CHEMICAL PRECIPITATION
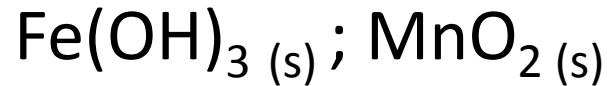
Practiced in water and wastewater treatment for

➢ Phosphorus removal (ww. treatment)
$AlPO_{4\ (s)}$, $FePO_{4\ (s)}$, $Ca_5(OH)(PO_4)_3$

➢ Hardness removal, water softening
$CaCO_{3\ (s)}$, $Mg(OH)_{2\ (s)}$

➢　　Iron and Manganese removal

　　$Fe(OH)_{3\,(s)}$; $MnO_{2\,(s)}$

➢　　Removal of heavy metals, radionuclei

　　As (V) or As (III), Ba, Cd, Hg, Zn, Ni, Cr (III)

　　precipitates in the form of As(V)

　　M^{n+} + n OH^- ⟶ $M(OH)_{n\,(s)}$

If discharge limitations are lower $S^=$ ppt. is preferred because solubility of sulfide salts is lower.

$M^{n+} + S^{2-}$ ⟶ $MS_{(s)}$

⟶ mostly in the form of $H_2S_{(g)}$

➤   Water conditioning
     (To control scale formation or corrosion)

➤   Sulfate removal from wastewaters
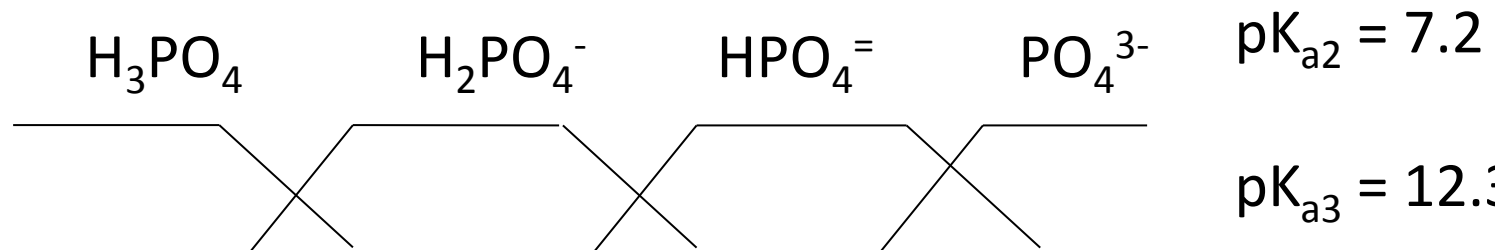 $CaSO_4$ (s) ; $BaSO_4$ (s)
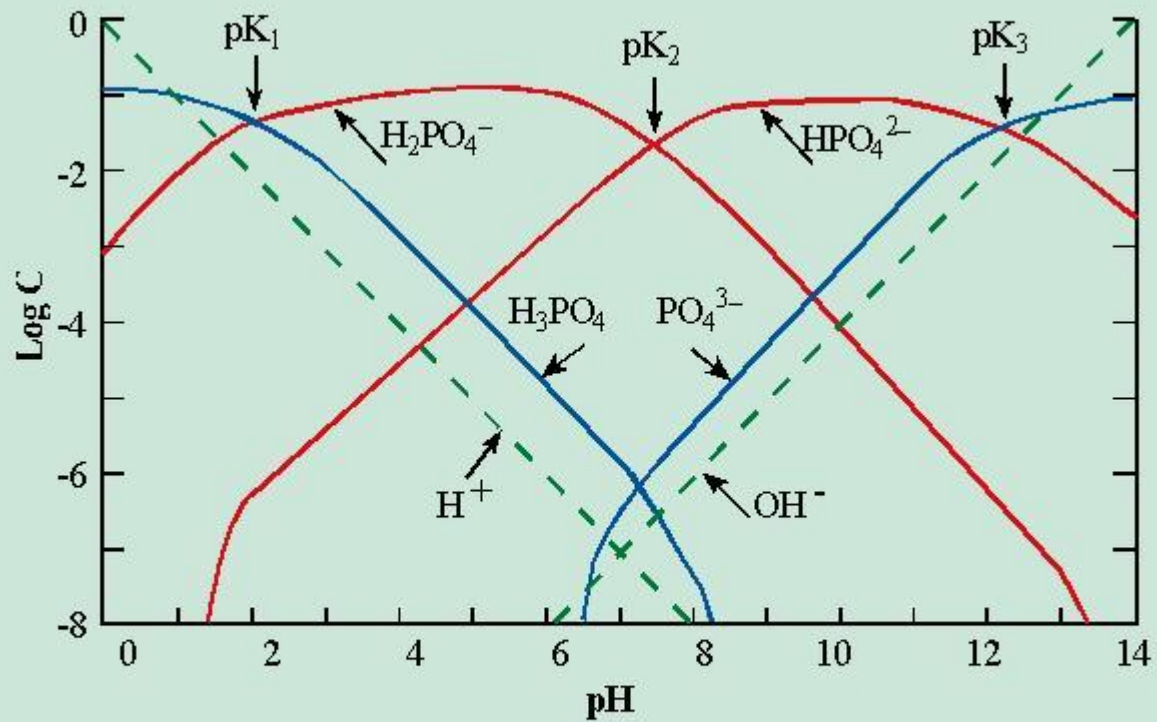
PHOSPHORUS REMOVAL

