK PLOT



The pulp density data agree well with the data obtained with the subsieve fractions, as shown in Figure 27. Whereas pulp densities necessary to approach maximum rates are impractical excessive grinding of the ore concentrate to increase the specific surface areas may be more practical. This could be combined with a higher pulp density. However, the increased grinding costs would have to be balanced against the improved rate of extraction. The highest extraction rate observed in any of the work reported in this thesis was about 1,160 mg/l hr; achieved with the smallest size fraction having a specific surface area of $6.90 \text{ m}^2/\text{g}$.

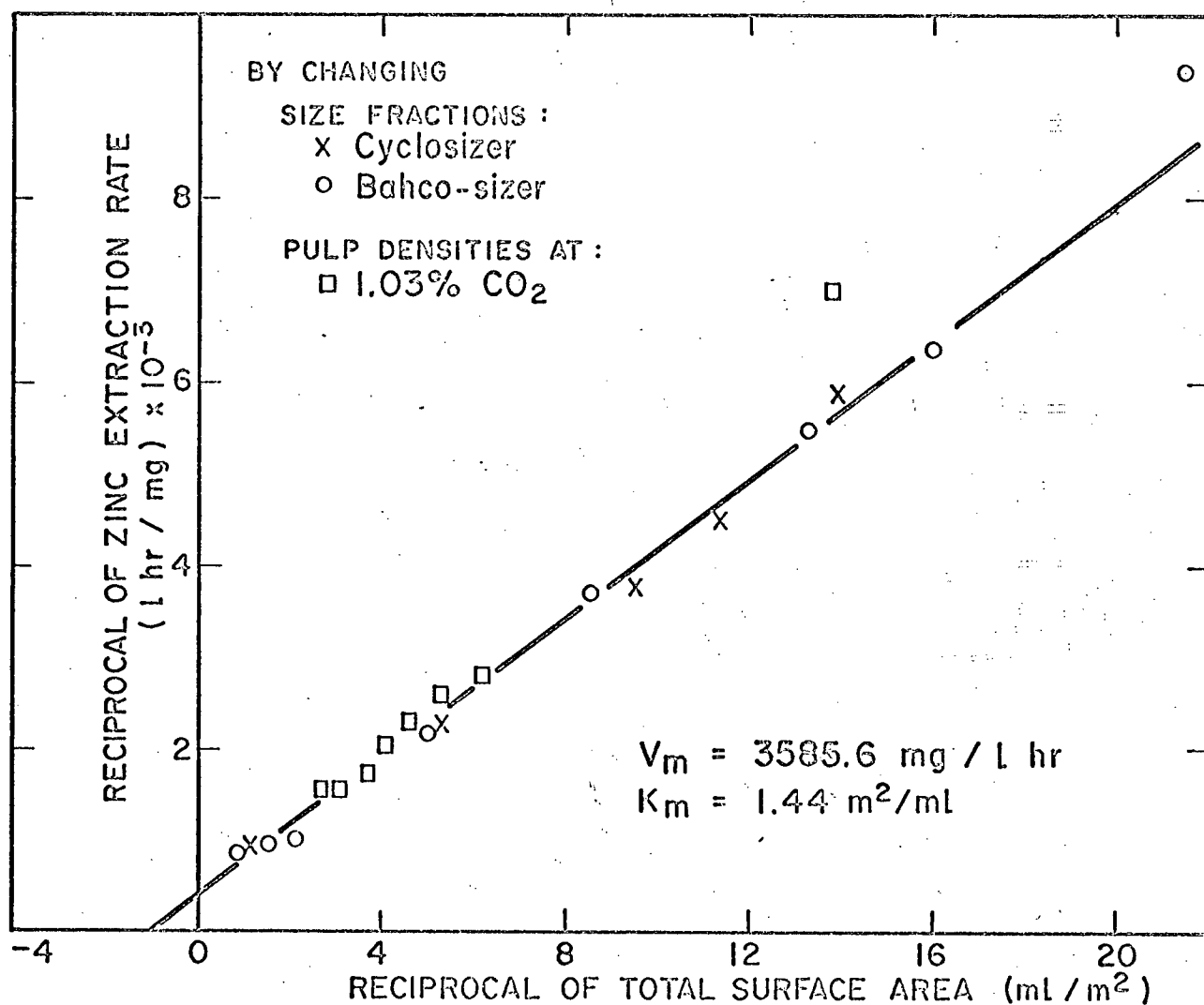
10. Mathematical description of bacterial leach curves

The generalized logistic equation (equation 21) was fitted to leach curves obtained under a variety of conditions. The results are presented in Tables 2 (A and B) to 10 (A and B) of Appendix 2.

The A tables contain the regression coefficients and associated statistical parameters as computed by a multiple regression analysis program⁽²⁰⁵⁾. Experimental data from a particular leach were fed into the program⁽²⁰⁵⁾ and fitted to equation 26. The high values obtained for the multiple correlation coefficients (R value) and for their squares suggest a good fit of the data by the generalized logistic equation. The goodness of this fit can be seen in the B tables where the experimental data are compared to the fitted data. The program reproduced in Table 1 of Appendix 2 was used to compute these B tables, by fitting the equations recorded in each A table. The independent variable is time (hr) and Y the dependent variable is the zinc concentration (mg/l). The maximum deviation observed between fitted and

Figure 27

EFFECT OF TOTAL SURFACE AREA AT 1.0% CO₂
 LINEWEAVER - BURK PLOT



observed values of zinc concentration was 5.5 g/l; agreement between most other data pairs was better.

Thus the generalized logistic equation as expressed by equation 21 can be used to fit a microbiological leach curve. This confirms the conclusions of Edwards⁽¹³⁵⁾ who suggested it for use with bacterial growth curves. It is of some importance that this kind of curve can fit the entire leach curve including the parts corresponding to the lag phase and the stationary phase.

Leaching curves obtained under a variety of conditions were fitted. The results in Table 2 of Appendix 2 were obtained in normal air, those of Tables 3 to 10 with carbon dioxide enriched air and various pulp densities. Under them some were fitted to data obtained with various size fractions (Table 7 and 8) and to data obtained in the larger scale, stirred tank experiments (Tables 9 and 10).

The technological feasibility of a batch microbiological leaching process using T. ferrooxidans for extracting zinc from a high-grade zinc sulfide concentrate has been demonstrated. This study provides useful information about the reaction mechanism involved in the oxidation process and explains certain phenomena, observed in this and other studies, which occur during the biological leaching of insoluble metal sulfides. These factors can be summarized as follows:

a) The zinc extraction rate was strongly dependent on temperature. Best results were observed at around 35°C.

b) The optimum pH was observed using both manual and automatic pH control to be about 2.3. At pH 2.3 the lag time was shortest, the zinc extraction rate was fastest and the final zinc concentration highest.

c) The nutrient concentrations present in the liquid medium⁽³⁷⁾ were found to be adequate and thus should not be rate limiting. Ammonium concentration controlled the final zinc concentration in solution and phosphate concentration controlled the rate of zinc extraction.

d) Zinc extraction rates were related to pulp density, specific surface area of the ore particles, mean diameter of the size fractions, and total surface area of ore per unit volume of leach liquor under various levels of carbon dioxide concentration in air. The results indicated that at low levels of these independent variables the extraction rates were proportional to these independent variables. At higher values of the independent variable the influence on the zinc extraction rates decreased. The use of total surface area permitted combination of

data from experiments on pulp density variations with those obtained using ore particles of various specific surfaces.

The maximum attainable zinc extraction rate increased as the carbon dioxide content of the air used for aeration of the fermentation increased.

Attempts were made to use a form of the Michaelis-Menten or Monod equation to correlate some of these data. This was reasonably successful but it should be considered as an empirical means only of determining maximum extraction rates. Maximum rates of 570 mg/l hr, 2,796 mg/l hr, 3,457 mg/l hr were estimated for carbon dioxide levels of normal air, 0.13%, and 0.23 to 7.92% respectively. Probably these rates are attainable only theoretically.

e) Larger scale experiments have shown that this microbiological leaching technique could produce zinc concentrations of the order of 120 g/l which are suitable for direct electrowinning of zinc. These larger scale stirred tank experiments gave similar zinc extraction rates to those observed in shake flasks for similar conditions. The final zinc concentrations were significantly higher in the stirred tank experiments. The ability of the organism T. ferrooxidans to grow under such high zinc concentration conditions is an important finding.

f) The generalized logistic equation 21 has been shown to be a suitable equation to use in fitting a mathematical expression to a complete leach curve.

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APPENDIX 1.

Experimental data

Table 1A

Effect of temperature

| Temperature °C | Time (hr) | Zinc extractions (g/l) | | |
|-------------------|--------------|------------------------|------|---------|
| | | A | B | Sterile |
| 25 | 0 | 1.62 | 1.54 | 0.196 |
| | 25 | 1.77 | 1.73 | 0.202 |
| | 46.5 | 3.18 | 3.10 | 0.205 |
| | 70.5 | 5.81 | 5.69 | 0.212 |
| | 100.5 | 6.60 | 6.60 | 0.223 |
| | 118.5 | 8.40 | 8.30 | 0.255 |
| | 143 | 9.30 | 9.10 | 0.270 |
| | 166 | 10.4 | 10.6 | 0.283 |
| | 191 | 12.2 | 12.2 | 0.294 |
| Zn-extr. rate | | 58.5 mg/1 hr | | |
| 30 | 0 | 1.40 | 1.50 | 0.178 |
| | 19 | 1.70 | 1.90 | 0.208 |
| | 46 | 4.50 | 4.30 | 0.351 |
| | 67 | 6.10 | 5.90 | 0.368 |
| | 91 | 8.10 | 8.30 | 0.375 |
| | 115 | 10.6 | 10.2 | 0.380 |
| | 140 | 11.8 | 11.8 | 0.385 |
| | 163 | 14.3 | 14.4 | 0.392 |
| Zn-extr. rate | | 83.7 mg/1 hr | | |
| 35 | 0 | 1.45 | 1.45 | 0.161 |
| | 19 | 1.80 | 1.80 | 0.205 |
| | 46 | 5.40 | 5.40 | 0.222 |
| | 67 | 7.50 | 7.70 | 0.399 |
| | 91 | 10.5 | 10.3 | 0.417 |
| | 115 | 13.8 | 13.8 | 0.430 |
| | 140 | 16.5 | 17.4 | 0.432 |
| | 163 | 19.0 | 19.2 | 0.433 |
| Zn-extr. rate | | 121.0 mg/1 hr | | |

Table 1B

Effect of temperature

| Temperature °C | Time (hr) | Zinc extractions (g/l) | | |
|-------------------|--------------|------------------------|------|---------|
| | | A | B | Sterile |
| 40 | 0 | 1.50 | 1.50 | 0.168 |
| | 19 | 1.80 | 1.80 | 0.200 |
| | 46 | 4.90 | 5.10 | 0.390 |
| | 67 | 7.10 | 7.10 | 0.395 |
| | 91 | 10.1 | 10.1 | 0.418 |
| | 115 | 13.1 | 13.3 | 0.434 |
| | 140 | 15.8 | 15.8 | 0.438 |
| | 163 | 18.0 | 18.1 | 0.439 |
| Zn-extr. rate | | 114.5 mg/l hr | | |
| 45 | 0 | 1.62 | 1.62 | 0.180 |
| | 18 | 2.10 | 2.30 | 0.205 |
| | 39 | 2.84 | 2.80 | 0.218 |
| | 63 | 2.92 | 3.04 | 0.219 |
| | 88 | 4.18 | 4.18 | 0.235 |
| | 112 | 4.60 | 4.80 | 0.245 |
| | 135 | 5.66 | 5.82 | 0.255 |
| | 159 | 6.12 | 6.04 | 0.265 |
| | 186 | 6.45 | 6.45 | 0.270 |
| | 208 | 7.15 | 7.35 | 0.278 |
| Zn-extr. rate | | 24.7 mg/l hr | | |

Table 2A

Effect of initial pH

pH = 1.5

| Time (hr) | A | | | B | | | Sterile | |
|---------------------------------|------|---------|---------|------|---------|---------|---------|---------|
| | pH | Zn(g/l) | Fe(g/l) | pH | Zn(g/l) | Fe(g/l) | Zn(g/l) | Fe(g/l) |
| 0 | 1.5 | 1.32 | 0.071 | 1.5 | 1.32 | 0.070 | 0.168 | 0.026 |
| 21 | 1.6 | 2.02 | 0.165 | 1.6 | 2.00 | 0.168 | 0.705 | 0.077 |
| 46 | 1.7 | 2.14 | 0.185 | 1.75 | 2.06 | 0.190 | 0.900 | 0.120 |
| 72 | 1.75 | 2.37 | 0.194 | 1.8 | 2.33 | 0.200 | 1.10 | 0.120 |
| 93 | 1.8 | 2.49 | 0.207 | 1.9 | 2.45 | 0.210 | 1.28 | 0.128 |
| 121 | 1.85 | 2.73 | 0.214 | 1.95 | 2.75 | 0.221 | 1.50 | 0.142 |
| 141 | 1.9 | 2.80 | 0.225 | 2.05 | 2.86 | 0.230 | 1.67 | 0.145 |
| 169 | 1.95 | 2.82 | 0.230 | 2.10 | 2.87 | 0.207 | 1.79 | 0.149 |
| 189 | 2.05 | 3.07 | 0.235 | 2.10 | 3.09 | 0.222 | 1.80 | 0.153 |
| 215 | 2.1 | 3.08 | 0.240 | 2.1 | 3.10 | 0.226 | 1.82 | 0.156 |
| 240 | 2.0 | 3.10 | 0.238 | 2.0 | 3.06 | 0.230 | 1.88 | 0.157 |
| 262 | 1.8 | 3.38 | 0.236 | 1.75 | 3.48 | 0.231 | 1.95 | 0.154 |
| 289 | 1.7 | 7.80 | 0.315 | 1.7 | 8.00 | 0.319 | 1.96 | 0.155 |
| 310 | 1.7 | 10.4 | 0.388 | 1.7 | 10.6 | 0.385 | 1.96 | 0.148 |
| 338 | 1.75 | 12.8 | 0.422 | 1.75 | 13.4 | 0.449 | 1.97 | 0.135 |
| 359 | 1.75 | 14.4 | 0.456 | 1.75 | 14.5 | 0.465 | 1.95 | 0.124 |
| 383 | 1.75 | 16.9 | 0.475 | 1.75 | 17.2 | 0.477 | 1.99 | 0.116 |
| 407 | 1.75 | 18.7 | 0.512 | 1.75 | 18.8 | 0.491 | 2.02 | 0.102 |
| 430 | 1.75 | 18.8 | 0.575 | 1.75 | 19.0 | 0.583 | 2.04 | 0.098 |
| 456 | 1.75 | 18.8 | 0.685 | 1.75 | 19.2 | 0.660 | 2.04 | 0.092 |
| 481 | 1.75 | 18.9 | 0.670 | 1.75 | 19.3 | 0.687 | 2.05 | 0.080 |
| Zinc-extr. rate (mg/l hr) | | 99.7 | | | | | | |

| Time (hr) | A | | | B | | | STERILE | |
|---------------------------|------|---------|---------|------|---------|---------|---------|---------|
| | pH | Zn(g/l) | Fe(g/l) | pH | Zn(g/l) | Fe(g/l) | Zn(g/l) | Fe(g/l) |
| 0 | 2.0 | 1.28 | 0.054 | 2.0 | 1.28 | 0.041 | 0.207 | 0.025 |
| 21 | 2.3 | 2.42 | 0.077 | 2.3 | 2.45 | 0.075 | 0.384 | 0.052 |
| 46 | 2.1 | 5.49 | 0.164 | 2.15 | 5.28 | 0.156 | 0.470 | 0.024 |
| 72 | 2.1 | 9.5 | 0.341 | 2.15 | 9.1 | 0.343 | 0.480 | 0.014 |
| 93 | 2.1 | 11.5 | 0.513 | 2.1 | 11.5 | 0.504 | 0.481 | 0.011 |
| 121 | 2.1 | 14.9 | 0.722 | 2.1 | 14.7 | 0.702 | 0.486 | 0.009 |
| 141 | 2.05 | 16.6 | 0.757 | 2.1 | 16.8 | 0.747 | 0.500 | 0.008 |
| 169 | 2.1 | 18.1 | 0.800 | 2.1 | 18.3 | 0.787 | 0.510 | 0.010 |
| 189 | 2.05 | 20.2 | 0.929 | 2.05 | 20.6 | 0.897 | 0.530 | 0.009 |
| 215 | 2.05 | 20.5 | 0.942 | 2.1 | 20.4 | 0.931 | 0.532 | 0.009 |
| 240 | 2.05 | 20.8 | 0.934 | 2.05 | 20.8 | 0.895 | 0.539 | 0.010 |
| 262 | 2.05 | 20.9 | 0.921 | 2.05 | 20.9 | 0.938 | 0.540 | 0.009 |
| Zn-extr.rate (mg/l hr) | | 106.4 | | | | | | |

Effect of initial pH
pH = 2.0

Table 2B

| Time (hr) | A | | | B | | | Sterile | |
|---------------------------------|-----------|---------|---------|-----------|---------|---------|---------|---------|
| | pH | Zn(g/l) | Fe(g/l) | pH | Zn(g/l) | Fe(g/l) | Zn(g/l) | Fe(g/l) |
| 0 | 2.5 | 1.29 | 0.039 | 2.5 | 1.26 | 0.034 | 0.200 | 0.022 |
| 21 | 2.8 → 2.5 | 1.74 | 0.042 | 3.0 → 2.5 | 1.72 | 0.052 | 0.209 | 0.010 |
| 46 | 2.45 | 3.94 | 0.076 | 2.45 | 4.26 | 0.070 | 0.213 | 0.009 |
| 72 | 2.35 | 8.40 | 0.271 | 2.35 | 8.00 | 0.265 | 0.222 | 0.009 |
| 93 | 2.3 | 10.2 | 0.446 | 2.3 | 9.8 | 0.424 | 0.232 | 0.009 |
| 121 | 2.25 | 13.3 | 0.656 | 2.25 | 13.1 | 0.648 | 0.272 | 0.008 |
| 141 | 2.25 | 14.7 | 0.670 | 2.2 | 14.9 | 0.687 | 0.285 | 0.010 |
| 169 | 2.2 | 16.8 | 0.761 | 2.2 | 17.1 | 0.769 | 0.287 | 0.012 |
| 189 | 2.2 | 17.9 | 0.862 | 2.2 | 18.1 | 0.868 | 0.301 | 0.011 |
| 215 | 2.2 | 18.6 | 0.895 | 2.2 | 18.9 | 0.912 | 0.312 | 0.016 |
| 240 | 2.2 | 19.9 | 0.897 | 2.2 | 20.1 | 0.875 | 0.329 | 0.017 |
| 262 | 2.2 | 20.0 | 0.902 | 2.2 | 20.1 | 0.888 | 0.410 | 0.011 |
| Zinc-extr. rate (mg/l hr) | | 119.5 | | | | | | |

Table 2C
Effect of initial pH
pH = 2.5

Table 2D

Effect of initial pH

pH = 3.0

| Time (hr) | A | | | B | | | Sterile | |
|---------------------------------|-----------|---------|---------|-----------|---------|---------|---------|---------|
| | pH | Zn(g/l) | Fe(g/l) | pH | Zn(g/l) | Fe(g/l) | Zn(g/l) | Fe(g/l) |
| 0 | 3.0 | 1.27 | 0.031 | 3.0 | 1.26 | 0.089 | 0.202 | 0.021 |
| 21 | 3.7 → 3.0 | 1.49 | 0.006 | 3.8 → 3.0 | 1.36 | 0.007 | 0.205 | 0.008 |
| 46 | 3.0 | 1.55 | 0.008 | 3.0 | 1.42 | 0.008 | 0.215 | 0.008 |
| 72 | 3.0 | 1.85 | 0.011 | 3.0 | 1.84 | 0.011 | 0.229 | 0.008 |
| 93 | 2.9 | 2.90 | 0.033 | 2.9 | 2.72 | 0.027 | 0.236 | 0.009 |
| 121 | 2.6 | 7.20 | 0.268 | 2.6 | 7.6 | 0.256 | 0.264 | 0.007 |
| 141 | 2.35 | 10.4 | 0.312 | 2.4 | 10.0 | 0.332 | 0.270 | 0.010 |
| 169 | 2.3 | 13.2 | 0.381 | 2.3 | 13.4 | 0.401 | 0.274 | 0.010 |
| 189 | 2.2 | 15.1 | 0.465 | 2.2 | 15.2 | 0.475 | 0.278 | 0.009 |
| 215 | 2.15 | 17.3 | 0.519 | 2.15 | 17.8 | 0.549 | 0.280 | 0.010 |
| 240 | 2.15 | 17.9 | 0.521 | 2.15 | 18.2 | 0.552 | 0.291 | 0.011 |
| 262 | 2.1 | 18.3 | 0.548 | 2.1 | 18.4 | 0.590 | 0.294 | 0.008 |
| 289 | 2.1 | 18.9 | 0.542 | 2.1 | 19.1 | 0.553 | 0.314 | 0.007 |
| 310 | 2.1 | 19.4 | 0.538 | 2.1 | 19.6 | 0.527 | 0.316 | 0.010 |
| 338 | 2.1 | 19.7 | 0.462 | 2.1 | 19.6 | 0.447 | 0.318 | 0.011 |
| 359 | 2.1 | 19.7 | 0.388 | 2.1 | 19.7 | 0.375 | 0.319 | 0.014 |
| Zinc-extr. rate (mg/1 hr) | | | | 116.3 | | | | |

