

ANAEROBIC TREATMENT OF A PAPER PLANT EFFLUENT

by

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SYNOPSIS

The objective of this study was to investigate the anaerobic biological treatment of an organic-bearing wastewater from a particular paper manufacturing process at laboratory scale. The process produces paper by re-pulping waste paper. Effluent from the process has a Chemical Oxygen Demand (COD) concentration of approximately 4500 mg/l with a sulphate content of approximately 300 mg SO_4^{2-} /l. The upflow anaerobic sludge bed (UASB) reactor was selected for the study.

Important information derived from the laboratory treatability study was: (1) the extent of COD removal possible; (2) the effluent quality; (3) the maximum COD loading rate (kgCOD/m^3 reactor/day) which can be achieved while maintaining reasonable COD removal, and the influence on loading rate of temperature; (4) the nature of the sludge produced in the reactor with particular reference to the extent of pelletisation; and (5) the effect of reactor effluent recycling on alkalinity requirements. The following specific conclusions may be itemised from the results obtained:

Wastewater characteristics and chemical addition:

- (1) The waste is amenable to anaerobic treatment in a UASB system.
- (2) The unbiodegradable COD content of the waste is in the region of 10 to 15 percent, and COD removals of approximately 85 percent are possible on a continuous basis.
- (3) The short chain volatile fatty acids acetic and propionic comprise approximately 45 percent of the COD in the influent. The remainder is made up principally of starch, carbohydrates and more complex organics.
- (4) The wastewater is deficient in the elements nitrogen and phosphorus. These elements must be supplemented through chemical addition in order to achieve complete anaerobic treatment.

- (5) The wastewater is acidic, with a pH in the range 5 to 6 generally. Alkalinity must be added to the waste prior to treatment to adjust the pH to approximately neutral.

Organic loading rates:

- (6) Organic loading rates of approximately 25 kgCOD/m³ reactor/day were attained at both 25 and 35°C. This corresponded to a hydraulic retention time of 5 hours at an influent COD concentration of 4500 mg/l. The loading rate was not constrained by limitations in the biological treatment capacity. Rather, difficulties associated with the settleability of the sludge were encountered; blockages of the under-designed laboratory reactor settler occurred.

Sludge characteristics:

- (7) A dense bed of biological sludge extended from the base to approximately half the height of the UASB reactors. This sludge had a granular, well-flocculated form with the flocs appearing to be in the size range 1-2 mm. Very fine sludge was also present within the bed. A small number of true sludge pellets (4-5 mm) were present within the dense sludge bed, particularly near the base.
- (8) The settleability of the dense granular sludge appeared reasonable, and the bed was not disturbed unduly by gas production. However, the settleability of the sludge was inferior to that of a well-pelletised sludge.
- (9) The absence of true sludge pellet formation appears to relate to the absence of a high hydrogen partial pressure zone in the lower region of the UASB reactor. With this particular wastewater two factors appear to reduce the possibility of creating a high partial pressure of hydrogen near the inlet, thus reducing the possibility of pellet formation. These are (1) the nature of the feed, and (2) the role of sulphate reduction.
- Nature of feed: Approximately 45 percent of the influent COD is in the form of acetic and propionic acid. Therefore, the amount of remaining substrate available for acidogenesis, with its associated

hydrogen production, is limited and the possibility of creating a high hydrogen partial pressure also is limited.

Sulphate reduction: The influent sulphate content appears to play an important role in suppressing the formation of pellets. Because sulphate reducing organisms have a high growth rate (greater than that of the methanogens) the influent sulphate is reduced rapidly on entering the reactor. These organisms can readily utilize hydrogen as an energy source; therefore it is likely that sulphate reduction results in a low hydrogen partial pressure at the base of the reactor. If sulphate were excluded from the waste (by not using alum) then it is likely that pelletisation of the sludge would occur. It is significant to note that, with batches of waste where the sulphate content was less than approximately 160 mg $\text{SO}_4^{2-}/\text{l}$, the degree of pelletisation increased within a few days.

- (10) The problems encountered in the laboratory as a result of incomplete sludge pelletisation will not necessarily be transferred to the full-scale application of the process. In a full-scale system, with an adequately designed settler unit, the problems of sludge blockages should not arise. Nevertheless, if it were possible to ensure the complete pelletisation of the sludge, this would be preferred.

Role of sulphate:

- (11) It has been demonstrated that sulphate plays an important role in the treatment process with respect to pelletisation. If alum were not used in the paper manufacturing process, and as a result sulphate were not present in the waste, it is likely that a well-pelletised sludge would form. However, exclusion of sulphate will not only influence pelletisation; sulphate has been shown to play an important part in pH regulation via the biological sulphate reduction process which consumes acidity. If sulphate were excluded from the waste the requirements for alkalinity addition, and therefore the operating costs of the process, possibly would be increased.

Recycling of effluent:

- (12) Alkalinity requirements can be reduced by recycling the reactor effluent back into the reactor with the fresh feed.
- (13) The presence of sulphate in the waste does not influence the use of recycling of effluent to reduce alkalinity requirements. The sulphide levels in the recycle stream did not have a deleterious effect on the process.
- (14) The sludge bed contained a higher proportion of fine material once recycling was employed. This appeared to be a result of recycling fines, and not generation of fines within the bed itself. The settleability of the sludge, however, was not adversely affected by the higher upflow velocity and finer bed material. A very slight expansion of the sludge bed occurred with recycling.

Re-starting the reactor:

- (15) During the study the 35°C UASB reactor was re-started after standing at 20°C without feed for a period of 2 months. Within a period of 10 days the load on the reactor could be re-instated with COD removals in excess of 80 percent.

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CHAPTER ONE

INTRODUCTION

1. BACKGROUND

The objective of this study was to investigate the anaerobic biological treatment of an organic-bearing wastewater from a particular paper manufacturing process. The process produces paper by re-pulping waste paper. Effluent from the process has a Chemical Oxygen Demand (COD) concentration of approximately 4500 mg/l with a sulphate content of approximately 300 mg SO_4^{2-} /l.

A Western Cape paper manufacturer produces two grades of paper for local and overseas markets. The two grades, fluting and liner, are produced from recycled waste paper. In the manufacturing cycle the waste paper is treated in a number of stages, many of which involve either addition or extraction of water. To minimize water usage it is attempted to follow the concept of a closed water system; that is, a system in which water is recycled between extraction and addition stages to minimize the overall consumption. In an ideal closed water system no water is withdrawn, and the water added to the system is that required to balance the amount lost by evaporation and that consumed in the process (by reaction, say). In this particular manufacturing process pollutants are introduced into the water at a number of stages. These pollutants consist principally of dissolved and particulate organics and sulphates. The introduction of pollutants necessarily prevents the adoption of an ideal closed water system as the pollutants accumulate in the system. Water must be purged at a rate sufficient to prevent build-up of the pollutant concentrations to levels unacceptable in the manufacturing process, and replaced with fresh make-up water.

The polluted water purged from this particular water system may be classified as a medium-strength organic waste, with the organic content consisting mainly of short chain fatty acids and carbohydrate which is derived from starch (Webb, 1985). The effluent stream of 400-500 m³/day has a Chemical Oxygen Demand (COD) of approximately 4500 mg/l. Other

characteristics of the waste are a low suspended solids content (± 200 mg/l), an unbiodegradable soluble COD content (10-15%) and a sulphate level varying from 200 to 600 mg SO_4^{2-} /l, depending on the grade of paper being produced.

Currently the effluent drains to the local municipal wastewater treatment plant and is treated in an aerobic biological activated sludge system together with domestic wastewater. Normal practice is that the municipality would charge the industry for accepting, conveying and treating the effluent. The charges are based on the volume and strength of the effluent and the formula for calculating the charges is laid down in municipal by-laws. For example, the formula utilized by Cape Town City Council for calculating charges levied on an organic waste is as follows (Cape Town City Council, 1986) :

$$C = V (R + T (0,33 + (\text{COD}-75)/1350)) \quad (1)$$

where C = charge per time period (Rands)
 V = volume received per time period (m^3)
 R = charge for conveying 1 m^3
 = R0,1144 as at 7 May 1986
 T = charge for treating 1 m^3
 = R0,2692 as at 7 May 1986
 COD = chemical oxygen demand (mg COD/l)

In the case of the paper manufacturer considered here, the cost calculated from Eq (1) would be R178460 per annum based on a flow of 450 m^3/d with a COD of 4500 mg/l. In addition to the charges for conveyance and COD content, penalties calculated as a percentage of the above sum also may be levied if the concentration of certain other pollutants (e.g. sulphate) exceeds specified limits.

An alternative to paying for treatment of effluents by the municipality would be to treat the waste on-site.

2. BIOLOGICAL TREATMENT OPTIONS

For organic wastes the treatment method generally will be a biological one, either aerobic or anaerobic. In the case of the medium-strength waste considered here anaerobic treatment would appear the more attractive option for a number of reasons:

1. **Low sludge production:** In aerobic systems approximately 66 percent of the COD applied to the system contributes to new sludge production. In contrast, with anaerobic systems only about 8 percent contributes to new sludge production; the remainder of the energy from the organic matter is converted into methane and carbon dioxide gas. Therefore, when compared with anaerobic systems, a disadvantage of aerobic systems is that it is necessary to dispose of substantial masses of excess solids.
2. **Net energy production:** Anaerobic systems produce a valuable by-product, methane gas, rather than negatively-valued surplus sludge as in aerobic systems. Also, aerobic systems are energy consuming in that oxygen must be supplied by aeration equipment in amounts sufficient to oxidise a substantial portion of the COD.

The way in which biogas from an anaerobic system would be used at a paper manufacturing plant would depend on the fuel already in use, (Webb 1985):

- i) At mills already using gaseous fuels such as natural gas, part of the existing boiler system could be modified to accept biogas or a blend of natural gas and biogas.
- ii) At mills using solid or liquid fuels, a special boiler could be installed to use biogas only.

3. **Anaerobic systems have low nutrient requirements:** In biological systems, certain nutrients (principally nitrogen and phosphorus) are utilised in the synthesis of new cellular material. Typically the nitrogen (N) and phosphorus (P) content in dry cell matter are in the region of 10 and 3 percent of the total mass, respectively. If these nutrients, and possibly certain micro-nutrients, are not present in the

wastewater to be treated biologically then chemical addition is necessary. In the treatment of paper plant wastewaters generally nitrogen and phosphorus must be supplemented; whether or not micro-nutrient addition is necessary will vary from location to location, depending principally on the constitution of the raw water. The amounts of N and P which must be added are dependent on the mass of sludge produced; this holds an advantage for anaerobic systems because the requirements will be roughly an order or magnitude less than for aerobic systems because of the small sludge production.

4. Intermittent operation is possible: The decay rate of anaerobic organisms is very low (approximately 0,01 per day). This means that the feed to anaerobic systems can be stopped and then re-started after an extended period. Examples of this mode of operation are found in the treatment of fruit canning wastewaters. The canning season may only extend for, say, three months; however, when the new season commences after nine months the anaerobic system can be brought back to full load in a matter of days because the sludge is still relatively active. The capacity for intermittent operation can be advantageous particularly in the treatment of industrial wastes where a continuous flow of wastes from the processing plant cannot be guaranteed. In contrast to anaerobic organisms, bacteria from aerobic systems have a high decay rate (of approximately 0,24 per day at 20°C). Therefore the feed to aerobic systems can only be stopped for periods in the order of hours compared to stoppages of months for anaerobic systems.

5. Loading capacity and capital costs: In the treatment of medium and high strength organic wastes anaerobic processes can cope with higher COD loading rates per unit reactor volume compared to aerobic systems. In either system the loading capacity is related to the sludge concentration in the reactor; the higher the sludge concentration the higher the loading capacity per unit reactor volume. In aerobic systems the oxygen demand increases with increasing sludge concentration for a fixed loading rate and operating sludge age. Therefore, the allowable sludge concentration in aerobic systems is constrained by the capacity to input oxygen; such a constraint does not exist for anaerobic systems. The nett result is that the maximum sludge concentration in anaerobic systems is approximately an order of magnitude higher than for aerobic

systems, and the reactor volume requirements for anaerobic systems treating wastes with CODs in excess of approximately 1000 mg/l are far smaller than for aerobic systems. Thus the capital cost for treatment of medium to high strength organic wastes generally is smaller for anaerobic systems compared to aerobic ones.

Given the advantages of anaerobic over aerobic treatment, the objective of this investigation has been to determine the feasibility of treating the paper manufacturing wastewater in an anaerobic system.

3. ANAEROBIC REACTOR SELECTION

Over the past decade there has been an upsurge of interest in the new generation of anaerobic digestion systems such as the upflow anaerobic sludge blanket and the anaerobic attached film expanded bed systems. These systems have been applied principally in the treatment of medium to high strength industrial and agricultural wastes, of an essentially soluble nature. The reason for their success is that with these systems a solution has been found for one of the major problems that beset the traditional systems (e.g. clarifester, anaerobic contact process); namely, retaining sludge within the system without having to resort to low sludge concentrations demanding excessively large reactors and settlers. The sludge in the new systems separates readily with virtually no loss in the effluent even though very high concentrations of sludge can be maintained, in excess of 100 kg m^{-3} (Pette and Versprille, 1981). As a consequence it is possible to reduce the hydraulic retention time in the system substantially; times as short as 1.5 to 2 hours even for low strength influents (1500 mg COD/l) have been reported (Lettinga et al. 1983; Schraa and Jewell, 1984).

Of the various "new" systems the upflow anaerobic sludge blanket (UASB) system is the least complex, and simplest to operate. In the other popular system, the anaerobic attached film expanded bed (AAFEB), the biological mass is attached to a support medium (e.g. sand) and it is necessary to recycle from above the bed at a controlled high rate to keep the medium/biological particles in suspension; no such high-rate recycle is required in the UASB process. This lack of complexity constitutes a significant advantage for the UASB, particularly for small

systems and in applications where the technical expertise with respect to biological systems is limited. For these reasons it was decided at the outset of the project to evaluate only the UASB in the treatability study.

4. OBJECTIVES

Once the process and reactor type for treatability study had been selected, the investigation centred on three aspects of the problem:

1. A laboratory treatability study on wastewater from the paper manufacturing plant. Operating conditions in the experimental study should take account of past experience from the literature regarding the UASB process.
2. Identification, during the treatability study, of problems which may be encountered in full-scale plant operation.
3. Development of design details for a pilot plant for treating the wastewater based on the results of the laboratory study.

CHAPTER TWO

ANAEROBIC TREATMENT IN THE UASB REACTOR

1. INTRODUCTION

This study centres on the treatability of a low/medium strength wastewater (4500 mg COD/l) in the UASB reactor system. Treatment of the waste may be influenced by the presence of sulphate. To assess the results of the laboratory treatability study demands a thorough understanding of the general principles of anaerobic fermentation and how these are manifested in the UASB system. The objective of this Chapter is to provide this background. The information presented here is derived largely from two sources: Sam-Soon et al (1987) and Sam-Soon et al (1988).

2. NORMAL MECHANISMS OF THE ANAEROBIC FERMENTATION PROCESS

Fermentation of a carbohydrate, lipid or protein substrate to methane gas, takes place in four stages involving three groups of organisms: solubilisation and acidogenesis (by acidogenic organisms), acetogenesis of short-chain fatty acid (by acetogenic organisms) and methanogenesis by methanogenic organisms) (McInerney et al., 1979). Product formation pathways for various substrates are set out in outline in Fig. 2.1 and for carbohydrate in greater detail in Fig. 2.2.

A crucial aspect in the process of anaerobic digestion concerns the symbiotic relationship between two of these organism groups; namely, the hydrogen producing acetogens and the methanogens. If the production rate of hydrogen by the acetogens exceeds the rate of hydrogen utilisation by the hydrogen-utilising methanogens then an increase in hydrogen partial pressure occurs. Should the partial pressure of hydrogen increase above a certain level the behaviour of the acetogens is affected; the production rate of acetic acid is reduced and increased amounts of propionic and butyric acid are formed. In this event the production of methane will decrease and propionic and butyric acid will accumulate in the system.

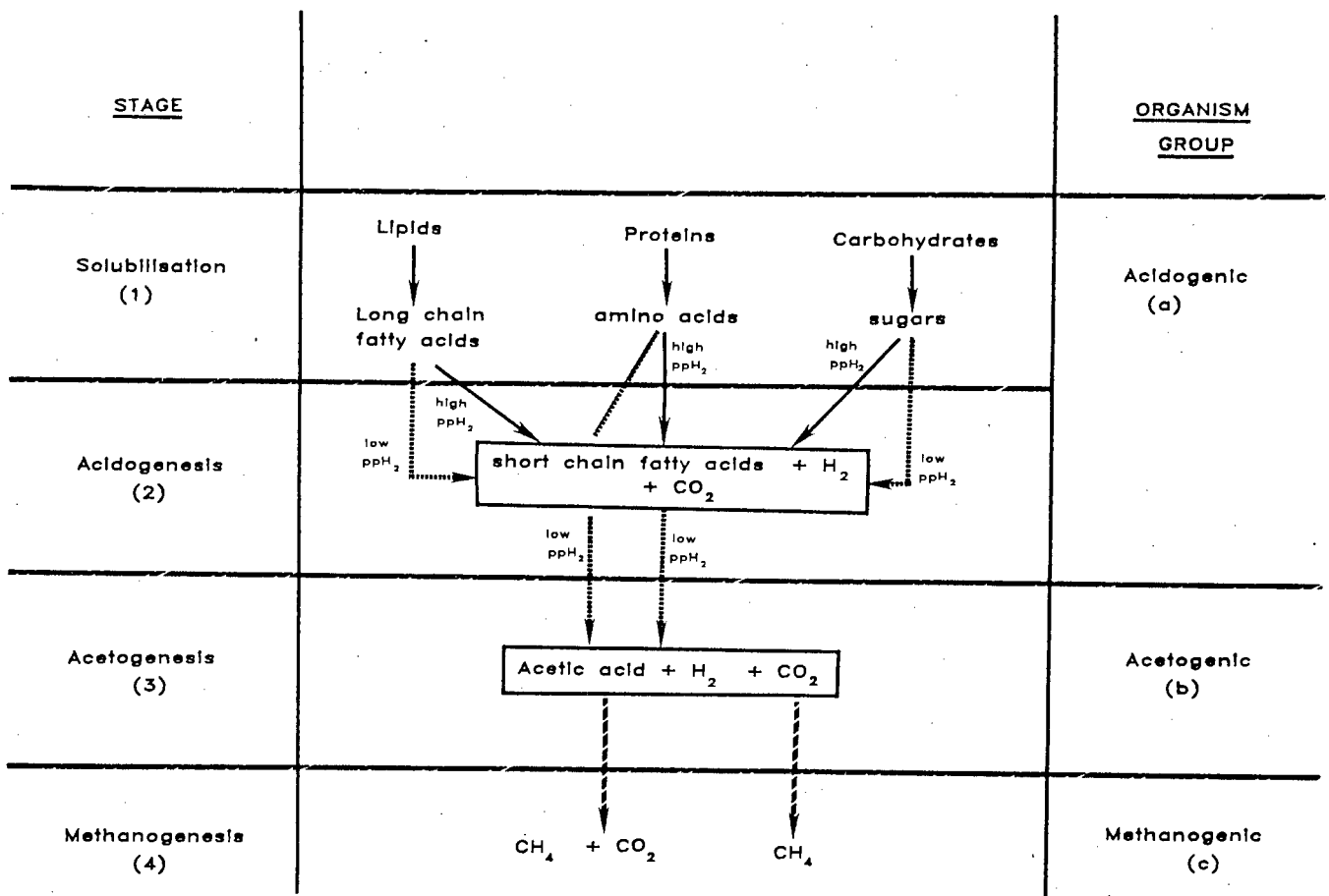


Figure 2.1: The four stages of the anaerobic methane fermentation process are effected by three groups of organisms. Note that for certain fatty acids, amino acids and sugars, depending on physiological conditions, the acidogenic and acetogenic phases may occur together, i.e. the substrate is converted directly to acetic acid, H₂ and CO₂.

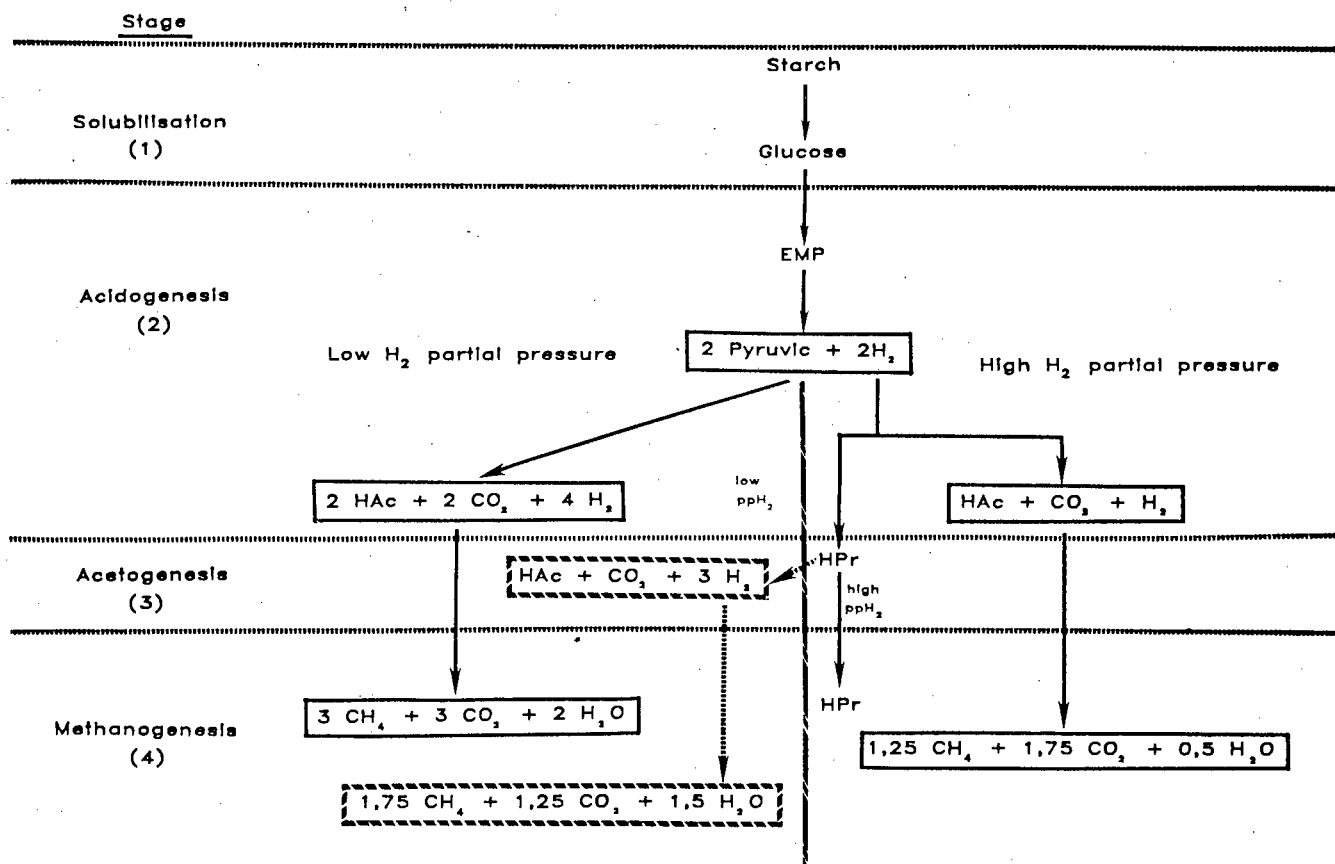


Figure 2.2: Methane fermentation of starch under high and low H₂ partial pressure conditions.

The accumulation of acids will cause a pH decrease which will further inhibit methanogenesis thus aggravating the problem; this can lead to system failure unless the load is reduced. In order to appreciate the factors which govern process behaviour and influence, for example, the symbiotic relationship described above, it is necessary to consider the steps involved in the biochemical degradation of substrate.

Stage 1: Solubilisation

In this stage complex long-chain macromolecules such as carbohydrates, lipids and proteins are solubilised extracellularly by acidogenic organisms to short-chain compounds: sugars, long-chain fatty acids and amino acids, respectively.

Stage 2: Acidogenesis

Substrate molecules from Stage 1 (i.e. fatty acids, amino acids and sugars) are ingested by the acidogenic organisms and fermented intracellularly to volatile fatty acids (e.g. acetic, propionic and butyric acids), carbon dioxide and hydrogen gas. The biochemical pathways by which the substrate is fermented and the nature of the end product (i.e. the type of volatile fatty acid produced) will depend primarily on the type of substrate and the hydrogen partial pressure. For example, long-chain fatty acids usually are fermented via the fatty acid spiral either to acetic acid and hydrogen under low hydrogen partial pressures, or, to butyric and propionic acids under high hydrogen partial pressures (Fig 2.1). Sugars usually are fermented via the Embden-Meyerhof pathway either to acetic acid, hydrogen and carbon dioxide under low hydrogen partial pressures, or, to acetic acid, propionic acid, carbon dioxide and hydrogen under high hydrogen partial pressures (Fig 2.2). Taking glucose as an example, the more detailed pathways under low and high hydrogen partial pressures are summarised in Figs 2.3a and b respectively. Under both low and high hydrogen partial pressure glucose is fermented first to pyruvic acid, via the Embden-Meyerhof pathway (EMP), thereafter the pathways differ depending on the types of electron sink: under low hydrogen partial pressure, only protons (H^+) act as the terminal electron acceptor; under high hydrogen partial pressures both pyruvic acid and protons act as the electron

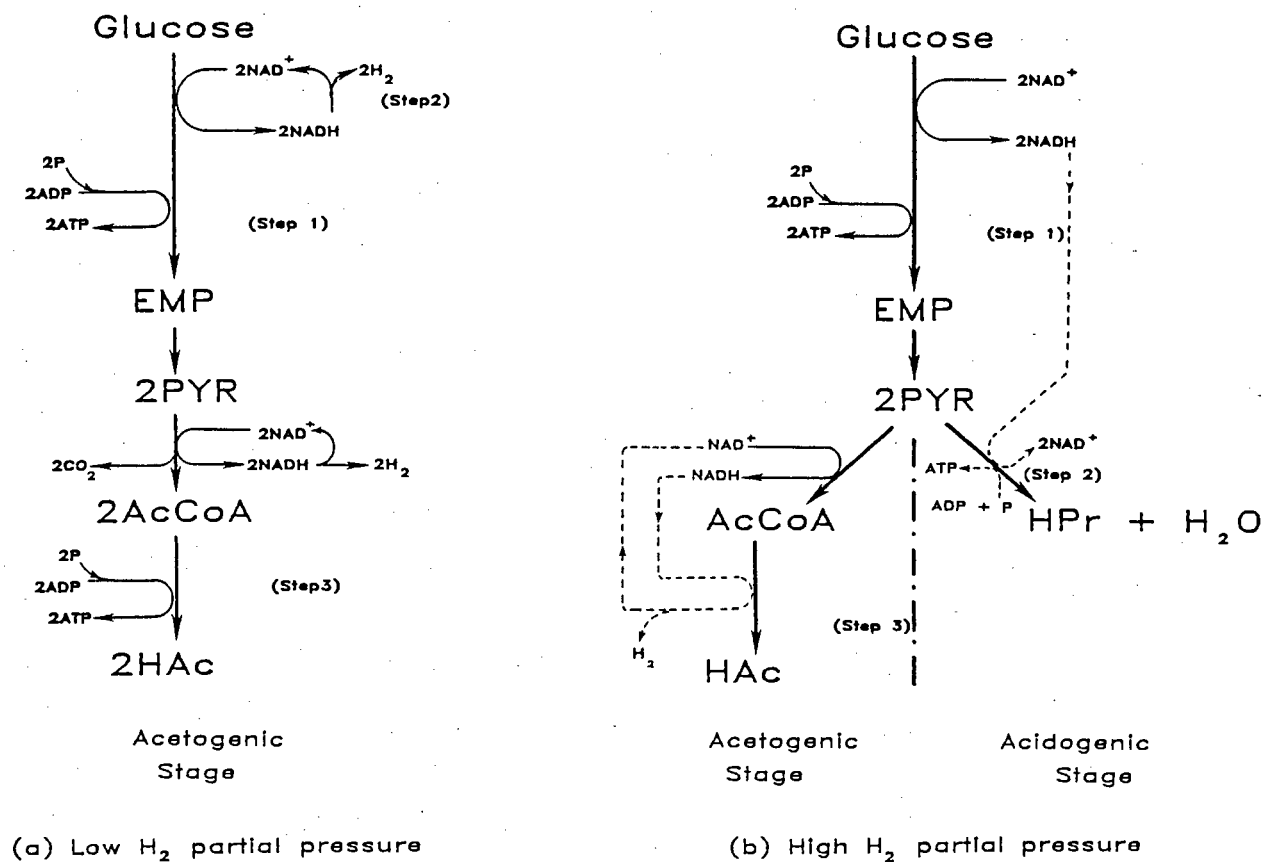
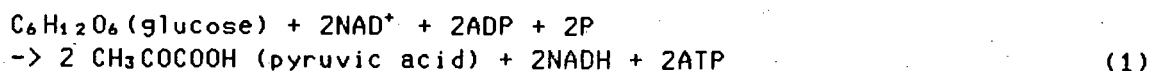


Figure 2.3: Acidogenic phase of glucose fermentation under low and high H_2 partial pressures to form acetic acid, propionic acid, H_2 gas and CO_2 . (Abbreviations: EMP - Embden-Meyerhof pathway; PYR - pyruvic acid; AcCoA - acetyl coenzyme A; HPr - propionic acid; HAc - acetic acid).

acceptor. The main steps whereby the electron transfer takes place in the respective acidogenic stages are described below.

Step 1:

(This step is via the Embden-Meyerhof pathway). Glucose is fermented to pyruvic acid and hydrogen. The hydrogen is attached to an electron-carrying co-enzyme, NAD⁺, and 2 moles ATP per mole glucose are conserved by the organisms, i.e.



That is, inter alia one mole of glucose generates 2 moles of pyruvic acid.

Step 1 is common to both high and low H₂ partial pressures.

Step 2:

The NADH formed in Step 1 needs to be dehydrogenated to maintain a high level of NAD⁺ in order that the Embden-Meyerhof pathway remains operative (NAD⁺ acts as the electron acceptor in this pathway). The dehydrogenation can take place in one of two ways depending on the hydrogen partial pressure:

Under low hydrogen partial pressures (less than about 10⁻⁶ atm), NADH is oxidised spontaneously to NAD⁺ and hydrogen gas, i.e.



(Step 2, Fig. 2.3a).

Under high hydrogen partial pressures, the forward reaction in Eq. (2) is no longer thermodynamically feasible. Consequently an alternative method for oxidising the NADH is needed. Usually this is effected by reducing pyruvic acid to propionic acid as follows (Wood, 1982):



(Step 2, Fig. 2.3b).

