Tema 9 – Procesos Aneróbicos
Anaerobic Procesos

CI7115 – Biotecnología Ambiental
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Descomposición anaeróbica de C orgánico

In the absence of oxygen, this is what occurs in soils, sediments, sludge, etc. to return organic matter to its simplest forms

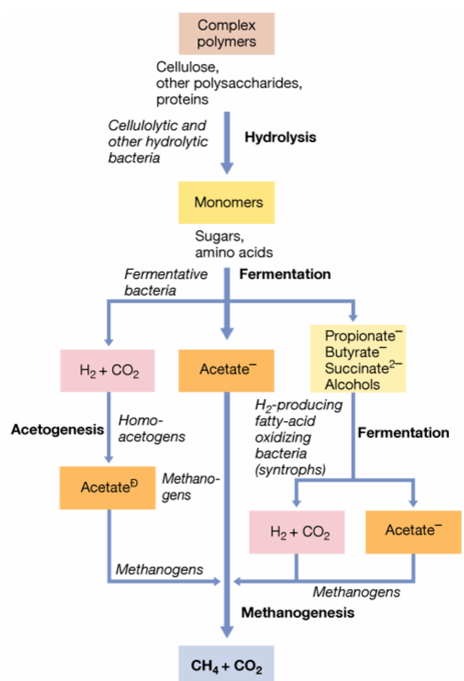

Figure 19.23. Anoxic decomposition. Shown is the overall process of anoxic decomposition, in which various groups of fermentative anaerobes cooperate in the conversion of complex organic materials ultimately to methane (CH4) and CO2.

Brock, 2000

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Flujo de C y e- en digestión anaeróbica

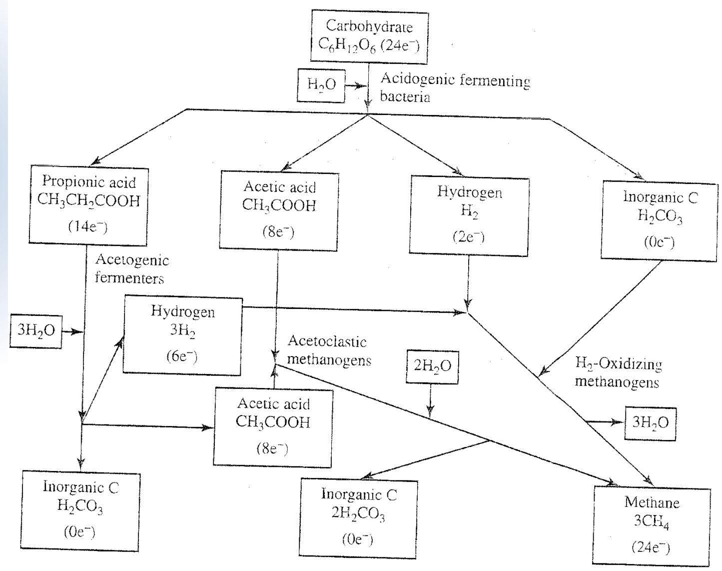
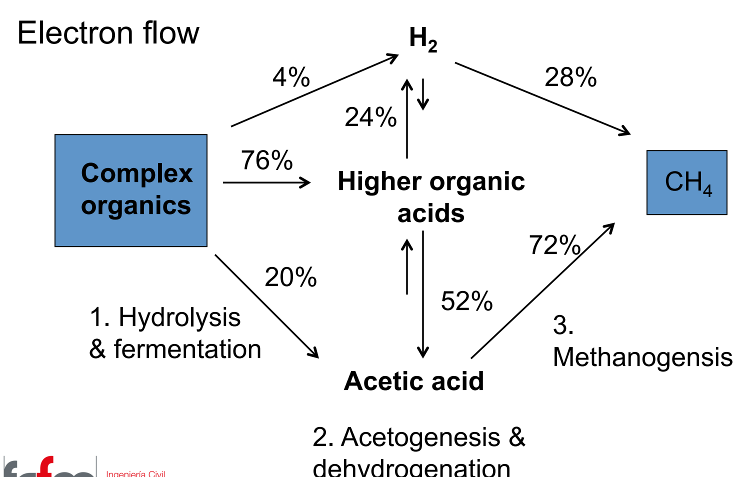


Figure 1.40 Flow of intermediate molecules in an anaerobic ecosystem that starts with carbohydrate, forms intermediate organic acids and H_2, and ultimately generates CH_4. The net reaction is $C_6H_{12}O_6 + 3\ H_2O \rightarrow 3\ CH_4 + 3\ H_2CO_3$, but four unique microbial groups are involved.

