Treatment of Effluents from Ammonia Plants – Part I
Biological Nitrification of an Inorganic Effluent from a Nitrogen-Chemicals Complex

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Abstract

The conditions for the biological oxidation of ammonia in an inorganic effluent containing high levels of ammonia and nitrate were investigated in continuous units. Successful and reliable nitrification of feed between 1 000–1 900 mg ℓ^{-1} NH_4–N (in the presence of an equivalent amount of NO_3–N) was achieved at pH 7,2 at 25°C and also 10°C.

It was found that experimental values fitted the relation $\frac{1}{R_s} = Y_t \frac{[N_i - N_e]}{X_v R} [1 + 0{,}15bR_s] - b$ where $Y_t = 0{,}1$ and $b = 0{,}04$

Introduction

An aqueous effluent from a nitrogen-chemicals complex (A) amounts to 1,6–1,7 million litres per day. The composition of this effluent is given in Table 1.

Such an effluent is being used as a liquid fertilizer and is distributed over a large area of land on which the grass *Eragrostis curvula* is grown (Lever 1966). Due to various circumstances, alternative methods of treating the effluent are required.

Air stripping, pressure driven membrane processes, ion-exchange, algal assimilation of nitrogen were considered but rejected in favour of a bacterial treatment method.

In another area, an ammonia plant (B) produces the necessary ammonia synthesis gas from naptha feed stock or refinery gas and in the reforming process a condensate (approximately 30 m^3h^{-1}) is produced. The composition of the effluent is shown in Table 2.

TABLE 1

COMPOSITION OF EFFLUENT FROM NITROGEN-CHEMICALS COMPLEX A.

	ppm
Calcium as Ca	1125
Phosphate as PO_4	not detected
Sodium as Na	309
Magnesium as Mg	43
Iron as Fe	<1
Potassium as K	27
Copper as Cu	0,2
Zinc as Zn	9,8
Chloride as Cl	220
Fluoride as F	~1
Sulphate as SO_4	3500
Ammonia as NH_4–N	1400
Nitrate as NO_3–N	1400

Aluminium as Al, Bismuth as Bi, Cadmium as Cd, Cobalt as Co, Chromium as Cr, Manganese as Mn, Nickel as Ni, Lead as Pb, Antimony as Sb, Mercury as Hg, Arsenic as As, and Molybdenum as Mo, present at values between 1 – 0,02 ppm. A light yellow colour is imparted to the effluent by various organic nitro-compounds present in low concentrations (below 20 ppm).

In this particular effluent, the odour nuisance is the problem and although the smell of amines can be prevented by avoiding alkaline conditions, it was considered advisable to seek methods which would destroy the amines. Two different

TABLE 2

COMPOSITION OF CONDENSATE FROM A REFORMING PROCESS

	ppm
Methanol	900 – 2000
Ammonia as NH_4–N	600
Methylamines (mono, di and tri) up to	200
Carbon dioxide	saturated
The amount of amine varies with catalyst activity; a particular effluent sample showed the following:	
Mono-methylamine	8 ppm
di-methylamine	2 ppm
tri-methylamine	4 ppm.

approaches were adopted (a) chemical oxidation involving the use of ozone and (b) biological oxidation of the carbon-one compounds.

The treatment processes will be described in four parts:

1. Biological nitrification of an inorganic effluent from a nitrogen-chemicals complex.
2. Biological oxidation of carbon-one compounds (amines and methanol) in an effluent from a reforming plant serving an ammonia complex.
3. Ozonation of amines in an effluent from a reforming plant serving an ammonia complex.
4. Biological denitrification of an inorganic effluent from a nitrogen-chemicals complex.

General

In line with common practice in environmental engineering the nitrifying bacteria are grouped into ammonia oxidising micro-organisms *(Nitrosomonas)* and nitrite oxidising organisms *(Nitrobacter)*.

The reactions may be represented simply as:

Cell synthesis

$$5\,Co_2 + NH_3 + 2H_2O \rightarrow C_5H_7O_2N + 5\,O_2$$

Energy reactions,

$$2NH_4^+ + 3\,O_2 \xrightarrow[\text{organisms}]{\text{nitrifying}} 2NO_2^- + 4H^+ + 2H_2O$$

$$2NO_2^- + O_2 \xrightarrow[\text{organisms}]{\text{nitrifying}} 2NO_3^-$$

The following equation has commonly been used to express the specific growth rate, μ, of micro-organisms

$$\frac{dx}{dt}\cdot\frac{1}{x} \equiv \mu = \frac{\mu_{max}\,N}{K_n + N} \qquad (1)$$

the relationship between rates of growth and substrate consumption is given by

$$\frac{dx}{dt} = \frac{-YdN}{dt} \qquad (2)$$

In the case of the autotrophic bacteria, *Nitrosomonas* and *Nitrobacter*, the usual difficulties in determining the concentration of bacteria in sludge is eliminated by being able to determine accurately the products of oxidation, nitrite and nitrate, which come only from the autotrophs.

In developing the relationships which follow, it is assumed that the reaction occurs in a completely homogeneous phase; the micro-organisms are dispersed in the fluid phase containing the substrate. It is assumed also that as nitrite is formed by *Nitrosomonas*, it is converted to nitrate by *Nitrobacter* and the level of nitrite is negligible in the effluent from a continuous stirred reactor. Thus the conversion of ammonia to nitrite is rate limiting and the model assumes conversion of nitrite to nitrate without interference from excess nitrite or free ammonia.

The influent is free from nitrifying micro-organisms. For a batch reactor,

net growth rate = synthesis rate – endogenous mass loss

$$\frac{dX_a}{dt} = \frac{dX_1}{dt} - \frac{dX_2}{dt} \qquad (3)$$

and since

$$\frac{dN}{dt} = \frac{-K_{mu}N\,X_a}{K_n + N} \text{ and } \frac{dX_a}{dt} = -Y_t\frac{dN}{dt}$$

$$\frac{dX_a}{dt} = Y_t\,\frac{K_{mu}\,N\,X_a}{K_n + N} - bX_a \qquad (4)$$

In a continuous stirred tank reactor, defining the growth rate of bacteria as $\psi = \frac{Y_t\,K_{mu}\,N\,X_a}{K_n + N} - bX_a$, various relationships may be obtained for operation with or without sludge retention. In view of the fact that the influent into the reactor may be regarded as steady, both with respect to concentration of substrate and volume of flow, the relationships may be developed for steady state conditions.