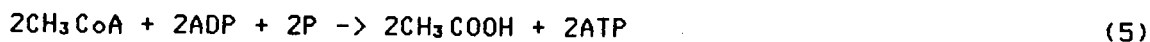
Step 3:

Pyruvic acid is oxidised to short chain fatty acids. The oxidation step follows one of two pathways again depending on the hydrogen partial pressure.

Under low hydrogen partial pressures (Fig. 2.3a), the 2 moles pyruvic acid generated in Step 1, are oxidised to Acetyl-CoA and carbon dioxide, with NAD^+ acting as an electron acceptor, i.e.



The 2 moles NADH formed [in Eq. (4)] are dehydrogenated by forming hydrogen gas, as in Eq. (2). The 2 moles acetyl-CoA formed [in Eq. (4)], are converted to 2 moles acetic acid with concomitant generation of 2 moles ATP, i.e.

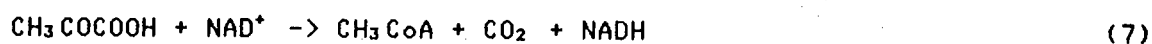


The overall fermentation reaction of 1 mole glucose under low hydrogen partial pressure is obtained by adding Eqs. (1, 2, 4 and 5) to give:



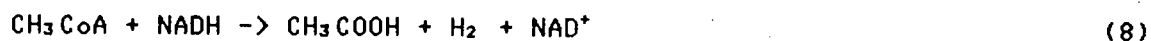
Thus one mole of glucose generates 2 moles of acetic acid, 2 moles of carbon dioxide, 4 moles of hydrogen and 4 moles of ATP.

Under high hydrogen partial pressures (Fig. 2.3b), already 1 mole of pyruvic acid has been converted to propionic acid (in order to oxidise NADH, Eq. (3) above). The single mole of pyruvic acid remaining is oxidised to acetyl CoA as in Eq. (4) i.e.

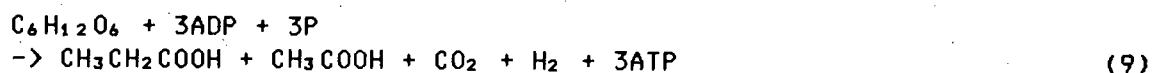


As noted earlier, under high hydrogen partial pressure, the NADH cannot be spontaneously oxidised to NAD^+ as the reaction is not thermodynamically favourable. However, the organism is capable of dehydrogenating the NADH by coupling this reaction with the thermodynamically favourable reaction in which acetyl-CoA forms acetic

acid. No ATP is generated in this step [cf. the low hydrogen partial pressure where 2 moles ATP are generated, Eq. (5)]. The coupled reaction is as follows:



The overall acidogenic fermentation reaction of glucose under high hydrogen partial pressure is obtained by adding Eqs. (1, 3, 7 and 8), giving:

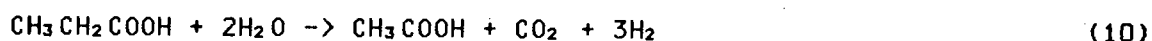


That is, one mole of glucose generates 1 mole of propionic acid, 1 mole of acetic acid, 1 mole of hydrogen, 1 mole of carbon dioxide and 3 moles of ATP.

Comparing Eqs. (6 and 9), in the acidogenic stage, under low hydrogen partial pressure, 4 moles ATP are conserved whereas under high hydrogen partial pressure only 3 moles ATP are conserved. Furthermore under low hydrogen partial pressures 2 moles of acetic acid are formed whereas under high hydrogen partial pressure one mole of propionic and one mole of acetic acid are formed.

Stage 3: Acetogenesis from short-chain fatty acids

Acetogenic organisms have an important intermediate role between acidogenesis and methanogenesis. Methanogenic organisms use formic acid, acetic acid (by cleavage), hydrogen, methanol and methylamines as substrate source to form methane; however short-chain fatty acids with more than 2 carbon atoms (i.e. $> \text{C}_2$) such as propionic and butyric acids cannot be fermented directly to methane. Hydrogen-producing acetogenic bacteria are capable of converting short-chain fatty acids longer than C_2 , to acetic acid, carbon dioxide and hydrogen gas, provided the hydrogen partial pressure is low, below 2×10^{-3} atm and 9×10^{-3} atm for the degradation of butyric and propionic acids respectively (McInerney et al., 1979). Under low hydrogen partial pressure, using propionic acid as an example,



that is, propionic acid is converted to acetic acid.

Under hydrogen partial pressure the forward reaction of Eq. (10) is thermodynamically unfavourable so that propionic acid remains unaltered in the system.

Stage 4: Methanogenesis

Methanogenic reactions take place optimally at pH near 7. Methanogenic organisms can utilise formic and acetic acids, hydrogen gas, methanol and methylamines as the electron donors. Taking acetate and hydrogen as examples, the following two reactions take place.

For acetate,



(Acetoclastic methanogenic organisms)

and for hydrogen,



The following points are worth noting:

The reaction described by Eq. (12) contributes to reducing the hydrogen partial pressure in the reactor; and

Both methanogenic reactions above take place irrespective of the hydrogen partial pressure, provided the pH remains near neutral.

With glucose as influent substrate, under low hydrogen partial pressure and with pH close to neutrality, in the acidogenic/acetogenic phase, 1 mole glucose produces 2 moles acetic acid and 4 moles hydrogen [(Eq. 6)]; in the methanogenic phase the 2 moles acetic acid produce 2 moles methane [Eq. (11)], and the 4 moles hydrogen produce 1 mole methane [Eq. (12)], giving an overall production of 3 moles methane, see Fig 2.2. Under high hydrogen partial pressure and with pH close to neutrality, the acidogenic/acetogenic phase reactions produce acetic acid plus propionic acid and hydrogen [Eqs. (3) and (7)]. The propionic acid is not degraded by the methanogenic organisms so that the fermentation

products for glucose as substrate are as follows: 1 mole glucose gives rise to 1 mole acetic acid, 1 mole propionic acid and 1 mole hydrogen [Eq. (9) and Fig 2.2]; the 1 mole acetic acid will give 1 mole methane, and the 1 mole hydrogen will give 0,25 moles methane, a total of 1,25 moles methane (cf. 3 moles methane when hydrogen partial pressure is low) and 1 mole propionic acid - that is, the methane production is reduced by 58 per cent relative to that when the hydrogen partial pressure is low.

3. BEHAVIOUR IN THE UASB REACTOR

The importance of the hydrogen partial pressure in the conversion of complex molecules to methane is readily apparent from the discussion above. Maximum conversion to methane gas is possible only at low hydrogen partial pressure; if the partial pressure should remain high, short chain fatty acids ($>C_2$) cannot be converted by the acetogens to acetic acid, hydrogen and carbon dioxide nor utilized directly by the methanogens. Consequently these acids are discharged in the effluent, and methane production is correspondingly low.

Completely mixed reactor systems normally are operated to maintain a low hydrogen partial pressure, to obtain maximal conversion to methane. However the sludges generated in these systems invariably have poor settling properties so that if a system is operated at low hydraulic retention times but with long sludge ages the flow must pass through some form of settling tank to give solid/liquid separation, the solids being returned to the reactor; if the separation is inadequate loss of sludge in the effluent could reduce the sludge age to a critically low value eventually to cause failure of the system.

The development of a new reactor system, the Upflow Anaerobic Sludge Bed (UASB) reactor, in the Netherlands in the late 70's appeared, in some instances, to have overcome the problems of liquid/solid separation, and retention of sludge mass (Lettinga, van Velsen, Hobma, de Zeeuw and Klapwyk, 1980). In the UASB reactor, which essentially is of the vertical plug flow type, the sludge generated often is in a very dense well defined pellet form. These pellets have excellent settleability and are readily retained in the reactor without the need for a settler -

high rates of loading of substrate per unit reactor volume are possible. However pellet formation in UASB reactors is not general but has been obtained with certain waste types only, e.g. with carbohydrate wastes but not with olive oil wastes (Boari, Brunetti, Passino and Rozzi, 1984).

Sam-Soon, Loewenthal, Dold and Marais (1987) endeavoured to establish the factors giving rise to pellet formation. In a laboratory scale UASB reactor treating an apple juicing waste they measured product formation along the line of flow and identified three zones of behaviour (see Fig. 2.4):

- (i) A lower active zone: In this zone volatile fatty acids (acetic and propionic acid) concentrations rise to a maximum - the bed level at which the peaks occur defines the upper limit of this zone; free and saline ammonia ($\text{NH}_3\text{-N}$) concentration reduces to a minimum and soluble organic nitrogen concentration increases to a maximum; pellet growth is restricted to this zone, the yield being approximately 0,36 mgVSS/mgCOD utilised, (this was verified by operating the lower active zone as a separate reactor); the pellets have a COD/VSS ratio of $1,23 \pm 0,06$ mgCOD/mgVSS; the soluble COD reduces to about half its influent value.
- (ii) An upper active zone: In this zone the soluble COD concentration reduces to a minimum; the propionic and acetic acid concentrations decrease to near zero - the bed level at zero acids concentrations defines the upper limit of this zone; $\text{NH}_3\text{-N}$ concentration remains near constant and soluble organic nitrogen decreases to a minimum; pellet breakup commences in this zone (established by monitoring the lower and upper zones in separate reactors in series).
- (iii) An upper inactive zone: This zone extends above the upper active zone to the top of the bed; no overt biokinetic reactions are observed except for pellet break up, the debris being discharged as organic fines into the suspended blanket above the bed.

Identical responses to those for the apple juicing waste were obtained with the UASB system receiving glucose as substrate.

In the lower active zone the continuous increase in propionic acid concentration indicates that the rate of generation and the rate of utilization of hydrogen is such that a high H_2 partial pressure is maintained. Indeed the lower active zone can be said to terminate at the bed level where the H_2 partial pressure falls to such a low value that the acetogens can convert the propionic acid to acetic acid, hydrogen and carbon dioxide. This conversion, of the propionic to acetic acid, indeed is observed in the upper active zone providing supporting evidence that it is a low H_2 partial pressure zone. The methanogens convert the acetic acid and hydrogen plus carbon dioxide to methane throughout the two zones.

The behaviour of the system with respect to acid transformation and methane generation conforms to established fermentation process behaviour. However there are responses in the lower active (high H_2 partial pressure) zone that are not consistent with normal fermentation process behaviour: (i) disappearance of NH_3-N and a generation of organic nitrogen, (ii) a volatile solids generation greater than that associated with COD utilization for cell synthesis, (iii) pellet breakup into fines in the upper active and upper inactive zones.

The abnormal responses described above led Sam-Soon et al (1987) to propose an hypothesis to describe pellet formation:

In the high H_2 partial pressure region a methano-organism develops, presumably *Methanobacterium Strain AZ* (M. Strain AZ), which uses hydrogen only as its energy source. This organism can produce all its amino acids, for cell synthesis, except cysteine (Zehnder and Wurhmann, 1977). Due to the high H_2 partial pressure, the M. Strain AZ is induced to produce all its amino acids (except cysteine) at a high rate but its growth is limited by the availability of cysteine from external sources e.g. from death of organisms or cysteine supply in the feed. The excess production of amino acids induces the organism to form extracellular long chain polypeptides. These polypeptide chains bind the species and others into pellets.

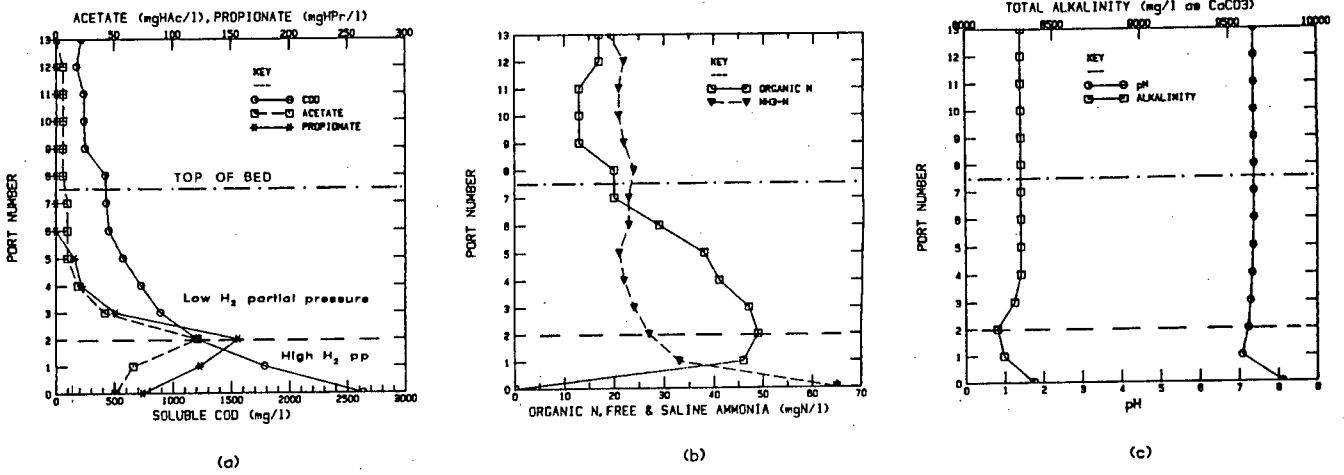


Figure 2.4: Concentration and pH profiles observed in the single reactor UASB system.

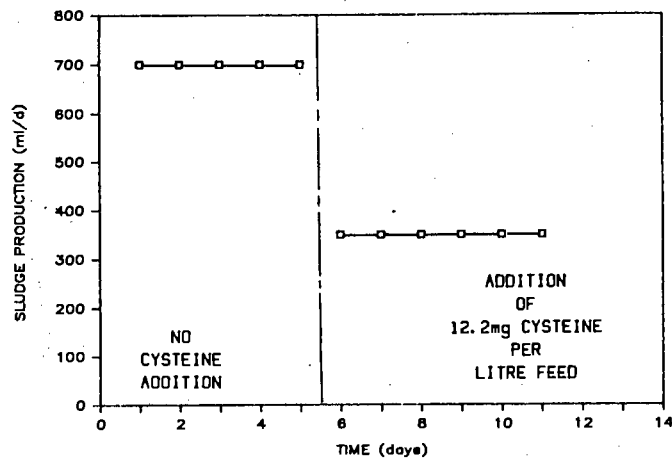


Figure 2.5: Effect of cysteine addition on pelletised sludge production in the high H₂ partial pressure reactor.

This hypothesis is supported by the following observations of Sam-Soon et al (1987): (i) growth of M. Strain AZ in pure culture results in an accumulation of amino acids in the solution medium (Zehnder and Wurhmann, 1977), (ii) pellet growth takes place only in the high H_2 partial pressure zone whereas there is a reduction in pellet mass in the low H_2 partial pressure zone, (iii) the specific sludge yield in the high H_2 partial pressure zone is an order of magnitude higher (0,36 mg VSS/mgCOD removed) than reported biomass yield values in "normal" anaerobic systems (0,03 mgVSS/mgCOD removed) (ten Brummeler, Hulshoff Pol, Dolfing, Lettinga and Zehnder, 1985) suggesting the production of a polymer, (iv) the COD/VSS ratio (1,23 mgCOD/mgVSS) coupled with a TKN/COD ratio of 0,09 mgN/mgCOD suggests that the pelletized sludge contains a large fraction of polypeptide polymer, (v) supplementation of the feed with cysteine decreased the specific sludge yield by 50 percent, see Fig. 2.5.

In terms of this hypothesis, a basic requirement for pellet formation is a high H_2 partial pressure. Hence not only must the substrate yield H_2 in the fermentation breakdown but also the H_2 partial pressure must have an opportunity to become high. No, or only poor, pelletization can be expected (via the suggested hypothesis) with influent substrates that do not yield hydrogen (e.g. acetate) or which can be broken down only under low H_2 partial pressure conditions (e.g. propionate, butyrate and lipids). Also, the reactor system should enable the establishment of a high H_2 partial pressure (at least in a part of the reactor); for example, the lower active zone of the UASB system of Sam-Soon et al (1987).

The requirement of a high H_2 partial pressure region to induce pellet formation is very significant when assessing the treatment of sulphate-containing wastes from the pulp and paper industry. Since sulphate reducing organisms have a higher affinity for hydrogen than the methano-organisms (Kristjansson, Schonheit and Thauer, 1982; Kristjansson and Schonheit, 1983), the generated hydrogen will be utilized virtually immediately to reduce sulphate ions to sulphide at the base of the UASB reactor. This will cause a reduction in the availability of hydrogen for pelletization and a reduction in the H_2 partial pressure. Therefore, a crucial aspect in any treatability study on a waste containing sulphate

is establishing the level of sulphate (or the influent SO_4/COD ratio) which can be tolerated without affecting pelletization.

4. ALKALINITY REQUIREMENTS

With phase separation into high and low H_2 partial pressure regions, UASB reactors require sufficient alkalinity to limit the decline in pH in the high H_2 partial pressure region due to the generation of acetic and propionic acids. In the low H_2 partial pressure region, because of the conversion of these acids to methane, virtually all the alkalinity is recovered, see Fig. 2.4. Thus, because of the phase separation, in a UASB system the alkalinity requirement to maintain the pH above say 6.6 at the interface between the lower and upper active zones (where pH is a minimum) will be larger than that for a completely mixed reactor.

One means for reducing the alkalinity requirement is by recycling from a region above the pelletized bed to the influent. However the recycle ratio cannot be increased at will (Sam-Soon et al, 1988): As the recycle ratio increases, the high H_2 partial pressure zone apparently spreads up the pelletized bed and, above a certain ratio, spreads throughout the whole bed. The propionate concentration now increases from the base to some level up the bed where all the carbohydrate present has been converted to propionic and acetic acids and then remains at the peak level throughout the rest of the bed. Sam-Soon et al (1988) reported that polypeptide formation appears to persist but pellets are no longer formed - the same high mass of polypeptide sludge is still generated but it is now in the form of fines which escape to the region above the bed as relatively inert material.

CHAPTER THREE

EXPERIENCE WITH ANAEROBIC TREATMENT OF PULP AND PAPER INDUSTRY WASTES

1. INTRODUCTION

Anaerobic treatment has been applied very little to date on wastewaters from pulp and paper industries. Amongst the reasons quoted for this are (Webb, 1982):

1. The very large effluent volumes.
2. The often low strength of the effluent.
3. The assumed low anaerobic biodegradability.
4. The presence of sulphates.
5. The presence of toxic chemicals in the waste which are thought to inhibit anaerobic degradation.
6. Low temperature of the effluents, together with high volumes, leading to high heating costs if treatment is carried out at elevated temperatures.

Pulp and Paper Industries use more water than any other branch of chemical industry. The large volume and low strength (200-2000 mgCOD/l) of these wastewaters have been inhibitory for the classical type of anaerobic digestion requiring a hydraulic retention time of several days and high influent concentrations.

Considering the development of modern anaerobic treatment units which allow for high hydraulic loading and the trend of closing down the water circuit in the mill to decrease fresh water intake, anaerobic treatment can now be reconsidered as an economically feasible alternative to activated sludge treatment or lagooning of the effluents. However, owing to the higher temperature and strength of recirculating waters in substantially closed systems, problems associated with anaerobic systems have been encountered. These include, among others, enhanced corrosion from anaerobic sulphate reducing bacteria and odour problems from sulphides and organic acids. Therefore pulp and paper mill wastewater characteristics will have a significant influence on whether or not anaerobic treatment is adopted.

Energy conservation is an important benefit of closing-up mill water systems (Webb, 1982), the specific energy loss being lower but the effluent temperature higher compared to open water systems. In addition to the degree of close-up, there are several other factors which control wastewater temperature, viz. use of live steam at wet-end; degree of refining and pumping; and the use of high temperature "pitch dispersion" processes. In closed mill systems ($<5\text{m}^3$ tonne⁻¹ water consumption), wastewater temperatures can reach 50°C (particularly during summer months) and some cooling may be necessary to run conventional aerobic treatment plants satisfactorily. However, there are a number of wastepaper-based UK mills with wastewater COD values of 2000-4000 mg l⁻¹ and water consumptions of 6-10m³ tonne⁻¹, where the effluent temperature rises above 30°C only during warm summer periods.

Together with substrate concentration removed, wastewater temperature determines the potential net energy yield at any operating temperature. The significance of a net energy surplus or deficit on anaerobic treatment will vary from mill to mill depending on the existing energy generating plant and patterns of energy consumption. For sub-30°C wastewaters, waste energy may be available from the paper machine to maintain treatment temperature within the optimal mesophilic range at low cost.

2.3 Suspended solids

In conventional aerobic treatment, suspended solids from the papermaking process would either dilute the active biomass with inert matter or consume oxygen during biodegradation. Therefore, aerobic systems are usually applied to the settled wastewater. In anaerobic treatment, however, the cellulosic solids may be fermentable to methane providing that they are relatively free of lignin i.e. the mill uses chemical or semi-chemical pulps rather than mechanical.

The only advantage from treating the unsettled rather than the settled wastewater is the extra methane that may be produced plus some savings on sludge disposal. The suspended solids will never be 100 percent degradable and there will, therefore, be some build-up of inert matter in the biomass; with reactors of the UASB type, the presence of non-

degradable solids may affect granulation and retention of biomass in the reactor. It is likely on balance that, unless the mill has a particular sludge disposal problem, anaerobic treatment would be applied to the settled rather than the raw wastewater.

2.4 Toxic substances

Partly due to anaerobic treatment being a sequential bacterial process in which non-functioning of any group of bacteria in the sequence will lead to process failure, anaerobic treatment systems are generally considered to be more sensitive to toxic substances than aerobic systems. For papermaking wastewaters, there are four areas of concern:

Hydrogen ions: Whilst the acetogenic bacteria have a fairly wide pH tolerance, particularly to acid conditions, the methane producers have a restricted activity outside the neutral pH range of pH 6.6-7.4. Some alkalinity is thus required as a buffer against the imbalances which occur between acid (VFAs, CO_2) production and acid consumption during methanogenesis. No data appears to be available on the natural alkalinity of papermaking effluents, but this is likely to vary considerably depending on the use of acid materials during papermaking (eg. alum), which would tend, as CaCO_3 , to destroy any alkalinity otherwise present, and the use of fillers, particularly chalk. Webb (1982) estimates that it is possible that augmentation of natural alkalinity would be necessary to the extent of $2-5 \text{ g l}^{-1}$ as CaCO_3 to give adequate reserve against acidification.

Sulphate: The utilisation of hydrogen and acetic acid by sulphate reducing bacteria is favoured thermodynamically over use by the methanogens. Whilst high levels of sulphate relative to organics can inhibit methane production completely, sulphate reducing and methane producing bacteria can co-exist over a wide range of sulphate concentrations. In sulphate reduction, organic matter is diverted from methane production to sulphide generation. For example, a reduction in dissolved sulphate (by, for example, replacing alum/rosin with neutral sizing) from 4 to 1 g l^{-1} (as SO_4) would increase potential methane production by 20 percent (from about 240 to $305 \text{ l CH}_4 \text{ kg}^{-1}$ organic COD removed). Unless the sulphide produced escapes with the biogas, the organic COD "removed" is simply transformed to inorganic (sulphide) COD.

Due to possible corrosion during biogas combustion, hydrogen sulphide in the biogas is clearly undesirable and, due to possible sulphide (actually hydrogen sulphide) toxicity in the reactor, high dissolved sulphide concentrations are equally undesirable. The benefits of minimising sulphate in the wastewater to be treated are thus obvious.

Biocides: Although the use of organic biocides is not universal, most paper mills control excessive slime growth in the machine system by the application of biocides on a daily, semi-continuous basis. Commercial formulations may incorporate more than one active component and dispersants may be included to assist rapid dissolution in the machine waters. At mills with closed water systems and high anaerobic slime activity, the biocide will be formulated to minimise problems from anaerobic deposits, particularly sulphate reduction. The possible deleterious effect on the microbial population in an anaerobic reactor is self evident. The use of anaerobic treatment by any paper mill must thus impose some constraints on the type of biocide used (notably its longevity in an active form and its toxicity to methanogens) and the type of dosing regime employed. Addition points should be chosen to minimise the possibility of short circuiting and, rather than employing high doses for short periods, continuous dosing at low level would appear to be preferable.

De-inking: A variety of chemicals are used to expedite de-inking of wastepapers; these include dispersants, detergents, soaps and bleaches. The latter should not present a problem, as little residual oxidant (peroxide or hypochlorite) should remain in the de-inking wastewater. Depending on their concentration anionic surfactants could be inhibitory, but this could be cured by the addition of a long chain aliphatic amine to co-precipitate the anionic material (Stanwick and Shurben, 1969).

2.5 Nutrients

Papermaking wastewaters usually have very low concentrations of the major inorganic nutrients needed for biological growth (nitrogen and phosphorous) as there is little use of N- or P- containing chemicals. Where used, gelatin can supply a significant proportion of the nitrogen requirements, but this chemical is no longer used widely. The low

biomass yield and hence low nutrient requirement of anaerobic compared to aerobic processes is thus a major cost saving in terms of purchased chemicals for the treatment of papermill wastewaters. Of the other macro-nutrients needed for biological growth, there should be adequate natural concentrations of sulphur, calcium and magnesium.

It is clear (Speece, 1983) that at least three heavy metal ions (iron, cobalt and nickel) are essential micro-nutrients for growth of methanogens. Given the degree of corrosion in many mill systems (particularly those with a high degree of close-up), iron concentrations should not be growth limiting, but there may be a need for addition of cobalt and nickel ions. No data would appear to be readily available on the levels of these ions in papermill wastewaters.

2.6 Conclusion on wastewater characteristics

The characteristics of papermaking wastewaters are wide-ranging, a reflection of the diverse range of products classified as "paper" and the range of additives used in their manufacture. In terms of biological treatment generally, the dissolved organic components of papermaking effluents (apart from any lignin residues derived from pulping) are biodegradable.

Additional factors are important in determining the suitability of a particular wastewater for anaerobic treatment, notably wastewater strength, temperature and sulphate concentration. It seems likely that the most suitable wastewaters will be generated by mills:

- (a) using a high proportion of wastepaper and/or starch;
- (b) with a substantially closed water system ($<10\text{m}^3$ tonne⁻¹ product);
and
- (c) using a synthetic neutral sizing system in preference to alum/rosin.

Given a treatable wastewater, the economic viability of anaerobic treatment will depend on a paper mill's scale of operation, its existing treatment system and the effluent standard required for discharge. In most circumstances, anaerobic treatment is likely to be cheaper to

install and operate than aerobic plants, giving pay-back periods of 2-3 years in the most favourable cases.

3. APPLICATION OF ANAEROBIC TREATMENT TO PULP AND PAPER INDUSTRY WASTES

Compared to work that has been conducted on wastes from other industries there have been relatively few investigations into anaerobic treatment of wastes from the pulp and paper industry. Table 3.1 summarises the performance of various types of anaerobic systems treating these wastes. Of these studies, the majority have concerned various waste streams from pulping operations, rather than from paper and board making. In this section the review is restricted to the two studies performed using UASB systems.

3.1 Application of the UASB Reactor for Anaerobic Treatment of Paper and Board Mill Effluent (Habets and Knelissen, 1985)

Within the holding of Buhrmann-Tetterode NV, 7 Dutch paper and board mills are operating, all of them using mainly waste paper as raw material. In 1981 research on anaerobic treatment (UASB reactors) was started using a 30 litre laboratory scale UASB reactor seeded with digested sewage sludge. Urea and phosphoric acid were used as nutrients to keep the COD:N:P ratio at 350:5:1, and the temperature was maintained at 30°C. Reactor pH was controlled between 6.5 and 7.5. Influent COD varied between 1600 and 2000 mgCOD/l.

After promising results had been achieved at laboratory scale further investigations were started on a pilot scale using a 50m³ UASB-reactor. In both cases the anaerobic seed sludge granulated after a period and loading rates up to 20 kg COD/m³/d could be handled. The COD removal was 70 percent, even when the hydraulic retention time was only 2.5 hours. Gas production was approximately 0.39-0.43 l biogas per gram COD removed. The biogas contained 80 percent methane, 19 percent carbon dioxide and about 1 percent hydrogen sulphide. It was also found that 30 to 40 percent of the wastewater COD was already present as volatile fatty acids (mainly acetic acid).

In April 1983 a 70 m³ practical scale UASB reactor was started up at the Dutch solid board mill at Ceres. Here solid board is produced from waste paper. The water circuit is almost closed and the process water has a temperature of 47 to 50°C and a maximum COD of 7000 mg COD/l. The surplus of 4 to 5 m³/h is buffered for cooling to mesophilic temperature and is fed to the UASB reactor. pH was almost neutral and nutrients were added in the same proportions used in the laboratory scale. After a year's operation loadings up to 9.5 kgCOD/m³/d were reached. A COD removal of 60 to 70 percent and a gas production of 0.41 m³/kgCOD removed was obtained. Another UASB pilot scale reactor operating under different loading conditions and wastewater strength only achieved a 52 percent COD removal (see Table 3.1, no. 1).

In October 1983 a full-scale plant was started up at Papierfabriek Roermond. This plant consists of a 1000 m³ UASB reactor and a 70 m³ gasholder. It is used for pretreatment of effluent, in order to reduce the loading on an activated sludge plant. The influent flow to the reactor was 2400 m³/d with a COD load of 10000 kgCOD/d (approximate COD of 4200 mg/l). The loading on the UASB reactor was 10 kgCOD/m³/d and a COD removal of 70 percent was achieved. Besides energy savings on the oxygen input, about 1 million m³/year of biogas is being generated and is used for steam production. Both plants are working satisfactorily. Investment costs appear to be relatively low. For the 70 m³ reactor at the Dutch board mill at Ceres, the pay-out time is 1.5 years, while at Papierfabriek Roermond wastewater treatment is cheaper than before, while capacity has doubled. A summary of the performances of the UASB reactors in this particular study is in Table 3.1, no. 10.

3.2 UASB Anaerobic Treatment of Fibre Board Mill Wastewater (Kroiss and Svardal, 1985)

An Austrian fibre board mill started a research programme to investigate the feasibility of applying anaerobic pre-treatment to their effluent. The wastewater to be treated was discharged at a rate of 35 m³/t of product. The COD after primary settling was 3100 mgCOD/l and the non-biodegradable COD content of the wastewater was 300 mg/l. The pH varied between 5.5 and 6.5 and its temperature was between 28 and 30°C.

Laboratory experiments were conducted initially using a slowly stirred upflow anaerobic reactor. Continuous feeding with neutralized wastewater ($2 \text{ g NaHCO}_3/\text{l}$) with the addition of the nutrients required was practised. After 20 weeks the reactor was operating stably. Retention time was 2.5 days. COD load was $1,58 \text{ kg/m}^3/\text{d}$ with a COD concentration in the influent of 3038 mgCOD/l . An average COD removal of 86 percent was attained. No volatile acids were present in the effluent. The biogas consisted of 81 percent methane, 18 percent carbon dioxide and 0,23 percent hydrogen sulphide. Gas production was $0,170 \text{ l biogas/g COD removed}$. This result indicates that anaerobic treatment of fibre board mill wastewater is possible when efficient neutralisation of the wastewater is achieved.

