APPENDIX A : GROWTH KINETICS AND BIOREACTOR MODELLING

1. Growth kinetics

Growth may be described through catabolic and anabolic pathways by which cell material is synthesised with an associated electron exchange (Lim 1998). In short, substrate is utilised to derive energy, building blocks (nutrients) and reducing power (for electron exchange) from it, with an ultimate transfer of electrons to a terminal electron acceptor. Biomass is produced from these products. Combined, substrate is utilised or consumed and biomass is produced, with a proportionally factor, **the true growth yield (Y)**, coupling the two overall biochemical reactions. The **observed growth yield (Y_{obs})** is less than the true growth yield, as Y is defined as yield without any maintenance energy taken into account. Y_{obs} decreases as the maintenance energy gets proportionally bigger (Grady *et al.* 1999). Growth may be expressed as :

$$r_{XB} = -Yr_S \qquad \text{(A1)}$$

with **r_{XB} the rate of biomass production** and **r_s the rate of substrate consumption** with Y the true growth yield, all expressed in units of chemical oxygen demand (COD). The rate of biomass production or the growth rate can be expressed as a first-order equation:

$$r_{XB} = \mu X_B \qquad \text{(A2)}$$

with **μ the specific growth rate coefficient** and **X_B the active biomass concentration**. Combining Eqs. A1 and A2 gives:

$$r_s = -\mu X_B / Y \qquad \text{(A3)}$$
$$= -(\mu/Y) X_B$$

μ/Y may be described as the specific substrate consumption rate.

Monod (1949) proposed an empirical equation describing the inter relationship between growth rate and substrate concentration and can be expressed as:

$$\mu = \mu_m S_s / (K_s + S_s) \qquad \text{(A4)}$$

where μ_m **is the maximum specific growth rate**, S_s **the substrate concentration** and K_s **the half-saturation coefficient for substrate**, which is the substrate concentration at half maximum specific growth rate. The equation is demonstrated in Chapter I, Fig. 1.1.

The substrate concentration represents the growth limiting nutrient concentration which can be the carbon source, the electron donor, the electron acceptor, or any other factor needed by the organism for growth (Grady *et al*. 1999). The specific growth rate increases as the growth limiting nutrient increases up to the maximum specific growth rate. The equation is generally accepted in literature as a good description of the relationship. The equation is also acceptable for the growth limiting nutrient to be measured in units of COD (Gaudy & Gaudy 1980).

The last biochemical process to describe is decay. Decay is the loss of biomass by predation and lysis for example. It is described by a first order expression similar to growth:

$$r_{XD} = -bX_B \qquad \text{(A5)}$$

with **b the decay coefficient** and $\mathbf{r_{XD}}$ **the reaction rate of biomass decay**.

2. Bioreactor modelling : The chemostat

Shown in Fig. A1 is a chemostat or CSTR with an influent and effluent stream and constant volume. Complete mixing is done by mechanical stirrer and/or gas mixing by the gas supplied for aeration.

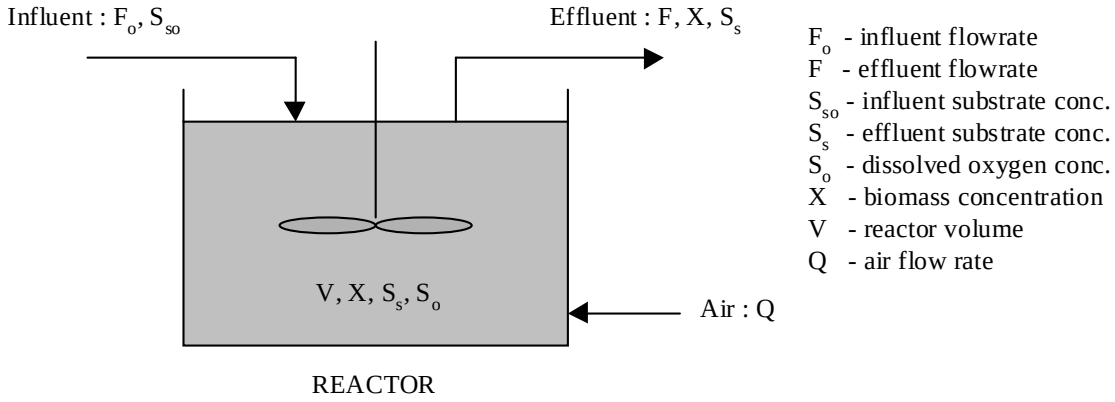

FIG. A1 - The chemostat or CSTR

The CSTR and its modelling is well described by Grady & Lim (1980) and may be explained by completing mass balances over the control volume, taken as the reactor volume (V), on; (i) substrate, (ii) biomass and (iii) COD.