The derivation of the various formula below is similar to that used by Marais (1973).

From a mass balance on biomass (Fig. 1)

$$Q[N_t–N_e]Y_t - bX_aV = wX_{ar} + (Q - w)\,X_{ae} \qquad (5)$$

$$X_a = Y_t\,\frac{(N_t–N_e)}{(1 + bR_s)}\,\frac{R_s}{R} \text{ where } R_s = \frac{XV_a}{wX_{ar} + (Q–w)\,X_{ae}} \qquad (6)$$

Similarly from a mass balance on N

$$N_tQ - N_eQ = \frac{K_{mu}NX_aV}{K_n + N} \qquad (7)$$

$$\text{or } N_t–N_e = \frac{K_{mu}N}{K_n + N}\,X_aR \qquad (8)$$

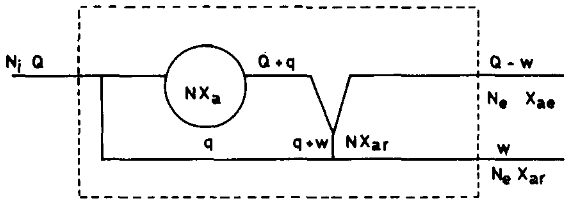

Figure 1
CST reactor with sludge retention

from which

$$\frac{K_{mu}N}{K_n + N} = \frac{1 + bR_s}{Y_t\,R_s} \tag{9}$$

$$\text{and } \frac{1}{R_s} = Y_t \frac{K_{mu}N}{K_n + N} - b \tag{10}$$

$$\text{and } N = \frac{K_n(1 + b\,R_s)}{R_s(Y_tK_{mu}-b) - 1} \tag{11}$$

Measurement of X_a

In practice volatile suspended solids X_v is normally measured. This measure includes any endogenous mass. Approximately 15–20% of cell mass may be regarded as endogenous mass or residue.

From Figure 1, at steady state

$$0{,}15\,b\,V\,X_a - [X_{ee}\,(Q-w) + X_{er}w] = 0 \tag{12}$$

$$\text{from which } X_e = 0{,}15\,b\,X_a\,R_s \tag{13}$$

Since the effluent concerned contains inert inorganics (soluble) and only a negligible amount of inert organics, these may both be neglected if controls are made on X_v since $X_v = X_a + X_e$.

It can thus be shown that

$$X_v = Y_t \frac{(N_t-N_e)}{1 + bR_s}\frac{R_s}{R}\,[1 + 0{,}15\,b\,R_s] \tag{14}$$

Relation between sludge age and unoxidised substrate

From equation (10),

$$\frac{1}{R_s} = Y_t \frac{K_{mu}N}{K_n+N} - b$$

and equation (11)

$$N = \frac{K_n[1 + bR_s]}{R_s\,(Y_tK_{mu}-b) - 1},$$

it can be seen that the unoxidised substrate in a CST reactor is a function of the sludge age.

From equation (14),

$$X_v = Y_t \frac{N_t-N_e}{1 + bR_s}\frac{R_s}{R}\,[1 + 0{,}15bR_s]$$

hence X_vV = mass of sludge in reactor

$$= Y_t\left[\frac{\text{mass of N oxidised}}{1 + bR_s}\right] R_s\,[1 + 0{,}15bR_s] \tag{15}$$

The constants Y_t and b

From equation (6),

$$X_a = Y_t \frac{(N_t-N_e)}{1 + bR_s}\frac{R_s}{R}$$

$$\text{hence } \frac{1}{R_s} = Y_t \frac{(N_t-N_e)}{X_aR} - b \tag{16}$$

and by applying equation (13),

$$\frac{1}{R_s} = Y_t \frac{(N_t-N_e)}{X_vR}\,.\,(1 + 0{,}15\,bR_s) - b \tag{17}$$

A plot of $\frac{1}{R_s}$ vs. $\frac{N_t-N_e}{X_vR}$ $(1 + 0{,}15\,bR_s)$ will give a slope of Y_t and an intercept on $\frac{1}{R_s}$ of –b. It will be seen however that the value of b is only available implicity.

From equation (14)

$$X_v = Y_t \frac{(N_t-N_e)}{1 + bR_s}\,.\,\frac{R_s}{R}[1 + 0{,}15\,bR_s]$$

hence

$$\frac{N_t-N_e}{X_vR} = \frac{1 + bR_s}{(1 + 0{,}15\,bR_s)\,R_sY_t}$$

$$\log\frac{(N_t-N_e)}{X_vR} = \log\left[{}^{(1 + bR_s)}/_{(1 + 0{,}15\,bR_s)R_s}\right] - \log Y_t$$

By plotting $\frac{1}{R_s}$ vs. $\left[{}^{1 + bR_s}/_{(1+0{,}15\,bR_s)R_s}\right]$ for a series of b values, a series of curves are obtained, the shape being a function of b only (Y = 1) Figure 2.

The value of b may be identified by plotting $\frac{N_t-N_e}{X_vR}$, the experimental value, vs $\frac{1}{R}$ the experimental condition, and superimposing the curve nearest to the experimental curve.

The value of Y_t can be found from equation (14) since

$$\frac{N_t-N_e}{X_vR} = \frac{1 + bR_s}{Y_tR_s\,(1 + 0{,}15\,bR_s)}$$

Data obtained from laboratory tests described in section 3 were used to show the applicability, in particular, of the equation

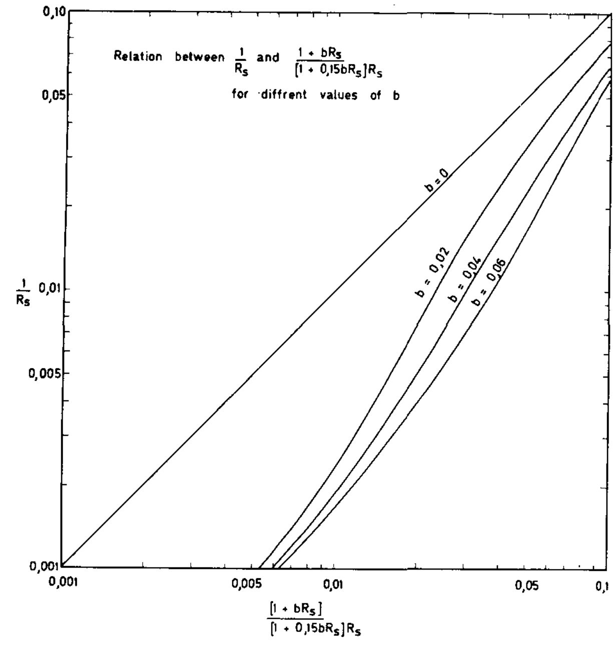

Figure 2

relating sludge age to biomass. Since both ammonia and nitrite under conditions which yield free ammonia or free HNO_2 are toxic to the biomass, only data obtained under conditions where this toxicity is eliminated should be used. These are of course the conditions for satisfactory effluent treatment.

