Nitrogen Removal

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BIOLOGICAL NITRIFICATION

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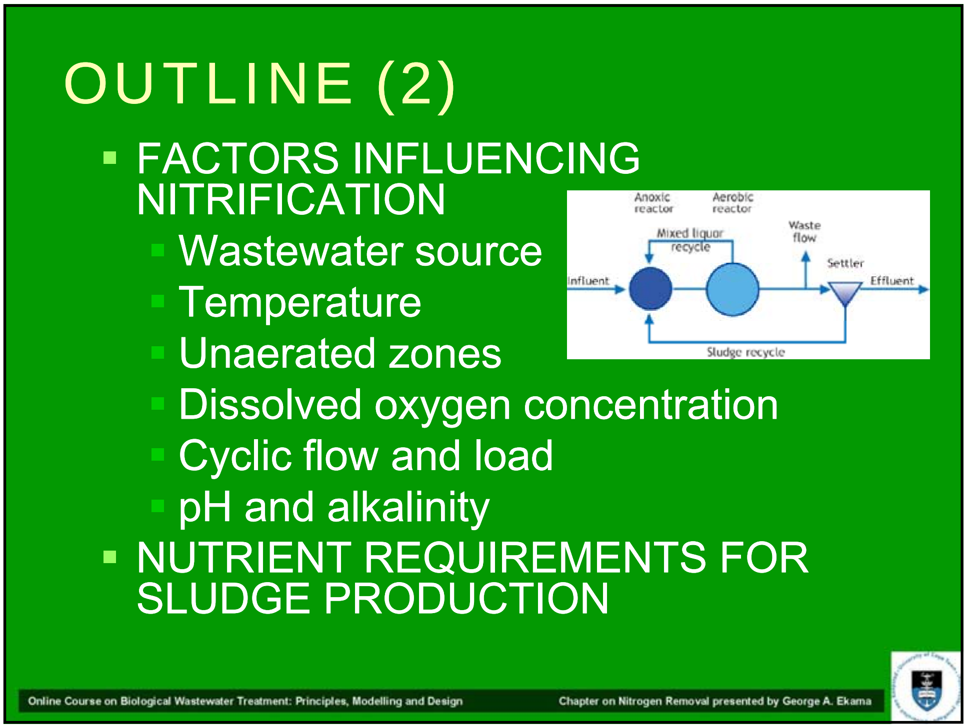
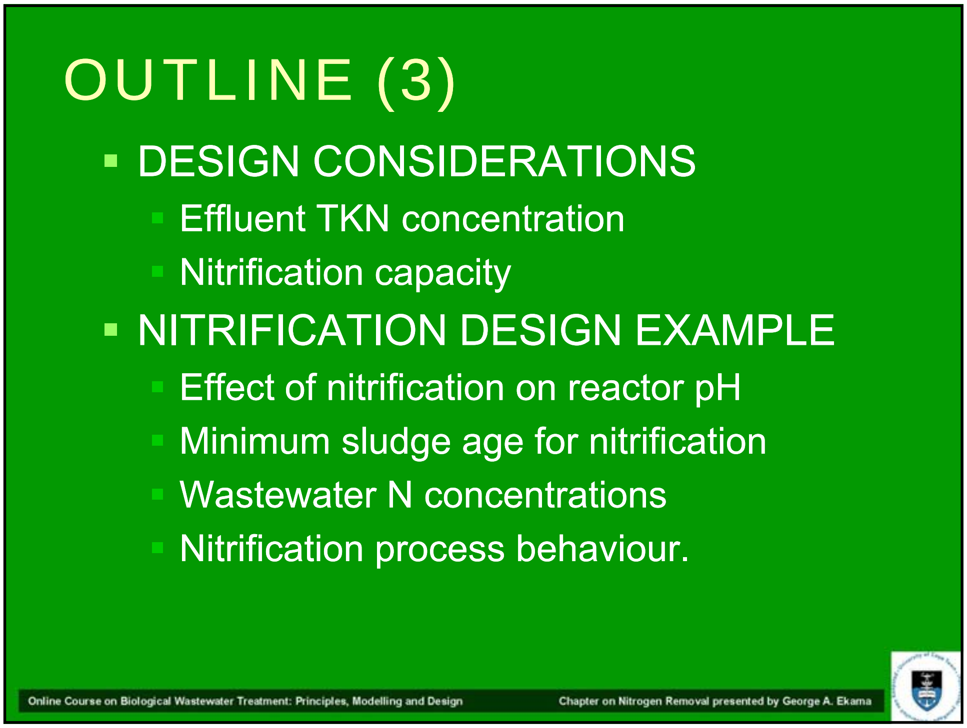
OUTLINE (1)

- GENERAL
- BIOLOGICAL KINETICS
  - Growth behaviour
  - Endogenous respiration
- PROCESS KINETICS
  - Effluent ammonia concentration
  - Minimum sludge age for nitrification



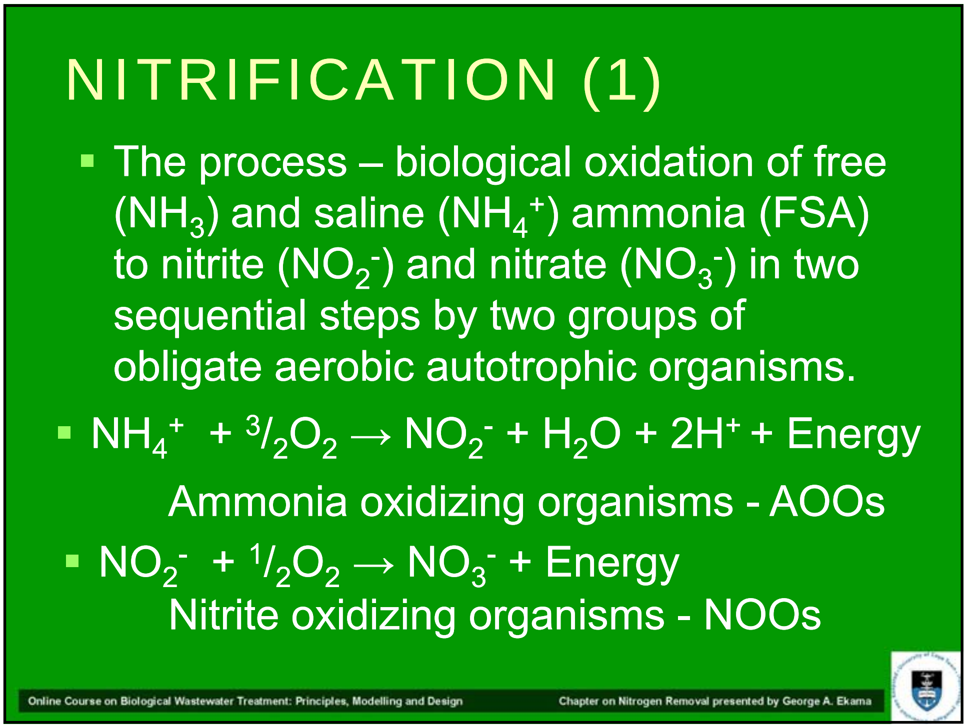
OUTLINE (2)