Fundamentos del proceso

I. Complex community ecology - multistage conversion of organic matter to methane.



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Fundamentos del proceso

II. Sources of methane:

- CO_2 reduction: $CO_2 + 4\ H_2 = CH_4 + 2H_2O$
  - *(Hydrogen oxidizers)*
- Acetic acid cleavage: $CH_3COOH = CH_4 + CO_2$
  - *(Aceticlastic methaogens, acetate utilizers)*

III. COD' to CH_4

(22.4 L) (64 g COD')

$CH_4 + 2O_2 = CO_2 + 2H_2O$

22.4 L÷ 64 g = 0.35 L CH_4/g COD' (@STP)

= **350 ml CH4/g COD' (@STP)**

= **0.35 m^3 CH_4/kg COD' (@STP)**

Fundamentos del proceso

IV. Effects of H_2 on reaction energetics:

TABLE 1

Conversion of ethanol to methane[a]

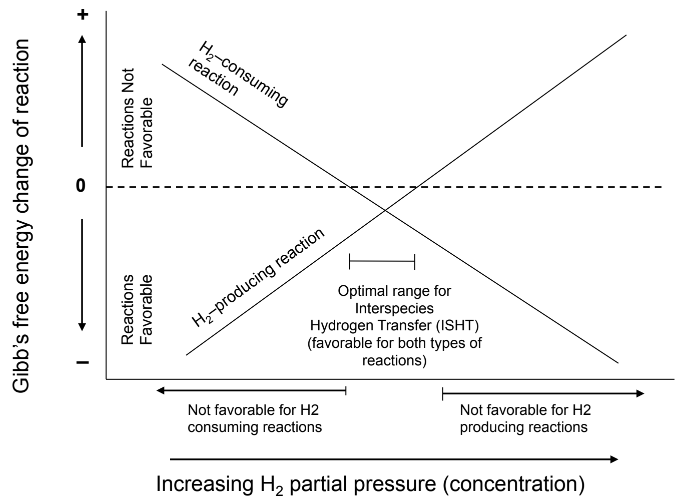
	$\Delta G^{o\prime}$ kJ
Ethanol	
$CH_3CH_2OH(aq) + H_2O(l) = CH_3COO^-(aq) + H^+(aq) + 2H_2(g)$	9.65
Hydrogen	
$2H_2(g) + 1/2CO_2(g) = 1/2CH_4(g) + H_2O(l)$	−65.37
Acetate	
$CH_3COO^-(aq) + H^+(aq) = CH_4(g) + CO_2(g)$	−35.83
Net	
$CH_3CH_2OH(aq) = 3/2CH_4(g) + 1/2CH_2(g)$	−91.55

[a]Thermodynamic values from Reference 4.

The first reaction cannot proceed unless the H_2-consuming organisms reduce the hydrogen partial pressure so that ΔG becomes negative

From McCarty and Smith (1986)

Interspecies Hydrogen Transfer



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Fundamentos del proceso

V. Nutrient requirements

NH_3-N - as needed
PO_4-P - as needed

See also Table 13.3 of textbook

	mg/L
KCl	50
$CaCl_2$	50
$MgSO_4.2H_2O$	300
$CoCl_2$	0.5
$FeCl_2$	10
$NiCl_2$	0.5

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Fundamentos del proceso

VI. pH and alkalinity requirements

- Normal range: pH 6.6-7.8

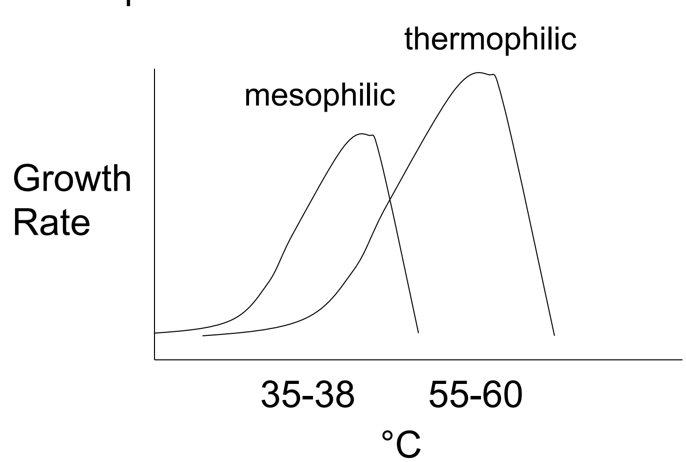
- To maintain pH, need 30-80 mM (1500-4000 mg/L as $CaCO_3$) alkalinity