The Types of P

1. <u>Orthophosphate H_3PO_4 , $H_2PO_4^-$, $HPO_4^=$, PO_4^{3-}</u>

As a fertilizer, phosphorus must be in the form of orthophosphate.

pH   2.1   7.2   12.3

H_3PO_4 $H_2PO_4^-$ $HPO_4^=$ PO_4^{3-}

pK_{a1} = 2.1

pK_{a2} = 7.2

pK_{a3} = 12.3

Distribution diagram for 0.1m orthophsphate solution
(pK₁ = 2.1; pK₂ = 7.2; pK₃ = 12.3)

In the pH range of wastewaters (around 7), the dominant forms of orthophosphate are $H_2PO_4^-$ and $HPO_4^=$. As the pH increases, the equation moves toward the formation of PO_4^{3-}.

2.   Condensed (polyphosphates)

When H_3PO_4 is heated, it decomposes, losing molecules of water forming the P - O - P bonds. The process of losing water is called condensation.
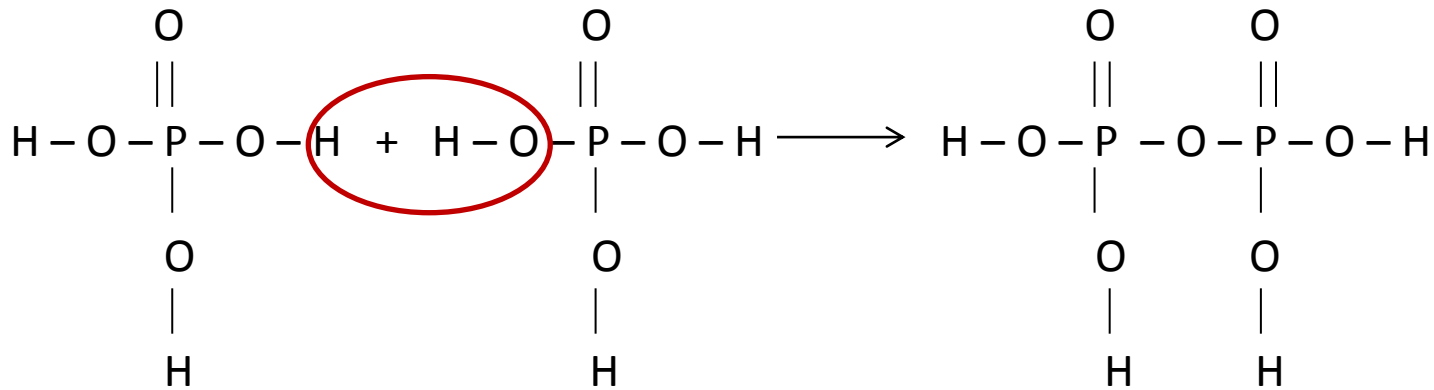
Orthophosphoric acid

Dipolyphosphoric acid or Pyrophosphoric acid

All of the hydrogen atoms are ionizable.

Properties of condensed phosphates

- Condensed phosphates are inorganic and contain more than one P per molecule.
- They are used in corrosion control and in detergents as complexation agents.

    Ex. *Pyrophosphate $H_4P_2O_7$ and its ionization products.*

- They do not form precipitates. But they undergo hydrolysis in aqueous solutions and transform into the orthophosphates.
- Microorganisms convert polyphosphates into orthophosphates.

3. Organic P : ATO, ADP, etc.

When organic compounds containing P are attacked by microorganisms, they also undergo hydrolysis into the orthophosphate forms.

➢ Typical municipal waste : 10 – 15 mg/L as P

30 % from human waste + 70 % from detergents (mostly in the form of polyphosphates)

➢ P being a nutrient, causes algal blooms (eutrophication)

$106\ CO_2 + 16\ NO_3^- + HPO_4^= + 18\ H^+ + 122\ H_2O \longrightarrow$
$C_{106}H_{263}O_{110}N_{16}P + 154\ O_2$
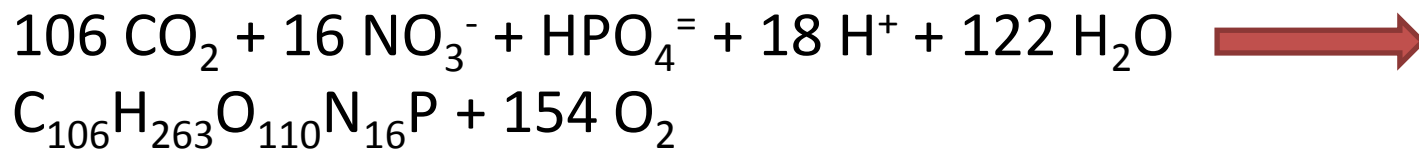
➢ In most lakes P is the growth limiting nutrient for algae. P > 0.01 mg/L stimulates algal growth.

