5.10
Distillation Process Examples

5.10.1
BSTILL – Binary Batch Distillation Column

The process is as described in Section 3.3.3.2 and consists of a distillation column containing seven theoretical plates, reboiler and reflux drum. Distillation is carried out initially at total reflux in order to first establish the column concentration profile. Distillate removal then commences at the required distillate composition under proportional control of reflux ratio. This model is based on that of Luyben (1973, 1990).
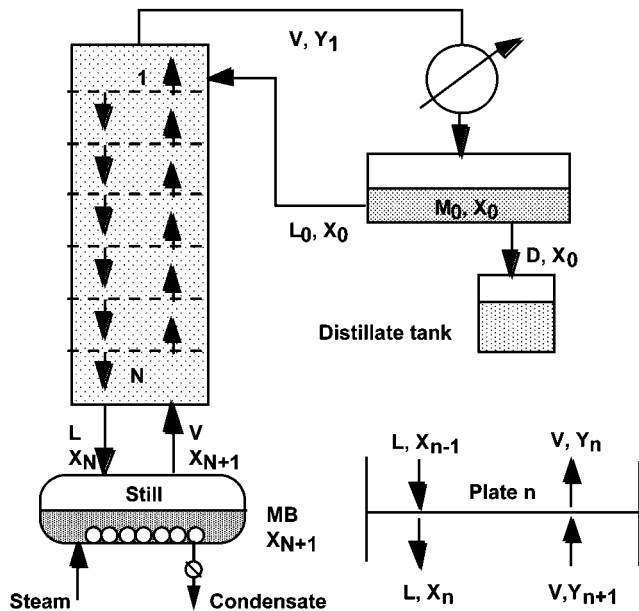

Fig. 1 Batch distillation column.

Model

The component balance for plate n, based on the more volatile component, is

$$M \frac{dX_n}{dt} = L\,X_{n-1} - L\,X_n + V\,(Y_{n+1} - Y_n)$$

For the still

$$\frac{dM_B}{dt} = L - V$$

and

$$\frac{d(M_B X_{N+1})}{dt} = L X_N - V Y_{N+1}$$

where the suffix N refers to the bottom plate and suffix N+1 relates to the still and column base, as represented in Fig. 1.

For the reflux drum and condenser, assuming constant holdup

$$M_0 \frac{dX_0}{dt} = V Y_1 - (L + D) X_0$$

The reflux ratio, R, is given by

$$R = L_0/D = L/D$$

for constant molar overflow, where

$$D = \frac{V}{R + 1}$$

and

$$L = V - D$$

Assuming theoretical plate behaviour

$$y_n = \frac{a X_n}{1 + (a - 1) X_n}$$

where a is the relative volatility.

The controller equations are given by:

for initial startup

$$R = R_{initial}$$

and for distillate withdrawal

$$R = K_C (X_D - X_{Dset})$$

Program

Start-up is at initially total reflux, with the reflux value set at an arbitrarily high value, $R = R_{init}$. Once the distillate composition, X_0, exceeds the set point composition, X_{0set}, control of reflux ratio is effected by varying the reflux ratio according to the proportional control relationship $R_C = K_C^*(X_{0set} - X_0)$. The change from initial start-up to controlled withdrawal of distillate is effected by means of the logical control variable FLAG.

Nomenclature

Symbols

α	Relative volatility	–
K_C	Controller gain	–
M	Molar holdup	kmol
L	Liquid flow rate	kmol/h
V	Vapour flow rate	kmol/h
D	Distillate rate	kmol/h
X	Liquid phase mole fraction	–
Y	Vapour phase mole fraction	–
R	Reflux ratio	–

Indices

1 to N	Plate number
B	Reboiler
0	Reflux drum
init	initial conditions
n	n-th plate
set	controller set point

Exercises

1. With only seven plates in the column, it is very difficult to maintain the required top product quality for very long. Study the effect of K_C on (i) the time for which required distillate composition can be maintained and (ii) the quantity of the total distillate of required composition obtained.
2. Also, as the problem is set up, further distillation should perhaps be discontinued, once the still composition has reached very low concentration levels. Modify the program to include this effect into the simulation.
3. Increase the number of plates in the column and study this effect on the separation obtained.

4. Modify the program to allow for continuous feeding of fresh feed into the still during the distillation. The feed rate should be adjusted to equal the rate of withdrawal of distillate. What is the effect of feeding on the distillation process?
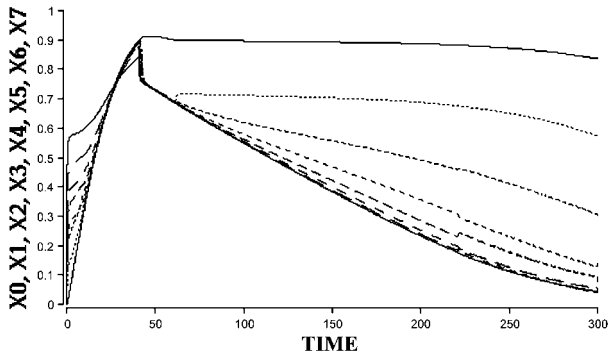
Results

Fig. 2 Composition profiles for distillate withdrawal at controlled reflux ratio, following the initial startup at total reflux. Number of plates = 7.
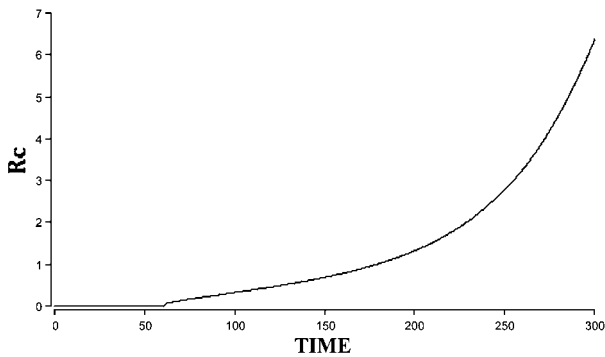

Fig. 3 The corresponding variation in the controlled value of reflux ratio.

Reference

Luyben, W. L. (1973, 1990) Process Modelling, Simulation and Control for Chemical Engineers, McGraw-Hill.

5.10.2
DIFDIST – Multicomponent Differential Distillation

System

A mixture of hydrocarbons A, B, C and D is charged to a batch still and is distilled over without reflux.
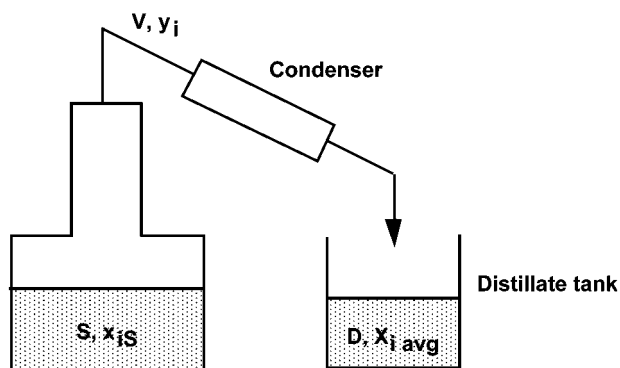

Fig. 1 Single multicomponent batch distillation.

Model

Total mole balance for the still

$$\frac{dS}{dt} = -V$$

Component mole balance

$$\frac{d(Sx_i)}{dt} = -Vy_i$$

The equilibrium is represented by

$$y_i = \frac{\alpha_i x_i}{\Sigma \alpha_i x_i}$$

For the receiver tank

$$\frac{dD}{dt} = V$$

$$\frac{dD_i}{dt} = Vy_i$$

where D is the total distillate in tank and D_i the mole quantity of component i.

Nomenclature

Symbols

S	Still liquid quantity	kmol
V	Distillate removal rate	kmol/h
x	Mole fraction composition in the liquid	–
y	Mole fraction composition in the vapour	–
a	Relative volatility	–

Indices

i	Component i
0	Initial condition
avg	Refers to average values in distillate tank

Exercises

1. Vary the relative volatilities of the mixture and study the effect on the distillation.
2. Vary the initial proportions of the four components.
3. Compare the computer predictions with the Rayleigh equation prediction, where

$$\ln \frac{s}{s_0} = \int_{x_i}^{x_{i0}} \frac{dy}{y^* - x}$$

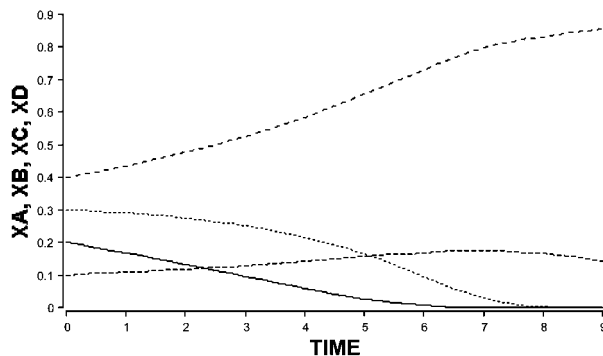4. Check the overall material balance in all the above exercises.

Results

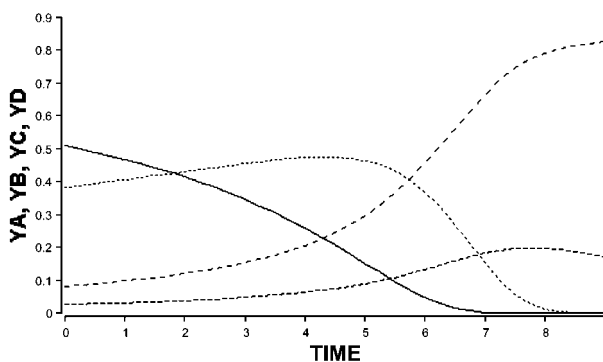**Fig. 2** Liquid compositions as a function of time during the course of the distillation.

Fig. 3 The corresponding vapour phase compositions.

5.10.3
CONSTILL – Continuous Binary Distillation Column

System

A continuous binary distillation column is represented below. The column is shown in Fig. 1 as consisting of eight theoretical plates, but the number of plates in the column may be changed, since the MADONNA program is written in array form.
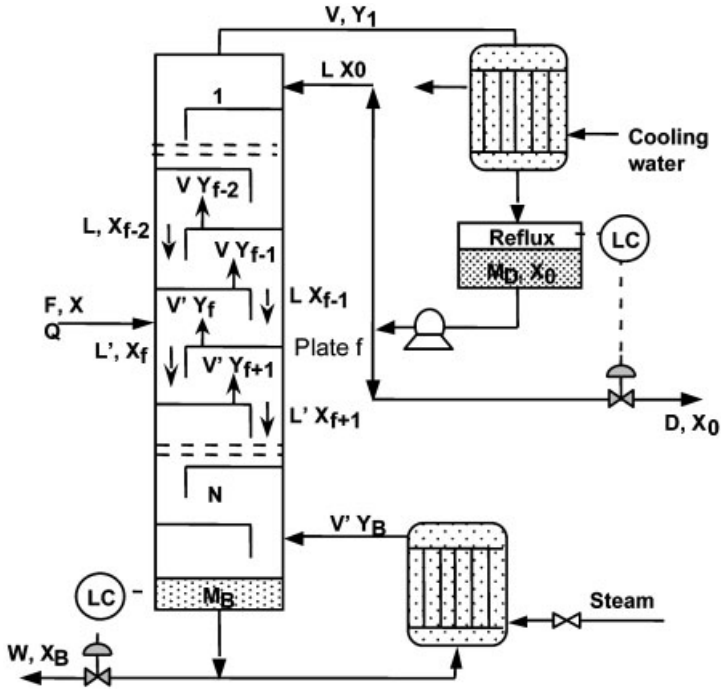
Fig. 1 An N-plate continuous distillation column.

Model

The model equations from Section 3.3.3.3 are

Reflux drum:

$$M_0 \frac{dX_0}{dt} = VY_1 - (L + D)X_0$$

Column enriching section:

$$M \frac{dX_n}{dt} = L(X_{n-1} - X_n) + V(Y_{n+1} - Y_n)$$

Column stripping section:

$$M \frac{dX_n}{dt} = L'(X_{m-1} - X_m) + V'(Y_{m+1} - Y_m)$$

Column feedplate:

$$M \frac{d(X_f)}{dt} = LX_{f-1} - L'X_f + V'Y_{f+1} - VY_f + FX_f$$

Reboiler:

$$M_B \frac{dX_B}{dt} = L'X_N - WX_W - V'Y_B$$

In the enriching section:
$$L = RD$$

and
$$V = (R + 1)D$$

In the enriching section:
$$L' = L + qF$$

and
$$V = V' - (1 - q)F$$

where for a saturated liquid feed with q=1, L'=L+F and V=V'.

Assuming theoretical plate behaviour in the column, the corresponding equilibrium vapour compositions are calculated by

$$Y_n = \frac{aX_n}{1 + (a - 1)X_n}$$

where a is the relative volatility.

Program

Note that the total number of plates, the feed plate location and reflux ratio can all be varied during simulation. The array form of the program also allows graphing the axial steady state tray-by-tray concentration profile. Part of the program is shown below.

{Example CONSTILL}

{CONDENSER AND REFLUX DRUM - index 1}
d/dt(X[1])=(V*Y[i+1]-(L+D)*X[i])/MD

{LIQUID PHASE COMPONENT BALANCES FOR PLATES 2 TO Nplates-1 }
d/dt(X[2..Fplate-1])=(L*(X[i-1]-X[i])+V*(Y[i+1]-Y[i]))/M
{Plates above the feed plate}

d/dt(X[Fplate])=(F*Xfeed+L*X[i-1]-L1*X[i]+V*(Y[i+1]-
Y[i]))/M {FEED PLATE}

```
d/dt(X[Fplate+1..Nplates1])=(L1*(X(i-1)-X(i))+V*(Y(i-1)-
Y[i]))/M  {Plates below the feed plate}
```

```
{REBOILER AND COLUMN BASE - index Nplates}
d/dt(X[Nplates])=(L1*X[i-1]-V1*Y[i]-W*X[i])/MR
```

```
{VAPOUR PHASE EQUILIBRIA}
Y[1..Nplates]=A*X[i]/(1+(A-1)*X[i])
```

```
{For plotting purposes}
XFplate=X[Fplate]
Xbottoms=X[Nplates]
Xdist=X[1]
```

Nomenclature

Symbols

D	Distillate rate	kmol/h
F	Feed rate	kmol/h
M	Liquid holdup	kmol
L	Liquid flow rate	kmol/h
q	Feed quality	–
R	Reflux ratio	–
V	Vapour flow rate	kmol/h
x	Liquid phase mole fraction	–
y	Vapour phase mole fraction	–
α	Relative volatility	–

Indices

|	
0	Refers to reflux drum
B	Refers to reboiler
f	Refers to feed plate
n	Refers to plate number
'	Refers to flows below the feed plate

Exercises

1. Study the response of the column to changes in the operating variables feed rate, feed composition and reflux ratio.
2. Verify that the overall steady-state balance is attained.
3. How long does it take for the steady state to be reached?
4. What influence does the reflux ratio have on the separation?
5. What influence does the term q have on the separation?

6. Use sliders for N_{plate}, F_{plate} and R with steady state array plots (choosing [i] as the X axis) to optimise the design of the column in terms of column separation efficiency. Compare your results with those obtained by more conventional calculation methods.

Results
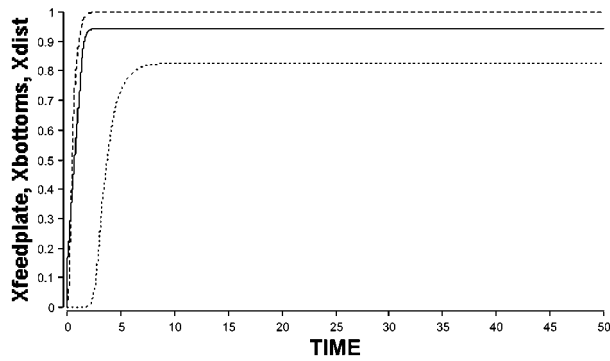
Fig. 2 Top product, feed plate and bottoms product composition variations as a function of time.
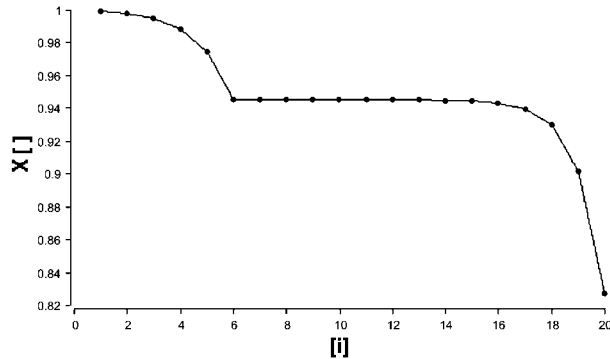
Fig. 3 Column steady state composition profiles. Note that N_{plate}, F_{plate} and R still need further optimisation to ensure good quality product at both ends of the column. Note the pinch region in the vicinity of the feed plate is very apparent.

5.10.4
MCSTILL – Continuous Multicomponent Distillation Column

System

This problem is similar to CONSTILL except that three components benzene, xylene and toluene are considered.
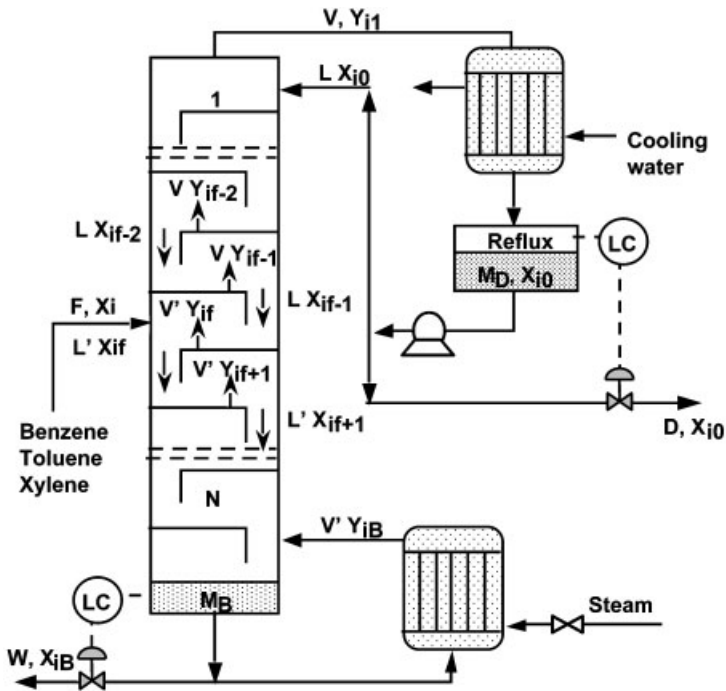

Fig. 1 The three-component, N_{plate}, continuous distillation column.

Model

The component balance equations for reflux drum, column enriching section, feed plate, column stripping section and the column base and reboiler are very similar to those derived previously for the binary distillation example CONSTILL, but are now expressed in multicomponent terms as described in Section 3.3.3.4.

Thus for any component i of the mixture in the enriching section of the column

$$\frac{M_n d(X_{in})}{dt} = L(X_{in-1} - X_{in}) + V(Y_{in+1} - Y_{in})$$

where $i = 1$ to j and where the corresponding vapour equilibrium composition is now represented by

$$Y_{in} = \frac{\alpha_{in} X_{in}}{\sum_{1}^{j} \alpha_{in} X_{in}}$$

Program

The simulation is based on a fixed vapour boilup rate. Component balance equations are represented for "benzene" and "toluene". The "xylene" concentrations are determined by difference, based on the sum of the mole fractions being equal to one.

Note that the plate numbering in the program is slightly different to that shown in Fig. 1, owing to the use of the vector notation to include both the reflux drum and the column base. In the program, index number 1 is used to denote the reflux drum and product distillate, and index $N_{plate} + 1$ is used to denote the reboiler and bottoms product. This is convenient in the subsequent plotting of the steady state composition profiles in the column. Both N_{plate} and the feed plate location F_{plate} are important parameters in the simulation of the resulting steady state concentration profiles and the resultant column optimisation.

The column start up is from an initial arbitrarily chosen composition profile. The steady state composition profile obtained from the first run can then be used as the starting profile for subsequent runs. With the MADONNA version for Windows, changes in operating parameters, such as feed rate, can be made with the CONTINUE feature. This can be programmed easily with IF-THEN-ELSE statements. In this way realistic dynamics can be obtained for the column conditions moving from one steady state to another.

Nomenclature

Symbols

D	Distillate rate	kmol/h
F	Feed rate	kmol/h
M	Liquid holdup	kmol
L	Liquid flow rate	kmol/h
q	Feed quality	–
R	Reflux ratio	–
V	Vapour flow rate	kmol/h
x	Liquid phase mole fraction	–
y	Vapour phase mole fraction	–
α	Relative volatility	–

Indices

′	Refers to flows below the feed plate
0	Refers to reflux drum
B	Refers to reboiler
f	Refers to feed plate
i	Refers to the component i
j	Refers to the number of components
n	Refers to plate number

Exercises

1. Study the response of the column to changes in the operating variables feed rate, feed composition and reflux ratio, while keeping the number of plates N_{plate} and feed plate location F_{plate} constant.
2. Verify that the overall steady-state balance is attained.
3. How long does it take for the steady state to be reached?
4. What influence does the reflux ratio have on the separation?
5. Repeat Exercises 1 to 4, but now varying the number of column plates and the feed plate.
6. Use sliders for N_{plate}, F_{plate} and R to determine the optimum design conditions for the column. For this the array index [i] can be chosen for the X axis to obtain steady-state axial profiles.
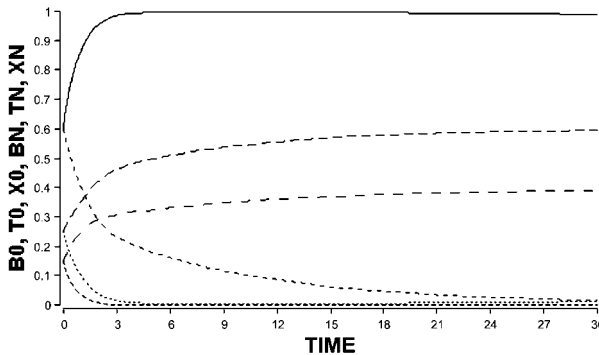
Results

Fig. 2 Column top and bottom product compositions approaching steady state from the rather arbitrary feed composition starting point.
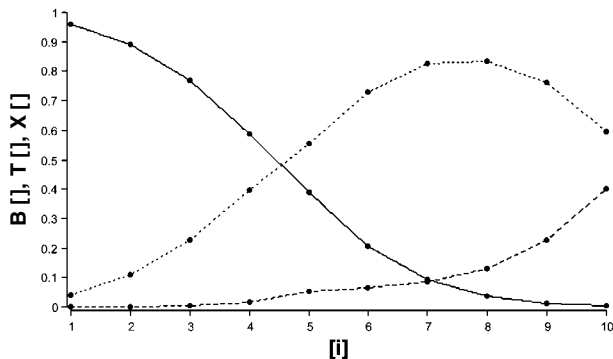
Fig. 3 Steady state column composition profiles for "benzene", "toluene" and "xylene".

5.10.5
BUBBLE – Bubble Point Calculation for a Batch Distillation Column

System

As in example BSTILL, a column containing four theoretical plates and reboiler is assumed, together with constant volume conditions in the reflux drum. The liquid behaviour is, however, non-ideal for this water–methanol system. The objective of this example is to illustrate the need for iterative calculations required for bubble point calculations in non-ideal distillation systems and to show how this can be achieved via the use of simulation languages.
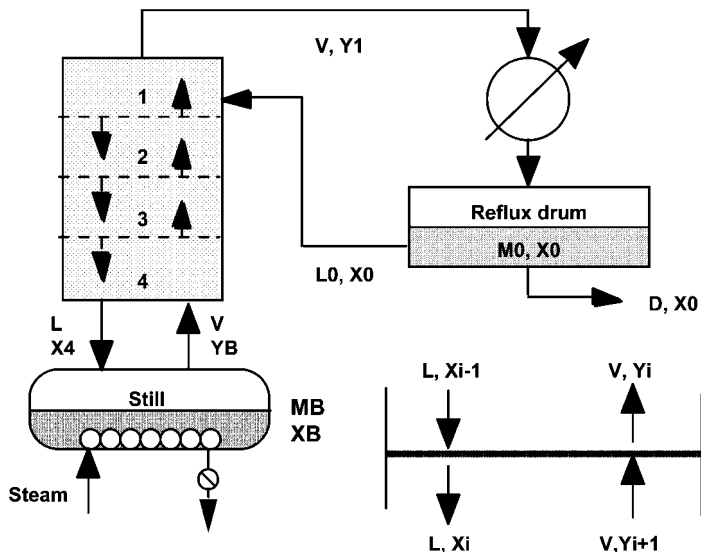

Fig. 1 The four-stage batch distillation column.