Fraction of species present under different pH conditions

Using the pK values for the following at 25°C and infinite dilution (Sillen and Martell 1964), the dependence of the molecular species on pH at any concentration of nitrite or ammonium ion was calculated and shown in Figure 3. (Correction for ionic strength should be made when considering the actual effluent.)

$H^+ + NO_2^- \rightleftharpoons HNO_2$ $\quad pK_1 = 3{,}35$

$H^+ + NH_3 \rightleftharpoons NH_4^+$ $\quad pK_1 = 9{,}25$

Under continuous operating conditions where the level of ammonium and nitrite ions should be low in effective operation, pH control can be used to keep the molecular species out of the reactor bearing in mind the effect of hydrogen and hydroxyl ions on the micro-organisms.

Sludge age

$$\frac{1}{R_s} = \frac{Y_t K_{mu} N}{K_n + N} - b \qquad \text{from equation 10}$$

The following cases apply

a) $\frac{1}{R_s} < \frac{Y_t K_{mu} N}{K_n + N} - b$

The nitrifying bacteria will be sustained in the reactor at a particular concentration and steady oxidation of ammonia and nitrite will take place.

As R_s decreases, so the nitrifying bacteria concentration decreases with effluent NH_4–N concentration remaining constant.

b) $\frac{1}{R_s} = \frac{Y_t K_{mu} N}{K_n + N} - b$

This is the critical age below which the effluent ammonia-N concentration changes.

It should be noted that the bacteria age based on the Monod equation is a function of NH_4–N and NO_2–N concentration and in the limiting case when $-N >> K_n$, the age becomes independent of the –N concentration,

and $\left.\frac{1}{R_s}\right|\ \lim = Y_t K_{mu} - b$ (18)

c) $\frac{1}{R_s} > \frac{Y_t K_{mu} N}{K_n + N} - b$

The loss of nitrifying bacteria is greater than that formed and the reaction will enter an unsteady state phase and NH_4–N concentration will change from the desired level. It would settle down at another level when the rate of formation of bacteria again equals the amount lost if there is no substrate or other toxicity or inhibitory effect.

μm or K_{mu} is dependent on a number of factors such as temperature, pH and toxic substances. In regard to temperature (which also affects K_n and b but not Y) the relation

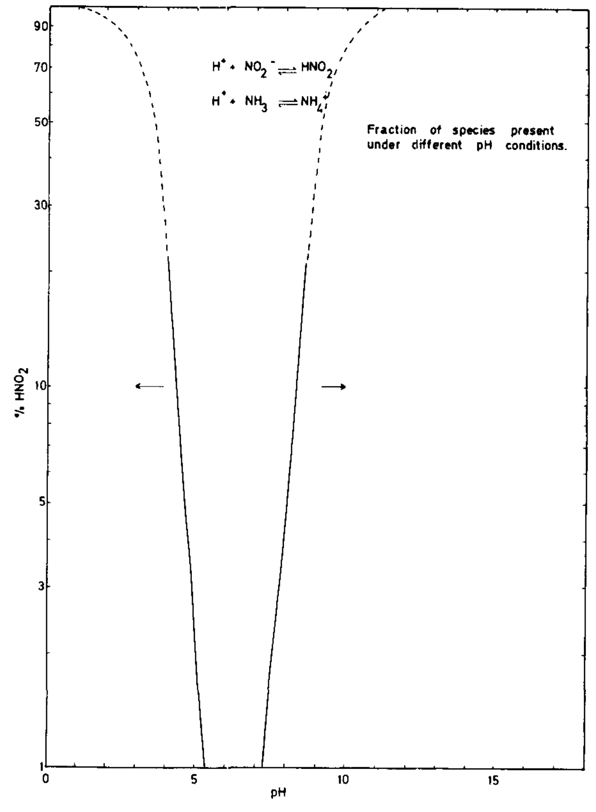

Figure 3

between temperature and growth rate constant is given by

$$\mu_{m\,T2} = \mu_{m\,T1}\, e^{x(T_2-T_1)}$$

x, according to Jenkins (1969) is 0,12; on the basis of sludge age therefore,

$$\frac{1}{R_{s\,T2}} = \frac{1}{R_{s\,T1}}\, e^{x(T_2-T_1)}$$

Oxygen consumption

Reactions involving oxygen may be shown as

(a) cells: $C_5H_7O_2N + 5\,O_2 = 5\,CO_2 + NH_3 + 2H_2O$ or 1 mg cells $\equiv$ 1,42 mg O_2

(b) energy: $2\,NH_4^+\,4\,O_2 = 2\,NO_3^- + 4\,H^+ + 2\,H_2O$ or 1 mg $NH_4^+ \equiv$ 4,6 mg O_2

From a mass balance on substrate (assuming that nitrite in the effluent from the CST reactor is negligible) it can be shown that the oxygen required per litre of reactor capacity

$$= 4{,}6\,\frac{\{N_{i\,NH4} - N_{e\,NH4}\}}{R} - \frac{1{,}42\,X_v}{R_s} - 4{,}6\,\frac{[0{,}1\,X_v]}{R_s} \qquad (19)$$

or the mass of oxygen required per day

$$= 4{,}6\,\frac{\{N_{i\,NH4} - N_{e\,NH4}\}}{R}\,Q - \frac{1{,}42\,X_vV}{R_s} - 4{,}6\,\frac{[0{,}1\,X_v]}{R_s}\,V \qquad (20)$$

where approximately 0,1 of the mass of sludge is nitrogen. Haug and McCarthy (1971) have indicated that the minimum level for constant oxidation is 1-2 mg $\ell^{-1} O_2$.

