Biological Fluidized Bed Treatment of Coke Plant Wastewater and Blast Furnace Scrubber Blowdown

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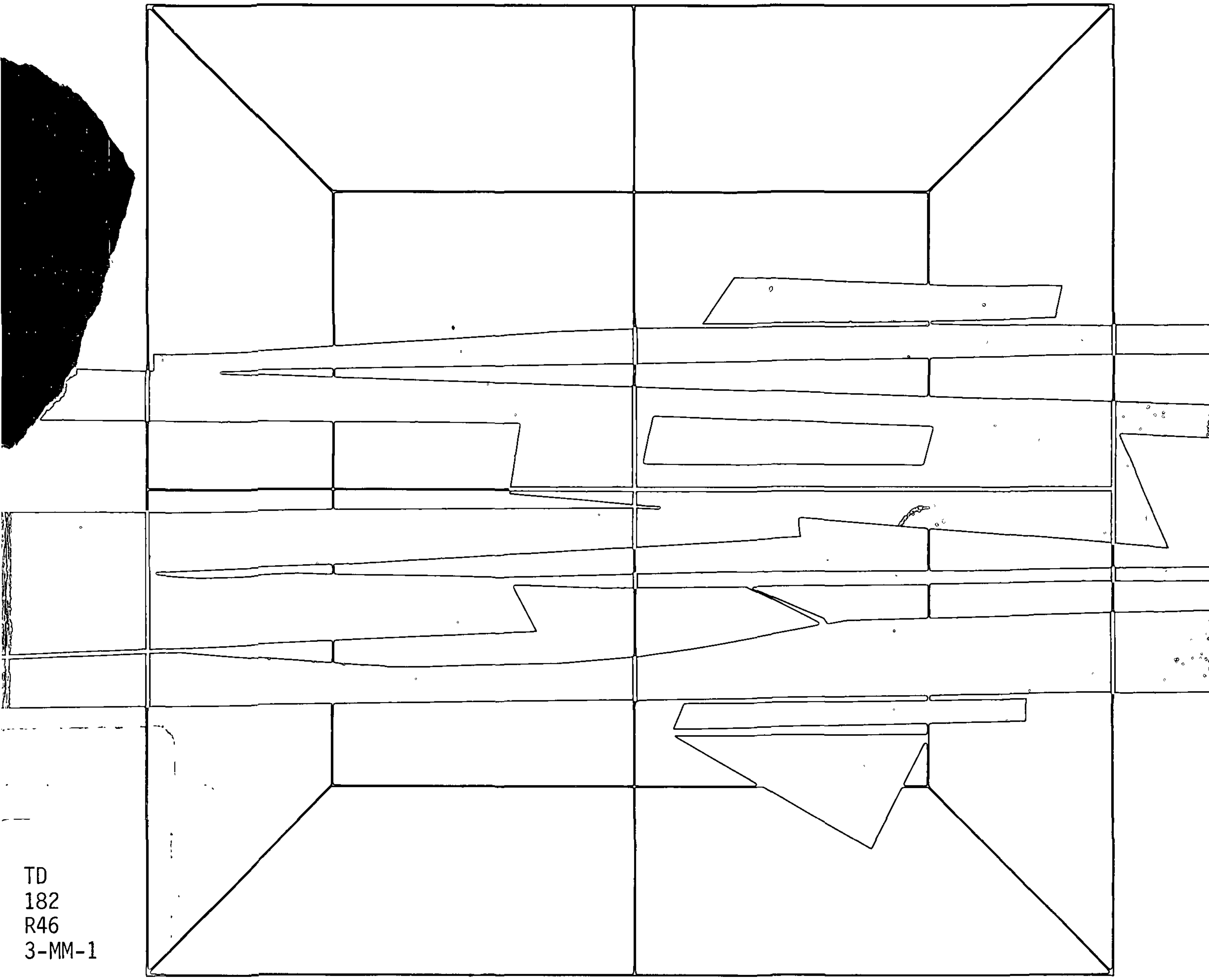

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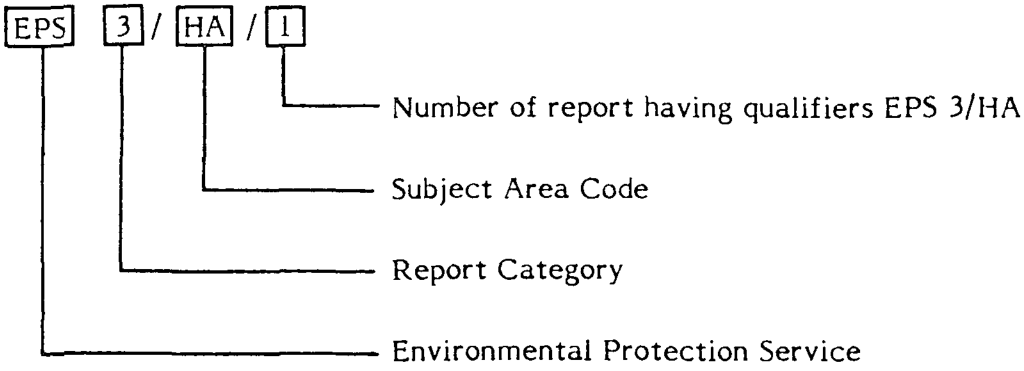

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BIOLOGICAL FLUIDIZED BED TREATMENT OF COKE PLANT WASTEWATER AND BLAST FURNACE SCRUBBER BLOWDOWN

L Report (Canada: Environmental Protection Service)

by

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for the

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Environmental Protection Service
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REVIEW NOTICE

This report has been reviewed by the Environmental Protection Programs Directorate, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute recommendation or endorsement for use. This report is based upon two separate project reports prepared by Dearborn Environmental Services, which contain all the raw data generated in the two studies. Any comments regarding the contents of this report should be directed to:

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ABSTRACT

Pilot-scale investigations were conducted at Environment Canada's Wastewater Technology Centre to assess the feasibility of using a coupled biological fluidized bed system in the treatment of:

a) coke plant wastewater (June 1980 - December 1981), and
b) a combined wastewater containing coke plant effluent and blast furnace scrubber blowdown (January - August 1982).

The fluidized bed system was shown to be capable of achieving complete nitrification and denitrification of undiluted coke plant wastewater at a total system hydraulic retention time (HRT) of approximately 16 hours. Total nitrogen removal efficiencies of more than 90 percent were maintained under steady and non-steady state conditions. Removal of conventional contaminants including filtered organic carbon, phenolic compounds and thiocyanate was consistently greater than 90 percent despite step changes in process loading and periodic reductions in the nitrification efficiency. The process also effected a high degree of trace organic contaminant control.

Complete nitrification and denitrification was also obtained when treating the combined wastewater stream. In this case, the total system HRT was significantly reduced to 4.5 hours. Effluent quality achieved was superior to that obtained during treatment of coke plant wastewater alone in terms of filtered organic carbon, phenolic compounds, thiocyanate, total cyanide, and suspended solids concentrations. Seven treated effluent samples from the fluidized bed process were analyzed for U.S. EPA organic priority pollutants and 24 non-priority pollutant trace organic compounds. Only di-n-butyl phthalate was identified at greater than trace concentrations (0.010 mg/L) despite the presence of a range of trace organics in the untreated wastewater at concentrations up to approximately 15 mg/L.

Full-scale process design data and capital and operating cost estimates for biological fluidized bed treatment of both wastewater streams were developed. Capital costs associated with treatment of 4950 m^3/d of combined wastewater were \$2 339 000, compared to \$2 357 000 for treatment of 1300 m^3/d of coke plant wastewater alone. Annual direct operating costs for treatment of the combined wastewater were estimated at \$252 400, equivalent to \$0.14 per m^3 of wastewater treated. Comparable costs for treatment of coke plant wastewater were \$150 900, equivalent to \$0.32 per m^3 of wastewater treated. The increased operating costs associated with treatment of the combined wastewater were primarily related to increased phosphoric acid requirements.

RÉSUMÉ

Des études en unité pilote ont été menées au Centre technique des eaux usées d'Environnement Canada pour évaluer la faisabilité d'un système biologique connecté, à lit fluidisé, pour le traitement:

a) des eaux résiduaires d'une cokerie (de juin 1980 à décembre 1981); et

b) des eaux résiduaires mixtes contenant l'effluent d'une cokerie et l'eau de purge des hauts fourneaux (de janvier à août 1982).

Le système s'est révélé capable d'une nitrification et d'une dénitrification complètes des eaux non diluées de cokerie, à un temps de rétention hydraulique (TRH), pour l'ensemble du système, d'environ 16 h. Des taux d'élimination de l'azote total de plus de 90% ont été maintenus dans des conditions à l'équilibre et non à l'équilibre. L'élimination des contaminants ordinaires, y compris du carbone organique filtré, des phénols et des thiocyanates, a constamment été supérieure à 90% malgré des variations brusques de charge et des baisses périodiques de l'efficacité de la nitrification. Le procédé s'est aussi révélé capable d'une forte maîtrise des traces de contaminants organiques.

Dans le cas des eaux mixtes, la nitrification et la dénitrification ont aussi été complètes, et le TRH a été réduit à 4,5 h. La qualité de l'effluent traité était supérieure à celle des seules eaux de cokerie, pour ce qui est du carbone organique filtré, des phénols, des thiocyanates, des cyanures totaux et des matières en suspension. Sept échantillons des effluents traités ont été prélevés, et on y a dosé les polluants organiques prioritaires pour l'EPA et 24 polluants organiques à l'état de trace non prioritaires. Seul le phtalate de di-n-butyle a été décelé à des concentrations supérieures aux traces (0,010 mg/L), malgré la présence de toute une gamme de matières organiques en traces dans les eaux brutes, à des concentrations pouvant atteindre environ 15 mg/L.

On a fait le calcul des installations à l'échelle et estimé les coûts d'exploitation et les investissements pour le traitement biologique en lit fluidisé des deux types d'effluents. Pour le traitement de 4 950 m^3/j d'eaux mixtes les investissements seraient de 2 339 000 $, comparativement à 2 357 000 $ pour le traitement de 1 300 m^3/j d'eaux de cokerie. Les frais annuels directs d'exploitation pour le traitement des eaux mixtes ont été estimés à 252 400 $, ce qui équivaut à 0,14 $/$m^3$ d'eau traitée, ceux du traitement des eaux de cokerie, à 150 900 $, ce qui équivaut à 0,32 $/$m^3$. Les frais accrus d'exploitation du traitement des eaux mixtes étaient surtout reliés à des besoins accrus en acide phosphorique.

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1 INTRODUCTION

Industrial activities such as organic chemical production, byproduct coke oven operation in the steel-making industry, and coal gasification/liquefaction processes generate complex wastewaters containing high concentrations of conventional contaminants such as ammonia, cyanide, thiocyanate, sulphides and a variety of oxygen-demanding organic carbon compounds. In addition, these wastewaters are known to contain a wide range of trace organic contaminants which have been shown to produce adverse long-term environmental effects.

The development of treatment technologies that can adequately deal with the contaminants present in such wastewaters has become an environmental priority. Although physical-chemical treatment has recently generated some interest, biological treatment techniques appear to be more cost-effective in most cases. In general, the emphasis of biological treatment has been on the control of conventional oxygen-demanding organic contaminants. However, increasingly stringent pollution control requirements for industrial wastewater discharges have led to a re-assessment of the biological processes with respect to the control of more specific contaminants than those traditionally monitored. Particular areas of concern have included the oxidation of ammonia to the less acutely toxic nitrate and nitrite species, complete control of nitrogenous compounds through a combination of nitrification and denitrification processes, and the biological removal of a variety of specific trace organic contaminants.

Blowdowns from blast furnace recycle systems contain lesser, although still significant, levels of ammonia and cyanide than coke plant wastewaters. Blast furnace blowdown streams are, however, relatively small contributors of organic contaminants. Treatment of blast furnace blowdown may be necessary in the future as increased process recycling results in more concentrated waste streams. The combined treatment of coke plant wastewater and blast furnace blowdown may be a practical alternative to separate treatment. Since freshwater dilution of coke plant wastewaters is widely practiced to improve nitrification efficiency (1, 2), the addition of blast furnace blowdown could be beneficial to the overall process economics. Data from a recent American study (3) indicates that combined treatment in a suspended growth biological system is technically feasible.

Studies conducted at Environment Canada's Wastewater Technology Centre (WTC) in Burlington, Ontario, have investigated the practicability of applying a single-sludge suspended growth biological treatment process, operated in the pre-denitrification-nitrification mode, to complex wastewaters generated from the organic chemicals industry and from steel industry metallurgical coke production operations. These studies demonstrated that complete nitrogen control and a high degree of trace contaminant control can be attained (1, 2, 4, 5, 6).

At the same time, the biological fluidized bed has been developed as a modification of more conventional fixed film processes such as the trickling filter. Investigations at the WTC (7, 8, 9, 10) confirmed some of the potential advantages of the fluidized bed process cited by other researchers. During the developmental work on biological nitrogen and contaminant control and investigations of the biological fluidized bed process, the possibility that a two-stage fluidized bed system, operated in the pre-denitrification-nitrification mode, might offer considerable advantage for the treatment of complex industrial wastes was recognized.

In this report, two pilot-scale studies of the applicability of the biological fluidized bed process for treatment of coke plant wastewater and blast furnace blowdown water are described. The first study (June 1980 - December 1981) evaluated the fluidized bed process operated in the pre-denitrification-nitrification flow mode as a high-rate system for treatment of coke plant wastewaters alone. In the second study (January - August 1982), treatment of a combined wastewater consisting of coke plant effluent and blast furnace blowdown water was assessed.

The major objectives of the two programs were as follows:

a) to operate a pilot-scale coupled anoxic-aerobic biological fluidized bed treatment system to treat coke plant effluents separately and combined with blast furnace blowdown water in order to develop basic design criteria;

b) to determine whether the fluidized bed process can effect nitrification of coke plant wastewater without dilution or addition of activated carbon to reduce the effect of inhibitory compounds;

c) to optimize the operation of the fluidized bed system to provide removal of conventional contaminants including phenolic compounds, cyanide, thiocyanate and ammonia;

d) to assess the degree of removal of trace organic contaminants effected by the biological fluidized bed process;

e) to compare the biological treatment requirements for the combined coke plant wastewater and blast furnace blowdown with the requirements for the treatment of coke plant wastewater alone; and

f) to develop preliminary capital and operating cost estimates for coupled biological fluidized bed systems designed to treat coke plant wastewaters alone and combined with blast furnace blowdown water.

The raw data for the two studies summarized in this report may be obtained from the Wastewater Technology Centre at the address given on the back of the title page.

2 TECHNICAL BACKGROUND

Liquid effluents resulting from coal gasification, liquefaction and carbonization processes are among the most complex industrial wastewaters. They typically contain high concentrations of ammonia, phenol, thiocyanate, cyanide, sulphides and lesser amounts of other trace contaminants. Biological treatment processes have been widely applied to control the organic constituents in these wastewaters, most notably phenolic compounds. However, increasingly stringent pollution control requirements will necessitate more intensive treatment of these wastewaters to eliminate acute toxicity and control various specific trace organics known to be present in the raw waste. Particular attention is being paid to nitrogenous compounds indigenous to coal processing wastewaters.

This section provides a background to biological processes capable of providing nitrogen control, documents the characteristics and treatability of coal processing wastewaters and blast furnace blowdown water, and reviews information on biological fluidized bed treatment technologies.

2.1 Biological Nitrogen Control

Nitrogen control in municipal and industrial wastewaters can be accomplished by either physical-chemical or biological means. In the case of high-strength wastewaters, physical-chemical technologies may be preferred; however, in most cases, biological nitrogen control is more cost-effective (11). Biological nitrogen control implies a two-stage process of nitrification and denitrification. The separate biological processes can be coupled to effect varying degrees of nitrogen control.

2.1.1 Nitrification. In biological nitrification, autotrophic organisms oxidize ammonia to nitrate under aerobic conditions. Although nitrification reduces the oxygen demand exerted by the treated waste on the receiving waters, it does not significantly reduce the nitrogen content of the waste stream. However, the conversion to oxidized nitrogen is necessary to allow subsequent biological nitrogen removal by the denitrification process.

Biological nitrification is a sequential process in which ammonia is oxidized to nitrite, principally by bacteria of the genus Nitrosomonas, and nitrite is subsequently further oxidized to nitrate, principally by bacteria of the genus Nitrobacter. The autotrophic organisms responsible for these nitrogen transformations derive energy for growth from the free energy released by the oxidation reactions. Inorganic carbon (carbon dioxide or bicarbonate) is the carbon source used for growth.

The conversion of ammonia to nitrite is the rate-limiting step in the nitrification process; however, as complete nitrification is a sequential reaction, biological systems must be operated to optimize the kinetics of both oxidative reactions. Nitrification rates are known to be affected by such environmental factors as temperature, pH and dissolved oxygen concentration.

The presence of heavy metals, such as copper, nickel and zinc, can inhibit the nitrification reactions (11). In addition, Downing et al. (12), and Hockenbury and Grady (13) identified a number of organic compounds selectively inhibitory to the ammonia oxidation or the nitrite oxidation reactions. The possibility of incomplete conversion of nitrite to nitrate due to Nitrobacter inhibition has been recognized by a number of researchers involved in the treatment of coke plant wastewaters (1, 14, 15).

Biological nitrification of municipal and industrial wastewaters has been effectively accomplished by either suspended growth processes (conventional activated sludge, contact stabilization, step aeration), in which the biological solids are suspended as a mixed liquor in the liquid stream by mechanical mixing, or by fixed film processes (trickling filters, rotating biological contactors, fluidized bed reactors), in which the biomass is retained in or on a solid support medium. In both cases, the processes can be operated in the separate-sludge mode, in which carbon oxidation and nitrification reactions are carried out in two distinct reactors without intermixing of the biological solids (16, 17), or in the single-sludge mode, in which carbon oxidation and nitrification reactions are carried out using the same biological sludge containing both heterotrophic and autotrophic organisms (3, 18). In some cases, suspended growth and fixed film processes have been combined to provide separate sludge carbon oxidation and nitrification (10, 19). In any specific application, one particular process design may offer advantages in terms of operation, process stability or economics.

2.1.2 Denitrification. In biological denitrification, the primary pathway for nitrogen removal is the conversion by heterotrophic organisms of oxidized nitrogen species to gaseous nitrogen under anoxic conditions. This pathway, in which oxidized nitrogen is utilized as a hydrogen acceptor during the oxidation of a carbon substrate, is termed dissimilatory denitrification. Denitrifiers are also capable of assimilatory denitrification in which oxidized nitrogen is converted to ammonia to satisfy the cellular nitrogen requirements; however, this metabolic pathway is of relatively minor importance, particularly in wastewaters containing adequate ammonia (20).

Biological denitrification requires organic carbon. In post-denitrification systems, in which the wastewater has undergone carbon oxidation and nitrification prior to the denitrification reactor, the carbon and energy source may be supplied by bypassing a portion of the raw wastewater to the denitrification reactor, by endogenous respiration of the cellular mass, or by the addition of an external carbon source. The latter approach is most commonly used (20). Methanol is the organic carbon source most frequently applied (20), although a wide variety of pure compounds and waste materials can be used, depending on the specific circumstances (21, 22, 23).

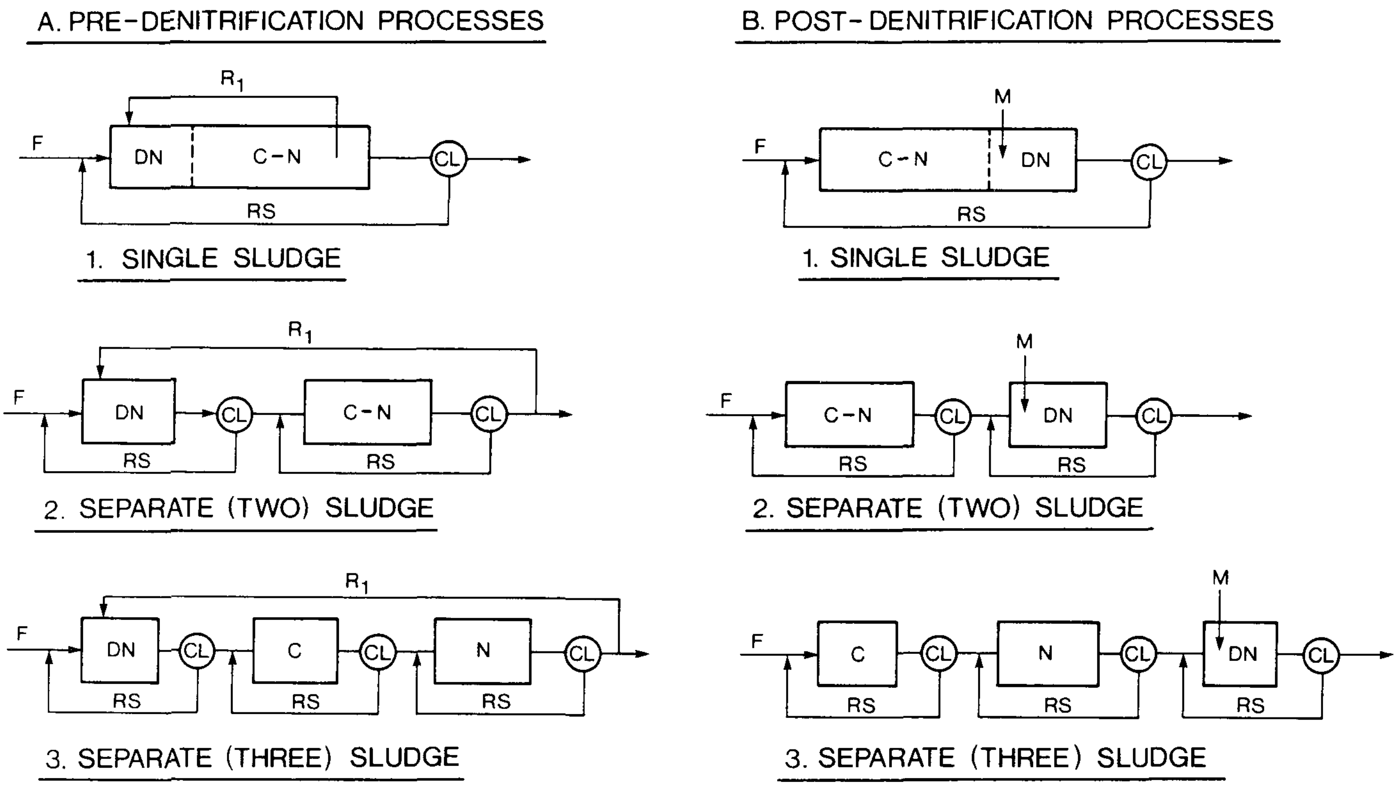
In pre-denitrification systems, the organic carbon present in the raw wastewater acts as the energy source and electron donor for the denitrification reactions. In this configuration, the raw wastewater is contacted with a recycle stream from the carbon oxidation-nitrification reactor which contains the oxidized nitrogen species.

As in other biological reaction processes, denitrification rates are affected by temperature and pH. Dissolved oxygen will also reduce the specific denitrification rates (24). In general, heterotrophic denitrifiers are less susceptible to adverse environmental conditions than autotrophic nitrifiers (11).

Biological denitrification has been successfully conducted on municipal and a wide variety of industrial wastes using both suspended growth (25, 26, 27) and fixed film processes (28, 29, 30).

2.1.3 Coupled Biological Nitrogen Control Processes. The nitrification and denitrification reactions can be coupled to provide biological nitrogen control. A number of reviews have been published describing in detail the process configurations available to the design engineer (20, 31, 32). Basically, the coupled systems can be classified according to the position of the denitrification reactor (pre-denitrification or post-denitrification) and according to the degree of separation of the organisms involved in the biological reactions (single-sludge or separate-sludge systems). Schematic flowsheets illustrating the major process options are presented in Figure 1. Suspended growth biological systems require a solid-liquid separation step between individual reactors if operated in the separate-sludge mode. Fixed film biological processes, in which the biological solids are retained in the reactor on a solid support medium, operate in the separate-sludge mode.

The pre-denitrification configuration offers some economic advantages. The use of the raw wastewater organic carbon compounds as electron donors for the denitrification process can reduce or eliminate the requirement for addition of an external carbon source such as methanol. In addition, the total oxygen requirements of



LEGEND: C = CARBON OXIDATION

N = NITRIFICATION

C-N = COMBINED CARBON OXIDATION AND NITRIFICATION

DN = DENITRIFICATION

R_1 = RECYCLE TO PRE-DENITRIFICATION REACTOR

CL = BIOMASS - LIQUID SEPARATION

RS = BIOMASS RECYCLE

F = FEED

M = EXTERNAL CARBON SOURCE

(NOTE: CLARIFICATION AND SLUDGE RETURN ARE NECESSARY FOR SUSPENDED GROWTH PROCESSES BUT ARE NOT REQUIRED TO MAINTAIN SEPARATE SLUDGES IN FIXED FILM PROCESSES)

FIGURE 1 SCHEMATIC FLOWSHEET OF BIOLOGICAL NITROGEN CONTROL PROCESS OPTIONS (Adapted from Wilson et al., 35) the treatment system can be reduced by the removal of a portion of the oxygen-consuming organic compounds under anoxic conditions in the denitrification reactor (33).

Single-sludge suspended growth pre-denitrification processes have been successfully operated at full scale for treatment of organic chemical industry wastewater (5, 34) and at bench scale for treatment of coke plant wastewater (1, 2, 4). The coupled fluidized bed process described in this report was operated as a separate (two) sludge fixed film pre-denitrification system.

2.2 Byproduct Coke-making Wastewaters

The production of metallurgical coke is an essential phase of the steel-making process in which coal is pyrolyzed to generate a variety of solid, liquid and gaseous products. In the byproduct coking process, used exclusively in Canada by the steel industry, the principal product by weight is coke for use in the operation of iron-making blast furnaces. In addition, a wide variety of valuable byproducts such as tars, light oils, phenol, ammonium compounds and naphthalene can be recovered from the distillation process off-gases. Detailed descriptions of the byproduct coking process are available in the literature (36, 37).

2.2.1 Characteristics. Figure 2 presents a simplified flowsheet illustrating the origin of the major wastewater streams associated with byproduct coke oven operation. Byproduct coke plants vary considerably in size, type of byproducts recovered, and byproduct recovery process. Therefore, the total plant wastewater flow and strength can vary considerably. The major process wastewaters associated with byproduct coking operations are excess flushing liquor, final cooler water, barometric condenser water and interceptor sump water from light oil refining operations (38).

Excess flushing liquor, also termed crude or weak ammonia liquor (WAL), is produced during the initial cooling of the coke oven gases. The off-gas stream is sprayed with a flushing liquid which condenses some of the tars, about 25 percent of the ammonia in the gas, phenolic compounds and organic nitrogen compounds (39). The tar is separated by gravity in the tar plant and a fraction of the liquid stream is recycled to the coke oven gas collection main. The excess WAL is discharged and represents the largest pollutant load from a byproduct coking operation (36).

In most coke plants, the excess WAL is steam-stripped to recover ammonia. Typically, ammonia recovery involves a free leg still for stripping the non-ionized ammonia and a fixed leg still, in which the liquor pH is made alkaline by the addition of lime or sodium hydroxide, for stripping the remaining ammonia compounds.

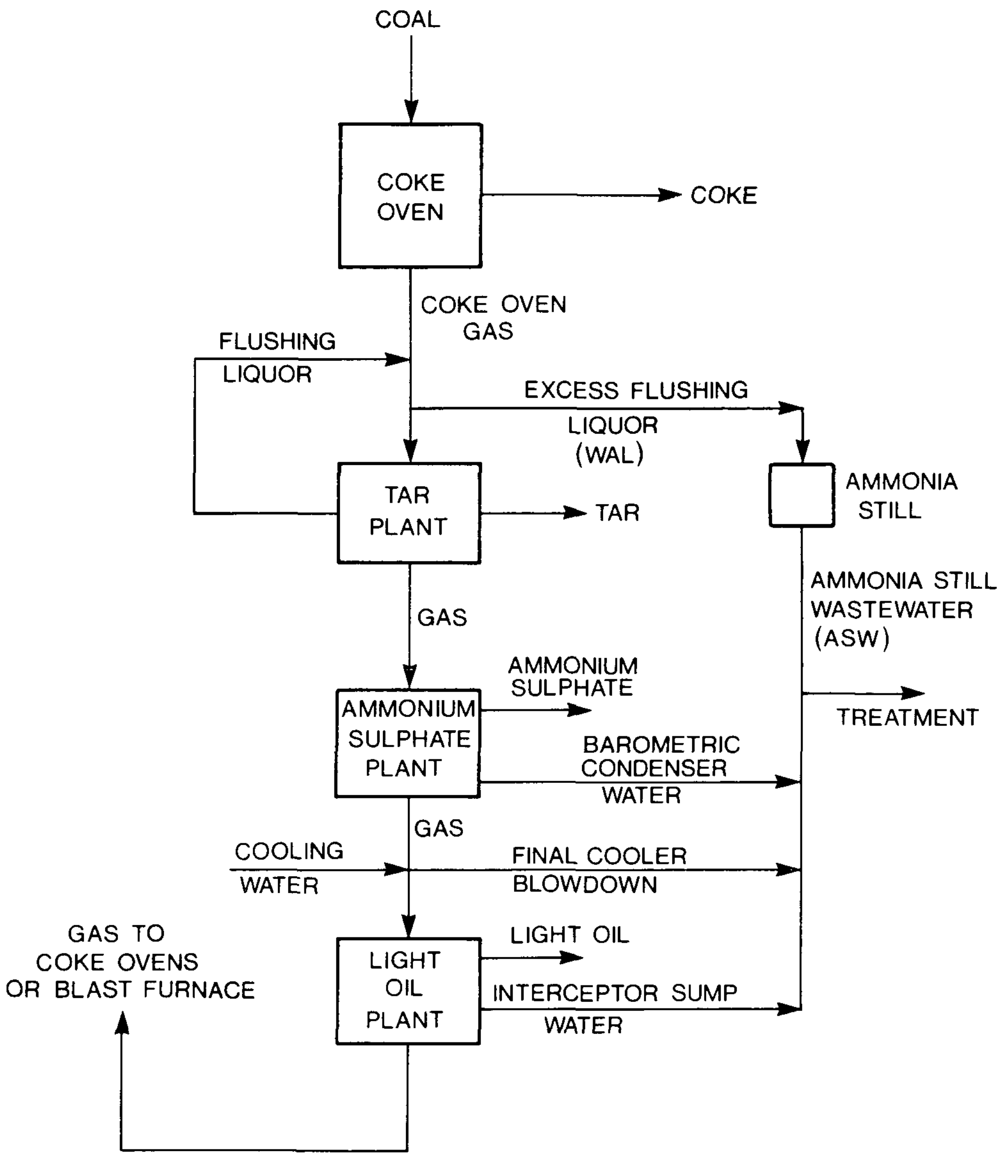


FIGURE 2 MAJOR WASTEWATER SOURCES IN BYPRODUCT COKING OPERATIONS

In reviewing the technical literature relating to coke oven wastewater characterization and treatment, it is important to differentiate between the characteristics of weak ammonia liquor (WAL) prior to ammonia removal and ammonia still wastewater (ASW) discharged from the ammonia stripping operation. Typical characteristics in terms of conventional contaminants for these wastewaters are summarized in Tables 1 (WAL) and 2 (ASW). The volumes of weak ammonia liquor generated in byproduct coking operations depend on the moisture content of the coal and the operation of the coke ovens and byproduct recovery plants. The rate of generation is typically in the range of 79 to 430 L/1000 kg of coke (36).

Final cooler water is produced from the direct contact cooling of the coke oven gases after ammonium sulphate recovery. Final cooler water can contribute a substantial fraction of the organic carbon, ammonia, cyanide and phenolic compounds to the total wastewater in some cases (39). Typical analyses for conventional contaminants are summarized in Table 3.

Interceptor sump water represents the aqueous discharge from the light oil or benzol plant oil-water separators as well as miscellaneous plant discharges. This wastewater can contribute significantly to the overall discharge of phenolic compounds, ammonia, thiocyanate and cyanide depending on plant operation (36, 37). Typical analyses in terms of conventional contaminants are summarized in Table 4.

These three wastewaters (weak ammonia liquor, final cooler water and interceptor sump water) contribute approximately equally to the total wastewater flow from most byproduct coking operations (36). Barometric condenser water from the ammonium sulphate crystallizer can result in a relatively large volume of contaminated water in plants using such systems. The major contaminant of concern in this waste stream is cyanide (37). Other minor contributors to the total coke plant wastewater include miscellaneous condensates, coke quench water, wet desulphurizer wastewater and discharges from various air pollution control devices.

2.2.2 Trace Organic Contaminants. The U.S. Environmental Protection Agency (EPA) has established that coke-making operations generate more toxic pollutants than any other industrial category examined. Sampling and analysis of byproduct coke plant wastewaters identified more than 40 toxic contaminants present in high concentrations (36). Of these, 29 trace organic contaminants appear to be characteristic of the raw wastewaters from byproduct coking operations, based on their presence at a number of coke plants. These trace organic contaminants are presented in Table 5. Of these 29

TABLE 1 CONCENTRATION OF CONVENTIONAL CONTAMINANTS IN WEAK AMMONIA LIQUOR FROM BYPRODUCT COKING OPERATIONS

	Contaminant Concentration (mg/L)					
Reference	COD	Phenolics	NH_3-N	CNS	TCN	Comment
U.S. EPA (36)	-	1 040	5 100	535	69	Average of 6 plants
Wong-Chong *et al*. (17)	-	1 245	4 500	-	55	Average of data from 11 plants
Schroeder & Naso (37)	-	2 000	5 000	-	20	5.5 x 10^6 kg/day plant
Cousins & Mindler (40)	5 000 - 10 000	1 000 - 2 800	4 000 - 5 000	700 - 1 300	20 - 80	4.3 x 10^6 kg/day plant
Kwasnoski (41)	-	870	6 900	860	40	
Luthy (42)	2 500 - 10 000	400 - 3 000	1 800 - 6 500	100 - 1 500	10 - 100	Based on references 43, 44, 45, 46

TABLE 2 CONCENTRATION OF CONVENTIONAL CONTAMINANTS IN AMMONIA STILL WASTEWATER FROM BYPRODUCT COKING OPERATIONS

	Contaminant Concentration (mg/L)							
Reference	COD	FOC	Phenolics	TKN	NH_3-N	CNS	TCN	Comment
Bridle *et al*. (2)	-	680	300	180	88	240	8	Includes light oil interceptor sump wastewater
Adams *et al*. (39)	6 650	1 200	1 620	179	41	-	4	Based on data from two plants
Wong-Chong & Caruso (47)	-	-	1 140	-	93	560	75	Unidentified wastewaters treated in ammonia still
Luthy & Jones (48)	3 400 - 5 700	-	620 - 1 150	-	22 - 100	230 - 590	2 - 6	Includes cooling liquor, tar and benzol plant effluents
Eklund & Irvin (49)	3 300	-	360	-	280	450	9.1	

TABLE 3 CONCENTRATION OF CONVENTIONAL CONTAMINANTS IN FINAL COOLER WATER

	Contaminant Concentration (mg/L)				
Reference	NH_3-N	TCN	CNS	Phenolics	Comment
U.S. EPA (36)	30	188	52	101	
Wong-Chong <u>et</u> <u>al</u> (17)	125 - 1 378	153 - 1 400	-	124 - 1 482	Ranges for three plants
Adams <u>et</u> <u>al</u> (39)	315	235	-	850	Average for two plants

TABLE 4 CONCENTRATION OF CONVENTIONAL CONTAMINANTS IN INTERCEPTOR SUMP WASTEWATER

	Contaminant Concentration (mg/L)				
Reference	NH_3-N	TCN	CNS	Phenolics	Comment
U.S. EPA (36)	276	0.01	252	291	Average for two plants
Wong-Chong <u>et</u> <u>al</u>. (17)	5-426	2.5-84	-	2.4-52	Ranges for three plants
Schroeder & Naso (38)	150	100	-	300	5.5 x 10^6 kg/day plant
Adams <u>et</u> <u>al</u>. (39)	10	10	-	140	Average for two plants

trace organic contaminants, the majority are base/neutral extractable compounds generated as a result of the destructive distillation of coal. Other characterization studies (2, 50, 51) have identified similar compounds in the wastewaters generated by coke plant operations. In addition to the U.S. EPA priority pollutants, Bridle <u>et</u> <u>al</u>. (2) reported 32 non-priority pollutants in coke plant wastewater, primarily base/neutral extractable heterocyclic nitrogenous compounds.

More detailed quantitative data with respect to trace contaminants in coke plant wastewaters are presented in Section 3.5 of this report.

TABLE 5 TRACE ORGANIC CONTAMINANTS IDENTIFIED IN COKE PLANT WASTEWATERS (36)

Class	Compound
1) Purgeable	Acrylonitrite
	Benzene
	Chloroform
	Ethylbenzene
	Toluene
	Xylene
2) Base/Neutral Extractable	Acenaphthylene
	Fluoranthene
	Isophorone
	Naphthalene
	Fluorene
	Pyrene
	Chrysene
	Benzo (a) pyrene
	Benzo (a) anthracene
	2,4 - Dinitrotoluene
	2,6 - Dinitrotoluene
	Bis (2-ethylhexyl) phthalate
	Butylbenzyl phthalate
	Di-n-butyl phthalate
	Di-n-octyl phthalate
	Diethyl phthalate
	Dimethyl phthalate
3) Acid Extractable	Phenol
	Pentachlorophenol
	2,4 - Dimethylphenol
	2,4,6 - Trichlorophenol
	Parachlorometacresol
	4,6 - Dinitro-o-cresol

2.2.3 Treatability. Although investigations have been conducted to assess the technical and economic feasibility of using physical-chemical methods, such as alkaline chlorination and activated carbon adsorption, to treat byproduct coke plant wastewaters (37, 52, 53), the application of these techniques to such wastewaters will be primarily limited to pretreatment, such as ammonia stripping and phenol extraction, due to the relative economics of physical-chemical and biological treatment technologies (36). U.S. EPA best practicable technology (BPT) and best available technology (BAT) effluent limitations are based on the application of biological treatment methods, except where advanced physical-chemical treatment systems have already been installed (36).

Biological treatment methods have been applied to coke plant wastewaters for a number of years and full-scale treatment systems are operating in Canada (54), throughout the United States (55) and in Europe (56). Most treatment systems are based on the activated sludge process, although fixed film processes, such as trickling filters, have been utilized in Europe (55). In most cases, the treatment processes have been designed and operated to provide organic carbon oxidation, particularly degradation of phenolic compounds. Few systems consistently nitrify wastewaters from coke plant operations and no full-scale systems currently practise nitrogen control (1).

Full-scale biological treatment systems have been shown to be capable of providing phenol removal efficiencies in excess of 99.9 percent (14, 17, 55, 57, 58) during treatment of either weak ammonia liquor or ammonia still wastewater. However, inhibition of the phenol oxidation rates due to high ammonia concentrations in the biological system has been identified in many cases (49, 57). To overcome the inhibitory effects, most American steel mills practise freshwater dilution of the raw wastewater (36, 57). Valiknac and Neufeld (59) also showed that low levels of thiocyanate inhibit phenol bio-oxidation and can limit the concentration of phenolic compounds achievable in the effluent from biological systems.

The reported efficiency of thiocyanate oxidation during biological treatment of coke plant wastewaters is very contradictory (14). Kostenbader and Flecksteiner (45) achieved oxidation efficiencies ranging from 10 to greater than 99 percent during treatment of weak ammonia liquor and offered no explanation for the wide variability in treatment efficiency. Similarly, Barker and Thompson (55) reported only partial removal of thiocyanate in the carbon oxidation stage of a three-stage biological treatment system, despite complete phenol oxidation. Investigations by the British Coke Research Association (60) showed that thiocyanate concentrations above 2200 mg/L could not be adequately treated despite hydraulic retention times of up to 30 hours. Cousins and Mindler (40) also showed inconsistent thiocyanate oxidation during full-scale biological treatment of weak ammonia liquor despite excellent phenol removal to effluent levels of less than 1 mg/L. The inconsistent thiocyanate removal attained has led a number of authors to question the ability of biological systems to maintain a high degree of thiocyanate oxidation (14, 49).

Recent investigations (61, 62) have determined that thiocyanate oxidation occurs after the completion of the phenol degradation reactions. Therefore, biological systems based on phenol degradation kinetics may not effectively oxidize thiocyanate.

Since thiocyanate oxidation is virtually complete prior to the onset of biological nitrification (47, 62), biological systems designed to effect some degree of nitrification will provide highly efficient thiocyanate oxidation in most cases. Data from a number of bench-, and pilot- and full-scale biological treatment plants confirm that effluent thiocyanate concentrations of approximately 1 mg/L can be maintained if the process is designed and operated to effect ammonia oxidation (nitrification) (1, 2, 50, 51, 62, 63).

The oxidation of thiocyanate results in the production of ammonia. This net increase in the ammonia concentration of the wastewater must be considered in the specification of design nitrification rates and aeration requirements.

Cyanide bio-oxidation reactions are also virtually complete prior to the onset of nitrification (47, 62). Erratic process performance in terms of cyanide removal (14, 55) may be a function of the relative quantities of free and complex cyanide present in the coke plant wastewater. Free cyanide is readily biodegradable, whereas complex cyanides can be highly resistant to biological treatment (50, 64). Biological systems designed for nitrification will produce effluent free cyanide concentrations typically less than 0.1 mg/L (62). Complex cyanides have been shown to pass through the biological system unaltered and without exerting an adverse effect on the process performance at concentrations up to approximately 100 mg/L (50).

The oxidation of cyanide also results in the generation of ammonia. As the concentration of free cyanide in coke plant wastewater is typically significantly lower than that of ammonia and thiocyanate, however, the contribution of oxidizable nitrogen due to cyanide degradation is relatively small.

Extensive research has been conducted at bench and pilot scale to define the conditions necessary for nitrification of coke plant wastewaters (1, 2, 39, 55, 60, 62, 63). Numerous authors have questioned the ability of biological systems to consistently maintain a high degree of nitrification during treatment of these wastewaters (14, 39, 49, 55). As coke plant wastewaters contain a variety of compounds inhibitory to nitrifying microorganisms, raw wastewater dilution has been widely considered necessary to ensure nitrification (14, 55). Virtually all American steel mills utilizing biological treatment for coke wastewaters practise freshwater dilution in an effort to optimize the bio-oxidation processes (36). Other researchers have advocated the use of growth factors to improve the stability of the nitrification process (65, 66).

Recently, a number of authors have reported the successful nitrification of coke plant wastewaters at bench or pilot scale (1, 2, 3, 50, 51, 62, 67, 68), as well as under full-scale conditions (69, 70). Both single-stage (combined carbon oxidation-nitrification) (3, 62, 70) and separate-stage (68, 71) processes have been used in these studies. Fixed film processes, specifically RBCs, have also been investigated as an alternative to suspended growth systems (3, 72). These studies have shown that long solids retention times (SRTs) are critical to stable operation of a nitrifying coke plant wastewater treatment system (1, 2, 3, 63). In most cases, the raw wastewater was diluted (1, 69, 70). In other cases, powdered activated carbon (PAC) was added to overcome the inhibitory effects of the raw wastewater (1, 2, 63). In some cases, both dilution and PAC addition have been practised (51, 72).

The specific nitrification rates reported for biological systems treating coke plant wastewaters are summarized in Table 6. The low specific rates, typically in the range 0.01 to 0.03 per day, relative to the rates cited for municipal wastewaters (20) are indicative of the inhibition resulting from the compounds present in the raw wastewater.

A number of researchers have investigated the possibility of coupling the nitrification and denitrification processes to achieve a high level of nitrogen control during treatment of coke plant wastewater (1, 2, 47, 55). Barker and Thompson (55) operated a three-stage, separate-sludge system and utilized molasses as a carbon source for the post-denitrification reaction. Their results indicated that denitrification was readily achieved; effective nitrogen control was completely dependent on the ability of the nitrification reactor to maintain a high level of ammonia oxidation. Wong-Chong and Caruso (47) showed that the phenolic compounds in the raw wastewater could be utilized as the carbon source for denitrification.

Bridle et al. (1, 2) reported extensive investigations of the single-sludge pre-denitrification suspended growth system applied to undiluted coke plant wastewaters. These studies confirmed that the organic carbon present in the raw waste was readily utilized as the energy source for the biological denitrification reactions.

Based on the technical literature, it is apparent that nitrification is the limiting reaction for advanced biological treatment of coke plant wastewaters. Nitrifying microorganisms are considerably more sensitive to environmental conditions than the autotrophic and heterotrophic organisms responsible for phenol degradation, cyanide and thiocyanate oxidation, and denitrification. Design of a biological system to effect nitrification will ensure degradation of the other components of the raw wastewater. Denitrification can be readily achieved, either in the pre- or post-denitrification flow configuration.

