AEROBIC TREATMENT OF CTMP WASTEWATER IN SEQUENCING BATCH REACTORS

by

Cara V. Dubeski

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Department of Bio-Resource Engineering

The University of British Columbia
Vancouver, Canada

Date April 28, 1993

ABSTRACT

This research evaluated the application of a bench-scale aerobic SBR system to the treatment of CTMP/TMP wastewater. The wastewater treated was from Quesnel River Pulp, and had a COD of approximately 7200 mg/l and BOD_5 of roughly 2700 mg/l. SBR cycle times used were 24 and 48 hours, with hydraulic retention times of 34.3 and 68.6 hours respectively. The 24-hour cycle consisted of 22 hours aeration, one hour settling and one hour decant. Sludge retention times were 20 days for most runs. By the end of the study, the sludge in the system had been run on effluent from the same source from the same mill for 1 and 1/2 years.

For the runs without pH adjustment, COD removals of 32-41% and BOD_5 reductions of 70-75% were achieved by the end of each 24-hour cycle (after one hour in-situ settling). When the decanted wastewater was settled for an additional three hours, COD reductions of 53-59% and BOD_5 reductions of 90-94% were obtained. From intermediate time point samples, it was found that most of the oxygen demand reduction occurred within the first 16 hours of the cycle.

Little improvement was found in effluent from 48-hour cycles compared to 24-hour cycles. The rate of COD removal was greatly decreased in the 48-hour cycles, even during the early hours of aeration. Comparison of columns with unregulated pH to pH-controlled columns at 6.5 and 7.5 pH showed little difference in COD removals. COD and BOD_5 percentage removals in samples after the longer settling, were almost as high as in other aerobic systems treating similar wastewaters, though the SBR system had a higher loading.

MLVSS concentrations were 3900 to 4600 mg/l at the end of 24-hour cycles, and Sludge Volume Indices ranged from 54 to 78 ml/g (for reactors without pH adjustment). Sludge yields in the 24-hour cycle runs were about 0.12 kg MLVSS per kg COD removed, and 0.15-0.18 kg MLVSS per kg BOD_5 removed. This is only about one quarter the sludge yields typical in AS systems, both on a COD and BOD_5 basis. Some recommendations for the design of an SBR pilot system for a pulp mill are made.

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INTRODUCTION

Over the past decade the production of chemithermomechanical pulp (CTMP) and other "alphabet" pulps has greatly increased. Much research has recently been done to bring the knowledge of wastewater treatment technology for these pulping processes up to that available for the kraft process. Although TMP (thermomechanical pulp) and CTMP wastewaters do not contain the organochlorines that are often a focus of environmental concern with kraft process effluents, they are highly toxic. This toxicity is primarily the result of the higher concentrations of resin and fatty acids liberated by the high temperatures and pressures of these pulping processes. B.C. has CTMP mills discharging effluent into both coastal and interior waters.

Aerobic treatment processes such as activated sludge (AS) and aerobic stabilization basins, are well established as successful treatment methods for pulping wastewaters, both in BOD reduction and detoxification. The sequencing batch reactor (SBR), though a proven technology for treatment of both municipal wastewater and various industrial effluents, has not often been considered for pulpmill wastewaters. The SBR process has several potential advantages that are as relevant to pulpmill wastewater treatment as to other industries where SBRs are now being used. Some of these advantages are increased process flexibility, the combination of equalization basin, reaction tank, and clarifier in one unit, and the lack of short-circuiting possibility for wastewater flow.

This research studies the application of an aerobic SBR process to CTMP pulpmill effluent treatment. Biological treatment runs are carried out in six ten-litre SBR columns using CTMP/TMP wastewater from an interior B.C. pulp mill (Quesnel River Pulp). The primary objectives of this thesis are to

a) study the oxygen transfer characteristics of our system for several CTMP effluent samples,

b) assess the performance of the test system with respect to such process variables as chemical and biological oxygen demand and sludge production,

c) estimate the highest effluent quality possible for this system by examining the impact of an extended hydraulic retention time,

d) compare runs with unregulated pH to pH-controlled runs to determine if any inhibitory effect from high pH is being exhibited in the non-controlled runs, and if pH control yields improvements in any process parameters,

e) generate design recommendations for a pilot scale CTMP/TMP wastewater treatment system.

CHAPTER 1

LITERATURE REVIEW

CTMP Wastewater

Wastewaters from thermomechanical pulping, including TMP and CTMP, contain oxygen demand, suspended solids, and materials toxic to aquatic life which must be removed prior to discharge. Table 1 presents the typical ranges of values for various water pollution parameters for TMP and CTMP, compiled from several sources [Cornacchio 1988, Urbantas 1985, Servizi 1986a, CH2M Hill 1989, Bathija 1990].

Table 1. Usual Range of TMP and CTMP Wastewater Characteristics

Parameter	TMP	CTMP
BOD mg/l	200 - 2800	1000 - 5000
BOD avg. kg/adt	12.5 - 46	21 - 82
COD mg/l	3000 - 7000	6000 - 9000
COD avg. kg/adt	36.3 - 68.8	73.7 - 200
COD/BOD typical	2.5 - 2.6	2.3 - 3
Flow m^3/adt	10 - 45	15 - 30
96-hr LC_{50}	1.3 - 35.3 %	0.83 - 1.8 %
pH	6.5 - 8	7 - 8
Resin acids total mg/l	2 - 100	26 - 300

Relative to kraft mill wastewater and domestic sewage, the COD and BOD_5 values are high. Typically for kraft whole mill effluent the BOD_5 is 300 mg/l, COD is 1200 mg/l and the COD/BOD_5 ratio is 4. For sewage the respective values are 220 mg/l, 500 mg/l and 2.3 [Metcalf 1979]. The high COD/BOD_5 ratio for TMP and CTMP indicates that much of the organic matter present in these wastewaters is not easily biologically degradable. However, since the BOD_5 of those nonbiologically

degradable components is negligible, there should be little oxygen depletion in the receiving water attributable to the discharge of biologically treated effluent.

The LC_{50} is the concentration of wastewater in pure water that kills 50% of the test organism (typically rainbow trout or daphnia) within the assay exposure period, usually 96 hours. The LC_{50} values shown for TMP and CTMP are quite low, indicating a high degree of toxicity. CTMP wastewater is usually more toxic than TMP wastewater, due to the greater liberation of wood extractives.

The TMP process entails presteaming wood chips at temperatures above 100°C, then refining them under pressure in one or more stages above 100°C [Mackie 1988]. The CTMP process primarily involves adding chemicals to the chips prior to the pressurized refining, mainly sodium sulfite on a 1-4% Na_2SO_3 per bone dry pulp basis [Mackie 1988]. The use of sodium sulfite in the CTMP process releases lignins, tannin, resin and fatty acids which are also released in the kraft process but not in TMP. However, in kraft production these components are captured in the cooking liquor and burned in the recovery boilers [Reeser 1990].

Toxic components in TMP and CTMP effluents are primarily natural organic compounds extracted from the wood during the pulping process. The major group of these is the resin acids, which account for 60-90% of the overall toxicity in mechanical pulping wastewaters [Leach 1976]. Of these, pimaric, palustric, isopimaric, abietic and dehydroabietic and levopimaric acid are major toxicants, with sandaracopimaric and neoabietic acid being minor toxicants. Resin acids have been shown to be biologically degradable [Leach 1977a, Servizi 1986b]. Toxicity is also generated by neutral constituents such as pimarol, isopimarol and juvabione [Leach 1976]. As similar wood species are used in TMP/CTMP and in kraft pulping, many of the same toxic compounds are released from the wood, though the quantities liberated by the different processes vary.

Quesnel River Pulp supplied almost all the wastewater used in this research. Table 2 gives the typical wastewater characteristics of the TMP and CTMP wastewaters from this mill, obtained from two recent studies at the mill. The first three rows of the table give information from Rankin *et al.* [1992], the rest of the values are from MacLean *et al.* [1990]. The TSS values given are likely for wastewater leaving the dissolved air flotation unit, as they are consistent with the value for that wastestream provided by technicians at the mill [personal communication March 1993]. The resin acid concentrations are high compared to the usual values shown in the previous table. This is due to the furnish used in the

interior mills which contains higher resin acid concentrations than the tree species used in B.C.'s coastal mills.

Table 2. Typical Wastewater Characteristics for Quesnel River Pulp TMP and CTMP Effluents

Parameter	TMP	CTMP
Wastewater Production	14-18 m^3/adt	17-20.5 m^3/adt
BOD_5	32 kg/adt	66-80 kg/adt
TSS	12 kg/adt	12-26 kg/adt
COD	4000 mg/l	7200 mg/l
BOD_5	1800 mg/l	3100 mg/l
COD/BOD_5	2.22	2.32
TSS	300 mg/l	400 mg/l
Resin acids	50-200 mg/l	50-550 mg/l
LC_{50}	0.5-1.5%	0.3-1.0%
Inorganic Sulfur	200 mg/l	300 mg/l
H_2O_2	0 mg/l	50-100 mg/l
pH	5-6	7-8

Quesnel River Pulp also produces some CTMP from aspen furnish, which has the same water use per ton as the other CTMP, but produces about 120 kg BOD_5 and 18 kg TSS per air dry tonne pulp (adt) [Rankin 1992]. The total TMP and CTMP production at the mill averages 900 adt per day [personal communication with QRP technicians, March 1993]. If the COD and BOD_5 values in table 2 are combined for a 2:1 CTMP:TMP ratio, they fall within the range of concentrations measured in the batches of combined wastewater used in this research, and within the current range specified by the QRP technicians for this wastewater stream.

From 10 to 30% of the BOD discharge of the QRP TMP/BCTMP (bleached CTMP) wastewater is due to the resin acid content, as the biodegradation of resin

acids exerts approximately 3 mg BOD_5 per mg resin acid [MacLean 1990]. The higher resin acid concentrations occur in this wastewater when there is a high fines content in the sewered whitewater, and during fresh wood usage or winter months [MacLean 1990]. The whitewater stream is specified as the major source of both soluble COD and toxicity for this wastewater.

McCarthy *et al.* [1991] found that resin acids inhibit anaerobic activity. From a comparison with results for a resin acid mixture, it was evident that the presence of resin acids alone cannot fully account for the toxicity of BCTMP wastewater to anaerobes. The wastewater studied was from Quesnel River Pulp and had a resin acid concentration of 36 mg/l. This is low for this wastewater, but within the range of values given for this effluent after dissolved air flotation (20-120 mg/l) [personal communication, Anna Rankin, QRP, 1993]. The mean resin acid percentages of BCTMP effluent samples from five separate occasions are shown in Table 3.

Table 3. Percentage of Total Resin Acid Content in Quesnel River Pulp BCTMP Wastewater for Specific Resin Acids

Resin acid	Percentage
Abietic	26
Dehydroabietic	22
Levopimaric / Palustric	21
Isopimaric	12
Pimaric	7
Sandaracopimaric	6
Neoabietic	6

Aerobic Treatment of CTMP Wastewaters

Although anaerobic treatment has advantages over aerobic treatment such as lower energy demand and the production of methane gas, it is unable to sufficiently detoxify CTMP wastewater [Lo 1991, MacLean 1990]. Resin acids are only slightly biologically degraded under anaerobic conditions, as has been evident from

experiences with full-scale anaerobic systems during BCTMP production [MacLean 1990]. Anaerobic treatment removes a maximum of 40-60% COD and 70-80% BOD_5 [Lo 1991]. Furthermore, as the information mentioned above on the toxicity of BCTMP to anaerobes illustrates, for biological treatment of strong CTMP wastewaters, aerobic treatment may be superior.

Various studies have examined the performance of a range of aerobic biological systems for the treatment of CTMP wastewaters, in bench-scale [Lo 1991], pilot-plants [Rankin 1992, Campbell 1990, Reeser 1990, Servizi 1986a] and full working systems [Bathija 1990, McAllen 1989]. However, there is still much less information available on the treatment of these wastewaters compared to kraft mill wastewaters, due to the more recent development of the TMP/CTMP industry.

A recent study examined the effectiveness of several strategies of AS treatment for the Quesnel River Pulp mill [Rankin 1992]. The different treatments compared were i) a two-stage AS system at 4-day HRT, ii) a two-stage AS system at 3-day HRT, iii) a single stage AS system at 3-day HRT, and iv) treating effluent from the current upflow anaerobic sludge blanket system (UASB) in a single stage AS system with 2-day HRT. The influent to i, ii and iii was 80% clarified preacidification effluent (the same wastewater used in our research except that our wastewater was obtained prior to clarification) and 20% gravity clarifier effluent (e.g. trench flows and cooling water).

Sludge retention times (SRT) in the single stage AS system was 20 days and 15 days (a 20-day SRT was used for most of our research). The two-stage AS system had an anoxic selector in the second stage. For the latter part of the study a 30 minute HRT anaerobic zone at the influent end of the system was added, improving the sludge settling characteristics. The single stage AS system with 3-day HRT, which had an 8 hour HRT anaerobic selector, had an average SVI of 105 ml/g and a MLSS of about 4000 mg/l. The 3-day HRT two-stage system had SVIs of around 150 ml/g.

All strategies resulted in LC_{50}s for trout and *Daphnia magna* of greater than 100%. Effluent pH ranged from about 7.9 to 8.3. Average COD removals ranged from 77-91%. BOD_5 values in the final effluent (after clarification) from the different phases of the study ranged from 14-50 mg/l. TSS concentrations ranged from 52-123 mg/l. These are both well below the current limits. It was concluded that successful treatment for this mill could be achieved with 1) a two-stage AS system with 64.5 hour or 96 hour HRT, 2) a single stage AS system with 64 hour HRT, or 3) a single stage AS system with 48-day HRT treating effluent from the UASB reactors.

One of the most comprehensive recent studies evaluated several parameters for the treatment of CTMP wastewater in aerated chemostats [Lo 1991]. Investigating the effect of pH using a 3-day HRT and pH levels of 5, 6, 7 and 8, more than 96% of BOD_5 and resin and fatty acids (RFA) were removed at each pH. However, COD reduction increased from 70 to 80% as pH increased from 5 to 7, then decreased to 74% as pH increased to 8. From 43% (pH 5) to 52% (pH 7) of the lignosulfonates in the wastewater were biodegraded, and it was suggested that the lignosulfonates released during CTMP pulping contain low molar mass compounds more easily biodegraded than the lignosulfonates in spent sulfite pulping liquor. Good sludge settling was achieved for all pH levels studied, with sludge volume indices (SVI) from 60-138 ml/g.

When the effect of HRT was studied, it was found that with an HRT of only 0.5 days (resulting in an F/M of approximately 4.5 kg BOD_5/kg MLSS·d) 88% reduction in BOD_5 and 96% reduction in RFA were obtained. BOD_5 and COD removals increased significantly as HRT increased from 0.5 to 2 days, but did not increase further for HRTs of 3 or 5 days. SVI increased as HRT increased from 0.5 to 3 days.

Investigation of the effect of dissolved oxygen (DO) levels from 2.5 to 8.2 mg/l demonstrated that a higher DO generally improved the removal of lignosulfonates. It was also found that at lower DOs the mixed liquor generated a bad odour and the wastewater was darker. No significant differences were found in the microbial populations under the different pH levels, DO concentrations or HRTs studied.

Evaluating the differences between treatment temperatures of 20, 30, 40 and 50°C, revealed that at the thermophilic temperature (thermophilic range is 45-75°C) BOD5 and COD removals greatly decreased. Other than for the 50°C temperature, the various other treatment conditions demonstrated little variation in BOD_5 and RFA removals, though COD removals were strongly influenced by changes in the parameters. SVIs obtained were all low, ranging from 30 to 138 ml/g (SVIs of under 150 ml/g are associated with easily settled sludge).

A study of full-scale activated sludge (AS) treatment of a variety of German pulp and paper mill wastewaters evaluated the ratio of BOD eliminated to COD eliminated [Mobius 1988]. The study concluded that DO levels had no effect on COD removal for levels above one mg/l. The best COD reduction was obtained in aeration cascade reactors (compared to completely mixed tank reactors) and two stage aeration reactors. It was recommended that to avoid bulking sludge, aeration cascade reactors should be operated at a BOD loading of about 0.2 kg/kg sludge·d,

and that the completely mixed tank systems should be operated at BOD loadings of 0.25-0.35 kg/kg·d. These values are typical loadings for conventional AS system [Metcalf 1979].

Many recent papers discuss the reduction of colour for kraft mill effluents, using such methods as activated carbon, ultrafiltration, ozone and ozone with peroxide oxidation [Amoth 1992], various peroxygens [Saugier 1991] and biotreatment with *Phanerochaete chryosporium* [Chambers 1991]. However, though many other papers mention the problem of colour development during aerobic biological treatment, no specific information was found on the reduction of colour for CTMP effluents.

Pulpmill wastewaters are generally nutrient deficient, both as to nitrogen and phosphorus [Vaananen 1988]. Though almost all the N and P in the wood dissolves and enters the effluent in the pulping and bleaching process, these nutrients comprise only 100-300 g P and 1500-2000 g N per ton pulp produced [Meloni 1991]. A typical BOD_7:N:P for pulp and paper mill wastewaters is roughly 100:1.0:0.2 [Vaananen 1988].

It has been established that nitrogen and phosphorus deficiency in AS causes deterioration of sludge settling characteristics, such as bulking or loss of flocculation or granulation [Jones 1965]. Due to the higher surface area to volume ratios, the filamentous organisms implicated in bulking problems are well suited for assimilating nutrients from dilute solutions [Gostick 1990]. The nutrient requirement ratio for extended aeration has been given as 100 BOD_5 to 0.8 N to 0.2 P [Gostick 1990], compared to the standard 100:5:1 or 100:3:0.6 used for activated sludge.

Nitrogen is normally added in the form of ammonium. As using nitrate instead may lower operational costs, a study by Corey and Benefield [1991] examined the performance of an activated sludge system when nitrate was the sole source of nitrogen. They found that wastewaters can be treated effectively with nitrate. The amounts of nitrogen and phosphorus required per unit biomass were lower for sludge grown with nitrate compared to ammonia. For each of the SRTs studied, the MLVSS was lower in the nitrate reactor and had a lower sludge yield. It was noted that this could result in lower costs for treatment due to the lower amounts of oxygen and nitrogen consequently required. Both nitrogen sources yielded similar levels of treatment and very good settling properties.

Foaming and Bulking in Activated Sludge Treatment

Bulking occurs when filamentous organisms protrude from flocs and interfere with the compaction and settling of sludge. These organisms are usually distinguished on a morphological basis, as some have not yet been isolated and grown in pure culture to be fully characterized [Soddell 1990]. Foaming, a common problem in AS plants worldwide, is also due to branching, filamentous bacteria, primarily nocardioform actinomycetes [Blackall 1991a]. It appears as a persistent, viscous, grey to cream-brown scum up to 30 cm deep or more [Blackall 1991b] on the liquid surface in the aeration chamber and sometimes in secondary clarifiers [Goddard 1987]. This foam is not the same as detergent-caused foams or those sometimes occurring at the startup of treatment plants [Soddell 1990 and references therein].

A common foam control strategy has been reduction in sludge age with the corresponding reduction in mixed liquor suspended solids [Blackall 1991b] and the use of anoxic selectors (a low oxygen period or a low-oxygen chamber prior to the aeration zone) [Soddell 1990]. Anoxic or anaerobic selectors are also used to reduce the growth of some filamentous organisms causing bulking [Albertson 1987, Flippin 1992, Flammino 1989]. Other bulking control methods are implementation of high to low F/M (food to microorganism) gradient, chlorination [Jeffries 1989], and pH control [Unz 1988, Hu 1991].

The Sequencing Batch Reactor Process

The treatability of a TMP/CTMP wastewater in an aerobic sequencing batch reactor (SBR) process was the focus of our investigations. The SBR process is a continuing cycle of fill, react (aerate with mixing), settle, decant and optional idle (see figure 1). Some portion of the settled sludge is retained for each subsequent cycle.

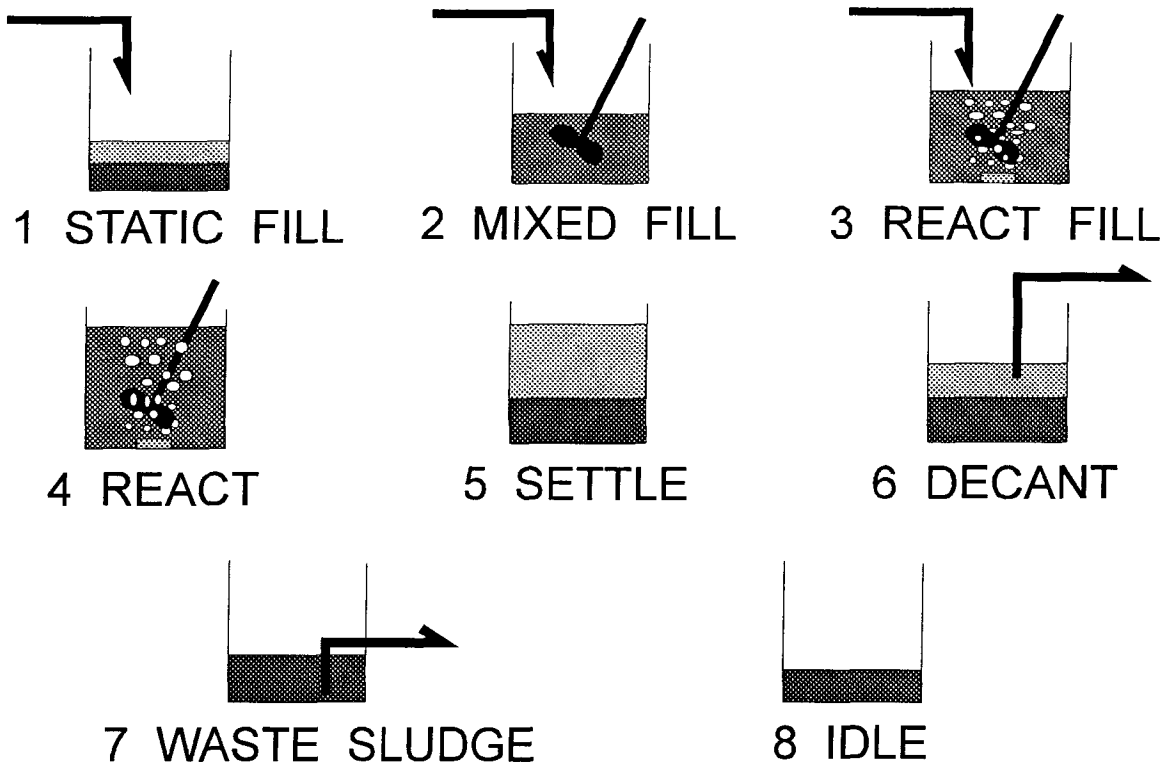

Figure 1. The Sequencing Batch Reactor Process

For the fill period, level sensing devices in addition to the ones at the minimum and maximum liquid volumes can be incorporated into the tank design to allow more flexible operating policies. For example, following a static fill period, a mixed fill or an aerated fill segment may be beneficial once some intermediate fill depth is reached. The react period completes the treatment which commenced during the fill period. React time may be set to a specific duration or may be related to the level in another SBR tank in a fill cycle. A major virtue of the SBR is its flexible react time compared to an aerated lagoon or continuous activated sludge process, where the hydraulic retention time is more or less fixed. Thus, in an SBR process, a difficult-to-treat batch of wastewater could be aerated for as long as necessary (within the maximum period available before filling must restart) to reach acceptable BOD levels.

The settling period is usually between 0.5 and 1.5 hours long [Irvine 1989]. Because the SBR system uses its entire volume for solids separation, it may provide more than ten times the settling volume of the secondary clarifier used in a comparable conventional AS plant. The SBR also precludes the need for a solids return underflow system, as mixed liquor does not leave the reactor, virtually all

sludge wasting occurs separately from the decanting of the treated effluent. As only clarified effluent is wasted, the SBR system also prevents the possibility of washout of the mixed liquor solids during hydraulic surges.

Withdrawal of effluent may use a pipe fixed at the desired depth and controlled by pump or automatic valve. However, a floating weir just below the liquid surface has the advantage of allowing maximum clarification of the effluent for the settling period allowed, in that effluent is always decanted from the most clarified zone. As the sludge blanket may begin to rise due to gas formation, the draw period should not be overly prolonged. During temporary extremely high influent flows to the treatment system, the draw period in one tank may be terminated before the minimum level is reached so filling can switch to that tank.

Idle is a holding period which may occur if another tank is being allowed to reach its maximum liquid level before flow is switched over. Sludge wasting may be carried out during this period. During long idles, aeration or mixing may be desired. Idle time can vary between different cycles if the influent flow rate varies because the fill time to maximum volume changes.

Surface scum is easily kept within the tank by withdrawing the effluent from just below the liquid surface so scum removal is usually not a problem in SBRs. The scum becomes well mixed with influent during the next fill and is therefore subject to digestion. Although if the scum level builds up it may require removal, this is not the continuous skimming and disposal problem common in continuous-flow AS [Irvine 1989].

Irvine and Ketchum note that because of the great impact of aeration and mixing strategies, the relationships between sludge age, HRT, mass loading and tank volume are not clear for SBRs [1989]. Also, a kinetic-based definition of sludge age is not possible because of the unsteady-state fill and react periods. Sludge age for this process therefore is defined simply as the biomass present divided by the mass of solids wasted per day.

For industries that generally or often operate close to 24-hours each day, an SBR system would usually comprise at least two tanks. If there are only two tanks, the time required for react, settle and decant in each tank cannot exceed fill time of the other tank. Adding a third tank of the same volume doubles the treatment capacity as the available time for react through idle stages is the sum of the fill durations for all other tanks, i.e. 1.5 times the volume with 1 1/3 times the daily react time available per tank, allows influent flow rate to be doubled. Similarly, the

capacity of a system increases if the total treatment volume is divided among more tanks. Use of multiple tanks also increases system flexibility, eliminates surge discharges and evens out the power requirement for aeration over the day.

As the SBR is a suspended growth, mixed culture system, it can in a general sense be considered an activated sludge process. However, the conventional AS process is spatially oriented whereas the SBR is a time-oriented periodic process which could be characterized as an unsteady-state AS system [Irvine 1989]. The SBR fulfills such functions as equalization, reaction and settling in sequential time periods, rather than sequential locations. This time orientation allows added operating flexibility. Through appropriate design of aeration protocol and tank volume, the SBR can replace any conventional continuous AS process, including contact stabilization and extended aeration [Irvine 1989]. Operation of the SBR can easily be adjusted to accommodate changing economic or regulatory conditions, changes in wastewater characteristics or fluctuations in flow rate.

The theoretically ideal reactor design for biological effluent treatment in terms of tank volume requirements, has been shown to be a completely mixed reactor, followed by a plug-flow reactor (PFR) [Bischoff 1966]. Irvine and Ketchum [1989] describe the basic kinetics of such a system to show that the SBR models this ideal configuration as far as reactor volume requirements. Due to the time-oriented nature of the SBR, both the continuous flow stirred tank reactor equivalent, the fill period, and the PFR equivalent, the react period, can be easily adjusted compared to the spatially-oriented conventional equivalents.

The SBR process has been applied for biological phosphorus removal, nitrogen removal, control of sludge bulking and hazardous waste treatment, and the degradation of a wide range of organic compounds in municipal and industrial applications. Irvine and Ketchum [1989] describe how the controlled growth rate variations and oxygen tension variations of an unsteady state AS system such as the SBR, can be used to mitigate the selective pressures of variations in influent to develop a beneficial organism distribution for such processes.

The objective of the SBR control policy is to regulate the selective pressures of growth rate and oxygen tension to enrich for the organism distribution which provides the optimal result. For example, using a static fill period allows feast conditions to be established. An extended react period provides famine conditions. It has been demonstrated that alternating feast and famine conditions can be used to control the growth of filamentous organisms [Albertson 1991, Mobius 1989]. An SBR system used in dairy wastewater treatment, where bulking problems are

common, has reported consistently good sludge volume indices with values as low as 25 ml/g [Albertson 1991].

Nitrification/denitrification can be achieved through manipulating oxygen tension during the fill period. The nitrite and nitrate produced during an aerated fill period are used as alternative electron acceptors during a following mixed fill. For biological phosphorus removal, anoxic and anaerobic conditions in a mixed fill can be used to select for the desired organisms. Recent work by Qasim *et al.* [1992] demonstrated that (continuous flow) anoxic-aerobic and anoxic-anaerobic-aerobic treatment processes gave superior performance for biological nutrient removal compared to a conventional aerobic process. The anoxic-aerobic process had the same nutrient removal capacity as the anoxic-anaerobic-aerobic process. All three processes had similar BOD removals and nitrification performance. SBR systems have been used in nutrient removal applications to provide anoxic-aerobic conditions sequentially in time similar to those created in such continuous flow systems in sequential chambers [Okada 1990, Ketchum 1987, Manning 1985, Palis 1985, Irvine 1983, Silverstein 1983, Alleman 1980].

Fill and draw treatment technology has been used with success for many decades. Irvine and Ketchum [1989] give a comprehensive review of the findings of many SBR investigations and list a large number of full-scale municipal SBR systems and industrial waste systems from across the U.S. Eight different full-scale municipal treatment facilities were evaluated in a study by Arora *et al.* [1985]. Though the plants all had similar water quality objectives, they were operated under a wide range of design criteria. HRT ranged from 7.6 hours to 49 hours and F/M ranged from 0.18 day^{-1} to 0.032 day^{-1}. The largest of the eight systems was designed for an average load of 3140 m^3 per day. All the plant operators reported the facilities were easier to operate than conventional continuous-flow systems.

A disadvantage of the process for pulpmill wastewater treatment has been uncertainty as to whether it can be operated feasibly on a large scale. Municipal SBR sewage plants have been built and operated to handle daily flows of up to 23,000 m^3/d (Oklahoma), and industrial SBR systems designed to handle flows as high as 3790 m^3/d (paper waste, Ontario) [Irvine, 1989]. Typical mechanical pulp effluent flows are of the order of 20 m^3/adt of pulp which, for a typical mill producing 350 t/d, means a daily wastewater flow of 7000 m^3/d. Although larger than industrial SBR applications found in the literature, this is well within the same order of magnitude.

Recently work has been done on adapting the IAWPRC activated sludge kinetic model to the computer-aided design of SBRs [Oles 1991]. The modified model gave a reliable simulation of experimentally determined concentration profiles. The model could be a useful tool in the optimization of treatment strategies for SBR research.

Other work applying a kinetic model of the SBR process to municipal wastewater treatment, concluded that increased aeration time per cycle can decrease the net sludge production (with resulting increase in energy requirement as oxygen) [Nakazawa 1991]. Increasing aeration time per cycle would also increase the percentage of inert suspended solids for a given SRT. Another conclusion was that using a fill period without aeration gives the lowest total oxygen consumption per cycle, but the highest peak oxygen consumption rate. It was also confirmed that using an anoxic period during fill is beneficial to control filamentous growth and prevent bulking.

Studying organic loading with a full-scale municipal SBR system, Irvine et al. [1985] found that under two different loadings (0.16 and 0.42 day^{-1}) the energy required per kg of BOD_5 oxidized was quite similar. Though both reactors achieved BOD_5 and suspended solids of less than 10 mg/l, slightly better effluent quality was achieved in the lower-loaded SBR, and the higher-loaded system was more difficult to operate. The more highly loaded system used approximately 30% less energy per kilogram BOD_5 applied, but also had a 46% higher sludge yield, which if sludge were treated aerobically could be expected to eliminate the cost savings.

CHAPTER 2

MATERIALS AND METHODS

The SBR System

The SBR system (shown in figure 2) is composed of six 76 cm (30 inch) deep acrylic columns with inside diameters of 14 cm (5.5 inch). Each column is filled with water or wastewater to a depth of 65 cm (25.6 inch). The aspect ratio is therefore 9.3. The liquid volume in each column is ten litres. In each column is centred a 1.3 cm (1/2 inch) stainless steel agitator shaft on which two 7.6 cm (3 inch) diameter stainless steel marine-type impellers are located. The first is 8 cm from the bottom, the second 50 cm. The top impeller is positioned such that it still remains fully below the liquid surface after all the samples required throughout the duration of a wastewater treatment run are taken. The impellers were rotated at their maximum speed of 150 RPM during all aeration periods, using a 1/2 hp Dayton DC gearmotor.

Each column is fitted with a non-airtight lid made of two semicircles of Plexiglas. In one semi-circle are fitted Swageloks to hold a 1.3 cm (1/2 inch) i.d. effluent withdrawal tube, and a 0.65 cm (1/4 inch) i.d. air line. Both of these tubes are rigid acrylic; flexible tubing is attached to both above the lid. Another Swagelok in each lid anchors a Omega T-type thermocouple linked to a ten-channel Omega 650 thermometer (Omega Engineering Inc., Stamford, CT).

Each column is equipped with one small-bubble diffuser positioned on the bottom of the column against the agitator shaft so that the bubbles must flow upward through the first impeller. During the aeration tests, 3 cm long glass particle airstones were used. However, these had to be replaced after the first biological runs as they were found to foul easily. This resulted in too much variation in bubble size because of differences in the blockage on airstones between the different columns. Each airstone was replaced by a 12 cm long strip of perforated flexible tubing, which created bubbles of similar sizes to the previous airstones at the same air flow rates. There was little adherence of biomass to this tubing. Both types of aerators are commonly available at aquarium supply stores. All biological runs documented in this thesis used the tubing-type aerators.

The six columns are positioned inside an insulated Plexiglas tank, which is used as a water-bath with a 1500 watt Colorabath circulating heater to maintain the liquid temperature in the columns at 35°C. A divider is positioned between the columns to prevent short-circuiting of the hot water between the entry and exit. Two Masterflex

(Cole Parmer, Niles, IL) peristaltic pumps with three standard size 18 heads each are used to decant the effluent from the columns. A Cole Parmer benchtop dissolved oxygen meter/controller and 30 cm long polarographic probe were used in some runs, with the probe positioned through a fitting in the column lid. In-situ pH control when used, was performed with two Cole Parmer 7142 control/pump systems and Broadley James pH probes (Broadley James Corporation, Santa Ana, CA).

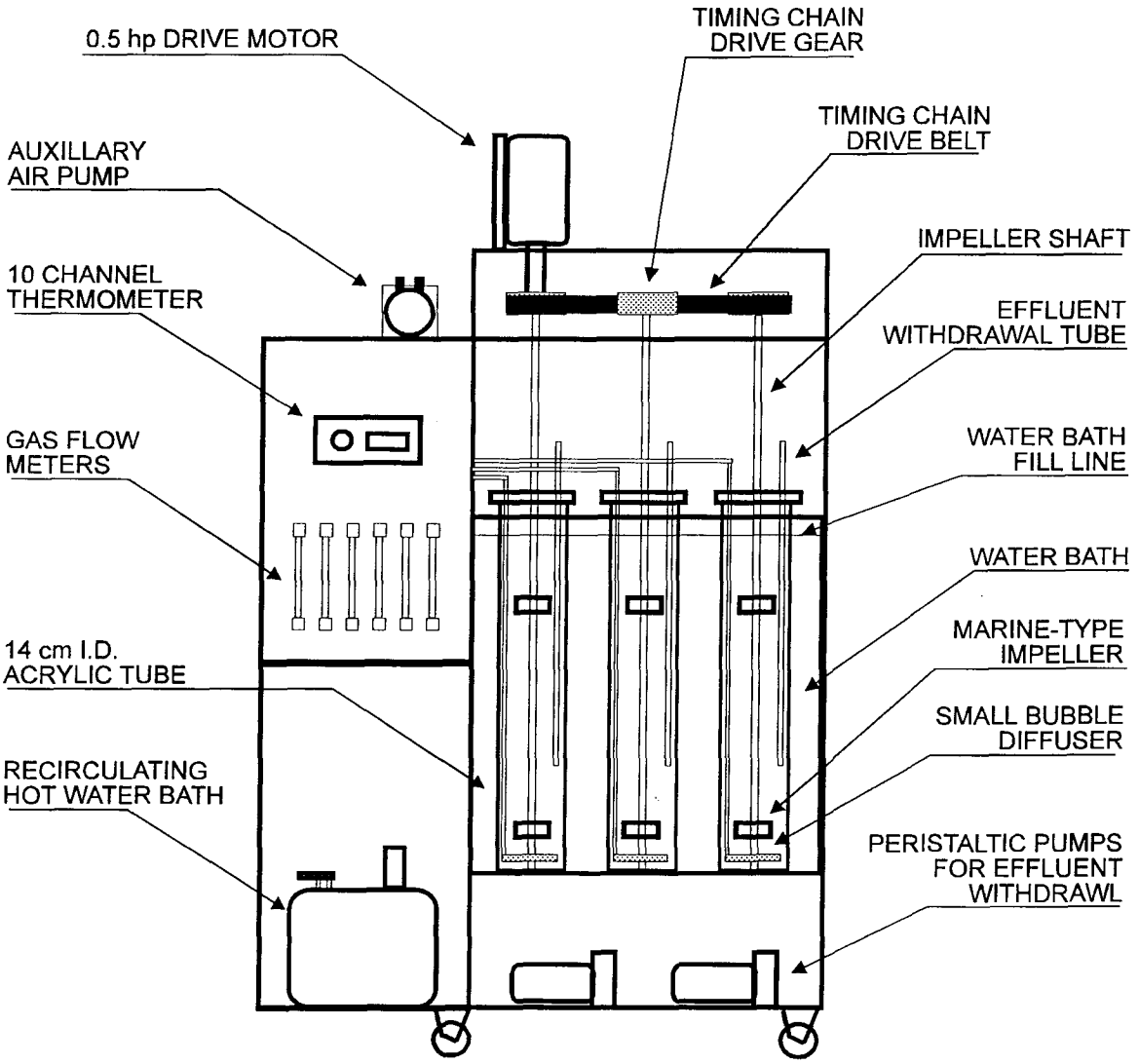

Figure 2. Illustration of the Experimental Sequencing Batch Reactors

Aeration tests

Aeration tests were performed using the unsteady-state aeration method [ASCE 1984]. This involves writing the oxygen transfer equation in the form of

$N/V = dC/dt = K_L a\ (C^* - C)$

and integrating it (see Appendix C for definition of symbols and a summary of the theory of oxygen transfer). From the slope of a semi-log plot of C^*-C vs. time, one determines $K_L a$, the overall mass transfer coefficient.