The semitechnical pilot investigation was conducted using a 100 litre UASB reactor which was slowly stirred. Its volume was 100 litres. A secondary clarifier was employed with discontinuous sludge return. Discontinuous neutralization and nutrient addition was practised, feeding only five days a week. During the first 10 months of operation COD removal efficiency improved from 18 percent to 65 percent. The investigation found that stable removal efficiencies were not achieved for long periods with discontinuous neutralisation of the waste-water, and where the sodium bicarbonate used for neutralisation was added directly to the reactor. Comparing with the laboratory experiments, it was concluded that a prerequisite for successful anaerobic treatment is a reliable neutralisation of the wastewater before entering the reactor.

TABLE 3.1: PERFORMANCES OF VARIOUS ANAEROBIC SYSTEMS ON PULP AND PAPER INDUSTRY WASTES

No.	Reactor		Source of Wastewater	Wastewater Strength (gCOD(BOD)/l)	Operating Temperature (°C)	Loading Rate (kg/m ³ /d)	Percent Removal of COD (or BOD)	Biogas production (l/kgCODr)	References
	Type	Size							
1	UASB	Pilot Scale	Wastepaper-based tissue mill	1,00 (COD)	33	4,00 (COD)	52 (COD)	-	Webb (1984)
2	Anaerobic Filter	Laboratory Scale	Mechanical Pulp Mill	1,5-3,4 (COD)	38	0,4-0,6 (COD)	73-50 (COD)	260	Norman and Hakansson (1977)
3	Anaerobic Filter	Laboratory Scale	Sulphite Pulp Mill (Spent Sulphite liquor)	-	-	-	75-85 (BOD)	-	Anonymous (1973)
4	UASB	Laboratory Scale	Kraft Pulp Mill (Unbleached wastewater)	1,9 (COD)	37	3,4 (COD)	38 (COD)	50	Maxham et al (1982)
5	Fluidised Bed	Full Scale	Kraft Pulp Mill (Bleached liquor)	-	30-40	1,5-2,5 (BOD)	60-70 (BOD)	-	Hakulinen et al (1981) and Hakulinen (1982)
6	Anaerobic Filter	Laboratory Scale	Pulping Condensates (Kraft liquor evaporation)	0,5-1,8 (COD)	38	0,32 (COD)	90 (COD)	-	Norman and Hakansson (1977)
7	Anaerobic Filter	Laboratory Scale	Pulping Condensate (SSL evaporation)	5,0 (COD)	35	3,2-16 (COD)	90-79 (COD)	330	Benjamin, Ferguson and Buggins (1981)
8	Anaerobic Filter	Laboratory Scale	Pulping Condensate (SSL evaporation)	4,5 (COD)	-	3,0 (COD)	90 (COD)	-	Webb (1984)
9	Anaerobic Filter	Laboratory Scale	Pulping Condensate (Magnifite/Kraft evaporation)	-	-	-	76 (BOD)	-	Scarлата and Pinardi (1982)

10	UASB	Laboratory Scale	Wastepaper-based Paper and Board Mill Wastewater	1,6-2,0 (COD)	30	20 (COD)	70 (COD)	390-430	Habets and Knelissen (1985)
		Pilot Scale		7,0 (COD)	30-35	9,5 (COD)	60-70 (COD)	410	
		Full Scale		4,0 (COD)	-	10 (COD)	70 (COD)	430	
11	UASB	Semi-Technical Scale	Fibre Board Mill Wastewater	3,1 (COD)	30	-	18-65 (COD)	-	Kroiss and Svardal (1985)
		Laboratory Scale		3,0 (COD)	30	1,58	86 (COD)	170	
12	Anaerobic Filter	Laboratory Scale	Varied proportions of starch hydrolysate and debarking plant water	-	34	-	80-0 (COD)	-	Rekunen et al. (1985)
13	Anaerobic Filter (with packing)	Laboratory Scale	1/3 debarking plant effluent and 2/3 white water	0,6 (BOD)	34	-	70-85 (BOD) (expanded grit packing)	0	Rekunen et al. (1985)
							80-90 (BOD) (activated carbon packing)	250 l/kg BOD ₇ removed	
14	UASB	Demonstration plant	Two Mills producing NSSC corrugating medium and exterior hardboard siding	7,0 (BOD)	-	10 (COD)	80 (BOD)	-	Hall (1986)

15	Contact Process	Pilot Scale	Fibreboard Wastewater	20-37 (COD)	35-37	1-2 (COD)	65 (COD)	200	Frostell (1981)
16	Contact Process	Pilot Scale	MSSC straw/hardboard (Sulphite Pulp Mill)	18 (COD)	35-37	5 (COD)	50 (COD)	310	Frostell (1981) and Huss (1982)
17	Contact Process	Pilot Scale	Pulping Condensates (SSL evaporation)	10-15 (COD)	35-37	4-5 (COD)	32 (COD)	300	Frostell (1983)
18	Contact Process	Pilot Scale	Pulping Condensates (SSL evaporation and yeast liquor)	12-13 (COD)	52-54	3,5-4,0 (COD)	82 (COD)	360	Takeshita et al. (1981)
19	Contact Process	Laboratory Scale	Pulping Condensates (SSL evaporation)	10-20 (COD)	37	5,0 (COD)	95 (COD)	-	Brune, Schoberth and Sahn (1982)
20	Contact Process	Laboratory Scale	Strawboard Wastewater	0,6-0,9 (BOD)	30	0,4 (BOD)	87 (BOD)	-	Bloodgood and Horgleroad (1948)
21	Contact Process	Full Scale	Newsprint Mill Wastewater	3,0 (COD)	35-38	-	60 (COD)	146 l/kg COD applied	Frostell, Bonkoski and Jan Sointio (1984)

CHAPTER FOUR

EXPERIMENTAL MATERIALS, METHODS AND PROGRAM

1. INTRODUCTION

The objective of the experimental study has centred on the treatability of the particular wastepaper processing plant wastewater in an Upflow Anaerobic Sludge Bed (UASB) Reactor. In this chapter the experimental program is described. Details are presented with respect to: (1) the laboratory reactors; (2) analytical methods; (3) the sequence of experiments; and (4) operating parameters.

Seven objectives were identified for investigation in the laboratory experimental program:

- (i) the extent of COD removal possible;
- (ii) the effluent quality;
- (iii) the maximum COD loading rate (kgCOD/m^3 reactor/day);
- (iv) the influence of operating temperature;
- (v) the nature of the sludge produced in the reactor with particular reference to the extent of pelletisation;
- (vi) influence of effluent recycling on alkalinity requirements;
- (vii) identification of possible operating problems with the UASB system.

2. APPARATUS

Two identical laboratory-scale upflow anaerobic sludge blanket reactors were constructed. Each reactor consisted of a perspex cylinder with a gas/liquid/solid separator arrangement at the top. The inside diameter of the reactors was 10.0 cm and the height 120.0 cm, giving a total effective reactor volume of 9.0 litres. Eleven sample ports were evenly spaced along the length of the reactor. The configuration of the two reactors is shown schematically in Fig 4.1, and in a photograph in Fig 4.2.

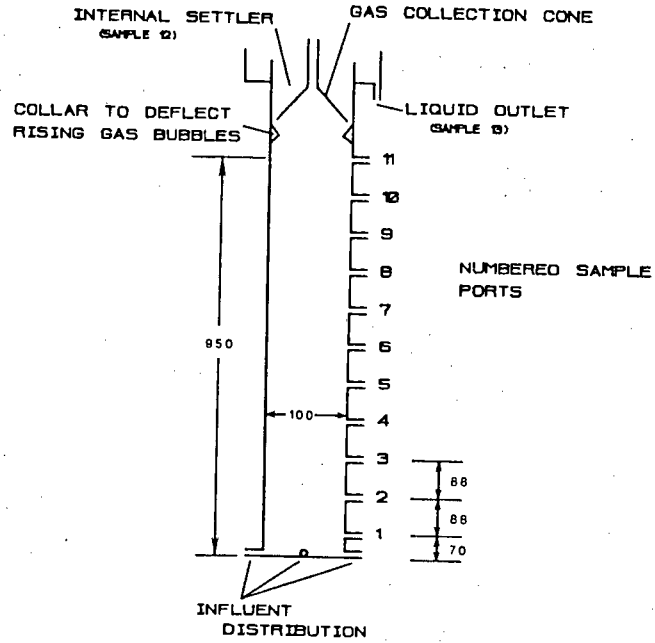


Figure 4.1: Schematic diagram of the laboratory-scale UASB reactors.

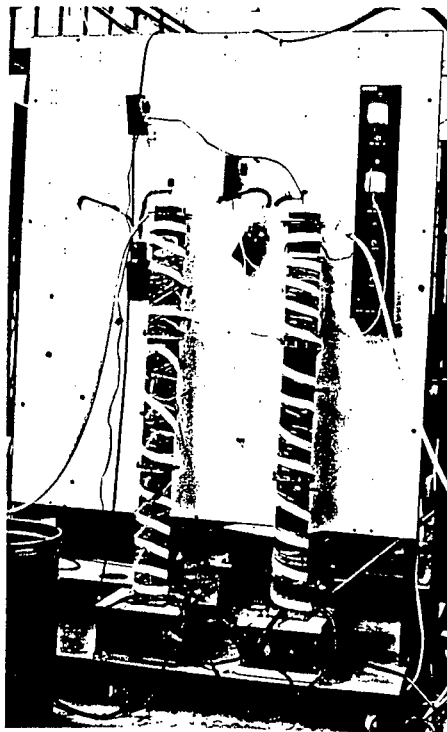


Figure 4.2: Photograph of the two laboratory-scale UASB reactors (without insulation)

Feed was made up each day and pumped to the reactor from a refrigerated vessel using a variable speed peristaltic pump. The feed line was split and connected to four inlet ports at the bottom of the reactor wall. During the start-up period an axially-mounted flat impeller was positioned 10 cm above the reactor base to allow mixing of the lower section of the reactor contents and to improve feed distribution, as suggested by Lettinga (1980).

The gas collection system at the reactor top was by means of a hollow cone. Rising gas bubbles were deflected into the cone by a collar around the inside wall of the reactor below the cone. Effluent gas flow was measured by a wet gas meter.

Liquid passed out of the reactor through the annular space between the gas collection cone and the reactor wall to enter a small solid/liquid separator (volume less than 500 ml). Clarified liquid flowed over a launder to the collection vessel while solids which settled out fell back into the reactor. The volume provided for solid/liquid separation was small relative to the reactor volume. This did not pose a problem for most of the experimental study because the sludge blanket usually only rose to a level of approximately two-thirds of the reactor height.

Temperature in the reactors was maintained at 25 or 35°C ($\pm 0,2^\circ\text{C}$) by on-off control of a heating wire wrapped around the length of the reactor. The reactors were insulated with sections of moulded pipe insulation.

3. WASTEWATER CHARACTERISTICS

The wastewater utilized in the study was collected in batches from the wastepaper processing plant, and stored at 4°C to prevent biological activity. New batches were collected at intervals of approximately one month. The constitution of each batch varied, depending on plant operating conditions at the time of collection. Approximate ranges of the concentrations in different batches of Chemical Oxygen Demand (COD), Total Kjeldahl Nitrogen (TKN), Phosphorus (P), Sulphate, and the pH range are listed in Table 4.1.

A fixed design parameter for the study was the influent COD concentration which was specified as 4500 mg COD/l at the start of the project. This was slightly less than the average COD of the waste from the plant over a period of several months before this investigation. The required concentration was obtained by diluting the batches of strong waste with tap water.

For a period during the latter part of the study the COD of batches collected from the plant varied between 2500 and 3000 mg/l, and it was not possible to maintain an influent COD of 4500 mg/l. In this instance the COD load to the laboratory reactors was held constant by increasing the daily volume of feed at the lower concentration. Approximately 45 percent of the COD was made up by the volatile fatty acids, acetic and propionic. Typically in a sample with total COD of 4500 mg/l, the concentrations of acetic and propionic acid were approximately 1200 and 900 mg/l (as COD) respectively.

The wastewater is deficient in the principal inorganic nutrients required for biological growth (nitrogen and phosphorus). These were supplemented by chemical addition, by adding 190 mg NH_4Cl and 55 mg K_2HPO_4 per 1000 mg COD. With this addition the influent COD:N:P ratio (neglecting N and P in the feed) was approximately 100:5:1. It was found later that the nitrogen and phosphorus supplements in the influent were far in excess of the actual requirements. Therefore these were reduced to 48 mg NH_4Cl and 14 mg K_2HPO_4 per 1000 mg COD; this gave a COD:N:P ratio in the influent of approximately 400:5:1. The reduced nutrient supplements in the influent still were in excess of the needs of the anaerobic bacteria in the UASB reactors.

In addition to N and P a trace metal solution, as suggested by Zehnder and Wuhrmann (1977) for enrichment cultures of methanogenic bacteria, was added to the feed over the initial period of operation. However, when the supplement was excluded from the feed no deterioration in performance was apparent. This would indicate that all trace nutrients are present in the wastewater in sufficient quantities.

The pH of the batches of wastewater generally was in the region of pH 5. This necessitated addition of alkalinity to the influent to adjust the

pH to a value close to neutral, a requirement for successful operation of the biological system. The alkalinity source in the study was through addition of NaHCO_3 ; for a raw wastewater of pH 5 approximately 0.9 mg NaHCO_3 per mg COD was added. This alkalinity requirement is substantial, and would constitute a large fraction of the running costs of the system. Therefore, pH and alkalinity variations within the system, and possible means for reducing the alkalinity addition, received attention in the study.

Table 4.1: Wastewater Characteristics (Ranges)

COD (mg/l)	TKN (mgN/l)	P (mgP/l)	SO_4^{2-} ($\text{mgSO}_4^{2-}/\text{l}$)	pH
2500 - 6700	20 - 30	5 - 10	150 - 750	5-7

4. ANALYTICAL METHODS

Reactor performance was assessed by measurement of the following parameters, using the methods listed:

- | | |
|--|---------------------------|
| 1. COD | Dichromate reflux method |
| 2. Gas production | Wet gas meter |
| 3. pH | Digital pH meter |
| 4. TKN and $\text{NH}_3/\text{NH}_4^+$ | Boric acid method |
| 5. Sulphate | Turbidimetric method |
| 6. P | Spectrophotometric method |
| 7. VFA concentration | Gas chromatography |

5. START-UP AND LOADING PROGRAM

Two UASB reactors were operated during the first part of the investigation, at temperatures of 25 and 35°C, respectively. The reactor at 25°C was seeded with three litres of pelletised sludge from a UASB system treating an apple processing wastewater also operated at 25°C. The 35°C reactor was seeded with a non-pelletised sludge from a municipal anaerobic digester treating a mixture of primary sewage sludge and waste activated sludge at 36°C. The objective of starting the

reactors with either pelletised or non-pelletised sludge was to ascertain whether or not pellets would form, and be sustained, with the paper wastewater.

To acclimatise the sludge to the substrate the feed initially was applied at a COD concentration of 500 mg/l of diluted wastewater and a flow rate of 9 l/day. Thereafter the feed rate was maintained at 9 l/d and the feed concentration increased stepwise until the design COD concentration of 4500 mg/l had been reached (see Fig 4.3). At each "step" the concentration was held constant for approximately one week. Once the design feed concentration had been reached i.e. 4500 mg/l the flow rate was increased stepwise to increase the loading on the reactors. Steady state performance was examined at each "step" in load; the "steady state" data quoted later are those measured once the COD removal efficiency and the gas production had been near-constant for a period of several days. Figure 4.4 (for the 25°C reactor) demonstrates the time-loading sequence; the slow rate of increase in load over the initial period should be noted in particular.

6. REACTOR CONCENTRATION PROFILES

The work of Sam-Soon et al (1986) has demonstrated that very useful information regarding the operation of the UASB reactor can be obtained by analysing certain parameters such as COD, VFAs, TKN, pH, along the length of the plug-flow reactor. This has been termed reactor "profiling". Analysis of samples taken along the reactor length has yielded information which forms the basis for a hypothesized mechanism for sludge pellet formation. In this respect the technique of profiling is very useful in that it allows an assessment of whether or not sludge pelletisation is likely to occur with a particular waste. Furthermore, information on aspects such as alkalinity and pH changes within the system, the role of sulphate, and the nitrogen species interactions, can be derived from the profiles. All these factors are of importance in assessing the treatability of the wastewater.

Samples for analysis were collected at fourteen different points. Eleven of the samples are taken from eleven sample ports situated along the length of the reactor, starting from the uppermost port. A further three

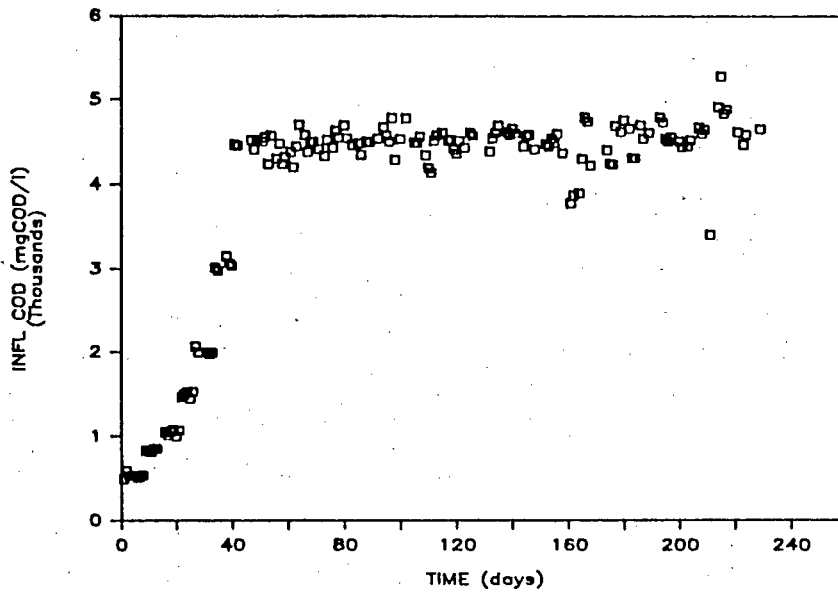


Figure 4.3: Concentration of influent to the 25°C UASB reactor. (Final design concentration = 4500 mg COD/l)

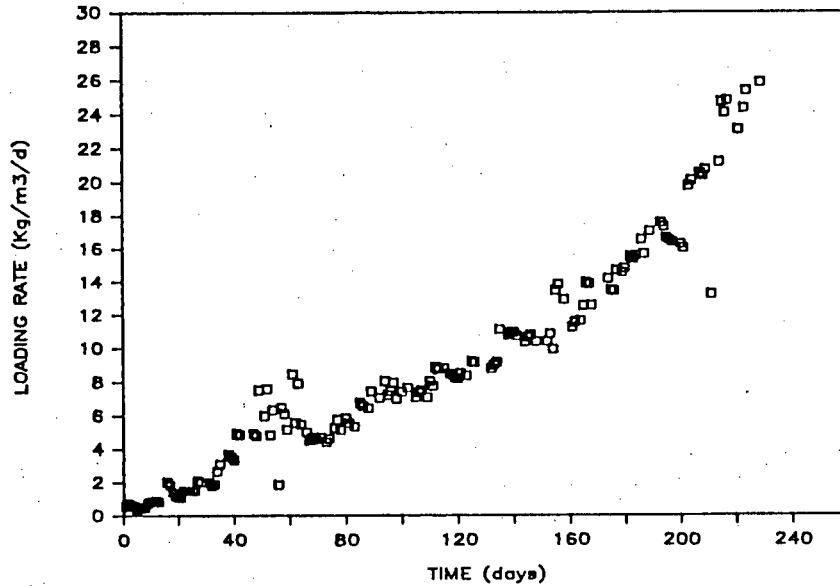


Figure 4.4: Sequence of increase in loading rate for the 25°C UASB reactor

samples are taken from the effluent and influent points and from the settler region. The sampling points are shown clearly in Figure 4.1. The samples were analysed for the following parameters:

- (i) COD
- (ii) Free and Saline Ammonia
- (iii) TKN
- (iv) pH
- (v) Sulphates
- (vi) Volatile Fatty Acids (Acetate and Propionate)
- (vii) Alkalinity

For the measurement of pH of samples taken from the eleven sample ports on the reactor, a special sampling apparatus must be used. This is because dissolved carbon dioxide formed during fermentation can escape from the sample if allowed to come into contact with the atmosphere. The resulting pH reading would be incorrect. The special apparatus illustrated in Figure 4.5 enables a sample to be taken without coming into contact with the atmosphere. After pH measurement the samples were filtered through Whatman No. 42 filter paper and tested for COD, Free and Saline Ammonia and TKN. The filtrate was filtered further through a 0.45 μm filter and analysed for Sulphate and Volatile Fatty Acids. Sludge in the samples was washed into a container and returned to the reactor after completion of sampling.

7. RECYCLING OF ALKALINITY

It was noted earlier in this chapter that NaHCO_3 addition to the raw wastewater is substantial, and would constitute a large fraction of the running costs of a UASB system. Alkalinity addition to the paper plant wastewater was necessary for two reasons. Firstly, the concentrations of acetic and propionic acid in the waste are appreciable, resulting in a pH of approximately 5. Alkalinity must be added to adjust the pH to above 6.6 to avoid inhibiting the biological behaviour in the reactor. The second reason relates to the behaviour within the reactor. At the entrance to the reactor there is a generation of volatile acids (acetic and perhaps propionic from carbohydrate in the waste;) this can result in a pH decrease to a minimum within the reactor. The influent

alkalinity should be sufficient to prevent the pH dropping below 6.6. On progressing through the reactor, the acids are removed in methane formation, and alkalinity is recovered. Because both the generated acids and the acids in the influent are removed, the effluent alkalinity can exceed that of the influent. Therefore, one means for reducing the addition to the influent would be to recycle from the effluent. After the reactor profiling results had been analysed the experimental program was extended to consider the effect of recycling from the effluent.

The effluent was recycled from the sample port immediately below the settler. A recycle ratio of 1:1 was chosen as any higher ratios would create a high upflow velocity in the reactor; this could possibly disturb solids settlement in the reactor. Alkalinity addition to the wastewater was maintained at the level prior to recycling for a period so that the system could reach steady state with respect to COD removal. Once steady state has been achieved a reactor profile was performed to assess the system behaviour during recycling. The alkalinity addition was then reduced by 50%. The reactor was operated at this reduced alkalinity and a reactor profile performed to assess how the alkalinity reduction had affected the measured parameters, especially pH variation and sulphate reduction.

Recycling of the reactor effluent would also show whether or not sulphide in the recycle stream would have a toxic effect on the anaerobic bacteria.

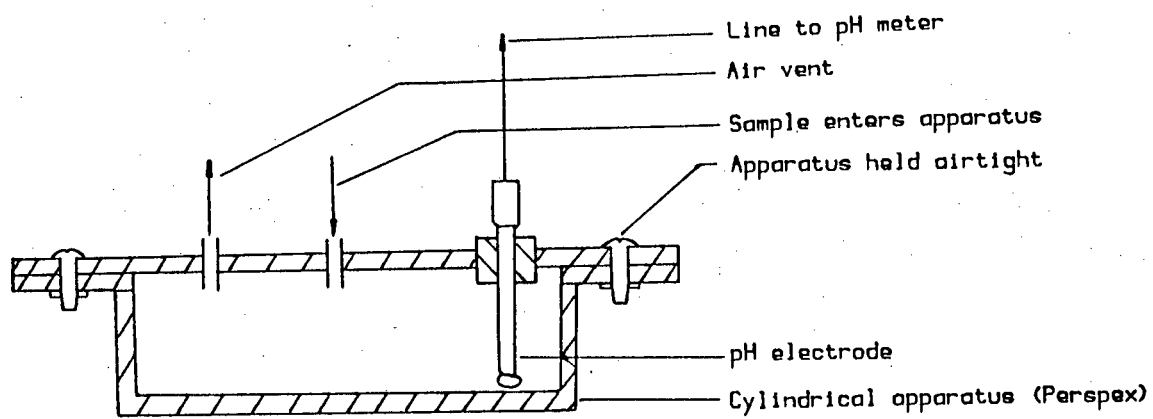


Figure 4.5: Sampling apparatus for reactor profiling

CHAPTER FIVE

EXPERIMENTAL RESULTS AND DISCUSSION

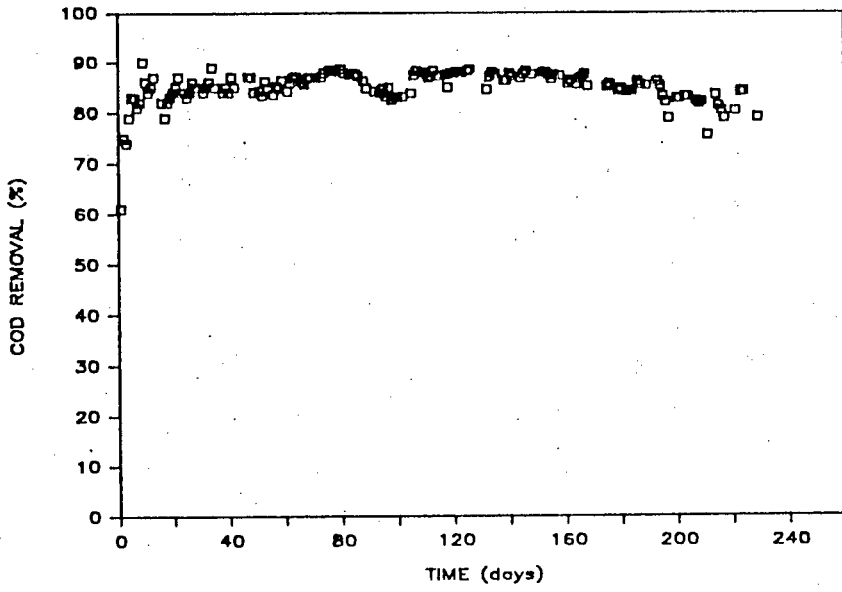
1. INTRODUCTION

The results gathered during the experimental study described in Chapter Four provided data sufficient to ascertain the wastewater treatability in a UASB system. Important information derived from the laboratory treatability study was: (1) the extent of COD removal possible; (2) the effluent quality; (3) the maximum COD loading rate (kgCOD/m^3 reactor/day) which can be achieved while maintaining reasonable COD removal, and the influence on loading rate of temperature; (4) the nature of the sludge produced in the reactor with particular reference to the extent of pelletisation; (5) identification of any operating problems; and (6) the effect of reactor effluent recycling on alkalinity requirements.

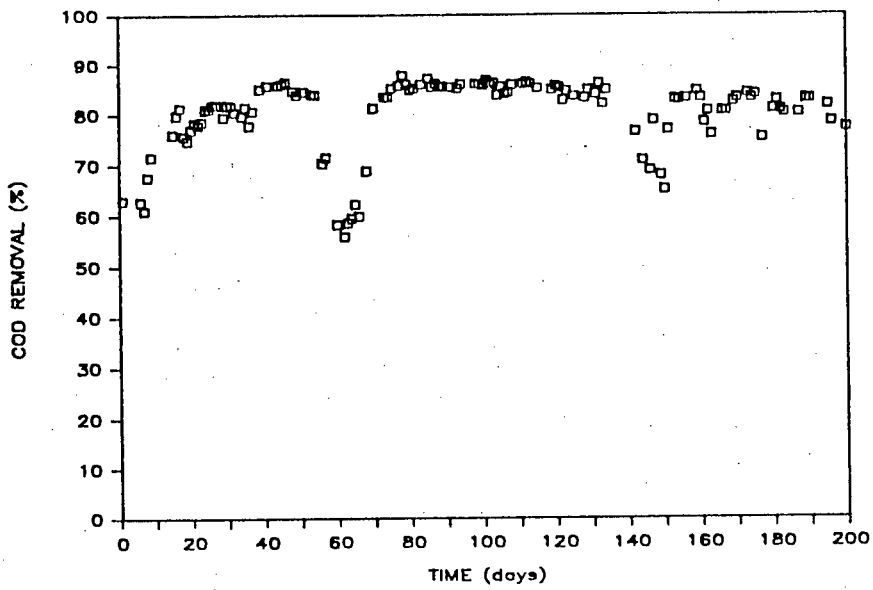
2. EXTENT OF COD REMOVAL

The percentage COD removal attained over a period of approximately eight months' operation is shown plotted for the 25 and 35°C reactors in Figs 5.1 (a) and (b), respectively. Over this period the loading rate was increased from zero to approximately $26 \text{ kg COD}/\text{m}^3/\text{day}$. It can be seen that, after sludge acclimatisation, the removal was relatively steady, in the region of 80-90 percent with the exception of two short periods for the 35°C reactor (discussed later).

From the data it would appear that the waste contains an unbiodegradable soluble COD portion (in the region of 10-15 percent) as the removal did not change with changes in loading rate/hydraulic retention time. This assertion is supported by two observations: Firstly, the volatile acid content (acetic and propionic) of the effluent was negligible, indicating complete anaerobic degradation of biodegradable influent material. Secondly, the removal for the system operated at 35°C was the same as for the system at 25°C.



(a)



(b)

Figure 5.1: COD removal (%) observed in the two UASB reactors. (a) 25°C (b) 35°C

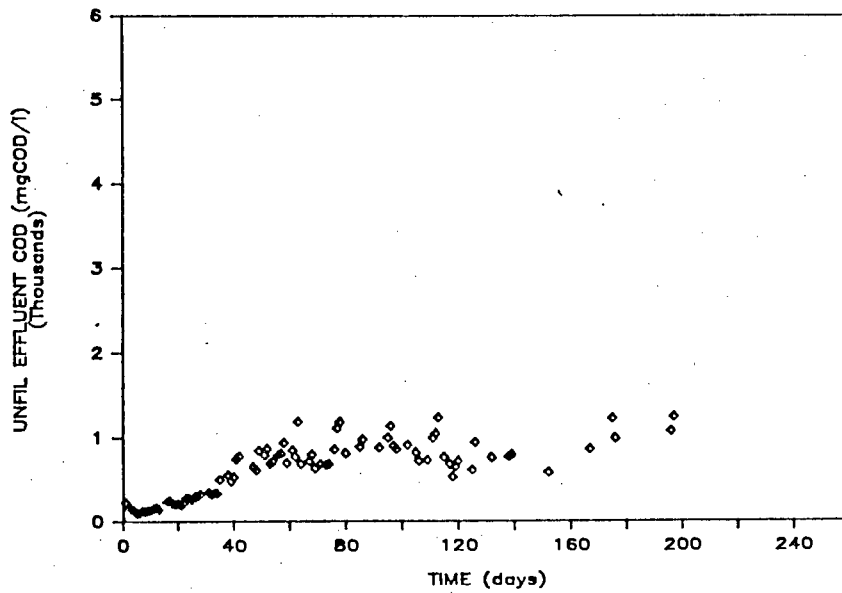
On two occasions the COD removal performance of the 35°C reactor declined (approximately Days 60 and 140). In the first instance the removal efficiency continued dropping to 55 percent, and it was necessary to reduce the loading rate to avert process failure. In the second instance the drop in efficiency was not as marked and no reduction in loading rate was necessary. The reasons for these operating problems were readily apparent and should not be of concern under normal operating circumstances; in each case, once the cause of the problem was removed the system recovered rapidly.

