

N in WASTEWATER

8-12 lb-N/year
per capita

DOMESTIC
WASTE

(~13 mg/L)
40%
Org-N

60%
NH₃ (~22 mg/L)

Tot-N
35 mg/L

CONVENTIONAL I^o + II^o TREATMENT
REMOVES ABOUT 25% OF N
REMAINDER IS ~ ALL NH₃
(~ 26 mg/L)

RECEIVING WATERS:

Organic N (also known as Total Kjeldahl Nitrogen: TKN)
INDICATOR OF ORGANIC
POLLUTION IN A RIVER

Tot-N_{org} < 1 mg-N/L TYPICAL STANDARD

AMMONIA - Toxic (as well as nutrient)

Tot-NH₃ < 1 mg-N/L for FISH protection

PRIMARY

MASS BALANCE

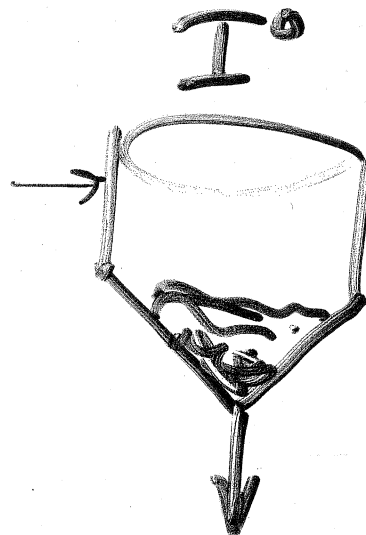
INPUT

$$N_{org} = 13 \text{ mg/L}$$

$$NH_3-N = 22 \text{ mg/L}$$

$$NO_3^- - N = 0 \text{ mg/L}$$

$$35$$



5 mg/L

(mg-N per
L w.w.
processed)

OUTPUT

$$N_{org} = 8 \text{ mg/L}$$

$$NH_3-N = 22 \text{ mg/L}$$

$$NO_3^- - N = 0 \text{ mg/L}$$

$$30$$

~15%

SECONDARY

WITH NO PLANNED ~~DE~~ NITRIFICATION

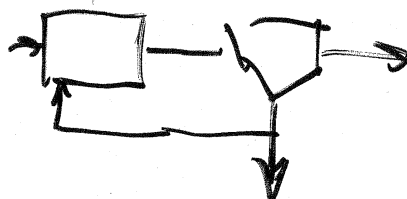
INPUT

$$N_{org} = 8$$

$$NH_3 = 22$$

$$NO_3 = 0$$

$$30$$



4 mg
PER L

-13% II°

-15% I°

~26% TOTAL REMOVAL

OUTPUT

$$N_{org} = 2 \text{ mg/L}$$

$$NH_3 = 24 \text{ mg/L}$$

$$NO_3 \approx 0$$

$$26$$

NITRIFICATION

- Conversion of NH_3 to nitrite & nitrate
 - NITRATE MUCH LESS TOXIC THAN NH_3
 - So, may want nitrification even though it does not BY ITSELF reduce N loading
 - Also eliminates NBOD oxygen consumption
-

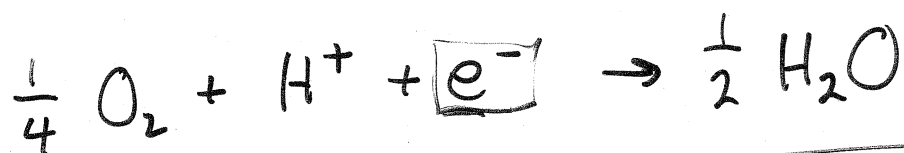
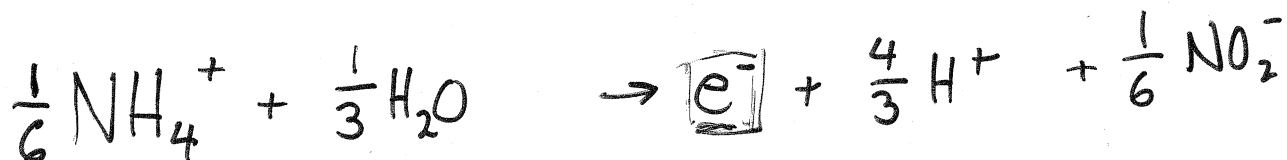
NITRIFIER BACTERIA:

"Chemoautotrophs"

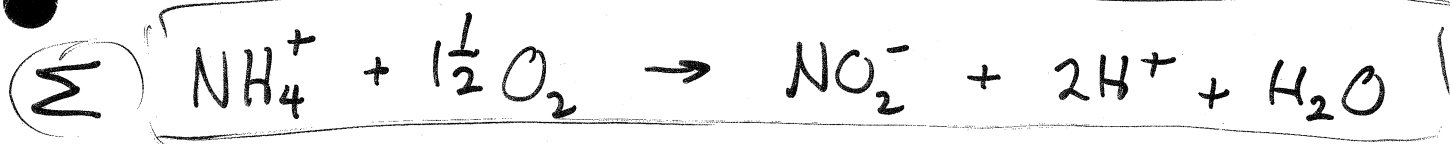
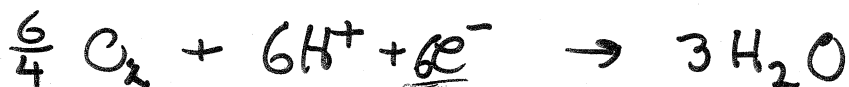
Make their own food, but use chemical energy instead of light energy.

TWO TYPES OF BACTERIA:

① NITROSOMONAS



MULTIPLY BY 6



$$+ \Delta G^\circ = -45.3 \text{ kJ/mol}$$

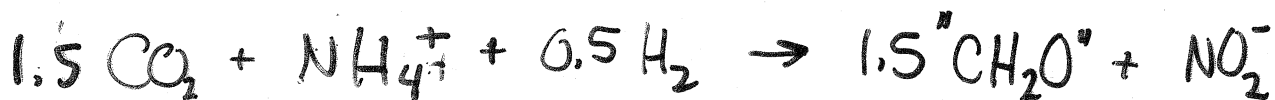
@ pH 7

They can also

fix carbon (make food)

with NH_4^+ :

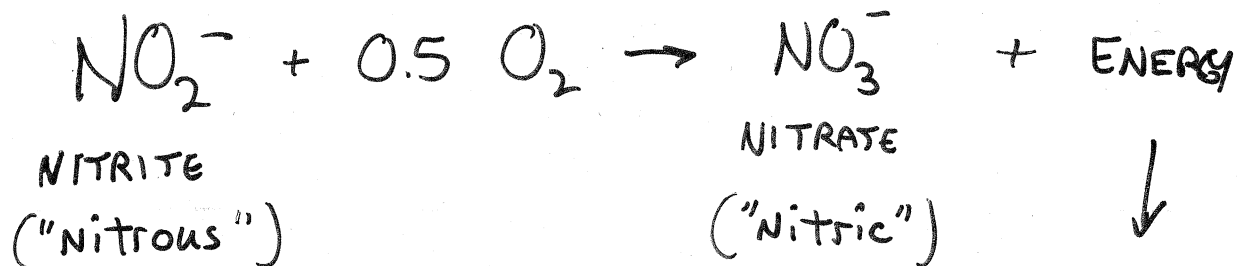
(COMPARE TO CARBOHYDRATE
OXIDATION: -119 kJ/mol)



REACTANTS	PRODUCTS
$\text{NH}_4^+, \text{CO}_2, \text{O}_2$	$\text{NO}_2^-, \text{H}^+, \text{"CH}_2\text{O"}$