  Alkalinity is typically the major operating expense (oxygen delivery and solids disposal are the major cost of aerobic systems)

- The type of alkalinity added can be important

Fundamentos del proceso

VII. Temperature



Cinética

- We design for the slowest growing organisms - most often the acetate utilizing methanogens. What does this mean about the choice of q_x^d?
- When the reaction rate is limited by acetate utilization, that step becomes an "obstruction" in the pathway. Volatile fatty acids (acetic acid, propionic acid, butyric acid) accumulate.
- To describe the resulting VFA concentration, a composite K value is used, called K_c [see equation in 13.38 in text].

Estoquiometría

<u>The entire microbial community participates in the overall reaction stoichiometry</u>

Use parameters for the entire community when calculating f_s, yield, or cell production rates.

Ejemplos

TABLE 2
Conversion of propionate and butyrate to methane[a]

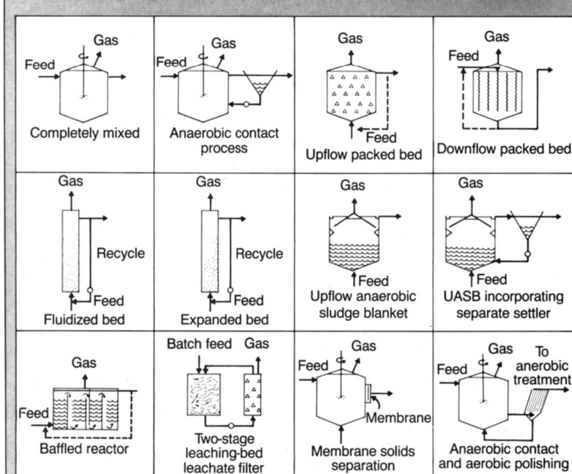
	$\Delta G^{o\prime}$ kJ
Propionate	
$CH_3CH_2COO^-(aq) + 2H_2O(l) = CH_3COO^-(aq) + 3H_2(g) + CO_2(g)$	71.67
Hydrogen	
$3H_2(g) + {}^3\!/_4CO_2(g) = {}^3\!/_4CH_4(g) + {}^3\!/_2H_2O(l)$	−98.06
Acetate	
$CH_3COO^-(aq) + H^+(aq) = CH_4(g) + CO_2(g)$	−35.83
Net	
$CH_3CH_2COO^-(aq) + H^+(aq) + {}^1\!/_2H_2O(l) = {}^7\!/_4CH_4(g)\ {}^5\!/_4CO_2(g)$	−62.22
Butyrate	
$CH_3CH_2CH_2COO^-(aq) + 2H_2O(l) = 2CH_3COO^-(aq) + 2H_2(g) + H^+(aq)$	48.30
Hydrogen	
$2H_2(g) + {}^1\!/_2CO_2(g) = {}^1\!/_2CH_4(g) + H_2O(l)$	−65.37
Acetate	
$2CH_3COO^-(aq) + H^+(aq) = 2CH_4(g) + 2\ CO_2(g)$	−71.66
Net	
$CH_3CH_2CH_2COO^-(aq) + H_2O(l) + H^+(aq) = {}^5\!/_2CH_4(g) + {}^3\!/_2CO_2(g)$	−88.73

[a]Thermodynamic values from Reference 4.

From McCarty and Smith (1986)

Configuraciones de reactor

FIGURE 4
Reactor configurations



Source: Reference 2. Adapted with permission from *Environmental Science & Technology* © 1983, American Chemical Society.

From McCarty and Smith (1986)

Digestores Anaeróbicos

Flared methane

Conventional digesters (floating top)

Egg-shaped digesters in Baltimore: designed to improve mixing and ease of solids removal (courtesy Sterling Fluid Systems)

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Fermentación de CH_4

<u>Natural Applications</u>

- Major end product of microbial decomposition of organic matter under anaerobic conditions.
- Main component of natural gas formed from decomposing vegetation in coniferous swamps.
- Produced in marshes and bogs
- Formed in the digestive track of ruminant animals and termites.