- FACTORS INFLUENCING NITRIFICATION
  - Wastewater source
  - Temperature
  - Unaerated zones
  - Dissolved oxygen concentration
  - Cyclic flow and load
  - pH and alkalinity
- NUTRIENT REQUIREMENTS FOR SLUDGE PRODUCTION



OUTLINE (3)

- DESIGN CONSIDERATIONS
  - Effluent TKN concentration
  - Nitrification capacity
- NITRIFICATION DESIGN EXAMPLE
  - Effect of nitrification on reactor pH
  - Minimum sludge age for nitrification
  - Wastewater N concentrations
  - Nitrification process behaviour.

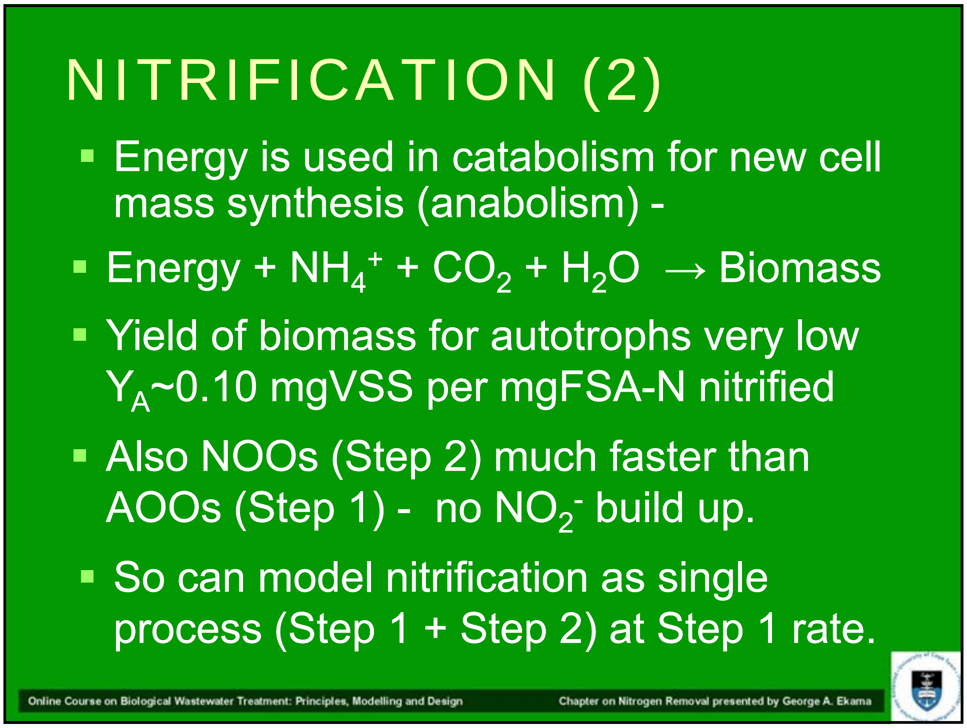


NITRIFICATION (1)

- The process – biological oxidation of free (NH_3) and saline (NH_4^+) ammonia (FSA) to nitrite (NO_2^-) and nitrate (NO_3^-) in two sequential steps by two groups of obligate aerobic autotrophic organisms.
- $NH_4^+ + {}^3/_2O_2 \rightarrow NO_2^- + H_2O + 2H^+ + \text{Energy}$

  Ammonia oxidizing organisms - AOOs
- $NO_2^- + {}^1/_2O_2 \rightarrow NO_3^- + \text{Energy}$

  Nitrite oxidizing organisms - NOOs



NITRIFICATION (2)

- Energy is used in catabolism for new cell mass synthesis (anabolism) -
- $\text{Energy} + NH_4^+ + CO_2 + H_2O \rightarrow \text{Biomass}$
- Yield of biomass for autotrophs very low Y_A~0.10 mgVSS per mgFSA-N nitrified
- Also NOOs (Step 2) much faster than AOOs (Step 1) - no NO_2^- build up.
- So can model nitrification as single process (Step 1 + Step 2) at Step 1 rate.

NITRIFICATION (3)

Overall process stoichiometry by autotrophic nitrifier organisms (ANOs)

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$

From above – per mgFSA-N nitrified -

- 4.57 mgO utilized (64mgO/14mgN)
- 7.14 mg/l as $CaCO_3$ consumed (2x50/14)
- 1 mgNO_3^--N generated.

NITRIFICATION (4)

If ammonia uptake by ANOs for biomass growth is taken into account, then products are negligibly lower -

Per mgFSA-N nitrified -

- 4.45 gO utilized (4.57mgO/mgN)
- 7.11 mg/l as $CaCO_3$ consumed (7.14)
- 0.99 mgNO_3^--N generated (1.00).