SECOND STAGE

② NITROBACTER



$$\Delta G^{\circ}_{\text{pH7}} = -37.6 \text{ kJ/mol}$$

OVERALL: ● $\text{NH}_3/\text{NH}_4^+$ CONSUMED

● O_2 CONSUMED

● H^+ PRODUCED, hence

Alkalinity CONSUMED
(pH will tend to DROP)

FOR EACH ● NEW CELLS (SLUDGE) PRODUCED

1 mg-N/L NH_3 :

➤ 4.2 mg/L O_2 CONSUMED

➤ 14.1 mg/L @ CaCO_3 ALK consumed

➤ 0.15 mg/L NEW CELLS (sludge) produced

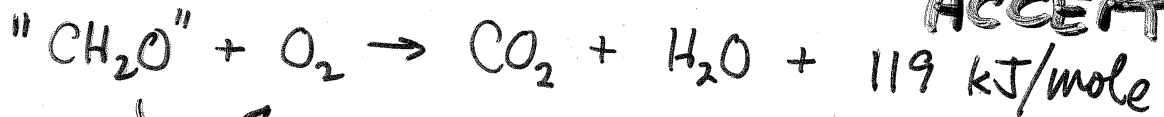
➤ 0.09 mg/L CO_2 CONSUMED

DENITRIFICATION

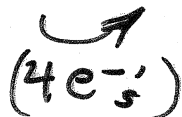
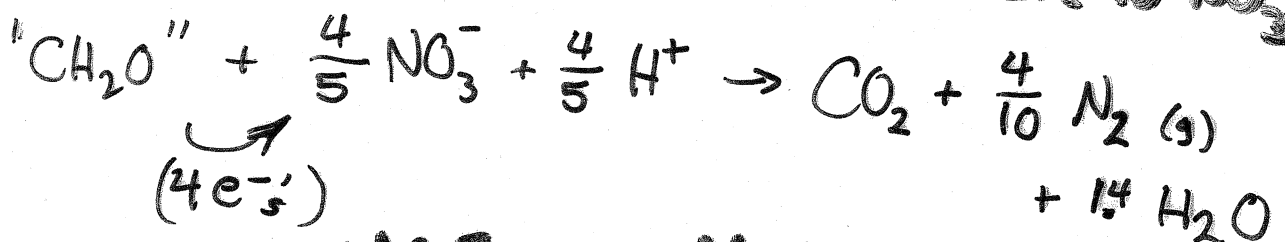
Completely different biochemical process than nitrification

Denitrification is where bacteria (heterotrophic) substitute NO_3^- for O_2 when oxidizing organic matter (respiration).

IN RESPIRATION: O_2 is "TERMINAL ELECTRON ACCEPTOR"
(AEROBIC)



IF NO O_2 PRESENT BUT NO_3^- PRESENT
MANY BUGS JUST SWITCH OVER TO NO_3^-



OVERALL in DENITRIFICATION

- Nutrient NO_3^- converted to "inert" gaseous N_2
- H^+ are consumed so Alkalinity is produced (PH tends to go up) *
- BOD is removed without having to add more O_2 (bugs using NO_3^-) *
- More cells (sludge) **PRODUCED**

* : SOMETIMES WE SAY ALK and O_2 have been "recovered"
(recovered from losses in the nitrification step.)

FOR EACH
1 mg-N/L
 NO_3^-

➤ 3 mg/L as CaCO_3 ALK is "recovered"

➤ 2.9 mg/L O_2 is "recovered"
(not consumed in BOD loss)

➤ ~ 0.4 mg/L VSS
CELLS (sludge) PRODUCED
PER 1 mg/L BOD removed)

WHY LITTLE OR NO NITRIFICATION IN CONVENTIONAL A.S.??

- Nitrifiers prefer warmth
& pH ~ 8

Conventional A.S. may not
provide these

- Ratio $\frac{BOD}{NH_3} \approx \frac{200}{35}$ ← MORE CELLS, FASTER
USING BOD
← FEWER CELLS
SLOWER ON NH_3

SINCE $\mu \propto \text{Conc}$ $\mu^{BOD} > \mu^{NH_3}$

SLUDGE AGE overall must be set
by majority of population

⇒ WASTING RATE \approx GROWTH RATE

→ TOO FAST for NH_3
USERS

NITRIFIERS GET "WASHED OUT" OF "CHEMOSTAT"

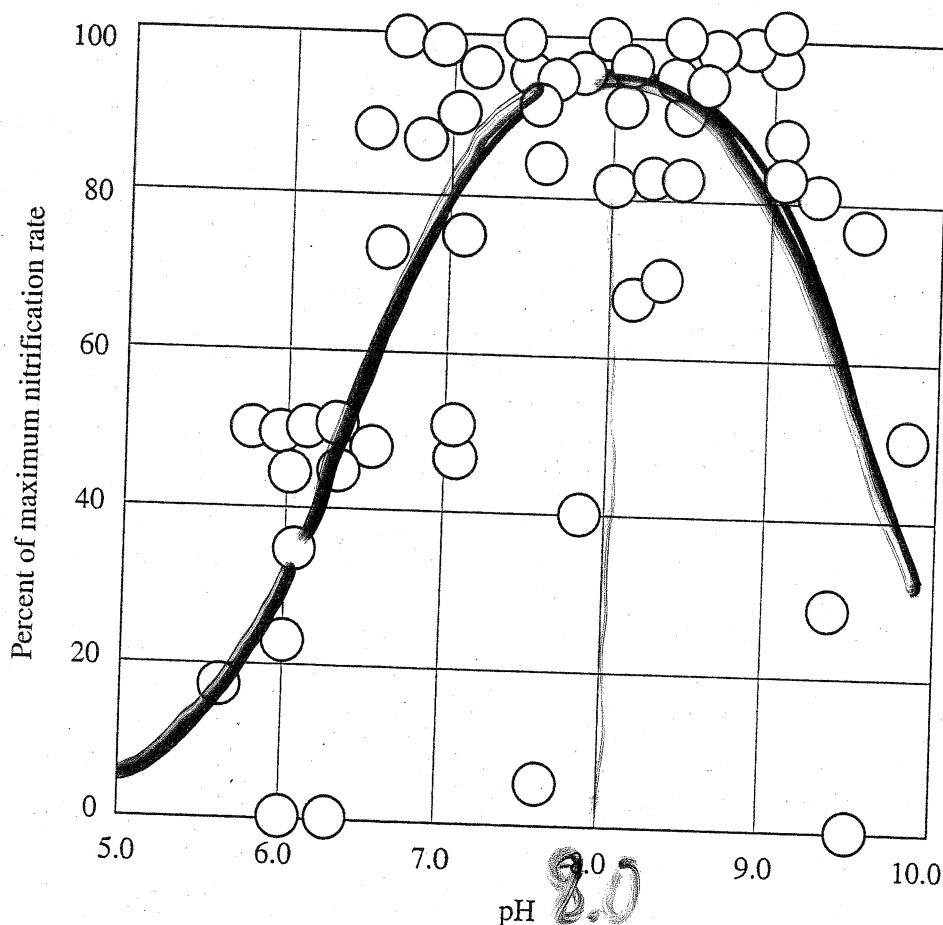


Figure 14.10 Rate of nitrification relative to maximum rate versus pH of the mixed liquor. [From: *Manual for Nitrogen Control*, Environmental Protection Agency, EPA/625/R-93/010 (September 1993): 93.]

No detectable inhibition of nitrification occurs at dissolved-oxygen levels above 1.0 mg/l. Nevertheless, a minimum dissolved-oxygen level of 2.0 mg/l is recommended in practice to prevent reduced nitrification during the passage of peak ammonia concentrations through the aeration tank.