i) On substrate:

$$V.\, dS / dt = F_o.S_{so} - F.S_s + r_s.V \qquad (A6)$$

where F_o and F are the volumetric flow rates for the influent and effluent and S_{so} and S_s the influent and effluent concentrations in COD, respectively. For steady state the equation simplifies to:

$$- r_s = (F/V)\ (S_{so} - S_s) \qquad (A7)$$

The **mean hydraulic residence time** (HRT) with symbol **τ**, is the inverse of the **dilution rate, D**, with:

$$\tau = V/F = 1/D \qquad (A8)$$

Combining Eqs. A3 and A7 and replacing with A8, gives :

$$(F/V)\ (S_{so} - S_s) = \mu X_B/Y$$
$$\therefore \quad X_B = Y(S_{so} - S_s) / \mu\tau \qquad (A9)$$

ii) On biomass: Completing a mass balance on active biomass concentration at steady state and using Eqs. A2, A5 and A8 with no biomass in the influent :

$$0 - FX_B + r_{XB}V + r_{XD}V = 0$$
$$\therefore \quad - X_BV / \tau + \mu X_BV - bX_BV = 0$$
$$\therefore \quad \mu = 1/\tau + b \qquad (A10)$$

Eq. A10 may be rewritten to define the dilution rate as :

$$D = \mu - b \qquad (A11)$$

showing that the growth rate must be faster than the dilution rate by the amount of the decay rate. Substituting μ in Eq. A9 with Eq. A10 gives Eq. A12:

$$X_B = Y\ (S_{so} - S_s)\ /\ (1 + b\tau) \qquad \text{(A12)}$$

The observed yield is the measured biomass formed per substrate removed taking decay into account and is defined by:

$$Y_{obs} = X / (S_{so} - S_s) \qquad \text{(A13)}$$

with **X** the measured **biomass concentration**. Assuming negligible biomass debris as part of X (influenced by τ), results in X being equal to X_B. Combining Eqs. A12 and A13 gives the correlation between Y and Y_{obs}:

$$Y_{obs} = Y / (1 + b\tau) \qquad \text{(A14)}$$

Eq. A4 may be rewritten for substrate determination and μ substituted with Eq. A10, giving:

$$S_s = \mu K_s / (\mu_m - \mu)$$
$$= [K_s (1/\tau + b)]\ /\ [\mu_m - (1/\tau + b)] \qquad \text{(A15)}$$

iii) On COD: Investigating the oxygen required for aerobic respiration, it can be said from basic stoichiometry that the electrons removed from the substrate must end up in either the electron acceptor or the biomass formed. With COD a measure of the flow of electrons, the substrate COD removed, equals the biomass formed in COD plus the oxygen used in COD (electron acceptor). Therefore, **RO, the mass rate of oxygen utilised**:

$$RO = F(S_{so} - S_s) - Y_{obs}.F\ (S_{so} - S_s)$$
$$= F(S_{so} - S_s)\ (1 - Y_{obs}) \qquad \text{(A16)}$$

APPENDIX B : EQUILIBRIUM CHEMISTRY

1. Theoretical background

Equilibrium chemistry is associated with the degree of dissociation of the weak acid / bases. Dissociation in turn is dependent on the dissociation constants, the total species concentrations and the ionic strength of electrolyte (Stumm & Morgan 1981). The pH of a solution can be calculated by equilibrium calculations, using (i) mass balance equations (total species concentrations), (ii) equilibrium relationships (equilibrium constants), (iii) correction for ionic strength (activity coefficients) and (iv) a proton condition (mass balance on protons) or charge balance (electro neutrality) (Snoeyink & Jenkins 1980). The method for the development of these equilibrium equations is well described in literature and will not be dealt with here. A comprehensive review and development on the topic were done by Loewenthal *et al.* (1989), Moosbrugger *et al.* (1993a, 1993b and 1993d) and Moosbrugger *et al.* (1993).

The development of equations for the solution in Chapter II Section 1.2, is as follows:

i) Mass balance equations for total species concentration:

$C_{TC} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$	(Total carbonate species concentration)
$C_{TA} = [HAc] + [Ac^-]$	(Total acetic acid species concentration)
$C_{TN} = [NH_4^+] + [NH_3]$	(Total nitrogen species concentration)
$C_{TP} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$	(Total phosphorus species concentration)
$C_{TNa} = [Na^+]$ (strong base)	(Total sodium concentration)

where: [ ] molar mass concentration, mol/*l*

$[H_2CO_3^*]$ the sum of dissolved carbon dioxide and carbonic acid = $[CO_2]_{aq} + [H_2CO_3]$ (Stumm & Morgan 1970)

ii) Equilibrium relationships or dissociation equations:

Water species:	$(H^+)(OH^-)$	=	K_W
Carbonate species:	$(H^+)(HCO_3^-) / (H_2CO_3^*)$	=	K_{C1}
	$(H^+)(CO_3^{2-}) / (HCO_3^-)$	=	K_{C2}
Acetic acid species:	$(H^+)(Ac^-) / (HAc)$	=	K_A

Nitrogen species:	$(H^+)(NH_3)$ / (NH_4^+)	=	K_N
Phosphorus species:	$(H^+)(H_2PO_4^-)$ / (H_3PO_4)	=	K_{P1}
	$(H^+)(HPO_4^{2-})$ / $(H_2PO_4^-)$	=	K_{P2}
	$(H^+)(PO_4^{3-})$ / (HPO_4^{2-})	=	K_{P3}

where: ( ) activity (active mass) concentration mol/*l*

K_x thermodynamic dissociation equilibrium constants, refer Table B1

K_w thermodynamic ion product constant, refer Table B1

The dissociation and ion product constants are temperature dependent and defined in Table B1 below (Benefield *et al.* 1982; Loewenthal *et al*. 1989).

TABLE B1 - Equilibrium constants (T = °K)

pK	Equation
pK_w	4787,3 / T + 7,1321 * log T + 0,010365 * T - 22,801
pK_{C1}	3404,7 / T - 14,8435 + 0,03279 * T
pK_{C2}	2902,4 / T - 6,498 + 0,02379 * T
pK_A	1170,5 / T - 3,165 + 0,0134 * T
pK_N	2835,8 / T - 0,6322 + 0,00123 * T
pK_{P1}	799,3 / T - 4,5535 + 0,01349 * T
pK_{P2}	1979,5 / T - 5,3541 + 0,01984 * T
pK_{P3}	12,023

iii) Total species concentrations are determined analytically, giving mass concentration. To enable calculation with mass concentrations the dissociation equations are corrected with activity coefficients. The hydrogen ion concentration is however determined by a pH measurement, measuring activity, and is an exception and is used without a correction, giving :

$$pH = -\log (H^+)$$

$$(OH^-) = f_m [OH^-]$$

water species:	$(H^+)\,[OH^-]$	=	K'_w	=	K_w/f_m
carbonate species:	$(H^+)[HCO_3^-]\ /\ [H_2CO_3^*]$	=	K'_{C1}	=	K_{C1}/f_m
	$(H^+)\,[CO_3^{2-}]\ /\ [HCO_3^-]$	=	K'_{C2}	=	$K_{C2}.f_m\ /\ f_d$
acetic acid species:	$(H^+)\,[Ac^-]\ /\ [HAc]$	=	K'_A	=	K_A/f_m
nitrogen species:	$(H^+)\,[NH_3]\ /\ [NH_4^+]$	=	K'_N	=	K_N/f_m
phosphorus species:	$(H^+)\,[H_2PO_4^-]\ /\ [H_3PO_4]$	=	K'_{P1}	=	K_{P1}/f_m
	$(H^+)\,[HPO_4^{2-}]\ /\ [H_2PO_4^-]$	=	K'_{P2}	=	$K_{P2}.f_m\ /\ f_d$
	$(H^+)\,[PO_4^{3-}]\ /\ [HPO_4^{2-}]$	=	K'_{P3}	=	$K_{P3}.f_d/f_t$

where: f_m, f_d and f_t, monovalent, divalent and trivalent activity coefficients, refer Table B2

K'_x apparent dissociation equilibrium constants, refer Table B2

K'_w apparent ion product constant, refer Table B2

The activity coefficients may be calculated using the Davies equation for solutions with ionic strength of less than 0,5 M (Stumm & Morgan 1981):

$$\log f_i = -Az_i^2\ [I^{½} / (1 + I^{½})\ -\ 0{,}3\ I] \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{ Davies Equation}$$

where: f_i activity coefficient for ionic species i, giving f_m , f_d and f_t

$A = 1{,}825 \times 10^6\ (\varepsilon T)^{-3/2}$

ε dielectric constant = 78,3

T temperature in Kelvin

z_i charge of the i^{th} species - mono = 1; di = 2 and tri = 3

I the ionic strength = $½ \Sigma\, c_i z^2_i$

c_i concentration of the i^{th} ionic species, mol/l (dissociated species)

Activity coefficients and equilibrium constants were calculated for an ionic strength of 0,1 M at a temperature of 25°C and shown in Table B2.