NITRIFIER GROWTH KINETICS (1)

Based on Monod growth kinetics –

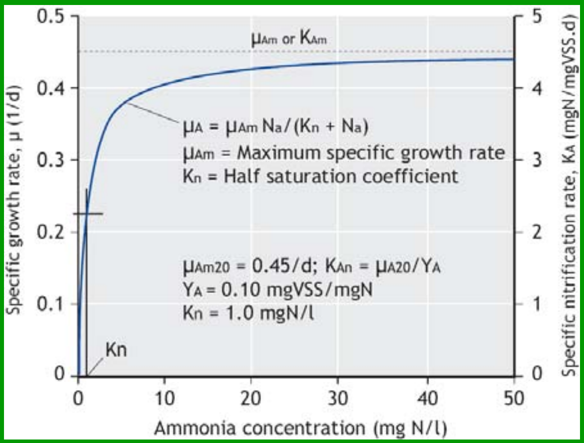
(1) ANO biomass (X_{BA}) generated is a fixed fraction (Y_A) of FSA (N_a) nitrified –

$$\frac{dX_{BA}}{dt} = Y_A \left[-\frac{dN_a}{dt} \right]$$

(2) Specific growth rate (μ_{AT}) related to bulk liquid FSA concentration (N_a) - Monod

$$\frac{dX_{BA}}{dt} = \mu_{AT} X_{BA} = \frac{\mu_{AmT} N_a}{K_{nT} + N_a} X_{BA}$$

NITRIFIER GROWTH KINETICS (2)



μ_{Am} = 0.45/d

K_n =1 mgN/l

Y_A = 0.10 mgVSS/ mgFSA-N

If N_a>4, ANOs nitrifying at maximum rate (μ_A), but it's difficult to get low N_a<1.0 mgN/l

NITRIFIER GROWTH KINETICS (3)

FSA (N_a) utilization rate, NO_3^- (N_n) generation rate and nitrification oxygen utilization (O_n) rate are linked to ANO biomass (X_{BA}) growth rate -

$$\frac{dN_n}{dt} = -\frac{dN_a}{dt} = \frac{1}{Y_A}\frac{\mu_{AmT} N_a}{K_{nT} + N_a} X_{BA}$$

$$\frac{dO_n}{dt} = 4.57\frac{dN_a}{dt} = 4.57\frac{dN_n}{dt}$$

NITRIFIER ENDOGENOUS RESPIRATION

Like all organisms, ANOs also undergo a biomass loss due to maintenance or endogenous energy requirements.

This is modelled in the same way in both steady state and simulation models as endogenous respiration for the ordinary heterotrophic organisms (OHOs) in steady state model, viz.

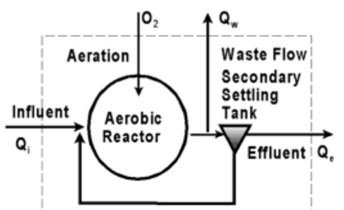
$$\frac{dX_{BA}}{dt} = -b_{AT} X_{BA}$$

b_{AT} = specific endogenous mass loss rate at T°C

= 0.04 /d at 20°C

PROCESS KINETICS

Derived from mass balances over AS system



(1) Mass balance on X_{BA} -

$$V_p \frac{\Delta X_{BA}}{\Delta t} = V_p \frac{\mu_{AmT} N_a}{K_{nT} + N_a} X_{BA} - V_p b_{AT} X_{BA} - V_p \frac{Q_W}{V_p} X_{BA} = 0$$

at steady state

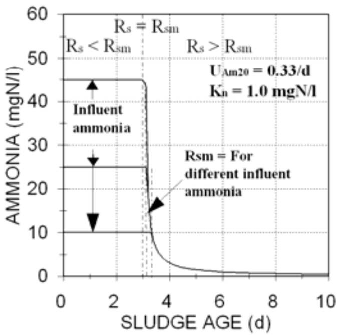
(2) Solving for N_a (= N_{ae}) yields -

$$N_a = N_{\text{æ}} = \frac{K_{nT}(b_{AT} + 1/R_S)}{\mu_{AmT} - (b_{AT} + 1/R_S)}$$

Independent of Y_A and N_{ai}

MINIMUM SLUDGE AGE (1)

Plotting N_{ae} vs R_s



(1) Above certain R_s, N_{ae} is very low.

(2) As R_s decreases, N_{ae} increases.

(3) When $N_{ae} = N_{ai}$, $R_s \approx R_{sm}$.

R_{sm} = minimum sludge age for nitrification.

Sludge age (R_s) is **<u>most</u>** important design parameter for systems required to nitrify!

MINIMUM SLUDGE AGE (2)

(1) If $R_s < R_{sm}$, no nitrification.

(2) If $R_s > 1.3 \times R_{sm}$, nitrification almost complete.

Setting $R_s = R_{sm}$ and $N_{ae}=N_{ai}$ yields for R_{sm}

$$R_{Sm} = \frac{1}{(1+\frac{K_{nT}}{N_{ai}})\,\mu_{AmT} - b_{AT}}$$

and with $K_{nT} << N_{ai}$

$$R_{Sm} = \frac{1}{\mu_{AmT} - b_{AT}}$$

So R_{sm} depends mainly on maximum specific growth rate of ANOs - μ_{Am}

NITRIFIER μ_{Am}

Depends on many factors -

(1) Wastewater composition (metals, salts).

(2) Wastewater temperature (T↓, μ_{Am}↓).

(3) Wastewater pH (pH↓, μ_{Am}↓).

(4) Reactor DO concentration (DO↓, μ_{Am}↓).

(5) ANO population selection.

Therefore μ_{Am} is considered a wastewater characteristic rather than kinetic constant

FACTOR OF SAFETY ON μ_{Am}

Nitrification is prerequisite for N removal, so to ensure nitrification, μ_{Am} is decreased by a factor of safety, S_f (1.2 – 1.3). This

(1) ensures $R_s > R_{sm}$,

(2) covers uncertainty in μ_{Am}

(3) ensures low effluent FSA concentration and near complete nitrification.

and under constant flow and load (steady state) $N_{ae} = K_{nT} / (S_f - 1)$.

FACTORS AFFECTING NITRIFICATION

(1) wastewater – magnitude of μ_{Am20},

(2) temperature,

(3) unaerated zones in reactor,

(4) aerobic reactor DO concentration,

(5) cyclic flow and load conditions

(6) reactor pH.

Each is discussed further below.

(A) WASTEWATER SOURCE

- Already mentioned - μ_{Am20} varies much between different wastewaters and so is a wastewater characteristic rather than a kinetic constant.
- Ideally should be measured on wastewater.
- μ_{Am20} values range between 0.3 - 0.75 /d.
- b_{A20} is accepted to stay constant (0.04/d).