Acid production

Acid production arises from the oxidation of ammonia,

$$2NH_4^+ + 3\,O_2 \rightarrow 2\,NO_2^- + 4H^+ + 2H_2O$$

Assuming the influent is near pH 7-7,2 and this is the value at which the reactor will be controlled, every mole of NH_4^+ oxidised will require 2 moles of OH^-.

Experimental

A series of preliminary batch tests was carried out by the author and Cook and was reported elsewhere (Neytzell-de Wilde 1975, Cook 1976). The Monod type equation appears to describe adequately the reactions under the conditions of the tests (ammonia oxidation to nitrite in the presence of the reaction nitrite → nitrate).

Utilization constants K_{mu} were found to be of the order of 0,07 – 0,09 hr^{-1} at 25°C for ammonia.

In batch tests nitrite tends to accumulate to a peak value and then decreases rapidly once the ammonia-N concentration is reduced to a few parts per million. For a given initial ammonia-N concentration, the maximum accumulation of nitrite increases with increase in pH.

Copper at levels as low as 0,4 mg ℓ^{-1} retarded reaction rates.

Continuous stirred tank reactor tests

Precipitation of biomass for continuous tests

A sample of activated sludge was obtained from a local sewage works and acclimated to a feed of synthetic sewage in a continuous stirred tank (CST) reactor maintained at pH 7. Thereafter, an additional feed of synthetic inorganic effluent was fed to the reactor in increasing quantities while the organic feed was simultaneously decreased until the only feed to the reactor was the synthetic inorganic feed.

The reactor was run under these conditions for some weeks before the biomass (now essentially buff-coloured nitrifying bacteria) so produced was used in subsequent tests.

The synthetic inorganic feed was made from technical grade salts and tap water and the nitrogen content was made to approach that of the industrial effluent:

Medium:	Potassium dihydrogen phosphate	0,125 g ℓ^{-1}
	Magnesium sulphate, $7H_2O$	0,1 g ℓ^{-1}
	Calcium chloride, $2H_2O$	0,15 g ℓ^{-1}
	Sodium chloride	0,2 g ℓ^{-1}
	Ammonium nitrate to give NO_3–N	1400 ppm
	NH_4–N	1400 ppm

It was assumed that sufficient trace elements would be present in the tap water.

The continuous experiments were designed to show
a) the relation between biomass and rate of utilisation of nitrogen and the advantages of the use of sludge retention (or sludge recycle or controlled sludge wastage) over once through or 'chemostat' type operation.
b) the reproducibility of tests and hence the likely reliability in large scale operation.

Standard conditions

Reactors: The type of reactor used is shown in Fig. 4. The reactors were made of clear Perspex, but were screened from light to prevent algal growth.

Temperature: Tests were carried out at ambient temperature 22 – 27°C and under controlled temperature conditions of 24 – 27°C and 10°C.

pH: Consideration was given to the dissociation of NH_4–N and NO_2–N and from the data given earlier, a pH of 7,2 ± 0,2 was used in all tests. The acid produced during reaction was neutralised with 1,0 molar sodium bicarbonate.

Oxygen: In all tests the supply of air to reaction vessels was sufficient to exceed 2 ppm (usually 4 – 6 ppm). In the quiet zone (primary settler) of the continuous reactors the oxygen value was usually greater than 1,5 – 2 ppm.

Sludge Wastage: Sludge was wasted by withdrawing a fixed volume of reactor mixed liquor at fixed intervals by pipette. Samples withdrawn for chemical analysis were taken from the main reactor or primary settler after the contents of both had been thoroughly mixed. Samples were filtered and biomass returned to the reactor with an equal volume of clear reactor effluent. Alternatively, where sludge was 'wasted' from the reactor, samples for analyses were taken from the volume

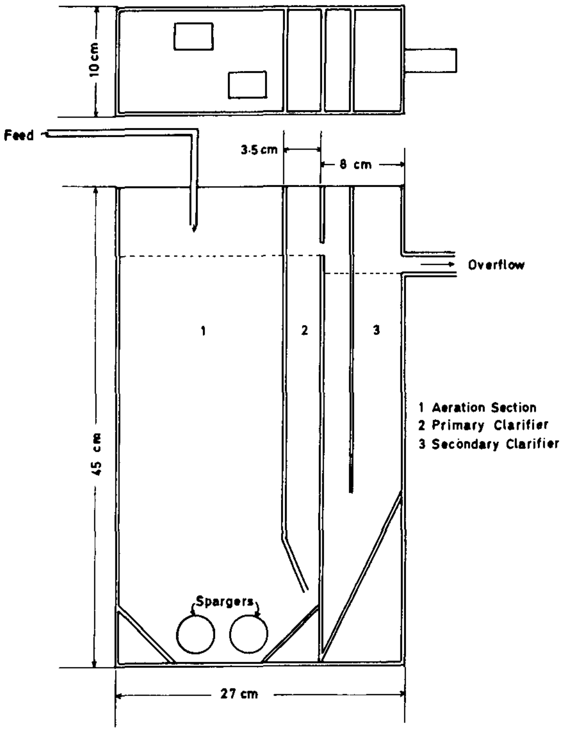

Figure 4
Laboratory scale activated sludge unit

withdrawn for sludge wastage. Any biomass settling out in the secondary settler was returned to the reaction zone at regular intervals.

Synthetic inorganic effluent runs

A batch of reactors was charged with medium supplemented with 2900 mg ℓ^{-1} nitrate-N and approximately 1500 mg ℓ^{-1} biomass which had been prepared as described above. A feed made up by supplementing the medium with ammonium nitrate to give about 1 400 mg ℓ^{-1} NH_4–N was fed to the reactors.

Two reactors also charged with medium supplemented with nitrate-N to which between 1 000 – 1 500 mg ℓ^{-1} biomass was added were fed with trade effluent supplemented only with phosphate. In one case, after running a reactor for over 90 days on trade effluent (test 9) the feed was switched to synthetic (test 10) to determine whether similar results would be obtained after a short period after the change.