TABLE 6 NITRIFICATION RATES IN BIOLOGICAL TREATMENT OF COKE PLANT WASTEWATERS

Reference	Biological System	Operating Conditions	Feed Characteristics (mg/L)	Specific Rate	Comments
Bridle *et al.* (1)	Pre-DN	T=22°C SRT=30 d	TKN = 130 NH_3-N = 75 CNS = 170	0.041 g TKN/g VSS•d	Diluted feed spiked with MeOH, phenol and CNS
Bridle *et al.* (2)	Pre-DN with PAC Addition	T=20-24°C SRT=30 d	TKN = 180 NH_3-N = 88 CNS = 240	0.015-0.023 g TKN/g VSS•d 0.013-0.017 g NH_3-N/g VSS•d	Undiluted feed 18-33 mg/L PAC in feed NH_3-N rate based on $\Delta(NH_3\text{-N} + 0.24\ \text{CNS} + 0.54\ \text{CN}_F)$
Wong-Chong & Hall (50)	Single-Stage A.S.	T=21-27°C	NH_3-N = 150 CNS = 300 Phenol = 500	0.025-0.030 g NH_3-N/g TVS•d	Maximum rate based on increasing NH_3-N feed concentration from 210 to 510 mg/L over 30 days
Wong-Chong & Caruso (47)	Single-Stage A.S.	T=20-25°C	Synthetic Feed ΣN = 429 ASW Feed ΣN = 264 - 434	0.015 g NH_3-N/g TVS•d	No difference in rate for synthetic or actual (ASW) waste
	Pre - DN	T=20-25°C	Synthetic Feed without CNS ΣN = 293	0.029 g NH_3-N/g TVS•d	Inhibition of nitrification due to CNS cited
Medwith & Lefelhocz (3)	Single-Stage Hybrid Suspended-Growth Fixed-Film Process	T=20-30°C	NH_3-N = 150 CNS = 200-550 TCN = 3 - 15	0.007-0.04 g NH_3-N/g VSS•d	Approximate rate based on volumetric rate = 0.82 lb/1000 US gal•d (0.10 kg/m^3•d) MLSS = 10 - 35 g/L MLVSS = 2.3 - 14 g/L Diluted wastewater
Ganczarczyk (66)	Second-Stage A.S.	T=19-22°C	NH_3-N = 86-560 SRT = 40-80 d	0.0096 - 0.0252 g NH_3-N/g TSS•d	Glucose added as "growth factor"
Wear *et al.* (69)	Full-Scale Single Stage A.S.	T=20-25°C	NH_3-N = 115 CNS = 175	0.015 - 0.020 g NH_3-N/g VSS•d	Feed consisted of: 52% Process Waste 18% Sanitary Waste 30% Dilution Water
Wilson *et al.* (51)	Single Stage A.S.	SRT=20, 60 d PAC=0-6000 mg/L	NH_3-N = 56 CNS = 370	0.00123 - 0.00734 g NH_3-N/g VSS•d	Feed diluted 26% with river water No effect of PAC or SRT apparent on nitrification rate

2.3 Blast Furnace Gas Cleaning Wastewaters

Off-gases from iron and steel industry blast furnaces are rich in carbon monoxide and are typically utilized in the steel-making process as a source of fuel (73). These off-gases also contain fine particulate matter, consisting primarily of calcium, silica and iron salts, as well as contaminant gases such as hydrogen cyanide and ammonia. For the gas to be utilized as a fuel source and to provide the necessary degree of air pollution control, the blast furnace gas stream is typically cleaned in high-energy scrubbers.

2.3.1 Characteristics. The scrubber water from the gas cleaning operation contains suspended particulate matter as well as ammonia, phenol and cyanide scrubbed from the blast furnace gas stream. In the past, the scrubber systems were typically operated on a once-through basis and scrubber water was clarified to remove suspended solids prior to discharge.

Recently, many steel mills have implemented recirculation for the blast furnace gas cleaning systems to minimize water use and to reduce effluent discharges (41). Scrubber water, after clarification for suspended solids removal and cooling, is recycled to the gas cleaning system. Chemical additions are generally required to control corrosion and scaling, and to prevent bacterial growth (41, 73). In addition, as clarification does not remove dissolved solids from the water, the discharge or blowdown of a fraction of the scrubber water flow is necessary to control the concentration of dissolved solids in the gas cleaning system. The fraction of the flow discharged from the gas cleaning circuit varies, depending on the water quality and blast furnace gas quality, and may range from more than 50 percent to less than 5 percent (74).

Recirculation of blast furnace gas cleaning water significantly increases the concentration of dissolved contaminants in the blowdown stream. Typical characteristics of blast furnace blowdown water are summarized in Table 7. Wherever possible, the percentage blowdown in the system has been cited. Contaminants of primary concern in blast furnace blowdown water are ammonia, cyanide and, in some cases, phenolic compounds.

2.3.2 Conventional Treatment. Treatment of blast furnace gas cleaning wastewater beyond that necessary to effect suspended solids removal is applied to reduce the concentrations of ammonia and cyanide in the discharge stream. Physical-chemical methods are typically utilized. The most commonly applied process is alkaline breakpoint

TABLE 7 CHARACTERISTICS OF BLAST FURNACE BLOWDOWN WATER

Reference	Estimated Blowdown (%)	Parameter*								
		pH	NH_3-N	TCN	CNS	Phenol	TOC	Zn	Fe	Conductivity
Gauthier et al. (75)	-	7.9	18.5	2.7	2.5	2.5	70.	0.07	5.40	2500
Gauthier et al. (75)	-	7.2	67.	2.2	0.3	3.4	48.	37.0	2.37	3600
Gauthier et al. (75)	-	7.3	428.	0.5	0.4	0.5	128.	0.07	1.06	6500
Gauthier et al. (75)	-	7.7	67.7	0.9	2.8	0.9	-	3.2	18.0	1500
Decaigny and Krikau (76)	100	8.5	9.1	0.3	-	0.05	-	-	12.0	-
Koehrsen and Krikau (77)	100	-	10.	0.3	-	0.075	-	-	-	-
Brower et al. (73)	0	8.1	-	15.8	-	-	-	-	-	-
Melcer (78)	-	7.1	16.7	3.9	-	0.006	-	0.45	2.2	-
Environment Canada (79)	100	-	6.	0.12	-	0.12	-	2.6	9.2	-

* Concentrations reported in mg/L except conductivity (μmhos/cm) and pH.

chlorination (74). Other physical-chemical methods that have been evaluated for blast furnace blowdown treatment include ozonation (52, 80), steam stripping (74, 81), reverse osmosis (52), and chemical oxidation using Caro's acid (74) or potassium permanganate (81).

Biological treatment processes are seldom applied to blast furnace blowdown streams due to the low concentrations of organic contaminants present in these wastewaters, although Radigan and Manda (82) reported the biological removal of ammonia, cyanide and phenolic compounds from blast furnace scrubber wastewater in waste stabilization lagoons. Biological systems designed to treat ammonia-bearing wastewaters that are low in organic contaminants are susceptible to upset due to the low biological growth rates and poor flocculation (20). In addition, the elevated heavy metal concentrations often present in blast furnace blowdown water can inhibit the nitrifying microorganisms.

The possibility of biological treatment of combined coke plant wastewater and blast furnace blowdown water has been discussed by various researchers (74) and was recently demonstrated at laboratory scale (75). The results indicated that the combined wastewaters could be successfully treated in a suspended growth system to achieve effluent concentrations of less than 0.1 mg/L phenolics, 1.0 mg/L thiocyanate and 1.0 mg/L ammonia. Moreover, the addition of blast furnace blowdown water to the coke plant wastewater eliminated the need for further freshwater dilution to reduce the inhibitory effect of the components of the coke plant waste. Specific ammonia oxidation rates as high as 0.15 mg NH_3-N/mg VSS•d were reported for the combined coke plant wastewater and blast furnace blowdown, compared to ammonia oxidation rates of 0.02 mg NH_3-N/mg VSS•d typically reported for coke plant wastewater.

2.4 Biological Fluidized Bed Treatment Technology

The biological fluidized bed treatment process has been developed as a modification of more conventional fixed film biological systems, such as the trickling filter, packed bed reactor or rotating biological contractor (RBC), for carbon oxidation, nitrification and denitrification of municipal and industrial wastewaters. The basic biological fluidized bed treatment concept involves passing a wastewater upward through a bed of granular media such as sand at a velocity sufficient to expand the bed beyond the point at which the frictional drag is equal to the net downward force of gravity. The upflow velocity of the liquid phase produces a fluidized state of motion in the granular bed. A population of microorganisms is developed as an attached film on the surface of the fluidized media. The support media provides a very large surface area (3000 to 4000 m^2/m^3) (83) for biomass growth, resulting in reactor biomass concentrations up to an order of magnitude higher than characteristic of conventional suspended growth processes.

Since the early 1970s when Beer and his co-workers (84, 85) reported the potential advantages of the biological fluidized bed process, numerous researchers have become involved in the evaluation of the technology for the treatment of potable water (86, 87, 88), as well as domestic (7, 30, 89, 90, 91, 92) and industrial (28, 29, 93, 94) wastewaters. All the basic biological treatment processes - carbon oxidation, nitrification and denitrification - have been assessed. The process has been evaluated in the anaerobic (95, 96), anoxic (30, 89, 92), aerobic (97, 98) and oxygenic (8, 10, 91, 93) (using pure oxygen) operating modes.

A flowsheet of the oxygenic fluidized bed process is shown in Figure 3. The process comprises the upflow reactor containing the support media, an oxygen transfer device with a recycle stream to ensure that adequate oxygen is available for the biological processes and that the reactor upflow velocity is sufficient to maintain fluidization, and a sand-biomass separator. The sand-biomass separator is required to control bed expansion and exert SRT control. As biological growth occurs on the support media, the overall particle density decreases, resulting in further bed expansion. To prevent loss of support media from the reactor due to expansion, the biomass-coated particles are subjected to shearing; the separated biomass is wasted and the clean sand returned to the reactor. Film thicknesses in the reactor are generally maintained in the range of 50 to 100 μ to minimize biofilm diffusion problems. In an anoxic denitrification fluidized bed system, the oxygen transfer device is unnecessary. An external carbon source may be required depending on the operating mode.

The principal advantage of the biological fluidized bed process, compared to conventional biological systems, is the reduced reactor volumes necessary to achieve a similar degree of treatment. The high volumetric conversion efficiencies characteristic of fluidized bed processes are a direct result of the high biomass concentrations achievable in these reactors. Biomass concentrations of 10 to 15 g VS/L have been achieved in fluidized bed reactors operated for carbon oxidation and combined carbon oxidation-nitrification (8, 90, 91, 92). For denitrification, biomass concentrations in the range of 20 to 40 g VS/L have been reported (89, 90, 92). These high biomass concentrations can result in up to an order of magnitude reduction in the reactor

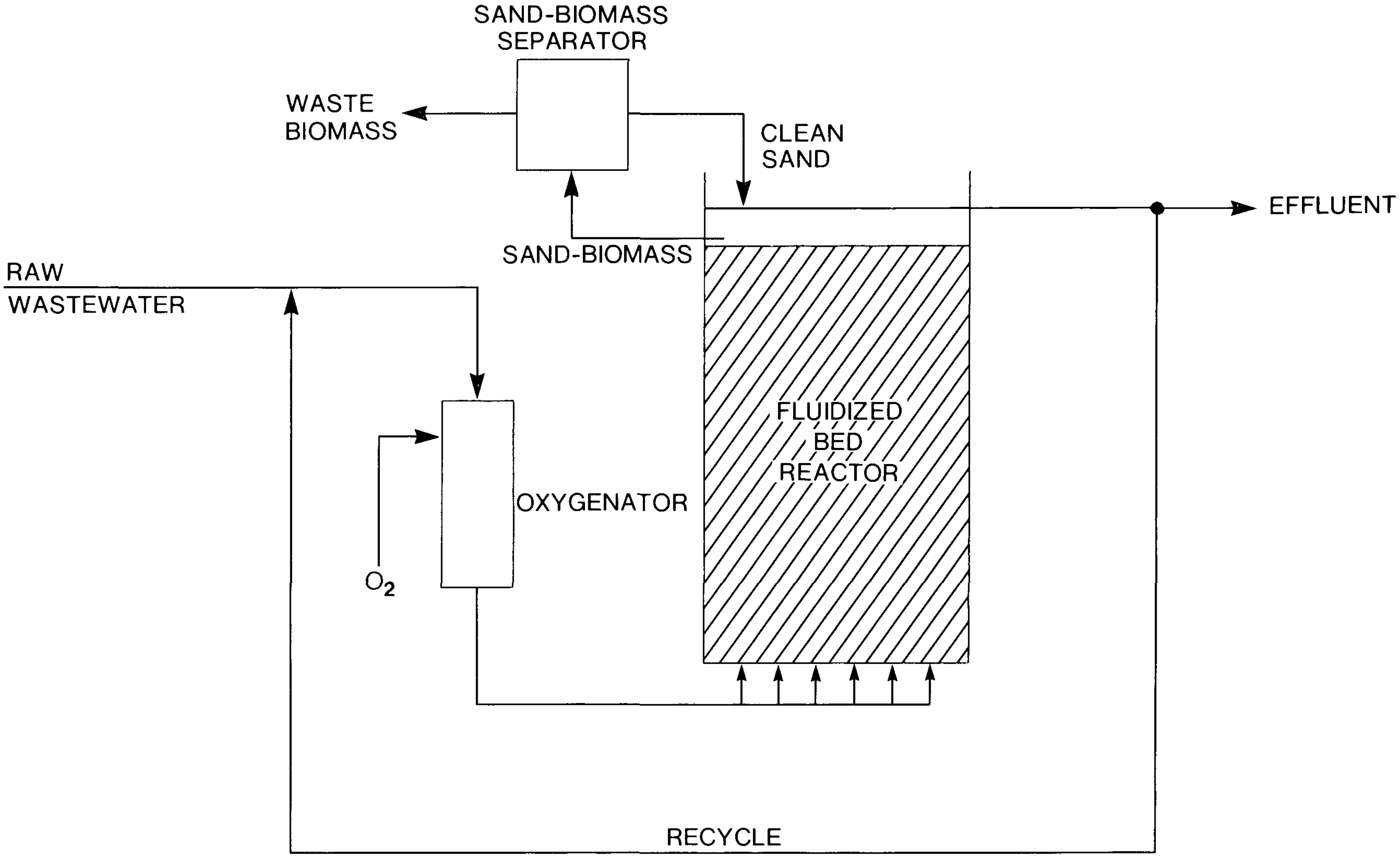


FIGURE 3 SCHEMATIC FLOWSHEET OF THE BIOLOGICAL FLUIDIZED BED PROCESS

hydraulic retention time (HRT) necessary to effect a given degree of treatment. In addition, the fixed film nature of the fluidized bed process can eliminate the need for secondary clarification of the wastewater in many instances.

Several recent technical reviews on the application of the biological fluidized bed process to industrial and municipal wastewaters have been published (77, 83). Pilot-scale industrial applications have included:

- denitrification of wastewaters from the nuclear industry (28), the explosives industry (29) and the petrochemical industry (83);
- carbon oxidation of a high carbohydrate wastewater (91, 93);
- combined carbon oxidation-nitrification of a fish farm effluent (83); and
- anaerobic treatment of agricultural wastes (99), pulp and paper wastes (100), brewery wastes (100) and bottling plant wastes (100).

Of particular interest is the work conducted at the Oak Ridge National Laboratory in which fluidized bed technology has been applied for the treatment of high-strength phenolic waste liquors (101). These investigations have demonstrated phenol degradation rates, on a volumetric basis, 10 to 50 times higher in a fluidized bed reactor than those reported for continuous stirred tank reactors. Volumetric thiocyanate conversion rates of up to 1.2 $kg/m^3 \cdot d$ were also observed and there were indications of nitrification during treatment of coal conversion wastewaters (101).

To date, no results have been published with respect to the successful coupling of fluidized bed reactors to attain nitrogen control through biological nitrification-denitrification processes. Cooper and Wheeldon (92) found that denitrification of nitrified municipal wastewater could be successfully completed in a fluidized bed reactor using settled raw sewage as the carbon source. Pilot-scale investigations are continuing at the Water Research Centre's Stevenage Laboratory using coupled anoxic and oxygenic reactors to effect denitrification, carbon oxidation and nitrification in a two-stage fluidized bed system operated in the pre-denitrification flow mode (83). Although no performance data are available, preliminary economic assessments indicate that, if an effluent is to be nitrified in a fluidized bed reactor, no additional operating cost is incurred by the addition of an anoxic fluidized bed reactor to denitrify the effluent. The extra cost of effluent recycling is more than counterbalanced by the cost savings resulting from the reduced oxygen demand in the oxygenic reactor (102).

3 FLUIDIZED BED TREATMENT OF COKE PLANT WASTEWATERS

3.1 Pilot Plant Description

A process flowsheet of the coupled fluidized bed pilot plant, located at Environment Canada's Wastewater Technology Centre, Burlington, is shown in Figure 4. The system was designed to operate as a two-stage separate-sludge pre-denitrification-nitrification (Pre DN-N) biological treatment process.

The pilot plant consisted of an anoxic denitrification fluidized bed reactor, 150 mm in diameter, and an oxygenic nitrification fluidized bed reactor, 290 mm in diameter. Both cylindrical reactors were 4.3 m in height and were designed with a conical entrance to improve inlet flow distribution. A downflow distributor and a perforated plate distributor were also used in the nitrification reactor to improve reactor hydraulics and minimize turbulence produced at high reactor upflow velocities.

The expanded bed heights were initially maintained at 3.9 m by manual and/or automatic valves installed on each reactor. At this expanded bed height, the empty bed reactor volumes were 58.5 L and 210 L for the anoxic and oxygenic reactors, respectively. The expanded bed heights and empty bed reactor volumes were adjustable by relocation of the position of the bed height control valves.

Pure oxygen was supplied to the oxygenic nitrification reactor through a proprietary downflow oxygen contactor developed by Dorr-Oliver Inc. Automatic dissolved oxygen control on the nitrification reactor effluent was provided by an analog PID feedback controller. Effluent dissolved oxygen concentrations in excess of 2 mg/L were maintained to ensure that dissolved oxygen concentration did not limit process performance. Influent and effluent dissolved oxygen concentrations were monitored continuously with in-line Beckman dissolved oxygen probes.

High internal recycle rates were necessary to both reactors to maintain the required fluidization fluxes, to ensure an adequate supply of oxygen to the nitrification reactor, and to return nitrate and nitrite to the pre-denitrification process. Recycle tanks and pumps were installed on the overflow from each reactor. The recycle tank at the anoxic reactor overflow was equipped with an automatic level controller to balance flows throughout the process. This recycle tank was also mechanically mixed to prevent sedimentation.

The sand-biomass mixture wasted from the reactors through the valves controlling expanded bed height could be processed mechanically or manually depending

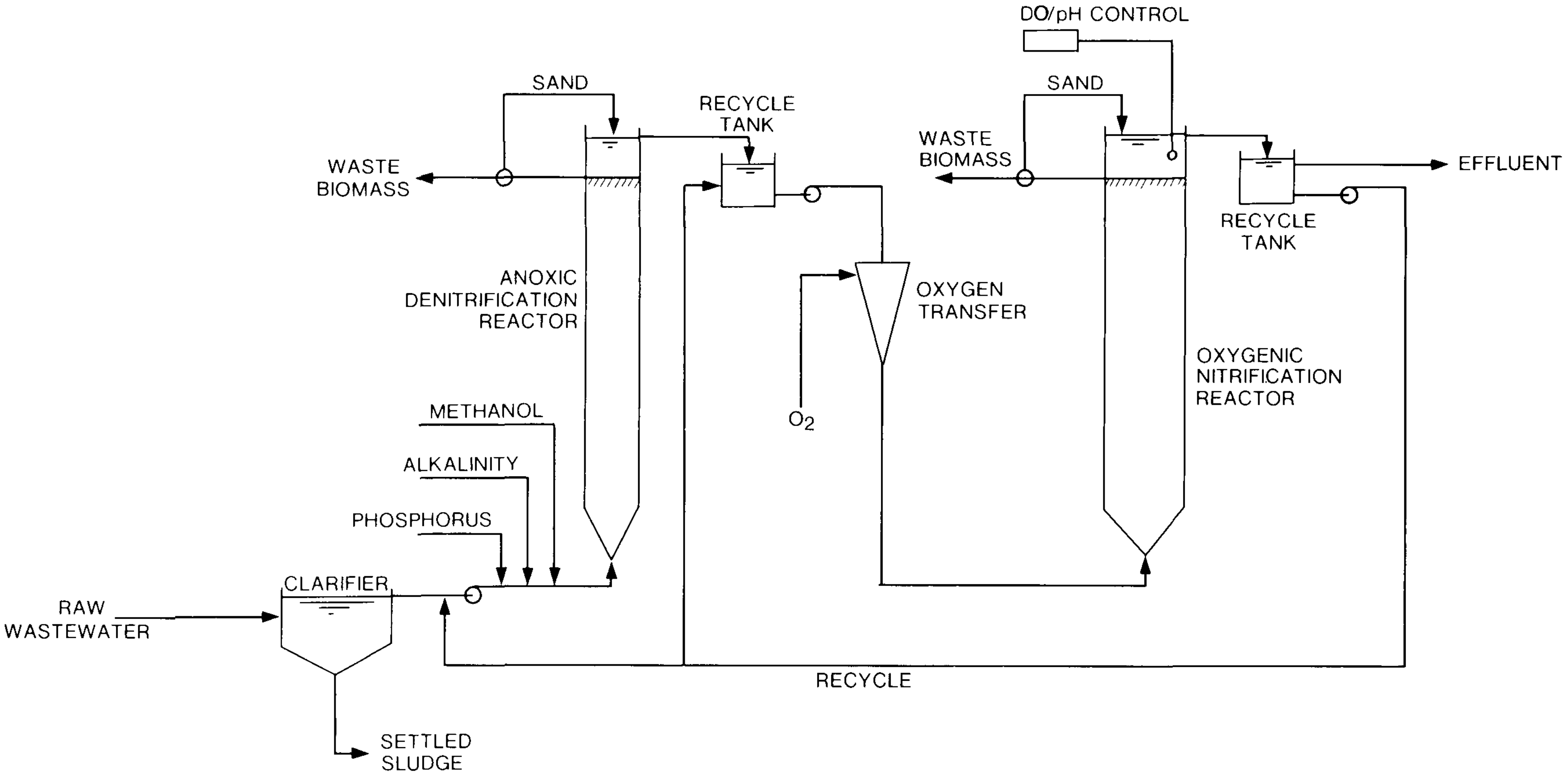


FIGURE 4 PROCESS FLOWSHEET OF TWO-STAGE FLUIDIZED BED BIOLOGICAL TREATMENT SYSTEM

on the biomass growth rates. Both reactors were equipped with mechanical systems to shear the biofilm from the sand and return the clean sand to the reactor. The mechanical system consisted of a collection hopper and a helical conveyor and was used primarily at high growth rates. At lower growth rates, the biofilms were sheared from the sand manually and the clean sand returned to the reactor manually. In both cases, the mass of excess biomass was measured to allow calculation of the individual reactor solid retention time (SRT).

Temperature control was included by means of immersion-type heaters and coolers. Initially, only an on/off heater was installed to maintain the reactor temperature approximately at 25°C. However, in response to problems related to excessively high (>30°C) reactor temperatures during the summer, a cooling coil operated from the municipal water supply was immersed in the nitrification reactor recycle tank.

A primary clarifier was installed upstream of the biological system to remove residual lime solids and free floating oils from the pilot plant feed. Food-grade phosphoric acid was added on a continuous basis to maintain a soluble phosphorus residual of 1 to 2 mg/L in the treated effluent. The pH of the nitrification reactor effluent was maintained at 7.0 by the automatic addition of sodium bicarbonate, which also provided supplemental alkalinity for the nitrification reactors. Feed systems were provided to allow methanol addition in case of carbon limitations in the denitrification reactor, and sodium nitrate addition to maintain a viable biomass in the denitrification reactor in the event of failure of the nitrification process.

The support medium in both the denitrification and nitrification fluidized bed reactors was quartzite sand with an effective size (d_{10}) of 0.48 mm and a uniformity coefficient (d_{60}/d_{10}) of 1.23. The particle size distribution characterizing the sand support media is given in Figure 5.

3.2 Pilot Plant Feed

The feed to the coupled fluidized bed pilot plant was obtained from the byproduct coke plant at Dofasco Inc. in Hamilton, Ontario. The wastewater consisted of ammonia still wastewater (ASW) obtained from the settling sump of a free- and fixed-leg still treating excess flushing liquor from the coke oven operations, plus a small flow of fractionator bottoms from the Phosam plant. This was essentially the same wastewater source used by Bridle et al. (1, 2, 4) in the evaluation of the single-sludge suspended growth biological treatment process.

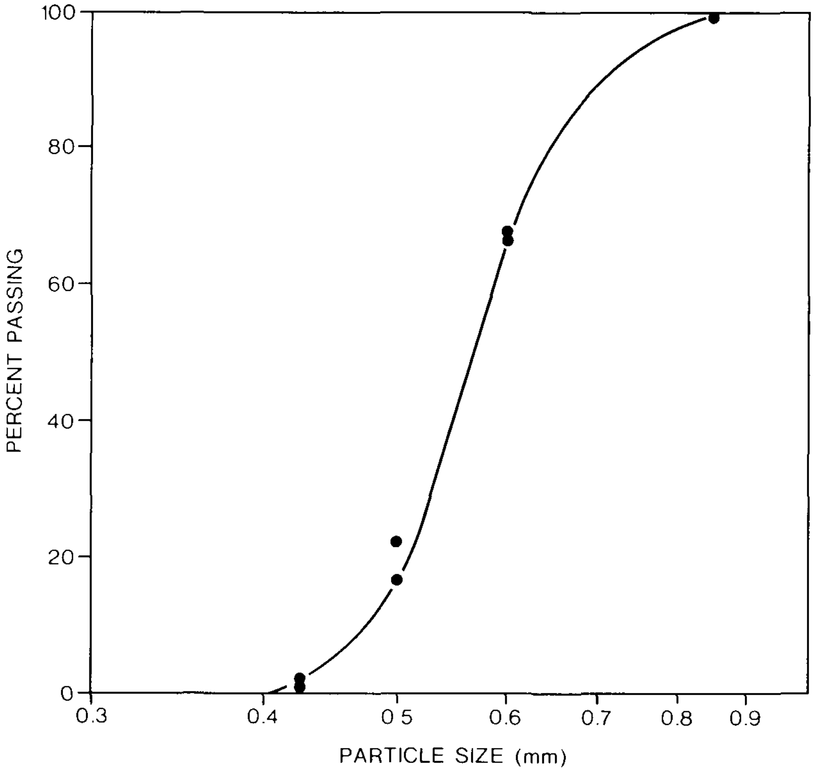


FIGURE 5 FLUIDIZED BED SAND PARTICLE SIZE DISTRIBUTION

Wastewater was collected from Dofasco in 7 to 10 m^3 batches, and stored in an insulated holding tank at the Wastewater Technology Centre (WTC). Details with respect to the characteristics of the raw feed are presented in Section 3.4.1.

3.3 Experimental, Sampling and Analytical Procedures

The pilot plant program involved three interrelated phases as follows:

Phase I	-	Start-up and Acclimation
Phase II	-	Pseudo-Steady State Operation
Phase III	-	Variable Feed Operation

During the start-up and acclimation period, the coupled biological process was operated on diluted coke plant wastewater supplemented as necessary with ammonium chloride, organic carbon (methanol) and nitrate until a viable population of microorganisms was established in each fluidized bed reactor. Dilution was then slowly eliminated and pseudo-steady state was assumed to be established when consistent process operation was attained.

The objective of the pseudo-steady state phase (Phase II) of the program was to establish the minimum hydraulic retention times required in the individual reactors to maintain adequate nitrogen control during treatment of undiluted coke plant wastewater. During this phase of the program, the pilot plant was operated at a number of pseudo-steady state loading conditions to define process performance. Pseudo-steady state conditions were assumed to have been attained when, after a step change in the process loading, the final effluent NH_3-N concentration had stabilized. This typically required from 20 to 40 days, depending on the magnitude of the step change. Pseudo-steady state performance data were collected for one to three weeks at each loading condition. These data do not represent true steady state in terms of the biomass as a constant biomass concentration and equilibrium SRT were not attained in the reactors. During the pseudo-steady state operating period, variation in raw feed characteristics was minimized as much as possible by storing a large volume of coke plant wastewater (approximately 40 m^3) and using this batch of feed for as much of Phase II as possible.

During Phase III, the impact of feed variability on process performance was assessed by obtaining small batches of raw feed on a frequent and regular basis from Dofasco. Pilot plant operating conditions were maintained as constant as possible throughout this phase of the experimental program.

During Phases II and III of the program, the sampling schedules were similar. Daily samples of treated process effluent (nitrification reactor effluent) were collected and analyzed for filterable organic carbon (FOC), ammonia-nitrogen (NH_3-N), nitrate (NO_3-N) and nitrite (NO_2-N) nitrogen, total and filterable Kjeldahl nitrogen (TKN), phosphorus and alkalinity. In addition, treated effluents were analyzed three times per week for phenolics, total and filterable chemical oxygen demand (COD), total cyanide (TCN), thiocyanate (CNS) and sulphide. Total and volatile suspended solids analyses were conducted five times per week.

Effluent from the anoxic denitrification reactor was monitored daily for FOC, NO_3-N, NO_2-N and TKN. The quality of the raw feed to the system was monitored weekly for FOC, TKN, NH_3-N, TCN, CNS, COD, phenolics, pH and alkalinity.

The concentration of biomass (bed volatile solids, BVS) in each reactor was measured once per week, based on compositing at least three individual samples from various locations in the reactors. Reactor biomass samples were obtained using a special sampling device designed to take a representative sample of the fluidized bed contents, including sand, biomass and liquid. In addition, liquid samples were syphoned from various positions within the individual reactors approximately once per week and analyzed for nitrogen species (TKN, NH_3-N, NO_2-N and NO_3-N) to define the concentration of individual species across the reactor profile. Dissolved oxygen measurements were made at each location using an immersible YSI dissolved oxygen probe.

All analyses were conducted at the Wastewater Technology Centre according to standard procedures (103).

In addition to the sampling and analyses of conventional contaminants to determine process performance, samples were also collected on a non-routine basis for trace contaminants and analyzed by the Laboratory Services Section, WTC, by gas chromatography/mass spectroscopy (GC/MS) techniques. Samples for GC/MS included raw feed and treated effluent aqueous samples and reactor biomass samples obtained during Phase II and Phase III of the experimental program. A detailed description of the sampling and analytical protocol, as well as the quality assurance/quality control (QA/QC) program, is given in Section 3.5.

3.4 Performance Evaluation

In this section of the report, the process performance in terms of conventional contaminants is reviewed for each stage of the experimental program. The performance in terms of trace contaminants is presented in Section 3.5.

3.4.1 Feed Characteristics. During the 18-month pilot-scale investigation, 13 batches of ammonia still wastewater were collected for treatment in the fluidized bed system. The characteristics of these coke plant wastewater samples are summarized in Table 8.

The quality of the coke plant wastewater was relatively consistent in terms of all conventional contaminants with the exception of ammonia nitrogen. The variability in ammonia nitrogen is almost totally responsible for the parallel variation in TKN. The thiocyanate concentration, which made up most of the non-ammoniacal nitrogen in the wastewater, showed a variability similar to the other contaminants such as FOC, COD and phenolic compounds.

The variability of the wastewater was greater during the start-up and acclimation phase of the program (wastewater batches A1 to A6). During this period, Dofasco was experiencing operational problems with the ammonia stills due to poor pH control and scale accumulation. During the steady state (batches SS1 and SS2) and the variable feed (batches V1 to V5) phases of the program, considerably better control of the still effluent ammonia concentration was maintained.

TABLE 8 COKE PLANT WASTEWATER CHARACTERISTICS

Wastewater Batch No. *	Date Rec'd	Contaminant Concentration (mg/L)										Comments
				COD			TKN					
		pH	FOC	UF	F	Phenolic Compounds	UF	F	NH_3-N	TCN	CNS	
A1	30/5/80	-	470	1940	1650	256	334	322	232	1.74	132	
A2	20/6/80	7.8	670	2460	2330	-	551	523	409	-	-	
A3	24/7/80	10.0	1300	4400	4200	845	710	700	510	11.7	274	
A4	31/7/80	11.2	590	2460	1660	375	160	150	75.1	6.27	147	
A5	9/9/80	12.0	485	2010	1900	310	502	498	351	7.95	229	High lime solids content
A6	10/10/80	11.8	821	2000	1950	286	36.4	33.7	29.6	6.32	247	
SS1	28/11/80	11.4	720	2770	2690	510	187	181	71.5	9.20	336	
SS2	28/5/81	9.0	831	3330	2990	455	184	180	88.9	7.28	386	
V1	21/10/81	8.1	401	1640	1390	118	247	244	181	1.42	81	Interceptor sump wastewater
V2	28/10/81	9.0	626	2780	2620	400	215	207	100	5.89	287	
V3	16/11/81	8.7	760	3210	2770	425	301	300	153	8.23	331	Average of two batches
V4	25/11/81	11.2	619	2330	2320	340	126	126	15.2	11.1	272	
V5	9/12/81	8.8	721	3940	2300	375	204	203	77.6	7.73	303	
Average		-	693	2713	2367	391	289	282	176	7.07	252	
Std. Deviation		-	225	817	733	176	191	187	156	3.13	91.1	
% Variability		-	32.5	30.1	31.0	44.9	66.1	66.2	88.9	44.3	36.1	

* Batches A1, A2, A3, A4, A5, and A6 were used during the start-up and acclimation phase (Phase I).
Batches SS1 and SS2 were used during the pseudo-steady state phase (Phase II).
Batches V1, V2, V3, V4 and V5 were used during the variable feed phase (Phase III).

Batch V1 represents primarily light oil interceptor sump wastewater as, at the time this wastewater was collected, the coke plant flushing liquor was being bypassed to the coke quench towers. Based on this single sample of the interceptor sump discharge, this wastewater appears to contain lower concentrations or organic contaminants, measured as FOC, COD or phenolic compounds, than ammonia still wastewater.

3.4.2 Phase I - Start-up and Acclimation. The fluidized bed reactors were started up in June 1980 with seeded sand which had been previously utilized during the assessment of separate-stage nitrification of municipal wastewaters (7). The stages of the start-up and acclimation phase of the program are shown in Figure 6. After 15 days of operation, the media from the nitrification reactor was removed because problems had developed in maintaining optimal biofilm growth in the system. The nitrification reactor was reseeded with sand of the same particle size distribution obtained from a Dorr-Oliver Inc. pilot-scale fluidized bed reactor which had been operated for combined carbon oxidation and nitrification of municipal wastewater. The reactors were filled to 2 m with seeded sand and hydraulically expanded 50 percent for the acclimation period.

Feed to the process at start-up was Dofasco plant wastewater (Batch A1) diluted 19:1 with secondary effluent from a pilot-scale extended aeration plant treating municipal wastewater. The feed was also augmented with sodium nitrate, methanol and ammonium chloride to balance the requirements of the coupled denitrification and nitrification reactors. Figure 6 shows the progressive reduction in the dilution of the raw feed over the initial 60 days of acclimation and accumulation of biological solids in the fluidized bed reactors. The concentration of volatile solids in the denitrification reactor doubled from a start-up level of about 6 g/L during the first 40 days of pilot plant operation. The increase in the volatile solids concentration in the nitrification reactor was less dramatic. While the bed volatile solids (BVS) concentration in the denitrification reactor continued to increase to more than 30 g/L, the concentration in the nitrification reactor appeared to stabilize at approximately 5 g/L. The adverse effect of turbulence on the establishment of high nitrifying biomass concentrations was identified as a controlling factor. This is discussed in more detail in Section 3.4.2.

In Figure 7, the specific denitrification rates (g NO_T-N removed/g BVS•d) and nitrification rates (g NO_T-N produced/g BVS•d) are shown during the acclimation period. It is evident that denitrification was established immediately in the system and the rate was affected only by the availability of oxidized nitrogen and carbon in the reactor. Decreasing dilution had no apparent effect on the activity of the denitrifiers in the reactor.

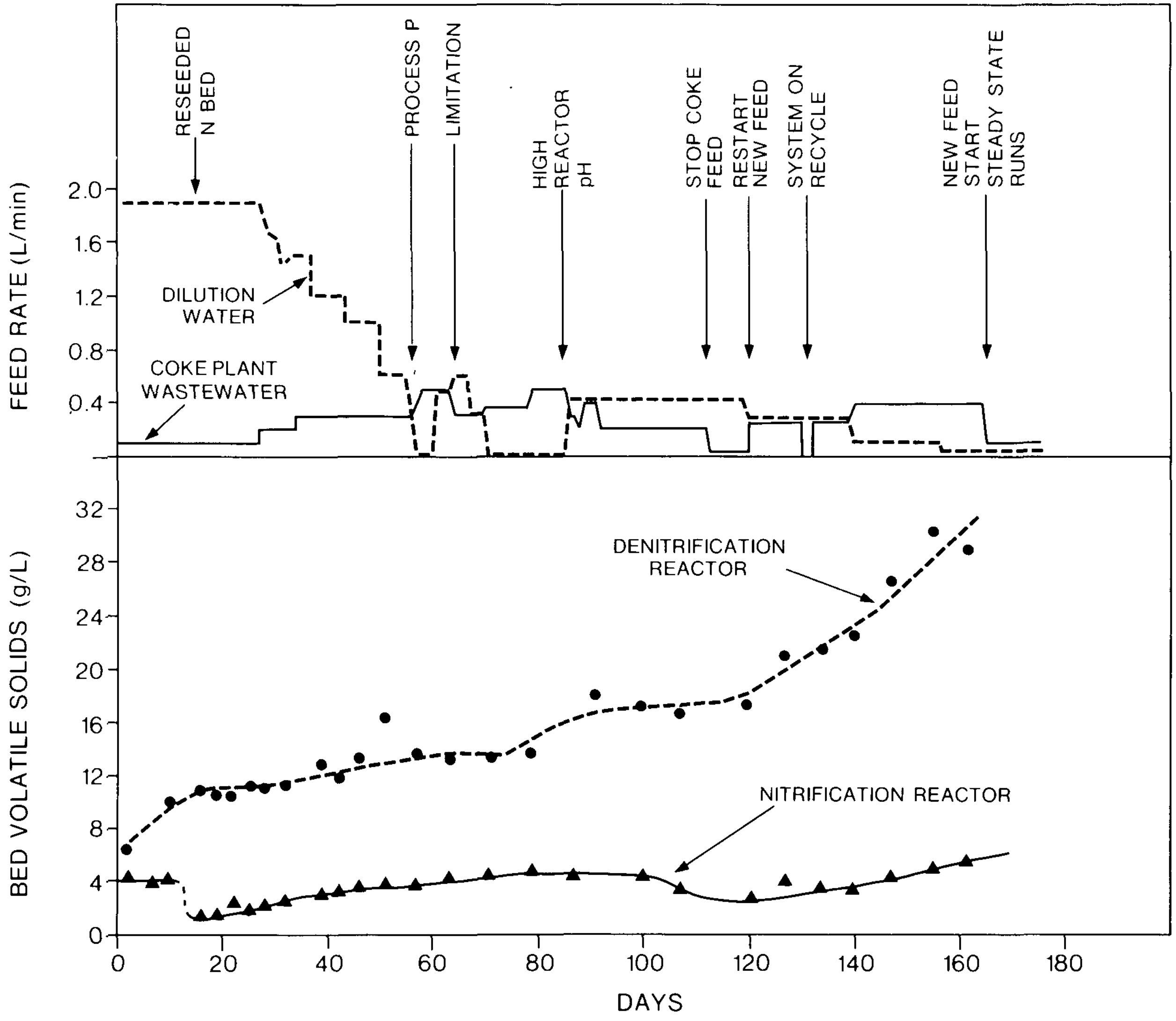


FIGURE 6 PROCESS START-UP CONDITIONS

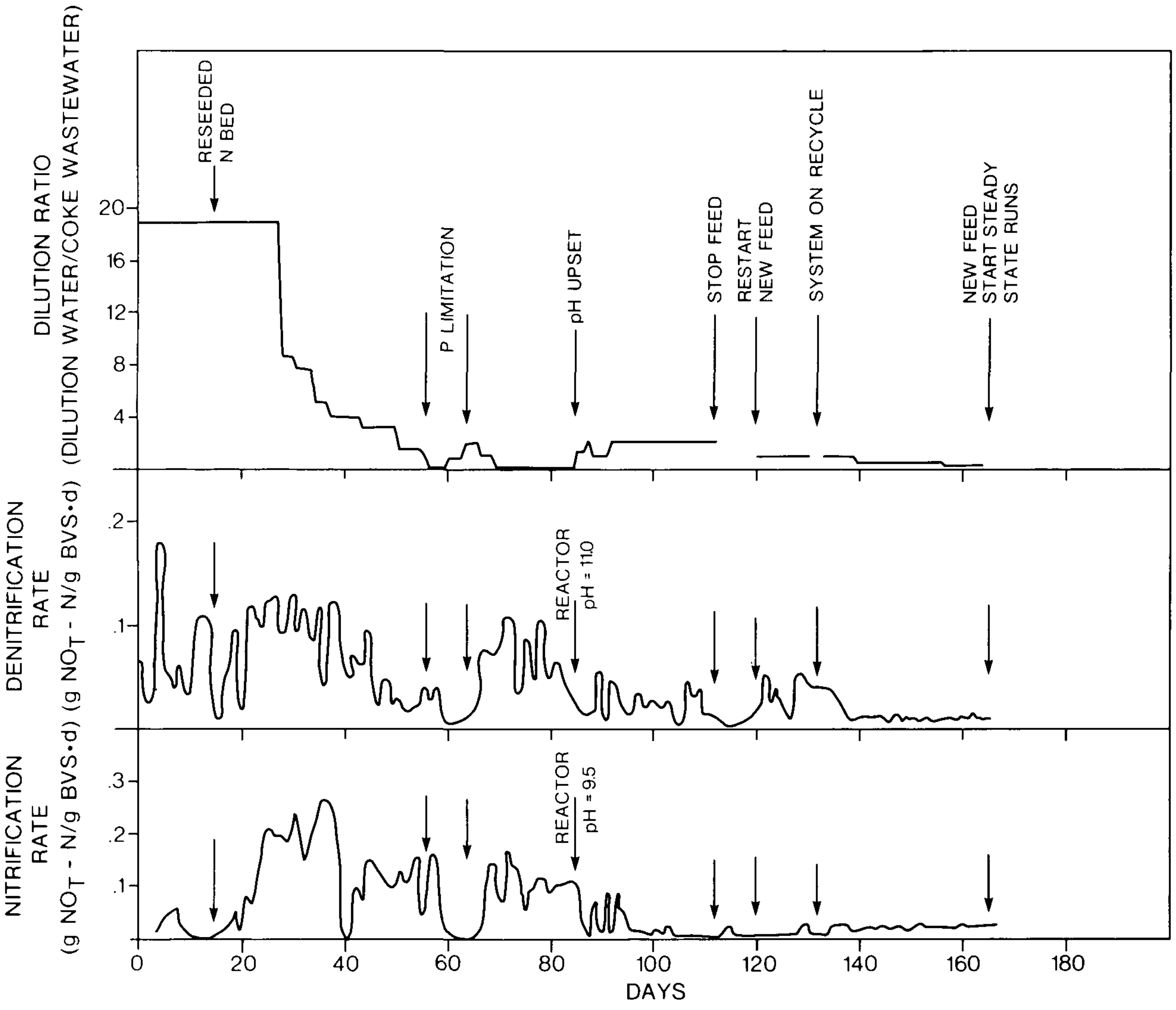


FIGURE 7 SPECIFIC REACTION RATES DURING ACCLIMATION PERIOD

After reseeding of the nitrification reactor, the specific nitrification rate showed a gradual increase to a level of approximately 0.2 d^{-1} despite a reduction in the dilution ratio from 19 to 6. Some inhibition of nitrification was evident as the dilution was further decreased; however, the process recovered rapidly and appeared to be completely acclimated to the undiluted coke plant wastewater approximately 50 days after the nitrification reactor was reseeded.

After 85 days of acclimation, a large batch of coke plant wastewater (Batch A5) was collected in preparation for initiating the pseudo-steady state phase of the experimental program. At the time this batch of wastewater was collected, the ammonia still experienced an upset and the still effluent contained an excessively high level of suspended lime solids. When this wastewater was fed to the fluidized bed system, the primary clarifier was overloaded and a lime slurry was pumped through the reactors. Before remedial measures could be taken, the pH had reached 11.0 in the denitrification reactor and 9.5 in the nitrification reactor.