Model

Component balances for the more volatile component on any plate n give

$$M \frac{dx_n}{dt} = L(x_{i-1} - x_n) + V(y_{i+1} - y_n)$$

for the still

$$\frac{dM_B}{dt} = L - V$$

$$\frac{d(M_B x_B)}{dt} = L x_4 - V y_B$$

where 4 refers to the bottom plate and B to the still and column base.

For the reflux drum and condenser

$$M_0 \frac{d(x_0)}{dt} = V y_1 - (L + D) x_0$$

where the reflux ratio, R, is given by L_0/D and

$$D = \frac{V}{(R + 1)}$$

Throughout the column the total mass balance gives

$$L = V - D$$

Theoretical plate behaviour in the column is assumed, where the liquid–vapour equilibrium is described by

$$p_i = \gamma_i x_i p_{pi}$$

Here p_{pi} is the vapour pressure of the pure fluid i, x_i is its mole fraction in the liquid phase, γ_i is its activity coefficient and p_i is the actual vapour partial pressure.

Vapour pressures p_{pi} are given by

$$\ln p_{pi} = c_i + \frac{d_i}{T_i}$$

For the estimation of activity coefficients the Van Laar equation is used.

$$\gamma_M = \exp\left[\frac{Ax_W^2}{\left(x_W + \dfrac{A}{B}x_M\right)^2}\right]$$

$$\gamma_W = \exp\left[\frac{Bx_M^2}{\left(x_M + \dfrac{B}{A}x_W\right)^2}\right]$$

These equations represent an implicit loop to satisfy the condition

$$P = p_W + p_M = \gamma_W x_W p_{pW} + \gamma_M x_M p_{pM}$$

Since P is constant, the temperature will adjust at each plate such that the above equation is satisfied.

Program

For convenience, only four stages were used in this model, since MADONNA does not have a ROOTS finder function in an array form. For this reason each stage needs to be programmed separately.

Nomenclature

Symbols

A, B	Coefficient in Van Laar equation	–
C	Constant in the vapour pressure relation	–
D	Distillate rate	kmol/h
d	Constants in the vapour pressure relation	–
L	Liquid flow rate	kmol/h
M	Molar holdup	kmol
R	Reflux ratio	–
p_P	Pure component vapour pressure	bar
P	Total pressure	bar
V	Vapour flow rate	kmol/h
x	Liquid phase mole fraction	–
y	Vapour phase mole fraction	–
α	Relative volatility	–
γ	Activity coefficient	–

Indices

0	Refers to reflux drum
1 to 4 and i	Refers to plate number
B	Refers to reboiler
M	Refers to methanol
W	Refers to water

Exercises

1. Investigate the response of the column to changes in the boilup rate V.
2. The program starts up the column at total reflux (R very high). After steady state is reached on all plates, vary the reflux ratio interactively and attempt to carry out the distillation in minimum time, while attempting to maintain a distillate composition, so far as is possible, that $x_0 > 0.9$ and note the response of the distillate composition x_0.
3. Recharge the column by changing x_B and M_B and note the transients on each plate.
4. Devise a control scheme, such that the column maintains a distillate composition at $x_0 > 0.9$.
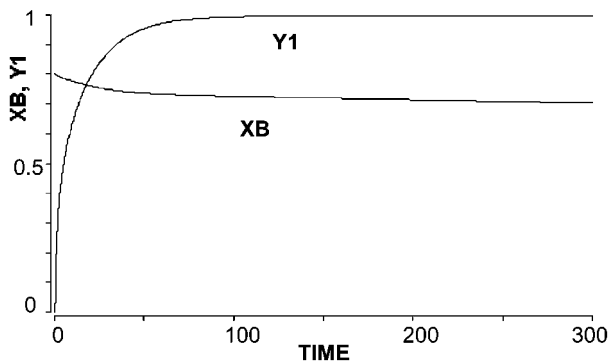
Results

Outputs are shown below.

Fig. 2 The column was started with total reflux; the reflux was then reduced to 10 at T=20.
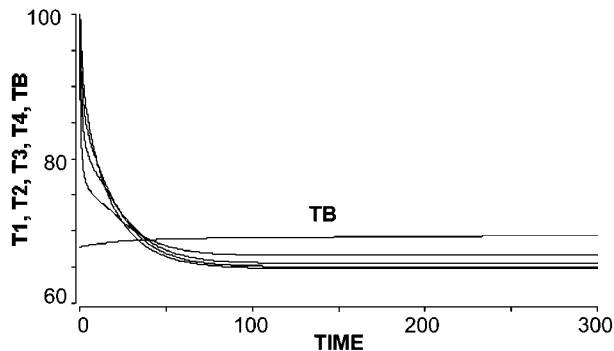
Fig. 3 The temperature profiles here are from the run of Fig. 2. The highest temperature is in the still (T_B) and the lowest is on the top plate (T_1).

Reference

Luyben, W. L. and Wenzel, L. A. (1988) Chemical Process Analysis, Prentice-Hall.

5.10.6
STEAM – Multicomponent, Semi-Batch Steam Distillation

System

This example is based on the theory and model description in Section 3.3.4 and involves a multicomponent, semi-batch system, with both heating and boiling periods. The compositions and boiling point temperatures will change with time. The water phase will accumulate in the boiler. The system simulated is based on a mixture of n-octane and n-decane, which for simplicity is assumed to be ideal but which has been simulated using detailed activity coefficient relations by Prenosil (1976).
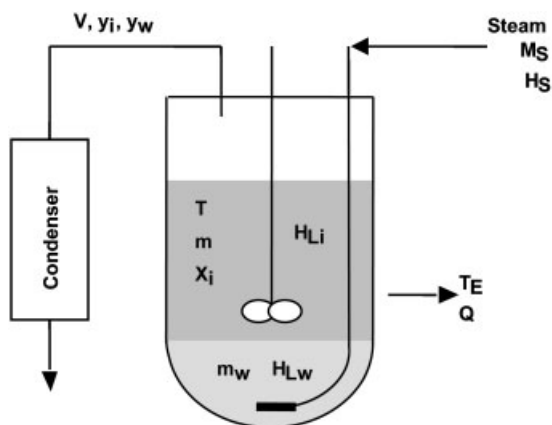

Fig. 1 Schematic of the semi-batch steam distillation.

Model

The model involves first a heating period and, when the boiling temperature is reached, then a distillation period.

All the steam is assumed to condense during the heating period, therefore the steam efficiency, E, equals 1.0. The standard state for enthalpy calculations is considered to be that of the pure liquid components at $0\,°C$ and 1 bar.

Program

The heating period begins with FLAG set initially to zero. When $\Sigma y > 1$ then FLAG becomes 1, and the distillation period begins. At each time interval the ROOT FINDER is used to make the iterative bubble point calculation. The component mass balance determines the removal of volatiles in the vapour, where the total molar flow rate, V, is determined from the energy balance.

Nomenclature

Symbols

c_p	Molar heat capacity	kJ/kmol K
H	Enthalpy	kJ/kmol
M_s	Flow rate of steam	kmol/min
m or M	Mass of organic phase in the still	kmol
m_w or M_w	Mass of water in the still	kmol
P	Total pressure	bar
P^*	Partial pressure	bar
P^0	Vapour pressure	bar
Q	Heat transfer rate	kJ/min
T	Absolute temperature	K
T_E	Absolute ambient temperature	K
U	Overall heat transfer coefficient	kJ/K min
V	Vapour flow rate	kmol/min
x	Mole fraction in the liquid	–
y	Mole fraction in the vapour	–

Indices

|	
0	Refers to initial
1, 2, i	Refers to organic components
Dist	Refers to distillate
L	Refers to liquid
S	Refers to steam
V	Refers to vapour
W	Refers to water
L	Refers to liquid

Exercises

1. Investigate the response of the system to changes in steam rate M_S.
2. Change the initial composition by varying the mole fractions X_{01} and X_{02}.

Results
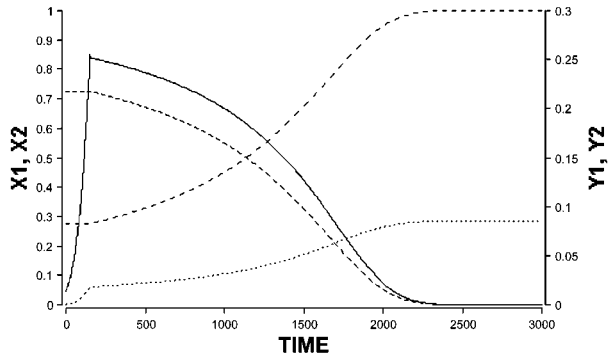
Fig. 2 The dynamic changes of the organic mole fractions in the gas and liquid phases are seen here.
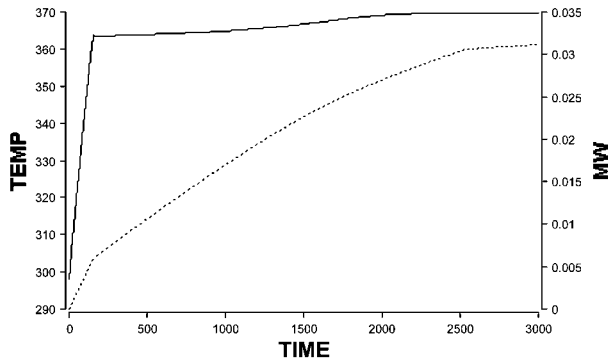
Fig. 3 Temperature and water mass variations in the still during the heating and distillation periods.

Reference

Prenosil, J. E. (1976) Multicomponent Steam Distillation: A Comparison between Digital Simulation and Experiment, Chem. Eng. J. 12, 59–68, Elsevier.

5.11
Heat Transfer Examples

5.11.1
HEATEX – Dynamics of a Shell-and-Tube Heat Exchanger

System

A shell-and-tube heat exchanger is to be investigated for both its dynamic and steady-state behaviour.
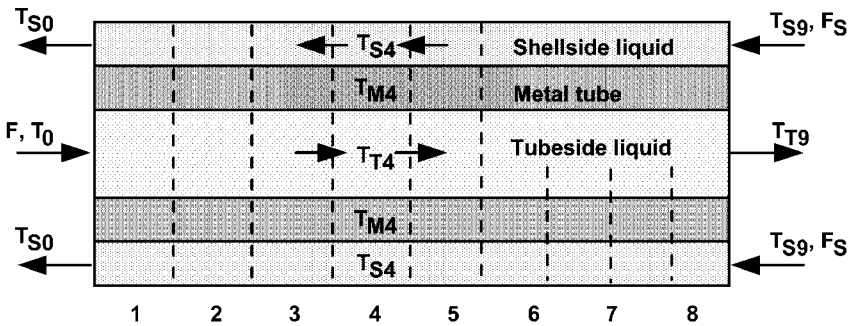

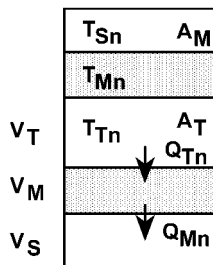**Fig. 1** Finite differencing the heat exchanger for dynamic modelling.

Fig. 2 Detail of section n showing heat flows, volumes and transfer areas.

Model

The model equations follow from Section 4.5.2.2. For section n, the rate of heat transfer from the tube contents to the metal wall is given by

$$Q_{Tn} = U_{TM}A_T(T_{Tn} - T_{Mn})$$

The rate of heat transfer from metal wall to shell-side content is

$$Q_{Mn} = U_{MS}A_M(T_{Mn} - T_{Sn})$$

For the tube-side fluid

$$c_{pT}\rho_T V_T \frac{dT_{Tn}}{dt} = F_T c_{pT}(T_{Tn-1} - T_{Tn}) - Q_{Tn}$$

For the metal wall

$$c_{pM}\rho_M V_M \frac{dT_{Mn}}{dt} = Q_{Tn} - Q_{Mn}$$

For the shell-side fluid

$$c_{pS}\rho_S V_S \frac{dT_{Sn}}{dt} = F_S c_{pT}(T_{Sn+1} - T_{Sn}) + Q_{Mn}$$

The respective volumes and area are calculated by

$$V_T = \Delta L \pi D_T^2 \,; \; A_T = \Delta L \pi D_T$$

$$V_M = \Delta L \pi (D_M^2 - D_T^2)\,, \; A_M = \Delta L \pi D_M$$

$$V_S = \Delta L \pi (D_S^2 - D_M^2)\,, \; A_S = \Delta L \pi D_S$$

where D_T, D_M, D_S are the respective diameters and A_T, A_M, A_S are the areas.

The tube inlet and outlet end sections are modelled by averaging the temperatures entering the section.

For example, for the shell-side section 1:

Entering shell-side temperature (averaged) $= \dfrac{(T_{S2} + T_{S1})}{2}$

Leaving shell-side temperature $= T_{S0}$

Thus

$$c_{pS}\rho_S V_S \frac{dT_{S1}}{dt} = F_S c_{pS}\left(\frac{(T_{S2} + T_{S1})}{2} - T_{S0}\right) + Q_{M1}$$

Program

The model is programmed using arrays. This permits varying the number of sections. As usual with such finite-differenced models, the end sections are treated separately. Part of the program is shown below.

```
{Example HEATEX}
{SHELL AND TUBE HEAT EXCHANGER}

{ELEMENT 1}
QT[1]=UTM*(TT[1]-TM[1])
```

```
QM[1]=UMS*(TM[1]-TS[1])
TS0=TS[1]+0.5*(TS[1]-TS[2])

d/dt(TT[1])=ZT*(TT0-0.5*(TT[1]+TT[2]))-QT[1]/YT
d/dt(TM[1])=(QT[1]-QM[1])/YM
d/dt(TS[1])=ZS*(0.5*(TS[1]+TS[2])-TS0)+QM[1]/YS

{ELEMENTS 2 TO ELEMENT Nelem-1}
{TUBE HEAT TRANSFER RATES, kJ/s}
QT[2..Nelem-1]=UTM*(TT[i]-TM[i])

{SHELL SIDE HEAT TRANSFER RATES, kJ/s}
QM[2..Nelem-1]=UMS*(TM[i]-TS[i])

{TUBE SIDE HEAT BALANCES}
d/dt(TT[2..Nelem-1])=ZT*(TT[i-1]-TT[i])-QT[i]/YT

{METAL WALL HEAT BALANCES}
d/dt(TM[2..Nelem-1])=(QT[i]-QM[i])/YM

{SHELL SIDE HEAT BALANCES}
d/dt(TS[2..Nelem-1])=ZS*(TS[i+1]-TS[i])+QM[i]/YS

{ELEMENT Nelem}
QT[Nelem]=UTM*(TT[i]-TM[i])
QM[Nelem]=UMS*(TM[i]-TS[i])
TTout=TT[Nelem]-0.5*(TT[Nelem-1]-TT[Nelem])
d/dt(TT[Nelem])=ZT*(0.5*(TT[i-1]+TT[i])-TTout)-QT[i]/YT
d/dt(TS[Nelem])=ZS*(TSIN-0.5*(TS[i-1]+TS[i]))+QM[i]/YS
d/dt(TM[Nelem])=(QT[i]-QM[i])/YM
```

Nomenclature

Symbols

A	Transfer area ($\Delta A = \pi D \Delta L$)	m^2
C	Specific heat	kJ/kg K
D_M	Outside diameter of metal wall	m
D_T	Internal diameter of tube wall	m
F	Mass flow velocity	m^3/s
H_{MS}	Film heat transfer coefficient from the wall to the shell	kJ/m^2 K s
H_T	Film heat transfer coefficient, tube-side	kJ/m^2 K s
Q	Heat transfer rate	kJ/s
T_{Mn}	Metal wall temperature in element n	K
T_{Sn}	Shell-side temperature in element n	K
T_{Tn}	Temperature in element n, tube-side	K

| V | Volumes of shell-side fluid, tube-side fluid and metal wall in length ΔL | m^3 |
| ρ | Density of the shell-side fluid, tube-side fluid and metal wall | kg/m^3 |

Indices

S	Refers to shell
M	Refers to metal
T	Refers to tube
1, 2, ..., n	Refers to section

Exercises

1. Establish that the overall steady-state balance is satisfied.
2. Investigate the response of the system to a change in entering temperatures.
3. Increase the heat transfer coefficients and observe the resulting trend in the temperatures T_T, T_M, and T_S.
4. Increase the flow of shell-side fluid and observe the effect on the inlet shell-side and outlet tube-side temperatures.
5. Increase the mass of the wall and observe the influence on the dynamics.
6. Derive a dimensionless form of the equations and thus obtain the important dimensionless groups governing the dynamic behaviour of the heat exchanger.
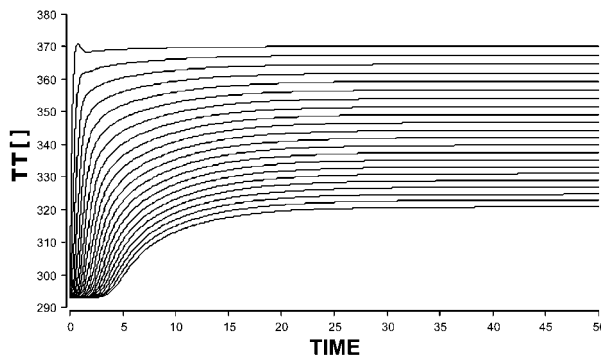
Results

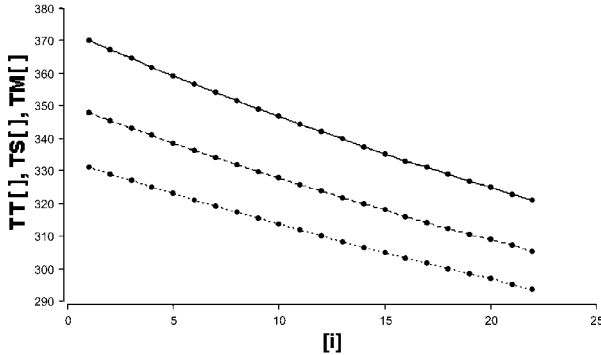**Fig. 3** Response of tube-side temperatures for a step change in the inlet tube-side temperature.

Fig. 4 Steady-state axial profile for the shell, metal and tube temperature corresponding to Fig. 3.

5.11.2
SSHEATEX – Steady-State, Two-Pass Heat Exchanger

System

A purified water stream for a food processing plant is raised to required temperature by heat exchange with warm untreated process water. A conventional two-pass heat exchanger is to be used. This problem is based on the formulation of Walas (1991) and data taken from Backhurst, Harker and Porter (1974).

In the first pass, both the hot and cold fluids flow in cocurrent flow through the heat exchanger, whereas in the second pass the cold fluid now flows countercurrent to the hot shell-side fluid. Half the heat exchange area is therefore in cocurrent flow and half in countercurrent flow.
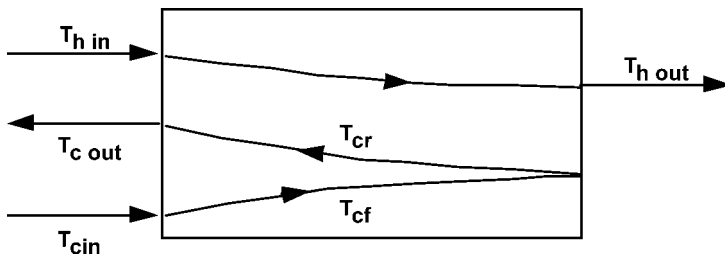

Fig. 1 Two-pass heat exchanger schematic, showing two passes for the cold fluid.

Model

The derivation of the model equations follows that of Section 4.5.2.1.

For the hot shell-side fluid

$$(Wc_p)_h \frac{dT_h}{dA} = -\frac{U(T_h - T_{cf})}{2} - \frac{U(T_h - T_{cr})}{2}$$

For the cold-side fluid in forward cocurrent flow

$$(Wc_p)_c \frac{dT_{cf}}{dA} = \frac{U(T_h - T_{cf})}{2}$$

and for the cold-side fluid in reverse countercurrent flow

$$(Wc_p)_c \frac{dT_{cr}}{dA} = \frac{U(T_h - T_{cr})}{2}$$

For a given inlet and outlet cold water temperature, the outlet hot water temperature is determined by an overall heat balance, where

$$(W)_h(T_{h\,in} - T_{h\,out}) = (Wc_p)_c(T_{c\,out} - T_{c\,in})$$

Program

Starting at the given temperature conditions $T_{c\,in}$, $T_{c\,out}$ and $T_{h\,in}$, the model equations are integrated to the condition that $T_{cf} = T_{cr}$, which must be true when the fluid reverses directions. It should be noted that a solution exists only for certain values of initial conditions and flow rates.

Nomenclature

Symbols

A	Area	m^2
c_p	Specific heat capacity	kJ/kg s
L	Length	m
T	Temperature	K
t	Time	s
U	Overall heat transfer coefficient	kJ/m^2 s K
W	Mass flow rate	kg/s

Indices

h, c	Refer to hot and cold fluids
f, r	Refer to the cold fluid in forward (cocurrent) and reverse (countercurrent) flow

Exercises

1. Study the effects of varying flow rates of both hot and cold fluids on the heat transfer area required.
2. Vary the hot fluid temperature in the range 383 to 353 K and study the effect on the area.
3. The model assumes a constant specific heat for water. If this varies with temperature, according to $c_p = a + bT$, how could this effect be implemented in the program, and what additional difficulties does it cause?
4. Is any advantage to be gained by changing the hot fluid to the two-pass arrangement?
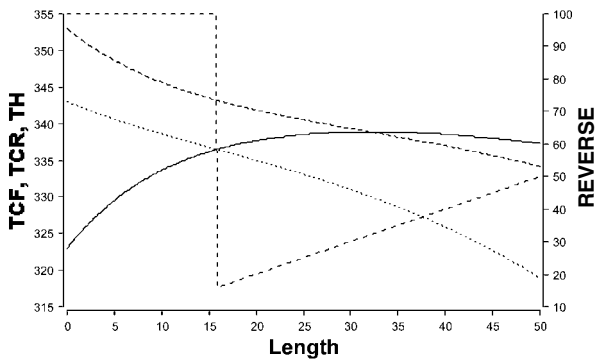
Results

Fig. 2 The steady state axial profiles for the cold and hot fluids. The variable REVERSE marks the length of exchanger needed, as shown by the vertical line.
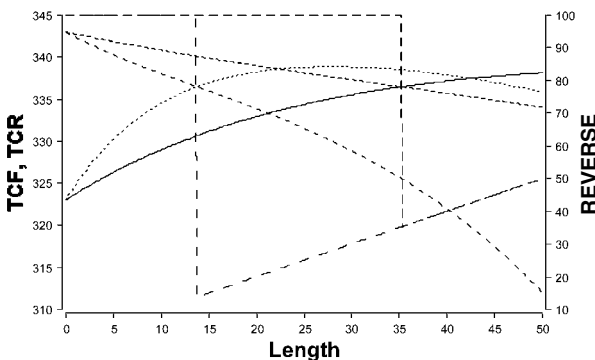

Fig. 3 Using an overlay plot gives the solutions for two values of the heat transfer coefficient.

References

Walas, S. M. (1991) "Modeling with Differential Equations in Chemical Engineering", Butter-worth.
Backhurst, J. R., Harker, J. H. and Porter, J. E. (1974) "Problems in Heat and Mass Transfer", Edward Arnold.

5.11.3
ROD – Radiation from Metal Rod

System

A metal rod of radius r is in contact with a constant temperature source at each end. At steady state the heat conducted towards the center is balanced by the heat loss by radiation. This leads to a symmetrical temperature profile in the rod, as shown.
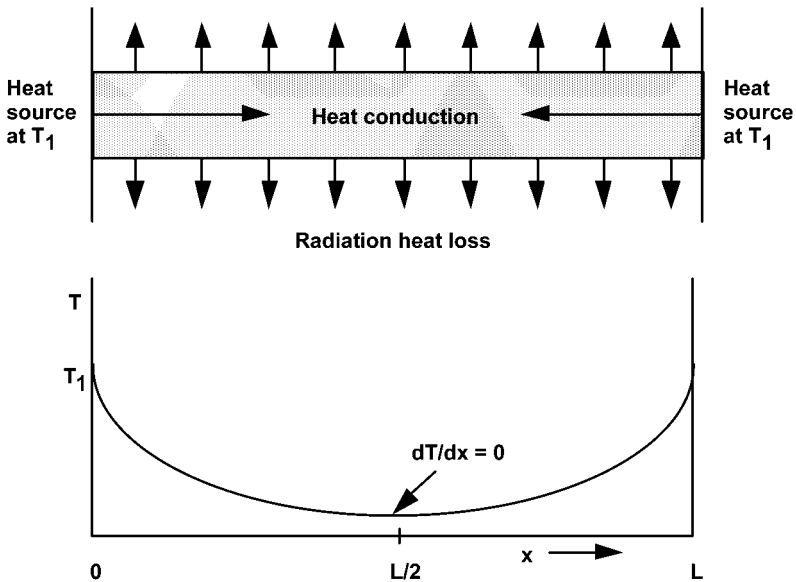

Fig. 1 The temperature profile is symmetrical for this heat conduction problem.