Thereafter three further reactors were operated on trade effluent to confirm the above tests and to allow the reactors to operate over a long period to test stability. A 'practical' sludge age of 40 days was used in one test operating at 25 °C (test 13) and a higher sludge age (approximately 300 days) in the remaining two tests operating at 10°C (tests 11 and 12).

A simple reactor without any preliminary settler or secondary clarifier was run along the lines of a chemostat (tests 19 and 15).

TABLE 3

SUMMARY OF RESULTS OF CONTINUOUS TESTS IN C.S.T. REACTORS

Exp. No.	Feed rate (includes alkali)	Feed type	NH_4–N Conc. in feed + alkali)	Biomass at steady value	Volume of reactor plus primary settler	Rate of withdrawal of mixed liquor	Temp.	Hydraulic retention time	R_s days	Effluent Composition		$\frac{1}{R_s}$	$\frac{N_t\text{-}N_e}{X_vR}$	$(N_t\text{-}N_e)\ \frac{(1+0{,}15bR_s)}{X_vR}$	$Y_t = \frac{X_vR}{(N_t\text{-}N_e)\ (1+0{,}15bR_s)}\left[\frac{1}{R_s}+b\right]$
			mg ℓ^{-1}	mg ℓ^{-1}		mℓ d^{-1}	°C	R days		NH_4–N ppm	NO_3–N ppm			where b = 0,04	where b = 0,04
1.	2572	S	1290	505	6,15	460	22–27	2,39	13,37	<1	10–100	0,075	1.07	1,16	0,099
2.	2800	S	1116	620	6,15	295	22–27	2,196	20,85	<1	10	0,048	0,82	0,92	0,096
3.	2700	S	1122	1200–1250	6,15	100	22–27	2,28	61,5	<1	1	0,016	0,39–0,41 0,4	0,53–0,56 0,54	0,106–0,10
4.	5950	S	1000	800	6,15	app. 510	22–27	1,034	12	app. 3	app. 10	0,083	1,21	1,29	0,095
5.	5390	S	1000	1000	6,15	app. 360	22–27	1,14	17	app. 1	app. 10	0,059	0,875	0,96	0,103
6.	1866	S	1181	808	6,15	150	24–27	3,30	41	<1	<1	0,0244	0,44	0,55	0,117
7.	1630	S	1181	634	6,15	150	24–27	3,77	41	<0,3	<1	0,0244	0,50	0,62	0,104
8.	2220	T	1198	1450	6,15	50	22–27	2,77	123	<1	5–10	0,008	0,298	0,518	0,093
9.	2100	T	1200	1050	6,15	100	22–27	2,93	61,5	<1	10	0,016	0,39	0,53	0,106
10.	2500	T–S	1109	1010	6,15	100	22–27	2,46	61,5	<1	5	0,016	0,446	0,61	0,092
11.	1545	T	1011	1900*[1]	6,15	20	10	3,97	307,5	<1	<2	0,0033	0,12	0,34	0,127
12.	1850	T	995	2000*[1]	6,15	20	10	3,32	307,5	<1	<2	0,0033	0,15	0,44	0,098
13.	1675	T	1054	525	6,15	150	25–26	3,67	41	<1	<1	0,0244	0,54	0,71	0,091
14.	1030	S	1272	120	10,0	*[2]	25–26	9,71	13,87	2,6	4,7	0,072	1,086	1,17	0,096
15.	746	S	1628	125	10,0	*[3]	25–26	13,4	16,7	<1	<2	0,060	0,97	1,09	0,109

*[1] Test not run long enough to give 3x reactor volume replacement.

*[2] Mass of sludge in reactor = 1200 mg; mass of sludge in effluent 86,5 mg.

*[3] Mass of sludge in reactor = 1250 mg; mass of sludge in effluent 75 mg.

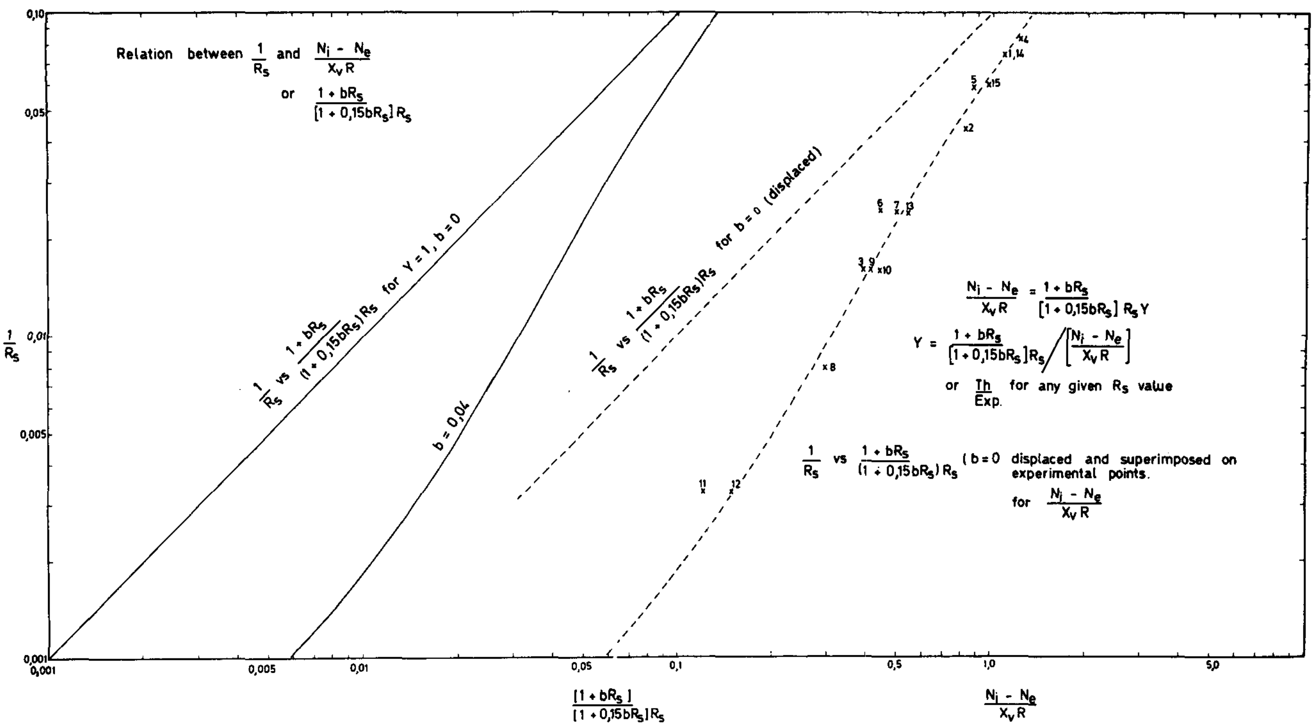

Figure 5

The results of these tests are summarised in Table 3. Values given in the table were for conditions when the MLVSS remained steady. Tests with very long sludge ages e.g. 8, 11, 12 were not run until 3x sludge age (days) had elapsed, but such tests were started with MLSS near to the predicted end MLSS.