Sludge age and temperature are interrelated factors in establishing and maintaining healthy nitrifier populations essential to efficient ammonia oxidation. In continuous-flow aeration systems, a long sludge age is required to prevent excessive loss of viable bacteria (i.e., the growth rate must be rapid enough to replace microbes lost through sludge wasting and washout in the plant effluent). The supply of organic matter controls the growth of heterotrophic organisms, while the quantity of ammonia applied governs

SOLUTION?

* WARM CLIMATE ($T \approx 20^{\circ}\text{C} +$)

- Extend aeration time
 - Control pH around 8.0
 - Watch wasting rate, keep it on low side ($\theta_c \approx \frac{1}{\mu'_N}$)
- CAN GET GOOD NITRIFICATION IN ONE-STAGE PROCESS

* COOL CLIMATE ($T \approx 10^{\circ}-15^{\circ}\text{C}$ SEASONALLY)

- Create a SECOND STAGE aeration basin
- Allows independ control of θ_c for optimizing on nitrifiers.
(Nitrosomonas)
- Allows focused pH control (keep pH up↑)
- Closed basins and/or heating might be an option as well

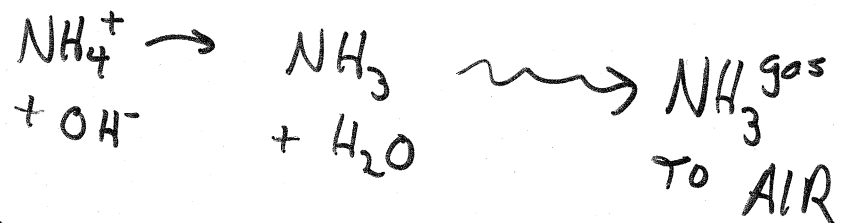
DENITRIFICATION

When total N load to receiving waters must be reduced

Options:

① Skip NITRIFICATION, use AMMONIA STRIPPING TO THE AIR

● Add alk (lime) to raise pH to > 9.0



● May not be acceptable if NH_3 stays in watershed

● May make sense for certain industrial wastes

② Let effluent (nitrified) go anaerobic, add a Carbon source, bup use NO_3^-
AEROBIC \rightarrow ANAEROBIC

③ Rearrange treatment scheme in II:
ANAEROBIC before AEROBIC

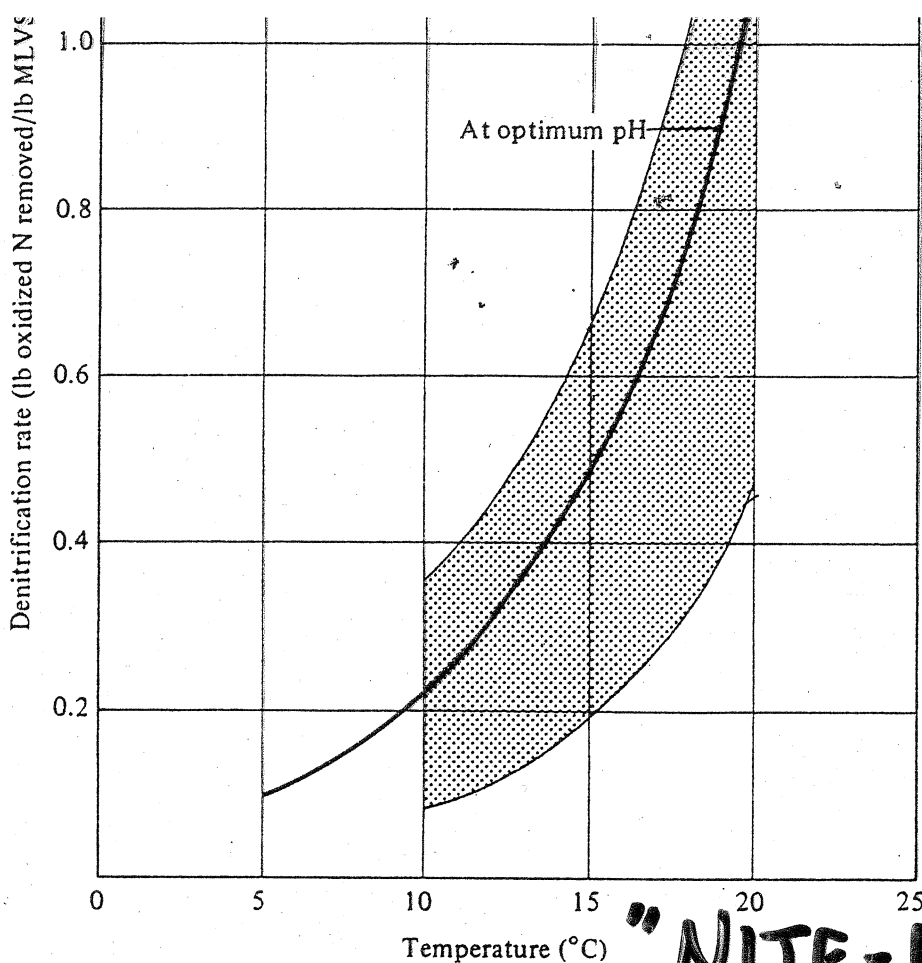


Figure 14.13 Effect of temperature on the rate of denitrification. [From *Nitrification and Denitrification Facilities*, Environmental Protection Agency, Technology Transfer (August 1973): 28.]

"NITE-DENITE" UNITS

CARBON SOURCE
CH₃OH

"DENITE" PART

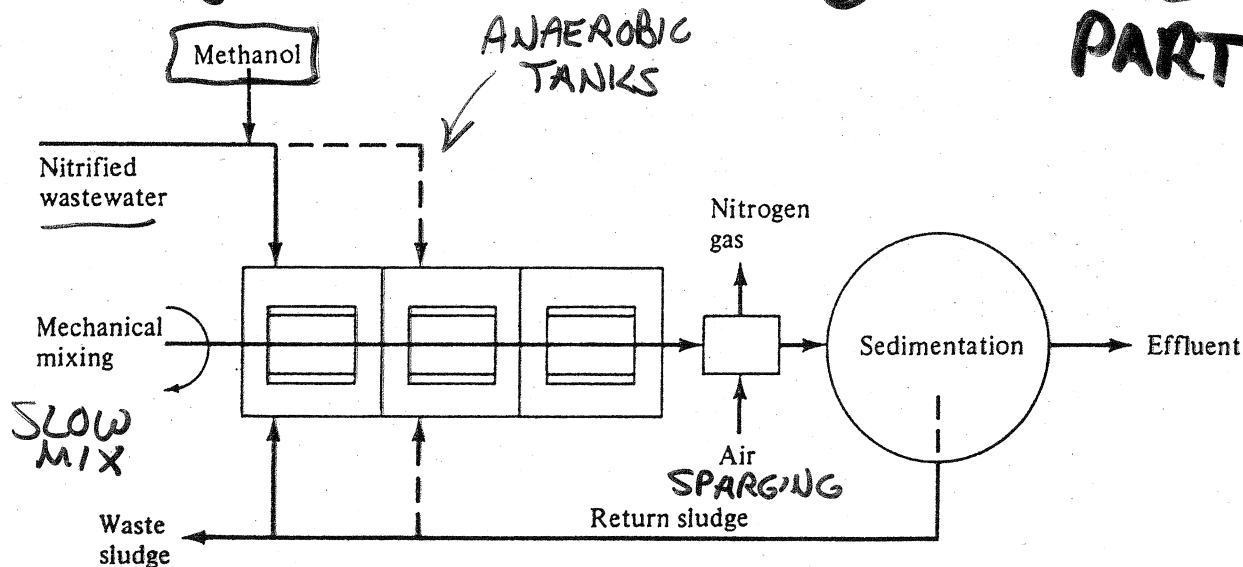


Figure 14.14 Flow diagram for a completely mixed, compartmented denitrification basin and clarifier.