Model

The model is based on the steady-state energy balance combined with Fourier's law which gives

$$\frac{d^2T}{dx^2} = \frac{2\sigma}{rk} \cdot T^4$$

or

$$\frac{d^2T}{dx^2} = \alpha T^4$$

where $\alpha = 1.25 \times 10^{-8}$ (1/m^2 K^3).

Boundary conditions are

$$T_1 = 2000 \text{ K} \quad \text{at} \quad x = 0$$

At the midpoint of the rod

$$\frac{dT}{dx} = 0 \quad \text{at} \quad x = \frac{L}{2}$$

This boundary condition is deduced from the symmetrical nature of the rod profile L=0.5 m.

Program

Knowledge of the derivative at the centre of the rod requires a solution involving repeated estimates of the temperature gradient at the rod end. The integration proceeds from the end to the rod centre. The required trial and error iteration can be easily done with a slider to adjust the parameter SLOPE.

Nomenclature

Symbols

| T	Temperature	K
σ	Emissivity	kJ/s m^2 K^4
k	Conductivity	kJ/s m K
x	Distance along rod	m
α	Constant	1/K^3 m^2
r	radius of rod	m

Exercises

1. Experiment with the various parameters of the model to see their influence.
2. Alter the program so that the conductivity and radius can be varied. Using various metals show how the value of k influence the solution.
3. Reformulate the problem in a dynamic form to be solved with respect to time and distance changes along the rod.

Results
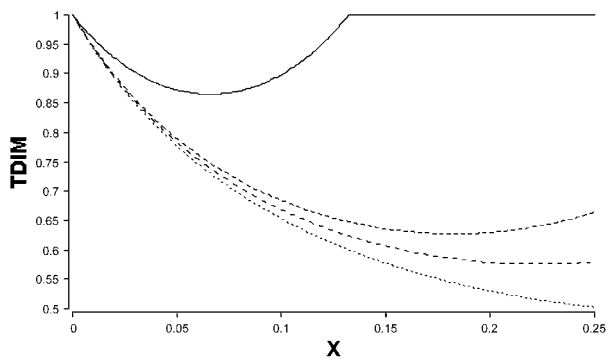
Fig. 2 Using a slider for SLOPE the correct value can be found to achieve a zero slope at the center of the rod at X=0.25.
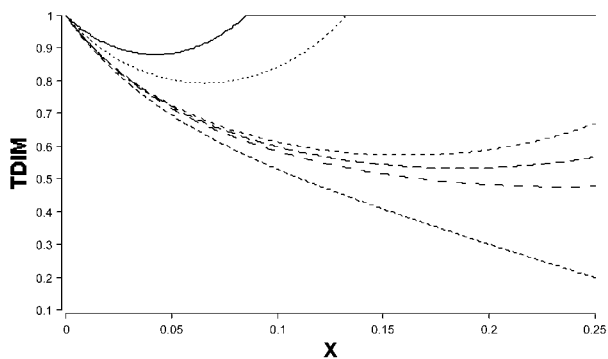
Fig. 3 Doubling Alpha compared with the run in Fig. 2 requires an increase in SLOPE.

5.12
Diffusion Process Examples

5.12.1
DRY – Drying of a Solid

System

A thin slab of solid material resting on a surface dries first by evaporation from the top surface and then by diffusion from the interior of the solid. The water movement towards the top surface is approximated by the diffusion equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2}$$
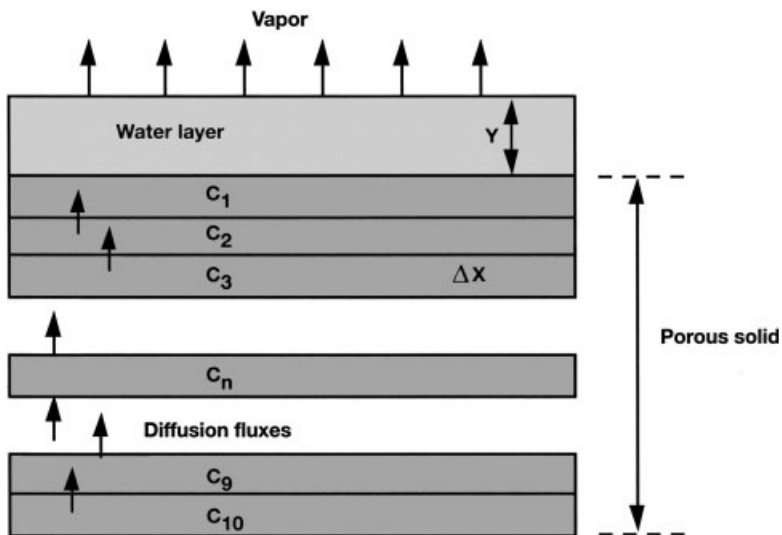

Fig. 1 Finite-differencing of the solid.

Model

Surface Drying

Water is removed from the top surface where $X=0$.

Drying rate

$$M_1 = UA \frac{T_g - T_w}{\Delta H}$$

Water mass evaporated

$$W_1 = \int_0^t M_1 dt$$

Depth of water at time t

$$Y = \frac{W - W_1}{\rho A}$$

where the initial water mass in the layer is

$$W = V_0 \rho$$

Solid Drying

At the instant that the depth of the water layer is reduced to zero, the drying of the solid begins. As shown in Fig. 1, the solid is considered as 10 finite difference elements, each of length ΔX.

For the water balance of element n and applying Fick's law

$$V_n \frac{dC_n}{dt} = D\left(\frac{C_{n+1} - C_n}{\Delta X}\right) A - D\left(\frac{C_n - C_{n-1}}{\Delta X}\right) A$$

with

$$V_n = A\Delta X$$

giving

$$\frac{dC_n}{dt} = D\left(\frac{C_{n+1} - 2C_n + C_{n-1}}{\Delta X^2}\right)$$

C_n represents the concentration at the midpoint of element n, and the gradient dC/dX is approximated by $\Delta C/\Delta X$.

The boundary conditions are as follows:

$$X = 0, \quad C_0 = \text{constant}$$

Corresponding to zero flux at the lower surface

$$X = L, \quad \frac{dC}{dX} = 0$$

This can be approximated by setting $C_{11} = C_{10}$.

The drying rate is obtained by approximating the concentration gradient at the surface

$$M_2 = DA \frac{C_1 - C_0}{\Delta X}$$

where C_0 is the water concentration of the outer solid in equilibrium with the air.

The total water removed from the solid is

$$W_2 = \int_0^t M_2 dt$$

Total water removed in both stages of drying

$$W_3 = W_1 + W_2$$

The water remaining is

$$W_4 = W + (ALC) - W_3$$

The percent dryness is

$$P = \frac{(W_3 \cdot 100)}{(W + A \cdot L \cdot C)}$$

Program

The program is written with two logical control variable flags, one takes the value of 1.0 to control the surface evaporation and the other a value of 1.0 to start the diffusional drying process. Array notation for the number of solid segments is used to allow plotting the concentration versus distance at any desired time.

Nomenclature

Symbols

A	Area	m^2
A	Surface area	m^2
C	Water concentration initially	$kmol/cm^3$
C_0	Surface equilibrium concentration	$kmol/cm^3$
C_n	Water concentration of solid	$kmol/cm^3$
D	Diffusion coefficient	m^2/s
ΔH	Latent heat of evaporation	$kJ/kmol$
ΔX	Depth of finite element	m

L	Depth of solid	m
L	Thickness	m
M_1	Drying rate of water layer	kmol/s
M_2	Drying rate of solid	kmol/s
P	Percent dryness	–
ρ	Water density	kmol/m^3
T_g	Air temperature	K
T_w	Water temperature (wet bulb)	K
U	Heat transfer coefficient	kJ/m^2 K s
V	Volume of water layer	m^3
W	Initial mass of water layer	kmol
W_1	Water mass evaporated	kmol
W_2	Water removed from solid	kmol
W_3	Total water removed	kmol
W_4	Remaining water	kmol
X	Length variable	m
Y	Water layer depth	m

Exercise

1. Run the program and graph the water concentrations in the solid versus time. Graph also the rate R1 versus percent dryness P.
2. The drying time for the solid can be characterised by L^2/D, a diffusion time. Verify this by simulation by varying D and L separately.
3. Improve the model by assuming a mass transfer rate at the solid surface, such that $M_2 = K_T A C_1$. Assume a suitable value for K_T.
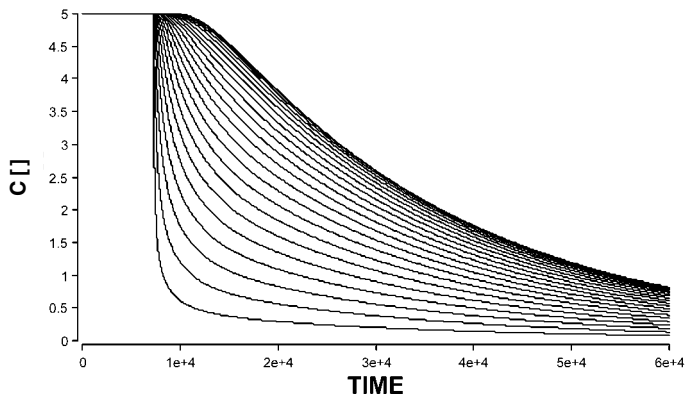
Results
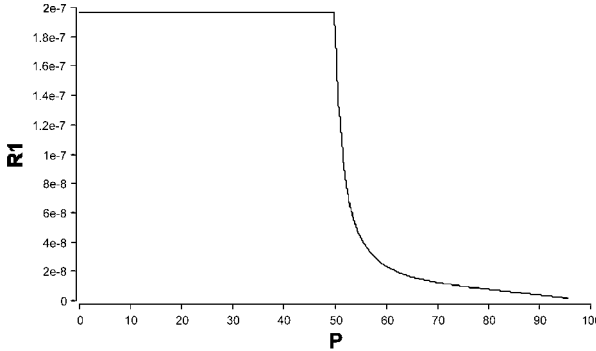

Fig. 2 Concentration-time profiles in the solid.

Fig. 3 Drying curve plotted as drying rate versus percent water remaining.

5.12.2
ENZSPLIT – Diffusion and Reaction: Split Boundary Solution

System

A rectangular slab of porous solid supports an enzyme. For reaction, reactant S must diffuse through the porous lattice to the reaction site, and, as shown in Fig. 1, this occurs simultaneously from both sides of the slab. Owing to the decreasing concentration gradient within the solid, the overall rate of reaction will generally be lower than that at the exterior surface. The magnitude of the concentration gradient determines the effectiveness of the catalyst.
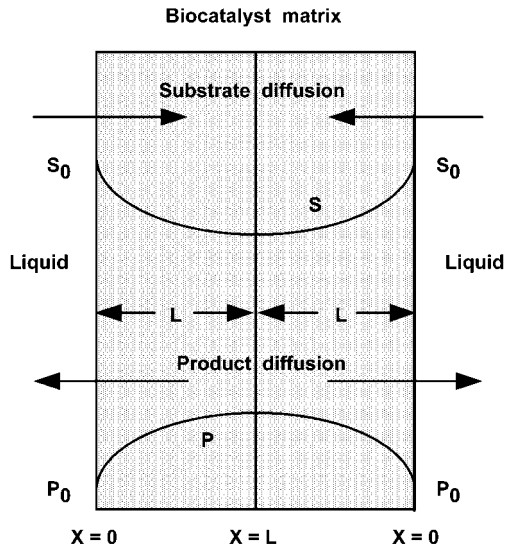

Fig. 1 Symmetrical concentration gradients for substrate and product.

Model

Under steady-state conditions

$$\begin{pmatrix} \text{Rate of diffusion of} \\ \text{reactant into the slab} \end{pmatrix} = \begin{pmatrix} \text{Rate at which reactant is} \\ \text{consumed by reaction} \end{pmatrix}$$

$$D_S \frac{d^2S}{dX^2} = R$$

A quasi-homogeneous form for the reaction term is assumed.

The boundary conditions are given by

At X = L

$$S = S_0, \quad P = P_0$$

At X = 0

$$\frac{dS}{dX} = \frac{dP}{dX} = 0$$

The external concentration is known, and the concentration profile throughout the slab is symmetrical.

The reaction rate for this enzyme kinetics example is expressed by the Michaelis–Menten equation and with product inhibition.

$$R = \frac{kES}{K_M(1 + P/K_I + S)}$$

where k, K_M and K_I are kinetic constants and E and P are the enzyme and product concentrations. At steady state, the rate of diffusion of substrate into the slab is balanced by the rate of diffusion of product out of the slab.

Assuming the simple stoichiometry $S \rightarrow P$,

$$D_S \frac{dS}{dX} = -D_P \frac{dP}{dX}$$

which on integration gives

$$P = (S_0 - S) \frac{D_S}{D_P}$$

where P is assumed zero at the exterior surface.

Defining dimensionless variables

$$S' = \frac{S}{S_0}, \quad P' = \frac{P}{S_0} \quad \text{and} \quad X' = \frac{X}{L}$$

Substituting gives

$$\frac{d^2 S'}{dX'^2} - \frac{L^2 R'}{D_S S_0} = 0$$

where

$$R' = \frac{kES'}{(K_M/S_0)(1 + (S_0 P'/K_I)) + S'}$$

and

$$P' = (1 - S')\frac{D_P}{D_S}$$

The boundary conditions are then given by

$$X' = 1, \quad S' = 1 \quad \text{and} \quad X' = 0, \quad \frac{dS'}{dX'} = 0$$

The catalyst effectiveness may be determined from

$$\eta = \frac{D_S S_0 (dS'/dX')_{X=1}}{L^2 R_0}$$

where R_0 is the reaction rate determined at surface conditions

$$R_0 = \frac{kES_0}{K_M(1 + P_0/K_I + XS_0)}$$

Program

The dimensionless model equations are used in the program. Since only two boundary conditions are known, i.e., S at $X' = 1$ and dS'/dX' at $X' = 0$, the problem is of a split-boundary type and therefore requires a trial and error method of solution. Since the gradients are symmetrical, as shown in Fig. 1, only one-half of the slab must be considered. Integration begins at the center, where $X' = 0$ and $dS'/dX' = 0$, and proceeds to the outside, where $X' = 1$ and $S' = 1$. This value should be reached at the end of the integration by adjusting the value of S_{guess} at $X = 0$ with a slider.

The MADONNA software allows an automatic, iterative solution of boundary value problems. Selecting **Model/Modules/Boundary Value ODE** prompts for the boundary condition input: Set $S = 1$ at $X = 1$ with unknowns S_{guess}. Allowing

S_{guess} to vary between 0.5 and 0.6 gives a solution that approaches $S_{guess} = 0.562$. After an additional RUN command the solution is shown. It is also instructive to use the manual slider method, as explained above.

The Thiele modulus is also calculated and explained in the program.

Nomenclature

Symbols

D	Diffusion coefficient	m^2/h
E	Enzyme concentration	mol/m^3
K	Kinetic constant	$kmol/m^3$
k	Reaction rate constant	$1/h$
L	Distance from slab centre to surface	m
P	Product concentration	$kmol/m^3$
R	Reaction rate	$kmol/m^3\ h$
S	Substrate concentration	$kmol/m^3$
X	Length variable	m
η	Effectiveness factor	–

Indices

I	Refers to inhibition
M	Refers to Michaelis–Menten
P	Refers to product
S	Refers to substrate
'	Refers to dimensionless variables
0	Refers to bulk concentration
guess	Refers to assumed value

Exercises

1. Vary the parameters L, D_S, S_0, k and E, but maintaining the Thiele parameter $[L^2\ k\ E/D_S\ S_0]$ at a constant value less than 0.1.
2. Vary the above parameters separately, noting the value of the Thiele parameter $(L^2\ k\ E/D_S\ S_0)$ and its influence.
3. Vary K_I and K_M and note their influence on the gradients and on η.
4. Alter the program for no reaction by setting E = 0 and note the results. Run with various bulk concentrations.
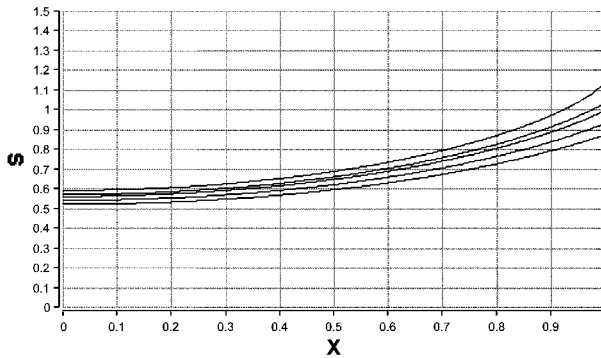5. Alter the program for nth-order kinetics.

Results

Fig. 2 A few iterations were required to find the solution by varying S_{guess} with a slider to reach $S=1$ at $X=1$.
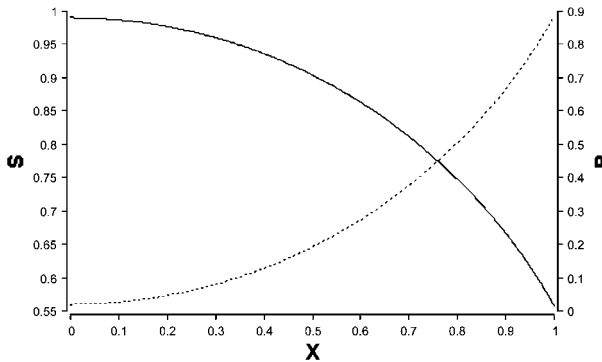

Fig. 3 The P and S profiles for the solution found in Fig. 2.

5.12.3
ENZDYN – Dynamic Diffusion with Enzymatic Reaction

System

This example involves the same diffusion-reaction problem as in the example, ENZSPLIT, except that here a dynamic solution is obtained, using the method of finite differencing. The substrate concentration profile in the porous biocatalyst is shown in Fig. 1.
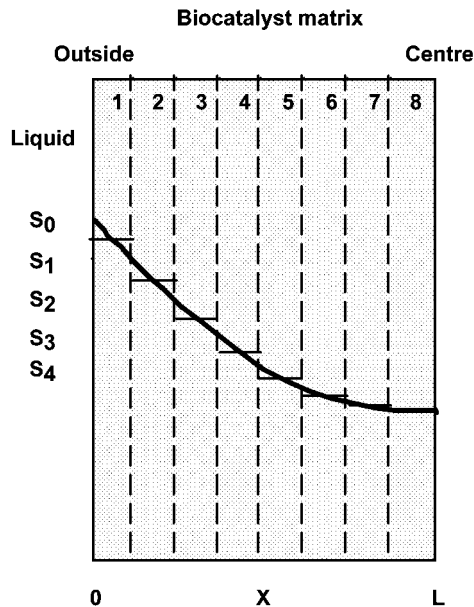
Fig. 1 Finite differencing for ENZDYN.

Model

With complex kinetics, a steady-state split boundary problem as solved in the example ENZSPLIT may not converge satisfactorily. To overcome this, the problem may be reformulated in the more natural dynamic form. Expressed in dynamic terms, the model relations become

$$\frac{\partial S}{dt} = D_s \frac{\partial^2 S}{\partial X^2} - R$$

$$\frac{\partial P}{\partial t} = D_p \frac{\partial^2 P}{\partial X^2} + R$$

where at the centre of the slab

$$\frac{dS}{dX} = \frac{dP}{dX} = 0$$

The kinetic equation used here is an enzymatic Michaelis–Menten form with product inhibition

$$R = \frac{kES}{S + K_M \frac{1 + P}{K_I}}$$

This behaves as a zero-order reaction if $S \gg K_M$ and $P \ll K_I/K_M$.

Using finite-differencing techniques for any given element n, these relations may be expressed in semi-dimensionless form using the definitions

$$S'_n = S_n/S_0, \quad P'_n = P_n/S_0 \quad \text{and} \quad \Delta X' = X/L$$

Here S_0 is the external substrate concentration and $\Delta X'$ is the length of the finite difference element.

This gives,

$$\frac{dS'_n}{dt} = \frac{D_s}{L^2}\left(\frac{S'_{n-1} - 2S'_n + S'_{n+1}}{\Delta X'^2}\right) - \frac{R'_n}{S_0}$$

$$\frac{dP'_n}{dt} = \frac{D_P}{L^2}\left(\frac{P'_{n-1} - 2P'_n + P'_{n+1}}{\Delta X'^2}\right) + \frac{R'_n}{S_0}$$

and

$$R'_n = \frac{kES'_n}{(K_M/S_0)(1 + S_0P'_n/K_I) + S'_n}$$

Boundary conditions are given by the external concentrations S_0 and P_0 and by setting $S_{N+1}=S_N$ and $P_{N+1}=P_N$, at the slab centre.

Catalyst effectiveness may be determined from the slope of the reactant concentration, S, at the solid surface

$$\eta_1 = \frac{D_s S_0}{L^2 R_0}\left(\frac{1 - S'_1}{\Delta X'}\right)$$

where

$$R_0 = \frac{kES_0}{K_M(1 + P_0/K_I + S_0)}$$

Program

The number of increments can be changed using the parameter ARRAY. The boundary conditions dictate the formulation of the first and last segments as follows: Center of slab (segment ARRAY), dS/dX=0 and dP/dX=0; surface conditions (segment 0), P_0 and S_0. With the same parameter values, the results of example ENZSPLIT should be exactly the same as the steady-state of ENZDYN.

Nomenclature

The nomenclature is the same as ENZSPLIT except as follows:

Symbols

ΔX Increment length   m

Indices

n   Refers to segment n

Exercises

1. Vary K_I and K_M and note the inhibition effects. It might be useful to plot the rates of reaction to see when inhibition becomes important.
2. Vary E and L and note the effect on the gradients and η.
3. Experiment with parametric changes, while keeping $(D_S S_0 / L^2 k E)$ constant. How is η influenced?
4. Vary L^2/D_S, and note that this influences the time to reach steady state.
5. Compare the steady-state results with those of ENZSPLIT.
6. Verify the form of the dimensionless equations. Rewrite the program in dimensional form.
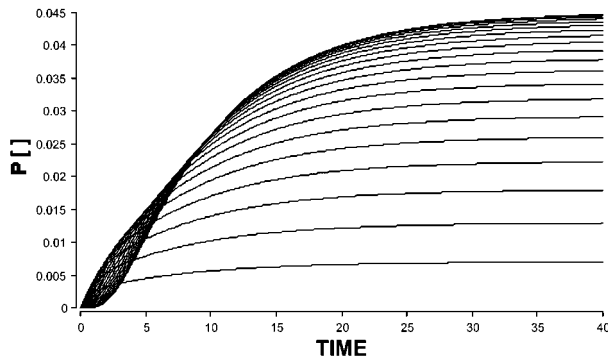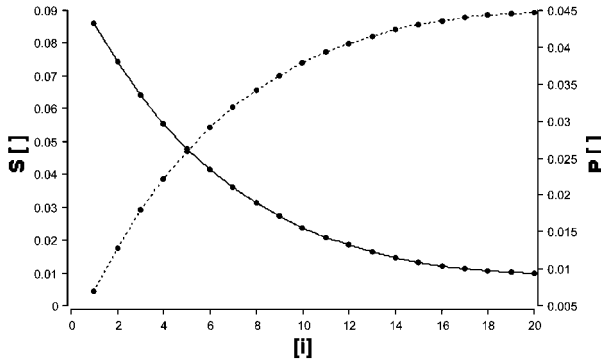7. Revise the program for a simple nth-order reaction.

Results

Fig. 2 A plot of P versus time for each segment.

Fig. 3 The substrate and product profiles plotted versus segment position for the steady state.

References

Blanch, H.W. and Dunn, I.J. (1973) Modelling and Simulation in Biochemical Engineering. In: Advances in Biochemical Engineering, Vol. 3, Eds. T.K. Ghose, A. Fiechter, N. Blakebrough, Vol. 3, Springer.

Goldman, R., Goldstein, L. and Katchalski, C.I. (1971) in Biochemical Aspects of Reactions on Solid Supports, Ed. G.P. Stark, Academic Press.

5.12.4
BEAD – Diffusion and Reaction in a Spherical Catalyst Bead

System

This example treats a diffusion-reaction process in a spherical biocatalyst bead. The original problem stems from a model of oxygen diffusion and reaction in clumps of animal cells by Keller (1991), but the modelling method also applies to bioflocs and biofilms, which are subject to potential oxygen limitation. Of course, the modelling procedure can also be applied generally to problems in heterogeneous catalysis.

