



# INFLUENCE OF THE DIGESTED COD CONCENTRATION ON THE ALKALINITY REQUIREMENT IN ANAEROBIC DIGESTERS

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## ABSTRACT

pH value and stability in anaerobic digesters are governed by the carbonic system. An expression is derived to determine the alkalinity requirement for maintaining a desired pH value in an anaerobic digester. The requirement is calculated from stoichiometric relationships and depends on measurable parameters of the influent (notably concentration of digestible material, influent VFA, alkalinity, acidity and organic nitrogen concentration) and operational conditions (temperature, recycle of effluent and/or biogas). The derived expression is applied to three cases of anaerobic digestion: dilute waste water (sewage), concentrated waste water (vinasse) and sludge. In each case it was calculated if the influent alkalinity was sufficient to maintain an adequate pH for digestion and when it was not, what was the alkalinity requirement to maintain the desired pH value. The calculated values of pH and alkalinity demand compared well with experimental data.

## KEYWORDS

Anaerobic digestion; pH stability; alkalinity; COD concentration.

## INTRODUCTION

Although usually several acid-base systems are present in anaerobic digesters, it has been well established that the carbonic system is by far the most important for the value and stability of pH (Capri and Marais, 1973; Li and Sutton 1983). This is due to the fact that the carbonic system has a high buffer capacity in the pH range that is required for methanogenesis ( $6.3 < \text{pH} < 7.8$  approximately) and because the carbonic system concentration is much greater than those of other acid base systems with a buffer capacity around the neutral pH value, unless one deals with very special waste waters with large concentrations of weak mineral acid-base systems or of unbiodegradable organic acid base systems. These exceptional cases will not be considered here.

The characteristics of many waste waters are such that a high buffer index near  $\text{pH}=7$  is obtained automatically, due to the dominating presence of the carbonic system. If this is not the case, a stable and neutral pH may be obtained by adding alkalinity to the influent or by subtracting acidity (carbon dioxide) from the digester. Acidity can be removed by recirculating the effluent or the biogas, after (partial) removal of  $\text{CO}_2$  from these flows.

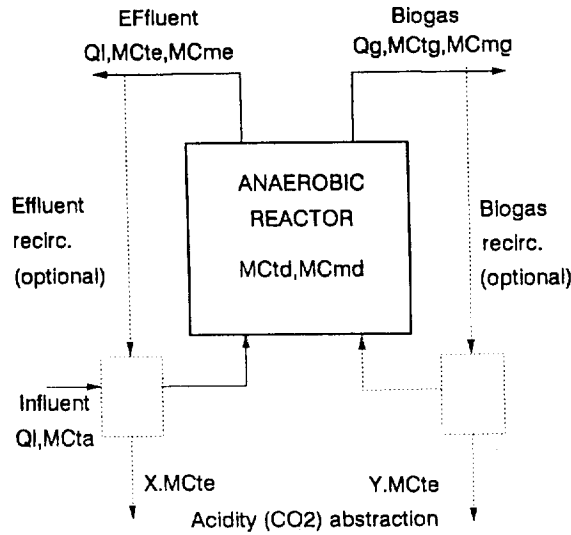


Fig. 1. Schematic representation of the mass flows of carbonic species and of methane in an anaerobic reactor (recirculations of effluent and biogas are optional).

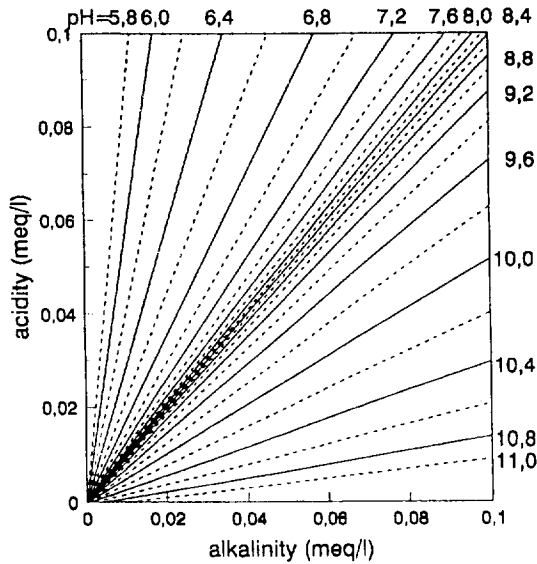


Fig. 2. Deffeyes diagram relating acidity and alkalinity at different pH values.

In this paper a method is described to assess if the characteristics of a particular waste water are adequate for direct anaerobic digestion and if not, how much alkalinity must be added and/or acidity subtracted to maintain a determined pH in the anaerobic reactor. The method is based on stoichiometric considerations with respect to the carbonic system. Only ionic equilibria and the gas-liquid equilibrium are considered.