Table 2E

Effect of initial pH

pH = 3.5

| Time (hr) | A | | | B | | | Sterile | |
|---------------------------------|-------------|---------|---------|-------------|---------|---------|---------|---------|
| | pH | Zn(g/l) | Fe(g/l) | pH | Zn(g/l) | Fe(g/l) | Zn(g/l) | Fe(g/l) |
| 0 | 3.5 | 1.23 | 0.029 | 3.5 | 1.24 | 0.025 | 0.174 | 0.013 |
| 21 | 3.8 - >3.5 | 1.37 | 0.007 | 3.8 - >3.5 | 1.37 | 0.007 | 0.190 | 0.006 |
| 46 | 3.75 - >3.5 | 1.43 | 0.008 | 3.75 - >3.5 | 1.42 | 0.008 | 0.196 | 0.008 |
| 72 | 3.75 - >3.5 | 1.53 | 0.008 | 3.75 - >3.5 | 1.54 | 0.007 | 0.220 | 0.008 |
| 93 | 3.7 - >3.5 | 1.62 | 0.013 | 3.7 - >3.5 | 1.70 | 0.012 | 0.240 | 0.010 |
| 121 | 3.7 - >3.5 | 1.79 | 0.008 | 3.7 - >3.5 | 1.78 | 0.009 | 0.261 | 0.008 |
| 141 | 3.85 - >3.5 | 1.84 | 0.012 | 3.8 - >3.5 | 1.87 | 0.011 | 0.269 | 0.009 |
| 169 | 3.75 - >3.5 | 1.92 | 0.017 | 3.75 - >3.5 | 1.96 | 0.014 | 0.272 | 0.010 |
| 189 | 3.45 | 2.61 | 0.020 | 3.45 | 2.73 | 0.025 | 0.286 | 0.010 |
| 215 | 2.85 | 4.9 | 0.098 | 2.85 | 5.20 | 0.112 | 0.287 | 0.011 |
| 240 | 2.55 | 8.0 | 0.274 | 2.50 | 8.1 | 0.291 | 0.289 | 0.012 |
| 262 | 2.4 | 10.8 | 0.363 | 2.4 | 11.3 | 0.364 | 0.290 | 0.008 |
| 289 | 2.3 | 14.0 | 0.439 | 2.3 | 15.4 | 0.445 | 0.304 | 0.009 |
| 310 | 2.2 | 16.1 | 0.452 | 2.2 | 16.2 | 0.461 | 0.305 | 0.009 |
| 338 | 2.2 | 17.3 | 0.486 | 2.2 | 17.6 | 0.488 | 0.324 | 0.015 |
| 359 | 2.15 | 18.5 | 0.554 | 2.15 | 18.4 | 0.537 | 0.341 | 0.012 |
| 383 | 2.1 | 18.9 | 0.562 | 2.1 | 19.0 | 0.541 | 0.345 | 0.015 |
| 407 | 2.1 | 19.2 | 0.584 | 2.1 | 19.3 | 0.531 | 0.381 | 0.016 |
| 430 | 2.05 | 19.3 | 0.402 | 2.05 | 19.5 | 0.408 | 0.401 | 0.010 |
| 456 | 2.05 | 19.3 | 0.365 | 2.05 | 19.6 | 0.354 | 0.407 | 0.012 |
| 481 | 2.05 | 19.4 | 0.315 | 2.05 | 19.6 | 0.330 | 0.432 | 0.015 |
| Zinc-extr. rate (mg/l hr) | | 108.4 | | | | | | |

Table 2F
Effect of initial pH
pH = 4.0

| Time (hr) | A | | | B | | | Sterile | |
|----------------------------|------------|---------|---------|-----------|---------|---------|---------|---------|
| | pH | Zn(g/l) | Fe(g/l) | pH | Zn(g/l) | Fe(g/l) | Zn(g/l) | Fe(g/l) |
| 0 | 4.00 | 1.23 | 0.029 | 4.00 | 1.24 | 0.025 | 0.185 | 0.021 |
| 21 | 3.85 | 1.37 | 0.006 | 3.85 | 1.41 | 0.007 | 0.192 | 0.006 |
| 46 | 3.80 | 1.42 | 0.007 | 3.80 | 1.40 | 0.007 | 0.194 | 0.008 |
| 72 | 3.75 | 1.54 | 0.008 | 3.80 | 1.47 | 0.009 | 0.200 | 0.009 |
| 93 | 3.80 | 1.59 | 0.012 | 3.80 | 1.56 | 0.009 | 0.204 | 0.011 |
| 121 | 3.80 | 1.74 | 0.006 | 3.80 | 1.70 | 0.009 | 0.233 | 0.008 |
| 141 | 3.85 | 1.84 | 0.010 | 3.85 | 1.82 | 0.011 | 0.240 | 0.009 |
| 169 | 3.95 | 1.91 | 0.012 | 3.95 | 1.84 | 0.014 | 0.262 | 0.011 |
| 189 | 4.05->4.00 | 1.98 | 0.016 | 4.15->4.0 | 1.92 | 0.012 | 0.264 | 0.009 |
| 215 | 4.25->4.0 | 1.97 | 0.022 | 4.25->4.0 | 1.96 | 0.016 | 0.268 | 0.010 |
| 240 | 4.35->4.0 | 1.96 | 0.023 | 4.35->4.0 | 1.97 | 0.019 | 0.269 | 0.012 |
| 262 | 4.30->4.0 | 1.97 | 0.026 | 4.30->4.0 | 1.98 | 0.021 | 0.270 | 0.008 |
| 289 | 4.30->4.0 | 2.04 | 0.026 | 4.30->4.0 | 2.02 | 0.026 | 0.291 | 0.009 |
| 310 | 4.30->4.0 | 2.06 | 0.029 | 4.30->4.0 | 2.07 | 0.029 | 0.310 | 0.012 |
| 338 | 4.20->4.0 | 2.09 | 0.030 | 4.20->4.0 | 2.09 | 0.028 | 0.322 | 0.009 |
| 359 | 3.80 | 2.10 | 0.038 | 3.8 | 2.08 | 0.040 | 0.341 | 0.011 |
| 383 | 3.7 | 2.14 | 0.036 | 3.8 | 2.18 | 0.042 | 0.364 | 0.013 |
| 407 | 3.7 | 3.87 | 0.074 | 3.8 | 3.92 | 0.068 | 0.394 | 0.017 |
| 430 | 3.1 | 6.7 | 0.240 | 3.4 | 6.5 | 0.198 | 0.411 | 0.008 |
| 456 | 2.6 | 9.9 | 0.310 | 2.7 | 9.8 | 0.305 | 0.435 | 0.010 |
| 481 | 2.3 | 11.7 | 0.488 | 2.5 | 11.9 | 0.435 | 0.472 | 0.011 |
| 505 | 2.3 | 14.3 | 0.557 | 2.3 | 14.5 | 0.514 | 0.480 | 0.013 |
| 526 | 2.2 | 16.4 | 0.538 | 2.2 | 16.2 | 0.527 | 0.484 | 0.013 |
| 552 | 2.2 | 17.7 | 0.556 | 2.2 | 17.8 | 0.541 | 0.488 | 0.012 |
| 557 | 2.2 | 18.0 | 0.537 | 2.2 | 18.0 | 0.532 | 0.492 | 0.012 |
| Zn-extr. rate (mg/l hr) | | 96.9 | | | | | | |

Table 3A

Effect of constant pH

| Time (hr) | pH=1.5 Zn(g/l) | |
|--------------|-------------------|------|
| | A | B |
| 0 | 1.83 | 1.81 |
| 24 | 2.13 | 2.18 |
| 46 | 2.76 | 2.74 |
| 69 | 3.24 | 3.30 |
| 92 | 3.91 | 3.98 |
| 117 | 4.5 | 4.4 |
| 141 | 6.8 | 6.9 |
| 165 | 9.7 | 9.9 |
| 189 | 11.3 | 11.5 |
| 213 | 13.4 | 13.3 |
| 243 | 17.0 | 16.8 |
| 265 | 19.5 | 19.7 |
| 288 | 19.9 | 19.8 |
| 311 | 19.7 | 19.9 |
| 340 | 19.8 | 19.8 |
| Zn-extr.rate | 99.2 mg/l hr | |

| Time (hr) | pH=2.0 Zn(g/l) | pH=2.5 Zn(g/l) |
|---------------------------|-------------------|-------------------|
| | Zn(g/l) | Zn(g/l) |
| 0 | 1.34 | 1.35 |
| 21 | 6.4 | 6.5 |
| 46 | 14.3 | 14.8 |
| 73 | 24.4 | 24.9 |
| 93 | 31.2 | 31.1 |
| 116 | 40.1 | 40.3 |
| 141 | 50.6 | 50.8 |
| 164 | 59.1 | 60.4 |
| 195 | 67.4 | 68.2 |
| 217 | 69.6 | 69.9 |
| 238 | 70.3 | 71.4 |
| Zn-extr.rate (mg/l hr) | 369.6 | 375.9 |

Table 3B

Effect of constant pH

| Time (hr) | pH=3.0 Zn(g/l) |
|---------------------------|-------------------|
| 0 | 1.61 |
| 17 | 2.07 |
| 43 | 3.42 |
| 69 | 13.0 |
| 96 | 23.2 |
| 117 | 30.4 |
| 141 | 40.0 |
| 168 | 50.2 |
| 187 | 53.6 |
| 212 | 54.0 |
| 236 | 54.2 |
| 259 | 54.1 |
| 290 | 54.3 |
| 309 | 54.2 |
| 321 | 54.4 |
| Zn-extr.rate (mg/l hr) | 373.7 |

| Time (hr) | pH=3.5 Zn(g/l) |
|---------------------------|-------------------|
| 0 | 1.65 |
| 17 | 1.82 |
| 43 | 1.96 |
| 69 | 2.02 |
| 96 | 3.18 |
| 122 | 12.8 |
| 149 | 22.2 |
| 170 | 30.5 |
| 194 | 38.2 |
| 221 | 47.1 |
| 240 | 48.3 |
| 265 | 49.0 |
| 289 | 49.2 |
| 312 | 49.4 |
| 343 | 49.3 |
| 362 | 49.5 |
| Zn-extr.rate (mg/l hr) | 326.8 |

| Time (hr) | pH=4.0 Zn(g/l) |
|---------------------------|-------------------|
| 0 | 1.60 |
| 17 | 1.74 |
| 43 | 1.88 |
| 70 | 1.91 |
| 91 | 1.97 |
| 115 | 2.06 |
| 142 | 3.88 |
| 169 | 8.9 |
| 190 | 14.8 |
| 214 | 21.0 |
| 241 | 28.3 |
| 260 | 33.4 |
| 285 | 35.6 |
| 309 | 36.2 |
| 321 | 36.3 |
| 345 | 36.4 |
| Zn-extr.rate (mg/l hr) | 255.1 |

Table 4

Effect of nutrient concentrations

| Time (hr) | ZINC EXTRACTIONS (g/l) ABSENT FROM THE BASAL MEDIUM (37): | | | | | |
|---------------------------|--|------|---------------------------------|------|--|------|
| | (NH ₄) ₂ SO ₄ | | K ₂ HPO ₄ | | KCl, MgSO ₄ , Ca(NO ₃) ₂ | |
| | A | B | A | B | A | B |
| 0 | 2.42 | 2.45 | 2.48 | 2.50 | 2.48 | 2.52 |
| 23 | 2.59 | 2.52 | 2.52 | 2.54 | 2.52 | 2.52 |
| 50 | 2.82 | 2.79 | 2.77 | 2.82 | 6.15 | 6.26 |
| 73 | 6.2 | 6.3 | 3.70 | 3.60 | 12.4 | 12.6 |
| 101 | 14.2 | 14.4 | 4.80 | 4.70 | 21.0 | 21.7 |
| 123 | 19.6 | 19.5 | 8.1 | 8.2 | 29.4 | 29.6 |
| 143 | 24.3 | 24.6 | 11.3 | 11.4 | 36.5 | 36.2 |
| 167 | 26.2 | 26.4 | 15.6 | 15.2 | 45.0 | 45.1 |
| 192 | 26.5 | 26.6 | 19.5 | 19.8 | 52.8 | 53.6 |
| 216 | 26.6 | 26.6 | 24.7 | 25.0 | 63.0 | 62.8 |
| 246 | 26.8 | 27.0 | 29.2 | 29.7 | 68.8 | 69.2 |
| 273 | 27.5 | 27.3 | 33.5 | 34.0 | 69.3 | 69.6 |
| Zn-extr.rate (mg/l hr) | 258.9 | | 171.8 | | 351.7 | |

Table 5A

Effect of ammonium concentration

| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | |
|---------------------------|---|------|---|------|---|------|
| | $(\text{NH}_4)_2\text{SO}_4 = 0.75\text{g/l}$ | | $(\text{NH}_4)_2\text{SO}_4 = 1.50 \text{ g/l}$ | | $(\text{NH}_4)_2\text{SO}_4 = 2.25\text{g/l}$ | |
| | A | B | A | B | A | B |
| 0 | 1.94 | 1.89 | 1.96 | 1.95 | 1.91 | 1.96 |
| 19 | 2.28 | 2.30 | 2.41 | 2.49 | 2.36 | 2.37 |
| 43 | 7.0 | 6.9 | 7.2 | 7.2 | 7.4 | 7.5 |
| 68 | 15.2 | 15.4 | 16.6 | 16.3 | 16.9 | 17.0 |
| 95 | 22.3 | 22.7 | 25.7 | 25.8 | 26.2 | 26.3 |
| 119 | 31.7 | 31.8 | 34.2 | 33.9 | 34.9 | 35.2 |
| 140 | 36.6 | 36.6 | 41.9 | 42.1 | 42.8 | 42.6 |
| 164 | 38.8 | 38.7 | 51.0 | 50.3 | 51.6 | 51.2 |
| 187 | 40.9 | 40.8 | 54.5 | 54.7 | 60.1 | 59.7 |
| 212 | 40.9 | 41.0 | 57.6 | 58.0 | 62.4 | 62.6 |
| 235 | 41.0 | 41.1 | 57.8 | 57.9 | 62.9 | 62.7 |
| Zn-extr.rate (mg/l hr) | 319.5 | | 357.5 | | 363.3 | |

Table 5B
Effect of ammonium concentration

| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | |
|---------------------------|---|------|---|------|---|------|
| | $(\text{NH}_4)_2\text{SO}_4 = 3.00\text{g/l}$ | | $(\text{NH}_4)_2\text{SO}_4 = 3.75\text{g/l}$ | | $(\text{NH}_4)_2\text{SO}_4 = 4.50\text{g/l}$ | |
| | A | B | A | B | A | B |
| 0 | 1.95 | 1.95 | 1.94 | 1.96 | 1.96 | 1.94 |
| 19 | 2.21 | 2.20 | 2.42 | 2.44 | 2.44 | 2.39 |
| 43 | 7.4 | 7.6 | 7.5 | 7.8 | 7.9 | 7.8 |
| 68 | 17.0 | 17.2 | 17.1 | 17.3 | 17.2 | 17.0 |
| 95 | 25.9 | 26.4 | 26.2 | 26.0 | 26.1 | 26.6 |
| 119 | 35.3 | 35.1 | 35.6 | 35.4 | 35.4 | 35.7 |
| 140 | 42.7 | 42.5 | 42.6 | 42.6 | 43.0 | 42.4 |
| 164 | 52.0 | 51.6 | 51.8 | 51.9 | 52.0 | 51.7 |
| 187 | 60.8 | 60.7 | 60.2 | 60.5 | 60.4 | 60.7 |
| 212 | 63.2 | 66.0 | 64.7 | 65.0 | 63.8 | 64.2 |
| 235 | 63.6 | 65.8 | 67.8 | 68.2 | 67.9 | 67.8 |
| Zn-extr.rate (mg/l hr) | 367.0 | | 364.5 | | 362.1 | |

Table 5C

Effect of ammonium concentration

| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | | | |
|---------------------------|---|------|--|------|--|------|---|------|
| | $(\text{NH}_4)_2\text{SO}_4=6.00\text{g/l}$ | | $(\text{NH}_4)_2\text{SO}_4= 7.50\text{g/l}$ | | $(\text{NH}_4)_2\text{SO}_4= 9.00\text{g/l}$ | | $(\text{NH}_4)_2\text{SO}_4= 10.50\text{g/l}$ | |
| | A | B | A | B | A | B | A | B |
| 0 | 1.93 | 1.91 | 1.94 | 1.93 | 1.94 | 1.92 | 1.92 | 1.94 |
| 19 | 2.32 | 2.32 | 2.40 | 2.41 | 2.36 | 2.36 | 2.32 | 2.38 |
| 43 | 7.9 | 7.9 | 8.0 | 8.4 | 8.2 | 8.0 | 7.9 | 8.0 |
| 68 | 17.4 | 17.1 | 17.6 | 17.3 | 17.4 | 17.6 | 17.3 | 17.7 |
| 95 | 26.0 | 26.3 | 26.5 | 26.6 | 26.9 | 26.3 | 26.8 | 26.7 |
| 119 | 35.8 | 35.6 | 35.7 | 35.9 | 35.3 | 35.8 | 35.5 | 35.9 |
| 140 | 43.1 | 42.7 | 43.0 | 43.2 | 43.1 | 43.0 | 43.3 | 43.3 |
| 164 | 51.9 | 51.8 | 51.7 | 51.6 | 52.4 | 52.3 | 52.4 | 52.5 |
| 187 | 60.6 | 60.4 | 60.7 | 60.8 | 60.3 | 60.9 | 60.5 | 60.7 |
| 212 | 64.3 | 64.7 | 64.8 | 64.5 | 64.2 | 64.4 | 64.5 | 64.5 |
| 235 | 68.4 | 68.2 | 68.5 | 68.5 | 68.8 | 68.5 | 68.9 | 69.4 |
| Zn-extr.rate (mg/l hr) | 364.3 | | 362.5 | | 364.1 | | 365.3 | |

Table 6A

Effect of phosphate concentration

| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | |
|---------------------------|--|------|--|------|--|------|
| | K ₂ HPO ₄ = 0.1g/l | | K ₂ HPO ₄ = 0.2g/l | | K ₂ HPO ₄ = 0.3g/l | |
| | A | B | A | B | A | B |
| 0 | 0.63 | 0.65 | 0.62 | 0.66 | 0.71 | 0.68 |
| 23 | 1.48 | 1.50 | 1.28 | 1.40 | 1.44 | 1.56 |
| 46 | 1.96 | 1.93 | 3.90 | 3.60 | 4.7 | 4.8 |
| 72 | 4.20 | 4.30 | 8.0 | 8.2 | 12.9 | 12.6 |
| 96 | 6.7 | 6.5 | 12.9 | 12.8 | 20.5 | 20.7 |
| 117 | 8.8 | 8.7 | 16.8 | 16.8 | 27.4 | 27.9 |
| 147 | 11.7 | 11.4 | 22.4 | 22.1 | 36.9 | 36.5 |
| 169 | 13.8 | 14.0 | 26.5 | 26.6 | 44.0 | 39.8 |
| 190 | 16.7 | 16.9 | 30.4 | 30.2 | 50.6 | 50.2 |
| 214 | 19.0 | 18.7 | 34.8 | 34.9 | 58.1 | 58.5 |
| 241 | 21.8 | 22.0 | 39.9 | 39.7 | 62.5 | 62.9 |
| 261 | 23.8 | 23.6 | 43.7 | 43.6 | 66.8 | 67.4 |
| 292 | 26.7 | 26.9 | 48.9 | 49.4 | 68.7 | 68.3 |
| Zn-extr.rate (mg/1 hr) | 104.1 | | 186.9 | | 315.8 | |