➢ 80 % removal of P or a residual of 1 mg/L as P is required in effluents discharged to streams which are tributaries to lakes.

➢ Effluent concentrations are commonly specified to be 1 mg/L or less to minimize environmental effects.

Primary clarification removes 5 – 10 % of P.
Primary + secondary treatment removes 10 – 20 % of P.

Phosphorus Removal

The most common method to remove phosphorus from a waste stream is chemical precipitation.
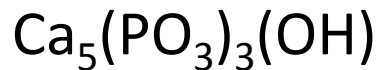The common precipitating cations used are Ca, Al and Fe.

Removal of P by Chemical Precipitation
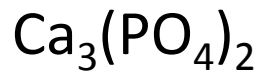
Salts of Al (III), Fe (III) and Ca(II)
Solubility Product Constants for Phosphate Precipitation

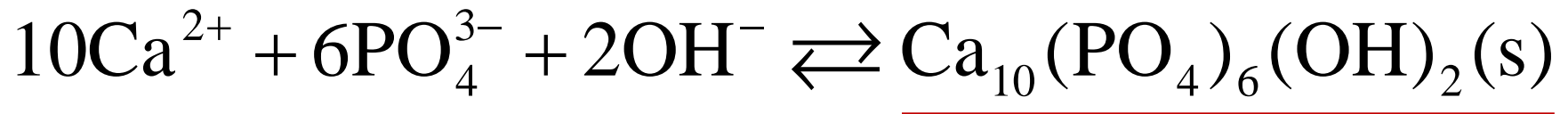| Precipitation Product	Solubility Product , K_{sp} at 25 ºC
$Ca_5(PO_3)_3(OH)$	$10^{-55.9}$
$Ca_3(PO_4)_2$	10^{-25}
$AlPO_4$	10^{-21}
$FePO_4$	$10^{-21.9}$

Precipitation by Calcium

Calcium is usually added as lime ($Ca(OH)_2$).
The reaction is represented as:

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightleftharpoons \underline{Ca_{10}(PO_4)_6(OH)_2(s)}$$

Calcium

- Lime dosage is primarily a function of system **alkalinity**.

- The key parameter here is pH.

- pH has to be elevated to somewhere between 10.5 and 11 to get effective P removal.

- As a rule of thumb, lime dose to attain this pH is about **1.5** times the alkalinity represented in mg/L as $CaCO_3$
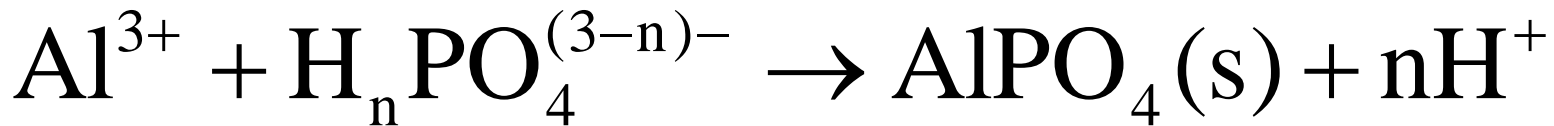
Disadvantages of lime addition
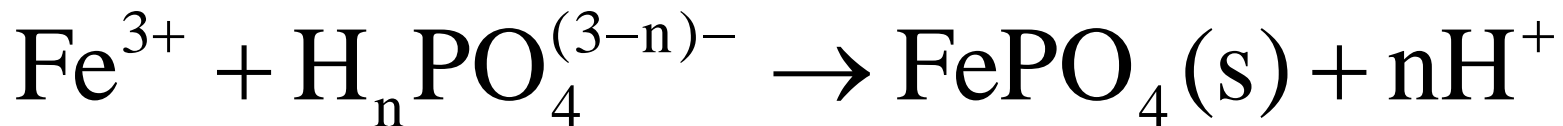
Lime addition is seldom practiced because

- it produces large amount of sludge, and

- the elevated pH has to be readjusted typically by recarbonation.

Precipitation by Al and Fe

Phosphate precipitation of by Al

$$Al^{3+} + H_nPO_4^{(3-n)-} \rightarrow AlPO_4(s) + nH^+$$

Phosphate precipitation of by Fe

$$Fe^{3+} + H_nPO_4^{(3-n)-} \rightarrow FePO_4(s) + nH^+$$

1 mol of Al or Fe precipitates 1 mol of phosphate. However, these reactions are simple and must be considered in the light of many <u>competing reactions</u>.

In general, with Ca, Al or Fe addition to precipitate PO_4^{3-} higher pH is favorable (more PO_4^{3-} as opposed to HPO_4^{2-} or $H_2PO_4^-$).

However, **soluble** Al-PO_4-OH complexes begin to form as pH increases.