The results are also reflected in Figures 5 and 6. In figure 5 the relation between sludge age and sludge utilisation is shown. The plot for the theoretical relation between $\frac{1}{R_s}$ and $\frac{1 + bR_s}{(1 + 0{,}15\ bR_s)\ R_s}$ is given for Y = 1 and b = 0 and for Y = 1 b = 0,04. This is compared with experimental values shown on the plot between

$$\frac{1}{R_s} \text{ and } \frac{N_i - N_e}{X_v R}$$

From the figure it will be seen that for Y = 0,1 and b = 0,04 a satisfactory fit is obtained.

In figure 6 the comparison is given between

$$\frac{1}{R_s} \text{vs.} \frac{N_i\text{–}N_e}{X_v R} \text{ with } \frac{1}{R_s} \text{vs.} \frac{1 + bR_s}{[1 + 0{,}15\ bR_s]}\ R_s Y$$

and between

$$\frac{1}{R_s} \text{vs.} \frac{N_i\text{–}N_e}{X_a R} \text{ or } \frac{1}{R_s} \text{vs.} \frac{N_i\text{–}N_e}{X_v R}\ [1 + 0{,}15\ bR_s]$$

with $\frac{1}{R_s}$ vs. $\frac{1 + bR_s}{YR_s}$

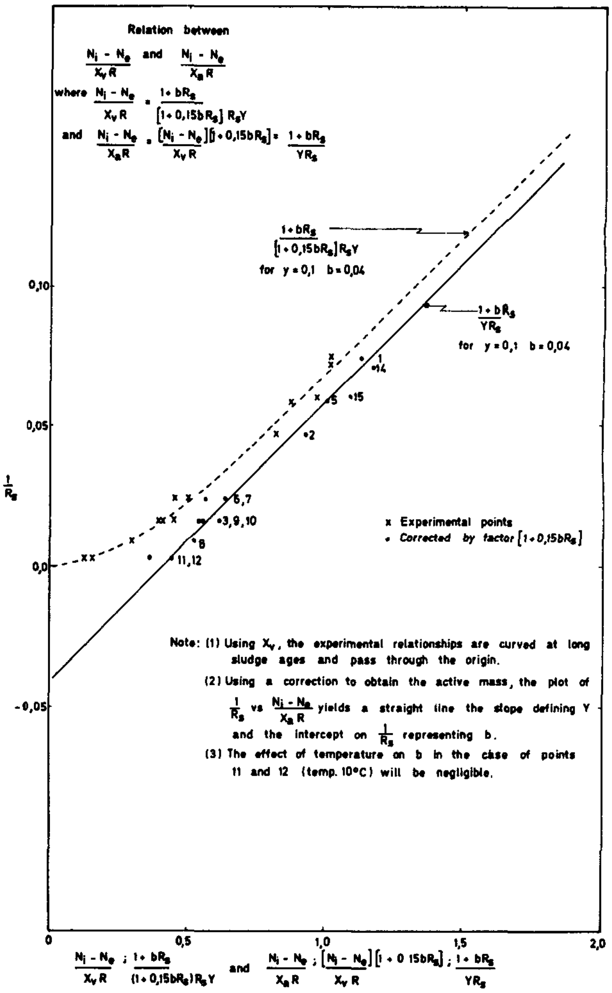

Figure 6

It can be seen that the experimental plot of

$$\frac{N_i - N_e}{X_v R} \text{ vs. } \frac{1}{R_s}$$

follows closely the curved relation of

$$\frac{1 + bR_s}{(1 + 0{,}15\ bR_s)\ R_s Y} \text{ vs. } \frac{1}{R_s} \text{ where } b = 0{,}04 \text{ and } Y = 0{,}1.$$

The plot using corrected X_v approximating to X_a yields a straight line and the b intercept is of course the same value as obtained from Figure 5.

The results confirm and justify the theoretical aspects used by Marais (1973) and appear to be sufficiently reliable to use for design purposes.

Application example

Effluent containing say 1 200 mg NH_4–N in presence of 1 200 mg NO_3–N $Y_t = 0{,}1$, $b = 0{,}04$

$$X_v = Y_t \frac{N_i - N_e}{1 + bR_s} \cdot \frac{R_s}{R} 1 + 0{,}15\ bR_s \quad \text{from equation 14.}$$

$$\therefore \log X_v = \log \left[Y_t \frac{(N_i - N_e)\ [1 + 0{,}15\ bR_s]}{1 + bR_s} \right] - \log R$$

Since N_i and N_e are known, Y_t and b are fixed and R_s is selected,

$\log X_v = \log [\text{Constant}] - \log R$ and a plot of

X_v vs. R may be obtained as shown in Figure 7.

Similarly for oxygen consumption, a plot may be derived, as shown also in Figure 7 from equation 19 relating oxygen and N, Y_t, R_s, R and b viz.

$$O_2 \text{ mg } \ell^{-1} \text{ d}^{-1} =$$

$$4{,}6 \frac{(N_i - N_e)}{R} - 0{,}96 \left[Y_t \frac{N_i - N_e\ [1 + 0{,}15\ bR_s]}{(1 + bR_s)} \right] \qquad (20)$$

For a unit operating at a rentention time of 1 day and a sludge age of 20 days ($R_s = 20$) the oxygen requirements are 5 400 mg $O_2 \ell^{-1}$ d^{-1}.