A fistulated cow

Fermentación de CH_4

Practical applications:

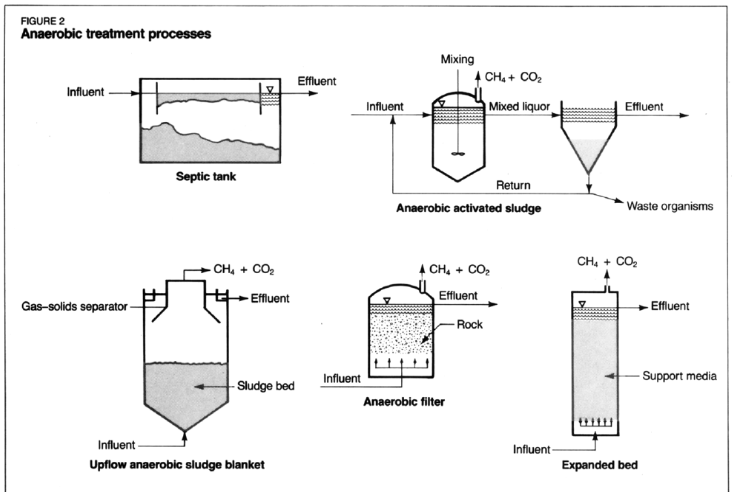
1) Stabilization of organic sludge from wastewater treatment
2) Energy production from farm residues
   - Household usage in China, Korea, India
   - Interest in large scale conversions in the United States
3) Treatment of high-strength industrial waste
4) Municipal solid waste: wet landfills and anaerobic composting
5) Direct treatment of sewage without primary settling.

Brazilian engineers (Foresti and coworkers) have recently demonstrated that upflow anaerobic sludge blanket reactors can achieve reliable sewage treatment at full scale (at least in warm climates).

Tratamiento anaeróbico para ARes doméstica

- Widely used in developed and developing nations (e.g. septic tank)
  - 24% of wastewater treatment in US in 1990 (EPA, 2002)
  - 30% of sanitation in Latin American countries is done using septic tanks and pit latrines (Noyola, 2007)
- Reduction of produced biomass (5% to 20% of aerobic process)
- Robust bioprocess
  - Reduced endogenous decay during starvation
  - Low cost and less maintenance requirement (Chernicharo, 2006)
- Energy bio-generation ($12x10^6$ BTU per 1000 kg of COD treated)
  - At least 50% of biogas is CH_4
    - Cleanest combustible fossil fuel available
    - Heating, electricity generation and pneumatic applications
- May not reach acceptable quality level for immediate reuse

Tratamiento anaeróbico para ARes doméstica

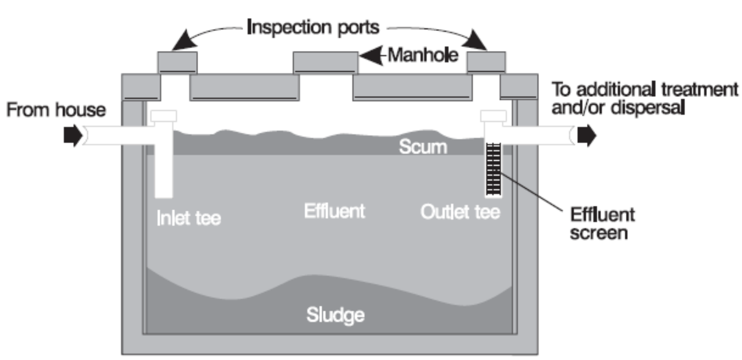


Source: Reference 8. Adapted with permission from *Proceedings of the Seminar/Workshop: Anaerobic Treatment of Sewage* © 1985, University of Massachusetts.

From William Jewell (1987)

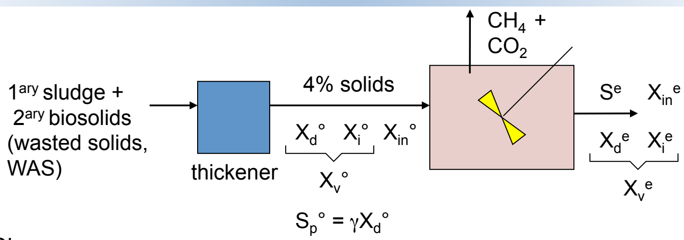
Tanques Sépticos

Typical single-compartment septic tank with at-grade inspection ports and effluent screen (EPA, 2002)



Source: NSFC, 2000.