Table 6B

Effect of phosphate concentration

| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | |
|----------------------------|------------------------|------|---------------------|------|----------------------|------|
| | $K_2HPO_4 = 0.4g/l$ | | $K_2HPO_4 = 0.5g/l$ | | $K_2HPO_4 = 0.75g/l$ | |
| | A | B | A | B | A | B |
| 0 | 0.66 | 0.72 | 0.66 | 0.63 | 0.63 | 0.62 |
| 23 | 1.46 | 1.52 | 1.48 | 1.43 | 1.41 | 1.44 |
| 46 | 4.9 | 4.9 | 5.2 | 5.4 | 5.0 | 5.1 |
| 72 | 14.1 | 14.2 | 14.8 | 14.4 | 14.9 | 14.6 |
| 96 | 22.6 | 22.3 | 23.7 | 23.8 | 23.9 | 24.1 |
| 117 | 30.2 | 30.0 | 31.5 | 31.9 | 31.3 | 31.6 |
| 147 | 40.9 | 41.0 | 42.6 | 42.4 | 42.5 | 42.4 |
| 169 | 48.7 | 49.0 | 50.8 | 50.5 | 50.7 | 50.6 |
| 190 | 55.5 | 55.8 | 58.1 | 58.3 | 57.9 | 58.1 |
| 214 | 61.2 | 61.1 | 63.2 | 63.6 | 62.9 | 63.3 |
| 241 | 64.5 | 64.8 | 66.7 | 66.5 | 67.3 | 67.0 |
| 261 | 67.4 | 67.3 | 68.0 | 68.3 | 68.2 | 68.5 |
| 292 | 68.5 | 68.6 | 68.3 | 68.7 | 69.0 | 68.7 |
| Zn-extr. rate (mg/l hr) | 354.8 | | 369.7 | | 368.0 | |

Table 6C

Effect of phosphate concentration

| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | | | |
|---------------------------|---|------|---|------|---|------|---|------|
| | K ₂ HPO ₄ = 1.00g/l | | K ₂ HPO ₄ = 1.25g/l | | K ₂ HPO ₄ = 1.50g/l | | K ₂ HPO ₄ = 1.75g/l | |
| | A | B | A | B | A | B | A | B |
| 0 | 0.66 | 0.63 | 0.63 | 0.69 | 0.68 | 0.66 | 0.67 | 0.68 |
| 23 | 1.45 | 1.44 | 1.46 | 1.46 | 1.46 | 1.48 | 1.50 | 1.47 |
| 46 | 4.8 | 4.6 | 4.9 | 5.3 | 4.9 | 4.8 | 5.2 | 5.3 |
| 72 | 14.3 | 14.5 | 14.7 | 14.9 | 14.2 | 14.6 | 14.5 | 14.3 |
| 96 | 23.6 | 23.3 | 24.8 | 24.2 | 24.5 | 24.3 | 24.5 | 24.7 |
| 117 | 31.8 | 31.4 | 31.3 | 31.4 | 31.2 | 31.1 | 31.2 | 31.0 |
| 147 | 42.3 | 43.0 | 42.3 | 42.6 | 42.5 | 42.3 | 42.2 | 42.5 |
| 169 | 50.2 | 50.4 | 50.7 | 50.4 | 50.3 | 50.7 | 50.5 | 50.5 |
| 190 | 57.7 | 57.3 | 57.7 | 57.8 | 56.9 | 57.6 | 57.8 | 58.0 |
| 214 | 62.7 | 63.5 | 63.1 | 63.0 | 62.9 | 63.4 | 63.2 | 62.8 |
| 241 | 66.5 | 67.1 | 67.2 | 67.1 | 66.5 | 67.2 | 66.9 | 66.7 |
| 261 | 67.3 | 67.4 | 68.3 | 69.0 | 67.4 | 67.7 | 67.5 | 67.3 |
| 292 | 68.1 | 68.4 | 68.8 | 69.2 | 68.5 | 68.7 | 69.2 | 68.7 |
| Zn-extr.rate (mg/1 hr) | 368.5 | | 365.6 | | 365.6 | | 366.3 | |

Table 7A

Effect of pulp density

Pulp density = 1%

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 1.34 | 1.34 | 0.050 |
| 13 | 1.77 | 1.74 | 0.155 |
| 37 | 2.24 | 2.19 | 0.239 |
| 61 | 2.38 | 2.31 | 0.240 |
| 85 | 2.35 | 2.45 | 0.242 |
| 109 | 2.68 | 2.71 | 0.258 |
| 134 | 2.98 | 2.95 | 0.305 |
| 158 | 3.20 | 3.25 | 0.338 |
| Zn-extr.rate (mg/l hr) | 8.5 | | |

Pulp density = 2%

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 1.41 | 1.31 | 0.069 |
| 13 | 2.04 | 2.05 | 0.174 |
| 37 | 2.68 | 2.62 | 0.250 |
| 61 | 3.40 | 3.32 | 0.320 |
| 85 | 4.60 | 4.65 | 0.346 |
| 109 | 5.40 | 5.60 | 0.387 |
| 134 | 6.40 | 6.20 | 0.412 |
| 158 | 7.20 | 7.30 | 0.428 |
| Zn-extr.rate (mg/l hr) | 35.8 | | |

Table 7B

Effect of pulp density

Pulp density = 4%

Pulp density = 5.3%

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 1.40 | 1.38 | 0.076 |
| 13 | 2.22 | 2.19 | 0.231 |
| 37 | 4.38 | 4.26 | 0.395 |
| 61 | 8.1 | 7.7 | 0.432 |
| 85 | 9.8 | 9.9 | 0.496 |
| 109 | 11.3 | 11.2 | 0.518 |
| 134 | 13.1 | 13.3 | 0.552 |
| 158 | 15.5 | 15.9 | 0.574 |
| Zn-extr.rate (mg/l hr) | 88.6 | | |

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 1.39 | 1.40 | 0.163 |
| 24 | 2.42 | 2.44 | 0.179 |
| 49 | 5.4 | 5.4 | 0.218 |
| 70 | 7.7 | 7.5 | 0.384 |
| 94 | 10.5 | 10.3 | 0.397 |
| 118 | 13.8 | 13.8 | 0.412 |
| 143 | 17.4 | 17.5 | 0.427 |
| 166 | 19.0 | 19.2 | 0.436 |
| Zn-extr.rate (mg/l hr) | 121.1 | | |

Table 7C

Effect of pulp density

Pulp density = 6%

Pulp density = 8%

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 1.44 | 1.48 | 0.156 |
| 13 | 2.36 | 2.31 | 0.277 |
| 37 | 6.48 | 6.96 | 0.297 |
| 61 | 10.6 | 10.9 | 0.317 |
| 85 | 13.9 | 13.8 | 0.385 |
| 109 | 16.5 | 16.9 | 0.473 |
| 134 | 19.6 | 19.8 | 0.594 |
| 158 | 22.2 | 22.1 | 0.682 |
| Zn-extr.rate (mg/l hr) | 126.0 | | |

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 1.72 | 1.65 | 0.201 |
| 13 | 2.20 | 2.16 | 0.358 |
| 37 | 6.8 | 6.9 | 0.492 |
| 61 | 13.5 | 13.1 | 0.577 |
| 85 | 17.5 | 17.8 | 0.653 |
| 109 | 21.5 | 21.6 | 0.681 |
| 134 | 26.6 | 27.1 | 0.688 |
| 158 | 30.9 | 31.2 | 0.699 |
| Zn-extr.rate (mg/l hr) | 195.2 | | |

Table 7D

Effect of pulp density

Pulp density = 10%

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 1.64 | 1.63 | 0.252 |
| 13 | 2.30 | 2.12 | 0.374 |
| 37 | 7.8 | 8.3 | 0.425 |
| 61 | 17.4 | 18.2 | 0.534 |
| 85 | 20.9 | 21.0 | 0.612 |
| 109 | 27.2 | 27.1 | 0.704 |
| 134 | 33.6 | 33.9 | 0.763 |
| 158 | 40.2 | 40.4 | 0.802 |
| Zn-extr.rate (mg/l hr) | 253.9 | | |

Pulp density = 12%

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 2.00 | 2.03 | 0.56 |
| 19 | 2.68 | 2.56 | 0.58 |
| 30 | 4.08 | 4.02 | 0.59 |
| 44 | 8.2 | 8.3 | 0.62 |
| 53 | 9.3 | 9.2 | 0.63 |
| 67 | 15.2 | 15.0 | 0.66 |
| 77 | 18.3 | 18.4 | 0.68 |
| 101 | 25.8 | 25.9 | 0.69 |
| 116 | 30.5 | 30.3 | 0.71 |
| 143 | 35.6 | 35.0 | 0.73 |
| 163 | 39.7 | 39.4 | 0.78 |
| 188 | 45.9 | 48.8 | 0.81 |
| 212 | 50.3 | 50.4 | 0.83 |
| 241 | 50.6 | 50.9 | 0.87 |
| 262 | 51.2 | 51.1 | 0.93 |
| 285 | 51.4 | 51.5 | 0.96 |
| 316 | 51.8 | 51.6 | 1.05 |
| 477 | | 52.3 | |
| Zn-extr.rate (mg/l hr) | 312.5 | | |

Table 7E

Effect of pulp density

Pulp density = 14%

Pulp density = 16%

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 1.97 | 2.03 | 0.50 |
| 19 | 2.58 | 2.57 | 0.54 |
| 30 | 4.16 | 4.34 | 0.56 |
| 44 | 8.5 | 8.4 | 0.68 |
| 53 | 11.6 | 11.7 | 0.70 |
| 67 | 16.4 | 16.2 | 0.72 |
| 77 | 19.5 | 19.8 | 0.75 |
| 101 | 28.6 | 28.5 | 0.76 |
| 116 | 33.0 | 33.2 | 0.78 |
| 143 | 41.9 | 41.1 | 0.79 |
| 163 | 44.2 | 44.9 | 0.80 |
| 188 | 50.0 | 49.2 | 0.82 |
| 212 | 51.2 | 51.4 | 0.83 |
| 241 | 51.9 | 52.2 | 0.89 |
| 262 | 52.5 | 52.8 | 0.96 |
| 285 | 53.0 | 53.2 | 1.02 |
| 316 | 53.8 | 54.0 | 1.09 |
| 477 | | 54.7 | |
| Zn-extr.rate (mg/l hr) | 335.4 | | |

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 2.10 | 2.15 | 0.57 |
| 19 | 2.58 | 2.60 | 0.61 |
| 30 | 4.2 | 4.3 | 0.64 |
| 44 | 9.1 | 9.0 | 0.69 |
| 53 | 12.4 | 12.3 | 0.74 |
| 67 | 17.0 | 17.1 | 0.77 |
| 77 | 20.4 | 20.4 | 0.81 |
| 101 | 29.9 | 29.8 | 0.84 |
| 116 | 35.3 | 35.1 | 0.89 |
| 143 | 42.3 | 41.6 | 0.90 |
| 163 | 49.8 | 50.4 | 0.91 |
| 188 | 57.4 | 58.2 | 0.93 |
| 212 | 59.4 | 60.1 | 0.96 |
| 241 | 61.9 | 61.7 | 1.04 |
| 262 | 62.6 | 62.8 | 1.12 |
| 285 | 63.2 | 63.3 | 1.17 |
| 316 | 63.6 | 63.5 | 1.20 |
| 477 | | 63.7 | |
| Zn-extr.rate (mg/l hr) | 343.3 | | |

Table 7F

Pulp density = 18%

Effect of pulp density

Pulp density = 20%

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 2.19 | 2.08 | 0.64 |
| 19 | 2.70 | 2.65 | 0.67 |
| 30 | 4.5 | 4.4 | 0.70 |
| 44 | 9.4 | 9.5 | 0.74 |
| 53 | 12.5 | 12.5 | 0.77 |
| 67 | 17.3 | 17.4 | 0.79 |
| 77 | 21.1 | 20.6 | 0.85 |
| 101 | 32.0 | 31.2 | 0.88 |
| 116 | 37.2 | 37.0 | 0.92 |
| 143 | 46.2 | 44.1 | 0.93 |
| 163 | 52.9 | 51.2 | 0.94 |
| 188 | 59.9 | 59.4 | 0.95 |
| 212 | 63.2 | 62.6 | 0.96 |
| 241 | 64.8 | 64.5 | 1.04 |
| 262 | 66.7 | 66.1 | 1.14 |
| 285 | 68.2 | 68.5 | 1.26 |
| 316 | 69.6 | 69.4 | 1.32 |
| 477 | | 70.1 | |
| Zn-extr.rate (mg/l hr) | 364.3 | | |

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 2.42 | 2.33 | 0.71 |
| 19 | 2.54 | 2.55 | 0.76 |
| 30 | 4.2 | 4.3 | 0.77 |
| 44 | 9.2 | 9.3 | 0.80 |
| 53 | 12.1 | 12.3 | 0.82 |
| 67 | 17.0 | 17.0 | 0.85 |
| 77 | 20.4 | 20.9 | 0.89 |
| 101 | 30.7 | 30.4 | 0.94 |
| 116 | 36.8 | 36.9 | 0.97 |
| 143 | 44.0 | 43.7 | 0.99 |
| 163 | 50.4 | 50.9 | 1.00 |
| 188 | 58.8 | 59.2 | 1.02 |
| 212 | 61.2 | 61.4 | 1.08 |
| 241 | 64.9 | 64.6 | 1.17 |
| 262 | 67.1 | 68.3 | 1.23 |
| 285 | 69.6 | 69.3 | 1.35 |
| 316 | 70.2 | 70.4 | 1.44 |
| 477 | | 70.6 | |
| Zn-extr.rate (mg/l hr) | 353.4 | | |

Table 7G

Pulp density = 24%

Effect of pulp density

Pulp density = 26.6%

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 2.25 | 2.31 | 0.66 |
| 22 | 2.86 | 2.74 | 0.74 |
| 45 | 3.04 | 3.07 | 0.86 |
| 68 | 4.18 | 4.30 | 0.87 |
| 92 | 6.8 | 6.7 | 0.90 |
| 117 | 15.2 | 15.3 | 0.94 |
| 142 | 23.6 | 23.4 | 0.96 |
| 165 | 31.3 | 31.5 | 0.97 |
| 189 | 39.4 | 39.1 | 0.98 |
| 213 | 46.1 | 46.5 | 1.03 |
| 236 | 54.2 | 54.4 | 1.05 |
| 260 | 60.4 | 61.0 | 1.10 |
| 284 | 64.2 | 64.7 | 1.15 |
| 308 | 66.7 | 67.0 | 1.22 |
| 333 | 68.9 | 69.0 | 1.30 |
| Zn-extr.rate (mg/l hr) | 327.5 | | |

| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
|---------------------------|------------------------|------|---------|
| | A | B | Sterile |
| 0 | 2.55 | 2.52 | 0.79 |
| 19 | 2.61 | 2.58 | 0.82 |
| 30 | 2.92 | 2.96 | 0.86 |
| 44 | 4.20 | 4.40 | 0.88 |
| 53 | 6.4 | 6.6 | 0.91 |
| 67 | 6.8 | 7.0 | 0.94 |
| 77 | 8.2 | 8.6 | 0.95 |
| 101 | 10.4 | 10.7 | 0.99 |
| 116 | 14.5 | 14.3 | 1.03 |
| 143 | 23.5 | 24.2 | 1.04 |
| 163 | 33.3 | 31.6 | 1.05 |
| 188 | 39.0 | 38.7 | 1.07 |
| 212 | 45.0 | 45.1 | 1.12 |
| 241 | 50.3 | 50.7 | 1.26 |
| 262 | 55.4 | 55.5 | 1.37 |
| 285 | 60.5 | 60.9 | 1.48 |
| 316 | 63.7 | 63.4 | 1.54 |
| 477 | | 69.9 | |
| Zn-extr.rate (mg/l hr) | 297.1 | | |

Table 7H

Effect of pulp density at increased agitation

| pulp density (%) | 12 | | 16 | | 20 | |
|---------------------------|--------------------------|------|--------------------------|------|--------------------------|------|
| Time (hr) | Zinc extraction (g/l) | | Zinc extraction (g/l) | | Zinc extraction (g/l) | |
| | A | B | A | B | A | B |
| 0 | 1.42 | 1.40 | 1.48 | 1.50 | 1.62 | 1.58 |
| 23 | 2.50 | 2.54 | 2.76 | 2.79 | 2.84 | 2.86 |
| 47 | 9.8 | 9.8 | 11.4 | 11.2 | 11.4 | 11.1 |
| 71 | 17.2 | 17.1 | 19.8 | 20.0 | 19.6 | 20.0 |
| 95 | 24.5 | 24.7 | 28.6 | 28.4 | 28.4 | 28.4 |
| 120 | 32.0 | 32.0 | 37.6 | 37.4 | 37.3 | 37.2 |
| 147 | 40.4 | 40.5 | 47.2 | 47.3 | 46.8 | 46.7 |
| 167 | 47.0 | 47.2 | 55.0 | 55.2 | 54.6 | 54.6 |
| 192 | 50.1 | 50.3 | 63.8 | 64.1 | 63.5 | 63.1 |
| 216 | 51.6 | 51.4 | 67.4 | 67.7 | 68.1 | 68.3 |
| 240 | 51.4 | 51.5 | 68.1 | 68.3 | 69.6 | 69.9 |
| 265 | 51.8 | 51.6 | 68.4 | 68.3 | 69.6 | 69.5 |
| Zn-extr.rate (mg/l hr) | 309.2 | | 363.8 | | 359.4 | |

Table 8A

Effect of particle size

| Sample | Cyclosizer fraction No. 1 | | | Cyclosizer fraction No. 2 | | |
|-------------------------------|------------------------------|------|---------|------------------------------|------|---------|
| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | |
| | A | B | Sterile | A | B | Sterile |
| 0 | 1.59 | 1.60 | 0.36 | 1.26 | 1.30 | 0.16 |
| 23 | 3.15 | 3.08 | 1.00 | 1.45 | 1.50 | 0.29 |
| 47 | 4.02 | 4.01 | 1.83 | 1.87 | 1.80 | 0.42 |
| 70 | 4.66 | 4.70 | 2.04 | 1.98 | 2.08 | 0.51 |
| 98 | 5.15 | 5.15 | 2.17 | 2.15 | 2.14 | 0.57 |
| 143 | 5.82 | 5.84 | 2.19 | 2.46 | 2.52 | 0.75 |
| 167 | 6.1 | 6.2 | 2.20 | 2.68 | 2.62 | 0.80 |
| 190 | 6.9 | 6.9 | 2.21 | 2.90 | 3.04 | 0.92 |
| 214 | 7.0 | 6.9 | 2.21 | 2.95 | 3.08 | 0.93 |
| 238 | 7.2 | 7.1 | 2.22 | 2.96 | 3.09 | 1.07 |
| 262 | 7.2 | 7.2 | 2.23 | 3.01 | 3.10 | 1.10 |
| 288 | 7.5 | 7.5 | 3.27 | 3.24 | 3.24 | 1.24 |
| 312 | 7.8 | 7.9 | 2.24 | 3.28 | 3.29 | 1.25 |
| 340 | 8.5 | 8.6 | 2.25 | 3.70 | 3.65 | 1.27 |
| 362 | 10.5 | 10.6 | 2.28 | 5.12 | 5.18 | 1.27 |
| 383 | 20.7 | 20.9 | 2.32 | 12.5 | 12.8 | 1.27 |
| 411 | 34.1 | 34.8 | 2.35 | 22.6 | 22.9 | 1.28 |
| 435 | 45.3 | 45.8 | 2.38 | 31.4 | 31.8 | 1.29 |
| 455 | 55.0 | 55.8 | 2.40 | 39.0 | 39.2 | 1.29 |
| 480 | 65.4 | 68.5 | 2.41 | 48.0 | 47.6 | 1.28 |
| 507 | 66.8 | 69.0 | 2.46 | 56.8 | 57.2 | 1.29 |
| 527 | 68.4 | 69.1 | 2.47 | 62.8 | 63.0 | 1.30 |
| 550 | 70.2 | 69.5 | 2.47 | 62.5 | 62.9 | 1.31 |
| 575 | 70.3 | 69.8 | 2.49 | 63.0 | 63.1 | 1.32 |
| Zn-extr. rate (mg/l hr) | 496.2 | | | 359.8 | | |