Can get 80-90% N-REMOVAL

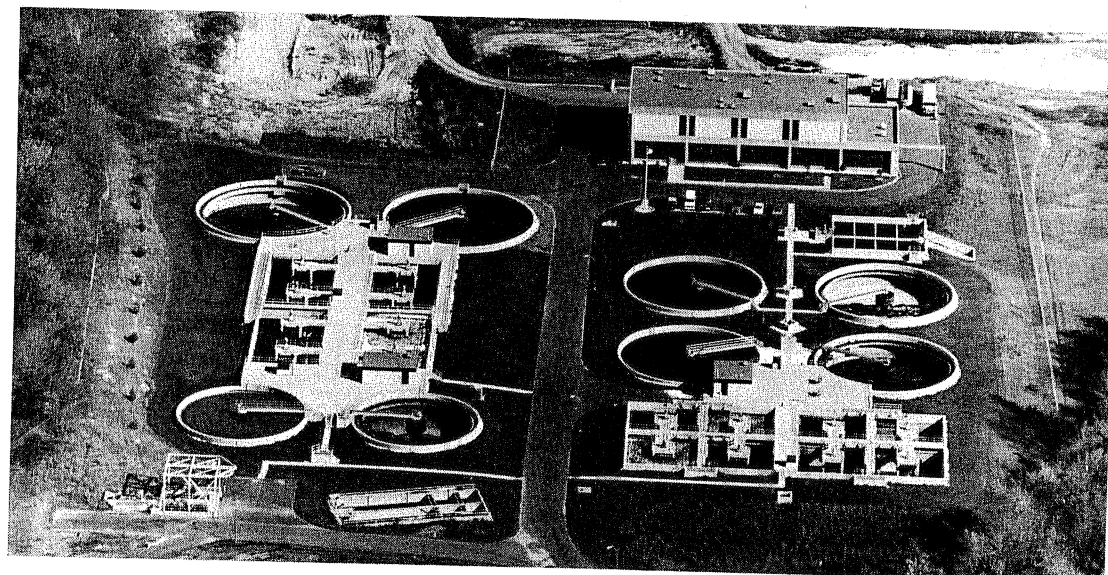
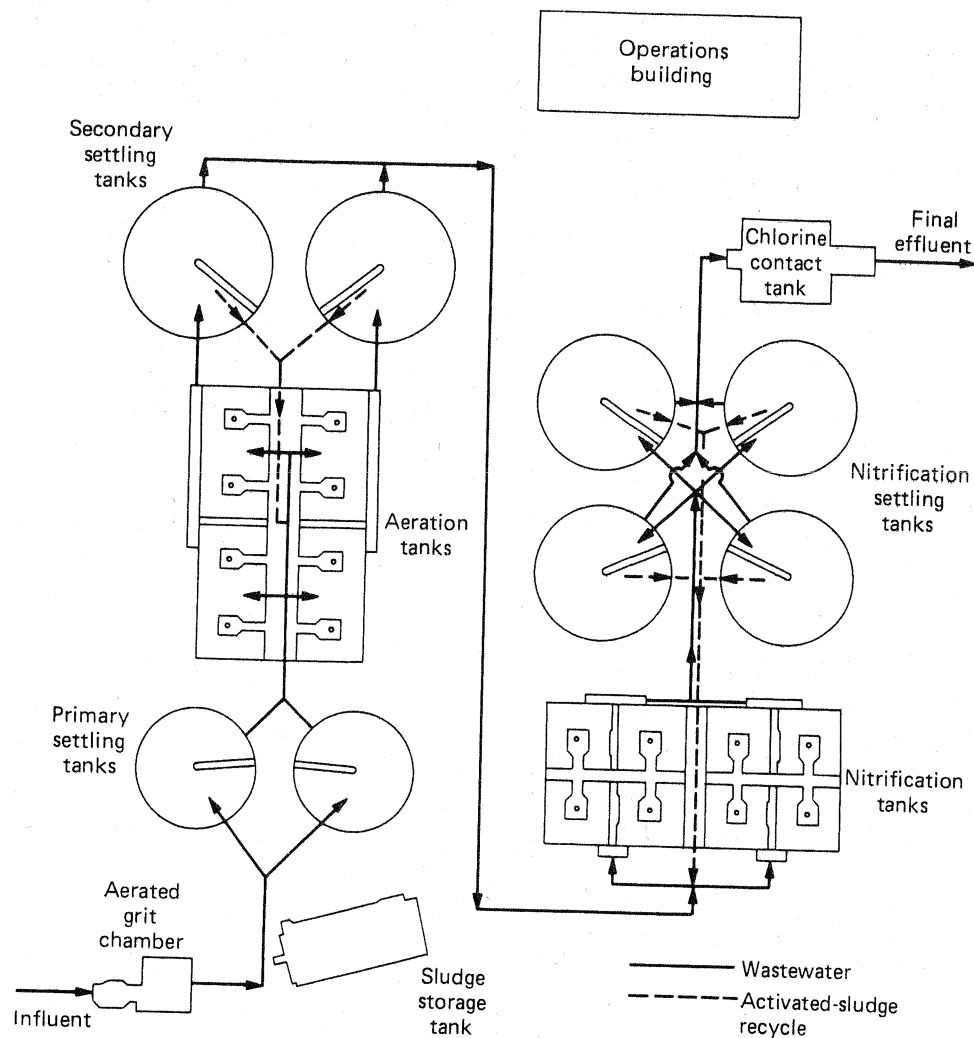
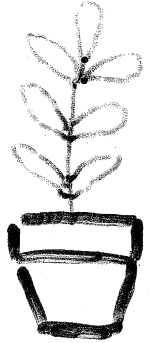


FIGURE 11-12

Flow diagram and aerial view of treatment plant with separate stages for carbon oxidation and nitrification (Marlborough, MA; design average flowrate = 5.5 Mgal/d).

Phosphate is good stuff, often “too good”

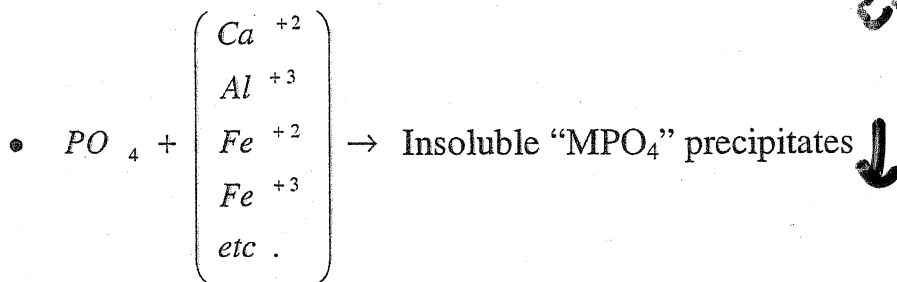
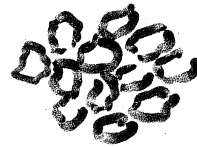
- Plants like all living things need small amounts of phosphorus (P)
- Not extremely common at earth's surface so plants really compete for it
- P loading leads to eutrophication, hence phosphate control essential water treatment technology.





- But phosphate is a vital resource: fertilizers, cleaning solutions and other chemical processes




- Mined as rock mineral Hydroxyapatite
- $PO_4 + NH_3 + CO_2 + \text{sunlight} \rightarrow$ green plants
- $PO_4 + BOD + NH_3 \rightarrow$ bacterial biomass



Why care about phosphorus removal?