The first problem (Day 60) occurred when the cooling system for maintaining the feed batches at 4°C failed for a period of several days. This resulted in the feedstock becoming septic. Problems in the operation of other biological systems in the same laboratory were also noted over this period. The second problem (Day 140) occurred when the temperature controller on the 35°C reactor failed and the reactor contents cooled to ambient temperature (approximately 20°C).

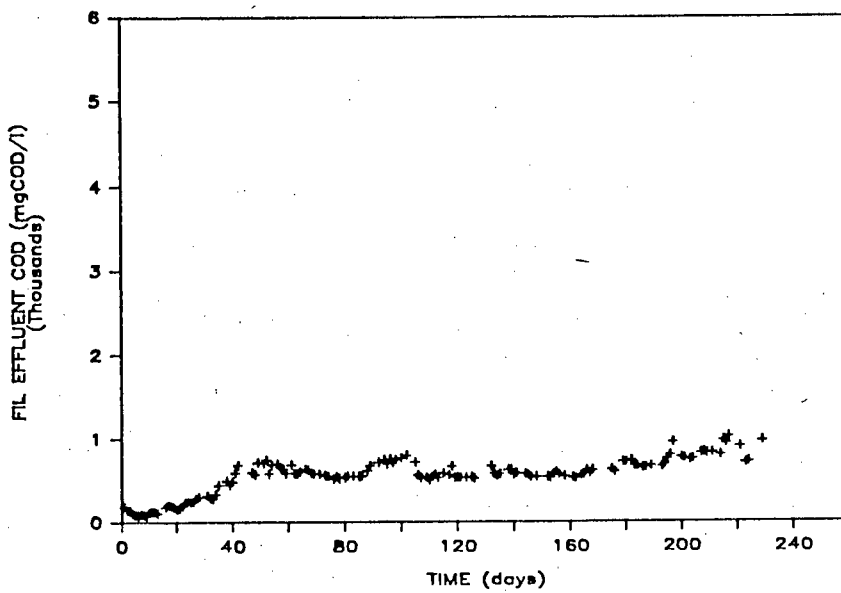
Comparison of the data in Figs 5.1 (a) and (b) shows that the acclimatisation period before the COD removal stabilised was longer for the 35°C reactor than for the 25°C system. This behaviour was to be expected in view of the different sludges used to start up the experiments. For the 35°C system the seed sludge was drawn from a municipal digester receiving an influent very different to the paper wastewater. In contrast, the 25°C system was seeded with well-pelletised sludge taken from a system treating a wastewater similar to the paper plant waste. Therefore, the shorter period of acclimatisation for the 25°C system was not unexpected.

3. EFFLUENT QUALITY

The filtered and unfiltered effluent COD concentrations over the eight months' operation are shown respectively in Figs 5.2 (a) and (b) for the 25°C reactor and Figs 5.3 (a) and (b) for the 35°C reactor. It should be noted that the influent COD only reached the design value of 4500 mg/l at approximately Day 40; data prior to this should be ignored.

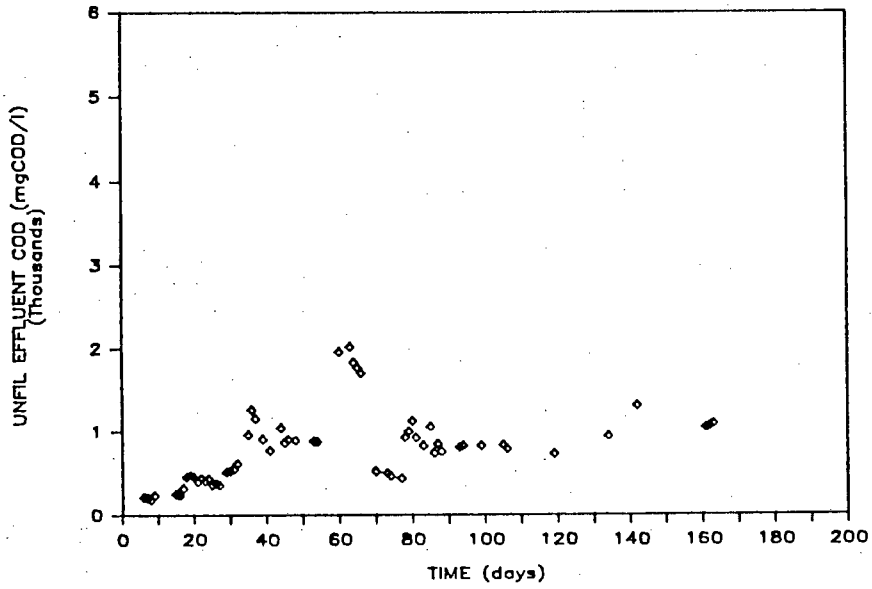


(a)

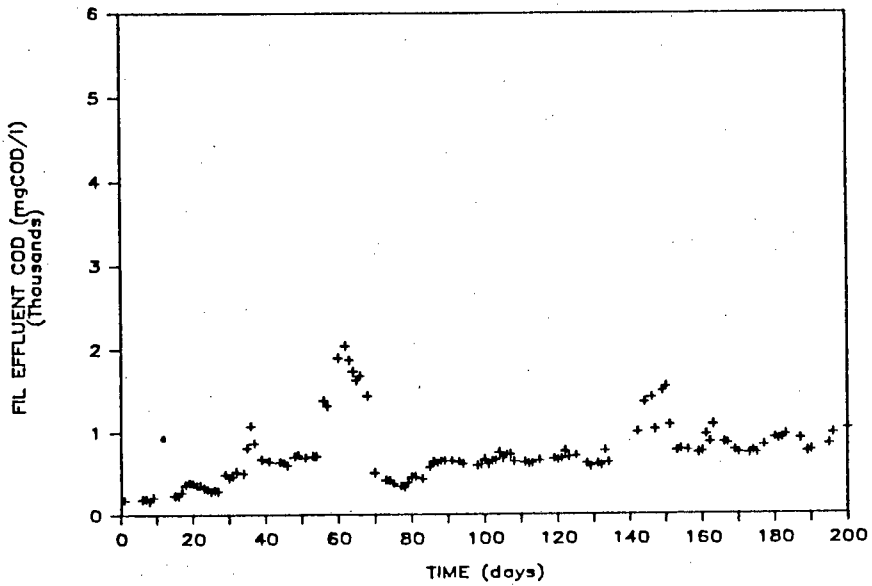


(b)

Figure 5.2: COD concentration in the effluent from the 25°C UASB reactor.
(a) Unfiltered (b) Filtered



(a)



(b)

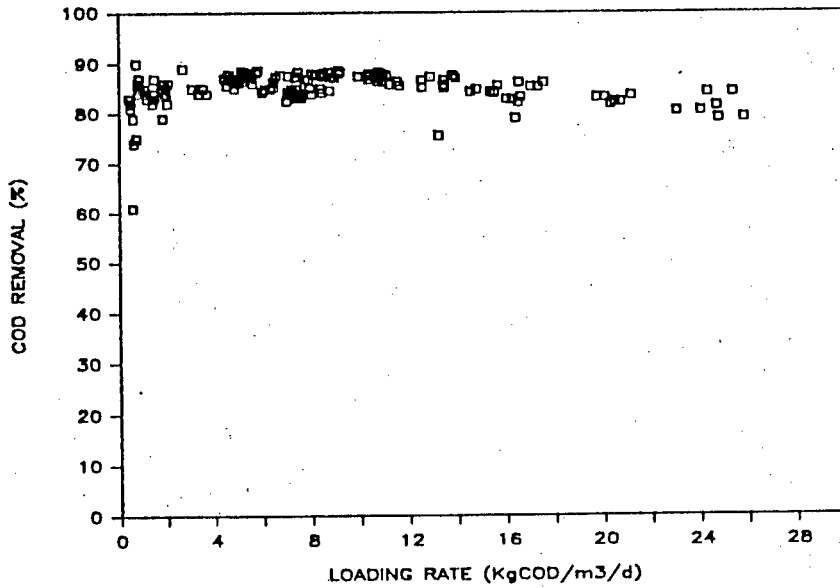
Figure 5.3: COD concentration in the effluent from the 35°C UASB reactor.
 (a) Unfiltered (b) Filtered

Two aspects are apparent in the data. Firstly, the effluent COD's were near constant from Day 40 until the end of the experimental period, even though the loading rate increased by a factor of approximately 10. This steady performance confirms the observation in Section 2 that approximately 10 to 15 percent of the influent COD is unbiodegradable. The second aspect of interest concerns the difference between the filtered and unfiltered effluent COD. Taking, for example, the data for the 25°C reactor, the approximate values of the unfiltered and filtered effluent COD's were 900 and 600 mg/l giving a difference of 300 mg/l. This difference corresponds to an effluent volatile suspended solids concentration of approximately 200 mg/l, the material consisting of cell debris which was eluted from the reactor. It is of interest to note that the concentration of eluted solids did not change significantly over the experimental period, even though the upflow velocity in the reactor increased by a factor of approximately 10 compared to the value at Day 40. This would indicate good sludge settling properties.

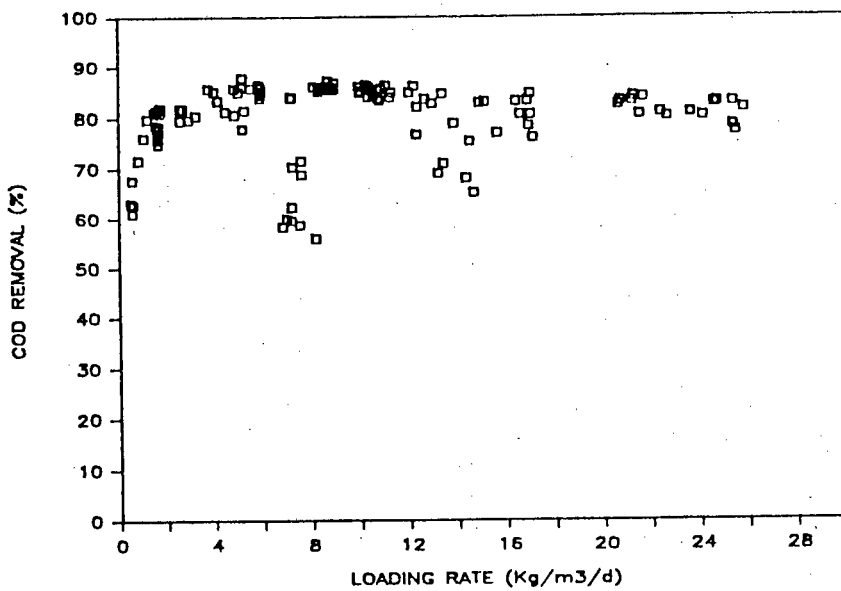
4. MAXIMUM COD LOADING RATE

The data on COD removal efficiency versus COD loading rate is presented in Figs 5.4 (a) and (b) for the 25 and 35°C reactors, respectively. The data shows that loading rates in the region of 25 kgCOD/m³/day (5 hour retention time at an influent COD concentration of 4500 mg/l) were attained for both reactors. This loading rate is based on the full reactor volume of 9 litres even though the sludge bed occupied only approximately 4.5 l.

As the loading rates were increased progressively there was only a minimal decrease in the COD removal efficiency (with the exception of the brief periods mentioned earlier). Although a significant fall off in COD removal with increasing loading rate was not observed for either the 25°C or the 35°C reactor it was decided that there was little purpose in increasing the load beyond 25 kgCOD/m³/d. This was because the sludge was not well-pelletised and the maximum loading rate is determined by the sludge settleability rather than by biological reaction rate limitations. This aspect is discussed in more detail in Sections 5 and 6.



(a)



(b)

Figure 5.4: COD removal (%) plotted versus COD loading rate for the two UASB reactors.
(a) 25°C (b) 35°C

5. RESULTS OF REACTOR "PROFILING" EXPERIMENTS : NO RECYCLE

Once the loading rates of $25 \text{ kgCOD/m}^3/\text{d}$ had been achieved while still maintaining satisfactory reactor performance for the two UASB systems, the 25°C reactor was shut down. The loading rate of the 35°C reactor was dropped to approximately $18\text{--}20 \text{ kgCOD/m}^3/\text{d}$ to overcome the problem of sludge blocking the exit pipes. It was then possible to study the reactor performance in greater detail and to observe sludge pelletisation. To this end two reactor profile analyses were performed. The 35°C reactor was selected because it was equipped with sample ports.

The results of the two reactor profiling experiments are presented in Figs 5.5 (Test 1) and 5.6 (Test 2). The data is plotted with the various parameters on the horizontal axis versus sample port number (i.e. reactor height) on the vertical axis (see Fig 4). The 35°C UASB reactor was being fed from the same batch of wastewater for both reactor profiles performed. As expected the two sets of results show very similar trends for all the parameters plotted. For purposes of discussion, the results of Fig 5.5 will be considered first. The response of various parameters is outlined briefly below. Interpretation of the results is dealt with in Section 6 where the results of Fig 5.5 are compared to those of Fig 5.6.

COD: The COD shows an exponential drop from the influent level of 4500 mgCOD/l to a steady state value of between 800 and 900 mgCOD/l by port 5. Port 5 corresponds to the height of the thick sludge bed.

Volatile fatty acids: The short chain volatile fatty acids acetic and propionic comprise approximately 45 percent of the COD in the influent; the remainder is made up principally of starch, carbohydrates and more complex organics. Acetic acid drops off from the influent value of 1200 mg/l to zero by port 5. Propionic acid remains constant to port 2 and then drops off from 500 mg/l to zero also at port 5.

Free and Saline Ammonia: A rapid drop in free and saline ammonia concentration occurs by port 1 from the influent value of 47 mgN/l to 30 mgN/l ; thereafter the concentration increases slightly to a steady value between 33 and 35 mgN/l by port 5.

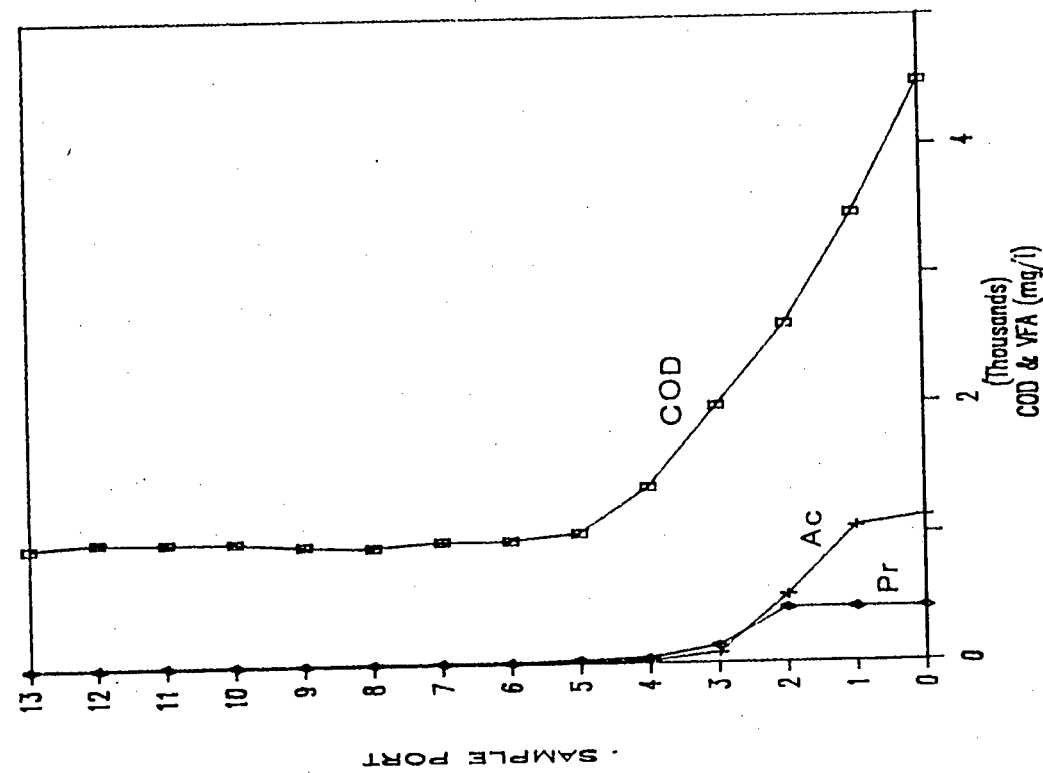


Figure 5.5: Reactor profiling experimental results - Test 1
 (a) Filtered COD, acetate and propionate

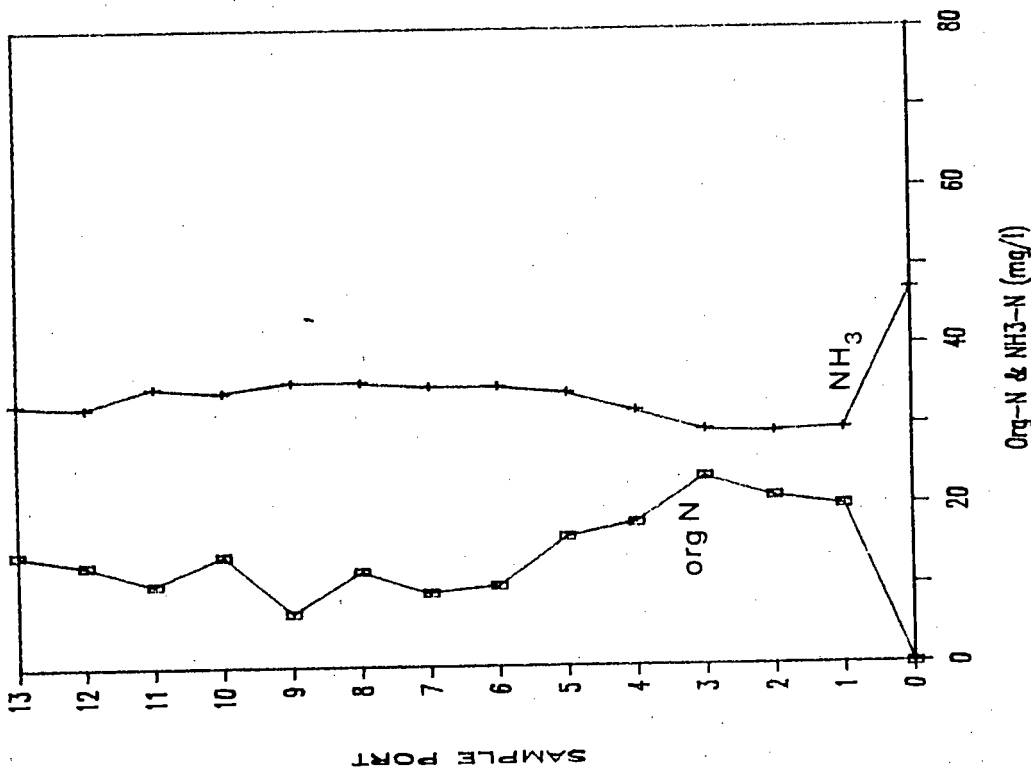


Figure 5.5: Reactor profiling experimental results - Test 1
 (b) Organic nitrogen and free ammonia

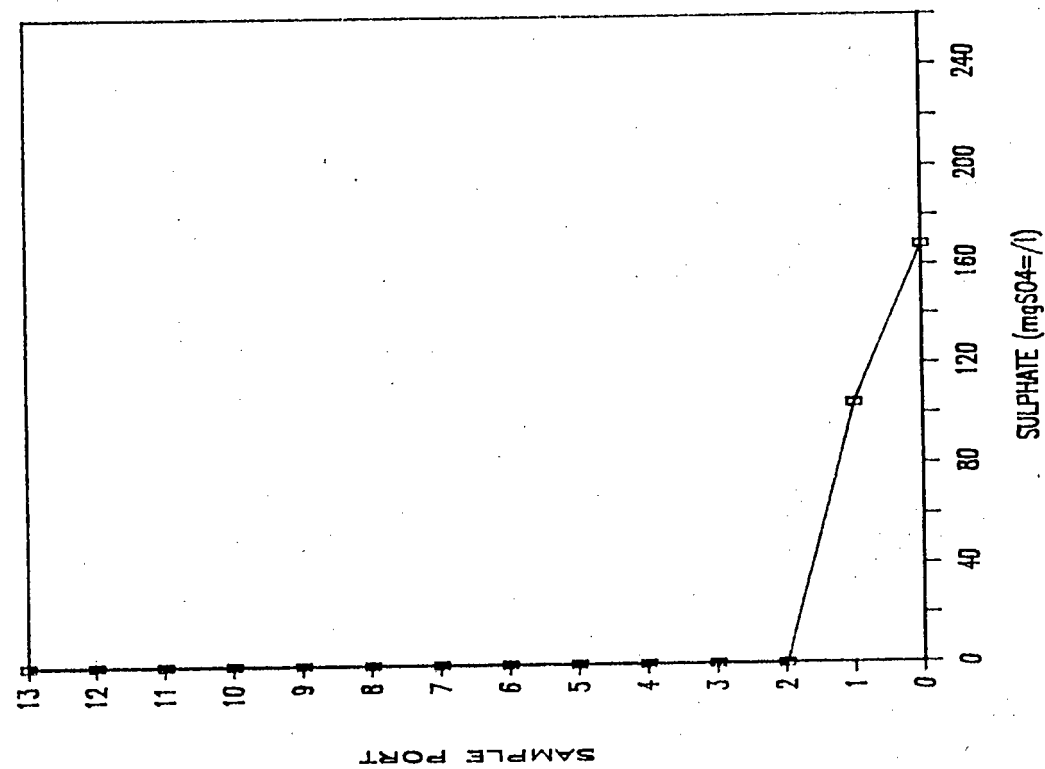


Figure 5.5: Reactor profiling experimental results - Test 1 (c) Sulphate

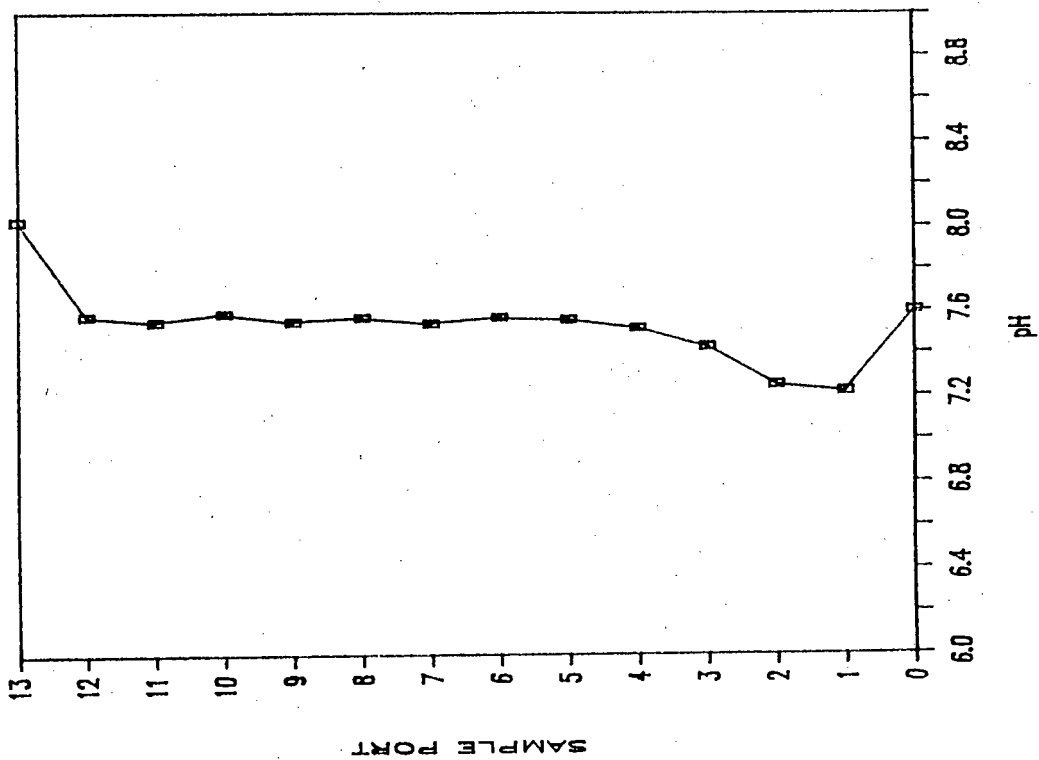


Figure 5.5: Reactor profiling experimental results - Test 1 (d) pH

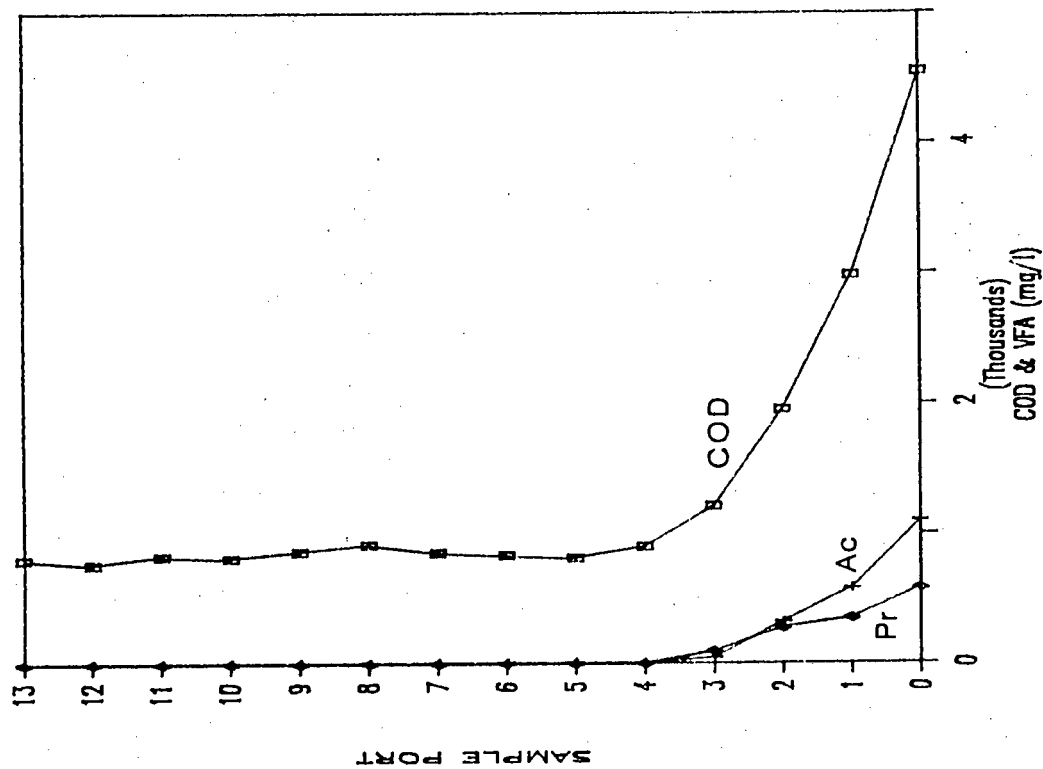


Figure 5.6: Reactor profiling experimental results - Test 2
 (a) Filtered COD, acetate and propionate

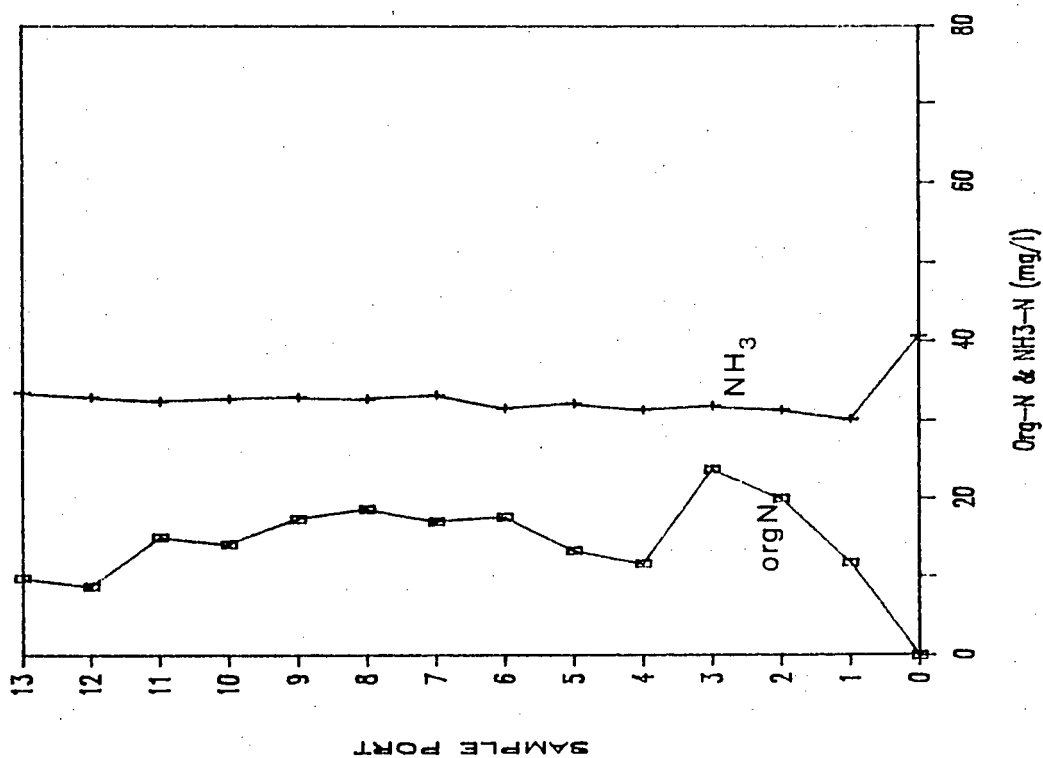


Figure 5.6: Reactor profiling experimental results - Test 2
 (b) Organic nitrogen and free and saline ammonia

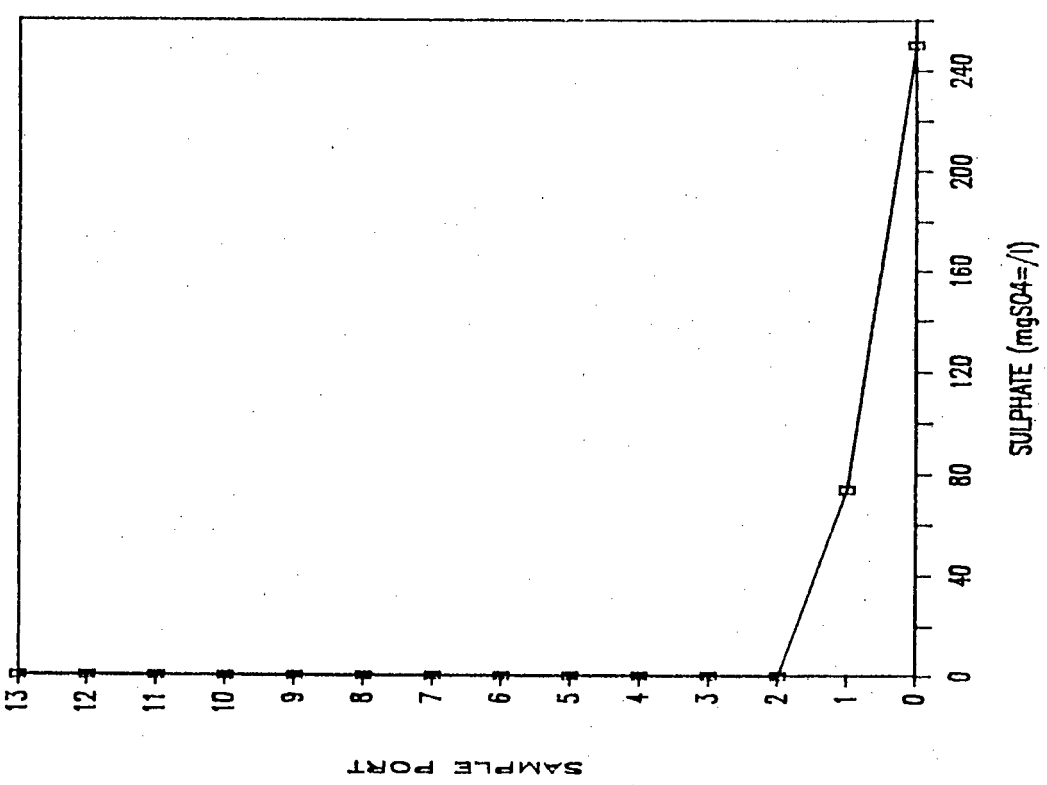


Figure 5.6: Reactor profiling experimental results - Test 2 (c) Sulphate

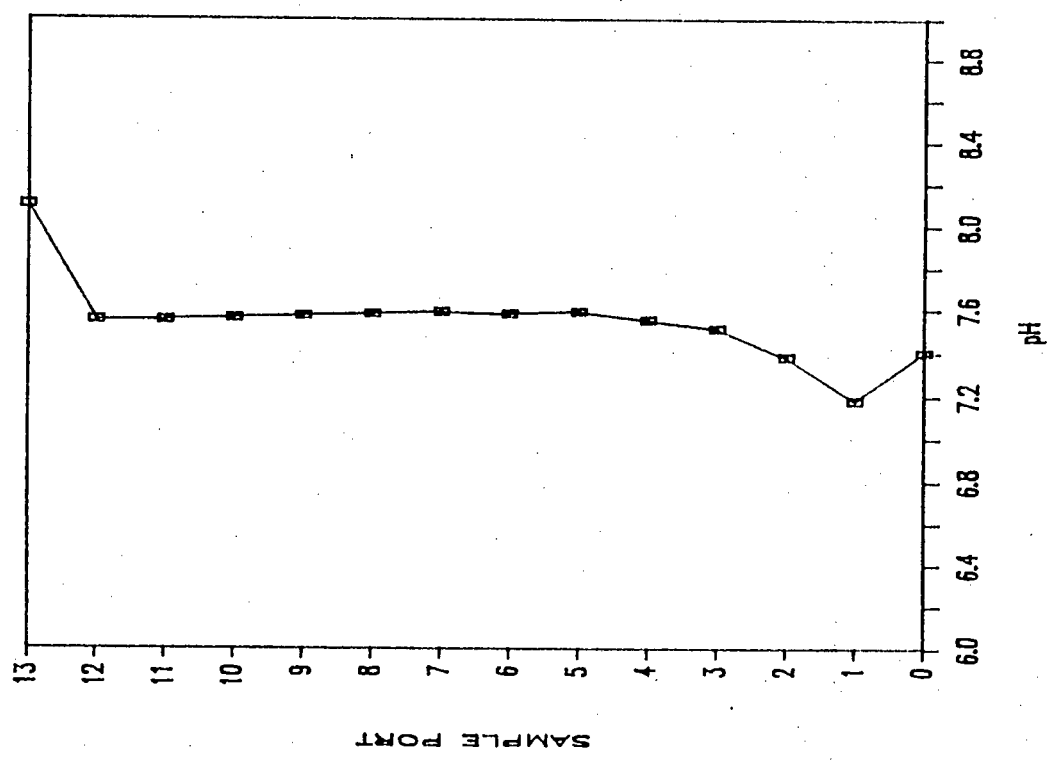


Figure 5.6: Reactor profiling experimental results - Test 2 (d) pH

Soluble Organic Nitrogen: This is calculated from the difference between the filtered TKN value and the free and saline ammonia value. Organic nitrogen shows a rapid increase i.e. a release of soluble organic nitrogen from zero in the influent to approximately 20 mgN/l by port 1 and then a slower increase to 25 mgN/l by port 3. Thereafter the concentration decreases to a steady value of approximately 10-15 mgN/l by port 5.