Diffusion and reaction takes place within a spherical bead of volume $= \frac{4}{3}\pi R_P^3$ and area $= 4\pi R_P^2$. It is of interest to find the penetration distance of oxygen for given specific activities and bead diameters. As shown, the system is modelled by dividing the bead into shell-like segments of equal thickness. The problem is equivalent to dividing a rectangular solid into segments, except that here the volumes and areas are a function of the radial position. Thus each shell has a volume of $\frac{4}{3}\pi(r_n^3 - r_{n-1}^3)$. The outside area of the nth shell segment is $4\pi\, r_n^2$ and its inside area is $4\pi\, r_{n-1}^2$.
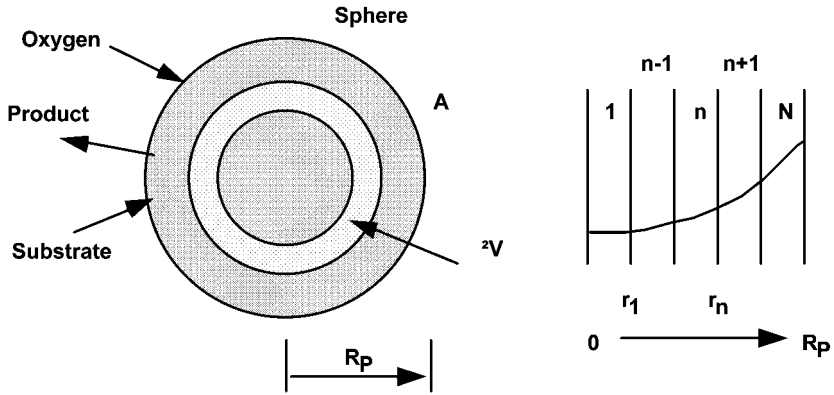
Fig. 1 The finite differencing of the spherical bead geometry.
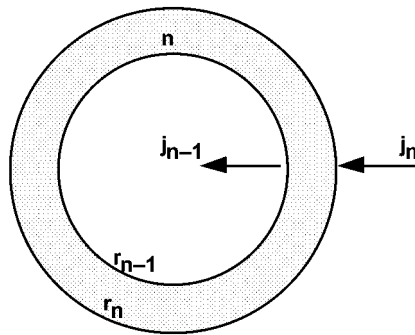
Fig. 2 The diffusion fluxes entering and leaving the spherical shell with outside radius r_n and inside radius r_{n-1}.

Model

Here the single limiting substrate S is taken to be oxygen.

The oxygen balance for any element of volume ΔV is given by

$$\frac{4}{3}\pi(r_n^3 - r_{n-1}^3)\frac{dS_n}{dt} = j_n 4\pi r_n^2 - j_{n-1} 4\pi r_{n-1}^2 + R_{sn}\frac{4}{3}\pi(r_n^3 - r_{n-1}^3)$$

The diffusion fluxes are

$$j_n = D_S \frac{S_{n+1} - S_n}{\Delta r}$$

$$j_{n-1} = D_S \frac{S_n - S_{n-1}}{\Delta r}$$

Substitution gives

$$\frac{dS_n}{dt} = \frac{3 \cdot D_S}{\Delta r(r_n^3 - r_{n-1}^3)}[r_n^2(S_{n+1} - S_n) - r_{n-1}^2(S_n - S_{n-1})] + R_{sn}$$

The balance for the central increment 1 (solid sphere not a shell) is

$$\frac{4}{3}\pi(r_1)^3\frac{dS_1}{dt} = j_1 4\pi r_1^2 + R_{sn}\frac{4}{3}\pi(r_1)^3$$

Since $r_1 = \Delta r$, this becomes

$$\frac{dS_1}{dt} = \frac{3D_S}{\Delta r^2}(S_2 - S_1) + R_{s1}$$

The reaction rate is expressed by a Monod-type equation

$$R_{Sn} = -OUR_{max}X\frac{S_n}{K_S + S_n}$$

where X is the biomass concentration (cell number/m^3) in the bead, OUR is the specific oxygen uptake rate (mol/cell s) and S_n is the oxygen concentration (mol/m^3) in shell n.

Program

The segments are programmed using the array facility of MADONNA, numbered from the outside to the centre. The effectiveness factor, expressing the ratio of the reaction rate to its maximum, is calculated in the program, part of which is shown below.

```
{Example BEAD}

INIT S[1..Array]=0
deltar=Radius/Array
r[1..Array]=((Array+1)-i)*deltar
RS[1..Array]=0

{SUBSTRATE OXYGEN BALANCES FOR EACH DELTA R ELEMENT}
{Outer shell}
d/dt(S[1])=3*D*( ((r[1]**2) * (S0-S[1])) - ((r[2]**2) *
(S[1]-S[2])))/(deltar*((r[1]**3) - (r[2]**3)) )+RS[1]

{Shells 2 to Array-1}
d/dt(S[2..(Array-1)])=3*D*( ((r[i]**2) * (S[i-1]-S[i])) -
((r[i+1]**2) *(S[i]-S[i+1])) )/(deltar*((r[i]**3) -
(r[i+1]**3)) )+RS[i]
```

```
{Inner spherical section}
d/dt(S[Array])=3*D*(S[(Array-1)]-
-S[Array])/(deltar**2)+RS[Array]
Sinner=S[array] {Defined for graphing}
```

Nomenclature

Symbols

D	Diffusion coefficient	m^2/s
K_S	Saturation constant in Monod equation	mol/m^3
OUR (max)	Maximum specific oxygen uptake rate	mol/cell s
r	Radius at any position	m
R_P	Outside radius of bead	m
R_S	Reaction rate in the Monod equation	$mol/s\ m^3$
S	Oxygen substrate concentration	mol/m^3
X	Biomass concentration	$cells/m^3$
Δr (Deltar)	Increment length, r/Array	m

Indices

1	Refers to segment 1
2	Refers to segment 2
n	Refers to segment n
P	Refers to particle
S	Refers to substrate

Exercises

1. Investigate the response of the bead to changes in the outside to the bulk concentrations. Can you relate the time constant to D/r^2?
2. Note the position of zero oxygen when changing D_{O2} and R_P.
3. Change the program to calculate the effectiveness factor.
4. Write the model in dimensionless form. What are the governing parameters for first and zero-order kinetics? Verify by simulation.
5. Develop a model and program for a rectangular slab geometry with diffusion from both sides and taking the thickness as $V_{bead}/A_{bead} = R_P$. Compare the results for the slab with those for the bead.
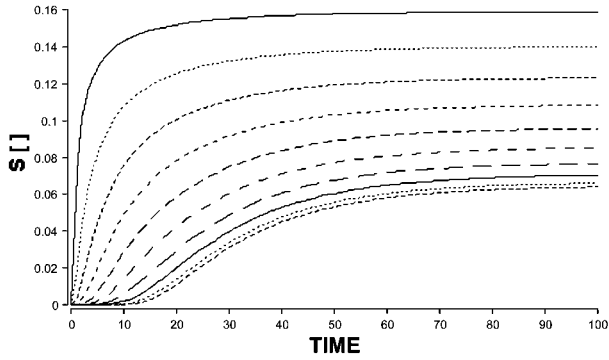
Results

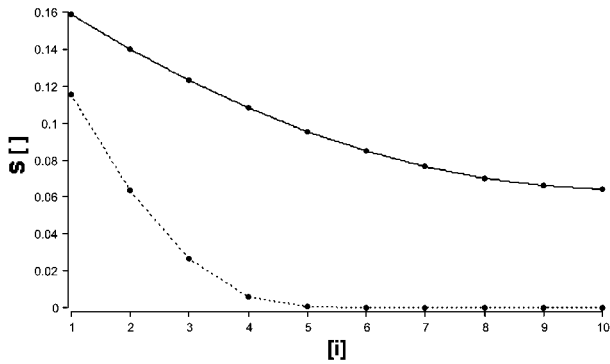**Fig. 2** Profiles of oxygen concentrations versus time for each shell.

Fig. 3 Doubling the bead radius causes oxygen deficiency inside the bead (lower curve) as these radial profiles show.

Reference

Keller, J. (1991) PhD Dissertation No. 9373, ETH Zurich.

5.13
Biological Reaction Examples

5.13.1
BIOREACT – Process Modes for a Bioreactor

System

The general balance equations for stirred tank bioreactor systems can be derived by referring to Section 3.2. Here the three principle modes of operation are considered, i.e., batch, fed batch and chemostat operation, as represented in Fig. 1. The important variables are biological dry mass or cell concentration, X, substrate concentration, S, and product concentration, P. The reactor volume V is assumed to be well mixed, and cell growth is assumed to follow Monod kinetics, based on one limiting substrate, as described in Section 1.3.6. Substrate consumption is related to cell growth by means of a constant yield factor $Y_{X/S}$. Product formation is the result of both growth and non-growth associated rates of production. The lag and decline phases of cell growth are not included in the model.
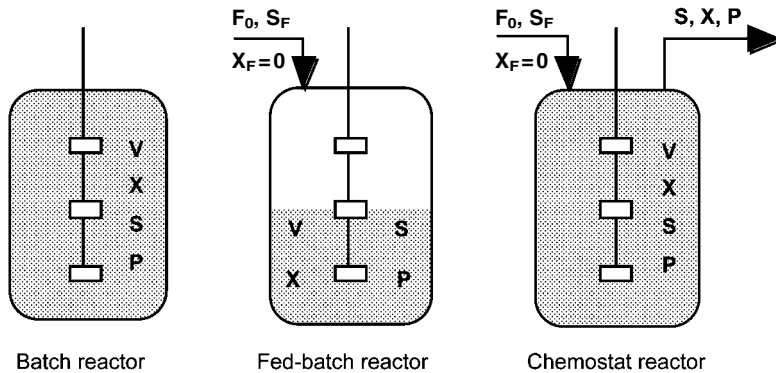

Fig. 1 Three modes of operation for a biological reactor.

Simple batch fermentation system is simulated within the program by setting the values of the input and outlet flow rates to zero.

For fed-batch fermentation, the model equations need to include the continuous feeding of sterile substrate to the fermenter, but zero outflow. The increase in volume (total accumulation of mass) that occurs in the fermenter due to the feeding is represented by a total mass balance relationship.

A continuous fermenter with sterile feed is referred to as a chemostat. For constant volume operation, the inlet volumetric flow rate is equal to that at the output. With this model chemostat start-up, resultant steady state behaviour and cell washout phenomena are easily investigated by simulation.

Model

The generalised material balances for a well-stirred tank fermentation can be represented as:

(Accumulation rate) = (In by flow) − (Out by flow) + (Production rate)

Total balance

$$\frac{dV}{dt} = F_0 - F_1$$

Cell balance

$$\frac{d(VX)}{dt} = -F_1 X + r_X V$$

Substrate balance

$$\frac{d(VS)}{dt} = F_0 S_F - F_1 S + r_S V$$

Product balance

$$\frac{d(VP)}{dt} = -F_1 P + r_P V$$

Knowing the mass quantities, VX, VS, and VP, the corresponding concentration terms are determined as

$$X = \frac{VX}{V} , \quad S = \frac{VS}{V} , \quad P = \frac{VP}{V}$$

The kinetic equations for the model are given by

$$r_X = \mu X$$

with μ being given by the Monod equation:

$$\mu = \frac{\mu_m S}{(K_S + S)}$$

and the rate of consumption of the limiting substrate

$$r_S = -\frac{r_X}{Y_{X/S}}$$

The rate of product formation is assumed to follow both a growth related and non-growth related kinetic form

$$r_P = (k_1 + k_2\mu)X$$

where k_1 is the non-growth associated coefficient and k_2 is the coefficient associated with growth.

Program

The MADONNA program, is designed to simulate the three reactor modes of operation by enabling the setting of appropriate values of the input and output flow rates.

Nomenclature

Symbols

D	Dilution rate ($= F_0/V$)	1/h
F_0	Volumetric feed rate	m^3/h
F_1	Volumetric outlet rate	m^3/h
k_1 and k_2	Product formation constants	1/h and kg/kg
K_S	Saturation constant	kg/m^3
M	Maintenance coefficient	kg/kg h
P	Product concentration	kg/m^3
r	Reaction rate	kg/m^3h
S	Substrate concentration	kg/m^3
V	Reactor volume	m^3
X	Biomass concentration	kg/m^3
Y	Yield coefficient	kg/kg
μ and U	Specific growth rate	1/h
τ	Time lag constant	h

Indices

1	Refers to non-growth association rate
2	Refers to growth-association rate
F	Refers to feed
m	Refers to maximum
P	Refers to product
S	Refers to substrate
X	Refers to biomass

Exercises for Batch Operation

1. Vary the kinetic parameters K_S and μ_m and observe the effects for the case of a batch reactor.
2. Vary the product kinetics constants (k_1 and k_2) and observe the effects. Note the shape of the P versus time curve when S reaches zero.
3. Vary the initial amount of biomass and note its influence on the batch performance.

Exercises for Chemostat Operation

1. Increase the volumetric flow rate successively until washout is obtained.
2. Change the feed concentration of substrate. Does this alter the steady state value of S in the reactor outlet? Why?
3. Under steady state conditions, the specific growth rate becomes equal to the dilution rate, $\mu = D$. Using the Monod equation, calculate a set of steady state S versus D values. Verify this result by simulation.
4. What is the effect of operating the chemostat at a dilution rate of $D > \mu_m$?
5. Operate the chemostat initially as a batch reactor with $D = 0$, and then switch to chemostat operation with $D < \mu_m$. Note the effect on the startup time.

Exercises for Fed-batch Operation

1. Start as a batch reactor and then switch to fed batch operation. Explain why this procedure is preferable to starting initially as a fed batch?
2. Operate the fed batch with high values of SF and low values of F. Note that it is possible to obtain a quasi steady state condition for which μ becomes equal to dilution rate $D = F/V$. It is seen from the simulations that this results in constant values of X but low and slowly decreasing values of S.
3. Operate at low SF and note the slope of the X versus time curve, which will eventually become linear, and note also that the slope is directly related to the feed rate. Why should this be so?
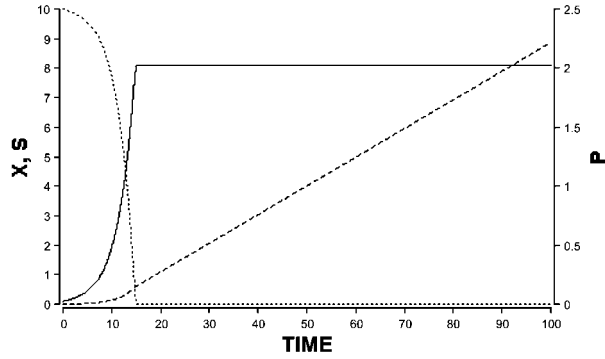
Results

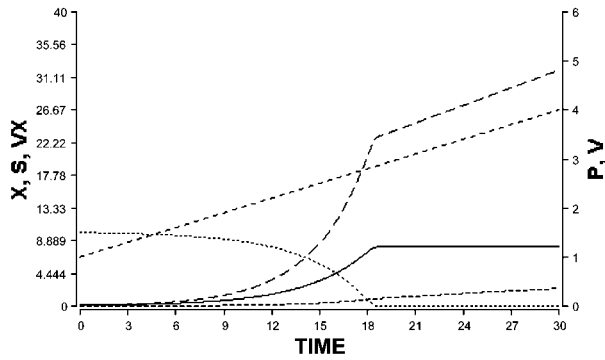**Fig. 2** Concentration profiles for a batch reaction.

Fig. 3 Results from a fed batch operation. Here both the biomass and the biomass concentration are plotted.
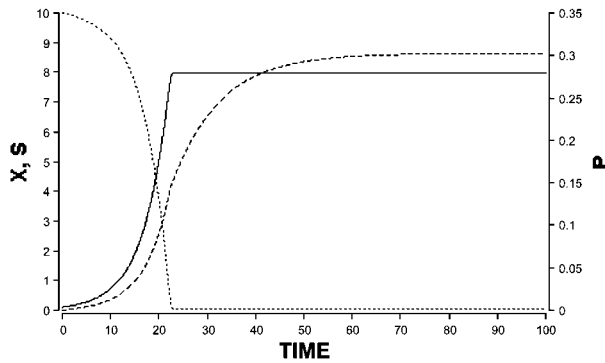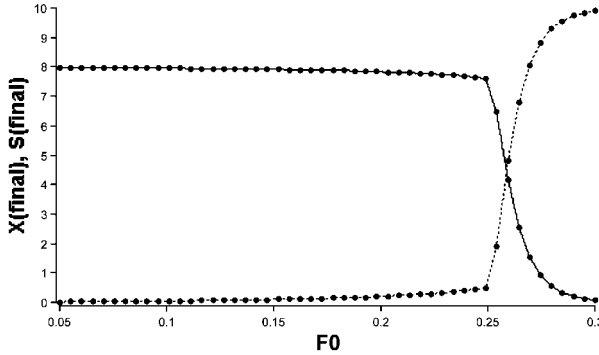

Fig. 4 Results from a chemostat run, where the steady state values of the concentrations can be observed.

Fig. 5 A parametric run for a chemostat varying F_0 versus final steady state values for X and S. Washout is shown in the region of UM. Here V = 1 and therefore D = F_0.

5.13.2
INHIBCONT – Continuous Bioreactor with Inhibitory Substrate

System

Inhibitory substrates at high concentrations reduce the specific growth rate below that predicted by the simple Monod equation. The inhibition function may often be expressed empirically as

$$\mu = \frac{\mu_m S}{K_S + S + S^2/K_I}$$

where K_I is the inhibition constant (kg m^{-3}).

In batch cultures the term S^2/K_I may be significant during the early stages of growth, even for higher values of K_I, owing to the initially high values of S. If substrate concentrations are low, the inhibition function reduces to the Monod equation. It can be shown that the value of μ passes through a maximum at $S_{max} = (K_S\ K_I)^{0.5}$.
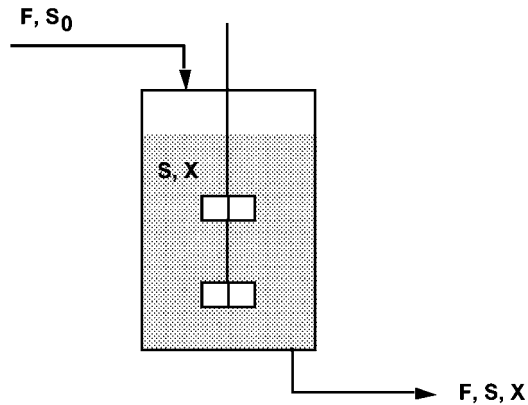
Fig. 1 Model variables for a continuous bioreactor.

Model

A continuous bioreactor with its variables is represented in Fig. 1.

Biomass balance

$$V\frac{dX}{dt} = \mu VX - FX$$

or

$$\frac{dX}{dt} = (\mu - D)X$$

where D is the dilution rate (= F/V). Thus steady-state behaviour, where dX/dt = 0, is represented by the conditions that $\mu = D$.

Substrate mass balance

$$V\frac{dS}{dt} = F(S_0 - S) - \frac{\mu XV}{Y}$$

or

$$\frac{dS}{dt} = D(S_0 - S) - \frac{\mu X}{Y}$$

where Y is the yield factor for biomass from substrate. Also from this equation at steady state, since $\mu = D$ and dS/dt = 0, the steady-state cell concentration is given by

$$X = Y(S_0 - S)$$

A continuous inhibition culture will often lead to two possible steady states, as defined by the steady-state condition $\mu = D$, as shown in Fig. 2.

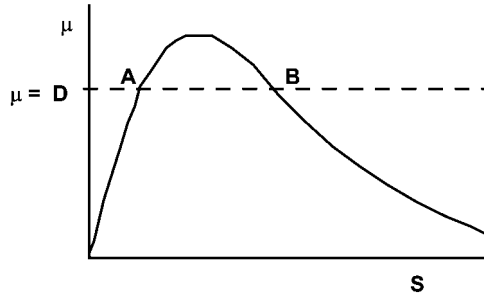**Fig. 2** Steady states A (stable) and B (unstable) for a chemostat with inhibition kinetics.

One of these steady states (A) can be shown to be stable and the other (B) to be unstable by reasoning somewhat similar to that described in Section 3.2.7. Thus only state A and the washout state (S = S$_0$) are possible. Using simulation techniques, the behaviour of the dynamic approach to these states can be investigated.

Program

When the system equations are solved dynamically, one of two distinct steady-state solutions is obtained, i.e., the reactor passes through an initial transient but then ends up under steady-state conditions either at the stable operating condition, represented by A, or the washout condition, for which X = 0. The initial concentrations for the reactor will influence the final steady state obtained. A PI controller has been added to the program, and it can be used to control a substrate setpoint below S$_{max}$. The controller can be turned on setting by K$_P$ > 0. The control constants K$_P$, τ_I and the time delay τ_F can be adjusted by the use of sliders to obtain the best results. Appropriate values of control constants might be found in the range 0.1 to 10 for K$_P$ and 0.1 to 10 for τ_I. Note that the control does not pass S$_{max}$ even though the setpoint may be above S$_{max}$. Another feature of the controller is a time delay function to remove chatter. The program comments should be consulted for full details.

Nomenclature

Symbols

D	Dilution rate	1/h
F	Flow rate	m^3/h
K$_I$	Inhibition constant	kg/m^3
K$_P$	Controller constant	kg/m^3
K$_S$	Saturation constant	m^6/kg h
S	Substrate concentration	kg/m^3
V	Volume	m^3
X	Biomass concentration	kg/m^3

| Y | Yield coefficient | kg/kg |
μ (U)	Specific growth rate coefficient	1/h
τ_I	Controller time constant	h
τ_F	Time constant controller delay	h

Indices

0	Refers to inlet
I	Refers to initial value
m, max	Refer to maximum

Exercises

1. Vary K_S and K_I to observe the changes in the inhibition curve by plotting versus S. Note especially the value of S at the maximum in μ.
2. Start the reactor with the initial concentration conditions of S = 0, X = 2 and $D < \mu_m$, and observe the approach to steady state. Did washout occur?
3. Start the reactor with $S > S_{max}$ and X = 0.1. What is the steady-state result?
4. Run a simulation under the conditions of Exercise 3 and program to stop the feed (D = 0) just before washout. Allow S to return to near zero. Plot μ versus S.
5. Rerun Exercise 2 with $S_0 = 20$. Stop the flow when $S > S_{max}$, and allow the system to return to $S < S_{max}$ before starting again.
6. Operate the model to include feedback control of the feed flow rate and experiment with various values of K_P, τ_I and τ_F.
7. Make suitable changes in the initial conditions of X and S, and plot the phase plane diagram X versus S. By making many runs at a range of initial conditions, the washout region can be identified.

Results
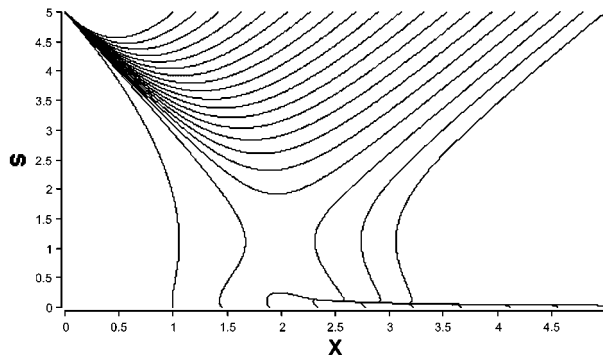
Fig. 3 A phase plane made by varying the initial conditions for S and X, with two Multiple Runs on an overlay plot.
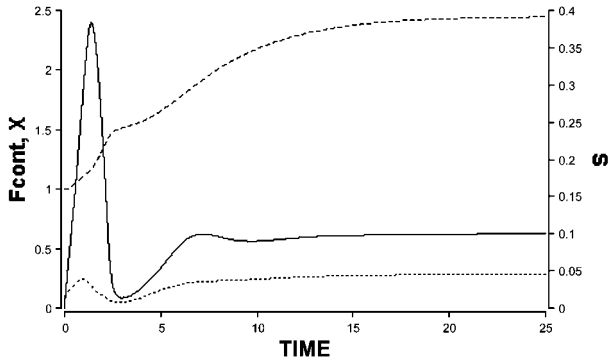
Fig. 4 A control simulation of the process with the setpoint below S$_{max}$.

Reference

Edwards, V. H., Ko, R. C. and Balogh, S. A. (1972) Dynamics and Control of Continuous Microbial Propagators Subject to Substrate Inhibition, Biotechnol. Bioeng. 14, 939–974.

5.13.3
NITBED – Nitrification in a Fluidised Bed Reactor

System

Nitrification is the sequential oxidation of NH_4^+ to NO_2^- and NO_3^- which proceeds according to the following reaction sequence:

$$NH_4^+ + \frac{3}{2}O_2 \rightarrow NO_2^- + H_2O + 2H^+$$

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^-$$
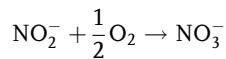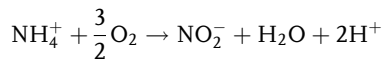
The overall reaction is thus

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$
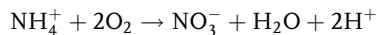
Both steps are influenced by dissolved oxygen and the corresponding substrate concentration. The nitrification as a wastewater treatment process benefits greatly from biomass retention, owing to the relatively slow growth rates of the nitrifiers.