- Until about 10 years ago- not mandated by law
 - Secondary treatment still all that's practiced in some parts of the country
 - Not needed when holding lagoons are used
 - Today engineered wetlands are sometimes used for nutrient removal
 - Like the wetlands within the Oregon Gardens
 - Untied sewer agency "Jackson Bottoms"-Hillsboro
 - Used where land is available- passive treatment
- Most important where effluent released to
 - Lakes 
 - Slow moving streams or rivers 

Phosphorus increased alga production in great lakes due to phosphorus in detergents. In much of the mid-west this type of detergent is now illegal.

- Locally the Tualatin River has a high P level
 - Some due to agriculture 
 - Some due to high P concentrations in groundwater
 - Originally due to some wastewater facilities
- Today wastewater standards for the Tualatin are lower than the natural river background levels
 - Normally rivers dilute wastewater discharges
 - Here effluent is diluting river water

Phosphorus can be removed either chemically or biologically

Removal of Phosphorus by Chemical Action

- Chemicals used produce insoluble or low-solubility salts
- Principal chemicals used are:
 - Alum
 - Sodium Aluminate
 - Ferric chloride or sulfate (pickle liquor)
 - Lime

Factors affecting the choice of chemical

1. Influent phosphorus level
2. Wastewater suspended solids
3. Alkalinity
4. Chemical cost (including transportation)
5. Reliability of chemical supply
6. Sludge handling facilities
7. Ultimate disposal methods
8. Compatibility with other treatment process

Actual Chemistry of PO₄

$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-$ Phosphoric Acid- Dominate at < pH 2

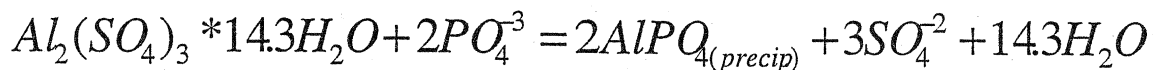
$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}$ Monobasic Phosphate- Dominate at pH 2-7

$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}$ Dibasic Phosphate – Dominate t pH 7-12

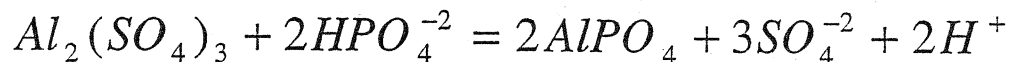
PO_4^{3-} Phosphate – Dominate at pH >12

Together they make up total phosphate or “PO₄⁻³”

Alum Removal of P



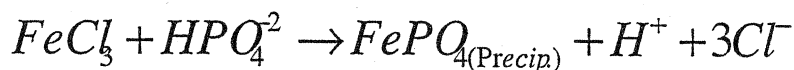
However near pH 7 the reaction is more like (with waters omitted):



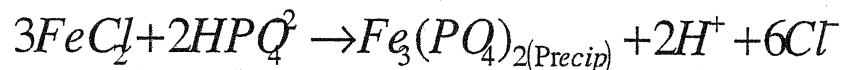
Consumes alkalinity and lowers the pH

Iron Removal of P

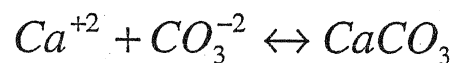
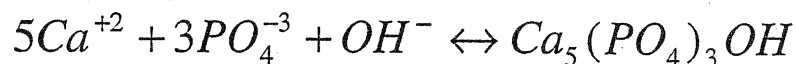
Ferric (Fe(III))



Ferrous (Fe(II))



Lime removal of P



PO₄ Removal via Fe precipitation

Two forms of iron can occur in water:

Ferrous- Fe(II) : Fe^{+2} , FeOH^+

Ferric- Fe(III): Fe^{+3} , FeOH^{+2} , Fe(OH)_2^+ , Fe(OH)_3

Fe(II) is fairly soluble at all pH but at $\text{pH} > 5$ it reacts with O_2 to form Fe(III)

Fe(III) is soluble below about pH 4 and very insoluble above about pH 6

Therefore excess Fe(III) can be removed just by raising the pH and flocculating

A cheaper alternative to buying these in tech or industrial grades is to use steel “pickling” solutions (Pickling: “removing surfaced impurities through the use of chemicals”)

Steel products are often pickled using HCl or H_2SO_4 Yielding primarily Fe(II): Ferrous chloride- FeCl_2 or Ferrous sulfate FeSO_4

If treated with O_2 or Cl_2 to oxidize the Fe^{+2} then you get: Ferric chloride FeCl_3 or Ferric sulfate $\text{Fe}_2(\text{SO}_4)_3$

Pickle liquor is cheap and sometimes free, but may contain a lot of “free acid” and sometimes metal impurities like Nickel and Chromium

