THE BIODEGRADATION OF CYANIDES IN WASTE WATER TREATMENT

Comparison between using a Fluidised Bed Reactor and a conventional Continuously Stirred Tank Reactor.

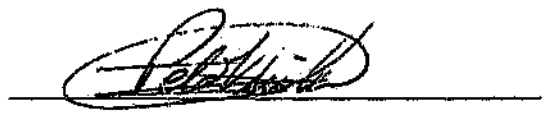
Peter Richard Ainley

A dissertation submitted to the Faculty of Engineering, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science in Engineering.

Johannesburg, 1998

Declaration

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.



(Signature of Candidate)

30 day of April 1998

Acknowledgment

I would like to thank firstly my supervisors, Dr A Grobicki for her theoretical background and Dr A Bryson for his help in the final analysis and the compilation of this dissertation; Dr A Pinches for his support and Mintek for the financial assistance during the past two years.

The members of staff in the Department of Chemical Engineering at the University of the Witwatersrand for their informative conversations that we have had, Sonja Reid for all her support and encouragement and the other post graduate students, especially Michael Ginter* for his guidance and suggestions.

The workshop staff, Mr. Peter Crockroft, Mr Theo Prassinos and Gift Mofeli for the construction of the experimental apparatus.

Last, but by no means least, my parents for their support and encouragement when I had had enough. Also my father, Michael, and Frank, my brother, for their help on the electronics side of things.

* Austrian

To my parents

Freya and Michael

Ainley

Abstract

A comparison is made between using a Fluidised Bed Reactor (FBR) and a conventional Continuously Stirred Tank Reactor (CSTR) for the removal of cyanides from waste water.

The two reactors were operated simultaneously under the same conditions to determine which of the two reactors would be the more efficient in cyanide degradation.

Initially, many problems were experienced with experimentation but thereafter operation of the equipment went more smoothly.

The results obtained indicate that the CSTR would still be the more efficient reactor, removing cyanides to almost 0 within a 10 hour retention period.

The maximum limit of 0.5 mg/ℓ, as stipulated by the government gazette, is then easily achieved. The FBR's removal rate did not achieve this limit within a 10 hour retention period and in 12 hours achieved only 81 % cyanide removal.

The major point that came to light during the final analysis phase of the project was whether the cyanides were biodegraded or removed by absorption and oxidative reactions in the presence of a catalyst, namely activated carbon, or more specifically dead microorganisms.

No clear conclusion could be drawn in this regard.

On the whole, more investigations need to be carried out on the FBR to determine the conditions under which it could perform better than the CSTR.

Contents

List of Figures

Abbreviations and Symbols

CN^-	-	Cyanide or cyanide ion
SCN^-	-	Thiocyanate or thiocyanate ion
ISCOR	-	Iron and Steel Corporation of South Africa

Definition of Terms

Retention time : The time spent by a substance in the reactor, based on the feed flow rate and the volume of the vessel;

Dilution rate : The hold up of substrate in the system before being removed in the effluent stream as a function of time.

Death rate . The term used in terms of substrate utilisation, for the combination of;

the rate of cell or microorganism deaths, and
the cell's endogenous metabolic rate.

Absorption/Oxidation : The combination of absorption and oxidative reactions occurring in a reactor.

Nomenclature

Variable		Definition	Value	Units
Alphabetic Characters				
c	-	Concentration factor		
D	-	Dilution rate of biomass		/hr
F	-	Flow rate		ℓ/hr
G	-	Sludge Age		/hr
g	-	Acceleration due to Gravity (set for Johannesburg)	9.81	m/s^2
h	-	Height		m
k_1	-	Absorption coefficient		/hr
k_o	-	Combine metabolism and death rate		/hr
K_s	-	Specific substrate constant (defined for specific substrates)		mg/ℓ
r	-	General rate expression		mg/ℓ.hr
r_s	-	Substrate utilisation rate		mg/ℓ.hr
r_x	-	Biomass reaction rate		mg/mg.ℓ.hr
S	-	Substrate concentration		mg/ℓ
t	-	Time		hr
V	-	Volume		ℓ
X	-	Quantity of biomass		mg
x	-	Biomass concentration		mg/ℓ
$Y_{x/s}$	-	Biomass/Substrate yield factor		mg bio./mg subst.

Greek Characters

α	-	Proportion constant	
Δ	-	Change	
ρ	-	Density of a liquid	kg/m^3
μ	-	Specific growth rate of biomass	/hr
μ_d	-	Death rate of biomass /hr	
μ_{max}	-	Maximum specific growth rate of biomass	/hr

Subscripts

0	-	Initial
1	-	Final
∞	-	Infinity
CSTR	-	Continuously Stirred Tank Reactor
FBR	-	Fluidised Bed Reactor
Recycle		Recycle
R	-	Reactor
s	-	Substrate
w	-	Waste
x	-	Biomass
v	-	Volume (Volumetric)

1 Prologue

One of the essential requirements for Man and a healthy community is the supply of clean water. He uses rivers and streams as a source of potable water and valuable food supplements supporting aquatic life and the irrigation of agricultural lands, not to mention his quest for some of life's comforts.

Yet despite its importance, rivers and streams throughout the world are generally badly treated and frequently used to carry off waste products produced by communities and industry. The pollution of our water resources by industrial effluent is a serious and ever increasing problem. Examples are the accidental spillage of chemical waste into the Rhine river in Germany and locally, the spillage from a paper mill into the Crocodile River. Run-off from rural communities has exposed Man to the contraction of water related diseases, such as cholera and typhoid, which can be fatal.

With the expansion of industry, chemical effluents such as those containing cyanide require expensive treatment before any of the effluent water may be returned to river systems. All over the world, legislation with regards to the discharge of industrial waste water, is being sharpened. Many industries are having to re-evaluate their waste water treatment processes or are being forced to change their attitudes towards waste discharge into natural waterways.

Unfortunately the problem of treating waste waters is a complex one, in particular the treatment of cyanide bearing waste waters. Not only is the capital cost of the treatment plant a problem, but also the ever increasing cost and availability of fresh water and additives. As a result of constant changes in manufacturing techniques, the discharge criteria are constantly being reviewed by the authorities.

2 Introduction and Literature Survey

2.1 Introduction

Cyanide occurs in numerous waste water streams, for example in the iron and steel industry and the mining industry (eg. the roasted almond smell around mine dumps on the Reef as a result of cyanide from the gold leaching process).
The mining industry has been using cyanide in gold leaching processes since the late nineteenth century after it was first introduced by Alfred James of the Cassel Gold Extraction Company in 1890 (Pohlandt-Watson 1990). This introduction increased the yield of gold extracted from ores, to above 90% from some 30% using a process of mercury amalgamation. Various chemical processes are available to treat these waste waters but are rather expensive.

With biotechnology now slowly taking its rightful place as a suitable, viable and more environmentally friendly process, the biodegradation of cyanides has enjoyed a fair amount of attention. Research into the biological treatment of cyanides was first recognised in the 1950's by Pettit and Mills {Alabama University (1983)}. Microbial destruction of cyanide is a developing technology capable of oxidising low concentrations of simple cyanides into CO_2 and NH_3 {Broadhurst (1990)}. The inability of most conventional bio-systems to treat cyanide concentrations of > 10 ppm or to even attempt to destroy complexed cyanides, have been major obstacles to the implementation of such systems {Broadhurst (1990)}.

It has been postulated that the biological approach to the treatment of effluent, and in particular waste waters containing cyanide, will be cheaper, hold more advantages and will become very much more popular due to the increasing amounts of industrial sewage in need of treatment {Howe (1965); Alabama University (1983); Shivaraman et al (1985); Whitlock & Mudder (1985); Broadhurst (1990); etc)}

2.2 Background Research Review

2.2.1 Sources of Cyanide Waste Waters

In the gold mining industry leaching is universally practised. The effluent from such plants is pumped into slimes dams and while some of the cyanide in solution may be oxidised by air, pollution of the surrounding ground water by seepage and run-off is inevitable.

The iron and steel industry in South Africa has relatively high levels of cyanide, thiocyanate and phenols in their effluent streams, coming from the coke quenching processes {ISCOR (1991)}.

2.2.2 Existing Chemical Processes for Cyanide Removal

Up until fairly recently (1965), it was thought that the biological route to waste water treatment was impractical or impossible, simply because it was believed that cyanide would inhibit certain enzymatic activity in a biological system (Howe 1965), if not kill the microorganisms completely.

The processes used and still being used, are all based on chemical reactions with cyanide to form less harmful and more stable compounds. These processes include {Broadhurst (1990); Alabama University (1983)}:

a) **Alkaline Chlorination**

This process uses chlorine or hypochlorite to oxidise cyanide to cyanates and ultimately to give NaCl, CO_2 and N_2.

This process is used fairly extensively on a commercial scale because of proven technolc id available expertise. Reagent costs are high, and toxic and corrosive chemicals are used, creating handling problems.

b) **Hydrogen Peroxide Oxidation**

Cyanide is oxidised to cyanates by the controlled addition of H_2O_2 solution

$$CN^- + H_2O_2 \xrightarrow{Cu^{2+}} CNO + H_2O \qquad (2.1)$$

The popularity of this process is its reliability and ease of operation. No toxic intermediates are formed. Excess H_2O_2 rapidly decomposes.

The disadvantage is high reagent consumption resulting in higher costs and in addition a Cu^{2+} catalyst (10 - 30 ppm) is required.

c) **The INCO Process - SO_2/Air Oxidation**

Air and SO_2 are used to oxidise the cyanide to cyanates in the presence of a Cu^{2+} catalyst

$$N^- + O_2 + SO_2 + H_2O \xrightarrow{Cu^{2+}} CNO^- + H_2S \qquad (2.2)$$

The acid is neutralised by lime.

All cyano-complexes are destroyed, except iron. The process is simplistic and easy to operate and no toxic intermediates are formed.

The process requires 30 ppm of Cu^{2+} catalyst for rapid and effective cyanide oxidation and a pH value of 10 is maintained with lime.

2.2.3 Previous Research into Biological Cyanide Removal

The Homestake Mining Company {Mudder & Whitlock (1984); Whitlock & Mudder (1985)}, in the United States, have been working on a process since 1977, that oxidises not only free and complexed cyanides but also thiocyanate and the oxidation by-product, ammonia. The company tested a variety of reactors and found the Rotating Biological Contactors (RBC's) performed the best, (an attached growth process). The flow diagram is shown in figure 2.1.

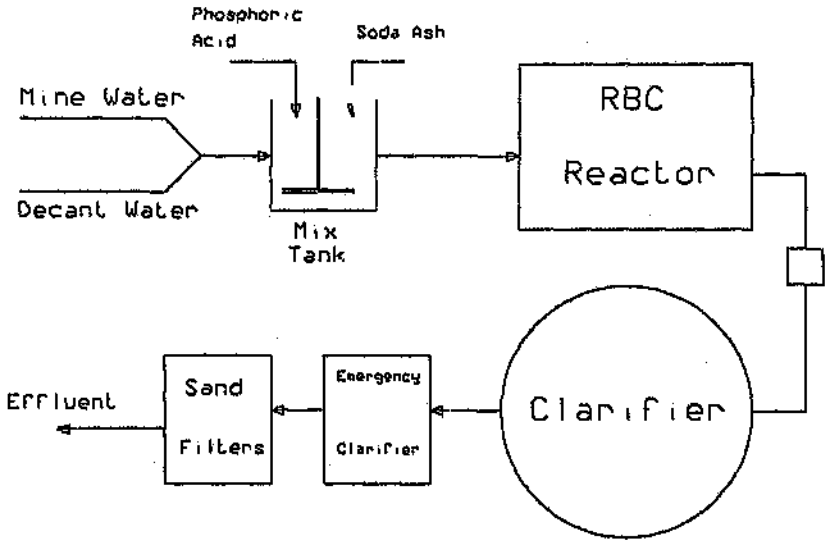


Figure 2.1 - Schematic of the Homestake Biological Treatment Plant

The average levels of cyanides being treated were :

Cyanide	=	15 mg/l
Thiocyanate	=	65 mg/l

The reactor consisted of a number of rotating contactors of different biomass densities. The contactors with low biomass density were used for the cyanide and thiocyanate removal and the high biomass density contactors for nitrification.

The reactors required only two chemical supplements :

1) an inorganic carbon source to aid nitrification (soda ash) and
2) phosphorous as trace nutrient (H_3PO_4).

Supplemental air was added to the reactor to provide enough dissolved oxygen (>= 0.4 mg/l) and to ensure biomass stripping.
The total hydraulic residence time was 5 hours at 21 000 m^3/day. The rate controlling oxidation step in the overall design was nitrification.
The total surface area of the contactors available for degradation was :

Cyanide degradation = 9 290 m^2
Nitrification = 13 935 m^2

Shivaraman et al (1985) used a completely mixed aeration system (CMAS), described in figure 2.2, to study the influence of phenols and cyanide on the biodegradation of thiocyanate. The levels of cyanides treated were :

Cyanide	=	45 mg/l
Thiocyanate	=	115 mg/l

This system follows the CSTR principle with subsequent settling of sludge.

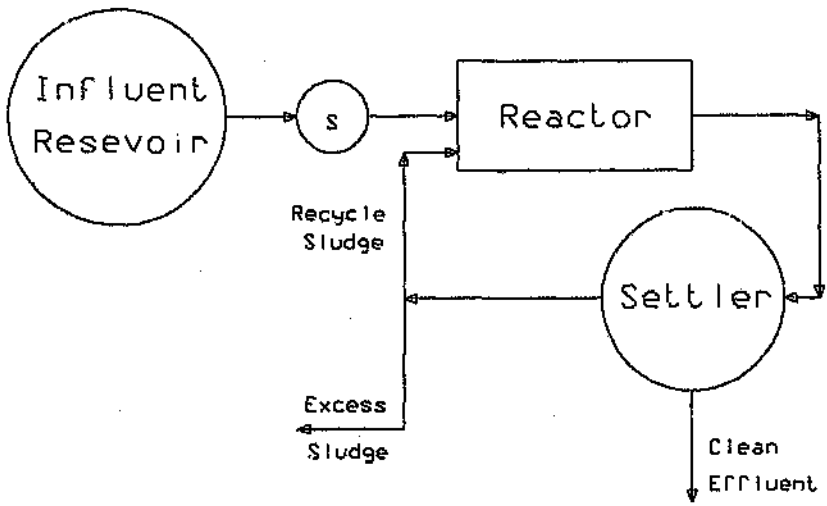


Figure 2.2 - Schematic of Bench Model CMAS

The bio-reactor is fed continuously from a reservoir. The liquid from the reactor was led into the bio-settler for settling of biomass. Part of the settled sludge was recycled back to the reactor and the remainder purged.
Recycling was on a semi-continuous basis. Retention times of the 2 units was 10±2 hours for the reactor and ≈2.3 hours for the settler.

A Hydrolytic Assist, figure 2.3, was used in conjunction with the extended aeration process by Gaudy et al, (1982) to study its effect on the degradation of cyanide (concentration = 10 - 20 mg/l).

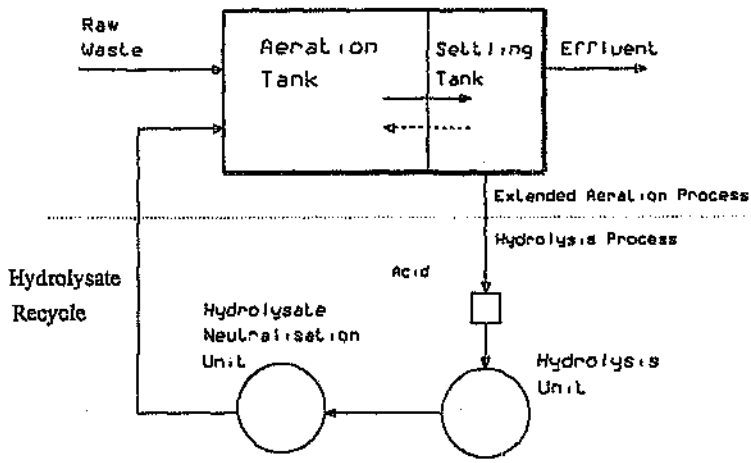


Figure 2.3 - Schematic of Extended Aeration Process including the "Hydrolytic Assist"

A known volume of sludge was withdrawn from the clarifier on a weekly basis and hydrolysed, acidified to pH 1, autoclaved and then neutralised to pH 7. The sludge was then recycled back to the reactor in smaller volumes each day.

The results of using the Hydrolytic Assist included, the advantage of decreasing the inhibitory effect of cyanide, and effectively removing organic matter as well as cyanide.

The idea of simultaneously using aerobic and anaerobic reactors for the treatment of cyanide laden waste waters was studied by Richards & Shieh (1989). They used a completely mixed, continuous-flow activated sludge reactor (oxic chamber) with an internal cell recycle (settling chamber) and a separated anoxic chamber. This may be seen in figure 2.4.

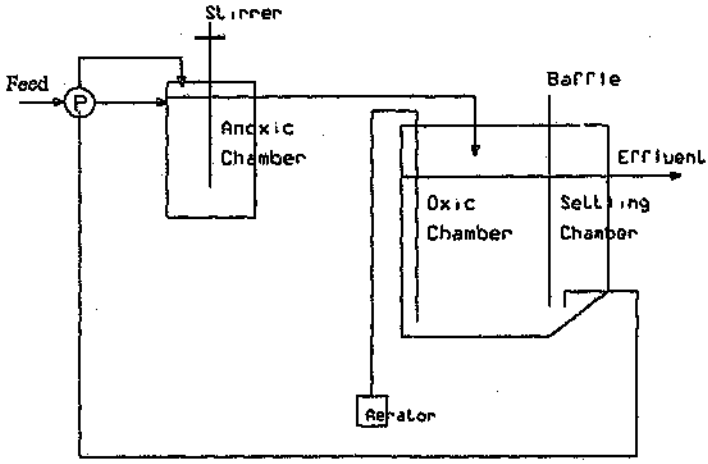


Figure 2.4 - Schematic of the Anoxic/Oxic Activated Sludge System

Cyanide levels were :

Cyanide	=	60 mg/l
Thiocyanate	=	100 mg/l

Cyanide degradation occurred in the oxic chamber where the dissolved oxygen concentration was maintained at 2.5 mg/l.

The anoxic chamber was then used for the subsequent nitrification of the effluent. This anoxic-oxic set up did not appear to impede the cyanide and phenol degradation in any way.

Alabama University (1983) used a simple CSTR and clarifier. The CSTR consisted of an aeration chamber with an overflow, which led to the clarifier. Any gases evolved were directed through NaOH solution to trap any volatilised cyanide. Settled sludge was recycled back to the aeration chamber and the treated effluent collected.

The cyanide levels treated in this reactor system were :

Cyanide	=	10 - 100 mg/l
Thiocyanate	=	100 -1500 mg/l

The efficiency obtained for cyanide degradation by this activated sludge process was 99 %.

The schematic flow diagram is much the same as the one by Shivaraman et al (1985), ie. the CMAS unit.

Ludzack (1960) used an adapted design from Dow Chemical Company, which consisted of the aeration chamber and a settler compartment inside the chamber. The settler was designed such that it formed a semi-circular section in the aeration chamber. The bottom end was cut to allow settled sludge to return to the aeration chamber.

2.2.4 The Possible Effect of Activated Carbon on Cyanide Removal

Results which will be presented later in this work suggest the possibility that another form of cyanide removal is taking place. The idea that cyanide may be removed from the system via a non-biological process, ie. absorption and oxidation in the presence of a catalyst should also be considered.

Cyanide may be removed form aqueous solution by two general types of reactions, namely hydrolysis reactions and oxidative reactions.

2.2.4.1 The Hydrolysis Reactions

The first is the hydrolytic reaction, occurring at low pH's, viz.:

$$CN^- + H_2O \rightarrow HCN + OH^- \qquad (2.3)$$

Some of the HCN formed will become volatilised and is removed through the escaping gas stream.

On the other hand, at high pH's and particularly at high temperatures, the reaction :

$$CN^- + 2H_2O \rightarrow NH_3 + HCO_2^- \qquad (2.4)$$

occurs, but is reported to take place very slowly at ambient temperatures {Adams (1990)}.

2.2.4.2 The Oxidative Reactions

Cyanide is easily oxidised to form cyanates or cyanogens in an aqueous solution as in this investigation. At high pH solutions the reactions are :

$$2CN^- \rightleftharpoons (CN)_2\ (g) + 2e^- \qquad (2.5)$$

(Cyanogens)

and

$$2OH^- + CN^- \rightleftharpoons CNO^- + H_2O + 2e^- \qquad (2.6)$$

(Cyanates)

The cyanates are further oxidised in the presence of the activated carbon catalyst to produce ammonium carbonate and small quantities of urea, according to the following reactions:

$$CNO^- + 2H_2O + H^+ \rightleftharpoons NH_4^+ + HCO_3^- \qquad (2.7)$$

and

$$CNO^- + NH_4^+ \rightleftharpoons CO(NH_2)_2 \qquad (2.8)$$

2.2.4.3 The Potential versus pH Diagram

When studying a diagram of the potential versus pH of the CN^--H_2O system at 25°C (figure 2.5){copied from Adams (1990)}, it is clear that the oxidation of cyanide to cyanates is thermodynamically favoured at ambient temperatures but is exceedingly slow in the absence of a catalyst. From work done by Adams (1990); {Broadhurst (1990)}, activated carbon is a suitable catalyst as well as being very good at absorbing cyanide.

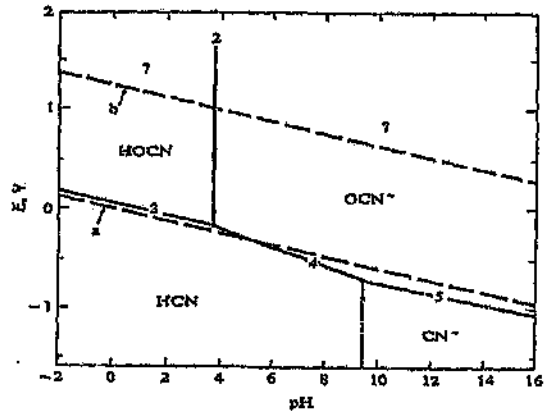


Figure 2.5 -

Homogeneous Equilibrium Diagram of Potential verses pH for the CN^--H_2O System (Adams (1990))

a	$2H_2O + 2e^- \rightleftharpoons 2OH^- + H_2$	$E = -0.0591\ pH - 0.0295 \log(p_{H2})$
b	$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	$E = +1.228 - 0.0591\ pH + 0.0147 \log(p_{O2})$
1	$HCN_{(aq)} \rightleftharpoons CN^- + ^+$	$\log \frac{[CN^-]}{[HCN]} = -9.39 + pH$
2	$HOCN_{(aq)} \rightleftharpoons OCN^- + H^+$	$\log \frac{[OCN^-]}{[HOCN]} = -3.89 + pH$
3	$HOCN_{(aq)} + H^+ + 2e^- \rightleftharpoons HCN_{(aq)} + H_2O$	$E = 0.021 - 0.0591\ pH + 0.0295 \log \frac{[HOCN]}{[HCN]}$

4 $OCN^- + 3H^+ + 2e^- \rightleftharpoons HCN_{(aq)} + H_2O$

$$E = 0.136 - 0.0883\ pH + 0.0295 \log \frac{[OCN^-]}{[HCN]}$$

5 $OCN^- + 2H^+ + 2e^- \rightleftharpoons CN^- + H_2O$

$$E = 0.141 - 0.0591\ pH + 0.0295 \log \frac{[OCN^-]}{[CN^-]}$$

? Reactions not identified by Bard {Adams (1990)}.