The system response to the pH shock is evident in Figures 6 and 7. Figure 6 shows a significant loss of biomass from the nitrification reactor. The decline in nitrifier activity is evident from Figure 7. After a period of unstable nitrification (days 85 to 95), there was a complete loss of nitrification in the system. Despite the higher pH in the denitrification reactor, no significant loss of biomass occurred, and the activity of the denitrifiers continued after the pH shock. The lower specific rates shown in Figure 7 are related to substrate (oxidized nitrogen) limitations in the denitrification system rather than to a long-term effect of pH on the biomass.

After the pH shock, dilution of the raw wastewater was re-instituted to re-establish nitrification. Approximately 40 days were required before stable nitrification of undiluted coke plant wastewater was attained.

Prior to the pH upset, specific nitrification rates of up to 0.25 d^{-1} were attained with diluted coke plant wastewater (dilution ratio of one part coke plant wastewater to five parts dilution water) and up to 0.15 d^{-1} with undiluted coke plant wastewater. These rates are almost an order of magnitude higher than nitrification rates cited by other researchers (Table 6) for the treatment of coke plant wastewater and were never reattained following the pH upset despite operation of the process for more than a year. A similar phenomenon was noted during fluidized bed nitrification of municipal wastewaters (7). At that time, it was postulated that the high specific rates were associated with an unstable, high concentration of nitrifiers in the biofilm which could not be maintained over long-term operation. Considerable additional investigation of the start-up and acclimation of fluidized bed nitrification reactors would be necessary to verify these findings.

As evident from Figure 6, high biomass concentrations were readily established in the denitrification reactor. From an initial concentration of approximately 6 g/L, the volatile solids concentration increased to more than 30 g/L by the completion of the start-up and acclimation phase. In some areas of the reactor, the volatile solids concentration exceeded 40 g/L. The development of stable biofilms, typically 100 to 200 µ thick, allowed the upflow velocity in the denitrification reactor to be reduced from an initial level of about 0.9 m/min to an operating level of about 0.5 m/min. The lower flux resulted in a significant reduction in the recycle rates to this reactor.

In the nitrification reactor, the volatile solids concentration stabilized at approximately 5 g/L during the acclimation period and continued operation did not result in a net increase in the BVS concentration. Upflow velocities in the range of 0.9 to 1.0 m/min were necessary to maintain adequate fluidization. To maintain these fluxes in the reactor, recycle ratios in the range of 400:1 to 600:1 were required. The high hydraulic fluxes through the reaction created excessive turbulence, preventing the establishment of high biomass concentrations.

The original reactor design included a conical entrance to the column and upflow entry of the feed stream. The inlet piping was redesigned such that the feed entered vertically downward into the apex of the cone. These modifications resulted in a slight increase in the concentration of biomass in the reactor; however, the biomass appeared to stabilize at approximately 5.5 g/L. A perforated distribution plate was designed for the reactor and the inlet piping was restored to the original upflow configuration. The changes in the nitrification reactor biomass concentration resulting from these modifications to the reactor inlet design are shown in Figure 8. In retrospect, according to Figure 8, the downflow distributor may have produced the same result as the perforated plate. The nitrification reactor BVS concentration increased to approximately 13 g/L over the next 100 days of operation. At that time, the plate was removed because plugging had become evident.

The emphasis during the start-up and acclimation period was on the establishment of nitrification and denitrification in the coupled fluidized bed process. However, after nitrification and denitrification were evident in the system, the pseudo-steady state monitoring schedule described in Section 3.3 was initiated. Data collection commenced approximately 30 days after start-up, when the raw feed dilution had been reduced to approximately 5:1 (dilution water: coke plant wastewater).

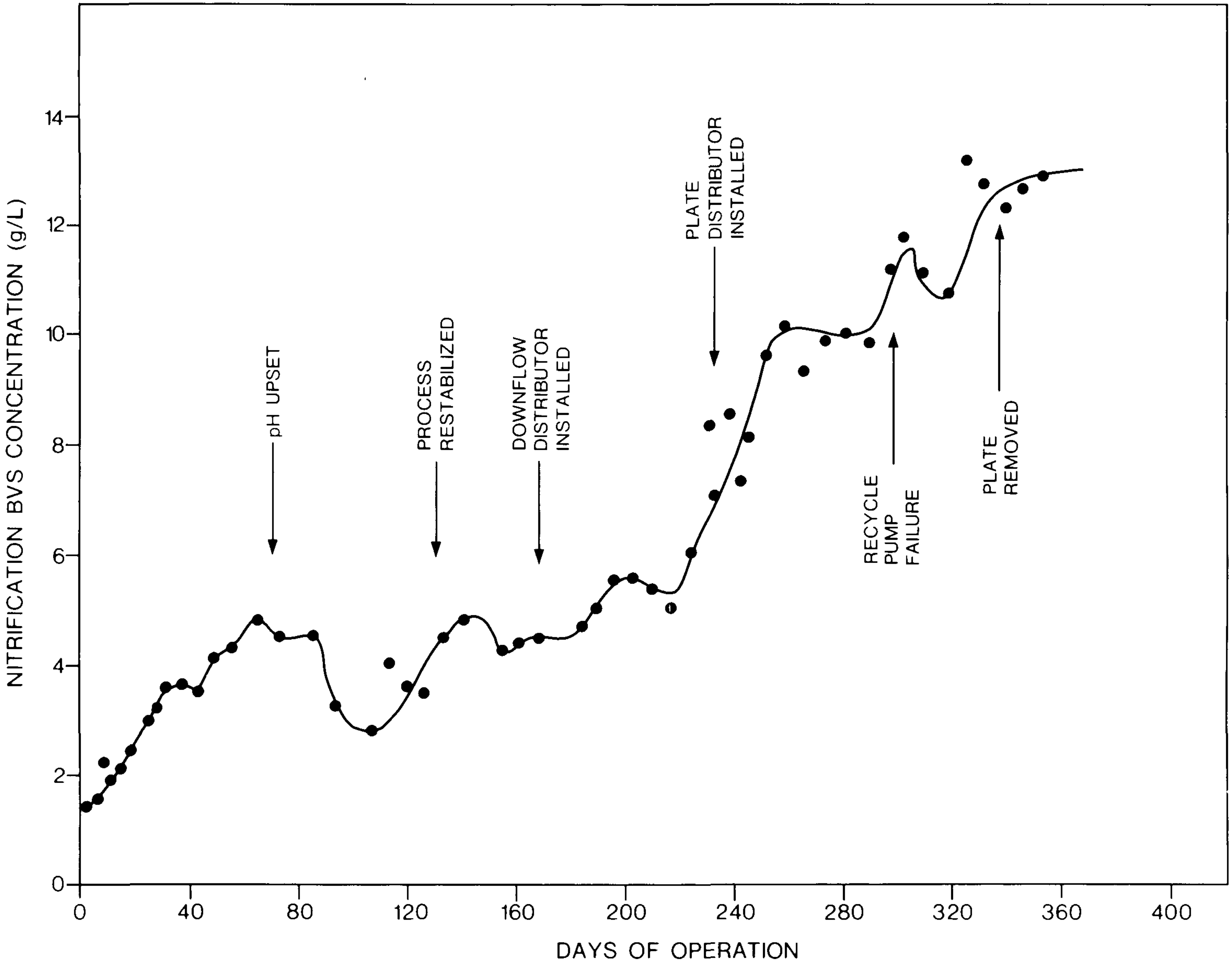


FIGURE 8 BIOMASS CONCENTRATION IN NITRIFICATION REACTOR

Data collected for conventional contaminants, including phenolic compounds, thiocyanate and total cyanide, indicated that throughout the acclimation period a high degree of removal was being attained (Table 9).

TABLE 9 REMOVAL OF PHENOLIC COMPOUNDS, THIOCYANATE AND CYANIDE DURING ACCLIMATION

	Feed (mg/L)			Effluent (mg/L)			
Parameter	Mean	Standard Deviation	% Var.	Mean	Standard Deviation	% Var.	Removal Efficiency (%)
Phenolic Compounds	178.9	111.5	62.3	0.120	0.048	40.0	>99.9
Thiocyanate	112.0	62.5	55.8	1.20	0.65	54.1	98.9
Total Cyanide	3.69	1.90	51.5	2.64	1.18	44.7	28.5

Over the entire acclimation period, the average removal of phenolic compounds was greater than 99.9 percent. Thiocyanate removal averaged 98.9 percent and total cyanide removal averaged 28.5 percent. The degree of total cyanide removal attained is related to the fraction of degradable cyanide in the raw wastewater. The data for phenolics, thiocyanate and cyanide include results collected during and immediately after the pH upset experienced in the process. High levels of phenolics (17.7 mg/L) and thiocyanate (up to 59.1 mg/L) were experienced for two to four days after the process upset. However, the high degree of removal obtained prior to the upset was rapidly re-established.

3.4.3 Phase II - Pseudo-steady State Operation. Five pseudo-steady state operating conditions were assessed during the pilot-scale investigation. The schedule of pseudo-steady state operations is outlined in Table 10. The pseudo-steady state performance data were collected using feed batches SS1 (Runs 1, 2, 3 and 4) and SS2 (Runs 4 and 5). These feed batches were similar in quality in terms of conventional contaminants, particularly ammonia nitrogen and thiocyanate concentrations.

The operating conditions for the anoxic denitrification reactor and the oxygenic nitrification reactor for each pseudo-steady state run are summarized in Table 11. The initial steady state run (Run 1) was conducted at loading conditions similar to

TABLE 10 SCHEDULE OF PSEUDO-STEADY STATE OPERATIONS

Year	Days*	Pilot Plant Operating Conditions
1980	332	Initiate pseudo-steady state runs
1980	333 - 338	Acclimate to pseudo-steady state loading condition 1
1980	339 - 347	Pseudo-steady state 1
1980	347	Increase system loading
1980/81	348 - 33	Acclimate and re-establish steady state
1981	34 - 56	Pseudo-steady state 2
1981	56	Increase system loading
1981	57 - 77	Acclimate and re-establish steady state
1981	78 - 93	Pseudo-steady state 3
1981	93	Increase system loading
1981	94 - 126	Acclimate and re-establish steady state
1981	127 - 162	Pseudo-steady state 4
1981	162	Increase system loading
1981	163 - 267	Acclimate and re-establish steady state
1981	267 - 272	Pseudo-steady state 5
1981	273 - 288	Mechanical equipment failure - re-establish steady state
1981	289 - 294	Pseudo-Steady State 5 (continued)

* Julian calendar

those determined by Bridle et al. (1,2,4) to be necessary to maintain consistent nitrification in suspended growth biological treatment systems treating similar wastewaters. The total system hydraulic retention time (HRT) during Run 1 was approximately 45 hours (1.9 days), where the system HRT was defined as the anoxic denitrification reactor HRT plus the oxygenic nitrification reactor HRT. The individual reactor HRT was based on the flow rate of coke plant wastewater and the empty bed reactor volume.

The experimental design of the pseudo-steady state phase of the program was based on stepwise increases in reactor loadings from those applied in Run 1 to establish the minimum HRT required in each reactor. At the end of Run 1, accumulated inorganic

TABLE 11 PSEUDO-STEADY STATE OPERATING CONDITIONS

	Anoxic Reactor							Oxygenic Reactor								System	
Run no.	HRT (h)	SRT (d)	Temp. (°C)	pH	BVS (g/L)	Hyd. Flux* (m/min)	Recycle Ratio	HRT (h)	SRT (d)	Temp. (°C)	pH	BVS (g/L)	Hyd. Flux* (m/min)	Recycle Ratio	DO (mg/L)	HRT (h)	SRT (d)
1	9.8	320.0	30-33	7.2	34.0	0.46	80	35.0	140.0	30-33	7.4	4.3	0.82	540	4.6-5.5	44.8	230.0
2	4.8	17.5	26-30	7.3	27.7	0.57	100	35.0	130.0	26-30	7.1	7.0	0.88	580	4.3-6.0	39.8	41.0
3	3.2	30.0	27-31	7.3	23.6	0.59	67	23.3	110.0	27-31	7.0	9.6	0.93	400	2.5-3.8	26.5	89.0
4	1.9	5.6	25-28	7.4	23.1	0.52	35	14.0	65.0	25-28	7.1	12.1	0.60	154	2.8-3.8	15.9	20.0
5	3.0	9.4	24-28	7.2	11.9	0.64	43	14.0	52.0	24-28	7.1	13.5	0.82	210	2.9-3.9	17.0	30.0

* Hydraulic flux defined as total volumetric flow per unit cross-sectional area of reactor.

deposits were adversely affecting fluidization in the denitrification reactor and high biomass concentrations were not being attained in the nitrification reactor. Therefore, between Runs 1 and 2, the volume of the denitrification reactor was reduced from approximately 59 L to 29 L by removing the upper 1.7 m of bed height and relocating the bed height control valve. The process loading to the nitrification reactor was not increased between Run 1 and Run 2; however, the reduction in anoxic reactor volume resulted in a denitrification HRT of 4.8 hours during Run 2, compared to 9.8 hours in Run 1.

In subsequent pseudo-steady state runs, the process loading was gradually increased until the system HRT had been reduced to approximately 16 hours in Run 4. During Run 4, feed batch SS1 was exhausted and a new batch of coke plant wastewater (batch SS2) was obtained. Operational and performance data related to Run 4 are based on 21 days during which batch SS1 was applied to the system and 15 days during which batch SS2 was applied as feed. The performance for Run 4, in terms of removal efficiency, was based on the average feed quality over the 36 day pseudo-steady state period.

As is evident from the schedule of pseudo-steady state runs in Table 10, considerable time was necessary from the completion of pseudo-steady state Run 4 to the re-establishment of steady state conditions for Run 5. At the end of Run 4 (day 162), the hydraulic loading on the system was increased such that the nitrification reactor HRT was reduced to approximately 9 hours. Under these loading conditions, problems were encountered in establishing stable nitrification and a significant increase in the effluent suspended solids concentration was noted. To re-establish stable nitrification and reduce biomass losses from the reactors, the process loading was decreased. Run 5 was conducted at loading conditions similar to those applied in Run 4 to verify that the performance attained during Run 4 could be duplicated.

The solid retention times (SRT) defined for the individual reactors in Table 11 were calculated based on assumptions that the effluent suspended solids represented biomass lost from the reactors and that each reactor contributed 50 percent of the total mass of volatile suspended solids present in the final effluent. Preliminary attempts, based on mass balances, specific ammonia oxidation rates of the effluent solids and nitrifier-specific plate counting techniques, failed to establish the relative contribution of the denitrification reactor and the nitrification reactor to the total mass of solids unintentionally lost to the final effluent.

The performance of the coupled fluidized bed process under pseudo-steady state loading conditions is summarized in Table 12. Stable process performance was maintained at a total system HRT of 16 to 17 hours. The overall removal of total nitrogen at these loading conditions was more than 90 percent. Effluent ammonia nitrogen concentrations of 1 to 2 mg/L were maintained despite the reduction in nitrification reactor HRT from 45 hours to 14 hours.

Under all conditions, oxidation of biodegradable carbonaceous matter in the raw wastewater was virtually complete. Treated effluent CNS concentrations were consistently less than 5 mg/L and generally in the range of 1 to 2 mg/L. Removal of total cyanide was more variable than that observed for other parameters and removal efficiency appeared to decline with prolonged storage of the raw wastewater. Although analyses to differentiate between free and complexed cyanide were not conducted on a routine basis, periodic analyses indicated that the concentration of cyanide amenable to chlorination in the treated effluent had been reduced to the level of detection. The cyanide present in the treated wastewater represented complexed cyanide not amenable to biological treatment.

Complete denitrification was consistently attained in the anoxic reactor throughout the pseudo-steady state runs (NO_T-N <1 mg/L) despite reduction of the anoxic reactor HRT to a minimum of approximately 2 hours. The relatively low final effluent oxidized nitrogen (NO_T-N) concentrations relate to the high rate of recycle from the oxygenic nitrification reactor to the anoxic denitrification reactor. The low concentration of effluent NO_T-N also contributes to the low total nitrogen concentration and the high overall nitrogen removal efficiency. Depending on site-specific discharge requirements, a full-scale system would probably be designed to operate at significantly lower recycle rates, resulting in higher concentrations of oxidized nitrogen (NO_T-N) in the final effluent.

Effluent suspended solids were consistently greater than 50 mg/L during the pseudo-steady state runs and, in Run 5, averaged more than 300 mg/L. Excessive losses of biomass from fluidized bed biofilms have not been identified as a problem in any other industrial or municipal fluidized bed studies (7, 93). However, Medwith and Lefelhocz (3) found that the effluent from a hybrid suspended growth-fixed film reactor nitrifying coke plant wastewater contained 100 to 500 mg/L suspended solids. It is possible that poor biofilm properties are characteristic of biological systems treating coke plant wastewater.

TABLE 12 PSEUDO-STEADY STATE PERFORMANCE OF TWO-STAGE BIOLOGICAL FLUIDIZED BED SYSTEM

	HRT (hours)[a]					COD			TKN								
Run no.	Anoxic	Oxygenic	System		FOC	UF	F	Phenolics	UF	F	NH_3-N[g]	TCN	CNS	NO_3-N	NO_2-N	TN	SS
1	9.8	35.0	44.8	Effluent[b]	40.0	270.0	220.0	0.08	9.0	7.5	1.0	4.5	1.8	0.0	2.5	10.0	132.0
				Removal (%)	95.1	91.1	92.2	>99.9	95.6	96.3	99.5	50.0	99.6	-	-	95.1	-
2	4.8	35.0	39.8	Effluent[c]	50.0	428.0	342.0	0.15	13.3	11.8	2.4	3.8	1.8	0.4	1.0	13.2	170.0
				Removal (%)	94.3	87.6	89.9	>99.9	94.6	95.1	98.8	57.8	99.6	-	-	94.5	-
3	3.2	23.3	26.5	Effluent[d]	45.0	355.0	250.0	0.17	9.8	8.8	0.4	6.2	1.6	0.0	1.8	10.6	104.0
				Removal (%)	94.1	89.1	91.3	>99.9	94.0	94.1	99.7	42.2	99.5	-	-	92.9	-
4	1.9	14.0	15.9	Effluent[e]	58.0	348.0	305.0	0.14	14.4	11.0	0.4	6.5	2.6	2.3	1.5	15.9	138.0
				Removal (%)	93.0	89.4	90.0	>99.9	92.1	93.8	99.8	18.2	99.3	-	-	90.9	-
5	3.0	14.0	17.0	Effluent[f]	70.0	513.0	339.0	0.20	21.5	13.0	1.8	4.5	3.0	2.2	2.3	17.5	315.0
				Removal (%)	90.6	83.4	88.0	>99.9	90.7	94.2	99.1	12.5	99.2	-	-	92.2	-

a Hydraulic retention time, based on empty bed reactor volume and coke waste feed rate.
b Median concentration, expressed in mg/L, based on 9 consecutive days of pseudo-steady state operation.
c Median concentration, expressed in mg/L, based on 23 consecutive days of pseudo-steady state operation.
d Median concentration, expressed in mg/L, based on 16 consecutive days of pseudo-steady state operation.
e Median concentration, expressed in mg/L, based on 36 consecutive days of pseudo-steady state operation.
f Median concentration, expressed in mg/L, based on 10 days (non-consecutive) of pseudo-steady state operation.
g Feed NH_3-N concentration based on coke wastewater (NH_3-N + 0.24 CNS) concentration.

TN - Total Nitrogen = Filt. TKN + NO_T-N
UF - Unfiltered
F - Filtered

The pilot-scale fluidized bed system was operated for a total of 326 consecutive days during Phase II. Feed and treated effluent quality in terms of average removals of FOC, phenolic compounds, thiocyanate and total cyanide are summarized in Table 13. These data include the time periods considered to be acclimation periods after step changes in the process loading, and the period between Runs 4 and 5 when difficulties were experienced in maintaining consistent nitrification. The coupled fluidized bed system was found to be capable of maintaining a consistently high degree of treatment in terms of FOC, phenolics, thiocyanate and total cyanide even during periods of unstable nitrification performance. Mechanical failures, including failure of recycle pumps which caused the entire contents of the reactors to settle and problems with maintaining adequate oxygen supply, had no long-term impact on the ability of the process to provide treatment in terms of these conventional contaminants.

TABLE 13 REMOVAL OF CONVENTIONAL CONTAMINANTS DURING PHASE II

	Median Concentration (mg/L)*		
Parameter	Feed	Effluent	Removal Efficiency (%)
FOC	780.0	50.0	93.6
Phenolics	495.0	0.16	>99.9
CNS	369.0	2.0	99.5
TCN	7.0	3.9	44.3

* Median concentration based on 326 consecutive days of operation.

The performance of the anoxic denitrification reactor was consistent throughout the pseudo-steady state experimental program. The support media seeded rapidly and high volatile solids concentrations (up to 40 g/L) were readily attained. The adverse effects of turbulence on the biomass concentrations in the nitrification reactor were not experienced in the denitrification reactor despite similar reactor inlet designs. Average volatile solids concentrations in the denitrification reactor ranged from 11.7 to 34.6 g/L during the pseudo-steady state runs, an order of magnitude higher than typically maintained in suspended growth biological systems.

At low denitrifier growth rates (high SRT), inorganic deposits accumulated in the anoxic reactor biofilms. By the completion of pseudo-steady state Run 1, these deposits had increased biofilm densities sufficiently that the reactor flux had to be increased from 0.44 to 0.59 m/min to maintain fluidization. Clean sand was added to the reactor to replace sand containing excessive amounts of calcium phosphate. Analyses of the biological matter indicated high concentrations of calcium and phosphorus. Based on these analyses, the mass ratio of calcium to phosphorus was approximately 2.8, indicative of tetrabasic calcium phosphate ($4CaO{\cdot}P_2O_5$). X-ray diffraction techniques confirmed the presence of tetrabasic calcium phosphate in the biofilms.

The deposition of inorganic matter in the denitrification reactor did not appear to affect the biological treatment efficiency; however, the fluidization difficulties prevented adequate control of bed expansion and reactor SRT. In Run 1, denitrification reactor SRT was more than 300 days. Subsequently, the volume of the anoxic reactor was decreased to increase the denitrifier growth rate and the reactor was operated at lower volatile solids concentrations. At a denitrification reactor SRT of 30 days or less, no further problems with the accumulation of calcium phosphate were experienced.

The maximum specific denitrification rates in the anoxic reactor were determined based on concentration profiles measured within the reactor. A typical denitrification reactor concentration profile for oxidized nitrogen species (NO_2-N + NO_3- N) and dissolved oxygen is shown in Figure 9. This particular concentration profile was determined during pseudo-steady state Run 3. Generally, the peak specific denitrification rate was attained in the upper 0.5-0.1 m of the reactor, after the residual dissolved oxygen content of the reactor feed had been removed by oxygenic organic carbon degradation. The reactor influent dissolved oxygen concentration varied with the recycle rate from the nitrification reactor and the nitrified effluent dissolved oxygen concentration.

Based on 17 reactor concentration profiles, the maximum specific denitrification rate averaged 0.11 g NO_T-N/g BVS•d (± 0.10 d^{-1}). The maximum rate data exhibited a high variability, ranging from 0.009 d^{-1} to 0.31 d^{-1}. Data developed for denitrification of municipal wastewater indicate that maximum specific rates at 25°C are typically in the range of 0.2 to 0.4 d^{-1} (20, 31). These data were generated from suspended growth systems in which methanol was utilized as the electron donor for denitrification. The U.S. Environmental Protection Agency (20) has cited denitrification rates approximately one-third of these rates when wastewater organics were substituted for methanol as the electron donor. Recent data from Beccari et al. (105) indicated that maximum denitrification rates at 25°C were 0.120 ± 0.020 d^{-1} when phenol was utilized as the carbon source. The rates attained from the pilot-scale fluidized bed system under actual coke plant wastewater treatment conditions correlate well with these data.

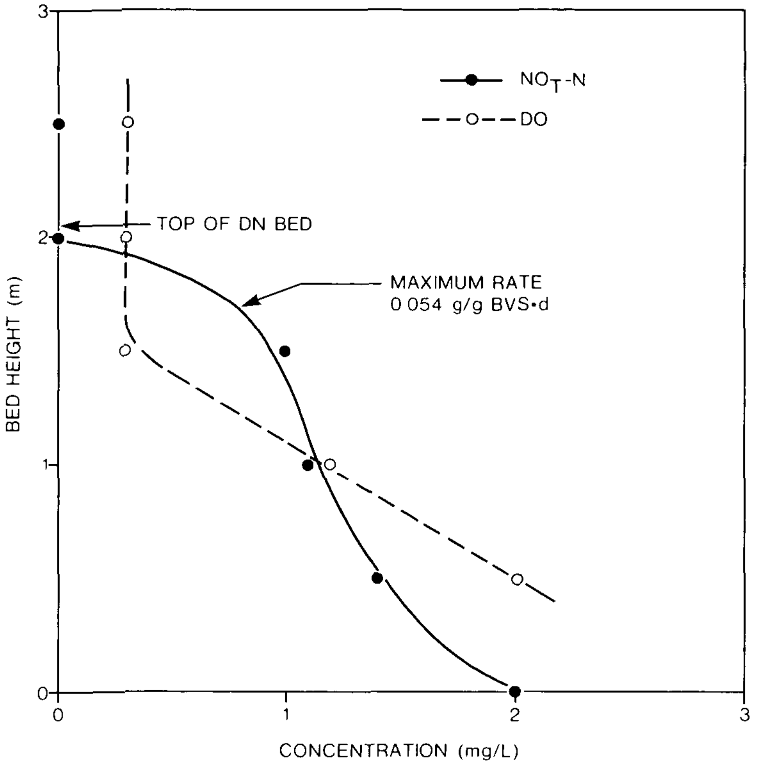


FIGURE 9 TYPICAL DENITRIFICATION REACTOR CONCENTRATION PROFILE

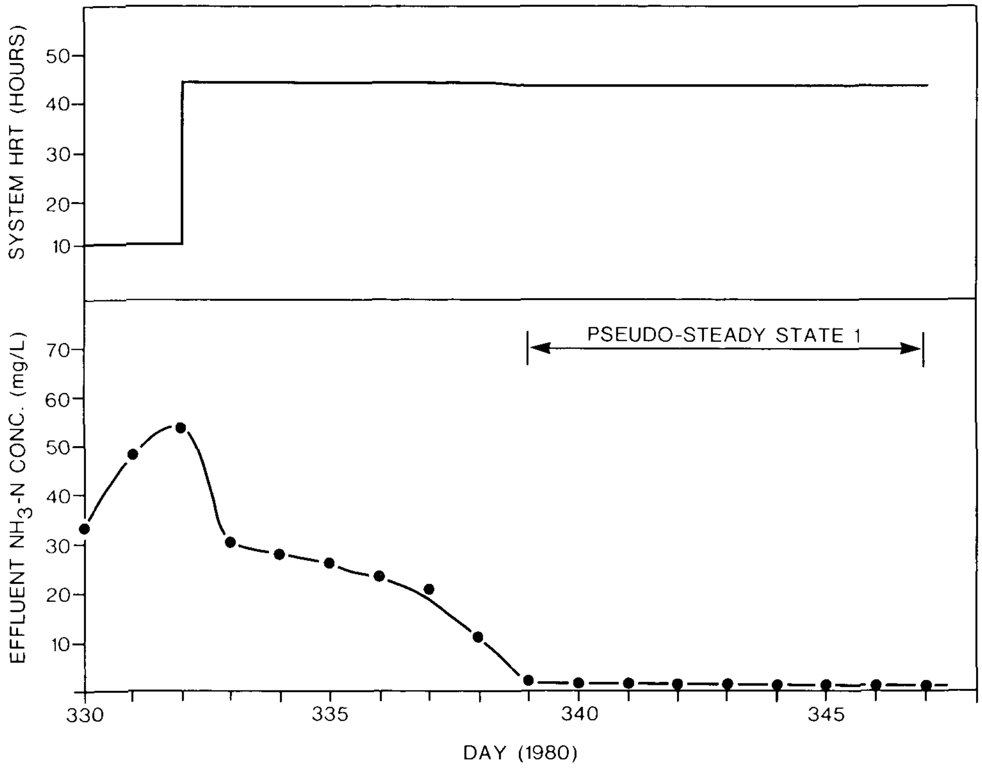


FIGURE 10 EFFLUENT AMMONIA NITROGEN CONCENTRATION - PSEUDOSTEADY STATE 1

Throughout the technical literature, difficulties in maintaining stable nitrification during treatment of undiluted coke plant wastewaters were cited (see Section 2.2.3). As in other biological systems, nitrification was the limiting step in the treatment of coke plant wastewater in the fluidized bed system. Although stable performance could be maintained in terms of other conventional contaminants such as phenolic compounds, FOC, thiocyanate, cyanide and oxidized nitrogen, the performance in terms of the effluent ammonia nitrogen concentration was susceptible to changes in loading.

The daily variations in effluent ammonia nitrogen concentration for each pseudo-steady state operating condition, including the acclimation period preceding steady state, are shown in Figures 10 to 14. The response of the nitrification process to step changes in process loading is evident, particularly in Runs 2, 3 and 4. The effluent ammonia nitrogen concentration increased immediately to approximately 100 mg/L. Up to 30 days of operation were necessary to re-establish stable nitrification in the system. Only at the end of Run 5 was it possible to impose step changes in the system without adversely affecting effluent quality. By the completion of Run 5, volatile solids concentrations in the nitrification reactor had attained levels of 14 to 15 g/L, significantly higher than the levels during previous steady state runs. It appears that transients in influent loading typical of full-scale ammonia still operation would have less impact on a well-seeded nitrification reactor; however, this would have to be verified under actual field conditions.

After 21 days of steady state operation in Run 4, feed SS2 was substituted for feed SS1. The change in feed had no apparent affect on the nitrification efficiency (Figure 13); however, an immediate increase in effluent suspended solids was noted. During operation with feed SS1, the effluent suspended solids concentration averaged 100 mg/L, similar to previous steady state data. After initiation of feed SS2, the average effuent suspended solids concentration increased to 165 mg/L, an apparent response to the change in feed quality. At the end of pseudo-steady state Run 4, the process loading was increased (system HRT reduced to 10.6 hours). Effluent suspended solids increased to approximately 500 mg/L and nitrification ceased in the process. A period of approximately 80 days was necessary to re-establish stable nitrification.

During the period of operation at a system HRT of 10.6 hours, the nitrification reactor SRT was in the range of 15 to 25 days, depending on the relative fraction of effluent solids contributed from the nitrification reactor. Bridle et al. (1) established that the minimum aerobic SRT to achieve complete nitrification was approximately 22 days. It appears that the loss of nitrification capacity is related to the reduction in reactor SRT

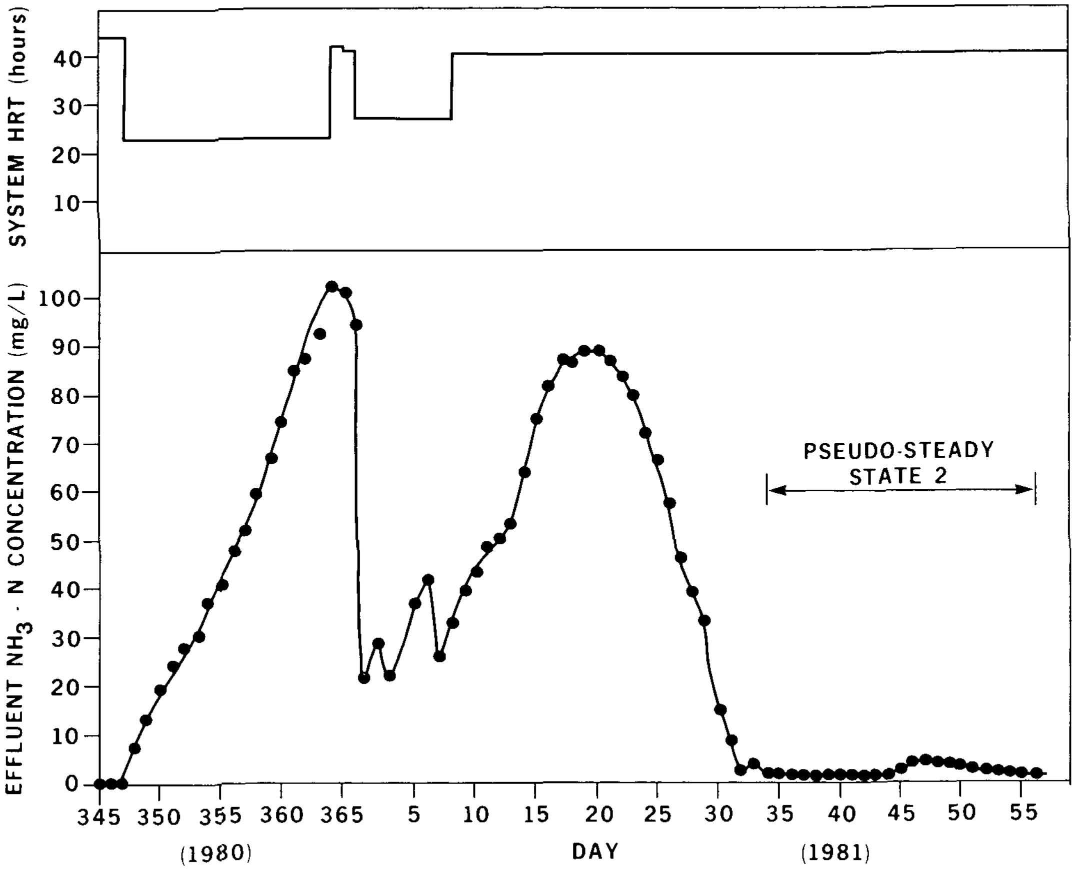


FIGURE 11 EFFLUENT AMMONIA NITROGEN CONCENTRATION - PSEUDOSTEADY STATE 2

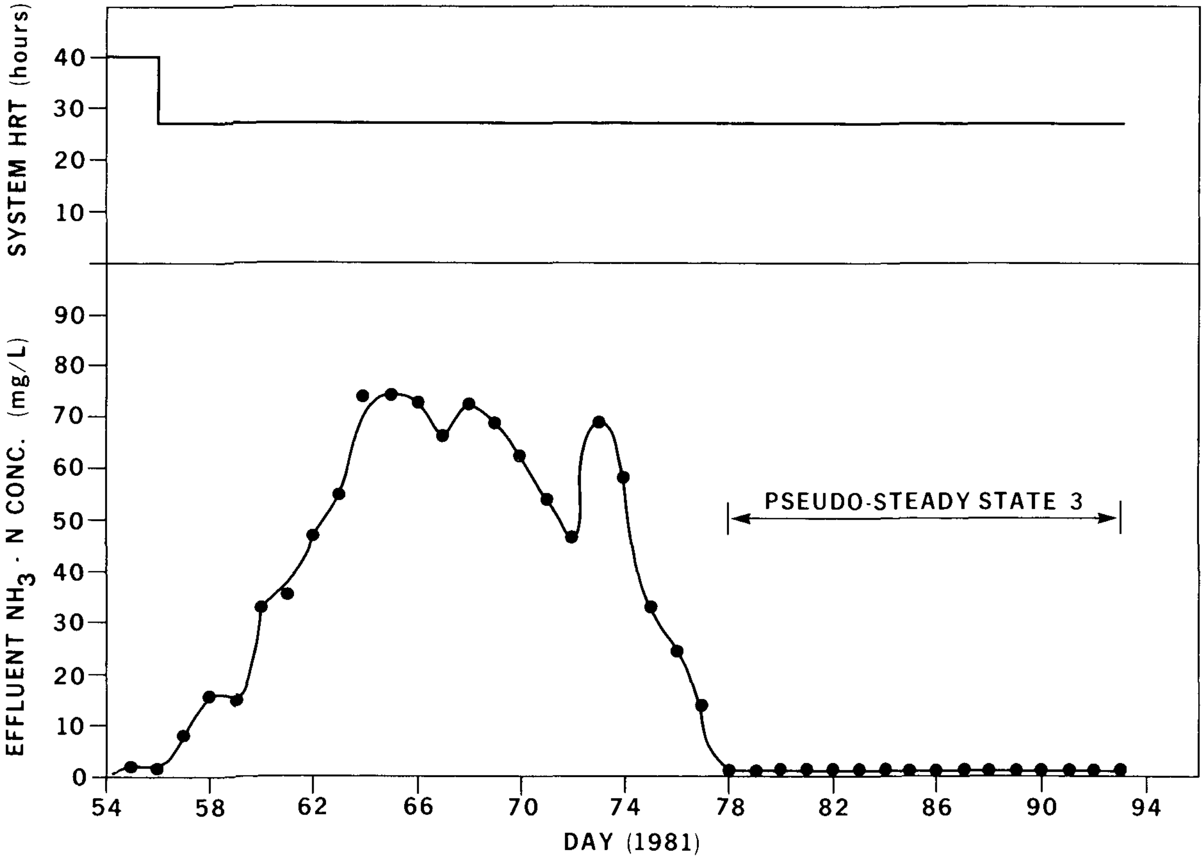


FIGURE 12 EFFLUENT AMMONIA NITROGEN CONCENTRATION - PSEUDOSTEADY STATE 3

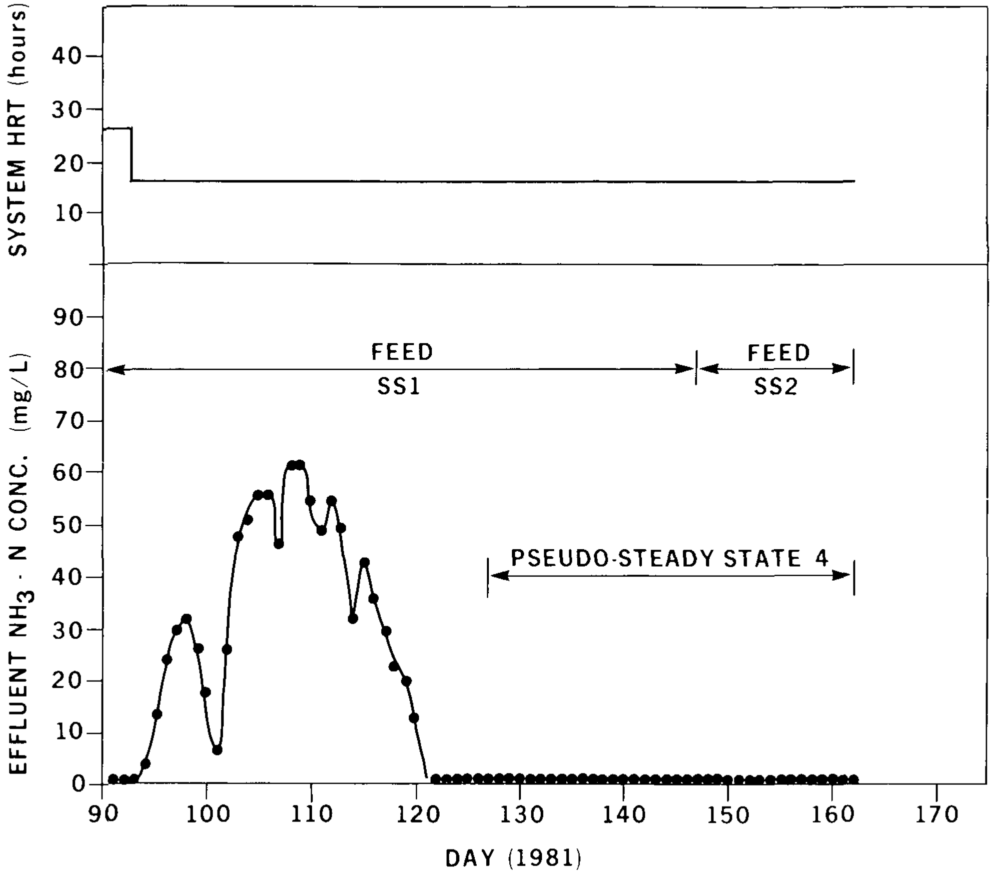


FIGURE 13 EFFLUENT AMMONIA NITROGEN CONCENTRATION - PSEUDOSTEADY STATE 4

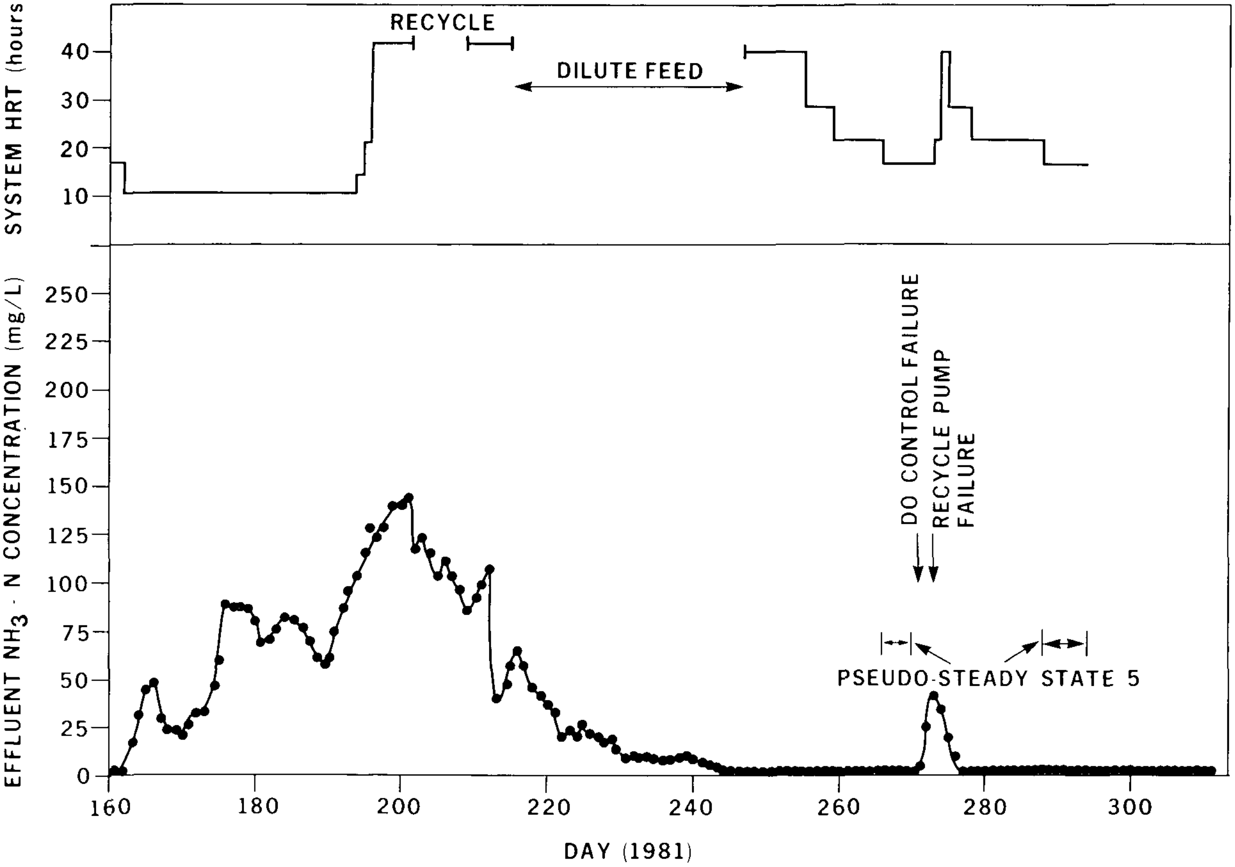


FIGURE 14 EFFLUENT AMMONIA NITROGEN CONCENTRATION - PSEUDOSTEADY STATE 5

associated with the loss of biomass to the effluent. Whether this biological response was related to the characteristics of feed SS2 or a function of overloading of the system could not be established. Process loadings similar to those imposed in Run 4 were eventually re-established in Run 5 with feed SS2; however, due to inadequate feed volume, higher loadings could not be imposed on the process to duplicate the conditions leading to failure of the nitrification system. Throughout pseudo-steady state Run 5, high effluent suspended solids concentrations were experienced, averaging 315 mg/L.

After the re-establishment of nitrification in Run 5, the dissolved oxygen control system failed, resulting in the entrance of oxygen bubbles to the nitrification reactor and a significant loss of biomass from the support media due to the high shear in the system. Two days later, the nitrification reactor recycle pump failed and the reactor contents settled. During the subsequent re-fluidization, additional biomass was sheared from the reactor. Remedial action involved reducing the hydraulic loading. Complete nitrification at the original loading was re-established within 20 days of the initial mechanical failure. The well-seeded reactor appeared to recover rapidly from the mechanical upsets. Removal of other conventional contaminants was unaffected during these periods of mechanical failure and nitrification instability.

The effect of nitrification reactor HRT on effluent ammonia nitrogen concentration is shown in Figure 15. Although in all cases ammonia oxidation efficiencies averaged approximately 99 percent, the relatively high slope of the data from Runs 2 and 5 indicates some process instability. Instability in Run 5 probably relates to the mechanical and process difficulties experienced in establishing steady state and the relatively short length of the pseudo-steady state period. During Run 2, the ammonia nitrogen loading was similar to that applied during Run 1 on a volumetric basis, but lower based on the mass of biomass in the reactor. Instability during Run 2 may be associated with changes in biofilm population dynamics.