For example, the following **soluble** species can form:

$$Al_2PO_4(OH)_3^0, \quad Al_2PO_4(OH)_2^+, \quad AlPO_4(OH)^-$$

$Al_2(SO_4)_3.XH_2O$ ➡️ Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$ etc.

forms below pH 2

$Al(OH)_{3\ (s)}$ according to pH.

tremendous waste of chemical.

- The chemistry of phosphate precipitate formation is complex because of complexes formed between phosphate and metals, and between metals and other ligands in the wastewater.
- Side reactions of the metals with alkalinity to form hydroxide precipitates are another factor to be considered.
- The amount of metal needed to remove phosphorus exceeds the stoichiometric amount at the low levels at which phosphorus is present in a wastewater.
- The common precipitates formed by the metals are given in the following table.

Table 15.5 Phosphate Precipitates

Metal	Precipitates	pH range	Comment
Ca^{+2}	Various calcium phosphates , e.g. , $Ca_3(PO_4)_2$, $Ca_5(OH)(PO_4)_3$, CaHPO4,	≥10	Produces lowest residual P concentrations. The alkalinity of the water determines the dose because of the formation of $CaCO_3$.
	$CaCO_3$	≤9.5	Residual P in the range of $1 - 2$ mg/L.
Fe^{2+}	$Fe_3(PO_4)_2$, $Fe_x(OH)_y(PO_4)_3$ $Fe(OH)_2$, $Fe(OH)_3$	$6 - 8.5$	There will be some oxidation of Fe^{2+} to Fe^{3+}.
Fe^{3+}	$Fe_x(OH)_y(PO_4)_z$, $Fe(OH)_3$	$6 - 8.5$	
Al^{3+}	$Al_x(OH)_y(PO_4)_3$, $Al(OH)_3$	$6 - 8.5$	

Purpose

$Al^{3+} + PO_4^- \longrightarrow Al(PO_4)_{(s)}$

So Al^{3+} required is more than 1:1 ratio.

Same for Fe (III)

$Fe^{3+} + PO_4^- \longrightarrow Fe(PO_4)_{(s)}$

- In order to determine the chemical requirement, site specific experiments, which involve testing the amount of phosphorus removal at different dosages, are needed.
- Chemical requirement depends upon
  - ✓ pH,
  - ✓ Alkalinity,
  - ✓ initial P_T, and
  - ✓ desired % P removal

- On-site tests under actual plant conditions are preferred.
- A reasonably good correlation can be obtained by plotting the **log of the fraction of soluble phosphorus remaining as a function of the weight ratio of metal to soluble phosphorus**.
- The required ratio of metal ion to influent soluble phosphorus for a specified phosphorus removal can be obtained from such a plot.
- This ratio is multiplied by the soluble influent phosphorus concentration in mg/L to determine the required chemical dose in mg/L.
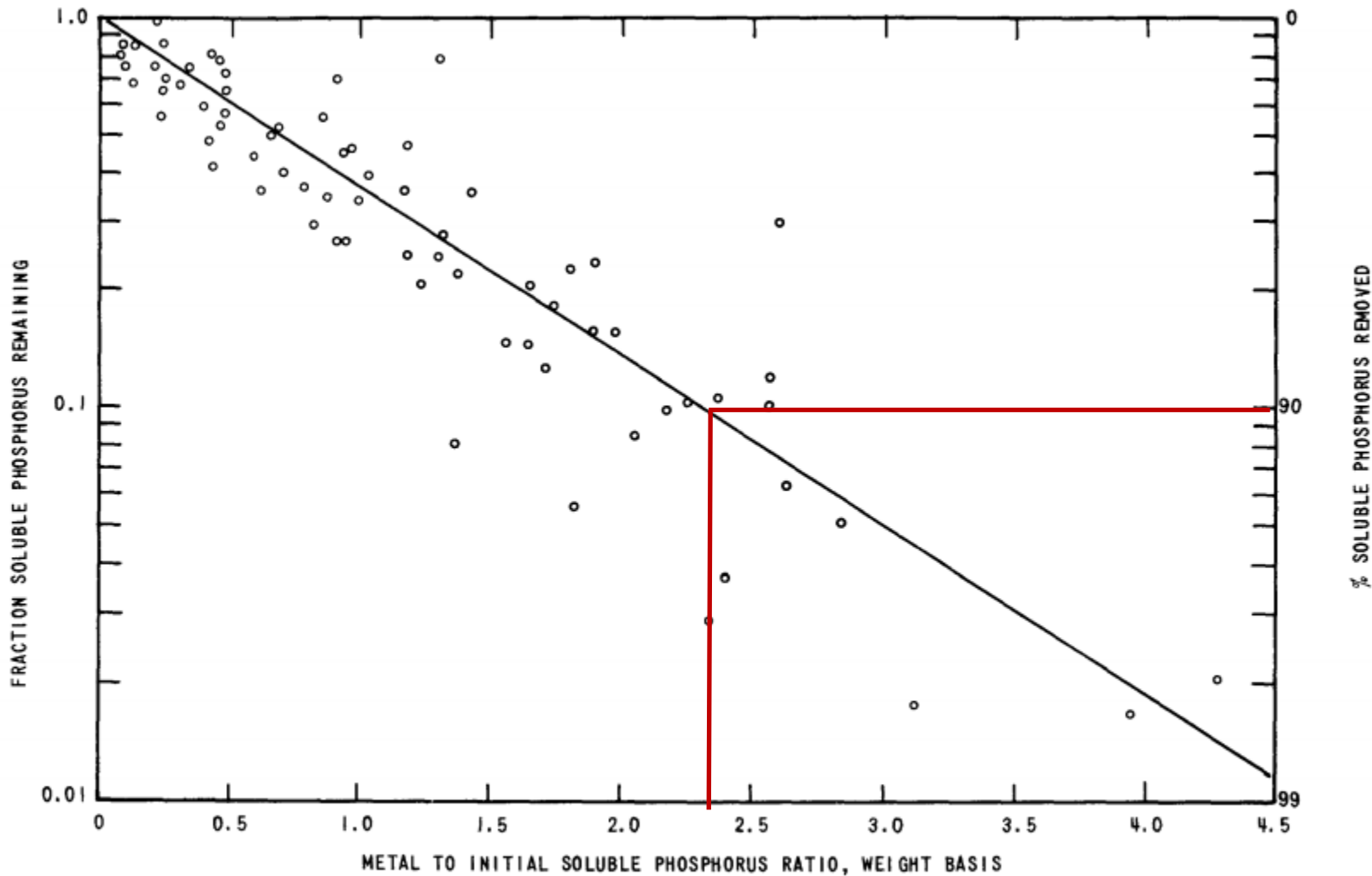
FIGURE 4-3 SOLUBLE PHOSPHORUS REMOVAL BY FERRIC CHLORIDE ADDITION