## INFLUENCE OF ORGANIC MATERIAL DIGESTION ON pH AND ALKALINITY

In an anaerobic digester the most important question with respect to pH and pH stability is whether the alkalinity present in the sewage plus the alkalinity eventually formed in the digester are sufficient to maintain the pH in the reactor above a certain minimum value, that assures stable operation. In this section an equation will be derived to calculate the required alkalinity for any particular pH value as a function of the concentration of digested organic material. It is convenient to formulate expressions of the mass flows of inorganic carbon and of methane in the incoming and outgoing liquid flows, and in the gas flow, as well as the mass flows generated in an anaerobic reactor. With the aid of Fig 1 one has:

$$\begin{array}{ll}
 \text{(1) For carbonic species:} & \text{(2) For methane:} \\
 MC_{i_i} = Q_i C_{i_i} & MC_{m_d} = Q_i C_{m_d} \\
 MC_{i_e} = Q_i C_{i_e} & MC_{m_e} = Q_i C_{m_e} \\
 MC_{i_d} = Q_i C_{i_d} & MC_{m_g} = Q_g p_{CH_4} / RT \\
 MC_{i_g} = Q_g p_{CO_2} / RT &
 \end{array}$$

When biogas is considered to be a mixture of only methane and carbon dioxide, its composition can be expressed by means of the partial pressures of the components:

$$\begin{aligned}
 p_{CO_2} &= MC_{i_g} / (MC_{i_g} + MC_{m_g}) \\
 &= (MC_{i_i} + MC_{i_d} - MC_{i_e}) / (MC_{i_i} + MC_{i_d} + MC_{m_d} - MC_{i_e} - MC_{m_e}) \\
 &= (C_{i_i} + C_{i_d} - C_{i_e}) / (C_{i_i} + C_{i_d} + C_{m_d} - C_{i_e} - C_{m_e})
 \end{aligned} \quad (1)$$

where

MC refers to daily mass flow (mol/d)

$C_i$  = carbonic species concentration (mol C/l)

$C_m$  = methane concentration (mol CH<sub>4</sub>/l)

$Q_i$  = waste water flow (m<sup>3</sup>/d)

$Q_g$  = biogas flow (m<sup>3</sup>/d)

Indices "i" and "e" refer to influent and effluent respectively

Index "d" refers to production in the digester

Index "g" refers to the gas phase

Equation (1) can be used to evaluate whether the sum of the influent and generated (bicarbonate) alkalinities are sufficient to maintain a pH with a suitable value for anaerobic digestion. To do so, first the terms of Eq(1) must be expressed in such a way that their values can be calculated.

### (1) Influent carbonic species concentration, $C_{i_i}$ .

For specified values of the influent pH and alkalinity, the influent acidity may be read off from the Deffeyes diagram that links alkalinity acidity and pH, using the definitions of the former two (Loewenthal and Marais, 1986):

$$Alk = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] \quad (2)$$

$$Ac = 2[CO_2] + [HCO_3^-] + [H^+] - [OH^-] \quad (3)$$

By using the dissociation equation of the carbonic system and water and the definition of pH a linear relationship between alkalinity and acidity can be derived for any value of pH as shown in Fig. 2:

$$Alk = [Ac + 10^{(pH-pK_w)} - 10^{-pH}] \times [1 + 2 \times 10^{(pH-pK_2)}] / [1 + 2 \times 10^{(pK_1-pH)}] \quad (4)$$

When both alkalinity and acidity of the influent are known, the value of  $C_{i_i}$  can be calculated by adding the definition equations Eqs (2 and 3):

$$C_{ti} = (Alk_i + Ac_i)/2 \quad (5)$$

In Eqs (2 to 5) Alk and Ac refer exclusively to the carbonic system. If a titrimetric method is used to determine Alk or Ac and if the titration is influenced by other acid base systems, the appropriate correction must be made.

### (2) Concentrations of generated CH<sub>4</sub> and CO<sub>2</sub>.

The concentrations of produced methane and of inorganic carbon, C<sub>md</sub> and C<sub>id</sub> respectively, depend upon the concentration and the composition of the organic material. The methane production can be estimated from the concentration of digested COD: stoichiometrically 1 g or 1/16 mol CH<sub>4</sub> is formed when 4 g of COD are digested. Hence there is a proportionality of 1/64 mol CH<sub>4</sub> produced per g COD digested. The production of CO<sub>2</sub> depends not only on the concentration of digested COD, but also on the composition of the organic material that is digested. For carbohydrates, the molar CO<sub>2</sub> production is equal to the molar CH<sub>4</sub> production and this proportion is also true in good approximation for protein digestion. In the case of fat digestion the proportion of CO<sub>2</sub> is lower than CH<sub>4</sub> production. Thus it is a conservative estimate, if it is assumed that the CO<sub>2</sub> production is equal to the CH<sub>4</sub> production and that both amount to 1/64 mol/g digested COD :

$$C_{id} = C_{md} = COD_d/64 \quad (6)$$

### (3) Alkalinity change in the reactor.

Alkalinity changes in the reactor are brought about basically by two processes: ammonification and VFA removal.