Sulphates: Sulphates are rapidly reduced from the influent level of 170 mg SO_4^{2-} /l to zero by port 2.

pH: pH drops off rapidly from the influent pH of 7.6 to a minimum of 7.2 at port 1 and then increases to 7.6 at port 5.

Sludge Characteristics: A dense bed of sludge extended from the base of the reactor to port 5. This sludge had a granular, well-flocculated form with the sludge flocs appearing to be in the range 1-2 mm in diameter. Very fine sludge was present within the bed. Also, a small number of true sludge pellets (4-5 mm in size) were present within the sludge bed particularly near the reactor base. Within the dense granular sludge bed the settleability appears to be satisfactory as the sludge bed height remained constant at sample port 5. The sludge, however, was not as well pelletised as that of Sam-Soon et al (1987) where the whole sludge bed consisted of well defined pellets with average sizes of 2-4 mm or greater. The region above the static sludge bed, from port 5 to the settler unit, was occupied by finely divided sludge kept in suspension by the turbulence caused by rising gas bubbles. A decrease in concentration from immediately above the sludge bed to the settler was noticeable. No biological activity was apparent in this region as the concentrations of all measured parameters remained constant.

6. INTERPRETATION OF REACTOR CONCENTRATION PROFILES

In Chapter 2 the basic theory of anaerobic digestion is used to explain the response observed in the UASB system treating a carbohydrate waste (free of sulphate). The mechanism for sludge pelletisation as proposed by Sam-Soon et al (1987) is also discussed. In this section the results of the two profiling experiments are analysed in terms of the theory and the proposed mechanism for pelletisation.

COD and Volatile Fatty Acid (VFA) Profiles: As noted earlier, approximately 45 percent of the influent COD is in the form of short chain volatile fatty acids (acetic and propionic acids). The remaining 55 percent is made up of biodegradable complex substrates (e.g. starch and carbohydrates) and unbiodegradable COD. The initial rapid drop in COD can be ascribed to the presence of the large amounts of readily biodegradable volatile fatty acids in the influent. These are rapidly utilised by the methanogens to produce methane and carbon dioxide and by the sulphate reducing bacteria for sulphide generation and cell synthesis.

The COD decreases to a steady value of 800 mgCOD/l which indicates that no more biodegradable material is left and that the COD in the effluent is made up of unbiodegradable material. This is supported by the observation that no VFA's are present in the effluent, indicating complete removal of all biodegradable substrates.

An important feature of the VFA profile in Fig 5.5 (Test 1) is that the concentration of propionic acid remains constant up to port 2, and only starts declining thereafter. The fact that propionic acid is not removed at the base of the reactor indicates that the hydrogen partial pressure in this region is high, despite the rapid hydrogen removal by sulphate reducing organisms. Under these conditions it would be expected that the hydrogen partial pressure is sufficient to allow generation of amino acids by methanogens; this in turn would lead to sludge pelletisation. This generation of amino acids is confirmed in Fig 5.5 by the rapid increase of soluble organic nitrogen at the base of the reactor. Therefore the fact that some large sludge pellets were observed at the base of the reactor was to be expected. The behaviour discussed here was not observed in Test 2 (Fig 5.6).

Fig 5.6 shows that in Test 2 there was an immediate decrease in propionic acid from the inlet. This would indicate a low hydrogen partial pressure in this region. The reason for the low partial pressure appears to relate to the role of the sulphate reducing organisms. In Test 2 the influent contained 250 mg SO_4^{2-} /l compared to 170 mg SO_4^{2-} /l in Test 1. As a result, in Test 2 the hydrogen removal would be greater, reducing the partial pressure sufficiently to allow propionate

utilisation by the acetogens. Also, the reduced availability of hydrogen for the methanogens would mean that generation of amino acids would be reduced as observed, and likewise the propensity to form sludge pellets.

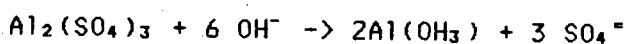
Organic Nitrogen and Free and Saline Ammonia: The raw wastewater, before chemical addition, contains no free and saline ammonia i.e. zero soluble TKN. All the TKN present in the wastewater is organic nitrogen associated with particulate matter at a concentration of approximately 25 mg N/l. To supply the nitrogen requirements for cell synthesis NH_4Cl was added to the influent to provide a soluble ammonia concentration of 47 mg/l. The free and saline ammonia shows a rapid drop of about 17 mg/l by port 1. Accepting a TKN/COD ratio for protoplasm of 0,086 mg N/mgCOD and a COD/VSS ratio of 1,42 mgCOD/mg VSS, the TKN/VSS ratio should be $0,086 \cdot 1,42$ i.e. 0,122 mg N/mg VSS. Accepting a biomass yield of 0,03 mg VSS/mgCOD removal, the COD associated with the utilisation of 17 mg N/l would be $(17/0,122)/0,03$ i.e. 4645 mg COD/l. However, the observed COD utilised by port 1 was only 1000 mg/l. Consequently the disappearance of the free and saline ammonia cannot be associated with carbonaceous-associated protoplasm generation only. In terms of the proposal of Sam-Soon et al (1987), the inflated disappearance of nitrogen is associated with polypeptide formation as a precursor to sludge pellet formation. However, it should be noted that the ratio of expected to actual COD removal was approximately 4,5:1 here; the ratio for Sam-Soon et al was 8:1. This would be indicative of limited pelletisation with the paper wastewater.

Soluble organic nitrogen reaches a peak of 23 mg N/l at port 3, and decreases to a level of 10 mg/l in the effluent. Two possible sources for this material can be identified. Firstly, if pelletisation occurs then this should be as a result over-production of soluble organic nitrogen, as observed by Sam-Soon et al (1986). However, because indications are that the degree of pelletisation is very limited, this source also will be limited. The second source of soluble organic nitrogen would be from hydrolysis of particulate organic nitrogen in the feed. Because the peak value of soluble organic nitrogen (23 mg N/l) corresponds closely to the amount of particulate organic nitrogen in the influent (25 mg N/l), it is likely that hydrolysis is the principal source.

Sulphate Reduction: The utilisation of hydrogen and acetic acid by sulphate reducing bacteria to produce sulphide (principally HS^- and H_2S at the prevailing pH) is favoured thermodynamically over use by the methanogens. The rapid decline in sulphate concentration at the reactor base indicates a rapid rate of conversion of sulphate to sulphide. It is likely that both hydrogen and acetate serve as the energy source for the sulphate reducing organisms. The function of the hydrogen utilizing organisms will be to maintain a low hydrogen partial pressure in the lower regions of the reactor.

pH Variation and Alkalinity Requirements: The pH in Fig 5.5 (Test 1) shows a drop of 0.4 units from 7.6 to 7.2 at the reactor base and then recovers to 7.6. The initial pH drop is of particular concern in operation of the UASB system. If the pH were to drop below approximately 6.6 the organisms (particularly the methanogens) would be inhibited, and the system eventually would fail. To avoid this situation it is necessary to add alkalinity to the influent to increase the pH of the raw waste which can be as low as pH 5.

The low pH of the waste is due to two components. Firstly, the influent in these tests contained a volatile fatty acid component (acetic and propionic) at a concentration of approximately 1750 mg/l as acetic (30 mmole/l). To restore the pH to neutral would require an addition of 30 mmole/l of alkalinity. The second factor is due to alum usage in the paper manufacturing process. A sulphate concentration of 288 mg $\text{SO}_4^{2-}/\text{l}$ correspond to an addition of 1 mmole $\text{Al}_2(\text{SO}_4)_3/\text{l}$. Assuming that the aluminium is precipitated as $\text{Al}(\text{OH})_3$:



to attain a sulphate concentration of 288 mg/l would cause a removal of 6 mmoles of alkalinity. In Tests 1 and 2 where the sulphate concentrations were approximately 170 and 250 mg $\text{SO}_4^{2-}/\text{l}$ respectively, the alkalinity requirements to neutralise the effect of alum addition would be approximately 4 and 6 mmole/l respectively. This is relatively small compared to the effect of the volatile acids, and differences in sulphate concentration would have little effect on alkalinity requirements for neutralisation.

The pH change at the inlet to the UASB system is due to a number of biochemical interactions; important amongst these are:

VFA production	[possible pH decrease]
Acetic and Propionic acid utilisation	[possible pH increase]
SO ₄ reduction and H ₂ S stripping	[possible pH increase].

It should be noted that the sulphate reduction plays an important role in that it reduces the pH drop substantially. If the sulphate were not present at such a high concentration (i.e. if alum were not used in the paper process) it is possible that increased alkalinity addition to the influent would be necessary to reduce the pH drop at the base of the reactor. This would add to process operating costs.

Rough calculations indicate that the cost of alkalinity addition would be appreciable, even though the requirements are somewhat reduced by the presence of sulphate in the feed. The reason for the large alkalinity requirement is the high concentration of volatile acids and low pH of the influent. As the concentration of influent acids, and any acids generated from complex influent substrate, is reduced to zero, the pH rises in the reactor. In Test 2 (Fig 5.6) the pH attains a value of 7,6 - 0,2 pH units higher than that of the influent. That is, there is a net removal of acidity from the influent to the effluent which corresponds to a generation of alkalinity. Therefore, a possible method for reducing the addition of alkalinity would be to recycle from the effluent to the influent. Such a scheme necessarily would mean that sulphide generated from sulphate reduction also would be recycled. It is possible that the presence of sulphide at the reactor base would have a deleterious effect on organism behaviour. This aspect, and quantification of the influence on alkalinity requirements, is discussed later.

Comments on Sludge Pelletisation and Settleability: Only limited pelletisation of the sludge was observed. Instead, a bed of well-flocculated finer material with good settling properties formed; within this bed small numbers of biopellets were found. The limited pelletisation was supported by the observation that only a small amount of ammonia in excess of that required for synthesis purposes was apparently directed into polypeptide formation. From the work of Sam-Soon et al (1987) it is evident that one of the requirements for good

pellet formation is the existence of a high hydrogen partial pressure zone in the lower region of the reactor. With this particular wastewater two factors appear to reduce the possibility of creating a high partial pressure of hydrogen near the inlet, thus reducing the possibility of pellet formation. These are (1) the nature of the feed, and (2) the role of sulphate reduction.

Nature of feed: Approximately 45 percent of the influent COD is in the form of acetic and propionic acid. Therefore, the amount of remaining substrate available for acidogenesis, with its associated hydrogen production, is limited and the possibility of creating a high hydrogen partial pressure is also limited.

Sulphate reduction: As with pH changes and alkalinity requirements, the influent sulphate content appears to play an important role in suppressing the formation of pellets. Because sulphate reducing organisms have a high growth rate (greater than that of the methanogens) the sulphate is reduced rapidly and is depleted by port 2. These organisms can readily utilize hydrogen as an energy source; therefore it is likely that sulphate reduction results in a low hydrogen partial pressure at the base of the reactor. If sulphate were excluded from the waste (by not using alum) then it is quite possible that pelletisation of the sludge would occur. This is supported by the observation that whenever the influent sulphate concentration was less than approximately $180 \text{ mg SO}_4^{2-}/\text{l}$ (as in Test 1) formation of large sludge pellets was observed and the response of certain parameters (e.g. ammonia and organic nitrogen) conformed to that observed in systems with good pelletising behaviour.

7. ALKALINITY REQUIREMENTS AND REACTOR EFFLUENT RECYCLING

It was decided to evaluate effluent recycling as a means for reducing alkalinity requirements on the basis of the first reactor profiling experiments. The 35°C reactor was also used for this part of the study, and was brought on line after standing at 20°C for a period of approximately 2 months. The reactor was started up with a low load and brought to 35°C immediately. The load was then increased step-wise, with increases being made once the COD removal exceeded 80 percent at each

loading rate. After a period of ten days the reactor was receiving a flow of 40 l/d at a concentration of approximately 2600 mgCOD/l; this corresponded to a load of 12 kgCOD/m³/day at a retention time of 5.4 hours. It had been intended to operate at a concentration of 4500 mgCOD/l so as to be able to compare the results to the profiles observed earlier. However, for an extended period the COD of effluent from the plant did not exceed 3000 mgCOD/l and it was unfortunately necessary to conduct the recycling experiments at the lower COD. Although the COD was lower, the concentration of sulphate remained in the range 200-300 mg SO₄²⁻/l.

When it was decided to operate at an influent COD of 2600 mg/l a profile was carried out to examine the behaviour at the lower concentration more closely. The results of this profile are shown in Fig 5.7. Several features should be noted:

- (i) At the time of conducting this profile steady state operation had not yet been attained in all respects. This is evident from the low COD removal of 77 percent. It can be seen that the COD profile had not leveled off by the top of the sludge bed (port 6) and therefore not all of the biodegradable COD had been removed.
- (ii) A second indication that the system had not reached steady state is given by the acetate profile. At the base of the reactor there is an accumulation of acetate and a peak in concentration is observed. Because this peak was not evident in the earlier experiments it indicated that the acetate-utilising methanogens were not yet operating at the previous rate.
- (iii) The sulphate concentration reduced rapidly from 310 mgSO₄²⁻/l in the influent to zero by port 2. This influent concentration was higher than at any time during the first part of the study when the influent COD was 4500 mg/l.
- (iv) The pH decrease at the base of the reactor was less than 0.1 of a unit. This was substantially less than the decrease of 0.4 observed in Fig 5.6, say. The smaller decrease was to be expected for two reasons. Firstly, the same amount of alkalinity was added

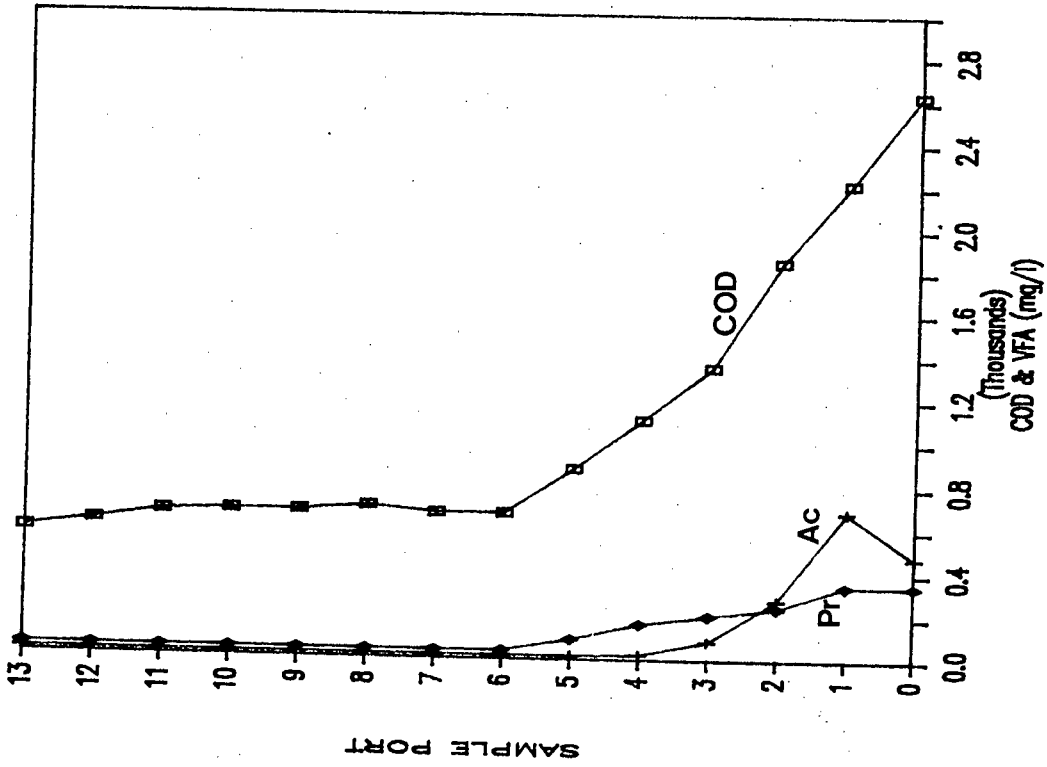


Figure 5.7: Reactor profiling experimental results - influent COD 2650 mg/l
 (a) Filtered COD, acetate and propionate

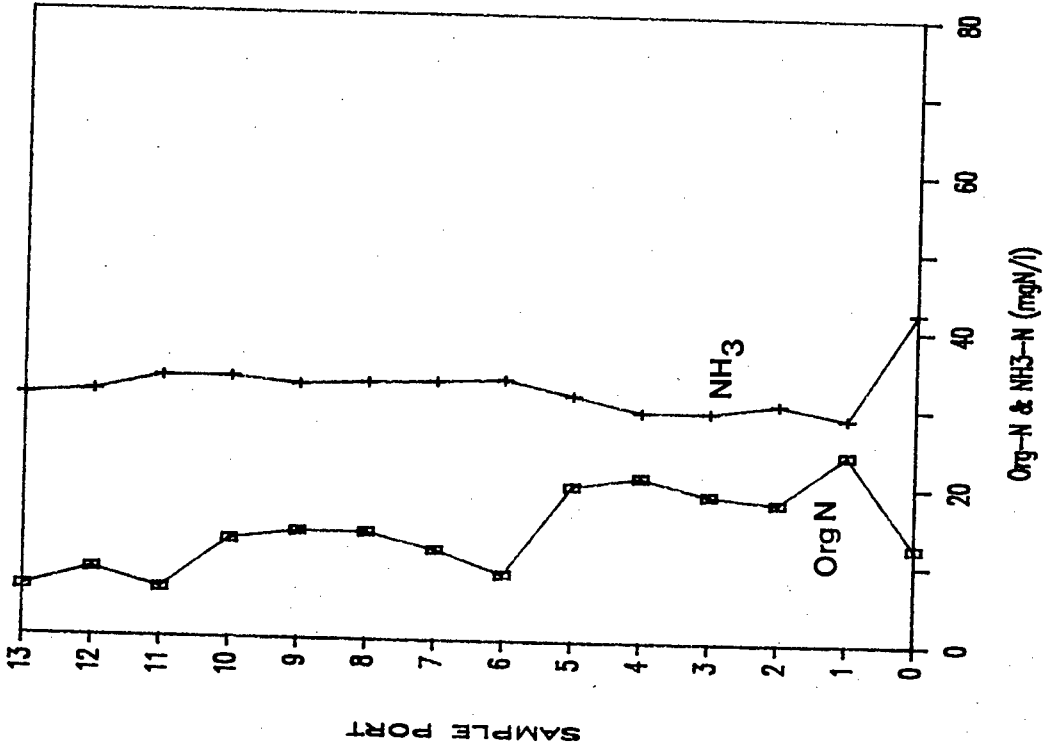


Figure 5.7: Reactor profiling experimental results - influent COD 2650 mg/l
 (b) Organic nitrogen and free and saline ammonia

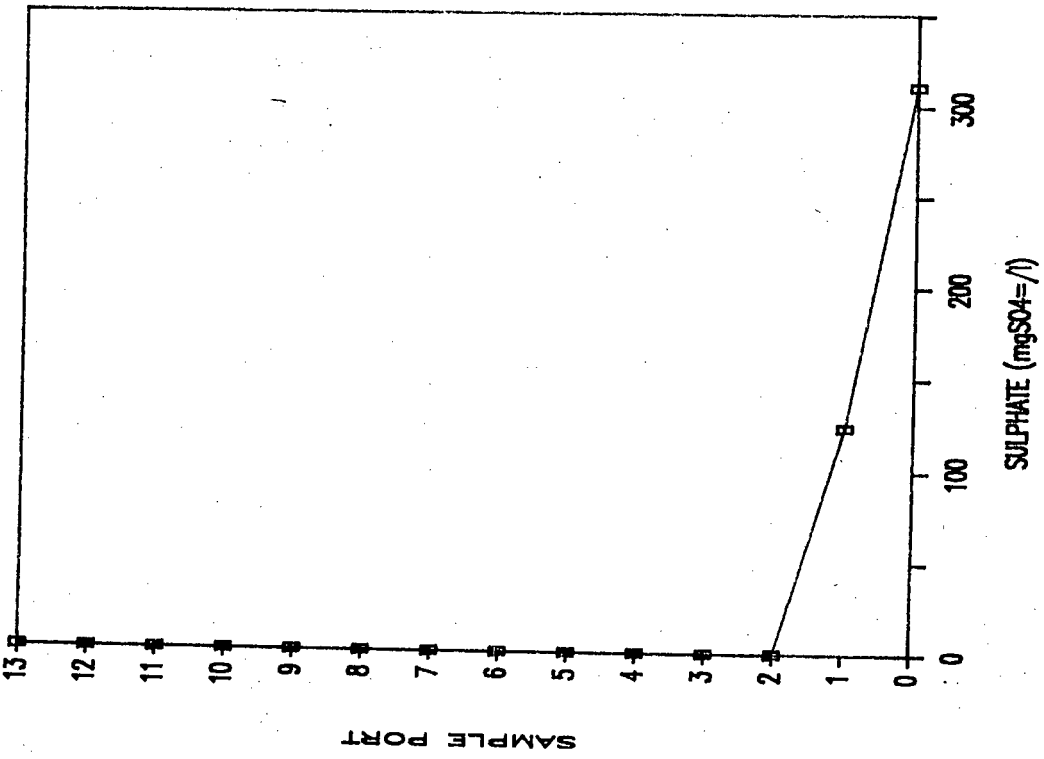


Figure 5.7: Reactor profiling experimental results - influent COD 2650 mg/l (c) Sulphate

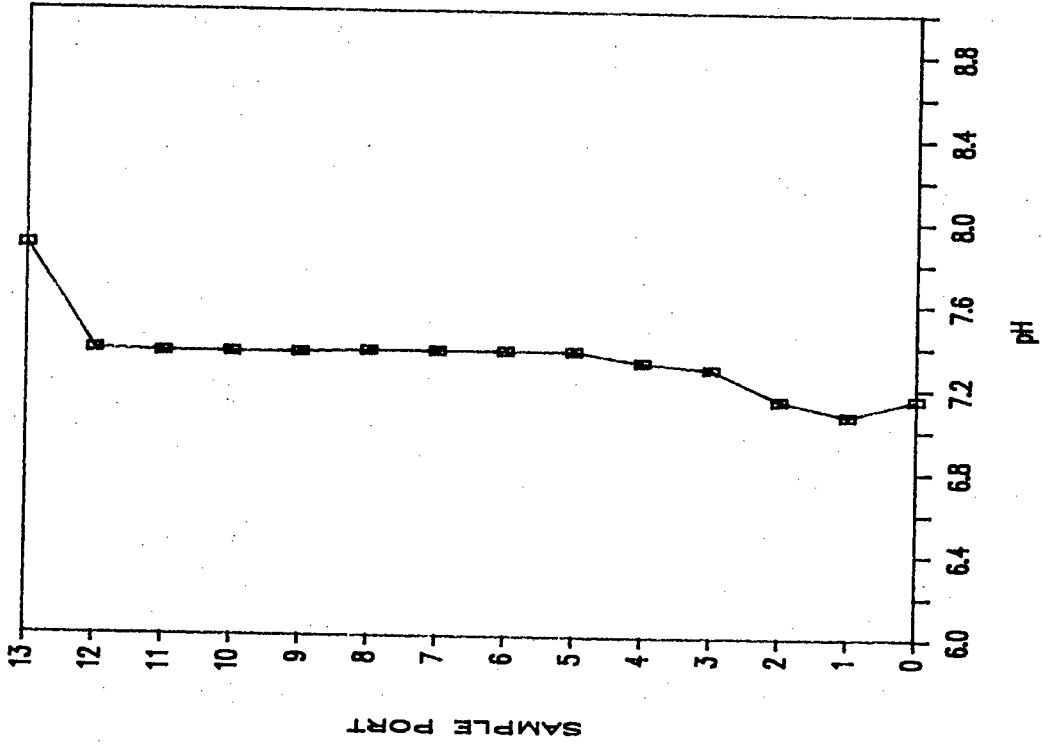


Figure 5.7: Reactor profiling experimental results - influent COD 2650 mg/l (d) pH

to the influent in each case ($6 \text{ g NaHCO}_3/\text{l}$), but in this case the extent of the volatile acid generation was much less because the influent COD was lower (2600 versus $4500 \text{ mgCOD}/\text{l}$). Secondly, in this case the influent sulphate concentration was higher (310 versus $250 \text{ mgSO}_4/\text{l}$). Because sulphate reduction consumes acidity thereby offsetting the effect of acids production, the high SO_4/COD ratio in this experiment resulted in an attenuated pH profile.

Recycling was commenced, without changing any of the operating parameters (including the alkalinity addition), once the behaviour of the system had stabilised. The recycle was taken from port 11 immediately below the settler and joined the feed pipe at the inlet to the reactor. The rate of the recycle stream was set equal to the feed rate (i.e. 1:1 recycle). Introducing the recycle did not appear to affect the stability of the reactor and the COD removal remained at between 80 and 85 percent. This would indicate that the increased concentration of sulphide at the base of the reactor did not have a deleterious effect.