In this example, a fluidised biofilm sand bed reactor for nitrification, as investigated by Tanaka et al. (1981), is modelled as three tanks-in-series with a recycle loop (Fig. 1). With continuous operation, ammonium ion is fed to the reactor, and the products nitrite and nitrate exit in the effluent. The bed expands in volume because of the constant circulation flow of liquid upwards through the bed. Oxygen is supplied external to the bed in a well-mixed gas-liquid absorber.

Fig. 1 Biofilm fluidised-bed recycle loop reactor for nitrification.

Model

The model balance equations are developed by considering both the individual tank stages and the absorber. Component balances are required for all components in e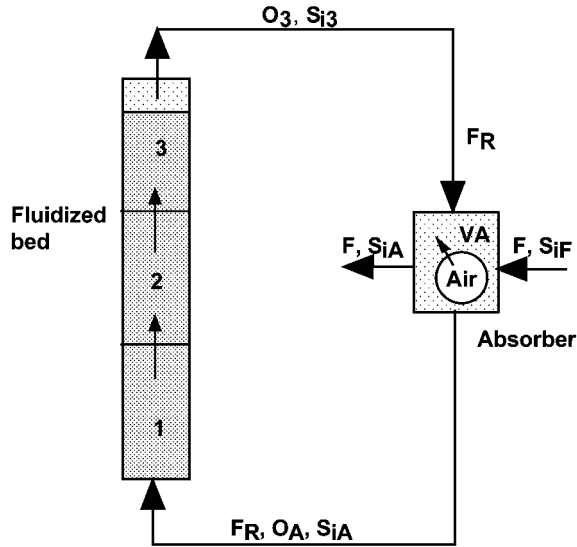ach section of the reactor column and in the absorber, where the feed and effluent streams are located. Although the reaction actually proceeds in the biofilm phase, a homogeneous model apparent kinetics model is employed, which is justified by its simplicity.

In the absorber, oxygen is transferred from the air to the liquid phase. The nitrogen compounds are referred to as S_1, S_2, and S_3, respectively. Dissolved oxygen is referred to as O. Additional subscripts, as seen in Fig. 1, identify the feed (F), recycle (R) and the flows to and from the tanks 1, 2 and 3, each with volume V, and the absorption tank with volume V_A.

The fluidised bed reactor is modelled by considering the component balances for the three nitrogen components (i) and also for dissolved oxygen. For each stage n, the component balance equations have the form

$$\frac{dS_{in}}{dt} = \frac{F_R}{V}\left(S_{i,n-1} - S_{i,n}\right) - r_{Sin}$$

$$\frac{dO_n}{dt} = \frac{F_R}{V}\left(O_{i,n-1} - O_{i,n}\right) - r_{on}$$

Similarly for the absorption tank, the balance for the nitrogen containing components include the input and output of the additional feed and effluent streams, giving

$$\frac{dS_{iA}}{dt} = \frac{F_R}{V_A}(S_{i,3} - S_{iA}) + \frac{F}{V_A}(S_{iF} - S_{iA})$$

The oxygen balance in the absorption tank must account for mass transfer from the air, but neglects the low rates of oxygen supply and removal of the feed and effluent streams. This gives

$$\frac{dO_A}{dt} = \frac{F_R}{V_A}(O_3 - O_A) + K_La(O_A^* - O_A)$$

For the first and second biological nitrification rate steps, the reaction kinetics for any stage n are given by

$$r_{1n} = \frac{v_{m1}S_{1n}}{K_1 + S_{1n}} \frac{O_n}{K_{O1} + O_n}$$

$$r_{2n} = \frac{v_{m2}S_{2n}}{K_2 + S_{2n}} \frac{O_n}{K_{O2} + O_n}$$

The oxygen uptake rate is related to the above reaction rates by means of the constant yield coefficients, Y_1 and Y_2, according to

$$r_{On} = -r_{1n}Y_1 - r_{2n}Y_2$$

The reaction stoichiometry provides the yield coefficient for the first step

$$Y_1 = 3.5 \text{ mg } O_2/(\text{mg } N_{NH_4})$$

and for the second step

$$Y_2 = 1.1 \text{ mg } O_2/(\text{mg } N_{NO_2})$$

Nomenclature

Symbols

F	Feed and effluent flow rate	L/h
F_R	Recycle flow rate	L/h
K_La	Transfer coefficient	h
K	Saturation constants	mg/L
K_1	Saturation constant for ammonia	mg/L
K_2	Saturation constant for ammonia	mg/L
O	Dissolved oxygen concentration	mg/L
O_S and O^*	Oxygen solubility, saturation conc.	mg/L
Our	Oxygen uptake rate	mg/L
r	Reaction rate	mg/L h
S	Substrate concentration	mg/L
V	Volume of one reactor stage	L
V_A	Volume of absorber tank	L

v_m	Maximum velocity	mg/L h
Y	Yield coefficient	mg/mg

Indices

1, 2	Refer to oxidation rates of ammonia and nitrite, resp.
1, 2, 3	Refer to ammonia, nitrite and nitrate, resp.
1, 2, 3	Refer to stage numbers
A	Refers to absorption tank
F	Refers to feed
ij	Refers to substrate i in stage j
m	Refers to maximum
O1 and O2	Refer to oxygen in first and second reactions
S1, S2	Refer to substrates ammonia and nitrite
S and *	Refer to saturation value for oxygen

Exercises

1. Assuming maximum reaction rates, choose a value of F and S_{1F}, and estimate the outlet substrate concentration at steady state. What oxygen supply rate would be required? Verify by simulation.
2. Vary K_La to give a low sufficient oxygen transfer capacity and note that low dissolved oxygen concentrations result in high nitrite concentrations. Investigate the reasons for this.
3. Vary the operating parameters and interpret the results in terms of the axial oxygen gradients in the reactor column.
4. Vary the rates of substrate and oxygen supply and note the interaction of both these factors on the outlet values of S_{13} and O_3.
5. Operate the reactor continuously with a K_La value of 40 1/h. With an ammonia feed concentration of 100 mg/L find the feed flow rate which will give 99% conversion to nitrate.
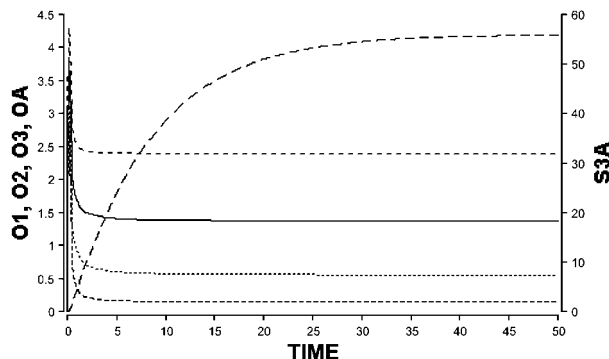
Results

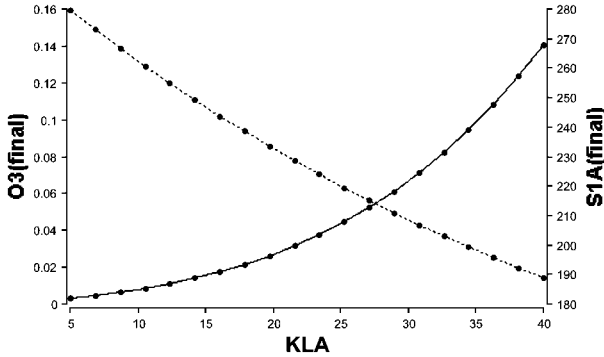**Fig. 2** Dynamic startup of continuous operation showing oxygen concentrations and nitrate in the effluent.

Fig. 3 Parametric run of continuous operation showing oxygen at the column top and ammonia in the effluent versus $K_L a$.

5.13.4
BIOFILM – Biofilm Tank Reactor

System

Active biomass can be retained effectively within continuous reactors by providing a carrier surface upon which a biofilm can develop. Examples are trickling filters (see BIOFILT) and fluidised bed reactors (see NITBED). In this example, biomass is retained within an aerated continuous tank reactor as a biofilm (Fig. 1). Wastewater entering the reactor is mixed throughout the tank and the pollutant S diffuses into the biofilm, along with oxygen, where it is degraded. The overall reaction rate in such a case will depend on the concentration gradients within the film. A diffusion model can be used to describe the biofilm diffusion-reaction process. As shown in Fig. 2, the biofilm is divided into segments for simulation purposes. Mass balances are written in terms of diffusion fluxes for each segment, and the diffusion fluxes at each position are expressed in terms of the corresponding concentration driving forces. An appropriate kinetic model is used for the local reaction rate, which depends on the local concentration within the segment. The bulk phase is coupled to the biofilm by means of an additional relationship representing the diffusion flux at the liquid-biofilm interface.
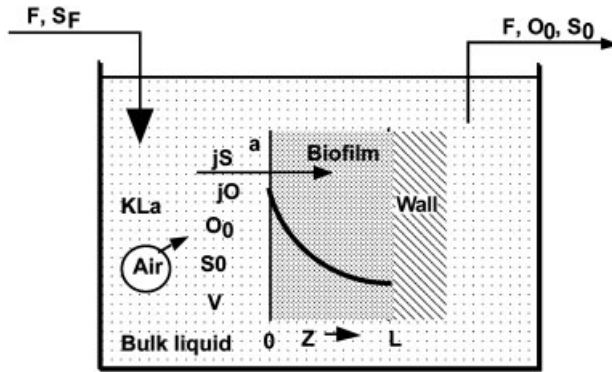
Fig. 1 Continuous tank reactor with biofilm.
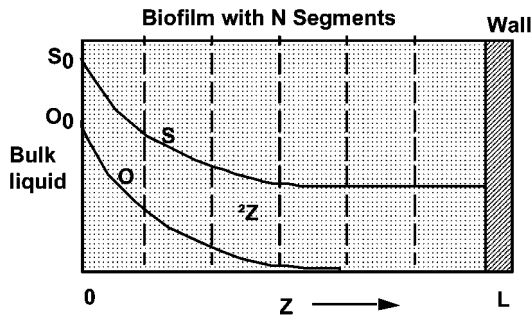
Fig. 2 Finite differencing of the concentration profiles within the biofilm into segments 1 to N.

Model

Multicomponent reaction within a biofilm can be described by diffusion-reaction equations. A component mass balance is written for each segment and for each component, respectively, where

$$
\begin{pmatrix} \text{Accumulation} \\ \text{rate} \end{pmatrix} = \begin{pmatrix} \text{Diffusion} \\ \text{rate in} \end{pmatrix} - \begin{pmatrix} \text{Diffusion} \\ \text{rate out} \end{pmatrix} + \begin{pmatrix} \text{Production rate} \\ \text{by reaction} \end{pmatrix}
$$

$$
A\Delta Z \frac{dS_n}{dt} = j_{n-1}A - j_n A + r_{Sn}A\Delta Z
$$

Using Fick's law, the diffusional flux can be described by

$$
j_{n-1} = D_S \frac{S_{n-1} - S_n}{\Delta Z}
$$

giving

$$\frac{dS_n}{dt} = D_S \frac{(S_{n-1} - 2S_n + S_{n+1})}{\Delta Z^2} + r_S$$

Thus N dynamic equations are obtained for each component at each position, within each segment. The equations for the first and last segment must be written according to the boundary conditions. The boundary conditions for this case correspond to the following: the bulk tank concentration is S_0 at the external surface of the biofilm where $Z=0$; a zero flux at the biofilm on the wall means that $dS/dZ=0$ at $Z=L$.

The kinetics used here consider carbon-substrate inhibition and oxygen limitation. Thus,

$$r_S = -v_m \frac{S}{K_S + S + (S^2/K_I)} \frac{O}{K_O + O}$$

A constant yield coefficient Y_{OS} describes the oxygen uptake rate

$$r_O = Y_{OS} r_S$$

For the well-mixed continuous-flow liquid phase shown in Fig. 1, the balance equations for oxygen and substrate must account for the supply of each component both by convective flow and by gas-liquid transfer, as well as by the diffusion rate into the biofilm.

For substrate with continuous inflow and outflow from the reactor:

$$\frac{dS_0}{dt} = \frac{F}{V}(S_F - S_0) - aD_S \frac{S_0 - S_1}{\Delta Z}$$

For oxygen transferred from the gas phase

$$\frac{dO_0}{dt} = K_L a(O_S - O_0) - aD_O \frac{O_0 - O_1}{\Delta Z}$$

In the above equations, symbol "a" represents the area of biofilm per unit volume of bulk liquid. The diffusion rates in and out of the biofilm are driven by concentration differences between the bulk liquid (0) and the outer biofilm segment (1).

Nomenclature

Symbols

a	Specific area perpendicular to the flux	1/m
A	Area perpendicular to diffusion flux	m^2
D	Diffusion coefficient	m^2/h

F	Volumetric flow rate	m^3/h
j	Diffusion flux	$g/m^2 \, h$
K_S	Saturation constant	g/m^3
K_I	Inhibition constant	g/m^3
$K_L a$	Oxygen transfer coefficient	$1/h$
L	Biofilm thickness	m
O	Dissolved oxygen concentration	g/m^3
O_S	Saturation concentration for oxygen	g/m^3
R, r	Reaction rate	$g/m^3 h$
S	Substrate conc. of carbon source	g/m^3
V	Volume of tank	m^3
v_m	Maximum reaction rate	$g/m^3 h$
Y_{OS}	Yield for oxygen uptake	–
Z	Length of element	m

Indices

0	Refers to bulk liquid
1–N	Refer to sections 1–N
I	Refers to inhibition
O	Refers to oxygen
S	Refers to carbon source
n	Refers to section n
F	Refers to feed

Exercises

1. Observe the response time of the reactor for changes in the operating parameters S_F, F and $K_L a$. Is the biofilm always the slowest to respond? Relate the response to the diffusion time constant L^2/D.
2. Experiment by varying the magnitude of the parameter K_I.
3. Vary the ratio of substrate and oxygen in the bulk phase, O_0/S_0, above and below the value of Y_{OS} for a series of runs. Note that the steady-state penetration limitation of one or the other substrates depends on whether the bulk ratio is greater or equal to the stoichiometric requirement, Y_{OS}.
4. Vary the amount of biomass by changing the numerical value of v_m and note the influence on the reaction rate.
5. Use the model to perform steady-state experiments to determine the apparent kinetics. Calculate the rates by sampling the substrate in the feed and effluent. Avoid the inhibition effect by setting K_I very high, while keeping S_0 high enough to maintain nearly zero order throughout the biofilm. By varying $K_L a$, run the reactor at various bulk dissolved oxygen concentrations. Plot the results as substrate uptake rate versus O_0 to determine the apparent K_S value for oxygen.
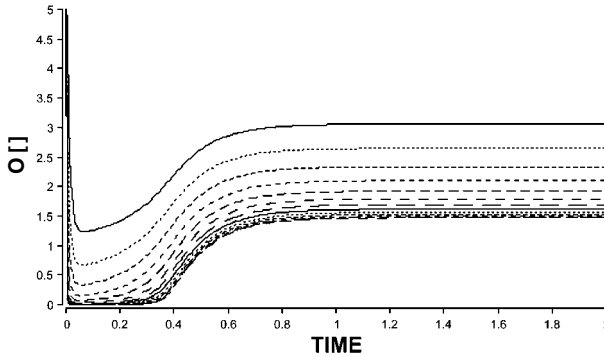6. Repeat Exercise 5 for substrate kinetics, while operating at constant O_0.

Results

Fig. 3 Response of the oxygen in the 12 segments of the biofilm.
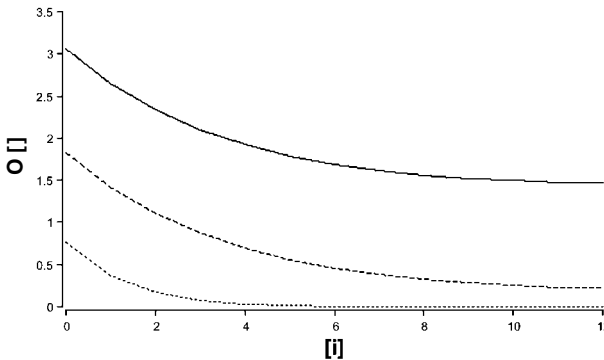
Fig. 4 Oxygen concentrations with distance from the outside (left side) to the inside of the film for three values of K_La.

5.13.5
BIOFILT – Biofiltration Column for Removing Ketone from Air

System

Biofiltration is an environmental process for treating contaminated air streams. Moist air is passed through a packed column, in which the pollutants in the contaminated air are adsorbed onto the moist packing. There the resident population of organisms oxidizes the pollutants biologically. Such columns can be run with a liquid phase flow (bio-trickling filter) or only with moist packing (biofilter). The work of Deshusses et al. (1994, 1995) investigated the removal of two ketones, methyl isobutyl ketone (MIBK) and methyl ethyl ketone (MEK) in such a biofilter The kinetics of this multi-substrate system is especially interesting since both substances exhibit mutual inhibitory effects on their rates of de-

gradation. Here the original dynamic model is greatly simplified in this example to calculate the steady-state concentration profiles in the column for the removal of only one component, MEK. The modelling concept is similar to the example of countercurrent gas-liquid absorption (Section 5.9.10, AMMONAB).
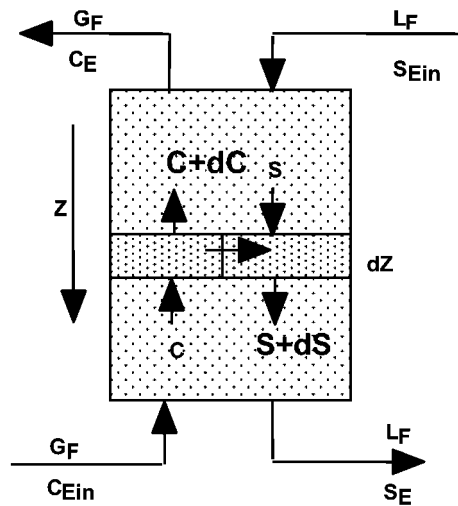
Fig. 1 Steady-state biofiltration column with countercurrent flow.

Model

The kinetics can be described approximately according to the Monod-type kinetics.

For MEK

$$r_{SE} = -\frac{v_{MSE}}{S_E + K_{SE}}$$

The steady-state mass balances for countercurrent flow can be formulated by considering changes in the component mass rates over a differential length of column. In this case, the length is measured from the top of the column ($Z=0$) to the bottom, as shown in Fig. 1. The column is assumed to consist of a moist solid or liquid phase with volume V_S, and a gas phase of volume V_G. The actual support volume is included in V_S.

Thus for MEK in the gas phase

$$\frac{dC_E}{dZ} = \frac{1}{v_{ZG}} K_L a (S_{ES} - S_E)$$

Thus in these equations for the steady-state, the convective terms are balanced by the transfer terms. Here the $K_L a$ value is based on the total volume V_T and is assumed to have the same value for each component. The linear velocities, expressed in terms of the volumetric flow rates and the empty tube cross-section, are for the gas and liquid phases

$$v_{ZG} = \frac{G_F}{A_T}$$

$$v_{ZL} = \frac{L_F}{A_T}$$

Assuming the reaction to occur within the wet packing volume V_S, the liquid phase balance for MEK is

$$\frac{dS_E}{dZ} = \frac{1}{v_{ZL}} K_L a (S_{ES} - S_E) + r_{SE} \frac{1}{v_{ZL}} (1 - \varepsilon)$$

The gas-liquid equilibrium relationship for the MEK is represented by

$$S_{ES} = M_E C_E$$

Very low liquid flow rates correspond to the case of biofilter operation and higher rates to the case of a trickling filter. The formulation of this problem for the two ketones would best be done with a tanks in series dynamic model. An alternative iterative steady state solution is given in Snape et al. (1995) for the two-component case with recycle.

Program

The program BIOFILT solves the steady-state countercurrent biofiltration operation for MEK removal. The integration is started at the top of the column by assuming a desired concentration in the outlet air. The required column length is determined when the inlet gas concentration exceeds the actual inlet value.

Nomenclature

Symbols

A_T	Cross-sectional area of empty tube	m^2
C	Concentration in gas phase	kg/m^3
D	Diameter	m
G_F	Gas flow rate	m^3/s
$K_L a$	Mass transfer coefficient	1/s
K_S	Monod coefficient	kg/m^3

L_F	Liquid flow rate	m^3/s
M	Partition coefficient	–
r	Reaction rate	kg/m^3s
S	Concentration in moist or liquid phase	kg/m^3
v_M	Maximum reaction velocity	kg/m^3s
v_{ZG}	Velocity of the gas phase	m/s
v_{ZL}	Velocity of the liquid phase	m/s
V_G	Volume of liquid phase	m^3
V_S	Volume of solid or liquid phase	m^3
Z	Length or height	m
ε	Bed porosity	–

Indices

E	Refers to MEK
G	Refers to gas
L	Refers to liquid
M	Refers to maximum
S	Refers to saturation
Z	Refers to axial direction

Exercises

1. Investigate the influence of the entering gas flow rate and entering concentration on the column length required to obtain 90% removal of MEK.
2. Alter the program to describe a cocurrent column. Compare the results with the countercurrent case for various extremes of liquid flow rate. Using the length found in Exercise 1, operate the column cocurrently to see whether the same degree of removal can be obtained. Show that the comparison depends on whether the column performance is reaction rate or transfer rate controlled.
3. The activity of the organisms v_M and the value of the mass transfer coefficient are important to the process. Vary these to determine their influence on the column length required.
4. Operate BIOFILT as a trickling filter by setting reasonably high values of liquid flow and investigate the influence of liquid flow rate.
5. Develop a model and program this for the case of a countercurrent column removing two components. Use a dynamic model to avoid the difficulty of making iterations for steady state.

Results
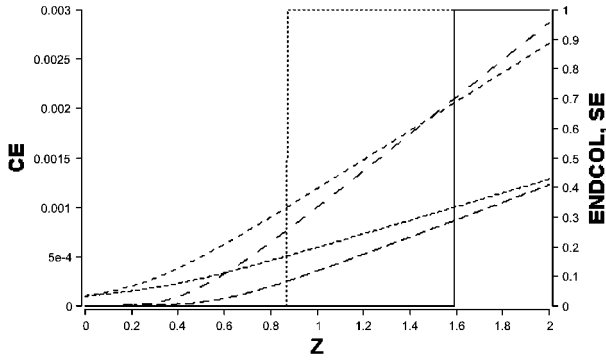
Fig. 2 Using two gas flow rates gave the respective column lengths required.

Fig. 3 Using very low and very high liquid flow rates gave these column lengths for the desired elimination.

References

Deshusses, M. A. (1994) ETH-Zurich, PhD Thesis, No. 10633.

Deshusses, M. A., Hamer, G. and Dunn, I. J. (1995) Part I, Behavior of Biofilters for Waste Air Biotreatment: Part I, Dynamic Model Development and Part II, Experimental Evaluation of a Dynamic Model, Environ. Sci. Technol. 29, 1048–1068.

5.14
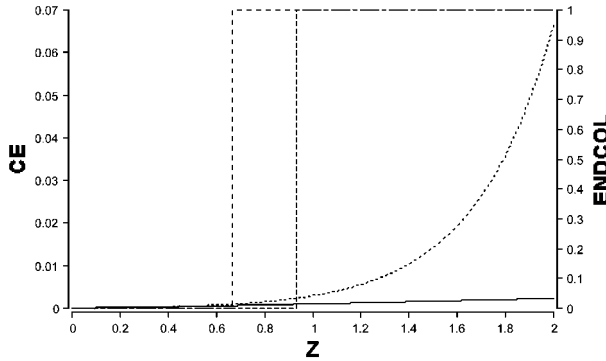**Environmental Examples**

5.14.1
BASIN – Dynamics of an Equalisation Basin

System

The flow rate and concentration of wastewater do not remain constant but vary during the course of the day and are also dependent on the time of year. If the flow rate is too high, loss of micro-organisms by washout may occur in secondary treatment processes. If the flow rate is too low, then the lack of nutrients will lead to a reduction of the micro-organism population. Wastewaters entering a treatment plant usually flow first into an equalisation basin, so that the flow rate out of the basin is maintained constant, or between prescribed limits, to protect the subsequent processes. The equalisation tank also reduces the effect of toxic shocks on the biological processes within the main treatment plant.
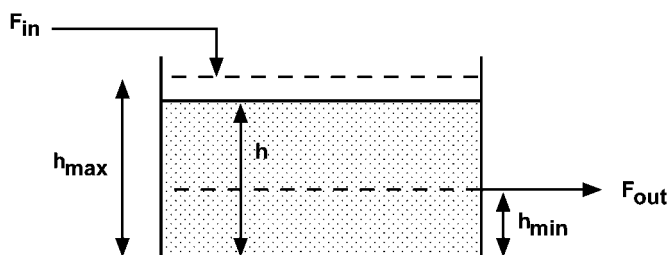
Model

Fig. 1 Basin for process flow equalisation.