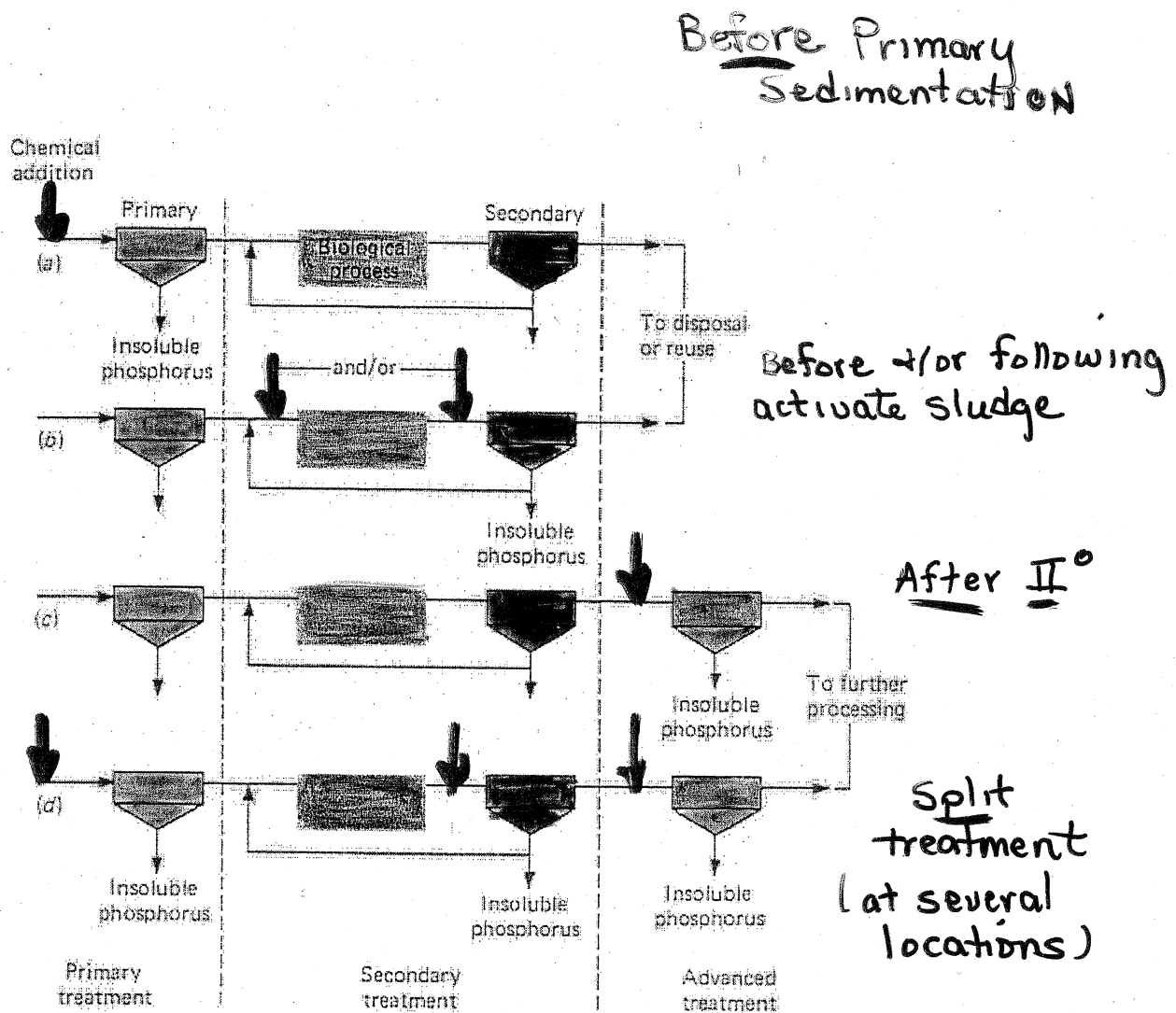


FIGURE 11-28

Alternative points of chemical addition for phosphorus removal: (a) before primary sedimentation, (b) before and/or following biological treatment, (c) following secondary treatment, and (d) at several locations in a process (known as "split treatment").

ALTERNATIVE POINTS OF CHEMICAL ADDITION FOR P-REMOVAL

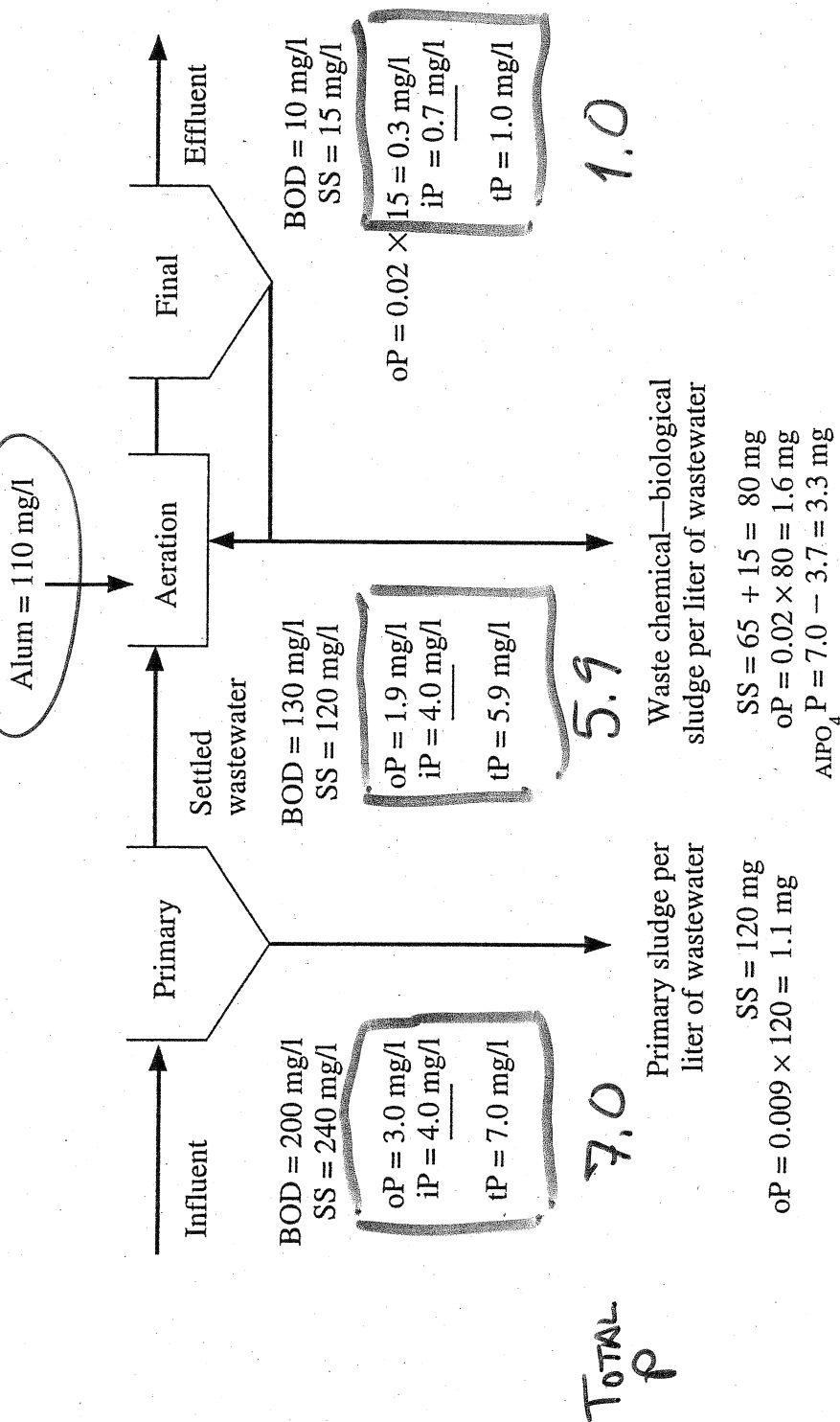
Alum Dose

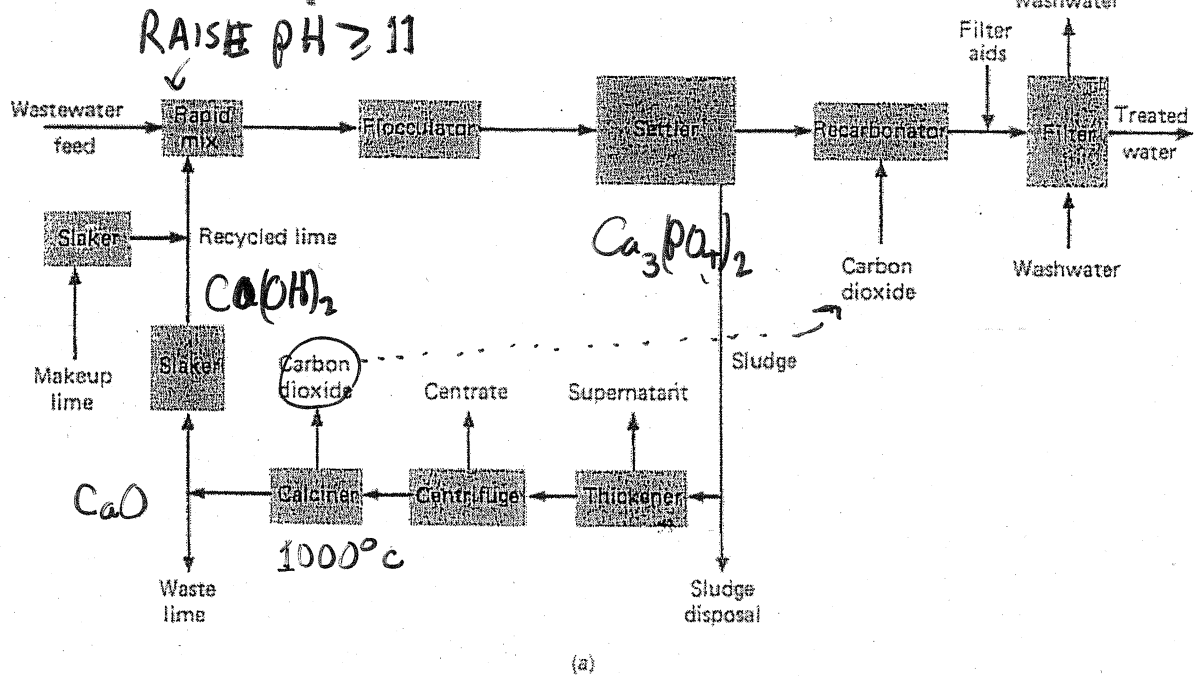
Figure 14.8 Tracing phosphorus through a biological—chemical treatment plant.

minimum alum dosage to reduce the effluent phosphorus concentration from 4.6 mg/l without coagulation to the maximum allowable tP of 1.0 mg/l is assumed to be 80 mg/l alum (molecular weight, 600). Addition of this coagulant also enhances the SS removal, reducing the effluent SS from 30 to 15 mg/l. The calculated oP in the effluent is therefore $0.02 \times 15 = 0.3$ mg/l, and the iP concentration is $1.0 - 0.3 = 0.7$ mg/l.