TABLE B2 - Apparent equilibrium constants corrected for ionic strength of 0,1 M at 25°C

pK	Value
pK'_w	13,891
pK'_{C1}	6,245
pK'_{C2}	10,008
pK'_A	4,648
pK'_N	9,143
pK'_{P1}	2,041
pK'_{P2}	6,878
pK'_{P3}	11,485
$f_m = 0,780$	$f_d = 0,371$ $f_t = 0,107$

iv) Proton Condition

The proton mass balance is established with reference to a reference level of protons. The reference level is taken as the species with which the solution was prepared. The species having protons in excess of the reference level are equated with the species having less protons than the reference level. This may be set out as in Fig. B1 resulting in the proton balance below :

$$[Na^+] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [Ac^-] + [NH_3] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [OH^-]$$

There are 14 unknown species and 14 equations to solve the solution species concentrations. The total species concentrations C_{TA}, C_{TN}, C_{TP} and C_{TNa} are known from preparation of the feed solution or are analytically determined. The total carbonate species, C_{TC}, may be determined from the carbonate alkalinity and pH measurement (WRC 1986) or as in this case, for an open system, it is a function of CO_2 partial pressure.

Species formed by									Na^+		H^+	
gain of one proton:									↑		↑	
Reference species:	**H_2CO_3***	**---**	**HAc**	**---**	**NH_4^+**	**---**	**H_3PO_4**	**---**	**NaOH**	**---**	**H_2O**	
	↓		↓		↓		↓				↓	
Species formed by loss of one proton:	HCO_3^-		Ac^-		NH_3		$H_2PO_4^-$				OH^-	
Species formed by loss of two protons:	↓ CO_3^{2-}						↓ HPO_4^{2-}					
Species formed by loss of three protons:							↓ PO_4^{3-}					

FIG. B1 - Proton balance

Using Henry's law constant, K_H, the dissolved CO_2 species may be calculated. The ratio of dissolved CO_2 to H_2CO_3 is fixed and equal to 99,76 : 0,24 at 25°C and is independent of pH and ionic strength (Stumm & Morgan 1970). The H_2CO_3* concentration may be approximated by the dissolved CO_2 concentration :

$$K_H \rho_{co2} = [CO_2]_{aq} \simeq [H_2CO_3^*]$$

with: $pK_H = -1760/T + 9,619 - 0,00753T$

ρ_{co2} partial pressure of CO_2. The University of Pretoria is at an elevation of 1400 m above sea level with atmospheric pressure of approximately 85,5 kPa giving a partial pressure for $CO_2 \simeq$ 0,00027 atmosphere.

These equations can now be solved simultaneously to yield the concentration of each chemical species.

2. Experimental

Computer Programme

The equations as developed above for an aerated solution with acetic acid, ammonium chloride, phosphoric acid and sodium hydroxide in distilled water were programmed in the spreadsheet program Excel(1998) for MSOffice. The pH was calculated for solutions with different total species concentrations by using the solver function, and compared to measured values of solutions prepared in a laboratory. Spreadsheet printouts of the programme are given below.

Solution preparation and pH measurement

Solutions of different concentrations were made up in freshly distilled water adding ammonium chloride, phosphoric acid, acetic acid and sodium hydroxide which was aerated. The solution concentrations are summarised in Table B3 below.

The pH was measured for each solution with a Mettler MP120 pH meter and Mettler Inlab413 temperature compensating probe. The accuracy stated by the manufacturer is $\pm$ 0,01 pH units. Chemicals of AR quality were used. Measurement was carried out under careful constant and similar stirring conditions for all the solutions. pH calibration was done with pH buffers of 4,01 and 7,01 pH and tested against a 1,68 pH buffer. All glassware was thoroughly washed with hydrochloric acid (Standard Methods 1995).

Results

The calculated and measured pH values are summarised in Table B3. The carbonate subsystem was only included in the calculation where indicated. A number of commercially available buffer solutions and self-prepared buffers were tested and compared. Big differences were noticed in some of them, notwithstanding guaranteed accuracies. The exercise emphasises the care that needs to be taken in using or selecting commercially available buffers for accurate calibration of pH meters.