Throughout the pilot-plant investigation, inhibition of Nitrobacter was evident based on the incomplete conversion of ammonia to nitrate. The relative fractions of nitrate and nitrite produced as a result of nitrification varied between experimental runs. In Runs 1 and 3, complete inhibition of Nitrobacter occurred and oxidized nitrogen was present only as nitrite in the final effluent. A lesser degree of inhibition was evident in the other pseudo-steady state runs. The inhibition may be related to the presence of various heterocyclic organic nitrogen compounds in the raw feed. The concentrations of free nitrous acid and free ammonia were considerably lower than levels which have been

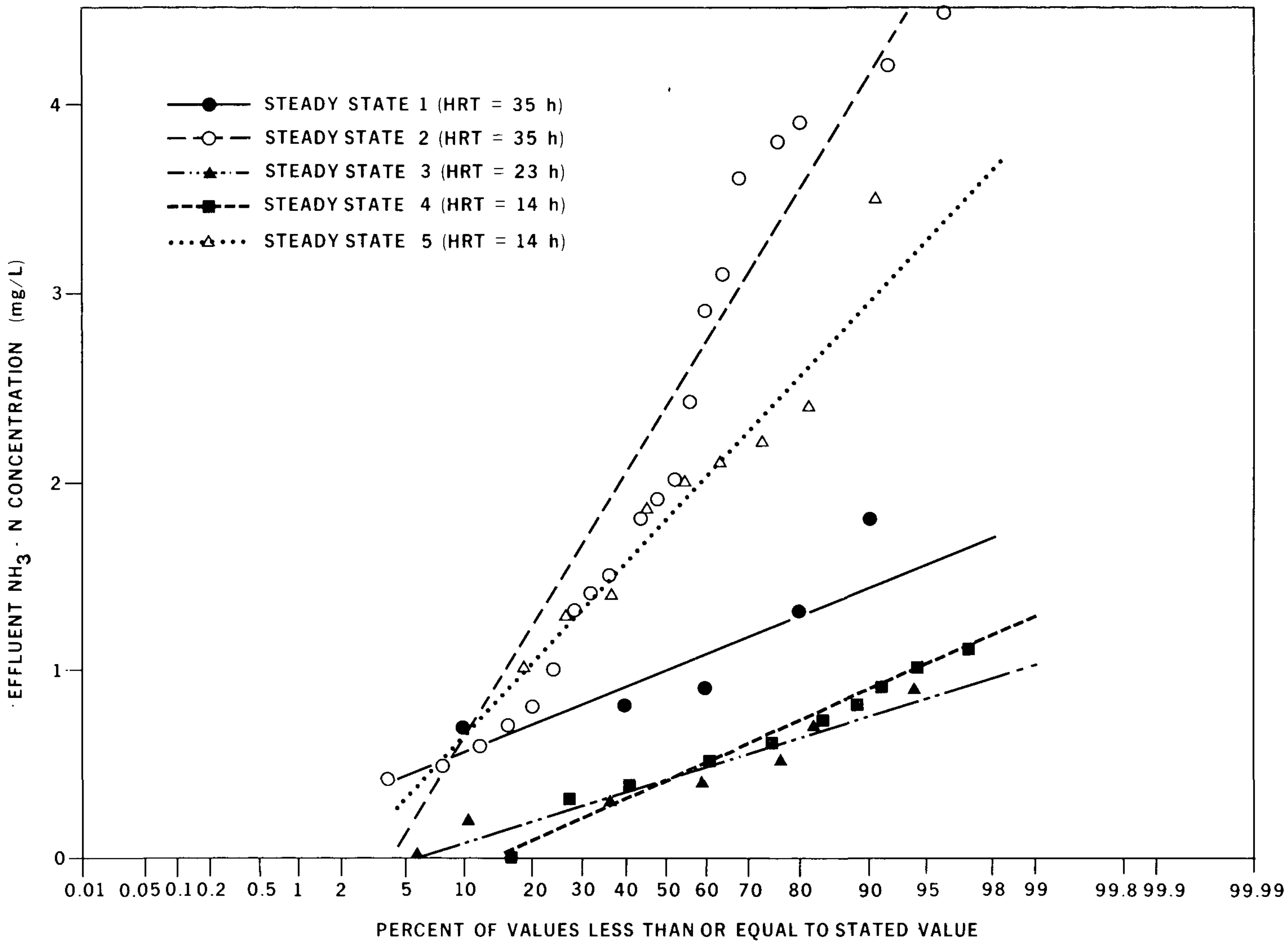


FIGURE 15 EFFECT OF NITRIFICATION REACTOR HRT ON EFFLUENT NH_3-N CONCENTRATION

found to cause Nitrobacter inhibition (106). The cause of the variability in degree of Nitrobacter inhibition for the same feed batch is presently unknown.

Ammonia nitrogen and oxidized nitrogen concentration profiles were also measured in the nitrification reactor in an attempt to define the maximum nitrification rate in a manner similar to that applied in the denitrification reactor. The high recycle rates and the excessive turbulence in the nitrification reactor created problems in accurately interpreting the profile data. The average specific nitrification rates for the individual pseudo-steady state runs are presented in Table 14. The ammonia nitrogen loadings have been based on the ammonia nitrogen concentration of the feed and the quantity of ammonia nitrogen generated from the oxidation of thiocyanate (62). The contribution of cyanide oxidation to the oxidizable nitrogen content of the feed was insignificant. The amount of nitrogen incorporated into cellular mass was not taken into account in the calculation of specific nitrification rates.

TABLE 14 PSEUDO-STEADY STATE SPECIFIC NITRIFICATION RATES

Pseudo-Steady State Run No.	Raw Feed Oxidizable Nitrogen (mg/L)	Mean BVS Conc. (g/L)	Temperature (°C)	Specific Nitrification Rate (g NH_3-N/g BVS•d)
1	172.7	4.3	31	0.027
2	188.9	7.0	28	0.019
3	156.1	9.6	29	0.017
4	142.7	12.1	26	0.022
5	176.7	13.5	26	0.024

* Based on raw feed (NH_3-N + 0.24 CNS) concentration.

The average specific nitrification rate during the pseudo-steady state runs was 0.022 g NH_3-N/g BVS•d ($\pm$ 0.005 d^{-1}). Specific nitrification rates determined by Bridle et al. (2) for similar wastewater were in the range of 0.013 to 0.017 d^{-1} (Table 6). The higher specific rates in the fluidized bed process probably relate to the separate-sludge operating mode which would tend to maximize the fraction of nitrifiers in the nitrification reactor compared to a single-sludge system. The specific rates attained in the fluidized bed system agree with those summarized in Table 6.

The pre-denitrification flow configuration reduces the requirement for supplemental carbon addition by utilizing the raw waste components as the carbon source for the denitrification reactions. Bridle et al. (1) established that complete denitrification of Dofasco coke plant wastewater required a feed FOC/TN ratio in excess of 3.5. The raw wastewaters utilized during the pseudo-steady state investigations (feeds SS1 and SS2) fulfilled this requirement and no supplemental carbon addition was necessary.

The data presented in Figure 16 show the relationship between organic carbon (FOC) removed in the denitrification reactor and the removal of oxidized nitrogen species (NO_T-N). The denitrification reactor was responsible for the removal of approximately 3 mg FOC per mg NO_T-N removed. The positive intercept in Figure 16 is associated with the aerobic removal of organic carbon compounds in the raw wastewater in the entrance zone of the anoxic reactor due to the presence of dissolved oxygen in the reactor feed. There is considerable scatter in the data presented in Figure 16 due to the high recycle rates and the small incremental changes in FOC and NO_T-N in the denitrification reactor.

Oxygen utilization in the oxygenic nitrification reactor was determined based on 24-hour average influent and effluent DO concentrations during two periods totalling 37 days when complete nitrification was attained. Average oxygen utilization based on the data collected during both periods was 1.03 g O_2 per L of coke plant wastewater treated (±0.15 g/L). There was no significant difference between the oxygen requirements during the two periods.

In Table 15, the actual oxygen requirement is compared with the theoretical requirement based on the feed composition. In the first case, the theoretical oxygen demand was calculated on the assumption that pre-denitrification of the coke plant wastewater was not practiced but the wastewater was completely nitrified. The organic carbon, thiocyanate and ammonia nitrogen would be removed aerobically from the raw wastewater. The demand associated with carbon oxidation was based on complete conversion to CO_2. Thiocyanate oxidation was assumed to proceed according to the pathway proposed by Luthy and Jones (61). The contribution of ammonia nitrogen generated from the thiocyanate oxidation was included in the calculated theoretical demand. On this basis, the theoretical demand for complete nitrification of these wastewaters is 3.1 g O_2 per L treated, approximately three timess the actual demand measured during the pilot plant investigation. The theoretical demand associated with organic carbon oxidation only is approximately 1.9 g O_2 per L treated.

The measured oxygen utilization of the oxygenic reactor is also compared with the theoretical demand exclusive of the organic carbon content of the raw wastewater. On this basis, the theoretical demand of wastewater was 1.23 g O_2 per L treated. The 20 percent discrepancy between the theoretical demand and the actual demand is probably

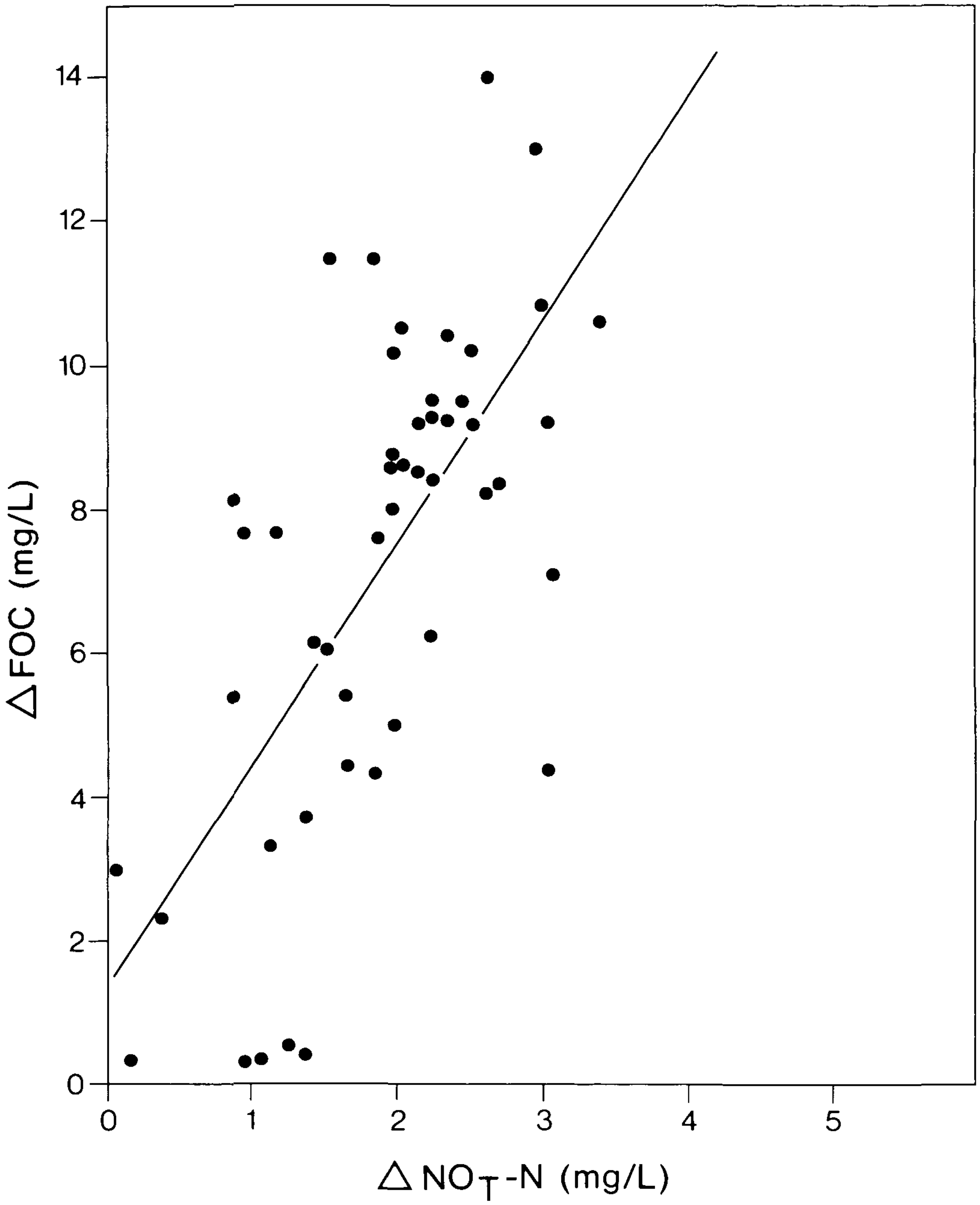


FIGURE 16 ORGANIC CARBON REQUIREMENTS FOR DENITRIFICATION

TABLE 15 OXYGEN UTILIZATION DURING COKE PLANT BIOLOGICAL TREATMENT

Period (days) 1981	Average Feed Quality			Average O_2 Utilization (g/L)	Theoretical O_2 Requirement (g/L)	
	NH_3-N	CNS	FOC		Including FOC Demand[a]	Excluding FOC Demand[b]
247 - 269	89.5	400	725	1.02	3.10	1.22
277 - 294	95.8	398	720	1.04	3.11	1.24

[a] Based on NH_3-N demand of 4.2 mg O_2 per mg NH_3-N (20), CNS demand of 1.1 mg O_2 per mg CNS (61) and FOC demand of 2.6 mg O_2 per mg FOC.

[b] Based on NH_3-N demand of 4.2 mg O_2 per mg NH_3-N (20) and CNS demand of 1.1 mg O_2 per mg CNS (61).

an indication of the amount of nitrogen utilized for cellular growth and not undergoing oxidation in the nitrification reactor.

Removal of organic carbon in the anoxic reactor was virtually complete (Figure 17). These data are representative of process performance throughout the experimental program. Operation in the pre-denitrification mode significantly reduced the total oxygen requirements associated with biological treatment of the coke plant wastewater due to anoxic removal of a large fraction of the wastewater organic carbon compounds.

The theoretical alkalinity requirement of the coupled denitrification-nitrification reactions is approximately 3.5 mg of alkalinity as $CaCO_3$ per mg nitrogen removed, based on an alkalinity consumption of 7.07 mg $CaCO_3$ per mg NH_3-N oxidized for nitrification and an alkalinity production of 3.57 mg $CaCO_3$ per mg NO_2-N or NO_3-N reduced to nitrogen gas (20).

Sodium bicarbonate was added to the fluidized bed pilot plant to maintain pH control. Alkalinity consumption and supplemental alkalinity requirements are summarized in Table 16 for pseudo-steady state periods 2, 3, 4 and 5. Data were not available from Run 1. During Runs 2 and 3, the alkalinity consumption per unit nitrogen removed was more than three times the theoretical requirement and considerably higher than the requirements determined for Runs 4 and 5. The higher demand in Runs 2 and 3 appeared to be associated with the higher rate of inorganic precipitation in the biofilms which was noted during operation at longer process SRTs. Phosphorus requirements were also significantly higher during Run 3 than during Runs 4 and 5. Phosphorus precipitation with calcium results in a net consumption of alkalinity (107).

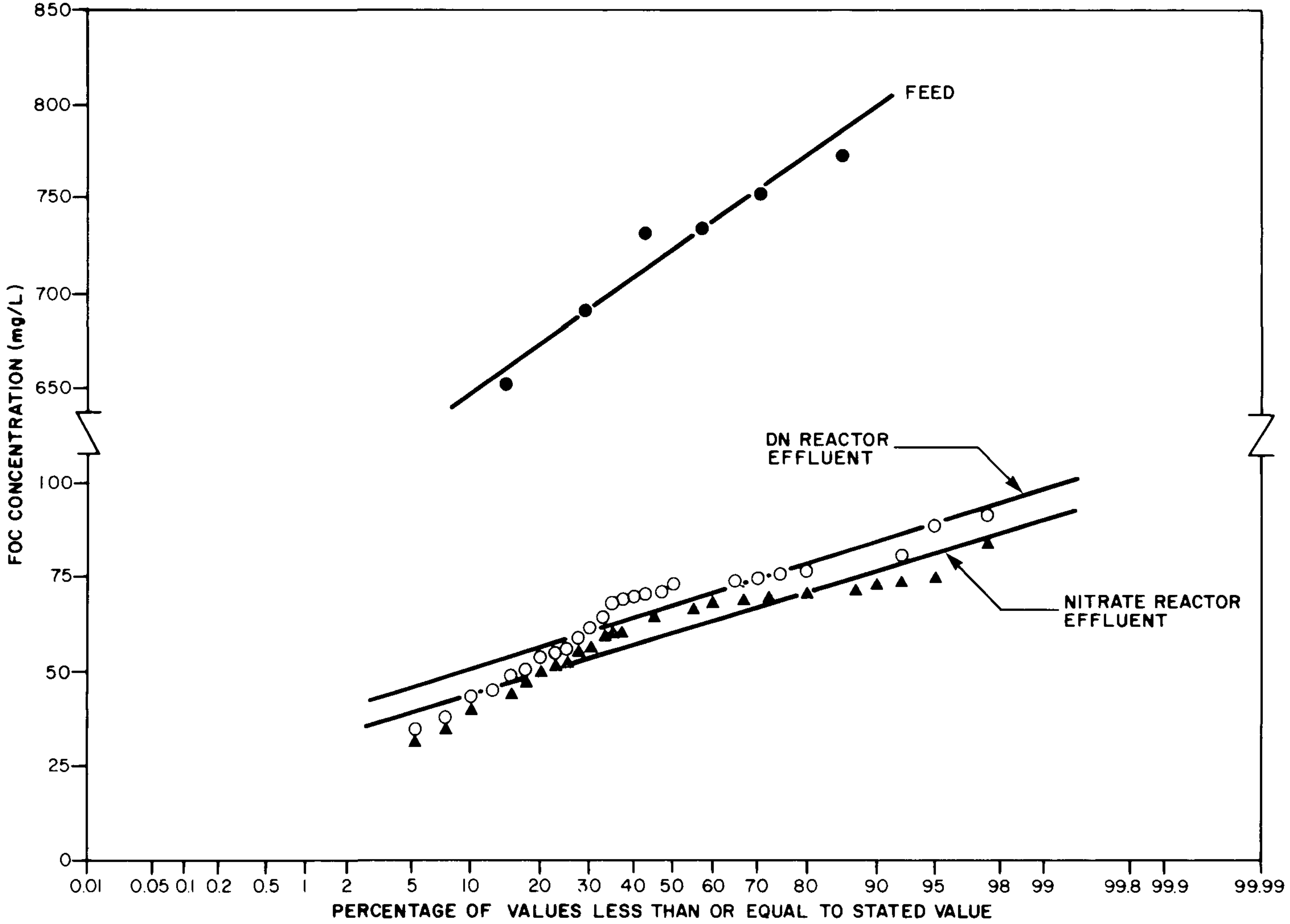


FIGURE 17 FOC CONTENT OF DENITRIFICATION AND NITRIFICATION REACTOR EFFLUENTS

TABLE 16 ALKALINITY CONSUMPTION DURING COKE PLANT BIOLOGICAL TREATMENT

Pseudo-steady State Run	Total Alkalinity Consumption (g $CaCO_3$/L)*	Supplemental Alkalinity Addition (g $CaCO_3$/L)*	Alkalinity Consumed Per Unit Nitrogen Removed (g $CaCO_3$/g TN)
2	2.99	1.82	13.8
3	2.02	1.05	13.5
4	0.80	0.33	5.2
5	0.99	0.95	4.7

* Per litre of wastewater treated.

Alkalinity consumptions during Runs 4 and 5 were closer to the theoretical requirement. As the organisms responsible for thiocyanate and sulphite oxidation are also autotrophic and utilize carbonate as their carbon source during cell synthesis (50), the total alkalinity demand would be expected to exceed that theoretically required for the coupled nitrification-denitrification reactors.

Phosphorus is required as a macro-nutrient for biological metabolism and was added to the phosphorus-deficient coke plant wastewater in the form of phosphoric acid. The precipitation of tetrabasic calcium phosphate resulted in an additional requirement for phosphorus. Bridle et al. (2) estimated that calcium phosphate precipitation was responsible for a tenfold increase in phosphoric acid requirements.

Phosphorus consumption in the fluidized bed process followed a pattern similar to that of alkalinity consumption. Highest demand was noted during Run 3, during which phosphorus was consumed in the system at an average rate of 0.167 g per litre of wastewater treated. Consumption during Runs 4 and 5 was significantly lower, 0.048 and 0.045 g P/L, respectively. Comparative data are not available for Runs 1 and 2.

Solids yield data for the pseudo-steady state periods are summarized in Table 17, on the basis of grams of volatile solids generated per litre of coke plant wastewater treated. The average total yield was 0.32 g VS per litre of wastewater treated. There was no significant difference between the yields from individual pseudo-steady state runs with the exception of Run 2, which produced a significantly higher yield from the anoxic reactor. The yield in the anoxic reactor was consistently higher than the yield in the oxygenic reactor, as would be expected based on the relative growth rates of

TABLE 17 SOLIDS YIELDS DURING COKE PLANT BIOLOGICAL TREATMENT

	SRT (days)			Solids Yield (g/L treated)		
Pseudo-steady State Run	DN Reactor	NIT Reactor	System	DN Reactor	NIT Reactor	Total
1	320	140	230	0.194	0.081	0.276
2	17.5	130	41	0.347	0.213	0.561
3	30.0	110	89	0.136	0.093	0.229
4	5.6	65	20	0.160	0.061	0.221
5	9.4	52	30	0.158	0.150	0.308

heterotrophic and autotrophic organisms (20). The average denitrification yield was 0.20 g VS/L treated compared to the nitrification yield of 0.12 g VS/L. These yields were calculated on the basis that half of the effluent suspended solids were generated in each reactor.

There was no significant correlation between the solids yield and the reactor SRT. During the pseudo-steady state investigations, constant biomass concentrations were not attained, particularly in the nitrification reactor. Therefore, true steady state was not achieved in the process in terms of the biomass and the calculated reactor SRTs do not represent the equilibrium SRT at that specific loading condition.

Although no optimization of waste sludge concentration was included in the pilot plant program, the waste sludge suspended solids concentrations were comparable to those that would be generated from the clarification stage of a suspended growth biological system. The median concentrations of waste sludge stripped from the support sand of the denitrification and nitrification reactors were 0.75 and 0.81 percent, respectively. The waste sludges were readily amenable to gravity thickening. Based on 30-minute quiescent settling tests, thickened sludge concentrations from the denitrification reactor averaged 2.4 percent and attained concentrations approaching 4 percent. In general, waste sludge from the nitrification reactor exhibited better thickening characteristics than waste sludge from the denitrification reactor. Median thickened sludge concentration was approximately 3.1 percent and concentrations approaching 7 percent were attained.

No studies have been conducted to evaluate the dewatering characteristics or the digestibility of fluidized bed sludges; however, it is not anticipated that the characteristics of these sludges should differ significantly from those of excess biomass generated in conventional suspended growth biological systems.

The experimental program did not include an assessment of the temperature coefficient related to coke plant biological treatment processes. The temperature of ammonia still effluent typically approaches 100°C and low temperature operation is, in general, not encountered in coke plant wastewater treatment.

High temperatures ($\geq$30°C) may be encountered in full-scale operations. During the initial pseudo-steady state experimental runs, no provision was made to reduce the reactor operating temperature. During the early summer months, reactor temperatures up to 33°C were encountered. Under these conditions, a possible correlation between high reactor operating temperatures ($\geq$30°C) and biomass losses from the fluidized bed support media was noted. A cooling water circuit was added to the pilot plant to maintain temperatures between 24 to 28°C for subsequent operations.

Wong-Chong and Hall (50) noted that, at temperatures from 27 to 35°C, there appeared to be oxidation or cellular destruction of biomass in suspended growth biological systems operated to achieve nitrification of coke plant wastewaters. A similar phenomenon in an attached growth system may affect the film-forming capabilities of the biomass and result in a loss of biological solids from the reactors. During the fluidized bed investigations, long-term operation at high temperatures was not assessed to determine if the biomass would acclimate to temperatures higher than 30°C.

Wong-Chong and Hall (50) observed optimal nitrification rates at temperatures between 21 and 27°C, the range over which the fluidized bed reactor was operated during subsequent experimentation.

As noted earlier, effluent suspended solids concentrations from the fluidized bed process were consistently greater than 50 mg/L. Effluent samples from the process were settled under quiescent conditions for 30 minutes, and the supernatant quality monitored. The effect of settling on the effluent suspended solids concentration is shown in Figure 18.

Based on these results, the effluent suspended solids exhibited poor settleability. The median effluent suspended solids concentration was reduced from approximately 115 to 98 mg/L. The effluent suspended solids were typically finely dispersed, consistent with the poor settleability shown in Figure 18.

During the assessment of the fluidized bed process for treatment of municipal wastewaters (7), chemical coagulation and granular media filtration were shown to be feasible polishing processes for fluidized bed effluents containing up to approximately

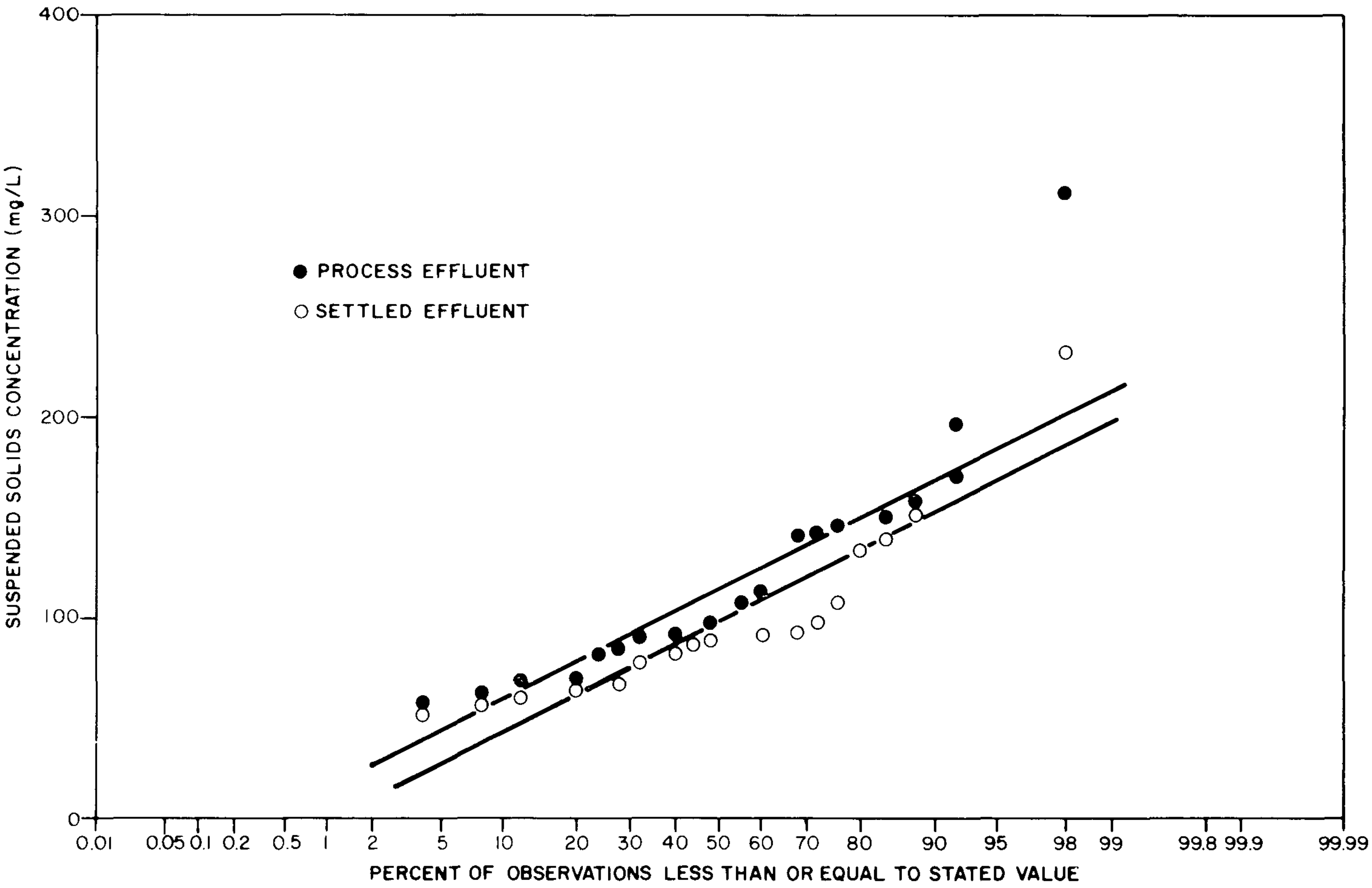


FIGURE 18 SETTLEABILITY OF EFFLUENT SUSPENDED SOLIDS

100 mg/L suspended solids. Rapid increases in headloss and short filter runs may adversely affect the feasibility of granular media filtration at the high suspended solids concentrations occasionally experienced during coke plant wastewater treatment. Further studies would be necessary to define the most cost effective solid-liquid separation process for this specific application.

Recycle in the nitrification reactor is necessary to ensure that the oxygen demand of the wastewater does not exceed the transfer capabilities of the oxygenator. Recycle of nitrified effluent from the oxygenic reactor to the denitrification reactor controls the concentration of oxidized nitrogen in the final treated effluent. In addition, recycle is required in both reactors to provide an adequate upflow velocity to maintain fluidization.

Due to the design of the coupled fluidized bed pilot plant, the recycle rates were controlled completely by the upflow velocities required in the individual reactors. Thus, the recycle ratios presented in Table 11 for the pseudo-steady state runs were significantly higher than would be necessary in a full-scale system. A recycle ratio of approximately 8:1 to the anoxic reactor would produce a final effluent containing about 15 mg/L of oxidized nitrogen. The cross-sectional area of the denitrification reactor would be designed based on this total flow to ensure that adequate fluidization velocities were attained.

In the case of the nitrification reactor, the minimum recycle required to fulfill the oxygen requirements would be approximately 20:1. However, to provide adequate reactor volume to meet the HRT and SRT requirements at this recycle ratio would result in excessively high reactors. Thus, the recycle ratio in the nitrification reactor would be controlled by the fluidization velocity requirements. Based on the pilot plant fluidization characteristics, the minimum recycle requirements for the nitrification reactor would be in the range of 50:1 to 60:1 for a maximum reactor height of 10 m.

3.4.4 Phase III - Variable Feed Operation. All pseudo-steady state data presented in Section 3.4.3 were collected during treatment of two batches of Dofasco coke plant wastewater. Unstable nitrification conditions were experienced after the completion of pseudo-steady state Run 4 during feeding of the second batch (batch SS2) of wastewater. To ensure that the performance attained during the pseudo-steady state period was representative of the effluent quality attainable under variable feed conditions, five batches of Dofasco wastewater were fed to the process over a period of approximately 60 days after completion of the pseudo-steady state period.

The characteristics of the individual batches (V1 to V5) were summarized in Table 8. As discussed in Section 3.4.1, feed batch V1 consisted primarily of light oil interceptor sump wastewater and produced a deterioration in nitrification efficiency in the fluidized bed process. In addition, the organic carbon content was inadequate to allow complete denitrification without supplemental methanol addition. Insufficient time was available to optimize process operation with this wastewater; therefore, data generated during operation with feed batch V1 are not included in the evaluation of process performance under variable feed conditions. The data for batches V2 to V5 represent process performance over a period of 48 days (Day 304 to Day 351 inclusive).

As the oxidizable nitrogen loading to the nitrification reactor (g NH_3-N/g BVS•d) had been defined as the most critical process control parameter during the pseudo-steady state investigations, the hydraulic loading during Phase III was varied to maintain a relatively constant oxidizable nitrogen loading (NH_3-N + 0.24 CNS) to the system in response to variations in feed concentration. The hydraulic and oxidizable nitrogen loadings during Phase III are shown in Figure 19. The actual NH_3-N loading varied over a twofold range from 0.014 to 0.028 d^{-1} (mean loading = 0.021 d^{-1}). However, this variation had no adverse effect on process performance.

The mean process operating conditions during Phase III are summarized in Table 18. The average system HRT was 17.7 hours, comprising 2.4 hours in the denitrification reactor and 15.3 hours in the nitrification reactor. Total system SRT was 42.0 days. The mean operating conditions for the process were comparable to the conditions during pseudo-steady state Runs 4 and 5.

The performance of the coupled biological fluidized bed system under variable feed conditions is summarized in Table 19. Nitrification efficiency was maintained consistently throughout the variable feed investigation despite a twofold variation in oxidizable nitrogen loading. Step changes in the reactor HRT had no discernible impact on the process. Median effluent NH_3-N concentration was 1.3 mg/L, equivalent to a removal efficiency of more than 99 percent. Removal of other conventional contaminants, including FOC, COD, phenolic compounds and thiocyanate, was consistently high. The overall performance was not significantly different from the performance attained under pseudo-steady state loading conditions in Phase II. Total nitrogen removal efficiency was approximately 93.3 percent during the seven-week investigation.

As evident from Figure 20, the denitrification reactor reduced the total oxidized nitrogen concentration (NO_T-N) to less than 1 mg/L without supplemental carbon

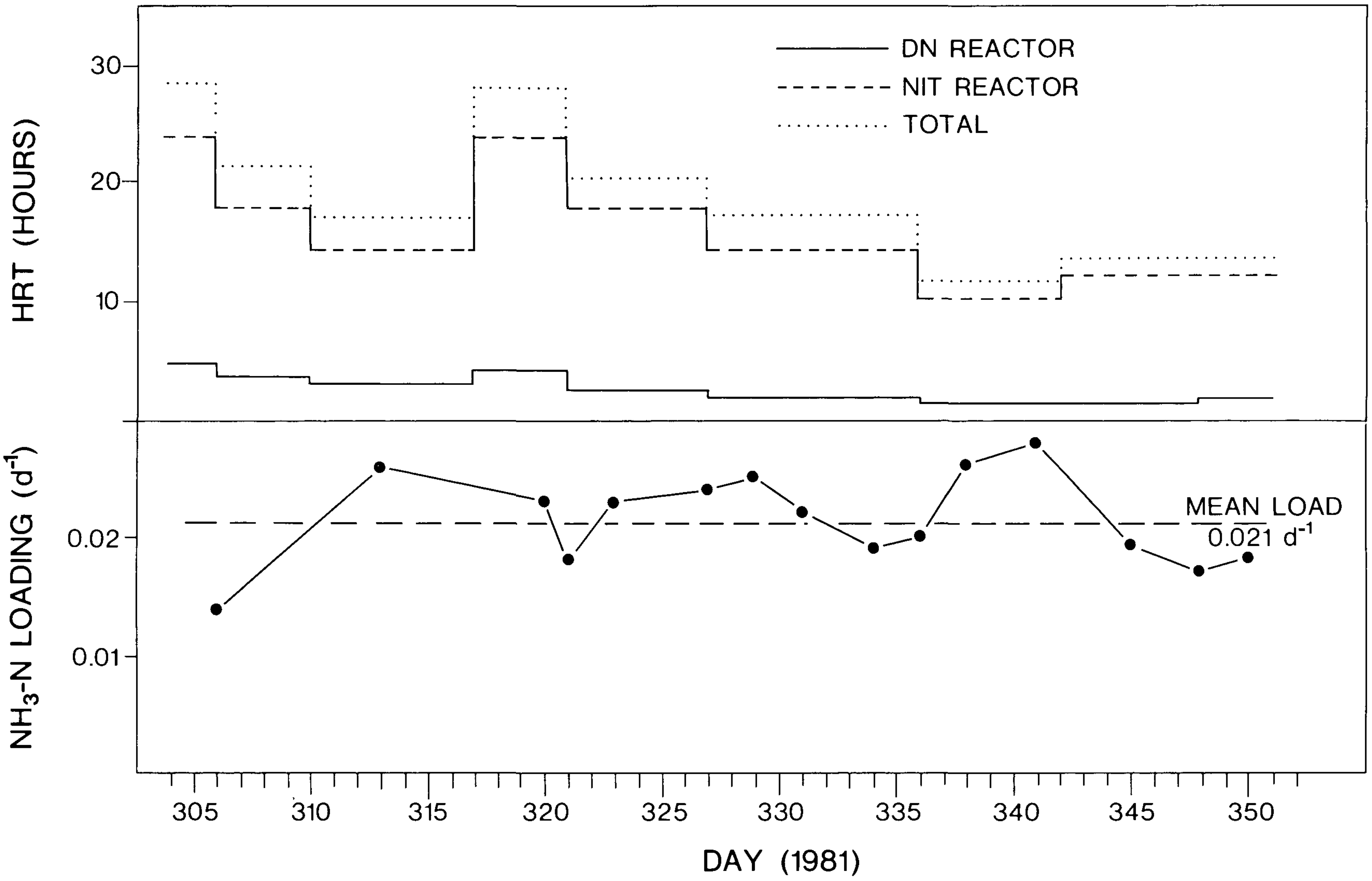


FIGURE 19 HYDRAULIC AND AMMONIA LOADING DURING PHASE III

TABLE 18 PROCESS OPERATING CONDITIONS - PHASE III

Parameter	Denitrification Reactor	Nitrification Reactor	System
HRT (hours)	2.4	15.3	17.7
SRT (days)	13.3	62.4	42.0
Temp. Range (°C)	25.2 - 28.0	25.5 - 28.0	-
pH Range	6.9 - 7.2	7.1 - 7.4	-
BVS (g/L)	16.3	14.5	-
Hyd. Flux (m/min)	0.57	0.85	-
Recycle Ratio	47.5	270.0	-
Eff. DO Range (mg/L)	-	2.9 - 3.7	-
Ammonia Loading* (g NH_3-N/g BVS•d)	-	0.021	-

* Includes contribution of CNS to oxidizable nitrogen concentration.

TABLE 19 PROCESS PERFORMANCE - PHASE III VARIABLE FEED CONDITIONS

Parameter	Feed (mg/L)			Effluent (mg/L)			Removal (%)
	Median	Std. Dev.	% Var.	Median	Std. Dev.	% Var.	
FOC	700	51.0	7.3	56.0	3.5	6.3	92.0
COD_F	2750	297.	10.8	478.	90.2	18.9	82.6
Phenolics	413	33.0	8.0	0.16	0.033	20.6	>99.9
TKN_F	247	40.5	16.4	11.9	1.55	13.1	95.2
NH_3-N	196	-	-	1.3	0.55	42.3	99.4*
CNS	346	60.7	17.5	2.4	0.47	19.4	99.3
TCN	8.0	1.4	18.0	6.1	1.4	22.1	23.8
NO_2-N	-	-	-	3.0	0.87	28.8	-
NO_3-N	-	-	-	1.6	0.78	48.8	-
TN	246	40.6	16.5	16.5	-	-	93.3
SS	-	-	-	232	75.6	32.5	-

* Includes contribution of CNS to oxidizable nitrogen concentration.

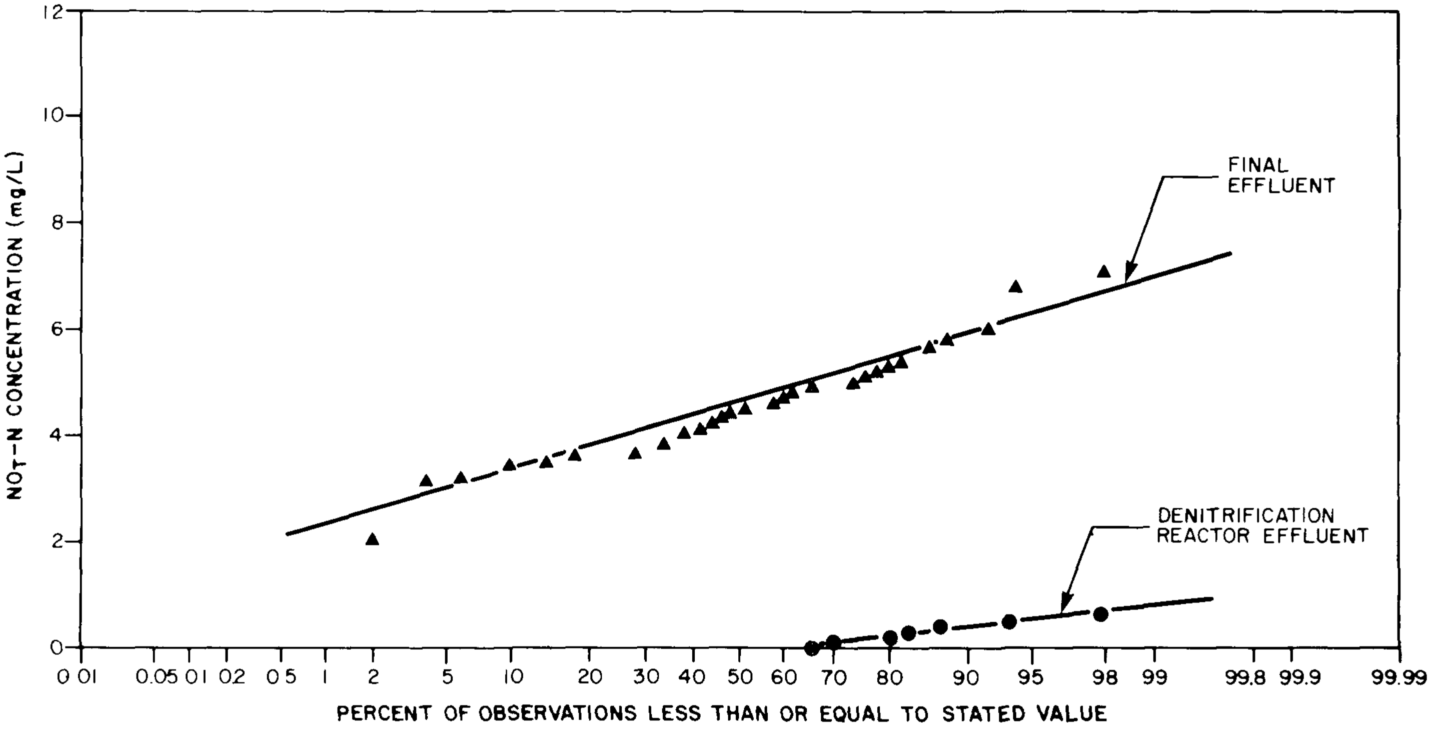


FIGURE 20 EFFLUENT NO_T-N CONCENTRATION UNDER VARIABLE FEED CONDITIONS

addition. The raw feed FOC/TN ratio averaged approximately 2.8 during the variable feed studies, significantly lower than the ratio of 3.5 found by Bridle et al. (1) to be required in suspended growth pre-denitrification system treating coke plant wastewater. These data agree with the overall removal of approximately 3 mg FOC per mg NO_T-N removed determined during the pseudo-steady state investigations. The lower FOC requirement in the fluidized bed process may be associated with the higher reactor biomass concentrations. As discussed in Section 3.4.3, the low effluent NO_T-N concentrations were associated with the high recycle rates required to maintain fluidization in the reactors.

The high effluent suspended solids concentrations noted at the completion of pseudo-steady state Run 4 and throughout the period when feed SS2 was fed to the process continued during the variable feed studies. Median effluent suspended solids concentration was approximately 230 mg/L (±32.5 percent).

Other process operation and performance parameters during Phase III were consistent with data generated during the pseudo-steady state operating period. Oxygen utilization averaged 0.97 g O_2 per litre of wastewater treated (±0.18 g O_2/L). The total alkalinity consumption was 0.92 g $CaCO_3$ per litre of wastewater treated, of which 0.62 g $CaCO_3$/L was supplied as supplemental alkalinity in the form of sodium bicarbonate. Phosphorus demand during the period of variable feed conditions was 0.065 g phosphorus as P per litre of wastewater treated. The total solids yield over the seven-week variable feed period was 0.322 g VS per litre of wastewater treated.

Based on seven weeks of operation with four batches of Dofasco coke plant wastewater, the coupled fluidized bed process was shown to be capable of maintaining efficient nitrification despite a two-fold variation in the oxidizable nitrogen loading. The consistent performance, in terms of the effluent NH_3-N concentration, during step changes in process loading confirmed the observations made prior to pseudo-steady state Run 5. A well-seeded nitrification reactor containing 12 to 16 g BVS/L appeared to be capable of withstanding a step change in ammonia loading without a significant effect on treated effluent quality. Assessment of the stability of the process under conditions of feed variability experienced at operating by-product coke plants was beyond the scope of this investigation and would require on-site pilot-scale studies.