Microorganisms consist mainly of carbon based molecules and as a result when the organisms die, the carbon in the organisms may have similar characteristics to that of activated carbon and could therefore be capable of absorbing cyanide {Raef et al (1977)}. It has been reported that activated carbon has the ability to absorb cyanide {Adams (1990)}.

The kinetics of the loss of cyanide in an aerated system can be adequately described by a first order rate law for all reactions that occur {Adams (1990)}.

Muir et al (1988) found that cyanide is oxidised by air in the presence of activated carbon, with losses between 65 and 95% over 24 hours. The oxidation process products are cyanates which are stable in alkaline solutions. In acidic solution hydrolysis occurs and ammonia and bicarbonate result.
As mentioned, at higher temperatures the hydrolysis reaction is favoured since the solubility of oxygen in water becomes very small.

Muir et al (1988) also found that the activated carbon should be in suspension to be most effective in cyanide destruction in aerated systems.
It is difficult to assess whether oxidation or hydrolysis of cyanide are the main destruction processes taking place and to what extent thi. occurs. There also exists

the possibility of HCN or CN^- absorption onto carbon.

Muir et al (1998) concluded that the main cause of cyanide loss is cyanide oxidation. Adams (1990) also concludes this fact but adds that absorption of cyanide also takes place but is not the primary cyanide removal mechanism.

2.2.4.4 Summary of Cyanide Losses in Aqueous Solution with Activated Carbon

Adams (1990) shows a table (table 2.2) which summaries all the reactions that take place in an aqueous solution in the presence of activated carbon. The results are based on batch experiments.

Table 2.1 - Mechanism of Cyanide Removal in Aqueous Solutions

	Reaction	% Contribution
CN^- in solution	-	26.74%†
CNO^- formed in solution	2.17	29.85%†
HCN evolved	2.14	5.60%†
CNO^- lost	2.18	9.95%†
CN^- absorbed	2.21	24.38%†
CN^- unaccounted for	-	3.48%†*

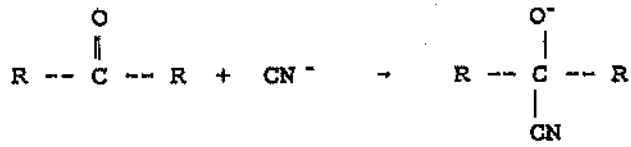
† Table values were calculated from table in Adams (1990).

* Calculated by difference. Not found in table of Adams (1990).

The reaction that causes the highest loss of cyanide is the carbon catalysed oxidation reaction described in detail in Adams (1990) and summaries as follows:

$$CN^- + {}^1/_2\, O_2 \rightarrow CNO^- \qquad (2.9)$$

The absorption reaction is displayed as follows:



(2.10)

2.3 Activated Sludge Systems in Biodegradation

2.3.1 The Activated Sludge Process

The activates sludge process is a continuous process in which aerobic biomass is mixed with the incoming waste water and aerated and then allowed to settle out by gravity usually in a separate settling tank. A portion of the settled biomass sludge is then returned back to the aeration tank and mixed with fresh waste water. The other portion of the settled sludge is removed to waste as the biomass is continually growing in the aeration vessel (Eckenfelder (1966); Eckenfelder et al (1970);).

In the conventional system the biomass absorption, flocculation and growth processes are all accomplished in a single step.

The sudden change in concentrations of toxins, acidity or alkalinity in the feed can have adverse effects on the activated sludge. Therefore since the 3 different processes all take place in a single sten, the mixing of the fresh waste water with the recycled biomass, provides greater stability and tolerance due to changes in the feed and loading characteristics. The limitation on the process is the degree of loading to achieve flocculation and the settling and separation of the biomass in the settling system.

In the completely mixed system, more commonly used in activated sludge treatment

of industrial waste waters, the oxygen utilisation rate and hence the aeration will remain constant throughout the process. This means that the soluble BOD in the effluent is the same as that in the aeration vessel.
Another use for aeration is to aid mixing and suspension of sludge and solids, strip-off volatile products and together with the agitator provide a uniform distribution of oxygen for microbial respiration {Bailey & Ollis (1986), Moser (1988)}.

Even though the activated sludge system can tolerate variations in the sludge loading and levels of acidity/alkalinity and toxins, extreme variation must first be treated to equalise the feed waste water {Eckenfelder (1966); Eckenfelder et al (1970)}.

The effect of recycling the settled biomass increases the residence time of the biomass in the system and thereby gives the microorganisms time to adapt to the surrounding waste water - cyanide and other nutrients. Not only must the organisms adapt to the presence of cyanides but the time they spend in contact with the cyanides in the system must be long enough to ensure the relevant biodegradation reactions can take place {Bailey & Ollis (1986)}.

The term 'activated sludge' was coined from the fact that one of the most important characteristics of organisms in the activated sludge is their propensity to produce a polysaccharide gel, which allows the microbes to flocculate together {Bailey & Ollis (1986)}.

2.3.1.1 Sludge Age

Sludge age is defined as the average length of time the biomass is under aeration. For a CSTR system the sludge age is expressed as

$$G = \frac{X}{X_w F_w} \qquad (2.11)$$

(The mass of biomass under aeration divided by the mass flow rate of wasted biomass) For a flow-through system such as the FBR, sludge age is defined simply as the inverse of the dilution rate (1/D). The reason for this is that the sludge, though moving upwards in a plug flow fashion, is partially back mixing through the length of the reactor and allowed to flow out over the weir. No sludge is recycled back to be aerated again. It is a once through process.

$$G = \frac{1}{D} \qquad (2.12)$$

After long periods of aeration small residual levels of BOD will remain because of the auto-oxidation of the sludge which results in the re-solubilisation of cellular materials which can then be used for synthesis of new and existing microorganisms. {Eckenfelder (1966), Curi & Eckenfelder (1980)}

2.3.1.2 Sludge Loading Rate

The loading rate of the sludge, ie the amount of all cyanides present that can be removed for a given amount of biomass in the reactor, may be defined quantitatively as follows:

$$Sludge\ Loading\ Rate = \frac{S_{total} \cdot F}{X_R} \qquad (2.13)$$

The sludge loading rate gives an indication of the activity of the biomass sludge when varying concentrations of substrate are fed into the activated sludge system, for a given amount of biomass in the reactor. The higher the loading the higher the utilisation of substrate for a given amount of biomass.

2.3.1.3 Sludge Settling

The settling and subsequent compaction of sludge is a primary requisite for the successful aeration of activated sludge systems. With poor settling, carry-over of solids into the effluent can occur, resulting is higher BOD levels than allowed. Poor compaction on the other hand will reduce the concentration of the recycled sludge which will affect the mixed liquor suspended solids level in the reactor. This may also cause filamentous organisms to proliferate and reduces the available substrate for bacterial utilisation. {Eckenfelder (1970)}

2.3.1.4 Aeration

Aeration is important for aerobic activated sludge systems which require a minimum of 0.4 mg/ℓ of oxygen. The dispersion of the oxygen is important to ensure that all the biomass is held in contact with oxygen to allow aerobic growth and endogenous respiration to take place unhindered.

2.3.2 Microorganisms present in Activated Sludge

Activated sludge consists of a large variety of microorganisms, which are capable of treating a myriad of wastes, with cyanide being just one of many waste substances. This mixed population of organisms include aerobes, anaerobes, bacteria, yeasts, moulds and fungi as well as many pathogens and viruses. As a result of the variety of

organisms present, acclimation of the organisms to the specific waste to be treated is required. Certain organisms will die off as they are not able to acclimatise to the waste (presented as toxins to these organisms) or the treatment process is operated under either aerobic or anaerobic conditions, not allowing certain metabolic processes to function.

Activated sludge is an agglomeration of flocs of organisms which result from the ability of aerobic organisms to synthesise a polysaccharide gel which binds them together. These flocs or activated sludge have a high affinity for suspended solids and so the absorbed particulates can be oxidised by the organisms.

In the aerated part of the process, the biological utilisation of these suspended solids or wastes occurs and also serves to restore the organisms' absorption capacity. All this promotes a healthy activated sludge, devoid of filamentous bacteria and flagellate protozoa.

These filamentous bacteria can not normally compete with heterotrophic bacteria present in healthy activated sludge while the protozoa preys on free ie. unflocced, bacteria, thus clarifying the effluent. Maintaining the correct conditions in the reactor system is thus important to prevent undesirables from taking over which are inherently present in a mixed population of organisms.

Various authors have found different microorganisms present in their activated sludges that are capable of degrading the various cyanides. In some of the papers, microbes have been found that have not degraded cyanides but appear to have helped the system in the degrading process {Gaudy et al (1982)}. These authors found *Bacillus* and *Klebsiella* to be predominately present in the biomass, but not to metabolise cyanide.

Shivaraman et al (1985) used the cyanide degrading microorganisms *Pseudomonas*

acidovorans and *Alcaligenes faecalis*, a c[illegible]le resistant phenol degrader.

Howe (1965), who discusses various authors' work in cyanide degradation, list some of the bacteria found :

Aspergillus niger for the oxidation of HCN,

Artrobacter,

Coccus,

Pseudomonas's, as the most prevalent ones.

Hor[illegible] Mining Company {Mudder & Whitlock (1984); Whitlock & Mudder (1985)} isolated a strain of *Pseudomonas sp.* which they found was indigenous to the area, and have inoculated their rotating biological contactors (RBC's) with the *Pseudomonas*.

Bacillus pumilus, *Artrobacter* and *Aspergillus niger* were found by Richard & Shieh (1989) to utilise cyanide as carbon and nitrogen source and produce ammonia. Autotrophic microbes were found to able to grow on thiocyanate. These microbes resulted in an efficiency of approximately 99 % degradation.

The enzyme Rhodanese, purified from the organism thermophile *B. stearothermophilus*, catalyses the formation of thiocyanate and sulphite from cyanide and has proved to be of value as an antidote for experimental cyanide poisoning in small animals {Atkinson (1975)}.

These various organisms are summaries in table 2.3.

Table 2.2 - List of Microorganisms

Microorganisms	Substrate	Reference
Rhodanese from *B. stearothermophilus*	Cyanide / Thiocyanate	Atkinson 1975 Potgieter 1991
Bacillus Klebsiella	Glucose / $(NH_4)_2SO_4$	Gaudy et al 1982
Aspergillus niger *Artobacter* *Coccus* *Pseudomonas*	Activated sludge/ Ammonium acetate/ Potassium phosphate	Howe 1965
Bacillus pumilus *Arthrobacter* *Aspergillus niger*	Phenols / $NaHCO_3$ / NH_4Cl / Cyanides	Richard & Shieh 1989
Pseudomonas acidovorans *Alcaligenes faecalis*	NH_4Cl / Phenols / Cyanides / Phosphate	Shivaraman et al 1985
Pseudomonas sp.	Cyanides / Thiocyanate	Whitlock & Mudder 1984/5
Fungi - *Marasmius oreades*, *Pholiota adiposa*, etc.	Primarily HCN	Potgieter 1991

2.3.3 Reactions of Microorganisms with CN^-/SCN^-

The bacteria in the activated sludge utilise the carbon in the cyanides for metabolic growth and the production of carbon dioxide, together with other organic nutrients, and the nitrogen is converted into ammonia.
This ammonia by-product is toxic and must therefore be detoxified.

2.3.3.1 Bacterial Pathways

Whitlock & Mudder (1985) formulated the following reaction (reaction order = 0) of thiocyanate with bacteria in the presence of oxygen :

$$SCN^- + 2\frac{1}{2}\ O_2 + 2H_2O \xrightarrow{\text{bacteria}} SO_4^{2-} + HCO_3 + NH_3 \qquad (2.14)$$

Recently a *Pseudomonas sp.* bacteria was isolated which can convert cyanide into formats and ammonia in the absence of oxygen :

$$CN^- + 2H_2O \longrightarrow HCOO^- + NH_3 \qquad (2.15)$$

The released ammonia could be used as a nitrogen source for further metabolism {Gokool (1990), Potgieter (1991)}.

2.3.3.2 Enzymatic Pathways

Enzymes are present in bacteria and it is these enzymes that give the bacteria their cyanide degrading capabilities. The assumption is being made that the enzymes are intracellular and not extracellular as no evidence to the contrary has been found in literature. If cyanide degrading enzymes are not present in the bacteria, the cyanide is toxic to the organisms. The enzymes utilise the cyanide directly and produce amino acids which the bacteria can then use as building blocks.

The general biochemical reaction for cyanide in the presence of an enzyme, is :

$$CN^- + \text{aldose} = \text{cyanohydrins} \qquad (2.16)$$

and is a first order reaction with respect to cyanide at a pH greater than 8. The cyanohydrins are immediately hydrolysed further into aldonic acids {Raef et al (1997)}.

Many of the reactions mentioned in papers occur in the presence of bacteria but use aldose, for instance glucose, in a first order chemical reaction {Raef et al (1977)}. The glucose-cyanide reaction products are however biodegradable, which are non-toxic to acclimatised organisms.

Enzymes often form part of biochemical cyanide reactions {Potgieter (1991)}. For instance :

Hydrogen cyanide can be converted into the neurotoxin β-cyanoalanine, with the aid of the enzyme β-cyanoalanine synthase. The reaction is as follows :

$$HCN + HSCH_2CHNH_2COOH \rightarrow CNCH_2CHNH_2COOH + H_2S \qquad (2.17)$$

(cysteine) (β-cyanoalanine)

β-cyanoalanine can be further converted into asparagine and aspartic acid by nitrile hydrase and amidase enzymes :

$$CNCH_2CHNH_2COOH \rightarrow CONH_2CH_2CHNH_2COOH \rightarrow COOHCH_2CHNH_2COOH \qquad (2.18)$$

(β-cyanoalanine) (asparagine) (aspartic acid)

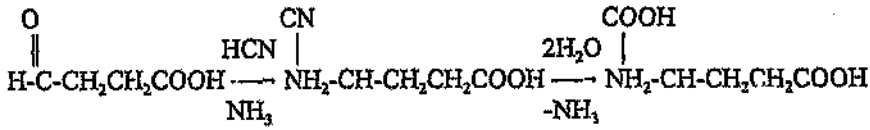
2.3.3.3 Fungi Pathways

Various fungi can incorporate HCN in alanine and to a lesser extent even in other amino acids. For instance {Potgieter (1991)}:

$$CH_3\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}H \xrightarrow[NH_3]{HCN} CH_3\text{-}\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle NH_2}{\overset{|}{C}}}}\text{-}CN \xrightarrow[-NH_3]{2H_2O} CH_3\text{-}\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle NH_2}{\overset{|}{C}}}}\text{-}COOH \qquad (2.19)$$

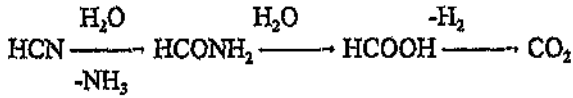
(acetaldehyde) (α-aminopropionitrile) (L-alanine)

In a method analogous to the above, glutamic acid, another important amino acid, can be formed.



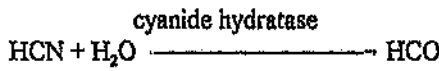
(succinic semi-aldehyde) (4-amino-4-cyano-butyric acid) (glutamic acid) *(2.20)*

Cyanide-forming fungi can also convert HCN into CO_2 via an unknown mechanism. An enzyme might be involved. A possible mechanism for the reaction is :



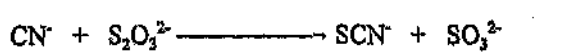
(2.21)

Certain fungi are pathogens to cyanide-forming plants, ie. the fungi can overcome the toxicity of the HCN released by the plant. The fungi form a cyanide hydratase enzyme which then converts the HCN into a non-toxic product, formamide. {Gokool (1990); Potgieter (1991)};



(2.22)

A possible reaction that could take place in the reactors is the direct conversion of cyanide CN^- to thiocyanate SCN^- and only then do bacteria or fungi utilise the cyanide in the thiocyanate form. This is the case with the Rhodanese enzyme, which occurs widely in plants, animals and microorganisms. This enzyme is active in sulphur transformations and can catalyse the CN^- to SCN^- conversion :



cyanide thiosulphate thiocyanate sulphite *(2.23)*

It should be mentioned that adsorption effects can be important as a cyanide removal mechanism {Raef et al (1976)}.

2.3.4 Advantages and Disadvantages of Biodegradation

Although biological degradation of cyanide bearing effluents only recently become an operational process at Homestake Mining Co. in 1984 {Whitlock (1989)}, the advantages have been realised and are reasonably well established {Howe (1965); Whitlock (1989)} :

- Biological treatment plants require considerably lower reagent chemicals, manpower, and installation costs, when compared to the equivalent chemical plant.
- To change an existing plant for cyanide degradation requires minimal cost as modifications required are relatively small.
- New plants built are also able to handle other biodegradable wastes and sewage of an industrial plant.
- The handling of chemicals is reduced to almost zero as very little reagents, if any, are required.
- The resulting low cyanide levels can be handled by the conventional sewage treatment works.
- No chlorine is required for water purification.
- The process is very much more resistant to changes in influent cyanide levels in so far as the efficiency does not drop off dramatically in an emergency. The biomass concentration will decrease but will rapidly regain its operational efficiency.
- Production of sludge is low.

The prime advantage of the biological plant to the chemical plant, therefore is the reduction of costs involved with the running of the plant, labour and chemicals.

On the other hand, the biological process for the degradation of cyanide, has the following disadvantages.

- Effluent streams containing small quantities of cyanide are more easily treated by chemical plants than biological plants, especially if no existing treatment plant is available.
- Chemical processes out-compete the biological processes for small industries due to the cost of capital equipment involved.
- If the concentrations of heavy metal ions in solution are high, they need to be removed before treatment, either chemically or biologically, in a separate unit. This incurs additional capital equipment costs.
- Extra provision must be made for safety protection, as any biological process can sometimes be upset. Cyanide-containing gases may be given off (air stripping) which pose a health hazard to personnel.
- Acclimation times are reasonably long (1 to 2 weeks). Therefore any interruption of the biological process may mean an interruption of the production process, ie. temporary shut down. This causes unnecessary loss of revenue.
- Proper nutrient supply is important and must be revised regularly.

Under certain conditions, the biodegradation of cyanide is both feasible and economical, but needs to be fully investigated in the proposed surroundings {Howe (1965); Gaudy et al (1982); Whitlock (1989)}.

2.4 Reactor Designs and Parameters

2.4.1 Reactor Design Criteria

Biological treatment plants are built outside and are therefore subject to the changes in the environment such as temperature. The microbial growth is affected by these changes, but activated sludge is more resistant to these ambient temperature fluctuations than are pure cultures.

Another design criterion that is important, is the hydraulic retention time of the sludge in the reactor, as this determines how efficient the bacteria degrade the cyanides in the reactor. Therefore the more contact that can be achieved through mixing the better, as this will reduce the residence time and hence the reactor size or increase the volumes of effluent that can be treated.

Increasing the contact per surface area through adequate mixing will reduce the mass transfer limitations for both oxygen and cyanides. In the support particles themselves the mass transfer is diffusion controlled and therefore the stagnant zone around the support particles needs to be minimised to increase the concentration of cyanide and oxygen in contact with the bacteria.

For an aerobic system, enough oxygen must be supplied for the needs of the bacteria. For the closed types of reactors, such as the FBR and CSTR, air will need to be compressed and fed to the reactor through spargers. Here a cost factor becomes important as compressed air is expensive. Therefore the design should optimise the utilisation of oxygen required, both for fluidising and aeration.

Recycle around the reactor facilitates rapid start-up and supplements the feed flow in

the event of very low feed flow conditions and therefore should be provided for, especially for the CSTR. For the FBR, the support particles remain in the reactor and therefore a recycle stream is not required.

The laboratory scale plant should be capable of approximating final plant performance. This is often very difficult to achieve.
Also the laboratory unit should be simple in construction and operation.

2.4.2 System Parameters

Different areas have different climatic conditions and hence the sewage treatment facilities operate under various conditions. For specific degradation processes like this one, conditions have to be kept reasonably constant or else the desired products are not obtained. Parameters such as pH, temperature and oxygen supply are important for sustained microbial growth. For different types of reactors investigated, different optimum conditions were found.

Fortunately many of these parameters fell within a certain range. The average was around the neutral pH and ambient to 35°C temperatures {Whitlock & Mudder (1985); Richards & Shieh (1989); Alabama Univ. (1983)}. It is very convenient to be able to operate the reactors at ambient and neutral conditions as it facilitates their control and reduces cost.

Dissolved oxygen concentrations have not been widely discussed. Whitlock and Mudder (1985), were supplying 4 mg/l or more of dissolved oxygen to their reactor. Others have stated that the dissolved oxygen required, is delivered during sparging and the velocity of the air required for fluidisation was the more important parameter {Cooper & Wheeldon (1980)}.

The retention times varied from 15 minutes {Cooper & Wheeldon (1980)} to as much as 12 hours {Shivaraman et al (1985); Shivaraman & Parhad (1984)}, depending on the reactor system.

Richards and Shieh (1989) reported that they had employed retention times of up to 30 hours in some of their test work. This is very much shorter than those retention times used in anaerobic processes, where hold-up time of up to 10 or 20 days are quite common. This is an advantage that the aerobic process has over the anaerobic ones.

Whitlock and Mudder (1985) reported that although the optimum pH for cyanide degradation was around 7.0 to 8.5, thiocyanate degradation took place at a slightly lower pH of between 6.7 and 7.2.
Shivaraman et al (1985) concluded that both cyanide and phenols inhibit the degradation of thiocyanate due to possibly an over growth of phenol-utilizing organisms.