TABLE B3 - Comparison of calculated and measured pH values

Solution	Subsystem species added	Concentration mg/*l*	Temp °C	Measured pH	Calculated pH	pH Difference	Calculated I (mol/*l*)
1a	NH_4Cl – N	449	24	5,23	5,33 (5,29)*	+0,10 (+0,06)*	0,0357
		125	24	5,43	5,65 (5,51)	+0,22 (+0,08)	0,0089
		50	24	5,49	5,86 (5,60)	+0,37 (+0,11)	0,0036
1b	H_3PO_4-P	620	25	2,09	2,04	-0,05	0,0100
		124	25	2,58	2,54	-0,04	0,0020
		62	25	2,82	2,79	-0,03	0,0010
1c	HAc	497	25	3,42	3,43	+0,01	0,0002
		99	27	3,80	3,79	-0,01	~ 0
		50	25	3,95	3,95	0	~ 0
2	P/N/HAc	50/50/50	23	2,89	2,86	-0,03	0,0044
	+NaOH	49/49/49+63,5	24	4,06	4,02	-0,04	0,005
	+NaOH	48/49/48+91,2	25	5,52	5,50	-0,02	0,0057
3	P/N/HAc	50/100/99	26	2,93	2,86	-0,07	0,0080
	+NaOH	49/98/97+63,5	26	3,89	3,84	-0,05	0,0087
	+NaOH	48/97/96+118,5	26	5,47	5,52	+0,05	0,0098
4	P/N/HAc	50/100/497	24	2,85	2,84	-0,01	0,0080
	+NaOH	49/99/494+119	24	4,04	4,05	+0,01	0,0101
	+NaOH	49/98/488+352	24	5,52	5,58	+0,06	0,0158
	+aerated (24h)	49/98/488/352	18	5,51	5,58	+0,07	0,0158

* Values in brackets includes the carbonate subsystem for an open system.

The differences between the calculated and measured pH values for the pure solutions were less than 0,1 pH units except for the NH_4Cl solutions. The reason for the bigger differences for these solutions is not clear, but is probably related to the very low buffer capacity of the solutions in the measured pH range. It is however still relative accurate with differences of less than 0,4 pH units. The difference decreases as the nitrogen concentration increases and together with the negligible buffer capacity in the acidic range, makes the differences not important for the purpose of this study. The mixed solution differences were less than 0,1 pH units, indication accurate modelling by the calculation method. The concentrations of all the different species of each solution are not shown but are known through the calculation method. The solutions are therefore completely characterised.

Comparing the pH values for the different solutions, it is seen that the pH values are different and decreases with increase in concentration. The increased N and HAc concentrations for solution 3 versus 2, decreased the pH for the same NaOH dose. A similar result may be noticed for an increased HAc concentration for solution 4 versus 3. These results are expected considering equilibrium chemistry and the shift in the equivalence point with increased reference species.

The added strong base (NaOH) increased the pH as would be expected. The carbonate subsystem had virtually no influence on the acidic pH of approximately 5,6 for solution 4, but will have an increased influence on an increased basic solution (Stumm & Morgan 1981).

Conclusions

The test work confirmed that the solution could completely be characterised by equilibrium chemistry. The programme gave accurate predictions and can be used to calculate the pH due to changes in chemical species concentrations. The most important aspect is the confirmation that the pH, the controlled parameter, is determined by the weak acid and base subsystems and strong acid and/or base added to the solution. The selected pH for the visualised chemo-pHauxostat will fix the total species and subsystem species concentrations for a given feed solution composition. It is thus possible to calculate and predict the species concentrations at the selected pH set point.

3. Computer program printouts

Properties

Temperature	T-C	**28.6**	oC
Ionic strength of solution feed	TDS feed	**920**	mg/l
Partial pressure of CO2 in atmosphere	Pco2	**0.00027**	atm
Ionic strength of solution effluent	TDSe effluent	**640**	mg/l
pH of solution (initial)	pHi	3.88	
pH of solution (final)	pHf	5.52	

Activity coefficients

Temperature	T	301.6	K	Effluent
Ionic strength of solution feed	I	0.023	Ie	0.016
Monovalent ions	fm	0.8654584	fme	0.882969
Divanlent ions	fd	0.5610283	fde	0.6078297
Trivalent ions	ft	0.2724054	fte	0.326219
Dielectric constant for water	D	78.3	??	
Henry's constant for [H2CO3*]	Kh	0.0307321	??	
	pKh	1.5124082		

Molar Mass

H2PO4-	MM1	96985.8	mg/mol
HPO42-	MM2	95977.9	mg/mol
PO43-	MM3	94970	mg/mol
CH3COO-	MM4	59043.7	mg/mol
NH4+	MM5	18038.6	mg/mol
Na+	MM6	22990	mg/mol
P	MM7	30974	mg/mol
N	MM8	14007	mg/mol
Hac	MM9	60051.6	mg/mol
NaOH	MM10	39996.9	mg/mol
HCl	MM11	36460.9	mg/mol
CH3CH2COOH	MM12	74078.4	mg/mol
CH3CH2CH2COOH	MM13	88105.2	mg/mol
COD/Hac (g/mol)		63.996	