The system was allowed to operate for a week before performing a reactor profile. The results of this analysis are shown in Fig 5.8. It should be noted that this figure shows one more sample port than the previous sets of profile results. The ports marked 0 to 13 correspond to those in Figs 5.5 to 5.7, with port 0 denoting the concentration at the inlet to the reactor. The additional port, denoted as port -1, represents the concentration of material in the feed container. This feed is mixed with the recycle from port 11 to give the concentration observed at port 0. The results were in accordance with the expectations:

- (i) The recycle merely attenuated the ammonia and organic nitrogen profiles, without changing the characteristics.
- (ii) The sulphate concentration was diluted from $310 \text{ mg SO}_4/\text{l}$ to 155 at the inlet of the reactor and was reduced to zero by port 1.
- (iii) The COD decreased exponentially from the inlet to a minimum at the top of the sludge bed at port 6. No high hydrogen partial pressure

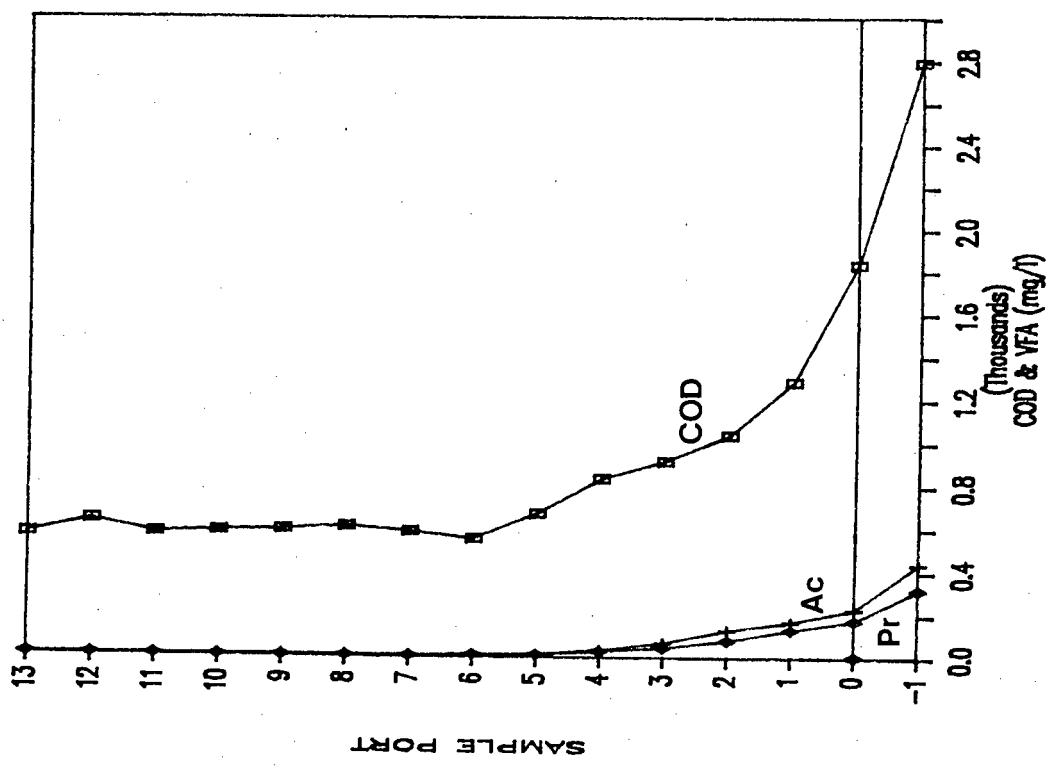


Figure 5.8: Reactor profiling experimental results - Recycle ratio 1:1, Alkalinity addition 6 g NaHCO₃/l (a) Filtered COD, acetate and propionate

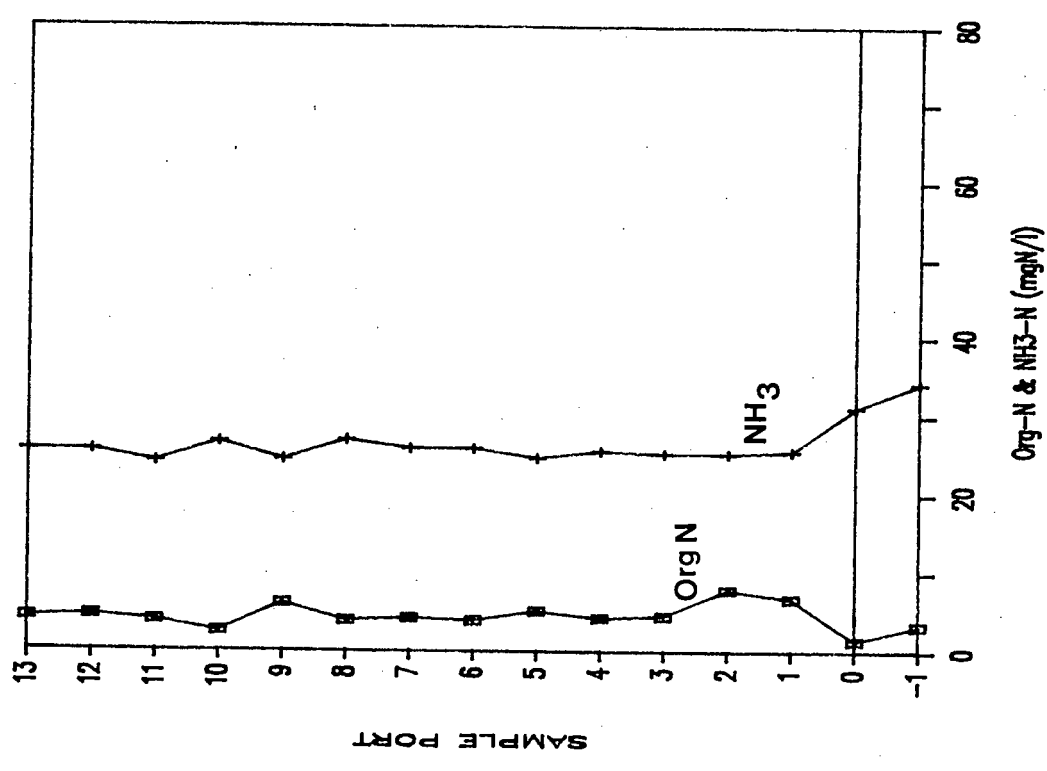


Figure 5.8: Reactor profiling experimental results - Recycle ratio 1:1, Alkalinity addition 6 g NaHCO₃/l (b) Organic nitrogen and free and saline ammonia

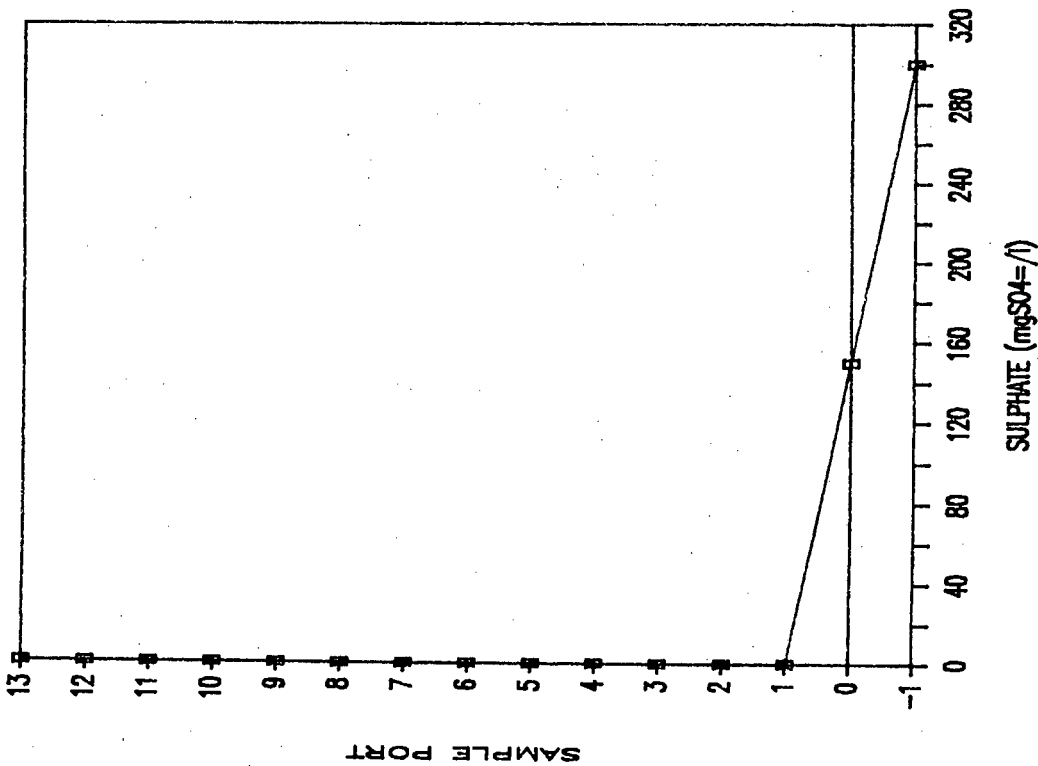


Figure 5.8: Reactor profiling experimental results -
Recycle ratio 1:1, Alkalinity addition
6 g NaHCO₃/l
(c) Sulphate

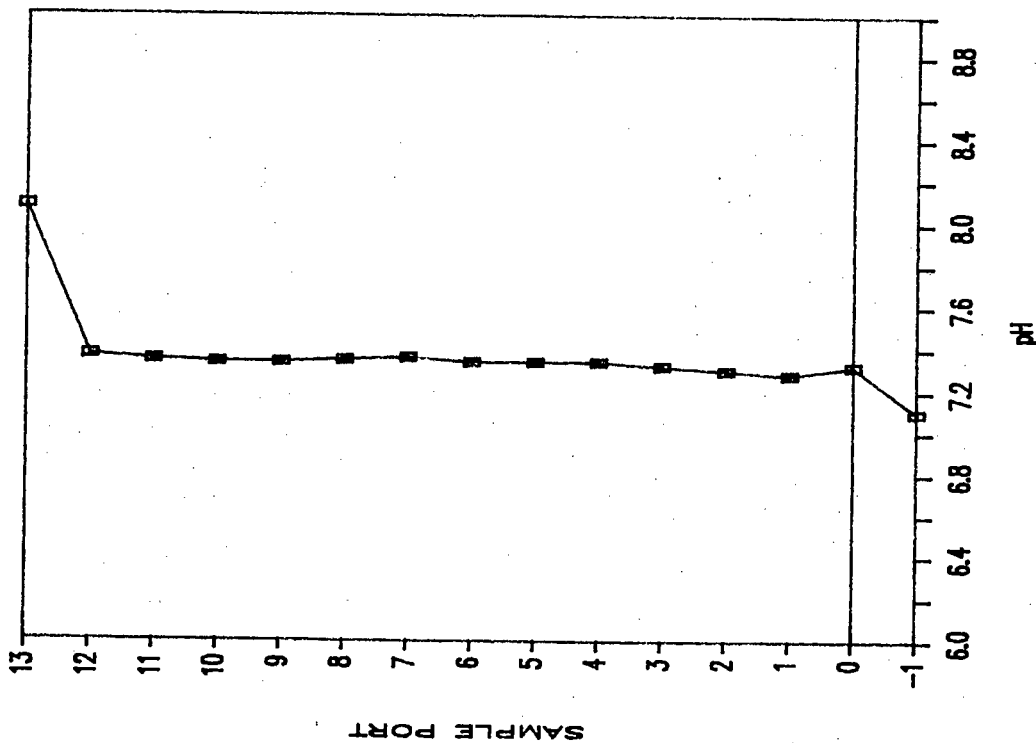


Figure 5.8: Reactor profiling experimental results -
Recycle ratio 1:1, Alkalinity addition
6 g NaHCO₃/l
(d) pH

zone existed at the base of the reactor as propionic acid concentration decreased from the inlet.

- (iv) The pH in the reactor was near constant at 7.35 throughout the reactor, without the characteristic decrease to a minimum at the base. This is 0.2 pH units higher than that of the feed. This result confirms that recycling from the effluent will allow a substantial reduction in the amount of alkalinity added to the feed.

The alkalinity addition to the feed was halved on the basis of the results of the first profile with recycling, and the system was allowed to stabilise for one week before taking a second profile of the reactor. The results of this profile with the alkalinity addition halved are shown in Fig 5.9. Again the results for COD, ammonia, organic nitrogen and sulphate are as expected and are very similar to those in Fig 5.8. However, it should be noted that the influent sulphate concentration was only $195 \text{ mgSO}_4/\text{l}$ compared to $300 \text{ mgSO}_4/\text{l}$ in Fig 5.8 (a new batch of waste from the plant was being used). The effect of the reduced amount of sulphate reduction at the base of the reactor would be to reduce the amount of acidity consumed in this region. This means that sulphate reduction would have a reduced capacity to offset the acidity produced by acidogenesis at the base of the reactor. Therefore, a pH drop at the base of the reactor would not be unexpected particularly as the alkalinity addition to the influent had been halved. However, from Fig 5.9 it can be seen that the pH decreased only marginally.

The results of Fig 5.9 indicate that the alkalinity addition to the feed could have been reduced further without adversely affecting reactor performance. It had been intended to perform profiles with further reductions in alkalinity. However, a burst pump tube resulted in a loss of a portion of the sludge from the reactor, and a period of several weeks would have been required to attain stable operation. Because the objective of testing the influence of recycling on alkalinity requirements and on system behaviour had been achieved successfully the laboratory experiments were terminated and attention was directed to the design of a pilot plant. Details concerning the pilot plant are given in Appendix A.

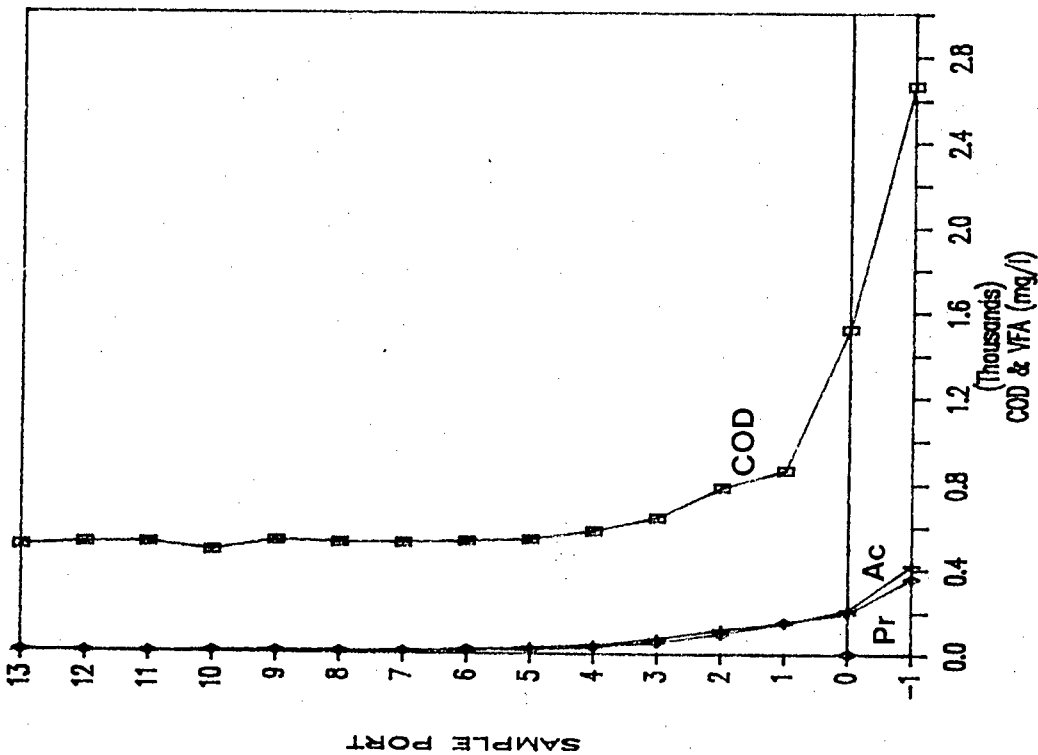


Figure 5.9: Reactor profiling experimental results -
 Recycle ratio 1:1, Alkalinity addition
 3 g NaHCO₃/l
 (a) Filtered COD, acetate and propionate

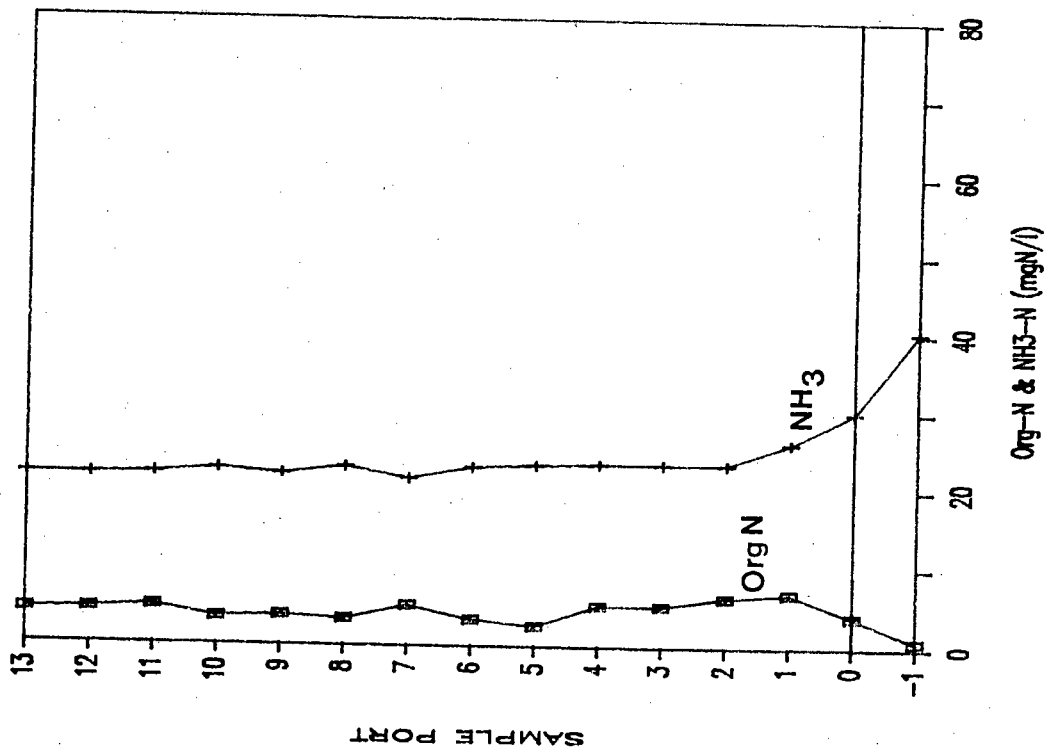
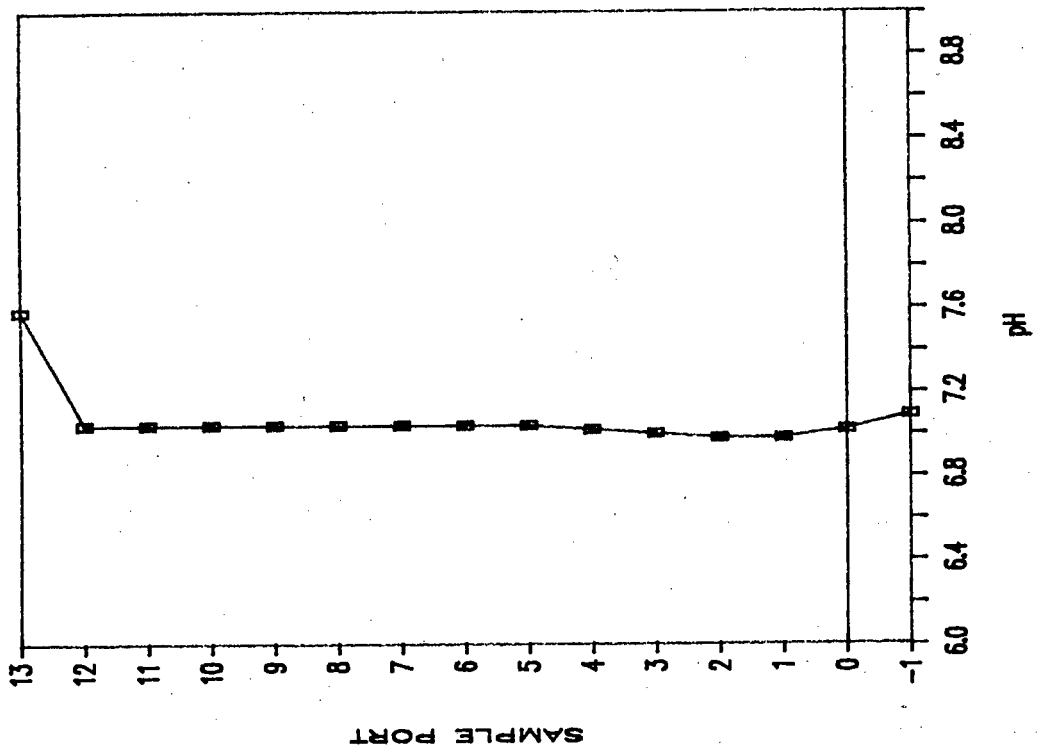
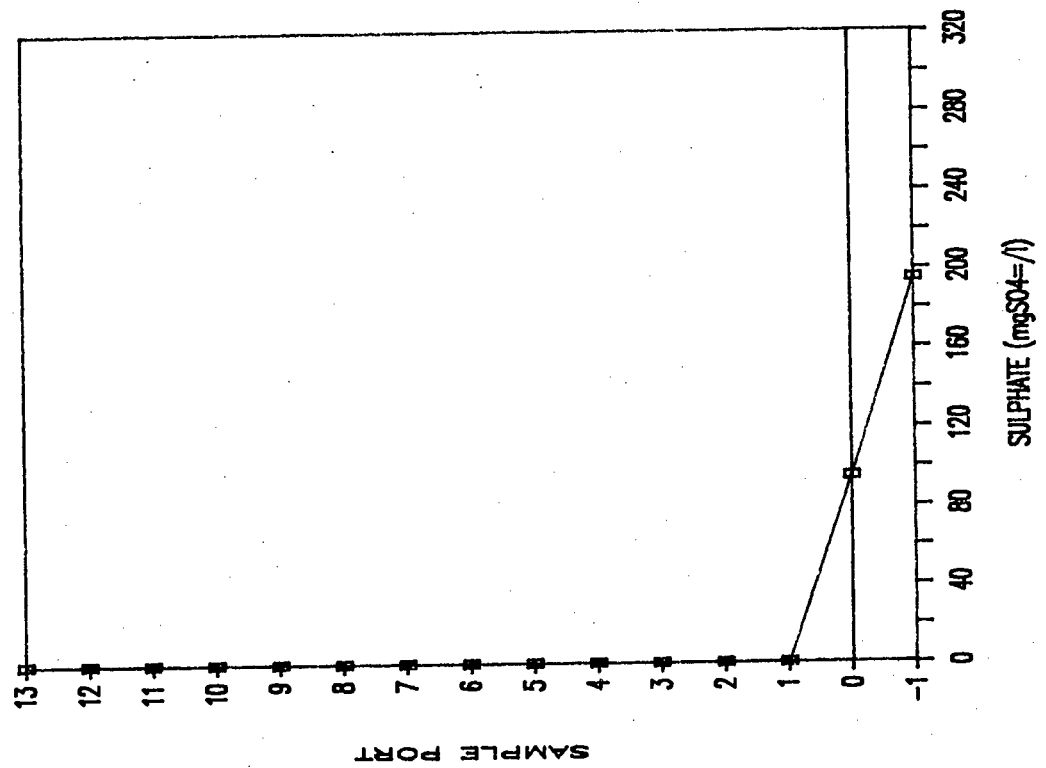


Figure 5.9: Reactor profiling experimental results -
 Recycle ratio 1:1, Alkalinity addition
 3 g NaHCO₃/l
 (b) Organic nitrogen and free and
 saline ammonia



Reactor profiling experimental results -
 Recycle ratio 1:1, Alkalinity addition
 3 g NaHCO₃/l
 (d) pH



Reactor profiling experimental results -
 Recycle ratio 1:1, Alkalinity addition
 3 g NaHCO₃/l
 (c) Sulphate

Figure 5.9:

CHAPTER SIX

CONCLUSIONS

The laboratory treatability study conducted on the wastewater from a waste paper re-pulping plant provided information on a wide range of factors. In general terms the important aspects were that the waste can be treated in a UASB system; guidelines on reactor loading rates were obtained; and that sulphate present in the wastewater plays an important role in the treatment system.

The following specific conclusions may be itemised from the results obtained in the study:

Wastewater characteristics and chemical addition:

- (1) The waste is amenable to anaerobic treatment in a UASB system.
- (2) The unbiodegradable COD content of the waste is in the region of 10 to 15 percent, and COD removals of approximately 85 percent are possible on a continuous basis.
- (3) The short chain volatile fatty acids acetic and propionic comprise approximately 45 percent of the COD in the influent. The remainder is made up principally of starch, carbohydrates and more complex organics.
- (4) The wastewater is deficient in the elements nitrogen and phosphorus. These elements must be supplemented through chemical addition in order to achieve complete anaerobic treatment.
- (5) The wastewater is acidic, with a pH in the range 5 to 6 generally. Alkalinity must be added to the waste prior to treatment to adjust the pH to approximately neutral.

Organic loading rates:

- (6) Organic loading rates of approximately 25 kgCOD/m³ reactor/day were attained at both 25 and 35°C. This corresponded to a hydraulic retention time of 5 hours at an influent COD concentration of 4500 mg/l. The loading rate was not constrained by limitations in the biological treatment capacity. Rather, difficulties associated with the settleability of the sludge were encountered; blockages of the under-designed laboratory reactor settler occurred.

Sludge characteristics:

- (7) A dense bed of biological sludge extended from the base to approximately half the height of the UASB reactors. This sludge had a granular, well-flocculated form with the flocs appearing to be in the size range 1-2 mm. Very fine sludge was also present within the bed. A small number of true sludge pellets (4-5 mm) were present within the dense sludge bed, particularly near the base.
- (8) The settleability of the dense granular sludge appeared reasonable, and the bed was not disturbed unduly by gas production. However, the settleability of the sludge was inferior to that of a well-pelletised sludge.
- (9) The absence of true sludge pellet formation appears to relate to the absence of a high hydrogen partial pressure zone in the lower region of the UASB reactor. With this particular wastewater two factors appear to reduce the possibility of creating a high partial pressure of hydrogen near the inlet, thus reducing the possibility of pellet formation. These are (1) the nature of the feed, and (2) the role of sulphate reduction.

Nature of feed: Approximately 45 percent of the influent COD is in the form of acetic and propionic acid. Therefore, the amount of remaining substrate available for acidogenesis, with its associated hydrogen production, is limited and the possibility of creating a high hydrogen partial pressure also is limited.

Sulphate reduction: The influent sulphate content appears to play an important role in suppressing the formation of pellets. Because

sulphate reducing organisms have a high growth rate (greater than that of the methanogens) the influent sulphate is reduced rapidly on entering the reactor. These organisms can readily utilize hydrogen as an energy source; therefore it is likely that sulphate reduction results in a low hydrogen partial pressure at the base of the reactor. If sulphate were excluded from the waste (by not using alum) then it is likely that pelletisation of the sludge would occur. It is significant to note that, with batches of waste where the sulphate content was less than approximately 160 mg $\text{SO}_4^{2-}/\text{l}$, the degree of pelletisation increased within a few days.

- (10) The problems encountered in the laboratory as a result of incomplete sludge pelletisation will not necessarily be transferred to the full-scale application of the process. In a full-scale system, with an adequately designed settler unit, the problems of sludge blockages should not arise. Nevertheless, if it were possible to ensure the complete pelletisation of the sludge, this would be preferred.

Role of sulphate:

- (11) It has been demonstrated that sulphate plays an important role in the treatment process with respect to pelletisation. If alum were not used in the paper manufacturing process, and as a result sulphate were not present in the waste, it is likely that a well-pelletised sludge would form. However, exclusion of sulphate will not only influence pelletisation; sulphate has been shown to play an important part in pH regulation via the biological sulphate reduction process which consumes acidity. If sulphate were excluded from the waste the requirements for alkalinity addition, and therefore the operating costs of the process, possibly would be increased.

Recycling of effluent:

- (12) Alkalinity requirements can be reduced by recycling the reactor effluent back into the reactor with the fresh feed.

(13) The presence of sulphate in the waste does not influence the use of recycling of effluent to reduce alkalinity requirements. The sulphide levels in the recycle stream did not have a deleterious effect on the process.

(14) The sludge bed contained a higher proportion of fine material once recycling was employed. This appeared to be a result of recycling fines, and not generation of fines within the bed itself. The settleability of the sludge, however, was not adversely affected by the higher upflow velocity and finer bed material. A very slight expansion of the sludge bed occurred with recycling.

Re-starting the reactor:

(15) During the study the 35°C UASB reactor was re-started after standing at 20°C without feed for a period of 2 months. Within a period of 10 days the load on the reactor could be re-instated with COD removals in excess of 80 percent.

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APPENDIX A

**ENVISAGED DESIGN, LAYOUT AND CHEMICAL
USAGE CALCULATIONS FOR THE UASB
PILOT SCALE PLANT**

SAPPI CAPE KRAFT

UASB PILOT PLANT

ENVISAGED DESIGN, LAYOUT
AND
CHEMICAL USAGE CALCULATIONS

INTRODUCTION

This document presents the envisaged design calculations, plant layout and chemical usage calculations for the UASB Pilot Plant to be operated at SAPPI CAPE KRAFT'S wastepaper processing paper mill. The UASB Pilot Plant will treat mill effluent which has an average COD of 4 000mgCOD/litre. Temperature varies from 18°C in Winter to 34°C in Summer. According to laboratory work 85% of the COD is biodegradable. The pH of the effluent is usually approximately pH5.

This document provides information on the UASB reactor and gives calculations on the pressures against which pumps will have to deliver influent to the reactor. Calculations to determine alkalinity addition to the effluent to adjust pH to optimum value for maximum biological activity are also laid down. Because of the low nutrient content of the effluent nitrogen and phosphate have to be added. Calculations based on adequate nutrient requirements for the UASB system to operate efficiently are also included.

Included also are detailed drawings of the UASB reactor tank and the pilot plant layout.

The major reasons for conducting a UASB Pilot Plant study are twofold :-

1. To see if the system operates efficiently under industrial situations where conditions vary appreciable. For example, COD varies from 3000mgCOD/litre to 6000mgCOD/litre, pH varies from pH 5 to pH7 and temperature varies from 18°C to 34°C.
2. To confirm the laboratory study performed at the University of Cape Town.

UPFLOW ANAEROBIC SLUDGE BLANKET REACTOR (UASB)

The UASB reactor will be an EVERITE TANK with an approximate volume of 4,5 cubic metres. Because the tank will also house a solid/liquid/gas separator in the top section, the effective reactor volume will be less than 4,5m³. It is estimated to be about 3,0m³.

The wastewater to be treated has an average COD concentration of 4000 mg COD/litre (Range 3000 to 5000 mg COD/litre).

$$\begin{aligned}\text{Mass load required} &= 20 \text{ kg COD/m}^3 \text{ reactor/day} \\ &= 20 \times 3 \text{ kg COD/day} \\ &= 60 \text{ kg COD/day}\end{aligned}$$

$$\begin{aligned}\text{Maximum Feed volume} &= \frac{60 \text{ kg COD/day}}{4 \times 10^{-3} \text{ kg COD/litre}} \\ &= 15 \text{ 000 litres/day} \\ &= 15,0 \text{ m}^3/\text{day}\end{aligned}$$

Initially the design flow requirement will be 5,0m³/day which can be increased to the maximum feed flow of 15,0m³/day into a tank of approximately 1,8m diameter. The liquid to be pumped is a settled wastewater from a wastepaper processing paper mill with suspended solids of average size less than 1mm in diameter. Therefore the minimum orifice size must be not less than 1mm. The distribution network will consist of 30 discharge outlets spaced evenly over the tank floor. Based on the fact that recycle of reactor effluent will be employed and that the recycle ratio will not be larger than 2:1 the following calculations were made:-

$$\begin{aligned}\text{Initial design flow} &= 15 \text{ 000 litres/day} \quad (2:1 \text{ recycle ratio}) \\ &= 5,787 \text{ cm}^3/\text{hole}/\text{sec} \\ \text{Area of 1 hole} &= \frac{\pi d^2}{4}\end{aligned}$$

Assuming a velocity of 3,5m/sec is adequate to ensure reasonable distribution of the liquid over the tank floor:-

$$\frac{\pi d^2}{4} = \frac{5,787}{350}$$

$$d = \sqrt{\frac{(4 \times 5,787)}{(\pi \times 350)}}$$

$$= 0,145\text{cm}$$

$$= 1,45\text{mm}$$

A hole diameter of 1,5mm was selected.