Data are from several ferric chloride phosphorus removal studies conducted in the Great Lakes region.

Ref: National Service Center for Environmental Publications (NSCEP)
Process Design Manual for Phosphorus Removal, April 1976

For iron and aluminum salts, without jar tests, the general guideline for the metal dose to achieve total soluble residual P concentrations of 1 to 2 mg P/L is

Typical Al or Fe requirement per mole P	% P removal
1.5	75
1.7	85
2.3	95

$$Al^{3+} + PO_4^{3-} \longleftrightarrow AlPO_4$$
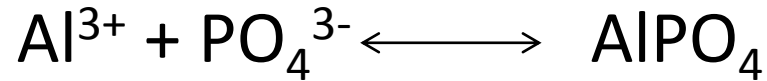
$$K_{sp} = [Al^{3+}][PO_4^{3-}]$$
$$K_{sp} = [Al^{3+}](\alpha_3 \cdot P_{total})$$

$$\alpha_3 = \frac{[PO_4^{3-}]}{[H_3PO_4] + [H_2PO_4^-] + [HPO_4^=] + [PO_4^{3-}]}$$

α_3 = fraction of PO_4^{3-} in total P species.

$$P_T = \frac{K_{sp}}{\alpha_3 \cdot [Al^{3+}]}$$

$[Al^{3+}] \downarrow$ as pH $\uparrow$ and $\alpha_3 \uparrow$ as pH $\uparrow$
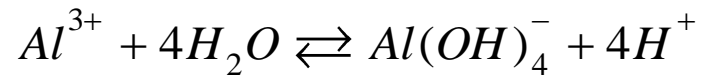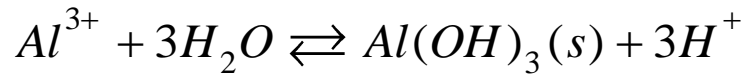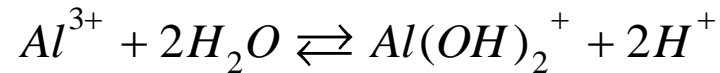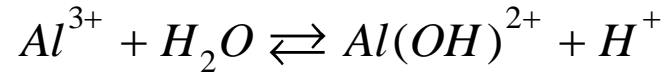
P solubility as a function of pH:
Pure metal phosphates are precipitated within the shaded area. Mixed complex polynuclear species are formed outside toward higher and lower pH values.
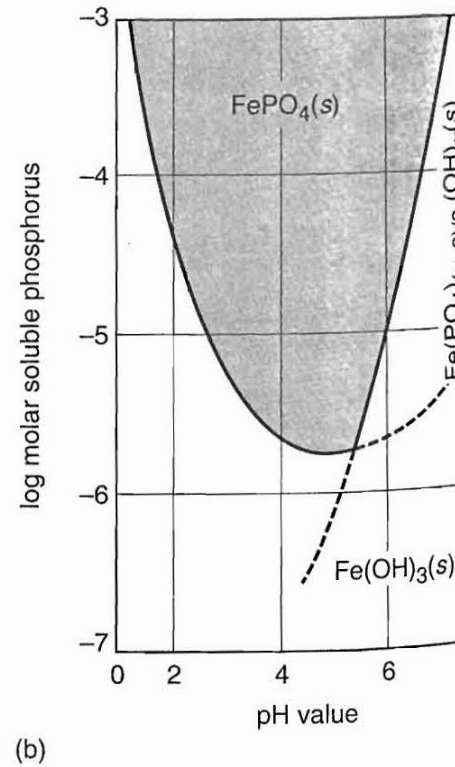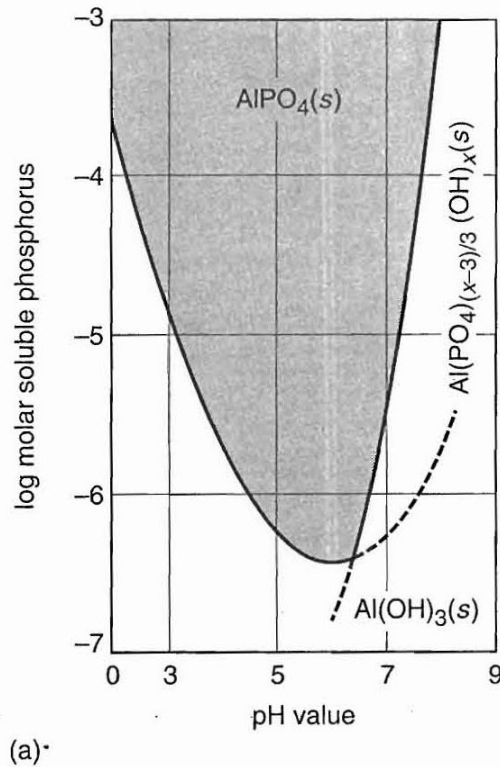
Figures : 6 – 12 a- b from Metcalf (pg:502)