Concentrations

				I = pH
Phosphate Subsystem initial **P**	Ptmi	**51**	mg/l	0.0230407
Acetic Subsystem initial **Hac**	Atmi	**5000**	mg/l	
Ammon. Subsystem initial **N**	Ntmi	**146**	mg/l	I = pHi
Caustic dose **NaOH**	NaOHmi	501.5	mg/l	0.0230407
Caustic dose **NaOH**	NaOHmf	501.5	mg/l	
Propionic **Hpr**	Prtmi	**0**	mg/l	
Butryric **Hbu**	Btmi	**0**	mg/l	
				I = pHf
Phosphate Subsystem final **P**	Ptmf	**16**	mg/l	0.015985
Acetic Subsystem final **Hac**	Atmf	**287**	mg/l	
Ammon. Subsystem final **N**	Ntmf	**52**	mg/l	
Propionic **Hpr**	Prtmf	**0**	mg/l	
Butryric **Hbu**	Btmf	**0**	mg/l	
Phosphate Subsystem initial	Pti	0.0016465	mol/l	
Acetic Subsystem initial	Ati	0.0832617	mol/l	
Ammonium Subsystem initial	Nti	0.0104234	mol/l	
Caustic dose NaOH	NaOHi	0.0125385	mol/l	
Caustic dose NaOH	NaOHf	0.0125385	mol/l	
Phosphate Subsystem final	Ptf	0.0005166	mol/l	
Acetic Subsystem final	Atf	0.0047792	mol/l	
Ammonium Subsystem final	Ntf	0.0037124	mol/l	

Dissociation constants' temperature dependency

Water	KwT	1.31327E-14	pKwT	13.881647
Carbonate	Kc1T	4.6264E-07	pKc1T	6.3347571
	Kc2T	5.00719E-11	pKc2T	10.300406
Phosphate	Kp1T	0.006834662	pKp1T	2.1652829
	Kp2T	6.4125E-08	pKp2T	7.1929729
	Kp3T	9.48418E-13	pKp3T	12.023
Acetate	KaT	1.7482E-05	pKaT	4.7574082
Ammonium	KnT	7.22291E-10	pKnT	9.1412879

Activity corrections

INFLUENT :

Water	Kw	1.51742E-14	pKw	13.818893
Carbonate	Kc1	5.3456E-07	pKc1	6.2720033
	Kc2	7.72423E-11	pKc2	10.112145
Phosphate	Kp1	0.007897159	pKp1	2.1025291
	Kp2	9.8921E-08	pKp2	7.0047115
	Kp3	1.9533E-12	pKp3	11.709231
Acetate	Ka	2.01997E-05	pKa	4.6946544
Ammonium	Kn	8.34576E-10	pKn	9.0785341

EFFLUENT :

Water	Kwe	1.48733E-14	pKwe	13.827592
Carbonate	Kc1e	5.23959E-07	pKc1e	6.2807026
	Kc2e	7.27373E-11	pKc2e	10.138243
Phosphate	Kp1e	0.007740546	pKp1e	2.1112284
	Kp2e	9.31517E-08	pKp2e	7.0308093
	Kp3e	1.76715E-12	pKp3e	11.752727
Acetate	Kae	1.97991E-05	pKae	4.7033536
Ammonium	Kne	8.18025E-10	pKne	9.0872334

Calculatons			pHi	**3.87939431232**	pHf	**5.52000000000**	
Calculate initial equilibrium (proton balance) :							
		solver H=	Hs	132009652.5		3.879394312323	pHs 3.8793943123
NH3i	6.58969E-08		H	0.000132009652454	pH	3.879394312323	
OHi	1.14948E-10		**solve no CO2 :**		**solve with CO2 :**		
Aci	0.01104968						
HCO3i	3.36006E-08		**No Na+**	12538438130.9572	**No Na+**	12538471732	Wp 0.016716094
CO3i	1.96606E-14						Xp 0.000749347
AlkH3PO4	0.001620704		**NaOHmi**	-33600.60204	**NaOHmi**	0	Yp 1.47966E-08
HPO4i			**NaOHmf**	-33600.60204	**NaOHmf**	0	
PO4i							Wn 158175.702
NaOHmi	**501.5**	mg/l					
NaOHmf	**501.5**	mg/l					

Solution : strong acid/base dose : initial and final known

Verander pHi en pHf bo

					pHi	3.879394312	pHf 5.52
AlkiHac	0.011049678		AlkfHac	0.004146726	Hi	0.00013201	Hf 3.01995E-06
AlkiH3PO4	0.001620704		AlkfH3PO4	0.000531818	Wai	6.535217506	Waf 0.15252943
AlkiH2CO3*	3.36006E-08		AlkfH2CO3*	1.43971E-06	Wni	158175.702	Wnf 3691.759254
AlkiNH4	6.58969E-08		AlkfNH4	1.00533E-06	Wpi	0.016716094	Wpf 0.000390147
AlkiH2O	-0.000152531		AlkfH2O	-3.4153E-06	Xpi	0.000749347	Xpf 0.030845417
					Ypi	1.47966E-08	Ypf 5.85157E-07
AlkiSol	0.01251795		AlkfSol	0.004677573			
Delta AlkSol	-0.007840377						
NaOH dose (mg/l)	-313.6		HCl dose(mg/l)	285.9			
NaOHmi-NaOHmf	0.0						