Ejemplo: Anaerobic digestion of mixed primary and secondary suspended solids



Given:

Solids from primary and secondary treatment = 2,400 kg/d

Thickener yields 4% solids

Degradable suspended solids concentration after thickening = 20 g vss/L

γ = 1.5 g COD/g vss

T=35°C

Y_{comm}= 0.078 g vss/g COD

K_c = 2.2 g COD/L

b = 0.015 d^{-1}

SF = 10

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What is Q°?

$$Q^\circ = \frac{\text{solids for treatment}}{\text{solids concentration after thickening}} = \frac{2{,}400\ \text{kg/d}}{40\ \text{kg/m}^3} = 60\ \text{m}^3/\text{d}$$

What are θ_x and V?

$$\left(\theta_x^{min}\right)_{lim} = \left(Y\hat{q} - b\right)^{-1}_{slow-growers} = \left(Y\hat{q} - b\right)^{-1}_{\substack{\text{acetate-utilizing}\\ \text{methanogens}}}$$

For the acetate-utilizing methanogens:

$Y = 0.04$ g vss/g COD, $b = 0.015\ d^{-1}$, $\hat{q} = 6.7$ g COD/g vss-d

$$\left[\theta_x^{min}\right]_{lim} = \left((0.04)(6.7) - (0.015)\right)^{-1} = 4 \text{ days}$$

$$\theta_x^d = SF\left[\theta_x^{min}\right]_{lim} = (10)(4) = 40 \text{ days} = \theta \text{ (no recycle)}$$

$V = Q°\theta = 60(40) = 2400\ m^3$

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How much solids are destroyed?

$$f_s^o = (0.078 \text{ g vss/g COD})(1.42 \text{ g COD/g vss}) = 0.111$$

$$f_s = f_s^o \frac{\left(1 + 0.2b\theta_x^d\right)}{1 + b\theta_x^d} = 0.111 \frac{\left(1 + 0.2(0.015)(40)\right)}{1 + (0.015)(40)} = 0.0777$$

$$f_e = 1 - f_s = 1 - 0.0777 = 0.9223$$

COD consumption rate = $Q°(S_{eff}° - S^e)$

$S_p° = \gamma X_d° = (1.5)(20 \text{ g vss/L}) = 30$ g COD/L

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How much gas is produced?

Assume k_{hyd} = 0.3 d^{-1}

$$S^o_{eff} = S^o + \frac{k_{hyd}\theta_x S^o_p}{1 + k_{hyd}\theta_x} = 0 + \frac{(0.3)(40)(30)}{1 + (0.3)(40)} = 27.69\ g/L$$

$$S^e = \frac{K_c(1 + b\theta_x)}{\theta_x(Yq - b) - 1} = \frac{2.2\ g\ COD/L(1 + (0.015)(40))}{40((0.04)(6.7) - (0.015)) - 1} = 0.39\ g\ COD/L$$

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COD consumption rate = $Q^o(S_{eff}^o - S^e)$ = 60(27.69-0.39) = 1638 kg COD/d (to cells and methane)

Rate of conversion to cells = f_s (COD consumed) = (0.0777)(1638) = 127 kg COD/d

VSS formed = 127 kg COD/d ÷ 1.42 kg COD/kg vss = 89 kg vss/d formed

Net vss destroyed = X_d degraded - vss formed = 1638/1.5 – 89 = 1003 kg/d destroyed

Rate of COD conversion to methane = f_e (COD consumed) = (0.9223)(1638) = 1510 kg COD/d

Volume methane produced at STP = (1510 kg COD/d)(0.35 m^3/kg COD) = 528 m^3/d

Volume methane produced at 35°C = $(529\ m^3/d)\left[\frac{273 + 35}{273}\right] = 597\ m^3/d$

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COD Balance:

Biodegradable COD in: 60(30) = 1800 kg/d

Biodegradable COD out:
- Cells as COD: 127 kg/d
- VFAs as COD: 60(0.39) = 23 kg/d
- Methane as COD: 1510 kg/d
- Undegraded S_p: 60(30)- 60(27.69)
  = 1800-1661 = 139 kg/d

