

### 4.1.3 Stoichiometrics of reactions with nitrogenous matter

#### 4.1.3.2 Effects on alkalinity

The effect of ammonification, nitrification and denitrification on the (carbonate) alkalinity of the mixed liquor can be calculated from simple stoichiometric relationships using the reaction equation of the three processes (Eqs. 4.1, 4.2 and 4.3). It can be noted that in all equations the hydrogen ion is involved: in the ammonification process and the denitrification process there is a consumption of 1 mol  $H^+$  per mol N, whereas during nitrification there is a release of 2 moles  $H^+$  per mol N. Knowing that the formation of 1 mol of  $H^+$  (mineral acidity) is equivalent to the consumption of 1 mol of alkalinity or  $\frac{1}{2}$  mol of  $CaCO_3$  (50 g  $CaCO_3$ ), the following alkalinity changes are calculated:

- Ammonification process: production of 50 g  $CaCO_3$  per mol N;
- Nitrification process: consumption of  $2 \cdot 50 = 100$  g  $CaCO_3$  per mol N;
- Denitrification process: production of 50 g  $CaCO_3$  per mol N.

The alkalinity changes may be expressed as:

$$(\Delta Alk/\Delta N)_{am} = 50/14 = 3.57 \text{ mg } CaCO_3 \cdot \text{mg } N^{-1} \quad (4.11a)$$

$$(\Delta Alk/\Delta N)_n = -100/14 = -7.14 \text{ mg } CaCO_3 \cdot \text{mg } N^{-1} \quad (4.11b)$$

$$(\Delta Alk/\Delta N)_d = 50/14 = 3.57 \text{ mg } CaCO_3 \cdot \text{mg } N^{-1} \quad (4.11c)$$

Where  $(\Delta Alk/\Delta N)$  = alkalinity variation in mg  $CaCO_3$  per mg N

The indices am, n and d refer to ammonification, nitrification and denitrification respectively. In the case of municipal sewage, the alkalinity effect of ammonification is usually very small, as the following analysis shows. The concentration of ammonified nitrogen in the activated sludge process is given by the difference between the organic nitrogen in the influent and the sum of the organic nitrogen concentrations in the effluent and the excess sludge (see Fig. 4.1) so that:

$$\Delta N_{am} = N_{oi} - N_{oe} - N_l \quad (4.12)$$

$$\Delta N_{am} = \text{ammonified nitrogen concentration in the activated sludge process} \\ \text{(mg } N \cdot l^{-1} \text{ influent).}$$

Normally in the case of municipal sewage, the organic nitrogen concentration in the effluent is very small, only 1 or 2 mg  $N \cdot l^{-1}$ , whereas the values of the  $N_{oi}$  and  $N_l$  concentrations are both approximately equal to 25 percent of the influent TKN concentration. Hence the variation of the organic nitrogen concentration in the activated sludge process is very small. Consequently the associated alkalinity change will also be small and can be expressed as:

$$\Delta Alk_{am} = 3.57 \cdot \Delta N_{am} = 3.57 \cdot (N_{oi} - N_{oe} - N_l) \quad (4.13)$$

The alkalinity change due to nitrification is calculated from the concentration of nitrified ammonium. This concentration is equal to the difference of the influent TKN concentration ( $N_{ki}$ ) and the sum of the TKN concentrations in the effluent ( $N_{ke}$ ) and the excess sludge ( $N_l$ ):

$$N_c = N_{ki} - N_{ke} - N_l \quad (4.14)$$

Where  $N_c$  = influent ammonium concentration, nitrified in the system ( $\text{mg N.l}^{-1}$ )

The effect of nitrification on alkalinity can be expressed as:

$$\Delta\text{Alk}_n = -7.14 \cdot N_c = -7.14 \cdot (N_{ki} - N_{ke} - N_l) \quad (4.15)$$

The alkalinity change due to denitrification depends on the removed nitrate concentration. This concentration can be calculated as:

$$\Delta N_d = N_{ni} + N_c - N_{ne}$$

Hence the alkalinity change due to denitrification can be expressed as:

$$\Delta\text{Alk}_d = 3.57 \cdot \Delta N_d = 3.57 \cdot (N_{ni} + N_{ki} - N_{ke} - N_l - N_{ne}) \quad (4.16)$$