In the aeration test the water or wastewater is stripped of dissolved oxygen (DO) by sparging it with N_2. When the DO is zero, air or O_2 is sparged in and the DO concentration is monitored using a calibrated DO probe. The probe is calibrated in a sample with zero DO and then in a sample of known DO concentration.

All tests were performed using the same column, airstone and rotameter. If significant variation from the desired test conditions for gas flow rate or liquid temperature occurred during a run, that run was discarded and repeated. All aeration tests were run at a liquid temperature of 34-35°C, except one additional series at 20°C. The impellers are rotated at 150 RPM during all aeration experiments as this is the maximum speed for the motor used and is the agitation chosen for the wastewater treatment trials. Air flow rates were 800 ml/min and 400 ml/min. Results presented are averages of duplicate runs.

All of the wastewaters used were untreated effluents from B.C. pulp and paper mills:

'Powell' is a CTMP chip wash effluent from MacMillan Bloedel in Powell River. It had a COD of approximately 5000 mg/l and a BOD_5 of roughly 1300 mg/l.

'Quesnel 1' is a CTMP wastewater from Quesnel River Pulp, composed of effluent from the chip washer and plug screw feeder. It contained no white-water or mill wash water. It had a COD of 13,000 mg/l and a BOD_5 of roughly 4,500 mg/l.

'Quesnel 2' is a combined final effluent from Quesnel River containing 70% CTMP and 30% TMP. It contained chip wash water, plug screw feeder wastewater and white-water. The COD was 7200 mg/l and the BOD_5 2670 mg/l.

'Crofton' is a CTMP final effluent from the Fletcher Challenge mill in Crofton. It had a COD of 2,550 mg/l and a BOD_5 of approximately 900 mg/l.

Oxygen solubilities for the wastewaters were measured using the Hach spectrophotometric method [Hach 1988]. Careful dilutions were required for

analysis of the Quesnel River wastewaters, due to high levels of colour and turbidity.

Biological Treatment Runs

A preliminary series of 22 consecutive two-day cycle treatment runs were conducted in the summer of 1990 using the Crofton CTMP wastewater. The seed sludge built up for these runs was 50% from the activated sludge (AS) system at the Crofton mill, and 50% from the Civil Engineering AS pilot plant at U.B.C. Nitrogen and phosphorus supplementation was used during the weeks in which the biomass was built up and during the run, at the typical AS dosing [Gostick 1990] of 1 g soluble phosphorus and 5 g ammonia nitrogen to approximately 100 g initial BOD_5. The runs were performed in triplicate, using three of the six SBR columns with a total volume of ten litres and a minimum volume of three litres after decanting. The columns were kept at 33-35°C. Aeration was applied for 46 hours of each 48-hour cycle, at an air flow rate of 800 ml/min per column.

Several runs were performed between September 1990 and May 1991 using Quesnel River Pulp wastewater, but did not reach completion due to inadequate wastewater supplies. Runs were abandoned when only 40 litres of wastewater remained, and then this remaining wastewater was carefully aliquotted to keep the sludge of one column fed until more wastewater arrived. By the end of the research, sludge had been grown continuously on this particular CTMP/TMP wastewater for 17 months.

Each time sludge from the one column was divided among additional columns to again grow up the required amount of biomass, nutrients were added at the rate of 3 g N to 0.6 g P to 100 g influent BOD_5 until the desired solids concentrations were established. Sludge wasting was not performed for the first two weeks during biomass regeneration, and then sludge wasting was resumed as usual. Most runs used sludge retention times of 20 days, so 1/20 of the sludge volume was wasted per day after thoroughly mixing the volume remaining after decanting.

One test successfully carried out in spring 1991 used four columns at 35°C, with a 24-hour cycle with 34.3 hour hydraulic retention time (HRT = 10 litre total liquid volume divided by flow rate of 7 litres per 24 hours). The sludge residence time (SRT) was 20 days and the liquid volumes were as per the Crofton tests. Two columns were fed nutrient at the beginning of each cycle based on 100 g initial BOD_5 to 3 g N to 0.6 g P, using urea and diammonium phosphate for nutrients. The other two columns had no nutrient added. For the runs on Quesnel River Pulp

wastewater a greatly increased air flow rate of 2.5 l/min per column was supplied. This was primarily to provide improved mixing, but part of the increase was also required because the $K_L a$ in the Quesnel CTMP effluent was only 3/4 the value in the Crofton CTMP wastewater.

The main biological treatment trials were carried out in the SBR system from June 1991 to February 1992. Three different batches of CTMP/TMP wastewater from Quesnel River Pulp were treated (referred to below as A, B and C). The experimental SBR system consisted of up to six columns run in parallel with a reactor volume of ten litres each, with seven litres of wastewater treated per cycle. The columns were kept at 35°C, and were supplied an air flow rate of 2.5 l/minute each, except where otherwise specified. The sludge used had, by the start of run A, been run on CTMP wastewaters for a year. However, it was reinoculated with seed sludge from the Civil Engineering pilot plant to maximize the variety of species available for selection under the various conditions of these later runs.

Each wastewater was used in a 24-hour cycle run for at least 20 days, followed by a 48-hour cycle run which lasted until that batch of wastewater was exhausted, typically another 22 days. The 24-hour cycles have 22 hours of aeration followed by one hour of settling. The treated wastewater is then decanted, a portion of sludge is wasted to maintain the desired sludge retention time (SRT), and the columns are refilled. The 48-hour cycles are the same except with 46 hours of aeration. HRT of the 24-hour cycle is 34.3 hours and 68.6 for the 48-hours cycle. All columns were run at 20-day SRTs, with the exception for wastewater C of one column run at 30-day sludge retention time (SRT).

If the SBR system had been automated, or if the assistance of a second person had been available, a shorter cycle time than 24 hours could also have been studied. An 18-hour cycle with 25.7 hour HRT would have been used for one run. The lower cycle times of 18 or 24 hours are closer to that expected for the scale-up of such a system than the 48-hour cycle. The SRTs of 20 days and 30 days specified in this research are nominal SRTs, as these were calculated based on the solids wasted intentionally at the end of each cycle and do not consider the small amount of biomass wasted in the treated effluent (discussed further in Results and Discussion).

Before the start of every run, all sludge was thoroughly removed from the system, mixed well and equally aliquotted back to each column. This was to ensure that all columns started each run without any differences in biomass carried over

from previous tests. This mixing and pouring of warm sludge was the only operation of the research to generate any emissions that annoyed other lab users.

Any sludge that accumulated on the inside walls of the columns (due to foaming) was thoroughly scraped back into the reactors every day. The head space allowed for in selecting the liquid volume for runs had been based on early treatment trials. It provided adequate room for the maximum expected foam layer, so that no biomass would be unintentionally wasted from the top of the columns. In all runs evaporative losses of the wastewater were not great (about 4% in 24-hour cycles of runs A, B and C), because of the fairly high aspect ratio of the columns.

Acid added and pH-controlled runs were performed to determine if the slow rates of COD removal after 16 hours aeration were in part due to inhibition by the high pHs which developed during the cycles. These runs were also used to examine pH effects on sludge settling characteristics and foaming. Other research [Unz 1988] has proposed pH adjustment as a possible aid in sludge bulking control.

Run A used three columns tested under the same standard conditions (2.5 l/minute air, uncontrolled pH, 20 day SRT). The 24-hour cycles ran starting June 12 through the cycle starting July 6 for a total of 25 cycles. The last 24-hour cycle was then continued an additional 24 hours, becoming the first 48-hour cycle (this was also done in runs B and C). This was done to maximize the number of 48-hour cycles possible from the quantity of wastewater remaining. The 48-hour cycles of run A continued to July 31 (13 cycles).

Run B had two columns (1 and 6) at standard conditions, and two columns (4 and 5) with 50 ml of 2 N sulphuric acid added to each at the four-hour mark immediately after removing the four-hour samples. The other two columns were run on pure oxygen, column 2 at 7 mg/l DO and column 3 around 20 mg/l DO. Run B 24-hour cycles started September 5 using an earlier batch of the Quesnel wastewater for the first 11 days (to maximize the duration of the 24-hour cycles), switching onto "B" wastewater on September 16. 24-hour cycles continued through the September 26 cycle, for a total of 22 cycles. The acid additions and pure oxygen activation were begun September 15, as it was desired to build up equal amounts of sludge in all columns before changing the conditions.

48-hour cycles ran from September 26 until October 18 (11 cycles). For the 48-hour cycles acid addition was discontinued, as the two previously acid-added columns were now being used primarily to maintain sludge for the next run. As this sludge would be mixed in with the other sludge, and 4 of the 6 columns in the next

run would not have pH control, it was desired that this sludge be reacclimatized to conditions of no pH adjustment. Though these two columns could not be considered replicates of the two columns which continued at standard conditions, analyses were still performed on them for the 48-hour cycles of run B.

The two columns that had in the 24-hour cycles had acid addition, as carefully run duplicates, provide a further quantification of between-column variation. It was also interesting to observe if they equilibrated at a different rate to the change to 48-hour cycles than the two standard conditions columns. They also provided some indication of what the 48-hour cycle COD removals would be for columns at slightly lower pH than the columns that had never had acid addition.

For the 24-hour cycles of run C, two columns were run at the standard conditions, one column was run at pH 6.5, one column was run at pH 7.5, one column was run using a controller to maintain the dissolved oxygen (DO) level at 3.0 mg/l, and one column was run with an SRT of 30 days. For the pH-controlled columns, sulphuric acid was used. In mill applications, other acids such as phosphoric acid might be used; here sulphuric acid was used specifically to avoid adding any nutrients to the controlled columns and so prevent introducing another variable between columns.

For the 48-hour cycles of run C, two columns were run at the standard conditions and one column was run at 30-day SRT. The 48-hour cycles of 30-day SRT did not continue long enough to ensure reaching 30-day SRT equilibrium conditions, but does provide information on where the longer SRT data was heading relative to the 20-day SRT results. The pH 6.5 column was also continued, but with pH control halted. It was being fed to keep sludge active for a possible subsequent run. As it was being operated anyway, samples were taken for analysis, as it might be informative to see how quickly the COD removals and sludge characteristics approached those of the standard conditions columns.

Run C 24-hour cycles started November 14 using another batch of wastewater, switching to wastewater C on November 20. The 24-hour cycles ended after the December 5 cycle, for a total of 22 cycles with the last 16 on wastewater C. The 48-hour cycles began December 5 and ended with the December 19 cycle (eight cycles).

All batches of Quesnel River Pulp wastewater used in this research were effluent specifically collected when the same combination of CTMP and TMP pulps were being produced using the same furnish. There was therefore almost no

reacclimatization necessary when the feeds were switched over to B and C batches of wastewater after the start of those runs. The data presented in the results are only from cycles after the wastewater source had been switched over to batches B or C.

After the wastewater for trial C had run out, and it had been four days since the last feeding, another student using the same batch of wastewater finished his run and made available to this project another 60 litres of wastewater. It was decided to use this wastewater by continuing on 96-hour cycles with the two standard conditions columns for another 16 days, for a total of five cycles ending January 8. Though such long retention times would not be designed for using an SBR system, these cycles could be used to provide some information on how such parameters as sludge settling characteristics in our system might change during a short near-starvation period, such as might occur if pulp production was temporarily decreased.

For these 96-hour cycles the sludge removal rate was halved, because little or no net sludge production would be expected with such a long treatment period. The sludge removed was the minimum necessary to allow full sludge measurements. Though this removal rate would correspond to an SRT of 40 days, an SRT is not mentioned for this run in subsequent discussion, as the columns were only beginning to approach that sludge age by the end of this short run, and the sludge concentrations were still clearly decreasing, so to specify an SRT would be erroneous.

SVIs were performed for three cycles in run A, and almost all cycles in runs B and C. Settled sludge volumes were noted for most cycles, including those early in the runs before sludge concentrations were measured. This was done because these volumes served as an indication of the system beginning to come to equilibrium. The sludge volumes were also found to be a reliable indicator of any change in system parameters, e.g. sludge volumes were quickly affected by any significant interruption in air supply.

Sampling Methods

Effluent samples were taken at the end of the settling period, i.e. at 23 or 47 hours into the cycle, with some samples also taken at 0, 2, 4 and 16 hours. Samples are designated according to the hours of aeration that had occurred prior to sampling, with the start of aeration being defined as zero hours, therefore samples are referred to as 0, 2, 4, 16, 22, 46 or 94-hour samples. Samples for COD

tests were frozen immediately after sampling. Samples for other tests were kept in tightly closed containers with almost no air space and stored in a refrigerator at 4°C until analysis.

Samples were taken from the columns with full mixing on, except in the case of final points, i.e. 22-hour sample of 24-hour cycles and 46-hour sample of 48-hour cycles, which were taken after settling. Except for these final samples, samples at all time points were settled for one hour after sampling (to equal the one hour settling the final samples had in the columns), and the clarified wastewater was used to fill the sample vials.

Additional samples for CODs were settled for a further three hours at room temperature in beakers, and the supernatant poured into sample vials. The extended settling was done in capped sample vials, to continue at the virtually zero DO that existed in the covered SBR columns by the end of one hour settling. This extended settling, though not necessarily identical in impact to exactly four hours added settling in-situ, would indicate if significant improvement in the effluent could be had with increased clarification. The samples collected after the additional settling were generally a clear supernatant, and are therefore referred to in the text either as four-hour settled samples or supernatant samples.

Each sludge sample was the biomass wasted from the column by subtracting the required fraction of the sludge after the decanting period. The sludge was mixed thoroughly before the samples were removed from each reactor. Sludge samples are designated by the date of the beginning of the cycle, with the sample being taken at the end of the cycle. As sludge samples were taken just before the columns were refilled, measurements on these samples accurately show the initial sludge concentrations for the following cycle. These are calculated by dividing the solids in the retained sludge volume over the total liquid volume after refilling, i.e. solids concentration * 3 l (sludge volume) / 10 l (filled total volume). These initial sludge concentrations are shown in the various graphs reporting solids measurements.

Wastewater for Main Treatment Runs

The Quesnel River Pulp wastewater consists of approximately two parts BCTMP wastewater and one part TMP wastewater. It is 65-70% whitewater and 30-35% wastewater. The furnish is approximately 55% white spruce, 40% lodgepole pine and 5% alpine fir. The effluent is obtained immediately upstream of the air flotation

unit. The average chemical oxygen demands (COD) of the batches used for runs A, B and C were: A - 5980 mg/l, B - 8990 mg/l, C - 6860 mg/l.

The average BOD_5 of wastewaters A, B and C were 2240 mg/l, 3190 mg/l and 2600 mg/l, for COD to BOD_5 ratios of 2.67:1, 2.82:1 and 2.64:1. The pH of wastewater A ranged from 6.55 to 6.67 with an average value of 6.60. The pH of B ranged from 5.82 to 5.93 and averaged 5.88. C ranged from pH 6.25 to 6.34, with an average of 6.29.

All wastewater used in the research, was stored in a walk-in refrigerator at the Pulp and Paper Centre, maintained at 2-4°C. Each batch of Quesnel River wastewater (shared by two or three research projects) was shipped in two one-tonne totes by truck, generally taking 2 days in transit. When the wastewater arrived it was pumped into 23 litre plastic pails, filled as fully as possible and tightly covered. It was requested of the person pumping the effluent to avoid entraining the fibrous settled solids at the bottom of the tank, as it would be impossible to distribute this material evenly among the pails, and would also be difficult in turn to divide evenly among the columns. It would also be impractical to try to withdraw the wastewater from the pails without risking resuspending some of this material, and would result in the wastage of too much wastewater.

If more cold storage space had been available, larger batches of wastewater could have been stored. This would have permitted far fewer runs to be performed as all runs could have been carried to completion, and would have enabled all treatment tests to be extended to a duration equal to several SRTs as is desirable. Wastewater for each cycle was taken out of the refrigerator 15 hours in advance to allow it to come to lab temperature (21°C).

Wastewater was screened through 1/4 inch mesh and then passed through a 0.5 mm mesh filter before being used. The filtering was done to maximize the homogeneity of the wastewater (both between different columns and different days), as occasionally small pieces of wood or clumps of fibres were found in the pails. It was particularly important for the accuracy of the solids analyses that such material be excluded from the columns. The screening was done just before the wastewater was poured into the columns, as it aerated the wastewater and it was not wished to introduce additional oxygen into the wastewater before it was used.

Near the end of runs B and C a few wastewater pails were found to have grown large fungus colonies on the surface of the wastewater. These pails of wastewater were not used for the runs.

Analytical Methods

Temperatures were measured in-situ using T-type Omega thermocouples (Omega Engineering Inc., Stamford, CT) connected to a Omega 650 ten-channel thermometer measuring to +/- 1°C. The temperature of at least one column was also verified each cycle using a glass thermometer with 0.5°C divisions. Sample pHs were measured using a Broadley James (Broadley James Corporation, Santa Ana, CA) pH probe and Cole Parmer meter (Cole Parmer, Niles, IL), and were done on all wastewater samples as soon as they were removed from the reactors. Redox measurements were made using a Broadley James combination electrode with the calibration checked in pH-buffered quinhydrone solutions. Dissolved oxygen readings were taken with a YSI meter and YSI 5700 DO probe (Yellow Springs Instruments, Yellow Springs, CO).

CODs were conducted on previously frozen samples using the closed vial method from Standard Methods for the Examination of Water and Wastewater [1989] for all earlier runs and run A. CODs for runs B and C were carried out using purchased Hach COD vials which come prefilled with reactants (potassium dichromate, mercuric sulphate and sulphuric acid similar to the standard method). CODs were performed on both the samples settled for one hour and the samples settled an additional four hours.

The coefficient of variation (CV) for CODs on the extended clarification samples was found to be quite low, permitting the use of only single COD vials for all subsequent tests of these samples. Duplicate vials were prepared for CODs on all one-hour settled samples, however, as these samples were less homogeneous and therefore the within sample variances were higher. A few CODs were also performed on centrifuged samples, to compare to values for the extended settling samples.

All other analyses were performed on samples settled for one hour, as this was the actual settling period in the SBR protocol used. BOD_5 and solids tests were also performed as outlined in Standard Methods, using fresh samples stored within the recommended time limits. Because samples for CODs could be frozen, CODs were performed on all the wastewater samples described, but BOD_5s could be performed on far fewer because of time demands during the running of the biological tests, and the many hundreds of BOD bottles that would have been required to analyze all the samples within the allowed storage period.

BOD_5s were done on one of the last two cycles of both the 24-hour and 48-hour cycles of each run, as it was desired to have BOD results for treatment as close to equilibrium as possible. The inoculant for the BOD dilution water (important for the untreated wastewater samples) was fresh sludge from the reactors. This seed sludge was therefore extremely well acclimatized to the samples tested.

Sludge Volume Index measurements were carried out similarly to the standard method but the settled sludge volume used in the calculation was determined from in-situ measurements. This was because not enough sludge was wasted per cycle to allow use of the one litre graduated cylinder described in Standard Methods (or an Imhoff cone). Therefore, the only significant differences between the two methods was that the 30-minute settled fraction was measured in a larger cylinder and was stirred near the vessel wall by slowly rotating the columns forward and backward, rather than with thin rods rotating around the periphery (recommended peripheral speed no greater than 1.3 cm/s). Sludge depths were measured to the nearest 1/4 inch. This was the greatest precision realistically possible in most cases, due to the slight unevenness of the surface of the sludge.

Zone settling rates were determined for all columns at the end of the 24-hour cycles of run C. Again these analyses were performed in-situ as far too little sludge could be removed without interfering with the runs, to allow the measurements to be conducted in a separate apparatus. The differences between our technique and the standard method, are that Standard Methods recommends the use of a cylinder at least one m high and the SBR columns were only 76 cm high, and the required peripheral stirring was supplied by slowly rotating the columns rather than by using rods circling within two rod diameters of the internal wall (as in the settled sludge volume method). This test was done at the end of one stage of the run because the columns were allowed to settle longer, a total of 100 minutes, for these tests and it was not wished to alter the settling period during a run.

Ammonia and nitrate analyses were carried out as per Hach Spectrophotometric methods: Ammonia Nitrogen - Salicylate method and the MR (mid-range) Nitrate - Cadmium Reduction method respectively [Hach 1988]. Orthophosphate analysis was also according to a Hach spectrophotometric method: Reactive Phosphate - PhosVer 3 (Ascorbic Acid) method. Four additional samples were analyzed using Standard Methods for total Kjeldahl nitrogen and total phosphorus, by Takis Elefsiniotis of Civil Engineering at U.B.C.

Resin acid analyses were performed on stored frozen samples by Alexandra Kwong at the Paprican Vancouver Laboratory using chemical extraction followed by

gas chromatography [Paprican internal procedures]. Microtox analysis was done on a few samples. The Microtox unit was not available and functioning properly until several months after the treatment runs were completed. A few samples from run C had been preserved at pH 2 and 4°C. It was thought that though these were not ideal storage conditions or durations, these conditions would have less potential impact on the toxicity than freezing of samples. These samples should allow some relative comparison of their toxicity. pH of the samples was adjusted to 7.0 before Microtox analysis, and both the additions of acid and base used in the dilution calculations.

CHAPTER 3

EXPERIMENTAL RESULTS AND DISCUSSION

Aeration Tests

The K_La values determined at an air flow rate of 800 ml/min for the four CTMP wastewaters tested, varied from 60 to 83% of the K_La values measured in water under the same conditions (Table 4). (The corresponding aeration capacities shown were calculated using equation 6 shown in Appendix C).

Table 4. K_La Values for 35°C and Air Flow Rate of 800 ml/min, and Corresponding Aeration Capacities

Liquid	K_La hr^{-1}	O_c g/h
Tap water	12.54	0.99
Powell	9.64	0.73
Quesnel 1	7.52	0.55
Quesnel 2	8.78	0.64
Crofton	10.43	0.80

Typical aeration curves for clean water and Quesnel 2 wastewater, are presented in Figure 3. The K_La graphs for those two runs follow (Figure 4), using the aeration data points between 20 to 80% oxygen saturation, adjusted such that the first point used appears at time zero.

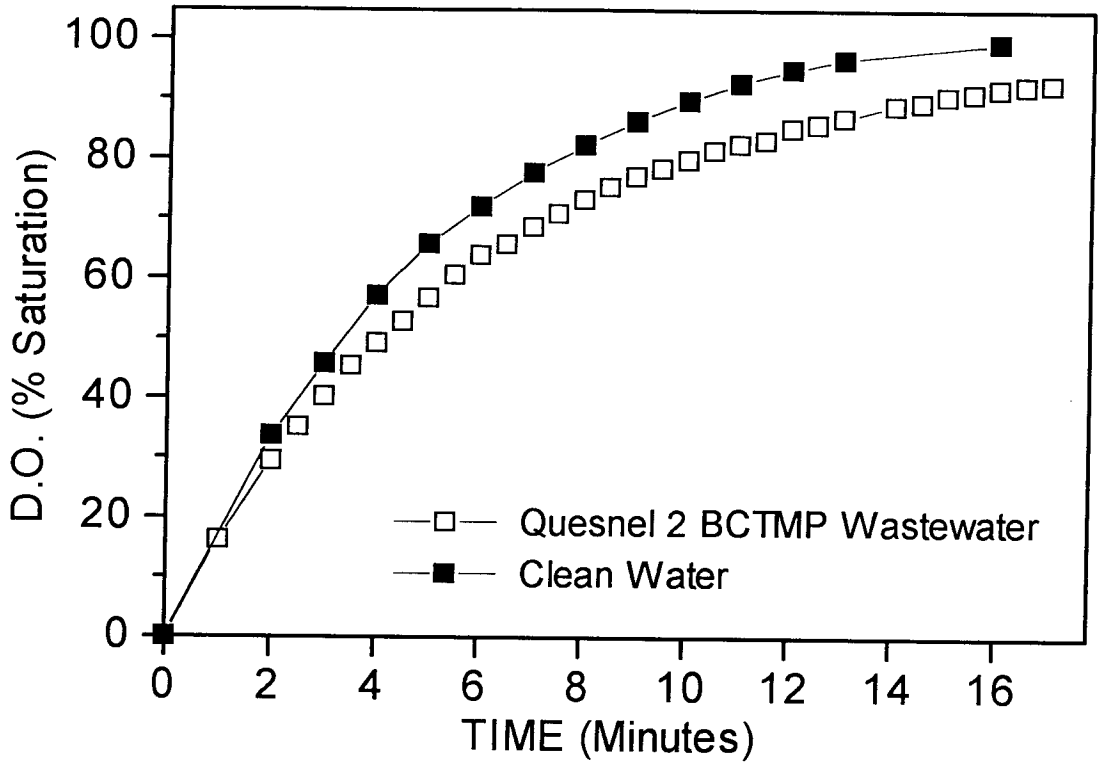

Figure 3. Example Aeration Curves for Water and Wastewater with Air

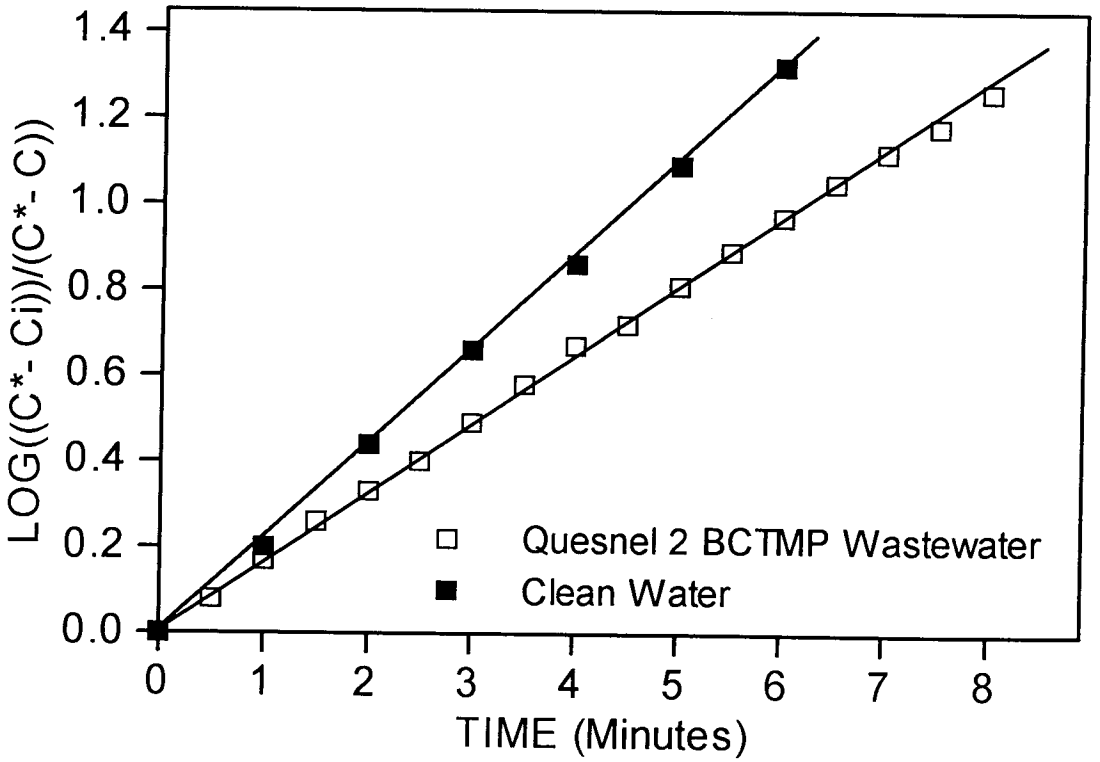

Figure 4. K_La Graphs of the Aeration Curves in Figure 3

Table 5. α Values from Aeration at 35°C and Air Flow Rate of 800 ml/min, with β Values for Each Effluent

Wastewater	α	β
Powell	0.77	0.96
Quesnel 1	0.60	0.92
Quesnel 2	0.70	0.93
Crofton	0.83	0.97

The wide range of alpha values for the CTMP wastewaters used (Table 5), illustrates the importance of aeration testing using the actual wastewaters to be treated, for design and optimization of aeration systems. If an assumed α value is used in aerator design, the probability exists that either under-design of the system, or significantly increased and unnecessary capital and operating costs would result.

Two series of aeration runs were performed at an air flow rate of 400 ml/min, half that used for the other air tests, to illustrate that K_La is not directly proportional to air flow rate. At 35°C in clean water, the K_La at 400 ml/min was 7.97 hr^{-1}, 64% of the corresponding value for 800 ml/min. At 35°C in Quesnel 1 wastewater, the K_La was 4.65 hr^{-1}, 62% of the value for 800 ml/min. The α value for the Quesnel 1 wastewater at 400 ml/min was 0.58.

Three aeration runs were conducted in Quesnel 1 wastewater at 20°C to determine if the generally accepted theta value of 1.024 for temperature correction would apply. For an air flow rate of 800 ml/min and agitation at 150 RPM, the $(K_La)_{20}$ was found to be 6.4 hr^{-1}, 85% of the $(K_La)_{35}$. Solving for θ (using equation 4 described in Appendix C):

$$(K_La)_{35}/(K_La)_{20} = \theta^{35-20}$$

$$1.17 = \theta^{35-20}$$

$$\theta = 1.011$$

Though this limited series of tests is not adequate to determine an accurate θ, it shows that the usual θ of 1.024 would be high for this case. Using 1.024 for θ here, would result in an overestimation of $(K_La)_{35}$ by 22%. Though the standard θ value is adequate for most applications between 10 and 30°C, researchers have observed θs from 1.01 to 1.05 depending on temperature [Bass 1977].

A second series of tests at 20°C performed in clean water gave a K_La of 11.0 hr^{-1}, 88% of the value for clean water at 35°C. Using a θ of 1.024 to adjust the $(K_La)_{20}$, would have overestimated the $(K_La)_{35}$ by 21%. From these aeration tests at 20°C, an α value of 0.58 was determined for Quesnel 1 wastewater at 20°C and an air flow rate of 800 ml/min.

The three α values determined for Quesnel 1 wastewater in the above tests varied slightly under the different conditions. However, the differences were small compared to the variability of K_La between different wastewaters in the first series of tests.

Two sets of aeration tests were performed at 35°C using pure oxygen at a flow rate of 800 ml/min. The K_La values for pure oxygen aeration of clean water and Quesnel 2 wastewater were 96% and 95% respectively of the corresponding values for air. The slight decrease in the values for oxygen was considered due to lag in the DO probe response, which only becomes noticeable at the high rate of increase in oxygen pressure that occurs during the pure oxygen tests. The effect of the DO probe lag could also be observed on the K_La graphs, as the curves for all of the pure oxygen tests were slightly concave from above.

A second series of aeration tests for pure oxygen was conducted for two of the wastewaters - Quesnel 2 and Crofton. The tests were performed at an oxygen flow rate equivalent to that in the air runs, i.e. at 20.9% of 800 ml/min, therefore 170 ml/min. The K_La values were 37 and 38% of the corresponding values for air, in the Quesnel 2 and Crofton wastewaters respectively. The corresponding aeration capacities for these two tests are 1.15 g/h and 1.47 g/h, approximately 1.8 times those at the same temperature with air at the same flow rate of oxygen. If it was assumed that the aeration capacity would be 4.8 times greater for pure oxygen delivery than for air containing the same quantity of oxygen, the flow rate of oxygen needed for this system would be greatly underestimated.

Biological Treatment Runs

As mentioned in Materials and Methods, several runs were unable to reach completion due to inadequate wastewater supplies. Several runs were also aborted after building power failures, as both the SBR temperature control and, most crucially, the aeration was shut down. One shorter power failure occurred while the researcher was present, so aeration was supplied by oxygen cylinders for the hour until power was restored. One run was reaching completion in March 1991 when

another student, seeing the aeration turned off during the decanting period, turned it back on, resulting in two thirds of the sludge being wasted.

In 1991 there were also problems with the air compressor in the Pulp and Paper Centre, which was the source of air for aeration. The compressor cut out several times, supposedly due to overheating from low UBC water pressure. During compressor failures, sludge was aerated using the oxygen cylinders which were always kept on hand for such emergencies. However, due to the temporary mid-cycle anoxic conditions which existed until the researcher observed the aeration stoppage, and the change in aeration while oxygen was used (fluctuations in DO, sometimes with very high DOs, and differences in DO among the columns, as only one dissolved oxygen controller was available), it was considered necessary to restart the two runs affected. To summarize, runs which could not be used for data because they were not completed were a result of extraneous factors, not problems with the SBR process itself.

The preliminary series of 22 consecutive 48-hour cycle treatment runs using the Crofton CTMP wastewater, were performed primarily to "debug" the system. Once COD removal efficiency stabilized, the runs consistently showed 31-35% COD reduction after 24 hours and 43-47% COD removal by the end of the 48-hour cycle. Except for the first hour after aeration was recommenced, the DO level was never found to be below 3 mg/l. The DO was usually near the saturation value of 6.7 mg/l during the final 34 hours of the 46 hours of aeration.

All other runs were performed using Quesnel River Pulp combined CTMP/TMP whitewater and wastewater. The pH, BOD_5 and COD for the specific batches A, B and C were presented in Materials and Methods. The overall range of characteristics for this wastewater stream were detailed by the technicians at the mill [personal communication, March 1993] and are presented in the following table. The values are for the combined wastewater before entering the dissolved air flotation clarifier, except for the resin acid value which is from immediately after. In the final column of the table are the typical values for the same parameters after treatment, before discharge into the Fraser River. This effluent has been treated in an upflow anaerobic sludge blanket (UASB) system with an HRT of 8-10 hours, and then an aerated stabilization basin with an HRT of 2.9 days.

Table 6. Characteristics of Quesnel River Pulp CTMP/TMP Wastewater

	Untreated Wastewater	Final Treated Effluent
COD	5,000-10,000 mg/l	1700 mg/l
BOD_5	1,500-3,500 mg/l	200 mg/l
COD/BOD_5	2-3	8.3
TSS	900-2,000 mg/l	480 mg/l
pH	5.75-6.75	not given
Total Resin Acids	20-120 mg/l	$\leq$ 2 mg/l
LC_{50}	< 1%	> 100%

The runs conducted on Quesnel wastewater to assess the need for nutrient addition showed no significant difference between the four columns. The influent COD was 6700 mg/l, final CODs in the nutrient added columns were 3940 mg/l and 4170, and in the no addition columns were 4140 mg/l and 4100 mg/l. The COD removals were therefore 41 and 38% for the two nutrient added columns, and 38 and 39% for the two columns without addition. The difference between the averages of the pairs is extremely small (65 mg/l) compared to between-column variation for replicate columns in some other runs. Though the decision to not use nutrient addition for the subsequent tests was based on these results, in retrospect this may have been premature. The effects on sludge settleability caused by nutrient scarcity may take longer to appear than the duration of this test.

Nutrient analysis of clarified samples of the influent and treated effluent from a column without nutrient addition (near the end of the run), showed that the levels were low but probably adequate. Total Kjeldahl nitrogen of the influent was 16 mg/l, and 5 mg/l in the 24-hour effluent. Total phosphorus was 4.7 mg/l in the influent and 2.5 mg/l in the 24-hour effluent.

Though the treatment system used was an activated sludge process, due to the long aeration periods and long hydraulic and sludge retention times used, and the low sludge yields produced in early runs, the nutrient requirements could be expected to be closer to the 100:0.8:0.2 BOD_5:N:P required for extended aeration [Gostick 1990] rather than the "rule of thumb" 100:5:1 generally allowed for AS. The wastewater used for runs in the spring of 1991 (including the nutrient to no

nutrient addition comparison run) had an average COD of 6700 mg/l, and BOD_5 of about 2300 mg/l, and average nutrient levels of 12 mg/l nitrate-N, 1.5 mg/l ammonia-N and 3.3 mg/l orthophosphate-P. The BOD_5:N:P ratio (including both nitrate and ammonium nitrogen) was approximately 100:0.59:0.14. Though this is only 73% the nutrient ratio recommended by Gostick, the nutrient concentrations present in the columns during treatment were never found to drop below acceptable levels. It should also be noted that much of the Kjeldahl nitrogen that was not initially in the form of ammonia was also utilized in the process, as shown by the decrease in Kjeldahl nitrogen levels mentioned above.

The recommendations given in a presentation on pulpmill wastewater treatment by the CH2M Hill engineering consulting company, were used as a guideline for levels of nutrients [CH2M Hill, 1989]. They are 1.5-2.5 mg/l ammonia nitrogen and 0.3-0.5 mg/l soluble phosphorus as minimum recommended operating levels for AS treatment. Based on the information cited in the literature review, which states that using nitrate as the primary nitrogen source should not impair treatment, both ammonia and nitrate nitrogen were added in calculating available nitrogen to meet this guideline.