2.5 Fluidised Bed Reactors

2.5.1 Fluidised Bed Reactors - FBR

A by-product of many biological treatment processes is ammonia. Subsequently this needs to be treated as well. Cooper & Wheeldon (1980), studied the concept of expanded and fluidised bed reactors for waste treatment, specifically nitrification.
The use of sand as bed particles, increases the surface area available for the biomass to grow on.
The reactor claimed some impressive advantages over ordinary activated sludge reactors : higher biomass concentrations, no need for secondary clarification, less

susceptibility to sudden changes in substrate concentration.

Donaldson (1983) reported on a fixed-film fluidised bed bio-reactor for the bio-oxidation of dissolved organics and noted the following advantages to conventional biological treatment processes:

- High biomass densities for high removal at low retention times;
- Better reactor geometries;
- Smaller reactors;
- Closed reactor systems to minimize health and environmental effects;
- Improved shock and toxin resistance provided by the fixed-film relative to the suspended growth system.

It was found that after short down times the reactor recovered very quickly, within several days, to the original performance levels. Degradation rates were found to be proportional to the flow rate, suggesting a liquid-solid mass transfer effect.
Also the reactor ought to be readily integrated with existing treatment systems. It is easily operated and is biologically stable.

The biomass in the reactor was attached to anthracite support particles. With the supply of air for the aerobic bacteria, the reactor becomes a 3 phase FBR: the solid phase is the biomass contained on the anthracite particles, so immobilising the biomass; the cyanides to be removed are in the aqueous liquid phase; and the gas phase for the supply of air for the aerobic degradation processes and bed fluidisation. Both the liquid and the gaseous phase are introduced at the bottom of the reactor.

Many of the fluidised bed reactor systems investigated, are based on the recycle principle, very few using support particles for containing their biomass. The support particles that can be used vary and the following section discusses support particles

other than the anthracite used by Donaldson (1983).

2.5.2 Use of Support Particles

Cooper & Wheeldon (1980) did research into using expanded - and fluidised bed reactors for the denitrification treatment of waste waters. They used sand (small particles) which gave a large surface area for the biomass to grow on.

The Thames Water Authorities in London were the first to use a full scale up flow expanded bed attached-growth system, for denitrification.
Many of the earlier work done on fluidised beds {Cooper and Wheeldon (1980)}, encountered many problems such as blockages and biomass wastage control from the system.

Atkinson, Black & Pinches (1981) did extensive work into the characteristics of various biomass support particles for expanded and fluidised bed reactors.
Advantages of support particles are :

- biomass is retained within the aeration tank obviating the need for recycle,
- very high concentrations of biomass can be maintained in the reactor compared to the CSTR type reactors,
- sludge can be removed directly from the particles, thus reducing the load on the clarifier.

It is important to prevent excessive accumulation of biomass associated with the particles so as to avoid blockages caused by the growing together of particles.
These reactors can be subject to periodic back washing to remove excess biomass.
Here use can be made of high air/liquid velocities.

There are many media suitable for the use as support particles, including sand, carbon, glass and other similar media in the size range 0.2 - 3 mm. Using reticulated foam particles will effectively increase the surface area for biomass film per unit reactor bed volume.

Biomass support particles can be used under continuous growth conditions with a constant biomass hold-up, without any loss of conversion efficiency. A normal concentration of biomass in the particles can take to 25 g (dry weight) / l (bed volume). Gas evolution can occur without shearing biomass from the particles. Also the biomass can easily be removed from the particles by squeezing or shaking.

A suitable biomass support particle to be used is the reticulated polyester foam particles, 5 mm cube with a nominal 30 pores per inch foam.
The cubic particles have some greater advantages to the spherical or toroidal particles in that the bed voidages are smaller and handling is better.

2.5.3 Motivation for FBR Design

With cost being an important design criterion, the smaller the reactor the less the capital cost involved will be. Therefore the use of expanded- or fluidised bed reactors, containing biomass support particles, will reduce the reactor size considerably and hence the cost.

The use of support particles in the reactor greatly increases the biomass concentration and hence reduces the retention times required for the efficient conversion. Also the shorter retention times needed allows more effluent to be treated per reactor. Increased biomass concentration will help maximise the achievable reaction rate.

Due to sparging in expanded- and fluidised bed reactors, the shear rate is high. This would cause high concentrations of biomass to be washed out and the effluent would have to be settled in order for sludge to be recycled.

Using support particles for the bed in the reactor, the biomass wash-out rate is greatly reduced as the biomass film on the support particles is much stronger. This reduces the need for a settler and again saves on cost {Cooper & Wheeldon (1980); Atkinson et al (1981); Donaldson (1983)}.

Air is required by the microbes in the system and therefore provides a suitable medium to expand or fluidise the bed at the same time. The flow rates of air to fluidise the bed are sufficient to maintain the required dissolved oxygen concentration in the reactor {Donaldson (1983)}.

2.6 Aims, Scope and Contribution of Research

The aim of this research project is to investigate the efficient use of a Fluidised Bed Reactor as apposed to the more conventional CSTR. The biomass is to be supported on reticulated foam particles in the FBR which would be neutral to the environment and would not require large quantities of energy to maintain them in a well mixed surrounding, such as sand or steel mesh balls.

A widely practised approach used in waste water treatment technology, will be used to compare the efficiency of the two reactor system. This approach is a semi-empirical one, initiated by Eckenfelder many years ago and involves the development of linear relationships which have approximate validity over the range of experiments performed herein.

In this investigation, a CSTR will be used as a means of comparing the performance of the FBR as well as a basis for determining kinetic parameters.

3 Theoretical Aspects

3.1 CSTR Kinetic Theory

The CSTR used in this investigation is better described, from a microbiological point of view, by a chemostat, where the biomass concentration in the reactor is changing with time (growth of bacteria) and a mixed culture is being utilised.
By definition for a completely mixed CSTR, the composition in the reactor vessel is uniform throughout the volume and is the same in the effluent stream.

Design of activated sludge systems usually use simple and idealised models. Hence the Monod kinetic model will be used with an additional term for endogenous metabolism and death rate of cells. The sludge is considered to be a single pseudo species, even though it is a mixed culture for the Monod equation to simplify a complex combination of microorganisms {Bailey & Ollis (1986)}.

$$\mu = \mu_{max} \frac{S}{K_s + S} - k_e \qquad (3.1)$$

The death rate may occur for two reasons; firstly the toxic effect of cyanide on the bacteria may cause some of the bacteria to die off, and secondly through the natural process of birth, growth and death of microorganisms. The endogenous metabolism of the microorganisms refers to the maintenance and new growth of cells which takes place continuously. The specific growth rate of biomass or microorganisms is related to the substrate available for growth and hence the relationship in Monods equation. The term K_s refers to the concentration level of the substrate where the specific growth rate has half its maximum valve, ie. It is the division between the substrate concentration range where the growth rate is linearly dependant on S and where the

growth rate become independent of the S.
This assumption has been used by many investigators and is therefore nothing new.

If the CSTR is assumed to function as a differential reactor (hence $\mu = D$), then at all points in the reactor the rate of biomass growth and substrate utilisation remains constant. This then enables the direct measurement of a growth rate [μ] for the reactor, without any complicated mathematical manipulation of the measurements as the reactor is assumed to be uniform. This is in line with the simplifying assumption that the sludge is considered to be a single pseudo species and the Monod equation above is defined for a single growth rate for the biomass in the reactor. This implies that the growth rate can be controlled by the amount of nutrient fed to the reactor.

3.2 The Rate of Biomass Growth - Cyanide Degradation

The rate expression for the CSTR is expressed in terms of the state of the system, ie. in terms of μ, X, S. The rate expression is defined to be :

$$r = - \frac{\mu . X}{Y_{X/S}} \qquad (3.2)$$

and hence substituting equation [3.1]

$$r = - \frac{X}{Y_{X/S}} \left(\frac{\mu_{max} S}{K_s + S} - k_e \right) \qquad (3.3)$$

The above expression is the rate expression for the CSTR in terms of biomass and substrate (cyanides) concentrations present in the reactor, measured under varying conditions.
This rate expression will be used in the mass balance expression

3.3 The Ideal CSTR with Biomass Settler and Recycle

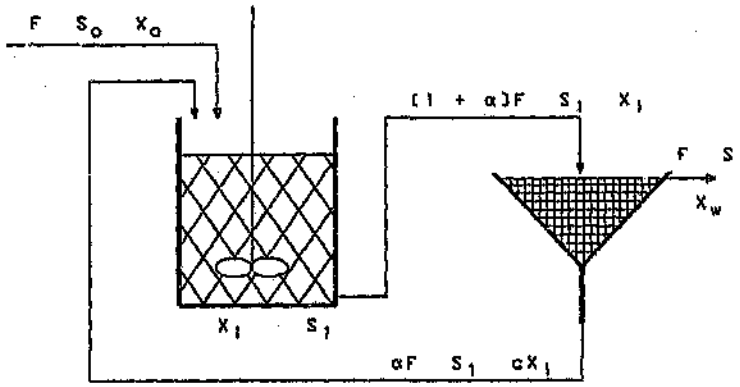


Figure 3.1 - The CSTR with Settler and Recycle

3.3.1 The Mass Balance

The mass balance for CSTR is taken over the whole CSTR system, including the settler and recycle stream and not the CSTR in its own right. The mass balance for the CSTR system is as follows :

$$FS_0 = FS_1 - rV \qquad (3.4)$$

Substituting equation (3.3) and dividing through by V, where D = F/V, the following expression results :

$$D(S_0 - S_1) = \frac{X}{Y_{X/S}}\left(\frac{\mu_{max} S_1}{K_s + S_1} - k_e\right) \qquad (3.5)$$

3.4 The 3 Phase FBR

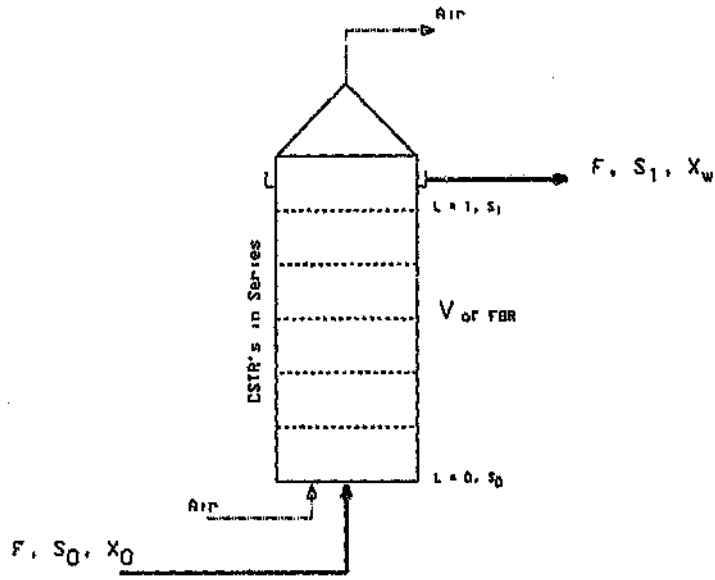


Figure 3.2 - The FBR

The 3 phase Fluidised Bed Reactor consists of a catalyst bed (biomass support particles) suspended in a cyanide and thiocyanate solution, which is fluidised with compressed air. Complete mixing of the catalyst particles is assumed to occur with the solution phase in ideal plug-flow with the feed at the bottom and outlet at the top, and no recycle stream.

The FBR may be assumed to consist of several CSTR's in series.

3.4.1 The Mass Balance

The following assumptions and conditions are used :

1) Biological catalyst particles (Biomass Support Particles) are of uniform size;
2) The fluid-phase density is constant;
3) The liquid phase is moving in a plug flow fashion with partial back mixing in the reactor (the aspect ratio is approximately 2.5 : 1);
4) The biomass support particles are well mixed in the cyanide solution and after approximately 2 retention times the excess biomass is washed out of the reactor;
5) The FBR behaves as several CSTR's in series.

The mass balance equation for the FBR is as follows :

$$\int_{S_0}^{S_1} FS = rV \qquad (3.6)$$

The integration of the CSTR rate expression into this mass balance equation as several CSTR's in series will yield an expression requiring integration up the height of the reactor and down the concentration gradient of substrate utilisation.

When comparing these two reactors, the CSTR has the settler and recycle stream included as part of the CSTR as the biomass in the CSTR is in suspension where as in the FBR the biomass is supported in support particles. Any biomass leaving the effluent stream from the FBR is lost but in the case of the CSTR the biomass in CSTR vessel effluent stream is concentrated up and returned to the CSTR vessel for re-use.

3.5 The Determination of Kinetic Parameters

Kinetic parameters are very often not presented in the literature and only a few make any mention of them. For mixed cultures, as activated sludge inherently is, defining kinetic parameters is somewhat difficult and hence finding lumped parameters for μ_{max}, K_s and k_s is easier instead of the individual parameters for each of the species present {Bailey & Ollis (1986)}. These lumped parameters are determined for the cyanide degraders in the activated sludge and not the sludge as a whole. As the cyanide is the only substrate available for consumption by microorganisms, therefore the lumped parameters are determined for cyanide only.

The CSTR will be used as a chemostat, for the growth studies, maintaining the dissolved oxygen concentration above the limiting concentration of 4 mg/ℓ and all the other parameters constant {Gaudy et al (1982)}.

The kinetic parameters, K_s, μ_{max} and k_s are determined by fitting a three parameter model to the data of the final substrate concentration at each dilution rate.To solve for these parameters, a simplex routine was used, using the Amoeba parameter solving function.

The kinetic parameters are intensive properties of the reactor and should be similar for both reactors as they are only a function of the substrate concentration and the same microorganisms in the reactors. Also the two reactors were operated under the same conditions.

Using the CSTR equation (3.5) and substituting the values for S and D and using a manual technique of Runge-Kutta is applied to find the values of the kinetic parameters.

Once a set of values for the parameters has been found, another CSTR is added into

the equation and a new set of parameters determined. This addition of CSTR's in series in the equation, continues until the variation in values of the kinetic parameters for the *n* and *n-1* CSTR's is zero to the 4th decimal place. Described in another way, the kinetic parameters do not change anymore with additional CSTR's.

The yield factor, $Y_{X/S}$, is a macroscopic parameter of the system. The yield factor for biomass as a function of substrate consumption is defined by Bailey and Ollis (1986) as follows :

$$Y_{X/S} = -\frac{\Delta X}{\Delta S} \approx -\frac{dX/dt}{dS/dt} = -\frac{r_X}{r_S} \qquad (3.7)$$

The r_s term, indicating substrate utilisation, is a negative term and hence the yield factor has a negative sign to make it a positive quantity.

3.6 The Comparison of the Reactors

The Eckenfelder approach for comparing reactors, essentially compares linear relationships of various components. These components include; the inverse of sludge age, effluent concentration and oxygen utilisation against the sludge loading rate.
The sludge loading rate is defined as the amount of substrate (cyanides) utilised for a given mass of biomass in the reactor.
The basis for these linear relationships come from the two equations that simlpy describe the aerobic biological treatment system. These equations are:

organics + (a')O_2 + N + P $\rightarrow$ (a)cells + CO_2 + H_2O + nondegradable soluble residue
(3.8)

and

cells + O_2 → CO_2 + H_2O + N + P + nondegradable cellular residue *(3.9)*

These reactions also occur in natural waters and streams. These equations may be schematically shown in the following figure 3.3.

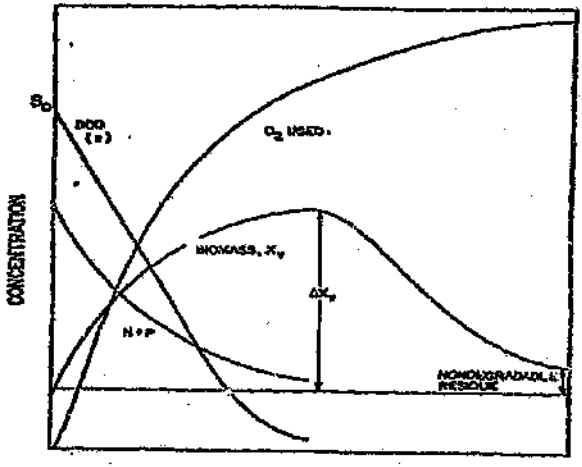


Figure 3.3 - Schematic of Aerobic Biological Process (Eckenfelder (1980))

This figure formed the basis from which the linear relationsh ... ere developed with the effluent concentration instead of the feed concentration as BOD being plotted against sludge loading rates calculated.

Tischler & Eckenfelder (1969) showed that the removal of specific compounds in an activated sludge process was zero order, ie. linear; down to very low levels of substrate concentrations. They also showed that for mixtures of organics, such as normally found in waste waters, each component simultaneously exhibited a linear or zero order removal process to low concentration levels.

In this investigation the inverse of the sludge age an ' effluent concentration of cyanides will be plotted against the sludge loading rate. A linear regression is then

fitted through the plotted points and the slope of the curves can be determined.

3.7 Cyanide Absorption by Dead Microorganisms

Dead microorganisms which are inherently present in the reactors due to normal growth cycles and possibly the toxic effect of cyanide, are a major source of carbon. Activated carbon is known for its absorption properties in filtration systems and is effective in removing cyanides. Hence the dead microorganisms, though not activated carbon, does show similar absorption characteristics to cyanide. Therefore a possible removal mechanism for cyanides is the absorption of cyanides by dead microorganisms.

Both Adam (1990) and Muir et al (1988) found that absorption of cyanide was first order and that this first order rate was true for all the reactions that were involved in the removal of cyanide in the presence of activated carbon {Adams (1990)}. Since the rate constant encompasses all the reactions taking place in the reactor, taking the average rate constant over all the runs performed with each reactor, will provide a useful predictive tool to determine the cyanide concentrations at any point during a run.

The conditions used for this particular investigation, are conditions similar to those used by Adams (1990). Therefore the expression for the kinetics of cyanide removal in a batch system, is as follows {Adams (1990)}:

$$\frac{-d[CN^-]}{dt} = k_1[CN^-] \qquad \textit{(3.10a)}$$

or

$$\frac{-dS}{dt} = k_1 S \qquad \textit{(3.10b)}$$

where

k_1 is the first order rate constant. Integrating the above expression yields the following

expression in semi-logarithmic form:

$$\ln(S_t) = \ln(S_0) - k_1 t \qquad (3.11)$$

Therefore a linear relationship exists in semi-logarithmic form, to define the kinetics of cyanide losses. A first order rate law will therefore describe the kinetics for all the reactions that are likely to occur in the reactors. An assumption is made here which states that, "The biodegradation of any cyanides is first order, however small the proportion of total cyanide removal".

Plotting the various rate constants from each run against the effluent levels of cyanide will yield a curve that describes the effect of activated carbon on the removal of cyanide in the reactor.

Rearranging equation (3.10) for substrate or cyanide removal :

$$r = -\frac{dS}{dt} = -\frac{d[CN^-]}{dt} \qquad (3.12)$$

4 Experimental Apparatus and Procedures

4.1 The CSTR Unit

The CSTR consisted of a 2 litre flanged glass vessel, onto which two valves were fitted; one outlet valve and one sample port (adjacent to outlet valve). The liquid level in the reactor vessel would be maintained to a 1.4 litres volume. A prefabricated stainless steel lid was fitted to the vessel, which contained a host of probes and other fittings, including pH, temperature, dissolved oxygen, stirrer, inlets.

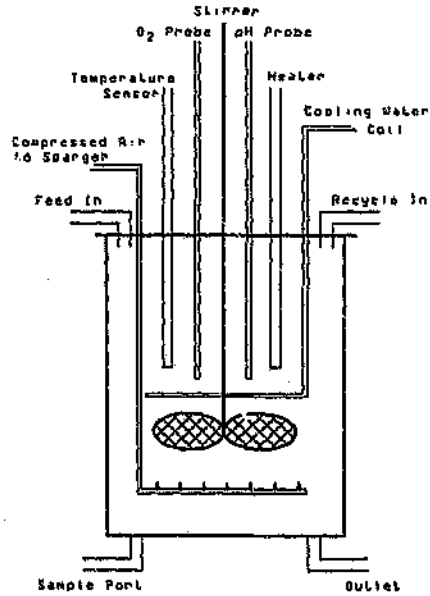


Figure 4.1 - Diagram of CSTR with Fittings

The effluent from the CSTR is pumped into a settler from where the concentrated activated sludge is recycled back to the CSTR. The settled effluent is discharged. The settler is continuously stirred, very slowly, to ensure that no biomass settles on

the walls and is properly recycled.

For three of the experiments, gases from the CSTR were bubbled through 2 absorbers to collect ammonia and carbon dioxide products. The first absorber contained Boric acid (0.5 M) for the absorption of NH_3 and the second absorber contained Potassium Hydroxide (0.5 M) to absorb CO_2.

The remaining experiments were carried out with NaOH absorbers for volatilised cyanide absorption.

The collection of NH_3 and CO_2 is important in order to complete the mass balance over the system and to determine the possible extent of NH_3 and CO_2 produced by the bacteria in the degradation process.

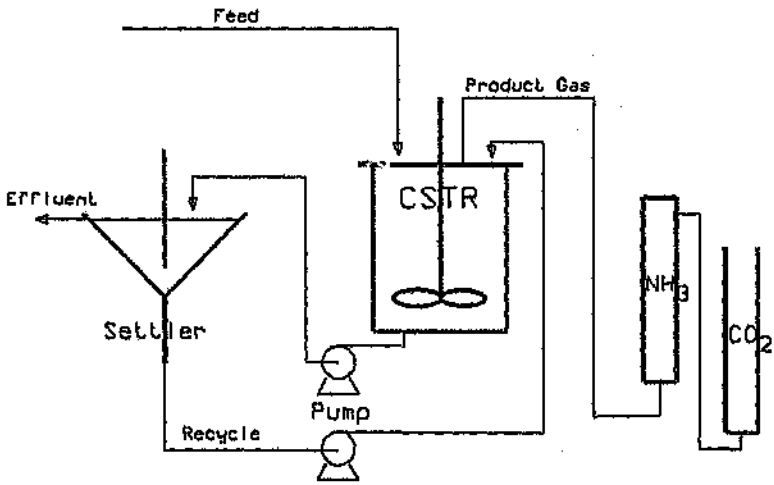


Figure 4.2 - CSTR Process System

4.2 The FBR Unit

The FBR is a 3 phase fluidised bed reactor where the biomass is contained in reticulated foam support particles which are mixed throughout a cyanide/thiocyanate solution using compressed air.

The reactor consists of a jacketed perspex cylinder, flanged at both ends. The feed inlet is situated at the bottom, together with the sparger for compressed air (oxygen) and bed fluidisation. Thermostat and heater rods are also mounted through the bottom. The pH, temperature and dissolved oxygen probes come in through the side of the vessel.

At the top of the vessel is a cone and weir assembly for the retainment of the biomass support particles and outflow of treated effluent. The exit gases from the FBR are passed through a NaOH absorber to absorb any volatilised cyanides.