(B) TEMPERATURE (1)

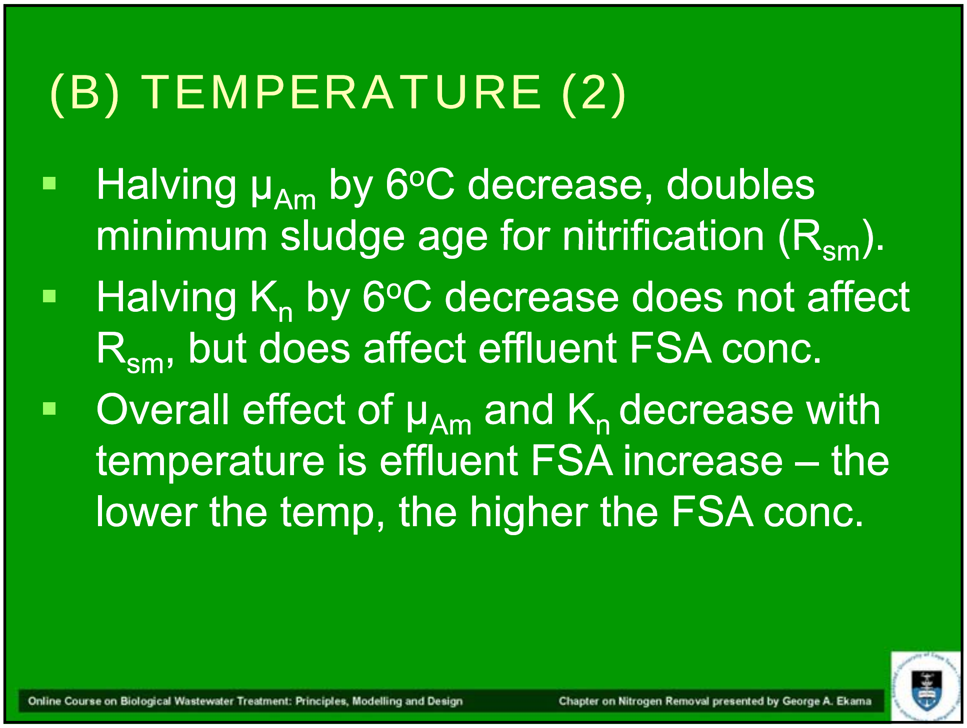
Nitrifier kinetic constants μ_{Am20}, b_{A20} and K_{n20} all decrease with temperature.

(1) $\mu_{AmT} = \mu_{Am20}(\Theta_n)^{(T-20)}$; Θ_n=1.123

(2) $K_{nT} = K_{n20}(\Theta_n)^{(T-20)}$; Θ_n=1.123

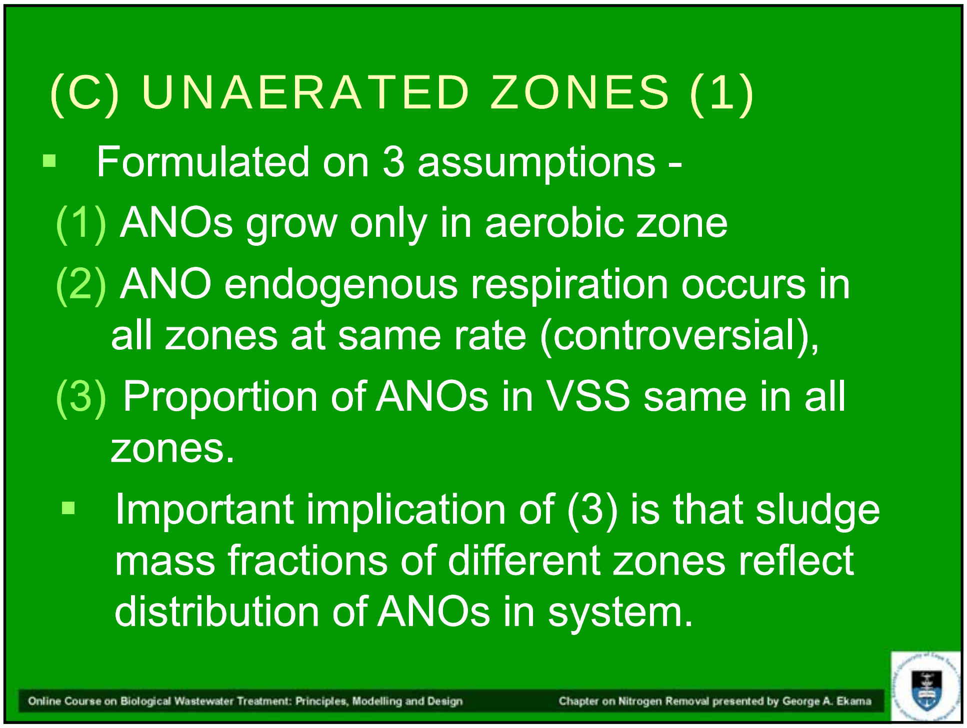
(3) $b_{nT} = b_{n20}(\Theta_b)^{(T-20)}$; Θ_b=1.029.

Θ_n=1.123 is equivalent to a 50% reduction every 6°C – if 0.45/d at 20°C, then is 0.23 at 14°C.



(B) TEMPERATURE (2)

- Halving μ_{Am} by $6^{o}C$ decrease, doubles minimum sludge age for nitrification (R_{sm}).
- Halving K_n by $6^{o}C$ decrease does not affect R_{sm}, but does affect effluent FSA conc.
- Overall effect of μ_{Am} and K_n decrease with temperature is effluent FSA increase – the lower the temp, the higher the FSA conc.



(C) UNAERATED ZONES (1)

- Formulated on 3 assumptions -

(1) ANOs grow only in aerobic zone

(2) ANO endogenous respiration occurs in all zones at same rate (controversial),

(3) Proportion of ANOs in VSS same in all zones.

- Important implication of (3) is that sludge mass fractions of different zones reflect distribution of ANOs in system.