Table 8B

Effect of particle size

| Sample | Cyclosizer fraction No. 3 | | | Cyclosizer fraction No. 4 | | |
|-------------------------------|------------------------------|------|---------|------------------------------|------|---------|
| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | |
| | A | B | Sterile | A | B | Sterile |
| 0 | 1.23 | 1.26 | 0.11 | 1.22 | 1.24 | 0.12 |
| 23 | 1.41 | 1.39 | 0.22 | 1.45 | 1.49 | 0.22 |
| 47 | 1.68 | 1.65 | 0.36 | 1.53 | 1.61 | 0.30 |
| 70 | 1.82 | 1.79 | 0.41 | 1.72 | 1.73 | 0.36 |
| 98 | 1.94 | 1.91 | 0.50 | 1.89 | 1.85 | 0.42 |
| 143 | 2.06 | 2.03 | 0.51 | 1.90 | 1.91 | 0.50 |
| 167 | 2.25 | 2.21 | 0.61 | 2.08 | 2.06 | 0.57 |
| 190 | 2.46 | 2.43 | 0.78 | 2.22 | 2.30 | 0.65 |
| 217 | 2.49 | 2.50 | 0.79 | 2.26 | 2.32 | 0.66 |
| 238 | 2.50 | 2.52 | 0.80 | 2.28 | 2.29 | 0.67 |
| 262 | 2.51 | 2.53 | 0.82 | 2.29 | 2.30 | 0.68 |
| 288 | 2.54 | 2.56 | 0.89 | 2.30 | 2.32 | 0.70 |
| 312 | 2.55 | 2.58 | 0.92 | 2.31 | 2.34 | 0.71 |
| 340 | 2.90 | 2.94 | 0.97 | 2.63 | 2.60 | 0.74 |
| 362 | 4.29 | 4.36 | 1.01 | 3.64 | 3.62 | 0.78 |
| 383 | 10.4 | 10.6 | 1.05 | 7.6 | 7.5 | 0.79 |
| 411 | 18.6 | 18.9 | 1.06 | 13.2 | 13.1 | 0.79 |
| 435 | 25.9 | 25.6 | 1.07 | 18.2 | 18.0 | 0.78 |
| 455 | 31.9 | 31.7 | 1.08 | 22.6 | 22.4 | 0.78 |
| 480 | 39.0 | 38.6 | 1.09 | 27.3 | 27.4 | 0.81 |
| 507 | 46.2 | 46.0 | 1.12 | 32.8 | 32.3 | 0.86 |
| 527 | 51.8 | 51.3 | 1.13 | 36.3 | 36.8 | 0.90 |
| 550 | 51.6 | 51.8 | 1.14 | 37.1 | 37.4 | 0.94 |
| 575 | 51.8 | 51.8 | 1.16 | 37.2 | 37.5 | 0.97 |
| Zn-extr. rate (mg/l hr) | 263.6 | | | 204.3 | | |

Table 8C

Effect of particle size

| Sample | Cyclosizer fraction No. 5 | | |
|---------------------------------|---------------------------|------|---------|
| Time (hr) | ZINC EXTRACTIONS (g/l) | | |
| | A | B | Sterile |
| 0 | 1.24 | 1.24 | 0.13 |
| 23 | 1.48 | 1.52 | 0.25 |
| 47 | 1.60 | 1.61 | 0.28 |
| 70 | 1.77 | 1.86 | 0.33 |
| 98 | 1.86 | 1.88 | 0.37 |
| 143 | 1.91 | 1.90 | 0.44 |
| 167 | 1.96 | 1.96 | 0.51 |
| 190 | 2.09 | 2.15 | 0.59 |
| 214 | 2.10 | 2.17 | 0.60 |
| 238 | 2.18 | 2.25 | 0.62 |
| 262 | 2.17 | 2.26 | 0.65 |
| 288 | 2.18 | 2.27 | 0.67 |
| 312 | 2.17 | 2.28 | 0.69 |
| 340 | 2.58 | 2.64 | 0.73 |
| 362 | 3.32 | 3.43 | 0.76 |
| 383 | 6.64 | 6.66 | 0.77 |
| 411 | 11.1 | 11.3 | 0.80 |
| 435 | 14.8 | 15.1 | 0.81 |
| 455 | 17.8 | 18.2 | 0.83 |
| 480 | 21.9 | 21.8 | 0.84 |
| 507 | 26.3 | 26.5 | 0.84 |
| 527 | 29.4 | 29.9 | 0.85 |
| 550 | 32.6 | 33.1 | 0.85 |
| 575 | 32.9 | 33.0 | 0.86 |
| Zinc-extr. rate (mg/l hr) | 158.0 | | |

Table 9A

Effect of particle size

| Sample | Bahco fraction No. 1 | | | Bahco fraction No. 1 | | |
|-------------------------------|-------------------------|------|---------|-------------------------|------|---------|
| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | |
| | A | B | Sterile | A | B | Sterile |
| 0 | 2.86 | 2.96 | 1.48 | 2.53 | 2.61 | 1.13 |
| 23 | 4.5 | 4.8 | 2.19 | 3.66 | 3.85 | 2.28 |
| 47 | 7.8 | 7.9 | 2.39 | 4.82 | 4.97 | 2.32 |
| 70 | 9.6 | 9.5 | 3.42 | 6.8 | 6.7 | 2.99 |
| 94 | 11.4 | 11.5 | 4.43 | 7.8 | 7.9 | 3.62 |
| 118 | 11.9 | 11.8 | 4.7 | 8.3 | 8.7 | 3.89 |
| 142 | 13.7 | 13.9 | 5.3 | 10.1 | 10.1 | 4.72 |
| 166 | 14.3 | 14.2 | 6.1 | 10.8 | 10.9 | 5.4 |
| 191 | 15.0 | 15.8 | 7.4 | 11.9 | 12.0 | 6.3 |
| 215 | 16.7 | 16.2 | 7.9 | 13.0 | 13.2 | 7.3 |
| 238 | 20.9 | 19.8 | 8.1 | 16.5 | 17.0 | 7.5 |
| 262 | 29.2 | 30.2 | 8.6 | 28.0 | 28.5 | 7.8 |
| 286 | 42.6 | 42.2 | 9.7 | 40.4 | 40.2 | 7.9 |
| 310 | 56.4 | 56.9 | 10.6 | 52.1 | 52.6 | 8.0 |
| 335 | 68.9 | 69.9 | 10.7 | 62.8 | 63.8 | 8.3 |
| 359 | 69.4 | 72.2 | 10.8 | 68.9 | 69.5 | 8.8 |
| 382 | 69.9 | 75.7 | 10.9 | 69.8 | 70.2 | 8.9 |
| Zn-extr. rate (mg/l hr) | 516.8 | | | 484.2 | | |

Table 9B
Effect of particle size

| Sample | Bahco fraction No. 3 | | | Bahco fraction No. 4 | | |
|---------------------------------|-------------------------|------|---------|-------------------------|------|---------|
| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | |
| | A | B | Sterile | A | B | Sterile |
| 0 | 1.96 | 1.96 | 0.62 | 1.91 | 1.90 | 0.46 |
| 23 | 2.73 | 2.85 | 0.99 | 2.26 | 2.14 | 0.61 |
| 47 | 3.36 | 3.37 | 1.18 | 3.96 | 3.87 | 0.65 |
| 70 | 4.86 | 4.90 | 1.35 | 10.4 | 10.6 | 0.93 |
| 94 | 5.8 | 5.8 | 1.85 | 17.2 | 17.9 | 1.36 |
| 118 | 6.7 | 6.5 | 2.27 | 25.9 | 25.7 | 1.73 |
| 142 | 7.8 | 7.7 | 2.82 | 36.4 | 36.3 | 1.88 |
| 166 | 12.6 | 11.3 | 2.86 | 46.7 | 47.2 | 2.00 |
| 191 | 22.5 | 22.0 | 2.91 | 51.8 | 51.4 | 2.10 |
| 215 | 33.9 | 34.1 | 3.26 | 56.8 | 57.2 | 2.33 |
| 238 | 45.8 | 45.2 | 3.58 | 59.0 | 59.2 | 2.58 |
| 262 | 54.8 | 54.6 | 3.72 | 60.2 | 60.6 | 2.87 |
| 286 | 64.9 | 64.7 | 4.04 | 60.8 | 61.2 | 3.04 |
| 310 | 65.2 | 65.6 | 4.24 | 61.4 | 61.2 | 3.21 |
| Zinc-extr. rate (mg/l hr) | 446.2 | | | 349.3 | | |

Table 9C

Effect of particle size

| Sample | Bahco fraction No. 5 | | |
|---------------------------------|------------------------|------|---------|
| Time | ZINC EXTRACTIONS (g/l) | | |
| (hr) | A | B | Sterile |
| 0 | 1.92 | 1.91 | 0.42 |
| 23 | 2.09 | 2.04 | 0.45 |
| 47 | 4.65 | 4.84 | 0.51 |
| 70 | 12.2 | 11.6 | 0.88 |
| 94 | 19.4 | 19.0 | 1.26 |
| 118 | 25.2 | 24.9 | 1.39 |
| 142 | 33.4 | 33.1 | 1.50 |
| 166 | 39.2 | 39.4 | 1.62 |
| 191 | 43.9 | 44.1 | 1.71 |
| 215 | 50.9 | 51.6 | 1.94 |
| 238 | 52.5 | 52.2 | 2.04 |
| 262 | 52.6 | 52.6 | 2.18 |
| 286 | 52.7 | 52.8 | 2.61 |
| 310 | 52.9 | 53.0 | 2.74 |
| Zinc-extr. rate (mg/1 hr) | 274.3 | | |

| Sample | Bahco fraction No. 6 | | |
|---------------------------------|------------------------|------|---------|
| Time | ZINC EXTRACTIONS (g/l) | | |
| (hr) | A | B | Sterile |
| 0 | 1.28 | 1.34 | 0.21 |
| 24 | 4.85 | 4.92 | 0.42 |
| 47 | 9.2 | 9.3 | 0.67 |
| 72 | 13.5 | 13.6 | 0.68 |
| 96 | 17.6 | 17.8 | 0.69 |
| 120 | 22.2 | 22.7 | 0.70 |
| 144 | 26.7 | 26.6 | 0.76 |
| 171 | 31.2 | 31.1 | 0.75 |
| 195 | 34.3 | 34.4 | 0.77 |
| 215 | 37.5 | 37.7 | 0.78 |
| 244 | 39.9 | 40.6 | 0.79 |
| 288 | 41.8 | 42.0 | 0.81 |
| 408 | 45.9 | 46.0 | 0.83 |
| 432 | 45.9 | 46.1 | 0.84 |
| Zinc-extr. rate (mg/1 hr) | 173.1 | | |

Table 9D
Effect of particle size

| Sample | Bahco fraction No. 7 | | | Bahco fraction No. 8 | | |
|---------------------------------|-------------------------|------|---------|-------------------------|------|---------|
| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | |
| | A | B | Sterile | A | B | Sterile |
| 0 | 1.18 | 1.30 | 0.13 | 1.21 | 1.28 | 0.13 |
| 24 | 4.16 | 4.11 | 0.40 | 2.65 | 2.72 | 0.39 |
| 47 | 7.2 | 7.4 | 0.63 | 3.17 | 3.26 | 0.62 |
| 72 | 10.5 | 10.6 | 0.71 | 5.4 | 4.9 | 0.64 |
| 96 | 13.6 | 13.4 | 0.76 | 6.4 | 6.6 | 0.73 |
| 120 | 16.9 | 17.2 | 0.80 | 7.7 | 8.1 | 0.76 |
| 144 | 21.4 | 21.5 | 0.83 | 10.0 | 9.7 | 0.83 |
| 171 | 23.2 | 23.4 | 0.84 | 12.4 | 12.2 | 0.84 |
| 195 | 27.4 | 27.0 | 0.83 | 14.2 | 14.0 | 0.88 |
| 215 | 29.3 | 29.2 | 0.84 | 15.3 | 15.6 | 0.92 |
| 244 | 31.9 | 31.5 | 0.84 | 18.4 | 18.0 | 0.94 |
| 288 | 32.9 | 32.8 | 0.85 | 20.3 | 20.2 | 0.94 |
| 408 | 38.9 | 38.4 | 1.00 | 27.7 | 26.9 | 1.20 |
| 432 | 39.0 | 38.8 | 1.02 | 27.9 | 27.4 | 1.27 |
| Zinc-extr. rate (mg/l hr) | 132.7 | | | 73.4 | | |

Table 10A

Effect of pulp density at 7.92% CO₂

| Pulp Density | 5.3% | | 12% | | 14% | | 26.6% | |
|---------------------------|------------------------|------|-------|------|-------|------|-------|------|
| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | | | |
| | A | B | A | B | A | B | A | B |
| 0 | 1.30 | 1.28 | 1.71 | 1.68 | 1.85 | 1.82 | 2.23 | 2.20 |
| 21 | 1.32 | 1.34 | 2.18 | 2.31 | 2.36 | 2.32 | 2.45 | 2.37 |
| 28 | 1.58 | 1.56 | 2.90 | 2.92 | 3.01 | 3.03 | 3.37 | 3.25 |
| 44 | 2.12 | 2.16 | 5.40 | 5.6 | 5.5 | 5.7 | 5.9 | 6.1 |
| 71 | 3.46 | 3.44 | 16.0 | 15.9 | 18.2 | 18.0 | 18.9 | 19.1 |
| 80 | 4.02 | 4.04 | 23.1 | 22.9 | 25.9 | 26.1 | 28.4 | 28.7 |
| 92 | 4.9 | 4.9 | 27.1 | 27.2 | 30.6 | 30.6 | 36.1 | 36.2 |
| 103 | 6.0 | 6.1 | 30.8 | 30.7 | 34.3 | 34.7 | 43.0 | 42.9 |
| 116 | 7.7 | 7.9 | 35.3 | 35.1 | 39.9 | 40.0 | 51.4 | 51.6 |
| 126 | 8.9 | 9.0 | 39.6 | 39.7 | 43.5 | 43.6 | 57.8 | 57.9 |
| 144 | 11.7 | 11.6 | 45.7 | 45.8 | 50.2 | 50.4 | 63.6 | 63.9 |
| 167 | 15.3 | 15.4 | 53.6 | 53.3 | 59.5 | 59.1 | 68.0 | 67.7 |
| 189 | 18.0 | 18.2 | 59.1 | 58.9 | 64.3 | 64.7 | 69.1 | 69.2 |
| 198 | 19.1 | 18.9 | 62.4 | 62.6 | 66.2 | 66.3 | 70.3 | 70.7 |
| Zinc-extr. rate (mg/l hr) | 141.3 | | 355.1 | | 383.0 | | 640.6 | |

Table 10B

Effect of pulp density at 7.92% CO₂

| Pulp Density | 16% | | | 18% | | | 20% | | | 24% | | |
|---------------------------|------------------------|------|---------|-------|------|---------|-------|------|---------|-------|------|---------|
| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | | | | | | | |
| | A | B | Sterile | A | B | Sterile | A | B | Sterile | A | B | Sterile |
| 0 | 1.92 | 1.96 | 0.52 | 1.96 | 1.98 | 0.64 | 2.10 | 2.00 | 0.70 | 2.10 | 2.10 | 0.73 |
| 21 | 2.30 | 2.35 | 0.66 | 2.33 | 2.31 | 0.67 | 2.33 | 2.36 | 0.77 | 2.38 | 2.41 | 0.77 |
| 28 | 3.00 | 3.05 | 0.75 | 3.05 | 3.10 | 0.69 | 3.20 | 3.30 | 0.80 | 3.20 | 3.28 | 0.78 |
| 44 | 5.6 | 5.8 | 0.81 | 5.7 | 5.6 | 0.71 | 5.8 | 5.9 | 0.88 | 5.9 | 6.0 | 0.82 |
| 71 | 18.9 | 18.7 | 0.82 | 18.8 | 18.9 | 0.74 | 18.9 | 19.0 | 0.89 | 19.0 | 19.0 | 0.87 |
| 80 | 28.2 | 28.0 | 0.83 | 28.2 | 28.1 | 0.78 | 28.3 | 28.2 | 0.92 | 28.2 | 28.4 | 0.90 |
| 92 | 33.3 | 33.6 | 0.85 | 34.0 | 34.2 | 0.80 | 35.5 | 35.0 | 0.93 | 36.0 | 35.8 | 0.92 |
| 103 | 38.2 | 38.6 | 0.91 | 39.3 | 39.5 | 0.81 | 41.6 | 41.6 | 0.94 | 42.8 | 42.9 | 0.93 |
| 116 | 43.9 | 43.7 | 0.92 | 45.9 | 45.7 | 0.84 | 49.0 | 49.2 | 0.99 | 51.3 | 51.5 | 0.97 |
| 126 | 48.3 | 48.3 | 0.93 | 50.6 | 50.5 | 0.86 | 55.0 | 54.8 | 1.01 | 57.4 | 57.8 | 0.99 |
| 144 | 56.2 | 56.5 | 0.97 | 58.9 | 60.1 | 0.90 | 62.7 | 62.5 | 1.03 | 63.7 | 63.6 | 1.03 |
| 167 | 62.5 | 62.2 | 1.02 | 66.7 | 66.3 | 0.93 | 67.3 | 67.7 | 1.10 | 67.8 | 67.9 | 1.10 |
| 189 | 66.4 | 66.9 | 1.03 | 68.9 | 69.1 | 0.96 | 68.8 | 68.9 | 1.12 | 68.9 | 69.0 | 1.16 |
| 198 | 68.3 | 68.4 | 1.07 | 69.8 | 69.7 | 1.07 | 69.7 | 69.9 | 1.16 | 69.8 | 69.7 | 1.17 |
| Zinc-extr. rate (mg/l hr) | 438.8 | | | 488.1 | | | 577.8 | | | 640.8 | | |

Table 11A
Effect of pulp density at 1.03% CO₂

| Pulp Density | 5.3% | | 12% | | 14% | | 16% | |
|---------------------------|------------------------|------|-------|------|-------|------|-------|------|
| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | | | |
| | A | B | A | B | A | B | A | B |
| 0 | 1.26 | 1.27 | 1.39 | 1.41 | 1.44 | 1.48 | 1.56 | 1.57 |
| 22 | 1.60 | 1.62 | 2.33 | 2.45 | 2.50 | 2.47 | 2.42 | 2.46 |
| 31 | 2.03 | 2.01 | 3.50 | 3.34 | 3.61 | 3.66 | 3.72 | 3.71 |
| 46 | 2.83 | 2.84 | 5.8 | 5.9 | 7.0 | 7.1 | 7.1 | 7.1 |
| 56 | 3.17 | 3.22 | 8.6 | 8.5 | 9.4 | 9.3 | 9.6 | 9.7 |
| 73 | 4.30 | 4.20 | 16.4 | 16.6 | 19.2 | 19.6 | 19.7 | 19.8 |
| 96 | 6.4 | 6.6 | 28.2 | 28.1 | 38.4 | 37.8 | 37.8 | 37.7 |
| 105 | 7.7 | 7.8 | 31.4 | 31.8 | 41.8 | 42.0 | 41.8 | 41.9 |
| 117 | 9.5 | 9.4 | 35.6 | 35.7 | 46.5 | 46.6 | 47.0 | 47.2 |
| 129 | 10.8 | 10.9 | 40.1 | 39.9 | 51.1 | 51.0 | 52.3 | 52.1 |
| 144 | 12.8 | 12.7 | 44.4 | 44.2 | 57.9 | 57.7 | 58.9 | 58.8 |
| 171 | 16.5 | 16.3 | 53.9 | 54.0 | 65.2 | 65.0 | 66.3 | 66.5 |
| 190 | 19.1 | 19.3 | 60.3 | 60.5 | 68.7 | 68.9 | 69.4 | 69.7 |
| Zinc-extr. rate (mg/l hr) | 133.9 | | 339.8 | | 405.2 | | 438.5 | |