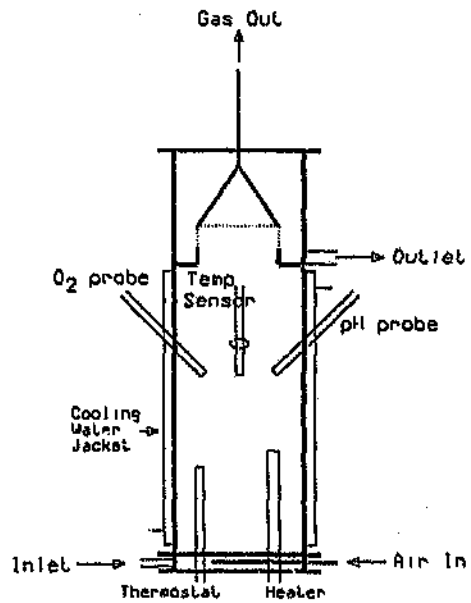


Figure 4.3 - Di... ...f FBR with Fittings

4.3 Parameter Monitoring and Control

Use was made of a personal computer for the monitoring the pH, dissolved oxygen concentration and temperature of the two reactors. A data acquisition card was employed for this purpose. These three parameters were recorded every hour for the duration of the run and daily averages and standard deviations were calculated.

The level in the CSTR vessel was monitored by light sensitive transistors and controlled by computer.
Using some of the basic software provided with the acquisition card, a fully integrated program was written for the monitoring and control.

4.4 Sampling

4.4.1 Cyanide and Thiocyanate

For the CSTR, the effluent samples from the reactor, ie the concentration in the reactor itself, were collected. On the FBR, the samples were collected from the outlet of the reactor.
Samples from the feed tank were also taken.

Samples were preserved by adding 0.1 M NaOH solution to them and storing them under refrigerated conditions. The ratio of sample to NaOH solution was 5:1. At the end of each run, the samples were analysed.

4.4.2 Biomass Samples

Biomass samples for the CSTR were taken from both the reactor (effluent stream) and the recycle stream to the reactor. Samples were taken on a daily basis together with the cyanide and thiocyanate samples.

For the FBR, biomass samples were only taken once a week. The number of particles removed was 10 and hence 10 inoculated particles were replaced to attempt to maintain the biomass concentration reasonably constant.
Any shorter sampling period would result in error due to the acclimatization required by the replacement particles. As there were only 2000 particles present in the reactor at any given time, taking more frequent samples would artificially change the biomass concentration for a particular run.

4.5 Analytical Procedures

4.5.1 Cyanide and Thiocyanate Concentrations

These samples were analysed according to the procedures listed in the instructions supplied with the Orion probes. The probes were specifically acquired for the direct measurement of cyanide as CN^- and thiocyanate as SCN^- in solutions. These were supplied by Labotech.

In cases where the concentrations were very low (< 2.6 mg/l) and the probes had difficulty obtaining a stable reading, known addition methods were used. The probes was unable to measure lower than 0.0001 M or 2.6 mg/l.

For the cyanide absorption experiments a titration method was used with a few drops of Rhodamine as an indicator. The samples were buffered and diluted with a standard NaOH solution and then titrated against a standard solution of silver nitrate titrant {Standard Methods (1985)}. This proved to be a very effective indicator when trying to determine the colour change at the equilibrium point.
The probes towards the end started to malfunction and therefore the titration method was employed for the remaining runs.
With this method it was found that much lower concentrations of cyanide could be measured to about 0.1 mg/l.

4.5.2 Biomass Concentrations

Biomass concentrations were determined using the dry-weight method as described in Standard Methods (1985), where a volume of reactor sludge was filtered using 45μm Whatman filter paper. The filter paper was first prepared by pre-drying and pre-weighing to determine the tare weight. The sample of biomass was washed out of the particles onto the prepared filter paper using distilled water, which was then placed in an oven at 105°C for a minimum of 3 hours and then weighed and the mass of biomass calculated and the concentration determined.

For the FBR, 10 support particles were removed and dried, and then weighed to determine the resident biomass mass. An average support particles mass was used for the initial mass, as it was assumed that all the particles have the same shape and dimension. This was verified quantitatively before hand.
From this information the concentration of biomass in the FBR was calculated.

4.5.3 Air Stripping Rates

The sparging in the FBR was more intense than in the CSTR and many authors point out that in an aerated system, cyanide can become volatilised and escapes as HCN gas. For this reason air stripping test were carried out to determine the extent to which this occurs in the FBR.

A NaOH absorber was used to collect any cyanide given off during a run where a cyanide feed was introduced. At various intervals, the cyanide concentration in the absorbers was measured together with the feed and effluent concentrations. From this information, a stripping rate was calculated and introduced into the general mass balance calculations for all the runs.

A stripping test was also carried out on the CSTR for mass balance purposes.

4.5.4 Absorption of Cyanide

The absorption of cyanide by dead microorganisms or activated carbon, is an important removal mechanism for cyanide. Adams (1990) found that activated carbon strongly absorbs cyanide and must therefore play an important part. Though dead microorganisms are not activated carbon, they would appear to exhibit a similar absorption characteristic for cyanide as activated carbon. Raef et al (1977) stated that anaerobic sludges have been reported to absorb cyanide although no clear evidence exists to state that the cyanide was absorbed and not removed by other mechanisms. The fact that anaerobic sludge appeared to remove cyanide by absorption suggests that organic matter in the form of microorganisms impact on the absorption process to a certain degree.

A batch absorption experiment was performed consisting of three different runs, each

with a different and known quantity of microorganisms and initial cyanide concentrations.

Concentration measurements were initially taken every half hour and then further apart as the concentrations levelled off, for a maximum of 24 hours.

4.6 Feed Stock Solutions

Two tanks were used for the feed stock to the reactors. One contained the cyanide solution while the other the thiocyanate solution.

A volume of 40 litres of each was made at a time. The compositions were as follows :

Cyanide 5 gm KCN

Thiocyanate 10 gm KSCN
2 gm KH_2PO_4
2 gm K_2HPO_4

The phosphate buffers were added to help maintain the pH at its desired level of around 8.

The feed solutions were contained separately as a white precipitate was found to form when the cyanide and thiocyanate were stored in the same container. The two solutions were then mixed just before entering the reactors.

5 Results

5.1 Forms of Cyanide Present

From the Pourbaix diagram (see section 2, figure 2.1) for the cyanide-water system, one finds that the cyanide is primarily present in the HCN form for the pH range present in the reactors.

It has been assumed that there is no CNO^- in the feed solution. The concentration of CNO^- in the reactor will be very low and can therefore be neglected. The oxidation of cyanide to cyanates is thermodynamically favoured at room temperature but the kinetics are exceedingly slow in the absence of a catalyst.

The introduction of air sparging and agitation will increase the rate of HCN formation {Adams (1990)}.

This means that HCN is the most common form of cyanide that may be found in the system and very little if any, as CN^-. All measured cyanide will then be measured as HCN and not CN^-. The equilibrium constant for the HCN-CN^- equilibrium is also very large at 1.6×10^9, favouring HCN in the system.

This was the initial line of thought followed.

5.2 Non Biological Aspects of Cyanide Removal

5.2.1 Cyanide losses due to Air Stripping

Cyanide is most likely stripped off in the form of HCN due to the pH of the solution. The system pH is around the 8.5 mark. The stripped off cyanide is broken down into CN^- and H^+ ions in the sodium hydroxide absorber solution and becomes HCN in solution.

Of the 2 reactors, the FBR exhibited the higher air stripping rate, most likely due to the higher gas flow rate required for fluidisation.
The stripping of cyanide in the FBR accounted for approximately 1.8% of the feed concentration and it was therefore decided that air stripping of cyanide may be neglected.

Air stripping of cyanide was found to be negligible in both the CSTR and the FBR when operating under the biodegradation operating conditions.
Data and a calculation may be found in Appendix C.

5.2.2 Cyanide losses in an "Open" System

In a system where no sparging or agitation takes place and the container is left open to the atmosphere, the concentration of cyanide was found to drop off somewhat but these amounts were found to be negligibly small. A beaker of cyanide solution was allowed to stand for a period of 4 hours. At the end of the period the concentration of cyanide was measured and found to have dropped by 1.2 mg/l from 64.5 mg/l.

5.3 Cyanide Degradation by Living Microorganisms

Living organisms can adjust to changes in their environments provided these changes are not too extreme. For instance waste containing cyanide is toxic to most organisms but there are those that adjust to these harsh conditions to survive and also to actively use cyanides as nutrients.

The CSTR is a commonly used type of reactor for activated sludge systems. It provides a suitable control reactor for comparison against the FBR.

5.3.1 The CSTR

The percentage cyanide degraded by the active biomass was calculated from the difference between feed and effluent stream concentrations as a function of the feed concentration. For the various retention times investigated (10,7.5,7,6,5,4 hrs), the percentage of cyanide and thiocyanate degraded are plotted against the number of retention time passed. The data is transient data and starts with time = 0.
The retention time of the cyanides in the reactor can only be increased until the cyanides degraded reach a maximum of 100%. Increasing the retention time further only serves to reduce the capacity of the reactor system.

All the cyanide degradation results for the CSTR may be found in appendix A.

The next three sub sections describe the degradation of cyanide, thiocyanate and total cyanides for the various retention times employed in the CSTR. As can be seen the figures are plotted against the number of retention times passe, giving the total runtime of each run, for example the 10 retention time run, the number of retention times passed was 28.8 which equates to 288 hours runtime. The graphs plotted show

the values obtained in the investigation, with no mathematical manipulation having been carried out. The data starts at the beginning of the experiment.

5.3.1.1 Cyanide Degradation

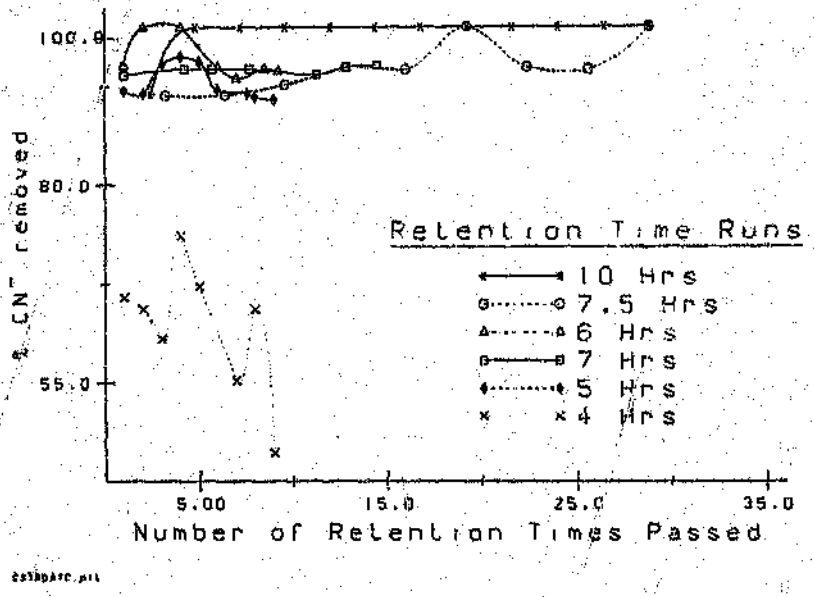


Figure 5.1 - CSTR Cyanide Degradation

The following observations can be made from figure 5.1:

i) The 10 hour retention time run removed all cyanide present in the feed once the process had stabilised after the first 48 hours;

ii) The higher capacity runs (shorter retention times) showed an initial high performance peak shortly after start which then dropped off steeply back to at least the initial degradation level;

iii) The 7.5 retention time run would appear to be struggling to cope with the level of incoming cyanide. Had the run been allowed to continue for at least the same time again, the degradation level might well have reached 100%;

iv) The 7 hour retention time run shows no spectacular result, remaining

reasonably constant throughout the run;

v) Both the 6 and 5 hour retention time runs show an early peak and then drop off in performance. Had the run been allowed to continue further, the early peak could possibly have been explained more;

vi) The run based on a 4 hour retention time, shows a few attempts to reach higher degradation level but overall describes a steady decline in performance.

Therefore one may conclude that the optimal retention time for cyanide removal must lie somewhere between 7.5 and 10 hour. At the 7.5 hour retention time the cyanide degraded would result in an effluent cyanide concentration of < 0.5 mg/ℓ (measured as CN^-) as stipulated in the Government Gazette [Vol (1), May 1984].

5.3.1.2 Thiocyanate Degradation

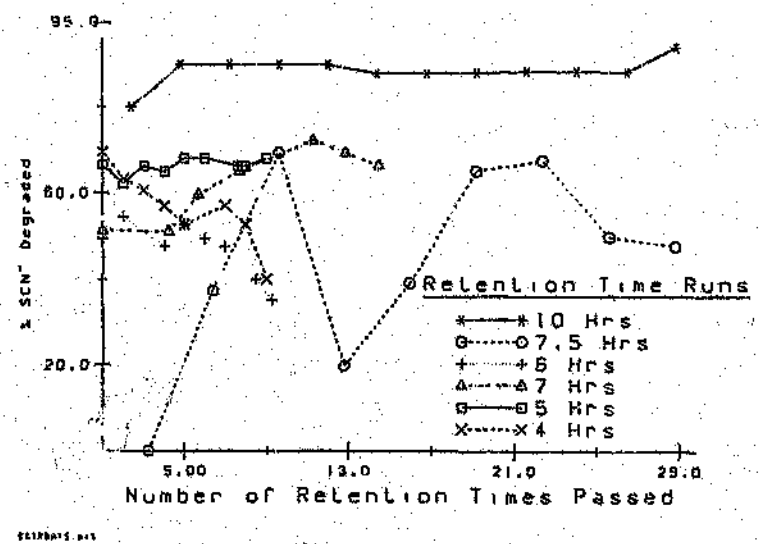


Figure 5.2 - CSTR Thiocyanate Degradation

The following observations can be made from figure 5.2:

i) The 10 retention time run removed an average of 88.6% of the incoming feed

thiocyanate. This is the most removed out of all the retention times indicated. Again there was the initial build up to the average degradation level as with the cyanide degradation;

ii) Other than the 10 hour run, the runs are erratic and the extremes indicated by the troughs could well be experimental error or noise in the measurements;

iii) The 4 and 6 hour retention time runs shows a general decline in thiocyanate degradation;

For thiocyanate a retention time of more than 10 hours would be required as the concentration of SCN^- in the effluent stream is an average 12.1 mg/ℓ (converted to CN^- = 5.76 mg/ℓ) and is required to be < 0.5 mg/ℓ (converted and measured as CN^-). It does however show that thiocyanate is being degraded but not as well as the cyanide. It would appear that cyanide is more effectively removed than thiocyanate, when mixed together in the same environment.

5.3.1.3 Total Cyanides Degradation

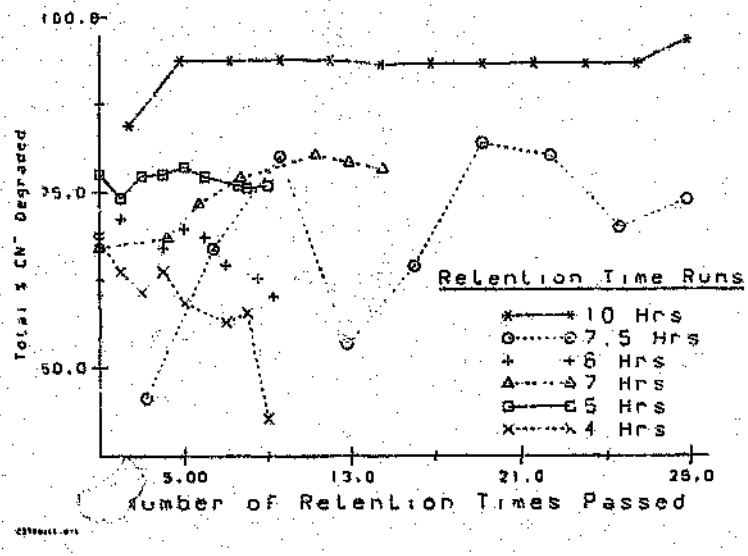


Figure 5.3 - CSTR Total Cyanides Degradation

The following observations can be made from figure 5.3:

i) The curves on this graph follow the patterns as displayed on the thiocyanate degradation graph (Fig 5.2). This is explained by the fact that cyanide degradation is relatively constant over time while thiocyanate fluctuates considerably at times;

ii) It is very clear that the 10 hour retention time run produces the best degradation with an average of 92.8% of the total cyanides degraded;

iii) Unfortunately with the 10 hour retention time run the total cyanides concentration left behind in the effluent stream is higher (5.6 mg/ℓ) than the legally required minimum level of 0.5 mg/ℓ total measured CN^-. Therefore a retention time, estimated at approximately 12 hours, would be required to total degrade all the cyanides to the acceptable limit.

5.3.1.4 Effect of Biomass Levels

When looking at the degradation of cyanides with respect to the biomass levels in the CSTR for all the runs:

Table 5.1 - Biomass Concentrations in CSTR

Run No.	Avg. Biomass Concentration	Avg. % CN^- Degraded	Avg. % SCN^- Degraded	Avg. % Total CN^- Degraded	Retention Time
	mg/ℓ	%	%	%	Hrs
1	550	99.3	88.6	92.8	10
2	650	94.9	44.1	68.3	7.5
3	562	94.6	62.2	74.7	7
4	487	95.9	47.1	66.6	6
5	521	93	66.3	76.6	5
6	566	62.1	56.7	59	4

it is clear that no obvious conclusion can be drawn as to the effect of biomass levels on the degradation of cyanides.

From table 5.1 it can be seen that most of the average biomass concentrations are in the mid 500 mg/ℓ region. Only run 2's value is comparatively on the high side and run 4 is on the low side. It was thought that for lower levels of biomass, less degradation would take place but the similarity of the degradation of cyanides for runs 2 and 4 indicate that biomass levels have not effect. The length of the retention time seems to be the over riding factor affecting the degradation process more so than the levels of biomass.

Variations in the degradation levels could also be affected by the toxicity effect of

cyanide.

5.3.1.5 Other Effects on Degradation in the CSTR

A certain amount of cyanides in a system can be tolerated by many organisms. Increasing this residual amount of cyanide (reducing the retention time), can cause some form of metabolic failure in the organisms, resulting in death and there by creating a mass of effectively activated carbon in suspension.
Activated carbon is known to remove cyanides from effluent streams by chemical reaction {Adams (1990) & Muir et al (1988)}.
Therefore if one considers that this phenomena could be taking place, then increasing the retention times allows either the organisms time to biodegrade the cyanides or the "activated carbon" to remove the cyanides by reactions and absorption. This will be discussed further later in section 5.4

5.3.2 The FBR

Plotting the results of % cyanide degraded against retention times, one arrives at a similar graphs to that for the CSTR.

All the degradation results for the FBR may be found in appendix B.

The next three sub sections describe the degradation of cyanide, thiocyanate and total cyanides for the various retention times employed in the FBR, against time. The graphs plotted show the values obtained in the investigation, with no mathematical manipulation having been carried out.

5.3.2.1 Cyanide Degradation

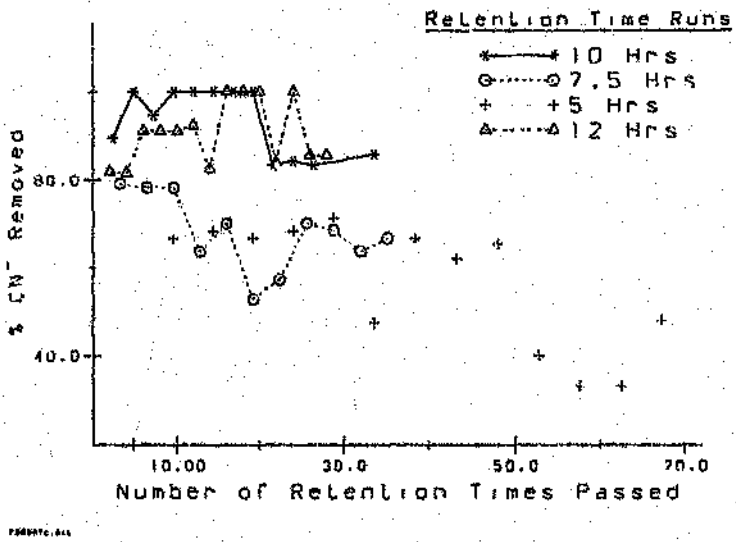


Figure 5.4 - FBR Cyanide Degradation

The following observations can be made from the above graph :

i) The 10 and 12 hour retention time runs produced the best results;

ii) The shorter the retention time, the less cyanide is removed from the system;

iii) Although the 10 hour retention time run displays very good removal of cyanide initially, this performance drops off towards the end, possibly indicating that after sometime the organisms are no longer able to cope with their task of cyanide degradation;

iv) The 5 hour retention time run shows a gradual decline in cyanide degradation. This could well be because of the rapid flow of cyanide through the reactor and therefore the inability of the organisms to degrade the given quantity of cyanide, and there by possibly killing off the organisms;

v) The 7.5 hour retention time run also gradually declines in performance;

vi) One might have expected that the 12 hour retention time run would be closer to removing 100% of the feed cyanide, more than the 10 hour run.

5.3.2.2 Thiocyanate Degradation

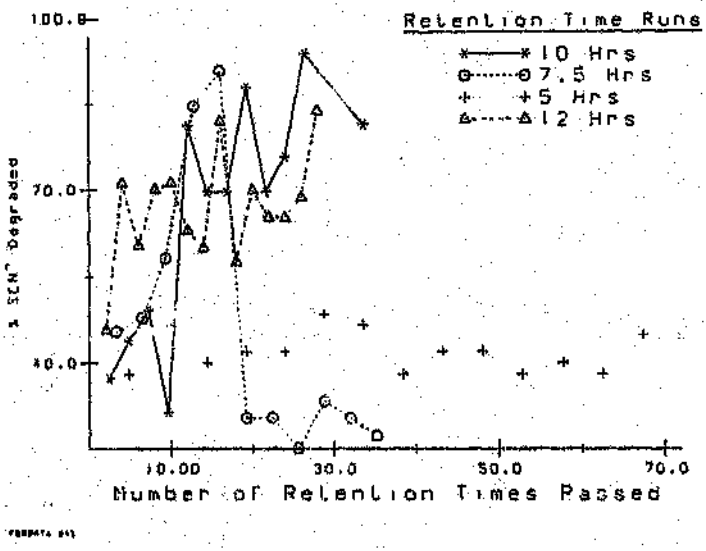


Figure 5.5 - FBR Thiocyanate Degradation

The following observations can be made from the graph on the following page :

i) The 10, 12 and 7.5 hour retention time runs all show erratic behaviour, with peaks and troughs, as with the 10 hour run at 9.6 retention time;

ii) The 5 hour retention time run displays reasonably smooth behaviour, especially compared to the others runs. This is also in contrast to the cyanide degradation curve for the 5 hour run;

iii) Comparing the average % degradation of the 10 and 12 hour retention time runs, the 12 hour run is marginally better at 66.7% with the 10 hour run at 65.9%;

iv) The 7.5 hour retention time run starts from an initial low to increase rapidly, only to drop off steeply again after its 91% peak, indicating that conditions could have been favourable initially. No equivalent behaviour is displayed by the cyanide degradation curve.