(C) UNAERATED ZONES (2)

- From 3 assumptions it can be shown that -

$$N_{ae} = \frac{K_{nT}\,(b_{AT} + 1/R_s)}{\mu_{AmT}\,(1 - f_{xt}) - (b_{AT} + 1/R_s)}$$

f_{xt} = unaerated mass fraction,

= fraction of total mass of sludge in system in unaerated zone(s).

= 0 for fully aerobic system.

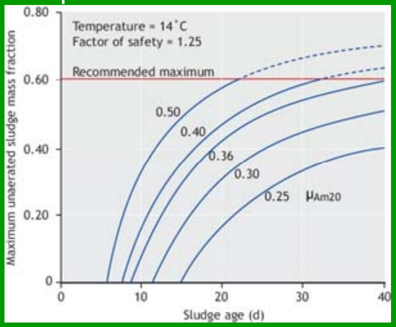
- Similarly, $R_{sm} = \dfrac{1}{\mu_{AmT}\,(1 - f_{xt}) - b_{AT}}$

(C) UNAERATED ZONES (3)

Alternatively, the maximum unaerated sludge mass fraction f_{xm} allowed at a sludge age of R_s to ensure nitrification with a safety factor of S_f is –

$f_{xm} = 1 - S_f\,(b_{AT} + 1/R_s)/\mu_{AmT}$

and the effluent FSA conc is still given by $N_{ae} = K_{nT} / (S_f - 1)$



(D) DO CONCENTRATION

- Effect of DO on μ_{Am} is formulated as -

$$\mu_{AmO} = \mu_{Am} \frac{O}{K_O + O}$$

O = DO conc in mixed liquor

K_O = Monod half saturation conc for DO = 0.3 to 2 mgO/L (depends on floc size, mixing).

- If reactor DO < K_O, nitrification rate is less than half the maximum.

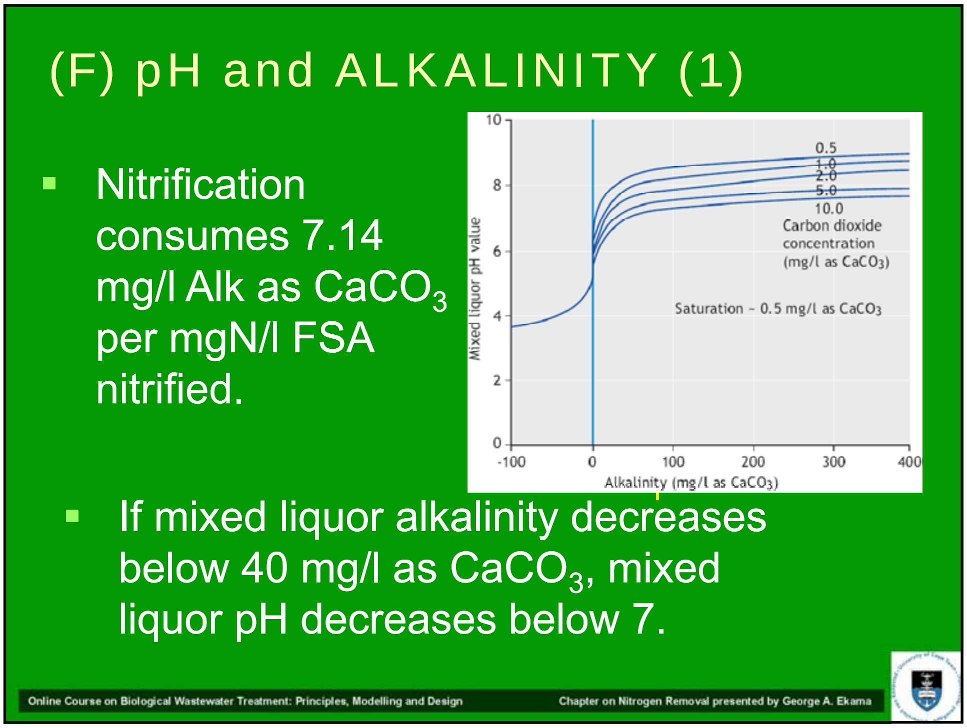
(E) CYCLIC FLOW AND LOAD

(1) Average effluent FSA conc under cyclic flow and load > steady state effluent FSA conc.

(2) So nitrification efficiency decreases under cyclic flow and load compared with steady state - the higher the variation, the lower the efficiency.

(3) Cyclic flow and load has similar effect as decreasing sludge age closer to R_{sm}

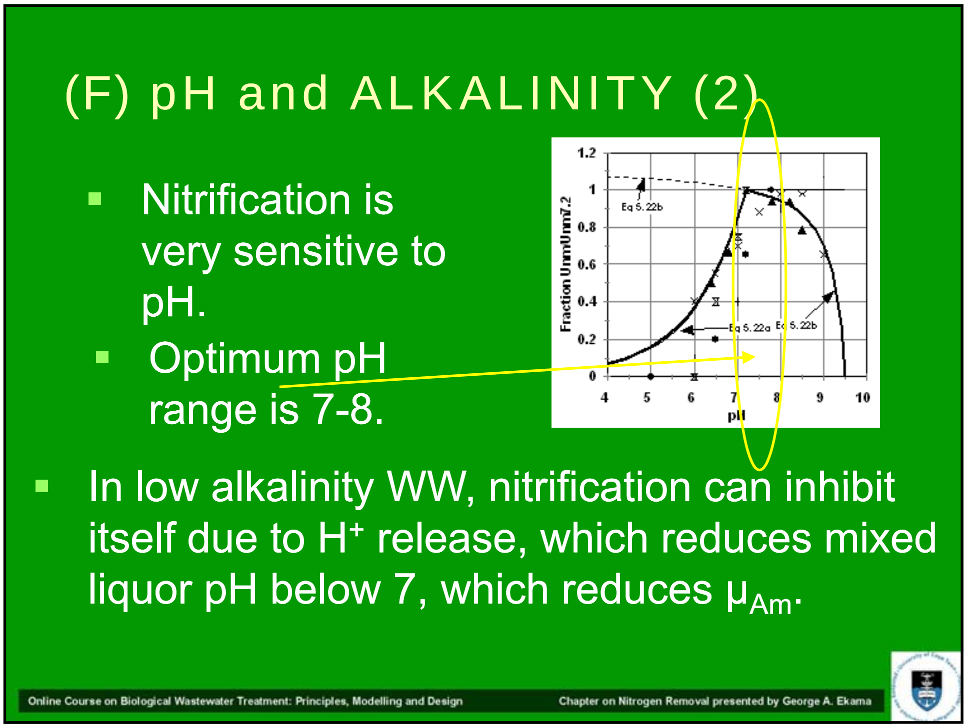
(4) So increase R_s to compensate for cyclic flow and load and keep effluent FSA low.