3.5 Trace Organic Contaminant Removal

Surveys conducted at nine by-product coke plants in the United States by the U.S. EPA identified six volatile organic compounds, six acid extractable organic compounds and 17 base/neutral extractable organic compounds considered to be characteristic of the raw wastewaters generated from these operations (36). These trace organic contaminants were identified in Table 5. The results of the U.S. EPA survey have been confirmed by other researchers who have quantified priority pollutant concentrations in coke plant wastewaters (2, 50, 51). Bridle et al. (2) quantified 16 base/neutral extractable and acid extractable priority pollutants in ammonia still wastewater. In addition, this investigation identified 32 base/neutral extractable trace organic compounds not included in the U.S. EPA priority pollutant classification as being present at detectable concentrations in coke plant wastewater. These compounds were primarily heterocyclic nitrogenous compounds including pyridine, quinoline, indole, and carbazole. Concentrations could not be quantified due to a lack of standards.

Recent investigations conducted with laboratory-scale, pilot-scale and full-scale biological systems treating a wide variety of municipal and industrial wastewaters have demonstrated that biological processes are effective for removal of the majority of trace organic compounds (6, 108, 109). A number of researchers have evaluated biological removal of trace organics during treatment of coke plant wastewaters. Wilson et al. (51) demonstrated significant reductions in the concentrations of priority pollutants in bench-scale activated sludge systems with and without PAC addition. On the basis of operation of activated sludge systems at a 60-day SRT treating coke plant wastewater after 26 percent dilution with river water, they concluded that carbon addition provided no significant additional reductions in the priority pollutants.

Wong-Chong and Hall (50) sampled full-scale and bench-scale biological systems treating coke plant wastewater and confirmed that biological processes were effective in the removal of the organic priority pollutants present in these wastewaters. HRT and SRT were noted as critical control parameters to maintain effective treatment.

Bridle et al. (2) showed that most organics present in coke plant wastewater were effectively removed from the aqueous phase at high SRT and HRT operating conditions with PAC addition. However, analyses of the biological sludges indicated the accumulation of some polynuclear aromatics (PNA's), notably indeno-pyrene, naphthalene, pyrene and benzo-a-anthracene. In addition, heterocyclic nitrogenous compounds including gH carbazole, gH anthracene carbonitrile, indolizene, phenanthridine and phenanthridinone were accumulated in the sludge. The relative effect of PAC addition to the biological process on the accumulation of trace organics could not be determined based on these studies.

3.5.1 Methodology. Grab samples of the untreated coke plant wastewaters fed to the fluidized bed system and treated effluent from the pilot plant process were manually collected on a non-routine basis and submitted for extraction and analysis by gas chromatography-mass spectrometry (GC/MS). In addition to U.S. EPA organic priority pollutants (acid extractable group and base/neutral extractable group), these analyses included quantification of 22 non-priority pollutant base/neutral extractable organic compounds selected based on the results of Bridle et al. (2).

Samples from feed batches A6, SS1, SS2 and V1 (refer to Table 8) were collected, extracted and analyzed for U.S. EPA organic priority pollutants. Feed batch SS1 was sampled four times in six-months. Samples from feed batches SS1, SS2, V3 and V5 were analyzed for non-priority pollutant base/neutral extractables. Feed batch SS1 was analyzed on three separate occasions for these compounds.

The fluidized bed system effluent was typically sampled at the completion of each steady state run to determine the ability of the process to effect trace contaminant control. Thus, samples were obtained during steady state runs 1, 2, 3 and 4 (SS1, SS2, SS3 and SS4) for extraction and analyses for U.S. EPA organic priority pollutants and non-priority pollutant base/neutral extractable compounds. In addition, three samples were analyzed for U.S. EPA organic priority pollutants and two samples were analyzed for non-priority pollutant base/neutral extractables to define process performance under variable feed conditions.

In addition to the aqueous samples analyzed for trace organic contaminants, the sludges from the fluidized bed reactors were sampled and analyzed by GC/MS. Samples collected for extraction represented both biomass separated from the sand and biomass/sand mixtures in cases where sufficient biomass could not readily be separated from the support media. Eleven samples were analyzed for U.S. EPA organic priority pollutants (seven samples from the denitrification reactor and four samples from the nitrification reactor). Nine samples were analyzed for the non-priority pollutant base/neutral extractable compounds (six samples from the denitrification reactor and three samples from the nitrification reactor).

Samples were not analyzed for volatile organic compounds (purgeables) or for pesticides. Extractions and analyses for trace organic contaminants were conducted by the Laboratory Services Section of the Wastewater Technology Centre.

These results represent analyses of samples collected over more than a year of pilot plant operation during which the methods were altered to accommodate improvements in the analytical methodologies. Throughout the program, duplicate samples of coke plant wastewaters, treated effluents and biological sludges were spiked with a "cocktail" containing a variety of priority and non-priority pollutant compounds.

Recovery of acid extractable compounds and both priority and non-priority base/neutral extractable compounds from untreated coke plant wastewater showed considerable variability, particularly for phenols. Current GC and GC/MS U.S. EPA protocols for priority pollutants are not suitable for complex untreated wastewaters, especially in cases where compounds of interest are present simultaneously at low and high concentrations. The analysis of μ g/L quantities of phenols in the presence of mg/L quantities of other organic contaminants is very difficult. Errors are compounded as a result of the large dilution factors that are required.

In general, the recovery of spiked compounds from treated effluent samples was more complete and more reproducible than from raw wastewaters. Recovery of acid extractable trace organics was consistently low and the concentrations determined by GC/MS were significantly less than those determined according to traditional wet chemical analyses. However, by the completion of the study, the base/neutral extraction results showed a consistent level of recovery in replicate extractions from a spiked sample. For U.S. EPA base/neutral priority pollutants, recoveries generally ranged from 80 to 120 percent with some specific exceptions such as anthracene/phenanthrene and butylbenzylphthalate. Similarly, consistent recovery of 50 to 90 percent of non-priority pollutant base/neutral extractables was ultimately attained. As in the case of untreated wastewaters, the absolute values reported for the treated effluent samples should be treated with caution; however, the order of magnitude reduction in trace organic concentration after fluidized bed biological treatment is considered valid on the basis of the quality assurance/quality control (QA/QC) results.

Only limited spike recovery data were available for sludge samples and no data were available for non-priority base/neutral extractable compounds. In general, recovery data for sludges were comparable to the data for treated effluents. Recoveries were more consistent and more complete for the three sludge samples analyzed than for the untreated coke plant wastewater samples.

3.5.2 Results. Analytical data characterizing trace organic compound concentrations in untreated coke plant wastewaters are presented in Table 20 (U.S. EPA organic priority pollutants) and Table 21 (non-priority pollutant base/neutral extractable compounds).

TABLE 20 TRACE ORGANICS (U.S. EPA PRIORITY POLLUTANTS) IN UNTREATED COKE PLANT WASTEWATERS

Compound	Concentration* (µg/L)						
	Feed A6 14/10/80	Feed SS1 1/12/80	Feed SS1 11/12/80	Feed SS1 1/04/81	Feed SS1 12/05/81	Feed SS2 1/06/81	Feed V1 20/10/81
ACID GROUP							
p-Chloro-m-cresol					4		
2-Chlorophenol							
2,4-Dichlorophenol							
2,4-Dimethylphenol				300	1098	5840	> 360
4,6-Dinitro-o-Cresol							
2,4-Dinitrophenol							
2-Nitrophenol							
4-Nitrophenol							
Pentachlorophenol							
Phenol				3400		206 000	>100 000
2,4,6-Trichlorophenol							
BASE NEUTRAL GROUP							
Polynuclear Aromatics:							
Acenaphthene	15	14	12	2	3	15	
Acenaphthylene	36	18	13	13	7	333	20
Anthracene/Phenanthrene	107	87	52			227	30
Benzo (a) anthracene/Chrysene							> 10
Benzo (b) fluoranthene							
Benzo (k) fluoranthene	tr	tr					
Benzo (ghi) perylene	tr						
Benzo (a) pyrene							
Dibenzo (ah) anthracene							
Fluoranthene		45	54	10	8	43	20
Fluorene		tr		6	4	33	10
Indeno (1,1,2-cd) pyrene	tr						
Naphthalene	81	37	26	10	3	67	20
Pyrene	15	3	13	5	5	49	20
Chlorinated Benzenes:							
1,2-Dichlorobenzene	tr	16	11	tr			< 10
1,4-Dichlorobenzene or		2					
1,3-Dichlorobenzene				tr	tr	227	50
1,2,4-Trichlorobenzene					tr	25	< 10
Hexachlorobenzene							
Nitrosamines:							
N-nitrosodimethylamine							
N-nitrosodiphenylamine	16	3	2	5	3		< 10
N-nitrosodi-n-propylamine							
Phthalate Esters:							
Butyl Benzylphthalate					tr		
Di-n-butylphthalate	5	17	5	13	3	173	20
Diethylphthalate	1	1	tr	2	tr	6	
Dimethylphthalate				tr	tr	5	< 10
Di-n-octylphthalate	tr						
bis-(2-ethylhexyl)phthalate	3		3	8	5		
Haloethers:							
4-Bromophenyl phenyl ether							
bis (2-Chloroethoxy)methane					tr	93	
bis (2-Chloroethyl)ether					431	7	< 10
bis (2-Chloroisopropy)ether	1		6				
4- Chlorophenyl phenyl ether							
Other Compounds:							
Benzidine							
2-Chloronaphthalene							
3,3-Dichlorobenzidine	tr		tr				
2,4-Dinitrotoluene							
2,6-Dinitrotoluene							
1,2-Diphenylhydrazine	30						
Hexachlorobutadiene							
Hexachlorocyclopentadiene							
Hexachloroethane							
Isophorone					124		
Nitrobenzene							

* tr < 1 µg/L

TABLE 21 ORGANICS (NON-PRIORITY POLLUTANTS) IN UNTREATED COKE PLANT WASTEWATER

	Concentration (µg/L)					
Compound	Feed SS1* 11/12/80	Feed SS1* 1/04/81	Feed SS1* 12/05/81	Feed SS2* 1/06/81	Feed V3* 24/11/81	Feed V5* 7/01/82
Benzonitrile						
3, 4 dimethyl pyridine		10	12			
Isoquinoline	7 000	1 000			6 000 ***	
2-methyl naphthalene	16	2	111	91	20	
Indole	26 000			23	9 000	3 000
2 and/or 8-methyl quinoline	2 000		84	67	1 000	
"7A"-methyl quinoline	2 000	451	66	187	560	
"7B"-methyl quinoline	691	10		2 680	150	
2, 6 and/or 2, 7 dimethyl quinoline	76	36	41	49	20	
2, 4 dimethyl quinoline	72	41			40	
3, 4 and/or 5, 6 benzoquinoline	148	58	46	191	80	
Carbazole	2 000	437	330	2 207	890	
2, 6 dimethyl pyridine						
Thiophenol						
3, 5 dimethyl pyridine		tr**	6			
Quinoline	10 000	2 000	805	7 550	17 000 ***	6 000
1-methyl naphthalene				40		
4-methyl quinoline	274	89	3	209	70	
Dibenzofuran	20	4	4	19	20	
7, 8 benzoquinoline	42	13	13	113		
9-anthracenecarbonitrile	36	tr	1			
aniline					80	600

* Refer to Table 8 for coding

** tr<1.0 µg/L

*** Column overload, quantitation inaccurate

Concentrations of acid extractable phenol compounds according to GC/MS analyses were consistently lower than data generated by traditional wet chemical methods (4-aminoantipyrine). Such discrepancies have been reported by several other investigators (50, 109).

The priority pollutant compounds identified in the base/neutral extractable group by GC/MS were consistent with results reported elsewhere in the literature (2, 36, 50, 51). Eighteen U.S. EPA base/neutral extractable priority pollutants were identified at greater than trace concentrations in more than one sample. Polynuclear aromatics such as acenaphthylene, acenaphthene, anthracene/phenanthrene, fluoranthene, naphthalene and pyrene were consistently found at higher than trace (1 μg/L) concentrations. In addition, 15 non-priority pollutant base/neutral extractable compounds, such as isoquinoline, indole, carbazole and quinoline, were consistently present at concentrations approaching or exceeding 1 mg/L.

Analyses of feed SS1 over six months, during which it was stored and used as feed to the fluidized bed process, indicated a consistent decrease in the concentrations of the majority of priority and non-priority base/neutral extractable compounds during storage.

Feed V1 consisted primarily of light oil interceptor sump wastewater (see Section 3.4.1) and, on the basis of GC/MS analysis, appeared to contain lower concentrations of base/neutral extractable priority pollutants. Non-priority pollutant base/neutral extractables were not analyzed in this feed.

As noted in Section 3.5.1, the absolute concentrations of trace organics in the raw wastewater should be treated with caution due to the difficulties in the extraction of such complex aqueous wastes.

The treated effluent quality from the biological fluidized bed process in terms of U.S. EPA priority pollutants and non-priority base/neutral extractable trace organics detected is presented in Tables 22 and 23, respectively. As was the case in all analytical results by GC/MS for acid extractable compounds, the concentration of phenol was consistently lower than the concentration of phenolic compounds determined by wet chemical methods. Maximum phenol concentration in the treated effluent according to the GC/MS procedure was 10 μg/L, compared to concentrations of phenolic compounds in the range from 50 to 150 μg/L according to the 4-aminoantipyrine method. However, it must be repeated that GC and GC/MS data are reported without correction for extraction efficiency.

TABLE 22 TRACE ORGANICS (U.S. EPA PRIORITY POLLUTANTS) IN FLUIDIZED BED PROCESS EFFLUENTS

	Experimental Run Date							
Compound (μ g/L)	SS1* 11/12/80	SS2* 12/02/81	SS2* 13/02/81	SS3* 1/04/81	SS4* 12/05/81	V.F.** 20/10/81	V.F.** 14/12/81	V.F.** 7/01/82
ACID GROUP								
2,4-Dimethylphenol			tr	tr	tr			
Pentachlorophenol							34	
Phenol					4	10		< 10
BASE NEUTRAL GROUP								
Polynuclear Aromatics:								
Acenaphthene	tr							
Acenaphthylene			tr	tr	tr			
Anthracene/Phenanthrene	3			tr	tr		21	
Benzo (b) fluoranthene Benzo (k) fluoranthene	tr							
Fluoranthene	tr		tr					
Fluorene	tr							
Naphthalene					tr			
Pyrene		tr	tr	tr	tr			
Chlorinated Benzenes:								
1,2-Dichlorobenzene						< 10		
1,4-Dichlorobenzene or 1,3-Dichlorobenzene						< 10		
Nitrosamines:								
N-nitrosodiphenylamine						< 10		
Phthalate Esters:								
Butyl Benzylphthalate				tr				
Di-n-butylphthalate		tr	6	9	4	90	22	< 10
Diethylphthalate			tr	1	tr			
Dimethylphthalate					tr			
Di-n-octylphthalate					tr			
bis-(2-ethylhexyl)phthalate	4	1	2	4	4			
Haloethers:								
bis (2-chloroethoxy)methane	tr							
bis (2-Chloroethyl)ether			tr	tr				
Other Compounds:								
Benzidine		tr						
1,2-Diphenylhydrazine			tr		tr			
Nitrobenzene			tr		1	10		

* Refers to steady state run number

** Variable Feed Operation

tr < 1.0 μ g/L

Note: The samples were screened for all the U.S. EPA acid and base-neutral priority pollutants. The above listing includes only those compounds that were positively identified.

TABLE 23 TRACE ORGANICS (NON-PRIORITY POLLUTANTS) IN FLUIDIZED BED PROCESS EFFLUENTS

	Experimental Run/Date							
Compound (µ g/L)	SS1* 11/12/80	SS2* 11/02/81	SS2* 12/02/81	SS2* 13/12/81	SS3* 1/04/81	SS4* 12/05/81	V.F.** 24/11/81	V.F.** 7/01/82
Benzonitrile			tr/ND/ND***					
3, 4 dimethyl pyridine	4	tr		2	7			< 10
Isoquinoline			5/ND/ND	1		3	10	< 10
2-methyl naphthalene			tr/3/10					
Indole		tr	tr/ND/ND	tr			20	
2 and/or 8-methyl quinoline	tr	27	tr/ND/tr	2	3	2	< 10	< 10
"7A"-methyl quinoline	28		tr/14/28	24	tr	1		
"7B"-methyl quinoline		3						
2, 6 and/or 2, 7 dimethyl quinoline	3	3	tr/1/2	3	2	tr	< 10	< 10
2, 4 dimethyl quinoline		tr	tr/2/3	4	3	3	< 10	< 10
3, 4 and/or 5, 6 benzoquinoline			tr/ND/tr			tr		
Carbazole			tr/ND/ND			tr	10	
2, 6 dimethyl pyridine						tr		
Thiophenol								
3, 5 dimethyl pyridine	2	2		2	tr	3		
Quinoline						1	20	< 10
1-methyl naphthalene			tr/ND/5					
4-methyl quinoline			tr/ND/ND			tr		
Dibenzofuran			tr/ND/ND					
7, 8 benzoquinoline			ND/ND/tr			tr	< 10	
9-anthracenecarbonitrile	tr	tr	ND/4/6		tr	tr	10	< 10
aniline							< 10	

* Refers to steady run number (Table 11)
** Variable Feed Operation
*** Analysis in triplicate
tr< 1.0 µ g/L
ND - Not Detected

Of the base/neutral group of priority pollutants, only four compounds were identified at greater than trace concentrations in more than one treated effluent sample. Two of these compounds were phthalate esters (di-n-butylphthalate and bis-(2-ethylhexyl) phthalate). These phthalate esters were also consistently quantified in the raw process feed and were noted by U.S. EPA (36) to be commonly present in by-product coke plant wastewaters. Batch biodegradability studies (110, 111) conducted by U.S. EPA have shown that all priority pollutant phthalate esters were significantly degraded but bis-(2-ethylhexyl) phthalate was one of the most bio-resistant. Phthalate esters are common plasticizers and the consistent presence of these compounds at low levels in the raw and treated wastewater may indicate contamination of the samples. Although care was taken during sample collection to prevent contact with plastic materials, many components of the pilot plant itself were plastic. Other base/neutral extractable priority pollutants identified in more than one treated effluent samples were anthracene/phenanthrene and nitrobenzene. Anthracene was also identified by Bridle et al (2) in the treated effluent from suspended growth systems treating coke plant wastewater. Nitrobenzene was not identified in any of the feed samples, but could be a reaction product of the oxidation of aniline, which was identified in the feed.

Of the non-priority pollutant base/neutral extractable compounds analyzed in the treated effluent, ten compounds were found at greater than trace concentrations in more than one sample. None of these compounds were detected at levels higher than 30 μg/L despite reported influent concentrations of more than 1 mg/L. Although direct comparison of influent and effluent concentrations is questionable due to the analytical difficulties encountered in analyzing the influent samples, it appears that the biological fluidized bed process is capable of effecting a high degree of contaminant control on the basis of the order of magnitude differences in influent and effluent trace organic contaminant concentrations.

Analytical results generated by GC/MS analysis of fluidized bed reactor sludge samples are presented in Tables 24 (U.S. EPA priority pollutants) and 25 (non-priority pollutant base/neutral extractable compounds). Phenol was not detected at levels in excess of 1 μg/g in the biomass samples. Of the base/neutral priority pollutants, five compounds were quantified at greater than trace concentrations in more than one sample.

Three of these compounds were phthalate esters (di-n-butylphthalate, diethylphthalate and bis-(2-ethylhexyl) phthalate) which accumulated in the sludge at concentrations between 10 and 30 μg/g. Bridle et al. (2) reported similar concentrations of these phthalate esters in biomass from suspended growth reactors treating coke plant

TABLE 24 TRACE ORGANICS (U.S. EPA PRIORITY POLLUTANTS) IN FLUIDIZED BED REACTOR SLUDGES

	Sample/Date										
Compound (µg/g)	DN Reactor Biomass 11/12/80	DN Reactor Sand/ Biomass 23/01/81*	DN Reactor (0.4 m) Sand/ Biomass 12/02/81	NIT Reactor (3.8 m) Sand/ Biomass 12/02/81	DN Reactor (2.0 m) Sand/ Biomass 13/02/81	DN Reactor Sand/ Biomass 1/04/81	NIT Reactor Sand/ Biomass 1/04/81	DN Reactor Biomass 20/10/81	NIT Reactor Biomass 20/10/81	DN Reactor Biomass 20/01/82	NIT Reactor Biomass 20/01/82
ACID GROUP											
Phenol	0.5	tr/ND			tr		tr	tr		1	
BASE NEUTRAL GROUP											
Polynucleear Aromatics:											
Acenaphthene					tr						
Acenaphthylene	0.8				0.2						
Anthracene/Phenanthrene		tr/tr	tr	tr	tr	tr	tr				
Benzo (b) fluoranthene					tr						
Dibenzo (ah) anthracene					tr						
Fluoranthene		ND/tr			tr		tr				<0.1
Fluorene					tr						
Pyrene	1	tr/0.2	0.2	tr	0.5	tr	tr			2	
Chlorinated Benzenes:											
1,2-Dichlorobenzene					tr		tr				
1,4-Dichlorobenzene or 1,3-Dichlorobenzene						tr					
Nitrosamines:											
N-nitrosodimethylamine				tr							
N-nitrosodiphenylamine		ND/0.2					tr				
Phthalate Esters:											
Di-n-butylphthalate	5	0.2/0.3	0.7	0.3	0.6	1	0.7	4	34	16	10
Diethylphthalate	0.4	tr/tr	tr	tr	tr	tr	tr			5	5
Dimethylphthalate		tr/tr	tr		tr	tr	tr				
Di-n-octylphthalate					tr						
bis-(2-ethylhexyl)phthalate		0.1/0.2	0.3	0.2	0.9	tr	0.2		13		3
Haloethers:											
4-Bromophenyl phenyl ether					tr						
Other Compounds:											
Benzidine		ND/10	tr								
Isophorone		tr/tr	tr	tr	tr	tr	tr				

* Analysis in duplicate

tr<0.1 µg/g

ND - Not Detected

Note: The samples were screened for all the U.S. EPA acid and base-neutral priority pollutants. The above listing includes only those compounds that were positively identified.

TABLE 25 TRACE ORGANICS (NON-PRIORITY POLLUTANTS) IN FLUIDIZED BED REACTOR SLUDGES

	Sample/Date								
Compound (µg/g)	DN Reactor 11/12/80	DN Reactor 23/01/81*	DN Reactor 12/02/81	NIT Reactor 12/02/81	DN Reactor 13/02/81	DN Reactor 1/04/81	NIT Reactor 1/04/81	DN Reactor 20/1/82	NIT Reactor 20/1/82
Benzonitrile	ND								ND
2-methyl naphthalene	ND							tr	ND
Indole	ND	tr/ND	tr		tr				ND
2 and/or 8-methyl quinoline*	ND				tr				ND
"7A"-methyl quinoline	ND				0.1				ND
2, 6 and/or 2, 7 dimethyl quinoline*	ND				tr				ND
2, 4 dimethyl quinoline	ND				tr				ND
Carbazole	ND	tr/ND	tr		0.2	tr			ND
2, 6 dimethyl pyridine	ND	tr/ND			0.1				ND
Quinoline	ND					tr			ND
Dibenzofuran	ND				tr			tr	ND
7, 8 benzoquinoline	ND		tr		tr				ND
9-anthracenecarbonitrile	ND	tr/tr	tr	tr	tr	tr	tr		ND
aniline	ND								ND

* Analysis in duplicate

tr<0.1 µg/g

ND - Not Detected

Note: The samples were examined for all the pollutants listed in Table 21. The above data show only those compounds that were positively identified.

wastewater. Other base/neutral priority pollutants consistently identified in the sludges were acenaphthylene and pyrene, found at concentrations up to 2 μg/g. Pyrene was also reported by Bridle et al. (2) at similar concentrations in suspended growth sludges. None of the non-priority pollutant base/neutral extractable compounds were consistently identified at greater than trace levels (0.1 μg/g). Bridle et al. (2) reported significant accumulations of several heterocyclic nitrogenous compounds in sludges, but the concentrations of these compounds were not quantified. There were insufficient data for trace organic concentrations in the individual sludges from the denitrification and nitrification reactors to identify differences in the relative concentrations in the separate sludges.

4 FLUIDIZED BED TREATMENT OF COMBINED COKE PLANT WASTEWATER AND BLAST FURNACE BLOWDOWN WATER

4.1 Pilot Plant Description

The pilot plant equipment utilized for the treatment of the combined coke plant wastewater and blast furnace blowdown stream was essentially the same as that used for the treatment of coke plant wastewater alone. Detailed descriptions of the pilot plant facilities and the sampling and analytical methodologies were provided in Sections 3.1 and 3.3.

A process flowsheet of the coupled biological fluidized bed plant was presented in Figure 4. The system was designed to operate as a two-stage separate sludge predenitrification-nitrification system to effect phenol oxidation, thiocyanate oxidation, cyanide removal and complete nitrogen control in separate anoxic and oxygenic biological reactors.

The anoxic denitrification reactor was cylindrical, 150 mm in diameter and 4.3 m in height. Fluidized bed height was controlled at approximately 2.2 m, equivalent to an empty bed reactor volume of approximately 31 L, although some variation in reactor height was allowed, depending on operating conditions. The reactor had a conical inlet design to improve influent flow distribution.

The oxygenic nitrification reactor was also cylindrical, 290 mm in diameter and 4.3 m in height. Fluidized bed height was controlled at approximately 3.9 m, equivalent to an empty bed reactor volume of approximately 210 litres. The nitrification reactor had a downflow inlet design to reduce turbulence and shear in the reactor. Pure oxygen was supplied to the reactor through a downflow oxygen contactor provided by Dorr-Oliver Inc. Oxygen supply was automatically controlled by an analog PID feedback controller in response to effluent dissolved oxygen concentration.

Tankage and pumps were provided to recycle treated effluent to the anoxic reactor and the oxygenic reactor as required to maintain fluidization of the reactors, to return nitrified effluent for denitrification and ensure adequate oxygen transfer for the biological processes. A primary clarifier was included in the process flow sheet but was not found to be necessary for efficient pilot plant operation.

The pilot plant included feed systems to supply phosphoric acid as a biological nutrient, sodium bicarbonate for pH control and as a source of supplemental alkalinity for the nitrification reactions, and methanol as a supplemental carbon source for the denitrification reactions. Temperature control was provided to maintain the reactors in the range from 25°C to 30°C.

The support media in both reactors was quartzite sand with an effective size (d_{10}) of 0.48 mm and a uniformity coefficient (d_{60}/d_{10}) of 1.23.

4.2 Pilot Plant Feed

Coke plant wastewater was obtained from the byproduct coke plant at Dofasco Inc. in Hamilton, Ontario. The wastewater consisted of ammonia still wastewater obtained from the settling sump of a free and fixed-leg still treating excess flushing liquor from the coke oven operation plus a small flow of fractionator bottoms from the Phosam plant.

Blast furnace blowdown water was obtained from a second integrated steel mill which included four blast furnaces (B, C, D and E) served by two separate gas cleaning water recirculation systems (BCD system and E system). Samples were obtained from both water recirculation systems during the pilot plant study. Recirculation system BCD was initially operating at a blowdown rate of approximately 50 percent, but during the six-month investigation, blowdown in the BCD system was reduced to approximately 15 percent. Recirculation system E operated at a blowdown of approximately 15 to 20 percent throughout the study.

Feed samples for the fluidized bed pilot plant were collected on a batch basis in volumes of approximately 7 m^3 per batch, mixed in the desired proportions and stored in an insulated holding tank at the WTC. In addition to the large batches utilized as feed for the pilot plant, grab samples of blast furnace blowdown water were also collected from both recirculation systems to provide additional characterization data.

4.3 Sampling and Analytical Procedures

The length of time that any batch of feed was utilized depended on the volume of wastewater collected and the pilot plant operating conditions. During the six months of plant operation, five separate feed batches were used. The duration of use for each batch varied from more than two months to less than three weeks.

Typically, the individual components of the feed (coke plant wastewater and blast furnace blowdown water) were sampled and analyzed at the time of delivery to the WTC. The actual mixed pilot plant feed was sampled weekly and analyzed for filterable organic carbon (FOC), phenolic compounds, total and filterable Kjeldahl nitrogen (TKN), ammonia nitrogen (NH_3-N), total cyanide (TCN) and cyanide amenable to chlorination (CN_A), thiocyanate (CNS) and total and filterable chemical oxygen demand (COD).

Daily samples of treated process effluent (nitrification reactor effluent) were collected and analyzed for NH_3-N, nitrate (NO_3-N) and nitrite (NO_2-N) nitrogen and total (TSS) and volatile suspended solids (VSS). Effluent FOC, TKN and phosphorus were determined five times per week and other parameters (COD, CNS, TCN, CN_A and phenolics) were determined three times per week.

Performance of the denitrification reactor was monitored by daily analysis of reactor effluent samples for oxidized nitrogen species (NO_2N and NO_3N). Concentrations of FOC, TKN, TSS and VSS were determined five times per week in the denitrification reactor effluent.

The concentration of biomass, measured as volatile solids, in each reactor was measured once per week. The quantity of biomass wasted from each reactor was routinely monitored to allow calculation of system SRT (solids retention time). Liquid samples were also obtained from various positions within the reactors and analyzed for nitrogen species (TKN, NH_3-N, NO_2-N and NO_3-N) to define concentration profiles within the reactors. Dissolved oxygen measurements were made in situ at each location.

All analyses were conducted at the Wastewater Technology Centre according to standard procedures (103).

In addition to sampling and analysis of conventional contaminants, influent and treated effluent samples were collected and analyzed for trace organic contaminants by gas chromatography/mass spectroscopy (GC/MS). These analyses included quantification of acid extractable and base-neutral extractable U.S. EPA organic priority pollutants as well as 24 base/neutral extractable compounds not included in the U.S. EPA priority pollutant listing but previously identified in coke plant wastewaters. All procedures used for trace organic analyses are available from the Wastewater Technology Centre.

4.4 Performance Evaluation

The pilot plant was operated for approximately six months treating the combined coke plant wastewater and blast furnace blowdown. The process loading on the biological reactors was progressively increased to determine the minimum reactor hydraulic retention times required to maintain nitrification of the combined wastewater and to achieve a treated effluent quality comparable to that attained during treatment of coke plant wastewater. Due to the short term of the experimental program, biological steady state conditions (in terms of SRT) were not attained in the process after step changes in the hydraulic loading.

During the six-month investigation, significant periods of process instability occurred in both the denitrification and nitrification systems due to changes in feed quality (FOC/TN ratio and zinc concentration) and process operating conditions. Therefore, the performance data in terms of the removal of conventional organic contaminants, thiocyanate and cyanide (Section 4.4.2), the denitrification efficiency (Section 4.4.3) and the nitrification efficiency (Section 4.4.4) are reviewed separately. A schedule indicating the periods of stability for the individual reactors and for the overall process is provided in Figure 21.

Removal of FOC, phenolic compounds, thiocyanate and cyanide was found to be virtually unaffected by feed quality or operating conditions. Therefore, the process performance was based on data collected over the entire operating period (196 consecutive days).

Because periods of stable nitrification and denitrification did not necessarily occur simultaneously, as indicated in Figure 21, it was difficult to define extended periods of pseudo-steady state performance for the coupled system. The primary factor affecting stability in the denitrification system was the ratio of FOC/TKN in the feed. During the first three months of pilot plant operation, considerable experimentation was conducted to establish the required FOC/TKN ratio. This experimentation adversely affected the performance of the nitrification system. Elevated zinc levels in the combined wastewater appeared to affect nitrification efficiency but had no apparent effect on denitrification performance. As discussed in Section 4.4.4, the performance of the nitrification system can be assessed in terms of seven pseudo-steady state operating periods shown in Figure 21. Stable denitrification was also achieved during three of these periods (periods 2, 3 and 6). During period 2, methanol was being added to the system to supplement the carbon content of the feed. During periods 3 and 6, no supplemental methanol was added. These three periods of operation were the primary basis for the assessment of denitrification performance discussed in Section 4.4.3.

4.4.1 Feed Characteristics.

Five different batches of feed were applied to the fluidized bed process. Grab samples from both blast furnace recirculation systems were also collected to provide additional characterization data.

The quality of the individual batches of coke plant wastewater used in the combined feed to the pilot plant is summarized in Table 26. As indicated in Table 26, the

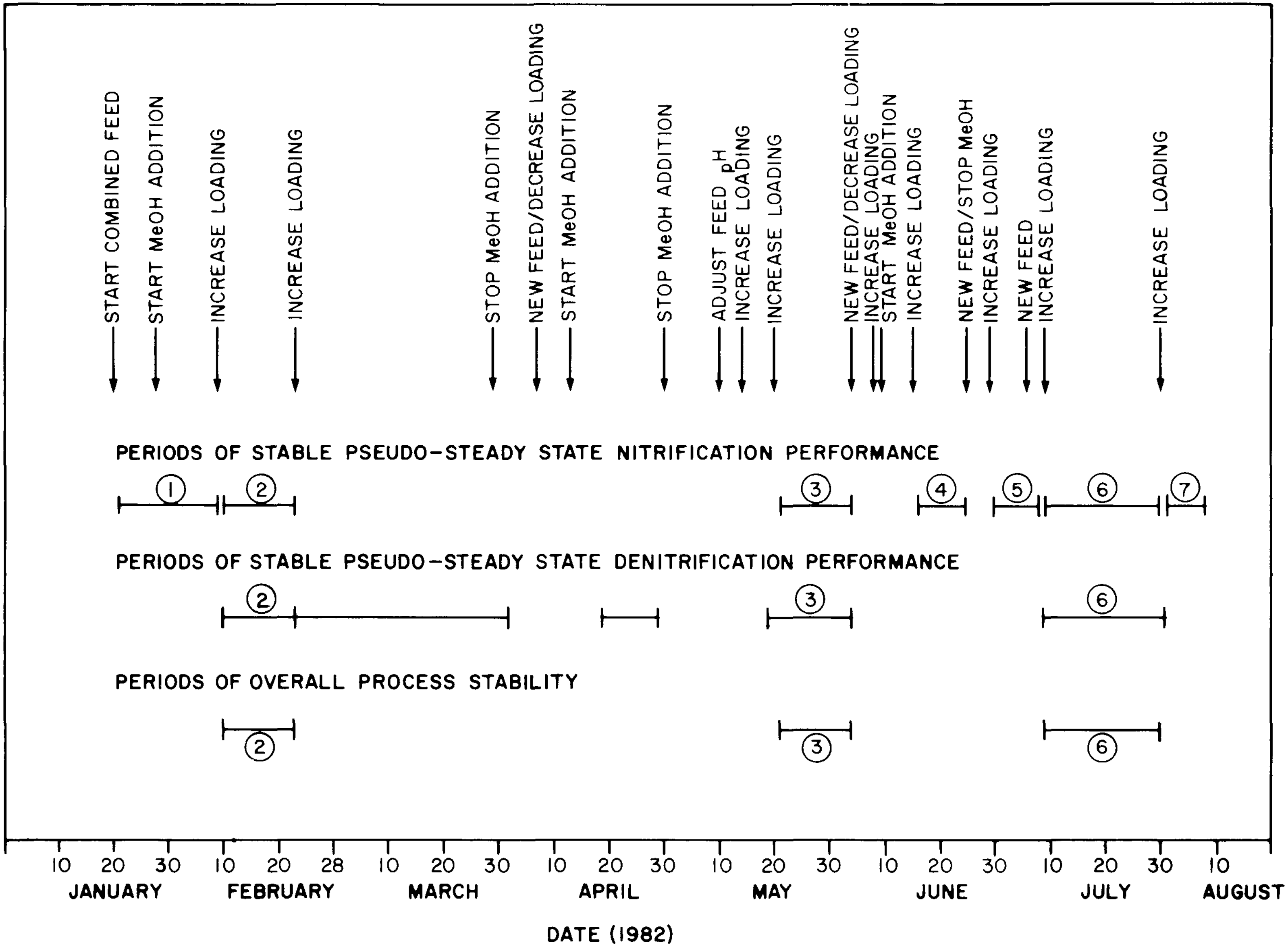


FIGURE 21 SCHEDULE OF EVENTS AND PROCESS OPERATING CONDITIONS - COMBINED WASTEWATER TREATMENT

TABLE 26 CHARACTERISTICS OF COKE PLANT WASTEWATERS

Sample Date	Parameter (mg/L)												
	COD	FOC	Phenolics*	TKN	NH_3-N	TCN	CN_A**	CNS	Ca	Zn	Fe	Ni	Pb
19/01/82	2432	675	327	197	87.7	8.94	-	342	632	0.58	1.8	0.01	0.06
7/04/82	2047	505	280	258	129.4	5.18	5.06	232	1345	0.27	3.8	<0.01	0.04
3/06/82	1780	413	230	508	384.0	0.80	0.04	290	662	0.65	6.5	0.02	0.08
24/06/82	2190	538	340	272	157.0	6.21	-	258	1264	0.16	5.3	<0.01	0.25
5/07/82	2470	621	325	300	158.0	3.70	1.97	329	2000	0.42	3.2	0.06	0.07
Average	2184	550	241	307	183.2	4.97	2.36	290	1180	0.42	4.1	<0.02	0.10
Coke Plant Wastewater Study	2173	693	391	289	176.0	7.07	-	252	-	-	-	-	-

* Phenolics refers to the total phenol concentration as determined by the 4-AAP determination (103).

** CN_A - Cyanide amenable to chlorination coke plant wastewaters used in the combined feed were similar to those used during the treatment of coke plant wastewater alone in terms of the concentrations of nitrogen compounds (TKN and NH_3) and thiocyanate. However, the concentration of organic contaminants, measured as COD, FOC and phenolics compounds, was lower during this investigation. The quality of the coke plant wastewater could have been affected by the longer coking times being used at Dofasco during this study.

The characteristics of the blast furnace blowdown waters from the two recirculation systems are shown in Table 27. Concentrations of organic contaminants as measured by COD and FOC were similar; however, the concentration of phenolic compounds was significantly higher in samples from the BCD system, due to elevated levels in four samples. All four of these samples were obtained from a tank truck upon delivery of a batch of blowdown water to the WTC. As the truck had previously been used to transfer coke plant wastewater, contamination of the blast furnace water with residual coke plant wastewater was probably responsible for the high concentrations.

The recirculation system on blast furnace E had significantly higher concentrations of nitrogenous compounds (TKN and NH_3-N), as would be expected due to the lower blowdown rate practised in the E system. The effect of decreasing the blowdown rate in the BCD system is apparent. When the first sample was collected from that system (13 January 1982), it was operating at approximately 50 percent blowdown. Subsequently, the blowdown was reduced to approximately 20 percent with a resultant increase in the concentration of nitrogen (TKN and NH_3-N) in the recirculation water to levels between 20 and 40 mg/L.

System BCD also contained significantly higher concentrations of cyanide (TCN and CN_A). In both systems, the fraction of the total cyanide that was amenable to chlorination exceeded 90 percent. Thiocyanate was also significantly higher in system BCD; however, as was the case for the phenolic results, the average thiocyanate concentration in BCD system is biased by elevated concentrations in three of the four tank truck samples and may represent the effect of contamination from the coke plant wastewater.

The concentration of zinc was consistently higher in blowdown from the BCD furnace recirculation system, indicative of the effects of sinter, a prepared feed material composed of iron oxide and scale, on the blast furnace operation.

The characteristics of the fluidized bed pilot plant feed during the six-month study are shown in Table 28. Ratios of blast furnace blowdown water to coke plant

TABLE 27 CHARACTERISTICS OF BLAST FURNACE BLOWDOWN WATER

Recirculation System	Sample Date	Parameter (mg/L)												
		COD	FOC	Phenolics	TKN	NH_3-N	TCN	CN_A	CNS	Ca	Zn	Fe	Ni	Pb
BCD Furnaces	13/01/82	49	5.6	0.18	11.1	6.7	4.44	4.34	-	55	10.0	7.4	0.10	0.33
	26/03/82	47	6.3	-	20.7	18.5	-	-	-	92	30.0	1.6	<0.01	0.15
	31/03/82	-	-	-	23.5	18.1	-	-	-	110	33.0	2.1	<0.01	0.18
	5/04/82	43	7.8	-	23.8	18.5	-	-	-	107	43.0	3.9	<0.01	0.25
	7/04/82	249	28.0	6.00	33.5	19.4	10.63	10.56	6.5	157	36.0	11.0	<0.01	0.41
	7/04/82	190	14.0	1.13	26.3	18.8	10.57	10.17	0.9	-	-	-	-	-
	15/04/82	-	-	-	28.0	17.1	-	-	-	98	17.0	3.6	<0.01	0.18
	29/04/82	-	8.3	-	-	28.3	-	-	-	104	26.0	1.9	<0.01	0.14
	19/05/82	199	9.0	0.21	30.5	24.3	4.63	4.53	0.6	104	17.0	1.7	<0.01	0.20
	31/05/82	250	5.3	0.30	32.3	25.8	0.52	0.46	0.6	85	5.1	4.8	<0.01	0.17
	3/06/82	134	23.0	13.0	45.2	39.8	3.07	2.88	6.8	109	6.9	1.1	<0.01	0.08
	24/06/82	133	24.0	20.0	34.9	27.7	4.77	-	7.1	135	17.0	2.3	0.01	0.20
	5/07/82	66	9.9	0.28	28.5	24.7	3.66	3.50	0.5	113	2.6	4.0	0.01	0.10
AVERAGE BCD	-----	136	10.5	5.14	28.2	22.1	5.30	5.21	3.3	106	20.3	3.2	<0.01	0.28
E Furnace	13/01/82	186	6.5	0.09	21.3	16.8	1.54	1.30	1.6	81	9.4	66.0	0.03	1.38
	20/01/82	77	12.2	0.08	30.8	26.0	2.35	2.25	2.2	93	3.7	10.3	0.03	0.28
	5/04/82	51	5.0	-	38.0	27.6	-	-	-	-	-	-	-	-
	31/05/82	220	6.3	0.05	56.9	48.5	0.92	0.82	1.2	85	5.1	4.8	<0.01	0.17
	21/06/82	-	11.0	-	53.0	48.0	-	-	-	-	-	-	-	-
AVERAGE E	-----	134	8.2	0.07	40.0	33.4	1.60	1.46	1.7	86	6.1	27.0	0.03	0.61

TABLE 28 CHARACTERISTICS OF COMBINED FEED TO THE FLUIDIZED BED PILOT PLANT

Feed Composition Ratio BFBD:CPWW*		Parameter (mg/L except pH)														
		pH**	COD	FOC	Phenolics	TKN	NH_3-N	TCN	CN_A	CNS	Alk. (as $CaCO_3$)	Ca**	Zn**	Fe**	Ni**	Pb**
2:1	Average	-	950	251	139	102.	51.9	2.15	6.72	114.	267.	532	2.38	2.27	0.03	0.03
	Std. Dev.	-	299	56	32	16.8	3.9	1.25	0.88	31.9	25.0	223	3.28	3.42	0.07	0.02
	Max.	7.8	1650	367	200	132.	56.8	5.50	2.98	168.	316.	992	7.94	15.0	0.30	0.06
	Min.	7.1	551	168	103	72.	43.2	0.74	0.00	68.	218.	265	0.08	0.20	0.01	0.01
3:1	Average	-	535	152	90	129.	91.9	1.13	0.25	67.2	238.	298	1.48	0.94	0.01	0.02
	Std. Dev.	-	90	19	17	29.3	28.4	1.12	0.47	21.1	69.0	129	1.09	0.63	0.01	0.01
	Max.	7.8	621	182	110	177.	142.	4.12	1.63	85.	410.	481	3.11	2.1	0.02	0.03
	Min.	7.4	270	126	57	99.	68.	0.20	0.00	62.	128.	181	0.13	0.27	<0.01	<0.01
Overall	Average	-	799	215	119	111.	66.4	1.78	0.54	98.1	257.	438	2.02	1.74	0.02	0.02
	Std. Dev.	-	316	66	36	25.2	25.9	1.29	0.78	32.7	58.6	192	2.82	2.91	0.05	0.01
	Max.	7.8	1650	367	200	177.	142.	5.50	2.98	168.	410.	992	7.94	15.0	0.30	0.06
	Min.	7.1	270	126	57	72.	43.2	0.20	0.00	62.	128.	181	0.08	0.20	<0.01	<0.01

* Blast Furnace Blowdown: Coke Plant Wastewater (ratio by volume)

** Unadjusted feed pH and metal concentrations.

wastewater of 2:1 and 3:1 (by volume) were used during the study to cover the range of conditions anticipated at full-scale at Dofasco. A ratio of 2:1 was used during the first four months and a ratio of 3:1 was used during the final two months of plant operation. Blowdown water from system E was used in the first mixed batch of feed covering the first 3 1/2 months of plant operation as system E contained a significantly higher nitrogen concentration than system BCD. All subsequent feed batches contained blowdown water from recirculation system BCD.