Though concentrations varied somewhat for the different batches of wastewater, in cycles without nutrient addition ammonia-N was generally around 0.2 mg/l at the end of 24-hour cycles, nitrate-N was about 6 mg/l and orthophosphate-P was about 0.7 mg/l, consistently exceeding the minimums cited above. It was found that nutrient concentrations at the end of 48-hour cycles were typically a little higher than at the end of 24-hour cycles. This is thought to be due to nutrients released in the digestion (during later hours of the 48-hour cycles) of some of the sludge that had built up during the 24-hour cycles. Some nutrient measurements from later runs B and C are shown in appendix C.

All these nitrate, ammonia and phosphate values are from supernatant from fully centrifuged samples as the spectrophotometric methods used would not be accurate for samples containing suspended solids. Though the organic solids of pulpmill wastewater are not high in nitrogen or phosphorus, the nutrients liberated from the solids during treatment likely contributed to the nutrient pool.

It must be noted that a portion of the solids wasted each cycle after settling, actually comprises suspended solids from the influent which became settleable matter during treatment. While some of the wastewater solids are broken down during treatment, some is also simply added to the biomass during settling. The

sludge added by these non-digested solids does not constitute any nitrogen or phosphorus demand.

Though there was not a drop in COD removal with no nutrient addition for these specific conditions, it must be noted that we are not suggesting that other applications of SBRs to pulpmill effluents would not require nutrient addition. If the wastewater were any lower in nutrient to BOD ratio than the effluent used here, or more rapidly degradable, or if a lower HRT or SRT were used, nutrient supplementation would be required. However, running the research system without adding unnecessarily high levels of nutrients is of relevance, given increasing concerns about effluent nutrient levels.

One batch of Quesnel wastewater not used in this research, would indeed have been too low in nutrients to maintain the desired biomass. Therefore, even for our low-demand system, not all batches of this wastewater could be assumed to be adequate without nutrient supplementation. Because of this fluctuation, in full-scale implementation of such a system at that mill, nutrients would be added to every cycle. Also in practice, due to the high cost of aeration, it would be better to incur the cost of a moderate dosing of nutrients rather than risk having to unnecessarily prolong aeration due to a decreased rate of substrate degradation from nutrient limitation.

It was not practical with our manually-operated system to use any cycle times under 24 hours. Lower cycle times were also not important for the study due to the high BOD_5 concentrations in the influent. In addition to the one-day cycle times (HRT of 34.3 hours), a second cycle time of 48 hours (HRT of 68.6 hours) was studied. Though the mass loadings for the 48-hour cycles (0.29-0.33 kg BOD_5 applied/kg MLVSS·d using average MLVSS values from final two cycles) were still within the range of conventional AS systems, this longer cycle time represents an extreme of SBR operation.

Information from the extended cycle time runs can serve to gauge the maximum possible BOD and COD reduction possible for our system, and verify whether or not the COD remaining after the shorter retention times could possibly have been reduced by any significant amount by further increasing the retention time. The results show that the organic load remaining after 34 hours retention time could not be significantly reduced simply by increasing the aerobic reaction time.

The early runs that did not come to completion did demonstrate what minimum final liquid volume was adequate to fully contain the settled sludge for our solids

concentrations and the range of sludge volume index experienced, and prevent solids from being drawn into the effluent withdrawal tube. This minimum volume was found to be about 2.8 l, therefore the minimum liquid volume for all subsequent runs was set at 3 litres - 30% of the total liquid volume.

In only one run was the allowed head space of 11 cm found to be inadequate to contain the foam generated near the end of each cycle. In late 1990, foaming on the columns filled the head space and it was necessary to reduce the liquid volume to 8.5 l. By the time the run was terminated (due to lack of wastewater), at the end of cycles the foam completely filled the 20 cm high space and was beginning to protrude through the openings in the lids. It was evident that foaming was a potential concern for the system (apparently due to the high pH reached near the end of cycles) so records on foaming were kept on subsequent runs.

Some cycles in a run in January 1991 were conducted using a two-hour settling period at the end of cycles instead of one hour, with no drop in COD removals at the four-hour sample points of the subsequent cycles. This indicates that the greater settling period did not have a significantly deleterious effect on the health of the sludge. The longer settling period did result in notably better COD removals at the end of the settling period.

Typical sludge settling times used in SBRs range between 0.5 and 1.5 hours [Irvine 1989], so a one-hour settling time was selected for all subsequent runs. It would not be recommended to extend the settling time for a full-scale system much over two hours without further study, as no examples of full-scale systems using a settling period of over two hours were found in the literature. Irvine [1989] recommends that the sum of settle and draw periods should usually be less than three hours.

At the end of March 1991, one column was completely cleaned of sludge and used to test the removal of volatile fatty acids (VFAs) from the wastewater by aeration alone. The column was aerated at 2.5 l/min air for 22 hours (at 35°C) and then influent and effluent samples were tested using high-performance liquid chromatography (HPLC). The wastewater used was a batch of the Quesnel CTMP/TMP wastewater with a COD of 8700 mg/l. The VFAs present in the untreated wastewater are shown in table 7 below. The total VFAs in the untreated wastewater were 2,277 mg/l, and 2,076 mg/l in the aerated wastewater, for a reduction of 8.8% during the aeration period. This indicates that during biological treatment, little of the reduction in volatile organics can be attributed simply to volatilization.

Table 7. Volatile Fatty Acids in Untreated Quesnel CTMP/TMP Wastewater

Acid	Acetic	N-Caproic	Formic	N-Valeric	Propionic	I-Butyric
mg/l	814	712	466	193	56	36

On two different days, influent for the next cycles did not come up to 21°C because the lab temperature was temporarily lower, so the wastewater was heated to 21°C using immersion heaters in the pails. The wastewater was continually mixed during heating so the wastewater was not locally heated much above the desired temperature. During all runs liquid temperature in the columns were very consistent, being 27-28°C when the fresh wastewater was first mixed into the columns, 34-35°C by two hours, and always 35°C before four hours. Once this temperature was reached, temperature fluctuation in the columns was generally within +/- 1°C, with 37°C occasionally being reached, but the temperature was not observed to drop below 34°C during runs A, B or C. In pulp industry application there would also be a temporal temperature gradient in the SBR, but this would be from a higher initial temperature.

In all runs that were interrupted due to power or air compressor failure, it was found that the aeration stoppage, even if only an hour long, was reflected in the pH at the next time point measured being significantly lower than the previous values for that sampling time. If pH is monitored during treatment, it might serve as an inexpensive early warning of any upset to the system as an adjunct to other monitoring systems such as dissolved oxygen.

In run A, at the beginning of each cycle (zero-hour time point) the DO was always higher than 4 mg/l. At both the two and four-hour points DOs were at least 1.5 mg/l. At the 16, 22 and 46-hour time points the oxygen concentration was saturated. In runs B and C, at the zero-hour mark DO levels were greater than 2 mg/l. At both the two and four-hour points during all cycles, DOs were at least 1 mg/l, but rarely over 2.5 mg/l. At the 16-hour sampling point, DO ranged between 5.5 mg/l and saturation. At the 22 and 46-hour marks the DO was at saturation.

The 24-hour cycle runs of A, B and C are considered to have reached or very nearly reached equilibrium conditions, as both the stable COD removals and sludge values show. The 48-hour runs are not considered long enough to have reached equilibrium, but the COD removal results from these runs probably do accurately indicate removals that would occur once steady-state was reached, as little

movement in these values was usually evident by the end of the runs. However, the solids concentrations still appeared to be moving towards lower values at the end of these runs so the final solids are probably still higher than equilibrium values, particularly for runs B and C.

After the one-hour settling of the zero and two-hour samples, (particularly the zero-hour samples from 48-hour cycles), a little of the material still suspended appeared to be small sludge flocs. However, the suspended solids wasted in the effluent at the end of cycles appeared indistinguishable from the fine suspended solids in the influent, i.e. most of the suspended material in the influent becomes settleable during treatment, but not all settles during the one hour. The sludge flocs settled much more quickly than this material, so in most cases (for the later time points), the primary difference between one-hour and four-hour settled samples is thought to be the result of the slow but eventual settling of these suspended wood solids.

Almost all flocculated biomass is already settled after one hour, with a little variation visible between different columns (there is also likely variation between columns in the small amount of non-flocculated cells still suspended in the wastewater). Therefore, though some VSS is wasted in the effluent, this is not considered to significantly affect the SRT, as at the end of all cycles most of the biomass appeared to have settled. (VSS measurements of a few effluent samples are discussed under run B.)

Eight samples from run A were centrifuged and compared to identical samples which instead of centrifugation had been given the additional settling of three hours, but in a refrigerator at 4°C to minimize biological activity. The CODs of the centrifuged samples gave values approximately equal to those of the samples from extended settling for six of the samples. The other centrifuged samples had CODs of 94% and 97% of the same samples subjected to the additional three-hour settling period, i.e. a significant amount of solids had remained suspended after four hours in only these two samples.

Because six of the eight extended settling samples had CODs similar to the centrifuged samples, it is evident that most of the clarification possible had occurred by the end of the three hours of additional settling, so little would be gained by further increasing this settling period. For almost all samples given the (room temperature) extended settling in runs A, B and C, the supernatant was visually found to be as clear as centrifuged samples and almost free of suspended solids.

Eight other samples (two each of time points 0, 4, 16 and 22 hours from run A) were settled for four hours in the refrigerator and compared to identical samples that instead had been settled at room temperature. The small amount of endogenous respiration which likely occurred in the settled biomass of room-temperature settled samples would have had no effect on the comparison to samples settled in refrigeration, as only the COD in the supernatant after settling was measured. It was found that there was good agreement between the refrigerated and room-temperature settled samples for the 16 and 22-hour point samples (room-temperature samples had CODs of 97-99% of the refrigerated samples). There were slightly lower CODs (4% lower) in the room temperature samples from the four-hour point, and a significant drop in the COD of the zero-hour point (9% lower than the refrigerated zero-hour sample).

This demonstrated that during the low-oxygen settling period, very little additional wastewater degradation will occur in the later samples to supplement the COD reduction that already occurred under favourable conditions during lengthy aeration. However, in the zero-hour samples, there are significant concentrations of easily-degradable organics of which some is utilized by the biomass in the sample (particularly until the dissolved oxygen is exhausted, although there is also assumed to be a little activity by facultative anaerobes). All other settling was conducted at room temperature, as refrigerated settling would have no relevance to full-scale treatment.

The small amount of biological activity during the extended settlings of samples is not very significant for the COD measurements, but results in a proportionally larger change in the BOD measurements (as the BODs are so much lower than CODs, especially at later time-points). Therefore, this biological activity likely accounts for a portion of the drop in BOD_5s between the one-hour and four-hour settled samples. The small amount of biomass still suspended after one-hour that settles out during the further three hours, would also cause a reduction in BOD_5 that would be more significant than in the COD measurements. The less digestible wood solids that settle out during the extended settling are thought to be the major part of the drop in CODs, but would be less significant in the BOD_5 measurements.

For all the graphs of COD removals in the following section it should be noted that results for zero-hour samples do not only reflect the drop in the influent COD that occurs upon mixing with the wastewater remaining in the column from the previous cycle. During the one or four hours of settling the samples are given after sampling, there is significant settling of the suspended material from the influent

and a small amount of biological activity occurs (as discussed above). Zero-hour samples were taken to determine the impact of this improved settling on CODs, so that the reduction in CODs by the two or four-hour time points would not erroneously be attributed merely to aerobic digestion of the wastewater organics.

The suspended matter in the influent does not settle during quiescent conditions in wastewater storage, but dramatically improves in settleability after being mixed with the sludge. This is considered due to the rapid absorption of a significant fraction of the organic matter onto the flocs, as in a contact stabilization process. The samples took up to ten times longer to fully clarify than for the flocs to settle. The material that settles much more slowly probably has little adsorbed biomass.

Run A Treatment Results

Run A was conducted to study the performance of the system under standard conditions and to determine the between-column variation, before runs were performed applying different conditions to various columns. This between-column variation is quantified throughout this section by averaging the columns on all graphs and showing error bars depicting the 90% confidence interval for agreement between columns.

Run A used three columns tested under the same standard conditions: 20-day SRT, 2.5 l/min air flow rate and no pH adjustment. BOD_5 of the influent was about 2300 mg/l, for a BOD_5 to COD ratio of approximately 1:2.6. The 24-hour cycles ran starting June 12, 1991 through the cycle starting July 6 for a total of 25 cycles. The last 24-hour cycle was then continued an additional 24 hours, becoming the first of the 48-hour cycles, which continued to July 31 (13 cycles).

Figure 5 shows pH values at the 0, 2, 4, 16 and 22-hour points during the final 24-hour cycles. After the axis break are shown pH values at the 0, 4, 16, 22 and 46-hour points of some of the 48-hour cycles. All values are averages of the three replicate columns. The error bars represent 90% confidence intervals for this and all other figures showing error bars. As the replication between columns is quite good, the fluctuation shown between different days during the run is accurate. This variation is greater than the fluctuations exhibited in COD removal and solids concentrations.

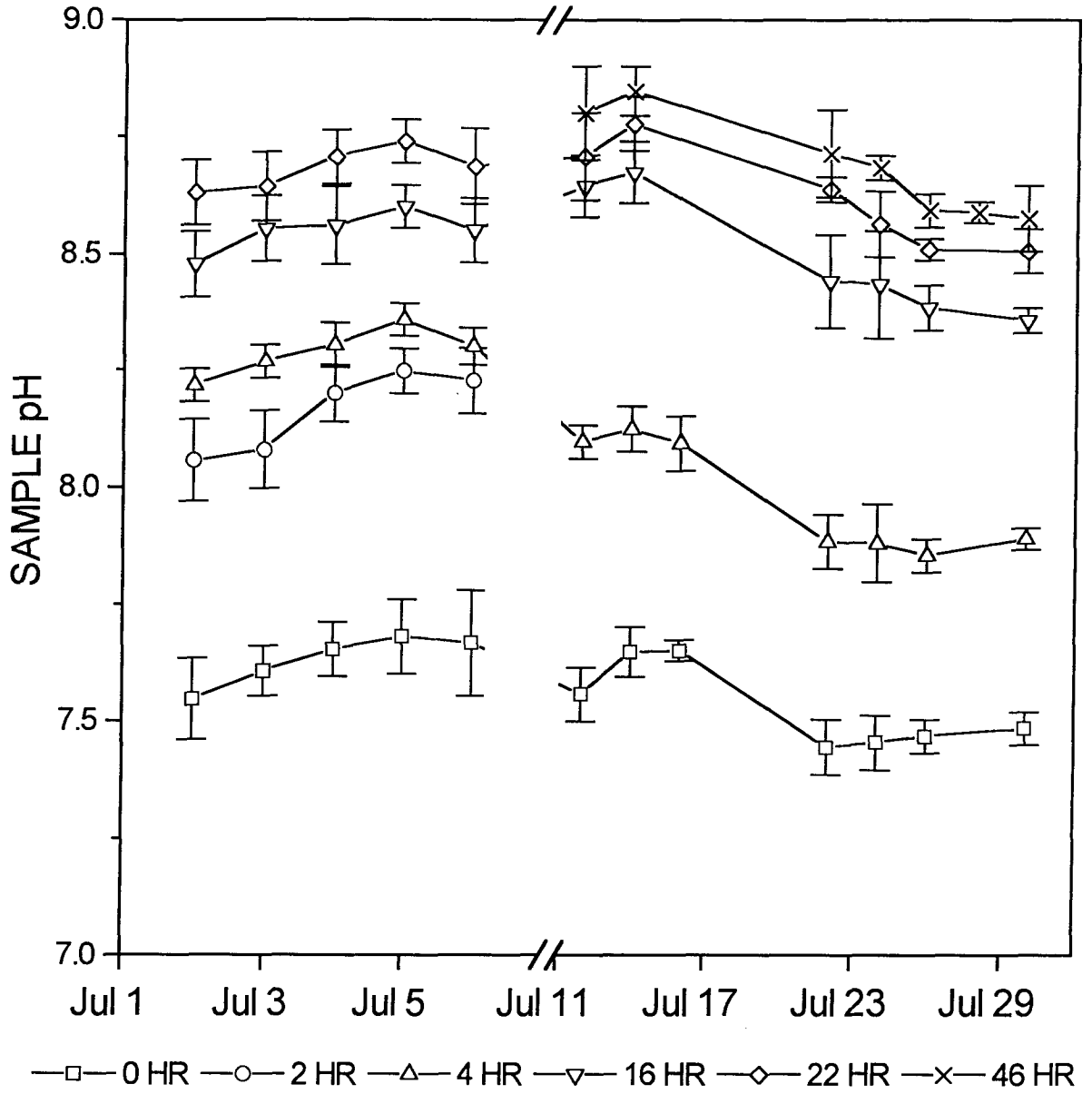

Figure 5. pH Values, Run A

This figure shows pH values at the 0, 2, 4, 16 and 22 hour points during some final 24-hour cycles of Run A, which started June 12, 1991. After the axis break are shown pH values at the 0, 4, 16, 22 and 46 hour points of some of the 48-hour cycles, which started July 6. All values are averages of the three replicate columns. The error bars represent 90% confidence levels. There is good replication between the columns. The readings appear to be stabilizing. Comparing the final few days of both portions, pH values at time points in the 24-hour cycles are significantly higher than the same time points during the 48-hour cycles. However, pH values at the end of 24-hour cycles are comparable to the pH reached in 48-hour cycles.

The pH readings from the last few 24-hour cycles appear to be stabilizing. Comparing the final few days of 24 and 48-hour cycles, pH values at time points in the 24-hour cycles are significantly higher than the same time points during the 48-hour cycles. However, pH values at the end of 24-hour cycles are comparable to the pHs reached at the end of 48-hour cycles.

COD removal percentages at the 0, 2, 4, 16 and 22-hour points during some final 24-hour cycles of Run A are shown in figure 6. After the axis break are shown COD removal percentages at the 0, 4, 16, 22 and 46-hour points of the final 48-hour cycles. All values are averages of the three replicate columns. The readings from the last few 24-hour cycles appear to have reached equilibrium. Comparing the final few days of both portions, COD removals at time points in the 24-hour cycles are significantly higher than the same time points during the 48-hour cycles.

Figure 7 shows COD removal percentages at the five time points each of the final 24-hour cycles and final 48-hour cycles, for supernatant from samples given an additional three hours settling after the initial one hour. All values are averages of the three replicate columns. The COD removals in these last 24-hour cycles appear to be stable. Comparing the final few days of both portions, COD removals at time points in the 24-hour cycles again are significantly higher than the same time points during the 48-hour cycles.

The COD error bars of both figures 6 and 7 show that there was a small amount of between-column variation, however the differences between the columns were consistent day-to-day in the 24-hour cycles, so the error bars are quite similar in size. The proximity of the zero-hour points to the four-hour points can be deceptive. Though a large amount of treatment occurs during the first four hours of aeration, some of this treatment is also accomplished during the extended settling of the zero-hour samples, raising the zero-hour line close to the four-hour data, particularly for the 48-hour cycles.

Average percentage COD removals are shown in figure 8 for the triplicate standard conditions columns of run A. The graph shows COD removal in both one-hour settled samples and supernatant from additional settling. An average of the last three cycles of each part of the run are used to calculate the five time points each of the 24-hour and 48-hour cycles. Though all 24-hour cycle points are higher than the result from the same aeration time in the 48-hour cycles, the difference is most dramatic for the zero to four-hour points. The biomass at the end of the 24-hour cycles must be much healthier, resulting in increased treatment during both the one-hour and four-hour (supernatant) settlings of the zero-hour samples.

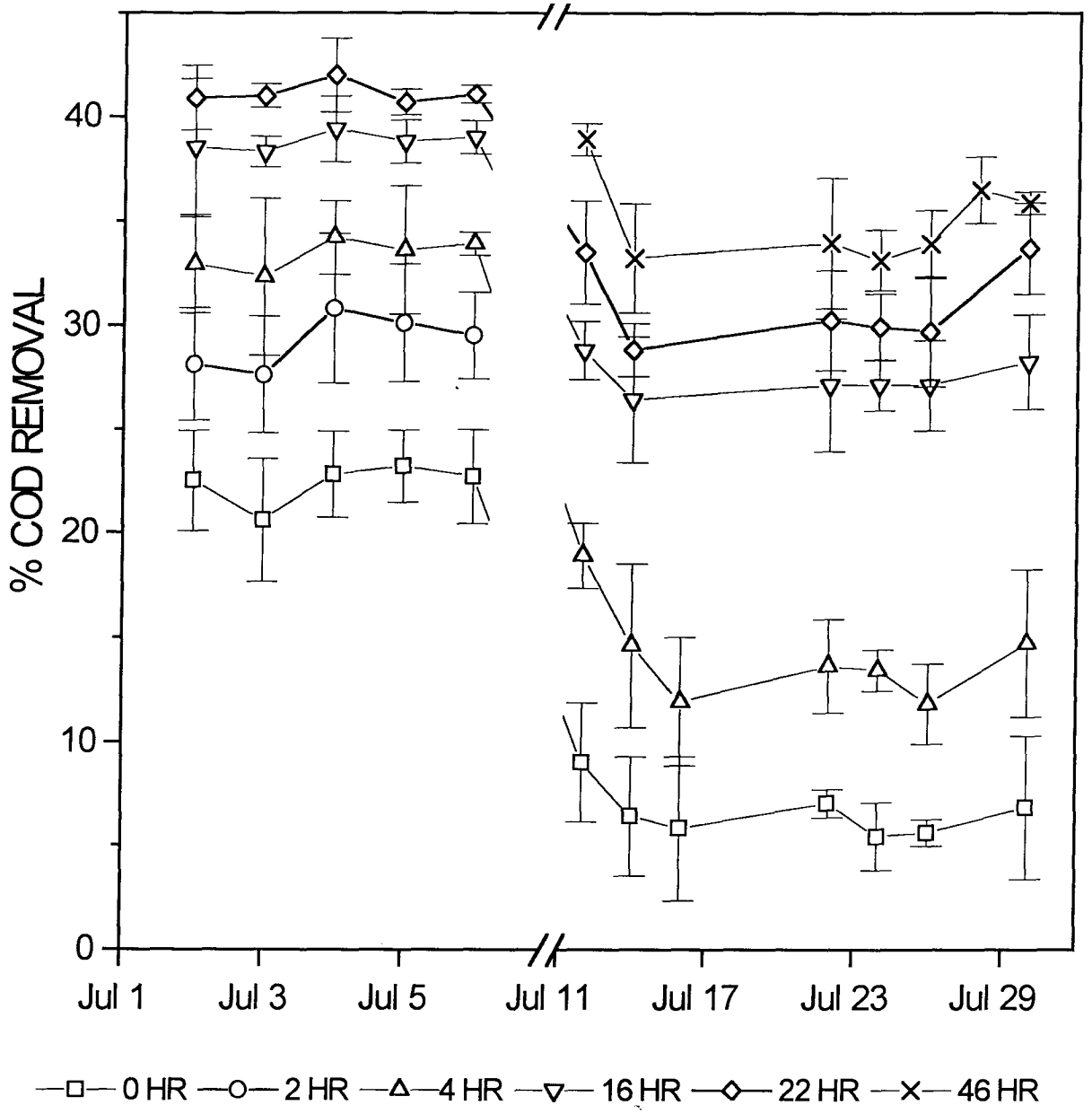

Figure 6. COD Removal (1-Hour Settled Samples), Run A

This figure shows COD removal percentages at the 0, 2, 4, 16 and 22 hour points during some final 24-hour cycles of Run A, which started June 12, 1991. After the axis break are shown COD removal percentages at the 0, 4, 16, 22 and 46 hour points of some of the 48-hour cycles, which started July 6. All values are averages of the three replicate columns. The error bars represent 90% confidence levels. The readings from these last 24-hour cycles appear to be stabilizing. Comparing the final few days of both portions, COD removals at time points in the 24-hour cycles are significantly higher than the same time points during the 48-hour cycles.

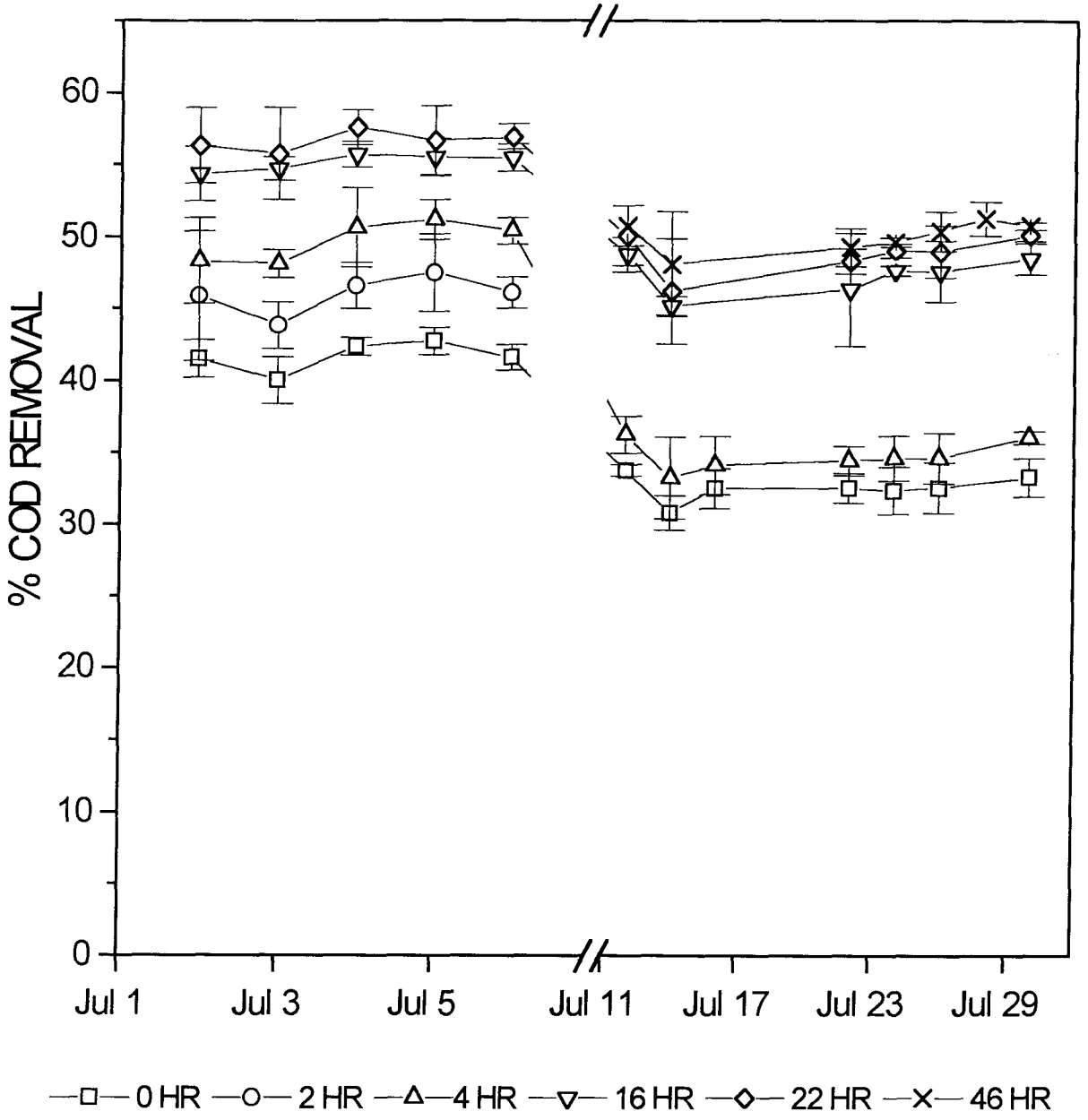

Figure 7. COD Removal (4-Hour Settled Samples), Run A

This figure shows COD removal percentages at the 0, 2, 4, 16 and 22 hour points during some final 24-hour cycles of Run A, which started June 12, 1991. After the axis break are shown COD removal percentages at the 0, 4, 16, 22 and 46 hour points of some of the 48-hour cycles, which started July 6. COD values shown are for supernatant from samples given four hours settling. All values are averages of the three replicate columns. The error bars represent 90% confidence levels. As in the previous graph, the readings from these last 24-hour cycles appear to be stable. Comparing the final few days of both portions, COD removals at time points in the 24-hour cycles are again higher than the same time points during the 48-hour cycles.

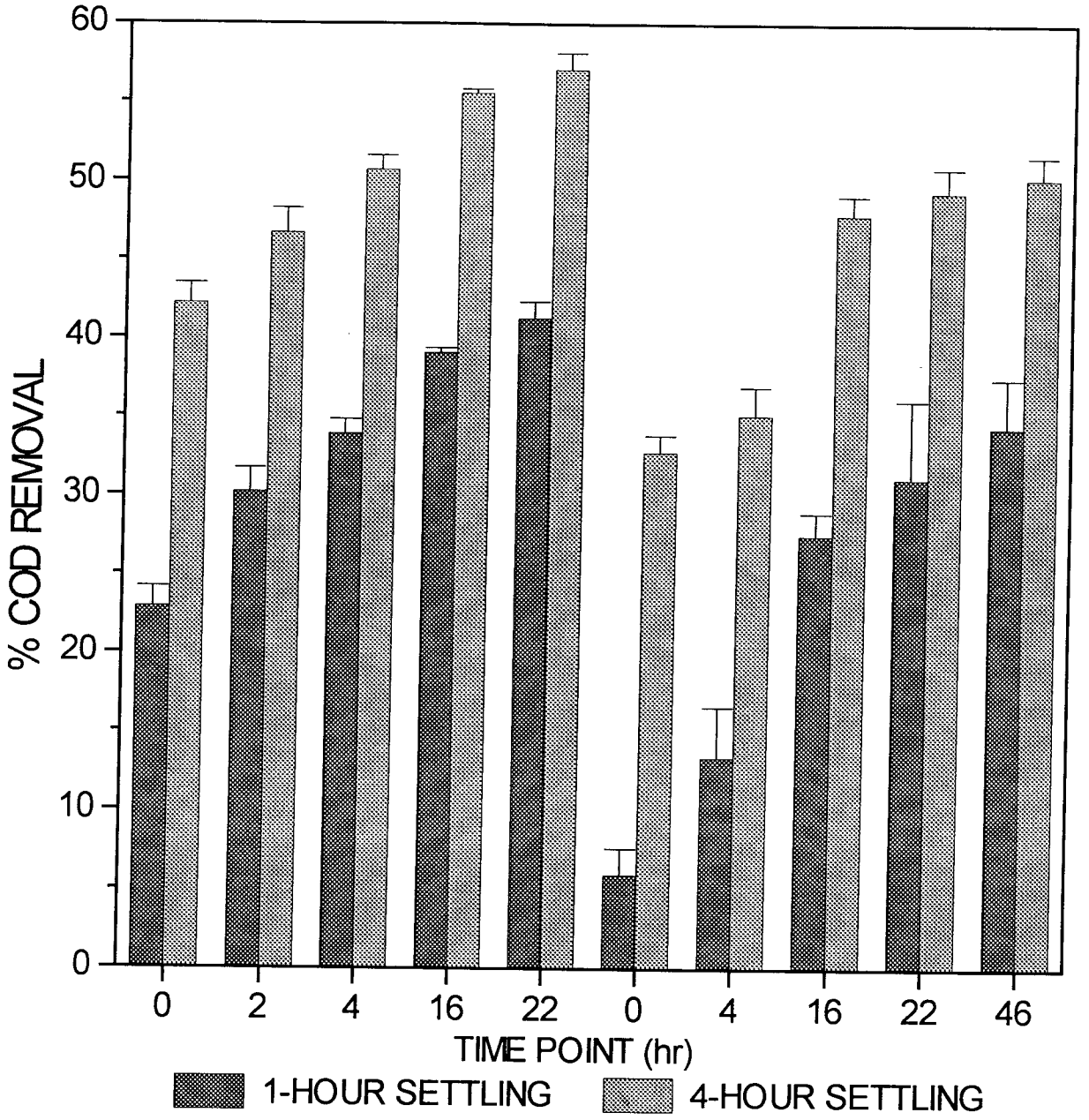

Figure 8. Average COD Removals in 1-Hour and 4-Hour Settled Samples, Run A

Average percentage COD removals are shown for the triplicate standard conditions columns of run A. An average of the last three cycles of each part of the run are used to calculate the 0, 2, 4, 16 and 22 hour points of the 24-hour cycles, and the 0, 4, 16, 22 and 46 hour points of the 48-hour cycles. Error bars show a 90% confidence interval for agreement between cycles. Though all 24-hour cycle points are higher than the result from the same aeration time in the 48-hour cycles, the difference is most dramatic for the 0 to 4 hour points. The biomass at the end of the 24-hour cycles must be more active, resulting in both increased treatment during the 1-hour and extended settlings of the zero-hour samples.

Figure 9 illustrates the cycling of COD removals and pH for the 0, 2, 4, 16 and 22 hour sample points of the last five 24-hour cycles, with zero hours of the cumulative time shown being set at the zero-hour point of the first of these five cycles. Both results from one-hour settled samples and supernatant from additional settling are shown. Though pH increase tapers off by the 16-hour points, there is still notable COD removal in both one-hour and four-hour settled samples between the 16 and 22 hour points. Both COD series appear to show equilibrium. pH equilibrium lags slightly behind, so in the first couple of these five cycles a small increase is still seen in pH.

A great amount of COD removal is effected simply by subjecting samples to one hour settling after fresh influent is mixed into the columns. In run A, these "zero" hour points show approximately 23% COD removal. This is a combination of three factors: a) the dilution of the influent with the three litres of treated wastewater remaining in the column, b) biological activity that continues during settling, particularly until the oxygen that entered the wastewater during straining is used up and c) the visible improvement in settleability of wastewater solids resulting from this hour of biological treatment.

As mentioned previously, settling that occurs during this hour would not have resulted by simply allowing the wastewater to remain under quiescent conditions without exposure to the biomass. The wastewater used has little settleable solids prior to this treatment as most settled out in the shipping containers. The settled matter in the individual stored buckets is not put into the columns (as discussed in Materials and Methods), partly because only buckets filled from near the bottom of the shipping containers have any noticeable amount, and it would amplify between-day variation in the influent to include this.

The difference between the zero hour COD removals from the 24-hour cycles and the 48-hours cycles is very large. The biomass must be far more active at the end of the 24-hour than at the end of the 48-hour cycles, and therefore is far more metabolically active during the hour of settling of the zero-hour points of the 24-hour runs. This difference is not due to any difference in DO at the beginning of the cycle, as the sludge remaining in the column was always at zero DO, the wastewater being poured into the columns was always subjected to the same method of straining, and the brief non-aerated mixing was of the same duration in both cycles and in any case would have added little to the DO. Though there were small differences in DO at the time the zero-hour samples were taken, this is

considered to be primarily due to the difference in the biomass activity affecting the speed at which the oxygen from the influent is exhausted.

In the 48-hour cycles, the zero-hour removal is actually only about 60% of what would be expected purely from the dilution of the influent with three litres treated wastewater. This means that the settleability of the biomass has actually decreased from the process of being mixed and undergoing another hour of settling. This must be because at the end of the hour of in-column settling the flocs are vulnerable to being broken up by mixing, some of which is carried out at the end of the cycle to allow the sludge sample to be taken, and the rest which occurs when fresh wastewater is mixed into the column. This destruction of the flocs is not experienced by the 46-hour samples because they are taken right at the end of the settling period (immediately before the sludge is mixed for sampling). The disruption of the flocs would also have been occurring in the 24-hour cycles, but the increased biological activity could recoup the COD removal losses, and in addition the healthier flocs may have been less susceptible to fragmentation.

Percentage removals of BOD_5 for samples from near the end of the 24-hour cycles and 48-hour cycles are given in table 8. All values are averages of quadruplicate tests. For the 22-hour samples an average of 19.6% additional BOD_5 removal results from the extended settling. The influent BOD_5 averaged 2240 mg/l.