5.3.2.3 Total Cyanides Degradation

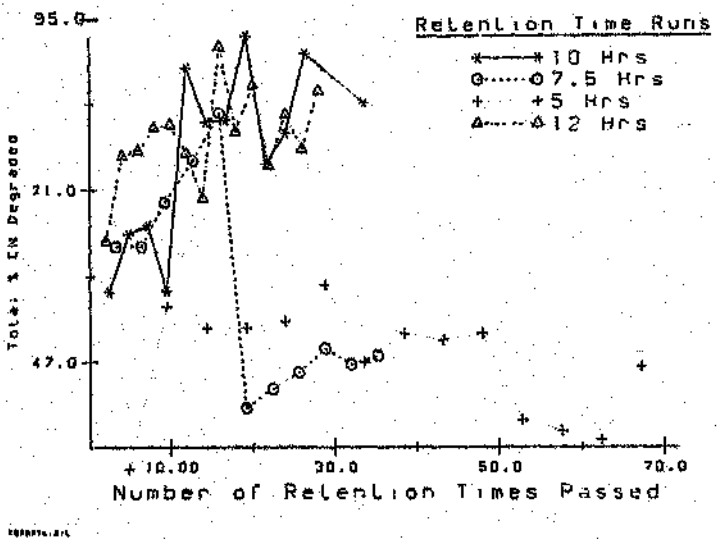


Figure 5.6 - FBR Total Cyanides Degradation

The following observations can be made from figure 5.6:

i) All 4 curves show erratic behaviour. Only the 5 hour retention time is more consistent than the others;

ii) Although the 10 hour retention time run appears to perform slightly better than the 12 hour retention time run, the average degradation for the 12 hour is better at 78.1% as compared to the 10 hour retention time run at 76% and also the data for the 12 hour retention time run are in a narrower band then the 10 hour run;

iii) The 5 hour retention time run displays a somewhat more erratic behaviour for thiocyanate than for cyanide degradation which therefore has a damping effect on the thiocyanate which then also results in the more damped total cyanide curve above.

5.3.2.4 Effects of Biomass Levels

Table 5.2 displays the biomass levels together with the levels of cyanide degraded.

Table 5.2 Biomass Concentrations in the FBR

Run No.	Avg. Biomass Concentration	Avg. % CN^- Degraded	Avg. % SCN^- Degraded	Avg. % Total CN^- Degraded	Retention Time
	mg/ℓ	%	%	%	Hrs
1	536	93.4	65.9	76.0	10
2	291	68.0	45.8	56.8	7.5
3	202	54.1	41.9	46.9	5
4	208	90.5	66.7	78.1	12

From the first 3 runs it would appear that decreasing the biomass levels decreases the total cyanide degradation. Then taking all 4 runs into account breaks down this theory as the biomass concentration for the 12 hour retention time run is at the lower end, very similar to the 5 hour run, but the degradation is the highest overall. No conclusion can be drawn as to the effect that biomass concentrations have on the degradation process.

5.3.2.5 Other Effects on Degradation in the FBR

As with the 4 hour retention time run on the CSTR, the 5 hour retention time run shows signs of increased degradation activity but the overall trend is decreasing as time passes. Again this could be indicating that the organisms' environment is at a constantly high level of cyanide, in fact it is increasing as degradation is decreasing.

These high levels of cyanide in the effluent stream are too high to adequately allow the given amount of biomass to effectively remove cyanide.
To what extent do dead organisms in the form of activated carbon, influence the biodegradation process or is it purely an activated carbon process taking place? The effect of activated carbon on the degradation of cyanides in waste water treatment will be considered at a later stage in this dissertation.

5.3.2.6 Biomass Support Particles

One experiment was briefly carried out with support particles that were larger (10 mm cubes as compared to 5 mm cubes) and had a more open structure, through which one could easily see.
It was found that hardly any biomass was retained in the particles, resulting in a negligible amount of cyanide removed. These results are displayed in table 5.3.

Table 5.3 - Results with larger Support Particles

	Biomass	Feed CN^-	Effluent CN^-	CN^- Removed
5 mm cubes	293 mg/l	30.5 mg/l	9.0 mg/l	70.5%
10 mm cubes	15 mg/l	28.5 mg/l	26.2 mg/l	8.1 %

As can be seen from the above values that the 10 mm cubes hold very much less biomass and therefore the cyanide removed by degradation would also be lower as indicated.

5.3.3 A Comparison between the CSTR and the FBR

Comparing the efficiencies of cyanide removal between the CSTR and the FBR, the runs with the most cyanide degraded for the two reactors were compared. When looking at the various cyanide degradations percentages, the different reactors performed differently depending on which degradation product is being analysed. Therefore the total cyanide is the most important degradation product to use as an overall efficiency criteria, as this takes into account both cyanide and thiocyanate and the fact that the legal limit is defined as total cyanide.

The individual cyanide degradation percentages and the overall efficiency of cyanide removed is displayed in table 5.4.

Table 5.4 - Comparison between the CSTR and the FBR

Reactor Type	CSTR	FBR	
Retention Time	10 hrs	10 hrs	12 hrs
Avg. % CN^- Degraded	99.3	93.4	90.5
Avg. % SCN^- Degraded	88.6	65.9	66.7
Avg. % total CN^- Degraded	92.8	76.0	78.1
CN^- levels in effluent	5.6 mg/ℓ	32 mg/ℓ	15.1 mg/ℓ
Biomass Conc.	550 mg/ℓ	536 mg/ℓ	208 mg/ℓ

In table 5.4 there are 2 runs depicted for the FBR, the 10 and 12 hour retention time runs. Comparing the individual cyanide percentages degraded, on cyanide the 10 hour run performs better than the 12 hour, but on thiocyanate the 12 hour run performs marginally better than the 10 hour run. Consequently, no significant conclusion can be drawn on the FBR. This is despite the difference in the biomass concentrations for the two runs.

The fact that the biomass concentrations are different and the levels of removal are

being achieved could possibly suggest that absorption and/or reactions with cyanides could be important removal mechanisms which would be an unexpected result to this investigation.

Table 5.5 - Concentration Comparison between the CSTR and the FBR

Reactor Type	CSTR	FBR	
Retention Time	10 hrs	10 hrs	12 hrs
CN^- levels in feed	77.5 mg/ℓ	133.6 mg/ℓ	69.1 mg/ℓ
CN^- levels in effluent	5.6 mg/ℓ	32 mg/ℓ	15.1 mg/ℓ
CN^- Removed	92.8 %	76 %	78.1 %
Biomass Conc.	550 mg/ℓ	536 mg/ℓ	208 mg/ℓ

From table 5.5 the first and most noticeable observation that can be made is that the CSTR was more successful in removing the cyanides as compared to the FBR. (Note that the toxic effect of cyanide was not considered.) This is evident from two different parameters; Firstly, the most important parameter is the concentration of cyanide remaining in the effluent stream after treatment. This is required by law to be less than 0.5 mg/ℓ. Therefore neither of the reactors has performed satisfactorily to remove the required amount of cyanide from the effluent stream under the experimental conditions used here. However the CSTR did the best job under the circumstances to remove all but 5.6 mg/ℓ of the cyanide present. Comparatively the FBR did not perform well at all and left as much as 32 mg/ℓ of cyanides in the effluent stream.

Secondly, the percentage of the total cyanide removed for a given retention time shows that the CSTR degraded 92.8% of the feed compared to only 76% in the FBR with similar biomass concentrations.

From the table above one notices that the effluent cyanide concentration would appear to be dependant on the feed concentration, disregarding the biomass concentration in the reactor.

One would have expected that the effluent concentration would be lower with the higher biomass concentration but this is not the case. This would tend to suggest that there maybe another form of cyanide removal taking place which may dependant on biomass concentration as the proportion of cyanide removed is the same is either case (76% and 78% removal respectively). However this was not verified by any independent experimentation as this observation was only made afterwards.

To conclude then, the CSTR out performed the FBR in all aspects considered but by no means performed to meet effluent regulations. From the results obtained it is clear that more detailed investigations are required to determine the optimal retention time for the CSTR and whether or not the FBR is capable of performing to similar standards of removal, thus making the FBR a feasible alternative worth considering. The aspect of cyanide absorption by organisms would require some further investigative work beyond this dissertation.

Comparing the retention times required to achieve the maximum allowable level of cyanide in the effluent stream, table 5.6 compares the CSTR and the FBR retention times required. These values were calculated by linear extrapolation to 100% removal.

Table 5.6 - Estimated Required Retention Times for the CSTR and FBR

	Retention Time Required
CSTR	ca. 12 hrs †
FBR	ca. 15 hrs †

† For maximum limit = 0.5 mg/l, measured as total cyanide.

These times were calculated based on the average trend of dilution rate against effluent cyanide concentration. It should be noted that these values are only an estimate as to the expected retention time required to achieve the required maximum limit.

These values however do show that the CSTR requires a shorter time than the FBR to achieve the same degree of cyanide degradation.

5.3.4 A Kinetic Model for the CSTR and the FBR

Taking the comparison between the CSTR and the FBR a step further, would be to use a simple kinetic model to describe the performance of the CSTR and the FBR, Bailey and Ollis (1986) show in their discussions on waste water treatment, that the simple Monod expression can be used to model activated sludge processes.

A CSTR has been described by various authors using the Monod model. One needs to include a term to define the death rate and endogenous metabolism of the organisms, hence equation (3.1) is used. The substrate terms are used as measured values of total cyanide and not as BOD values of substrate.

To solve the Monod equation parameters, one needs to solve the mass balance equation [equation (3.4)], which contains the Monod expression [equation (3.1)]. In order to solve for the 3 parameters, the Simplex routine was utilised as the solving algorithm. First the 2 parameters were solved to facilitate an initial estimate of the parameter values. Finally the 3 parameters were solved and are recorded in table 5.7. Calculations may be found in appendix A.

Table 5.7 - CSTR Kinetic Parameters

	2 Parameter Monod Model	3 Parameter Monod Model Variation
μ_{max}	3.9266 /hr	3.926456 /hr
K_s	0.006106 mg/ℓ	0.006048 mg/ℓ
k_e	-	-0.000052 /hr

From these results the following can be concluded :

i) A negative parameter for endogenous metabolism and death rate, would not be possible with a system containing live and active organisms;

ii) The negative parameter indicates that substrate (cyanide) is not used for metabolic growth and maintenance and organisms are dying off. In fact it could indicate that cyanide is being produced, which is highly unlikely;

iii) The similarity of the first two parameters in the two models supports the result that $k_e \rightarrow 0$, which we know can not be the case as cyanide is the only substrate present in the feed. The organisms would require some substrate to maintain their existence.

5.3.4.1 The CSTR and the Monod Kinetic Model

As can be seen from the various cyanide degradation figures for the CSTR and the FBR, the results are not fitted to a model, but are joined by points indicating which retention time gave the best degradation of cyanides. Tables 5.8 show the levels of total cyanides removed for each of the various retention time runs for the CSTR.

The average kinetic removal efficiencies that the Monod model predicts should be achievable with the parameters from table 5.7 for the investigated retention times, are compared against the actual average removal efficiency achieved in table 5.9.

Table 5.8 - Actual Cyanide Removal Data for the CSTR

% Total Cyanide Degraded	Retention Times [hrs]					
	10	7.5	7	5	5	4
	84.4%	45.7%	67.0%	69.1%	77.5%	68.0%
	93.6%	66.8%	68.4%	71.1%	74.1%	63.6%
	93.6%	80.0%	73.2%	67.0%	77.3%	60.7%
	93.7%	53.3%	76.9%	69.7%	77.5%	63.7%
	93.6%	64.3%	80.2%	68.4%	78.5%	59.2%
	93.0%	81.9%	79.1%	64.5%	77.1%	56.4%
	93.1%	80.0%	78.2%	62.7%	75.9%	57.7%
	93.0%	69.8%		60.1%	75.5%	42.8%
	93.1%	73.4%			75.9%	
	93.0%					
	93.0%					
	96.4%					
Avg	92.3%	68.4%	74.7%	66.6%	76.6%	59.0%

Table 5.9 - Actual vs Kinetic Degradation Removal for the CSTR

	Retention Times					
	10	7.5	7	6	5	4
Actual	92.3%	68.4%	74.7%	66.6%	76.6%	59.0%
Kinetic	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%

According to the Monod kinetic model 100% of all cyanide should be removed in the CSTR under the retention times employed in this investigation. The actual values presented in table 5.8 indicate otherwise. This clearly shows that the Monod kinetic model does not adequately describe the cyanide removal process in the CSTR.

As the kinetic model for the CSTR failed, no further attempt was made to use it to describe the FBR as no suitable comparison would then exist.

5.3.4.2 Why Would the Monod Kinetic Model Fail ?

If the organisms were killed off with the introduction of cyanide into the system, the Monod model without the combined death rate and endogenous metabolism term could easily be solved and values for the substrate or final reactant concentration and system parameters would yield similar results.

Therefore from the table and comments above of kinetic parameter values, the process of cyanide removal being a non-biological mechanism is strongly supported. Again the possibility of cyanide absorption by dead organisms could be very likely.

Based on the results of the CSTR it was decided not to kinetically model the FBR as a comparison on that basis would be meaningless.

Therefore to conclude:

i) Using a kinetic model like Monod's is not possible as it would appear that the system is not entirely, if at all, biodegrading cyanides, and

ii) that another form of cyanide removal could possibly be taking place preferentially.

5.4 Absorption of Cyanides onto Microorganisms

In the light of all the results presented up till now, there would appear to be another form of cyanide removal taking place instead of those originally thought, ie.. biodegradation of cyanides.

At the end of experimentation a brief test was carried out to determine the extent of absorption, using the organisms that were heated to 140°C to ensure that all the organisms were dead. This was a convenient time as the organisms (should there be any alive), could be killed off as they were no longer required.

The question however still remains as to the exact reason for the possible dying off of the organisms. There could be two possible reasons :

* The first and most obvious one is the fact that cyanide is highly toxic to most living organisms. The toxic effect would have the result of killing off those microorganisms which do not have a resistance to cyanide. Hardly any literature that was surveyed made mention of the toxic effect;
* The second reason for dead microorganisms is the natural cycle the bacteria go through. They become old and are unable to sustain an active metabolism.

The resulting dead organisms are essentially composed of carbon and hence show very similar characteristics to that of activated carbon. Cyanide has been found to be readily absorbed by activated carbon {Adams (1990)}. Hence the suggestion that dead microorganisms exhibit similar characteristics as activated carbon to cyanide absorption. Raef et al (1977) mentions that treating the waste with anaerobic process solids first, allowed the aerobic process to treat the sludge further without being affected by cyanide toxins. They indicated that absorption by digester solids may be a possible mechanism of cyanide removal.

5.4.1 Cyanide losses in a Dead Microorganism System

Table 5.10 shows how the dead microorganisms appear to have absorbed and oxidised most of the cyanide in the feed. This experiment was done by taking a known volume of activated sludge and heating it to render all the microorganisms dead. All the dead microorganism were then assumed to behave similar to activated carbon. These dead organisms were then used as the "activated sludge" in the CSTR system for a run under the same conditions as the other CSTR runs.

Table 5.10 - Cyanide Levels in a CSTR containing Dead Microorganisms

	Feed	Effluent	Absorber	Absorbed / Evolved / Oxidised
Average	55.1 mg/ℓ	0.4 mg/ℓ	1.56 mg/ℓ	54.7 mg/ℓ
Total	199.9 mg	1.54 mg	0.22 mg	198.14 mg
			Total CN^- removed =	198.14 mg
			=	99.1%

From table 5.10, it is clear that the cyanide in the CSTR was absorbed and oxidised by the dead organisms and that virtually no cyanide (0.22 mg) was released into the air stream as indicated by the air stripping test (section 5.2). The CSTR system was operated as per normal experimental conditions.

Therefore it can be concluded that the 'activated carbon' effect is significant in the removal of cyanides from waste waters. From the paper by Adams (1990), the effect of cyanide volatilisation is small, accounting for some 5% of the cyanide removal in the experimentation that Adams (1990) undertook. If we therefore take this into account and propose that the cyanide is oxidised to form cyanates in the presence of

a carbon catalyst, then the extent of the cyanide removed from the system will fall in line with Adams conclusions.
The agitation of the activated carbon mass results in the suspension of the dead microorganisms, which increases the surface area available for oxidation and absorption {Muir et al (1988)}.

Based on these results, the cyanide present in the reactors system is unlikely to be HCN as the oxidation effect of the dead microorganisms would oxidise most of the cyanide to cyanates before the hydrolysis reaction of cyanide and water can produce HCN (a very slow reaction at ambient temperatures). Therefore the statement made earlier that the cyanide in the reactors is in the form of HCN is not correct when proposing that cyanide removal is taking place by oxidative reactions and absorption.

Hence should a large portion of the microorganisms in the CSTR system be dead, a large amount of cyanide will be oxidised by and absorbed onto the activated carbon and the biodegradation results would appear better than they actually are.

The determination of the proportion of dead microorganisms to live microorganisms and the analysis of cyanates in the reactors, was not carried out as the possible absorption aspect was an unexpected result and its possible role only proposed after final experimentation was complete.

The results for the dead microorganisms tests may be found in appendix D.

5.4.2 Batch Absorption Tests

Batch absorption test were carried out to determine how quickly the cyanide might be absorbed onto the dead microorganisms. It was assumed that the absorption of cyanide follows a first order process under any given set of conditions and is true for

all cyanide loss reactions taking place {Adams (1990)} and therefore equation. (3.11) was used. The operating conditions for these experiments were the same for all three batch. Only the biomass concentrations and initial cyanide concentrations were altered.

Plotting the semi-logarithmic curve of the cyanide concentration with time, yields the first order rate constant k_1 as the slope. The data and results may be found in appendix D. Table 5.11 summaries the values for the three batch runs undertaken.

Table 5.11 - First Order Rate Constant

	Biomass [mg]	$[CN^-]_0$ [mg/ℓ]	$[CN^-]_t$ [mg/ℓ]	% CN^- Removal	k_1 [/hr]
	264	90.51	1.54	98.3 %	0.09
	672	100.66	1.39	98.6 %	0.10
	1504	119.13	1.39	98.8 %	0.22
Ave	813.33	103.43	1.44	0.99	0.14

From table 5.11, the higher biomass concentration yielded a higher rate constant, as would be expected. The absorption constant increases with the increase in biomass level. However as the results for cyanide removal show very little variation, no significant conclusion can be drawn as to the effect of biomass concentration on the absorption of cyanide by dead microorganisms.

Plotting the curves of the cyanide concentrations changes with time for each of the batch tests, all on one graph, results in figure 5.7:

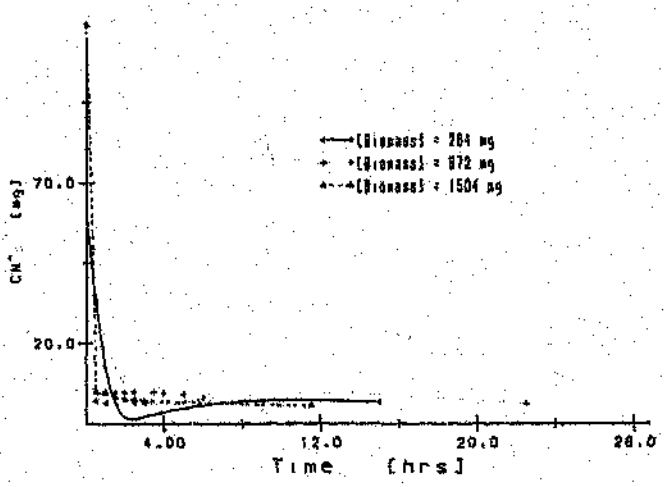


Figure 5.7 - Absorption of Cyanide in Batch Runs

The most striking aspect of the above figure (5.7) is the behaviour of each of the curves levelling out to approximately the same final cyanide concentration level. This indicates that the cyanide concentration achieves an equilibrium concentration at around the 1.44 mg/ℓ level, regardless of the initial cyanide or biomass concentrations. Most of the cyanide is absorbed very rapidly at the beginning, as indicated by the steep slope of the initial part of the curve.

Increasing the biomass concentration to excess levels might well result in a higher equilibrium concentration of cyanide.

Actual results may be found in appendix D.

5.4.3 CSTR Absorption Results

Using the results obtained for the CSTR under the "biodegradation" experiments, the results were analysed using the approach that biodegradation was not occurring but absorption and oxidation was.

Solving for the first order rate constant for absorption in the CSTR system using the Simplex routine again, the following value is obtained :

First Order Rate Constant	0.37 /hr

Changing the dilution rate or retention time of the CSTR system, changes the rate at which cyanides are removed from the system. Therefore the rate constant gives an indication of the expected cyanide removal as a function of time. This may be represented by the following graph :

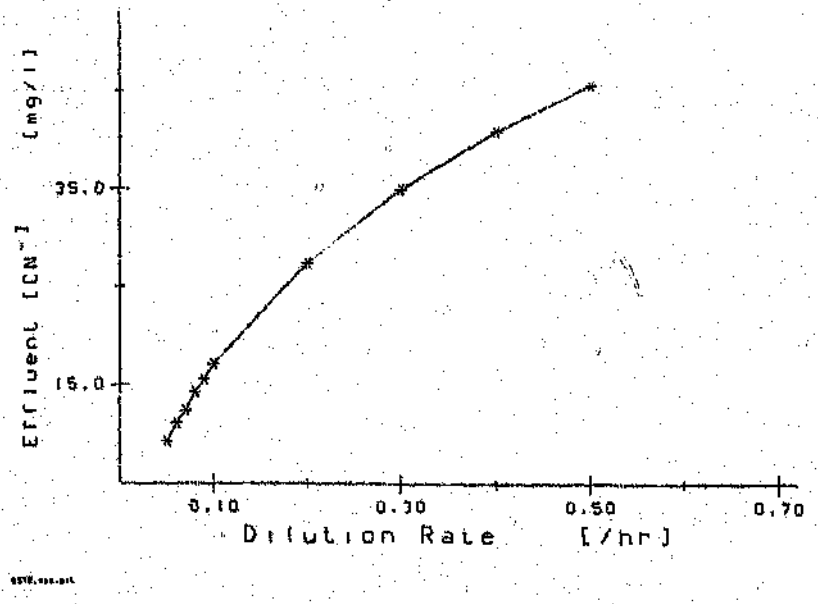


Figure 5.8 - CSTR - Cyanide Removal with Time

As can be seen from the curve, the longer the retention time (lower dilution rate) the more cyanide can be removed from the system. This follows the line that the more time available for absorption/oxidation, the more will be removed via these

mechanisms. To attain the minimum required by law (0.5 mg/l), the dilution rate required is 0.0024/hr , which equates to a retention time of 423 hrs, a rather long retention time.