(F) pH and ALKALINITY (1)

- Nitrification consumes 7.14 mg/l Alk as $CaCO_3$ per mgN/l FSA nitrified.

- If mixed liquor alkalinity decreases below 40 mg/l as $CaCO_3$, mixed liquor pH decreases below 7.



(F) pH and ALKALINITY (2)

- Nitrification is very sensitive to pH.
- Optimum pH range is 7-8.

- In low alkalinity WW, nitrification can inhibit itself due to H^+ release, which reduces mixed liquor pH below 7, which reduces μ_{Am}.

(F) pH and ALKALINITY (3)

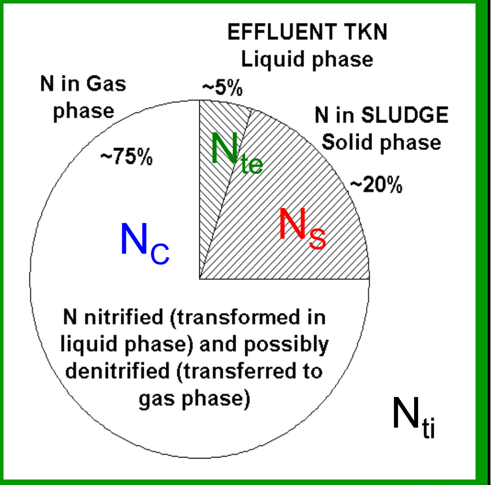
- If influent Alk = 200 and 24 mgN/l FSA is nitrified, effluent Alk = 200 – 7.14x24=29 mg/l. Less than 40, so mixed liquor pH will decrease below 7.
- In this event, either
  - Introduce anoxic zones to denitrify nitrate and recover half Alk lost, or
  - Dose lime to keep pH > 7.0.

N REQUIREMENTS FOR SLUDGE GROWTH

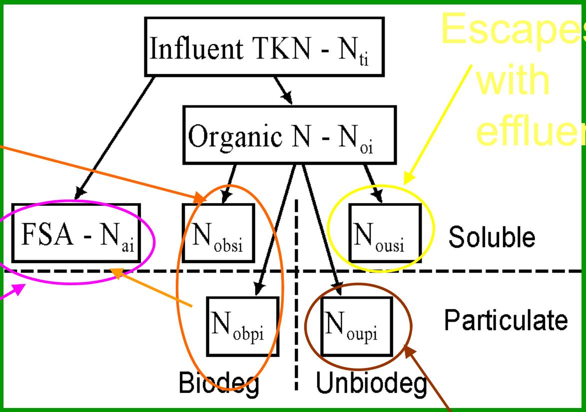
(1) About 15-20% of influent TKN is required for AS sludge growth (N_s).

(2) N_s decreases with R_s and settled WW.

(3) Influent biodeg OrgN adds to FSA pool in reactor and nitrified.



FATE OF INFLUENT TKN



Released as FSA and adds to FSA pool.

Escapes with effluent

Some taken up for growth, rest nitrified to nitrate. Effluent FSA (N_{ae}) low.

Effluent TKN
$N_{te}=N_{ae}+N_{ousi}$

Included with waste sludge

NITRIFICATION CAPACITY

Nitrification capacity (N_c) = Concentration of nitrate per litre influent flow generated by nitrification (mgN/l).

$$N_c = N_{ti} - N_s - N_{te}\ ;\ N_s = f_n\,(V_p.X_v)/(R_s.Q_i)$$

$$N_{te} = N_{ae} + N_{ousi}\ ;\ f_n = N \text{ content of VSS}$$

$$N_{ae} = \frac{K_{nT}\,(b_{AT} + 1/R_s)}{\mu_{AmT}\,(1 - f_{xt}) - (b_{AT} + 1/R_s)}$$

DESIGN PROCEDURE (1)

Calculation of sludge age (R_s) and unaerated sludge mass fraction (f_{xt}) most important part of design procedure!

With WW characteristics known and R_s and f_{xt} selected -

(1) Calculate influent N concentrations (N_{oi}, N_{ousi}, N_{oupi}).

(2) Calculate effluent OrgN ($N_{ouse} = N_{ousi}$).

(3) Calculate N for sludge production (N_s).

DESIGN PROCEDURE (2)

(4) Calculate R_{sm}.

(5) If $R_s < R_{sm}$ – no nitrification, then -

Effluent Nitrate (N_{ne}) = 0.

Effluent FSA (N_{ae}) = $N_{ti} - N_s - N_{ouse}$

= FSA available for nitrification (N_{an}).

Effluent TKN (N_{te}) = $N_{ae} + N_{ouse} = N_{ti} - N_s$

Nitrifier sludge mass $MX_{BA} = 0$

Nitrification oxygen demand $MO_n = 0$

DESIGN PROCEDURE (3)

(6) If $R_s > R_{sm}$ – nitrification occurs, then –

Effluent FSA = $$N_{ae} = \frac{K_{nT}\,(b_{AT} + 1/R_s)}{\mu_{AmT}\,(1 - f_{xt}) - (b_{AT} + 1/R_s)}$$

If N_{ae} is negative or $>N_{an}$, set $N_{ae} = N_{an}$

Effluent TKN: $N_{te} = N_{ae} + N_{ouse}$ (mgN/l)

Effluent Nitrate: $N_{ne} = N_{an} – N_{ae}$ (mgN/l)

$= N_{ti} – N_s – N_{te}$ (mgN/l)

DESIGN PROCEDURE (4)