Table 8. BOD_5 Percentage Removals for Run A

Date	Sample hr	Column	1-hr settling % BOD_5 Removal	4-hr settling % BOD_5 Removal
July 05	22	4	73.77	92.99
July 05	22	5	71.69	92.30
July 05	22	6	75.00	93.87
July 05	22	average	73.49	93.05
July 30	46	4	77.29	90.61
July 30	46	5	78.02	92.48
July 30	46	6	78.89	91.92
July 30	46	average	78.07	91.67

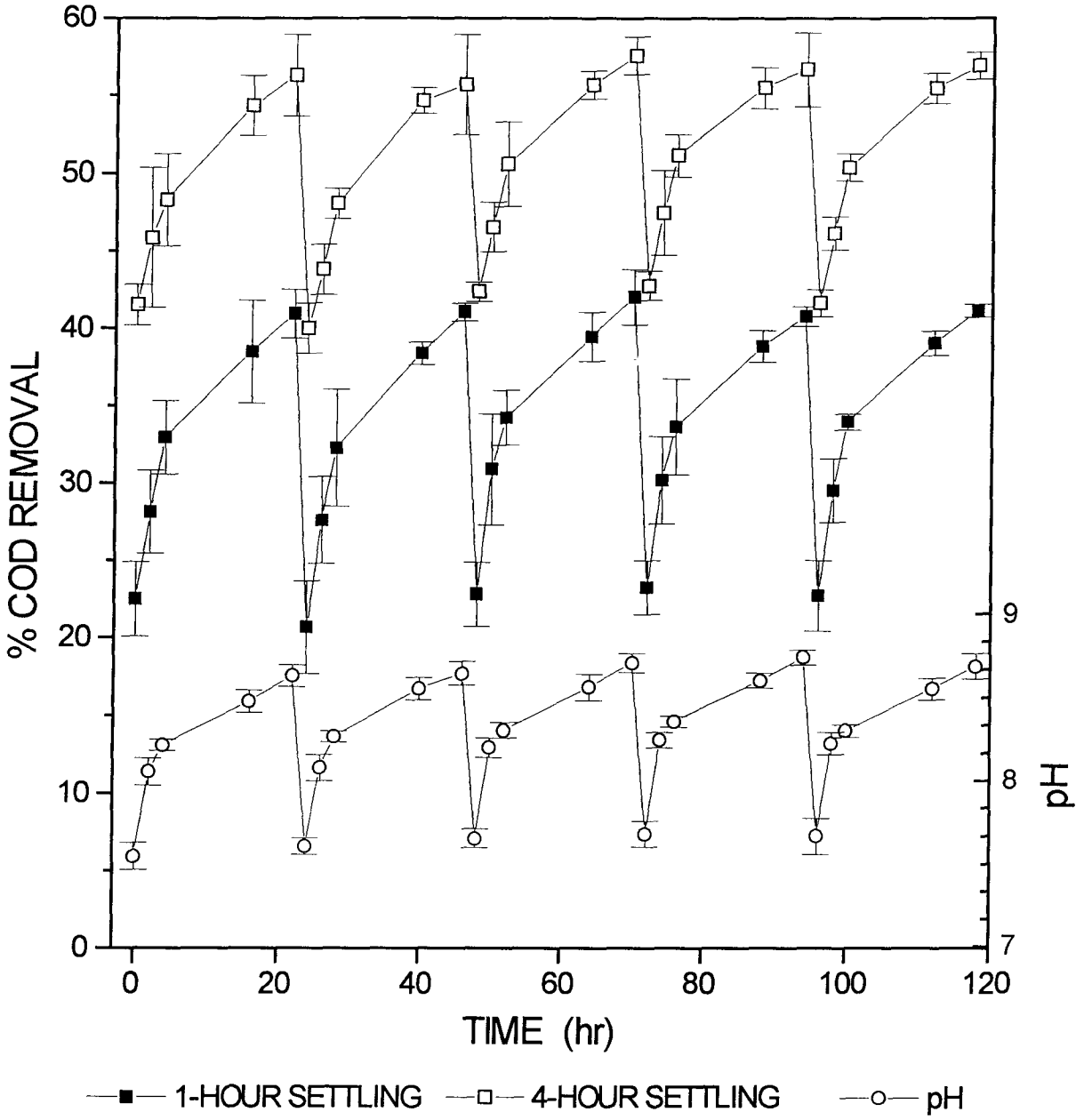

Figure 9. COD Removals in 1-Hour and 4-Hour Settled Samples and pH Values, For Last Five 24-Hour Cycles of Run A

This figure shows COD removals and pH for the 0, 2, 4, 16 and 22 hour sample points of the last five 24-hour cycles of run A, with 0 hours of the cumulative time shown being set at the 0-hour point of the first of these five cycles. Error bars represent 90% confidence levels. Though pH increase tapers off by the 16-hour points, there is still notable COD removal in both 1-hour and 4-hour settled samples between the 16 and 22 hour points. Both COD series appear to show equilibrium. pH equilibrium lags slightly behind, so in the first couple of these five cycles a small increase is still seen in pH.

Foam heights at the end of the aeration periods increased slightly during the early 24-hour cycles of run A, stabilizing at heights of 8 to 10 cm (occasionally reached the underside of the column lids 11 cm above liquid surface). The foam had some substance, but dissipated within three minutes of aeration being halted. During the first 48-hour cycles, the foam reached heights of 9-11 cm (during the first cycle also filled the small opening in the lid). However, by the end of the run the foam heights were typically 7 to 9 cm.

Mixed liquor total solids, total suspended solids and volatile suspended solids for run A are shown in figure 10. All values are averages of the three replicate columns. The values for June 25 to July 5 are from the final 24-hour cycles, and later dates show values from some 48-hour cycles near the end of the run. Values from the 24-hour cycles show quite stable levels for all three solids measurements. The concentrations from 48-hour cycles are slowly decreasing. The final 48-hour values and corresponding wasted sludge rates are approximately 60% of the 24-hour values. From the sludge volumes measured for one of the 24-hour cycles and three of the 48-hour cycles of this run, the SVIs for the 24-hour cycles were 57-61 ml/g and 63-76 ml/g in the 48-hour cycles.

The sludge concentrations in the individual columns show more cycle-to-cycle variation than is evident in this graph, as averaging the three columns tends to smooth this fluctuation. This is also seen in the figures of sludge concentrations for run B which show averages of duplicate columns.

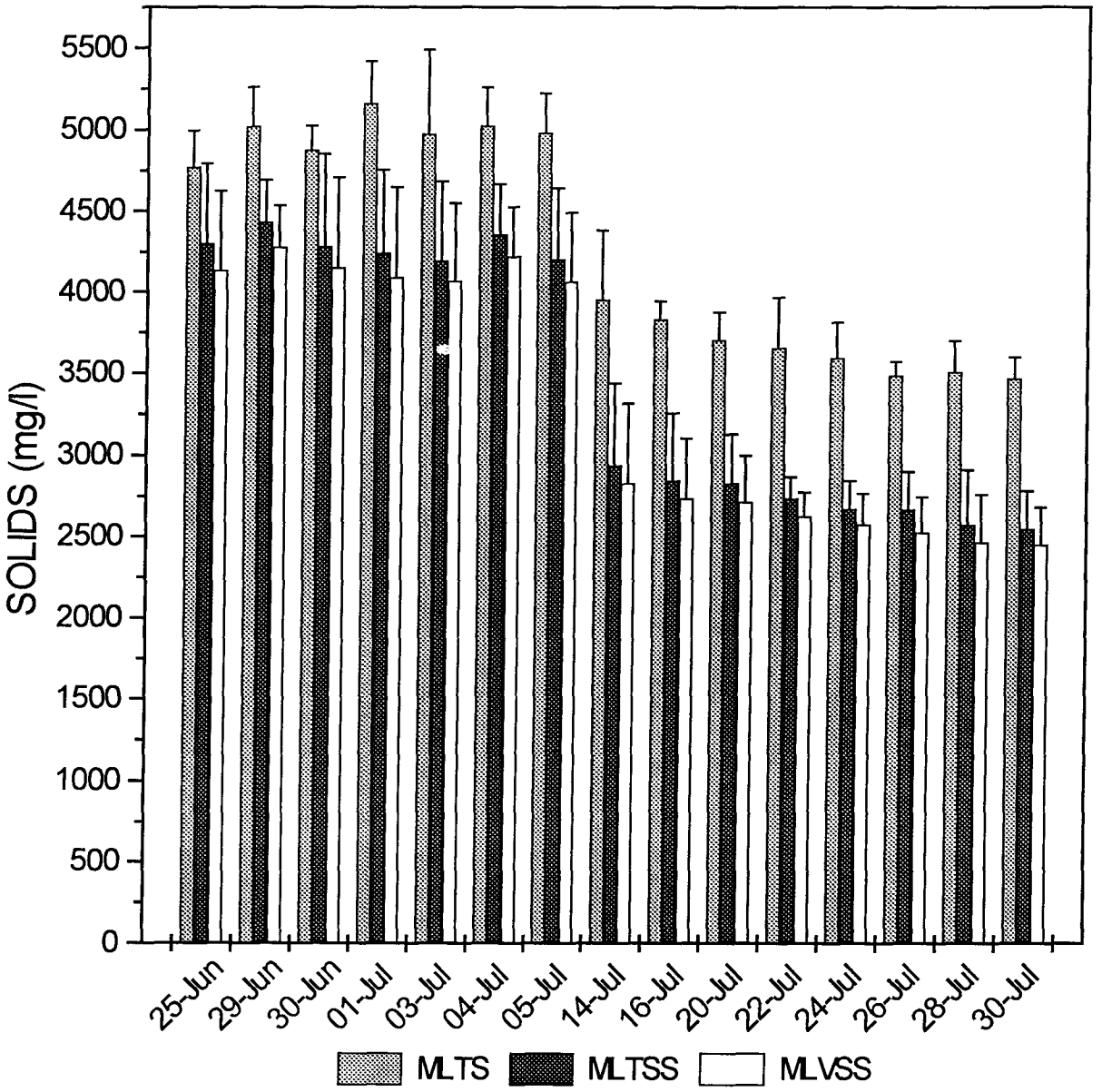

Figure 10. Solids Concentrations, Run A

Mixed liquor total solids, total suspended solids and volatile suspended solids are shown. All values are averages of the three replicate columns. The error bars represent 90% confidence levels. The values for June 25 to July 5 are from the 24-hour cycles which started June 12, 1991, and later dates show values from the 48-hour cycles which started July 6. Values from both parts of the run show quite stable levels for all three solids measurements, though the values from the 24-hour cycles portion show slightly less variation. This might be expected as the first part of the run was of longer duration. The 48-hour values and corresponding wasted sludge rates are roughly 60% of the 24-hour values.

Run B Treatment Results

Recommended pH operating ranges for AS systems are 6.5 to 8.5, with the optimum pH between 6.8 and 7.5 [CH2M Hill 1989]. The reactors in run A reached a pH of approximately 8.7 by the end of 24-hour cycles, and earlier runs had reached pHs as high as 8.8 in 24-hour cycles. Run B was performed to determine if the high pH being reached at the end of all cycles was limiting the activity of the biomass during the later hours of aeration. This was assessed by comparing results from columns run at standard conditions to columns having acid added during each cycle to limit the pH reached. It was also attempted to compare the standard columns to columns using pure oxygen-activation, but this was not successful.

Run B had two columns (1 and 6) at standard conditions. Two columns (4 and 5) were run identically to these except that 50 ml of 2 N sulphuric acid were added into each column immediately after the four-hour samples were taken (for pH control and possibly sludge bulking control). Columns 2 and 3 were run on pure oxygen.

The pure oxygen-activated columns had lower COD removals than the other columns and falling sludge concentrations, but this is considered likely due to the decreased mixing caused by the lower gas flow rates required. It was observed that the sludge flocs in the air-activated columns were being broken up to a far greater degree. Once the columns were switched over to pure oxygen, the sludge concentrations began dropping significantly Because of the poor mixing in the oxygen columns, the results from those columns are not considered representative of oxygen-activation and the those results are not discussed further here.

Run B 24-hour cycles started September 5, 1991 using an earlier batch of the Quesnel wastewater for the first 12 days, switching onto "B" wastewater on September 17. 24-hour cycles continued through the September 26 cycle, for a total of 22 cycles. 48-hour cycles ran from the beginning of the last 24-hour cycle until October 18 (11 cycles).

Figure 11 shows pH values at the 0, 4 and 22-hour points during the 24-hour cycles. All values are averages of the duplicate columns. The two standard columns appear to be at equilibrium. The readings for the two acid-added columns were still dropping at the first dates shown, but this change appears to be slowing at the final dates. It had been desired to achieve a pH reduction of about 0.75 - 1 pH unit compared to the 22-hour point of nonadjusted columns and this was met using this level of acid addition. The agreement between duplicate columns was very good for the zero and 22-hour points. It is understandable that the four-hour points

had more variation, as pH levels are changing rapidly during the early hours of treatment.

Figure 12 shows COD removal percentages at the 0, 4 and 22-hour points during 24-hour cycles of run B. All values are averages of the duplicate columns. Standard columns demonstrate slightly superior COD removals, particularly noticeable for the four-hour points. Even early in the run, before the pH after the 4-hour point might have dropped too far, the acid-added runs did not have significantly superior COD reductions.

Figure 13 illustrates COD removal percentages at the three time points during 24-hour cycles, for supernatant given the additional three hours settling. All values are averages of the duplicate columns. Acid-added columns have dramatically higher removals for the zero-hour points, but much of this improvement over the standard columns is lost by the four-hour point. By the 22-hour point the two treatments are not significantly different.

The pH values resulting immediately after the addition of acid appeared to reach equilibrium values of approximately 5.28 and 5.20 for columns 4 and 5 by September 24. This stabilization at the lowest pH values coincided with the small but consistent drop in COD removals for the one-hour settled samples near the end of the run. However, there was little corresponding drop in the COD removals in the supernatant samples, so the activity of the biomass had not been affected, only the settleability of suspended solids. As the SVIs were unaffected, it was primarily the influent suspended solids that decreased in settling speed rather than the flocs. It is possible that the temporary low pH conditions existing after the four-hour points near the end of the run somehow caused a poorer adsorption of organic matter onto the flocs.

hese temporarily low pHs were a little lower than intended. If discrete acid aliquots were used for pH adjustment in a full scale system, it would be advisable to use multiple smaller aliquots to obtain less variation in pH levels over the cycle. If pH limitation was desired for a full-scale application, pH controllers would likely be used, eliminating the problem of either pH extreme. Two pH controllers became available for use in run C, so it was possible to compare run B to results where a low pH was maintained with less fluctuation during the cycle.

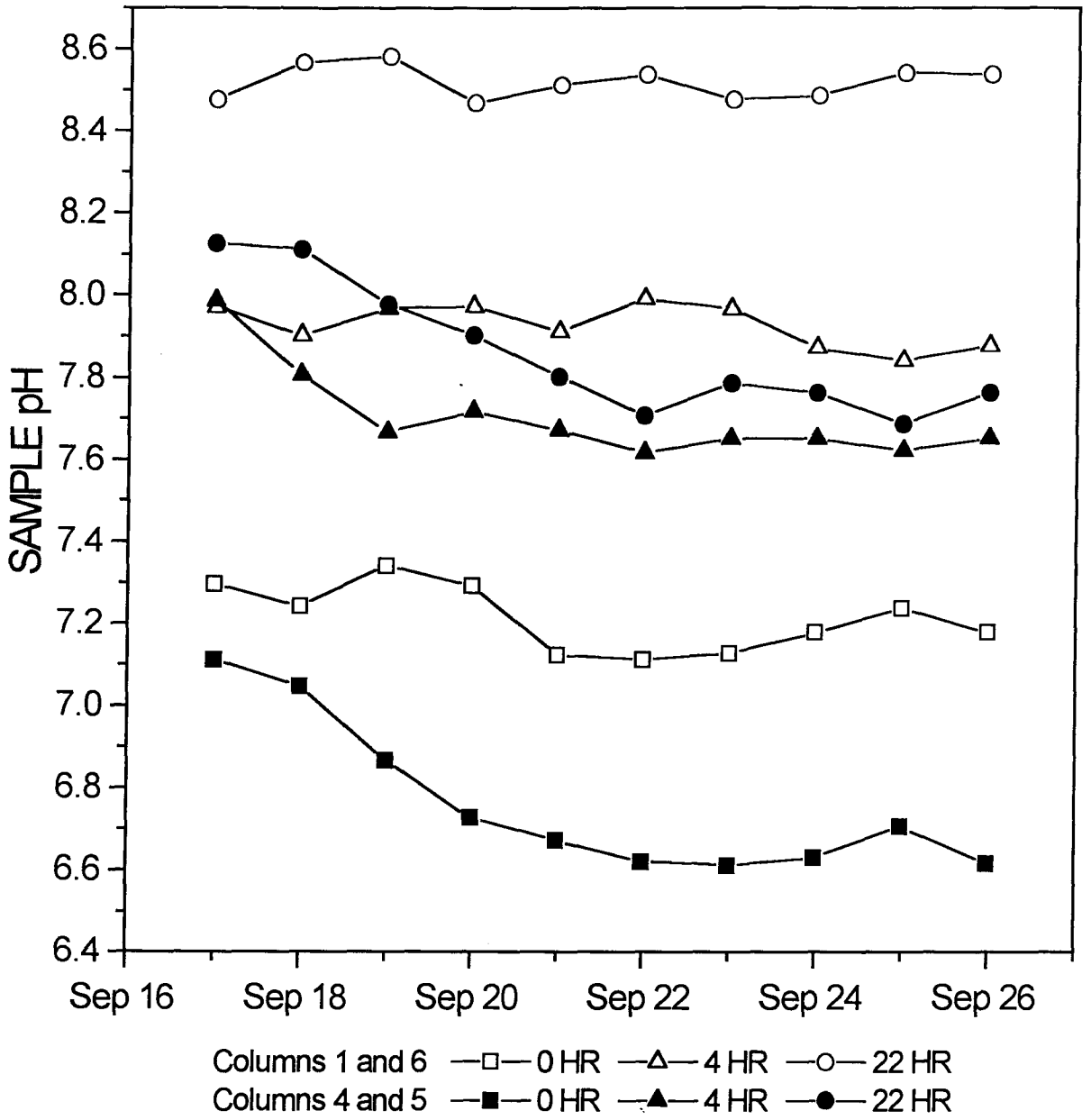

Figure 11. pH Values, Run B

This figure shows pH values at the 0, 4 and 22 hour points during 24-hour cycles of Run B, which ran from September 5 to 27, 1991. All values are averages of the duplicate columns. Columns 1 and 6 were run at standard conditions. Columns 4 and 5 were run identically except that 50 ml of 2 N sulphuric acid were added into each immediately after the 4 hour samples were taken. The standard columns appear to be at equilibrium. The readings for the acid-added columns are still dropping at the first dates shown, but appear to be stabilizing at the final dates. It had been desired to achieve a pH reduction of about 0.75 - 1 unit compared to the 22 hour point of nonadjusted columns and this was met using this level of acid addition.

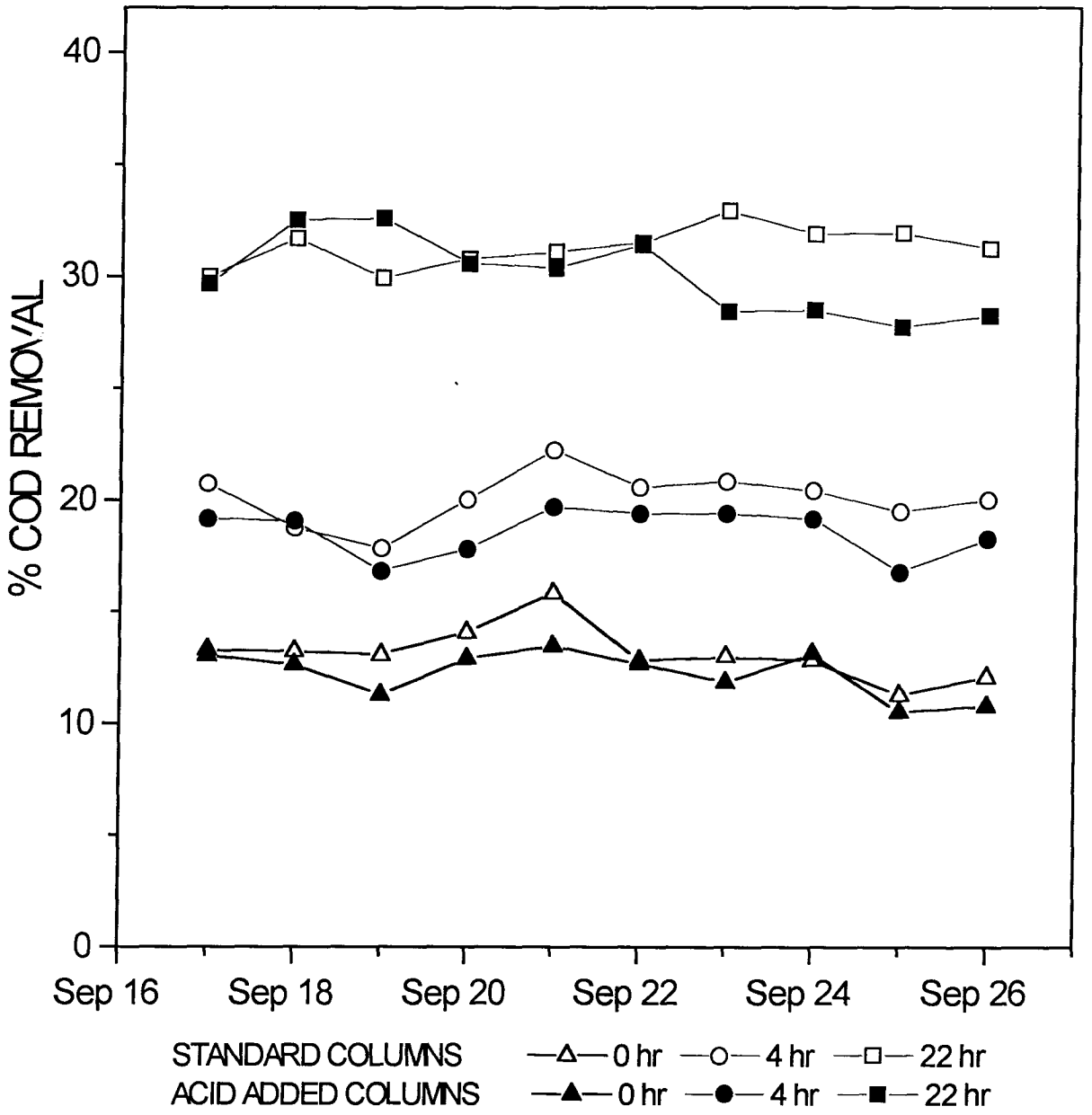

Figure 12. COD Removal (1-Hour Settled Samples), Run B

This figure shows COD removal percentages at the 0, 4 and 22 hour points during 24-hour cycles of Run B, which ran from September 5 to 27, 1991. All values are averages of the duplicate columns. Columns 1 and 6 were run at standard conditions and had no pH adjustment. Columns 4 and 5 were run identically except that 50 ml of 2 N sulphuric acid were added into each immediately after the 4-hour samples were taken. The standard columns generally have slightly higher COD removals. The largest difference occurs at the 22-hour point for the last few cycles, where the reduction in the acid-added columns appears to be reaching a new equilibrium.

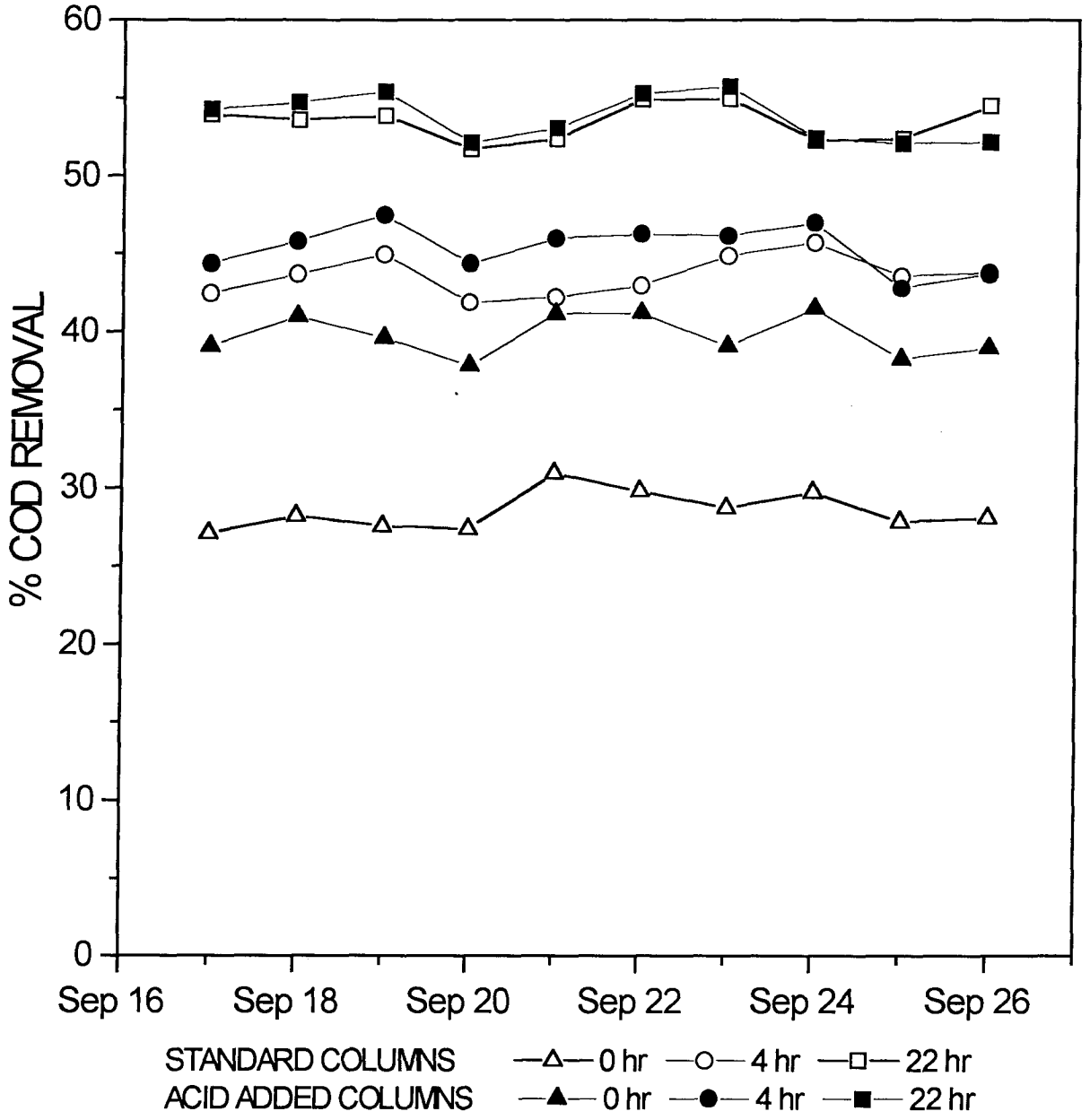

Figure 13. COD Removal (4-Hour Settled Samples), Run B

This figure shows COD removal percentages at the 0, 4 and 22-hour points during 24-hour cycles of Run B, which ran from September 5 to 27, 1991. COD values shown are for supernatant from samples given 4 hours settling. All values are averages of the duplicate columns. Columns 1 and 6 were run at standard conditions and had no pH adjustment. Columns 4 and 5 were run identically except that 50 ml of 2 N sulphuric acid were added into each immediately after the 4 hour samples were taken. The difference between the acid-added and standard columns were small except for the 0-hour point where COD removals in the acid-added columns were nearly as great as in the 4-hour samples.

Shown in figure 14 are the average percentage COD removals for the 0, 4 and 22-hour time points of the 24-hour cycles and the 46-hour point of the 48-hour cycles of Run B for the two standard conditions columns. COD removals for both one-hour settled samples and supernatant from additional settling are graphed. The values are averages of the last three cycles of each part of the run. The error bars are much smaller on supernatant as would be expected, as the only one-hour settled samples can have significant variation in the amount of biomass still suspended. Removals at the end of 48-hour cycles are only moderately higher than at the end of 24-hour cycles.

Percentage COD removals for both one-hour settled and additional-settled samples are shown in figure 15 for the three time points. All values shown are averages of duplicate columns. The averages from the standard columns are on the left of each pair, the acid-added columns to the right. The numbers used are averages of the last three 24-hour cycles. The standard conditions results are consistently higher than the acid-added removals for the one-hour settled samples. The acid-added columns had the advantage however when the samples were given the additional settling, resulting in dramatically higher removals for the zero-hour samples. The suspended material in the wastewater is quite effectively settled during the additional three hours clarification after being mixed with the biomass from the end of the previous acid-added cycle. However, most of this improvement over the standard columns was lost by the 22-hour point.

This run indicates that pH was not limiting near the end of the cycles in the standard columns, as the acid-added columns had only slightly superior supernatant COD removals at the 22-hour point. In fact, during the latter part of each cycle when the pH was high, was when the nonadjusted columns made up some of the large deficit in removal evident at the beginning of each cycle. Though pH is not thought to have been limiting in the nonadjusted columns, the addition of acid did confer an advantage for the removal of COD in the supernatant samples of the early time points, particularly the zero-hour point. However, because the standard columns had almost as good final CODs for the extended settling samples, and did have slightly better results for the more typical settling period, the addition of the acid is not considered to have been an advantage in this run.

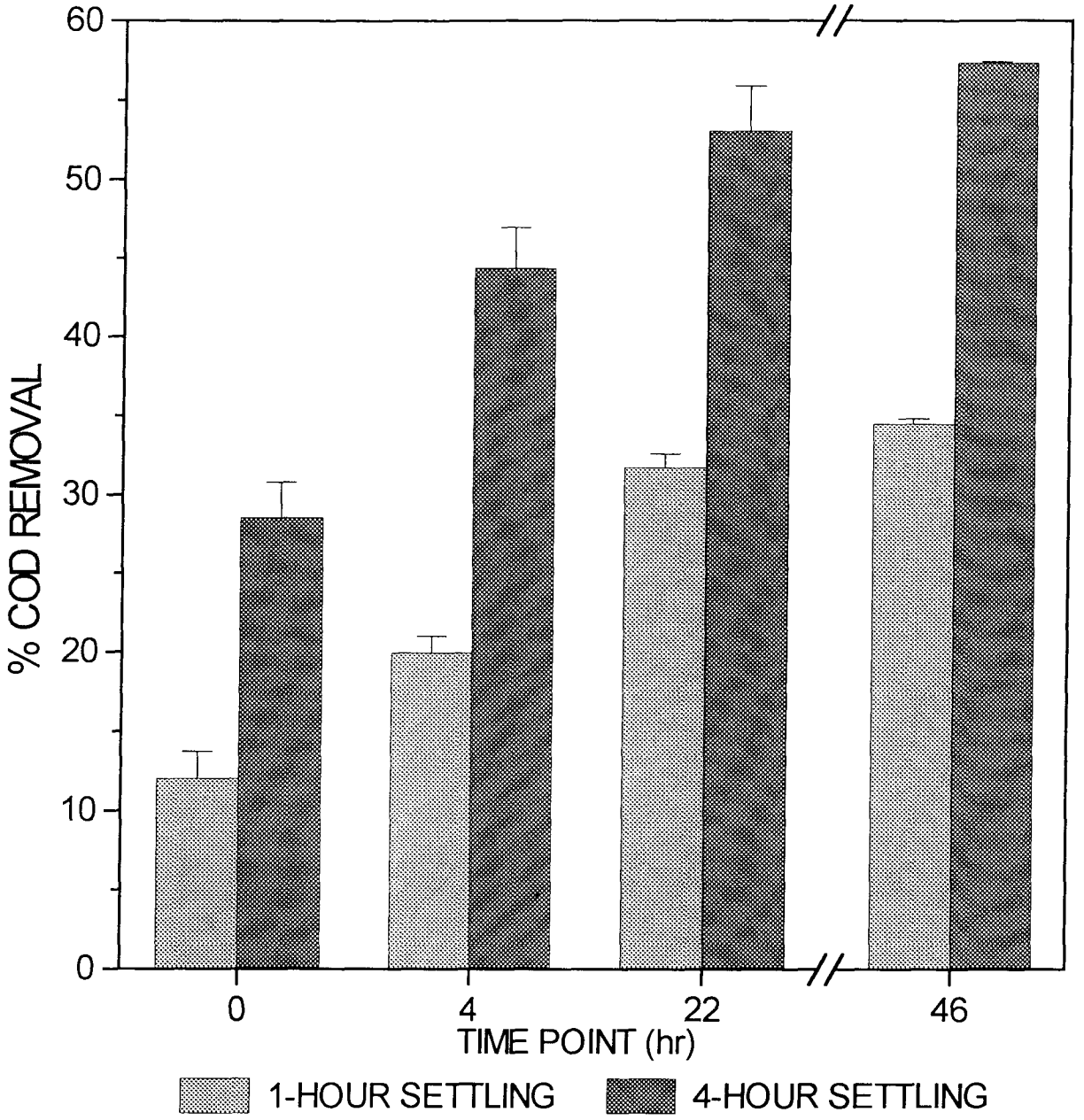

Figure 14. COD Removals in 1-Hour and 4-Hour Settled Samples, Run B

Shown are the average percentage COD removals for the 0, 4 and 22 hour time points of the 24-hour cycles and the 46 hour point of the 48-hour cycles of Run B for the two standard conditions columns. The values are averages of the last three cycles of each part of the run. Error bars show 90% confidence intervals for agreement between cycles. Error bars are much smaller on the supernatant from extended settling, as would be expected because the samples settled for only one hour can have significant variation in the amount of biomass still suspended. Removals at the end of 48-hour cycles are only moderately higher than at the end of 24-hour cycles.

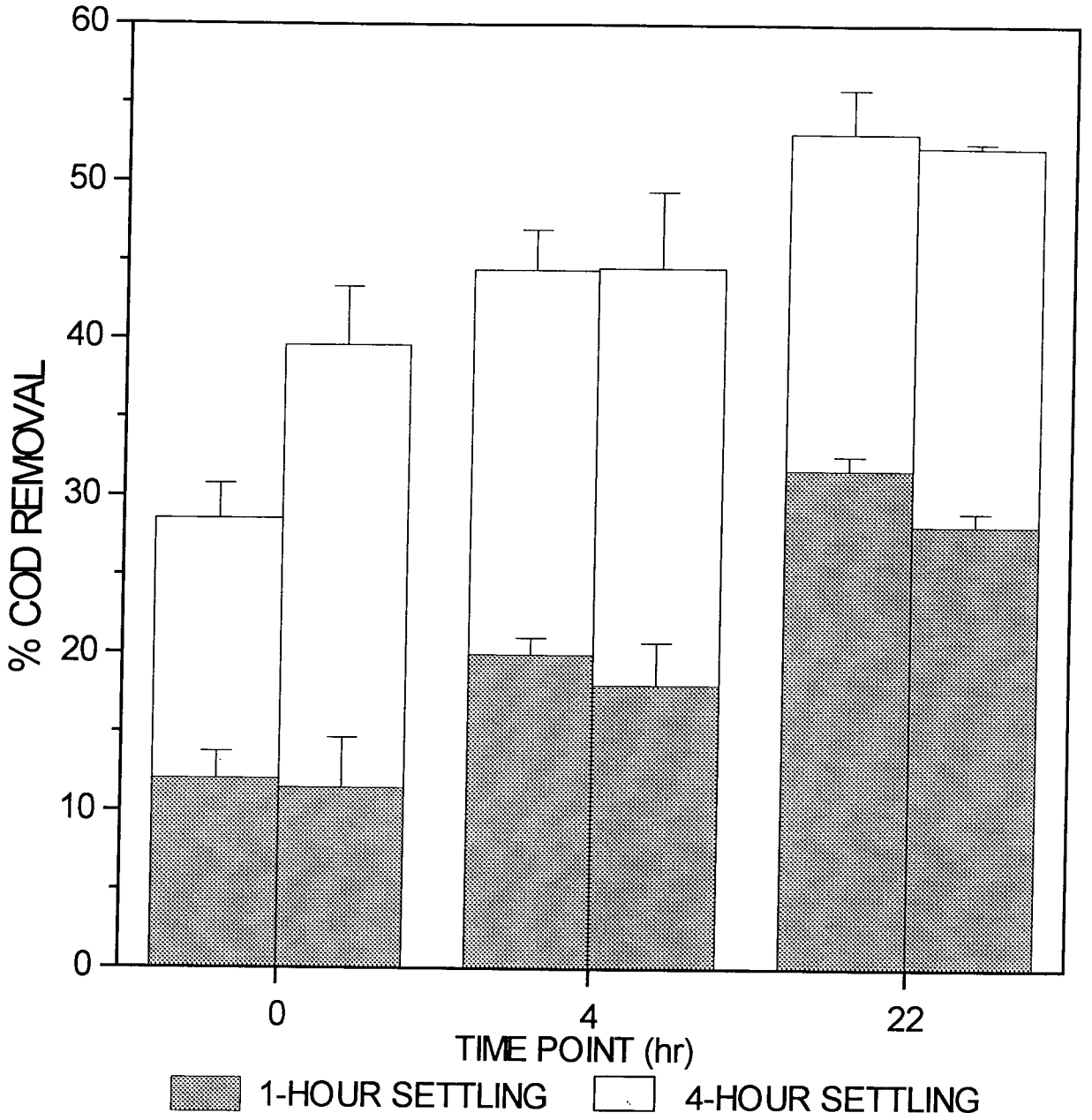

Figure 15. Average COD Removals in 1-Hour and 4-Hour Settled Samples for Standard Conditions Columns and Acid-Added Columns, Run B

COD removals for both 1-hour and 4-hour settled samples are shown for three different time points of run B. Averages of the duplicate columns are used, with the standard columns shown on the left in each pair, the acid-added columns to the right. The numbers used are averages of the last 3 24-hour cycles. Error bars represent 90% confidence intervals for the cycle-to-cycle variation. The standard conditions results are consistently at least slightly higher than the acid-added removals, with the exception being the result for the zero-hour point in the supernatant from extended settling.

BOD_5 reductions at the final time points at the end of the 24-hour cycles and 48-hour cycles are listed in table 9. These removals are slightly lower than the results from run A (which had a lower BOD_5 loading). There is a greater difference between the standard and acid-added columns for the one-hour settled samples than four-hour settled samples, which was also the case for the COD measurements. The BOD_5 of the untreated wastewater averaged 3190 mg/l.