As would be expected based on the characteristics of blast furnace blowdown water and coke plant wastewater, the feed containing more coke plant wastewater had significantly higher concentrations of organic contaminants (COD, FOC and phenolic compounds). However, the concentrations of nitrogenous compounds (TKN and NH_3-N) were actually higher in feeds containing less coke plant wastewater. This relates directly to the concentrations of these compounds in the coke plant wastewater batches used to prepare these feeds (Table 26).

Overall, the pilot plant feed contained an average concentration of total nitrogen of 111 mg TKN/L, and an average concentration of organics of 215 mg FOC/L, equivalent to an FOC/TKN ratio of approximately 2. This is considerably lower than that found necessary for complete denitrification of coke plant wastewater in previous studies.

The variability data presented in Table 28 represent the variation in feed quality to the pilot plant during the study. They do not represent the actual variability of feed to an on-line system at an actual steel mill. Storage time for individual feed batches varied from three to eleven weeks. There was relatively little change in feed quality upon extended storage for most conventional contaminants with the exception of cyanide.

Data illustrating the effect of storage on feed quality for one specific feed batch is shown in Figure 22. The concentration of cyanide compounds amenable to chlorination (CN_A) was significantly reduced upon storage. The total cyanide concentration showed a parallel decline indicating that, during storage, the fraction of non-biodegradable cyanide compounds, such as those complexed with iron, represented a progressively higher fraction of the total cyanide present in the feed.

4.4.2 Removal of Organic Compounds, Thiocyanate and Cyanide in the Fluidized Bed Process. Prior to this evaluation, the coupled fluidized bed system had been operated for more than two years treating coke plant wastewater. Thus, when the initial batches of blast furnace blowdown water and coke plant wastewater were obtained, the denitrification and nitrification reactors were completely seeded with active biomass at a

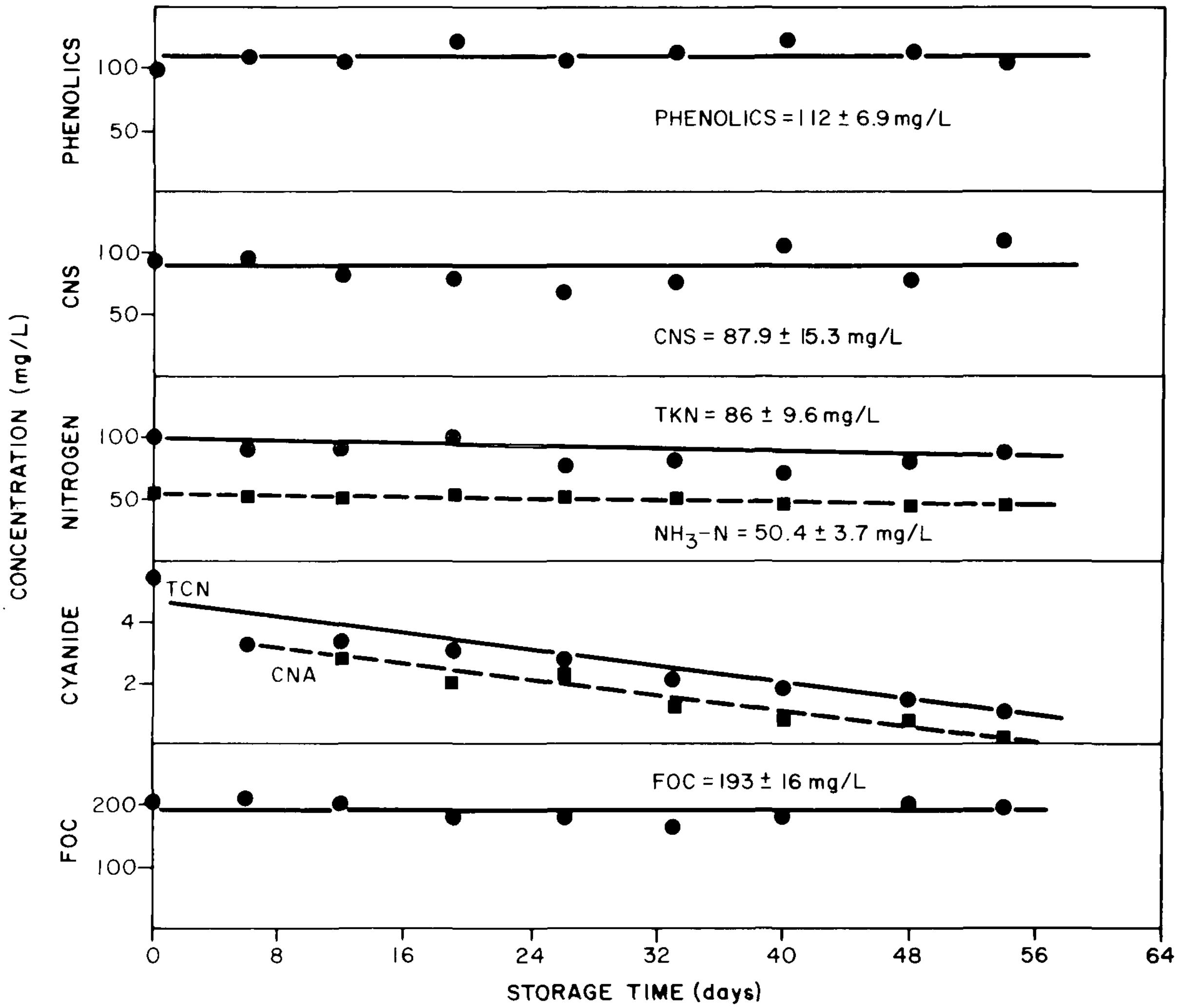


FIGURE 22 EFFECT OF STORAGE TIME ON FEED QUALITY

concentration of approximately 20 g VS/L. Extended start-up and acclimation periods were not required and, upon receipt of batches of wastewater, feed to the process was initiated at a low rate and subsequently increased step-wise over the six-month investigation.

The addition of blast furnace blowdown water had no apparent effect on the operation of the biological processes in terms of the removal of organic carbon (FOC and phenolic compounds), thiocyanate and cyanide (TCN and CN_A). Monitoring of process performance commenced immediately. In terms of all of these parameters, stable process performance was maintained throughout the study despite step changes in process loading, mechanical problems, and reductions in nitrification efficiency resulting from changes in oxidizable nitrogen loading and in wastewater characteristics. The performance of the system in terms of these parameters (FOC, phenolic compounds, CNS, TKN and CN_A) is summarized in Table 29.

Table 30 compares the effluent quality attained based on 196 days of operation on the combined coke plant wastewater and blast furnace blowdown water with data collected for the same contaminants during 326 days of treatment of coke plant wastewater using the same pilot plant configuration. In all cases, the effluent quality attained during treatment of the combined wastewater was superior to that achieved during treatment of coke plant wastewater alone (except CN_A, for which prior data were not available).

4.4.3 Denitrification Process Performance.

The performance of the denitrification process is shown in Figure 23. Periods of stable operation based on Figure 21 are indicated in Figure 23.

Prior to the initiation of the combined feed to the system, complete denitrification was consistently being attained as is evident by the absence of oxidized nitrogen (NO_3-N and NO_2-N) in the denitrification reactor effluent. Upon initiation of the combined coke plant wastewater and blast furnace blowdown feed to the process, an immediate increase in the denitrification reactor effluent NO_T-N concentration was noted. A critical parameter controlling denitrification is the ratio of organic carbon to nitrogen in the wastewater which can be measured as the FOC/TKN ratio in the feed or, more precisely, as the ratio of FOC to total oxidized nitrogen (NO_T-N) removed in the anoxic reactor. The feed during this period contained approximately 280 mg FOC/L and 110 mg TKN/L, equivalent to an FOC/TKN ratio of 2.5. Data generated for denitrification of coke plant wastewater alone in the fluidized bed process indicated that the organic

TABLE 29 REMOVAL OF CONVENTIONAL CONTAMINANTS (FOC, CNS, PHENOLICS, TCN, CN_A) FROM COMBINED FEED BY FLUIDIZED BED PROCESS

Parameter	Feed* Average	Feed* Std. Dev.	Effluent* Average	Effluent* Std. Dev.	Percent Removal
FOC	215.0	66.0	23.0	5.6	89.3
Phenolics	119.0	36.0	0.085	0.038	>99.9
CNS	98.1	32.0	0.7	0.5	99.3
TCN	1.78	1.29	0.75	0.88	57.9
CN_A	0.54	0.78	0.12	0.27	77.8

* Concentration in mg/L based on 196 consecutive days of pilot plant operation.

TABLE 30 COMPARISON OF EFFLUENT QUALITY ACHIEVED DURING TREATMENT OF COKE PLANT WASTEWATER AND COMBINED COKE PLANT WASTEWATER/BLAST FURNACE BLOWDOWN

Parameter	Effluent Concentration (mg/L) Coke Plant Wastewater*	Effluent Concentration (mg/L) Combined Wastewater**
FOC	50.	23.
Phenolics	0.16	0.085
CNS	2.0	0.7
TCN	3.9	0.75
CN_A	N.A.	0.12

* Median concentration based on 326 consecutive days of pilot plant operation.
** Average concentration based on 196 consecutive days of pilot plant operation.
N.A. - Not analyzed

carbon requirement for denitrification was in the range of 2.8 to 3.0 times the concentration of oxidized nitrogen removed (NO_T-N). Therefore, it was suspected that the increase in effluent NO_T-N concentration was related to a carbon limitation in the denitrification system and the addition of methanol to the anoxic reactor was commenced to supplement the amount of organic carbon available in the raw wastewater. In retrospect, based on subsequent performance data, it appears that the denitrification

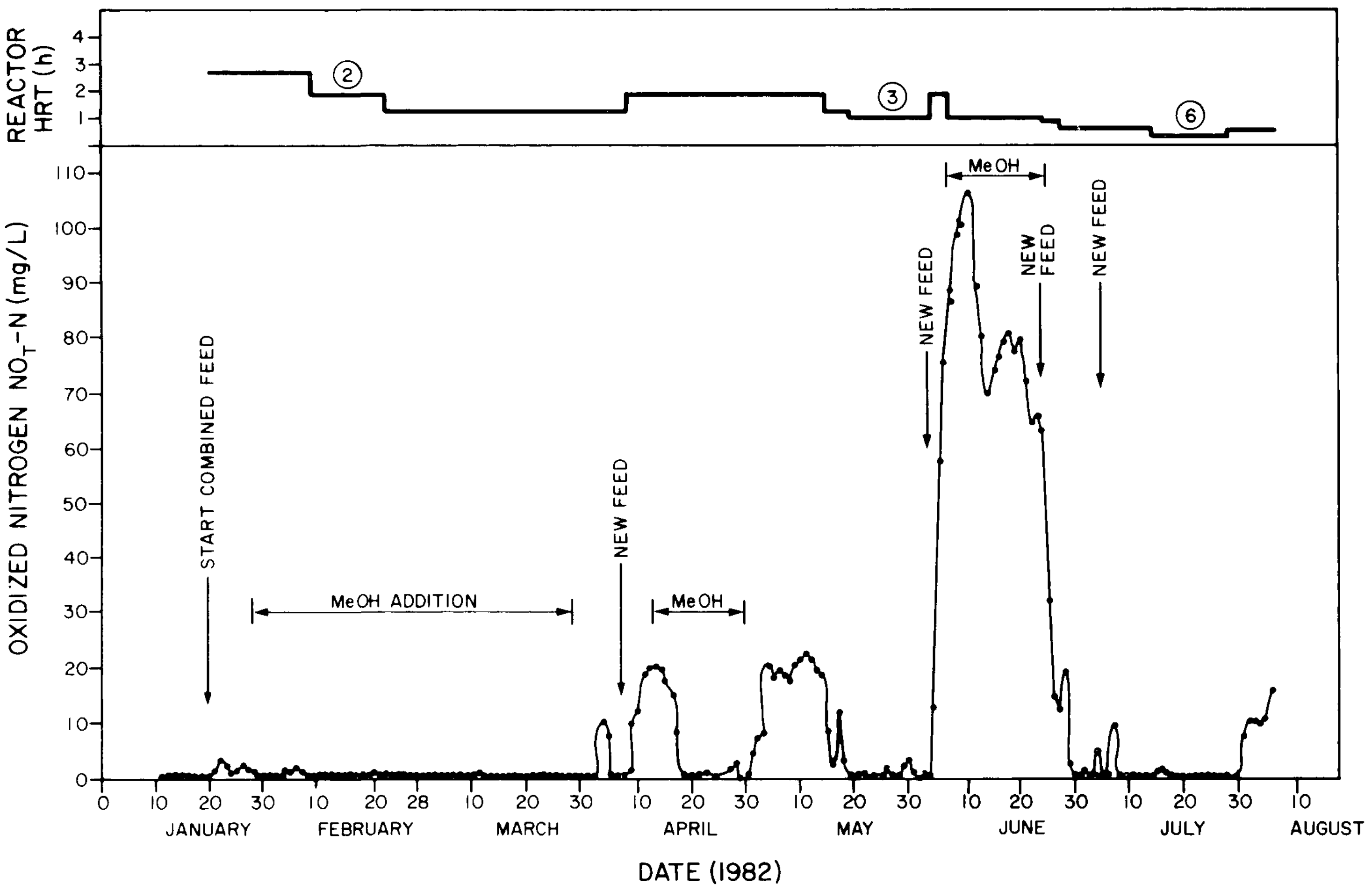


FIGURE 23 PERFORMANCE OF DENITRIFICATION SYSTEM - COMBINED WASTEWATER TREATMENT

instability was related to the change in feed characteristics which required some acclimation of the denitrifying biomass. It is probable that complete denitrification of this feed would have been attained without the addition of supplemental carbon.

Methanol addition continued for about 60 days. At this point, instability in the efficiency of nitrification, possibly related to the breakthrough of organic carbon from the anoxic bed, was identified and methanol addition was discontinued. After a short-term increase in the effluent NO_T-N concentration, during which the heterotrophic organisms responsible for denitrification reacclimated to the utilization of the wastewater organics, complete denitrification was attained despite the low FOC/TKN ratio in the feed. Unfortunately, there was insufficient feed available to allow long-term operation without methanol addition.

The second feed batch contained approximately 205 mg FOC/L and 85 mg TKN/L, equivalent to an FOC/TKN ratio of 2.4. The process responded to this feed with an increase in oxidized nitrogen concentration in the anoxic reactor effluent to approximately 20 mg NO_t-N/L. Methanol addition to supplement the organic carbon content of the feed resulted in an immediate decrease in the effluent NO_T-N concentration. Essentially complete denitrification was maintained for approximately 10 days; however, instability in nitrification efficiency continued during methanol addition (Section 4.4.4). To confirm the possible relationship between methanol addition and nitrification instability, methanol addition was stopped on April 30, 1982. After about 20 days, complete denitrification was attained and continued for the remainder of the period that this wastewater was utilized.

The last three batches of feed, which contained 75 percent blast furnace blowdown water, compared to 66 percent in the prior two feed batches, had FOC/TKN ratios of 0.80, 1.23 and 1.54, respectively. Operation at the lowest FOC/TKN ratio resulted in an accumulation of oxidized nitrogen to levels in excess of 100 mg NO_T-N/L, at which point methanol addition was initiated to prevent process inhibition. The latter two feeds, however, were completely denitrified without the addition of supplemental carbon, despite the low FOC/TKN ratios. There was a short-term increase in effluent NO_T-N concentration in response to the change in feed on July 8, 1982. The instability of the denitrification process at the end of the study (July 31 to August 5) appeared to be related to dissolved oxygen control problems during this period, which resulted in high dissolved oxygen concentrations in the anoxic reactor, rather than to carbon limitations in the process feed.

Based on feed quality, it is apparent that complete denitrification of the combined coke plant wastewater and blast furnace blowdown water was attainable at significantly lower FOC/TKN ratios than those required for similar treatment of coke plant wastewater alone. Mass balances were conducted on the anoxic reactor to determine the relative quantities of organic carbon and oxidized nitrogen removed during denitrification. The data analysis was conducted during periods of stable denitrification process performance and separate analyses were conducted for periods of supplemental methanol addition (February 10 to March 25) and periods without supplemental methanol addition (May 10 to June 3 and July 10 to July 30). The relationship between FOC and NO_T-N removal in the anoxic reactor during periods of operation without methanol addition is shown in Figure 24. Similar data generated during periods of supplemental methanol addition are shown in Figure 25. In both cases, there was considerable variability in the data because of the relatively small differences in FOC and NO_T-N concentrations across the reactors due to the high recycle rates used.

The data indicate the anoxic removal of between 0.84 and 1.26 mg FOC per mg NO_T-N removed, compared to the anoxic removal of 2.8 to 3.0 mg FOC per mg NO_T-N measured during treatment of coke plant wastewater alone. There was no significant difference in the ratio of FOC to NO_T-N removed as measured with and without the addition of methanol to the system. These data agree with the observed impact of feed quality on denitrification process performance. While feed containing an FOC/TKN ratio of 0.80 was not completely denitrified, feeds containing FOC and TKN in ratios in excess of 1.23 could be completely denitrified without supplemental carbon.

The requirement of approximately 1 mg FOC per mg NO_T-N removed during denitrification approaches the theoretical requirement (20). According to the chemical stoichiometry, the methanol requirement for denitrification is 2.47 mg CH_3OH per mg NO_3-N removed, equivalent to a carbon requirement of 0.93 mg FOC per mg NO_3-N. The requirement for removal of nitrite nitrogen is 1.53 mg CH_3OH per mg NO_2-N, equivalent to 0.57 mg FOC per mg NO_2-N. In this study, nitrite nitrogen (NO_2-N) represented from 25 to 75 percent of total oxidized nitrogen (NO_T-N) generated in the nitrification process. The significant reduction in organic carbon required to denitrify the combined wastewater compared to the requirement to denitrify coke plant wastewater cannot be explained on the basis of existing data.

Maximum specific denitrification rates in the anoxic reactor were determined based on the concentration profiles of oxidized nitrogen and volatile solids measured in

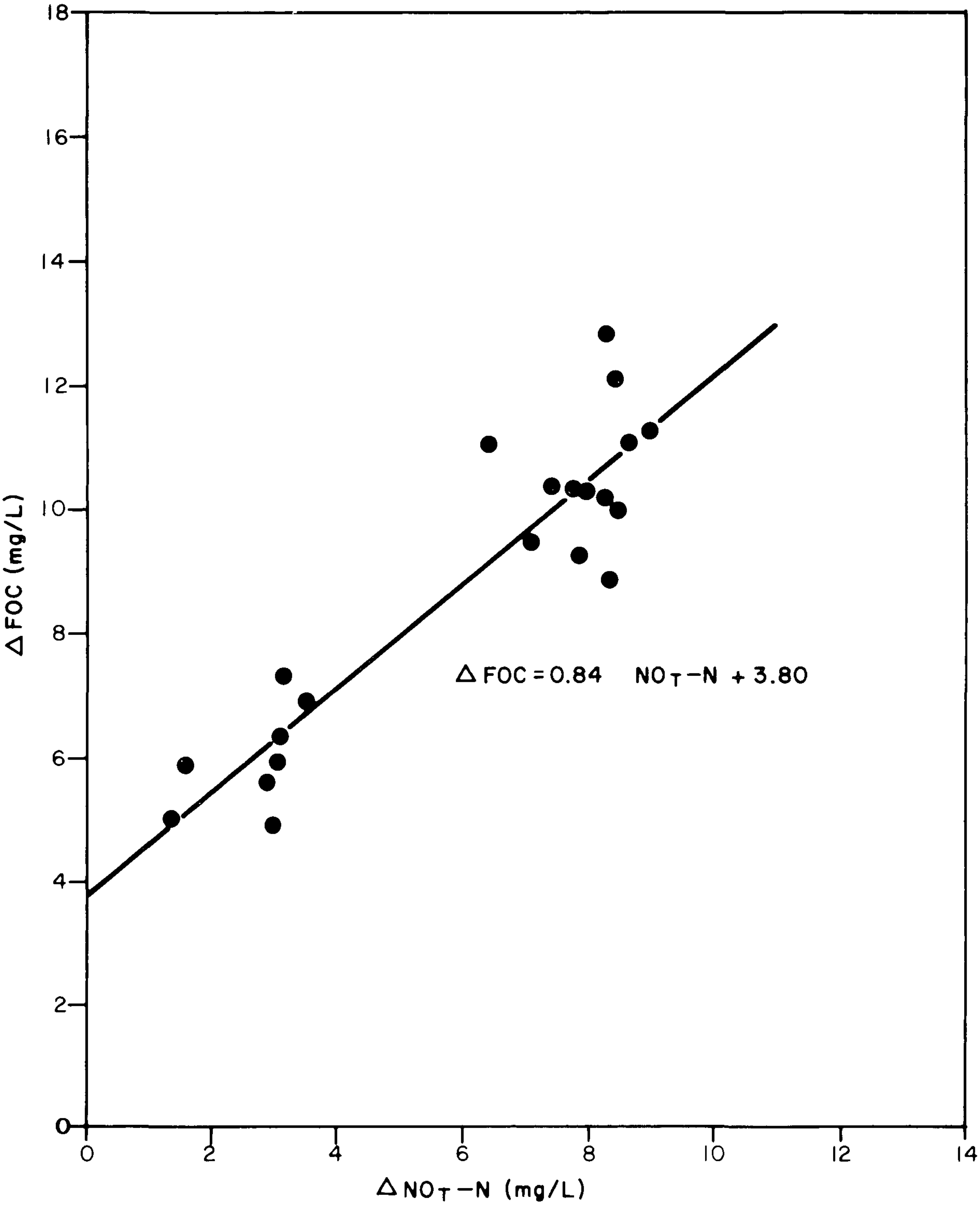


FIGURE 24 RELATIONSHIP BETWEEN ORGANIC CARBON AND OXIDIZED NITROGEN REMOVAL FOR DENITRIFICATION WITHOUT METHANOL ADDITION

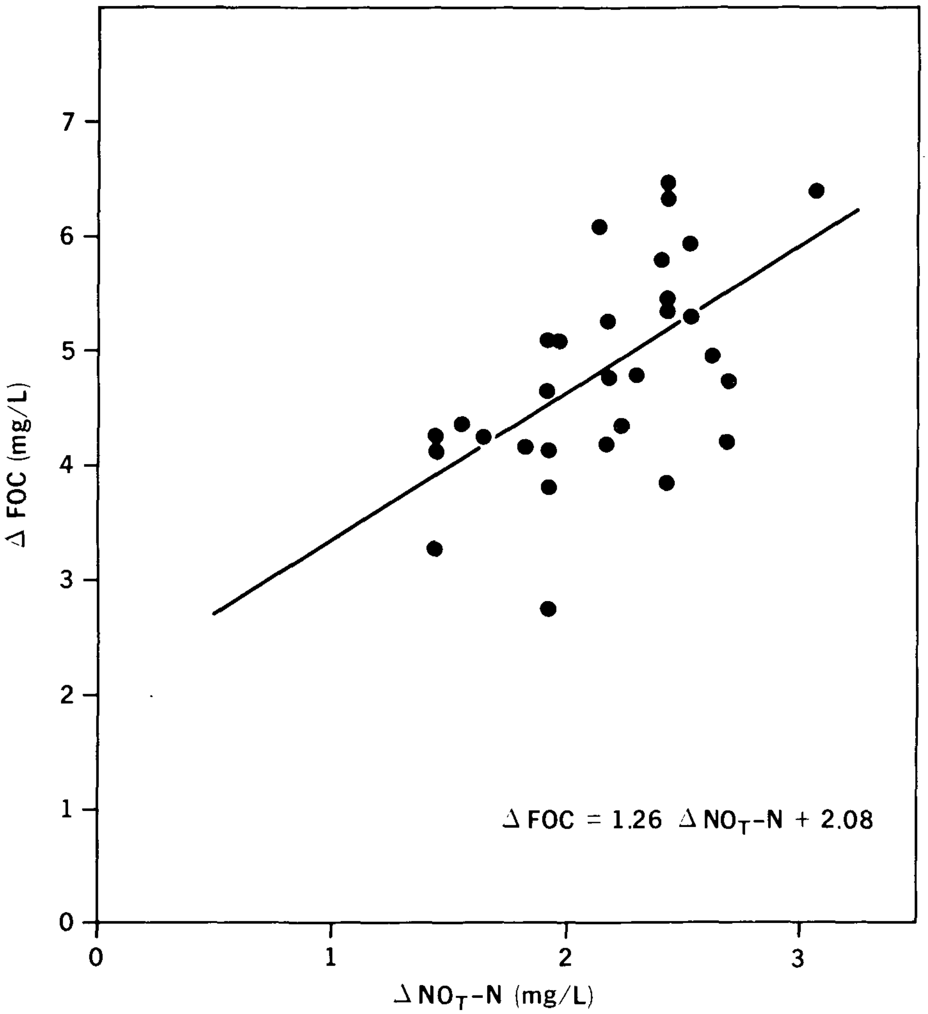


FIGURE 25 RELATIONSHIP BETWEEN ORGANIC CARBON AND OXIDIZED NITROGEN REMOVAL FOR DENITRIFICATION WITH METHANOL ADDITION

the reactor. The results are summarized in Table 31, which compares denitrification rates for the combined wastewater with and without methanol addition to the rate attained during treatment of coke plant wastewater alone. There was no significant difference between these rates at the 90 percent confidence level.

TABLE 31 MAXIMUM DENITRIFICATION RATES IN THE FLUIDIZED BED PROCESS

Feed	Carbon Source	Maximum Denitrification Rate ($g\ NO_T\text{-}N/g\ VS \cdot d$)
Coke Plant Wastewater and Blast Furnace Blowdown	Wastewater Organics	0.18 ± 0.04
Coke Plant Wastewater and Blast Furnace Blowdown	Supplemental Methanol	0.13 ± 0.03
Coke Plant Wastewater	Wastewater Organics	0.11 ± 0.10

Volatile solids concentrations in the denitrification reactor ranged from 8.9 g/L to 26.8 g/L, averaging 14.7 g/L (±4.9 g/L) over the course of the pilot plant investigation. The reactor biomass concentration progressively declined from an initial concentration of 25.2 g/L to an equilibrium concentration of approximately 11 g/L due to the low reactor loadings and resultant low biomass yields. During the final six weeks of pilot plant operation at higher loading conditions, the average denitrification reactor volatile solids concentration was 18.4 g/L.

The accumulation of inorganic deposits of tetrabasic calcium phosphate encountered during treatment of coke plant wastewater alone was not experienced to the same degree during treatment of the combined wastewater, despite operation over a similar range of SRT, probably due to the lower concentration of calcium in the combined feed. Some reduction in fluidization efficiency was noted at the completion of the study but appeared to be more related to operation at a low reactor upflow velocity (0.4 to 0.5 m/min) in the small reactor than to the accumulation of an inorganic precipitate. The poor fluidization in the reactor during this final week of operation may have contributed to the decrease in denitrification efficiency at the end of the study period as shown in Figure 23.

4.4.4 Nitrification Process Performance. The performance of the nitrification process during the six months of pilot plant operation is summarized in Figure 26. The sequential presentation of effluent ammonia nitrogen data in Figure 26 indicated periods of instability in the nitrification process efficiency when elevated concentrations of NH_3-N were present in the final effluent. This instability in the efficiency of nitrification could be related to one of three factors:

i) the unnecessary addition of supplemental carbon (as methanol) to the denitrification reactor;
ii) the presence of elevated concentrations of zinc in the process feed; and/or
iii) operation of the process at ammonia loadings in excess of the maximum specific nitrification rate of the biomass.

As indicated in Figure 26, some instability in the nitrification efficiency was experienced prior to the initiation of combined wastewater feed to the systems on January 20, 1982. Upon initiation of the combined feed at a hydraulic loading equivalent to a nitrification reactor HRT of 17.5 hours, the effluent ammonia-nitrogen concentration stabilized at approximately 1.0 mg/L. A subsequent increase in the process loading to reduce the nitrification reactor HRT to 11.7 hours had no significant effect on process performance. However, a further increase in loading to a reactor HRT of 8.8 hours resulted in a dramatic increase in the effluent NH_3-N concentration and stable performance could not be obtained despite operation at this loading for a period of approximately 35 days. The oxidizable nitrogen loading on the nitrification system during this period was approximately 0.011 g NH_3-N/g VS•d, significantly lower than the nitrification rates measured in the fluidized bed during treatment of coke plant wastewater alone. Throughout this period, methanol was being added to the system as a supplemental carbon source. On March 29, the addition of methanol was stopped. Nitrification reactor effluent NH_3-N declined dramatically from an average level of approximately 25 mg/L to approximately 1.4 mg/L within 10 days. As discussed in Section 4.4.3, supplemental carbon was not necessary to ensure complete denitrification of this wastewater. It appears that the unnecessary addition of supplemental carbon to the system may result in a break-through of carbon from the denitrification reactor to the nitrification reactor with a resultant increase in the relative fraction of heterotrophic organisms present in the biomass. The increased yield of heterotrophs would reduce the specific nitrification rate of the total biomass. Unfortunately, there was insufficient volume of this feed to allow

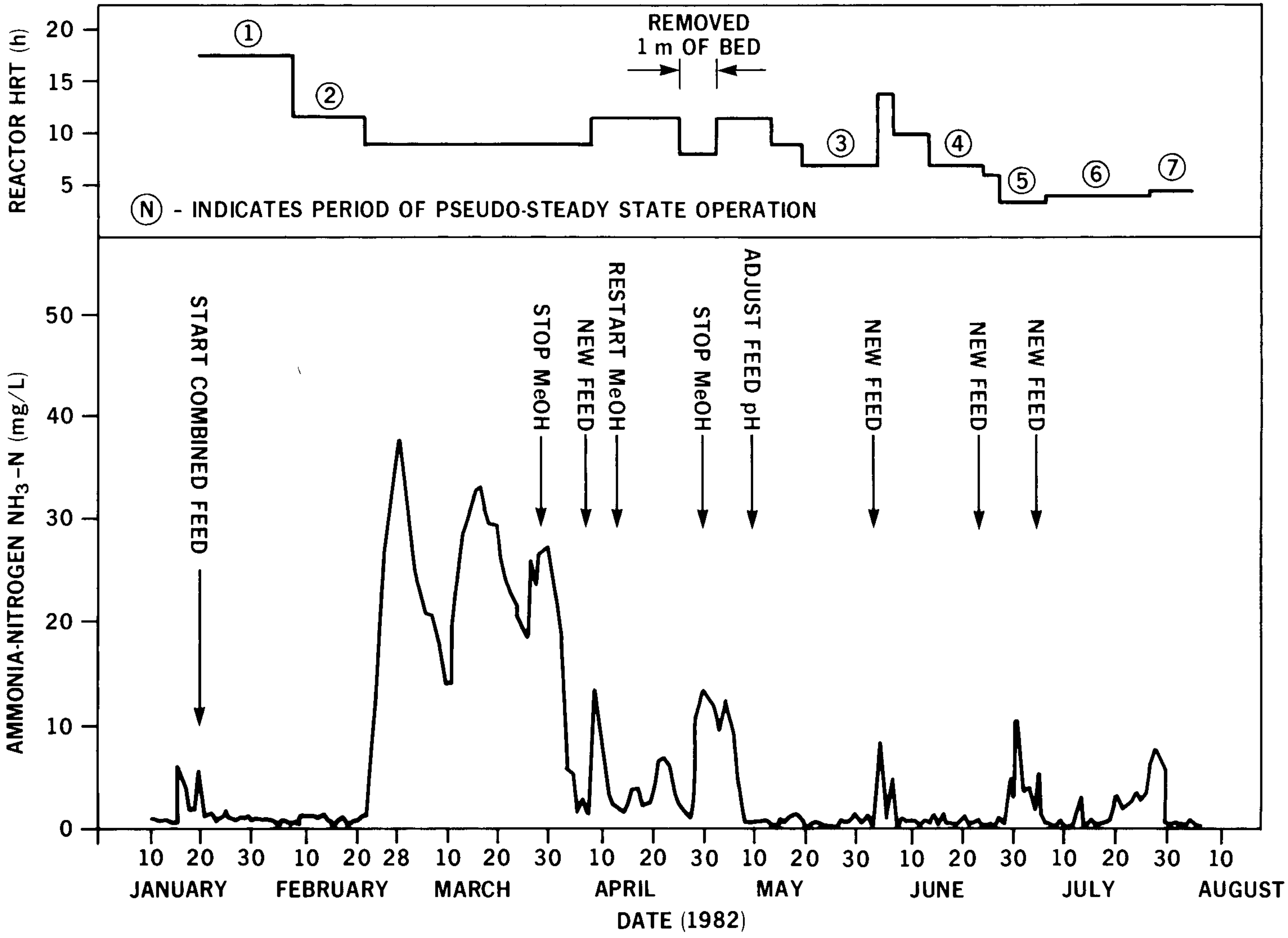


FIGURE 26 PERFORMANCE OF NITRIFICATION SYSTEM - COMBINED WASTEWATER TREATMENT

long-term operation without methanol addition to establish the maximum nitrification rate attainable.

Instability in the performance of the nitrification system continued after a new batch of feed was obtained on April 7, 1982. The oxidizable nitrogen loading applied was approximately 0.008 g NH_3-N/g VS•d during this period. As in the previous case, methanol was being added to the system to supplement what was considered to be an inadequate FOC concentration in the feed (Section 4.4.3). Stopping the addition of methanol to the reactor resulted in a significant increase in nitrification efficiency as the effluent NH_3-N concentration declined from approximately 13 mg/L to less than 1 mg/L within eight days. At the same time, analysis indicated that the zinc concentration of the feed batch being utilized was approximately 7.0 mg/L of which approximately 6.5 mg/L was present in soluble form. The literature indicates that inhibition of nitrification due to zinc can occur at concentrations as low as 1 mg/L (112). To eliminate the possibility of zinc inhibition to the nitrifiers, the pH of the feed was raised from 7.8 to 10.0 by the addition of sodium hydroxide to the storage tank to precipitate soluble zinc as zinc hydroxide. This treatment reduced the zinc concentration of the process feed to approximately 0.4 mg/L. Further information on zinc removal from the combined wastewater is presented in Section 4.4.5.

Subsequent to the removal of zinc from the feed, stable nitrification was maintained despite stepwise increases in the loading to an oxidizable nitrogen loading of 0.013 g/g VS•d at an oxygenic reactor HRT of 7.0 hours. On the basis of the data shown in Figure 26, it cannot be concluded that a similar degree of ammonia oxidation could not have been attained in the presence of 7.0 mg Zn/L as effluent ammonia concentrations of less than 1 mg/L were achieved prior to the precipitation of zinc from the feed. Subsequent batches of feed were not treated to precipitate zinc. Zinc concentrations up to 3.4 mg/L occurred in these feeds with no discernible effect on the biological processes. The maximum zinc concentration which could be applied to the process without affecting nitrification efficiency cannot be defined on the basis of these pilot plant results. Researchers have demonstrated that biological inhibition is primarily related to the presence of soluble heavy metals (113, 114). Therefore, simple pH adjustment to precipitate zinc as zinc hydroxide should eliminate nitrification inhibition associated with soluble zinc in the process feed without the requirement to remove the precipitated zinc hydroxide from the feed by physical means.

The fluidized bed system was operated for a further three month period during which four feeds were applied. Stable nitrification was maintained throughout this period with short-term excursions in the effluent NH_3-N concentrations up to a maximum level of 10 mg/L in response to changes in feed, step changes in process loading and operation at loading conditions in excess of the maximum nitrification rate of the process.

As indicated in Figure 26, seven operating periods were selected as indicative of pseudo-steady state process performance over the range of loading conditions applied. These data should not be considered to represent true steady state operation due to the short duration at each operating condition necessitated by the time constraints of the program.

The operating conditions imposed on the nitrification system for each pseudo-steady period are summarized in Table 32. With the exception of run 4 when nitrate concentrations exceeded 100 mg/L, methanol was not added to the system during the last three months of operation. Reactor HRT was progressively decreased from 17.5 hours to approximately 4 hours, providing a range of oxidizable nitrogen loadings from 0.005 g NH_3 -N/g VS•d to 0.037 g NH_3-N/g VS•d, including the ammonia generated as a result of thiocyanate oxidation (50). Reactor volatile solids concentrations ranged from 16.6 to 24.0 g/L. The calculated nitrification reactor solid retention time (SRT) ranged from 72 days to more than 600 days. These values, particularly the long SRT's calculated for operating periods early in the study which were conducted at relatively low loadings, should not be considered steady state values due to the short duration of the individual operating periods. The lack of correlation between the nitrogen loading and reactor SRT is indicative of a non-steady state. The high recycle rates cited in Table 32 are function of the pilot plant design, as discussed in detail in Section 4.4.7.

The performance of the system at each pseudo-steady state operating condition is summarized in Table 33 in terms of conventional contaminants. As discussed in Section 4.4.2, removal of organic carbon (FOC), phenolic compounds, thiocyanate and cyanide was consistent throughout the investigation. Under all operating conditions, oxidation of biodegradable carbonaceous matter in the raw wastewater was virtually complete and phenol oxidation efficiency was 99.9 percent or greater. Treated effluent thiocyanate concentrations were consistently less than 2.5 mg/L. The removal of total cyanide varied from 10 percent to more than 70 percent efficiency depending on the proportion of CN_A present in the raw feed.

Final effluent suspended solids concentrations were significantly lower during treatment of the combined wastewater than the effluent quality achieved during treatment of coke plant wastewater alone. Figure 27 demonstrates the dramatic reduction in effluent suspended solids immediately upon switching from coke plant

TABLE 32 NITRIFICATION PROCESS OPERATING CONDITIONS - COMBINED WASTEWATER TREATMENT

Pseudo-Steady State Run no.	Date/1982	Reactor HRT (h)	SRT (d)	Ammonia-N Loading* (g/g•d)	Hydraulic Flux (m/min)	Recycle Ratio	Reactor VS (g/L)	Effluent DO (mg/L)	Temp. Range (°C)
1	Jan. 21 - Feb. 8	17.5	650	0.005	0.84	270	24.0	4.7 - 5.6	25 - 27
2	Feb. 9 - Feb. 22	11.7	530	0.008	0.83	178	22.7	3.6 - 4.5	25 - 27
3	May 21 - June 3	7.0	89	0.013	0.84	108	17.9	2.8 - 5.4	24 - 31
4	June 15 - June 24	7.0	160	0.031	0.84	108	16.6	3.0 - 3.3	27 - 30
5	June 29 - July 7	3.5	72	0.037	0.83	53	17.4	2.8 - 4.8	26 - 30
6	July 8 - July 29	3.9	114	0.033	0.83	59	17.0	1.8 - 2.7	26 - 29
7	July 30 - Aug. 6	4.4	108	0.030	0.82	66	17.0	N.A.	26 - 27

* Ammonia-N loading based on feed (NH_3-N + 0.24 CNS) concentration (50)

N.A. - Not Available

TABLE 33 PERFORMANCE OF NITRIFICATION PROCESS - COMBINED WASTEWATER TREATMENT

Pseudo-Steady State Run No.	Effluent Removal	Parameter							
		FOC	Phenolics	TKN	NH_3-N*	CNS	TCN	CN_A	SS
1	Mean (mg/L)	27.	0.018	10.9	0.8	0.7	1.64	0.02	57
	(%)	90.8	>99.9	90.2	99.1	99.5	10.1	95.7	-
2	Mean (mg/L)	26.	0.081	6.9	1.0	1.1	1.26	0.01	14
	(%)	90.6	>99.9	93.7	98.8	99.2	27.8	98.0	-
3	Mean (mg/L)	22.	0.044	5.8	0.8	0.6	0.52	0.12	51
	(%)	89.2	>99.9	93.2	98.9	99.4	50.8	77.4	-
4	Mean (mg/L)	19.	0.059	2.1	0.8	0.2	0.18	0.13	32
	(%)	85.2	>99.9	98.8	99.5	99.7	14.3	38.1	-
5	Mean (mg/L)	19.	0.110	9.9	3.8	0.2	0.36	0.02	15
	(%)	86.2	99.9	90.8	95.9	99.7	72.9	99.0	-
6	Mean (mg/L)	19.	0.059	6.0	2.3	0.6	0.37	0.07	32
	(%)	88.7	>99.9	94.6	97.5	99.3	50.0	-	-
7	Mean (mg/L)	20.	0.080	3.8	0.7	0.5	0.33	0.00	44
	(%)	88.1	>99.9	96.6	99.2	99.4	55.4	-	-

* Removal of ammonia-N is based on total oxidizable nitrogen in feed.

wastewater to combined wastewater as system feed. The relatively high effluent suspended solids concentration reported in Table 33 during pseudo-steady state run 1 was related to the short acclimation time which did not allow steady state conditions to be attained in the biological reactors. Effluent suspended solids concentrations were less than 30 mg/L approximately 60 percent of the time. Higher effluent suspended solids concentrations during later stages of the study were generally caused by mechanical problems or were associated with disturbances within the reactors due to sampling or removal of biomass and sand.

The most significant impact of variations in process loading on system performance was related to nitrification efficiency. Operation at oxidizable nitrogen loadings of up to 0.031 g NH_3-N/g VS•d (Runs 1, 2, 3, 4, and 7) resulted in the production of a treated effluent containing consistently less than 2.0 mg/L NH_3-N. At higher loading conditions (Runs 5 and 6), instability in the efficiency of nitrification occurred. Figure 28 indicates the effect of process loading on effluent quality in terms of NH_3-N concentration. At loadings up to 0.031 g NH_3-N/g VS•d, average effluent ammonia nitrogen concentrations of less than 1 mg/L were attained. At higher loadings, a deterioration in effluent quality was evident as the loading exceeded the maximum specific nitrification rate of the system. For comparison, specific nitrification rates achieved in the coupled fluidized bed process during treatment of coke plant wastewater alone were 0.022 g NH_3-N/g VS•d.

4.4.5 **Removal of Zinc From the Process Feed.** Of the metals quantified in the coke plant wastewater (Table 26), blast furnace blowdown water (Table 27), and the combined feed (Table 28), only zinc was present at concentrations which could produce a toxic effect on the biological processes. Zinc was present at concentrations of up to approximately 8 mg/L in the combined feed.

Comparison of the total and filterable zinc content of the individual components of the feeds with the measured concentrations of total and filterable zinc in the feed to the pilot plant indicated that significant zinc precipitation occurred upon mixing of the blast furnace blowdown water with the coke plant wastewater. Furthermore, a progressive reduction in the total and filterable zinc concentrations of the feed was noted during storage. To assess the effect of blending blast furnace blowdown water with coke plant wastewater on the concentrations of total and filterable zinc, grab samples of wastewater from each source were combined and mixed for approximately 30 minutes. Samples of the mixed wastewater were then analyzed for total and filterable zinc. In addition, the mixed samples were allowed to settle under quiescent condition for approximately 16 hours and the supernatant analyzed for total zinc. The results of these experiments are shown in Table 34.