Now consider phosphorus removal by the biological—chemical process. The waste biological solids include 65 mg of SS resulting from the applied BOD (Fig. 14.7) plus

TRUE TERTIARY TRTMT : Post-II° LIME TREATMENT SYSTEM

Single Stage System



Two Stage System

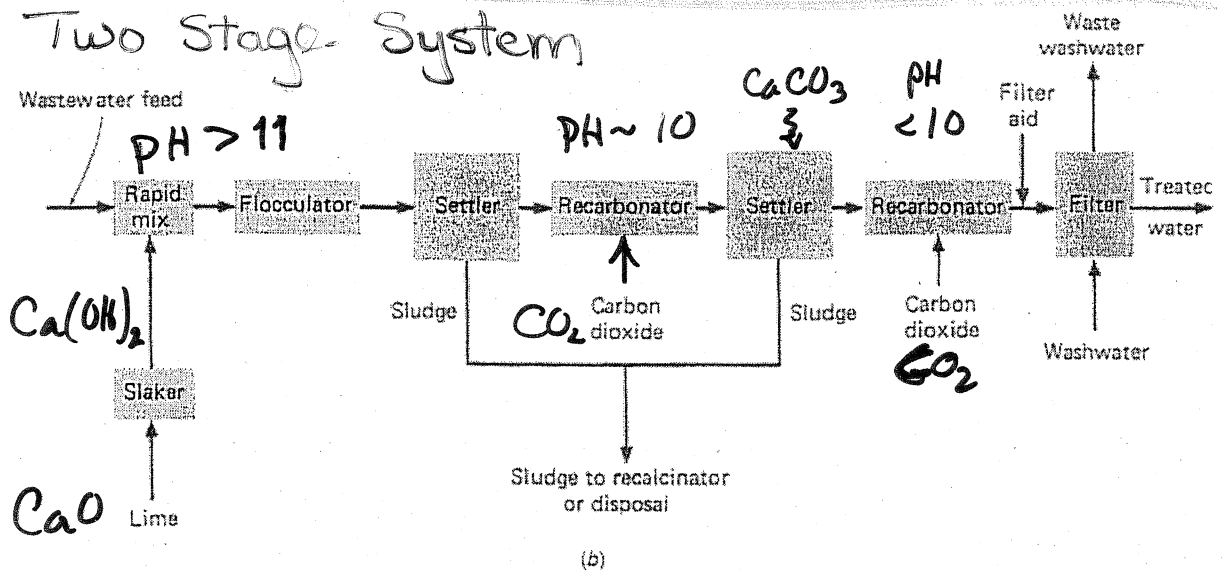
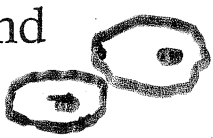


FIGURE 11-30

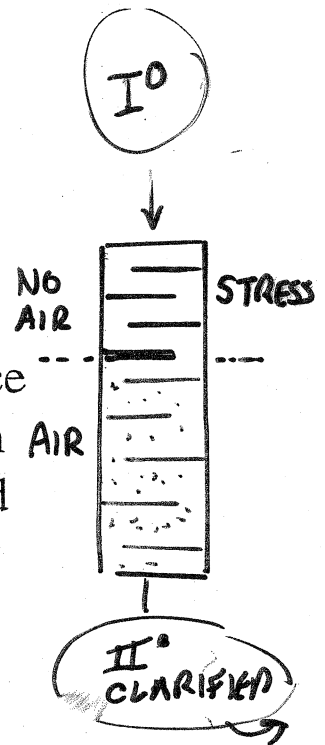
Typical lime treatment process flow diagrams for phosphorus removal: (a) single-stage system and (b) two-stage system.

Removal of P by Biological Methods

- Alternatives to chemical treatment by means of incorporating orthophosphate, polyphosphate and organically bound phosphorus into cell tissue 
- The key to biological phosphorus removal is the exposure of the microorganisms to alternating anaerobic and aerobic conditions
- This stresses the organisms so that their uptake of P rises (P is used for cell maintenance, synthesis, energy transport and stored for subsequent use)
- The resulting sludge containing the excess P is then wasted
- Process can either be in the mainstream of the plant processing or in the return-sludge “side stream”
- These processes are proprietary
 1. The A/O process used for mainstream Phosphorus removal
 2. The PhoStrip process for side stream Phosphorus removal
 3. The sequencing batch reactor (SBR) is used for smaller wastewater flows (it can also remove Nitrogen)

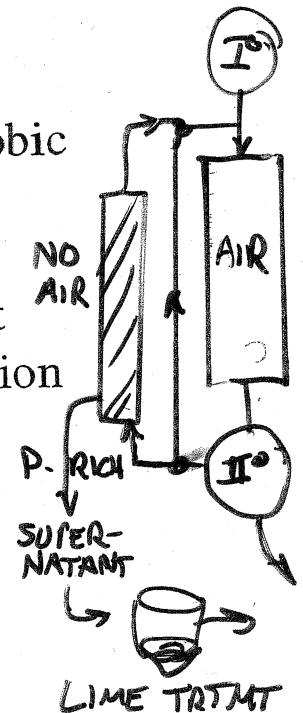
A/O Process (Mainstream Phosphorus Removal)

- Used for combined carbon oxidation and P removal
- Single-sludge suspended-growth system
- Combines anaerobic and aerobic sections in sequence
- If aerobic time lengthened can also remove Nitrogen
- Settled sludge returned to influent end of reactor and mixed with incoming wastewater
- Under anaerobic conditions P released as soluble phosphates
- Under aerobic this P is taken up by the cell mass



PhoStrip Process

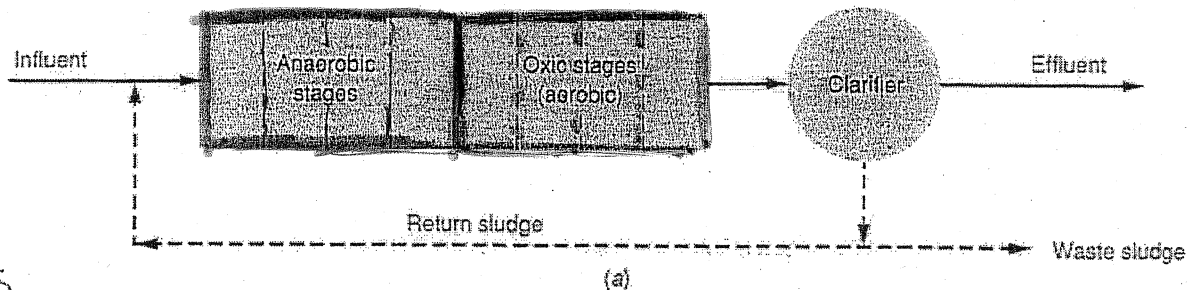
- Portion of return activated sludge diverted to anaerobic phosphorus stripping tank
- Retention time 8-12 hours.
- Phosphorus released passes out of tank in supernatant
- Phosphorus-poor activated sludge returned to aeration tank
- Phosphorus-rich supernatant is treated with lime in a separate tank, flocculated and clarified.