Table 11B

Effect of pulp density at 1.03% CO₂

| Pulp Density | 18% | | 20% | | 24% | | 26.6% | |
|---------------------------|------------------------|------|-------|------|-------|------|-------|------|
| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | | | |
| | A | B | A | B | A | B | A | B |
| 0 | 1.59 | 1.61 | 1.72 | 1.71 | 1.78 | 1.79 | 1.86 | 1.92 |
| 22 | 2.43 | 2.44 | 2.45 | 2.45 | 2.41 | 2.43 | 2.48 | 2.44 |
| 31 | 3.65 | 3.72 | 3.75 | 3.72 | 3.74 | 3.71 | 2.7 | 2.80 |
| 46 | 6.9 | 6.8 | 7.0 | 7.1 | 6.8 | 6.9 | 7.2 | 7.0 |
| 56 | 10.1 | 9.9 | 10.2 | 10.3 | 10.1 | 10.2 | 10.2 | 10.4 |
| 73 | 21.2 | 21.0 | 20.8 | 21.2 | 21.3 | 21.2 | 21.4 | 21.3 |
| 96 | 38.3 | 38.1 | 38.5 | 38.7 | 38.7 | 38.8 | 38.8 | 38.8 |
| 105 | 43.4 | 43.5 | 43.7 | 43.5 | 44.6 | 44.8 | 44.5 | 44.6 |
| 117 | 49.6 | 49.9 | 50.7 | 50.6 | 52.3 | 52.1 | 52.2 | 52.0 |
| 129 | 55.0 | 55.3 | 57.6 | 57.4 | 60.0 | 60.2 | 59.8 | 59.9 |
| 144 | 61.7 | 61.6 | 64.7 | 65.1 | 66.2 | 66.5 | 65.4 | 65.7 |
| 171 | 67.8 | 67.3 | 68.8 | 68.9 | 68.9 | 69.0 | 68.9 | 69.3 |
| 190 | 69.8 | 70.1 | 70.2 | 70.0 | 70.5 | 70.3 | 70.4 | 70.7 |
| Zinc-extr. rate (mg/l hr) | 513.3 | | 574.6 | | 644.4 | | 636.9 | |

Table 12A

Effect of pulp density at 0.23% CO₂

| Pulp Density | 5.3% | | 12% | | 14% | | 16% | |
|------------------------|------------------------|------|-------|------|-------|------|-------|------|
| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | | | |
| | A | B | A | B | A | B | A | B |
| 0 | 1.38 | 1.39 | 1.68 | 1.69 | 1.73 | 1.71 | 1.77 | 1.79 |
| 21 | 1.45 | 1.48 | 1.83 | 1.86 | 2.03 | 2.05 | 2.15 | 2.13 |
| 44 | 2.20 | 2.24 | 4.45 | 4.41 | 4.5 | 4.6 | 4.67 | 4.65 |
| 70 | 3.30 | 3.40 | 11.3 | 11.3 | 12.2 | 12.1 | 12.5 | 12.7 |
| 80 | 4.2 | 4.3 | 15.2 | 15.3 | 16.0 | 15.9 | 16.5 | 16.4 |
| 102 | 5.9 | 5.8 | 25.2 | 25.1 | 26.4 | 26.1 | 26.8 | 26.7 |
| 120 | 8.1 | 8.2 | 31.3 | 31.2 | 33.5 | 33.6 | 34.7 | 34.8 |
| 140 | 10.6 | 10.5 | 38.1 | 38.3 | 41.5 | 41.4 | 43.5 | 43.5 |
| 164 | 13.1 | 13.2 | 46.3 | 46.4 | 51.0 | 51.2 | 54.0 | 54.3 |
| 189 | 16.2 | 16.1 | 54.8 | 54.7 | 61.1 | 61.0 | 65.1 | 64.9 |
| 212 | 19.0 | 19.1 | 62.6 | 62.3 | 66.1 | 65.9 | 69.3 | 69.6 |
| 236 | 20.1 | 20.3 | 65.4 | 64.9 | 68.5 | 68.3 | 70.2 | 69.8 |
| Zinc-extr. rate (mg/l) | 118.5 | | 339.4 | | 399.7 | | 439.8 | |

Table 12B

Effect of pulp density at 0.23% CO₂

| Pulp Density | 18% | | 20% | | 24% | | 26.6% | |
|---------------------------|------------------------|------|-------|------|-------|------|-------|------|
| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | | | |
| | A | B | A | B | A | B | A | B |
| 0 | 1.87 | 1.83 | 1.91 | 1.95 | 2.03 | 2.04 | 2.05 | 2.17 |
| 21 | 2.20 | 2.21 | 2.25 | 2.24 | 2.27 | 2.30 | 2.33 | 2.31 |
| 44 | 4.8 | 4.9 | 5.1 | 5.2 | 5.2 | 5.2 | 5.3 | 5.2 |
| 70 | 12.8 | 12.8 | 13.0 | 13.2 | 13.3 | 13.1 | 13.3 | 13.2 |
| 80 | 16.9 | 16.6 | 17.1 | 17.0 | 17.3 | 17.3 | 17.2 | 17.4 |
| 102 | 26.8 | 26.9 | 27.3 | 27.1 | 27.5 | 27.7 | 27.6 | 27.8 |
| 120 | 35.7 | 35.6 | 37.6 | 37.7 | 39.0 | 38.8 | 39.1 | 39.0 |
| 140 | 45.6 | 45.7 | 49.1 | 49.0 | 51.8 | 51.5 | 51.9 | 51.7 |
| 164 | 57.5 | 57.7 | 63.9 | 63.7 | 67.0 | 67.1 | 67.2 | 67.1 |
| 189 | 64.5 | 64.6 | 67.4 | 67.6 | 69.7 | 69.9 | 69.5 | 69.8 |
| 212 | 68.8 | 68.3 | 69.8 | 69.9 | 70.8 | 71.0 | 71.0 | 70.9 |
| 236 | 69.9 | 70.0 | 70.4 | 70.2 | 72.1 | 71.6 | 71.4 | 71.2 |
| Zinc-extr. rate (mg/l hr) | 496.5 | | 589.0 | | 636.6 | | 636.5 | |

Table 13A

Effect of pulp density at 0.13% CO₂

| Pulp Density | 5.3% | | 12% | | 14% | | 16% | |
|---------------------------|------------------------|------|-------|------|-------|------|-------|------|
| Time (hr) | ZINC EXTRACTIONS (g/l) | | | | | | | |
| | A | B | A | B | A | B | A | B |
| 0 | 1.32 | 1.36 | 1.66 | 1.71 | 1.52 | 1.58 | 1.88 | 1.93 |
| 23 | 1.96 | 1.92 | 2.18 | 2.23 | 2.41 | 2.37 | 2.28 | 2.26 |
| 33 | 2.60 | 2.63 | 2.99 | 3.01 | 3.10 | 3.20 | 3.41 | 3.44 |
| 47 | 4.35 | 4.28 | 5.2 | 5.1 | 5.3 | 5.4 | 5.8 | 5.8 |
| 59 | 5.8 | 5.7 | 7.4 | 7.6 | 7.8 | 7.6 | 9.1 | 9.0 |
| 72 | 7.4 | 7.3 | 11.6 | 11.3 | 12.1 | 12.0 | 15.0 | 15.2 |
| 95 | 10.1 | 10.0 | 19.4 | 19.6 | 20.8 | 20.9 | 26.2 | 26.5 |
| 106 | 11.4 | 11.5 | 23.1 | 23.0 | 25.7 | 25.6 | 31.1 | 31.0 |
| 120 | 13.2 | 13.0 | 27.8 | 27.9 | 32.2 | 32.6 | 37.3 | 37.2 |
| 131 | 14.6 | 14.5 | 31.6 | 31.8 | 36.5 | 36.2 | 42.2 | 42.0 |
| 148 | 16.5 | 16.6 | 37.3 | 37.3 | 43.3 | 43.6 | 49.7 | 49.9 |
| 168 | 18.9 | 18.7 | 43.4 | 43.4 | 51.2 | 51.0 | 58.6 | 58.8 |
| 192 | 19.5 | 19.7 | 51.7 | 51.8 | 60.7 | 60.5 | 66.4 | 66.3 |
| 216 | 20.2 | 20.1 | 60.3 | 60.5 | 66.2 | 66.6 | 69.8 | 67.7 |
| Zinc-extr. rate (mg/l hr) | 107.6 | | 331.3 | | 414.3 | | 444.2 | |

Table 13B

Effect of pulp density at 0.13% CO₂

| Pulp Density | 18% | | 20% | | 24% | | 26.6% | |
|---------------------------|-------|------|------------------------|------|-------|------|-------|------|
| Time (hr) | A | B | ZINC EXTRACTIONS (g/l) | | | | A | B |
| | A | B | A | B | A | B | A | B |
| 0 | 1.88 | 1.91 | 1.95 | 1.98 | 2.08 | 2.06 | 2.14 | 2.19 |
| 23 | 2.31 | 2.34 | 2.33 | 2.35 | 2.36 | 2.35 | 2.31 | 2.33 |
| 33 | 3.20 | 3.20 | 3.20 | 3.25 | 3.42 | 3.53 | 3.45 | 3.44 |
| 47 | 5.7 | 5.4 | 6.1 | 6.3 | 6.1 | 6.2 | 6.1 | 6.3 |
| 59 | 12.1 | 11.7 | 9.9 | 9.8 | 10.3 | 10.2 | 10.2 | 10.4 |
| 72 | 21.9 | 22.2 | 17.2 | 17.4 | 17.5 | 17.7 | 17.6 | 17.7 |
| 95 | 28.3 | 28.7 | 27.1 | 26.9 | 27.4 | 27.3 | 27.5 | 27.3 |
| 106 | 33.8 | 33.7 | 33.2 | 33.3 | 33.9 | 33.8 | 33.8 | 33.5 |
| 120 | 40.6 | 40.5 | 40.8 | 40.9 | 41.9 | 42.0 | 41.7 | 41.6 |
| 131 | 46.1 | 46.3 | 46.8 | 46.5 | 48.2 | 48.1 | 47.8 | 47.8 |
| 148 | 54.5 | 54.3 | 56.2 | 56.3 | 57.9 | 58.0 | 57.4 | 57.1 |
| 168 | 64.4 | 64.1 | 62.4 | 63.0 | 65.1 | 65.3 | 66.5 | 66.3 |
| 192 | 68.7 | 69.0 | 66.8 | 66.5 | 68.4 | 68.1 | 68.4 | 68.7 |
| 216 | 70.2 | 70.8 | 69.7 | 69.5 | 69.9 | 70.0 | 69.3 | 69.8 |
| Zinc-extr. rate (mg/l hr) | 490.7 | | 549.0 | | 576.2 | | 563.6 | |

Table 14A

Effect of specific surface area at 1.0% CO₂

| Cyclosizer Fraction | No. 1 | No. 2 | No. 3 | No. 4 | No. 5 |
|--------------------------------|------------------------|-------|-------|-------|-------|
| time (hr) | Zinc Extractions (g/l) | | | | |
| 0 | 2.68 | 1.68 | 1.49 | 1.42 | 1.36 |
| 22 | 5.2 | 2.97 | 2.32 | 2.15 | 2.05 |
| 34 | 18.6 | 5.2 | 4.3 | 4.10 | 3.65 |
| 50 | 36.3 | 12.1 | 9.4 | 7.3 | 6.4 |
| 58 | 45.3 | 15.2 | 11.6 | 8.9 | 7.8 |
| 70 | 58.8 | 20.5 | 14.8 | 11.3 | 9.9 |
| 81 | 67.3 | 25.6 | 17.8 | 13.5 | 11.8 |
| 94 | 68.7 | 31.5 | 21.3 | 16.1 | 14.0 |
| 106 | 69.3 | 36.9 | 24.6 | 18.6 | 16.1 |
| 118 | 69.6 | 42.5 | 27.7 | 20.8 | 18.0 |
| 130 | 70.1 | 47.7 | 30.9 | 23.2 | 20.2 |
| 145 | 70.3 | 53.1 | 34.9 | 26.1 | 22.4 |
| Zinc Extraction Rate (mg/l hr) | 1,115.5 | 441.9 | 268.7 | 198.6 | 170.2 |

Table 14B

Effect of specific surface area at 1.0% CO₂

| Bahco-sizer Fraction | No.1 | No.2 | No.3 | No.4 | No.5 | No.6 | No.7 | No.8 |
|---|---|---------|-------|-------|-------|-------|-------|-------|
| Time (hr) | Z i n c E x t r a c t i o n s (g/l) | | | | | | | |
| 0 | 3.35 | 2.96 | 2.47 | 1.82 | 1.63 | 1.51 | 1.47 | 1.39 |
| 22 | 5.4 | 5.2 | 5.1 | 3.32 | 2.31 | 2.25 | 2.14 | 2.11 |
| 34 | 20.3 | 17.9 | 17.3 | 4.90 | 4.20 | 3.63 | 3.57 | 3.27 |
| 50 | 38.4 | 35.1 | 33.1 | 12.3 | 9.4 | 6.6 | 6.0 | 5.0 |
| 58 | 47.5 | 43.7 | 41.0 | 15.9 | 11.6 | 8.1 | 7.2 | 5.8 |
| 70 | 60.9 | 56.5 | 52.9 | 21.5 | 14.9 | 10.3 | 10.1 | 7.1 |
| 81 | 68.2 | 64.3 | 63.5 | 26.6 | 17.8 | 12.3 | 11.7 | 8.2 |
| 94 | 70.5 | 67.7 | 66.7 | 32.6 | 21.4 | 14.7 | 13.6 | 9.6 |
| 106 | 70.8 | 69.1 | 68.0 | 38.1 | 24.7 | 16.9 | 15.3 | 10.9 |
| 118 | 71.1 | 69.8 | 69.4 | 43.6 | 28.1 | 19.2 | 17.1 | 12.2 |
| 130 | 71.3 | 70.1 | 69.9 | 49.2 | 31.3 | 21.4 | 18.8 | 13.5 |
| 145 | 71.3 | 70.4 | 70.2 | 56.0 | 34.9 | 24.0 | 20.9 | 15.2 |
| Zinc Extraction Rate (mg/l hr) | 1,152.3 | 1,068.3 | 989.8 | 460.9 | 271.6 | 184.1 | 157.6 | 107.0 |

APPENDIX 2

Curve fittings

Table 1

Program for curve fitting

```
DIMENSION X(220),Y(220),YF(220),X1(220),X2(220),X3(220),  
1X4(220),X5(220),A(53)  
REAL K
```

```
C      K=FINAL EXTRACTION
```

```
C      Y(I)=EXTRACTION
```

```
100 READ(5,1)N
```

```
1  FORMAT(I3)
```

```
READ(5,6)K
```

```
6  FORMAT(F10.0)
```

```
WRITE(6,88)
```

```
88  FORMAT(17HFINAL EXTRACTION:)
```

```
WRITE(6,5)K
```

```
WRITE(6,2)
```

```
2  FORMAT(5X,15HNO OF DATAPAIRS,/)
```

```
WRITE(6,3)N
```

```
3  FORMAT(10X,I3,/) )
```

```
DO 10 I=1,N
```

```
READ(5,4)X(I),Y(I)
```

```
4  FORMAT(2F10.0)
```

```
10  CONTINUE
```

```
DO 40 I=1,N
```

```
X1(I)=X(I)
```

```
X2(I)=X(I)*X1(I)
```

```
X3(I)=X(I)*X2(I)
```

```
X4(I)=X(I)*X3(I)
```

```
X5(I)=X(I)*X4(I)
```

```
40  CONTINUE
```

Table 1

Continuation

```
DO 60 I=1,6
READ(5,5)A(I)
5 FORMAT(E13.6)
60 CONTINUE
WRITE(6,18)
18 FORMAT(1X,25HPOLYNOMIAL PARAMETERS ARE,/)
DO 70 I=1,6
70 WRITE(6,15)A(I)
15 FORMAT(4X,E13.6)
WRITE(6,19)
19 FORMAT(5X,/)
DO 20 I=1,N
31 YF(I)= K/(1.+EXP(A(1)+A(2)*X1(I)+A(3)*X2(I)+A(4)*X3(I)+A(5)*X4(I)+
1A(6)*X5(I)))
20 CONTINUE
WRITE(6,7)
7 FORMAT(50H VALUES OF X VALUES OF Y FITTED VALUES OF Y )
DO 30 I=1,N
WRITE(6,8)X(I),Y(I),YF(I)
8 FORMAT(1X,8G15.5)
30 CONTINUE
WRITE(6,9)
9 FORMAT(1H1)
GO TO 100
END
```

Table 2A

Effect of pulp density (16%) at 0.03% CO₂

| INDEPENDENT VARIABLE | REGRESSION COEFFICIENT | STANDARD DEVIATION |
|-------------------------|---------------------------|-----------------------|
| X | -0.456878D-01 | 0.634035D-02 |
| X2 | 0.178017D-03 | 0.106921D-03 |
| X3 | -0.736080D-06 | 0.707001D-06 |
| X4 | 0.136661D-08 | 0.194600D-08 |
| X5 | -0.750941D-12 | 0.184276D-11 |

CONSTANT TERM = 0.361672E 01
 STANDARD ERROR OF ESTIMATE = 0.184501E 00
 RESIDUAL VARIANCE = 0.340408E-01
 MULTIPLE CORRELATION COEFFICIENT = 0.99804
 R SQUARED = 0.99608

The logistic equation describing these data is:

$$P = 64000 / (1 + \exp(f(t)))$$

$$\begin{aligned}
 \text{where } f(t) = & 3.6167 - 4.5688 * 10^{-2} * t + 1.7801 * 10^{-4} * t^2 - 7.3608 * 10^{-7} * t^3 \\
 & + 1.3666 * 10^{-9} * t^4 - 7.5094 * 10^{-13} * t^5
 \end{aligned}$$

Table 2B

Effect of pulp density (16%) at 0.03% CO₂

| VALUES OF X | VALUES OF Y | FITTED VALUES OF Y |
|-------------|-------------|--------------------|
| 0.0 | 2100.0 | 1674.7 |
| 0.0 | 2150.0 | 1674.7 |
| 19.000 | 2580.0 | 3641.0 |
| 19.000 | 2600.0 | 3641.0 |
| 30.000 | 4200.0 | 5384.3 |
| 30.000 | 4300.0 | 5384.3 |
| 44.000 | 9100.0 | 8374.9 |
| 44.000 | 9000.0 | 8374.9 |
| 53.000 | 12400. | 10785. |
| 53.000 | 12300. | 10785. |
| 67.000 | 17000. | 15276. |
| 67.000 | 17100. | 15276. |
| 77.000 | 20400. | 18974. |
| 77.000 | 20400. | 18974. |
| 101.00 | 29900. | 28904. |
| 101.00 | 29800. | 28904. |
| 116.00 | 35100. | 35268. |
| 116.00 | 35100. | 35268. |
| 143.00 | 42300. | 45530. |
| 143.00 | 41600. | 45530. |
| 163.00 | 49800. | 51442. |
| 163.00 | 50400. | 51442. |
| 188.00 | 57400. | 56642. |
| 188.00 | 58200. | 56642. |
| 212.00 | 59400. | 59748. |
| 212.00 | 60100. | 59748. |
| 241.00 | 61700. | 61848. |
| 241.00 | 61900. | 61848. |
| 262.00 | 62600. | 62679. |
| 262.00 | 62800. | 62679. |
| 285.00 | 63200. | 63209. |
| 285.00 | 63300. | 63209. |
| 316.00 | 63600. | 63576. |
| 316.00 | 63500. | 63576. |
| 477.00 | 63700. | 63699. |

Table 3A

Effect of pulp density (16%) at 0.13% CO₂

| INDEPENDENT VARIABLE | REGRESSION COEFFICIENT | STANDARD DEVIATION |
|-------------------------|---------------------------|-----------------------|
| X | 0.217935D-01 | 0.200241D-01 |
| X2 | -0.172928D-02 | 0.653294D-03 |
| X3 | 0.195213D-04 | 0.814307D-05 |
| X4 | -0.906010D-07 | 0.426204D-07 |
| X5 | 0.146010D-09 | 0.790459D-10 |

CONSTANT TERM = 0.357914E 01
 STANDARD ERROR OF ESTIMATE = 0.281981E 00
 RESIDUAL VARIANCE = 0.795135E-01
 MULTIPLE CORRELATION COEFFICIENT = 0.99394
 R SQUARED = 0.98792

The generalized logistic equation describing these data is:

$$P = 70000 / (1 + \exp(f(t)))$$

$$\begin{aligned}
 \text{where } f(t) = & 3.5791 + 2.1794 * 10^{-2} * t - 1.7293 * 10^{-3} * t^2 + 1.9521 * 10^{-5} * t^3 \\
 & - 9.0601 * 10^{-8} * t^4 + 1.4601 * 10^{-10} * t^5
 \end{aligned}$$