Solution : weak acid/base dose (Ac) : initial and final known FOR YIELD

AlkiAc	-0.07221205		AlkfAc	-0.000632498	-0.07157955		
AlkiH3PO4	0.001620704		AlkfH3PO4	0.000531818	0.001088886		
AlkiCO3	-1.66289E-05		AlkfCO3	-1.8035E-05	1.40604E-06		
AlkiNH4	6.58969E-08		AlkfNH4	1.00533E-06	-9.3943E-07		
AlkiH2O	-0.000152531		AlkfH2O	-3.4153E-06	-0.00014912		
AlkiSol	-0.07076044		Alk others	-0.00012112	-0.07063932		
AlkfAc calcul	0.07063932				SRT	15.3	
Atf calcul	-0.533759			delta	HRT	3.1	
Atmf calcul	-32053.1	287.0	Atmf	-32340.1	X	4.63	
Atmi-Atmf calcul	-37053.1	-4713	Atmi-Atmf	32340.1	I	64	
					Yobs	0.344	
delta/Atmi-Atmf	6.861883344	112.683	delta/Atmf		Yalk	1.657805776	
%	686.19	11268.31	%				

Solution : weak acid/base dose (HAc) : initial and final known

AlkiHAc	0.011049678		AlkfHAc ?	
AlkiH2PO4	-2.58386E-05		AlkfH2PO4	1.52555E-05
AlkiH2CO3*	3.36006E-08		AlkfH2CO3*	1.43971E-06
AlkiNH3	-0.010423294		AlkfNH3	-0.003711424
AlkiH2O	-0.000152531		AlkfH2O	-3.4153E-06
AlkiSol	0.00044805		Alk others	-0.00369814
AlkfHAc calcul	0.004146			
Atf calcul	0.004779			delta
Atmf calcul	287.0	287.0	Atmf	0.0
Atmi-Atmf calcul	-4713.0	-4713	Atmi-Atmf	0.0
delta/Atmi-Atmf	7.83326E-06	0.000	delta/Atmf	
%	0.00	0.01	%	

APPENDIX C : ALKALINITY

1. Defining alkalinity

Alkalinity is a measure against the equivalence point of an equivalent solution. Different alkalinities can be defined for different equivalent solutions depending on the reference species, with each alkalinity having its own equivalence point (Loewenthal *et al*. 1989). In terrestrial waters the carbonate subsystem normally dominates which resulted in the general practice to refer to carbonate alkalinity (alkalinity relative to the carbonic acid equivalence point) when mentioning Alkalinity. In effluents a number of other subsystems may however be present and may include the ammonia, phosphoric and SCFA subsystems as for the feed under discussion. The alkalinity of the feed is a solution alkalinity and is a combination of the different subsystem equivalent solutions, forming one combined equivalent solution with a solution equivalence point. The solution alkalinity is the proton accepting capacity of the solution relative to the solution equivalence point.

Loewenthal *et al.* (1991) defined the solution alkalinity as the sum of the alkalinities of the individual weak acids/bases relative to their respective selected reference species, plus the water subsystem alkalinity. The alkalinities for the different weak acid/base subsystems may be derived from a proton balance. Considering the conventional equation for Alkalinity:

$$\text{Alkalinity} = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+]$$

which may be explained by completing a proton balance on a H_2CO_3* equivalent solution with addition of base BOH, depicted by:

$$\begin{array}{lccccc} & B^+ & & & & H^+ \\ & \uparrow & & & & \uparrow \\ \textbf{Reference species:} & \textbf{BOH} & \textbf{---} & \textbf{H}_2\textbf{CO}_3^* & \textbf{---} & \textbf{H}_2\textbf{O} \\ & & & \downarrow & & \downarrow \\ & & & HCO_3^- & & OH^- \\ & & & \downarrow & & \\ & & & CO_3^{2-} & & \end{array}$$

FIG. C1 - Proton balance for Alkalinity

The proton accepting capacity (Alkalinity) of the solution is now equivalent to the amount of base added to the equivalent solution. This amount will be back titrated to the equivalence point during alkalinity determination. The base added is:

$$[B^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+]$$

giving the conventional equation for Alkalinity and demonstrating that it is, and may be defined as $H_2CO_3^*$ alkalinity. Alkalinities for individual weak acid/base subsystems may similarly be derived and defined, giving:

HAc alkalinity	=	$[Ac^-] + [OH^-] - [H^+]$
H_3PO_4 alkalinity	=	$3[PO_4^{3-}] + 2[HPO_4^{2-}] + [H_2PO_4^-] + [OH^-] - [H^+]$
NH_4^+ alkalinity	=	$[NH_3] + [OH^-] - [H^+]$
$H_2CO_3^*$ alkalinity	=	$2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+]$

Considering these alkalinities, each alkalinity can be expressed as the sum of two alkalinities, associated with its reference species. Referring to Fig. C1, the two subsystem reference species in this case are $H_2CO_3^*$ and H_2O. These individual subsystem alkalinities were defined and expressed by Loewenthal and co-workers (1991) as "Alk (reference species)" giving:

$$H_2CO_3^* \text{ alkalinity} = \text{Alk } H_2CO_3^* + \text{Alk } H_2O$$
$$= 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+]$$

with: Alk $H_2CO_3^*$ - alkalinity of the carbonate subsystem with reference species $H_2CO_3^*$ and equivalent to $2[CO_3^{2-}] + [HCO_3^-]$

Alk H_2O - alkalinity of the water subsystem with reference species H_2O and equivalent to $[OH^-] - [H^+]$

giving the general equation:

$$\text{Solution alkalinity} = \Sigma \text{Alk}_i + \text{Alk } H_2O$$

with: Alk_i - the subsystem alkalinity for the i^{th} weak acid / base subsystem relative to its selected reference species.

Note that the water subsystem Alk H_2O is only added once. The solution alkalinity for the feed and the reactor can now be defined as:

$$\text{Solution alkalinity} = \text{Alk HAc} + \text{Alk } H_3PO_4 + \text{Alk } NH_4^+ + \text{Alk } H_2CO_3^* + \text{Alk } H_2O$$

with reference species: HAc, H_3PO_4, NH_4^+, $H_2CO_3^*$ and H_2O respectively,

and :

$$\text{Alk HAc} = [Ac^-]$$

$$\text{Alk } H_3PO_4 = [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$$

$$\text{Alk } NH_4^+ = [NH_3]$$

$$\text{Alk } H_2CO_3^* = [HCO_3^-] + 2[CO_3^{2-}]$$

$$\text{Alk } H_2O = [OH^-] - [H^+]$$

The SCFA subsystem alkalinities may for simplicity be represented by the acetic acid subsystem alkalinity because the ionisation constants for the SCFA's, typically of concern (acetic, propionic, butyric and valeric), differs only slightly from that of acetic acid and with HAc concentration normally the highest. The SCFA concentration are converted to HAc concentration and then considered as HAc, giving:

$$\text{Alk SCFA} \simeq \text{Alk HAc} = [Ac^-]$$

It was concluded in Chapter II that equilibrium chemistry can be used to characterise the feed and the reactor solutions. All chemical species concentrations are thereby known and the solution alkalinity can be calculated using the above equations.

2. Calculating alkalinity

Equations for the total species concentrations, dissociation equations and subsystem alkalinities for the substrate were given in Chapter II and above. These equations may be combined as demonstrated by Loewenthal *et al*. (1991) to simplify alkalinity calculations. Developed equations are summarised below:

$$\text{Alk HAc} = C_{TA} / (1 + W)$$

$$\text{Alk } Ac^- = - C_{TA}.W / (1 + W)$$

$$\text{Alk } H_3PO_4 = C_{TP} . (1 + 2X + 3XY) / (1 + W + X + XY)$$

$Alk\ H_2PO_4^- = C_{TP} . (-W + X + 2XY) / (1 + W + X + XY)$

$Alk\ NH_3 = -C_{TN} . W / (1 + W)$

$Alk\ NH_4^+ = C_{TN} / (1 + W)$

$Alk\ H_2O = 10^{pH-pK'_w} - 10^{-pH} / f_m$

$Alk\ H_2CO_3^* = 2[CO^{2-}_3] + [HCO_3^-]$

$= K_H\rho_{CO2} [2(K'_1K'_2 (10^{pH})^2 + K'_1 10^{pH}]$

$Alk\ CO_3^{2-} = -2 [H_2CO_3^*] - [HCO_3^-]$

$= K_H\rho_{CO2} (-2 - K'_1 10^{pH})$

with: $W = 10^{pK'_1-pH}$

$X = 10^{pH-pK'_2}$

$Y = 10^{pH-pk'_3}$

K'_1 = first apparent dissociation equilibrium constant

K'_2 = second apparent dissociation equilibrium constant

K'_3 = third apparent dissociation equilibrium constant