5.4.4 FBR Absorption Results

Solving for the first order rate constant for absorption in the FBR using the Simplex routine again, the following value is obtained :

First Order Rate Constant	0.23 /hr

A similar result for the FBR is presented, though a lower rate of absorption than that of the CSTR. The graph on the following depicts the nature of the curve which has a very similar characteristic as the curve for the CSTR.

Again the longer the retention time (lower dilution rate) the greater the cyanide removal. To meet the government specifications, a dilution rate of 0.001 /hr is required, which equates to a retention time of approximately 780 hrs.

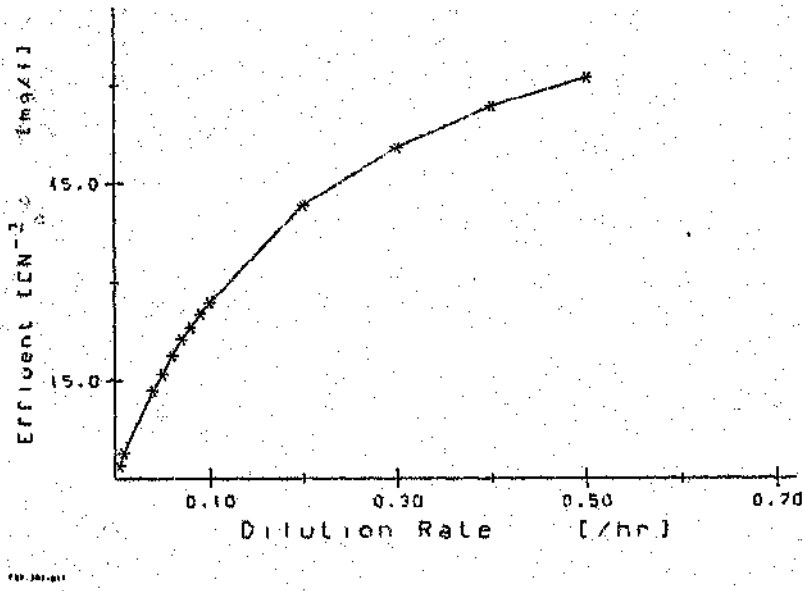


Figure 5.9 - FBR - Cyanide Removal with Time

5.4.5 Comparison of the Absorption Results

Comparing the rate constant for absorption for the two reactors, the CSTR still out performs the FBR and taking into account the retention times required for the required cyanide removal from the waste water stream, which are very long indeed and not really practical.

Looking at the two reactors from a macroscopic point of view, the biomass in the CSTR is in a mixed free suspension, which will increase the available surface area for reaction/absorption significantly more, as compared to the FBR's support particles. The support particles in the FBR are possibly restricting the available surface area for reaction/absorption by restricting the flow of cyanide into the particle sufficiently to

enable the removal reactions to take place.

5.5 Comparison between Cyanide Absorption and Biodegradation

Comparing the effect of biodegradation and absorption/oxidation as cyanide removal mechanisms, the factor that can be used is the retention times required to achieve the maximum legal limit for cyanides in any effluent stream. As no other parameters were measured this is the only feasible parameter to look into.

It is not 100 percent clear yet as to which process is the most likely to have taken place as certain measurements were not carried out at the time of experimentation as it was not anticipated that absorption/oxidation would be the possible removal process to biodegradation. The fact that the reactors were not fed anything else other than cyanides, ie. no additional nutrients or trace elements, might lead one to say that biodegradation was unlikely to occur and microorganisms could not survive in an environment without these elements. Also the toxic effect of cyanides on living organisms can be detrimental to a number of activated sludge microorganisms.

Table 5.12 gives a summary of the two alternative processes and the retention times required.

Table 5.12 - Comparison of Absorption/Oxidation and Biodegradation

Retention Times Required		
	Absorption/Oxidation	**Biodegradation**
CSTR	423 hrs	ca. 12 hrs
FBR	780 hrs	ca. 15 hrs

How believable the absorption/oxidation retention times are is questionable. The method used to determine the required retention times differ here. The absorption times are based on the first order rate constant for absorption/oxidation as defined by Adams (1990) and the biodegradation values are calculated by plotting a second order polynomial through the points of the dilution rates against the effluent cyanide concentrations.

Using the same technique for the absorption/oxidation retention times the following retention times result :

Table 5.13 - Estimated Retention Time for Absorption/Oxidation & Biodegradation

Estimated Retention Times Required		
	Absorption/Oxidation	Biodegradation
CSTR	22 hrs	11 hrs
FBR	58 hrs	15 hrs

These values are more realistic for absorption/oxidation than the values in table 5.12. These values show that the biodegradation is the more efficient process in terms of the time required to achieve the same goal. in both cases (absorption versus biodegradation) the CSTR would fare better than the FBR, noticeably so in the absorption/oxidation case. The difference in times for the biodegradation is not as marked.

These results would indicate that the expression for the first order absorption rate does not hold true at lower dilution rate (longer retention times). This could give rise to the very long retention times required for removal. Therefore the above values were calculated from the fitting of a second order polynomial to the values calculated using the rate constant over the retention times investigated.

This then also brings the cut off points for the first order rate constant into question as to where these lie.

5.6 Comparison of Reactors

The comparison of the two reactors was carried out using a technique used by Eckenfelder. The inverse of the sludge age and the effluent concentration of the cyanides were plotted against the sludge loading rate for the two reactors. The resultant graph is shown in figure 5.10:

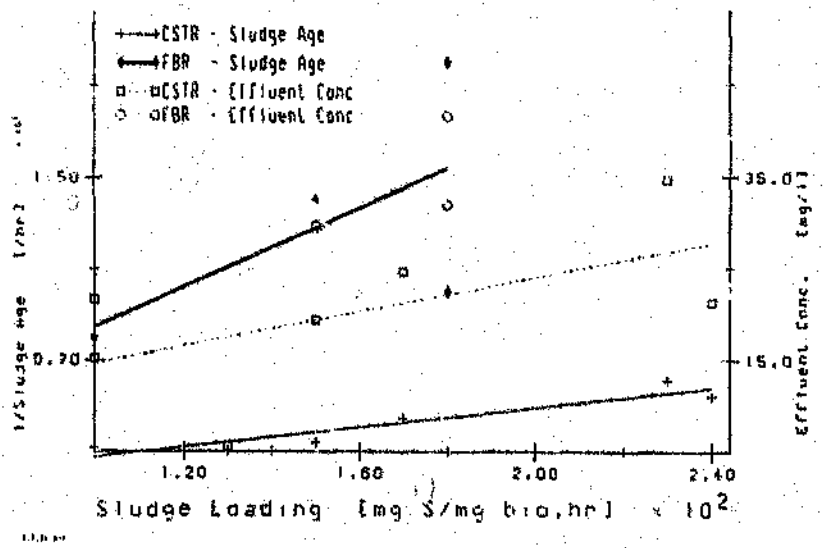


Figure 5.10 - Comparison of Reactors

The graph shows a general tendency for the FBR to have steeper slopes than the CSTR for the inverse sludge age and the effluent concentration of cyanides as a function of the sludge loading rate.

5.6.1 Sludge Age Comparison

From the graph it can be seen that the sludge age in the CSTR is longer than that for the FBR. This would allow the "biodegradation" process to tend to greater completion of its task of removing cyanides present in the waste water.
It is also noted that as the sludge loading rate increases, the sludge age becomes shorter (the inverse of the sludge age is increasing).

5.6.2 Effluent Concentration Comparison

From the graph it can be clearly seen that the effluent concentration of cyanides increases as the sludge loading rate increases. This means that the cyanide removing capabilities of the biomass decrease as the sludge loading rate increases. The CSTR is able to remove more cyanides for given sludge loading rate than the FBR.
The slope of the FBR effluent concentration curve is much steeper than the slope of the CSTR effluent concentration curve.

	FBR	CSTR
Slope	2702.8	937.4

This shows that the slope of the FBR curve is 2.88 times greater as compared to the CSTR curve. This would indicate that the FBR is a less efficient reactor for the utilisation of incoming substrate or the biodegradation of cyanides present in waste waters.

6 Conclusion

The investigation into the biodegradation of cyanides in a CSTR and FBR yielded an interesting result in that cyanides are not necessarily being removed by biological degradation only but by an oxidative reaction in the presence of a catalyst and absorbed onto a suitable substrate, namely activated carbon or dead microorganisms. Though it can not be categorically proven that oxidation and absorption are taking place and not biodegradation, or for that matter a combination of the all 3 processes, the results would tend to indicate that the absorption/oxidation mechanisms are more likely route for cyanides removal.

The results also show that there is a lot of potential for the FBR. Specifically for the FBR using biomass support particles to contain the active agent for cyanide removal, even though not much emphasis was placed on this aspect of the investigation.

From the biodegradation results the CSTR proved to be the better cyanide removing reactor, requiring only an estimated 12 hours to remove cyanides to the legal limit of 0.5 mg/ℓ, as compared to the 15 hours for the FBR. Describing the CSTR using the Monod kinetic model under these condition proved unsuccessful with the determining of a negative parameter for the combined death rate and endogenous metabolism of microorganisms. As a result it was decided not to continue and try to describe the FBR for comparative purposes using kinetics.

The results presented for the absorption/oxidation of cyanides in the CSTR and FBR showed that although removal of cyanide initially is high, much higher than the biodegradation, the decrease in this removal rate proved to be a problem when the concentrations of cyanides became low, as a very long retention time was then

required to reduce the concentrations to the legal limit. It was also shown that using the rate constant to determine the retention time (or dilution rate required for the removal of the remaining cyanides), does not satisfactorily describe the removal process, as a retention time of approximately 40 times the investigated times would be required. This becomes unrealistic when compared to the biodegradation retention times required. To determine the required retention times for the two removal processes, a second order polynomial fit was used on the data to achieve an 12 hour retention time for the biodegradation and 22 hours for the absorption/oxidation processes in the CSTR.

In comparison the FBR required a 58 hour retention time for absorption/oxidation as compare : to only 15 hours for biodegradation.

This highlighted another aspect of the first order rate constant for absorption/oxidation as to the regime in which it applies, ie. what are the boundaries in terms of retention times.

From the approach used by Eckenfelder to compare two reactors, the CSTR showed to be the better than the FBR. The CSTR operated under lower sludge loading rates as compared to the FBR, thereby making it less susceptible to variations in the feed concentration of cyanides.

Therefore, despite not knowing exactly which process is taking place in the CSTR and the FBR, the CSTR still proved to be the better cyanides remover. However the FBR should not be discarded as an unsuitable reactor as it is felt that more investigative work is required to prove the final effectiveness of the reactor.

7 Recommendations for Further Investigations

Based on the interesting results discovered in this investigation about the possible mechanisms of cyanide removal, an even larger field exists for future research and investigations. There are many aspects that could be looked into, specifically in the biodegradation and absorption/oxidation fields of cyanide removal, with possible implications for the treatment of waste waters in general.

i) Probably the most obvious area for immediate investigation is the extent to which the biodegradation and absorption/oxidative processes are taking place simultaneously in both a CSTR and FBR (with support particles). Are sufficient microorganisms able to survive in the cyanide environment to be able to actively degrade cyanide and those microorganisms which do not survive and hence form the activated carbon portion of the particles in the system? To what extent do these dead microorganisms absorb cyanide and catalyse oxidative reactions, thereby contributing to the overall cyanide removal process?

ii) The FBR should by no means be discarded as an unsuitable reactor for waste water treatment. The physical parameters and operating conditions for the optimal running of the FBR for cyanide removal should be investigated more closely, specifically the number and size of support particles. Improvements in the design of the reactor should not be ignored.

iii) The size of the particles should not be very much larger than the ones used in this investigation, viz. 5 mm cubes. The larger the particle, the

more difficult the containment of the microorganisms.

What structure will increase the available surface area for reaction and therefore the flow of solution through the particle to feed the microorganisms or activated carbon particles? A structure that is too open will cause the microorganisms to be washed out as the flow of cyanide solution through the particle will be very much more turbulent. Hence the shear rates on the microorganisms is higher and they are unable to remain attached to the particle surfaces.

iv) The use of other alternative for the suspension and containment of the biomass on particles within a reactor. A Norwegian company 'Kaldnes' has developed a reactor system for the treatment of waste waters using a support particle consisting of small cross sectioned extruded plastic piping. This eliminated loss of biomass film due to friction in the turbulent environment of the FBR and also provided enough surface area for the biomass to grow and receive the required nutrients and substrates. Therefore the use of the a similar type of support particles could improve the performance of the FBR {Kaldnes (1996)}.

v) The applicable regime where the first order rate constant for absorption and oxidation mechanisms for cyanide removal in a CSTR and FBR should be investigated.

References

1. Adams M. D., (1990), " **The chemical behaviour of cyanide in the extraction of gold - Part 1&2** ", J. S. Afr. Inst. Min. Metall., vol 90, no. 2, pp 37-44.
2. Adams M. D., (1992), " **The removal of cyanide from aqueous solution by the use of ferrous sulphate**", J. S. Afr. Inst. Min. Metali., vol 92, no 1, pp 17-25.
3. Alabama Univ. in Birmingham, (1983)," **Adaptation of an Activated sludge process to the treatment of Coke-plant waste water containing high levels of cyanide** ", Bureau of Reclamation, Washington DC.
4. Atkinson A., (1975), " **Bacterial cyanide detoxification** ", Biotechnology and Bioengineering, vol 17, pp 457.
5. Atkinson B., Black G. & Pinches A., (1981), " **The characteristics of solid support and biomass support particles when used in Fluidised Beds** ", Cooper P. & Atkinson B. (eds) In: Biological Fluidised Bed Treatment of Water and Waste Water, pp 75, Ellis Horwood, Chichester.
6. Atkinson B, Cunningham J. D., Pinches A., May (1984), " **Biomass Hold-up and Overall Rates of Substrate (glucose) Uptake of Support Particles containing a mixed Microbial Culture** ", Chem Eng Res Des, Vol . 62,.
7. Babu G.R.V, Wolfram J. H., & Chapatwala K.D., (1992), " **Conversion of sodium cyanide to carbon dioxide and ammonia by immobilized cells of *Pseudomonas putida*** ", J. Ind. Microbiology, 9, pp 235-238.
8. Bailey J. & Ollis D., (1986), " **Biochemical Engineering Fundamentals** ", Mc Graw Hill.
9. Broadhurst J., Nov (1990), " **Literature survey and evaluation of processes for the removal of cyanide and thiocyanate from effluent streams** ", GENMIN Process Research.

10. Cooper P. F. & Wheeldon D. H. V (1980), " **Fluidised- and Expanded-Bed reactors for waste water treatment** ", Wat. Pollut. Control, pp 286-301.

11. Curi K. & Eckenfelder W. W. Jr., (1980), **"Theory and Practice of Biological Wastewater Treatment"**, Series E, pp 105-119, Sijhoff & Noordhoff, Netherlands.

12. Donaldson T. L., June (1983), " **Fixed-Film, Fluidised-Bed Bio-reactors for Bio-oxidation of Coal Conversion Waste Waters** ", 3rd Biennial Synfuels Waste Wat. Workshop, West Virginia.

13. Eckenfelder W. W. Jr., (1966), **"Industrial Water Pollution Control"**, McGraw-Hill.

14. Eckenfelder W. W., (1970), **"Water Quality Engineering for Practicing Engineers"**, Cahners Int., Boston, pp 163,164,179-183.

15. Ekama G. A., Pitman A. R., Smollen M., Marais G.vR., (1984), " **Secondary Settling Tanks** ", Theory, Design and operation of nutrient removal activated sludge processes, Ch 8, Water research Commission, pp 8.1 - 8.14.

16. Finnegan I., Toerien S., Abbott L. & Raubenheimer H., " **Precipitation of Gold Cyanide from Dicyanoaurate solution by an acinetobacter sp** ", RAU - Dept. Chemistry & Biochemistry

17. Ganczarczyk J. & Elion D., May (1978), " **Extended Aeration of Coke-Plant Effluent** ", Paper 33rd Purdue Ind. Waste Wat. Conf., Purdue Univ., Indiana.

18. Gaudy A. F., Gaudy E. T., Feng Y. J. & Brueggemann G., Feb (1982), **"Treatment of cyanide waste by the extended aeration process "**, Journal WPCF, pp 153-164.

19. Germain J. E. & Patterson K. E., (1974), " **Plating and Cyanide Wastes** ", Journal WPCF, vol 46., no. 6, pp 1301-1315.

20. Gerrard A. M. & Stephenson T., Nov (1990), " **Some economic targets for inoculum enhanced activated sludge processes** ", Trans. IChemE, vol 68, Part B, pp 269-272.

21. Gokool P., (1990), " **Biological Degradation of Cyanide** ", Biotechnology Div., Research & Development dept., NCP.

22. Government Gazette, (1984), " **Vol (1), No. 991, pp. 9225, May 1984** ".

23. Grau P. et al, (1987), " **Notation for use in the Description of Waste Water Processes** ", Water Research, Vol 21, No 2, pp 135-139.

24. Hedley N. & Tabachnick H., Dec (1968), " **Chemistry of Cyanidation**", Mineral Dressing Notes, American Cyanamid Company, No 23.

25. Howe R., (1965), " **Bio-destruction of cyanide waste - advantages and disadvantages** ", Int. J. Air Wat. Poll., Pergamon Press, pp 463-478.

26. Kaldnes, Spring (1996), "**How the Moving Bed Evolved**", Int. Environment & Safety News, Vol 14, No 1, pp 11.

27. Kostenbader P. D. & Flecksteiner J. W., Feb (1969), " **Biological Oxidation of coke plant weak ammonia Liquor** ", Journal WPCF, vol 41, no 2, part 1, pp 199-207.

28. Luthy R. G., Mar (1981), " **Treatment of coal coking and coal gasification waste waters** ", Journal WPCF, vol 52, no 3, pp 325-339.

29. Luthy R. G., Bruce S. G., Walters R. W. & Nakles D. V., Sept (1979), **"Cyanide and thiocyanate in coal gasification waste waters** ", Journal WPCF, vol 51, no 9, pp 2267-2281.

30. Ludzack F. J., June (1960), " **Laboratory model activated sludge unit** ", Journal WPCF, vol 32, no 6, pp 605-609.

31. Ludzack F. & Schaffer R., " **Activated sludge treatment of cyanide, cyanate and thiocyanate** ", Proc 15th Ind. Waste Conf., Purgen Univ., pp 439-460.

32. Melcer H., Nutt S., Marvan I., Sutton P.,, Feb. (1984), " **Combined**

treatment of cake plant waste water and blast furnace blowdown water in a coupled biological Fluidised Bed System ", Journal WPCF, Vol. 56, No 2.

33. Meyers P. R., Gokool P., Rawlings D. E., Woods D. R., (1991), " **An Efficient Cyanide-degrading *Bacillus pumilus* strain** ", Journal of General Microbiology, vol. 137, pp 1397-1400.

34. Moser A., (1988), " **Bioprocess Technology** ", Springer Verlag.

35. Mudder T. & Whitlock J., Aug (1984), " **Biological treatment of Cyanidation Waste Waters** ", Homestake Mining Co. Lead, South Dakota.

36. Muir D. M., Aziz M., Hoecker W., (1998), " **Cyanide losses under C.I.P conditions and effect of carbon on cyanide oxidation** ", Proc. Ist Internat. Conf. on Hydrometallurgy (ICHM '88), Eds Zheng Yulian & Xu Jiazhong, int Academic Publishers.

37. Nutt S. G., Melcer H., Pries J. H., July (1984), " **Two-stage biological fluidised bed treatment of coke plant waste water for Nitrogen control** ", Journal WPCF, Vol 56, No 7.

38. Osseo-Asare K., Xue T. & Ciminelli V. S. T., " **Solution chemistry of cyanide leaching systems** ", supplied by MINTEK, pp 173-197.

39. Paruchuri Y. L., Shivaraman N., Kumaran P., (1990), " **Microbial Transformation of Thiocyanate** ", Environmental pollution, Vol 68, pp 15-28.

40. Pettit A. E. J.& Mills E. V., Aug (1954), " **Biological treatment of cyanides, with and without sewage** ", J. appl. chem., 4, pp 434-444.

41. Pohlandt-Watson C. & Jones E. A., Oct (1990), " **Historical, analytical and environmental aspects of the Cyanide process in South Africa** ", ChemSA, pp 267-269.

42. Porter A. J. & Dutch P. H., June (1960), " **Phenol-cyanide removal in a**

plastic-packed trickling filter ", Journal WPCF, vol 32, no 6, pp 622-631.

43. Pujol R & Canler J. P., (1992), ' **Biosorption and Dynamics of Bacterial Populations in Activated Sludge** ", Water research, Vol 26, No 2, pp 209-212.

44. Raef S. F., Characklis W. G., Kessick M. A. & Ward C. H., (1977), " **Fate of cyanide and related compounds in aerobic microbial systems Part I & II**", Water Research, vol 2, Pergamon Press, pp 477-492.

45. Richards D. & Shieh W., (1989), " **Anoxic-Oxic activated sludge treatment of cyanide and phenols** ", Biotechnology & Bioengineering, vol 33, Wiley & Sons, pp 32-38.

46. Schiller J. E., (1983), " **Removal of cyanide and metals from mineral processing waste waters** ", Bureau of Mines Report of Investigation, United States Department of the Interior.

47. Shivaraman N., et al, (1985), " **Microbial Degradation of Thiocyanate, Phenol and Cyanide in a Completely Mixed Aeration System** ", Environmental Pollution (Series A), vol 39, pp 141-150.

48. Shivaraman N., et al, " **Cyanide and Thiocyanate removal from LTC Waste Waters** ", Asian Environment, pp 10-15.

49. Shivaraman N. & Parhad N., (1984), " **Biodegradation of Cyanide in a Continuously Fed Aerobic System** ", J. Enviro. Biol., vol 5, no 4, pp 273-284.

50. Tischler L. F. & Eckenfelder W. W., (1969), " **Linear Substrate removal in the activated sludge process**", In Advances in Water Pollution Research, 361, Pergamon Press, Oxford, England.