Table 3BEffect of pulp density (16%) at 0.13% CO₂

| VALUES OF X | VALUES OF Y | FITTED VALUES OF Y |
|-------------|-------------|--------------------|
| 0.0 | 1880.0 | 1900.0 |
| 0.0 | 1930.0 | 1900.0 |
| 23.000 | 2280.0 | 2307.7 |
| 23.000 | 2260.0 | 2307.7 |
| 33.000 | 3410.0 | 3272.9 |
| 33.000 | 3440.0 | 3272.9 |
| 47.000 | 5800.0 | 5813.6 |
| 47.000 | 5800.0 | 5813.6 |
| 59.000 | 9100.0 | 9419.9 |
| 59.000 | 9000.0 | 9419.9 |
| 72.000 | 15000. | 14784. |
| 72.000 | 15200. | 14784. |
| 95.000 | 26200. | 25934. |
| 95.000 | 26500. | 25934. |
| 106.00 | 31100. | 31079. |
| 106.00 | 31000. | 31079. |
| 120.00 | 37300. | 37242. |
| 120.00 | 37200. | 37242. |
| 131.00 | 42200. | 41999. |
| 131.00 | 42000. | 41999. |
| 148.00 | 49700. | 49632. |
| 148.00 | 49900. | 49632. |
| 168.00 | 58600. | 58589. |
| 168.00 | 58800. | 58589. |
| 192.00 | 66400. | 66139. |
| 192.00 | 66300. | 66139. |
| 216.00 | 69800. | 68998. |
| 216.00 | 67700. | 68998. |

Table 4A

Effect of pulp density (24%) at 0.23% CO₂

| INDEPENDENT VARIABLE | REGRESSION COEFFICIENT | STANDARD DEVIATION |
|-------------------------|---------------------------|-----------------------|
| X | -0.240356E-02 | 0.170125D-01 |
| X2 | -0.681870D-03 | 0.492853D-03 |
| X3 | 0.595578D-05 | 0.552764D-05 |
| X4 | -0.250921D-07 | 0.263025D-07 |
| X5 | 0.412513D-10 | 0.445235D-10 |

CONSTANT TERM = 0.360096E 01

STANDARD ERROR OF ESTIMATE = 0.242196E 00

RESIDUAL VARIANCE = 0.586590E-01

MULTIPLE CORRELATION COEFFICIENT = 0.99683

R SQUARED = 0.99368

The generalized logistic equation describing these data is:

$$P = 72800 / (1 + \exp(f(t)))$$

$$\begin{aligned} \text{where } f(t) = & 3.6010 - 2.4036 * 10^{-3} * t - 6.8187 * 10^{-4} * t^2 + 5.9558 * 10^{-6} * t^3 \\ & - 2.5092 * 10^{-8} * t^4 + 4.1251 * 10^{-11} * t^5 \end{aligned}$$

Table 4B

Effect of pulp density (24%) at 0.23% CO₂

| VALUES OF X | VALUES OF Y | FITTED VALUES OF Y |
|-------------|-------------|--------------------|
| 0.0 | 2030.0 | 1934.5 |
| 0.0 | 2040.0 | 1934.5 |
| 21.000 | 2270.0 | 2589.0 |
| 21.000 | 2300.0 | 2589.0 |
| 44.000 | 5200.0 | 5055.8 |
| 44.000 | 5200.0 | 5055.8 |
| 70.000 | 13300. | 12216. |
| 70.000 | 13100. | 12216. |
| 80.000 | 17300. | 16832. |
| 80.000 | 17300. | 16832. |
| 102.00 | 27500. | 30601. |
| 102.00 | 27700. | 30601. |
| 120.00 | 39000. | 43435. |
| 120.00 | 38800. | 43435. |
| 140.00 | 51800. | 55666. |
| 140.00 | 51500. | 55666. |
| 164.00 | 67000. | 64997. |
| 164.00 | 67100. | 64997. |
| 189.00 | 69700. | 69571. |
| 189.00 | 69900. | 69571. |
| 212.00 | 70800. | 71249. |
| 212.00 | 71000. | 71249. |
| 236.00 | 72100. | 71822. |
| 236.00 | 71600. | 71822. |

Table 5A

Effect of pulp density (24%) at 1.03% CO₂

| INDEPENDENT VARIABLE | REGRESSION COEFFICIENT | STANDARD DEVIATION |
|-------------------------|---------------------------|-----------------------|
| X | 0.136909D-02 | 0.827012D-02 |
| X2 | -0.112858D-02 | 0.308046D-03 |
| X3 | 0.117130D-04 | 0.434311D-05 |
| X4 | -0.564931D-07 | 0.257424D-07 |
| X5 | 0.107215D-09 | 0.542016D-10 |

CONSTANT TERM = 0.369511E 01
 STANDARD ERROR OF ESTIMATE = 0.100037E 00
 RESIDUAL VARIANCE = 0.100075E-01
 MULTIPLE CORRELATION COEFFICIENT = 0.99931
 R SQUARED = 0.99863

The generalized logistic equation describing these data is:

$$P = 72400 / (1 + \exp(f(t)))$$

$$\text{where } f(t) = 3.6951 + 1.3691 * 10^{-3} * t - 1.1286 * 10^{-3} * t^2 + 1.1713 * 10^{-5} * t^3 \\ - 5.6493 * 10^{-8} * t^4 + 1.0722 * 10^{-10} * t^5$$

Table 5B

Effect of pulp density (24%) at 1.03% CO₂

| VALUES OF X | VALUES OF Y | FITTED VALUES OF Y |
|-------------|-------------|--------------------|
| 0.0 | 1780.0 | 1755.2 |
| 0.0 | 1790.0 | 1755.2 |
| 22.000 | 2410.0 | 2597.7 |
| 22.000 | 2430.0 | 2597.7 |
| 31.000 | 3740.0 | 3591.3 |
| 31.000 | 3710.0 | 3591.3 |
| 46.000 | 6800.0 | 6722.8 |
| 46.000 | 6900.0 | 6722.8 |
| 56.000 | 10100. | 10332. |
| 56.000 | 10200. | 10332. |
| 73.000 | 21300. | 20113. |
| 73.000 | 21200. | 20113. |
| 96.000 | 38700. | 38650. |
| 96.000 | 38800. | 38650. |
| 105.00 | 44600. | 45792. |
| 105.00 | 44800. | 45792. |
| 117.00 | 52300. | 53905. |
| 117.00 | 52100. | 53905. |
| 129.00 | 60000. | 60024. |
| 129.00 | 60200. | 60024. |
| 144.00 | 66200. | 65097. |
| 144.00 | 66500. | 65097. |
| 171.00 | 68900. | 69372. |
| 171.00 | 69000. | 69372. |
| 190.00 | 70500. | 70322. |
| 190.00 | 70300. | 70322. |

Table 6A

Effect of pulp density (24%) at 7.92% CO₂

| INDEPENDENT VARIABLE | REGRESSION COEFFICIENT | STANDARD DEVIATION |
|--|---------------------------|-----------------------|
| X | 0.156638D-01 | 0.800185D-02 |
| X2 | -0.146572E-02 | 0.281942D-03 |
| X3 | 0.144663D-04 | 0.387674D-05 |
| X4 | -0.627694D-07 | 0.224352D-07 |
| X5 | 0.101064D-09 | 0.459414D-10 |
| CONSTANT TERM = 0.349736E 01 | | |
| STANDARD ERROR OF ESTIMATE = 0.106098E 00 | | |
| RESIDUAL VARIANCE = 0.112568E-01 | | |
| MULTIPLE CORRELATION COEFFICIENT = 0.99932 | | |
| R SQUARED = 0.99864 | | |

The generalized logistic equation describing these data is:

$$P = 70600 / (1 + \exp(f(t)))$$

$$\begin{aligned} \text{where } f(t) = & 3.4974 + 1.5664 * 10^{-2} * t - 1.4657 * 10^{-3} * t^2 + 1.4466 * 10^{-5} * t^3 \\ & - 6.2769 * 10^{-8} * t^4 + 1.0106 * 10^{-10} * t^5 \end{aligned}$$

Table 6B

Effect of pulp density (24%) at 7.92% CO₂

| VALUES OF X | VALUES OF Y | FITTED VALUES OF Y |
|-------------|-------------|--------------------|
| 0.0 | 2100.0 | 2074.8 |
| 0.0 | 2100.0 | 2074.8 |
| 21.000 | 2380.0 | 2506.3 |
| 21.000 | 2410.0 | 2506.3 |
| 28.000 | 3200.0 | 3139.3 |
| 28.000 | 3280.0 | 3139.3 |
| 44.000 | 5900.0 | 6076.3 |
| 44.000 | 6000.0 | 6076.3 |
| 71.000 | 19000. | 19186. |
| 71.000 | 19000. | 19186. |
| 80.000 | 28200. | 26048. |
| 80.000 | 28400. | 26048. |
| 92.000 | 36000. | 35889. |
| 92.000 | 35800. | 35889. |
| 103.00 | 42800. | 44351. |
| 103.00 | 42900. | 44351. |
| 116.00 | 51300. | 52576. |
| 116.00 | 51500. | 52576. |
| 126.00 | 57400. | 57423. |
| 126.00 | 57800. | 57423. |
| 144.00 | 63700. | 63405. |
| 144.00 | 63600. | 63405. |
| 167.00 | 67800. | 67505. |
| 167.00 | 67900. | 67505. |
| 189.00 | 68900. | 69271. |
| 189.00 | 69000. | 69271. |
| 198.00 | 69800. | 69644. |
| 198.00 | 69700. | 69644. |

Table 7A

Effect of specific surface area at 1.0% CO₂. Cyclosizer fraction No. 1

| INDEPENDENT VARIABLE | REGRESSION COEFFICIENT | STANDARD DEVIATION |
|-------------------------|---------------------------|-----------------------|
| X | -0.124841D-01 | 0.419484D-01 |
| X2 | -0.165177D-02 | 0.206551D-02 |
| X3 | 0.112255D-04 | 0.378458D-04 |
| X4 | 0.187596D-07 | 0.290916D-06 |
| X5 | -0.212228D-09 | 0.793635D-09 |

CONSTANT TERM = 0.326576E 01
 STANDARD ERROR OF ESTIMATE = 0.244258E 00
 RESIDUAL VARIANCE = 0.596619E-01
 MULTIPLE CORRELATION COEFFICIENT = 0.99774
 R SQUARED = 0.99548

The generalized logistic equation describing these data is:

$$P = 71200 / (1 + \exp(f(t)))$$

$$\begin{aligned}
 \text{where } f(t) = & 3.2658 - 1.2484 * 10^{-2} * t - 1.6518 * 10^{-3} * t^2 + 1.1226 * 10^{-5} * t^3 \\
 & + 1.8760 * 10^{-8} * t^4 - 2.1223 * 10^{-10} * t^5
 \end{aligned}$$

Table 7BEffect of specific surface area at 1.0% CO₂

Cyclosizer fraction No. 1

| VALUES OF X | VALUES OF Y | FITTED VALUES OF Y |
|-------------|-------------|--------------------|
| 0.0 | 2680.0 | 2617.6 |
| 22.000 | 5200.0 | 6403.1 |
| 34.000 | 18600. | 14215. |
| 50.000 | 36300. | 36201. |
| 58.000 | 45300. | 48383. |
| 70.000 | 58800. | 60728. |
| 81.000 | 67300. | 66041. |
| 94.000 | 68700. | 68598. |
| 106.00 | 69300. | 69513. |
| 118.00 | 69900. | 69895. |
| 130.00 | 70100. | 70075. |
| 145.00 | 70300. | 70303. |

Table 8A

Effect of specific surface area at 1.0% CO₂

Bahco-sizer fraction No. 1

| INDEPENDENT VARIABLE | REGRESSION COEFFICIENT | STANDARD DEVIATION |
|-------------------------|---------------------------|-----------------------|
| X | -0.711331D-02 | 0.448937D-01 |
| X2 | -0.159162D-02 | 0.221054D-02 |
| X3 | 0.840387D-05 | 0.405030D-04 |
| X4 | 0.327378D-07 | 0.311342D-06 |
| X5 | -0.209468D-09 | 0.849358D-09 |

CONSTANT TERM = 0.305298E 01
STANDARD ERROR OF ESTIMATE = 0.261408E 00
RESIDUAL VARIANCE = 0.683339E-01
MULTIPLE CORRELATION COEFFICIENT = 0.99771
R SQUARED = 0.99542

The generalized logistic equation describing these data is:

$$P = 71900 / (1 + \exp(f(t)))$$

$$\text{where } f(t) = 3.0530 - 7.1133 * 10^{-3} * t - 1.5916 * 10^{-3} * t^2 + 8.4039 * 10^{-6} * t^3 \\ + 3.2738 * 10^{-8} * t^4 - 2.0947 * 10^{-10} * t^5$$

Table 8BEffect of specific surface area at 1.0% CO₂

Bahco-sizer fraction No. 1

| VALUES OF X | VALUES OF Y | FITTED VALUES OF Y |
|-------------|-------------|--------------------|
| 0.0 | 3350.0 | 3241.9 |
| 22.000 | 5400.0 | 7029.9 |
| 34.000 | 20300. | 14970. |
| 50.000 | 38400. | 37604. |
| 58.000 | 47500. | 50237. |
| 70.000 | 60900. | 62766. |
| 81.000 | 68200. | 67858. |
| 94.000 | 70500. | 70132. |
| 106.00 | 70800. | 70884. |
| 118.00 | 71100. | 71174. |
| 130.00 | 71300. | 71273. |
| 145.00 | 71300. | 71299. |

Table 9A

Leaching in unbaffled tank at 1.0% CO₂

| INDEPENDENT VARIABLE | REGRESSION COEFFICIENT | STANDARD DEVIATION |
|--|---------------------------|-----------------------|
| X | -0.360925D-01 | 0.620146D-02 |
| X2 | 0.367240D-03 | 0.112604D-03 |
| X3 | -0.289729D-05 | 0.813377D-06 |
| X4 | 0.936691D-08 | 0.250395D-08 |
| X5 | -0.110220D-10 | 0.274728D-11 |
| CONSTANT TERM = 0.424634E 01 | | |
| STANDARD ERROR OF ESTIMATE = 0.119222E 00 | | |
| RESIDUAL VARIANCE = 0.142140E-01 | | |
| MULTIPLE CORRELATION COEFFICIENT = 0.99933 | | |
| R SQUARED = 0.99866 | | |

The generalized logistic equation describing these data is:

$$P = 112500 / (1 + \exp(f(t)))$$

$$\begin{aligned} \text{where } f(t) = & 4.2463 - 3.6093 * 10^{-2} * t + 3.6724 * 10^{-4} * t^2 - 2.8973 * 10^{-6} * t^3 \\ & + 9.3669 * 10^{-9} * t^4 - 1.1022 * 10^{-11} * t^5 \end{aligned}$$

Table 9B

Leaching in unbaffled tank at 1.0% CO₂

| VALUES OF X | VALUES OF Y | FITTED VALUES OF Y |
|-------------|-------------|--------------------|
| 0.0 | 1440.0 | 1587.9 |
| 20.000 | 3060.0 | 2850.8 |
| 24.000 | 3300.0 | 3127.2 |
| 44.000 | 4800.0 | 4597.4 |
| 48.000 | 5200.0 | 4912.5 |
| 68.000 | 6600.0 | 6675.0 |
| 72.000 | 7300.0 | 7081.6 |
| 92.000 | 8600.0 | 9560.9 |
| 96.000 | 9200.0 | 10174. |
| 120.00 | 14300. | 15088. |
| 144.00 | 20800. | 23014. |
| 164.00 | 34400. | 32680. |
| 168.00 | 37800. | 34963. |
| 188.00 | 51000. | 47827. |
| 192.00 | 54500. | 50611. |
| 212.00 | 64200. | 64761. |
| 216.00 | 67500. | 67525. |
| 240.00 | 82500. | 82558. |
| 260.00 | 91400. | 92413. |
| 264.00 | 92300. | 94081. |
| 288.00 | 0.10070E 06 | 0.10220E 06 |
| 312.00 | 0.10750E 06 | 0.10759E 06 |
| 336.00 | 0.11120E 06 | 0.11074E 06 |
| 360.00 | 0.11210E 06 | 0.11210E 06 |
| 365.00 | 0.11220E 06 | 0.11223E 06 |

Table 10A

Leaching in baffled tank at 1.0% CO₂

| INDEPENDENT VARIABLE | REGRESSION COEFFICIENT | STANDARD DEVIATION |
|-------------------------|---------------------------|-----------------------|
| X | -0.276813D-01 | 0.641820D-02 |
| X2 | 0.416842D-03 | 0.119612D-03 |
| X3 | -0.455291D-05 | 0.901220D-06 |
| X4 | 0.183833D-07 | 0.293197D-08 |
| X5 | -0.256570D-10 | 0.342962D-11 |

CONSTANT TERM = 0.406040E 01
 STANDARD ERROR OF ESTIMATE = 0.119072E 00
 RESIDUAL VARIANCE = 0.141782E-01
 MULTIPLE CORRELATION COEFFICIENT = 0.99930
 R SQUARED = 0.99860

The generalized logistic equation describing these data is:

$$P = 120000 / (1 + \exp(f(t)))$$

$$\begin{aligned}
 \text{where } f(t) = & 4.0604 - 2.7681 * 10^{-2} * t + 4.1684 * 10^{-4} * t^2 - 4.5529 * 10^{-6} * t^3 \\
 & + 1.8383 * 10^{-8} * t^4 - 2.5657 * 10^{-11} * t^5
 \end{aligned}$$

Table 10B

Leaching in baffled tank at 1.0% CO₂

| VALUES OF X | VALUES OF Y | FITTED VALUES OF Y |
|-------------|-------------|--------------------|
| 0.0 | 2100.0 | 2034.0 |
| 20.000 | 2900.0 | 3069.9 |
| 26.000 | 3100.0 | 3348.9 |
| 43.000 | 4300.0 | 4115.1 |
| 49.000 | 4700.0 | 4402.5 |
| 67.000 | 5800.0 | 5460.3 |
| 72.000 | 6100.0 | 5837.8 |
| 91.000 | 8000.0 | 7824.1 |
| 97.000 | 8500.0 | 8697.7 |
| 116.00 | 10100. | 12616. |
| 121.00 | 13500. | 14013. |
| 141.00 | 21500. | 21572. |
| 147.00 | 25600. | 24523. |
| 163.00 | 36300. | 33933. |
| 174.00 | 43800. | 41485. |
| 187.00 | 52100. | 51042. |
| 198.00 | 59700. | 59210. |
| 212.00 | 68500. | 69161. |
| 217.00 | 71900. | 72521. |
| 222.00 | 73500. | 75766. |
| 235.00 | 83500. | 83684. |
| 240.00 | 86400. | 86552. |
| 246.00 | 89900. | 89891. |
| 259.00 | 96600. | 96811. |
| 265.00 | 0.10130E 06 | 99881. |
| 270.00 | 0.10250E 06 | 0.10237E 06 |
| 285.00 | 0.10910E 06 | 0.10932E 06 |
| 292.00 | 0.11150E 06 | 0.11212E 06 |
| 307.00 | 0.11630E 06 | 0.11668E 06 |
| 314.00 | 0.11810E 06 | 0.11804E 06 |
| 327.00 | 0.11950E 06 | 0.11943E 06 |
| 333.00 | 0.11980E 06 | 0.11972E 06 |
| 338.00 | 0.11980E 06 | 0.11986E 06 |

APPENDIX 3

Determination of specific surface area

Determination of specific surface area

The Cyclosizer and Bahco-sizer subsieve fractions have been characterized by determination of the mean particle diameter. However, only regular particles, e.g., spheres or cylinders, possess a definite diameter as well as known volume and surface area. Irregular particles such as those contained in the size fractions (see their microscopic pictures in Figure 11 and 12) have a definite volume and surface area only. Therefore, a better characterization of the subsieve zinc sulfide material can be achieved through determination of its specific surface area, which is the surface area per unit mass of solids.