Table 9. BOD_5 Percentage Removals for Run B

Date	Sample hr	Column	1-hr settling % BOD_5 Removed	4-hr settling % BOD_5 Removed
Sep-26	22	standard	70.23	89.65
Sep-26	22	acid-added	67.04	88.11
Oct-16	46	standard	76.58	94.62

Wastewater B had a total solids concentration of 8,625 mg/l, TSS of 950 mg/l and VSS of 930 mg/l. This TSS is near the bottom of the range of 900-2000 mg/l specified by the Quesnel mill technicians for combined whitewater and wastewater from that mill, which is probably because the measurement of wastewater B does not include the fraction of solids that settled out during shipping and storage. However, this is higher than the concentration in the wastewater entering the Quesnel mill's biological treatment system, which has been clarified in a dissolved air flotation system and has a TSS of about 150-300 mg/l.

The treated wastewater from the September 24, 24-hour cycle had a TSS of 500 mg/l (+/-16 mg/l at 90% C.I.) and a VSS of 480 mg/l (both averages of four samples). This just meets the TSS regulation in effect for Quesnel River Pulp which, based on production and effluent flow rate, works out to a daily maximum of 837 mg/l and a maximum of 502 mg/l for the monthly average. TSS regulations will likely become even stricter in the near future [personal communication, Vernon E. McAllen of H.A. Simons Ltd. 1993]. The Quesnel River Pulp final effluent has an average TSS of 480 mg/l.

During the 24-hour cycles the standard columns had significantly more foam at the end of aeration periods (7-10 cm) than the acid-added columns (2-4 cm). Comparing foam heights between duplicate columns, showed that the column operating at slightly higher pH also had slightly more foam. The foam on the acid-added columns also broke up within three seconds after the aeration stopped, while in the standard columns the foam lingered for one to two minutes. The acid addition

had a large impact on foaming, but the SVIs of the acid-added columns remained similar to those in the standard columns.

Mixed liquor total solids, total suspended solids, volatile suspended solids and sludge volume index for run B are shown in figure 16. All values are averages of the duplicate columns at standard conditions. The values for September 18 to 26 are from some final 24-hour cycles; later dates show values from 48-hour cycles near the end of the run. The SVIs are steady at between 54 and 60 ml/g for the 24-hour cycles, and then clearly deteriorate during the 48-hour cycles.

Values from the 24-hour cycles are relatively stable by this stage of the run for all sludge measurements. The solids wasted per cycle at the end of the run of 48-hour cycles were still greater than the equilibrium values expected for the very low organic loading. The concentrations in the final 48-hour cycles are approximately 73% of the 24-hour cycle values, which is high compared to run A. At the end of the run the solids concentrations are still declining from sludge built up during the 24-hour cycles, and the SVIs are still deteriorating.

Shown in figure 17 are the mixed liquor total solids, total suspended solids, volatile suspended solids and sludge volume index for the 24-hour cycles of run B, comparing the standard and acid-added columns. The acid-added columns have slightly lower solids concentrations, but SVIs are similar. Agreement was high between the two standard columns.

Resin acids and fatty acids were determined by GC for the influent and a 24-hour cycle treated wastewater sample. The treated sample was the one-hour settled sample of the 22-hour point in standard column 1, from the September 26 cycle. The results are shown in table 10. High resin acid concentrations were expected for this batch of wastewater as its COD and BOD_5 were the highest of all the batches of wastewater used. The resin acids present in the highest concentrations are dehydroabietic and abietic acid, consistent with the resin acid percentages for the QRP wastewater in a recent study [McCarthy 1991]. The 41.9% reduction in total resin acids is low compared to that of other aerobic treatment systems mentioned in the literature review, but cannot be considered as typical for the system without the analysis of further samples.

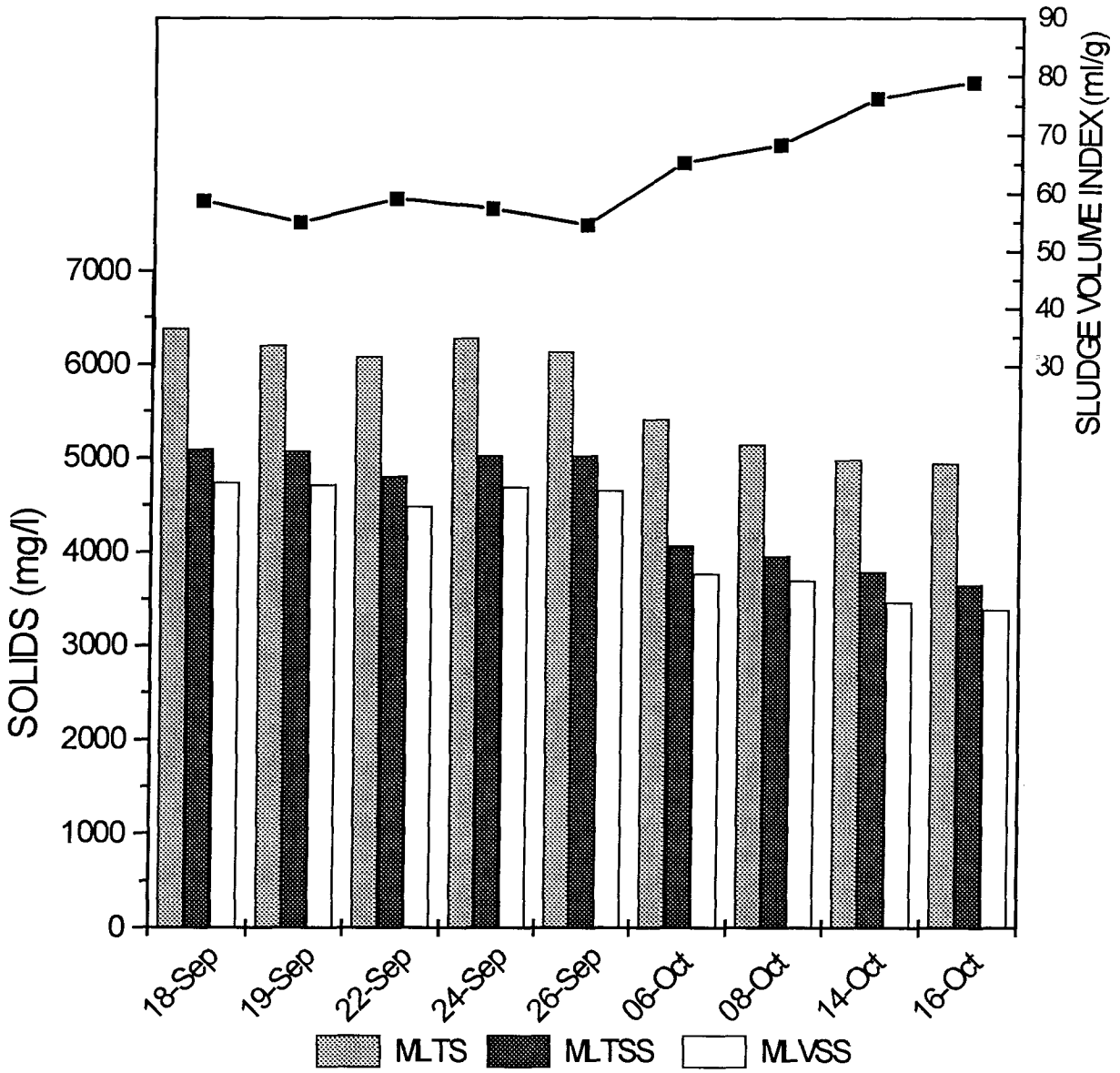

Figure 16. Solids Concentrations and Sludge Volume Index for Standard Columns, Run B

Mixed liquor total solids, total suspended solids, volatile suspended solids and sludge volume index are shown. All values are averages of the duplicate columns at standard conditions. The values for September 18 to 26 are from the 24-hour cycles which started September 5, 1991. Later dates show values from the 48-hour cycles which started September 26. Values from the 24-hour cycles are relatively stable by this stage of the run for all sludge measurements. Though the solids concentrations of the 48-hour cycles are only slowly decreasing during the dates shown, the SVIs are still deteriorating. The final 48-hour cycle MLVSS is 73% of the average 24-hour cycle values, and is probably still above equilibrium levels.

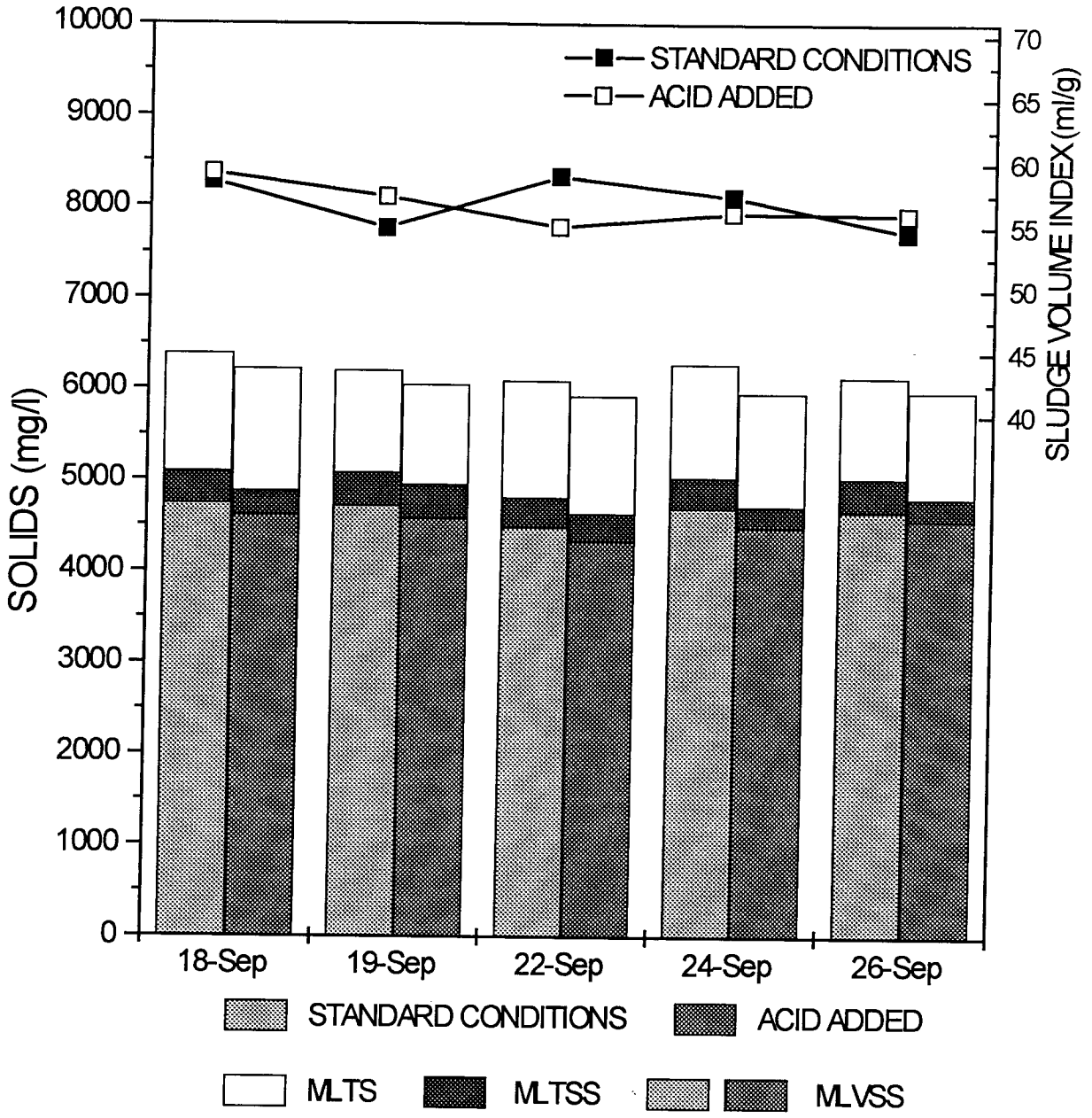

Figure 17. Solids Concentrations and SVIs for Standard and Acid-Added Columns, Run B

This figure illustrates the mixed liquor total solids, total suspended solids, volatile suspended solids and sludge volume index for the 24-hour cycles of run B, comparing the standard and acid-added columns. Acid-added columns consistently have slightly higher SVIs, and slightly lower solids concentrations. Solids measurements for both treatments appear to be at equilibrium.

Table 10. Resin Acids and Fatty Acids in Untreated Wastewater and 22-Hour Sample, Run B

	Untreated	22-Hour Sample	% Reduced
Resin Acid	mg/l	mg/l	%
Dehydroabietic	95.82	66.90	30.2
Abietic	67.77	36.48	46.2
Levopimaric & Palustric	62.70	20.60	67.1
Isopimaric	54.01	40.33	25.3
Pimaric	41.51	28.97	30.2
Neoabietic	21.87	6.25	71.4
Sandaracopimaric	4.13	2.67	35.3
Total resin acids	347.81	202.20	41.9
Fatty acid	mg/l	mg/l	%
Linoleic	80.00	11.56	85.6
Oleic	58.41	0.00	100.0
Pinolenic	24.46	0.00	100.0
Stearic	12.08	8.14	32.6
Palmitic	10.19	0.49	95.2
Palmitoleic	1.78	0.00	100.0
Myristic	1.52	0.91	40.6
Lignoceric	1.14	1.41	-23.7
Lauric	1.06	0.33	68.6
Caproic	0.55	0.00	100.0
Total fatty acids	191.19	22.83	88.1

Run C Treatment Results

Run C was carried out to investigate if lower, controlled pH conditions would cause any improvement in COD removal or sludge settleability. A column was also run using an on-off DO controller to limit the aeration to maintaining adequate DO levels, to assess the effect of less mixing. The air flow rate used for this column was set at about 2 l/min, so that the column would not take much longer to come up to acceptable DO levels than the other columns. This flow rate was also chosen so that the problems encountered from the even lower gas flow rates of the oxygen-activation columns in run B could be decreased. In addition, one column was run with a lower fraction of sludge wasting, to study the effects of a longer SRT on sludge concentrations and COD removal.

In run C all columns were run at standard conditions of 20-day SRT, 2.5 l/min air flow rate and uncontrolled pH except as specified. For the 24-hour cycles, Column 1 was controlled at a pH of 6.5. Column 2 was controlled at a DO of 3 mg/l. Column 3 was run at an SRT of 30 days. Column 4 was controlled at a pH of 7.5. Columns 5 and 6 are a duplicate at standard conditions. For the 48-hour cycles, columns 5 and 6 were still at standard conditions, column 3 was continued at 30-day SRTs, and column 1 was continued but without pH control. As with the pure oxygen-activated columns of run B, it was observed that in the 3 mg/l DO column the flocs were fluffier, and the lower degree of mixing was again easily visible.

Run C 24-hour cycles started November 14, 1991 using another batch of wastewater, switching to wastewater C on November 20. The 24-hour cycles ended after the December 5 cycle, for a total of 22 cycles with the last 16 on wastewater C. The 48-hour cycles began December 5 and ended with the December 19 cycle (eight cycles).

Results from the two columns run on four-day cycles at the end of run C are not included in the various figures in this section. This is because these were only measurements of transient conditions and it would be misleading to include them next to data from near-equilibrium conditions. The four-day cycles provide information on what might happen during a short period of low organic loading, such as might happen during a production decrease, a work stoppage, or a major equipment breakdown on one of the pulping lines.

Figure 18 shows pH values at the 22-hour sample point during the 24-hour cycles. The 3 mg/l DO column had significantly lower pH levels than the other three columns without pH control. The differences between the standard columns and the

longer SRT column, though consistent, are not larger than between-column variations demonstrated in the previous runs. pHs in all the columns in the 24-hour cycles appear to have reached equilibrium.

The fluctuations shown for the columns with controlled pH are primarily due to the increase in pH that occurred once the samples were removed from the columns. This change was faster the lower the sample pH was. In all runs, this change in the sample pH was minimized by measuring the pHs immediately after the samples were removed from the reactors, and measuring the different samples in as rapid succession as possible.

The reduction-oxidation (Redox) potential measured during settling of column 6 at the end of the December 4 cycle is shown in the following table (11). As dissolved oxygen had always been zero by the end of the settling periods, it was interesting to find out how low the Redox dropped. Though the mixed liquor remained aerobic for most of the settling period, it was well into the anoxic region by the end of the hour of settling. At the end of the 30-minute decanting period (at 1.5 hours after aeration halted) immediately before refilling with wastewater, the sludge was quickly mixed manually and the Redox potential measured to be -209 mV.

Table 11. Reduction-Oxidation Potential During Settling Period

Minutes into settling	0	15	25	40	50	60
Redox Potential, mV	42	19	14	8	-10	-45

Figure 19 shows COD removal percentages of cycles late in each segment of run C. Before the axis break are COD removals at the 22 hour sample point during 24-hour cycles. After the axis break are shown COD removal percentages at the 46-hour sample point during 48-hour cycles. The greatest COD removal was achieved in the 3 mg/l DO column. The longer SRT and pH 7.5 columns are next in COD removal, with the standard columns consistently below them. The pH 6.5 column typically had the poorest COD removal.

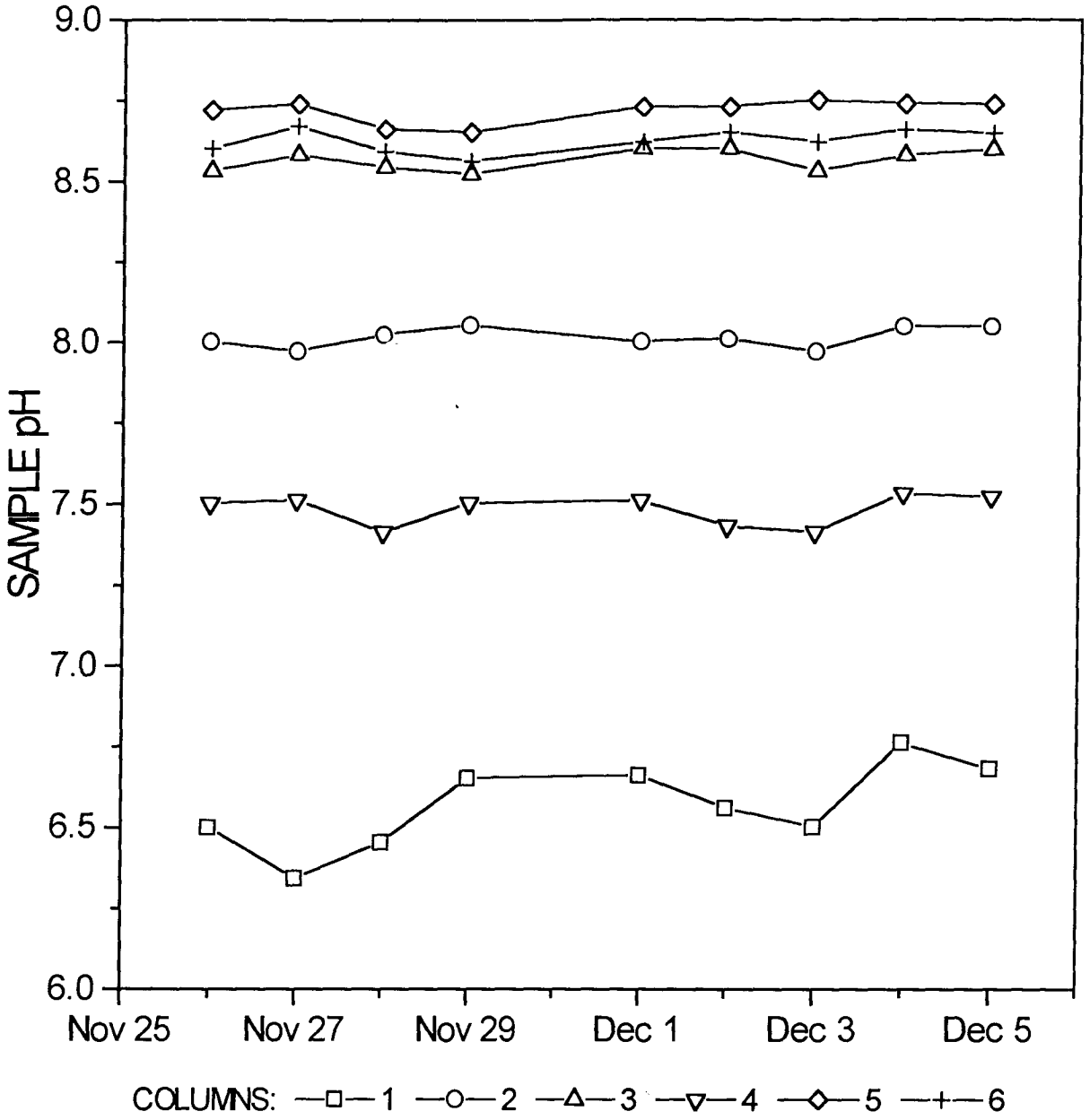

Figure 18. pH Values, Run C

Shown above are pH values at the 22 hour sample point during 24-hour cycles of Run C, which ran from November 14 to December 6, 1991. All columns were run at standard conditions of 20-day SRT, 2.5 l/min air flow rate and uncontrolled pH except as specified. Column 1 was controlled at a pH of 6.5. Column 2 was controlled at a DO of 3 mg/l. Column 3 was run at an SRT of 30 days. Column 4 was controlled at a pH of 7.5. Columns 5 and 6 are a duplicate at standard conditions. The 3 mg/l DO column had significantly lower pH levels than the other three columns without pH control. All columns without pH control appear to be at pH equilibrium.

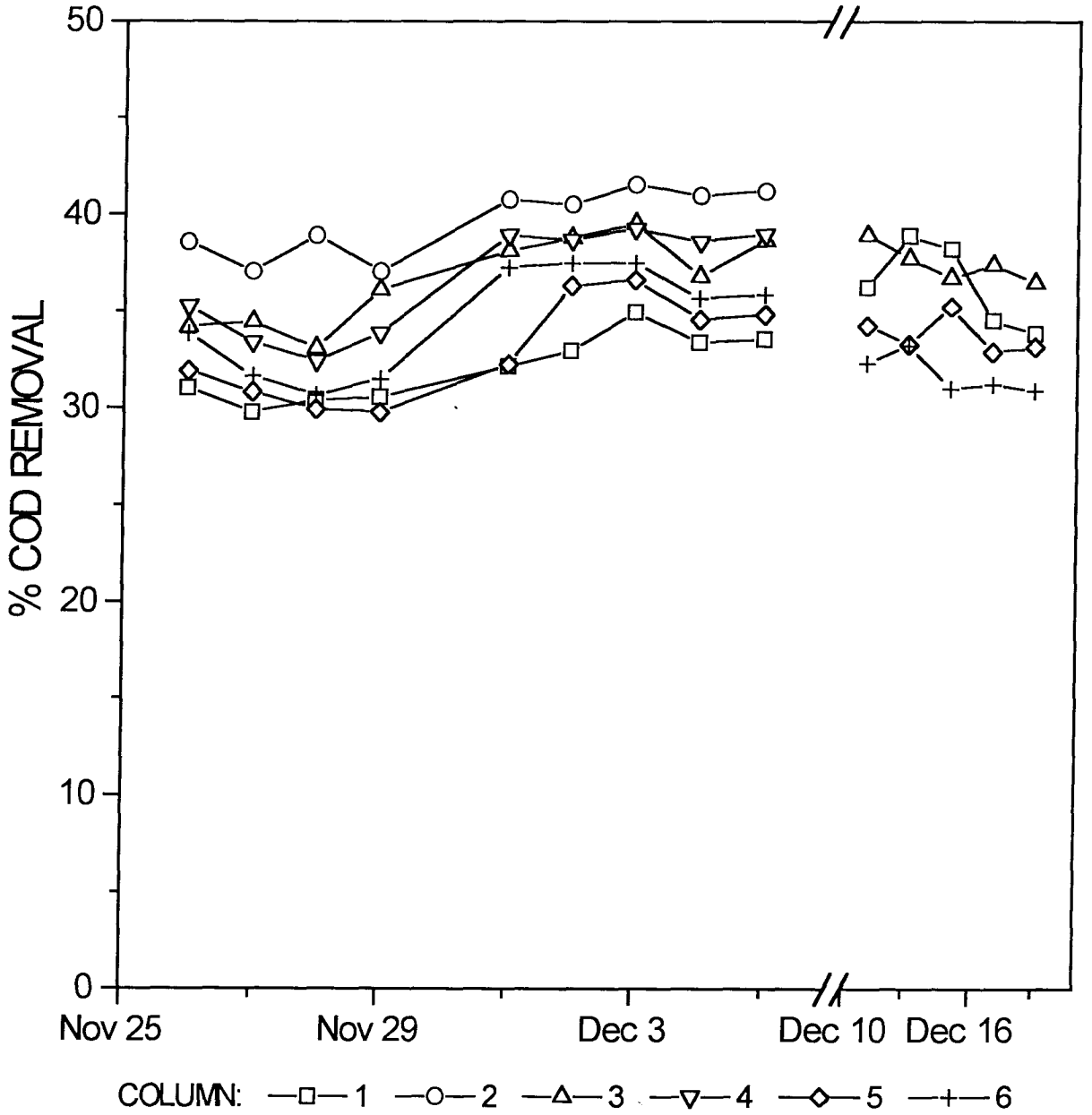

Figure 19. COD Removal (1-Hour Settled Samples), Run C

Before the axis break are shown COD removal percentages at the 22-hour point during 24-hour cycles of Run C, which ran from November 14 to December 6, 1991. After the axis break are removals at 46 hours during 48-hour cycles, which ran from the last 24-hour cycle to December 21. Columns were run at standard conditions except as follows. For the 24-hour cycles, Column #1: pH 6.5; #2: 3 mg/l DO; # 3: 30-day SRT; # 4: pH 7.5. For the 48-hour cycles, columns #5 and 6 were still at standard conditions, #3 was continued at 30-day SRT, and #1 was continued but without pH control. In the 24-hour cycles the 3 mg/l DO column had the best reduction. In 48-hour cycles, the previously pH 6.5 column was at similar levels to the longer SRT column but appeared to be dropping towards the standard columns.

For the 48-hour cycles, the longer SRT column was still marginally more effective than the standard columns. The column which had been previously controlled at pH 6.5 was at similar levels to the longer SRT column, but appears to be dropping towards the results of the standard columns. This initial improvement in its COD removal is consistent with the similarity between the longer SRT and pH 7.5 columns in the 24-hour cycles. This might be expected while the previously pH 6.5 column temporarily still has its average pH closer to 7.5 than to the pHs of the standard columns.

For the supernatant from samples that were given the additional three hours of settling, COD removal percentages of the later cycles are shown in figure 20. Before the axis break are shown COD removal percentages at the 22-hour sample point during 24-hour cycles. After the axis break are shown COD removal percentages at the 46 hour sample point during 48-hour cycles. The COD removals appear to be fairly stable at the end of the run of 24-hour cycles, though with more variation than the previous two runs.

For the 24-hour cycles, the pH 6.5 column had marginally higher COD removals, followed by the pH 7.5 column and the longer SRT column which had similar removals. The other three columns were roughly similar to each other with slightly lower removals. There was less difference between the COD removals in these supernatant samples than in the samples from the shorter settling period shown in the previous graph. At the end of the 48-hour cycles, the 30-day SRT column and the two standard columns were perhaps beginning to stabilize. The previously pH 6.5 column still had the highest COD removal (63.1%), but appeared to be continuing to drop towards the values of the other columns. The higher SRT column again had slightly better removal than the two standard columns.

There is a small gap between the COD removals (figure 19) of the standard condition duplicates, columns 5 and 6. However, looking at the supernatant COD removals (figure 20), this gap virtually disappears. The variation between these columns may be because a small increase developed in the air bubble size in column 5. Even though the difference in bubble size was small, the slight change in mixing could account for the minor difference in settling noticed in the columns and demonstrated in the difference between their one-hour settled COD values. All the other columns had no discernible difference in bubble size, all being similar to column 6.

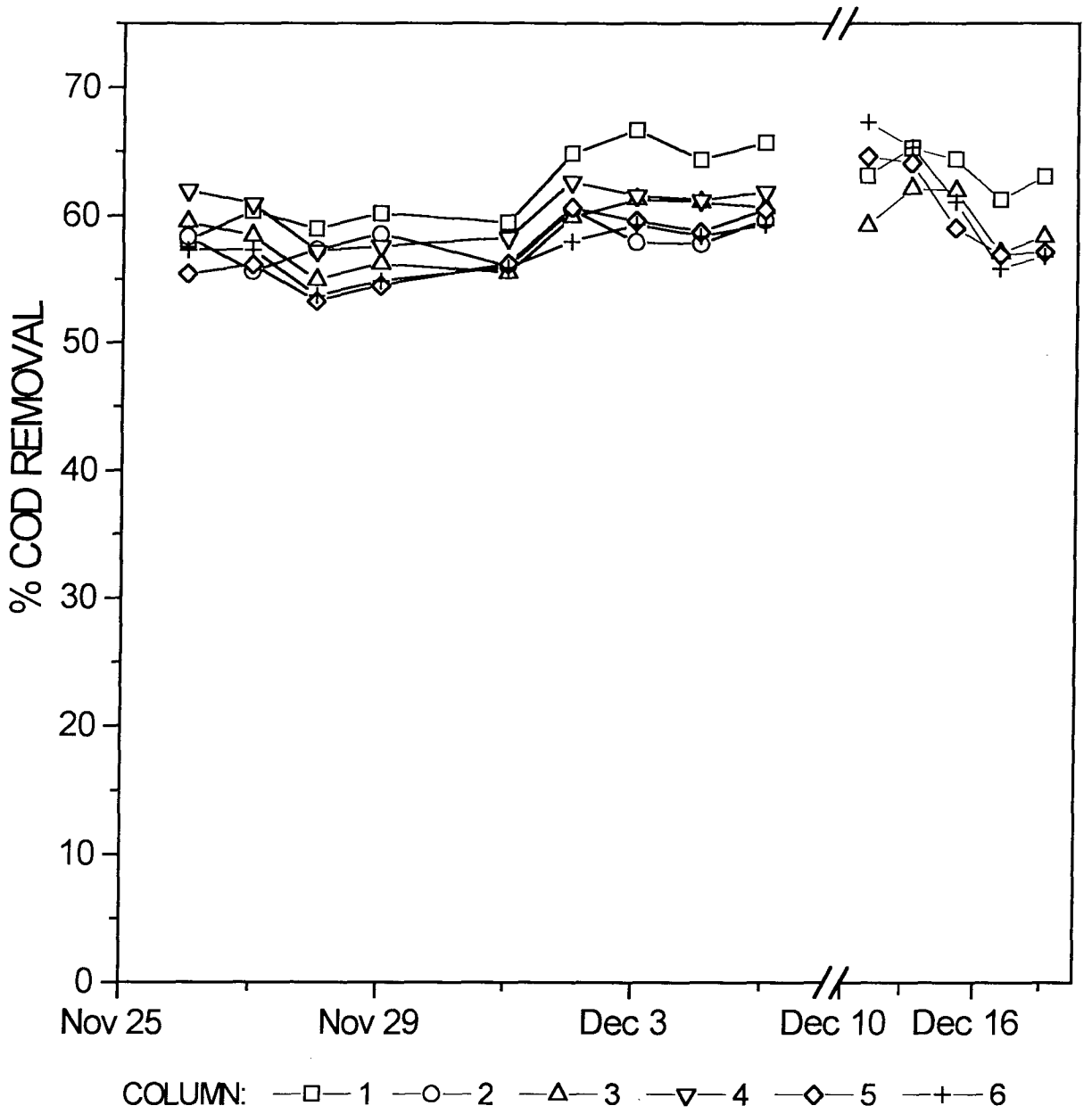

Figure 20. COD Removal (4-Hour Settled Samples), Run C

Before the axis break are shown COD removals at the 22-hour point during final 24-hour cycles of Run C. After the break are removals at 46 hours during final 48-hour cycles. Values shown are for supernatant samples after 4 hours settling. All columns were run at standard conditions of 20-day SRT, 2.5 l/min air flow rate and uncontrolled pH except as follows. For the 24-hour cycles, Columns #1: pH 6.5; #2: 3 mg/l DO; #3: 30-day SRT; #4: pH 7.5. For the 48-hour cycles, columns #5 and 6 were still at standard conditions, #3 was continued at 30-day SRT, and # 1 was continued but without pH control. The pH 6.5 column had marginally highest removals. In the 48-hour cycles, the previously pH 6.5 column still had the best removal, but was dropping towards the other columns.

Of note is that when samples only experienced one hour of settling, the 3 mg/l DO column which had much lower air flow, had removals slightly higher than any of the five other columns. Yet when samples were given an additional three hours of settling, this column then yielded some of the lowest COD removal results. What appears to have been occurring, both from COD and SVI results and observation of the columns, was that the flocs in the lower air flow rate column were far less broken up than in the other columns.

The fluffier sludge caused slightly higher SVIs, and the lower mixing resulted in slightly lower COD removals in the supernatant. However, after only a short period of settling, COD results were better because more of the biomass settled out of the supernatant. As the flocs were much less broken up, significantly less biomass existed in the columns outside the flocs compared to the other columns. As SVIs are important in determining required SBR reactor volume, and the SBR system would be operated on the basis of thorough settling, this slight improvement in the CODs for the 3 mg/l DO column for one-hour settled samples would not be considered an advantage.

Figure 21 shows the average percentage COD removals for the two standard conditions columns, for the 4, 16 and 22 hour points of the 24-hour cycles and the 46-hour point of the 48-hour cycles. COD removals for one-hour and four-hour settled samples are compared. The values are an average of the last three cycles of each part of the run. There is a deterioration in removals in the 48-hour cycles, particularly in the CODS of samples settled for only one hour, indicating that in addition to not achieving better treatment, sludge settleability has also fallen.

Percentage COD removals for both one-hour settled and additional-settled samples are shown in figure 22 for three different time points for the six columns of run C. The numbers used are again averages of the last three 24-hour cycles. Even though the 6.5 pH column settled very well, at four and 22 hours it had lower COD removals after the one-hour settling period than the other columns. This was likely due to its significantly higher biomass concentrations resulting in more biomass suspended in the partially-clarified wastewater. However, at all three time-points the 6.5 pH column had the best COD removal in the supernatant from additional settling. Though the four-hour settled COD removal of the 3 mg/l DO column was lowest by 22 hours, it had the best one-hour settled COD removals at four and 22 hours, likely due to its less broken up sludge resulting in less suspended biomass after the shorter settling period. Limitation of mixing velocities

has been shown in other research to improve settleability and effluent suspended solids [Galil 1991].

BOD_5 values for samples from the final 24-hour and 48-hour cycles and the second to last 96-hour cycle are shown in table 12. The initial BOD_5 of the wastewater was 2600 mg/l. All the 22-hour effluents after one hour of settling had at least 72% removal, or less than 725 mg/l BOD_5. All the 22-hour samples after extended settling had at least 90% removal, or BOD_5s of less than 257 mg/l.

Table 12. BOD_5 Percentage Removal Results for Run C

Date	Sample hr	Column	1-hr settle % BOD_5 Removal	4-hr settle %BOD_5 Removal
Dec-05	4	std (5)	62.55	78.74
Dec-05	4	std (6)	64.04	77.73
Dec-05	16	std (5)	67.80	86.64
Dec-05	16	std (6)	69.96	85.96
Dec-05	22	pH 6.5	72.12	94.45
Dec-05	22	3 mg/l DO	77.09	90.12
Dec-05	22	30-d SRT	74.44	92.40
Dec-05	22	pH 7.5	75.00	93.64
Dec-05	22	std (5)	72.91	90.77
Dec-05	22	std (6)	73.67	91.31
Dec-19	46	prev pH 6.5	80.63	95.79
Dec-19	46	30-d SRT	81.91	93.03
Dec-19	46	std (5)	80.65	93.38
Dec-19	46	std (6)	79.28	91.31
Dec-31	94	std (5)	82.24	95.73
Dec-31	94	std (6)	83.32	97.54

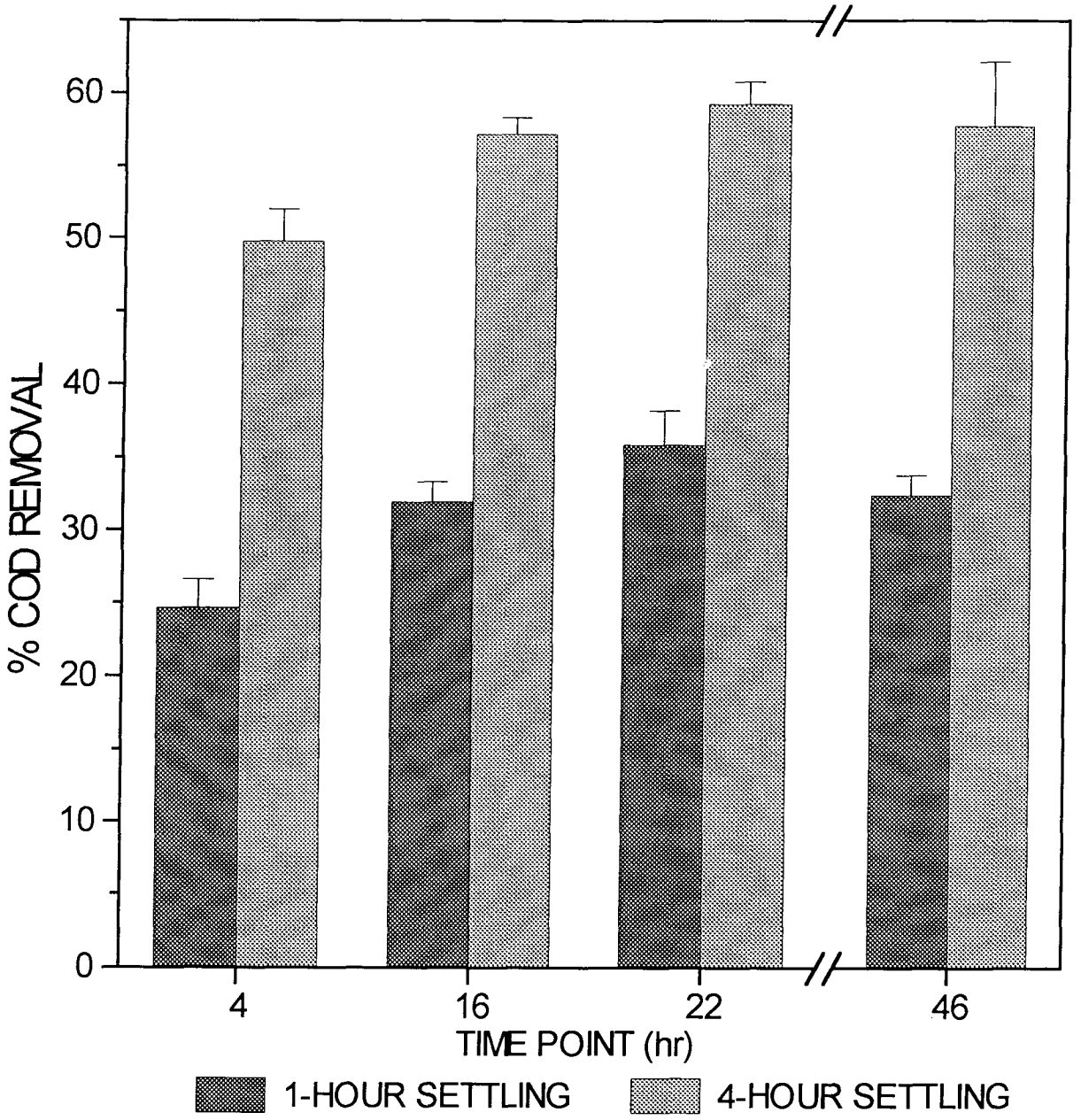

Figure 21. Average COD Removals in 1-Hour and 4-Hour Settled Samples for Standard Conditions Columns, Run C

This figure shows the average percentage COD removals for the two standard conditions columns of run C, for the 4, 16 and 22 hour points of the 24-hour cycles and the 46 hour point of the 48 hour cycles. The values are an average of the last three cycles of each part of the run. 90% confidence intervals are shown for agreement between cycles. There is a deterioration in removals in the 48 hour cycles, particularly in the one-hour settled CODs, indicating that in addition to not achieving better treatment, settleability of suspended solids has also fallen.