The total alkalinity change in the activated sludge process, due to the reactions of nitrogenous matter, will be equal to the sum of the effects calculated for ammonification, nitrification and denitrification.

$$\begin{aligned} \Delta\text{Alk}_t &= \Delta\text{Alk}_{am} + \Delta\text{Alk}_n + \Delta\text{Alk}_d \\ &= 3.57 \cdot (N_{oi} - N_{oe} - N_l) - 7.14 \cdot (N_{ki} - N_{ke} - N_l) + 3.57 \cdot (N_{ni} + N_{ki} - N_{ke} - N_l - N_{ne}) \end{aligned} \quad (4.17)$$

Knowing that the TKN concentration ( $N_k$ ) is the sum of the concentrations of organic ( $N_o$ ) and ammonium nitrogen ( $N_a$ ), Eq. (4.17) can be simplified to:

$$\Delta\text{Alk}_t = -3.57 \cdot (N_{ai} - N_{ni} - N_{ae} + N_{ne}) = 3.57 \cdot (\Delta N_a - \Delta N_n) \quad (4.18)$$

Where:

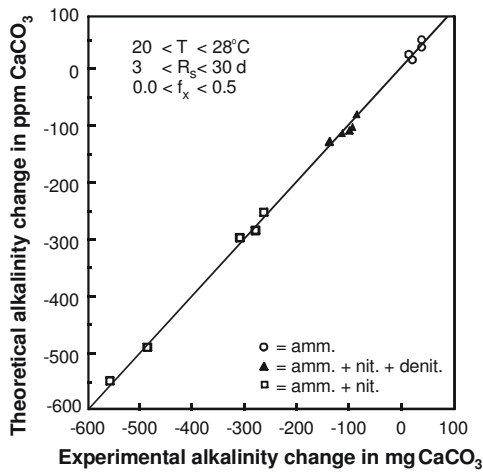
$\Delta N_a$  = variation of the ammonium concentration in the activated sludge process ( $\text{mg N.l}^{-1}$ )

$\Delta N_n$  = variation of the nitrate concentration in the activated sludge process ( $\text{mg N.l}^{-1}$ )

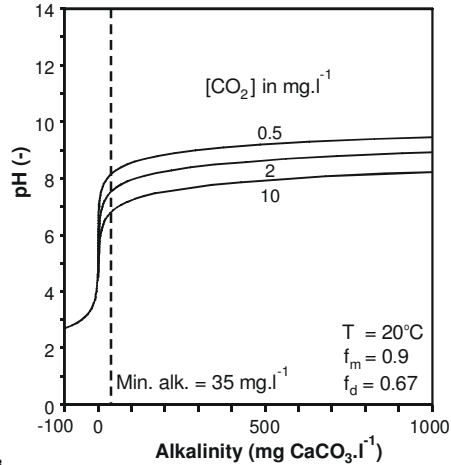
All parameters on the right hand side of Eq. (4.18) can be determined experimentally by standard tests. Hence it is possible to calculate the stoichiometric alkalinity change due to the combined effect of ammonification, nitrification and denitrification in the activated sludge process. On the other hand, it is also possible to measure the alkalinity change directly.

In Fig. 4.4 the calculated (according to Eq. 4.18) and the experimentally determined values of alkalinity change in different activated sludge processes have been compared. The data in Fig. 4.4 refers to systems with a different extent of nitrogen removal: (a) without nitrification, (b) with nitrification but without denitrification and (c) with both nitrification and denitrification.

Fig. 4.4 shows that in all cases there is an excellent correlation between the calculated and the experimentally observed alkalinity changes, for a very large range of changes ( $\Delta\text{Alk}$  between -600 and +100 ppm  $\text{CaCO}_3$ ) and for very diverse operational conditions. Thus, the conclusion is justified that the alkalinity change in an activated sludge process is due to the stoichiometric effects of the reactions with nitrogenous material: ammonification, nitrification and denitrification.