The effluent flow rate is assumed to show a diurnal variation with maximum values occurring in the morning and early evening. This variation can be approximated by a sine wave function:

$$F_{in} = F_{av} + F_{amp} \sin\left(\frac{2\pi t}{12} - \pi\right)$$

where t is the time in hours, F_{av} the average flow rate and F_{amp} the amplitude of the variation in flow rate. This function gives maximum flow rates at 9 am and 9 pm, assuming that t=0 at midnight and accounts for the average time taken for water to travel from household to the treatment plant. A random component may be added to the flow rate to give more realistic variations in flow rate. Variations in the concentration of organics (S), both in the wastewater and in the tank, are not considered in this simplified example.

   The purpose of the tank (Fig. 1) is to ensure that the flow rate out of the tank, F_{out}, is kept constant at a value equal to F_{con} for as long as the depth of the liquid in the basin does not exceed some maximum value or fall below a minimum value, i.e.,

$$F_{out} = F_{con} \quad \text{for} \quad h_{min} < h < h_{max}$$

If the liquid depth exceeds the maximum depth of the tank, then the outlet flow F_{out} will equal the inlet flow F_{in}, so long as F_{in} exceeds the required flow rate to the plant F_{con}. If F_{in} falls below the value of F_{con}, the outlet flow F_{out} will be maintained equal to F_{con} for as long as possible. This prevents the tank from overflowing and allows the liquid level to fall when the inlet flow is reduced.

$$F_{out} = F_{in} \quad \text{for} \quad h > h_{max} \quad \text{and} \quad F_{in} > F_{con}$$

$$F_{out} = F_{con} \quad \text{for} \quad h > h_{max} \quad \text{and} \quad F_{in} < F_{con}$$

The magnitude of the inlet flow similarly regulates the outlet flow rate whenever the water level drops below the minimum depth. This prevents the tank from running dry and allows the tank to fill up again when the inlet flow is increased. In this case, the regulation of outlet flow is expressed by

$$F_{out} = F_{in} \quad \text{for} \quad h < h_{min} \quad \text{and} \quad F_{in} < F_{con}$$

$$F_{out} = F_{con} \quad \text{for} \quad h < h_{min} \quad \text{and} \quad F_{in} > F_{con}$$

The tank is assumed to have vertical sides so that the depth of liquid can be related to the volume (V) and tank cross-sectional area (A) by

$$V = Ah$$

A total mass balance for the tank gives the relationship

$$\frac{dV}{dt} = F_{in} - F_{out}$$

i.e., the rate of change in the volume of the tank contents with respect to time is equal to the difference in the volumetric flow rate to and from the tank.

Substitution gives

$$\frac{d(Ah)}{dt} = F_{in} - F_{out}$$

which for constant tank cross-sectional area this becomes

$$\frac{dh}{dt} = \frac{F_{in} - F_{out}}{A}$$

Nomenclature

A	Cross-sectional area	m^2
F_{in}	Volumetric flow rate into basin	$m^3\ h^{-1}$
F_{av}	Daily average volumetric flow rate	$m^3\ h^{-1}$
F_{amp}	Daily variation in flow rate	$m^3\ h^{-1}$
F_{con}	Constant flow rate	$m^3\ h^{-1}$
F_{out}	Flow rate out of basin	$m^3\ h^{-1}$
F_{storm}	Storm flow rate	$m^3\ h^{-1}$
L	Length of basin	m
h_{max}	Maximum depth of water in basin	m
h_{min}	Minimum depth of water in basin	m
h	Depth of water at time t	m
Q_{av}	Annual average volumetric flow rate	$m^3\ h^{-1}$
Q_{amp}	Annual variation in flow rate	$m^3\ h^{-1}$
S_{in}	Concentration of organics in inflow	$g\ m^{-3}$
S	Concentration of organics in tank	$g\ m^{-3}$
t	Time	h
V	Volume of basin	m^3
W	Width of basin	m

Exercises

1. During a storm the flow rate of wastewater will increase significantly. This effect can be simulated by programming conditional (IF.THEN.ELSE) changes in F_{STORM} at certain times. Simulate storms of varying duration and severity and study how the basin can cope with these varying demands while maintaining a constant outlet flow rate.

2. One problem with the above control strategy is that when the tank fails there is a rapid change in the flow rate entering the main treatment plant. Modify the program so that the flow rate leaving the tank is controlled such that the flow is proportional to the depth of liquid in the tank. The result of this should be that although oscillations in the flow rate are damped and not eliminated entirely, the risk of complete and sudden failure is reduced.

3. Modify the program to allow for inlet variation in the concentration of organics. This can be simulated by inclusion of the component balance equation

$$\frac{d(VS)}{dt} = F_{in}S_{in} - F_{out}S$$

where $S = VS/V$. The magnitude of the inlet organic concentration S_{in} will need to be defined.

Is constant flow rate the best strategy to avoid variations to subsequent processes?

4. As well as daily variations in flow rate and concentration there are also annual variations. These can be simulated by assigning a variable function to the value of F_{av}. For instance, the following sine function could be used:

$$F_{av} = Q_{av} + Q_{amp} \sin\left(\frac{2\pi t}{365 \times 24}\right)$$

where Q_{av} and Q_{amp} are the annual average flow rate and amplitude of the annual variations in flow rate, respectively. Include this in the model and see how this additional factor affects the operation of the basin.

5. In practice not all basins are rectangular in shape and the cross-sectional area of the basin can vary with height. Include this effect in the model assuming a basin with a trapezoidal cross-sectional area, where the height and volume of liquid are related by the following formula:

$$V = h(L + 2h)(W + 2h)$$

where L and W are the length and width of the base of the basin, respectively (i.e., a basin for which the walls are at 45° to the vertical).

6. Use a conditional statement to simulate the effect of a shock load on the system: i.e., change the value of S_{in} for a short time and follow the resulting variations in the value of S.

7. Modify the program to operate at constant organic concentration rather than constant flow rate and repeat the Exercises 1 to 6. Which strategy gives the minimum variation in load to subsequent processes? Devise a strategy that takes into account both changes in flow rate and concentration.

8. Modify the program so that the organic concentration is reduced in the basin by the biological action of bacteria in the wastewater. Assume that the basin remains well mixed so that the concentration in the outflow is the same as that in the basin.
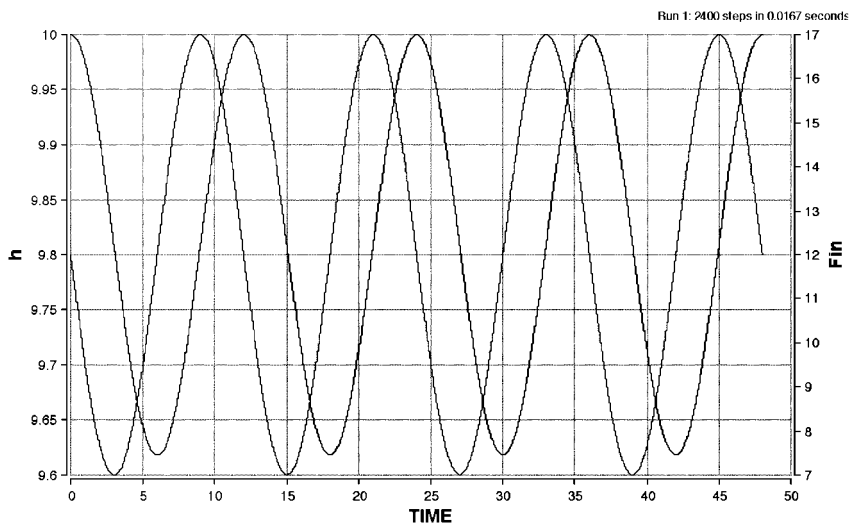
Results

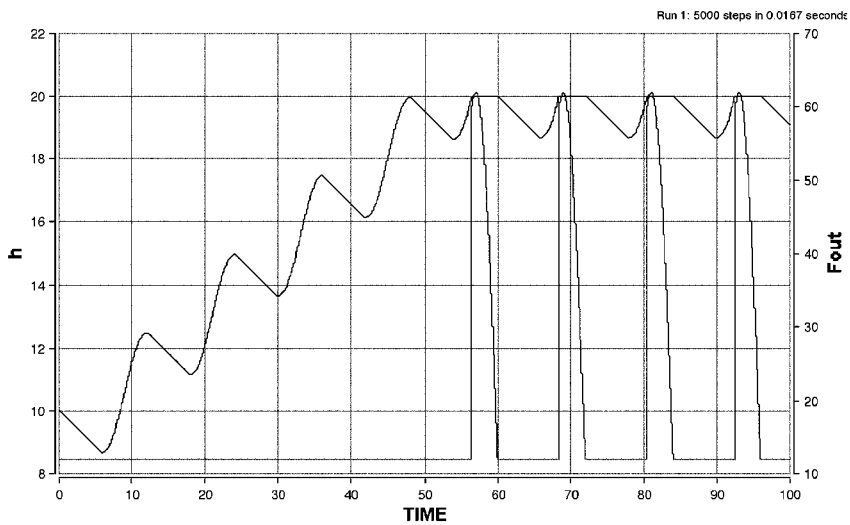**Fig. 2** Variation in height with inlet flow, maintaining outlet flow constant.

Fig. 3 Variation in height and outflow for very large inlet fluctuations.

5.14.2
METAL – Transport of Heavy Metals in Water Column and Sediments

System

Heavy metals find their way into the water cycle via the natural processes of erosion, weathering and volcanic activity. In addition the human activities of mining, smelting and burning fossil fuels contribute significantly to the metals found in natural waters. These metals can be accumulated by some micro-organisms and thus enter into the food chain, so presenting a possible toxic risk to wildlife and humans. Rivers passing through industrial and mining areas transport metals, partly as metal in solution and partly as metal adsorbed to suspended material. This suspended material sediments out in lakes and estuaries and there accumulates in the sediment. The model presented here, based on van de Vrie (1987), aims at predicting the concentration of zinc, cadmium and lead in the sediment and water of a lake in the southwest of the Netherlands.
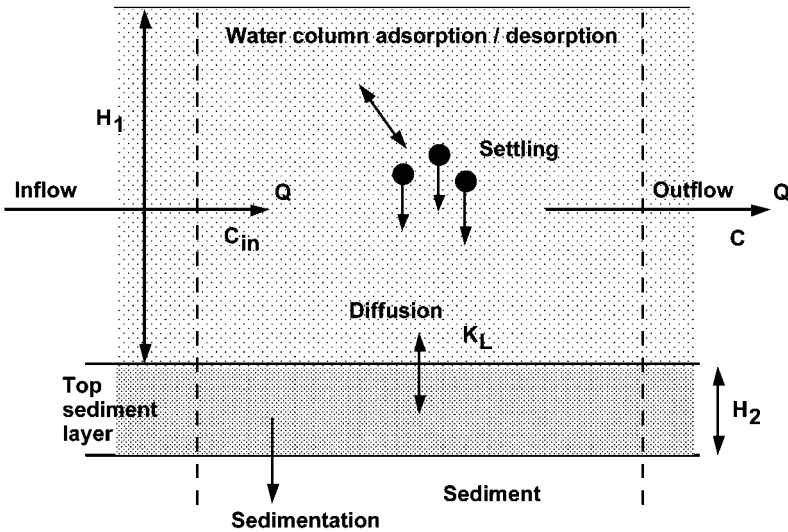
Model

Fig. 1 Balance regions for heavy metal transport for a lake in the Netherlands.

The whole lake is divided into a number of vertical elements, each comprising a column of water and the top layer of sediment. In this simulation only one such element is considered in order to improve the speed of execution. The general principle however can be extended to many elements.

It is assumed that the metals are distributed homogeneously in the water column as well as in the upper sediment layer. In both compartments, the metals can exist in either a dissolved form or as adsorbed to solid particles.

$$C_T = C_d + C_a$$

$$C_d = f_d C_T$$

The dissolved fraction, f_d, is given by the distribution coefficient, K_D:

$$f_d = \frac{1}{1 + mK_D}$$

where m is the total concentration of the suspended particles.

The suspended particles settle with a velocity v_s, and enter the top sediment layer, at a rate given by

$$J_s = v_s A C_a = v_s A (1 - f_d) C_T$$

The particles in the top layer of sediment also settle until they reach a certain depth at which they are no longer influenced by the water column.

There is a diffusion exchange between the two compartments owing to differences in the dissolved metal concentration in the water column and in the top layer of the sediment. The rate of this exchange is proportional to the concentration difference and the area of the sediment-water interface and is defined by proportionality constant K_L.

$$J_d = K_L A (C_{d1} - C_{d2})$$

Water flows into the water column at a volumetric flow rate Q containing a total metal concentration C_{in}. It is assumed that water flows out from the column at the same rate and at the same concentration as in the water column. Mass balances on the water column and top sediment layer give

$$V_1 \frac{dC_{T1}}{dt} = Q(C_{in} - C_{T1}) - J_{s1} - J_d$$

$$V_{''} \frac{dC_{T2}}{dt} = J_{s1} + J_d - J_{s2}$$

where V_1 and V_2 are the volumes of the water column and top layer of sediment, respectively, and H_1 and H_2 are the corresponding heights.

Substituting and rearrangement gives

$$\frac{dC_{T1}}{dt} = Q(C_{in} - C_{T1}) - \frac{v_s}{H_1}(1 - f_d)C_T - \frac{K_L}{H_1}(C_{d1} - C_{d2})$$

$$\frac{dC_{T2}}{dt} = \frac{v_{s1}}{H_1}(1 - f_{d1})C_{T1} + \frac{K_L}{H_2}(C_{d1} - C_{d2}) - \frac{v_{s2}}{H_2}(1 - f_{d2})C_{T2}$$

Nomenclature

Symbols

A	Area of water-sediment interface in each element	m^2
C	Concentration of metal	$g\ m^{-3}$
f_d	Fraction of metal that is dissolved	–
H_1	Height of water column	m
H_2	Depth of top sediment layer	m
J	Fluxes of metals	$g\ m^{-2}\ day^{-1}$
K_D	Distribution coefficient	g^{-1}
K_L	Diffusion exchange coefficient	$m\ day^{-1}$
m	Concentration of suspended particles	$g\ m^{-3}$
Q	Volumetric flow rate of water into water column	$m^3\ day^{-1}$
t	Time	days
V_1	Volume of water column	m^3
V_2	Volume of top sediment layer	m^3
v_s	Sedimentation velocity	$m\ day^{-1}$

Indices

1	Water column
2	Top sediment layer
a	Adsorbed
d	Dissolved
s	Settling
T	Total

Exercises

1. Run the model with the following parameters and compare the relative rates of accumulation for the different metals.

Parameters for METAL:

Parameter	Zinc	Cadmium	Lead
Thickness of top sediment layer (m)	0.39	0.37	0.26
Distribution coefficient water column (g^{-1})	114	81	309
Distribution coefficient sediment (g^{-1})	18.8	22.0	38.0
Diffusion exchange coefficient ($m\ day^{-1}$)	1.0	8.1	0.88

Results

Run 1: 269 steps in 0 seconds

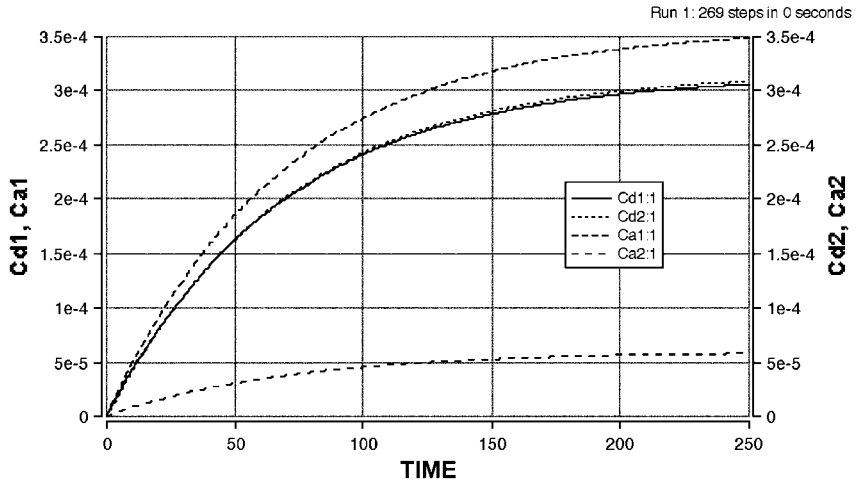**Fig. 2** Variation in adsorbed (A) and dissolved (D) metal both in the water column (1) and in the sediment (2).

Run 3: 269 steps in 0 seconds

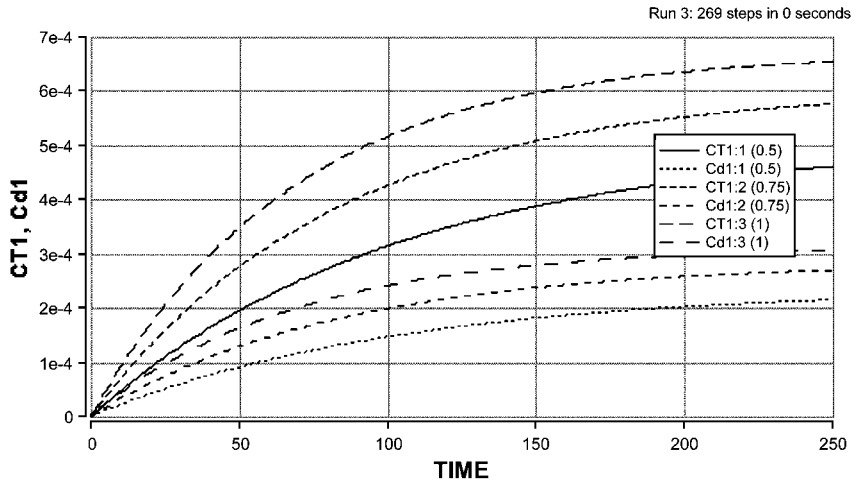**Fig. 3** Dissolved and total metals concentration at three flow rates (1.0, 0.75 and 0.5 m^3 d^{-1}).

References

van de Vrie, E. M. (1987) Modelling and Estimating Transport and Fate of Heavy Metals in Water Column and Sediment Layer in Some Enclosed Branches of the Sea in the SW Netherlands, In: Dynamical Systems and Environmental Models (eds. Bothe, H. G., Ebeling, W., Kurzhanski, A. B. and Peschel, M.), Akademie, Berlin.

Salomons, W. and Förstner, U. (1984) Metals in the Hydrocycle, Springer Verlag, Berlin.

5.14.3
OXSAG – Classic Streeter-Phelps Oxygen Sag Curves

System

When wastewaters are discharged into rivers the degradable organic compounds are utilised by micro-organisms, causing the dissolved oxygen concentration to be reduced. Simultaneously, oxygen is transferred from the air and at a certain distance downstream the transfer rate will equal the oxygen uptake rate; the dissolved oxygen level will be at a minimum. When the organics are used up, further downstream, the dissolved oxygen will start to increase to its saturation value. Streeter and Phelps in 1925 developed a simple model for this system. The plot of dissolved oxygen concentration versus the distance along the river is known as the sag curve, which is shown in below.
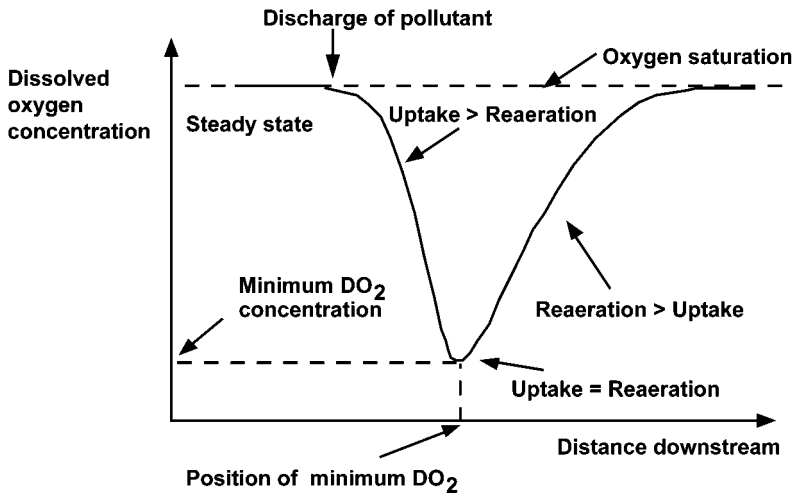

Fig. 1 Oxygen sag curve characteristics.

Model

The Streeter Phelps equation relates the dissolved oxygen concentration (DO) at any point in the river to the rate of aeration (R_{air}) and the rate of utilisation of oxygen by the river micro-organisms (R_{bio}):

$$\frac{dDO}{dt} = R_{air} + R_{bio}$$

The rate of reaeration is assumed to be a first order process, which is proportional to the oxygen deficit (i.e., the saturation dissolved oxygen concentration minus the actual dissolved oxygen concentration.):

$$R_{air} = K_{air}(DO_{sat} - DO)$$

The rate of substrate utilisation is assumed to follow Monod kinetics as

$$\frac{dS}{dt} = R_S$$

where

$$R_S = -R_{max}\frac{S}{K_S + S}$$

and

$$R_{bio} = \frac{R_S}{Y_{SO}}$$

Here Y_{SO} is a yield coefficient relating the rate of substrate utilisation to the rate of oxygen uptake.

Assuming plug flow, the distance downstream from the point of discharge, Z, is related to the average river velocity, v, and the time of travel, t, by

$$Z = vt$$

Nomenclature

DO	Dissolved oxygen concentration	$g\ m^{-3}$
DO_{sat}	Saturated dissolved oxygen conc.	$g\ m^{-3}$
K_{air}	Reaeration coefficient	h^{-1}
K_s	Monod constant	$g\ m^{-3}$
R_{air}	Rate of reaeration	$g\ m^{-3}\ h^{-1}$
R_{bio}	Rate of biological oxidation	$g\ m^{-3}\ h^{-1}$
R_{max}	Maximum reaction rate	h^{-1}

S	Substrate concentration	$g\ m^{-3}$
t	Time	h
v	Average river velocity	$m\ h^{-1}$
Y_{SO}	Yield coefficient, substrate/oxygen	–
z	Distance along river	m

Exercises

1. Vary the concentration of the discharge between 10 and 100 $g\ m^{-3}$ and see how the distance downstream and the value of the minimum dissolved oxygen concentration vary with the concentration of the discharge.
2. Vary the velocity of the river between 200 and 1000 $m\ h^{1}$ and see how this influences the distance downstream and the value of the minimum dissolved oxygen concentration.
3. Vary the reaeration coefficient K_{air} and see how this influences the dissolved oxygen profiles.

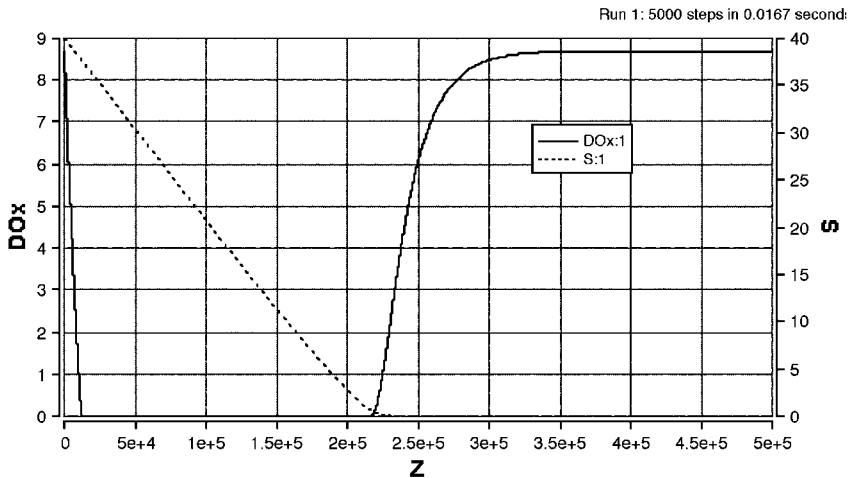Fig. 2 Typical oxygen sag curve. Reaeration occurs after the BOD is consumed.
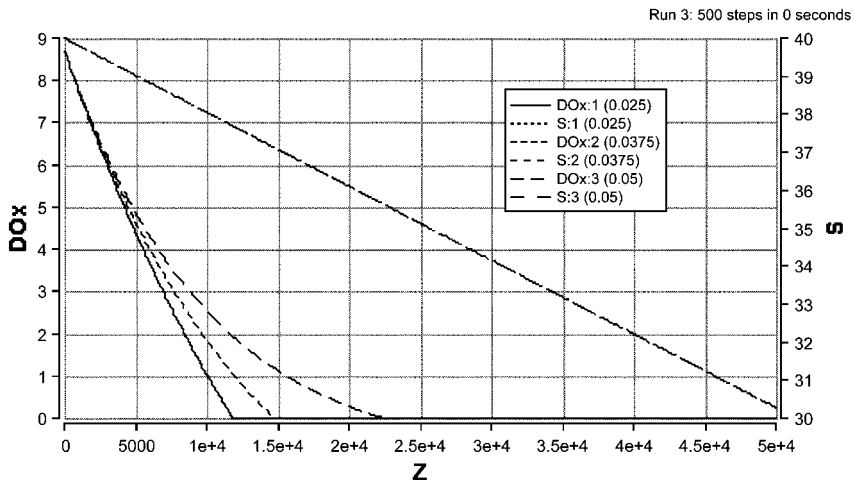
Fig. 3 Oxygen profiles for 3 values of K_{air}.