The blast furnace blowdown water contained an average total zinc concentration of 25.4 mg/L, of which approximately 70 percent was in a soluble form (17.9 mg/L). After mixing in ratios of 1:1 to 3:1 with coke plant wastewater, the samples contained an average total zinc concentration of 16.6 mg/L, in agreement with the concentration calculated based on the individual components of the mixture. However, soluble zinc represented only approximately 29 percent of the total zinc present in the mixture. Extended contact time resulted in further zinc precipitation from the sample. The supernatant after 16 hours settling contained an average total zinc concentration of 2.9 mg/L, approximately 17.5 percent of the total zinc present in the mixed sample. Blending

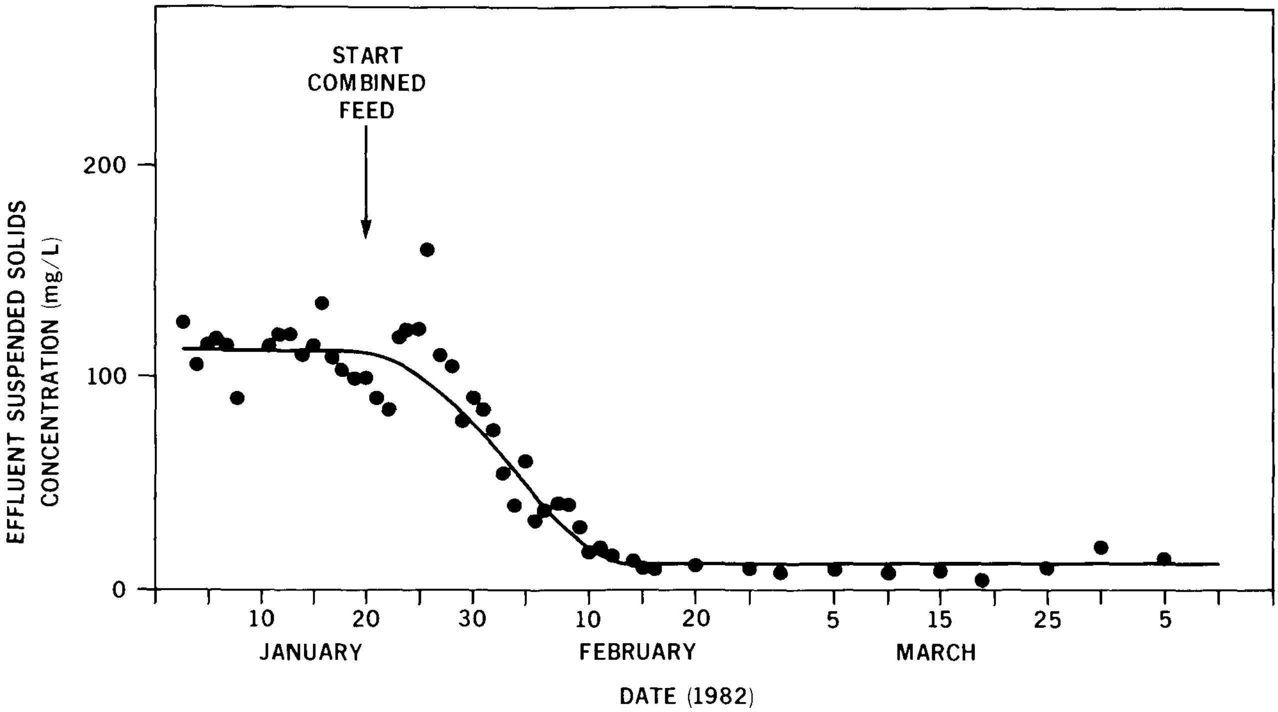


FIGURE 27 EFFECT OF COMBINED FEED ON PROCESS EFFLUENT SUSPENDED SOLIDS CONCENTRATION

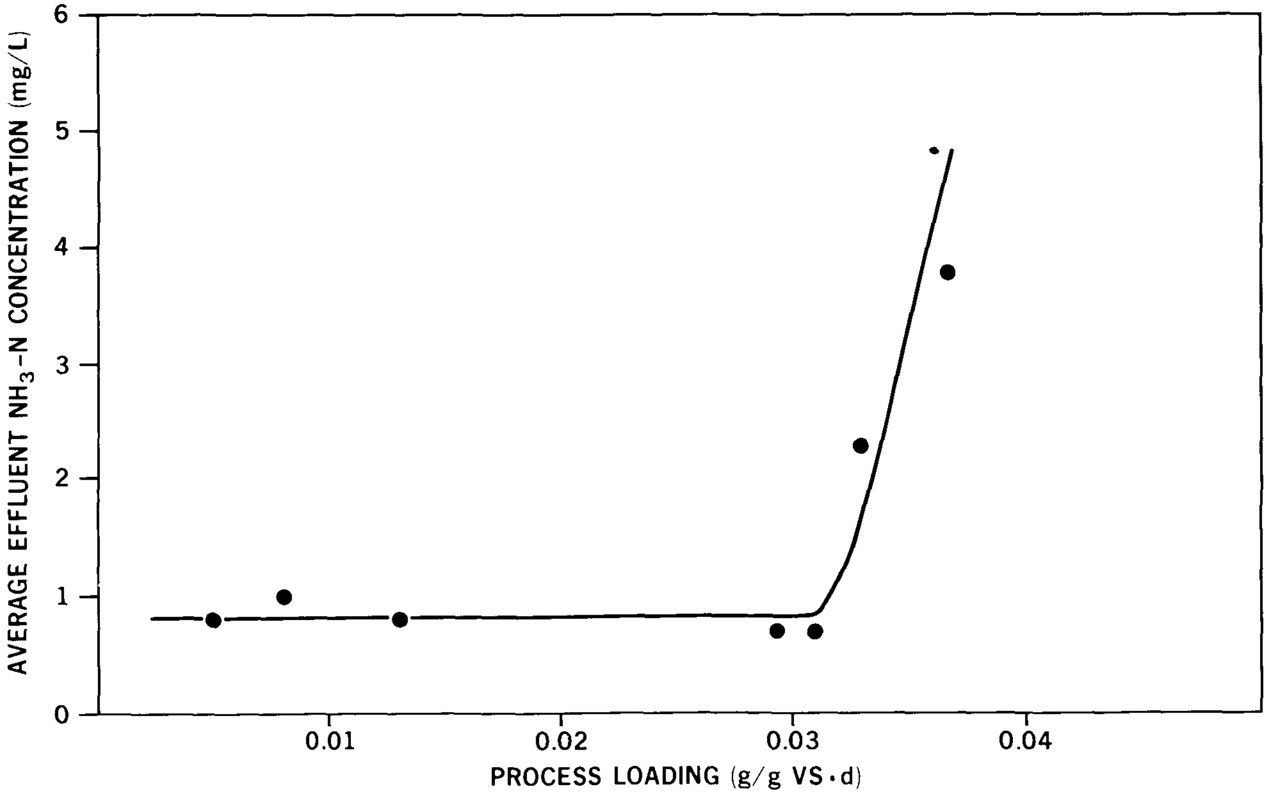


FIGURE 28 EFFECT OF PROCESS NITROGEN LOADING ON NITRIFICATION EFFICIENCY

TABLE 34 EFFECT OF COMBINING COKE PLANT WASTEWATER AND BLAST FURNACE BLOWDOWN ON ZINC CONTENT

Sample Date	Ratio BFBD:CPWW	Zinc Concentration (mg/L)								
		Blast Furnace Blowdown		Coke Plant Wastewater		Mixed Sample		Settled Sample	Calculated Conc.	
		Total	Filtrable	Total	Filtrable	Total	Filtrable	Total	Total	Filtrable
19/03/82	1:1	11.0	8.4	0.14	0.08	5.4	0.38	0.28	5.6	4.2
26/03/82	2:1	30.0	26.0	0.08	0.08	19.0	3.5	3.5	20.0	17.4
31/03/82	3:1	33.0	17.0	0.26	0.17	27.0	2.7	1.3	24.8	12.8
5/04/82	1:1	43.0	30.0	0.52	0.21	23.0	6.6	4.0	21.8	15.1
7/04/82	2:1	36.0	23.0	0.27	0.05	26.0	14.0	4.6	24.1	15.4
13/04/82	2:1	24.0	22.0	0.67	0.13	17.0	2.4	2.1	16.2	14.7
15/04/82	1:1	17.0	15.0	1.05	1.05	10.0	8.8	8.8	9.0	8.0
27/04/82	2:1	15.0	12.0	0.12	0.11	9.6	5.3	1.9	10.0	8.0
28/04/82	2:1	19.0	14.0	0.10	0.06	12.0	3.4	0.9	12.7	9.4
29/04/82	2:1	26.0	12.0	0.44	0.06	17.0	1.7	1.9	17.5	8.0
Average	-	25.4	17.9	0.37	0.20	16.6	4.9	2.9	16.2	11.3

the blast furnace blowdown water with the coke plant wastewater resulted in a final pH of 7.6 to 8.5, depending on the ratio of the individual components and their pH. On the basis of these preliminary experiments, it appears that a well-designed equalization facility upstream of the biological system could minimize the impact on the biological system of zinc by allowing precipitation of zinc from the combined feed.

Despite the precipitation of zinc from the feed upon mixing of the blast furnace blowdown with the coke plant wastewater, concentrations in the pilot plant feed of up to approximately 8 mg/L total zinc and 7 mg/L filterable zinc occurred. As discussed in Section 4.4.4, these elevated zinc levels in the feed may have contributed to the instability of the nitrification process during April 1982.

The biological system effectively removed zinc from the wastewater feed. From April 13 to May 10, when feed zinc concentrations averaged 6.9 mg/L, the effluent zinc concentration averaged 0.20 mg/L. The zinc removed from the wastewater accumulated in the biological reactor biomass as shown in Figure 29. Prior to the period of elevated feed zinc levels, zinc concentrations in the biomass did not significantly increase over levels measured before initiation of the combined feed. Over a month, the biomass zinc concentration increased to 9.5 mg/g in the denitrification reactor and 8.5 mg/g in the nitrification reactor. After removal of the zinc from the feed on May 10, zinc concentrations declined. A second peak in the biomass zinc concentration was experienced in June when the feed contained an average total concentration of 2.41 mg/L. In July when the feed zinc concentration averaged 0.55 mg/L, the biomass zinc concentration progressively declined to levels approaching the base-line level measured prior to the start of the study. The low peak concentration and more rapid decrease in zinc in the denitrification reactor relates to the lower SRT in the denitrification reactor compared to the nitrification reactor.

As discussed in Section 4.4.4, the pH of the storage tank contents was raised to 10.0 with sodium hydroxide on May 10 to precipitate zinc from the feed. Figure 30 illustrates the effect of wastewater pH on the soluble zinc content of this particular feed. At a pH of 9.5, the solubility of zinc was approximately 1 mg/L. Further testing would be necessary to confirm these data. It was not possible, within the context of this study, to determine if any inhibitory effects of zinc could be eliminated by pH adjustment to render zinc ions insoluble or if physical removal of precipitated zinc hydroxide would be necessary.

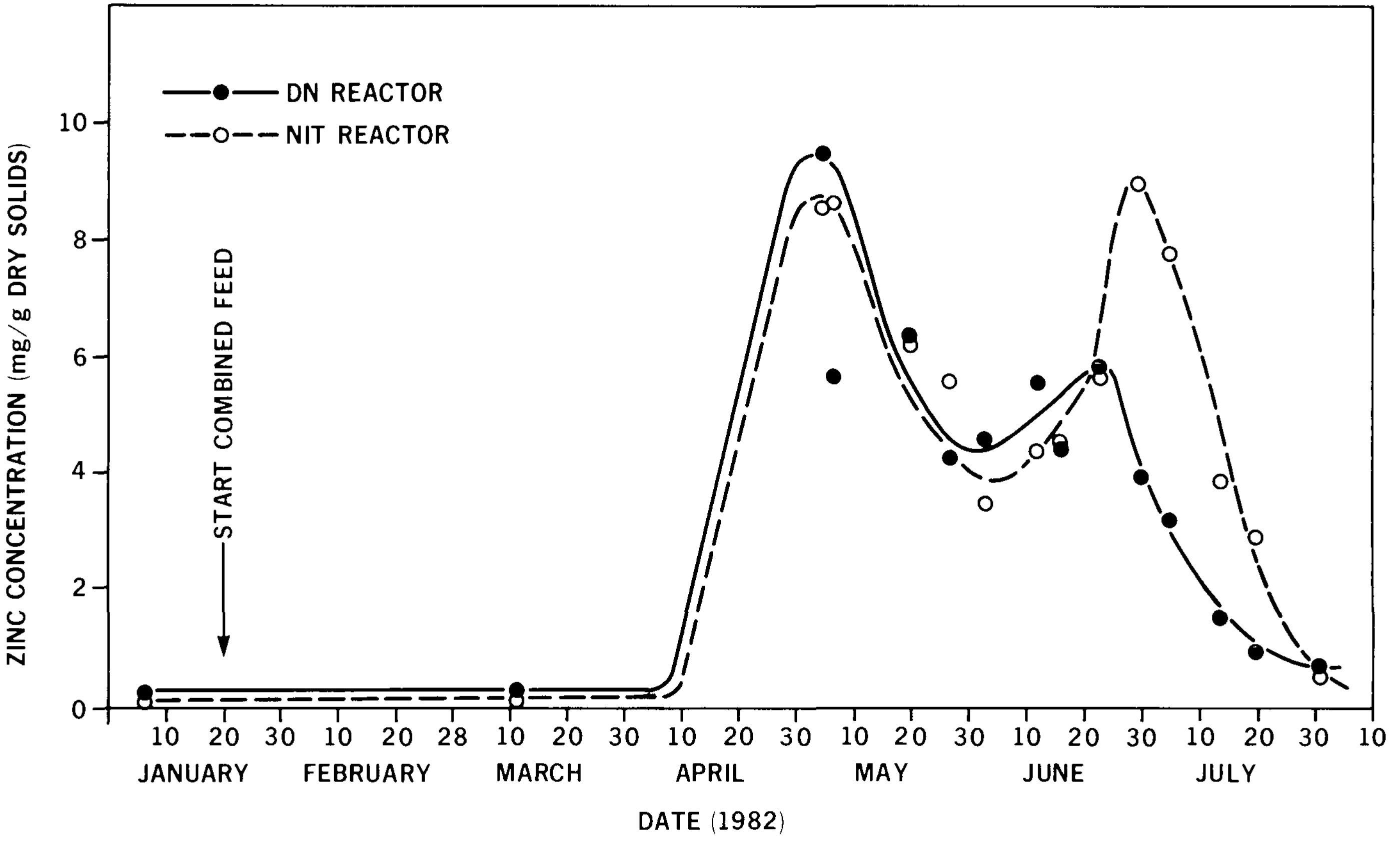


FIGURE 29 ZINC ACCUMULATION IN REACTOR BIOMASS

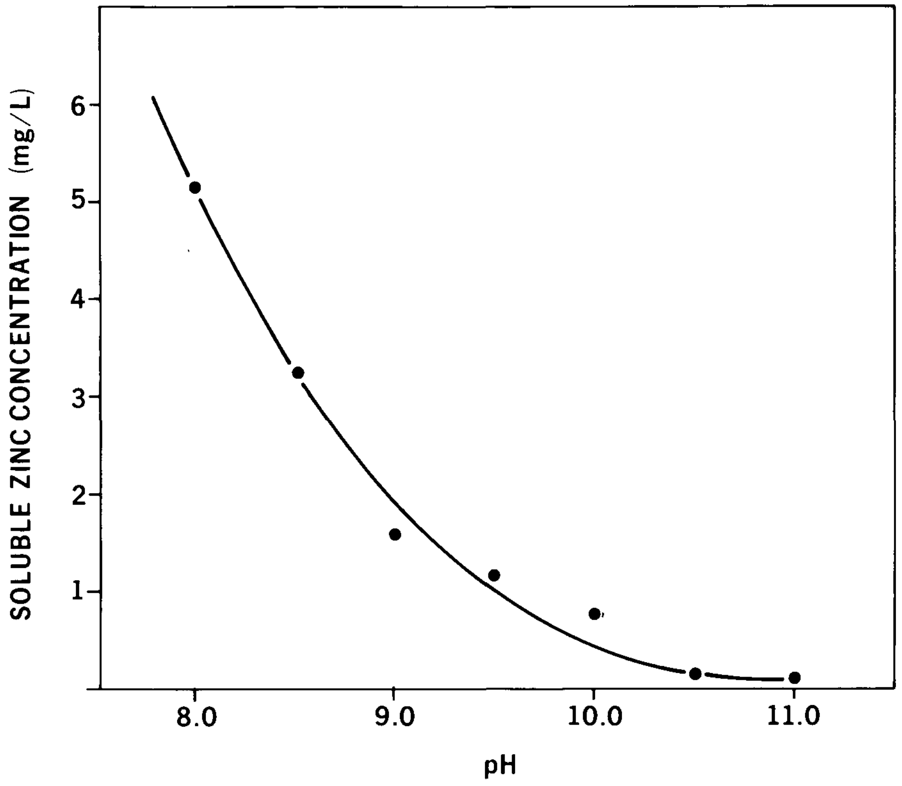


FIGURE 30 EFFECT OF pH ON ZINC SOLUBILITY IN COMBINED WASTEWATER

4.4.6 **Chemical Consumption.** To establish the chemical consumption (oxygen, phosphorus and alkalinity) associated with treatment of combined coke plant wastewater and blast furnace blowdown in the coupled biological fluidized bed process, data generated from May 21 to June 3, July 1 to July 4 and July 7 to July 28, were analyzed. These represented periods of relatively stable nitrification and denitrification during which no methanol was added to the process and the nitrification system was operated at relatively high ammonia loadings. In all cases, longer term operation at stable process conditions would be useful in precisely establishing the chemical consumption associated with the process.

Oxygen consumption was determined based on on-line influent and effluent DO measurements obtained at 15-second intervals and automatically averaged for 24-hour periods. The calculated consumption is summarized in Table 35. The average consumption during the three operating periods analyzed ranged from 0.17 to 0.25 g O_2 per litre of wastewater treated. There was a positive correlation between the oxygen consumed and the concentration of oxidizable nitrogen in the process feed.

TABLE 35 OXYGEN CONSUMPTION DURING TREATMENT OF COMBINED WASTEWATER

Period (1982)	Average Feed Quality (mg/L) NH_3-N	CNS	FOC	Oxygen Consumption (g/L)	Theoretical O_2 Requirement (g/L) N-Compounds*	Total**
May 21 - June 3	45.5	99	205	0.17 ± 0.03	0.40	0.88
July 1 - July 4	73.5	68	138	0.22 ± 0.04	0.45	0.76
July 7 - July 28	71.7	82	168	0.25 ± 0.05	0.47	0.86

* Oxygen demand associated with nitrogenous compounds based on NH_3-N demand of 4.2 mg O_2 per mg NH_3-N (20) and CNS demand of 1.1 mg O_2 per mg CNS (48).

** Total oxygen demand based on NH_3-N demand of 4.2 mg O_2 per mg NH_3-N (20), CNS demand of 1.1 mg O_2 per mg CNS (48) and FOC demand of 2.6 mg O_2 per mg FOC.

As indicated in Table 35, the measured consumption was only 50 percent of the theoretical oxygen requirement associated with the thiocyanate and oxidizable nitrogen present in the feed. A fraction of the nitrogen present in the feed would be utilized for biological growth and would not undergo oxidation in the nitrification reactor; however, it is unlikely that this alone would account for the difference between the measured and theoretical oxygen requirement. The absolute difference between the measured and theoretical oxygen consumption (approximately 0.23 mg O_2 per litre of wastewater) was similar to the difference measured previously during treatment of coke plant wastewater alone.

Also included in Table 35 is the theoretical oxygen requirement for nitrification of the combined wastewater without the pre-denitrification stage. In this case, all nitrogenous and carbonaceous components of the wastewater would have to be oxidized aerobically in the presence of oxygen. For the purposes of the calculation, the demand associated with carbon oxidation was based on complete conversion to CO_2. Thiocyanate oxidation was assumed to proceed according to the pathway proposed by Luthy and Jones (28). The contribution of ammonia nitrogen generated from thiocyanate oxidation was included in the theoretical demand. On this basis, the total theoretical demand for these wastewaters ranged from 0.76 to 0.88 g O_2 per litre treated. The measured demand was approximately 25 percent of the total theoretical demand. Operation in the pre-denitrification flow mode is primarily responsible for the significant reduction in the oxygen requirements associated with treatment of this wastewater.

The theoretical alkalinity requirement of the coupled denitrification-nitrification reactions is approximately 3.5 mg of alkalinity as $CaCO_3$ per mg nitrogen removed, based on an alkalinity consumption of 7.07 mg $CaCO_3$ per mg NH_3-N oxidized for nitrification and an alkalinity production of 3.57 mg $CaCO_3$ per mg NO_2-N or NO_3-N reduced to nitrogen gas (20).

Alkalinity was added to the fluidized bed pilot plant in the form of sodium bicarbonate to maintain pH control. The average alkalinity consumption, calculated for the same operating periods cited previously, was 0.67 g $CaCO_3$ per litre of wastewater treated. Supplemental alkalinity in the form of sodium bicarbonate contributed 0.54 g $CaCO_3$ per litre of the total consumption. On a total nitrogen basis, the total alkalinity consumption averaged approximately 8.0 g $CaCO_3$ per g TN removed, considerably higher than the theoretical requirement associated with coupled nitrification and denitrification. As was the case during treatment of coke plant wastewater alone, the higher alkalinity demand would appear to be associated with the precipitation of calcium phosphate from the wastewater. Alkalinity consumption during treatment of coke plant wastewater alone ranged from 0.80 to 2.99 g $CaCO_3$ per litre treated, equivalent to 4.7 to 13.8 g $CaCO_3$ per g TN removed.

The average phosphorus requirement for the coupled fluidized bed process during the operating periods analyzed was 0.028 g P per litre of wastewater treated. Comparative data for treatment of coke plant wastewater alone in the fluidized bed process indicate phosphorus requirements ranging from 0.045 to 0.167 g P/L. As noted in the discussion of alkalinity consumption, the precipitation of calcium phosphate in the system results in an increase in the phosphorus requirements beyond that needed for biological metabolism; however, the relative increase associated with calcium phosphate precipitation cannot be estimated based on these data. In the case of coke plant wastewater treatment, Bridle et al (2) estimated that the precipitation of calcium phosphate was responsible for a ten-fold increase in phosphoric acid requirements.

4.4.7 Other Design Considerations. Recycle in the nitrification reactor is necessary to ensure that the oxygen demand of the wastewater does not exceed the transfer capabilities of the oxygenator. Recycle of nitrified effluent from the oxygenic reactor to the denitrification reactor controls the concentration of oxidized nitrogen in the final treated effluent. In addition, recycle is required in both reactors to provide an adequate upflow velocity to maintain fluidization. Due to the design of the coupled fluidized bed pilot plant the recycle rates were controlled completely by the upflow velocities required in the individual reactors. Thus, the recycle ratios used during these pilot-scale studies were significantly higher than would be necessary in a full-scale system.

A recycle ratio of approximately 4:1 to the anoxic reactor would produce a final effluent containing approximately 15 mg/L of oxidized nitrogen. The cross-sectional area of the denitrification reactor would be designed based on this total flow to ensure that adequate fluidization velocities were attained.

In the case of the nitrification reactor, the minimum recycle required to fulfill the oxygen requirements would be approximately 4:1. However, to provide adequate reactor volume to meet the HRT and SRT requirements at this recycle ratio would result in excessively high reactors. Thus, the recycle ratio in the nitrification reactor would be controlled by the fluidization velocity requirements. Based on the pilot plant fluidization characteristics, the minimum recycle requirements for the nitrification reactor would be approximately 25:1 for a maximum reactor height of 7.6 m.

For a biological treatment process designed to nitrify a complex wastewater such as the combined coke plant wastewater and blast furnace blowdown water investigated during this study, the principal process design parameter should be system solids retention time (SRT). In this particular study, time constraints did not allow the long operating times necessary to achieve steady state in the system. Therefore, SRT data do not represent steady state values.

July 8 to July 28 represents the longest operating period during which the process loading conditions were constant and representative, and process performance was relatively stable. Therefore, this operating period was utilized to estimate the biological growth rates and solid yields in the reactors.

For this period, the individual reactor SRT's were approximately 13 days in the denitrification reactor and 114 days in the nitrification reactor, based on the mass of biomass present in the individual reactors, the mass wasted intentionally from each reactor and the biomass unintentionally wasted in the effluent proportioned equally between the reactors. This was equivalent to a system SRT of 49 days (based on total system biomass and total intentional and unintentional biomass wastage). Solids yields on the basis of grams of volatile solids generated per litre of wastewater treated were 0.031 g VS/L for the denitrification reactor and 0.024 g VS/L for the nitrification reactor, equivalent to a total yield of 0.055 g VS per litre of wastewater treated. Average solids yield during treatment of coke plant wastewater alone was 0.32 g VS/L. The higher yield relates to the higher concentration of contaminants in the coke plant wastewater compared to the combined wastewater.

4.4.8 Removal of Trace Organic Contaminants. Grab samples of the combined coke plant wastewater and blast furnace blowdown used as feed to the biological fluidized bed process and treated effluent from the pilot plant system were collected manually and submitted for extraction and analysis by GC/MS. In addition, samples of coke plant wastewater and blast furnace blowdown were submitted separately for similar analysis. Excess biomass separated from the support media in the individual reactors was also sampled and analyzed for trace organics. The analytical results are presented in Tables 36 (untreated wastewater), 37 (fluidized bed effluent) and 38 (fluidized bed sludges). In the tabular presentation of these data, only Table 36 shows all those U.S. EPA organic priority pollutants identified in at least one sample or included in the analytical QA/QC program. In addition, all non-priority pollutants that were to be quantified in the samples are included. These compounds were primarily heterocyclic nitrogenous compounds. Samples were not analyzed for volatile organic compounds (purgeables) on the U.S. EPA priority pollutant list. Tables 37 and 38 show only trace organics actually detected.

As a routine portion of the WTC analytical QA/QC program, duplicate samples of wastewaters, treated effluents and sludges were spiked with a variety of trace organic compounds and the recovery efficiency measured. Although there was significant variability in the spike recovery from compound to compound, the recovery was generally higher and more consistent from treated fluidized bed samples than from untreated wastewater samples. Recovery of base-neutral group priority pollutants was generally more consistent than recovery of acid group priority pollutants in both cases. Recovery of non-priority pollutant trace organic compounds was comparable to the recovery achieved for base-neutral group priority pollutants. Recovery of spiked compounds from sludge samples was generally lower than the recovery of similar compounds from aqueous samples, although fewer spiked sludge samples were submitted for analyses.

On the basis of two untreated coke plant wastewater samples analyzed individually for trace organic compounds (Table 36), the concentration of trace organics was significantly lower than previously identified in these wastewaters during the study of treatment of coke plant wastewater alone. This observation is consistent with the lower gross organic content, as measured by FOC. On the same basis, the blast furnace blowdown water was found to be relatively free of trace organic contaminants.

Seven combined coke plant wastewater/blast furnace blowdown samples were collected for trace organic analysis. Acid group U.S. EPA priority pollutants, in particular phenol, were identified in most samples but at levels significantly lower than

TABLE 36 TRACE ORGANIC COMPOUNDS IN UNTREATED WASTEWATER SAMPLES

Compound	Concentration* (mg/L) Coke Plant Waste** Sample 82 - 13/14 January 7/82	Blast Furnace Water Sample 82 - 45 January 20/82	Blast Furnace Water Sample 82 - 47 January 20/82	Coke Plant Waste*** Sample 82 - 401 July 6/82	Combined Waste Sample 82 - 179 April 2/82
BASE NEUTRAL GROUP					
Polynuclear Aromatics					
Acenaphthene					
Acenaphthylene					
Anthracene					
Phenanthrene					
Benzo (a) anthracene and/or Chrysene				0.16	
Benzo (b) and/or Benzo (k) fluoranthene				0.41	
Benzo (ghi) perylene					
Benzo (a) pyrene				0.24	
Fluoranthene				0.07	
Fluorene					
Naphthalene		<0.01	<0.01	0.01	
Pyrene				0.05	
Chlorinated Benzenes					
1,3- and/or 1,4-Dichlorobenzene		0.01	0.02		0.02
Hexachlorobenzene					
Nitrosamines					
N-nitrosodiphenylamine					0.13
Phthalate Esters					
Butyl benzylphthalate					
Di-n-butylphthalate	ND / 0.05	<0.01	0.02		3.44
Diethylphthalate					
Dimethylphthalate					
Di-n-octylphthalate					0.58
Bis(2-ethylhexyl)phthalate		<0.01			
Haloethers					
Bis(2-chloroethyl)ether					
Other Compounds					
Hexachlorobutadiene					
ACID GROUP					
2-Chlorophenol			<0.01		
2,4-Dimethylphenol		<0.01			
Pentachlorophenol					
Phenol	53/21.2				
2,4,6-trichlorophenol					
NON-PRIORITY POLLUTANTS					
2,4-dimethyl pyridine					
Aniline	0.6/0.92				
Benzonitrile					
Isoquinoline		<0.01	<0.01		0.24
3,4-dimethyl pyridine					
2-methyl naphthalene	ND / 0.04	<0.01	<0.01		
Indole	3/2.7				1.00
7A-methyl quinoline					
7B-methyl quinoline					
2,6 and/or 2.7 dimethyl quinoline					
2,4-dimethyl quinoline					
3,4 and/or 5,6 benzoquinoline					
Carbazole		<0.01	<0.01		
2 or 8 methyl quinoline	ND / 0.2		<0.01		
2,6 dimethyl pyridine					
3,5 dimethyl pyridine					
Quinoxaline					
Benzothiazole		<0.01			
Quinoline	6/7.5	0.01	0.02		1.24
1-methyl naphthalene	ND / 0.05		<0.01		0.14
4-methyl quinoline			<0.01		
Dibenzofuran					
7,8-benzoquinoline					0.03
9-anthracenecarbonitrile					0.03

ND = Not Detected

* Detection limits of 0.010 mg/L for base-neutral group, 0.025 mg/L for acid group except dinitrophenol and dinitrocresol (0.250 mg/L) unless noted.

** Analysed in duplicate. Detection limit 0.2 mg/L for base-neutral group, 0.6 mg/l for acid group in sample 82 - 13.

*** Analysed for PNA's only. Detection limit 0.01 mg/L.

TABLE 36 TRACE ORGANIC COMPOUNDS IN UNTREATED WASTEWATER SAMPLES (Continued)

	Concentration* (mg/L)					
Compound	Combined Waste Sample 82 - 200 April 20/82	Combined Waste Sample 82 - 230 May 10/82	Combined Waste Sample 82 - 359 June 22nd/82	Combined Waste* Sample 82 - 427 June 2nd/82	Combined Waste** Sample 82 - 472 July 23/82	Combined Waste*** Sample 82 - 548 June 2nd/82
BASE NEUTRAL GROUP						
Polynuclear Aromatics						
Acenaphthene				<0.01		0.003
Acenaphthylene						0.005
Anthracene						0.003
Phenanthrene					<0.003	0.006
Benzo (a) anthracene and/or Chrysene						
Benzo (b) and/or Benzo (k) fluoranthene						
Benzo (ghi) perylene						
Benzo (a) pyrene						
Fluoranthene						
Fluorene						0.004
Naphthalene				0.01	<0.003	0.007
Pyrene						0.002
Chlorinated Benzenes						
1,3- and/or 1,4-Dichlorobenzene	0.08	0.02		0.02		
Hexachlorobenzene						
Nitrosamines						
N-nitrosodiphenylamine						
Phthalate Esters						
Butyl benzylphthalate						
Di-n-butylphthalate	0.04	0.04	1.53	0.94		
Diethylphthalate						
Dimethylphthalate						
Di-n-octylphthalate						
Bis(2-ethylhexyl)phthalate						
Haloethers						
Bis(2-chloroethyl)ether						
Other Compounds						
Hexachlorobutadiene						
ACID GROUP						
2-Chlorophenol						
2,4-Dimethylphenol	0.01	0.12	0.08			
Pentachlorophenol						
Phenol	0.05	10.20	14.68			
2,4,6-trichlorophenol						
NON-PRIORITY POLLUTANTS						
2,4-dimethyl pyridine						
Aniline	0.93	0.88				
Benzonitrile	0.02					
Isoquinoline	2.92		0.91			
3,4-dimethyl pyridine						
2-methyl naphthalene						
Indole	9.96	9.92	5.7			
7A-methyl quinoline	0.19	0.14	0.10			
7B-methyl quinoline	0.04					
2,6 and/or 2.7 dimethyl quinoline						
2,4-dimethyl quinoline						
3,4 and/or 5,6 benzoquinoline						
Carbazole	0.89	0.77	0.41			
2 or 8 methyl quinoline	0.34	0.26				
2,6 dimethyl pyridine						
3,5 dimethyl pyridine						
Quinoxaline	0.04					
Benzothiazole						
Quinoline	9.92	8.58	2.50			
1-methyl naphthalene						
4-methyl quinoline	0.27	0.17				
Dibenzofuran						
7,8-benzoquinoline	0.03					
9-anthracenecarbonitrile						

* Non-priority pollutants not analysed in sample 82 - 427

** Analysed for PNA's only. Detection limit 0.003 mg/L

*** Analysed for PNA's only. Detection limit 0.001 mg/L

TABLE 37 TRACE ORGANIC COMPOUNDS IN FLUIDIZED BED EFFLUENT

	Concentration* (mg/L)						
Compound	Sample 82 - 181 April 6/82	Sample 82 - 202 April 20/82	Sample 82 - 232 May 10/82	Sample 82 - 236 May 20/82	Sample 82 - 280 June 2/82	Sample 82 - 361 June 22/82	Sample 82 - 474 July 23/82**
<u>BASE-NEUTRAL GROUP</u>							
<u>Polynuclear Aromatics</u>							
Fluoranthene							<0.005
Napthalene							<0.005
Pyrene							<0.005
<u>Chlorinated Benzenes</u>							
1,3- and/or 1,4- Dichlorobenzene	<0.01	<0.01					
<u>Phthalate Esters</u>							
Di-n-butylphthalate	0.01	<0.01	<0.01	0.09	0.07	0.57	
Bis (2-ethylhexyl) phthalate						0.01	
<u>NON-PRIORITY POLLUTANTS</u>							
Aniline	<0.01						

* Detection Limits: 0.010 mg/L for base-neutral group, 0.025 mg/L for acid group except dinitrophenol and dinitrocresol (0.250 mg/L).

** Analysed for PNA's only. Detection limit 0.005 mg/L.

TABLE 38 TRACE ORGANIC COMPOUNDS IN FLUIDIZED BED SLUDGES (μg/g)

Compound	DN Sludge* Sample 82 - 49 January 20/82	NIT Sludge Sample 82 - 50 January 20/82	DN Sludge Sample 82 - 204 April 20/82	NIT Sludge Sample 82 - 206 April 20/82	DN Sludge** Sample 82 - 336 June 7/82	NIT Sludge** Sample 82 - 337 June 7/83	DN Sludge** Sample 82 - 410 July 8/82	NIT Sludge** Sample 82 - 412 July 8/82	NIT Sludge** Sample 82 - 555 August 16/82	DN Sludge** 82 - 553 August 16/82
BASE-NEUTRAL GROUP										
Polynuclear Aromatics										
Anthracene									0.2	
Phenanthrene	ND/0.2/ND				<0.2	<0.2			0.7	0.4
Benzo(a)anthracene and/or Chrysene						<0.2	<0.2	1.9	5.8	3.3/24
Benzo(b) and/or Benzo(k) fluoranthene								1.8	1.0	
Benzo(ghi)perylene										
Benzo(a)pyrene								<0.2	1.3	
Fluoranthene	2/ND/ND	< 0.1			2	0.4	1.2	2.2	6.9	5.7
Naphthalene	ND/0.2/ND				<0.2	<0.2	<0.2	<0.2		0.2
Pyrene	5/1.9/2				3	2.0	0.7	2.3	6.1	5.0
Chlorinated Benzenes										
1,3 - and/or 1,4-Dichlorobenzene	ND/0.2/ND									
Hexachlorobenzene	ND/0.9/ND									
Phthalate Esters										
Butyl benzylphthalate	ND/0.4/ND									
Di-n-butylphthalate	14/10.3/16	10.0	14							
Diethylphthalate	1/4.5/5	5.0								
Dimethylphthalate	ND/0.3/ND									
Bis (2-ethylhexyl-phthalate)	2/2/2	3.0	3.0	4.0						
ACID GROUP										
Phenol	ND/0.4/1									
NON-PRIORITY POLLUTANTS										
2-methyl naphthalene	ND/0.1/<0.1									
Carbazole	2/ND/ND		1							
Benzothiazole	<0.1/0.7/0.7	0.9								
Quinoline	ND/0.3/ND									
Dibenzofuran	ND/ND/<0.1									
9-anthracenecarbon-itrile	3/ND/ND									

* Analysed in triplicate. Second set of results are average of 2 MS quantifications.

** Analysed for PNA's only. Detection limit 0.2 μg/g.

ND - Not Detected

those measured by traditional wet chemical methods (4-aminoantipyrine). Such discrepancies were noted in analysis of coke plant wastewater alone and have been reported by other investigators (50). Base-neutral group U.S. EPA priority pollutants, specifically PNA's such as acenaphthene, phenanthrene and naphthalene were identified in more than one untreated sample; however, these compounds were present at relatively low levels (0.01 mg/L). Di-n-butylphthalate was measured at levels up to 3.4 mg/L in the combined wastewater. Of the non-priority pollutant trace organic compounds, quinoline, indole and isoquinoline were identified in concentrations in excess of 1 mg/L. Aniline and carbazole were present at concentrations approaching 1 mg/L. Other compounds identified in more than one feed sample included 7A-methyl quinoline, 4-methyl quinoline and 7,8 benzoquinoline; however, these compounds were present at relatively low concentrations.

Seven treated fluidized bed effluent samples were collected and analyzed. As shown in Table 37, only di-n-butylphthalate was identified consistently in the treated effluent at greater than trace (0.01 mg/L) concentrations.

Di-n-butylphthalate was also identified in fluidized bed effluents produced during treatment of coke plant wastewater alone. Phthalate esters are common plasticizers and the consistent presence of di-n-butylphthalate at low levels in the treated wastewater may be indicative of sample contamination. None of the U.S. EPA base-neutral PNA's or the non-priority pollutant heterocyclic nitrogenous compounds were found at greater than trace levels (0.01 mg/L) in the treated effluent samples.

The concentrations of trace organic compounds in fluidized bed sludges are summarized in Table 38. Sludges from both the denitrification (DN) reactor and the nitrification (NIT) reactor were analyzed. On the basis of the limited amount of data available, no significant difference between the trace organic content of the individual sludges could be established.

Samples from both reactors were analyzed prior to the start of feeding the combined wastewater to the system to establish the concentration of trace organics initially present. As shown in Table 38, the denitrification reactor sludge appeared to contain a broader range of trace organic contaminants than the nitrification reactor sludge. However, the denitrification sludge was analyzed in triplicate and many of the trace organic compounds were not recovered consistently. Phthalate esters, in particular di-n-butylphthalate, were quantified at levels up to 14 μ g/g in both sludges. Benzothiazole was identified in both sludges. As this compound had not been previously found in coke plant wastewaters, the source of benzothiazole in the sludge cannot be established.

Only one pair of sludge samples were analyzed for the complete range of trace organics after initiation of the combined feed (samples 82-204 and 82-206). These samples were taken after approximately three months of pilot plant operation of the combined feed. As shown in Table 38, with the exception of phthalate esters, only carbazole was identified. Subsequently, five sludge samples were analyzed for U.S. EPA priority pollutant base-neutral group polynuclear aromatic compounds. The data presented in Table 38 suggests an accumulation of these compounds in the sludges during the study. There were insufficient data available to conclude that the increase in concentration of PNA's in the sludges was significant.

4.4.9 Comparison of Fluidized Bed Effluent Quality With U.S. EPA BPT and BAT Effluent Limitations. To evaluate the performance of the fluidized bed process the effluent quality achieved in the pilot-scale system was compared to Best Practicable Technology (BPT) and Best Achievable Technology (BAT) effluent limitation guidelines recently promulgated by the U.S. EPA for the iron and steel manufacturing point source category (115). These guidelines were developed on the basis of separate effluent limitations for by-product coke-making and iron blast furnace operation. For the purposes of the comparison, the effluent limitations from the individual sectors were summed to provide a total discharge limitation for the combined operations. Both BPT and BAT limitations are production-based (kg of contaminant per unit of production). The calculated effluent limitation guidelines for the by-product coke plant were based on the actual Dofasco coke oven production (3850 kkg/d). In the case of the blast furnace, the theoretical production was based on the anticipated blast furnace blowdown flow (3650 m^3/d) and the actual blowdown rate for recirculation system BCD (605 L/kkg). This calculation results in a theoretical blast furnace production rate of 6030 kkg/d. The discharge loadings from the fluidized bed system were based on the average concentration of phenol and cyanide achieved by the pilot plant over the six-month study, and effluent ammonia-nitrogen and total suspended solids concentrations of 1 mg/L and 30 mg/L, respectively. Total combined wastewater flow was assumed to be 4950 m^3/d, based on the actual Dofasco coke plant wastewater flow (1300 m^3/d) and blast furnace blowdown rate equivalent to 2.8 times the coke plant wastewater flow (3650 m^3/d).

Based on these assumptions, the fluidized bed treated effluent loadings are compared with U.S. EPA BPT and BAT effluent limitation guidelines in Tables 39 and 40. It is apparent that all BPT discharge limitations are readily met by the fluidized bed system. In the case of BAT limitations, guidelines for ammonia and cyanide are met by the treated effluent. Phenol limitations are exceeded by approximately 40 percent.

TABLE 39 COMPARISON OF FLUIDIZED BED EFFLUENT QUALITY WITH U.S. EPA BPT EFFLUENT LIMITATIONS (Basis: Byproduct Coke Plant Production = 3850 kkg/d*, Iron Blast Furnace Production = 6030 kkg/d**, BPT effluent limitations shown as average of daily values for 30 consecutive days.)

Parameter	By product Coke Plant Limitations (BPT) (kg/kkg)	(kg/d)	Iron Blast Furnace Limitations (BPT) (kg/kkg)	(kg/d)	BPT Total Discharge Limitations (kg/d)	Fluid Bed Treated Effluent Discharge*** (mg/L)	(kg/d)
Ammonia-N	0.0912	351.1	0.0537	323.8	674.9	1.0	4.95
Phenols (4AAP)	0.0015	5.78	0.00210	12.7	18.5	0.085	0.42
Cyanide	0.0219	84.3	0.00782	47.2	131.5	0.75	3.71
TSS	0.1310	504.4	0.0260	156.8	661.2	30.	148.5

* Based on actual Dofasco coke oven production.

** Based on pro-rated recirculation system blowdown of 605 L per kkg and design blowdown flow of 3650 m^3/d.

*** Based on average fluidized bed effluent quality, coke plant wastewater flow of 1300 m^3/d and blast furnace blowdown flow of 3650 m^3/d.

TABLE 40 COMPARISON OF FLUIDIZED BED EFFLUENT QUALITY WITH U.S. EPA BAT EFFLUENT LIMITATIONS (Basis: Byproduct Coke Plant Production = 3850 kkg/d*, Iron Blast Furnace Production = 6030 kkg/d**, BAT effluent limitations shown as average of daily values for 30 consecutive days.)

Parameter	Byproduct Coke Plant Limitations (BAT) (kg/kkg)	(kg/d)	Iron Blast Furnace Limitations (BAT) (kg/kkg)	(kg/d)	BAT Total Discharge Limitations (kg/d)	Fluid Bed Treated Effluent Discharge*** (mg/L)	(kg/d)
Ammonia-N	0.0180	69.3	0.00292	17.6	86.9	1.0	4.95
Phenols (4AAP)	0.0000319	0.12	0.0000292	0.18	0.30	0.085	0.42
Cyanide	0.00351	13.5	0.000292	1.76	15.3	0.75	3.71
TSS	-	-	-	-	-	30.	148.5

* Based on actual Dofasco coke oven production.

** Based on pro-rated recirculation system blowdown of 605 L per kkg and design blowdown flow of 3650 m^3/d.

*** Based on average fluidized bed effluent quality, coke plant wastewater flow of 1300 m^3/d and blast furnace blowdown flow of 3650 m^3/d.

5 PROCESS DESIGNS AND PRELIMINARY COST ESTIMATES

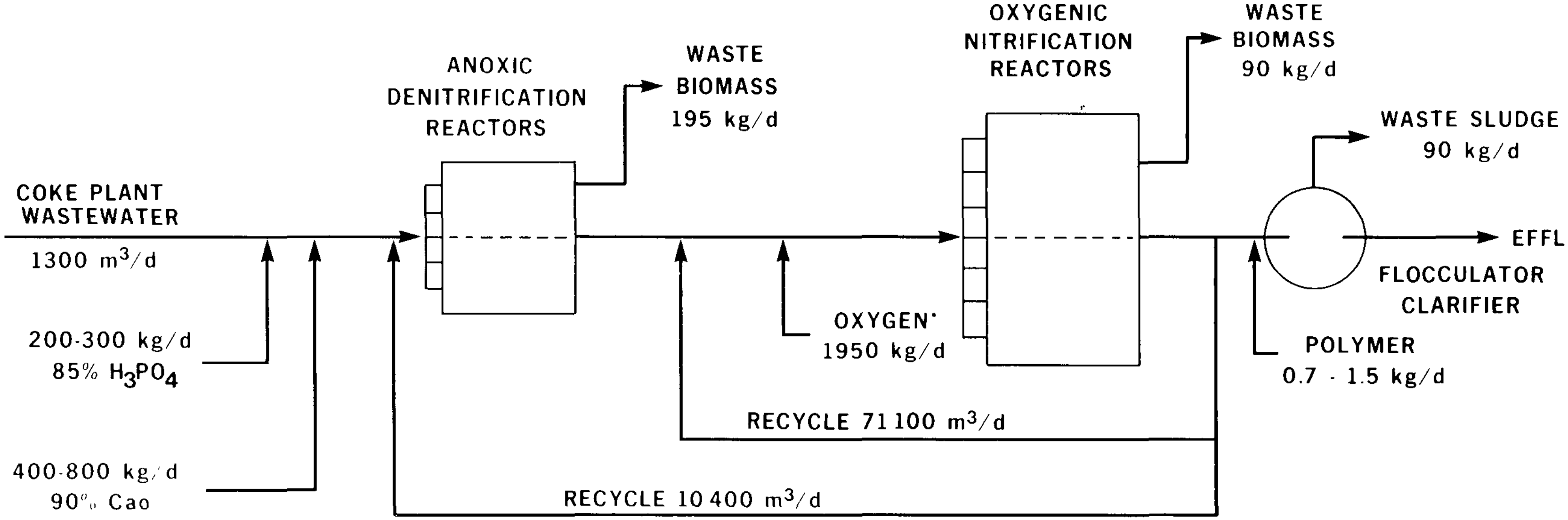
5.1 Coke Plant Wastewater Treatment

On the basis of the pseudo-steady state and non-steady state performance data, process design details for a coupled biological fluidized bed process treating coke plant wastewater were developed. The process flowsheet is shown schematically in Figure 31. Process capital and operating cost estimates were developed for the full-scale treatment facility and are summarized in the following subsections.