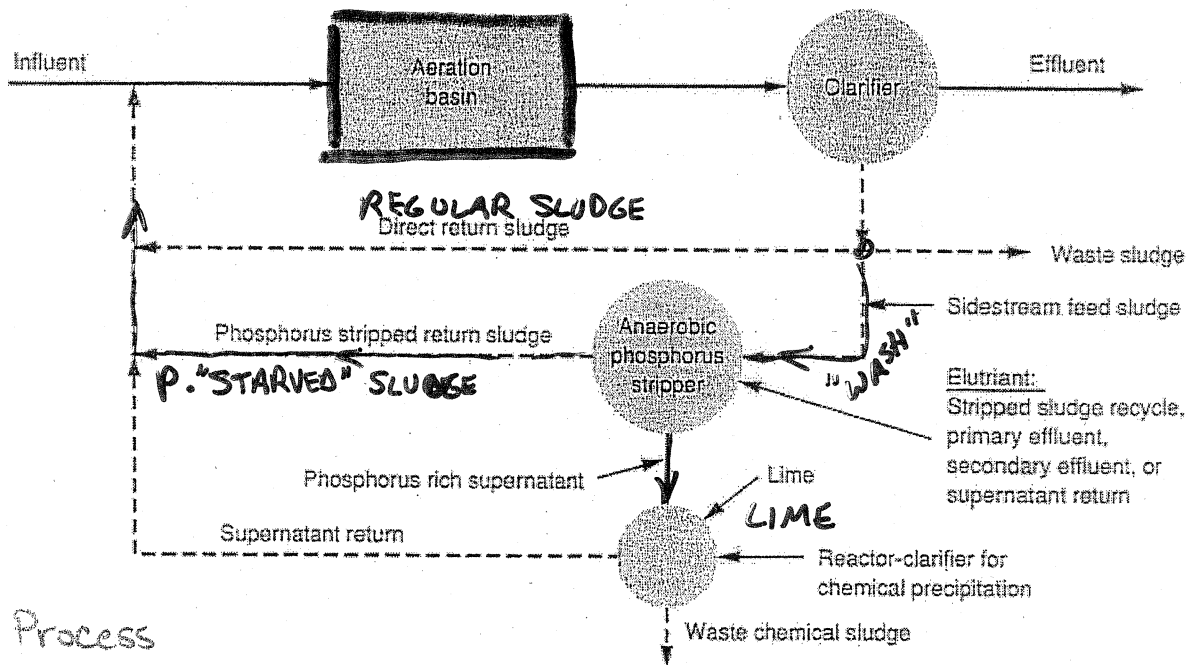
Sequencing Batch Reactor

- Can be used for P and N removal
- With or without chemical additions
- P can be removed by coagulant addition or biologically
- Overall cycle times 3-24 hours
- Carbon source required in anoxic phase to support denitrification

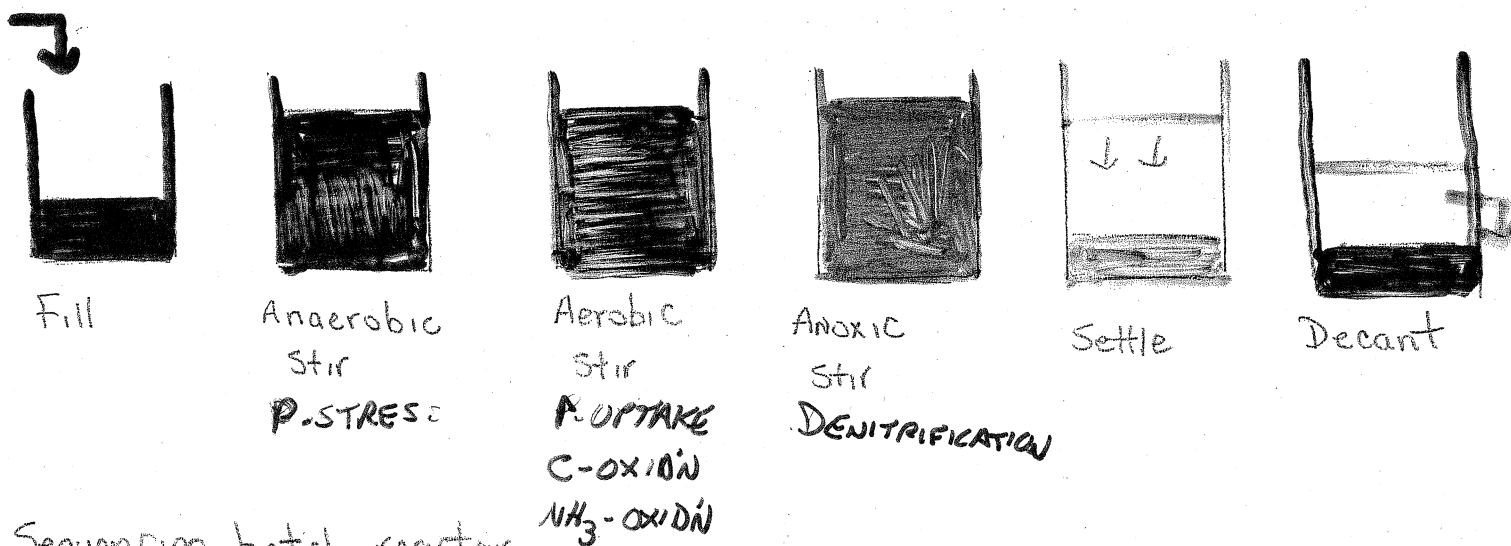
Biological Phosphorus Removal



A/O Process



PhoStrip Process



Sequencing batch reactor

TABLE 11-26

Advantages and disadvantages of biological phosphorus removal processes^a

Process	Advantages	Disadvantages
A2/O	<p>Operation is relatively simple compared to other processes.</p> <p>Waste sludge has a relatively high phosphorus content (3–5%) and has fertilizer value.</p> <p>Relatively short hydraulic retention time.</p> <p>Where reduced levels of phosphorus removal efficiency are acceptable, process may achieve complete nitrification.</p>	<p>Is not capable of achieving high levels of nitrogen and phosphorus removal simultaneously.</p> <p>Performance under cold weather operating conditions uncertain.</p> <p>High BOD/P ratios are required.</p> <p>With reduced aerobic cell detention time, very high-rate oxygen-transfer devices may be necessary.</p> <p>Limited process control flexibility is available.</p>
PhoStrip	<p>Can be incorporated easily into existing activated-sludge plants.</p> <p>Process is flexible; phosphorus removal process is not controlled by BOD/phosphorus ratio.</p> <p>Several installations in U.S.</p> <p>Significantly less chemical usage than mainstream chemical precipitation.</p> <p>Can achieve reliably effluent orthophosphate concentrations of less than 1.5 mg/L.</p>	<p>Requires lime addition for phosphorus precipitation.</p> <p>Requires higher mixed-liquor dissolved oxygen to prevent phosphorus release in final clarifier.</p> <p>Additional tankage required for stripping.</p> <p>Lime scaling may be a maintenance problem.</p>
Sequencing batch reactor	<p>Process is very flexible for combining nitrogen and phosphorus removal.</p> <p>Process is simple to operate.</p> <p>Mixed-liquor solids cannot be washed out by hydraulic surges.</p>	<p>Suitable only for smaller flows.</p> <p>Redundant units are required.</p> <p>Effluent quality depends upon reliable decanting facility.</p> <p>Limited design data available.</p>