#### (a) Ammonification

If the effluent ammonia concentration is higher than the influent concentration, the difference is due to ammonification of organic nitrogen. This process produces alkalinity as can be seen from the reaction equation:



From the reaction equation it can be noted that ammonification is essentially a hydrolysis reaction. The conversion of 1 "mol" TKN (14 gN) leads to the creation of 1 equivalent of alkalinity, so the alkalinity production from ammonification is equal to 1/14 = 0.071 meq/mgN.

#### (b) Change of the VFA concentration

A second source of alkalinity production in the reactor is the digestion of VFA. Provided the concentration of VFA in the influent is higher than in the effluent, there will be an increase of (bicarbonate) alkalinity in the reactor, equal to the net decrease of the VFA concentration. Clearly, if there is VFA production in the digester (which may occur when methanogenesis is not efficient), there will be a decrease of the alkalinity corresponding to the increase of the VFA concentration. If no other reactions with alkalinity consumption or production occur, the effluent alkalinity can be estimated from the influent alkalinity and the changes in VFA and NH<sub>4</sub><sup>+</sup> concentrations as:

$$Alk_e = Alk_i + VFA_i - VFA_e + (NH_4^+_e - NH_4^+_i)0.071 \quad (8)$$

where Alk and VFA are expressed in meq/l and NH<sub>4</sub><sup>+</sup> in mgN/l.<sup>1</sup>

<sup>1</sup>In Eq(8) it is assumed that the pH of the influent and of the effluent are significantly greater than 4.7 (the pK value of acetic acid), so that the volatile acids are largely dissociated.

#### (4) Concentration of carbonic species in the effluent.

The concentration of carbonic species can be linked to the bicarbonate concentration and hence to alkalinity in the effluent. If the effluent pH is near the neutral value, then the carbonate concentration in the effluent will be low and the concentration of carbonic species can be expressed as:

$$C_{te} = [\text{CO}_2] + [\text{HCO}_3^-] \\ = [\text{HCO}_3^-](1 + [\text{H}^+]/K_1) \quad (9)$$

At relevant pH values for anaerobic digestion the concentrations of  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$  and  $\text{H}^+$  are all much smaller than  $\text{HCO}_3^-$ , so that, to good approximation, alkalinity equals the bicarbonate concentration:

$$C_{te} = \text{Alk}_e(1 + 10^{(\text{pK}_1 - \text{pH})}) \\ = \text{Alk}_e(1 + f_e) \quad (9a)$$

where

$$f_e = 10^{(\text{pK}_1 - \text{pH})} \quad (10)$$

#### (5) Dissolved methane concentration, $C_{me}$ .

The concentration of methane dissolved in the effluent will obey Henry's law and therefore it will depend on the  $\text{CH}_4$  partial pressure and on the value of Henry's constant for methane. The solubility of methane at a partial pressure of 1 atm. is about 1 mmol/l in the range of temperatures from 20 to 35°C (Perry, 1963). This means that the dissolved methane represents at its maximum (i.e. when the methane partial pressure approaches 1 atm) a digested COD concentration of 64 mg/l (viz. the digestion of 64 mg COD generates 1 mmol of  $\text{CH}_4$ ). Thus, the dissolved methane will only be a significant fraction of the COD if the digested COD concentration is low (i.e. not very much greater than 64 mg/l). In that case the dissolved methane concentration can be taken as 1 mmol/l. If the digested COD concentration is high, the mass flow of dissolved methane is insignificant relative to the methane mass flow in the gas phase. Hence, in any case only a small error is made, when  $C_{me}$  is equalled to 1 mmol.l<sup>-1</sup>

Taking the above into consideration, Eq(1) can be rewritten as:

$$p_{\text{CO}_2} = (C_{\text{H}} + \text{COD}_d/64 - \text{Alk}_e(1 + f_e)) / (C_{\text{H}} + \text{COD}_d/32 - 0.001 - \text{Alk}_e(1 + f_e)) \quad (11)$$

On the other hand the  $\text{CO}_2$  partial pressure can also be expressed by Henry's law as:

$$p_{\text{CO}_2} = [\text{CO}_2]/K_{\text{H}} = [\text{HCO}_3^-][\text{H}^+]/(K_1 K_{\text{H}}) \\ = \text{Alk}_e f_e / K_{\text{H}} \quad (12)$$

where

$$K_{\text{H}} = \text{Henry's constant for carbon dioxide in water} \\ (\text{pK}_{\text{H}} = 1.12 + 0.0138t \text{ for } 0 < t < 35^\circ\text{C, Loewenthal and Marais, 1986})$$

Equations (11 and 12) form the basis for calculations to determine if the alkalinity present in a particular waste water plus the alkalinity formed in an anaerobic digester will be sufficient to maintain an adequate pH and, if not, what is the alkalinity demand to maintain a certain desired pH.