5.1.1 Design Basis. The characteristics of the coke plant wastewater treated in the coupled fluidized bed system were based on the actual characteristics of the weak ammonia liquor collected from Dofasco and used as feed during the course of the pilot-scale studies. The characteristics of the feed and final effluent from the process are summarized in Table 41. For the purposes of the design, a variability of ± 50 mg NH_3-N/L was included for sizing of the oxygenation equipment. Design flow for the process was 1300 m^3/d, based on the actual flows from the Dofasco system.

The design specifications and cost estimates were developed for the biological process and related solid-liquid separation equipment only. Cost estimates were not included for pre-treatment processes such as ammonia stills, wastewater equalization or primary clarification as the design and costs of these unit processes would be common to any biological system treating coke plant wastewater. In a full-scale system, the functions of equalization and primary clarification to protect the biological system from variations in feed quality and from excessively high concentrations of free floating oil or carry-over of lime from the stills could be combined in a single unit. In addition, costs associated with waste sludge handling and disposal were not included. Sludge yields measured in the fluidized bed process were comparable to those determined by other researchers for suspended growth systems; therefore, sludge disposal costs would be similar to those resulting from the operation of an activated sludge system providing an equivalent degree of treatment.

The anoxic denitrification reactor was designed to provide an HRT of 2.0 hours at design flow, equivalent to a total anoxic reactor volume of approximately 109 m^3. Parallel reactors 7.62 m in height were provided in the design. The design recycle ratio for the anoxic reactor was 8:1, providing a hydraulic flux of 0.4 m/min in accordance with typical design practice for full-scale fluidized bed reactors. Design denitrification



* OXYGEN REQUIREMENTS ARE STATED AS A MAXIMUM VALUE.

FIGURE 31 PROCESS DESIGN FLOWSHEET FOR COUPLED FLUIDIZED BED TREATMENT OF COKE PLANT WASTEWATER

TABLE 41 DESIGN COKE PLANT WASTEWATER AND FINAL EFFLUENT CHARACTERISTICS

	Concentration (mg/L)	
Parameter	Coke Plant Wastewater	Final Effluent
FOC	700	50
NH_3-N	100*	1
CNS	300	2
TKN	200	-
NO_T-N	-	15
SS	-	30

* Range of coke plant wastewater NH_3-N concentration 50-150 mg/L.

SRT was 10 days, at an operational reactor biomass concentration of 25 g/L, equivalent to a biomass wasting rate of 195 kg VS/d.

The oxygenic nitrification reactor was designed to provide an HRT of 14.0 hours at design flow, equivalent to a total oxygenic reactor volume of approximately 760 m^3. As in the anoxic reactor design, parallel reactors were provided. Reactor height is 7.6 m. Design hydraulic flux in the nitrification reactor was 0.48 m/min at a recycle ratio of 55:1. The design flux was significantly lower than the operating level in the pilot-scale reactor at WTC. Discussions with Dorr-Oliver Inc. indicated that this flux had been shown to be adequate even under start-up conditions in larger-scale fluidized bed pilot plants. The higher flux requirements in the WTC pilot plant appear to be related to the poor flow distribution properties of the small-scale reactor inlet design.

Design nitrification SRT, at an operational reactor biomass concentration of 15 g VS/L, was 70 days. Ammonia loading to the nitrification process under these operating conditions, including the ammonia generated as a result of thiocyanate oxidation, was 0.014 to 0.025 g NH_3-N/g BVS•d. Steady-state biomass wastage from the oxygenic reactor was 90 kg VS/d on the basis of measured pilot plant yields and equivalent reactor effluent suspended solids concentrations.

The process design details for the anoxic and oxygenic biological reactors are summarized in Table 42.

TABLE 42 DESIGN SPECIFICATIONS FOR BIOLOGICAL REACTORS TREATING COKE PLANT WASTEWATERS

Parameter	Anoxic Reactor	Oxygenic Reactor
HRT (hours)	2.0	14.0
Fluidized Bed Height (m)	5.49	6.4
Reactor Height (m)	7.62	7.62
Reactor Area (m^2)	19.88	119.0
Hydraulic Flux (m/min)	0.40	0.48
Recycle Ratio	8.0	54.9
Sand Inventory (tonnes)	87.0	609.0

Maximum oxygen requirements for the nitrification process were 1950 kg/d. Average requirements, based on an influent NH_3-N concentration of 100 mg/L, were 1300 kg/d. The normal oxygen requirement of the process was approximately 15 mg/L per pass through the nitrification reactor. Theoretically, air could be used to supply the requirements of the process rather than pure oxygen. Oxygenator pressures of between 300 and 425 kPa would be necessary to dissolve the oxygen required at normal and maximum ammonia loading conditions. These operating pressures result in excessively deep oxygenator pits for the design. In addition, the presence of nitrogen in the liquid phase could interfere with oxygen transfer and the possible release of nitrogen gas within the fluidized bed reactors could adversely affect biofilm adhesion. Therefore, the supply of pure oxygen to the nitrification reactor was assumed. At many steel mills, pipeline oxygen is available from the cryogenic generator supplying the basic oxygen furnace (BOF). Where pipeline oxygen is not available, alternatives include the purchase and storage of bulk liquid oxygen (LOX) or on-site production in a pressure swing adsorption (PSA) or a cryogenic generation facility.

The process design included the addition of phosphoric acid and lime at the rates shown in Figure 31, based on pilot plant operating data. There is no provision for methanol addition in the process flowsheet because no supplemental carbon would be necessary for denitrification at the design feed quality.

To meet the effluent quality objectives outlined in Table 41, effluent polishing for suspended solids removal is provided in the process flowsheet by means of polymer addition to a conventional flocculator-clarifier designed at a conservative hydraulic loading of 40.8 $m^3/m^2 \cdot d$. An evaluation of the coagulation and sedimentation characteristics was not in the scope of the pilot plant studies and these design parameters would need to be confirmed.

5.1.2 Capital Cost Estimates. Preliminary cost estimates were developed for the major capital items of the coupled biological fluidized bed process, including the flocculator-clarifier for effluent suspended solids removal. The major capital costs are summarized in Table 43. In the development of these costs, it was assumed that pipeline oxygen would be available from the cryogenic generator associated with the BOF. Providing a dedicated PSA generation facility would result in an additional capital cost of approximately $930 000 for a PSA capacity of 2700 kg/d, including liquid oxygen storage for two days as backup to the generator. Oxygen generation in a dedicated cryogenic plant is not competitive with PSA generation at this demand, despite the higher oxygen purity and lower power requirements associated with cryogenic plants.

TABLE 43 CAPITAL COST ESTIMATES FOR COUPLED BIOLOGICAL FLUIDIZED BED PROCESS TREATING COKE PLANT WASTEWATERS

Item	Cost (1982 Canadian $ x 1000)
1) Equipment, instrumentation and engineering for two 9.8 x 6.1 m nitrification reactors, two 2.4 x 4.3 m denitrification reactors and 7.6 m diameter clarifier with polymer system	1010
2) Concrete reactors, oxygenator pits, pump sumps and 7.6 m diameter x 3.7 m SWD clarifier basin	460
3) Pumps and prefab pump rooms	292
4) Piping and valves (erected basis)	283
5) Installation of equipment, motor control center, power wiring, site work	312
TOTAL	2357

It was also assumed that lime requirements can be satisfied from the lime feeding facilities associated with the fixed-leg ammonia still. Costs for a dedicated lime slaking facility and lime slurry tank were, therefore, not included in the cost estimate.

On this basis, the estimated capital cost for a coupled fluidized bed process to treat coke plant wastewater was $2 357 000.

5.1.3 Direct Operating Costs. Annual direct operating costs for chemicals (phosphoric acid, lime, oxygen and polymer) and power are summarized in Table 44. As noted in Section 5.1.1 supplemental carbon addition would not be required based on the design feed quality. Annual direct operating costs for the coupled fluidized bed process treating coke plant wastewater were $150 900.

TABLE 44 ANNUAL DIRECT OPERATING COSTS FOR COUPLED BIOLOGICAL FLUIDIZED BED PROCESS TREATING COKE PLANT WASTEWATER

Item	Cost (1982 Canadian $)
1) Phosphoric Acid - 250 kg/d 85% H_3PO_4 @ $0.90 per kg	82 100
2) Lime - 600 kg/d bulk quicklime (90% CaO) @ $0.061 per kg	13 400
3) Oxygen - 1300 kg/d @ 0.06 per kg*	28 500
4) Polymer - 1.0 kg/d @ $6.30 per kg	2 300
5) Electrical @ $0.03 per kWh	24 600
TOTAL	150 900

* Based on pipeline oxygen from cryogenic generator supplying BOF.

The addition of phosphoric acid to the biological system contributed more than 50 percent of the total annual direct operating costs. The high demand for phosphorus was a direct result of the precipitation of tetrabasic calcium phosphate in the system as discussed in Section 3.4.3. Upstream removal of calcium from the wastewater by recarbonation with carbon dioxide could reduce the phosphoric acid requirements by up to 90 percent based on data generated by Bridle et al (2). The effect on operating and capital costs of wastewater recarbonation warrants further investigation.

The operating costs shown in Table 44 were based on the availability of pipeline oxygen from the cryogenic generator at the BOF at a cost of $60 per tonne. Bulk liquid oxygen would cost approximately $57 000 annually if oxygen were not available from this source.

Power costs associated with the operation of a dedicated 2700 kg/d PSA oxygen generation facility would amount to approximately $16 500 annually. At the oxygen demands of the process, bulk LOX supply would appear to be the more cost-effective alternative on the basis of investment cost and operating cost over a period of three to five years.

5.2 Combined Treatment of Coke Plant Wastewater and Blast Furnace Blowdown

Process design details for a coupled biological fluidized system to treat a combined stream of coke plant wastewater and blast furnace blowdown water were developed based on the treatability results generated from the six-month pilot-scale investigation. The process flowsheet is shown schematically in Figure 32. Preliminary capital and operating cost estimates were generated for a full-scale treatment facility and are summarized in the following sections.

5.2.1 Design Basis. To allow a comparison between the process requirements and costs associated with treatment of combined wastewater with those generated for treatment of coke plant wastewater alone, a similar design basis was used.

Design flow of coke plant wastewater was 1300 m^3/d and the same wastewater characteristics were assumed. The design flow of blast furnace blowdown water was 3650 m^3/d, equivalent to 2.8 times the flow of coke plant wastewater. The characteristics of the blast furnace blowdown water were based on the actual measured characteristics of blowdown water from recirculation system BCD. The characteristics of the individual components of the feed, the combined wastewater and the final effluent from the process are summarized in Table 45. A variability of ± 50 mg NH_3-N/L in the coke plant wastewater and ± 10 mg NH_3-N/L in the blast furnace blowdown water was included.

TABLE 45 DESIGN WASTEWATER AND FINAL EFFLUENT CHARACTERISTICS - COMBINED TREATMENT OF COKE PLANT WASTEWATER AND BLAST FURNACE BLOWDOWN

Parameter	Coke Plant Wastewater	Blast Furnace Blowdown	Combined Wastewater	Final Effluent
Flow (m^3/d)	1300	3650	4950	4950
FOC (mg/L)	700	10	190	20
NH_3-N (mg/L)	100 $\pm$ 50	30 $\pm$ 10	48 $\pm$ 20	1
CNS (mg/L)	300	1	80	1
TKN (mg/L)	200	40	82	-
NO_T-N (mg/L)	-	-	-	15
SS (mg/L)	-	-	-	30

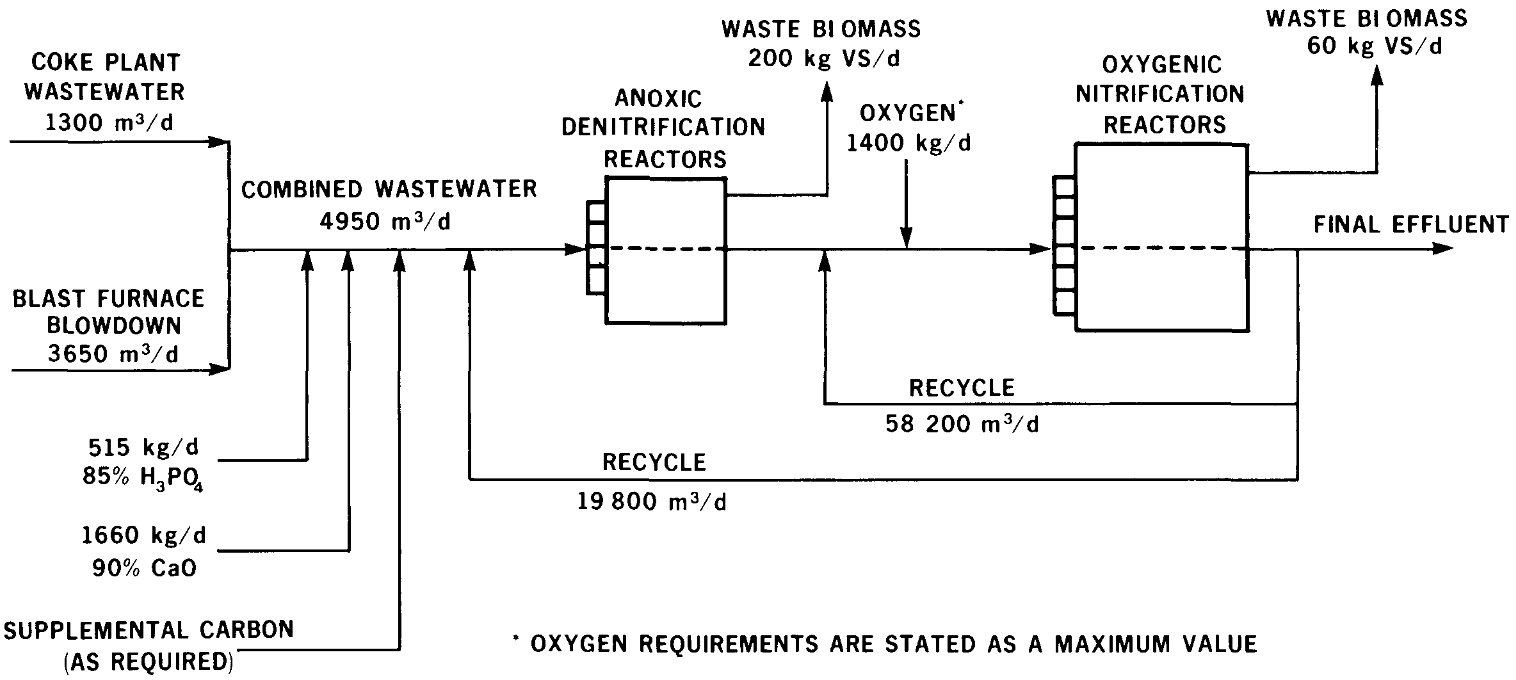


FIGURE 32 PROCESS DESIGN FLOWSHEET FOR COUPLED BIOLOGICAL FLUIDIZED BED TREATMENT OF COMBINED COKE PLANT WASTEWATER/BLAST FURNACE BLOWDOWN

The biological process SRT's were based on the measured SRT's under pseudo-steady state pilot plant conditions. Similarly, chemical requirements (oxygen, phosphoric acid and lime) were based on the consumption rates measured under pseudo-steady state operating conditions. In both cases, these are considered to be approximations of the actual equilibrium values; longer-term operating data would be necessary to confirm the requirements under steady state conditions.

Design and cost data were not developed for primary clarification or equalization facilities for the raw wastewater. Furthermore, there was no provision for zinc removal from the combined wastewater as the requirement for zinc precipitation would depend on the zinc content of the blast furnace blowdown water at the specific site. In cases where zinc precipitation and/or zinc removal are necessary, these functions, could be accomplished in an appropriately-designed equalization basin.

The process flowsheet includes provision for the addition of supplemental carbon as required to maintain denitrification. Based on the design feed quality, supplemental carbon would not be necessary on a routine basis as the raw wastewater contains adequate organic carbon to ensure complete denitrification in the anoxic reactor. However, a system to supply supplemental carbon should be included to allow for major changes in the nitrogen and carbon content of the feed. The initiation of addition of supplemental carbon to the system would be based on increasing effluent oxidized nitrogen concentrations rather than on changes in the feed FOC/TN ratio to ensure that supplemental organic carbon would not adversely affect the nitrification system performance. More economical sources of supplemental organic carbon than methanol have been described in the literature (21, 22).

The anoxic denitrification reactor was designed to provide an HRT of approximately 0.5 hours, equivalent to a total anoxic reactor volume of approximately 110 m^3. Parallel reactors 4.6 m in height were provided. The design recycle ratio to the anoxic reactors was 4:1 to produce an effluent comparable in quality in terms of oxidized nitrogen (NO_T-N) concentration to that generated by the fluidized bed system previously designed to treat coke plant wastewater. Hydraulic flux in the denitrification reactor was 0.4 m/min, in accordance with typical design practice for full-scale fluidized bed reactors. Design denitrification process SRT was 10 days, at an operational reactor biomass concentration of 25 g VS/L, equivalent to a biomass wasting rate of approximately 200 kg VS/d.

The oxygenic nitrification reactor was designed to provide an HRT of 3.7 hours at design flow, equivalent to a total oxygenic reactor volume of approximately 760 m^3.

As in the anoxic reactor design, parallel reactors were provided. Reactor height was 7.6 m. Fluidized bed height was 6.4 m. Design hydraulic flux in the nitrification reactor was 0.48 m/min at a recycle ratio of approximately 16:1. The design hydraulic flux was significantly lower than the operating flux in the pilot-scale reactor at WTC. The higher flux requirements in the WTC pilot plant appear to be related to poor flow distribution characteristics of the small-scale reactor inlet design. Design nitrification SRT at an operational reactor biomass concentration of 17.5 g VS/L was 100 days. Ammonia nitrogen loading to the process under these operating conditions, including ammonia generated as a result of thiocyanate oxidation, ranged from 0.018 to 0.032 g NH_3-N/g VS•d, based on the design quality of the combined feed. Biomass wastage from the oxygenic reactor was 60 kg VS/d based on the measured pilot plant yield and equivalent reactor effluent suspended solids concentrations.

The process design details for the anoxic and oxygenic biological reactors are summarized in Table 46. Comparison of these design data with similar data generated for a coupled biological fluidized bed system treating coke plant wastewater alone indicate that the reactor volumes required to accomplish a similar degree of treatment are essentially identical despite the increase in design flow from 1300 m^3/d for the coke plant treatment application to 4950 m^3/d for treatment of the combined wastewater. The reduction in reactor HRT is a direct result of the increased nitrification rate achievable during treatment of the combined wastewater due to the dilution of inhibitory compounds in coke plant wastewater by the addition of blast furnace blowdown. A treatment plant layout is shown in Figure 33. Total area dedicated to the reactors would be approximately 100 m^2.

Maximum oxygen requirements for the nitrification process were 1400 kg/d based on the measured consumption during the pilot plant operation. Average requirements for a feed containing 48 g NH_3-N/L were approximately 1000 kg/d. The average oxygen requirement of the process was approximately 12 mg/L per pass through the nitrification reactor. At many steel mills, pipeline oxygen is available from the cryogenic generator supplying the basic oxygen furnace (BOF). Where pipeline oxygen is not available, alternatives include the purchase and storage of bulk liquid oxygen (LOX) or on-site production in a pressure swing adsorption (PSA) or a cryogenic generator facility.

On the basis of the pilot plant operating data, suspended solids removal from the final effluent would not be required to meet the design effluent requirements. Therefore, no provision was made in the design for effluent polishing by filtration or coagulation-sedimentation.

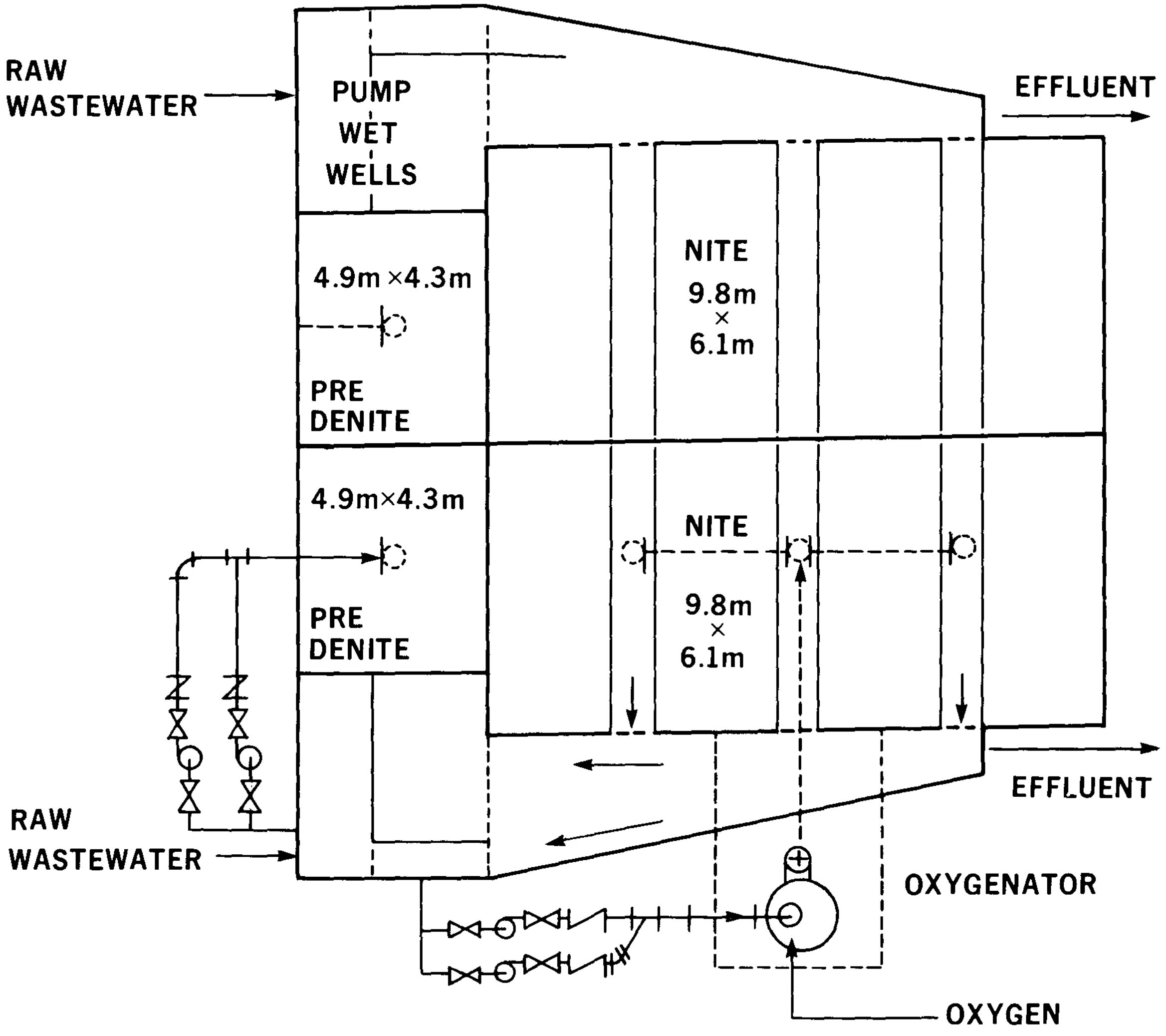


FIGURE 33 FLUIDIZED BED PROCESS LAYOUT FOR TREATMENT OF COMBINED WASTEWATER (Courtesy of Dorr-Oliver Inc.)

TABLE 46 DESIGN SPECIFICATIONS FOR BIOLOGICAL REACTORS TREATING COMBINED WASTEWATER

Parameter	Anoxic Denitrification Reactor	Oxygenic Nitrification Reactor
HRT (hours)	0.53	3.7
Fluidized Bed Height (m)	2.6	6.4
Reactor Height (m)	4.6	7.6
Reactor Area (m^2)	42.2	119.
Hydraulic Flux (m/min)	0.40	0.48
Recycle Ratio	4.0	15.8
Sand Inventory (tonnes)	87.	609.

5.2.2 Capital Cost Estimates. Preliminary cost estimates were developed for the major capital items of the coupled biological fluidized bed process and are presented in Table 47. Capital cost estimates were generated by Dorr-Oliver Inc. in U.S. dollars (1982) and have been converted to Canadian dollars directly on the basis of current exchange rates (1 U.S. \$ = 1.2 Canadian \$). In the development of these costs, it was assumed that pipeline oxygen would be available from the cryogenic generator associated with the BOF. Providing a dedicated PSA generation facility would result in an additional capital cost of approximately \$930 000 for a PSA capacity of 2700 kg/d, including liquid oxygen storage for two days as backup to the generator. Oxygen generation in a dedicated cryogenic plant is not competitive with PSA generation at this demand despite the higher oxygen purity and lower power requirements associated with cryogenic plants. It is also assumed that the lime requirements can be satisfied from the lime feeding facilities associated with the fixed-leg ammonia still. Costs for a dedicated lime slaking facility and lime slurry tank are, therefore, not included in the cost estimate.

On this basis, the estimated capital cost for a coupled fluidized bed system to treat 4950 m^3/d of a combined wastewater stream containing coke plant wastewater and blast furnace blowdown was \$2 339 000.

5.2.3 Direct Operating Costs. Annual direct operating costs for chemicals (phosphoric acid, lime and oxygen) and power are summarized in Table 48. These costs were generated on the basis of estimates provided by Canadian suppliers, exclusive of freight.

TABLE 47 CAPITAL COST ESTIMATES FOR COUPLED FLUIDIZED BED TREATMENT OF COMBINED COKE PLANT WASTEWATER AND BLAST FURNACE BLOWDOWN

Item	Cost (1982 Canadian \$ x 1000)
1) Equipment, instrumentation and engineering for: two 9.8 x 6.1 m nitrification reactors and two 4.8 x 4.3 m denitrification reactors	1050
2) Concrete reactors, oxygenator pits and pump sumps	413
3) Pumps and prefab pump rooms	300
4) Piping and valves (erected basis)	276
5) Installation of equipment, motor control center, power wiring and site work	300
TOTAL	2339

TABLE 48 ANNUAL DIRECT OPERATING COSTS ASSOCIATED WITH TREATMENT OF COMBINED WASTEWATER

Item	Cost (1982 Canadian \$)
1) Phosphoric Acid - 515 kg/d 85% H_3PO_4 @ \$0.90 per kg	\$169 300
2) Lime - 1660 kg/d bulk quicklime (90% CaO) @ \$0.061 per kg	\$ 37 000
3) Oxygen - 1000 kg/d @ \$0.06 per kg*	\$ 21 900
4) Electrical @ \$0.03 per kWh	\$ 24 250
TOTAL ANNUAL COST	\$252 450

* Based on use of pipeline oxygen from cryogenic generator supplying BOF.

Annual direct operating costs associated with treatment of the combined wastewater amount to $252 450.

Phosphoric acid requirements for the biological system constitute approximately two-thirds of these annual operating costs. As noted in Section 4.4.6, a fraction of the phosphoric acid consumption is directly related to the precipitation of calcium phosphate from the wastewater. Removal of calcium from the wastewater by recarbonation upstream of the fluidized bed process could significantly reduce the phosphorus consumption.

The operating costs provided in Table 48 were based on the availability of pipeline oxygen from the cryogenic generator at the BOF at a cost of $60 per tonne. Bulk liquid oxygen costs would be approximately $44 000 annually if oxygen were not available from this source. Alternatively, power costs associated with the operation of a dedicated 2700 kg/d PSA oxygen generation facility would be approximately $16 500 annually. At the oxygen demands of the process, bulk LOX supply would appear to be the more cost-effective alternative on the basis of investment cost and operating cost over a period of three of five years.

5.3 Comparison of Capital and Operating Costs for Fluidized Bed Systems Treating Coke Plant Wastewater and Combined Wastewater

In Table 49, the capital costs of the fluidized bed system designed to treat the combined wastewater stream are compared with cost data developed for treatment of coke plant wastewater alone. The capital costs associated with treatment of the combined wastewater are essentially the same as those associated with treatment of coke plant wastewater alone.

Table 50 compares the annual direct operating costs associated with treatment of the combined wastewater with those developed for treatment of coke plant wastewater alone. Operating costs for treatment of the combined wastewater are approximately $100 000 per year higher than similar costs for treatment of coke plant wastewater. The cost difference is primarily a result of the increased costs associated with phosphoric acid utilization during treatment of the combined wastewater. However, on a unit cost basis ($ per m^3 treated), operating costs associated with treatment of the combined wastewater are less than half the costs associated with treatment of coke plant wastewater alone.

In assessing the capital and operating cost implications of the two wastewater management concepts evaluated in this study; that is, biological treatment of coke plant wastewater alone and in combination with blast furnace blowdown, it must be considered

TABLE 49 COMPARISON OF CAPITAL COSTS ASSOCIATED WITH TREATMENT OF COMBINED WASTEWATER AND COKE PLANT WASTEWATER

Item	Capital Cost (1982 Canadian $ x 1000)	
	Combined Coke Plant Wastewater and Blast Furnace Blowdown*	Coke Plant Wastewater**
1) Equipment, instrumentation and engineering for reactors and clarifiers***	1050	1010
2) Concrete reactors, oxygenator pits, pump sumps and clarifier basin***	413	460
3) Pumps and prefab pump rooms	300	292
4) Piping and valves	276	283
5) Installation	300	312
TOTAL	2339	2357

* Design Flow = 4950 m^3/d
** Design Flow = 1300 m^3/d
*** No clarification stage required for treatment of combined wastewater.

TABLE 50 COMPARISON OF CAPITAL COSTS ASSOCIATED WITH TREATMENT OF COMBINED WASTEWATER AND COKE PLANT WASTEWATER

Item	Capital Cost (1982 Canadian $)	
	Combined Coke Plant Wastewater and Blast Furnace Blowdown*	Coke Plant Wastewater**
1) Phosphoric Acid	169 300	82 100
2) Lime	37 000	13 400
3) Oxygen	21 900	28 500
4) Polymer	N/A	2 300
5) Electrical	24 250	24 600
TOTAL ANNUAL COST	252 450	150 900
UNIT COST ($ per m^3 treated)	0.14	0.32

* Design Flow = 4950 m^3/d

** Design Flow = 1300 m^3/d

that the costs associated with the first alternative (biological treatment of coke plant wastewater alone) do not incorporate any provision for separate treatment of blast furnace blowdown water. In this instance, a separate dedicated treatment facility, based on alkaline chlorination or a similar technology, would be required to treat the blast furnace blowdown water. Development of capital and operating cost information for a dedicated blast furnace blowdown treatment system was outside the scope of this investigation; however, these costs must be considered in the overall economic comparison of alternative waste management schemes for coke plant wastewater and blast furnace blowdown water at an integrated steel mill.

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Fluidized Bed Treatment of Coke Plant Wastewater

The results of pilot-scale evaluation of the coupled pre-denitrification-nitrification biological fluidized bed process conducted at the Wastewater Technology Centre demonstrated that the technology is technically feasible for treatment of coke plant wastewater. Effective nitrogen control can be attained at significantly reduced hydraulic retention times compared to conventional suspended growth systems treating similar wastewaters, without raw wastewater dilution or the addition of powdered activated carbon to the biological reactors.

The following specific conclusions and recommendations can be drawn with respect to the application of the biological fluidized bed process to coke plant wastewaters.

1) The fluidized bed process was capable of achieving complete nitrification and denitrification of undiluted coke plant wastewater without the addition of powdered activated carbon to the system. Total nitrogen removal efficiencies of more than 90 percent were maintained in the fluidized bed process at a total system HRT of approximately 16 hours. Based on a separate study (1, 2) with a similar wastewater, a system HRT of up to 60 hours and the addition of low levels of PAC were necessary to attain the same degree of treatment in a suspended growth biological process.
2) The higher volumetric removal efficiencies of the fluidized bed process are primarily related to the high biomass concentrations attainable in the reactors. Volatile solids concentrations in the denitrification reactor approached 40 g/L. Volatile solids concentrations in the nitrification reactor approached 20 g/L.
3) Operation of the denitrification reactor at long SRT's (more than 30 days) resulted in the accumulation of inorganic deposits of tetrabasic calcium phosphate which inhibited bed expansion and SRT control. At higher growth rates (lower SRT), these problems were eliminated.
4) Flow distribution was determined to be a critical factor in achieving high biomass concentrations in the nitrification reactor.
5) Operation of the coupled process in the pre-denitrification mode reduced the theoretical oxygen demand of the wastewater by approximately 66 percent due to the removal of a substantial fraction of the degradable organic carbon under anoxic

conditions in the denitrification reactor. Mass balances around the denitrification reactor indicated the anoxic removal of approximately three parts of organic carbon (FOC) per part of oxidized nitrogen (NO_T-N) removed. Oxygen requirements for complete nitrification were approximately 1.0 g/L of coke plant wastewater treated.

6) After the establishment of an acclimated biomass in the fluidized bed reactors, the process consistently attained more than 90 percent removal of organic carbon, thiocyanate and phenolic compounds despite step changes in loading conditions and periodic reductions in the efficiency of nitrification. The removal efficiency for total cyanide depended on the amount of biodegradable cyanide in the wastewater.

7) Eighteen U.S. EPA base/neutral extractable priority pollutants were identified at greater than trace concentrations (1 µg/L) in more than one untreated coke plant wastewater sample, including polynuclear aromatics such as acenaphthylene, acenaphthene, anthracene/phenanthrene, fluoranthene, naphthalene and pyrene. An additional 15 base/neutral extractable compounds not included in the U.S. EPA priority pollutant classification were identified at greater than trace levels in more than one untreated sample. Heterocyclic nitrogenous compounds such as isoquinoline, indole, carbazole and quinoline were consistently present at elevated concentrations.

8) Only four base/neutral extractable priority pollutants were identified at greater than trace concentrations (1 µg/L) in more than one sample collected after treatment in the biological fluidized bed process. Two of these four compounds were phthalate esters. Ten base/neutral extractable non-priority pollutants were found at greater than trace concentrations in more than one treated effluent sample. None of these compounds were detected at concentrations in excess of 30 µg/L.

9) Five base/neutral extractable priority pollutants were quantified in reactor sludge samples, including three phthalate esters, acenaphthylene and pyrene. None of non-priority pollutants analyzed for were consistently found in the biological sludges at greater than trace levels (0.1 µg/g).

10) On the basis of the pilot-scale performance data, process design details for a full-scale coupled biological fluidized bed process treating coke plant wastewater were developed. Estimated installed costs of a fluidized bed system to treat coke plant wastewater at a design flow of 1300 m^3/d were $2 357 000 (1982) including the costs associated with final effluent clarification.

11) Annual direct operating costs (chemicals and power) associated with the coupled fluidized bed process amounted to approximately \$150 900 (1982). The cost of phosphoric acid addition contributed more than 50 percent of the total annual direct operating costs.

The following recommendations were made relating to the treatment of coke plant wastewaters alone.

1) Although non-steady state feed conditions were simulated during the pilot-scale evaluation, the impact of process feed variability on the stability of the coupled fluidized bed process should be assessed under typical coke plant operating conditions. This would require on-site pilot plant investigations.
2) The coupled biological fluidized bed process was demonstrated to be a technically feasible process for application to coke plant wastewaters. In light of the advantages demonstrated for this technology, its applicability to other complex industrial wastes, such as coal liquefaction wastewater, should be evaluated.
3) As the fluidized bed process is capable of high volumetric removal efficiencies and the response time is an order of magnitude less than conventional systems, suitable process control strategies and instrumentation should be developed to capitalize on the intrinsic advantages of the process.
4) The analytical methodologies applied for quantification of trace organic compounds in the coke wastewater, treated effluents and biological sludges were screening methods designed to identify a wide range of trace contaminants. Based on these results, specific analytical methods for the compounds identified should be developed and applied to these wastewaters, effluents and sludges.

6.2 Fluidized Bed Treatment of Coke Plant Wastewater and Blast Furnace Blowdown

The results of pilot-scale evaluations of the coupled biological fluidized bed process conducted at the Wastewater Technology Centre demonstrated that the technology is technically feasible for treatment of a combined stream containing coke plant wastewater and blast furnace blowdown water.

The following specific conclusions and recommendations can be drawn with respect to the application of the process to the combined wastewater stream.

1) Complete nitrification and denitrification of the combined coke plant wastewater and blast furnace blowdown water was achieved in the fluidized bed system at

significantly reduced reactor hydraulic retention times compared to those required to achieve a similar degree of treatment for coke plant wastewater alone. Total system HRT requirements for the combined wastewater were approximately 4.5 hours compared to approximately 16 hours for equivalent treatment of coke plant wastewater.

2) Under these operating conditions, effluent quality in terms of FOC, phenolic compounds, thiocyanate, total cyanide and suspended solids concentrations was superior to that achieved during fluidized bed treatment of coke plant wastewater.

3) The organic carbon requirements associated with denitrification of the combined wastewater were significantly lower than those measured during treatment of coke plant wastewater alone. Mass balances around the denitrification reactor indicated the anoxic removal of approximately one part of organic carbon (FOC) per part of oxidized nitrogen (NO_T-N) removed from the combined wastewater compared to the removal of approximately three parts FOC per part NO_T-N removed from coke plant wastewater.

4) The addition of methanol or other supplemental organic carbon was not necessary under conditions of typical feed quality. The unnecessary addition of methanol adversely affected the performance of the nitrification process.

5) Concentrations of zinc in the pilot plant feed of up to approximately 3.4 mg/L did not appear to affect the performance of the biological system. At concentrations of 7 mg/L, there appeared to be some inhibition to the nitrification system but further data are necessary to confirm this observation. Blending of coke plant wastewater with blast furnace blowdown resulted in a net reduction in the soluble zinc content of the combined feed. Further precipitation of soluble zinc was achieved by pH adjustment to the range of 9 to 10. Additional work is required to determine whether removal of insoluble zinc from the feed is necessary to prevent inhibition of the nitrification system.

6) On the basis of seven treated effluent samples collected from the fluidized bed pilot plant and analyzed for U.S. EPA organic priority pollutants and 24 non-priority pollutant trace organic compounds, only di-n-butylphthalate was identified at greater than trace concentrations (0.01 mg/L) after treatment despite the presence of a range of trace organics in the untreated wastewater at concentrations up to approximately 15 mg/L. There were indications of an accumulation of a number of base-neutral group polynuclear aromatic compounds including fluoranthene, pyrene, benzo(a)pyrene and benzo(a)anthracene and/or chrysene in the fluidized bed sludges.

7) On the basis of pilot plant performance data, the estimated capital costs associated with treatment of 4950 m^3/d of combined wastewater were \$2 339 000 (1982). The capital cost was essentially identical to the cost developed for similar treatment of 1300 m^3/d of coke plant wastewater alone.

8) Annual direct operating costs (chemical and power) for treatment of 4950 m^3/d of combined wastewater were \$252 450 (1982), of which approximately two-thirds was related to the consumption of phosphoric acid. Although annual costs for treatment of the combined wastewater were approximately 67 percent higher than for treatment of coke plant wastewater, the treatment costs per unit volume of combined wastewater were less than 50 percent of those for treatment of coke plant wastewater alone (\$0.14 per m^3 and \$0.32 per m^3, respectively.)

The following recommendations were made based on the pilot plant study of fluidized bed treatment of the combined wastewater stream.

1) Longer term operating data should be acquired to confirm biological process SRT's, process stability and chemical requirements (oxygen, alkalinity and phosphorus) under steady state operating conditions.

2) The impact of feed variability on the stability of the fluidized bed process should be evaluated under typical coke plant and blast furnace operating conditions. This would require on-site plant investigations.

3) The concentrations of total and soluble zinc in the combined feed at which significant inhibition to the nitrification process occurs should be more precisely defined. Furthermore, the necessity to physically remove insoluble zinc from the process feed needs to be evaluated.

4) Due to the contribution of phosphoric acid addition to the total direct operating costs of the system, the effect of reducing the influent calcium concentration by recarbonation on the phosphorus requirements should be investigated.

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ABBREVIATIONS AND SYMBOLS

A1→A6 - process feeds during acclimation period
Alk - alkalinity
A.S. - activated sludge
ASW - ammonia still wastewater
BAT - Best Available Technology
BOD_5 - biochemical oxygen demand
BOF - basic oxygen furnace
BPT - Best Practicable Technology
BVS - bed volatile solids
CaO - quicklime
$4CaO \cdot P_2O_5$ - tetrabasic calcium phosphate
CN_F - free cyanide
CNS - thiocyanate
CO_2 - carbon dioxide
COD - chemical oxygen demand
°C - Celsius degrees
d_{10} - effective size
d_{60}/d_{10} - uniformity coefficient
F - filterable
FOC - filterable organic carbon
g - gram
g/L - gram per litre
GC/MS - gas chromatography/mass spectroscopy
$g\ NH_3\text{-}N/g\ VSS \cdot d$ - specific ammonia oxidation rate
h - hour
H^+ - hydrogen ion
H_2O - water
H_3PO_4 - phosphoric acid
HRT - hydraulic retention time
kg - kilogram
kkg - thousand kilogram (tonne)
kg/d - kilogram per day
$kg/m^3 \cdot d$ - kilogram per cubic metre per day

kWh	-	kilowatt - hour
L	-	litre
L/min	-	litre per minute
LOX	-	liquid oxygen
m	-	metre
mm	-	millimetre
m^3	-	cubic metre
m^2/m^3	-	square metre per cubic metre
m^3/d	-	cubic metre per day
m/min	-	metre per minute
$m^3/m^2 \cdot d$	-	cubic metre per square metre per day
mg	-	milligram
mg/L	-	milligram per litre
N	-	nitrogen
NH_3-N	-	ammonia nitrogen
NH_4+	-	ammonium ion
NO_2-	-	nitrite ion
NO_2-N	-	nitrite nitrogen
NO_3-	-	nitrate ion
NO_3-N	-	nitrate nitrogen
NO_T-N	-	total oxidized nitrogen
O_2	-	oxygen
P	-	phosphorus
PAC	-	powdered activated carbon
PID	-	proportional-integral-derivative (controller)
PNA	-	polynuclear aromatics
PSA	-	pressure swing adsorption
Pre - DN	-	pre-denitrification (process)
Pre - DN-N	-	pre-denitrification-nitrification (process)
Q	-	flow
QA/QC	-	quality assurance/quality control
RBC	-	rotating biological contractor
$SO_4^=$	-	sulphate ion
SRT	-	solids retention time
SS	-	suspended solids

SS1→SS5	-	process feeds during steady state
T	-	temperature
TCN	-	total cyanide
TKN	-	total kjeldahl nitrogen
TN	-	total nitrogen
TVS	-	total volatile solids
UF	-	unfiltered
U.S. EPA	-	United States Environmental Protection Agency
V1→V5	-	process feeds during variable feed phase
VS	-	volatile solids
VSS	-	volatile suspended solids
WAL	-	weak ammonia liquor
WTC	-	Wastewater Technology Centre
CN_A	-	cyanide amenable to chlorination
BFBD	-	blast furnace blowdown
Ca	-	calcium
Zn	-	zinc
Fe	-	iron
Ni	-	nickel
Pb	-	lead
PNA	-	polynuclear aromatics
µ	-	micron
µg	-	microgram
µg/L	-	microgram per litre
µg/g	-	microgram per gram
µmho/cm	-	micromho per centimetre

CONVERSION FACTORS

1 centimetre (cm)	=	0.394 inches (in)
1 metre (m)	=	3.28 feet (ft)
1 square centimetre (cm^2)	=	0.155 square inches (in^2)
1 square metre (m^2)	=	10.76 square feet (ft^2)
1 litre (L)	=	0.22 Imperial gallons (Igal)
	=	0.26 U.S. gallons (gal)
1 cubic metre (m^3)	=	220 Imperial gallons (Igal)
	=	264 U.S. gallons (gal)
1 kilogram (kg)	=	2.2 pounds (lb)
1 centimetre per second (cm/s)	=	0.394 inches per second (in/sec)
1 metre per second (m/s)	=	3.28 feet per second (ft/sec)
1 Celsius degree	=	1.8 Fahrenheit degree
1 litre per minute (L/min)	=	0.22 Imperial gallons per minute (Igal/min)
1 cubic metre per day (m^3/d)	=	220 Imperial gallons per day (Igal/day)
1 metre per hour (m/h)	=	0.05 feet per minute (ft/min)
1 cubic metre per square metre-day ($m^3/m^2 \cdot d$)	=	20.4 Imperial gallons per square foot-day ($Igal/ft^2$-d)
1 kilogram per 1000 square metres-day (kg/1000 $m^3 \cdot d$)	=	0.204 pounds per 1000 square feet-day (lb/1000 ft^2-d)