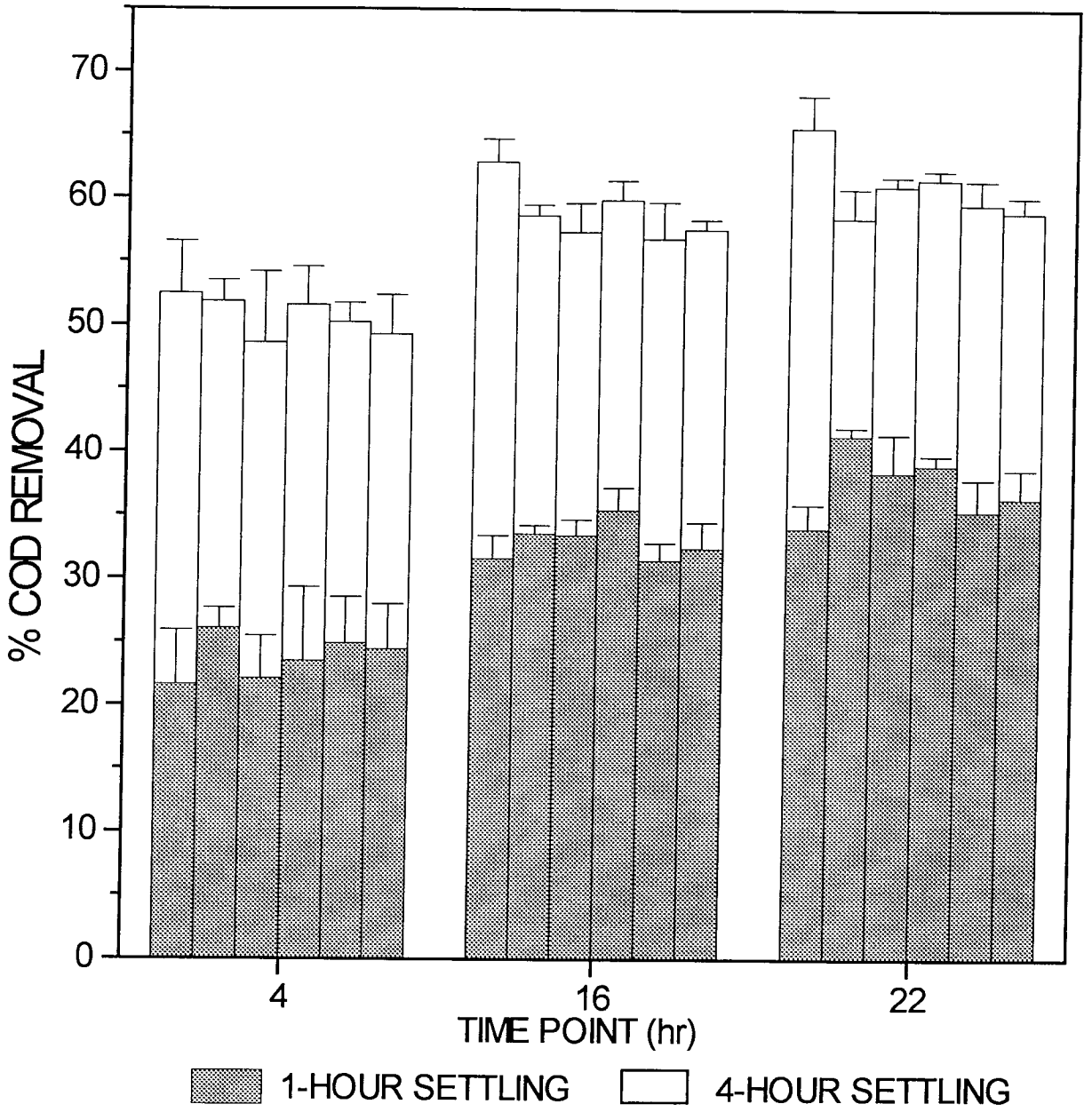

Figure 22. Average COD Removals in 1-Hour and 4-Hour Settled Samples, Run C

Percentage COD removals for regular and additional-settled samples are shown for run C, going from column 1 to 6, left to right. The values used are averages of the last three 24-hour cycles. All columns were run at standard conditions except as specified. Columns 1 and 4 were controlled at pH 6.5 and 7.5 respectively. Column 2 was controlled at 3 mg/l DO. Column 3 had a 30-day SRT. Even though the 6.5 pH column (1) settled very well, it had lower 1-hour settled COD removals than the others at 4 and 22 hours. However, the 6.5 pH column had the best COD removal at all three points in the supernatant from additional settling. The 3 mg/l DO column (2) had the best regular CODs at 4 and 22 hours, but did not have superior 4-hour settled COD removals.

The following observations on foam depths uses descriptions similar to those employed in a study by Blackall *et al.* [1991a]. In the 24-hour cycles it was observed that the mixed liquor in the pH 6.5 column reacted to aeration as did the pure Quesnel wastewater during aeration tests. The bubbles had no stability so no foam layer formed. The pH 7.5 column had 1 to 2.5 cm of foam with fragile bubbles, and insufficient stability to form films. The foam collapsed within a second or two of aeration being stopped. The standard columns, 3 mg/l DO column and 30-day SRT column had foam with some stability, 5-10 cm in height (3 mg/l DO column the lowest, standard column 5 the most). The foams lasted up to two minutes after aeration ceased.

In the latter part of the 48-hour cycles, standard column 5 still had the greatest foam height (10 cm); standard column 6 and the 30-day SRT column had foam depths of 7-8 cm. The pH 6.5 column started the 48-hour cycles with virtually no foam, but by the end of the run had 3-4 cm of foam.

Figure 23 shows mixed liquor total solids, total suspended solids, volatile suspended solids and sludge volume index for dates near the end of the 24-hour cycles portion of run C. The sludge concentrations appear to be stabilizing for most of the columns by the last dates shown. The pH 6.5 column has significantly higher sludge concentrations and lower SVIs. The 30-day SRT and pH 7.5 columns have slightly higher sludge concentrations than the lower DO and standard columns.

The differences between the lower DO and standard columns for all sludge measurements are not significant when compared to the variation exhibited between the replicate columns at standard conditions. Excluding the pH 6.5 column, SVIs are not significantly different among the columns. During the run, pH-controlled columns had appeared to have denser sludge packing by the end of the hour of settling (SVIs are measured at 30 minutes) than the other columns, but with the 6.5 pH column settling more rapidly and compactly than the 7.5 pH column. In the 48-hour cycles, the 30-day SRT column had the most densely packed, granular-appearing sludge. The final sludge measurements in the 48-hour cycles showed that the MLVSS had dropped by 9% (30-day SRT column) to 22% (standard column 5) from the concentrations during the 24-hour cycles.

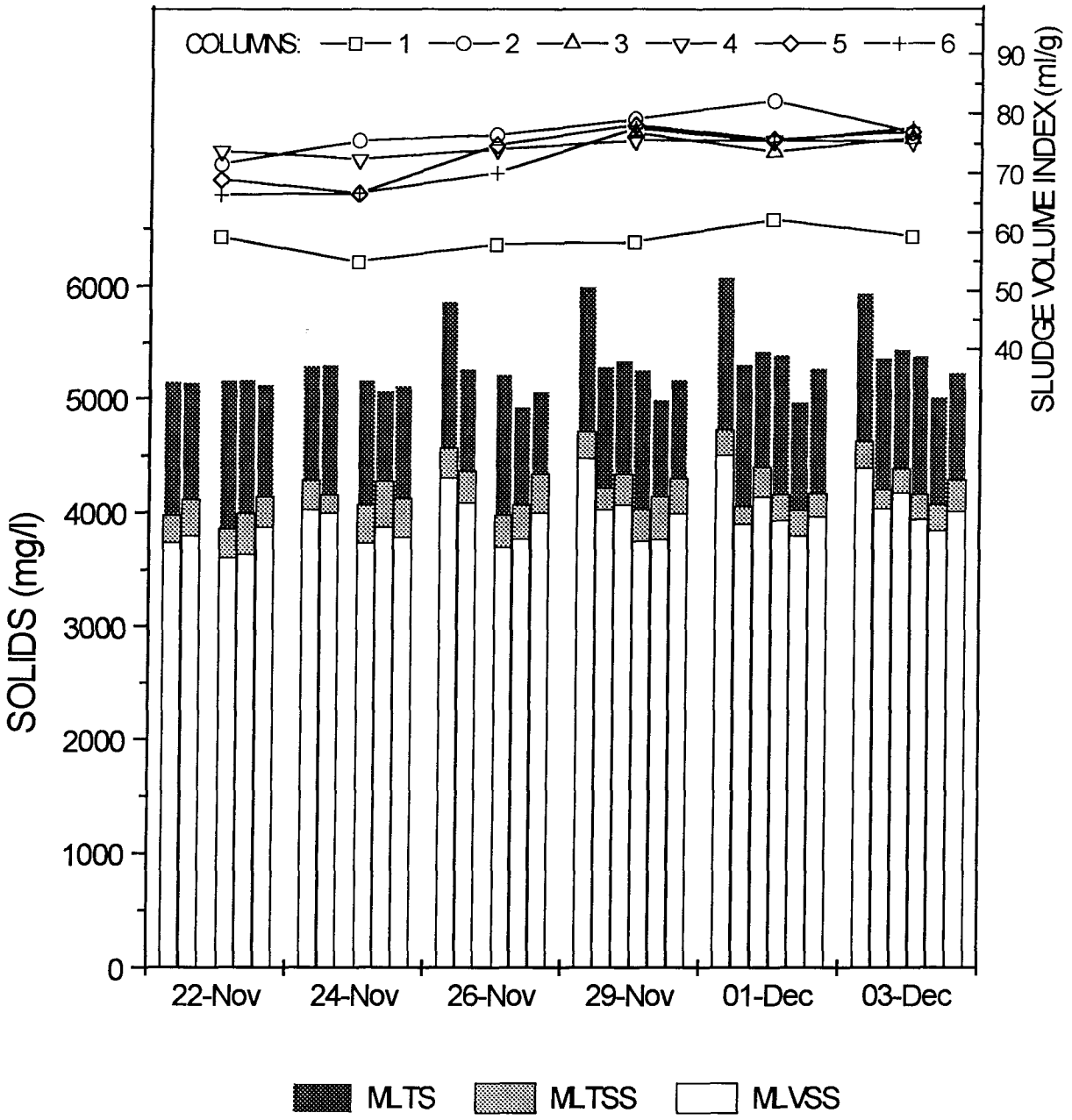

Figure 23. Solids Concentrations and Sludge Volume Index for Run C

Mixed liquor total solids, total suspended solids, volatile suspended solids and SVIs are shown for dates near the end of the 24-hour cycles of Run C, which ran from November 14 to December 6, 1991. All columns were run at standard conditions of 20-day SRT, 2.5 l/min air flow rate and uncontrolled pH except as specified. Columns 1 and 4 were controlled at pH 6.5 and 7.5 respectively. Column 2 was controlled at 3 mg/l DO. Column 3 was run at 30-day SRT. Sludge concentrations appear to be stabilizing for most columns. Column 1 had significantly higher concentrations and lower SVIs. Columns 3 and 4 had marginally higher solids than 2, 5 and 6. SVIs are not significantly different among columns 2 through 6.

The fact that the pH 6.5 column had only slightly better supernatant COD removals than the other columns while its solids concentrations were significantly increasing, means that increased digestion of the wastewater cannot alone account for the higher sludge concentrations. It appears that the sludge underwent less destruction during the later hours of each cycle. This is also supported by the observation that there was a greater decrease in the supernatant CODs between 16 and 22 hours for this column than the other columns. Whereas some of the other columns had little or no further improvement in the COD removals in supernatant samples (four-hour settled samples), the supernatant COD removal for the pH 6.5 column still improved between these time points. In the other columns, though a small amount of wastewater digestion is likely still occurring in addition to endogenous respiration, the breakdown of some of the biomass may release a little soluble organic material back into the supernatant. This was demonstrated in a few samples where the overall COD did drop slightly between 16 and 22-hour points, but the supernatant COD slightly increased.

Zone settling rates were measured at the end of the December 3 24-hour cycle. These are shown in Table 13. The sizable differences between the settling rates of columns 2 through 6 are not echoed by the SVIs, which showed little variation between these columns.

Table 13. Zone Settling Rates for a 24-hour Cycle of Run C

Column	Zone Settling Rate, cm/min
# 1 pH 6.5	3.81
# 2 3 mg/l DO	1.83
# 3 30-day SRT	2.51
#4 pH 7.5	3.05
#5 standard	2.67
#6 standard	2.29

The 96-hour cycles yielded final COD removals that were a little poorer than in the 48-hour cycles for column 5, but a little higher in column 6. The solids concentrations continued to drop. The SVIs were clearly deteriorating, but by the end of the five cycles were still settling well compared to sludge volumes occurring in some AS systems for pulpmill wastewaters [Jeffries 1989]. This indicated that the system could survive a short-term low loading situation, without exacerbating the

sludge reduction by decanting large amounts of biomass with the treated wastewater.

Microtox results presented in Table 14 show that the wastewater has high toxicity which, though reduced by two orders of magnitude, was not fully detoxified during treatment. This wastewater batch was particularly toxic. Later batches of the same type of Quesnel River pulp mill effluent used in other research projects had 15-minute EC_{50}s that ranged from about 0.3-3%. For these Microtox tests the "r" values, giving the correlation coefficient of the line estimated from serial dilutions of each sample, ranged between 0.985 and 0.997.

Table 14. 15-minute Microtox EC_{50} for Samples from Run C

Date	Sample	Column	EC_{50}, %	95% C.I.
91-12	Influent		0.22	0.16-0.31
12-05	22 hour	pH 6.5	15	11.8-19.1
12-05	22 hour	standard	21	16.5-26.8
12-19	46 hour	30-d SRT	32	26.1-39.2
12-19	46 hour	standard	25	20.3-30.8

The two 48-hour cycle samples gave a higher EC_{50} for the 30-day SRT column than for column 6 at standard conditions, consistent with the fact that the 30-day SRT column also had higher COD reduction. For the 24-hour cycles, the difference between the EC_{50}s for the pH 6.5 and standard column is not reflected in the CODs. As rainbow trout and daphnia bioassays on the wastewater must have LC_{50}s of 100% to meet the effluent regulations, the examination of toxicity reduction using these bioassays would be a critical part of further research on this system.

Comparison of Runs A, B and C

Measurements of four-hour settled CODs, solids concentrations, SVIs and pH values were very stable for the last few 24-hour cycles of each run. The one-hour settled CODs showed a little more variability. This high degree of between-cycles agreement would not be expected in pilot-plant or full-scale applications. In normal pulpmill operation the BOD and COD concentrations in the untreated wastewater can change greatly from one day to the next, as the type of pulp being produced or the furnish used changes.

A summary of pH at various sample times for runs A, B and C is shown in Figure 24. All time points shown except 46 hours are for samples taken during 24-hour cycles. Points plotted use an average of the last three cycles of the 24-hour cycles or 48-hour cycles segment of each run, with error bars showing the agreement between the three cycles. Run A points are an average of three columns; B and C points are each an average of two columns. All data shown in this figure is from the columns at standard conditions (i.e. uncontrolled pH, 2.5 l/min air flow and 20-day SRT). In the 24-hour cycles, run A had the highest pHs except at the 16-hour point.

The pH increase with treatment time was significant in all three runs, particularly for the early hours of treatment. For runs B and C, pH at the end of the 48-hour cycles was consistently higher than pH at the end of the 24-hour cycles. The uncontrolled pH columns typically had a pH of at least 8.5 by the end of 22 hours aeration, 8.5-8.9 by 46 hours aeration, and 9.0 by 94 hours. With all pH-unadjusted runs the relationship held that for a given batch of wastewater the columns which developed the highest pHs had the highest overall COD removals.

The colour of all columns except pH-controlled columns darkened greatly during treatment. Colour was found to be very pH dependent, with the samples around 6.5 pH from the early hours of treatment in uncontrolled columns not being discernible in colour from samples from the end of treatment from the 6.5 pH column (the samples were different in turbidity). Colour of the acid-added columns of run B at the end of cycles, was similarly comparable to the colour of the standard columns earlier in each cycle. It was also observed qualitatively that a significant amount of the colour increase in the samples from the uncontrolled-pH columns could be reversed by neutralizing the pH. As darkening of the effluent is a common problem in the aerobic treatment of pulpmill wastewater, the colour-pH relationship in this SBR system merits further investigation.

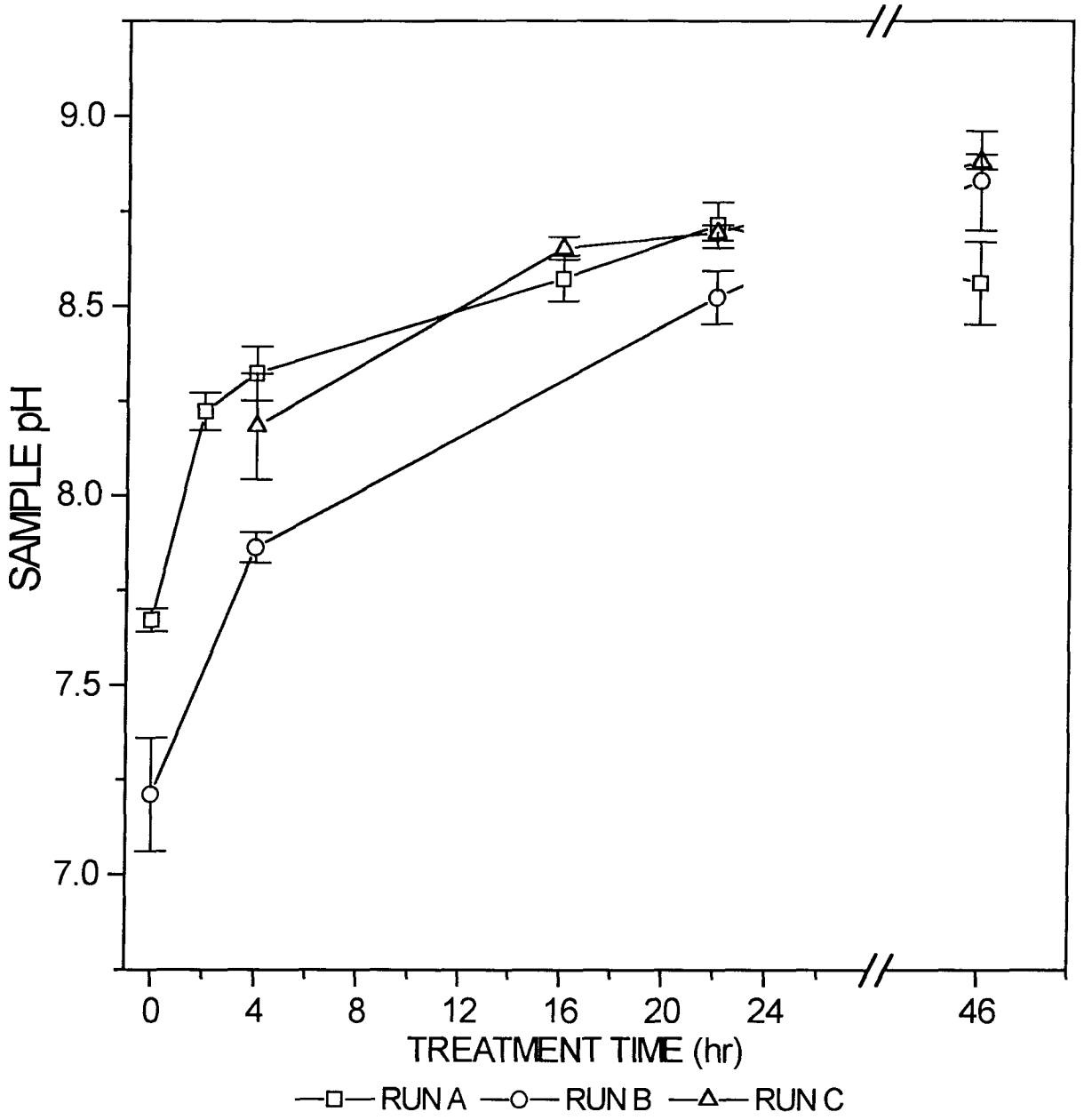

Figure 24. pH Summary for Runs A, B and C

A summary of pH at various sample times for Runs A, B and C is shown. All time points shown except 46 hours are for samples taken during 24-hour cycles. Points plotted use an average of the last three cycles of the 24-hour cycles or 48-hour cycles segment of each run. Run A points are an average of three columns; B and C points are each an average of two columns. Error bars (for variation between cycles) depict a 90% confidence interval. All data shown in this figure is from columns at standard conditions, i.e. uncontrolled pH, 2.5 l/min air flow and 20-day SRT. pH increase with treatment time was significant in all three runs, particularly for the early hours of treatment. For runs B and C, pH at the end of the 46 hour cycles was higher than pH at the end of the 24 cycles.

Percentage COD removals from all the time points of the 24-hour cycles and the 46-hour time point of the 48 hour cycles are illustrated by figure 25. The values shown are averages of the three standard conditions columns of run A, the two of run B and the two of run C. Both COD removals from one-hour settled samples and supernatant from additional settling are charted. Each value is an average of the last three cycles of the 24-hour cycles or, in the case of the 46-hour point, the last three 48-hour cycles. Run A shows the best COD removal, run B the poorest. The 48-hour cycle removals were generally slightly lower than the end of the 24-hour cycles. The relationship between different time points is quite consistent between runs.

In all three runs, the most rapid COD removal occurred in the first four hours. Very little, if any, additional COD removal was achieved by running the system on 48-hour cycles rather than 24-hour cycles. It was clear from the COD data (especially obvious from comparing the time points of the 48-hour cycles to the 24-hour cycles in run A) that the use of a 48-hour cycle greatly decreased removal efficiency, treatment was greatly slowed and took longer than 22 hours of aerated treatment to meet what was achieved in the 24-hour cycles by 16 hours aeration.

CODs of the supernatant from extended settling showed little reduction between the 16-hour and 22-hour points. Therefore, even though some one-hour settled CODs still showed significant improvement between the 16 and 22 hour points, if the system is run with adequate clarification, there is no benefit to having a longer reaction period than 16 hours. The amount of sludge digested during the extra six hours of treatment would not likely be considered sufficient compensation for the greatly increased operating cost.

Fluctuations in COD values between cycles near the end of the runs were primarily due to differences in settling characteristics, as much of the fluctuation disappears if results from the extended settling samples are examined rather than those from the one-hour settled samples. Indeed, for most samples where CODs were found to vary significantly from the average, it had been noted in lab records that the column had experienced a drop in settling performance - for example that there was an increase in the amount of fine, feathery flocs, which tend not to settle, or that there was sludge floating on the wastewater surface, some of which occasionally got mixed into the supernatant as the sample was being taken.

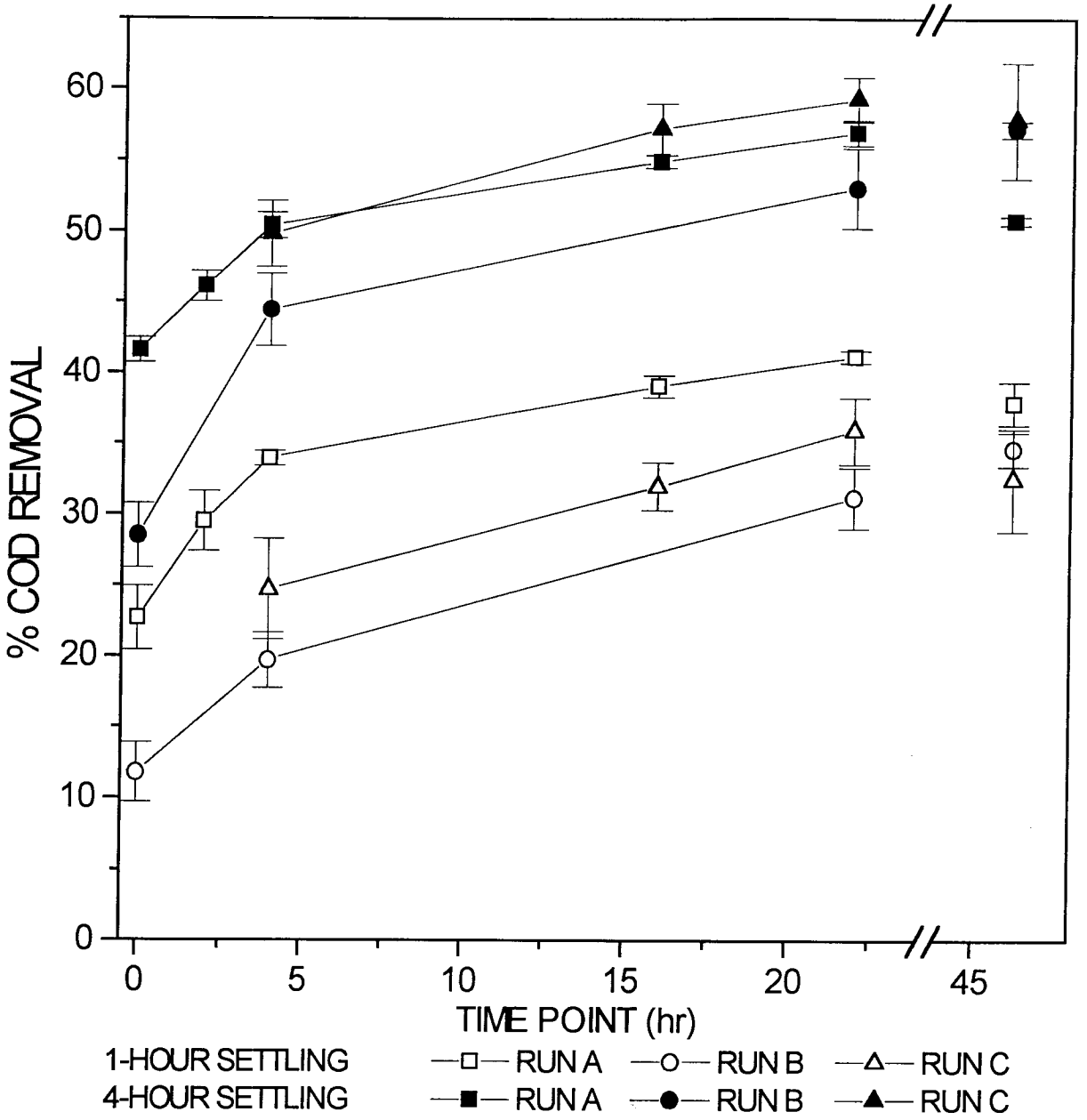

Figure 25. Comparison of Average COD Removals in 1-Hour and 4-Hour Settled Samples for the Standard Conditions Columns of Runs A, B and C

Percentage COD removals from all the time points of the 24-hour cycles and the 46-hour time point of the 48 hour cycles are illustrated. The values shown are averages of the three standard conditions columns of run A, the two of run B and the two of run C. Each value is an average of the last three cycles of the 24 hour cycles or, in the case of the 46-hour point, the last three 48-hour cycles. 90% confidence intervals show the agreement between cycles.

Both of these situations had little impact on samples from additional settling as there was virtually no suspended matter in the supernatant. Because most of the cycle-to-cycle variations in the one-hour settled samples appear to be the result of fluctuations in settling characteristics, with the average sample having experienced very good settling, most COD values lower than the median are distributed over a far smaller range than values higher than the median.

Table 15 gives the percentage COD removals from the various scenarios of 24-hour cycles of runs A, B and C for the 4 and 22-hour time points. Run A had the highest COD removals in one-hour settled samples, matched by the 3 mg/l DO column for the 22-hour point but not the four-hour point. The best COD removals in the four-hour settled samples occurred in the pH 6.5 column.

Table 15. Summary of Percentage COD Removals From 24-hour Cycle Runs

	1-hour settled samples		4-hour settled samples	
Run	4 hours	22 hours	4 hours	22 hours
A: standard (avg of 3 columns)	33.88	41.25	50.69	57.05
B: standard (avg of 2 columns)	19.92	31.70	44.35	53.03
B: acid-added (avg of 2 columns)	18.01	28.15	44.48	52.21
C: standard (avg of 2 columns)	24.68	35.82	49.74	59.24
C: D.O. limited to 3 mg/l	26.05	41.24	51.82	58.41
C: Extended SRT of 30 days	22.11	38.33	48.62	60.93
C: pH controlled at 6.5	21.62	33.93	52.43	65.52
C: pH controlled at 7.5	23.51	38.95	51.58	61.49

The increase in COD removals in the pH 6.5 and 7.5 columns compared to the higher pH, standard columns is consistent with the research results on CTMP wastewater of Lo *et al.* summarized in the literature review. In their study the pH 7 reactor had a higher COD removal than the pH 8 reactor. They also found that reactors with HRTs of 3 or 5 days did not have greater COD removals than reactors at a 2-day HRT. This is similar to the lack of improvement in the 66-hour HRTs compared to the 33-hour HRTs found in this SBR research.

COD concentrations are very high immediately after the fresh wastewater is mixed into the columns as the wastewater is only diluted with the three litres of liquid retained. These initial CODs are far higher than what would occur in the

continuous mixed conditions of even most high-rate AS systems. All runs tolerated this shock loading, as indicated by the large amount of COD removed in the first few hours, and the high oxygen consumption in evidence from the slow increase in DO levels despite high air flows. (During aeration tests with 800 ml/min air flow per column, other batches of this wastewater saturated within 20 minutes, while during treatment with 2.5 l/min air flow saturation always took well over four hours. At several points during the study, air flow was temporarily halted while oxygen uptake rate measurements were attempted, but the mixing throughout the column was inadequate without air flow to allow more than localized DO measurements.)

Average BOD_5s in the untreated wastewater were 2240, 3190 and 2600 mg/l for runs A, B and C respectively. BOD_5 reductions in the one-hour settled samples were typically 73% at the 22-hour point of 24-hour cycles and 79% at the 46-hour point of 48-hour cycles. The BOD_5 removals in the supernatant from extended settling were approximately 92% and 93% for the final points of the 24-hour and 48-hour cycles respectively. All the four-hour settled samples met the BOD_5 regulation for Quesnel River Pulp which, based on the reference production rate, works out to 335 mg/l [personal communication with Quesnel River Pulpmill technicians, 1993].

The BOD_5 results showed less variation than the COD results. This drop in the spread of values was true for results of columns with different conditions, the 24-hour and 48-hour cycles of the same run, and different runs. This means that under various scenarios, the reactors were able to utilize the more easily degradable organics with similar effectiveness. The larger differences occurred in the ability to break down the COD that was not initially present as BOD_5, reflected in the greater fluctuations in COD measurements. This is consistent with the findings of the Lo *et al.* study [1991], which found that under a wide range of operating conditions, bench-scale aerated chemostats treating CTMP wastewater yielded very similar BOD reductions, though COD removals varied.

Control of foaming using measured acid aliquots or pH control were both successful, but with the pH 6.5 column having the only complete elimination of foam. In all cycles, no foam was present during the first hours of aeration, but consistently developed by the 16-hour sample points (except for pH 6.5 column), and slowly increased in height as the cycle continued. In the columns without pH control, foam filled most of the 11 cm head space by the time the pH reached 8.5. At the equivalent points in the cycles, the acid-added and pH-controlled columns showed little or no foam and also had no lumps of the floating sludge which occasionally occurred in the other columns. It was observed that in comparing foam

on different columns within a run that the columns reaching the highest pHs at the end of cycles also consistently had the greatest foam heights.

In figure 26 the total solids, total suspended solids, and volatile suspended solids are shown for the 24-hour and 48-hour cycles of runs A, B and C. All values shown are for columns run at standard conditions, with run A values being averages of triplicate columns, and runs B and C averages of duplicate columns. An average of the last three sludge samples for the 24-hour cycles is used, and an average of the final two sludge samples used for the 48-hour cycles. The run using wastewater of the highest concentration yielded the highest sludge concentrations, and the run with most dilute wastewater, the lowest solids. Run B had slightly greater between-cycle variation in sludge concentrations, which is demonstrated by the larger error bars.

The average mass loadings for the 24-hour cycles of standard condition columns, in terms of kg BOD_5 applied/MLVSS·d were 0.38 for run A, 0.48 for B and 0.47 for C. These values would be slightly lower if it were possible to determine the average MLVSS present during the cycle and use this in the calculation rather than the concentration present at the end of cycles (which is assumed to be slightly lower). Run A, which had the lowest mass loading, consistently had the highest COD removals in the treated effluent decanted from the system (i.e. after one hour settling).

30-minute settled sludge volumes were slightly more variable between cycles than the one-hour depths observed, as while the sludge is still noticeably settling both variations in compactibility and settling speed impact on the measured volumes. By one hour, settling is basically complete and the sludge is only slowly compacting further, therefore the depths at this point were less variable. Because the sludge volume index uses 30-minute settled volumes, these values subsequently fluctuate more on both a cycle-to-cycle and between columns basis than the corresponding solids concentrations and the sludge volumes observed at the end of the settling periods. The columns which settled most rapidly consistently had the highest fractions of granular-appearing sludge, e.g. the pH 6.5 column.

Error bars on the solids concentrations shown in the various solids graphs illustrate both between-column variation and the heterogeneous nature of the sludge. In cases where there were slightly larger chunks of sludge in the column, it was more difficult with one sample to obtain as accurately representative a sample as possible in cycles or columns where the sludge flocs were of more uniform, smaller size.