**Figure 4.4**  
Calculated change of the alkalinity versus experimentally observed alkalinity change in a number of activated sludge processes



**Figure 4.5**  
pH value as function of the alkalinity in mixed liquor

Having established the relationship between the reaction of nitrogenous matter and the alkalinity change in an activated sludge process, it is now possible to evaluate the effect of these reactions on the pH of the mixed liquor. First it must be recognised that the pH in activated sludge processes is dictated by the carbonic system  $\text{CO}_2 \leftrightarrow \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-}$ , because this system is present at much higher concentrations than other acid-base systems.

The equilibrium of the weak acid and associated base  $\text{NH}_4^+ \leftrightarrow \text{NH}_3$  is not important when the pH is in the neutral range as in the case of mixed liquor: almost all ammonium will be present in the ionised form. Other equilibria with a pK value (negative logarithm of the dissociation constant) in the neutral pH range, for example  $\text{H}_2\text{PO}_4^- \leftrightarrow \text{HPO}_4^{2-}$  (pK = 7.2) and  $\text{H}_2\text{S} \leftrightarrow \text{HS}^-$  (pK = 7.0) are not important because the concentrations of phosphate and sulphide in mixed liquor are much lower than the concentrations of the carbonic system (Van Haandel et al., 1994). For the carbonic system, the relationship between the alkalinity and pH can be derived from the model developed by Loewenthal and Marais (1976). This model describes the interrelationship between alkalinity, acidity and pH in aqueous solutions.

For the carbonic systems,  $\text{CO}_2 \leftrightarrow \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-}$  the alkalinity is defined as:

$$\text{Alk} = [\text{HCO}_3^-] + 2 \cdot [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (4.19)$$

Where [X] = concentration of X in  $\text{mol.l}^{-1}$

In order to correlate pH and alkalinity, it is necessary to eliminate the concentrations  $[\text{HCO}_3^-]$ ,  $[\text{CO}_3^{2-}]$  and  $[\text{OH}^-]$  from Eq. (4.19). This can be done using the relevant dissociation equations:



From Eq. (4.20), the chemical equilibrium can be written as:

$$k_1 = [\text{HCO}_3^-] \cdot [\text{H}^+] / [\text{CO}_2] \text{ or } [\text{HCO}_3^-] = k_1 / f_m \cdot [\text{CO}_2] / [\text{H}^+] = k_1^* \cdot [\text{CO}_2] / (\text{H}^+) \quad (4.23)$$

Where:

- [X] = activity of X in mol.l<sup>-1</sup>  
 $k_1$  = thermodynamic constant of the CO<sub>2</sub> dissociation = 4.45·10<sup>-7</sup> (at 20°C)  
 $k_1^*$  = “real” dissociation constant of the CO<sub>2</sub> dissociation (on molar base)  
 $f_m$  = activity coefficient for a monovalent ion in the mixed liquor

Similarly one has:

$$k_2 = [\text{CO}_3^{2-}] \cdot [\text{H}^+] / [\text{HCO}_3^-] \text{ or}$$

$$[\text{CO}_3^{2-}] = k_2 \cdot (f_m / f_d) \cdot [\text{HCO}_3^-] / (\text{H}^+) = k_1^* \cdot k_2^* \cdot [\text{CO}_2] / (\text{H}^+)^2 \quad (4.24)$$

$$k_w = [\text{OH}^-] \cdot [\text{H}^+] \text{ or } [\text{OH}^-] = (k_w / f_m) / [\text{H}^+] = k_w^* / [\text{H}^+] \quad (4.25)$$

Where:

- $k_2$  = thermodynamic constant for bicarbonate dissociation = 4.69·10<sup>-11</sup> at 20°C  
 $k_w$  = thermodynamic constant for the dissociation of water = 10<sup>-14</sup> at 20°C  
 $f_d$  = activity for a bivalent ion