The equation for head loss through an orifice is as follows:-

$$V = C_d \sqrt{2gH}$$

$$Q = C_d A \sqrt{2gH} = C_d \left(\frac{\pi d^2}{4} \right) \sqrt{2gH}$$

where Q is the flow (m³/sec)

V is the velocity (m/sec)

A is the orifice area (m²)

d is the orifice diameter (m)

H is the head loss (m)

g is the gravitational constant (9,8m/sec²)

Cd is the discharge coefficient

For orifices Cd is approximately 0,6 where the orifice diameter : pipe diameter ratio is less than 0,2.

$$Q = 3,477 C_d d^2 \sqrt{H}$$

Since the wastewater will be pumped from a holding tank approximately 1,4m high to the reactor which is approximately 1,8m high, there will be a static head. Both tanks will operate at full capacity. This will result in a static head of 0,4m which will add to the dynamic heads already calculated.

$$\begin{aligned} \text{i.e. at initial flow, } H &= 1,5 + 0,4 \\ &= 1,9\text{m} \\ \text{at maximum flow, } H &= 13,7 + 0,4 \\ &= 14,1\text{m} \end{aligned}$$

Adding on approximately 1,0m for losses through the piping network we have a head loss variation from 2,9m of water at initial flow to 15,1m of water at maximum flow while employing a 2:1 recycle ratio. Therefore, it is established that the pumps must be capable of delivering a maximum of 45,0m³/day against a total head of 14,1m of water. For this purpose the air-operated double-diaphragm pumps were selected as ideal to deliver constant flow (controlled by air pressure) against heads ranging from 0 to 150 kPa.

NUTRIENT AND ALKALINITY SUPPLEMENT

It has been decided that the pretreatment of the influent to the reactor would best be achieved by adopting the following scheme.

Clarified water will be fed from the Clarified Water Tank into a holding tank. The head of water in the Clarified Water Tank will be sufficient to maintain wastewater flow into the holding tank. This flow will be controlled using a ball valve, which will maintain the tank at a constant level. The holding tank will have a volume of approximately 1,5 cubic metres, and will be continuously stirred.

Since the wastewater is acidic, pH adjustment is necessary. Concentrated sodium hydroxide solution, available at the mill, will be used for this purpose. This will be pumped into the holding tank at a controlled rate, determined by the feed flow to the U A S B reactor.

To supply the required nitrogen and phosphate requirements, a suitable fertilizer will be pumped as an aqueous solution into the holding tank at a rate determined by the feed flow to the U A S B reactor.

(1) Sodium Hydroxide Usage

The wastewater, generally, has a pH of about 5. In laboratory work at the University of Cape Town sodium bicarbonate was used to adjust the pH to about 7,2. For a system with no recycle the sodium bicarbonate dosage was 5,0 grams per litre of wastewater and for a system at a recycle ratio of 1 : 1 it was possible to decrease the dosage to 2,5 grams per litre. To be on the safe side a dosage of 3,0 grams of sodium bicarbonate per litre was assumed to be adequate.

However, since concentrated sodium hydroxide solution is to be used instead of sodium bicarbonate, the above dosage will have to be converted to alkalinities to determine the sodium hydroxide dosage.

The alkalinity equation is as follows:-

$$\text{Total Alkalinity} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

([] refers to concentration of species)

Each mmole of HCO_3^- added is equivalent to an addition of 1 mmole alkalinity, according to the above equation.

$$\begin{aligned} 3,0\text{g/litre of NaHCO}_3 &= 3000 \text{ mg/litre} \\ &= 36 \text{ mmole/litre of NaHCO}_3 \end{aligned}$$

i.e. Total alkalinity addition required = 36 mmole/litre

Now, for 1 mmole of sodium hydroxide added, it can be seen from the Total Alkalinity equation that 1 mmole of alkalinity is being added.

$$\begin{aligned} \text{NaOH dosage} &= \text{Total Alkalinity required} \\ &= 36 \text{ mmole/litre} \\ &= 36 \times 40 \\ &= 1440 \text{ mg NaOH/litre} \end{aligned}$$

$$\begin{aligned} \text{Maximum feed flow} &= 15\text{m}^3/\text{day} \\ &= 15000 \text{ litres/day} \end{aligned}$$

$$\begin{aligned} \text{NaOH usage} &= 15000 \times 1440/1000 \\ &= 21600 \text{ g/day} \\ &= 21,6 \text{ kg/day} \end{aligned}$$

Available sodium hydroxide is a 47% solution with a specific gravity of about 1,48.

$$\begin{aligned} \text{NaOH solution usage} &= 21,6/0,47 = 46,0 \text{ kg/day} \\ &= 46,0/1,48 = 31,1 \text{ litres/day} \end{aligned}$$

Therefore, at maximum feed flow, maximum sodium hydroxide solution (47%) usage will be 31,1 litres/day (21,60 ml/min).

(2) Nitrogen and Phosphate Addition

From laboratory work performed at the University of Cape Town, it was observed that a COD:TKN:P ratio of 1000:5:1 was adequate to supply the required nitrogen and phosphate for the system to operate at maximum efficiency.

For the mass load of 60kg COD/day:-

$$\begin{aligned}\text{Nitrogen requirement} &= 60 \times 5/1000 \\ &= 0,30 \text{ kg N/day}\end{aligned}$$

$$\begin{aligned}\text{Phosphate requirement} &= 60 \times 1/1000 \\ &= 0,06 \text{ kg P/day}\end{aligned}$$

The cheapest source of nitrogen and phosphate is fertilizer and the most suitable one has been found to be a WONDER fertilizer with a N:P:K ratio of 3:1:5 and contains 8,7% N and 2,9% P. Based on the nitrogen requirement calculated above, the fertilizer usage is calculated as follows:-

$$\begin{aligned}\text{Fertilizer Usage} &= \frac{0,30 \text{ kg N/day}}{0,087 \text{ kg N/kg fertilizer}} \\ &= 3,45 \text{ kg fertilizer/day}\end{aligned}$$

Therefore, the actual COD:TKN:P ratio will be 600:3:1.

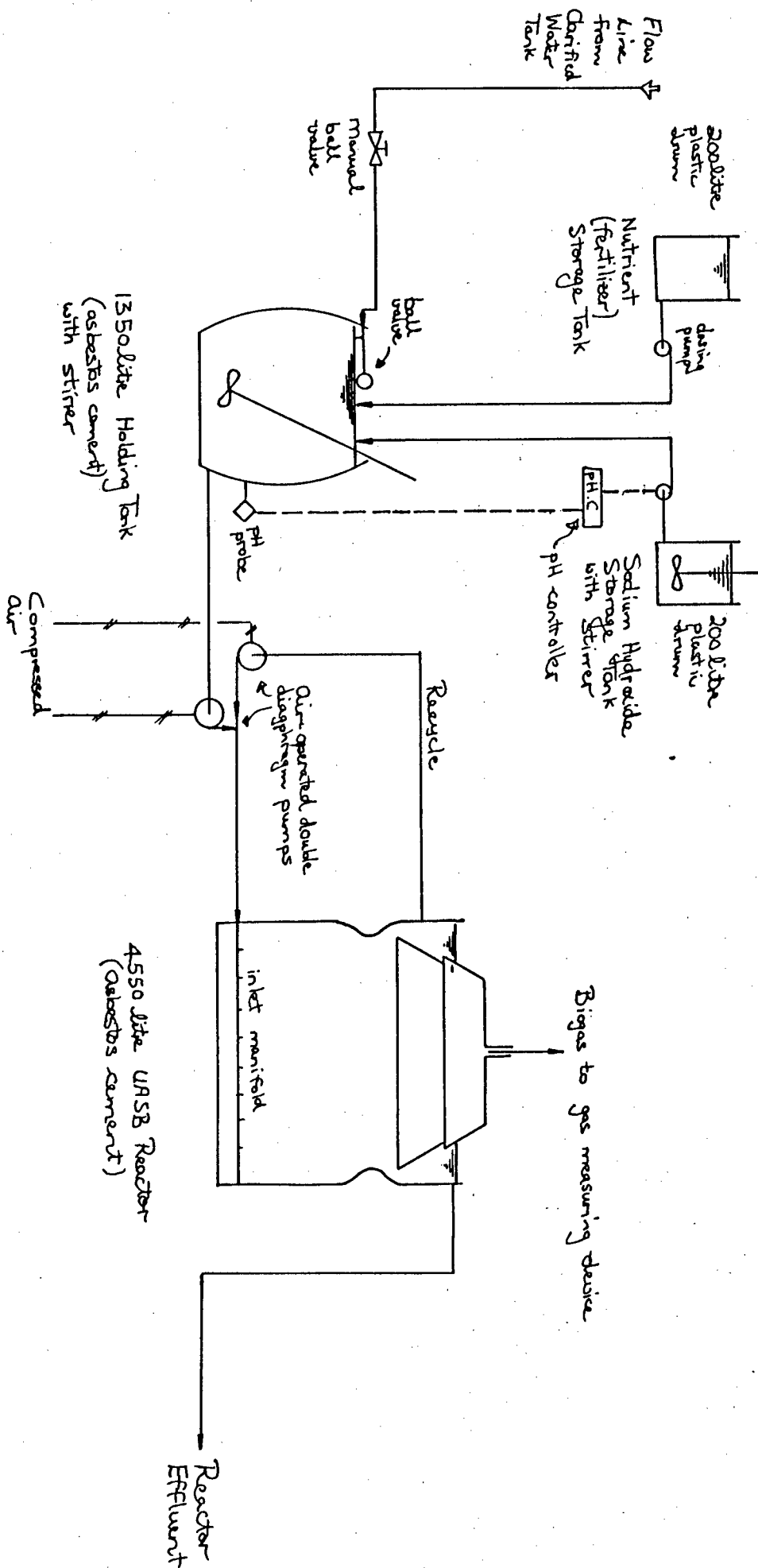
The fertilizer will be pumped as an aqueous solution at a concentration of 100 mg/litre using a suitable dosing pump.

$$\begin{aligned}\text{Fertilizer usage} &= 3,45 \text{ kg/day} \\ \text{Fertilizer concentration} &= 100 \text{ mg/litre} \\ \text{Flow rate} &= 34,5 \text{ litres/day} \\ &\quad (24,0 \text{ ml/min})\end{aligned}$$

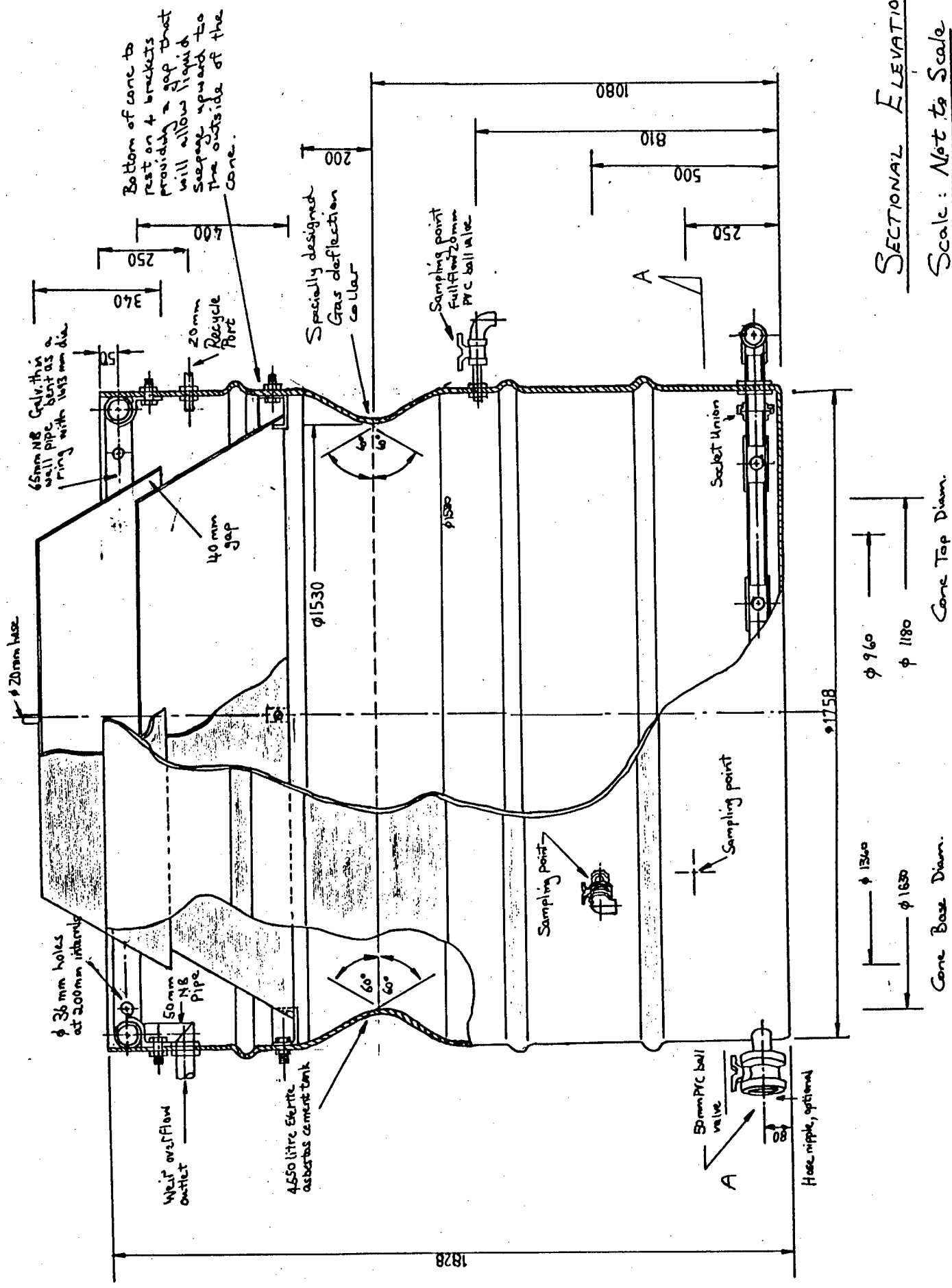
BUDGET FIGURES FOR UASB PILOT PLANT

<u>CAPITAL COSTS</u>	<u>SUPPLIER</u>	<u>COST</u>
4550 litre Asbestos Tank	Everite	R 570,00
Collar and Cones	Everite	R 560,00
1350 litre Asbestos Tank	Everite	R 235,00
3 x 200 litre Plastic Drums	Sappi	R 0,00
PVC Pipes and Fittings	Astore Africa	R 815,00
Air operated double Diaphragm pumps (2)	Wilco Howard	R1 372,00
pH Control Pump (NaOH)) in one	Autrex	R 850,00
Dosing pump (fertilizer)) cabinet	Autrex	R 450,00
Stirrer (for fertilizer)	Sappi	R 0,00
Stirrer (for holding tank)	Sappi	R 0,00
Bitumen coating for asbestos tanks	Everite	<u>R 100,00</u>
	TOTAL	<u>R4 952,00</u>

<u>RUNNING COSTS (at maximum flow)</u>	<u>USAGE/DAY</u>	<u>COST/DAY</u>
Sodium Hydroxide (47%)	46,0 kg	R 32,53
Fertilizer	3,45 kg	<u>R 2,75</u>
	TOTAL	<u>R 35,28/day</u>

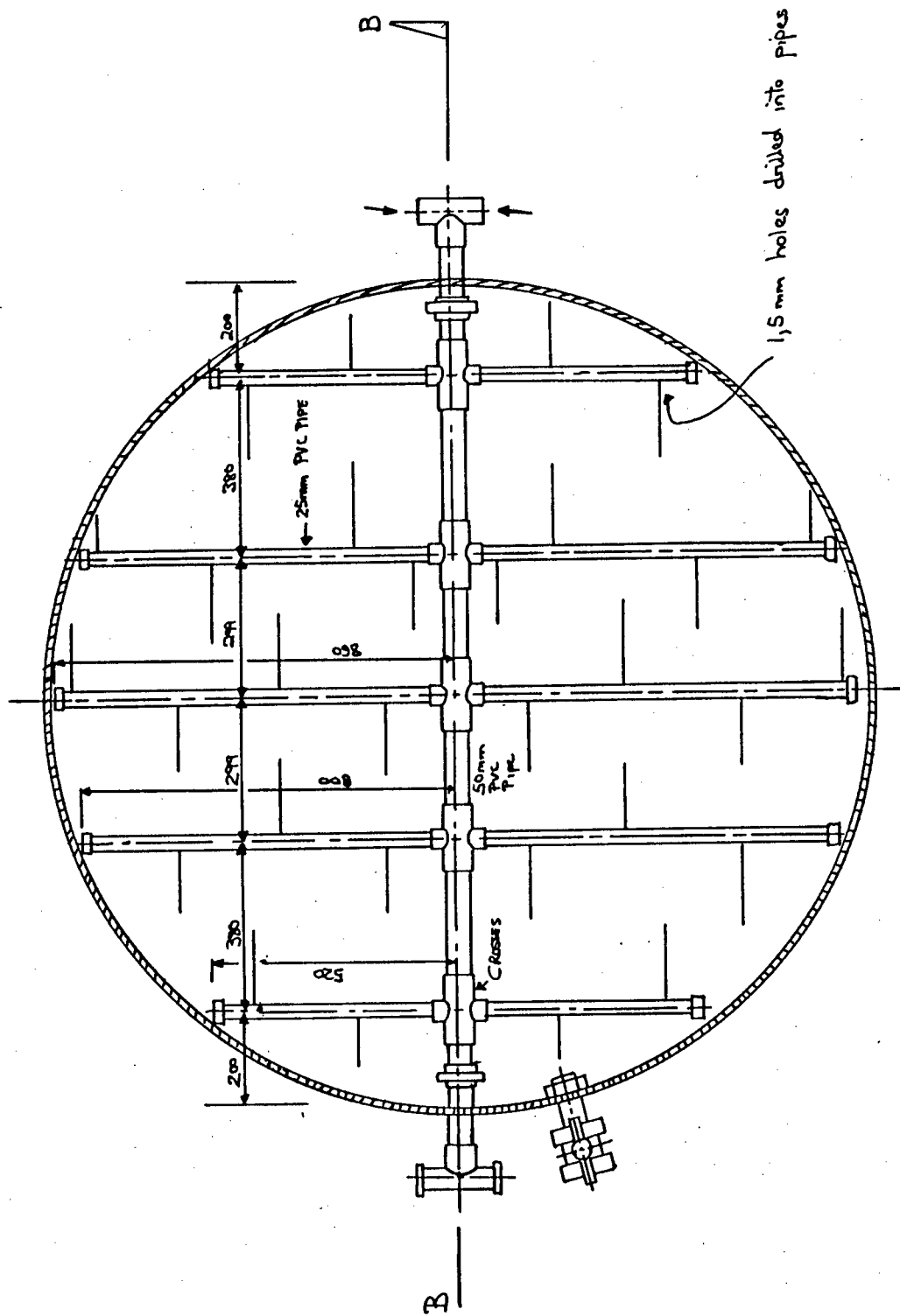


ENVISAGED LAYOUT OF THE USB PILOT PLANT (NOT TO SCALE)



SECTIONAL ELEVATION AT B-B

Scale: Not to Scale



PLAN AT A-A
 Scale: Not to Scale

APPENDIX B

**DAILY RESULTS FOR THE 25°C AND
35°C UASB LABORATORY REACTORS**

SAPPI 25 degC REACTOR

Date	Day	Influent Flowrate (l/day)	Influent COD (mgCOD/l)	Filtered Effl. COD (mgCOD/l)	Unfiltered Effl. COD (mgCOD/l)	Influent pH	Effluent pH	Loading Rate (Kg/m ³ /d)	COD Removal (%)	Retention Time (hours)
13-2-86	1	10.5	490	189	228	7.6	8.1	0.57	61	20.6
14-2-86	2	11.4	592	148	176	7.2	8.0	0.75	75	18.9
15-2-86	3	11.0	522	137	152	7.0	7.1	0.64	74	19.6
16-2-86	4	10.0	532	112	136	7.0	7.0	0.59	79	21.6
17-2-86	5	7.0	532	90	102	7.1	6.9	0.41	83	30.9
18-2-86	6	8.0	505	84	102	7.1	6.9	0.45	83	27.0
19-2-86	7	8.5	521	101	128	7.3	6.9	0.49	81	25.4
20-2-86	8	8.5	535	96	121	7.4	7.0	0.51	82	25.4
21-2-86	9	8.0	831	84	127	7.5	7.1	0.74	90	27.0
22-2-86	10	9.0	820	118	135	7.5	7.2	0.82	86	24.0
23-2-86	11	9.0	816	128	155	7.6	7.3	0.82	84	24.0
24-2-86	12	9.5	848	126	170	7.5	7.3	0.90	85	22.7
25-2-86	13	9.0	854	112	147	7.4	7.2	0.85	87	24.0
26-2-86	14	NA	NA	NA	NA	NA	NA	NA	NA	NA
27-2-86	15	NA	NA	NA	NA	NA	NA	NA	NA	NA
28-2-86	16	17.4	1054	187	238	7.4	7.3	2.04	82	12.4
1-3-86	17	16.4	1015	209	250	7.7	7.1	1.85	79	13.2
2-3-86	18	12.0	1061	191	216	7.6	7.1	1.42	82	18.0
3-3-86	19	9.8	1077	183	204	7.6	7.1	1.18	83	22.0
4-3-86	20	9.8	1002	160	215	7.6	7.1	1.10	84	22.0
5-3-86	21	9.2	1073	165	192	7.6	7.1	1.10	85	23.5
6-3-86	22	9.2	1469	195	218	7.6	7.2	1.50	87	23.5
7-3-86	23	9.0	1500	235	287	7.7	7.2	1.50	84	24.0
8-3-86	24	9.0	1522	246	281	7.7	7.2	1.50	84	24.0
9-3-86	25	9.0	1450	242	256	7.7	7.2	1.50	83	24.0
10-3-86	26	9.0	1534	250	304	7.7	7.3	1.50	84	24.0
11-3-86	27	9.0	2071	282	299	7.6	7.3	2.10	86	24.0
12-3-86	28	9.0	1998	307	326	7.7	7.2	2.00	85	24.0
13-3-86	29	NA	NA	NA	NA	NA	NA	NA	NA	NA
14-3-86	30	NA	NA	NA	NA	NA	NA	NA	NA	NA
15-3-86	31	9.0	1998	325	350	7.8	7.3	2.00	84	24.0
16-3-86	32	8.3	1975	293	324	7.7	7.3	1.80	85	26.0
17-3-86	33	8.5	1991	283	336	7.7	7.3	1.90	86	25.4
18-3-86	34	8.0	3018	339	339	7.6	7.2	2.70	89	27.0
19-3-86	35	9.4	2977	449	506	7.6	7.2	3.11	85	23.0
20-3-86	36	NA	NA	NA	NA	NA	NA	NA	NA	NA
21-3-86	37	NA	NA	NA	NA	NA	NA	NA	NA	NA
22-3-86	38	10.6	3156	503	563	7.6	7.2	3.70	84	20.4
23-3-86	39	10.4	3064	453	486	7.7	7.2	3.54	85	20.8
24-3-86	40	10.0	3037	491	538	7.7	7.2	3.37	84	21.6
25-3-86	41	10.0	4473	599	753	7.6	7.3	4.97	87	21.6
26-3-86	42	9.8	4459	691	784	7.7	7.3	4.86	85	22.0
27-3-86	43	NA	NA	NA	NA	NA	NA	NA	NA	NA
28-3-86	44	NA	NA	NA	NA	NA	NA	NA	NA	NA
29-3-86	45	NA	NA	NA	NA	NA	NA	NA	NA	NA
30-3-86	46	NA	NA	NA	NA	NA	NA	NA	NA	NA
31-3-86	47	9.8	4525	599	657	7.4	7.1	4.94	87	22.0
1-4-86	48	9.8	4412	581	619	7.4	7.2	4.80	87	22.0
2-4-86	49	15.0	4526	720	852	7.5	7.2	7.54	84	14.4

3-4-86	50	NA	NA	NA	NA	NA	NA	NA	NA	NA
4-4-86	51	12.0	4506	710	803	7.5	7.1	6.01	84	18.0
5-4-86	52	15.0	4557	755	877	7.5	7.2	7.60	83	14.4
6-4-86	53	10.3	4239	586	697	7.5	7.2	4.85	86	21.0
7-4-86	54	12.5	4577	695	724	7.5	7.2	6.36	85	17.3
8-4-86	55	NA	NA	NA	NA	NA	NA	NA	NA	NA
9-4-86	56	3.9	4304	708	798	7.5	7.2	1.87	84	55.4
10-4-86	57	13.0	4488	661	820	7.5	7.1	6.48	85	16.6
11-4-86	58	13.0	4243	645	948	7.5	7.1	6.13	85	16.6
12-4-86	59	10.8	4325	588	708	7.6	7.2	5.19	86	20.0
13-4-86	60	NA	NA	NA	NA	NA	NA	NA	NA	NA
14-4-86	61	17.4	4386	694	861	7.6	7.2	8.48	84	12.4
15-4-86	62	12.0	4202	590	782	7.6	7.1	5.60	86	18.0
16-4-86	63	16.0	4454	588	1190	7.7	7.1	7.92	87	13.5
17-4-86	64	10.5	4707	608	695	7.7	7.2	5.49	87	20.6
18-4-86	65	NA	NA	NA	NA	NA	NA	NA	NA	NA
19-4-86	66	9.9	4585	640	NA	7.7	7.2	5.04	86	21.8
20-4-86	67	9.3	4383	630	727	7.7	7.1	4.53	86	23.2
21-4-86	68	9.4	4505	598	810	7.3	7.1	4.71	87	23.0
22-4-86	69	9.2	4505	586	639	7.3	7.1	4.61	87	23.5
23-4-86	70	NA	NA	NA	NA	NA	NA	NA	NA	NA
24-4-86	71	9.6	4418	582	695	7.3	NA	4.71	87	22.5
25-4-86	72	NA	NA	NA	NA	NA	NA	NA	NA	NA
26-4-86	73	9.2	4337	564	681	NA	NA	4.43	87	23.5
27-4-86	74	9.2	4528	552	693	NA	NA	4.63	88	23.5
28-4-86	75	NA	NA	NA	NA	NA	NA	NA	NA	NA
29-4-86	76	10.7	4431	518	870	NA	NA	5.27	88	20.2
30-4-86	77	11.2	4636	551	1116	NA	7.1	5.77	88	19.3
1-5-86	78	10.2	4554	528	1190	7.5	7.0	5.16	88	21.2
2-5-86	79	NA	NA	NA	NA	NA	NA	NA	NA	NA
3-5-86	80	11.2	4698	535	822	7.6	7.0	5.85	89	19.3
4-5-86	81	11.0	4544	553	NA	7.6	7.1	5.55	88	19.6
5-5-86	82	NA	NA	NA	NA	NA	NA	NA	NA	NA
6-5-86	83	10.8	4465	557	NA	7.6	7.1	5.36	88	20.0
7-5-86	84	NA	NA	NA	NA	NA	NA	NA	NA	NA
8-5-86	85	13.6	4485	553	897	7.7	7.2	6.78	88	15.9
9-5-86	86	13.6	4352	557	983	7.8	7.3	6.58	87	15.9
10-5-86	87	NA	NA	NA	NA	NA	NA	NA	NA	NA
11-5-86	88	12.9	4506	619	NA	7.5	7.2	6.46	86	16.7
12-5-86	89	14.9	4495	682	NA	7.4	7.2	7.44	85	14.5
13-5-86	90	NA	NA	NA	NA	NA	NA	NA	NA	NA
14-5-86	91	NA	NA	NA	NA	NA	NA	NA	NA	NA
15-5-86	92	14.0	4539	720	885	7.5	7.1	7.06	84	15.4
16-5-86	93	NA	NA	NA	NA	NA	NA	NA	NA	NA
17-5-86	94	15.5	4674	753	NA	7.5	7.2	8.05	84	13.9
18-5-86	95	14.2	4581	701	1009	7.2	7.2	7.23	85	15.2
19-5-86	96	14.9	4508	761	1144	7.2	7.2	7.46	83	14.5
20-5-86	97	15.0	4787	720	906	7.1	7.2	7.98	85	14.4
21-5-86	98	14.7	4292	752	869	7.3	7.1	7.01	82	14.7
22-5-86	99	NA	NA	NA	NA	NA	NA	NA	NA	NA
23-5-86	100	14.7	4538	771	NA	7.4	NA	7.41	83	14.7
24-5-86	101	NA	NA	NA	NA	NA	NA	NA	NA	NA
25-5-86	102	14.4	4783	805	920	7.6	7.3	7.65	83	15.0
26-5-86	103	NA	NA	NA	NA	NA	NA	NA	NA	NA
27-5-86	104	NA	NA	NA	NA	NA	NA	NA	NA	NA
28-5-86	105	14.2	4492	728	829	7.5	7.2	7.09	84	15.2