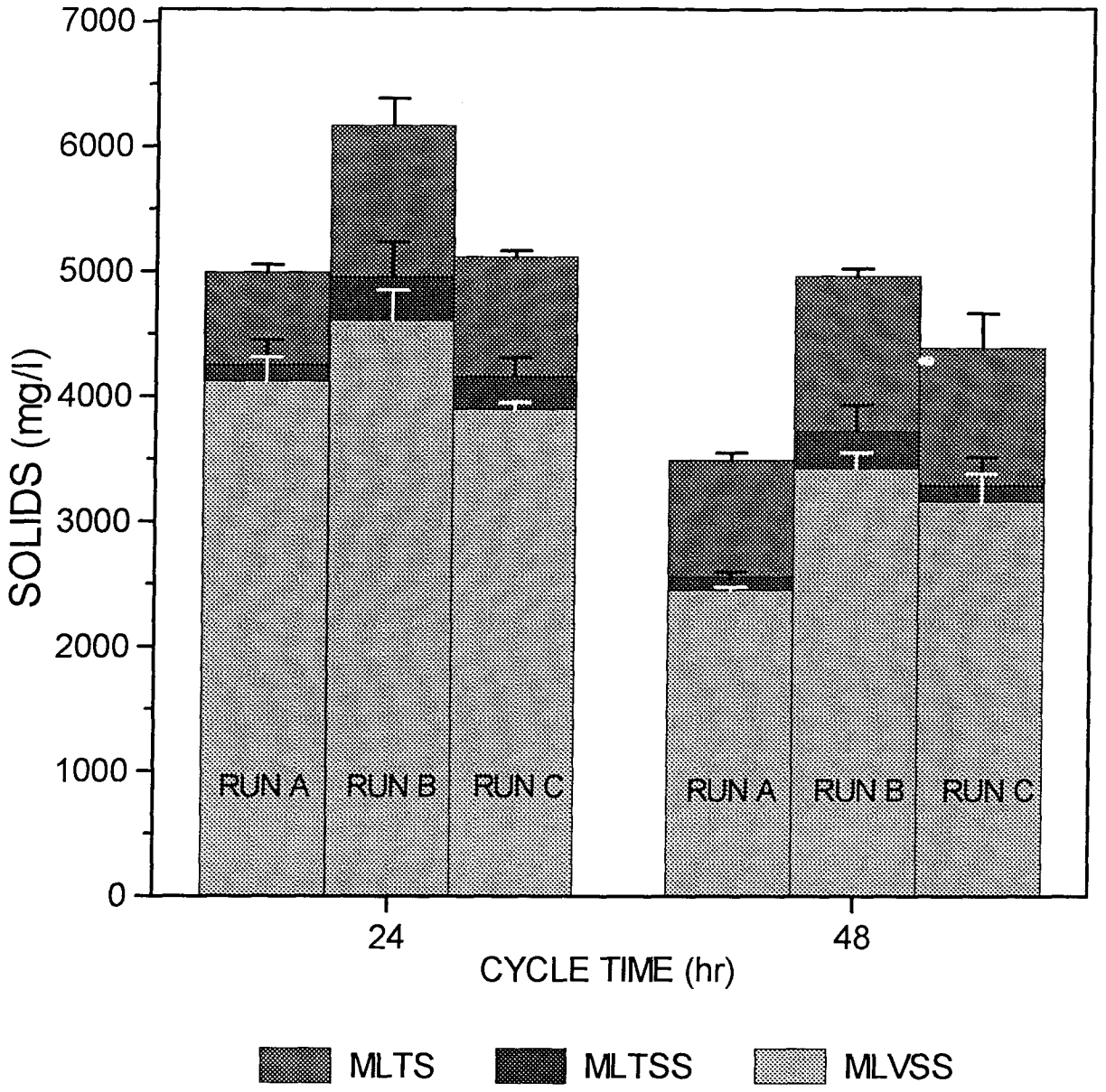

Figure 26. Solids Concentrations for the Standard Conditions Columns of Runs A, B and C

The total solids, total suspended solids, and volatile suspended solids are shown for averages of the standard conditions columns from the 24-hour cycles of runs A, B and C, followed by the same measurements from the 48-hour cycles. An average of the last three sludge samples is used for the 24-hour cycles and an average of the last two samples for the 48-hour cycles. Error bars give the 90% confidence intervals for agreement between the averaged cycles. The run using wastewater of the highest concentration yielded the highest sludge concentrations, and the run with most dilute wastewater, the lowest solids.

Listed below in Table 16 are average mixed liquor volatile suspended solids (MLVSS) values from the three runs. Listed in the fourth column is the quantity of sludge MLVSS removed from each SBR column per litre of wastewater treated, in mg per day. The fifth column gives the sludge yield - the mg of VSS wasted per cycle divided by the mg of total mg of COD removed from the wastewater per cycle. The sixth column also gives sludge yield, but on the basis of BOD_5 removed. The values are averages from the final three cycles of solids measurements for the 24-hour cycles, and averages of the last two cycles measured for the 48-hour cycles (as the solids concentrations in the 48-hour cycles were still decreasing). The values for standard conditions columns are also averages of the triplicate columns of run A and the duplicate columns of runs B and C.

Table 16. Summary of MLVSS Concentrations and Sludge Yields

Run and cycle hr	Column	MLVSS mg/l	mg/d VSS removed per l ww treated	kg VSS/ kg COD	kg VSS/ kg BOD_5
A, 24	standard	4115	294	0.119	0.179
A, 48	standard	2455	175	0.166	0.203
B, 24	standard	4609	329	0.116	0.147
B, 24	acid-added	4461	319	0.126	0.151
B, 48	standard	3422	244	0.158	0.200
C, 24	standard	3892	278	0.113	0.146
C, 24	pH 7.5	3872	277	0.104	0.142
C, 24	pH 6.5	4455	318	0.137	0.170
C, 24	3 mg/l DO	3983	285	0.101	0.142
C, 24	30 d SRT	4124	196	0.075	0.102
C, 48	standard	3157	226	0.203	0.217

The pH 6.5 column had the highest sludge yield for 24-hour cycles. The sludge yields for the 48-hour cycles are higher than the 24-hour cycles because the sludge concentrations are still falling from levels built up during the 24-hour cycles. Typical sludge yields for AS systems are 0.4 (range from 0.25 - 0.5) mg VSS / mg COD and 0.6 (range from 0.4-0.8) mg VSS / mg BOD_5 [Metcalf 1979]. This SBR process produced only 1/4 the typical sludge yield on both the COD and BOD_5 basis (for the 20-day SRT). This indicates that this system was able to incorporate some sludge digestion into the cycles.

If the fraction of the VSS leaving the system in the supernatant that is generated biomass rather than wood solids could be determined, and were added to the calculation of sludge wasted, this would slightly increase the sludge yield values. However, if the quantity of sludge that is composed of wood solids that have settled out during treatment were determined and the corresponding fraction removed from the calculation of the sludge wasted, it would reduce the sludge yield value. This would at least partially counterbalance the increase in the calculated value from including the microbial matter wasted in the supernatant. The settling of much of the suspended wood solids that occurred in the SBRs during treatment would likely be performed by a primary clarifier process in an AS system, so the sludge wasted from the AS system would be almost entirely sludge created through wastewater digestion.

From the data presented in the Rankin *et al.* study [1992] of conventional AS wastewater treatment at QRP, it is calculated that the 3-day HRT single stage AS system with a 15-day SRT, had a sludge yield of 0.5 kg MLVSS/kg BOD_5 removed. This further corroborates that the sludge yields from the SBR research system are much lower than expected for a continuous-flow system under similar conditions.

Statistical Analysis

Using quadruplicate tests performed on the same sample (except for the BOD_5 between-samples result), the coefficient of variation for the methods used are shown in the following table.

Table 17. Standard Deviation and Coefficient of Variation for Analytical Methods

Analysis	Standard Deviation	Coefficient of Variation, %
COD	97 mg/l	2.7
COD settled sample	51 mg/l	1.8
BOD_5 within	32 mg/l	6.3
BOD_5 between	38 mg/l	7.2
TS	61 mg/l	1.6
TSS	52 mg/l	2.2
VSS	35 mg/l	1.6
Ammonia - N	0.005 mg/l	9.5
Nitrate -N	0.05 mg/l	4.3
Orthophosphate	0.024 mg/l	3.5

The ammonia nitrogen tests were found to have a large coefficient of variation and this was expected as the readings were near the bottom of the range of that spectrophotometric method.

CHAPTER 4

DESIGN AND SCALE-UP OF THE SBR SYSTEM

Because of the fairly long HRT required for effective treatment of this wastewater, a minimum of three tanks would be recommended for a full-scale application of this process. For only one or two tanks, some aeration during fill would be required due to the extended fill period. Therefore feast conditions could not be maximized before aerobic digestion began. Also, the shorter fraction of the cycle occupied by the react period requires that more of the fill period be utilized for treatment as an aerated-fill period. For example, if just two tanks are used for an 18-hour cycle, the protocol might be a 9-hour fill with 1 hour aeration every 2 hours (for 4.5 hours total aerated fill), then 6 hours react, 1.5 hours settle and 1.5 hours decant. For four tanks providing the same aeration time per 18-hour cycle, a fill period of 4.5 hours could be used including two 0.5 hour aerated fill periods, followed by 9.5 hours react, 1.5 hours settle, 1.5 hours decant and 1 hour idle. A larger number of tanks increases the total time available for react per cycle, and lowers the ratio of fill to decant times. It also increases system flexibility by increasing time allotted as idle time which acts to increase the safety margin of the design, and by allowing greater adaptability in total reactor volume as one or more reactors can be taken in or out of service as needed.

The biggest change that would occur in a full-scale version of the research SBRs would be the increase in the fill period duration. This is because the test system used a very short fill period in which stored wastewater was poured into the reactors. In the full-scale system with four reactors, fill time would equal one third the total react, settle, decant and idle periods of each tank (time of react + settle + decant + idle = Σ time of fill of all other tanks). This extended fill period could be used for a phosphorus or nitrogen removal strategy, but this is not required for the nutrient levels present in pulpmill wastewaters. The fill stage will therefore serve primarily as an equalization period with a low level of substrate removal (much of the period will probably be anoxic). By minimizing aeration until fill is complete, the temporary feast conditions useful to select for organisms with good settling characteristics, can be maximized.

The other major change between the research system and a pilot-scale and full-scale system would be the change from a consistent feed source to the highly variable on-line wastestream. An important research objective for a pilot-scale test

would be to determine if solids loading and SVIs stayed fairly stable under these variable loading conditions.

An idle period is also incorporated into the design to provide a buffer of time to be drawn from for fill time fluctuations due to flow rate variations (and for some react time adjustments as changes in mill processes of furnish dictate).

The choice of sludge wasting rates (and corresponding SRT) is largely a design trade-off between sludge digestion in the reactor and sludge treatment after removal. A higher sludge wasting rate would correspond to lower aeration energy requirements, but increased manpower and sludge treatment requirements. The decision is a compromise based on expected costs of the extended aeration and the resulting increase in tank volume required, versus the costs of sludge disposal and treatment.

If the SBR incorporates solids clarification which would otherwise be performed in a preclarifier, this would increase the total concentration of MLVSS that must be retained in the reactor. At least the same concentration of active biomass would still be needed, but a significant fraction of the MLVSS would now consist of wood solids. This increase in the sludge loading would increase the reactor volume required because the minimum liquid level would have to increase to contain the greater volume of sludge. However, for influent solids levels that are not excessively high, and SVIs that are reasonably low, this increase in reactor volume could still be significantly lower than the additional volume that would be required if a separate preclarifier were used.

During non-aerated fill, the SBR acts as a stepwise equalization tank. Equalization and buffering requirements can often be accommodated through proper design of the minimum liquid level and of the mixing and aeration periods during fill. The Quesnel River CTMP effluent includes no compounds that are known to be significantly inhibitory of aerobic organisms at the concentrations present. Therefore for this design, providing buffering capacity with the liquid volume retained after each cycle is not a concern.

The greater the fraction of wastewater decanted per cycle, the more the feast conditions are maximized at the beginning of aeration. However, minimum liquid level and SRT are not independent. For any MLSS and SVI there is a maximum biomass that can be contained in the tank, therefore setting a limit on sludge age for any minimum liquid volume fraction. For our typical MLSS of 4000 mg/l and an expected SVI of 125 ml/g or less after 1.5 hours settling, the minimum liquid volume

would be 0.5 times the maximum volume (4g/l mixed liquor x 0.125 l sludge/g = 0.5 l sludge per l mixed liquor). Similarly, adequate tank volume is also determined once mass loading and desired MLVSS are specified. It has been suggested that at around 0.4 kg BOD_5/kg MLVSS/d and lower, the SBR is not stressed and acceptable effluent quality should result [Irvine 1989].

Almost all SBRs now in operation use jet aerators [Irvine 1989], which also provide mixing when the blowers are off. If separate recirculation pumps are installed for mixing, or if nonaerated mixing (for nutrient removal) is not required than a wide range of diffused air or floating mechanical aerators can be used.

Using approximated rates of oxygen consumption from Irvine and Ketchum's review paper [1989], results in a rough estimate of adequately supplied oxygen consumption rate of 20 g/kg MLVSS-h during aerated fill and the first few hours of react, and 15 g/kg MLVSS-h during the rest of the react period. Actual demand during the end of the react period may fall even lower because the BOD_5 degradation rate has dropped so far by then, and sludge growth and respiration is therefore slowed. For the pilot system proposed below, 20 g/kg MLVSS-h works out to a consumption of 80 g O_2 per hour per 1000 l tank.

The results of the research are used to make the following recommendations for a pilot plant SBR for the Quesnel River Pulp mill. The pilot-scale system would be installed to receive the combined wastewater and whitewater that enters the dissolved air flotation clarifier (DAF) prior to anaerobic bio-treatment (the same wastewater source used in the research). This wastewater had a COD of 5000-10,000 mg/l, a BOD_5 of 1500-3500 mg/l (average of roughly 2300 mg/l) and a TSS of 900-2000 mg/l [personal communication with Quesnel River Pulp technician Anna Rankin, 1993]. Alternately, if the SBR were installed after the DAF, this would reduce the usual influent COD to 2000-5000 mg/l, BOD_5 to 800-2800 mg/l (average of approximately 1650 mg/l) and TSS to 150-300 mg/l.

The proposed pilot plant (summarized in table 18), is composed of four 1000 l tanks, each handling 500 l per cycle, or 667 l per day. The following specifications use an HRT slightly greater than that of the 24-hour cycles in the research system.

Table 18. Recommended Initial Protocol for Pilot Plant

Volume out per tank	0.5 x maximum volume = 500 l
Static fill	3.5 hours
Aerated fill	1 hour
React	9.5 hours
Settle	1.5 hours
Draw	1.5 hours
Idle	1 hour
Total cycle	18 hours
Cycles/tank	1.33 per day
Ratio draw / fill	0.33
Residence time	36 hours
Loading	0.42 kg BOD_5/kg MLSS-d
Estimated Sludge wasted	0.33 kg/cycle per tank
Sludge age	12 days

The loading is based on a BOD_5 of 2500 mg/l. Uncommonly high BOD_5 loadings could be accommodated by utilizing the buffer capacity provided by the idle period, or by increasing the fraction of the fill period that is aerated. Common F/M (mass loading, i.e. food to microorganism) ratios for conventional AS systems are 0.2-0.4. High rate systems typically have F/M ratios between 0.4 and 1.5 [Metcalf 1979]. The waste sludge concentration is approximately 10,000 mg/l for a final SVI of 100 ml/g, as wastage occurs after settling. Therefore the waste sludge flow rate is 133 l/day for the total 4000 l system.

Sludge yields would likely be a little higher than in the research system, due to the total aerated time comprising a smaller fraction of each day (14 hours rather than 22 hours). The reduction in sludge age is based on the higher wasting rate required to allow for an increase in the sludge yield by up to 100% (to 0.3 kg/kg BOD_5 from the value of 0.15 typical in the research system). The sludge age is

based on maintaining an MLVSS of 4000 mg/l with the expected maximum sludge yield and an average reduction of 90% of the influent BOD_5 (using an influent BOD_5 of 2500 mg/l).

The actual sludge age would be adjusted based on early results, to establish the desired solids loading. The sludge wasted could be significantly reduced if the sludge yield is closer to the yields that occurred in the research system. The daily volume of wastewater the reactors could treat might also increase if the SVIs are closer to the research results than the more typical value allowed for, permitting a greater fraction of the treated wastewater to be decanted (as long as final BODs under the slightly shorter HRT remained acceptable).

Under the recommended operation conditions, both TSS and BOD_5 regulations would be easily met by the pilot plant if results corroborate the findings of the bench-scale research. A major objective in the assessment of the pilot-plant would be to evaluate toxicity reduction with regular trout and/or daphnia bioassays.

Quesnel River Pulp currently uses nutrient addition for the biological treatment system that is aimed at 3 parts N and 0.7 parts P to 100 parts influent BOD_5 [personal communication, Anna Rankin 1993]. This would be a suitable, conservative starting level for the SBR pilot plant, with decreases likely possible depending on early results, based on maintaining adequate soluble N and P levels in the reactors at all times. Unless nutrient restrictions were implemented, it would not be advisable to attempt to decrease nutrient addition too far, as it would necessitate more stringent monitoring of nutrient concentrations than is necessary under a reasonably generous rate of supplementation.

A microcomputer would be used to control the SBR cycles, with float controls used for maximum and minimum liquid levels. The aerated fill period could be controlled by timer or triggered by a level sensing device (e.g. to start when tank is 3/4 full) or a DO probe (e.g. to terminate aeration period once a DO of 1.0 mg/l was reached).

The decanter should be designed to follow the fall of the liquid level, to continually draw from the most clarified region. This, accompanied by a longer settling period, would improve both the BOD_5 and TSS of the effluent compared to those obtained with the bench-scale research system. The entrance to the decanter should be positioned to draw effluent from 15-20 cm below the surface [Shubert 1986] to prevent any floating scum from entering. Entrance turbulence should be minimized to avoid resuspending sludge as the decanter system approaches the

depth of the settled sludge. A skimming device is probably not required as little scum accumulated during operation of the bench-scale system, and would not be drawn into a properly-designed decanting system.

It is recommended that the pilot-scale system have a depth as close as practical to the typical SBR design, to allow proper assessment of settling. Full-scale systems typically have at least a 2.4 m minimum depth [Shubert 1986]. For a 4000 l pilot plant with a 1.2 m minimum depth, example dimensions are 2.4 m maximum liquid depth and 73 cm diameter for each of four reactors. For the full-scale plant, the separate reactors might share common walls between rectangular chambers.

The aerator system sizing is based on the ability to adequately meet the peak demand periods. The actual oxygen requirement (AOR) is calculated from a generous allowance for expected oxygen required per quantity BOD_5 removed, i.e. 1.5 kg O_2/kg BOD_5 (would also include an oxygen allowance for nitrification if there were larger concentrations of ammonia), or oxygen per quantity MLVSS per hour as mentioned above. The standard oxygen requirement (SOR) is calculated by dividing the AOR by a correction factor for oxygen transfer conditions such as liquid temperature, atmospheric pressure and wastewater characteristics.

For an operating temperature of 35°C, a fine bubble diffuser depth of 2 m, α of 0.7 and β of 0.95 (estimated from the oxygen transfer measurements on Quesnel River Pulp wastewater), and 2.0 mg/l residual DO, using the standard equation [Shubert 1986] the correction factor is calculated to be 0.529. The rate at which oxygen must be applied to the system is then calculated by dividing the SOR by the efficiency of the air delivery system (e.g. approximately 5.9% per m of immersion depth for a fine bubble diffuser [Shubert, 1986]. For the example given above of 80 g O_2/hour per 1000 l tank, this works out to 1280 g O_2 per hour, or 0.25 m^3 of air per minute per tank.

Scaling up the pilot plant based on the maximum expected flow rate of 21,000 m^3/d (including all wastewater sources) would require a system with a volume of 31,500 m^3. Though this is very large it would have to be judged against an AS system of comparable HRT and flow rate, including the volume of the equalization basin and clarifier for the AS system, which would generally be unnecessary for an SBR system. The ASB at Quesnel River Pulp is 53,000 m^3.

The SBR volume might be reduced somewhat based on favourable results in the pilot plant, but major reductions could not be made because the system must allow for possible fluctuations in SVIs and the large swings in BOD_5 loading possible.

Due to the highly variable wastewater characteristics the system must be significantly oversized compared to one capable of handling only the average loading.

For an example maximum (filled) depth of 8 m with a minimum (decanted) depth of 4 m, the surface area of this system would be 3938 m^2, i.e. 62.7 m square. Depth selected would depend on both the aerator system chosen and the land area available.

There are several municipal SBR systems in place treating this large a flow rate, but they are much smaller due to the lower HRTs. No examples were found in the literature of an industrial wastewater treatment SBR system designed for more than 4000 m^3/d, and most applications are under 1000 m^3/d [Irvine 1989].

It is expected that few companies would seriously consider a system that was not already in place on a similar scale treating similar wastewaters, unless strong evidence was given supporting an expectation of substantial cost savings. The bench-scale research system demonstrated several assets, such as low sludge yield and low SVIs, which could be translated into direct cost savings on sludge treatment, but similar results in a long-term pilot plant would have to be shown to generate more interest in applying the SBR system to pulpmill wastewater treatment.

CHAPTER 5

CONCLUSIONS

Because the development of the TMP/CTMP industry is relatively recent, much less research has been performed on the treatment of CTMP pulp mill wastewaters than kraft mill wastewaters. Furthermore, though the sequencing batch reactor process has been applied to a wide variety of industrial wastewaters, little information exists on its application to pulp mill wastewaters. This research examined the application of an SBR system to the aerobic treatment of CTMP/TMP wastewater.

Aeration tests

Alpha values for the wastewaters studied with the bench-scale SBR system, ranged from 0.60 to 0.83. Beta values determined ranged from 0.92 to 0.97. Though the aeration tests were performed to determine the oxygen transfer characteristics of the particular system with the wastewaters that were to be used in biological treatment research, a few more general conclusions can be drawn:

As with other complex industrial wastewaters, there is a wide range of effluent characteristics possible from different TMP/CTMP mills and from different pulping runs in the same mill. This results in a greater range of possible alpha, beta and theta values than would be encountered in municipal aerobic treatment design. As the expense of either over-design or under-design for aerobic treatment can be very great, these results demonstrate that adequate testing is needed for these coefficients to predict oxygen transfer under actual operating conditions. Care is also needed when choosing samples representative of the range of wastewater characteristics that will be produced.

Biological Treatment Runs

Throughout the work, several potential benefits of the SBR system over conventional activated sludge systems were apparent: much lower sludge yield, better sludge settling than often occurs in AS systems for pulpmill wastewater, the possibility of combining equalization basin, reactor and clarifier in one unit, and high system flexibility. However, these advantages demonstrated in a bench-scale system are unlikely to change the practices of engineers designing CTMP wastewater treatment facilities. An SBR pilot plant would have to be installed treating CTMP effluent wastewater, and show stable long-term results with a

significant improvement in cost efficiency over AS treatment, before a full-scale plant would be considered. If the demonstrated benefits were not sizable, designers could be expected to stay with the proven AS system.

Using Quesnel River CTMP/TMP wastewater, average COD reductions (in one-hour settled samples) near the end of runs with a 24-hour cycle time and 34.3-hour HRT were 28-41%, and 31-37% for 48-hour cycles with 68.6-hour HRT. For samples taken after an additional three hours of settling in beakers, these ranges were 52-66% and 51-63% respectively. The extended HRT runs demonstrated that almost all the COD that could be removed by this process was removed during 24-hour cycles. COD removals were roughly 26% by four hours aeration, and 35% by 16 hours aeration. The SBR reactors were able to tolerate the shock loadings of very high COD and BOD_5 loadings (and high concentrations of toxins) at the beginning of cycles.

These results experienced generally minor variation between columns, including the 6.5 or 7.5 pH trials, trials with acid added at four hours, or the extended SRT trial. The pH-adjusted runs demonstrated that the low rates of removal after the first 16 hours of aeration were not the result of inhibition by the high pH in uncontrolled pH columns. BOD_5 in the one-hour settled samples for the various treatment conditions were 67-77% for the 24-hour cycle runs, and 88-94% for samples after three hours additional settling. For the 48-hour cycles, BOD_5 removal in the one-hour settled samples were 77-82%, and 91-96% in the four-hour settled samples.

BOD_5 and COD removal percentages for the one-hour settled samples were low compared to aerobic treatment results for similar wastewaters reviewed in the literature. The removal percentages in the four-hour settled samples were only slightly lower than values from the literature, though the SBR was generally subjected to much higher BOD_5 loadings.

Though nutrient levels were consistently low, the dissolved N and P levels at the end of the cycles were still adequate. The colour of all columns except the pH-controlled columns darkened greatly during treatment. Colour was found to be very pH dependent, with the samples around 6.5 pH from the early hours of treatment in uncontrolled columns not being discernibly different in colour from the samples at the end of treatment in the 6.5 pH column. SVIs for this system were between 53 and 82 ml/g in 24-hour cycles, and 58-96 ml/g in 48-hour cycles. The settling characteristics varied little between columns, except for the pH 6.5 column which consistently settled more compactly. This column also accumulated a significantly greater concentration of sludge.

Sludge yields for this system were uniformly low. The values for the 24-hour cycles were 0.11-0.12 kg MLVSS per kg COD removed and 0.15-0.18 kg MLVSS per kg BOD_5 removed. Both are about 1/4 the typical ratios for conventional AS systems. The values for the 48-hour cycles were higher (0.16-0.20 and 0.20-0.22 respectively) as the sludge concentrations were still falling from levels established during the 24-hour cycles. The low sludge yields would translate directly into savings in sludge treatment costs.

Recommendations for the design of a pilot-plant for a BCTMP pulp mill were made. Though an often-mentioned benefit of the SBR is the combination of reaction tank and clarifier in one unit, for our system separate additional settling time was more effective than the diminishing returns of continuing aeration beyond 16 hours. In scale-up of the system, if no separate clarifier were used, the settling period should be made as long as possible without seriously deteriorating the health of the sludge. Based on the results, a total aeration time of about 12 hours with a cycle time of 18 hours and HRT of 36 hours, is suggested as the initial protocol for a pilot plant based on this system for comparable wastewater. A primary focus for the pilot plant would be to determine if adequate reduction in toxicity could be achieved during that retention time.

6. NOMENCLATURE SUMMARY

Symbols

a	interfacial area per unit volume of liquid (A/V)
A	interfacial area between the gas and liquid phases
C	actual dissolved oxygen concentration in the liquid phase
C^*	dissolved oxygen saturation concentration
C_{si}	saturation concentration of DO at equilibrium with the gas entering the liquid at an equivalent pressure to the liquid above the aerator
F/M	food to microorganism ratio
H	Henry's law constant
K_L	mass transfer coefficient
K_La	volumetric oxygen mass transfer coefficient
N	mass of O_2 transferred per unit time
O_c	aeration capacity, i.e. the rate of oxygen transfer during aeration for a specified temperature and in water that is completely deoxygenated
p_g	partial pressure of a specific gas in the gas phase.
Q	volumetric flow rate
V	liquid volume
α	ratio of K_La measured in process water to K_La in clean water under equivalent conditions of temperature, mixing and geometry
β	ratio of C^* in process water to C^* in clean water at the same conditions of partial pressure and temperature
θ	empirical temperature correction coefficient

Abbreviations

AOR	actual oxygen requirement
BCTMP	bleached chemithermomechanical pulp
BOD	biochemical oxygen demand

BOD_5	BOD exerted in a 5-day test period
C.I.	confidence interval
COD	chemical oxygen demand
CTMP	chemithermomechanical pulp
DAF	dissolved air flotation
DO	dissolved oxygen
EC_{50}	effective concentration to reduce light output to 50% of unchallenged Microtox cultures
HRT	hydraulic retention time
LC_{50}	lethal concentration causing the death of 50% of test organism
MLSS	mixed liquor suspended solids
MLVSS	mixed liquor volatile suspended solids
PFR	plug flow reactor
QRP	Quesnel River Pulp mill
RFA	resin acids and fatty acids
SBR	sequencing batch reactor
SOR	standard oxygen requirement
SRT	solids retention time
SVI	solids volume index
TMP	thermomechanical pulp
TS	total solids
TSS	total suspended solids
UASB	upflow anaerobic sludge blanket
VS	volatile solids
VSS	volatile suspended solids

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APPENDIX A. Theory of Oxygen Transfer

Since the SBR process studied is aerobic, oxygen must be supplied to the microorganisms that are removing the BOD. Following is an overview of the theory of oxygen transfer.

Oxygen transfer from a gas phase to a liquid phase can be described by equation 1.

$$N = K_L A (C^* - C) \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

where N is the mass of O_2 transferred per unit time,

K_L is the mass transfer coefficient,

A is the interfacial area between the gas and liquid phases,

C^* is the solubility of oxygen in the liquid phase when in equilibrium with the gas phase, and

C is the actual dissolved oxygen concentration in the liquid phase.

Consider the individual terms in equation 1 with respect to their effects on O_2 transfer in a wastewater treatment system:

The required N is determined by the BOD of the wastewater. Thus if the inlet BOD of the wastewater is x mg/l, the desired outlet BOD is y mg/l and the daily flowrate of wastewater is Q l/d, then N is Q(x-y) mg of O_2/d. Adequate levels of oxygen must also be provided for the respiration requirements of the biomass, even once most of the wastewater BOD has been removed. Dissolved oxygen (DO) levels are always maintained at least slightly higher levels than theoretically required, to ensure that despite changing wastewater and biomass conditions an oxygen deficit does not occur.

K_L, the mass transfer coefficient, is determined by the physical properties of the liquid and gas. The relevant properties are the gas - liquid density difference, liquid viscosity, diffusivity of the gas in the liquid, and the molecular weight of the gas. Thus for a particular gas and liquid at a given temperature, K_L is fixed.

A is the interfacial area between the liquid and gas phases. To put this in terms of interfacial area per unit volume of liquid, a, divide both sides of equation 1 by the liquid volume V, thus

$$N/V = K_L a [C^* - C] \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

where a = A/V.

A and a are affected by the parameters of the oxygen delivery system, including superficial gas velocity and power input per unit volume. Provision of adequate values of a is the major expense in aerobic biological wastewater treatment. This expense is associated with the cost of running compressors and/or agitators. Since values for a are difficult to measure and values for $K_L a$ are not, data correlations are usually done in terms of the product $K_L a$, the volumetric mass transfer coefficient. Aerator suppliers sometimes also rate their equipment in terms of $K_L a$.

C is the level of dissolved oxygen present in the wastewater. It is desirable to keep this value as low as practical, to maximize transfer rates.

C^* is the concentration of dissolved oxygen in the liquid in equilibrium with the gas phase, i.e. the oxygen saturation concentration. Henry's law states that C^* for a gas in a liquid is directly proportional to the partial pressure of the gas in the atmosphere in contact with the liquid. Oxygen is only slightly soluble in water, so Henry's law can be used as an equilibrium relationship.

$$C^* = H \cdot p_g \quad \text{..... (3)}$$

where H is the Henry's law constant for oxygen and

p_g is the partial pressure of oxygen in the gas phase.

Note that C^* is affected by the mole fraction of oxygen in the gas phase and the total pressure on the system. C^* is also a function of temperature since the Henry's law constant is temperature dependent - the higher the temperature the lower the solubility. For example, in pure water at 20°C exposed to an atmosphere containing 21% oxygen, C^* is 9.17 mg/l, whereas at 30°C, it is 7.63 mg/l. C^* is also affected by the composition of the wastewater through the presence of dissolved solids, being particularly affected by electrolytes. Values quoted in textbooks and handbooks are usually those for pure water.

Pure oxygen is sometimes used in aeration because the value of P_g is 1.0 compared to 0.209 at atmospheric pressure for air. Thus C^* should be 4.78 times higher when pure O_2 is used. If pure O_2 is used as the oxygen source then, because C^* is much higher, the driving force is much greater. So if the oxygen demand is the same, the $K_L a$ value necessary for an O_2 system should be significantly less. This should lead to reduced capital and operating costs for the aeration system. These savings of course must be balanced against the increased costs of the pure O_2. There are now over 200 oxygen-activated plants in operation around the world for the treatment of both industrial and municipal wastewaters [WPCF 1988].

In comparing air and O_2 treatment systems, it should be borne in mind that the size of the aeration tank is determined by BOD removal kinetics and sludge settling characteristics. Provided there is an adequate level of dissolved O_2, BOD removal rates are not affected by this parameter. However, with a pure oxygen system a higher level of microbial cell concentration can be maintained in the reactor without DO becoming rate-limiting, and therefore the rate of BOD reduction per unit volume can be higher.

Values for C should be at least 1-2 mg/l to ensure that dissolved O_2 is not rate-limiting. In systems like the SBR and activated sludge, in which organisms grow in flocs, the higher the DO level, the greater the penetration of DO into the floc. This can affect the species mix in the floc's microbial population and can affect the settleability of the flocs in the settling stage of an SBR or in the clarifier of an activated sludge process [Lau 1984].

In addition to K_La, aeration can also be characterized using the three factors alpha, beta and theta, and the aeration capacity. The ratio of K_La measured in mixed liquor (wastewater and biomass) or process water to K_La measured in clean water under the same conditions, is designated alpha. Beta is defined as the ratio of C^* in the wastewater to C^* in clean water, both in equilibrium with the same gas composition at the same temperature and pressure.

A theta factor (θ) is used to correct the molecular diffusion rate of oxygen for temperature. It is commonly used to standardize test data collected at operating temperature to the standard liquid temperature of 20°C. Equation 4 illustrates this.

$$(K_La)_T = (K_La)_{20} \times (\theta)^{T-20} \quad \text{..... (4)}$$

where $(K_La)_T$ is the value of the coefficient at the specified temperature,

$(K_La)_{20}$ is the value of the coefficient at 20°C, and

T is the temperature in °C.

The standard theta value of 1.024 is usually adequate for most applications between 10 and 30°C [Bass 1977].

If values of C^* and K_La obtained in water are to be used in the design of an aeration system for wastewater treatment, rewrite equation 2 as

$$N = \alpha \cdot (K_La)_{20} \cdot \theta^{T-20} \cdot (\beta C^* - C) \quad \text{..... (5)}$$

where K_La and C^* are values for clean water.

The aeration capacity (O_c) is often defined as the rate of oxygen transfer during aeration for a specified temperature and in water that is completely deoxygenated. It can be calculated using equation 6.

$$O_c = K_L a \cdot V \cdot C_{si} \quad \text{..... (6)}$$

where V is the liquid volume, and

C_{si} is the saturation concentration of DO at equilibrium with the air or oxygen entering the liquid at an equivalent pressure to the liquid above the aerator [Boon 1980].

In this research oxygen saturation values at atmospheric pressure were measured and used to calculate β values. For the aeration capacity calculations these values are corrected for the mid-depth pressure of the reactor.