Finally by substituting Eqs. (4.23, 4.24 and 4.25) in Eq. (4.19) the following expression is obtained:

$$\text{Alk} = [\text{CO}_2] \cdot (k_1^* / [\text{H}^+] + 2 \cdot k_1^* \cdot k_2^* / [\text{H}^+]^2) + k_w^* / [\text{H}^+] - [\text{H}^+] \quad (4.26)$$

Knowing that pH = -log[H<sup>+</sup>] one has [H<sup>+</sup>] = 10<sup>-pH</sup> and

$$\text{Alk} = [\text{CO}_2] \cdot 10^{(\text{pH}-\text{pk}1^*)} \cdot (1 + 2 \cdot 10^{(\text{pH}-\text{pk}2^*)}) + 10^{(\text{pH}-\text{pk}w^*)} - 10^{-\text{pH}}$$

From Eq. (4.26), the pH can be calculated for any alkalinity value if the dissolved carbon dioxide concentration is known. This concentration depends on the production rate of this gas from the oxidation of organic matter and the removal efficiency from the liquid phase caused by the stripping effect of the aeration system.

In Fig. 4.5 pH curves as a function of alkalinity have been drawn for CO<sub>2</sub> concentrations ranging from 0.5 mg CO<sub>2</sub>.l<sup>-1</sup> (the saturation concentration at 20°C) to 10 mg CO<sub>2</sub>.l<sup>-1</sup> (i.e. 20 times super-saturated). To construct the diagram, a temperature of 20°C and activity coefficients  $f_m = 0.90$  and  $f_d = 0.67$  were assumed. These values correspond to a ionic force of 0.01 as calculated from the Debye-Hückel theory, as shown by Loewenthal et al, 1976 and are fairly typical for sewage. Fig. 4.5 shows that for alkalinities greater than 35 ppm CaCO<sub>3</sub>, the pH does not vary significantly when alkalinity changes.

For example, an alkalinity increase from 35 to 500 ppm results in an increase of the pH value of less than one unit. In contrast, for alkalinities smaller than 35 ppm, pH depends strongly on the alkalinity value. An alkalinity decrease from 35 to 0 ppm causes the pH to drop from the neutral range to a value of approximately 4.2. A low pH value affects the activity of micro-organisms. In particular the activity of Nitrosomonas and Nitrobacter, both active in the nitrification process, has been shown to decrease at low pH values. In Section 4.2.1 it will be shown that below a pH of 6 the nitrification activity virtually ceases. Hence to ensure stable and efficient nitrification, it is necessary that the alkalinity is maintained at a value larger than 35 ppm CaCO<sub>3</sub>, so that approximately neutral pH is guaranteed.

It is interesting to note that Haug and McCarty (1971) on the basis of an experimental investigation, established the same minimum alkalinity value as the one calculated from theory above. Now it is possible to estimate the minimum influent alkalinity to ensure a stable and neutral pH value in an activated sludge process:

$$\Delta \text{Alk}_t = \text{Alk}_e - \text{Alk}_i = 35 - \text{Alk}_i = 3.57 \cdot (\Delta N_a - \Delta N_n)$$

$$\text{Or approximated: } \text{Alk}_i > 3.57 \cdot (\Delta N_n - \Delta N_a + 10) \quad (4.27)$$

$\text{Alk}_i$  = influent alkalinity (mg CaCO<sub>3</sub>·l<sup>-1</sup>)

$\text{Alk}_e$  = effluent alkalinity (mg CaCO<sub>3</sub>·l<sup>-1</sup>)

In practice the neutral alkalinity of waste waters may be less than the value required to maintain a stable pH in the activated sludge process. This is a particular risk when nitrification without subsequent denitrification occurs in the process. In such cases it is necessary to increase the influent alkalinity, which is usually done by lime addition.

Without the addition of alkalinity, the behaviour of the activated sludge process will be irregular; there will be periods with nitrification and the consequential decrease of alkalinity and pH, until a pH value is established that is inhibitory for nitrification. When nitrification ceases, alkalinity automatically increases and pH rises, so that once again favourable conditions for nitrification are established and a new cycle of instability is initiated. If denitrification is included as a treatment step, the decrease of alkalinity will be smaller and often there will be no need for lime addition, because the denitrification process produces alkalinity.