Hydro-Complexes of Aluminum

$$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+$$

$$Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2{}^+ + 2H^+$$

$$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3(s) + 3H^+$$

$$Al^{3+} + 4H_2O \rightleftharpoons Al(OH)_4^- + 4H^+$$

- pH drops and alkalinity of water is reduced due to acid formation.
- If $Al(OH)_3$ precipitate is formed, 3 equivalents of alkalinity is reduced per mole of Al^{3+} added.

A similar set of reactions can be written for Fe^{3+}.

- So there is a minimum point for P_{total} at about pH = 6–7. For $FePO_4$, minimum P_{total} is at about pH = 5–6.

- Use Fe salts if alkalinity is low.

- When salts are added, pH drops (hydrolysis reactions and alkalinity consumption).

- This helps the precipitation, if the pH is above the minimum solubility point.
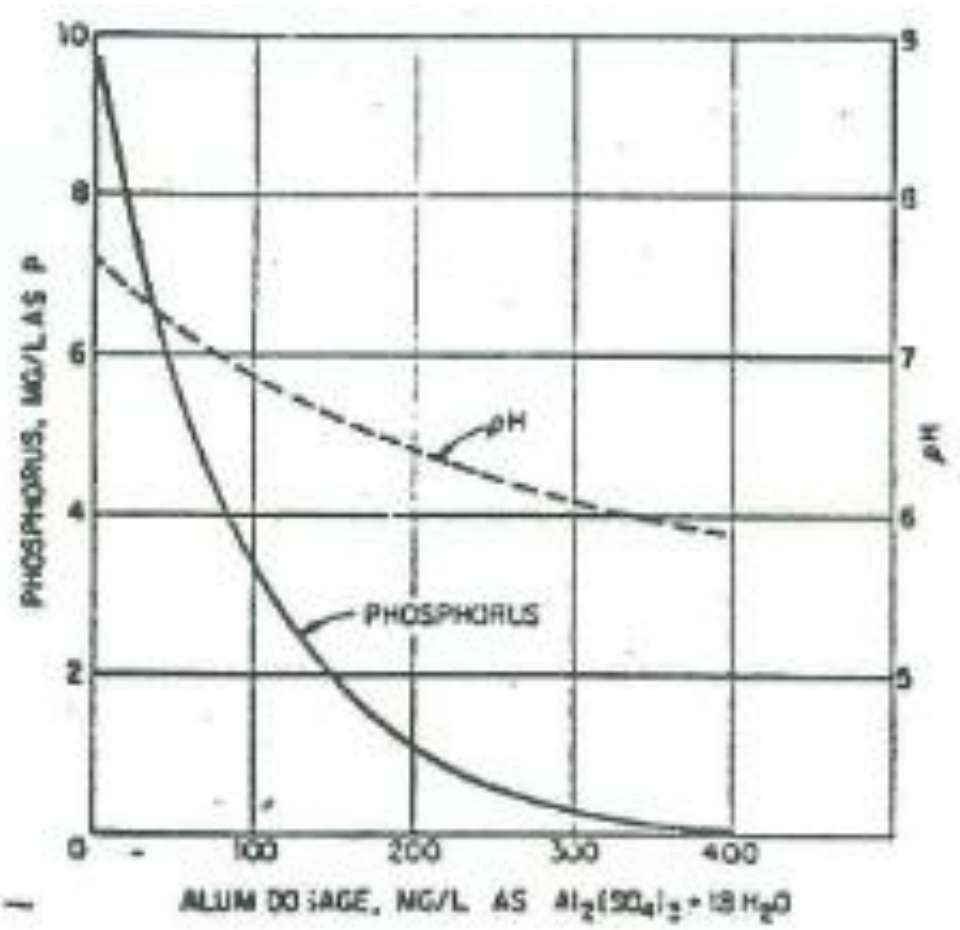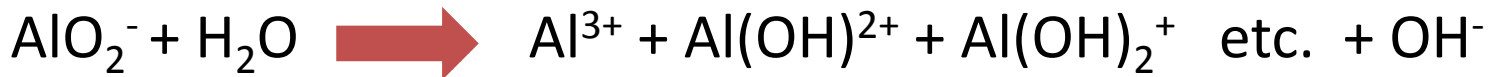
- Otherwise, pH drop is detrimental.