#### Estimate of pH without alkalinity addition

If the alkalinity in the system is sufficient, a pH value in the adequate range for anaerobic digestion will be established. The value of this pH can be calculated by equating Eqs (11 and 12). The solution of the quadratic expression, implicit after equating Eqs (11 and 12) is given by:

$$f_e = (b - \sqrt{b^2 - 4c}) * 0.5 \tag{13}$$

where:

$$b = (K_H + C_{ii} + C_{td} + C_{md} - C_{me} - Alk_e) / Alk_e$$

$$c = K_H (C_{ii} + C_{td} - Alk_e) / Alk_e^2$$

(a = 1)

Having determined the factor  $f_e$ , the effluent pH can easily be calculated:

$$f_e = 10^{(pK_1 - pH)}$$

or

$$pH_{eff} = pK_1 - \log f_e \tag{14}$$

Estimate of required alkalinity addition

The validity of Eqs (11) and (12) to calculate pH is limited by the fact that it is presupposed that methanogenesis will occur. Of course, when the calculated pH is low (for example below 6.3) this presupposition is not valid. In that case an alternative approach must be made: The required alkalinity to maintain some desired pH value must be calculated. The alkalinity demand for anaerobic digestion of a waste water can be determined when the minimum required operational pH is specified.

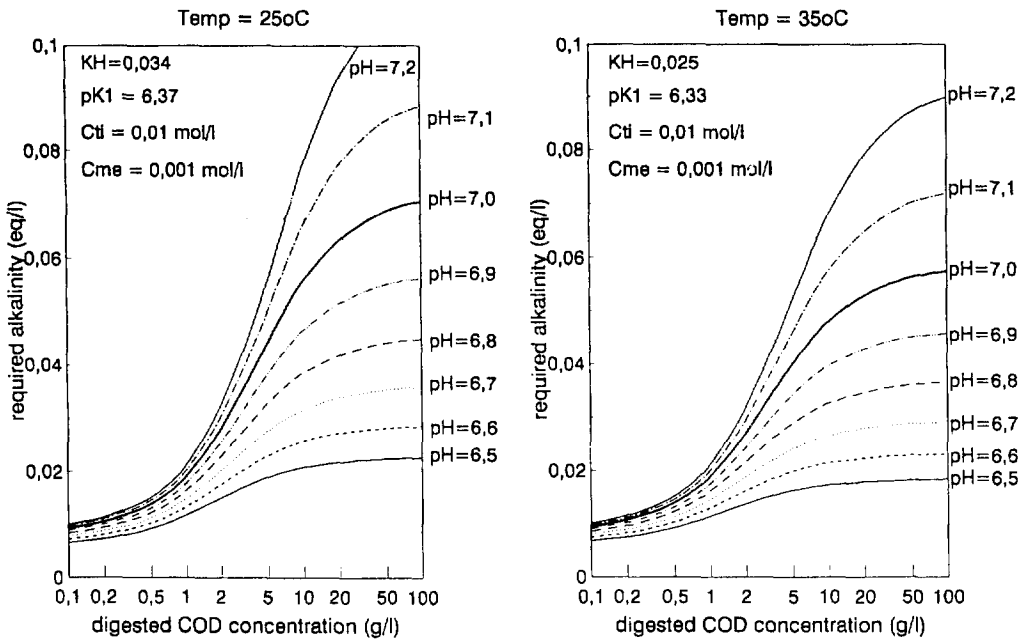


Fig. 3. Required alkalinity in an anaerobic digester as a function of the digested COD concentration for different pH values in the digester (and effluent) and for temperatures of 25 (3a, left) and 35 °C(3b, right).

In that case Eqs(11 and 12) can be rewritten as:

$$P_{CO_2} = (C_{\bar{u}} + C_{\bar{td}} - Alk_r(1+f_r)) / (C_{\bar{u}} + 2C_{\bar{td}} - C_{\bar{ml}} - Alk_r(1+f_r)) \quad (15)$$

and

$$P_{CO_2} = [CO_2] / K_H = [HCO_3^-][H^+] / (K_1 K_H) = Alk_r f_r / K_H \quad (16)$$

where

$pH_r$  = required pH value for efficient methanogenesis

$f_r = 10^{(pK_1 - pH_r)}$

$Alk_r$  = required alkalinity to maintain  $pH_r$

The value of  $pH_r$  is set at a determined value, for example  $pH_r = 7.0$ . The required alkalinity can be determined from Eqs (15) and (16) by solving the implicit quadratic expression after equating the two equations:

$$Alk_r = 0.5(b \pm \sqrt{b^2 - 4ac}) / a \quad (17)$$

where

$a = (1+f_r) \cdot f_r$

$b = (C_{\bar{u}} + 2C_{\bar{td}} - C_{\bar{ml}}) f_r + k_H(1+f_r)$

$c = k_H(C_{\bar{u}} + C_{\bar{td}})$

The result of Eq(17) is the required alkalinity to maintain the pH value that has been assumed ( $pH_r$ ). If the real alkalinity is smaller than the required value, the difference must be added to the influent. Of course if the alkalinity is higher than the desired pH, the actual pH will be higher than the chosen  $pH_r$  value and may be calculated from Eq(14). Figure 3a and b show the required alkalinity as a function of the digested COD concentration for different pH values in the digester at 25 and at 35°C. To construct the diagrams an influent carbonic species concentration of 10 mmol.l<sup>-1</sup> has been assumed.

### Influence of effluent or biogas recycle

If the operational pH of the anaerobic digester is too low for stable digestion, alkalinity addition is not the only alternative: acidity may be removed by CO<sub>2</sub> subtraction from the liquid or from the gas phase by recirculating effluent or biogas respectively as indicated in Fig 1. Carbon dioxide will desorb from the effluent when this is placed in contact with the atmosphere, but acidity removal by effluent recirculation becomes particularly efficient when it is mixed with a low influent pH. In this case the effluent bicarbonate will be transformed into CO<sub>2</sub> and most of the carbonic species concentration will desorb from the supersaturated mixture. CO<sub>2</sub> can also be absorbed from the biogas by contact with an alkaline solution, so that (bi)carbonate is formed. It can be demonstrated that normally it is more economical to recirculate effluent than biogas, by considering that the gas phase has a much lower concentration of carbonic species than the effluent, whereas the pumping costs per unit volume are in principle the same for both recirculations (the same head is required). Thus normally the effluent will be recirculated.

If it is assumed that the removed carbonic species fluxes due to effluent recirculation and biogas recirculation are a factor X and Y respectively of the flux discharged in the effluent (and that no methane is lost in the recycles), Eqs (15) and (16) may be rewritten to calculate pH and required alkalinity for a system with effluent and biogas recirculations. The effect of recirculation is equivalent to a decrease of Henry's constant by a factor (1+X+Y) i.e. the apparent Henry constant may be written as:

$$K_H' = K_H / (1+X+Y) \quad (18)$$

where

$K_H'$  = apparent Henry constant in a digester with recirculation

$X$  = ratio of the carbonic species flux desorbed from recirculated effluent to the carbonic species flux discharged in the effluent

$Y$  = ratio of carbonic species flux absorbed from recirculated biogas to the carbonic species flux discharged in the effluent

As an example in Fig 4 the required alkalinity for a waste water with a digestible influent COD of 32 g/l and zero influent alkalinity and carbonic species is plotted as a function of the combined recycle ratio ( $X+Y$ ).

## APPLICATIONS OF THE THEORY

### 1. Sewage digestion

In Fig. 5 the value of pH is plotted as a function of the digestible COD concentration in sewage both for a relatively high influent alkalinity of 500 mg.l<sup>-1</sup> and pH=7.5 and a low alkalinity 300 ppm CaCO<sub>3</sub> and pH =7.0. It was further assumed that there is an alkalinity production of 3 meq.g<sup>-1</sup> influent COD due to ammonification. The influent VFA concentration was estimated at 3 meq/gCOD or 180 mgHAc/gCOD (as 1 mgHAc has a COD of 1.067mg, this means that a fraction of 180x1.067 mgCOD per g COD i.e. 20% of the influent COD enters the digester already acidified). The relationship is shown plotted for methanogenic digestion efficiencies of 100, 60 and 20 per cent (in the digestion process acid fermentation is assumed to be 100 per cent efficient and to produce only acetic acid). It can be seen from Fig 5 that the pH only becomes too low for high rate methanogenesis (<6.3), when there is a combination of unfavourable factors: high concentration of digestible organic material, low influent alkalinity and low methanogenic fermentation efficiency. Hence it is possible that souring of sewage occurs and this can indeed be observed in sewer system with a long retention time (septic sewage); in that case the retention time in the sewerage system may be sufficient to develop the relatively fast growing acid fermentation population but not the methanogens. In anaerobic treatment systems with a low methanogenic efficiency such as anaerobic ponds, souring may also occur, particularly if there is a sudden increase of the organic load. In modern anaerobic waste water treatment systems generally methanogenic fermentation efficiency is well above 60 per cent and pH is not lowered significantly even when the influent alkalinity is low and the digestible COD concentration is high. Thus in none of the full scale and demonstration scale upflow anaerobic sludge blanket (UASB) reactors has souring been a problem, not even during start-up, when the methanogenic population is still small. (Haskoning, 1989; Draaijer *et al.*, 1991; Schellinkhout and Collazos, 1991; Vieira and Souza, 1986; Van Haandel *et al.*, 1992)