Total out = 127+23+1510 +139 = 1799 kg/d

(close enough)

% Reduction in Volatile Suspended Solids

Volatile suspended solids in: 60(20) = 1200 kg/d

Volatile suspended solids out:
- Cells: 89 kg/d
- Undegraded X_d = 139/1.5 = 90 kg/d

Net vss destroyed = in-out = 1200-90-89 = 1021 kg/d destroyed (close enough)

Percent reduction = (1021/1200) x 100 = 85%

Check with methane and COD data = 1510/1800 = 84% (close enough)

Control de pH

1. Microbial processes require specific pH ranges.
2. Many microbial process produce or consume alkalinity.

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Rango de pH óptimo para procesos biológicos

Organisms	Function	pH range
Nitrifiers	Oxidize ammonia	6-9
Denitrifiers	Reduce nitrate to N_2	6-9
Acidogens	Convert BOD_L to VFAs	6
Acetogens	Convert propionic acid and butyric acid to acetic acid	7 optimal
H_2-utilizing methanogens	Convert H_2 + CO_2 to methane	7 optimal
Acetoclastic methanogens	Convert acetic acid to methane	> 6.6 (7 optimal)
PAOs	Accumulate excess phosphorus	>7.2

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CO_2 accumulation in closed reactors causes pH change

Methane fermentation

- Sufficient buffer must be present for CO_2 and for potential accumulation of volatile fatty acids
- pH of 6.6-7.8 is needed (Best at pH > 6.8)
- Bicarbonate buffering controls the pH
- % CO_2 in the gas controls CO_2 in solution
- Typical alkalinity requirement: 1500-4000 mg/L as $CaCO_3$

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Fuentes de bufer alcalino

Alkaline buffer (salt/base)	Dissolution and Neutralization reactions	How many kg of the buffer are equivalent to one kmol of alkalinity?	Comments	1995 Cost($) per kmol Alkalinity
$CaCO_3$	$CaCO_3 + 2H^+ = Ca^{2+} + H_2CO_3$ $CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^-$	100 g of $CaCO_3$ neutralizes **2** moles of strong acid, 100 g of $CaCO_3$ reacts with CO_2 to make **2** moles of HCO_3^-. We have 100 ÷ 2 = 50 kg $CaCO_3$ per kmol of alkalinity.	Poor solubility restricts alkalinity to 1400-1500 mg/L as $CaCO_3$	Not available (cheap)
Na_2CO_3	$Na_2CO_3 + 2H^+ = 2Na^+ + H_2CO_3$ $Na_2CO_3 + H_2O + CO_2 = 2Na^+ + 2HCO_3^-$	106 ÷ 2 = 53 kg	Na is inhibitory at 3,500 mg/L. Na deflocculates soil.	11.55
K_2CO_3	Like Na_2CO_3	136÷ 2 = 68 kg	K is inhibitory at > 2,500 mg/L.	Not available
$(NH_4)_2CO_3$	$(NH_4)_2CO_3 = 2NH_4^+ + CO_3^{2-}$ $CO_3^- + 2H^+ = H_2CO_3$	96 ÷ 2 = 48 kg		Not available
CaO (lime)	$CaO + 2H_2O = Ca(OH)_2$ $Ca(OH)_2 + 2H^+ = Ca^{2+} + 2H_2O$ $Ca(OH)_2 + 2CO_2 = Ca^{2+} + 2HCO_3^-$	56÷ 2 = 28 kg	Can cause severe scaling @ pH>6.8. Can create a vacuum in a closed system.	3.74
MgO	Like CaO	40 ÷ 2 = 20 kg	Low solubility reduces chance of pH overshoot.	7.71
$NaHCO_3$	$NaHCO_3 + H_2O = Na^+ + HCO_3^-$ $HCO_3^- + H^+ = H_2CO_3$	84 kg	Exactly the right form, but expensive.	36.89
NaOH	$NaOH + H^+ = Na^+ + H_2O$ $NaOH + CO_2 = Na^+ + HCO_3^-$	40 kg	Can create a vacuum in a closed system	35.20
KOH	Like NaOH	56 kg	Can create a vacuum in a closed system	Not available
NH_3	$NH_3 + H^+ = NH_4^+$ $NH_3 + CO_2 + H_2O = NH_4^+ + HCO_3^-$	17 kg	Can be toxic. Released as protein degrades.	Not available

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