Figure 2–4 Alum coagulation of sewage.

Sodium Aluminate

$$NaAlO_2 \longrightarrow Na^+ + AlO_2^-$$

$$AlO_2^- + H_2O \longrightarrow Al^{3+} + Al(OH)^{2+} + Al(OH)_2^+ \quad etc. \ + OH^-$$

- **$NaAlO_2$ is more expensive than Alum but you generate OH^- instead of H^+.**

- **OH^- is released in the reaction. So, aluminate behaves as a base and pH increases.**

- **If water is acidic, use $NaAlO_2$ not $Al_2(SO_4)_3$ or use a mixture to adjust to the optimum pH.**

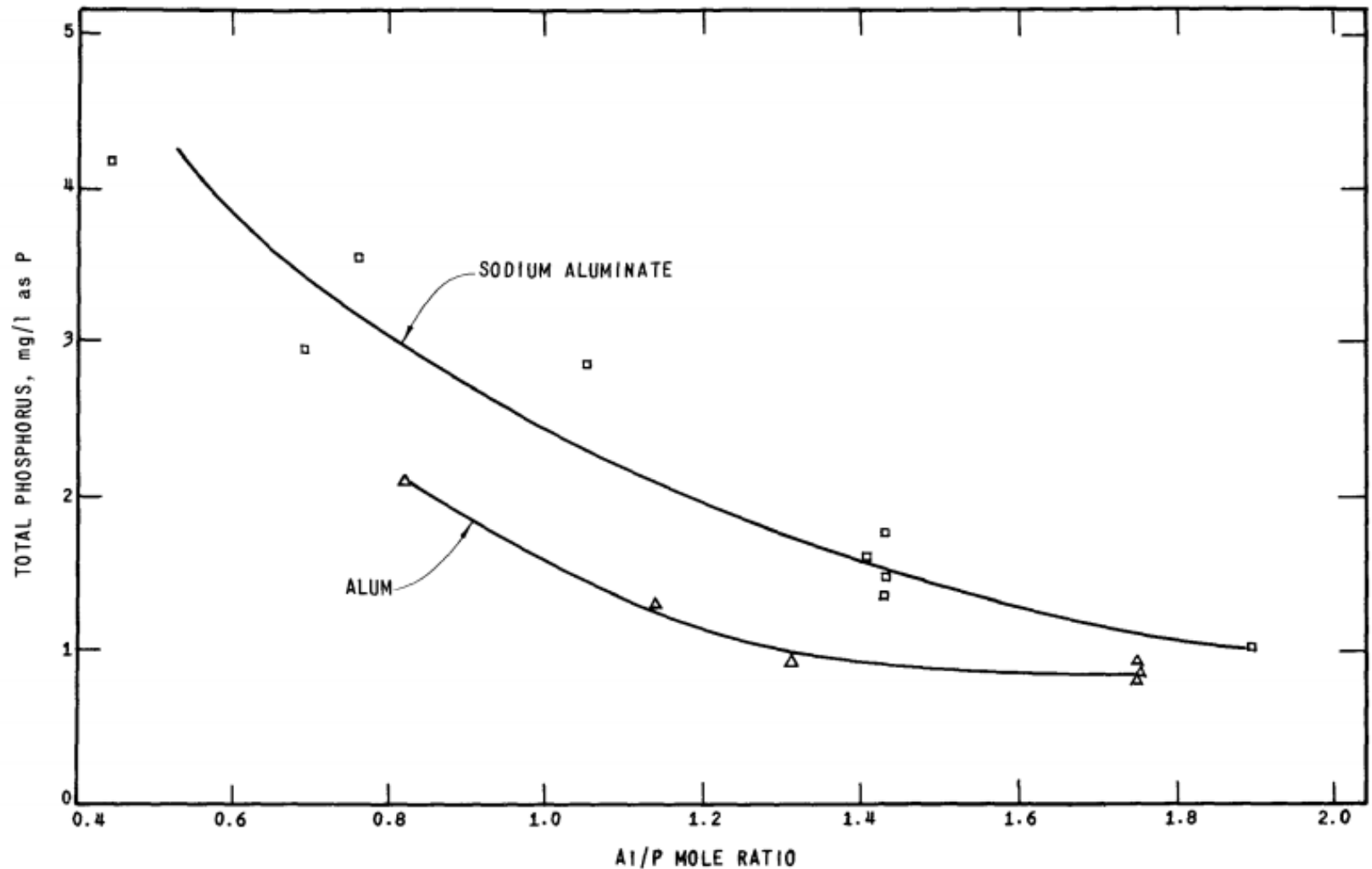- **Higher Al (III) requirement with aluminate than alum.**