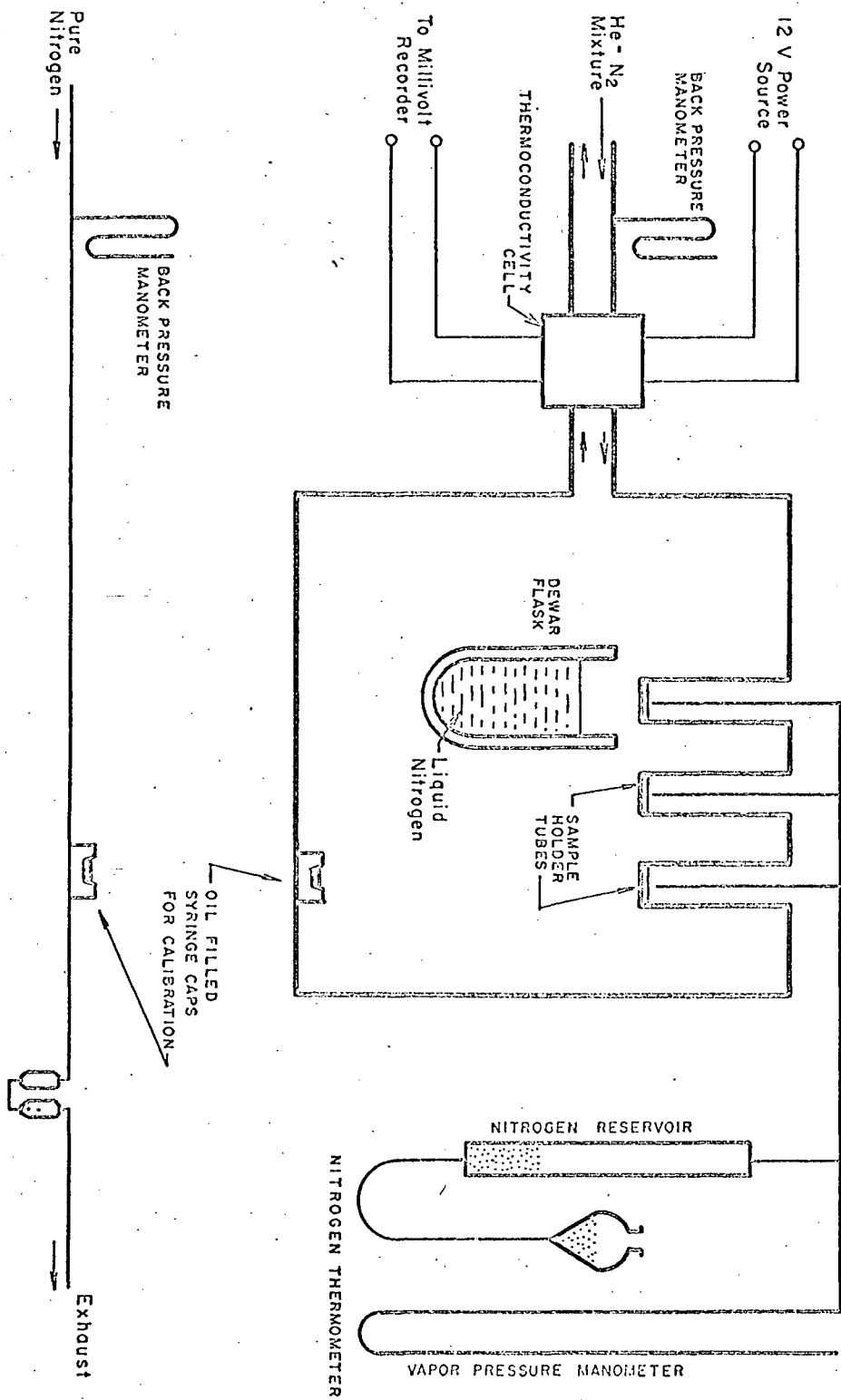
Figure 1 is a schematic representation of the dynamic nitrogen adsorption apparatus used for determination of specific surface area of the unfractionated -400 mesh subsieve zinc sulfide concentrate and of the different subsieve size (Cyclosizer and Bahco-sizer) fractions.

1. Experimental procedure

Three different samples of known weight were introduced into the sample-holders and placed in the circuit as indicated in Figure 1. A known mixture of helium and nitrogen content was passed at a constant flow (12 ml per minute) through the system to replace the air originally present. When this was achieved a steady base line was obtained on the recorder chart. Then the first sample was slowly immersed in the liquid nitrogen bath. Adsorption of nitrogen by the solid was indicated by a peak on the recorder chart. After the recorder pen returned to its base line position, the polarity switch was reversed in order to take advantage of the full range of the recorder scale, prior to desorption of nitrogen. The sample tube was then warmed up by removal from the liquid nitrogen bath, while the desorption peak for the nitrogen was

SCHEMATIC DIAGRAM OF THE DYNAMIC NITROGEN ADSORPTION APPARATUS

Figure 1



recorded. The areas under these two peaks (adsorption and desorption) were equal and constitute a measure of the amount of adsorbed nitrogen. The complete sequence of this procedure was repeated several times to enhance the validity of the results. Then the entire procedure was repeated on the second and the third samples. Calibration of the apparatus was achieved by injecting known volumes of pure nitrogen into the system under adsorption conditions.

In addition the whole process was repeated with two more gas mixtures. In this study, gas mixtures containing 25, 15 and 5% of nitrogen in helium were used.

Figure 2 shows some typical examples of adsorption, desorption and calibration (due to injection of nitrogen) peaks together with their disc integrator traces, used to determine peak area.

2. Calculation of specific surface area

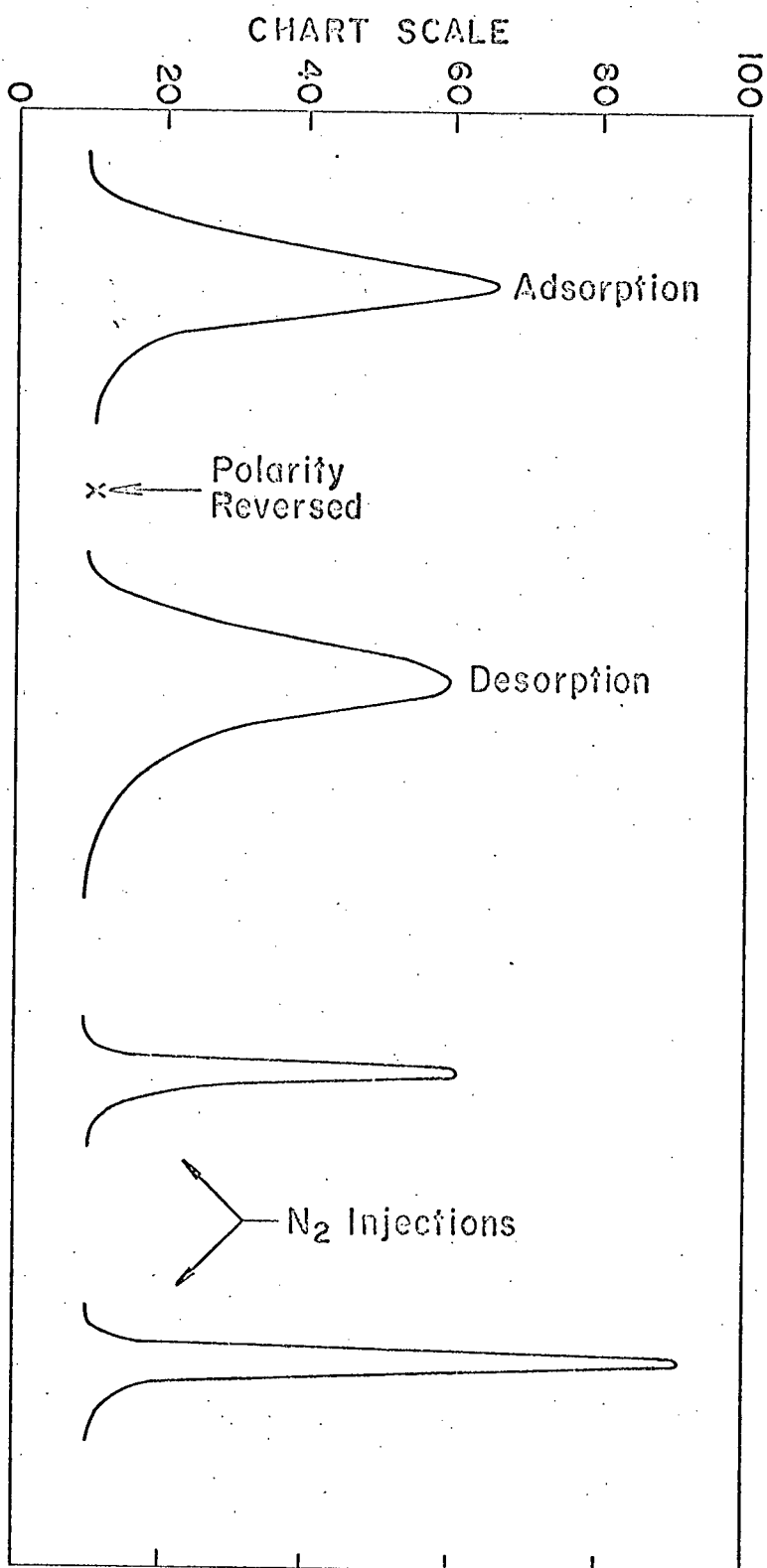
The computer programs 1 and 2 present the calculations of the specific surface area of the subsieve zinc sulfide samples.

In program 1, the relationship between injected volume of pure nitrogen and area under the adsorption and desorption curves was determined by the least squares technique. Using this relationship, the volume of nitrogen adsorbed on the sample is determined, then it is recalculated for standard temperature and pressure conditions. Thereafter, the B.E.T.-coordinates are calculated. All these determinations have been carried out on data obtained at 25, 15 and 5% N_2 levels.

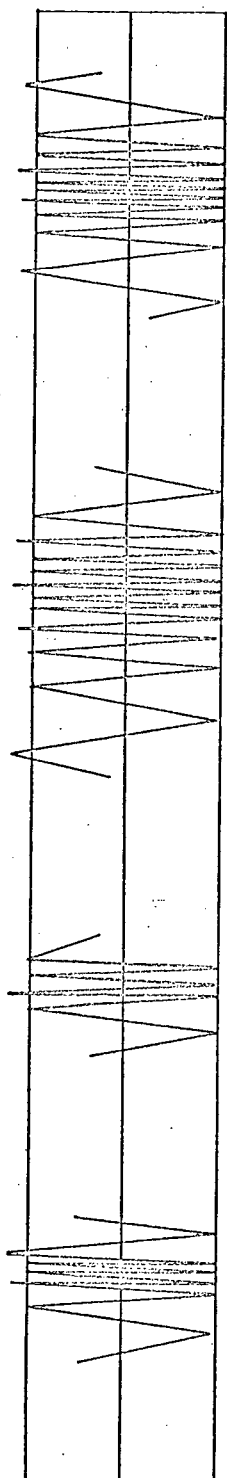
In program 2, the specific surface area of the samples has been calculated through application of the Brunauer, Emmett and Teller (B.E.T.) equation:

Figure 2

TYPICAL ADSORPTION AND DESORPTION CURVES



ELECTRONIC INTEGRATION OF PEAK AREAS



$$\frac{P}{V_{\text{ads}} (P_o - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \left(\frac{P}{P_o} \right) \quad (1)$$

where P = partial pressure of nitrogen (in the gas mixture)

P_o = saturation pressure of nitrogen at temperature of liquid
nitrogen

V_{ads} = volume of nitrogen adsorbed on the sample (STP)

V_m = volume of adsorbed nitrogen due to monolayer coverage

C = constant

This is the equation of a straight line having $P/V_{\text{ads}} (P_o - P)$ as the dependent and P/P_o as the independent variable (B.E.T.-coordinates). Through least squares fitting of these data the slope $((C - 1)/V_m C)$ and the intercept $(1/V_m C)$ of the straight line were ascertained. From these values, the monolayer capacity (V_m) and the specific monolayer capacity (V_mspc) were derived. When this latter is multiplied with a factor (F), the specific surface area of the sample is obtained. The value of the factor (F) is given in the following form:

$$F = \frac{6.02 * 10^{23} * 16.2 * 10^{-20} * 10^{-6}}{22.414} = 4.3532 * 10^{-3} \quad (2)$$

where $6.02 * 10^{23}$ = Avogadro's number (molecules/mole)

16.2 = area covered by a N₂ molecule (square Angstroms/
molecule)

10^{-20} = conversion of square Angstroms to square meters

10^{-6} = conversion of microliters to liters in V_mspc

22.414 = volume of a mole of nitrogen gas under standard
conditions (liter per mole)

Determination of the specific surface area will be demonstrated for Cyclosizer fraction No. 1.

The output of computer program 1 for the calibration data obtained at 25, 15 and 5% nitrogen levels is presented in Table 1A to 1C and the corresponding B.E.T.-coordinates in Table 1D. The least squares fit of the B.E.T.-data and the value for the specific surface area of the sample, Cyclosizer fraction No. 1, are presented in Table 2, as the output of computer program 2. The fitted values for the calibration data in Tables 1A to 1C and the B.E.T.-coordinates in Table 2 are in close agreement with those derived experimentally.

The calibration data are graphed in Figure 3. Each point of the individual plots for 25, 15 and 5% nitrogen levels, is the arithmetic average of all measurements made under the indicated conditions. For all three nitrogen concentrations a precise straight line relationship is obtained, with a zero intercept.

The B.E.T.-plot for the Cyclosizer fraction No. 1 is presented in Figure 4. Here again, each point represents the average of numerous measurements. An excellent straight line relationship has been obtained. The intercept and the slope of this straight line were used for determination of the monolayer capacity.

The specific surface areas of the rest of Cyclosizer and Bahco-sizer fractions and of the -400 mesh infractionated subsieve zinc sulfide concentrate were determined in a similar way to that outlined above. The results of these determinations are summarized in Table 3. To demonstrate the reproducibility of the results, the specific surface area of the third size fraction produced by both Cyclosizer and Bahco-sizer fractionation techniques, has been determined twice. As Table 3 shows, the duplicate data agree well, e.g., values for the specific

Figure 3

CALIBRATION CURVES FOR CYCLOSIZER FRACTION No. 1

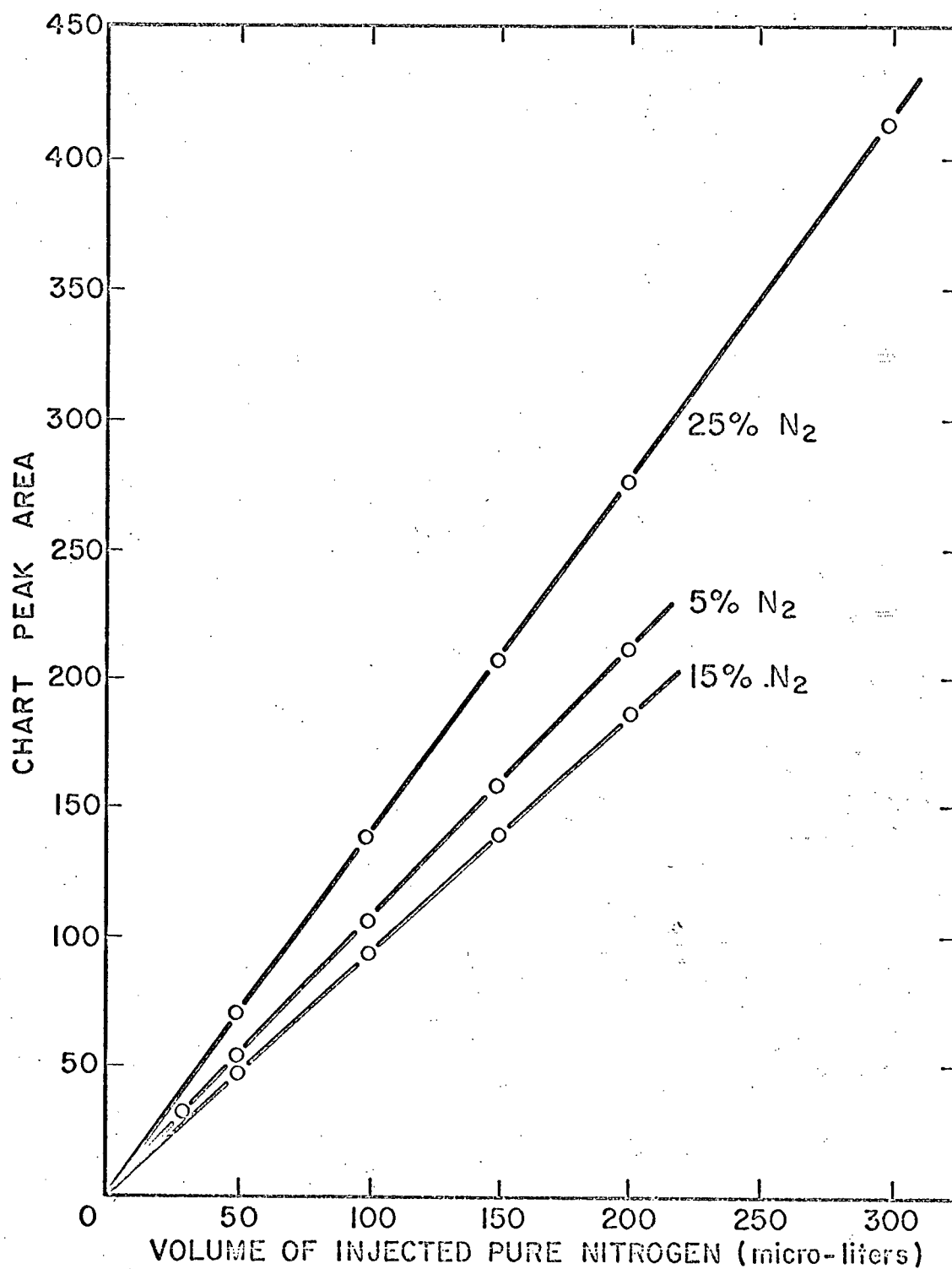


Figure 4
B.E.T. PLOT FOR CYCLOSIZER FRACTION No. 1

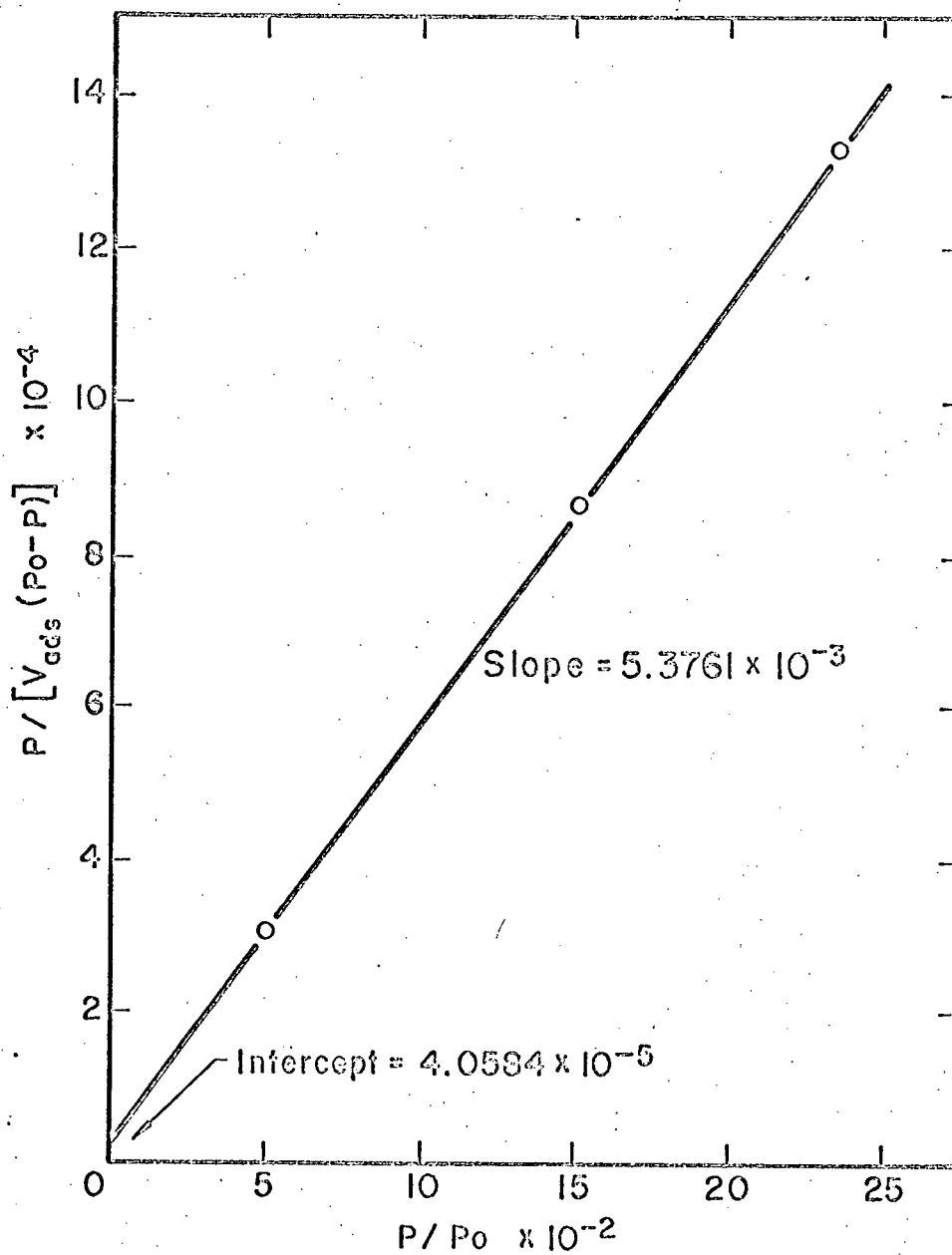


Table 3

Summary of B.E.T.-specific surface areas

| Sample | Sample Weight (g) | Slope $\frac{c-1}{V_m C} * 10^{-2}$ | Intercept $\frac{1}{V_m C} * 10^{-4}$ | V _m spc (micro-liter/g) | Spec. surface area (m ² /g) |
|------------|----------------------|--|--|---------------------------------------|--|
| C.S. No. 1 | 0.1323 | 0.5376 | 0.4058 | 1,395.45 | 6.07 |
| 2 | 0.1582 | 2.2446 | 4.4764 | 276.11 | 1.20 |
| 3 | 0.3452 | 1.9001 | 3.7863 | 149.48 | 0.65 |
| 4 | 0.2670 | 2.4915 | 4.1861 | 147.84 | 0.64 |
| 5 | 1.1916 | 0.6375 | 2.6739 | 126.35 | 0.55 |
| | 1.5117 | 0.6211 | 1.9115 | 103.32 | 0.44 |
| B.S. No. 1 | 0.3900 | 0.1583 | 0.3403 | 1,585.95 | 6.90 |
| 2 | 0.5632 | 0.1865 | 0.1723 | 943.17 | 4.11 |
| 3 | 0.2490 | 0.5812 | 3.0918 | 656.10 | 2.86 |
| 4 | 0.3953 | 0.3845 | 0.3992 | 651.16 | 2.83 |
| 5 | 0.6975 | 0.4914 | 0.7220 | 287.53 | 1.25 |
| 6 | 0.7575 | 0.7768 | 1.3267 | 167.09 | 0.73 |
| 7 | 1.1588 | 0.7872 | 1.7079 | 107.30 | 0.47 |
| 8 | 1.4055 | 0.7832 | 1.8476 | 88.75 | 0.39 |
| | 1.5627 | 0.9549 | 0.8913 | 66.39 | 0.29 |
| -400 mesh | 0.3357 | 0.9339 | 1.0370 | 315.48 | 1.37 |

Where C.S. = Cyclosizer fractions
 B.S. = Bahco-sizer fractions

surface area of the Cyclosizer fraction No. 3 were 0.65 and 0.64 m²/g and for the corresponding Bahco-sizer fraction, 2.86 and 2.83 m²/g.