51. Trautman L. & Owen R., " **Cyanide removal test work at Homestake Gold Mine** ", Homestake Gold Mine.

52. Vergunst R. D. et al, " **Heap pad detoxification at Snow Caps Mine**

using the INCO process ", INCO Exploration and technical services

53. Wen C., et al, (1989), " **Adsorption-Enhanced bio-process for water treatment** ", Water Treatment, vol 4, pp 223-230.

54. Whitlock J., Dec (1989), " **The Advantages of Biodegradation of Cyanide** ", JOM, pp 46-47.

55. Whitlock J. & Mudder T., (1985), " **The Homestake Waste Water Treatment Process : Biological removal of toxic parameters from cyanidation waste waters and bioassay evaluation** ", Process Metallurgy, Fundamentals & Applied Biohydrometallurgy, pp 327-339.

56. Whitlock J. & Smith R., Aug (1989), " **Operation of Homestake's Cyanide Biodegradation Waste Water system based on multi-variable trend analysis**", Int. Symposium on Bio-hydrometallurgy.

Appendices

Index to Appendices

Appendix A

CSTR Analysis Calculation Tables

CSTR Data

Volume of CSTR : 1.4 *l*
Volume of settler : 5 *l*

Run No.:	2			Feed flow rate =	0.14	l/hr	β =	0.28	
Retention Time =	10	hrs		Recycle flow rate =	3.78	l/hr	Effluent flow rate =	0.10	l/hr
Dilution rate =	0.10	/hr		Waste flow rate =	0.036	l/hr	Effluent biomass = negligibly small		

Sample	Time as retentions (hrs)	Time past after start (hrs)	Cyanide Feed (mg/l)	Cyanide Effluent (mg/l)	Cyanide Degraded (mg/l)	Cyanide % Degraded (% of feed)	Thiocyanate Feed (mg/l)	Thiocyanate Effluent (mg/l)	Thiocyanate Degraded (mg/l)	Thiocyanate % Degraded (% of feed)	Total CN in Feed (mg/l)	Total CN in Effluent (mg/l)	Total CN Degraded (mg/l)	Total CN % Degraded (% of feed)	Biomass Conc in reactor (mg/l)	Conc in recycle (mg/l)	Mass in reactor (mg)	Conc. factor c	Biomass Wastage (mg/hr)	Sludge Age (hr)	Sludge Loading (SCN/X.hr)	dx/dt (mg/l.hr)	dS/dt (mg/l.hr)	= Yx/s (-)	ln(CN-) (mg/l)
1	2.4	24	31.0	2.5	29.4	91.8	118.2	23.2	95.0	80.9	93.1	13.9	79.1	84.4	480	700	672	1.46	25.1	28.7	0.015				2.56
2	4.8	48	29.7	0.0	29.7	100.0	118.2	11.8	106.4	90.0	83.8	5.2	78.6	93.8	570	738	798	1.30	20.2	30.4	0.013	-8.8	-7.7	-1.1	1.65
3	7.2	72	29.7	0.0	29.7	100.0	118.2	11.8	106.4	90.0	83.8	5.2	78.6	93.8	640	755	896	1.18	27.1	33.1	0.012	-7.0	-7.7	-0.9	1.65
4	9.6	96	31.8	0.0	31.8	100.0	118.2	11.8	106.4	90.0	83.1	5.2	77.9	93.7	615	685	861	1.13	25.6	34.5	0.013	3.5	-7.8	0.3	1.65
5	12.0	120	29.1	0.0	29.1	100.0	118.2	11.8	104.0	90.0	81.2	5.2	76.0	93.6	650	710	910	1.09	25.5	35.7	0.012	-4.5	-7.6	-0.5	1.66
6	14.4	144	31.0	0.0	31.0	100.0	95.8	11.8	84.3	87.8	74.0	5.2	68.8	93.0	520	665	728	1.28	21.5	31.9	0.013	13.0	-4.9	1.9	1.65
7	16.8	168	32.5	0.0	32.5	100.0	95.8	11.8	84.3	87.6	75.3	5.2	70.1	93.1	600	685	840	1.18	25.0	33.7	0.012	-8.0	-7.0	-1.1	1.65
8	19.2	192	31.0	0.0	31.0	100.0	95.8	11.8	84.3	87.5	74.0	5.2	68.8	93.0	580	635	812	1.08	22.9	35.6	0.012	2.0	-4.9	0.3	1.65
9	21.6	216	31.0	0.0	31.0	100.0	98.8	11.8	87.2	88.3	75.3	5.2	70.1	93.1	565	600	791	1.06	21.5	36.7	0.012	1.6	-7.0	0.2	1.65
10	24.0	240	26.7	0.0	26.7	100.0	99.4	11.8	87.8	88.3	74.2	5.2	69.0	93.0	450	635	630	1.41	22.8	27.6	0.015	11.5	-4.8	1.7	1.65
11	26.4	264	26.7	0.0	26.7	100.0	98.8	11.8	87.2	88.3	74.8	5.2	69.6	93.0	480	516	672	1.08	18.3	36.7	0.014	-3.0	-5.9	-0.4	1.65
12	28.8	288	29.8	0.0	29.8	100.0	95.9	6.8	90.1	94.8	72.8	2.6	70.3	96.4	450	550	630	1.22	18.7	31.9	0.016	3.0	-7.8	0.4	0.95
Averages			30.4	0.2	30.2	99.3	105.1	12.1	93.1	88.6	77.5	5.6	71.9	92.8	550	656	770	1.20	23.5	32.9	0.013	0.3	-7.2	0.062	1.5

Run No.:	2			Feed flow rate =	0.19	l/hr	β =	0.20	
Retention Time :	7.5	hrs		Recycle flow rate =	3.78	l/hr	Effluent flow rate =	0.15	l/hr
Dilution rate =	0.14	/hr		Waste flow rate =	0.036	l/hr	Effluent biomass = negligibly small		

Sample	Time as retentions (hrs)	Time past after start (hrs)	Cyanide Feed (mg/l)	Cyanide Effluent (mg/l)	Cyanide Degraded (mg/l)	Cyanide % Degraded (% of feed)	Thiocyanate Feed (mg/l)	Thiocyanate Effluent (mg/l)	Thiocyanate Degraded (mg/l)	Thiocyanate % Degraded (% of feed)	Total CN in Feed (mg/l)	Total CN in Effluent (mg/l)	Total CN Degraded (mg/l)	Total CN % Degraded (% of feed)	Biomass Conc in reactor (mg/l)	Conc in recycle (mg/l)	Mass in reactor (mg)	Conc. factor c	Biomass Wastage (mg/hr)	Sludge Age (hr)	Sludge Loading (SCN/X.hr)	dx/dt (mg/l.hr)	dS/dt (mg/l.hr)	= Yx/s (-)	ln(CN-) (mg/l)
1	3.2	24	35.9	3.1	32.8	91.4	90.2	80.15	9.7	9.1	71.8	38.9	32.8	45.7	749	838	1049	1.11	31.4	33.2	0.006				3.66
2	6.4	48	35.9	3.1	32.8	91.4	66.8	41.6	25.0	37.4	65.8	21.8	44.0	66.9	710	795	994	1.12	30.1	33.1	0.006	4.8	-6.0	0.8	3.08
3	9.6	72	28.6	2.1	26.5	92.7	75.9	23.7	52.3	68.3	62.4	12.5	49.9	80.0	655	720	917	1.10	27.2	33.7	0.010	7.5	-6.6	1.1	2.51
4	12.8	96	31.2	1.6	29.6	94.9	87.1	68.7	17.4	20.0	70.2	32.8	37.4	53.3	696	790	952	1.14	28.9	31.9	0.007	-3.4	-5.1	-0.7	3.48
5	16	120	29.7	1.6	28.1	94.6	80.3	48.8	31.4	39.2	65.8	23.5	42.2	64.3	690	785	826	1.10	29.7	31.1	0.009	2.7	-6.7	0.5	3.18
6	19.2	144	32.8	0	32.8	100.0	80.2	27.8	52.3	65.2	68.7	12.5	56.2	81.8	610	775	854	1.27	29.3	28.2	0.013	6.9	-7.8	0.9	2.53
7	22.4	168	31.2	1.9	29.8	94.8	93.7	27.1	66.6	67.8	68.7	13.7	55.0	80.0	625	780	875	1.25	28.5	29.7	0.012	-2.0	-7.5	-0.3	2.62
8	25.6	192	26.7	1.6	25.1	94.6	83.7	41.8	41.8	50.1	67.2	20.3	46.9	69.8	600	780	[illegible]	1.31	28.7	28.5	0.011	6.1	-6.4	1.0	3.01
9	28.8	216	34.4	0	34.4	100.0	80.2	41.8	38.4	47.9	78.5	16.7	51.9	73.4	585	715	819	1.22	27.8	30.2	0.012	-8.7	-7.0	-0.1	2.83
Averages			32.2	1.6	30.5	94.9	79.7	44.3	35.8	44.3	67.9	21.7	46.2	68.3	650	772	910	1.18	29.2	31.2	0.010	2.7	-6.8	0.354	2.7

Run No.:	4			Feed flow rate =	0.23	l/hr	β =	0.23	
Retention Time :	6	hrs		Recycle flow rate =	3.78	l/hr	Effluent flow rate =	0.18	l/hr
Dilution rate =	0.16	/hr		Waste flow rate	0.052	l/hr	Effluent biomass = negligibly small		

Sample	Time as retentions (hrs)	Time past after start (hrs)	Cyanide Feed (mg/l)	Cyanide Effluent (mg/l)	Cyanide Degraded (mg/l)	Cyanide % Degraded (% of feed)	Thiocyanate Feed (mg/l)	Thiocyanate Effluent (mg/l)	Thiocyanate Degraded (mg/l)	Thiocyanate % Degraded (% of feed)	Total CN in Feed (mg/l)	Total CN in Effluent (mg/l)	Total CN Degraded (mg/l)	Total CN % Degraded (% of feed)	Biomass Conc in reactor (mg/l)	Conc in recycle (mg/l)	Mass in reactor (mg)	Conc. factor c	Biomass Wastage (mg/hr)	Sludge Age (hr)	Sludge Loading (SCN/X.hr)	dx/dt (mg/l.hr)	dS/dt (mg/l.hr)	= Yx/s (-)	ln(CN-) (mg/l)
1	1	6	33.1	1.8	31.8	96.2	98.8	49.8	48.8	49.5	77.3	23.9	53.4	69.1	515	648	721	1.24	31.4	21.8	0.017				3.17
2	2	12	28.4	0	28.4	100.0	108.1	49.3	58.8	54.4	77.3	22.3	55.0	71.1	435	565	609	1.30	29.6	20.6	0.021	13.1	-8.9	1.5	3.11
3	4	24	28.4	0	28.4	100.0	109.1	56.9	52.2	47.8	77.3	25.5	51.8	67.0	515	670	721	1.36	35.9	20.0	0.017	-13.1	-8.5	-1.6	3.24
4	5	30	31.8	1.8	30.0	94.3	105.8	49.8	56.0	52.8	78.9	23.9	55.0	69.7	480	630	644	1.15	27.7	23.3	0.020	9.2	-8.8	1.0	3.17
5	6	36	31.8	1.8	30.0	94.3	98.8	49.8	48.9	49.6	75.8	23.8	51.9	68.4	645	825	903	0.87	33.1	27.2	0.013	-30.4	-8.5	-3.6	3.17
6	7	42	24.7	1.6	23.1	93.5	95	49.8	45.2	47.6	67.3	23.9	43.3	64.5	510	595	714	1.17	31.1	23.8	0.014	22.2	-7.1	3.1	3.17
7	8.5	51	30	1.6	28.4	94.7	95	56.9	38.1	40.1	72.6	27.1	45.5	62.7	370	485	518	1.31	25.3	20.5	0.020	23.0	-7.5	3.1	3.30
8	9.25	55.5	29.4	1.6	28.8	94.4	89	56.9	31.1	35.3	67.8	27.1	40.7	60.1	445	636	623	1.43	27.7	22.6	0.015	-12.3	-6.7	-1.8	3.30
Averages			29.5	1.2	28.3	95.9	99.9	52.5	47.4	47.1	74.3	24.7	49.6	66.8	467	581	652	1.29	30.3	22.4	0.017	1.6	-7.9	0.212	2.8

Run No.:	7		Feed flow rate =	0.2	l/hr		B =	0.21
Retention Time:	7	hrs	Recycle flow rate =	3.78	l/hr	Effluent flow rate =	0.18	l/hr
Dilution rate =	0.14	/hr	Waste flow rate =	[illegible]	l/hr	Effluent biomass = negligible		mg/l

Sample	Time on retention (hrs)	Time past after start (hrs)	Cyanide Feed (mg/l)	Cyanide Effluent (mg/l)	Cyanide Degraded (mg/l)	Cyanide % Degraded (% of feed)	Thiocyanate Feed (mg/l)	Thiocyanate Effluent (mg/l)	Thiocyanate Degraded (mg/l)	Thiocyanate % Degrade (% of feed)	Total CN in Feed (mg/l)	Total CN in Effluent (mg/l)	Total CN Degraded (mg/l)	Total CN % Degrade (% of feed)	Biomass Conc in reactor (mg/l)	Conc in recycle (mg/l)	Mass in reactor (mg)	Conc. factor c	Biomass Wastage (mg/hr)	Sludge Age (hr)	Sludge Loading (1/X hr)	dX/dt (mg/l/hr)	dS/dt (mg/l/hr)	= Y/X (–)	ln[CN-] (mg/l)
1	1.0	7.0	[illegible]	1.6	22.2	94.8	102	49.8	52.2	51.2	72.3	23.9	48.9	67.6	620	728	868	1.18	31.1	27.9	0.011				3.17
2	4.2	28.5	30	1.6	28.4	94.7	100	48.8	62.2	51.2	75.7	23.9	51.8	68.4	530	430	740	1.18	25.9	27.7	0.014	12.4	-7.4	1.7	3.17
2	9.7	48.9	30	1.6	28.4	94.7	108.8	42.7	62.8	58.8	77.3	26.7	58.6	73.2	600	785	852	1.11	32.2	29.5	0.012	-21.0	-8.1	-2.8	3.03
3	7.7	54.0	30	1.6	28.4	94.7	102	35.5	66.5	65.2	75.7	17.5	58.2	76.9	647	535	786	0.88	22.8	33.5	0.015	10.0	-8.3	2.3	2.88
4	11.2	73.1	26.8	1.6	25.2	94.0	102	28.4	73.6	72.2	72.6	14.3	58.2	80.2	613	600	856	0.88	25.6	33.5	0.014	-8.4	-8.3	-1.1	2.86
4	12.8	98.8	31.6	1.6	30.0	94.8	110.15	35.5	88.7	68.4	83.8	17.5	66.1	79.1	425	575	585	1.35	24.8	24.2	0.022	38.9	-9.4	2.6	2.88
5	14.5	101.5	33.1	1.4	31.6	95.2	105.6	35.5	70.1	66.4	80.4	17.5	62.9	78.2	516	550	721	1.07	23.5	30.7	0.017	-12.9	-8.0	-1.4	2.96
Averages			29.6	1.6	28.2	94.6	105.1	38.6	66.5	62.2	76.8	19.3	57.6	74.7	562	625	787	1.12	26.7	29.6	0.015	2.5	-8.4	0.208	2.3

Run No.:	8		Feed flow rate =	0.29	l/hr		B =	0.23
Retention Time:	5	hrs	Recycle flow rate =	3.78	l/hr	Effluent flow rate =	0.22	l/hr
Dilution rate =	0.20	/hr	Waste flow rate =	[illegible]	l/hr	Effluent biomass = negligible		mg/l

Sample	Time on retention (hrs)	Time past after start (hrs)	Cyanide Feed (mg/l)	Cyanide Effluent (mg/l)	Cyanide Degraded (mg/l)	Cyanide % Degraded (% of feed)	Thiocyanate Feed (mg/l)	Thiocyanate Effluent (mg/l)	Thiocyanate Degraded (mg/l)	Thiocyanate % Degrade (% of feed)	Total CN in Feed (mg/l)	Total CN in Effluent (mg/l)	Total CN Degraded (mg/l)	Total CN % Degrade (% of feed)	Biomass Conc in reactor (mg/l)	Conc in recycle (mg/l)	Mass in reactor (mg)	Conc. factor c	Biomass Wastage (mg/hr)	Sludge Age (hr)	Sludge Loading (1/X hr)	dX/dt (mg/l/hr)	dS/dt (mg/l/hr)	= Y/X (–)	ln[CN-] (mg/l)
1	1	5	36.3	2.9	33.4	92.0	105.8	35.9	70.1	66.4	83.0	18.8	64.8	77.5	725	830	1015	1.14	53.4	18.8	0.018				2.93
2	2	10	34.7	2.2	31.0	91.5	112.6	42.7	69.9	62.5	85.1	22.5	63.1	74.1	475	556	665	1.17	35.7	18.6	0.027	50.0	-12.8	4.0	3.09
3	3	15	34.7	1.5	33.1	95.4	136.7	42.7	94.6	69.3	91.5	20.7	70.7	77.3	336	485	748	1.24	42.8	17.5	0.028	-12.0	-14.1	-0.8	3.03
4	4	20	37.8	1.4	36.4	96.3	125.7	44.4	82.3	65.9	94.8	21.3	73.3	77.5	610	455	854	1.14	44.7	19.1	0.024	-16.6	-14.7	-1.1	3.06
5	6	25	38.3	1.6	34.7	95.6	133.7	42.7	91.0	68.1	98.2	20.7	76.5	78.5	586	675	818	1.15	43.4	18.9	0.025	5.9	-18.1	0.3	3.03
6	6	30	36.3	2.5	33.4	92.0	133.7	42.7	91.9	68.1	96.2	22.0	74.2	77.1	580	710	812	1.22	45.7	17.8	0.029	1.9	-14.8	0.1	3.09
7	7.5	35	34.7	2.9	31.8	91.6	126.7	42.7	84.0	66.3	91.5	22.0	69.4	75.9	585	465	833	1.12	42.8	19.5	0.025	-3.0	-13.8	-0.2	3.09
8	8	40	33.1	2.9	30.2	91.2	126.7	42.7	84.0	66.2	90.0	22.0	67.8	75.5	545	640	763	1.17	41.2	18.5	0.025	10.0	-13.8	0.7	3.09
9	9	45	36.6	2.9	28.6	90.0	133.7	42.7	91.0	68.1	91.4	22.0	68.4	75.9	555	665	777	1.25	44.7	17.4	0.025	-2.0	-13.9	-0.1	3.09
Averages			35.8	2.4	32.8	93.0	125.5	42.3	83.6	66.3	91.1	21.3	69.8	76.6	576	581	810	1.18	43.6	18.5	0.024	4.5	-14.1	0.316	2.8

Run No.:	9		Feed flow rate =	0.35	l/hr		B =	0.22
Retention Time:	4	hrs	Recycle flow rate =	2.78	l/hr	Effluent flow rate =	0.27	l/hr
Dilution rate =	0.25	/hr	Waste flow rate =	[illegible]	l/hr	Effluent biomass = negligible		mg/l

Sample	Time on retention (hrs)	Time past after start (hrs)	Cyanide Feed (mg/l)	Cyanide Effluent (mg/l)	Cyanide Degraded (mg/l)	Cyanide % Degraded (% of feed)	Thiocyanate Feed (mg/l)	Thiocyanate Effluent (mg/l)	Thiocyanate Degraded (mg/l)	Thiocyanate % Degrade (% of feed)	Total CN in Feed (mg/l)	Total CN in Effluent (mg/l)	Total CN Degraded (mg/l)	Total CN % Degrade (% of feed)	Biomass Conc in reactor (mg/l)	Conc in recycle (mg/l)	Mass in reactor (mg)	Conc. factor c	Biomass Wastage (mg/hr)	Sludge Age (hr)	Sludge Loading (1/X hr)	dX/dt (mg/l/hr)	dS/dt (mg/l/hr)	= Y/X (–)	ln[CN-] (mg/l)
1	1	4	36.3	12.4	23.9	65.8	116.1	36.5	79.6	68.4	86.3	28.3	58.0	66.8	720	725	1008	1.01	65.1	18.3	0.021				3.34
2	2	8	34.7	12.4	22.3	64.3	118.3	42.7	73.4	63.2	92.7	31.6	58.2	63.6	665	735	931	1.10	55.2	16.9	0.021	13.0	-13.4	5.8	3.45
3	3	12	31.5	12.4	19.1	60.6	130.7	40.8	79.8	69.7	90.3	34.7	51.6	60.7	645	750	[illegible]	1.16	57.1	15.7	0.021	8.3	-11.4	8.5	3.55
4	4	16	34.7	9.2	25.5	73.5	110.1	40.8	69.3	57.1	80.7	31.5	56.2	63.7	436	635	608	1.23	48.4	15.1	0.032	57.3	-11.8	3.7	3.45
5	5	20	37.3	12.4	25.4	67.2	110.8	40.8	56.8	52.8	85.1	34.7	50.4	58.2	370	600	785	1.05	45.4	17.8	0.022	-33.8	-12.6	-2.7	3.56
6	7	25	34.7	15.5	19.3	55.3	116.1	40.8	65.3	57.1	86.7	37.8	48.8	56.4	610	695	854	1.14	52.6	16.3	0.020	-18.0	-12.2	-0.8	3.63
7	8	32	34.7	12.4	22.3	64.3	105.8	48.8	59.8	52.8	82.0	34.7	47.3	57.7	415	400	581	1.30	37.8	15.4	0.028	48.8	-11.8	4.1	3.55
8	9	38	34.7	18.7	18.0	48.1	95	56.8	38.5	42.1	77.3	44.3	33.1	42.8	475	550	665	1.18	41.8	16.0	0.017	-15.0	-8.5	-1.8	3.78
Averages			34.9	13.2	21.7	62.1	112.2	46.8	64.2	56.7	85.1	34.7	50.5	59.8	568	657	793	1.13	48.1	16.4	0.023	8.8	-12.3	[illegible]	3.1

Run Averages for CSTR

Run No.	Dilution Rate (/hr)	Total CN- Feed (mg/l)	Total CN- Effluent (mg/l)	Total CN- Removed (mg/l)	Biomass (mg/l)	Sludge Age (hr)	Sludge Loading (/hr)
2	0.105	77.92	6.40	71.50	558	32.8	0.013
3	0.136	87.57	21.80	48.22	658	34.2	0.049
6	0.164	74.27	24.70	49.56	487	22.4	0.017
7	0.143	76.82	19.34	57.48	562	29.6	0.015
8	0.200	91.10	21.30	69.80	576	18.5	0.024
9	0.250	85.13	34.60	50.45	568	16.4	0.023