### 2. Vinasse treatment

Vinasse is the waste water from the bottom of an alcohol distillation tower. In order to suppress the organisms competing with alcohol fermenting yeasts the pH is lowered by H<sub>2</sub>SO<sub>4</sub> addition, so that the pH of the waste is very low. Table 1 gives the typical waste composition at the Sao Luiz Distillery at Maraiial in Brazil. From the pH and VFA concentration it can be noted that the vinasse is equivalent to a 6 g/l VFA or 0.1 N HAc (pK=4.7) with an additional organic material concentration of 26 g.l<sup>-1</sup> and no carbonic species. At the distillery the vinasse is digested anaerobically in UASB reactors. Initially alkalinity was added in the form of caustic soda (NaOH). The required dosage for a stable pH of 7.0 was 3 g/l or 0.075 eq/l, which corresponds well to the calculated value of 0.072 mol/l (See Fig. 5). To reduce costs, caustic soda was substituted by lime (80 per cent purity) and operation continued with a dosage of 2.5 gCaO<sub>80%</sub>/l, again corresponding to the calculated requirement. However a gradual decline of the removal efficiency indicated a reduction of the sludge activity and when tests were carried out it was established that the mineral fraction of the sludge had increased by a factor of 3 from 8 to 25 per cent.



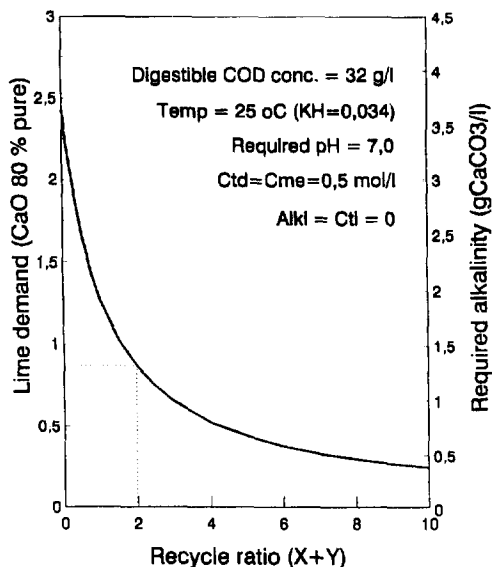


Fig 4:  
Required alkalinity for vinasse treatment  
as a function of the recirculation rate of  
effluent and/or biogas

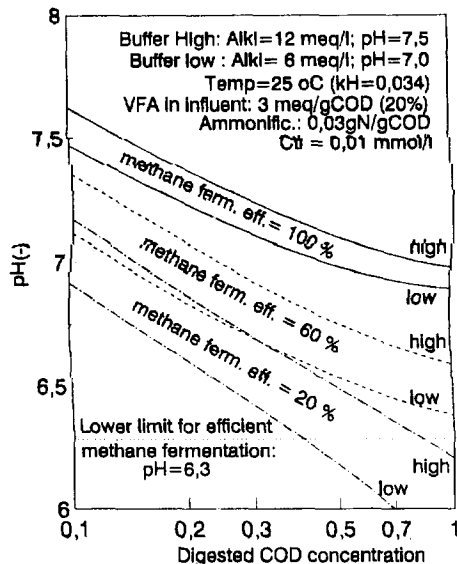


Fig 5:  
pH as a function of the digestible COD  
concentration for different influent  
alkalinities and methanogenic  
fermentation efficiencies

TABLE 1. Average Vinasse Characteristics after Settling in an Accumulation Lagoon (Influent) and after Anaerobic Digestion in a UASB Reactor with a Retention Time of 1.5 Days

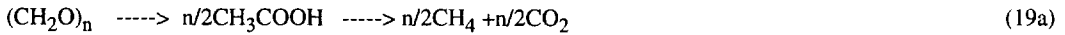
Parameter	Unit	UASB Influent	UASB Effluent
COD	mg/l	32.000	880
BOD	mg/l	18.000	245
TSS	mg/l	8.000	650
pH	-	3,0	7,0
Alkalinity	eq/l	0	0,072
VFA	mg/l HAc	6.000	160
Ammonia	mgN/l	470	380
Phosphate	mgP/l	150	115
Temperature	°C	25	25