Reference

Streeter, H.W. and Phelps, E.B. (1925) A Study of the Pollution and Natural Purification of the Ohio River, Public Health Bulletin 146, US Public Health Service, Washington D.C.

5.14.4
DISCHARGE – Dissolved Oxygen and BOD Steady-State Profiles Along a River

System

Wastewater treatment plants and most factories discharge water into a river system. The wastewater will differ from the river water in temperature, BOD and dissolved oxygen concentration and nitrogen content. If the wastewater is discharged at an approximately constant rate then it may be assumed that steady state will be attained at some point along the length of the river with respect to temperature, BOD and dissolved oxygen. The minimum dissolved oxygen concentration likely to be encountered in the river and its position downstream from the point of the discharge can therefore be predicted.
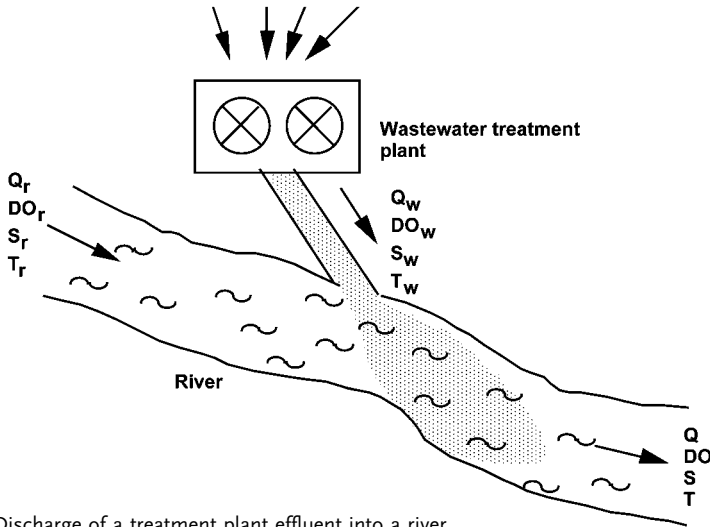
Fig. 1 Discharge of a treatment plant effluent into a river.

Model

Wastewater flows into a river and is immediately mixed with the river water. The flow rate of the river is increased as a result, where

$$Q = Q_r + Q_w$$

Similarly, the dissolved oxygen concentration (DO), BOD (S), nitrates (N) and temperature of the river will also be effected according to

$$DO = \frac{DO_r Q_r + DO_w Q_w}{Q}$$

$$S = \frac{S_r Q_r + S_w Q_w}{Q}$$

$$Temp = \frac{Temp_r Q_r + Temp_w Q_w}{Q}$$

$$N = \frac{N_r Q_r + N_w Q_w}{Q}$$

The dissolved oxygen deficit can be defined as the difference between the actual dissolved oxygen concentration and the saturation concentration for oxygen in the river at the same conditions.

$$\varepsilon = DO_{sat} - DO$$

The saturated dissolved oxygen concentration can be related to the temperature:

$$DO_{sat} = 14.652 - 0.41\,\text{Temp} + 0.008\,\text{Temp}^2$$

Oxygen is consumed by micro-organisms as they utilise the substrate and also as a result of nitrification, but oxygen is gained by the river by processes of surface aeration, so that

$$\frac{d\varepsilon}{dt} = aK_nN + K_sS - K_a\varepsilon$$

The rate of nitrification is assumed to be first order with respect to nitrate concentration, and the value of the rate constant, K_n, is a function of temperature.

$$K_n = K_{n20}\,1.07^{(\text{Temp}-20)}$$

$$\frac{dN}{dt} = -K_nN$$

The rate of pollutant degradation is also first order and temperature dependent:

$$K_s = K_{s20}\,1.05^{\text{Temp}-20}$$

$$\frac{dS}{dt} = -K_sS$$

The rate of reaeration is dependent on the velocity, v, of the river and its depth D, where

$$K_{a20} = \frac{2.26v}{D^{0.667}}$$

The reaeration rate is also temperature dependent:

$$K_a = \frac{K_{a20}}{24}e^{0.024(\text{Temp}-20)}$$

Assuming steady-state conditions, the distance downstream (km) can be related to the time of passage along the river (hours) by

$$z = 3.6vt$$

The velocity of the river is related to the volumetric flow rate and the river depth:

$$v = \frac{Q}{3600DW}$$

where this assumes approximately rectangular cross-sectional area of the river, W being the width.

Nomenclature

Symbols

ε	Oxygen deficit	mg L^{-1}
a	Stoichiometric parameter	–
D	Depth of river	m
DO	Dissolved oxygen concentration	mg L^{-1}
DO$_{sat}$	Saturated dissolved oxygen concentration	mg L^{-1}
K$_a$	Reaeration coefficient	h^{-1}
K$_n$	Nitrification rate coefficient	h^{-1}
K$_s$	Biodegradation rate coefficient	h^{-1}
N	Nitrate concentration	mg L^{-1}
Q	Volumetric flow rate	m^3 h^{-1}
S	BOD substrate concentration	mg L^{-1}
t	Time	h
Temp	Temperature	°C
v	Velocity of river	m s^{-1}
W	Width of river	m
z	Distance downstream	km

Indices

r	River
w	Wastewater
20	Reference temperature (°C)

Exercises

1. Compare the results obtained with those for the model OXSAG. What assumptions are appropriate to each particular model, and how valid are these likely to be in reality?
2. Investigate the discharge of a pollutant into rivers of different sizes, flow rates and velocities. What is the best and the worst type of river for the discharge of industrial wastewaters (from the point of view of minimising environmental damage)?
3. Model seasonal variations in temperature, flow rate and river depth. At what time of year is the river most at risk?
4. Is there any difference between the discharge of a small volume of highly concentrated waste and a large volume of more dilute waste if the overall amount of pollutant is the same?
5. Is it more worthwhile to reduce the temperature of the wastewater by 10% or the concentration by 10%? Is this always the case or does it depend on the absolute values?
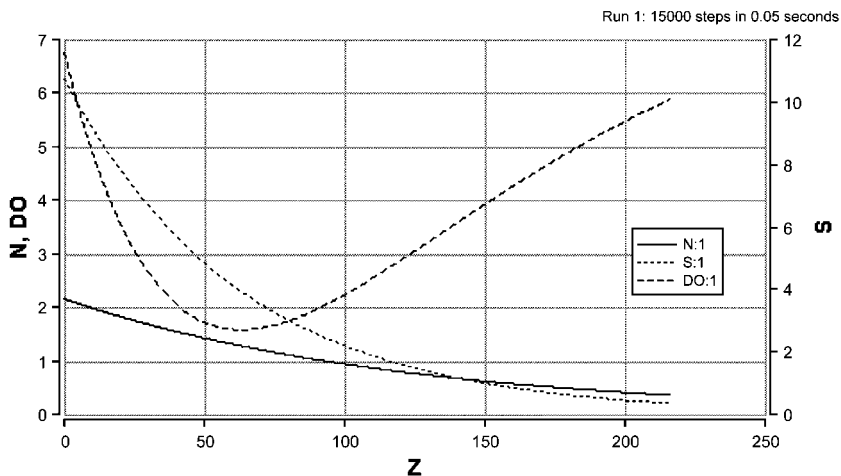
Results

Fig. 2 Dissolved oxygen, BOD and nitrate concentration-time profiles (25 °C wastewater).
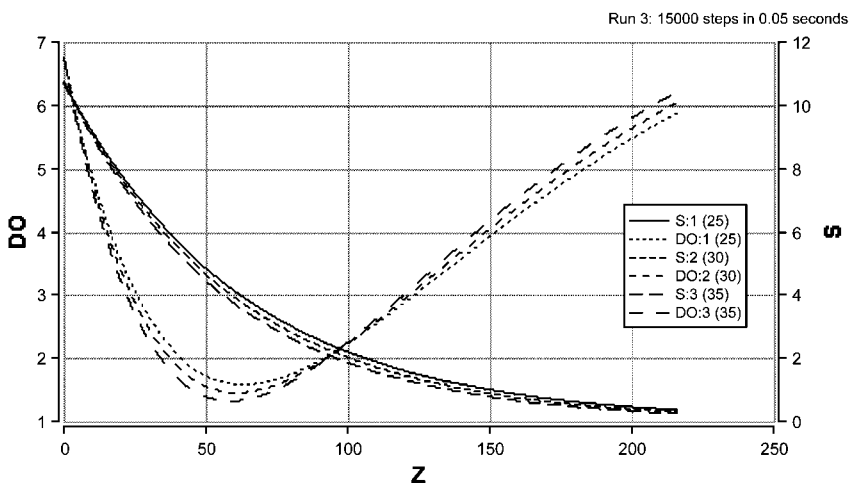

Fig. 3 Dissolved oxygen and BOD profiles for the discharge of three different wastewaters (15, 25 and 35 °C). Note that the higher temperature leads to a lower minimum dissolved oxygen concentration that occurs nearer to the discharge point, but also recovers more quickly.

Reference

Jorgensen, S. E. (1986) Fundamentals of Ecological Modelling, Elsevier.

5.14.5

ASCSTR – Continuous Stirred Tank Reactor Model of Activated Sludge

System

The activated sludge process, depicted in Fig. 1, involves basically the aeration and agitation of an effluent in the presence of a flocculated suspension of micro-organisms which are supported on particulate organic matter. After a predetermined residence time (usually several hours) the effluent is passed to a sedimentation tank where the flocculated solids are separated from the treated liquid. A reduction of BOD from 250–350 mg L^{-1} to a final value of 20 mg L^{-1} is achieved under typical operating conditions. Part of the settled sludge is usually recycled to the aeration tank in order to maintain biological activity.

In this model the aeration tank is modelled as a continuous stirred tank reactor.
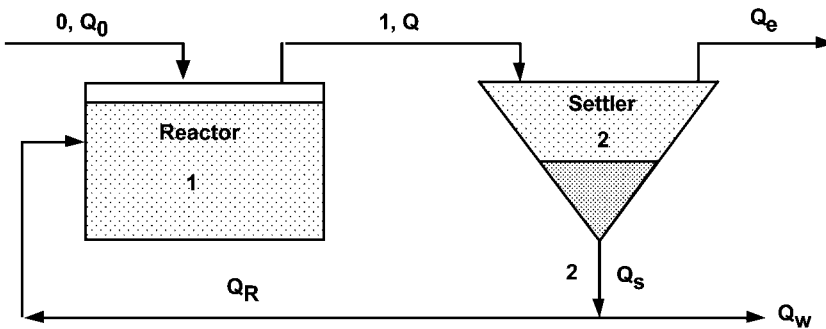
Fig. 1 Continuous stirred tank reactor and settler with sludge recycle.

Model

The total volumetric flow rate entering and leaving the reactor, Q, is the sum of the influent and recycle flow rates:

$$Q = Q_0 + Q_R$$

The recycle ratio is defined as

$$R = \frac{Q_R}{Q_0}$$

Combining the above equations gives

$$Q = (1 + R)Q_0$$

The reactor residence time is defined by the volume of the reactor divided by the volumetric influent flow rate:

$$\theta = \frac{V}{Q_0}$$

The concentration factor β is defined as the ratio of the recycle biomass to effluent biomass concentrations:

$$\beta = \frac{X_R}{X} \quad \beta > 1$$

The growth of biomass in the reactor is assumed to follow Monod kinetics with a first-order death rate. A mass balance on the biomass in the reactor yields the following differential equation (assuming that no biomass enters the reactor in the feed):

$$\frac{dX}{dt} = \frac{X}{\Theta}(\beta R - 1 - R) + \mu_m \frac{XS}{K_S + S} - K_d X$$

Similarly, assuming there is only negligible substrate in the recycle, a mass balance on the substrate (BOD) in the reactor gives

$$\frac{dS}{dt} = \frac{S_0 - S}{\Theta} - \frac{\mu_m}{Y}\frac{XS}{(K_s + S)} - K_d X$$

Various operating parameters can be calculated from the above equations as follows:

(1)   Substrate to micro-organism ratio or process load factor:

$$\text{Load} = \frac{\text{Substrate consumed per day}}{\text{Biomass in the reactor}}$$

$$\text{Load} = \mu_m \frac{\dfrac{XSV}{Y(K_s + S)}}{XV}$$

$$\text{Load} = \mu_m \frac{S}{Y(K_s + S)}$$

(2)   Mean solids residence time in the reactor θ_m:

$$\theta_m = \frac{\text{Solids in the reactor}}{(\text{Rate of biomass synthesis}) + (\text{Solids input to reactor})}$$

(3)   The sludge age θ_c:

$$\theta_c = \frac{\text{Biomass in the reactor}}{\text{Rate of biomass generation}}$$

$$\theta_c = \frac{XV}{Q_W X_R + Q_e X_e}$$

Nomenclature

Symbols

K_d	Death rate constant	h^{-1}
K_s	Monod constant	$g\ m^{-3}$
Load	Loading factor	h^{-1}
Q	Volumetric flow rate	$m^3\ h^{-1}$
R	Recycle ratio	–
S	Substrate concentration	$g\ m^{-3}$
V	Volume	m^3
X	Biomass concentration	$g\ m^{-3}$
Y	Yield biomass/substrate	–
β	Sludge concentration factor	–
μ_m	Maximum growth rate	h^{-1}
θ	Reactor residence time	h
θ_c	Sludge age	h
θ_m	Mean solids residence time	h

Indices

0	Refers to inlet
e	Refers to effluent
R	Refers to recycle
w	Refers to waste

Exercises

1. Vary the recycle ratio and see how this influences the process performance.
2. Change the model so that the reactor is modelled as two or more tanks in series and compare the results with those obtained for the single tank model.
3. Simulate a shock loading by changing the values of either the flow rate or the effluent concentration interactively.
4. Add a calculation of the operating parameters substrate consumption rate to micro-organisms ratio (Load), solids residence time (θ_m) and sludge age (θ_c) to the program. Experiment with variations in the values of these parameters under various conditions of flow and feed concentration to test their value as process control parameters.
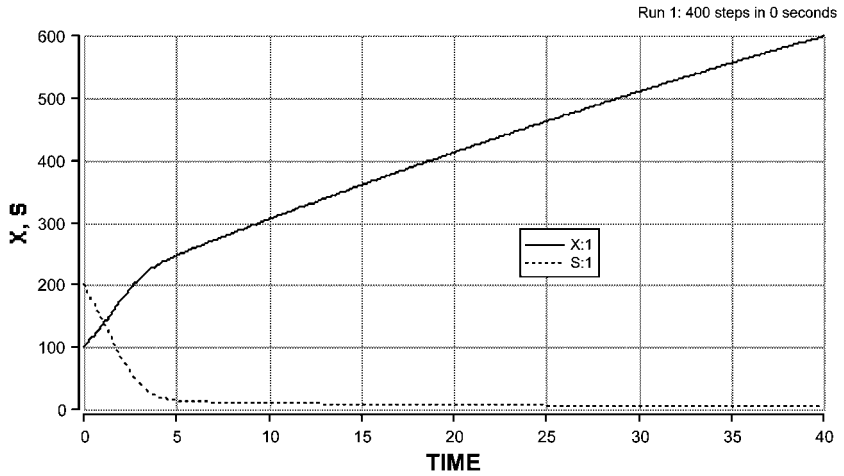
Results

Fig. 2 Startup of the continuous activated sludge reactor with recycle ratio R=0.3.
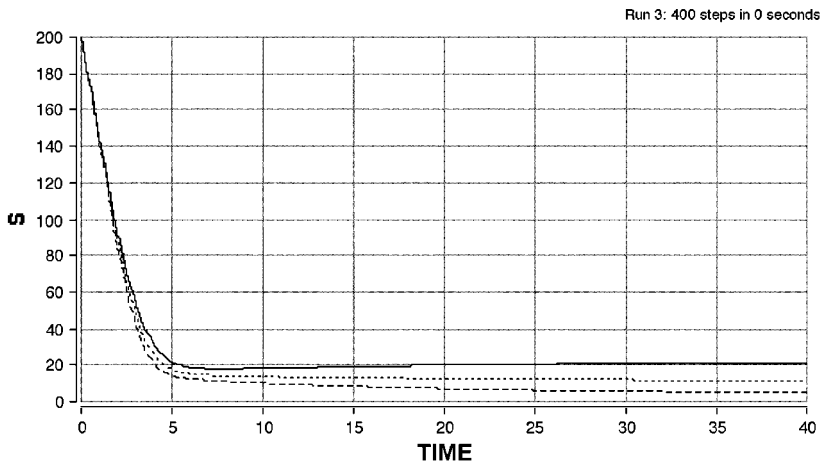

Fig. 3 Substrate concentration profiles for different values of the recycle ratio.

Reference

Grady, C. P. L. and Lim, H. C. (1980) Biological Wastewater Treatment: Theory and Applications. Pollution Engineering and Technology 12, Chapter 16.

5.14.6
DEADFISH – Distribution of an Insecticide in an Aquatic Ecosystem

System

The environmental impact of a new product needs to be assessed before it can be released for general use. Chemicals released into the environment can enter the food chain and be concentrated in plants and animals. Aquatic ecosystems are particularly sensitive, in this respect, since chemicals, when applied to agricultural land, can be transported in the ground water to rivers and then to the lakes, where they can accumulate in fish and plant life. The ecokinetic model presented here is based on a simple compartmental analysis and is based on laboratory ecosystem studies (Blau et al., 1975). The model is useful in simulating the results of events, such as the accidental spillage of an agrochemical into a pond, where it is not ethical to perform actual experimental studies.

The distribution of the insecticide Dursban in a simple aquatic environment consisting of water, fish, soil and plants is simulated, as shown in Fig. 1. The kinetic constants were obtained from radio label experiments in a test aquarium.
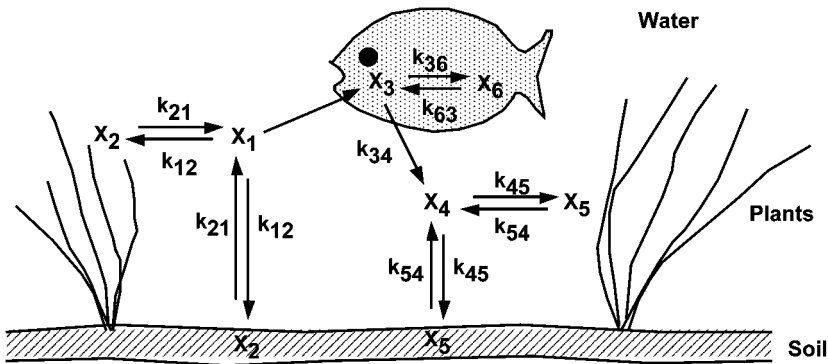

Fig. 1 Kinetic model of the water-fish-plant-soil interactions.

Model

It is assumed that at time zero a defined quantity of Dursban enters a lake and is distributed subsequently between the fish, the soil and the plants. The soil and plants are lumped together as one compartment. The quantities in each compartment are expressed as a percentage of the initial contamination.

Dursban in the pond water can be taken up by the soil and plants and also by the fish in the pond, and it is assumed that there is an equilibrium between the amount of insecticide in the plants and soil and in the pond water. Inside the fish, Dursban is metabolised to pyridinol and then excreted. Some insecti-

cide is stored separately within the fish. The released pyridinol is taken up by the soil and plants but not again by the fish.

In this model only the quantities of the components in the different compartments are considered, and therefore no assumptions have to be made about the sizes of the different compartments.

Writing mass balances for compartments 1 to 6 and referring to Fig. 1 we obtain:

For the Dursban in the water

$$\frac{dX_1}{dt} = -k_{13}X_1 - k_{12}X_1 + k_{21}X_2$$

For the Dursban in the plants and soil

$$\frac{dX_2}{dt} = -k_{21}X_2 + k_{12}X_1$$

For the Dursban in the fish

$$\frac{dX_3}{dt} = k_{13}X_1 + k_{63}X_6 - k_{36}X_3 - k_{34}X_3$$

For the Pyridinol in the water

$$\frac{dX_4}{dt} = k_{34}X_3 - k_{45}X_4 + k_{54}X_5$$

For the Pyridinol in the plants and soil

$$\frac{dX_5}{dt} = k_{45}X_4 - k_{54}X_5$$

For the stored Dursban in the fish

$$\frac{dX_6}{dt} = k_{36}X_3 - k_{63}X_6$$

Nomenclature

Symbols

k_{ij}	Rate constant for reaction from compartment i to compartment j	h^{-1}
t	Time	h
X_i	Percentage insecticide in compartment i	%

Indices

1	Dursban in water
2	Dursban in plants and soil
3	Dursban in fish
4	Pyridinol in water
5	Pyridinol in plants and soil
6	Stored Dursban in fish

Exercises

1. Compare the accumulation of the insecticide in the fish in systems with and without the plant and soil compartments.
2. Modify the model to simulate the slow release of insecticide (for instance via runoff) into the lake.
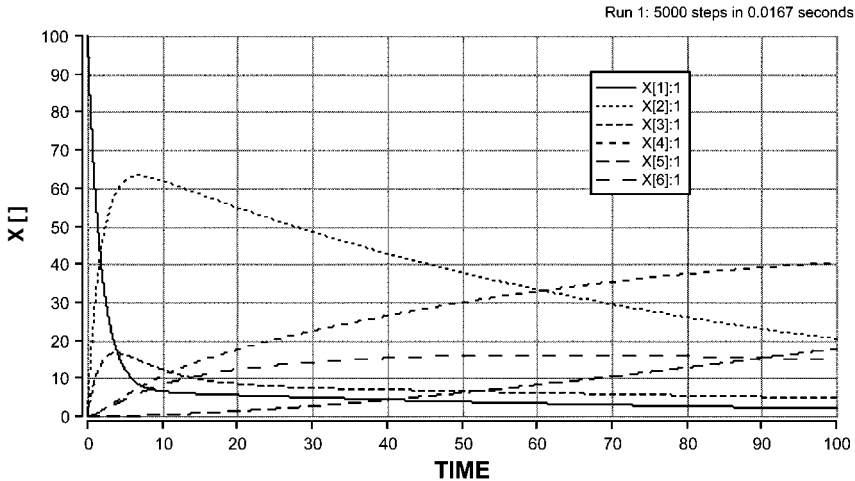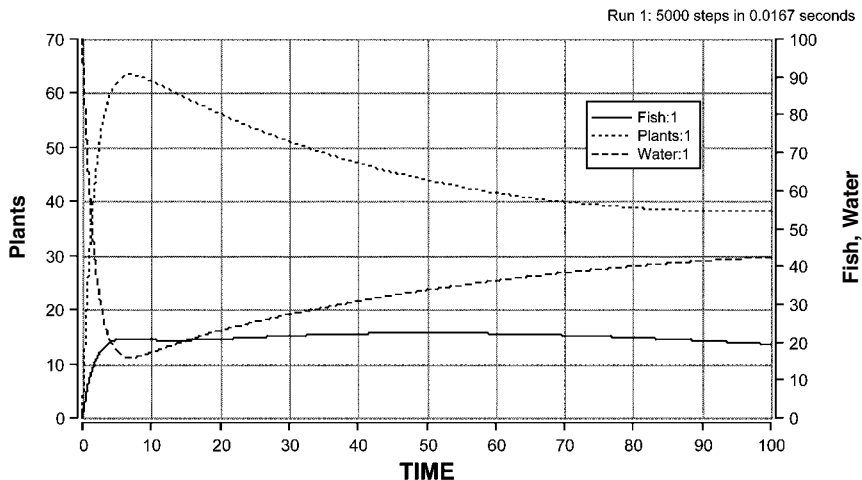
Results

Fig. 2 Insecticide distribution (percent) between the various compartments as a function of time.

Fig. 3 For the same run, insecticide plus metabolite distribution (percent) between the fish, plants and water.