Overall Average for CSTR

Total Feed CN- =	78.91 mg/l
Total Effluent CN- =	18.37 mg/l
Total CN- Removed =	58.55 mg/l
Average Biomass =	565 mg/l

Kinetic Parameters according to Monod

μmax =	3.925450 /hr
Ks =	0.000048 mg/l
kd =	-5.2E-05 /hr

[illegible] "[illegible]"

Appendix B

FBR Analysis Calculation Tables

FBR Data

Volume of FBR: [illegible]

Run No.: 2 Retention Time = 10 hr; Dilution rate = 0.10 /hr; Feed flow rate = 0.28 l/hr

Sample	Time on retention (hr)	Time past after start (hr)	Cyanide Feed (mg/l)	Cyanide Effluent (mg/l)	Cyanide Degraded (mg/l)	Cyanide % Degraded (% of feed)	Thiocyanate Feed (mg/l)	Thiocyanate Effluent (mg/l)	Thiocyanate Degraded (mg/l)	Thiocyanate % Degraded (% of feed)	Total CN in Feed (mg/l)	Total CN in Effluent (mg/l)	Total CN Degraded (mg/l)	Total CN % Degraded (% of feed)	Biomass Conc in reactor (mg/l)	Biomass Conc in effluent (mg/l)	Biomass Mass in reactor (mg)	Sludge Age	Sludge Loading	Other Parameters dx/dt (mg/l/hr)	ds/dt (mg/l/hr)	= Yx/s (-)
1	2.4	24	48.4	6.2	44.2	89.6	185.6	116.2	69.4	37.4	132.6	57.3	70.3	55.8								
2	4.8	48	48.4	0.0	48.4	100.0	186.6	104.8	81.8	43.9	132.9	46.8	86.1	64.8							-8.6	0.0
3	7.2	72	48.4	2.8	46.9	94.7	186.8	96.9	92.8	48.2	134.0	48.9	85.6	64.0							-8.8	0.0
4	9.6	96	48.4	0.0	48.4	100.0	195.8	127.2	89.1	31.3	152.7	57.3	78.4	58.8	490	22	1344	12..		-48.0	-7.5	-6.4
5	12	120	48.8	0.0	48.8	100.0	188.9	34.9	150.7	81.2	129.8	15.8	114.3	88.0						48.0	-11.4	4.2
6	[illegible]	144	48.8	0.9	48.9	100.0	187.6	68.1	119.3	68.6	132.6	28.0	106.5	80.4							-10.7	0.0
7	[illegible]	168	48.4	0.0	49.4	100.0	191.4	58.1	133.3	69.8	136.1	28.0	108.1	80.7							-18.9	0.0
8	19.2	192	52.0	0.0	52.0	100.0	191.4	23.2	168.2	87..	137.7	10.4	127.4	92.8							-12.7	0.0
9	21.9	216	48.8	7.8	39.8	83.3	191.4	58.1	133.3	[illegible]	[illegible]	33.8	98.7	74.5							-9.9	0.0
10	36	240	48.4	7.8	41.6	84.2	194.4	48.5	144.9	[illegible]	[illegible]	28.0	108.6	78.3	529	32	1486	12.7	0.020		-10.7	0.0
11	26.4	264	48.8	7.8	39.8	83.3	185.4	11.8	174.9	[illegible]	[illegible]	13.0	110.8	80.8						32.8	-11.7	4.4
14	33.6	336	54.0	7.8	46.2	85.7	186.5	34.0	158.8	81.2	37.2	23.4	114.4	83.0	607	38	1780	13.2	0.019	-40.7	-11.4	-6.3
Averages			49.2	3.3	45.3	93.4	188.7	64.2	124.2	65.2	133.6	32.0	101.8	76.8	536	30.0	1600	14.4	0.018	-2.2	-10.4	-0.275

Run No.: 3 Retention Time = 7.5 hrs; Dilution rate = 0.14 /hr; Feed flow rate = 0.35 l/hr

Sample	Time on retention (hr)	Time past after start (hr)	Cyanide Feed (mg/l)	Cyanide Effluent (mg/l)	Cyanide Degraded (mg/l)	Cyanide % Degraded (% of feed)	Thiocyanate Feed (mg/l)	Thiocyanate Effluent (mg/l)	Thiocyanate Degraded (mg/l)	Thiocyanate % Degraded (% of feed)	Total CN in Feed (mg/l)	Total CN in Effluent (mg/l)	Total CN Degraded (mg/l)	Total CN % Degraded (% of feed)	Biomass Conc in reactor (mg/l)	Biomass Conc in effluent (mg/l)	Biomass Mass in reactor (mg)	Sludge Age (hr)	Sludge Loading (/hr)	Other Parameters dx/dt (mg/l/hr)	ds/dt (mg/l/hr)	= Yx/s (-)
1	3.2	24	37.46	7.8	29.7	79.2	76.7	41.9	34.8	45.5	71.6	26.5	45.3	63.0								
2	6.4	48	36.01	7.8	28.1	78.3	80.2	41.9	38.4	47.8	71.8	26.5	45.3	63.1	311	25.6	871	12.6	0.025		-4.6	0.0
3	9.6	72	36.01	7.8	28.1	78.5	66.8	27.3	34.8	64.2	69.9	20.3	45.6	69.2						42.3	-4.8	9.3
4	12.8	96	38.8	19.4	18.2	63.6	76.5	11.8	63.9	84.5	62.4	15.6	46.8	78.0							-4.7	0.0
5	16	120	31.23	9.36	21.9	70.0	87.1	8.0	79.1	90.8	70.2	12.8	57.3	81.8							-6.7	0.0
6	19.2	144	29.67	14	15.7	52.8	80.2	56.8	24.4	30.4	66.6	38.8	27.8	40.6	400	30	1120	14.3	0.008		-3.7	0.0
7	22.4	168	32.79	14	18.8	57.3	80.2	55.8	24.4	30.4	65.7	30.0	28.7	43.2						54.7	-3.0	18.4
8	25.6	192	31.23	9.36	21.9	70.0	83.7	62.7	21.0	25.0	68.7	37.4	31.3	45.6							-3.1	0.0
9	28.8	216	29.67	9.36	20.3	68.5	83.7	55.8	27.9	33.3	67.1	34.4	32.8	48.8	544	32.5	1523	17.8	0.008		-3.5	0.0
10	32	240	34.35	12.6	21.8	63.6	80.2	55.8	24.4	30.4	79.3	37.5	32.8	46.4						73.8	-3.3	22.6
11	35.2	264	37.48	12.6	25.0	68.8	78.7	58.8	20.9	27.2	71.8	37.5	34.3	47.8	167	25	462	9.3	0.024		-3.4	0.0
Averages			33.1	10.4	22.7	68.0	78.1	43.0	34.2	46.8	68.6	29.7	38.5	56.6	291	28.0	1018	13.4	0.015	38.8	-3.8	5.622

Run No.: 4 Retention Time = 5 hrs; Dilution rate = 0.20 /hr; Feed flow rate = 0.56 l/hr

Sample	Time on retention (hr)	Time past after start (hr)	Cyanide Feed (mg/l)	Cyanide Effluent (mg/l)	Cyanide Degraded (mg/l)	Cyanide % Degraded (% of feed)	Thiocyanate Feed (mg/l)	Thiocyanate Effluent (mg/l)	Thiocyanate Degraded (mg/l)	Thiocyanate % Degraded (% of feed)	Total CN in Feed (mg/l)	Total CN in Effluent (mg/l)	Total CN Degraded (mg/l)	Total CN % Degraded (% of feed)	Biomass Conc in reactor (mg/l)	Biomass Conc in effluent (mg/l)	Biomass Mass in reactor (mg)	Sludge Age (hr)	Sludge Loading (/hr)	Other Parameters dx/dt (mg/l/hr)	ds/dt (mg/l/hr)	= Yx/s (-)
1	4.8	24	23.42	18.7	4.7	20.2	101.1	62.7	38.4	38.0	68.7	46.8	21.8	31.9								
2	9.6	48	31.23	10.4	20.8	66.7	104.6	55.8	48.8	46.6	78.1	35.4	42.7	54.7							-4.3	0.0
3	14.4	72	32.79	10.4	22.4	68.3	104.6	62.7	41.9	40.6	79.9	38.5	41.1	51.7	416	33.5	1300	23.2	0.017	-57.2	-4.1	-18.5
4	19.2	96	31.25	10.4	20.8	66.7	108.1	62.7	41.4	42.0	79.7	38.5	41.2	51.7							-4.1	0.0
5	24	120	32.8	10.4	22.4	68.3	108.1	62.7	45.4	42.0	81.2	38.5	42.7	52.6							-4.3	0.0
6	28.8	144	32.8	9.4	23.4	71.3	108.1	55.8	52.3	48.4	81.2	34.4	46.8	57.5							-4.7	0.0
7	33.6	168	29.69	15.6	14.1	47.4	104.6	55.8	48.8	46.6	78.8	40.8	38.0	45.9	376	29.6	1050	19.9	0.019	-40.8	-3.8	-14.2
8	38.4	192	37.45	12.5	25.0	66.6	101.1	62.7	38.4	38.0	82.7	40.8	42.1	50.9							-4.2	0.0
9	43.2	216	32.8	12.5	20.3	61.9	108.1	62.7	45.4	42.0	81.2	40.8	40.6	50.0							-4.1	0.0
10	48	240	28.9	10.4	18.0	64.2	109.1	62.7	45.4	42.8	78.5	38.5	39.8	49.6							-4.8	0.0
11	52.8	264	31.2	18.7	12.5	40.1	101.1	62.7	38.4	38.0	76.5	48.8	28.7	36.8							-3.0	0.0
12	57.6	288	32.8	21.9	10.9	33.2	104.6	62.7	41.9	40.0	78.6	50.8	28.8	37.2	411	30	1151	21.5	0.014	-66.5	-3.0	-16.9
13	62.4	312	32.8	21.9	10.9	33.2	101.3	62.7	38.4	38.0	78.1	50.0	28.1	36.0							-2.9	0.0
14	67.2	336	35.9	18.7	17.2	47.9	101.1	55.8	45.3	44.5	81.2	43.7	37.6	46.2	332	32.1	930	18.2	0.023	-45.1	-3.7	-12.0
Averages			31.3	14.4	17.5	54.1	104.5	60.7	43.8	41.8	78.7	41.5	37.1	46.9	202	31.2	1129	20.2	0.018	-51.7	-3.8	-4.718

[illegible]

Run No.	5		Feed flow rate =	0.25	l/hr
Retention Time =	12	hr			
Dilution rate =	0.08	/hr			

Sample	Time since reductions (hr)	Time past after start (hr)	Cyanide Feed (mg/l)	Cyanide Effluent (mg/l)	Cyanide Degraded (mg/l)	Cyanide % Degraded (% of feed)	Thiocyanate Feed (mg/l)	Thiocyanate Effluent (mg/l)	Thiocyanate Degraded (mg/l)	Thiocyanate % Degraded (% of feed)
1	2	24	34.3	4.2	28.1	87.8	77	41.8	38.2	48.7
2	4	48	31.5	5.8	25.7	81.8	88.7	25.4	63.1	71.1
3	6	72	31.5	2.8	28.7	91.1	84.7	25.8	58.1	69.4
4	8	96	31.5	2.8	28.7	91.1	86.6	25.0	60.9	70.1
5	10	120	31.5	2.5	28.7	91.1	88.7	25.6	63.1	71.5
6	12	144	33.2	2.8	31.2	92.1	84.4	34.0	55.5	65.9
7	14	168	31.8	6.2	24.7	[illegible]	87.7	34.8	52.3	60.0
8	16	192	34.36	0	34.4	100.0	75.86	13.9	62.1	81.9
9	18	216	31.28	0	31.3	100.0	68.25	29	39.3	57.5
10	20	240	37.06	0	37.1	100.0	74.96	23.2	51.8	69.0
11	22	264	32.9	5.2	27.0	84.1	80.16	27.0	52.3	65.2
12	24	288	31.2	0	31.2	100.0	80.16	27.9	52.3	65.2
13	26	312	36.8	6.2	30.7	85.5	88.86	27.8	61.0	68.6
14	28	336	36.8	5.2	30.7	85.5	71.16	11.6	59.6	83.7
Averages			33.9	3.3	[illegible]	90.5	80.6	26.8	53.9	66.7

Sample	Total Cyanide: Total CN in Feed (mg/l)	Total CN in Effluent (mg/l)	Total CN Degraded (mg/l)	% Degraded (% of feed)	Biomass: Conc in reactor (mg/l)	Conc in effluent (mg/l)	Mass in reactor (mg)	Sludge Age (hr)	Sludge Loading (hr)	Other Parameters: dx/dt (mg/l/hr)	ds/dt (mg/l/hr)	− Yx/s (–)
1	88.8	34.9	43.9	43.8								
2	71.2	17.3	54.5	75.6	488	51.4	1310	8.8	0.008	-63.5	-5.4	-11.9
3	88.5	14.3	46.2	78.4						63.5	-4.8	13.7
4	88.6	14.3	55.5	79.6							-5.8	0.0
5	71.2	14.3	57.6	80.0							-5.7	0.5
6	118.1	18.2	87.3	78.5							-5.8	0.0
7	88.8	20.5	48.1	88.8	418	28.6	1178	9.1	0.006	-58.7	-4.8	-11.0
8	88.8	8.2	82.8	91.0						58.7	-6.5	9.1
9	61.8	13.6	48.8	78.0							-4.9	0.0
10	71.6	10.4	61.1	85.5	329	26	921	9.1	0.015	-44.7	-6.1	-7.3
11	88.7	17.7	51.6	74.2						44.7	-6.1	8.8
12	67.1	12.6	54.5	81.4							-6.6	0.0
13	75.7	17.7	58.0	76.6							-6.6	0.0
14	67.8	10.4	57.4	84.7	164	32.1	1034	13.1	0.007	-44.1	-6.2	-7.3
Averages	80.1	15.1	54.0	78.1	308	29.6	1309	10.0	0.010	-4.3	-5.5	-0.528

Run Averages for FBR

Run No.	Dilution Rate (/hr)	Total CN Feed (mg/l)	Total CN Effluent (mg/l)	Total CN Removed (mg/l)	Sludge Age (hr)	Sludge Loading (hr)	Biomass (mg/l)
2	0.06	133.04	31.06	101.59	8.79	0.018	336
3	0.16	71.79	29.79	38.87	8.14	0.015	291
4	0.20	79.39	41.83	37.12	0.25	0.008	302
5	0.08	80.14	18.14	64.31	10.08	0.010	308

Overall Average for FBR

Total Feed CN =	91.32	mg/l
Total Effluent CN =	31.67	mg/l
Average Biomass =	308	mg/l

N:\CDIA\SAT\...xls – "FBR data"

Appendix C

Air stripping of Cyanide in the CSTR

Air Stripping of Cyanide in the CSTR

Run #1

Average pH = 9

Time		Feed [mg/l]	Effluent [mg/l]	Absorber [mg/l]
15:30	0	86.63	10.48	0.00
16:00	0.5	85.85	11.88	1.31
17:00	1 1.5	86.37	14.24	1.57
17:30	2	89.43	15.11	1.62
Average		87.07	12.93	1.12

Run #2

Average pH = 7

Time		[mg/l]	Effluent [mg/l]	Absorber [mg/l]
11:30	0	70.13	12.05	0.00
12:00	0.5	71.13	9.69	4.72
13:00	1.5	71.67	12.14	16.59
13:30	2	72.88	11.00	25.94
Average		71.45	11.22	11.81

Run #3

Average pH = 9

Time		Feed [mg/l]	Effluent [mg/l]	Absorber [mg/l]
8:00	0	50.57	6.86	0.00
8:30	0.5	50.74	7.86	1.48
9:00	1	49.43	7.77	2.53
9:30	1.5	50.13	8.91	2.10
Average		50.22	7.85	1.53

MSCDATA1.wb3 - "AirStripping"

Run #4

Average pH = 8

Time		Feed	Effluent	Absorber
		[mg/l]	[mg/l]	[mg/l]
10:30	0	43.32	12	0.00
11:00	0.5	42.23	11.96	3.32
11:30	1	43.06	7.86	6.20
12:00	1.5	43.36	8.82	8.82
Average		42.99	9.19	4.59

Run #5

Average pH = 8.5

Time		Feed	Effluent	Absorber
		[mg/l]	[mg/l]	[mg/l]
13:00	0	34.15	10.04	0.00
13:30	0.5	33.80	9.78	4.45
14:00	1	33.89	9.61	5.24
14:30	1.5	34.45	10.22	6.38
Average		34.07	9.91	4.02

Calculation

	Feed	Effluent	Absorber	% loss	
Run #1	87.07	12.93	1.62	0.21	%
Run #2	71.45	11.22	25.94	4.10	%
Run #3	50.22	7.85	2.1	0.47	%
Run #4	42.99	9.19	8.82	2.32	%
Run #5	34.07	9.91	6.38	2.11	%
			avg	1.84	%

Vol CSTR = 1.4 l
Vol Absorber = 0.158 l

Appendix D

Cyanide Absorption Run #1

Cyanide Absorption Run #2

Cyanide Absorption Run #3

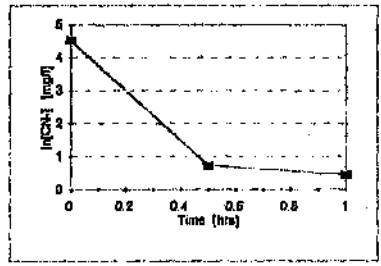
Absorption by Dead Microorganisms

Cyanide Batch Absorption Tests

Batch Runs #1

Times	Time past	[CN-] in Beaker	CN- in Beaker	ln[CN-]	CN- Absorbed per Time
		[mg/l]	[mg]	[mg/l]	[mg/hr]
7:30	0.0	90.51	90.51	4.51	
8:00	0.5	2.05	1.65	0.73	177.70
8:30	1.0	1.56	1.25	0.45	0.42
9:00	2.5	1.56	1.25	0.45	0.00
9:30	3.0	1.56	1.25	0.45	0.00
21:30	15.0	1.54	1.23	0.43	0.00

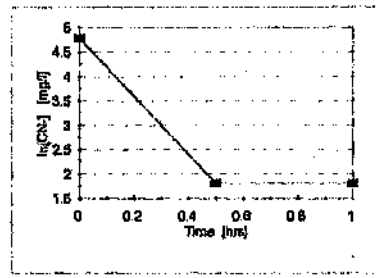
Biomass Quantity =	264.00	mg
Absorption Coefficient =	6.0157	/hr
Equilibrium [CN-] =	1.0188	mg/l
First order rate constant =	-0.0990	/hr
Temperature =	ambient	°C



Batch Runs #2

Times	Time past	[CN-] in Beaker	CN- in Beaker	ln[CN-]	CN- Absorbed per Time
		[mg/l]	[mg]	[mg/l]	[mg/hr]
9:10	0.0	119.13	119.13	4.78	
9:40	0.5	6.16	4.92	1.82	228.40
10:10	1.0	6.11	4.62	1.81	0.40
10:40	1.5	4.68	3.18	1.54	0.89
11:10	2.0	4.25	2.83	1.45	0.27
11:40	2.5	4.07	2.25	1.40	0.14
12:10	3.0	3.99	1.99	1.38	0.10
20:10	11.5	1.39	0.81	0.33	0.12

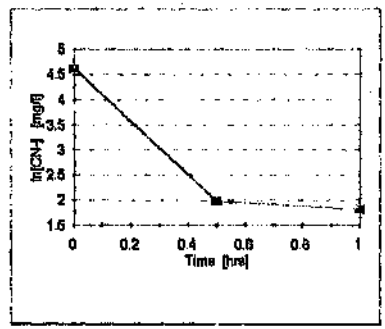
Biomass Quantity =	1504.00	mg
Absorption Coefficient =	1.7233	/hr
Equilibrium [CN-] =	1.0746	mg/l
First order rate constant =	-0.2176	/hr
Temperature =	ambient	°C



Batch Runs #3

Times	Time past	[CN-] in Beaker	CN- in Beaker	ln[CN-]	CN- Absorbed per Time
		[mg/l]	[mg]	[mg/l]	[mg/hr]
9:50	0.0	100.55	80.53	4.61	
10:20	0.5	7.20	6.76	1.97	149.64
10:50	1.0	6.16	4.92	1.82	0.83
11:20	1.5	6.05	4.44	1.71	0.32
11:50	2.0	5.72	4.88	1.74	-0.07
12:20	2.5	6.16	4.62	1.82	-0.14
13:20	3.5	6.56	4.79	1.79	0.04
13:50	4.0	6.55	4.44	1.71	0.09
14:50	5.0	5.12	4.09	1.63	0.07
15:50	6.0	3.90	3.12	1.36	0.16
8:20	22.5	1.39	1.11	0.33	0.09

Biomass Quantity =	672.00	mg
Absorption Coefficient =	1.0637	/hr
Equilibrium [CN-] =	2.0424	mg/l
First order rate constant =	-0.1016	/hr
Temperature =	ambient	°C



Cyanide losses in a Dead Microorganisms System

Sample	Time	Time Past [hrs]	CN- in Feed [mg/l]	Cum. CN- in Feed [mg]	CN- in Effluent [mg/l]	Cum. CN- in Effluent [mg]	Absorber [mg]	CN- Removed [mg/l]	Cum. CN- Removed [mg]	
1	9:30	0:00	65.57	21.64	1.56	0.51		64.01	21.12	
2	10:00	0.50	40.59	35.03	0.00	0.51		40.59	34.52	
3	10:30	1.00	62.45	55.64	0.00	0.51		62.45	55.13	
4	11:00	1.50	49.96	72.13	0.00	0.51		49.96	71.61	
5	11:30	2.00	53.08	89.64	0.00	0.51		53.08	89.13	
6	12:30	3.00	46.84	105.10	0.00	0.51		46.84	104.59	
7	13:30	4.00	56.20	123.65	0.00	0.51		56.20	123.13	
8	22:30	13.00	62.45	144.26	0.00	0.51		62.45	143.74	
9	9:00	23.50	53.08	161.77	0.00	0.51		53.08	161.26	
10	10:00	24.50	59.33	181.35	1.56	1.03		57.77	180.32	
11	11:00	25.50	56.20	199.90	1.56	1.54	0.22	54.64	198.35	
Averag			55.07		0.43			54.64		mg/l
Total		25.5		199.90		1.54	0.22		198.35	mg

Flow rate = 0.33 l/hr
Absorber Volume 0.143 l

Summary of Absorption test

Total CN- Removed = 198.13 mg
99.12 %

MSCDATA1.wb3 - "DeadBugs"