APPENDIX B. Example Nutrient Levels from Runs B and C

			Ammonia	Nitrate	Orthophosphate
Date	Column	Sample, hr	Nitrogen, mg/l	Nitrogen, mg/l	Phosphorus, mg/l
10.16	1	22	0.25		0.39
10.16	4	22	0.40		0.44
10.16	5	22	0.45		0.68
10.16	6	22	0.45		0.65
12.03	5	4	0.20	10.5	1.31
12.03	6	4	0.15	8.5	1.20
12.03	5	16	0.10	8.5	1.28
12.03	6	16	0.10	8.5	1.15
12.03	5	22	0.10	8.5	0.92
12.03	6	22	0.15	8.0	1.03
12.15	5	46	0.20	9.5	1.33
12.15	6	46	0.15	8.0	1.13
91.09		IN	1.10	14.0	3.38
91.09		IN	1.15	13.5	3.59
91.12		IN	0.75	11.5	2.05
91.12		IN	0.75	12.0	2.15

All nutrient measurements are of supernatant from fully clarified samples

Appendix C. Solids Concentrations in Runs A, B and C

	COL 1							COL 1	COL 2							COL 2
	g/l SL	mg/l	g/l SL	mg/l	g/l SL	mg/l	depth, in	ml/g	g/l SL	mg/l	g/l SL	mg/l	g/l SL	mg/l	depth, in	ml/g
CYCLE	TS	MLTS	TSS	MLTSS	VSS	MLVSS	SETTLE	SVI	TS	MLTS	TSS	MLTSS	VSS	MLVSS	SETTLE	SVI
625																
629																
630																
701																
703																
704		NOTE	g/l SL:	gives actual concentration in g/l of the sludge remaining in the 3 litres after decanting												
705			mg/l:	these measurements are the corresponding calculated mixed liquor concentrations												
714																
716																
720																
722																
724																
726																
728																
730																
918	21.70	6510	17.16	5148	15.90	4770	7.50	56.9	20.17	6051	16.32	4896	14.95	4485	9.00	71.8
919	20.62	6186	16.90	5070	15.69	4707	7.00	53.9	19.35	5805	15.88	4764	14.49	4347	8.00	65.6
922	20.65	6195	16.32	4896	15.23	4569	7.50	59.8	17.03	5109	13.95	4185	12.67	3801	7.50	70.0
924	20.86	6258	17.07	5121	15.92	4776	7.50	57.2	16.74	5022	13.16	3948	12.10	3630	8.25	81.6
926	20.26	6078	16.69	5007	15.47	4641	7.00	54.6	15.92	4776	12.03	3609	11.50	3450	7.50	81.2
1006	17.47	5241	12.53	3759	11.72	3516	6.50	67.5							6.50	
1008	16.96	5088	12.43	3729	11.67	3501	6.75	70.7							6.00	
1014	16.55	4965	12.21	3663	11.05	3315	7.00	74.6							6.75	
1016	16.52	4956	11.67	3501	11.07	3321	7.00	78.1							6.50	
1122	17.20	5160	13.26	3978	12.46	3738	6.00	58.9	17.17	5151	13.71	4113	12.65	3795	7.50	71.2
1124	17.66	5298	14.27	4281	13.43	4029	6.00	54.7	17.69	5307	13.85	4155	13.32	3996	8.00	75.2
1126	19.56	5868	15.23	4569	14.35	4305	6.75	57.7	17.56	5268	14.54	4362	13.62	4086	8.50	76.1
1129	19.98	5994	15.69	4707	14.92	4476	7.00	58.1	17.62	5286	14.05	4215	13.41	4023	8.50	78.8
1201	20.27	6081	15.75	4725	15.00	4500	7.50	62.0	17.69	5307	13.51	4053	12.98	3894	8.50	81.9
1203	19.81	5943	15.40	4620	14.63	4389	7.00	59.2	17.87	5361	14.00	4200	13.44	4032	8.25	76.7
1213	17.79	5337	14.44	4332	13.88	4164	8.50	76.6								
1217	16.71	5013	13.59	4077	13.02	3906	8.25	79.0								
1223																
1227																
1231																
104																

Appendix C. Solids Concentrations in Runs A, B and C

	COL 3							COL 3	COL 4							COL 4
	g/l SL	mg/l	g/l SL	mg/l	g/l SL	mg/l	depth, in	ml/g	g/l SL	mg/l	g/l SL	mg/l	g/l SL	mg/l	depth, in	ml/g
CYCLE	TS	MLTS	TSS	MLTSS	VSS	MLVSS	SETTLE	SVI	TS	MLTS	TSS	MLTSS	VSS	MLVSS	SETTLE	SVI
625									15.42	4626	13.61	4083	13.06	3918		
629									17.20	5160	14.78	4434	14.14	4242		
630									16.21	4863	14.19	4257	13.78	4134		
701									16.67	5001	13.05	3915	12.47	3741		
703									15.50	4650	12.93	3879	12.54	3762		
704									17.00	5100	14.33	4299	13.79	4137		
705									16.88	5064	13.28	3984	12.81	3843	6.00	58.8
714									13.63	4089	10.80	3240	10.40	3120	5.25	63.3
716									12.97	3891	10.23	3069	9.80	2940		
720									12.70	3810	10.04	3012	9.63	2889	5.00	64.8
722									12.83	3849	9.36	2808	9.03	2709		
724									12.43	3729	9.22	2766	8.89	2667	4.75	67.1
726									11.45	3435	9.30	2790	8.80	2640		
728									11.47	3441	9.25	2775	8.81	2643		
730									11.30	3390	8.93	2679	8.57	2571		
918	20.91	6273	16.48	4944	15.40	4620	8.25	65.2	21.01	6303	15.99	4797	15.05	4515	7.25	59.0
919	20.67	6201	16.05	4815	15.06	4518	8.25	66.9	19.55	5865	15.94	4782	14.88	4464	7.00	57.2
922	17.30	5190	14.03	4209	12.71	3813	7.00	65.0	19.52	5856	14.78	4434	14.03	4209	6.50	57.3
924	17.01	5103	13.22	3966	12.39	3717	7.75	76.3	19.70	5910	15.44	4632	14.72	4416	6.75	56.9
926	15.67	4701	11.84	3552	11.11	3333	8.00	88.0	19.58	5874	15.73	4719	15.10	4530	6.75	55.9
1006							7.25		19.70	5910	15.80	4740	14.38	4314	7.00	57.7
1008							6.00		19.01	5703	15.13	4539	14.05	4215	6.75	58.1
1014							8.25		16.96	5088	13.57	4071	12.76	3828	7.00	67.2
1016							8.00		16.90	5070	13.22	3966	12.55	3765	7.00	68.9
1122							6.50		17.24	5172	12.86	3858	12.01	3603	7.25	73.4
1124							7.50		17.24	5172	13.55	4065	12.44	3732	7.50	72.1
1126							7.50		17.40	5220	13.25	3975	12.31	3693	7.50	73.7
1129	17.81	5343	14.46	4338	13.56	4068	8.50	76.5	17.53	5259	13.41	4023	12.50	3750	7.75	75.3
1201	18.10	5430	14.65	4395	13.79	4137	8.25	73.3	17.97	5391	13.85	4155	13.09	3927	8.00	75.2
1203	18.14	5442	14.61	4383	13.89	4167	8.50	75.8	17.95	5385	13.84	4152	13.13	3939	8.00	75.3
1213	17.04	5112	13.56	4068	13.05	3915	7.25	69.6								
1217	16.49	4947	12.98	3894	12.45	3735	7.50	75.2								
1223																
1227																
1231																
104																

Appendix C. Solids Concentrations in Runs A, B and C

	COL 5							COL 5	COL 6							COL 6
	g/l SL	mg/l	g/l SL	mg/l	g/l SL	mg/l	depth, in	ml/g	g/l SL	mg/l	g/l SL	mg/l	g/l SL	mg/l	depth, in	ml/g
CYCLE	TS	MLTS	TSS	MLTSS	VSS	MLVSS	SETTLE	SVI	TS	MLTS	TSS	MLTSS	VSS	MLVSS	SETTLE	SVI
625	16.15	4845	15.35	4605	14.79	4437			16.12	4836	14.02	4206	13.47	4041		
629	16.33	4899	15.24	4572	14.77	4431			16.67	5001	14.29	4287	13.84	4152		
630	16.54	4962	15.36	4608	14.89	4467			16.00	4800	13.26	3978	12.83	3849		
701	17.46	5238	14.81	4443	14.35	4305			17.49	5247	14.54	4362	14.10	4230		
703	17.25	5175	14.54	4362	14.05	4215			17.00	5100	14.46	4338	14.09	4227		
704	17.00	5100	15.16	4548	14.70	4410			16.25	4875	14.06	4218	13.68	4104		
705	16.83	5049	14.88	4464	14.37	4311	6.50	56.9	16.08	4824	13.88	4164	13.42	4026	6.50	61.0
714	13.63	4089	9.60	2880	9.25	2775	4.75	64.4	12.27	3681	8.98	2694	8.64	2592	4.75	68.9
716	12.55	3763.71	9.51	2853	9.11	2733			12.76	3828	8.71	2613	8.45	2535		
720	12.12	3636	9.25	2775	8.89	2667	5.00	70.4	12.22	3666	8.97	2691	8.61	2583	5.00	72.6
722	11.77	3531	9.09	2727	8.72	2616			11.93	3579.03	8.89	2667	8.48	2544		
724	11.79	3537	8.90	2670	8.64	2592	5.00	73.2	11.70	3510	8.59	2577	8.19	2457	5.00	75.8
726	11.70	3510	8.92	2676	8.44	2532			11.73	3519	8.45	2535	8.00	2400		
728	12.10	3630	8.42	2526	8.05	2415			11.50	3450	8.04	2412	7.75	2325		
730	11.62	3486	8.46	2538	8.18	2454			11.77	3531	8.06	2418	7.73	2319		
918	20.45	6135	16.49	4947	15.70	4710	7.50	59.2	20.88	6264	16.80	5040	15.67	4701	7.75	60.1
919	20.72	6216	17.03	5109	15.62	4686	7.50	57.3	20.71	6213	16.95	5085	15.73	4719	7.25	55.7
922	19.93	5979	16.11	4833	14.83	4449	6.50	52.5	19.92	5976	15.73	4719	14.66	4398	7.00	57.9
924	19.96	5988	15.98	4794	15.16	4548	6.75	55.0	20.99	6297	16.46	4938	15.34	4602	7.25	57.4
926	20.22	6066	16.32	4896	15.37	4611	7.00	55.8	20.62	6186	16.80	5040	15.55	4665	7.00	54.3
1006	19.03	5709	15.04	4512	13.75	4125	7.00	60.6	18.60	5580	14.59	4377	13.38	4014	7.00	62.5
1008	18.45	5535	14.99	4497	13.58	4074	7.00	60.8	17.33	5199	13.93	4179	12.98	3894	7.00	65.4
1014	17.63	5289	14.37	4311	13.13	3939	6.75	61.2	16.69	5007	13.02	3906	12.03	3609	7.75	77.5
1016	17.01	5103	13.38	4014	12.46	3738	6.75	65.7	16.46	4938	12.66	3798	11.47	3441	7.75	79.7
1122	17.26	5178	13.29	3987	12.12	3636	7.00	68.6	17.10	5130	13.80	4140	12.91	3873	7.00	66.0
1124	16.92	5076	14.25	4275	12.91	3873	7.25	66.2	17.08	5124	13.75	4125	12.61	3783	7.00	66.3
1126	16.44	4932	13.55	4065	12.56	3768	7.75	74.5	16.89	5067	14.46	4338	13.32	3996	7.75	69.8
1129	16.66	4998	13.80	4140	12.54	3762	8.25	77.8	17.25	5175	14.33	4299	13.29	3987	8.50	77.2
1201	16.58	4974	13.38	4014	12.64	3792	7.75	75.4	17.59	5277	13.88	4164	13.21	3963	8.00	75.0
1203	16.73	5019	13.55	4065	12.80	3840	8.00	76.9	17.45	5235	14.27	4281	13.36	4008	8.50	77.6
1213	14.06	4218	10.62	3186	10.08	3024	7.25	88.9	15.78	4734	11.75	3525	11.44	3432	7.75	85.9
1217	13.61	4083	10.15	3045	9.85	2955	7.50	96.2	15.03	4509	11.25	3375	10.72	3216	8.25	95.5
1223	13.20	3960	9.74	2922	9.36	2808	7.75	103.6	13.91	4173	10.11	3033	9.76	2928	7.75	99.8
1227	12.41	3723	8.84	2652	8.41	2523	8.00	117.8	13.68	4104	9.99	2997	9.63	2889	8.00	104.3
1231	12.44	3732	8.76	2628	8.26	2478	8.00	118.9	13.59	4077	9.91	2973	9.51	2853	8.25	108.4
104	11.97	3591	8.37	2511	7.88	2364	8.00	124.5	13.21	3963	9.38	2814	8.88	2664	8.50	118.0

APPENDIX D. COD Measurements from Runs A, B and C

In the following tables there are several abbreviations that do not appear in the main body of the text. These are explained here.

Sample Names:

A 16 hour sample point, with sample taken 16 hours into aeration. Samples are then settled for one hour in beakers and supernatant used as actual sample.

B 22 hour sample point, with sample taken following 22 hours aeration and 1 hour in-situ settling in 24-hour cycles, or following 22 hours aeration in 48-hour and 96-hour cycles and then settled for one hour in beakers and supernatant used as in 16-hour point.

C 46 hour sample point, with sample taken following 46 hours aeration and 1 hour in-situ settling in 48-hour cycles, or following 46 hour aeration in 96-hour cycles and then settled for one hour as in 16-hour point.

S-COD COD of supernatant from additional three hours of settling.

Appendix D. COD Measurements From Runs A, B and C

RUN A		COL 4							COL 5				
DATE	TIME	pH	COD	%REM	S-COD	%REM	DATE	TIME	pH	COD	%REM	S-COD	%REM
7.01	B	8.61	3569	40.33	2819	52.87	7.01	B	8.57	3729	37.65	2731	54.34
7.02	0	7.59	4566	23.65	3534	40.91	7.02	0	7.53	4651	22.23	3463	42.09
7.02	2	8.10	4227	29.32	3364	43.75	7.02	2	8.03	4373	26.88	3235	45.91
7.02	4	8.23	3949	33.97	3188	46.69	7.02	4	8.20	4077	31.82	3041	49.14
7.02	A	8.47	3580	40.13	2672	55.32	7.02	A	8.45	3756	37.20	2748	54.04
7.02	B	8.60	3492	41.60	2549	57.37	7.02	B	8.63	3577	40.18	2690	55.02
7.03	0	7.62	4652	22.20	3592	39.93	7.03	0	7.58	4797	19.78	3633	39.24
7.03	2	8.11	4250	28.93	3411	42.97	7.03	2	8.04	4343	27.38	3358	43.85
7.03	4	8.25	3933	34.23	3112	47.97	7.03	4	8.28	4112	31.23	3077	48.55
7.03	A	8.52	3700	38.13	2696	54.92	7.03	A	8.56	3697	38.18	2701	54.83
7.03	B	8.63	3545	40.71	2684	55.12	7.03	B	8.62	3521	41.13	2713	54.63
7.04	0	7.63	4634	22.51	3469	41.99	7.04	0	7.65	4666	21.98	3440	42.48
7.04	2	8.17	4233	29.21	3241	45.81	7.04	2	8.22	4134	30.87	3153	47.28
7.04	4	8.28	3911	34.60	2912	51.30	7.04	4	8.31	3992	33.24	2912	51.30
7.04	A	8.53	3615	39.54	2678	55.22	7.04	A	8.55	3671	38.61	2631	56.00
7.04	B	8.68	3490	41.65	2543	57.47	7.04	B	8.71	3507	41.35	2567	57.08
7.05	0	7.64	4623	22.69	3399	43.16	7.05	0	7.70	4616	22.81	3446	42.38
7.05	2	8.23	4205	29.68	3129	47.67	7.05	2	8.24	4091	31.58	3077	48.55
7.05	4	8.34	4006	33.00	2965	50.42	7.05	4	8.36	3875	35.20	2901	51.49
7.05	A	8.58	3636	39.20	2631	56.00	7.05	A	8.60	3691	38.27	2655	55.61
7.05	B	8.72	3528	41.01	2532	57.67	7.05	B	8.74	3557	40.52	2584	56.78
7.06	0	7.61	4652	22.21	3498	41.50	7.06	0	7.69	4666	21.98	3516	41.20
7.06	2	8.20	4247	28.97	3252	45.61	7.06	2	8.22	4152	30.57	3194	46.59
7.06	4	8.29	3952	33.92	2989	50.02	7.06	4	8.29	3940	34.11	2942	50.81
7.06	A	8.52	3633	39.25	2637	55.90	7.06	A	8.58	3642	39.10	2690	55.02
7.06	B	8.65	3510	41.30	2573	56.98	7.06	B	8.69	3522	41.11	2602	56.49

Appendix D. COD Measurements From Runs A, B and C

RUN A		COL 6				
DATE	TIME	pH	COD	%REM	S-COD	%REM
7.01	B	8.62	3513	41.25	2825	52.77
7.02	0	7.52	4695	21.49	3504	41.40
7.02	2	8.04	4297	28.15	3118	47.87
7.02	4	8.22	4007	32.99	3053	48.95
7.02	A	8.51	3706	38.03	2772	53.65
7.02	B	8.66	3533	40.91	2602	56.49
7.03	0	7.62	4787	19.96	3545	40.71
7.03	2	8.09	4401	26.40	3323	44.44
7.03	4	8.27	4109	31.29	3129	47.67
7.03	A	8.58	3664	38.74	2737	54.24
7.03	B	8.68	3517	41.19	2549	57.37
7.04	0	7.68	4556	23.81	3440	42.48
7.04	2	8.21	4038	32.47	3200	46.50
7.04	4	8.32	3907	34.66	3041	49.14
7.04	A	8.60	3586	40.03	2643	55.81
7.04	B	8.73	3416	42.87	2502	58.16
7.05	0	7.70	4538	24.11	3440	42.48
7.05	2	8.27	4237	29.15	3223	46.10
7.05	4	8.37	4031	32.59	2901	51.49
7.05	A	8.62	3656	38.86	2701	54.83
7.05	B	8.76	3557	40.52	2660	55.51
7.06	0	7.70	4552	23.87	3469	41.99
7.06	2	8.26	4251	28.91	3229	46.01
7.06	4	8.32	3969	33.63	2977	50.22
7.06	A	8.55	3674	38.57	2666	55.41
7.06	B	8.72	3533	40.91	2555	57.27

Appendix D. COD Measurements From Runs A, B and C

RUN A		COL 4							COL 5				
DATE	TIME	pH	COD	%REM	S-COD	%REM	DATE	TIME	pH	COD	%REM	S-COD	%REM
7.12	0	7.56	5497	8.08	3970	33.61	7.12	0	7.58	5482	8.33	3950	33.95
7.12	4	8.08	4809	19.58	3780	36.79	7.12	4	8.10	4894	18.16	3810	36.29
7.12	A	8.61	4227	29.31	3035	49.25	7.12	A	8.66	4245	29.01	3065	48.75
7.12	B	8.67	3958	33.82	3010	49.67	7.12	B	8.70	3921	34.43	2925	51.09
7.12	C	8.77	3670	38.63	2975	50.25	7.12	C	8.78	3630	39.29	2905	51.42
7.14	0	7.62	5545	7.27	4110	31.27	7.14	0	7.66	5688	4.88	4135	30.85
7.14	4	8.10	5103	14.67	3930	34.28	7.14	4	8.13	5000	16.39	3970	33.61
7.14	A	8.64	4376	26.83	3265	45.40	7.14	A	8.69	4330	27.59	3280	45.15
7.14	B	8.75	4261	28.75	3125	47.74	7.14	B	8.80	4294	28.19	3210	46.32
7.14	C	8.82	3997	33.16	2995	49.92	7.14	C	8.86	4061	32.10	3140	47.49
7.16	0	7.64	5739	4.02	4075	31.86	7.16	0	7.65	5576	6.76	4040	32.44
7.16	4	8.09	5327	10.92	4005	33.03	7.16	4	8.07	5173	13.50	3915	34.53
7.22	0	7.47	5552	7.17	4005	33.03	7.22	0	7.44	5582	6.66	4045	32.36
7.22	4	7.91	5233	12.49	3920	34.45	7.22	4	7.88	5118	14.41	3895	34.87
7.22	A	8.46	4448	25.61	3090	48.33	7.22	A	8.47	4345	27.33	3250	45.65
7.22	B	8.65	4188	29.97	3120	47.83	7.22	B	8.63	4227	29.31	3085	48.41
7.22	C	8.76	3994	33.21	3045	49.08	7.22	C	8.69	4015	32.86	2995	49.92
7.24	0	7.48	5606	6.25	4050	32.27	7.24	0	7.45	5679	5.04	4000	33.11
7.24	4	7.89	5197	13.09	3925	34.36	7.24	4	7.91	5185	13.30	3865	35.37
7.24	A	8.44	4397	26.47	3125	47.74	7.24	A	8.48	4352	27.23	3130	47.66
7.24	B	8.53	4200	29.77	3055	48.91	7.24	B	8.59	4230	29.26	3035	49.25
7.24	C	8.67	4000	33.11	3020	49.50	7.24	C	8.69	4036	32.50	3005	49.75
7.26	0	7.45	5627	5.90	4065	32.02	7.26	0	7.48	5661	5.34	3980	33.44
7.26	4	7.84	5303	11.32	3860	35.45	7.26	4	7.87	5303	11.32	3920	34.45
7.26	A	8.36	4421	26.07	3085	48.41	7.26	A	8.40	4352	27.23	3125	47.74
7.26	B	8.52	4283	28.38	3050	49.00	7.26	B	8.50	4197	29.81	3105	48.08
7.26	C	8.59	3994	33.21	2925	51.09	7.26	C	8.61	3954	33.87	2990	50.00
7.28	C	8.58	3843	35.74	2900	51.51	7.28	C	8.59	3794	36.55	2950	50.67
7.30	0	7.47	5673	5.13	4015	32.86	7.30	0	7.50	5563	6.97	3950	33.95
7.30	4	7.89	5140	14.05	3840	35.79	7.30	4	7.88	5167	13.60	3820	36.12
7.30	A	8.37	4233	29.21	3080	48.49	7.30	A	8.35	4357	27.15	3050	49.00
7.30	B	8.53	3946	34.02	2970	50.33	7.30	B	8.50	3920	34.45	2990	50.00
7.30	C	8.61	3831	35.93	2935	50.92	7.30	C	8.57	3823	36.07	2940	50.84

Appendix D.

COD Measurements From Runs A, B and C

		COL 6				
DATE	TIME	pH	COD	%REM	S-COD	%REM
7.12	0	7.53	5355	10.46	3965	33.70
7.12	4	8.11	4855	18.82	3850	35.62
7.12	A	8.66	4300	28.09	3100	48.16
7.12	B	8.75	4052	32.25	3030	49.33
7.12	C	8.85	3664	38.74	2965	50.42
7.14	0	7.66	5561	7.01	4175	30.18
7.14	4	8.14	5212	12.84	4080	31.77
7.14	A	8.69	4491	24.90	3300	44.82
7.14	B	8.78	4224	29.36	3325	44.40
7.14	C	8.86	3918	34.48	3185	46.74
7.16	0	7.66	5576	6.76	4000	33.11
7.16	4	8.12	5306	11.27	3905	34.70
7.22	0	7.42	5548	7.22	4060	32.11
7.22	4	7.86	5142	14.01	3950	33.95
7.22	A	8.39	4276	28.50	3295	44.90
7.22	B	8.63	4100	31.44	3075	48.58
7.22	C	8.69	3858	35.49	3065	48.75
7.24	0	7.43	5685	4.94	4090	31.61
7.24	4	7.84	5145	13.96	3945	34.03
7.24	A	8.38	4333	27.54	3145	47.41
7.24	B	8.57	4145	30.68	3060	48.83
7.24	C	8.69	3958	33.82	3020	49.50
7.26	0	7.47	5655	5.44	4060	32.11
7.26	4	7.85	5212	12.84	3955	33.86
7.26	A	8.39	4303	28.04	3200	46.49
7.26	B	8.51	4140	30.77	3005	49.75
7.26	C	8.58	3906	34.69	2990	50.00
7.28	C	8.60	3757	37.17	2890	51.67
7.30	0	7.48	5487	8.25	4010	32.94
7.30	4	7.90	4990	16.56	3820	36.12
7.30	A	8.35	4290	28.26	3110	47.99
7.30	B	8.49	4034	32.54	2985	50.08
7.30	C	8.55	3851	35.59	2950	50.67

Appendix D. COD Measurements From Runs A, B and C

RUN B		COL 1							COL 4				
DATE	TIME	pH	COD	%REM	S-COD	%REM	DATE	TIME	pH	COD	%REM	S-COD	%REM
9.17	0	7.29	7843	12.75	6590	26.70	9.17	0	7.10	7733	13.98	5655	37.10
9.17	4	7.98	7060	21.47	5230	41.82	9.17	4	7.96	7349	18.26	4970	44.72
9.17	B	8.45	6351	29.35	4095	54.45	9.17	B	8.10	6343	29.45	4140	53.95
9.18	0	7.23	7840	12.79	6600	26.59	9.18	0	7.04	7853	12.64	5365	40.32
9.18	4	7.88	7323	18.54	5080	43.49	9.18	4	7.81	7233	19.54	4770	46.94
9.18	B	8.53	6343	29.45	4155	53.78	9.18	B	8.08	6026	32.97	4110	54.28
9.19	0	7.31	7683	14.53	6465	28.09	9.19	0	6.86	7840	12.79	5400	39.93
9.19	4	8.02	7320	18.58	4935	45.11	9.19	4	7.65	7410	17.58	4615	48.67
9.19	B	8.56	6389	28.94	4365	51.45	9.19	B	7.95	6051	32.69	4005	55.45
9.20	0	7.28	7883	12.31	6650	26.03	9.20	0	6.71	7830	12.90	5550	38.26
9.20	4	8.00	7107	20.95	5450	39.38	9.20	4	7.73	7390	17.80	4990	44.49
9.20	B	8.55	6300	29.92	4325	51.89	9.20	B	7.85	6151	31.57	4280	52.39
9.21	0	7.13	7600	15.46	6400	28.81	9.21	0	6.67	7710	14.24	5460	39.27
9.21	4	7.95	7003	22.10	5310	40.93	9.21	4	7.70	7170	20.24	4760	47.05
9.21	B	8.56	6180	31.26	4210	53.17	9.21	B	7.78	6094	32.21	4195	53.34
9.22	0	7.15	8000	11.01	6505	27.64	9.22	0	6.63	7793	13.31	5415	39.77
9.22	4	8.12	7253	19.32	5260	41.49	9.22	4	7.60	7237	19.50	4775	46.89
9.22	B	8.55	6340	29.48	4150	53.84	9.22	B	7.69	6023	33.00	4055	54.89
9.23	0	7.14	7863	12.53	6485	27.86	9.23	0	6.62	7870	12.46	5310	40.93
9.23	4	8.07	7230	19.58	5045	43.88	9.23	4	7.66	7263	19.21	4790	46.72
9.23	B	8.48	6143	31.67	4270	52.50	9.23	B	7.79	6386	28.97	3920	56.40
9.24	0	7.19	7920	11.90	6490	27.81	9.24	0	6.63	7743	13.87	5325	40.77
9.24	4	7.96	7280	19.02	4915	45.33	9.24	4	7.68	7220	19.69	4740	47.27
9.24	B	8.50	6294	29.99	4360	51.50	9.24	B	7.77	6354	29.32	4295	52.22
9.25	0	7.26	7997	11.05	6695	25.53	9.25	0	6.72	8073	10.20	5530	38.49
9.25	4	7.95	7343	18.32	5000	44.38	9.25	4	7.63	7477	16.83	5140	42.83
9.25	B	8.63	6337	29.51	4425	50.78	9.25	B	7.72	6477	27.96	4215	53.11
9.26	0	7.18	7960	11.46	6580	26.81	9.26	0	6.63	8053	10.42	5515	38.65
9.26	4	7.96	7253	19.32	5120	43.05	9.26	4	7.67	7230	19.58	5000	44.38
9.26	B	8.59	6326	29.64	4250	52.73	9.26	B	7.76	6406	28.75	4240	52.84
10.06	B	8.62	6813	24.22	4005	55.45	10.06	B	8.42	6243	30.56	4190	53.39
10.06	C	8.78	6085	32.31	3815	57.56	10.06	C	8.62	6108	32.06	3935	56.23
10.08	C	8.81	5975	33.54	3905	56.56	10.08	C	8.71	6138	31.73	3885	56.79
10.10	C	8.88	5935	33.98	3895	56.67	10.10	C	8.80	5760	35.93	3725	58.57
10.14	C	8.75	5863	34.79	3830	57.40	10.14	C	8.76	5843	35.01	3735	58.45
10.16	C	8.80	5880	34.59	3820	57.51	10.16	C	8.80	5868	34.73	3760	58.18

Appendix D. COD Measurements From Runs A, B and C

RUN B		COL 5							COL 6				
DATE	TIME	pH	COD	%REM	S-COD	%REM	DATE	TIME	pH	COD	%REM	S-COD	%REM
9.17	0	7.12	7910	12.01	5310	40.93	9.17	0	7.30	7753	13.76	6520	27.47
9.17	4	8.01	7191	20.01	5035	43.99	9.17	4	7.96	7194	19.97	5120	43.05
9.17	B	8.15	6306	29.86	4085	54.56	9.17	B	8.50	6243	30.56	4190	53.39
9.18	0	7.05	7863	12.53	5255	41.55	9.18	0	7.25	7770	13.57	6310	29.81
9.18	4	7.80	7327	18.50	4980	44.61	9.18	4	7.92	7293	18.87	5055	43.77
9.18	B	8.14	6114	31.99	4040	55.06	9.18	B	8.60	5943	33.89	4195	53.34
9.19	0	6.87	8117	9.71	5470	39.15	9.19	0	7.37	7953	11.53	6565	26.97
9.19	4	7.68	7550	16.02	4835	46.22	9.19	4	7.91	7457	17.06	4970	44.72
9.19	B	8.00	6074	32.43	4020	55.28	9.19	B	8.60	6220	30.81	3940	56.17
9.20	0	6.74	7840	12.79	5640	37.26	9.20	0	7.30	7577	15.72	6410	28.70
9.20	4	7.70	7397	17.72	5025	44.10	9.20	4	7.94	7280	19.02	5010	44.27
9.20	B	7.95	6340	29.48	4335	51.78	9.20	B	8.38	6154	31.54	4365	51.45
9.21	0	6.67	7860	12.57	5130	42.94	9.21	0	7.11	7540	16.13	6025	32.98
9.21	4	7.64	7277	19.06	4960	44.83	9.21	4	7.87	6983	22.32	5085	43.44
9.21	B	7.82	6431	28.46	4250	52.73	9.21	B	8.46	6217	30.84	4360	51.50
9.22	0	6.61	7917	11.94	5165	42.55	9.22	0	7.07	7683	14.53	6125	31.87
9.22	4	7.63	7267	19.17	4895	45.55	9.22	4	7.86	7033	21.76	5000	44.38
9.22	B	7.72	6309	29.83	3995	55.56	9.22	B	8.52	5980	33.48	3965	55.90
9.23	0	6.60	7990	11.12	5655	37.10	9.23	0	7.11	7790	13.35	6335	29.53
9.23	4	7.64	7240	19.47	4900	45.49	9.23	4	7.86	7010	22.02	4875	45.77
9.23	B	7.78	6486	27.86	4045	55.01	9.23	B	8.47	5917	34.18	3835	57.34
9.24	0	6.63	7887	12.27	5205	42.10	9.24	0	7.16	7763	13.64	6155	31.54
9.24	4	7.62	7323	18.54	4795	46.66	9.24	4	7.78	7037	21.73	4850	46.05
9.24	B	7.75	6503	27.67	4270	52.50	9.24	B	8.47	5951	33.80	4230	52.95
9.25	0	6.69	8027	10.72	5585	37.88	9.25	0	7.21	7963	11.42	6290	30.03
9.25	4	7.61	7497	16.61	5145	42.77	9.25	4	7.73	7143	20.54	5145	42.77
9.25	B	7.65	6517	27.51	4400	51.06	9.25	B	8.45	5897	34.41	4140	53.95
9.26	0	6.60	8000	11.01	5470	39.15	9.26	0	7.17	7857	12.61	6360	29.25
9.26	4	7.63	7477	16.83	5125	42.99	9.26	4	7.79	7137	20.62	4985	44.55
9.26	B	7.76	6497	27.73	4360	51.50	9.26	B	8.48	6034	32.88	3930	56.28
10.06	B	8.41	6723	25.22	4145	53.89	10.06	B	8.56	6100	32.15	3815	57.56
10.06	C	8.62	6178	31.28	3825	57.45	10.06	C	8.80	5945	33.87	3650	59.40
10.08	C	8.71	6070	32.48	3875	56.90	10.08	C	8.85	6038	32.84	3905	56.56
10.10	C	8.78	5773	35.79	3970	55.84	10.10	C	8.92	5830	35.15	3785	57.90
10.14	C	8.73	5780	35.71	3660	59.29	10.14	C	8.82	5915	34.20	3835	57.34
10.16	C	8.72	6040	32.81	3690	58.95	10.16	C	8.83	5940	33.93	3855	57.12

Appendix D. COD Measurements From Runs A, B and C

RUN C		COL 1							COL 2				
DATE	TIME	pH	COD	% REM	S-COD	% REM	DATE	TIME	pH	COD	% REM	S-COD	% REM
11.26	B	6.50	4733	31.00	2880	58.02	11.26	B	8.00	4215	38.55	2860	58.31
11.27	B	6.34	4820	29.74	2725	60.28	11.27	B	7.97	4318	37.06	3047	55.58
11.28	B	6.45	4777	30.37	2820	58.89	11.28	B	8.02	4191	38.90	2930	57.29
11.29	B	6.65	4766	30.53	2735	60.13	11.29	B	8.05	4321	37.01	2845	58.53
12.01	B	6.66	4658	32.11	2785	59.40	12.01	B	8.00	4063	40.78	3020	55.98
12.02	4	6.61	5223	23.86	3280	52.19	12.02	4	7.93	4903	28.52	3360	51.02
12.02	A	6.42	4755	30.69	2660	61.22	12.02	A	8.00	4435	35.35	2685	60.86
12.02	B	6.56	4603	32.91	2415	64.80	12.02	B	8.01	4083	40.49	2715	60.42
12.03	4	6.73	5230	23.76	3155	54.01	12.03	4	8.06	5015	26.90	3250	52.62
12.03	A	6.62	4643	32.33	2610	61.95	12.03	A	8.02	4540	33.82	2830	58.75
12.03	B	6.50	4465	34.91	2290	66.62	12.03	B	7.97	4010	41.55	2890	57.87
12.04	4	6.77	5491	19.96	3230	52.92	12.04	4	8.10	5103	25.61	3310	51.75
12.04	A	6.63	4690	31.63	2530	63.12	12.04	A	8.04	4563	33.48	2865	58.24
12.04	B	6.76	4572	33.35	2450	64.29	12.04	B	8.05	4050	40.96	2900	57.73
12.05	4	6.74	5409	21.15	3405	50.36	12.05	4	8.09	5100	25.66	3355	51.09
12.05	A	6.67	4755	30.69	2500	63.56	12.05	A	8.10	4581	33.22	2815	58.97
12.05	B	6.68	4560	33.53	2355	65.67	12.05	B	8.05	4032	41.22	2770	59.62
12.11	C	8.67	4373	36.25	2530	63.12							
12.13	C	8.65	4188	38.95	2385	65.23							
12.15	C	8.66	4235	38.27	2445	64.36							
12.17	C	8.71	4493	34.50	2660	61.22							
12.19	C	8.67	4539	33.83	2530	63.12							

Appendix D. COD Measurements From Runs A, B and C

RUN C		COL 3							COL 4				
DATE	TIME	pH	COD	% REM	S-COD	% REM	DATE	TIME	pH	COD	% REM	S-COD	% REM
11.26	B	8.53	4518	34.14	2780	59.48	11.26	B	7.50	4442	35.24	2610	61.95
11.27	B	8.58	4500	34.40	2854	58.40	11.27	B	7.51	4573	33.35	2685	60.86
11.28	B	8.54	4594	33.04	3095	54.88	11.28	B	7.41	4638	32.39	2940	57.14
11.29	B	8.52	4385	36.08	3005	56.20	11.29	B	7.50	4540	33.81	2910	57.58
12.01	B	8.60	4245	38.12	3055	55.47	12.01	B	7.51	4190	38.92	2865	58.24
12.02	4	8.05	5203	24.15	3490	49.13	12.02	4	7.39	5097	25.70	3200	53.35
12.02	A	8.55	4405	35.79	2920	57.43	12.02	A	7.51	4428	35.46	2780	59.48
12.02	B	8.60	4200	38.78	2755	59.84	12.02	B	7.43	4208	38.67	2565	62.61
12.03	4	7.95	5310	22.59	3355	51.09	12.03	4	7.51	5042	26.50	3370	50.87
12.03	A	8.46	4563	33.49	2900	57.73	12.03	A	7.51	4400	35.86	2710	60.50
12.03	B	8.53	4148	39.53	2660	61.22	12.03	B	7.41	4166	39.27	2640	61.52
12.04	4	7.96	5260	23.32	3520	48.69	12.04	4	7.39	5327	22.35	3215	53.13
12.04	A	8.46	4609	32.81	2875	58.09	12.04	A	7.51	4495	34.48	2750	59.91
12.04	B	8.58	4335	36.81	2675	61.01	12.04	B	7.53	4212	38.60	2665	61.15
12.05	4	8.08	5460	20.41	3700	46.06	12.05	4	7.34	5373	21.68	3380	50.73
12.05	A	8.52	4533	33.92	3010	56.12	12.05	A	7.47	4403	35.82	2805	59.11
12.05	B	8.60	4209	38.64	2705	60.57	12.05	B	7.52	4186	38.98	2620	61.81
12.11	C	8.72	4188	38.95	2800	59.18							
12.13	C	8.59	4270	37.76	2600	62.10							
12.15	C	8.61	4340	36.73	2610	61.95							
12.17	C	8.77	4293	37.42	2945	57.07							
12.19	C	8.76	4354	36.53	2856	58.37							

Appendix D. COD Measurements From Runs A, B and C

RUN C		COL 5							COL 6				
DATE	TIME	pH	COD	% REM	S-COD	% REM	DATE	TIME	pH	COD	% REM	S-COD	% REM
11.26	B	8.72	4673	31.88	3060	55.39	11.26	B	8.60	4539	33.83	2930	57.29
11.27	B	8.74	4748	30.79	3010	56.12	11.27	B	8.67	4693	31.60	2930	57.29
11.28	B	8.66	4809	29.91	3210	53.21	11.28	B	8.59	4760	30.62	3180	53.64
11.29	B	8.65	4819	29.75	3125	54.45	11.29	B	8.56	4702	31.46	3100	54.81
12.01	B	8.73	4650	32.22	3005	56.20	12.01	B	8.62	4305	37.24	3025	55.90
12.02	4	8.21	5133	25.17	3475	49.34	12.02	4	8.14	5220	23.91	3645	46.87
12.02	A	8.70	4505	34.33	2910	57.58	12.02	A	8.64	4538	33.86	2845	58.53
12.02	B	8.73	4370	36.30	2705	60.57	12.02	B	8.65	4290	37.46	2885	57.94
12.03	4	8.14	5081	25.94	3395	50.51	12.03	4	8.08	5116	25.42	3520	48.69
12.03	A	8.71	4658	32.11	2905	57.65	12.03	A	8.61	4643	32.33	2920	57.43
12.03	B	8.75	4348	36.62	2775	59.55	12.03	B	8.62	4288	37.49	2795	59.26
12.04	4	8.26	5093	25.76	3380	50.73	12.04	4	8.21	5310	22.59	3370	50.87
12.04	A	8.68	4741	30.89	2925	57.36	12.04	A	8.59	4699	31.50	2935	57.22
12.04	B	8.74	4490	34.55	2835	58.67	12.04	B	8.66	4415	35.64	2860	58.31
12.05	4	8.23	5280	23.03	3470	49.42	12.05	4	8.17	5123	25.32	3550	48.25
12.05	A	8.70	4713	31.30	3070	55.25	12.05	A	8.61	4575	33.31	2890	57.87
12.05	B	8.74	4472	34.81	2715	60.42	12.05	B	8.65	4402	35.83	2795	59.26
12.11	C	9.01	4510	34.26	2430	64.58	12.11	C	8.90	4645	32.29	2245	67.27
12.13	C	8.86	4578	33.27	2465	64.07	12.13	C	8.72	4583	33.19	2380	65.31
12.15	C	8.94	4443	35.23	2810	59.04	12.15	C	8.83	4735	30.98	2670	61.08
12.17	C	8.96	4605	32.87	2955	56.92	12.17	C	8.82	4721	31.18	3030	55.83
12.19	C	8.91	4587	33.13	2940	57.14	12.19	C	8.84	4742	30.87	2964	56.79
12.19	E	8.98	4563	33.48	2934	57.23	12.19	E	8.93	4539	33.83	2790	59.33
12.23	E	9.10	4812	29.85	2922	57.41	12.23	E	9.05	4560	33.53	2964	56.79
12.27	E	9.00	4948	27.87	3024	55.92	12.27	E	8.97	4449	35.15	2802	59.15
12.31	E	9.10	4899	28.59	3210	53.21	12.31	E	9.01	4887	28.76	2988	56.44
1.04	E	9.00	4501	34.39	3180	53.64	1.04	E	8.91	4398	35.89	3096	54.87