For an influent of 1 700 000 ℓ d^{-1} containing 1200 mg ℓ^{-1} NH_4–N to be treated to trace values of NH_4–N and NO_2–N in the effluent, the total oxygen requirement is 9 180 kg d^{-1}. Most surface aeration units will transfer say 2,12 kg/Kwh, under standard conditions. The daily load in NH_4–N oxygen demand is 9 180 kg d^{-1}; corrected for transfer efficiency the oxygen required is say 9 180 x 1,28 = 11 750 kg d^{-1}, which corresponds to 230 kw (or approximately 308 h p).

Volume to be treated = 1 700 000 ℓ so two tanks of say 900 m^3 capacity each would be suitable. Aerators would then be selected and the dimensions of the tanks fixed so that the oxygen requirements are met and adequate scouring provided at the bottom of the tanks.

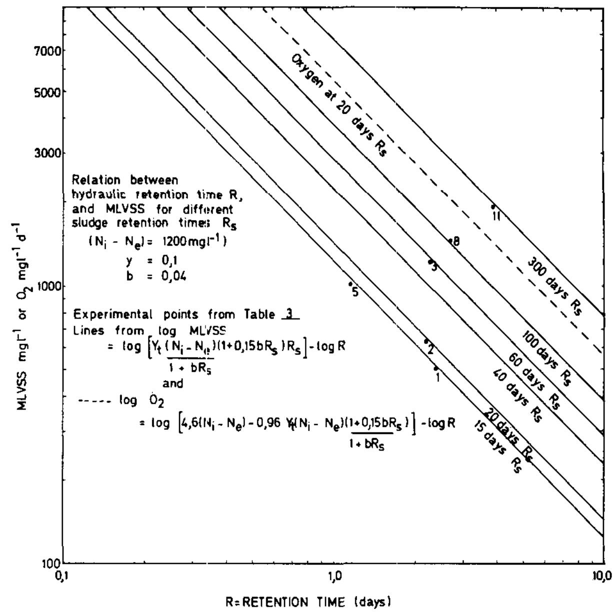

Figure 7

CONTROL

After selection of the sludge age R_s, irrespective of the flow through the plant, a fixed volume of the reactor ($V_w = V/R_s$) should be removed every day and the sludge from this volume (V_w) discarded. The sludge settled in the main clarifier should all be returned to the reactor (preferably continuously) and if clarification is not effective the loss of biomass here must be allowed for in V_w.

Because of the effect of temperature on growth rate and so on R_s, the sludge withdrawn for discarding must be decreased as temperature decreases.

Equation 17, viz $\frac{1}{R_s} = Y_t \frac{(N_i - N_e)}{X_v R} (1 + 0{,}15\ bR_s) - b$

has been found valid for sludge ages of 13 days or more where N_e can be taken as near to zero at 25°C (see Table 3.). Below this value of 13 days, there tended to be breakthrough of ammonia and nitrite.

Taking K_{mu} as 0,07 hr^{-1} or 1,68 d^{-1} at 25°C (section 3.1.) from equation 10 the limiting R_s value is given by

$$\frac{1}{R_s} = Y_t \frac{(K_{mu} N)}{K_n + N} - b$$

and when N (or N_e) is large

$$\frac{1}{R_s} = Y_t K_{mu} - b, \text{ hence } R_s \text{ (limiting)} = 7{,}8 \text{ days.}$$

From experiment, for N_e to be near zero at 25°C the value of R_s should be closer to 13 days, and in practice of course a safety factor must be allowed and plants should operate at say 20 days or higher at 25°C.

TABLE 4

NITRIFICATION AT 25°C AND pH 7 – 7,1

Period	Feed Conc. after Alkali addition		Total nitrate after nitrification	Feed Rate (including alkali)	Volume Reactor	Rate of withdrawal of mixed liquor	Hydraulic Retention time	Sludge Age	Effluent Composition		Biomass (MLVSS)	$\frac{N_i-N_e}{X_v R}$
	NH_4-N mgℓ^{-1}	NO_3-N mgℓ^{-1}		ml d^{-1}	ℓ	ml d^{-1}	R = d	R_s = d^{-1}	NH_4-N ppm	NO_3-N ppm	mgℓ^{-1}	
15/11/76 6 /12/76	1558	1136	2694	7808	6,12	150	0,78	41	<<1	<4	5100	0,39
7/12/76 11/12/76	1597	2329	3926	7616			0,80	41			5380	0,37
12/12/76 21/12/76	1533	3354	4887	7934			0,77	41			5312	0,37
Average	1556	—	—	7817			0,78	41			5203	0,38

The relation between sludge age and temperature is given by

$$\frac{1}{R_{sT_2}} = \frac{1}{R_{sT_1}} e^{.52\,(T_1-T_2)} \qquad \text{(section 2.5)}$$

Hence if 7,8 d is taken as the limiting sludge age at 25°C, the corresponding limiting age at 10°C would be at least 47 days. However in practice, at this low temperature, it would be wise to operate at a very much higher sludge age. In the experimental work a very high age of 300 days was used, but operation at say 120 days would probably be satisfactory.

pH

Automatic pH control is essential to achieve consistent nitrification and at pH 7 – 7,2 satisfactory operation can be expected provided the NH_4^+ level is low enough in the continuous reactor to avoid any free NH_3.

Nitrification in the presence of high nitrate concentrations

Biomass taken from experiments in which the influent consisted of approximately 1 400 mg ℓ^{-1} NH_3–N and 1 400 mg ℓ^{-1} NO_3–N, was washed with medium and freeze-dried for storage. Some two years later this biomass was used to carry out further tests with special reference to nitrification in high nitrate concentrations.

The reactor was charged with biomass and medium without NH_4–N. Feed was started at a low rate and gradually increased to 7 – 8 ℓd^{-1} with sludge withdrawal to give 41 days sludge age. The results given in Table 4 were obtained after about 15 days operation at 7 – 8 ℓd^{-1} feed rate.

High nitrate values in the effluent (up to 4 800 ppm NO_3–N) did not appear to upset the system.

As in previous tests adequate pH control, and sufficient oxygen prevented the build up of free ammonia and nitrite. Settling properties of the biomass were excellent at all nitrate concentrations as may be seen in Figure 8.