Apparently the high lime dosage led to  $\text{CaCO}_3$  precipitation on the flocs, thus reducing the accessibility of substrate for the bacteria. It was decided introduce a 2:1 recycle of the effluent and mix it with the influent in a tank with a 15 min retention time. The pH in the tank was 4.5 to 5 and the lime demand decreased to 1.1 g/l CaO, slightly more than the calculated value of 0.85 to the calculated value (see Fig. 5). Possibly the difference can be attributed to incomplete  $\text{CO}_2$  stripping in the mixing tank: lime is added immediately before the mixture enters into the digester and any  $\text{CO}_2$  present would be converted into bicarbonate. Although the calculated ionic product remained well above the thermodynamical solubility constant of  $\text{CaCO}_3$  ( $\text{pK}=8.3$ ; Truesdale and Jones, 1973), the mineral fraction of the sludge gradually decreased and digestion efficiency increased. It is concluded that  $\text{CaCO}_3$  precipitation is no longer a problem, possibly due to the shielding effect of the phosphate, present in the digester (Capri and Marais 1973). In the case of vinasse treatment, effluent recirculation proved to be an excellent provision that not only reduced the lime demand by more than half, but also led to an improvement of the plant performance.

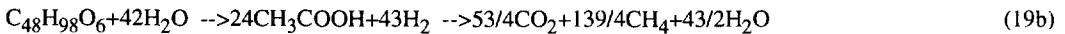
### 3. Sludge digestion

Primary sludge is generated by settling of suspended solids in waste waters and in most cases is composed mainly of carbohydrates (general formula  $(\text{CH}_2\text{O})_n$ ) and lipids (for example glycerine palmitate,  $\text{C}_{48}\text{H}_{98}\text{O}_6$ ). Secondary sludge is generated in waste treatment plants and has a large proportion of bacterial mass, i.e. proteic matter. McCarty (1964) proposed a structural formula of  $\text{C}_5\text{H}_7\text{O}_2\text{N}$  for bacterial mass. The acid and methanogenic fermentations of the three main organic materials can be expressed as:

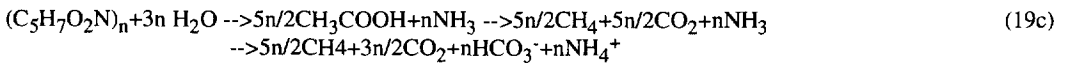
(a) carbohydrates:



(b) lipids:



(c) proteins:



From Eqs (19a,b and c) it can be seen that alkalinity is produced in the case of protein digestion: the ammonification of organic nitrogen leads to an alkalinity increase of 1 eq/molN. In the case of pure bacterial mass there is 1 mol of organic N in 113 g (molecular weight of  $\text{C}_5\text{H}_7\text{O}_2\text{N}$ ) of volatile sludge mass, so that there is an alkalinity increase of  $1/113 = 0.0088$  eq per gram VSS digested. As 1 gVSS pure bacterial mass has a stoichiometric COD of 1.42 g, an alkalinity increase of  $0.0088/1.42 = 0.0062$  eq/gCOD is calculated. From Eq (19c) a nitrogen mass fraction of  $14/113$  mgN/mgVSS or 12.4 per cent is calculated for pure proteins. The mass fraction in sludges is lower than the figure calculated for pure proteins: Typical nitrogen mass fractions of 10 per cent and 4 per cent of the VSS mass or 7 and 2.8 of the COD mass (COD/VSS ratio = 1.42, McCarty, 1964) have been found for secondary sludges (waste activated sludge, Water Research Commission, 1984) and primary sludges (USEPA, 1979) respectively. Thus, it can be assumed that the alkalinity increases in secondary and primary sludge are a fraction of  $10/12.4$  and  $4/12.4$  of the calculated value of 0.0062 eq/gCOD, so that one can estimate increases of 0.0050 eq/gCOD for secondary sludge and 0.0020 eq/gCOD for primary sludge. In Fig. 6a and b the alkalinities after digestion of secondary sludge (0.067gN/gCOD) and primary sludge (0.027gN/gCOD) have been plotted as a function of the digested COD concentration (an initial alkalinity of 0.01 eq/l and a temperature of 25°C have been assumed). In the same diagram curves have been plotted, linking the required alkalinity to the digested COD concentration for several pH values. It can be noted that the alkalinity release increases more than the required alkalinity so that at high concentrations the actual alkalinity is amply sufficient to maintain a stable pH: in the case of primary sludge digestion at 25°C the pH is above 7.0, when the digested COD concentration is above about 24 gCOD/l, which in practice will usually be the case.