29-5-86	106	14.8	4492	565	732	7.3	7.2	7.39	87	14.6
30-5-86	107	14.8	4564	535	NA	7.3	NA	7.51	88	14.6
31-5-86	108	NA	NA	NA	NA	NA	NA	NA	NA	NA
1-6-86	109	14.7	4348	543	740	7.3	NA	7.10	88	14.7
2-6-86	110	17.3	4194	506	NA	7.2	7.3	8.06	88	12.5
3-6-86	111	16.9	4138	545	1002	7.4	7.3	7.77	87	12.8
4-6-86	112	17.7	4519	577	1054	7.4	7.2	8.89	87	12.2
5-6-86	113	17.2	4579	537	1245	7.4	7.4	8.75	88	12.6
6-6-86	114	NA	NA	NA	NA	NA	NA	NA	NA	NA
7-6-86	115	17.2	4609	589	774	7.4	7.3	8.81	87	12.6
8-6-86	116	NA	NA	NA	NA	NA	NA	NA	NA	NA
9-6-86	117	16.9	4517	566	691	7.4	7.2	8.48	87	12.8
10-6-86	118	16.7	4528	678	538	7.5	7.2	8.40	85	12.9
11-6-86	119	16.8	4415	540	662	7.5	7.2	8.24	88	12.9
12-6-86	120	16.9	4364	538	732	7.5	7.3	8.19	88	12.8
13-6-86	121	17.0	4517	540	NA	7.4	7.2	8.53	88	12.7
14-6-86	122	NA	NA	NA	NA	NA	NA	NA	NA	NA
15-6-86	123	17.0	4436	540	NA	7.4	7.2	8.38	88	12.7
16-6-86	124	NA	NA	NA	NA	NA	NA	NA	NA	NA
17-6-86	125	18.0	4610	543	622	7.4	7.2	9.22	88	12.0
18-6-86	126	18.0	4579	526	949	7.4	7.3	9.16	89	12.0
19-6-86	127	NA	NA	NA	NA	NA	NA	NA	NA	NA
20-6-86	128	NA	NA	NA	NA	NA	NA	NA	NA	NA
21-6-86	129	NA	NA	NA	NA	NA	NA	NA	NA	NA
22-6-86	130	NA	NA	NA	NA	NA	NA	NA	NA	NA
23-6-86	131	NA	NA	NA	NA	NA	NA	NA	NA	NA
24-6-86	132	18.0	4388	679	769	7.5	7.3	8.78	85	12.0
25-6-86	133	17.8	4548	584	NA	7.2	7.3	8.99	87	12.1
26-6-86	134	17.9	4608	556	NA	7.3	7.3	9.16	88	12.1
27-6-86	135	21.3	4699	580	NA	7.3	7.3	11.12	88	10.1
28-6-86	136	NA	NA	NA	NA	NA	NA	NA	NA	NA
29-6-86	137	NA	NA	NA	NA	NA	NA	NA	NA	NA
30-6-86	138	21.0	4618	631	779	7.2	7.3	10.78	86	10.3
1-7-86	139	21.5	4585	629	806	7.2	7.2	10.95	86	10.0
2-7-86	140	21.2	4657	570	NA	7.2	NA	10.97	88	10.2
3-7-86	141	21.0	4605	592	NA	NA	7.3	10.75	87	10.3
4-7-86	142	NA	NA	NA	NA	NA	NA	NA	NA	NA
5-7-86	143	NA	NA	NA	NA	NA	NA	NA	NA	NA
6-7-86	144	21.0	4451	588	NA	7.5	7.4	10.39	87	10.3
7-7-86	145	21.0	4575	568	NA	7.4	7.3	10.68	88	10.3
8-7-86	146	21.2	4588	541	NA	7.4	7.3	10.81	88	10.2
9-7-86	147	NA	NA	NA	NA	NA	NA	NA	NA	NA
10-7-86	148	21.2	4416	551	NA	7.4	7.4	10.40	88	10.2
11-7-86	149	NA	NA	NA	NA	NA	NA	NA	NA	NA
12-7-86	150	NA	NA	NA	NA	NA	NA	NA	NA	NA
13-7-86	151	NA	NA	NA	NA	NA	NA	NA	NA	NA
14-7-86	152	20.9	4477	547	592	7.1	7.3	10.40	88	10.3
15-7-86	153	22.0	4447	535	NA	7.4	7.3	10.87	88	9.8
16-7-86	154	19.7	4545	575	NA	7.3	NA	9.95	87	11.0
17-7-86	155	27.0	4494	601	NA	NA	7.4	13.48	87	8.0
18-7-86	156	27.1	4597	575	NA	7.4	NA	13.84	87	8.0
19-7-86	157	NA	NA	NA	NA	NA	NA	NA	NA	NA
20-7-86	158	26.6	4371	554	NA	NA	7.3	12.92	87	8.1
21-7-86	159	NA	NA	NA	NA	NA	NA	NA	NA	NA
22-7-86	160	NA	NA	NA	NA	NA	NA	NA	NA	NA
23-7-86	161	26.8	3776	538	NA	7.0	7.1	11.24	86	8.1

24-7-86	162	26.9	3868	525	NA	7.1	7.1	11.56	86	8.0
25-7-86	163	NA	NA	NA	NA	NA	NA	NA	NA	NA
26-7-86	164	26.9	3896	563	NA	NA	7.2	11.64	86	8.0
27-7-86	165	26.3	4304	575	NA	7.1	7.1	12.58	87	8.2
28-7-86	166	26.2	4794	624	NA	7.2	7.2	13.96	87	8.2
29-7-86	167	26.3	4743	590	871	7.1	7.2	13.86	88	8.2
30-7-86	168	26.8	4223	624	NA	7.2	7.2	12.58	85	8.1
31-7-86	169	NA	NA	NA	NA	NA	NA	NA	NA	NA
1-8-86	170	NA	NA	NA	NA	NA	NA	NA	NA	NA
2-8-86	171	NA	NA	NA	NA	NA	NA	NA	NA	NA
3-8-86	172	NA	NA	NA	NA	NA	NA	NA	NA	NA
4-8-86	173	NA	NA	NA	NA	NA	NA	NA	NA	NA
5-8-86	174	29.0	4405	NA	NA	7.4	7.4	14.19	NA	7.4
6-8-86	175	28.6	4243	634	1234	7.4	7.2	13.48	85	7.6
7-8-86	176	28.6	4233	606	998	7.2	7.3	13.45	86	7.6
8-8-86	177	28.2	4692	NA	NA	7.4	7.4	14.70	NA	7.7
9-8-86	178	NA	NA	NA	NA	NA	NA	NA	NA	NA
10-8-86	179	28.4	4617	726	NA	7.4	7.4	14.57	84	7.6
11-8-86	180	28.0	4761	726	NA	7.4	7.3	14.81	85	7.7
12-8-86	181	NA	NA	NA	NA	NA	NA	NA	NA	NA
13-8-86	182	30.0	4658	743	NA	7.5	7.4	15.53	84	7.2
14-8-86	183	32.1	4309	677	NA	7.5	7.4	15.37	84	6.7
15-8-86	184	32.5	4309	677	NA	7.5	7.4	15.56	84	6.6
16-8-86	185	NA	NA	NA	NA	NA	NA	NA	NA	NA
17-8-86	186	31.7	4701	650	NA	7.5	7.4	16.56	86	6.8
18-8-86	187	31.1	4538	658	NA	7.5	7.4	15.68	86	6.9
19-8-86	188	NA	NA	NA	NA	NA	NA	NA	NA	NA
20-8-86	189	33.3	4609	675	NA	7.5	7.3	17.05	85	6.5
21-8-86	190	NA	NA	NA	NA	NA	NA	NA	NA	NA
22-8-86	191	NA	NA	NA	NA	NA	NA	NA	NA	NA
23-8-86	192	NA	NA	NA	NA	NA	NA	NA	NA	NA
24-8-86	193	33.0	4792	666	NA	7.5	7.4	17.57	86	6.5
25-8-86	194	33.0	4731	696	NA	7.5	7.3	17.35	85	6.5
26-8-86	195	33.0	4536	762	NA	7.6	7.4	16.63	83	6.5
27-8-86	196	33.0	4506	805	1081	7.7	7.3	16.52	82	6.5
28-8-86	197	32.4	4557	959	1253	7.5	7.3	16.41	79	6.7
29-8-86	198	NA	NA	NA	NA	NA	NA	NA	NA	NA
30-8-86	199	NA	NA	NA	NA	NA	NA	NA	NA	NA
31-8-86	200	32.5	4506	778	NA	7.6	7.2	16.27	83	6.6
1-9-86	201	32.5	4440	764	NA	7.4	7.2	16.03	83	6.6
2-9-86	202	NA	NA	NA	NA	NA	NA	NA	NA	NA
3-9-86	203	40.0	4450	750	NA	7.4	7.3	19.78	83	5.4
4-9-86	204	40.0	4521	762	NA	7.5	7.3	20.09	83	5.4
5-9-86	205	NA	NA	NA	NA	NA	NA	NA	NA	NA
6-9-86	206	NA	NA	NA	NA	NA	NA	NA	NA	NA
7-9-86	207	39.5	4674	829	NA	7.5	7.3	20.51	82	5.5
8-9-86	208	39.8	4599	840	NA	7.5	7.3	20.34	82	5.4
9-9-86	209	40.2	4645	826	NA	7.5	7.3	20.75	82	5.4
10-9-86	210	NA	NA	NA	NA	NA	NA	NA	NA	NA
11-9-86	211	35.0	3403	834	NA	7.5	7.3	13.23	75	6.2
12-9-86	212	NA	NA	NA	NA	NA	NA	NA	NA	NA
13-9-86	213	NA	NA	NA	NA	NA	NA	NA	NA	NA
14-9-86	214	38.8	4916	809	NA	7.5	NA	21.19	84	5.6
15-9-86	215	42.2	5274	985	NA	7.6	7.4	24.73	81	5.1
16-9-86	216	44.8	4834	948	NA	7.7	7.3	24.06	80	4.8
17-9-86	217	45.7	4885	1028	NA	7.6	7.3	24.80	79	4.7

SAPPI 35 degC REACTOR

Date	Day	Influent Flowrate (l/day)	Influent COD (mgCOD/l)	Filtered Effl. COD (mgCOD/l)	Unfiltered Effl. COD (mgCOD/l)	Influent pH	Effluent pH	Loading Rate (Kg/m3/d)	COD Removal (%)	Retention Time (hours)
17-3-86	1	9.0	506	187	NA	7.8	7.2	0.51	63	24.0
18-3-86	2	NA	NA	NA	NA	NA	NA	NA	NA	NA
19-3-86	3	NA	NA	NA	NA	NA	NA	NA	NA	NA
20-3-86	4	NA	NA	NA	NA	NA	NA	NA	NA	NA
21-3-86	5	NA	NA	NA	NA	NA	NA	NA	NA	NA
22-3-86	6	10.6	518	193	211	7.8	7.1	0.61	63	20.4
23-3-86	7	10.4	500	195	205	7.8	7.1	0.58	61	20.8
24-3-86	8	10.0	519	168	181	7.9	7.1	0.58	68	21.6
25-3-86	9	10.0	765	217	235	7.9	7.1	0.85	72	21.6
26-3-86	10	NA	NA	NA	NA	NA	NA	NA	NA	NA
27-3-86	11	NA	NA	NA	NA	NA	NA	NA	NA	NA
28-3-86	12	NA	NA	NA	NA	NA	NA	NA	NA	NA
29-3-86	13	NA	NA	NA	NA	NA	NA	NA	NA	NA
30-3-86	14	NA	NA	NA	NA	NA	NA	NA	NA	NA
31-3-86	15	9.8	1000	239	250	7.7	7.1	1.09	76	22.0
1-4-86	16	9.8	1139	230	236	7.8	7.1	1.24	80	22.0
2-4-86	17	9.8	1495	279	319	7.8	7.1	1.63	81	22.0
3-4-86	18	9.8	1521	369	456	7.7	7.1	1.66	76	22.0
4-4-86	19	9.8	1546	389	468	7.7	7.1	1.68	75	22.0
5-4-86	20	9.4	1649	379	450	7.7	7.1	1.72	77	23.0
6-4-86	21	9.4	1644	356	396	7.7	7.2	1.72	78	23.0
7-4-86	22	9.0	1618	358	439	7.7	7.3	1.62	78	24.0
8-4-86	23	9.0	1561	335	404	7.8	7.3	1.56	79	24.0
9-4-86	24	9.8	1642	312	435	7.7	7.3	1.79	81	22.0
10-4-86	25	9.0	1520	288	357	7.7	7.3	1.52	81	24.0
11-4-86	26	9.8	1663	303	379	7.7	7.3	1.81	82	22.0
12-4-86	27	9.8	1601	290	357	7.7	7.3	1.74	82	22.0
13-4-86	28	NA	NA	NA	NA	NA	NA	NA	NA	NA
14-4-86	29	9.8	2397	492	510	7.5	7.3	2.61	79	22.0
15-4-86	30	9.4	2485	451	520	7.4	7.3	2.60	82	23.0
16-4-86	31	9.6	2545	464	546	7.6	7.2	2.71	82	22.5
17-4-86	32	10.9	2697	528	614	7.6	7.1	3.27	80	19.8
19-4-86	33	NA	NA	NA	NA	NA	NA	NA	NA	NA
20-4-86	34	10.8	2470	503	NA	7.6	7.2	2.96	80	20.0
21-4-86	35	10.8	4404	816	962	7.5	7.0	5.28	81	20.0
22-4-86	36	9.6	4868	1079	1265	7.4	7.2	5.19	78	22.5
23-4-86	37	9.7	4518	872	1157	7.3	7.2	4.87	81	22.3
24-4-86	38	NA	NA	NA	NA	NA	NA	NA	NA	NA
25-4-86	39	10.0	4518	675	908	7.2	NA	5.02	85	21.6
26-4-86	40	NA	NA	NA	NA	NA	NA	NA	NA	NA
27-4-86	41	9.6	4528	649	769	NA	NA	4.83	86	22.5
28-4-86	42	NA	NA	NA	NA	NA	NA	NA	NA	NA
29-4-86	43	NA	NA	NA	NA	NA	NA	NA	NA	NA
30-4-86	44	11.0	4503	642	1045	NA	NA	5.50	86	19.6
1-5-86	45	11.8	4513	635	862	NA	NA	5.92	86	18.3
2-5-86	46	11.9	4441	605	903	7.4	7.2	5.87	86	18.2
3-5-86	47	NA	NA	NA	NA	NA	NA	NA	NA	NA
4-5-86	48	11.6	4605	707	894	7.4	7.2	5.94	85	18.6
5-5-86	49	11.8	4503	728	NA	7.4	7.2	5.90	84	18.3

6-5-86	50	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
7-5-86	51	11.9	4485	696	NA	7.5	7.2	5.93	84	18.2	NA
8-5-86	52	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
9-5-86	53	14.6	4454	713	883	7.5	7.2	7.23	84	14.8	14.8
10-5-86	54	14.6	4424	713	875	7.6	7.4	7.18	84	14.8	14.8
11-5-86	55	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
12-5-86	56	14.0	4659	1384	NA	7.5	7.3	7.25	70	15.4	15.4
13-5-86	57	14.9	4598	1313	NA	7.4	7.3	7.61	71	14.5	14.5
14-5-86	58	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
15-5-86	59	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
16-5-86	60	13.5	4550	1898	1965	7.5	7.1	6.83	58	16.0	16.0
17-5-86	61	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
18-5-86	62	15.9	4643	2047	NA	7.5	7.2	8.20	56	13.6	13.6
19-5-86	63	15.0	4529	1872	2022	7.2	7.2	7.55	59	14.4	14.4
20-5-86	64	15.1	4291	1737	1830	7.2	7.1	7.20	60	14.3	14.3
21-5-86	65	15.0	4322	1629	1768	7.3	7.0	7.20	62	14.4	14.4
22-5-86	66	15.0	4200	1685	1706	7.9	7.2	7.00	60	14.4	14.4
23-5-86	67	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
24-5-86	68	14.9	4609	1436	NA	7.5	NA	7.63	69	14.5	14.5
25-5-86	69	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
26-5-86	70	14.8	2724	511	515	7.6	7.2	4.48	81	14.6	14.6
27-5-86	71	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
28-5-86	72	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
29-5-86	73	14.8	2539	422	500	7.5	7.1	4.18	83	14.6	14.6
30-5-86	74	14.9	2519	417	461	7.3	7.1	4.17	83	14.5	14.5
31-5-86	75	14.2	2539	376	NA	7.4	NA	4.01	85	15.2	15.2
1-6-86	76	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2-6-86	77	14.0	2426	348	436	7.5	NA	3.77	86	15.4	15.4
3-6-86	78	17.0	2746	335	928	7.3	7.2	5.19	88	12.7	12.7
4-6-86	79	16.7	2796	391	1002	7.5	7.3	5.19	86	12.9	12.9
5-6-86	80	17.5	3046	463	1130	7.4	7.3	5.92	85	12.3	12.3
6-6-86	81	17.2	3126	463	922	7.4	7.3	5.97	85	12.6	12.6
7-6-86	82	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
8-6-86	83	17.2	3106	437	826	7.5	7.2	5.94	86	12.6	12.6
9-6-86	84	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
10-6-86	85	17.3	4538	581	1059	7.3	7.1	8.72	87	12.5	12.5
11-6-86	86	17.0	4489	652	738	7.4	7.1	8.48	85	12.7	12.7
12-6-86	87	17.3	4548	630	850	7.4	7.2	8.74	86	12.5	12.5
13-6-86	88	17.4	4436	646	756	7.4	7.1	8.58	85	12.4	12.4
14-6-86	89	17.9	4497	650	NA	7.4	7.3	8.94	86	12.1	12.1
15-6-86	90	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
16-6-86	91	17.8	4489	654	NA	7.4	7.1	8.88	85	12.1	12.1
17-6-86	92	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
18-6-86	93	17.2	4351	645	804	7.4	7.2	8.32	85	12.6	12.6
19-6-86	94	18.0	4413	620	825	7.4	7.3	8.83	85	12.0	12.0
20-6-86	95	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
21-6-86	96	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
22-6-86	97	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
23-6-86	98	17.1	4372	595	NA	NA	7.5	8.31	86	12.6	12.6
24-6-86	99	17.0	4297	610	821	7.5	7.5	8.12	86	12.7	12.7
25-6-86	100	17.1	4719	675	NA	7.2	7.3	8.97	86	12.6	12.6
26-6-86	101	17.4	4639	612	NA	7.3	7.3	8.97	87	12.4	12.4
27-6-86	102	20.0	4679	654	NA	7.3	7.4	10.40	86	10.8	10.8
28-6-86	103	20.8	4799	657	NA	7.3	7.4	11.09	86	10.4	10.4
29-6-86	104	20.7	4679	759	NA	7.3	7.3	10.76	84	10.4	10.4
30-6-86	105	20.0	4689	679	831	7.3	7.3	10.42	86	10.8	10.8

1-7-86	106	20.5	4544	726	790	7.3	7.2	10.35	84	10.5
2-7-86	107	20.3	4688	736	NA	7.3	NA	10.57	84	10.6
3-7-86	108	20.2	4585	646	NA	NA	7.3	10.29	86	10.7
4-7-86	109	NA	NA	NA	NA	NA	NA	NA	NA	NA
5-7-86	110	NA	NA	NA	NA	NA	NA	NA	NA	NA
6-7-86	111	20.3	4595	642	NA	7.4	7.4	10.36	86	10.6
7-7-86	112	20.2	4575	621	NA	7.4	7.4	10.27	86	10.7
8-7-86	113	20.2	4444	619	NA	7.4	7.4	9.97	86	10.7
9-7-86	114	NA	NA	NA	NA	NA	NA	NA	NA	NA
10-7-86	115	20.2	4477	662	NA	7.4	7.3	10.05	85	10.7
11-7-86	116	NA	NA	NA	NA	NA	NA	NA	NA	NA
12-7-86	117	NA	NA	NA	NA	NA	NA	NA	NA	NA
13-7-86	118	NA	NA	NA	NA	NA	NA	NA	NA	NA
14-7-86	119	20.0	4507	680	728	7.2	7.4	10.02	85	10.8
15-7-86	120	21.0	4668	668	NA	7.4	7.5	10.89	86	10.3
16-7-86	121	20.7	4668	681	NA	7.3	NA	10.74	85	10.4
17-7-86	122	26.0	4494	775	NA	NA	7.6	12.98	83	8.3
18-7-86	123	26.5	4555	698	NA	7.5	NA	13.41	85	8.2
19-7-86	124	NA	NA	NA	NA	NA	NA	NA	NA	NA
20-7-86	125	26.0	4391	718	NA	NA	7.5	12.69	84	8.3
21-7-86	126	NA	NA	NA	NA	NA	NA	NA	NA	NA
22-7-86	127	NA	NA	NA	NA	NA	NA	NA	NA	NA
23-7-86	128	26.1	3735	624	NA	7.0	7.2	10.83	83	8.3
24-7-86	129	26.1	3899	587	NA	7.1	7.1	11.31	85	8.3
25-7-86	130	NA	NA	NA	NA	NA	NA	NA	NA	NA
26-7-86	131	26.2	3866	620	NA	NA	7.2	11.25	84	8.2
27-7-86	132	25.6	4304	596	NA	7.1	7.1	12.24	86	8.4
28-7-86	133	25.5	4366	783	NA	7.2	7.2	12.37	82	8.5
29-7-86	134	25.7	4213	634	945	7.1	7.2	12.03	85	8.4
30-7-86	135	NA	NA	NA	NA	NA	NA	NA	NA	NA
31-7-86	136	NA	NA	NA	NA	NA	NA	NA	NA	NA
1-8-86	137	NA	NA	NA	NA	NA	NA	NA	NA	NA
2-8-86	138	NA	NA	NA	NA	NA	NA	NA	NA	NA
3-8-86	139	NA	NA	NA	NA	NA	NA	NA	NA	NA
4-8-86	140	NA	NA	NA	NA	NA	NA	NA	NA	NA
5-8-86	141	25.2	4404	NA	NA	7.4	7.4	12.33	NA	8.6
6-8-86	142	26.0	4274	1000	1312	7.4	7.2	12.35	77	8.3
7-8-86	143	26.7	4202	NA	NA	7.2	7.2	12.47	NA	8.1
8-8-86	144	25.8	4692	1363	NA	7.4	7.3	13.45	71	8.4
9-8-86	145	NA	NA	NA	NA	NA	NA	NA	NA	NA
10-8-86	146	26.0	4576	1420	NA	7.4	7.3	13.22	69	8.3
11-8-86	147	25.6	4874	1030	NA	7.4	7.3	13.86	79	8.4
12-8-86	148	NA	NA	NA	NA	NA	NA	NA	NA	NA
13-8-86	149	27.7	4668	1496	NA	7.5	7.3	14.37	68	7.8
14-8-86	150	29.8	4432	1547	NA	7.5	7.4	14.67	65	7.2
15-8-86	151	30.0	4701	1081	NA	7.5	7.4	15.67	77	7.2
16-8-86	152	NA	NA	NA	NA	NA	NA	NA	NA	NA
17-8-86	153	29.7	4589	775	NA	7.5	7.5	15.14	83	7.3
18-8-86	154	29.0	4630	793	NA	7.4	7.4	14.92	83	7.4
19-8-86	155	NA	NA	NA	NA	NA	NA	NA	NA	NA
20-8-86	156	31.8	4650	781	NA	7.5	7.5	16.43	83	6.8
21-8-86	157	NA	NA	NA	NA	NA	NA	NA	NA	NA
22-8-86	158	NA	NA	NA	NA	NA	NA	NA	NA	NA
23-8-86	159	31.3	4895	750	NA	7.4	7.5	17.02	85	6.9
24-8-86	160	33.0	4608	770	NA	7.5	7.4	16.90	83	6.5
25-8-86	161	33.6	4536	979	1040	7.7	7.3	16.93	78	6.4

26-8-86	162	43.0	4506	872	1057	7.7	7.4	21.53	81	5.0
27-8-86	163	33.8	4557	1090	1090	7.5	7.4	17.11	76	6.4
29-8-86	164	NA	NA	NA	NA	NA	NA	NA	NA	NA
30-8-86	165	NA	NA	NA	NA	NA	NA	NA	NA	NA
31-8-86	166	34.0	4506	872	NA	7.6	7.4	17.02	81	6.4
1-9-86	167	33.6	4440	858	NA	7.4	7.3	16.58	81	6.4
2-9-86	168	NA	NA	NA	NA	NA	NA	NA	NA	NA
3-9-86	169	41.8	4450	778	NA	7.4	7.5	20.67	83	5.2
4-9-86	170	41.3	4521	756	NA	7.5	7.5	20.75	83	5.2
5-9-86	171	NA	NA	NA	NA	NA	NA	NA	NA	NA
6-9-86	172	NA	NA	NA	NA	NA	NA	NA	NA	NA
7-9-86	173	41.0	4674	740	NA	7.5	7.3	21.29	84	5.3
8-9-86	174	41.5	4599	769	NA	7.5	7.4	21.21	83	5.2
9-9-86	175	42.0	4645	747	NA	7.5	7.4	21.68	84	5.1
10-9-86	176	NA	NA	NA	NA	NA	NA	NA	NA	NA
11-9-86	177	38.4	3403	839	NA	7.5	7.3	14.52	75	5.6
12-9-86	178	NA	NA	NA	NA	NA	NA	NA	NA	NA
13-9-86	179	NA	NA	NA	NA	NA	NA	NA	NA	NA
14-9-86	180	41.0	4916	932	NA	7.5	NA	22.40	81	5.3
15-9-86	181	42.0	5274	908	NA	7.6	7.4	24.61	83	5.1
16-9-86	182	44.0	4834	920	NA	7.7	7.3	23.63	81	4.9
17-9-86	183	44.5	4885	963	NA	7.6	7.3	24.15	80	4.9
18-9-86	184	NA	NA	NA	NA	NA	NA	NA	NA	NA
19-9-86	185	NA	NA	NA	NA	NA	NA	NA	NA	NA
20-9-86	186	NA	NA	NA	NA	NA	NA	NA	NA	NA
21-9-86	187	44.2	4614	912	NA	7.5	7.4	22.66	80	4.9
22-9-86	188	NA	NA	NA	NA	NA	NA	NA	NA	NA
23-9-86	189	49.8	4471	758	NA	7.5	7.1	24.74	83	4.3
24-9-86	190	49.8	4589	779	NA	7.1	7.1	25.39	83	4.3
25-9-86	191	NA	NA	NA	NA	NA	NA	NA	NA	NA
26-9-86	192	NA	NA	NA	NA	NA	NA	NA	NA	NA
27-9-86	193	NA	NA	NA	NA	NA	NA	NA	NA	NA
28-9-86	194	NA	NA	NA	NA	NA	NA	NA	NA	NA
29-9-86	195	50.0	4653	848	NA	7.2	7.2	25.85	82	4.3
30-9-86	196	50.0	4570	984	NA	7.2	7.2	25.39	78	4.3
1-10-86	197	NA	NA	NA	NA	NA	NA	NA	NA	NA
2-10-86	198	NA	NA	NA	NA	NA	NA	NA	NA	NA
3-10-86	199	NA	NA	NA	NA	NA	NA	NA	NA	NA
4-10-86	200	50.0	4591	1042	NA	7.2	7.0	25.51	77	4.3

APPENDIX C

**35°C UASB LABORATORY REACTOR
PROFILING RESULTS**

Reactor profiling experimental results - Test 1

Sample Port	COD (mgCOD/l)	Organic-N (mgN/l)	NH3-N (mgN/l)	Sulphate (mgSO4=l)	VFA-HAc (mg/l)	VFA-HPr (mg/l)	pH
0	4488	0.0	47.0	168	1125	425	7.60
1	3474	19.9	29.4	104	1050	425	7.22
2	2606	21.0	29.1	0	525	425	7.25
3	1985	23.5	29.4	0	80	135	7.43
4	1365	17.9	31.9	0	13	40	7.52
5	1013	16.2	34.2	0	16	25	7.56
6	962	10.1	35.0	0	13	10	7.57
7	962	9.2	35.0	0	13	10	7.54
8	920	12.0	35.6	0	13	10	7.57
9	939	6.7	35.6	0	5	7	7.55
10	972	14.0	34.4	0	5	7	7.59
11	972	10.4	35.0	0	8	7	7.55
12	980	12.9	32.5	0	5	0	7.58
13	939	14.3	33.0	0	5	0	8.03

Reactor profiling experimental results - Test 2

Sample Port	COD (mgCOD/l)	Organic-N (mgN/l)	NH3-N (mgN/l)	Sulphate (mgSO4=l)	VFA-HAc (mg/l)	VFA-HPr (mg/l)	pH
0	4544	0.0	40.6	250	1100	575	7.40
1	2981	11.8	30.2	74	575	350	7.18
2	1953	20.1	31.4	0	325	275	7.38
3	1213	23.8	31.9	0	50	100	7.51
4	900	11.7	31.4	0	6	0	7.55
5	812	13.4	32.2	0	12	0	7.59
6	833	17.7	31.6	0	9	0	7.58
7	853	17.1	33.3	0	9	0	7.59
8	915	18.7	32.8	0	6	0	7.58
9	859	17.4	33.0	0	6	0	7.57
10	810	14.2	32.8	0	6	0	7.56
11	827	15.1	32.5	0	3	0	7.55
12	761	8.7	33.0	0	3	0	7.55
13	802	9.8	33.6	0	0	0	8.10

Reactor profiling experimental results - COD of influent 2600 mg/ℓ

Sample Port	COD (mgCOD/l)	Organic-N (mgN/l)	NH3-N (mgN/l)	Sulphate (mgSO4=l)	VFA-HAc (mg/l)	VFA-HPr (mg/l)	pH
0	2632	12.3	42.3	311	478	344	7.15
1	2220	24.1	28.8	124	689	344	7.07
2	1850	17.9	30.5	0	278	244	7.14
3	1357	18.8	29.4	0	85	207	7.29
4	1110	21.0	29.4	0	22	167	7.32
5	884	19.8	31.4	0	16	93	7.37
6	678	8.4	33.3	0	16	38	7.37
7	678	11.5	33.0	0	16	38	7.37
8	707	13.7	32.8	0	16	38	7.37
9	683	13.7	32.5	0	16	38	7.36
10	683	12.6	33.3	0	16	38	7.36
11	674	6.2	33.3	0	16	38	7.36
12	625	8.6	31.4	0	16	38	7.37
13	584	6.2	30.8	0	16	38	7.87

Reactor profiling experimental results - recycle ratio 1 : 1, alkalinity addition 6g NaHCO₃/ℓ

Sample Port	COD (mgCOD/l)	Organic-N (mgN/l)	NH3-N (mgN/l)	Sulphate (mgSO4=l)	VFA-HAc (mg/l)	VFA-HPr (mg/l)	pH
-1	2795	3.3	34.2	300	438	320	7.10
0	1836	1.4	31.1	150	228	175	7.32
1	1285	6.7	25.5	0	168	130	7.28
2	1040	7.8	25.2	0	129	80	7.30
3	918	4.5	25.2	0	68	45	7.32
4	836	4.2	25.5	0	32	26	7.34
5	673	5.1	24.6	0	12	10	7.34
6	555	3.9	25.8	0	8	10	7.34
7	588	4.2	25.8	0	6	4	7.36
8	612	3.9	25.9	0	6	4	7.35
9	596	6.1	24.4	0	6	2	7.34
10	588	2.5	26.6	0	4	2	7.34
11	579	3.9	24.1	0	4	2	7.35
12	637	4.5	25.5	0	4	2	7.37
13	571	4.2	25.5	0	4	2	8.08

Reactor profiling experimental results - recycle ratio 1 : 1,
alkalinity addition 3g NaHCO₃/ℓ

Sample Port	COD (mgCOD/l)	Organic-N (mgN/l)	NH ₃ -N (mgN/l)	Sulphate (mgSO ₄ =/l)	VFA-HAc (mg/l)	VFA-HPr (mg/l)	pH
-1	2667	0.9	40.3	195	418	355	7.09
0	1521	3.9	30.0	95	210	195	7.02
1	862	6.8	26.0	0	148	150	6.98
2	781	6.2	23.2	0	118	95	6.98
3	639	5.1	23.2	0	72	55	7.00
4	577	5.1	23.2	0	40	32	7.02
5	537	2.5	23.0	0	28	18	7.04
6	527	3.3	22.7	0	16	18	7.04
7	519	5.0	21.3	0	10	10	7.04
8	519	3.3	22.7	0	4	8	7.04
9	527	3.7	21.8	0	4	8	7.04
10	479	3.4	22.4	0	2	6	7.04
11	515	4.8	21.8	0	0	0	7.04
12	511	4.4	21.6	0	0	0	7.04
13	495	4.2	21.6	0	0	0	7.58