Nomenclature

b = endogenous mass coefficient (d^{-1})

K_{mu} = maximum substrate utilisation rate constant (d^{-1})

K_n = substrate concentration when the rate at which substrate disappears is ½ K_{mu} (mg ℓ^{-1})

N = concentration of substrate surrounding the organisms (mg ℓ^{-1})

N_e = total NH_4–N in effluent (also N_{eNH4}) (mg ℓ^{-1})

N_i = total NH_4–N in influent (also N_{iNH4}) (mg ℓ^{-1})

q = return flow (ℓ d^{-1})

Q = base flow through reactors (ℓ d^{-1})

R = hydraulic retention time = V/Q (d)

R_s = holding or retention time of biomass

$$= \text{sludge age} = \frac{\text{sludge in reactor}}{\text{sludge wasted per day}}\ (d)$$

V = reactor volume plus settler volume as per Fig. 1.

w = sludge waste flow (ℓ d^{-1})

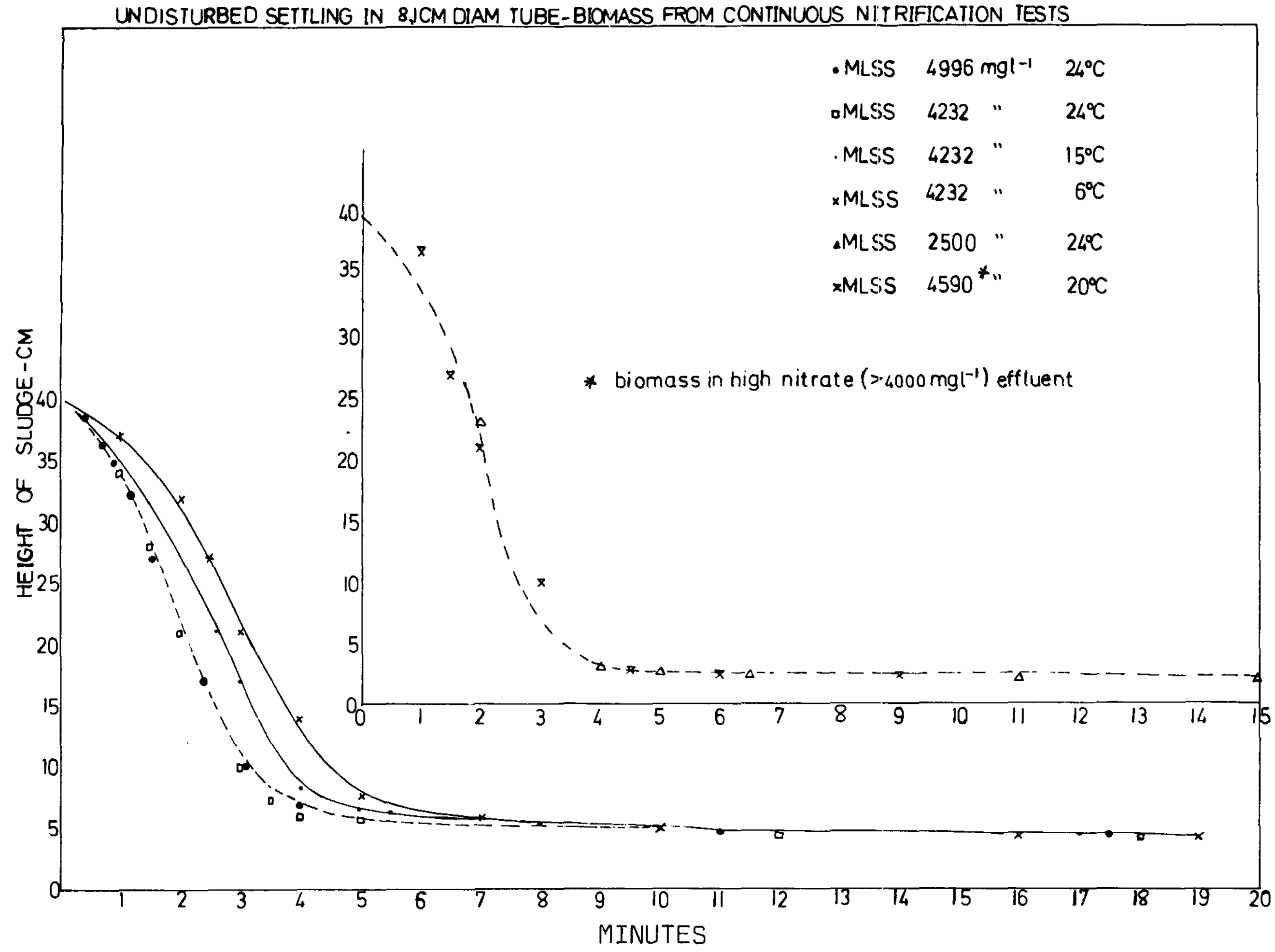

Figure 8
Undisturbed settling in 8,1 cm diam tube-biomass from continuous nitrification tests

X = sludge concentration (also concentration of micro-organisms generally) (mg ℓ^{-1})

X_1 = concentration of micro-organisms synthesised (mg ℓ^{-1})

X_2 = endogenous mass loss (mg ℓ^{-1})

X_a = concentration of 'active' organisms (mg ℓ^{-1})

X_{ae} = sludge concentration in effluent ('active') (mg ℓ^{-1})

X_{ar} = sludge concentration recycle ('active') (mg ℓ^{-1})

X_e = endogenous mass (mg ℓ^{-1})

X_{ee} = endogenous mass in effluent (mg ℓ^{-1})

X_{er} = endogenous mass in recycle (mg ℓ^{-1})

X_v = mixed liquor volatile suspended solids = MLVSS (mg ℓ^{-1})

Y $= \text{growth yield} = \dfrac{\text{mass of bacteria formed}}{\text{mass of substrate consumed}}$

Y_t = total growth yield or total mass of organisms/mass of substrate fully converted from NH_4-N to NO_3-N. (This constant includes *Nitrosomonas* and *Nitrobacter*).

μ = specific growth rate constant (hr^{-1} or d^{-1})

μ_m also μ max = maximum value of specific growth rate constant (hr^{-1} or d^{-1})

pK = log acidity constant

$\psi = Y_t \dfrac{K_{mu}\, N\, X_a}{K_n + N}$ (mg ℓ^{-1} d^{-1})

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