(6) If $R_s > R_{sm}$ – nitrification occurs, then –

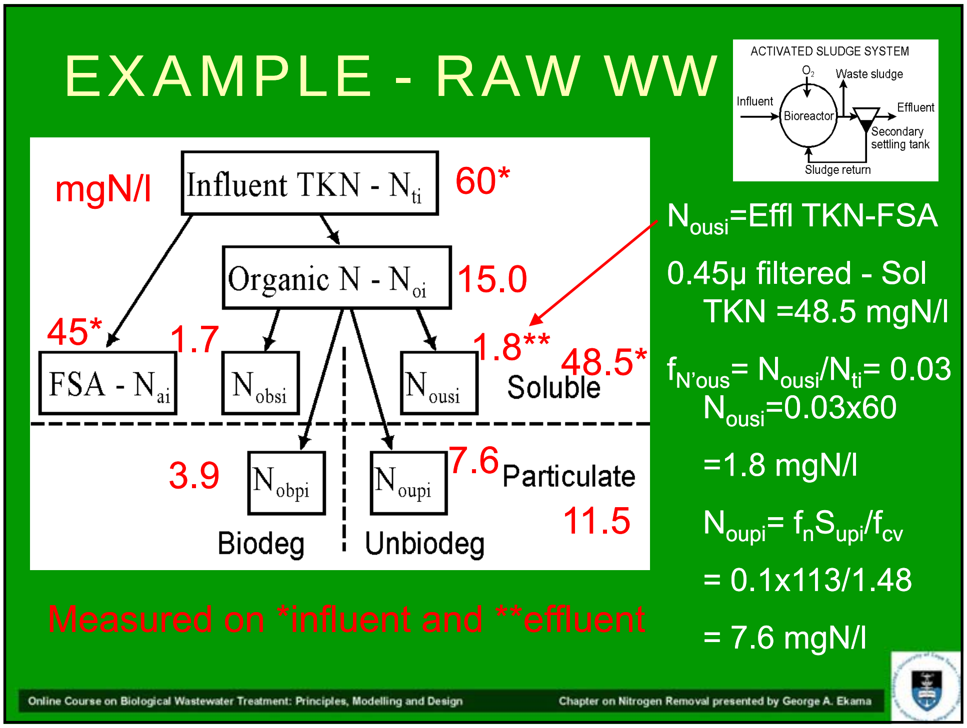
Analogous to mass of ordinary heterotrophic organisms (OHOs) in reactor, mass of ANOs is $MX_{BA} = (Q_i\,N_{ne})\,Y_A R_s/(1+b_{AT}R_s)$

where $Q_i\,N_{ne}$ = mass of nitrate generated

$= N_{ne}\,(Q_e + Q_w)$ mgN/d

Nitrification oxygen demand (mgO/d) =

$MO_n = 4.57\,(Q_i\,N_{ne})$ mgO/d.