References

Blau, G. E., Neely, W. B. and Branson, D. R. (1975) Ecokinetics: A Study of the Fate and Distribution of Chemicals in Laboratory Ecosystems, AIChE J. 21, 5, 854–861.
Butte, W. (1991) Mathematical Description of Uptake, Accumulation and Elimination of Xenobiotics in a Fish/Water System, In: Bioaccumulation in Aquatic Systems: Contributions to the Assessment (eds. Nagel, R. and Loskill, R.), VCH, Weinheim.

5.14.7
LEACH – One-Dimensional Transport of Solute Through Soil

System

Groundwater is a major source of drinking, industrial and agricultural water. Its quality is a primary environmental concern, not only for health reasons, but also because of the decrease in crop productivity caused by pollutants. The ability to model the migration of pollutants through the vadose soil layer plays an important part in the combat against the degradation of groundwater.

Model

In this model from Corwin et al. (1991), the transport of a solute such as a pesticide through the soil is simulated from ground level to the water table. As shown in Fig. 1, the soil column is divided into N elements each of thickness z, with element 1 at the surface and element N directly above the water table.

Hence

$$z = \frac{W_{table}}{N}$$

The water fraction for any element n is expressed as the ratio of the volume of water to the total volume of the element:

$$F_n = \frac{W_n}{V_n}$$

The water fraction of each element of soil can not exceed a certain maximum value, known as the field capacity. If the water content is less than the field capacity, then no water is able to leave the element. If the water content is equal to or greater than the field capacity, then water is able to leave the element at the same rate as water enters. The water is also taken up by the roots of plants. Here it is assumed that the uptake rate of water is proportional to the length of root. If the water content falls below a critical value, the plants can no longer take up water, and they wilt and eventually die.
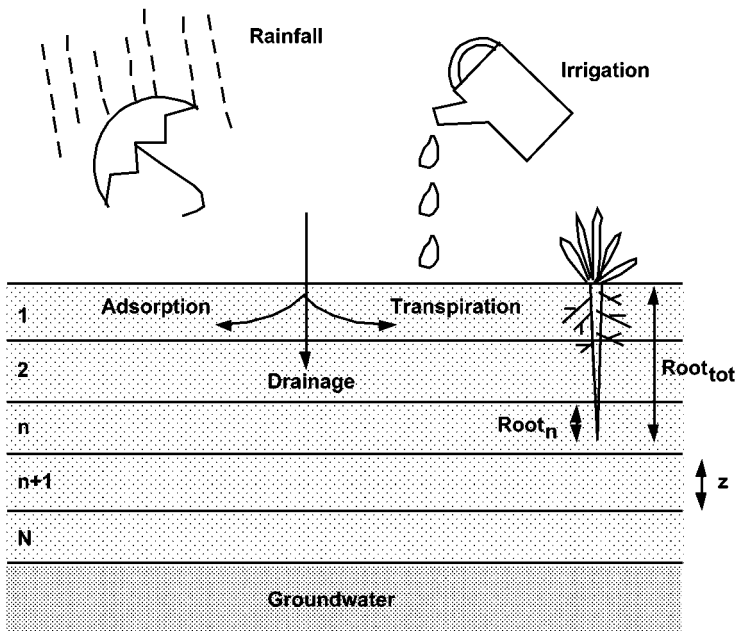

Fig. 1 Solute transport through the vadose layer.

A mass balance based on the volume of water in each element leads to the following equation:

$$\frac{dW_n}{dt} = Q_{n-1} - Q_n - ET_n$$

where Q_{n-1} and Q_n are the volumetric flow rates of water in and out of element n, and ET_n is the rate of assimilation by the plant or evapotranspiration rate.

The limiting behaviour on the rate of evapotranspiration is expressed by the logical condition, that with

$$ET_n = 0 \qquad \text{when } F_n < F_{min}$$

$$ET_n = ET\,Root_n \quad \text{when } F_n > F_{min}$$

and F_{min} is the minimum water content for plant growth. The water leaving any element is described by the following logical condition statements:

$$Q_n = 0 \qquad \text{when } F_n < FC$$

$$Q_n = Q_{n-1} \qquad \text{when } F_n > FC$$

where FC is the field capacity value.

The roots are assumed to grow at a constant rate (GR), so that the length of the root at any time t is given by

$$Root_{tot} = Root_0 + GR\,t$$

where $Root_{tot}$ is the total root length at time t, and $Root_0$ is the root length at time t=0.

The growth stops if the water content is too low, given by the condition

$$GR = 0 \quad \text{if } F_n < F_{min}$$

If the water content is less than the minimum then growth stops. Thus the root length in any element n is given by

$$Root_n = z \quad \text{for } Root_{tot} > nz$$

Thus the root occupies the total length of the element for those elements less than the total root length. When the root penetrates only part way into the soil element, as shown in Fig. 1,

$$Root_n = Root_{tot} - (n-1)z \quad \text{for } (n-1)z < Root_{tot} < nz$$

and

$$Root_n = 0 \quad \text{for } Root_{tot} < (n-1)z$$

The input of water to the top element is by rain or via human irrigation. A water balance for the top element 1 therefore leads to the mass balance

$$\frac{dW_1}{dt} = A(\text{Rain} + \text{Irrig}) - Q_1 - ET_1$$

where Rain and Irrig are specific rates given in cm day^{-1}, and the cross-sectional area, A, of the soil column is related to the height, z, and the volume, V, of each element by

$$A = \frac{V}{z}$$

If a pesticide, or any other solute, is sprayed onto the field it will travel in the water through the soil, but may also be adsorbed onto the soil. It is assumed that the process of adsorption occurs almost instantaneously, as compared to the slower rate of transport through the soil. Only solute dissolved in the mobile water column is transported from one element to the next.

A mass balance on the total solute concentration, C, including both adsorbed and mobile solute for element n yields the following relationship:

$$V_n \frac{dC_n}{dt} = Q_{n-1} Cs_{n-1} - Q_n Cs_n$$

where Cs, the concentration in the soil water, is related to the total and adsorbed solute concentrations by the water fraction, F_n, i.e.,

$$C_n = F_n Cs_n + (1 - F_n) C_{ads}$$

An assumed instantaneous distribution between the adsorbed and free solute is modelled by a Langmuir-type adsorption isotherm, where

$$C_{ads} = C_{max} \frac{Cs}{Cs + K}$$

C_{max} is the maximum concentration of solute that can be adsorbed by the soil, and K is the Langmuir adsorption coefficient. Combining the above two equations, a quadratic equation can be derived in terms of Cs, which on solving for the positive root gives

$$Cs = \frac{-b + (b^2 - 4as)^{0.5}}{2a}$$

where

$a = F$
$b = F\ K - C + C_{max}\ (1 - F)$
$s = -C\ K$

Hence the corresponding values for C, Cs and C_{ads} can be determined for each element.

It is assumed that the plants do not take up solute and that the solute is not bio-degraded. As water is taken up by the plants at a greater rate than the rate of supply, the value of F will decrease, and the solute will become more concentrated.

Program

Five elements are used to model the soil column.

Nomenclature

a	Constant in quadratic equation	–
A	Cross-sectional area of soil column	cm^2
b	Constant in quadratic equation	–
C	Solute concentration in irrigation water	$g \ cm^{-3}$
C_n	Total solute concentration in element	$g \ cm^{-3}$
C_{ads}	Concentration of adsorbed solute	$g \ cm^{-3}$
Cs	Concentration of solute in liquid phase	$g \ cm^{-3}$
C_{max}	Maximum adsorbed solute conc.	$g \ cm^{-3}$
ET_n	Evapotranspiration rate in element n	$cm^3 \ day^{-1}$
F_n	Water fraction in element n	$cm^3 \ cm^{-3}$
FC	Field capacity fraction	–
F_{min}	Minimum moisture content for plant growth	–
GR	Plant root growth rate	$cm \ day^{-1}$
Irrig	Specific rate of human irrigation	$cm \ day^{-1}$
K	Langmuir adsorption coefficient	$g \ cm^{-3}$
N	Number of elements in the soil model	–
Q_n	Volumetric flow rate from element n	$cm^3 \ day^{-1}$
Rain	Specific rainfall rate	$cm \ day^{-1}$
$Root_n$	Length of root in element n	cm
$Root_{tot}$	Total length of root	cm
s	Constant in quadratic equation	–
t	Time	day
V	Volume of one element	cm^3
W_n	Water content in element n	cm^3
W_{table}	Depth of water table	cm
z	Height of one soil element	cm

Exercises

1. Run the simulation under the following conditions: (a) Dry conditions time 0 to day 2, (b) spraying day 2 to day 5 and (c) rain day 8 to day 13. See how the concentrations of adsorbed and unadsorbed solute vary with time and depth. Vary the time of spraying to before, during and after rainfall.

2. Change the chemical equilibrium parameters (K and C_{max}) to see how they effect the distribution and transport of the solute (see Lyman et al. (1982) for a comprehensive set of data). Experiment by using a different model for the adsorption of the solute. e.g., Freundlich linear adsorption.

3. In practise some water will always be transported through the soil even if the local water content is less than the field capacity owing to preferential flow through cracks and large pores in the soil structure. This can be modelled simply by defining a bypass parameter to account for the fraction of water that can pass through each element. Modify the model to include bypass and see how this influences the solute profiles (see Corwin et al. (1991) for further details).

4. Different soil types have differing field capacities and minimum water contents.

   Typical values are:

 | Soil type | Field capacity (cm³ cm⁻³) | Minimum water content (cm³ cm⁻³) |
   |---|---|---|
   | Sandy soil | 0.08 | 0.05 |
   | Clay soil | 0.35 | 0.16 |

   Vary the parameters within the above ranges. How does the soil type affect the transport of solutes? Modify the model so that the soil characteristics vary with depth, e.g., a sandy soil near the surface becoming clay deeper below the surface.

5. The assumption of linear water uptake along the length of the plant roots is not usually true in practise. Often the uptake is divided $40:30:20:10$ i.e. 40% of water is taken up by the top quarter of the roots, 30% by the second quarter and so on. Modify the model to take this into account. Try other models of water uptake (e.g., $44:31:19:6$).

6. Modify the model for a solute that is capable of being biodegraded or being assimilated by the plants. An appropriate kinetic relationship must be assumed.

Results
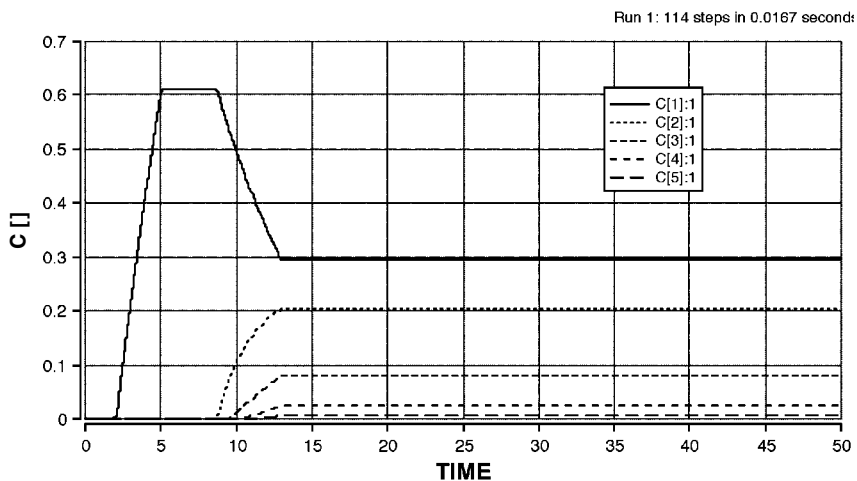
Fig. 2 Time profiles for the overall concentration of solutes at five different depths. Irrigation between days 2 and 5. Rain on days 8 to 13.
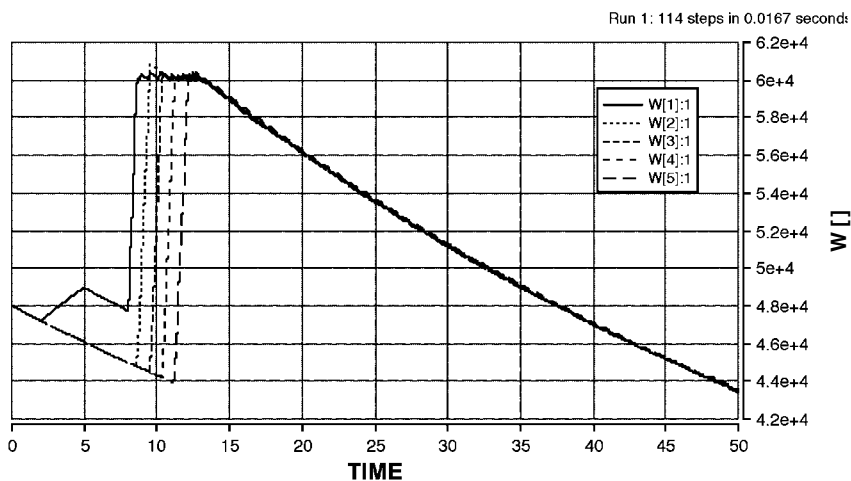
Fig. 3 Water fractions for the same run. The influence of irrigation and rain is clearly seen near the surface at depth 1.

References

Corwin, D. L., Waggoner, B. L. and Rhoades, J. D. (1991) A Functional Model of Solute Transport that Accounts for Bypass, J. Environ. Qual. 20, 647–658.

Lyman, W. J., Reehl, W. F. and Rosenblatt, D. H. (1982) Handbook of Chemical Property Estimation Methods, Chapter 4, Adsorption Coefficients for Soils and Sediments, McGraw-Hill.

5.14.8
SOIL – Bioremediation of Soil Particles

System

Soil that has been contaminated with an organic compound can be cleaned by naturally occurring soil bacteria. These bacteria are present as suspended forms existing within the liquid in the pores of the soil particles as well as existing as microcolonies attached to the solid surface. The micro-organisms utilise the organic compounds as a carbon source but also require oxygen. Oxygen and the contaminant are transported by diffusion within the liquid phase of the soil particles. The time required for the contaminated soil to be cleaned, or the bioremediation time, is an important parameter in influencing the course of action to minimise the environmental impact of the contamination.
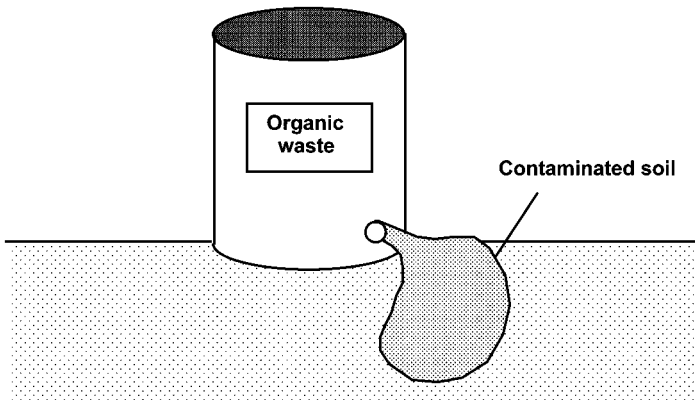
Fig. 1 Leaching of an organic compound into the soil.

Model

The soil aggregates are assumed to be spherical in form and to have constant temperature and to contain initially uniform distributions of substrate (contaminant) and biomass. The external concentrations of biomass and substrate are assumed to be zero and the external oxygen concentration is constant. Substrate is adsorbed onto the solid phase to an extent determined by an equilibrium partition coefficient.

Thus for the substrate

$$S_{sol} = S_{liq}K_{ps}$$

and for the biomass

$$X_{sol} = X_{liq} K_{px}$$

Substrate is present in both the liquid and soil phases of the soil particle. A factor F_s can be defined such that all the substrate can be considered to be found in the total volume V, where

$$S_{liq} F_s V = S_{liq} V E_a + S_{sol} V (1 - E_a)$$

This can be simplified to

$$F_s = E_a + (1 - E_a) \frac{S_{sol}}{S_{liq}}$$

which is

$$F_s = E_a + (1 - E_a) K_{ps}$$

A similar expression can be derived for biomass, which gives

$$F_x = E_a + (1 - E_a) K_{px}$$

where E_a is the volumetric fraction of liquid, and K_{ps} and K_{px} are the partition coefficients. The factors F_s and F_x are introduced to avoid having to use separate differential biomass and substrate balances for both the solid and liquid phases.

Oxygen is assumed to be present only in the liquid phase. The biomass is assumed to follow Monod growth kinetics, depending on both the oxygen and substrate concentrations in the liquid phase and to decline according to a first order decay term, where

$$\frac{R_x}{VF_x} = \mu_{max} X \frac{S}{K_s + S} \frac{O}{K_o + O} - K_d X$$

The rates of uptake of substrate and oxygen are related to the biomass growth rate by appropriate yield constants:

$$\frac{R_s}{VF_x} = -\frac{\mu_{max} X}{Y_s} \frac{S}{K_s + S} \frac{O}{K_o + O}$$

$$\frac{R_o}{VF_x} = -\frac{\mu_{max} X}{Y_o} \frac{S}{K_s + S} \frac{O}{K_o + O}$$

Oxygen, substrate and biomass are all transported by diffusion within the liquid phase contained in the aggregate. The modelling of this process is achieved via the use of a finite differencing technique. In this, the spherical aggregate is divided into a number of shells, as seen in Fig. 1.
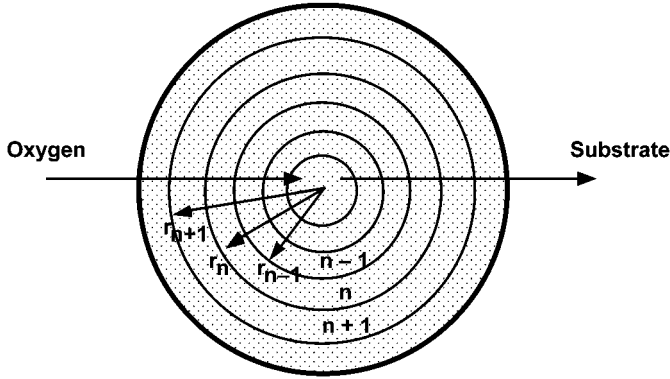
Fig. 2 Finite differencing of a soil particle.

The outer diameter of the nth shell is r_n and its inner diameter is r_{n-1}. Therefore the volume of shell n is given by

$$V_n = \frac{4}{3}\pi\left(r_n^3 - r_{n-1}^3\right)$$

and the outside area of the shell by

$$A_n = 4\pi r_n^2$$

Mass balances for element n give

$$F_x V_n \frac{dX}{dt} = J_{x,n} + R_{x,n}$$

$$F_s V_n \frac{dS}{dt} = J_{s,n} + R_{s,n}$$

$$E_a V_n \frac{dO}{dt} = J_{o,n} + R_{o,n}$$

where J_x, J_s and J_o are the respective net rates of diffusion of biomass, substrate and oxygen into the nth element which are approximated by

$$J_{x,n} = D_x^* \frac{A_n(X_{n+1} - X_n) - A_{n-1}(X_n - X_{n-1})}{r_n}$$

$$J_{s,n} = D_s^* \frac{A_n(S_{n+1} - S_n) - A_{n-1}(S_n - S_{n-1})}{r_n}$$

$$J_{o,n} = D_o^* \frac{A_n(O_{n+1} - O_n) - A_{n-1}(O_n - O_{n-1})}{r_n}$$

D_x^*, D_o^*, and D_s^* are the diffusion coefficients for biomass, oxygen and substrate in the liquid phase of the aggregates. It is assumed that the rates of diffusion in the solid phase are negligible compared to those in the liquid phase. The biomass diffusion coefficient also incorporates the effect of cell motility. The rate of diffusion through the aggregate will depend on the volume fraction of liquid in the aggregates and the degree of tortuosity of the pore space. The diffusion constants in the aggregates can be related to the diffusion constants in free liquid by the following relationship

$$D_i^* = D_i \frac{E_a}{\tau}$$

where i is substrate, biomass or oxygen, E_a is the liquid volume fraction in the aggregate and τ is a measure of the degree of tortuosity of the pore space.

Program

The model equations are very stiff and require a suitable integration method.

Nomenclature

Symbols

A	Outside area of shell	cm^2
D	Diffusion coefficient	$cm^2\ s^{-1}$
DO	Dissolved oxygen concentration	$g\ cm^{-3}$
E_a	Liquid fraction in aggregate	–
F_x	Biomass concentration correction factor	–
F_s	Substrate concentration correction factor	–
J	Diffusion rate	$g\ s^{-1}$
K_d	First order cell death constant	s^{-1}
K_s	Monod constant for substrate	$g\ cm^{-3}$
K_o	Monod constant for oxygen	$g\ cm^{-3}$
K_{ps}	Partition coefficient substrate	–
K_{px}	Partition coefficient biomass	–
r	Radius of aggregate	cm
R	Reaction rates	$g\ s^{-1}$
S	Substrate (contaminant) concentration	$g\ cm^{-3}$
t	Time	s
V	Volume of aggregate	cm^3
X	Biomass concentration	$g\ cm^{-3}$
Y_o	Yield oxygen/biomass	–
Y_s	Yield substrate/biomass	–
μ_{max}	Maximum growth rate	s^{-1}
τ	Tortuosity of the pore space	–

Indices

ex	External
liq	Liquid phase
n	Element number (1 to 6)
o	Oxygen
sol	Solid phase
s	Substrate
x	Biomass
in	Initial

Exercises

1. Vary the radius of the soil aggregates in the range 0.1 to 10 cm and see how this influences the bioremediation time.
2. Vary the substrate partition coefficient in the range 1 to 1500 and see how this also influences the bioremediation time.
3. Also vary the initial substrate concentration, i.e. the degree of contamination in the range 1.0×10^{-6} to 0.1, and see how this influences the bioremediation time.
4. Compare the bioremediation time for a small, highly contaminated particle to that of a larger, less contaminated particle having an equal initial mass of contaminant.
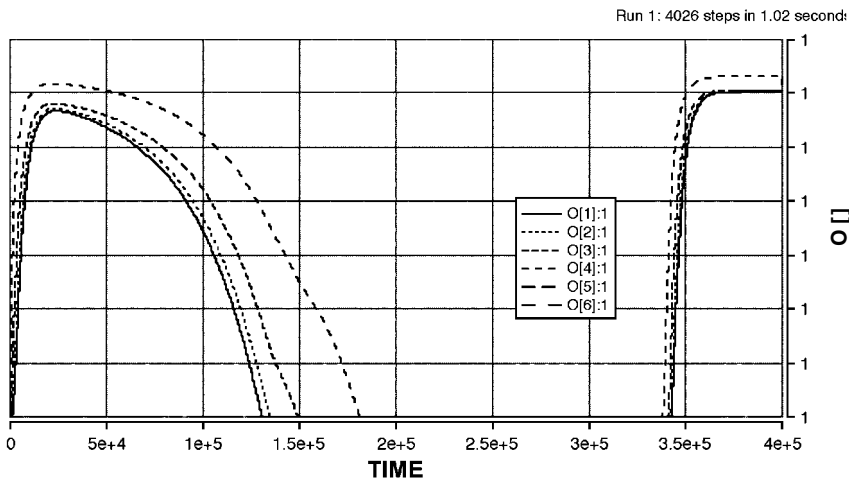
Results

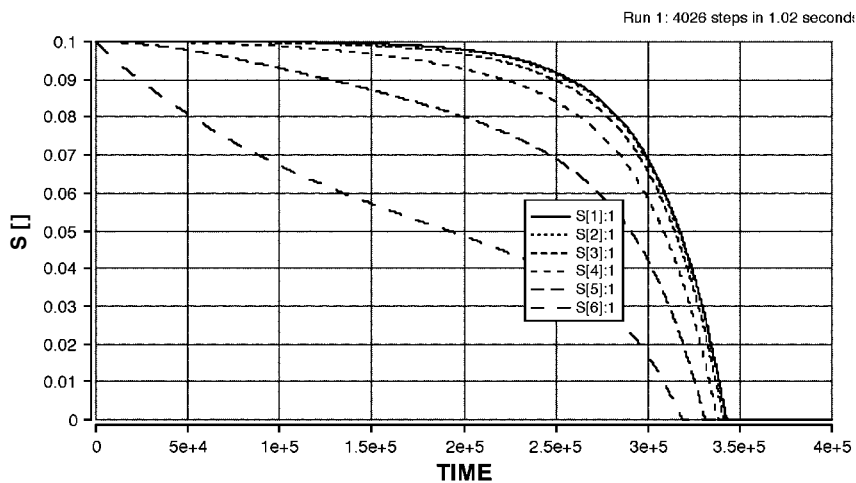**Fig. 3** Variation in oxygen concentrations with time.

Fig. 4 Variation in substrate concentrations with time for the same run as in Fig. 3.

Reference

Dhawan, S., Fan, L. T., Erickson, E. and Tuitemwong, P. (1991) Modeling, Analysis and Simulation of Bioremediation of Soil Aggregates, Environmental Progress 10, 4, 251–260.