Program 1

```
C
C      LEAST SQUARES FIT
C      CALIBRATION
      DIMENSION X(200),Y(200),YF(200),W(200),E1(50),E2(50),P(50)
      1,DIFF(200),XX(200),YY(200),VSTP(200),PO(200)
      2,X1(200),Y1(200)
      3 READ(5,1)N,M,NI
      1 FORMAT(3I5)
      DO 39 I=1,5
39 P(I)=0.0
      DO 57 I=1,N
      READ(5,2)X(I),Y(I)
      2 FORMAT(8F10.0)
57 CONTINUE
      EXTERNAL AUX
      CALL LQF(X,Y,YF,W,E1,E2,P,0.,N,M,NI,ND,EP,AUX)
      IF(ND.EQ.0) GO TO 3
      WRITE(6,40)
40 FORMAT(66H ESTIMATES OF ROOT MEAN SQUARE STATISTICAL ERROR IN THE
1PARAMETERS)
      WRITE(6,5)(E1(I),I=1,M)
      WRITE(6,4)
      4 FORMAT(60H ESTIMATES OF ROOT MEAN SQUARE TOTAL ERROR IN THE PARAME
1TERS)
      WRITE(6,5)(E2(I),I=1,M)
      5 FORMAT(1X,8G15.5)
      WRITE(6,6)
      6 FORMAT(65HMICROLITER OF N2 CHART PEAK AREA FITTED VALUE OF CHART
```

Program 1 (continued - 1)

```
1PEAK AREA)
DO 7 I=1,N
7 WRITE(6,5)X(I),Y(I),YF(I)
C=1./P(2)
D=-P(1)/P(2)
READ(5,1)NN
READ(5,2)P1,T,S
C      P1 IS THE ATM. PRESSURE(MMHG)
C      T IS THE ABS. TEMP. IN KELVIN-DEGREE
C      S IS THE NITROGEN CONTENT OF GAS MIXTURE
DO 60 I=1,NN
READ(5,2)DIFF(I),YY(I)
60 CONTINUE
C      DIFF(I) IS THE PARTIAL PRESSURE OF LIQUID NITROGEN
DO 61 I=1,NN
61 XX(I)=D+C*YY(I)
C      XX(I) IS THE VOLUME OF ADSORBED NITROGEN
DO 62 I=1,NN
VSTP(I)=0.359408*(P1/T)*XX(I)
62 CONTINUE
C      THE CONSTANT TERM IS EQUAL TO 273.15/760.
PP=S*P1
C      PP IS THE PARTIAL PRESSURE OF NITROGEN IN GAS MIXTURE
C      PO IS THE SATURATION PRESSURE OF NITROGEN
C      AT TEMPERATURE OF LIQUID NITROGEN (MMHG)
DO 64 I=1,NN
PO(I)=P1+DIFF(I)
```

Program 1 (continued - 2)

C DETERMINATION OF THE B.E.T.-COORDINATES

 X1(I)=PP/PC(I)

64 Y1(I)=PP/(VSTP(I)*(PO(I)-PP))

 WRITE(6,88)

88 FORMAT(1H1)

 WRITE(6,70)

70 FORMAT(75HADS. PEAK AREA VOL. ADS. N2 VOLUME IN STP P/PO

 1 P/(VADS(PC-P)),//)

 DO 55 I=1,NN

55 WRITE(6,5)YY(I),XX(I),VSTP(I),X1(I),Y1(I)

 WRITE(6,8)

 8 FORMAT(1H1)

 GO TO 3

 END

 FUNCTION AUX(P,D,X,L)

 DIMENSION P(50),D(50)

 D(1)=1.

 AUX=P(1)

 DO 10 J=2,5

 D(J)=D(J-1)*X

10 AUX=AUX+P(J)*D(J)

 RETURN

 END

Program 2

C
C
C
C

DETERMINATION OF SPECIFIC SURFACE AREA
LEAST SQUARES FIT

```
DIMENSION X(200),Y(200),YF(200),W(200),E1(50),E2(50),P(50)
3 READ(5,1)N,M,NI
1 FORMAT(3I5)
DO 39 I=1,5
39 P(I)=0.0
DO 57 I=1,N
  READ(5,2)X(I),Y(I)
  2 FORMAT(4F15.5)
57 CONTINUE
  READ(5,22)WE
  22 FORMAT(8F10.0)
  EXTERNAL AUX
  CALL LQF(X,Y,YF,W,E1,E2,P,0.,N,M,NI,ND,EP,AUX)
  IF(ND.EQ.0) GO TO 3
  WRITE(6,40)
40 FORMAT(66H ESTIMATES OF ROOT MEAN SQUARE STATISTICAL ERROR IN THE
  1PARAMETERS)
  WRITE(6,5)(E1(I),I=1,M)
  WRITE(6,4)
  4 FORMAT(60H ESTIMATES OF ROOT MEAN SQUARE TOTAL ERROR IN THE PARAME
  1TERS)
  WRITE(6,5)(E2(I),I=1,M)
  5 FORMAT(1X,8G15.5)
  WRITE(6,93)
```

Program 2 (continued - 2)

```
93 FORMAT(37H                                B.E.T.-COORDINATES)
   WRITE(6,6)
6  FORMAT(53HVALUES OF P/PC  P/(VADS(PC-P))  FITTED P/(VADS(PC-P)),/)
   DO 7 I=1,N
7  WRITE(6,5)X(I),Y(I),YF(I)
   VM=1./(P(1)+P(2))
   VMSPC=VM/WE
   SSA=0.0043532*VMSPC
   WRITE(6,41)
41  FORMAT(1H0,57HWEIGHT OF SAMPLE MONOLAYER CAPACITY SPECIFIC SURFACE
1  AREA,/)
   WRITE(6,5)WE,VM,SSA
   WRITE(6,8)
8  FORMAT(1H1)
   GO TO 3
   END

   FUNCTION AUX(P,D,X,L)
   DIMENSION P(50),D(50)
   D(1)=1.
   AUX=P(1)
   DO 10 J=2,5
   D(J)=D(J-1)*X
10  AUX=AUX+P(J)*D(J)
   RETURN
   END
```

Table 1A

Curve fitting of calibration data at 25% N₂

for Cyclosizer fraction No. 1

INTERMEDIATE ESTIMATES OF PARAMETERS, SUM OF SQUARES

| | | |
|--------------|--------|-------------|
| 0.0 | 0.0 | 0.14117E 07 |
| -0.47469E-01 | 1.3721 | 253.38 |

FINAL ESTIMATES OF PARAMETERS

| | |
|--------------|--------|
| -0.46432E-01 | 1.3721 |
|--------------|--------|

| | |
|----------------|--------|
| SUM OF SQUARES | 253.38 |
|----------------|--------|

ESTIMATES OF ROOT MEAN SQUARE STATISTICAL ERROR IN THE PARAMETERS

| | |
|---------|-------------|
| 0.46291 | 0.24495E-02 |
|---------|-------------|

ESTIMATES OF ROOT MEAN SQUARE TOTAL ERROR IN THE PARAMETERS

| | |
|--------|-------------|
| 1.6905 | 0.89452E-02 |
|--------|-------------|

MICROLITER OF N₂ CHART PEAK AREA FITTED VALUE OF CHART PEAK AREA

| | | |
|--------|--------|--------|
| 50.000 | 64.300 | 68.556 |
| 50.000 | 70.500 | 68.556 |
| 50.000 | 67.200 | 68.556 |
| 50.000 | 70.700 | 68.556 |
| 100.00 | 139.00 | 137.16 |
| 100.00 | 140.10 | 137.16 |
| 100.00 | 137.00 | 137.16 |
| 100.00 | 137.10 | 137.16 |
| 150.00 | 211.30 | 205.76 |
| 150.00 | 207.80 | 205.76 |
| 150.00 | 205.40 | 205.76 |
| 150.00 | 205.30 | 205.76 |
| 200.00 | 275.60 | 274.36 |
| 200.00 | 273.10 | 274.36 |
| 200.00 | 267.30 | 274.36 |
| 200.00 | 266.00 | 274.36 |
| 300.00 | 416.40 | 411.57 |
| 300.00 | 411.00 | 411.57 |
| 300.00 | 407.80 | 411.57 |
| 300.00 | 415.50 | 411.57 |
| 300.00 | 412.80 | 411.57 |

Table 1B

Curve fitting of calibration data at 15% N₂
for Cyclosizer fraction No. 1

INTERMEDIATE ESTIMATES OF PARAMETERS, SUM OF SQUARES

| | | |
|-------------|---------|-------------|
| 0.0 | 0.0 | 0.29163E 06 |
| C.48510E-01 | 0.92232 | 72.151 |

FINAL ESTIMATES OF PARAMETERS

| | |
|-------------|---------|
| C.48084E-01 | 0.92233 |
|-------------|---------|

| | |
|----------------|--------|
| SUM OF SQUARES | 72.151 |
|----------------|--------|

ESTIMATES OF ROOT MEAN SQUARE STATISTICAL ERROR IN THE PARAMETERS

| | |
|---------|-------------|
| 0.55736 | 0.40406E-02 |
|---------|-------------|

ESTIMATES OF ROOT MEAN SQUARE TOTAL ERROR IN THE PARAMETERS

| | |
|--------|-------------|
| 1.1836 | 0.85804E-02 |
|--------|-------------|

MICROLITER OF N₂ CHART PEAK AREA FITTED VALUE OF CHART PEAK AREA

| | | |
|--------|--------|--------|
| 50.000 | 48.700 | 46.164 |
| 50.000 | 48.100 | 46.164 |
| 50.000 | 45.900 | 46.164 |
| 50.000 | 48.400 | 46.164 |
| 50.000 | 44.600 | 46.164 |
| 100.00 | 92.500 | 92.281 |
| 100.00 | 89.200 | 92.281 |
| 100.00 | 91.500 | 92.281 |
| 100.00 | 90.300 | 92.281 |
| 150.00 | 140.10 | 138.40 |
| 150.00 | 137.20 | 138.40 |
| 150.00 | 137.60 | 138.40 |
| 150.00 | 135.30 | 138.40 |
| 200.00 | 186.00 | 184.51 |
| 200.00 | 181.50 | 184.51 |
| 200.00 | 184.80 | 184.51 |
| 200.00 | 187.10 | 184.51 |
| 200.00 | 187.30 | 184.51 |

Table 1C

Curve fitting of calibration data at 5% N₂
for Cyclosizer fraction No. 1

INTERMEDIATE ESTIMATES OF PARAMETERS, SUM OF SQUARES

| | | |
|-------------|--------|-------------|
| 0.0 | 0.0 | 0.26627E 06 |
| 0.40710E-01 | 1.0432 | 56.982 |

FINAL ESTIMATES OF PARAMETERS

| | |
|-------------|--------|
| 0.40609E-01 | 1.0432 |
|-------------|--------|

| | |
|----------------|--------|
| SUM OF SQUARES | 56.982 |
|----------------|--------|

ESTIMATES OF ROOT MEAN SQUARE STATISTICAL ERROR IN THE PARAMETERS

| | |
|---------|-------------|
| 0.45337 | 0.36676E-02 |
|---------|-------------|

ESTIMATES OF ROOT MEAN SQUARE TOTAL ERROR IN THE PARAMETERS

| | |
|---------|-------------|
| 0.91466 | 0.73991E-02 |
|---------|-------------|

MICROLITER OF N₂ CHART PEAK AREA FITTED VALUE OF CHART PEAK AREA

| | | |
|--------|--------|--------|
| 30.000 | 30.700 | 31.336 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 30.000 | 31.000 | 31.336 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 30.000 | 30.900 | 31.336 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 30.000 | 31.100 | 31.336 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 30.000 | 30.800 | 31.336 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 50.000 | 53.900 | 52.200 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 50.000 | 51.500 | 52.200 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 100.00 | 108.30 | 104.36 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 100.00 | 105.10 | 104.36 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 100.00 | 100.00 | 104.36 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 150.00 | 159.90 | 156.52 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 150.00 | 156.90 | 156.52 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 200.00 | 208.40 | 208.68 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 200.00 | 206.30 | 208.68 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 200.00 | 208.80 | 208.68 |
|--------|--------|--------|

| | | |
|--------|--------|--------|
| 200.00 | 208.30 | 208.68 |
|--------|--------|--------|

Table 1D

Output of data derived on Cyclosizer fraction No. 1
at gas mixture (contained 5% nitrogen)

| ADS. PEAK AREA | VOL. ADS. N2 | VOLUME IN STP | P/PO | P/(VADS(PO-P)) |
|----------------|--------------|---------------|-------------|----------------|
| 198.60 | 190.34 | 174.41 | 0.48347E-01 | 0.29129E-03 |
| 197.30 | 189.09 | 173.27 | 0.48719E-01 | 0.29558E-03 |
| 197.20 | 189.00 | 173.18 | 0.48719E-01 | 0.29573E-03 |
| 192.40 | 184.40 | 168.96 | 0.48719E-01 | 0.30311E-03 |
| 187.20 | 179.41 | 164.40 | 0.48719E-01 | 0.31153E-03 |

Table 1D (continued - 1)

Output of data derived on Cyclosizer fraction No. 1
at gas mixture (contained 15% nitrogen)

| ADS. PEAK AREA | VOL. ADS. N2 | VOLUME IN STP | P/PO | P/(VADS(PO-P)) |
|----------------|--------------|---------------|---------|----------------|
| 202.80 | 219.83 | 201.78 | 0.15061 | 0.87872E-03 |
| 218.00 | 236.31 | 216.91 | 0.15061 | 0.81744E-03 |
| 208.50 | 226.01 | 207.45 | 0.15061 | 0.85469E-03 |
| 207.80 | 225.25 | 206.76 | 0.15003 | 0.85371E-03 |
| 209.60 | 227.20 | 208.55 | 0.15003 | 0.84638E-03 |
| 214.00 | 231.97 | 212.93 | 0.15003 | 0.82897E-03 |
| 198.00 | 214.62 | 197.00 | 0.15003 | 0.89597E-03 |

Table 1D (continued - 2)

Output of data derived on Cyclosizer fraction No. 1
at gas mixture (contained 25% nitrogen)

| ADS. PEAK AREA | VOL. ADS. N2 | VOLUME IN STP | P/PO | P/(VADS(PO-P)) |
|----------------|--------------|---------------|---------|----------------|
| 345.90 | 252.14 | 232.06 | 0.23863 | 0.13506E-02 |
| 347.20 | 253.09 | 232.93 | 0.23863 | 0.13455E-02 |
| 360.80 | 263.00 | 242.06 | 0.23863 | 0.12948E-02 |
| 342.30 | 249.51 | 229.65 | 0.23863 | 0.13648E-02 |
| 367.20 | 267.66 | 246.35 | 0.23715 | 0.12619E-02 |
| 353.90 | 257.97 | 237.43 | 0.23656 | 0.13051E-02 |
| 357.70 | 260.74 | 239.98 | 0.23656 | 0.12912E-02 |

Table 2

Determination of specific surface area of Cyclosizer fraction No. 1

INTERMEDIATE ESTIMATES OF PARAMETERS, SUM OF SQUARES

| | | |
|-------------|-------------|-------------|
| 0.0 | 0.0 | 0.17639E-04 |
| 0.40585E-04 | 0.53760E-02 | 0.12055E-07 |

FINAL ESTIMATES OF PARAMETERS

| | |
|-------------|-------------|
| 0.40584E-04 | 0.53761E-02 |
|-------------|-------------|

| | |
|----------------|-------------|
| SUM OF SQUARES | 0.12055E-07 |
|----------------|-------------|

ESTIMATES OF ROOT MEAN SQUARE STATISTICAL ERROR IN THE PARAMETERS

| | |
|---------|--------|
| 0.53326 | 3.0900 |
|---------|--------|

ESTIMATES OF ROOT MEAN SQUARE TOTAL ERROR IN THE PARAMETERS

| | |
|-------------|-------------|
| 0.14200E-04 | 0.82285E-04 |
|-------------|-------------|

B.E.T.-COORDINATES

| VALUES OF P/P0 | P/(VADS(P0-P)) | FITTED P/(VADS(P0-P)) |
|----------------|----------------|-----------------------|
|----------------|----------------|-----------------------|

| | | |
|-------------|-------------|-------------|
| 0.23863 | 0.13506E-02 | 0.13235E-02 |
| 0.23863 | 0.13455E-02 | 0.13235E-02 |
| 0.23863 | 0.12948E-02 | 0.13235E-02 |
| 0.23863 | 0.13648E-02 | 0.13235E-02 |
| 0.23715 | 0.12619E-02 | 0.13155E-02 |
| 0.23656 | 0.13051E-02 | 0.13123E-02 |
| 0.23656 | 0.12912E-02 | 0.13123E-02 |
| 0.15061 | 0.87872E-03 | 0.85027E-03 |
| 0.15061 | 0.81744E-03 | 0.85027E-03 |
| 0.15061 | 0.85469E-03 | 0.85027E-03 |
| 0.15003 | 0.85271E-03 | 0.84715E-03 |
| 0.15003 | 0.84638E-03 | 0.84715E-03 |
| 0.15003 | 0.82897E-03 | 0.84715E-03 |
| 0.15003 | 0.89597E-03 | 0.84715E-03 |
| 0.48247E-01 | 0.29129E-03 | 0.30050E-03 |
| 0.48719E-01 | 0.29558E-03 | 0.30250E-03 |
| 0.48719E-01 | 0.29573E-03 | 0.30250E-03 |
| 0.48719E-01 | 0.30011E-03 | 0.30250E-03 |
| 0.48719E-01 | 0.31153E-03 | 0.30250E-03 |

WEIGHT OF SAMPLE MCNCLAYER CAPACITY SPECIFIC SURFACE AREA

| | | |
|---------|--------|--------|
| 0.13230 | 184.62 | 6.0746 |
|---------|--------|--------|