Up to now it has been assumed tacitly that methanogenic digestion takes place at 100 per cent efficiency, which in practice will not be the case. If part of the organic material in the sludge is only acidified but not methanised, along with ammonification there will be a production of VFA. In that case the alkalinity change can be expressed with the aid of Eq(8) as:

$$\Delta\text{Alk} = 0.071(\text{NH}_4^+_{\text{e}} - \text{NH}_4^+_{\text{i}}) + \text{Alk}_i + \text{VFA}_i - \text{VFA}_e \quad (8)$$

$$= [0.071f_n - (1-E_m)/(60 \times 1.067)]\Delta\text{COD}$$

Where:

- $\Delta\text{Alk}$  = alkalinity change in the digester  
 $\Delta\text{COD}$  = COD concentration of lysed (acidified) organic material  
 $E_m$  = methanogenic fermentation efficiency  
 $f_n$  = fraction of N in the acidified material (mgN/mgCOD)

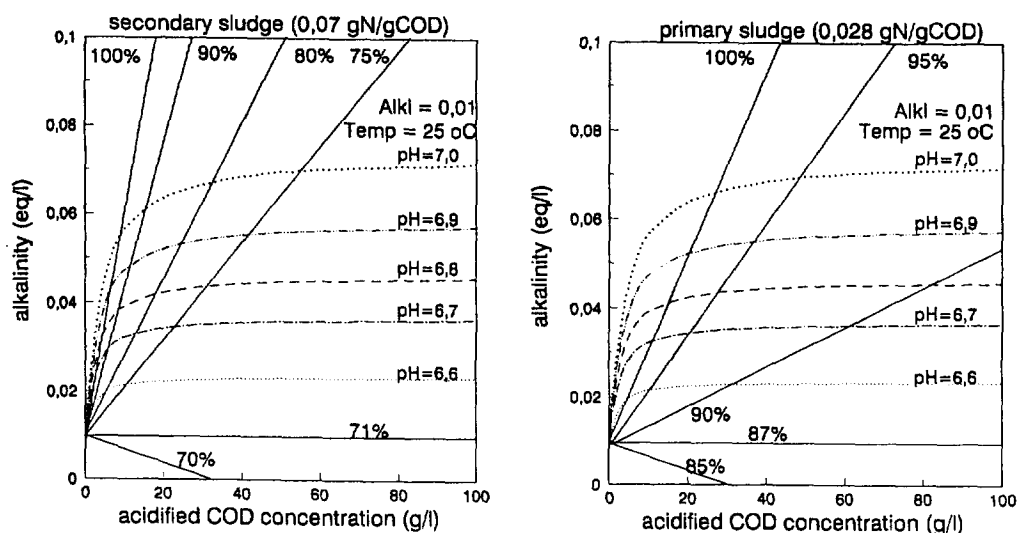


Fig. 6. Alkalinity release as a function of the digested concentration of primary and secondary sludges (nitrogen mass fractions of 0.028 and 0.07 mgN/mgCOD respectively) for different efficiencies of methanogenic fermentation. The required alkalinities for different pH values are also indicated.

Depending on the TKN/COD ratio of the sludge and the efficiency of the methanogenic bacteria in removing the VFA, the produced alkalinity may or may not be sufficient to maintain a certain desired pH in the sludge digester. In Fig 6 the alkalinity release in a sludge digester has been plotted as a function of the digested COD concentration for different efficiencies of the methanogenic fermentation both for secondary sludge (0.07 gN/gCOD) and primary sludge (0.028 gN/gCOD). The diagrams show that it is only possible to maintain a suitable pH value in the digester (pH around 7.0) when the methanogenic fermentation efficiency is high. The alkalinity does not increase for  $E_m$  values below 0.71 for secondary sludge and 0.87 for primary sludge. If the alkalinity does not increase the digester will probably fail because the influent alkalinity will typically be much lower than the value required for an adequate pH. However methanogenic fermentation efficiencies obtained in practice are normally higher than the minima calculated here: an effluent VFA concentration of more than 2 to 3 gHAc.l<sup>-1</sup> is atypically high and indicates operational problems, not necessarily related to pH.

## CONCLUSIONS

- The alkalinity requirement for stable anaerobic digestion can be calculated from stoichiometric considerations and depends on the influent characteristics, notably the digestible COD, VFA, influent carbonic species and organic nitrogen concentrations and the influent alkalinity and on the operational conditions (temperature).
- The alkalinity in raw municipal sewage is such that a stable pH in an anaerobic treatment unit can be maintained, unless the methanogenic fermentation efficiency is very low, the digestible material concentration is high and influent alkalinity is low.
- If the alkalinity of waste waters is insufficient to maintain a stable pH in an anaerobic digester, an alternative to alkalinity addition is removal of acidity by recirculation of the effluent. For effluent recirculation to be efficient it is necessary that CO<sub>2</sub> stripping occurs, which is achieved expeditiously when the recirculation flow is mixed with acid influent.
- CO<sub>2</sub> absorption from biogas and recirculation of the resulting methane is an alternative to effect acidity removal, but effluent recirculation is more attractive economically.

- In anaerobic sludge digesters the source of alkalinity is ammonification of the organic nitrogen. The released alkalinity is sufficient to maintain an adequate and stable pH if methanogenesis is efficient. The minimum methanogenic fermentation efficiency depends on the nitrogen mass fraction of the sludge to be digested.

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