EXAMPLE - RAW WW

mgN/l

Influent TKN - N_{ti} 60*

Organic N - N_{oi} 15.0

45* FSA - N_{ai}

1.7 N_{obsi}

N_{ousi} 1.8**

48.5* Soluble

3.9 N_{obpi}

N_{oupi} 7.6 Particulate

11.5

Biodeg | Unbiodeg

Measured on *influent and **effluent

N_{ousi}=Effl TKN-FSA

0.45μ filtered - Sol TKN =48.5 mgN/l

$f_{N'ous}$= N_{ousi}/N_{ti}= 0.03

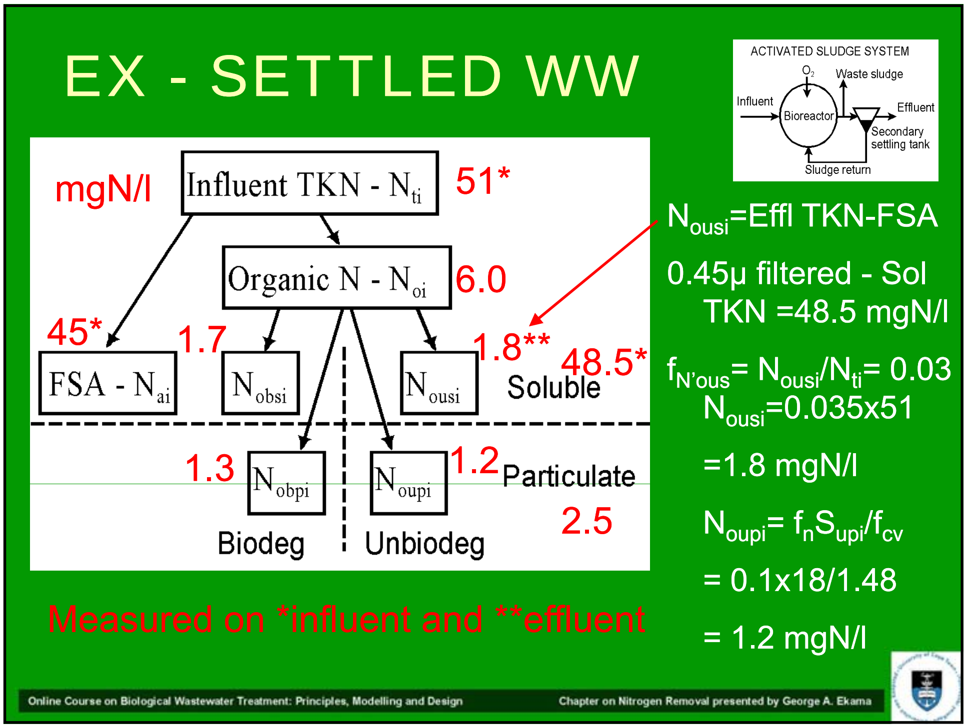
N_{ousi}=0.03x60

=1.8 mgN/l

N_{oupi}= $f_n S_{upi}/f_{cv}$

= 0.1x113/1.48

= 7.6 mgN/l



EX - SETTLED WW

mgN/l

Influent TKN - N_{ti} 51*

Organic N - N_{oi} 6.0

45* FSA - N_{ai}

1.7 N_{obsi}

N_{ousi} 1.8**

48.5* Soluble

1.3 N_{obpi}

N_{oupi} 1.2 Particulate

2.5

Biodeg | Unbiodeg

Measured on *influent and **effluent

N_{ousi}=Effl TKN-FSA

0.45μ filtered - Sol TKN =48.5 mgN/l

$f_{N'ous}$= N_{ousi}/N_{ti}= 0.03

N_{ousi}=0.035x51

=1.8 mgN/l

N_{oupi}= $f_n S_{upi}/f_{cv}$

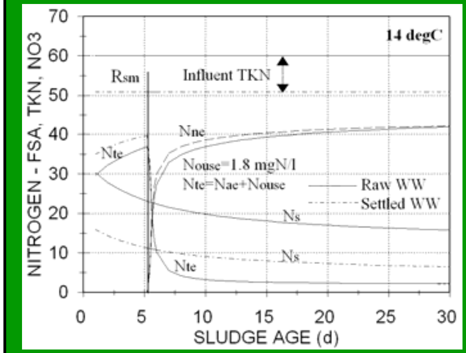
= 0.1x18/1.48

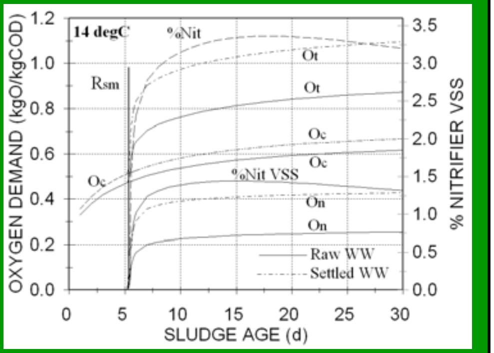
= 1.2 mgN/l

DESIGN EXAMPLE

- Following the design procedure with the example raw and settled wastewaters in the notes at 14 and 22^{o}C -

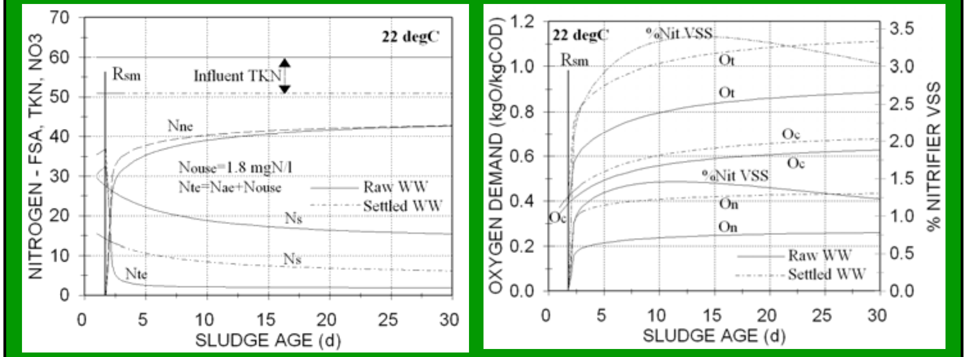
DESIGN RESULTS – 14^{o}C





Fully aerobic – raw and settled wastewater.
Minimum sludge age for nitrification ≈ 5d.
Effluent TKN & NO_3 concs virtually the same.
Influent TKN and N_s lower for settled than raw.

DESIGN RESULTS – 22^{o}C



Fully aerobic – raw and settled wastewater.

Minimum sludge age for nitrification ≈ 2d.

Effluent TKN & NO_3 concs virtually the same.

Influent TKN and N_s lower for settled than raw.

EFFECT OF PRIMARY SETTLING ON NITRIFICATION

PSTs do not have significant influence on nitrification because -

(1) Not much N is removed in PSTs (10-15%) – usually most TKN is FSA,

(2) N for sludge production (N_s) for settled wastewater is lower than for raw.

(1)≈(2) so nitrification capacity (N_c) for settled and raw wastewaters are similar.

NITRIFICATION: INFLUENCE ON SYSTEM (1)

(1) Sludge age: Nitrification requires $R_s > R_{sm}$, so has major influence on selection of R_s.

(2) Reactor volume and sludge production: For the same sludge age, no influence. Nitrifiers < 4% of VSS mass in reactor (TKN load << COD load and $Y_A << Y_H$). However, nitrification usually needs longer R_s so reactor volume larger and sludge production lower.

NITRIFICATION: INFLUENCE ON SYSTEM (2)

(3) Oxygen demand (OD): Increases significantly with nitrification – by about 40-60% of COD removal OD depending on influent TKN/COD conc ratio.

Also, if nitrification requires longer sludge age, COD removal OD increases.

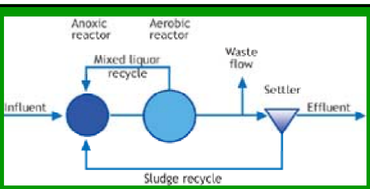
(4) In low DO conditions, COD removal OD takes preference and nitrification will be partial – DO should be >2 mgO/l.

NITRIFICATION: INFLUENCE ON SYSTEM (3)

(5) Effluent quality: No difference in COD, low FSA, high nitrate, reduced alkalinity, lower pH – possibly aggressive to concrete surfaces.

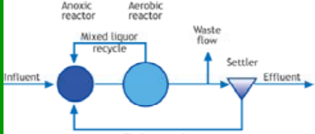
(6) When nitrification can take place, by design or accident, include denitrification and hydraulic control of sludge age, especially for warm WW, to reduce nitrate and oxygen demand, recover alkalinity, raise pH and minimize rising sludge in SST.

SUMMARY (1)



- (1) Maximum specific growth rate of nitrifiers (μ_{Am20}) fixes the sludge age of the AS system.
- (2) Unaerated zones, low WW temperature and cyclic flow and load increase sludge age over minimum for nitrification.
- (3) Selection of unaerated mass fraction and sludge age is the most important decision in the design for nitrification.
- (4) At fixed sludge age, nitrification has negligible effect on sludge production.

SUMMARY (2)



- (5) Nitrification increases oxygen demand by 40 to 60% over that for organic removal.
- (6) When nitrification can take place, include denitrification to recover half the Alkalinity and oxygen used in nitrification and minimize rising sludge in the SST.
- (7) Control sludge age hydraulically by wasting directly from the reactor to fix sludge age and “guarantee” nitrification rather than control reactor concentration (system fails via high ESS rather than on nitrification).

ACKNOWLEDGEMENTS

University of Cape Town

And others