FIGURE 7-5 COMPARISON OF THE EFFECTIVENESS OF ALUM AND SODIUM ALUMINATE ON PHOSPHORUS REMOVAL

Ref: National Service Center for Environmental Publications (NSCEP)
Process Design Manual for Phosphorus Removal, April 1976

Addition of Ca

- Lime is cheaper than alum, $FeCl_3$ or $Fe_2(SO_4)_3$.

- It can achieve the lowest residual phosphate concentration because of the formation of apatites, $Ca_5(OH)(PO_4)_3$.

- Apatites are highly insoluble Ksp = $10^{-55.0}$, however a high pH must be attained to realize their formation.

- Because calcium forms $CaCO_3$ near pH 9.5 and pHs higher than 9.5 are required for significant apatite formation, the alkalinity of water is the governing factor for the required dose of lime.

Very high doses of lime are required, which makes this choice costly compared to other metal agents, although the lowest residual P concentrations can be achieved.

$Ca(OH)_2$, CaO : Both Ca^{++} and OH^- source.

$$5\ Ca^{2+} + OH^- + 3\ PO_4^{3-} \longleftrightarrow Ca_5(OH)(PO_4)_{3\ (s)}$$

$$Ca^{2+} + CO_3^= \longleftrightarrow CaCO_{3\ (s)}$$

This reaction is not our purpose but we cannot prevent its formation.

➢ Ca requirement for P removal is a function of carbonate alkalinity. Avoid if alkalinity is too high. ($CaCO_3$ sludge) See Fig. 6-11 from Met-Calf&Eddy

➢ High pH is required (pH : 10 – 11) See Fig. 2-2

➢ Neutralize or recarbonate (CO_2) to bring the pH down after precipitation.

Figure 6-11

Lime dosage required to raise the pH to 11 as a function of untreated wastewater alkalinity.
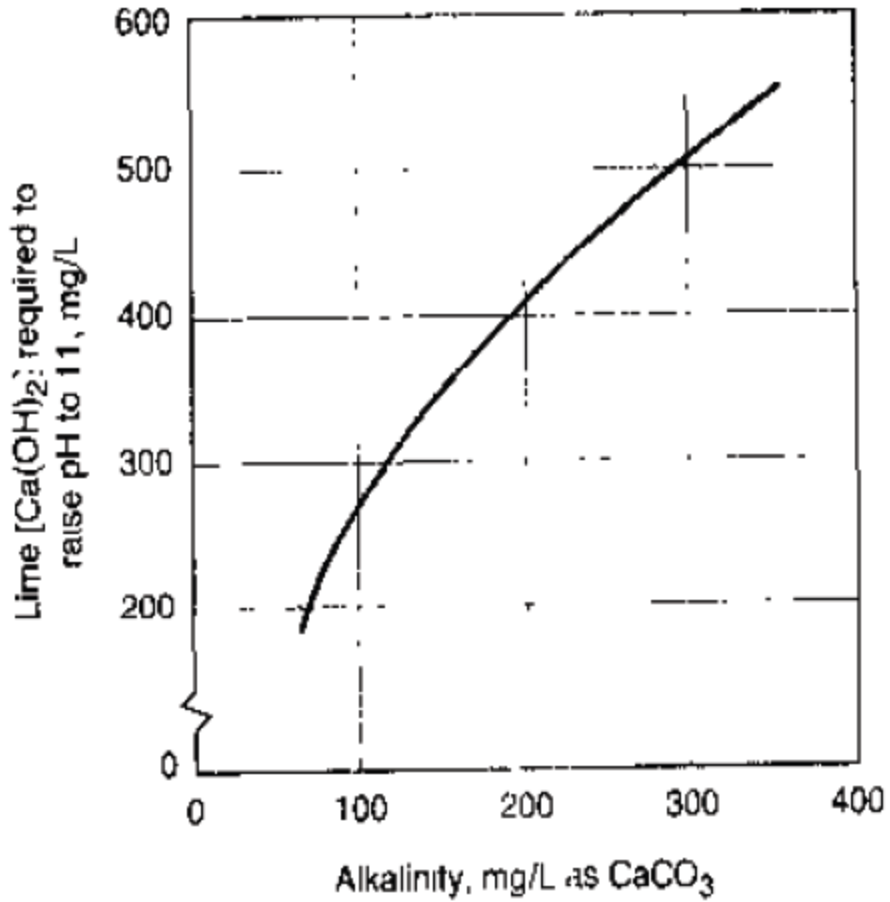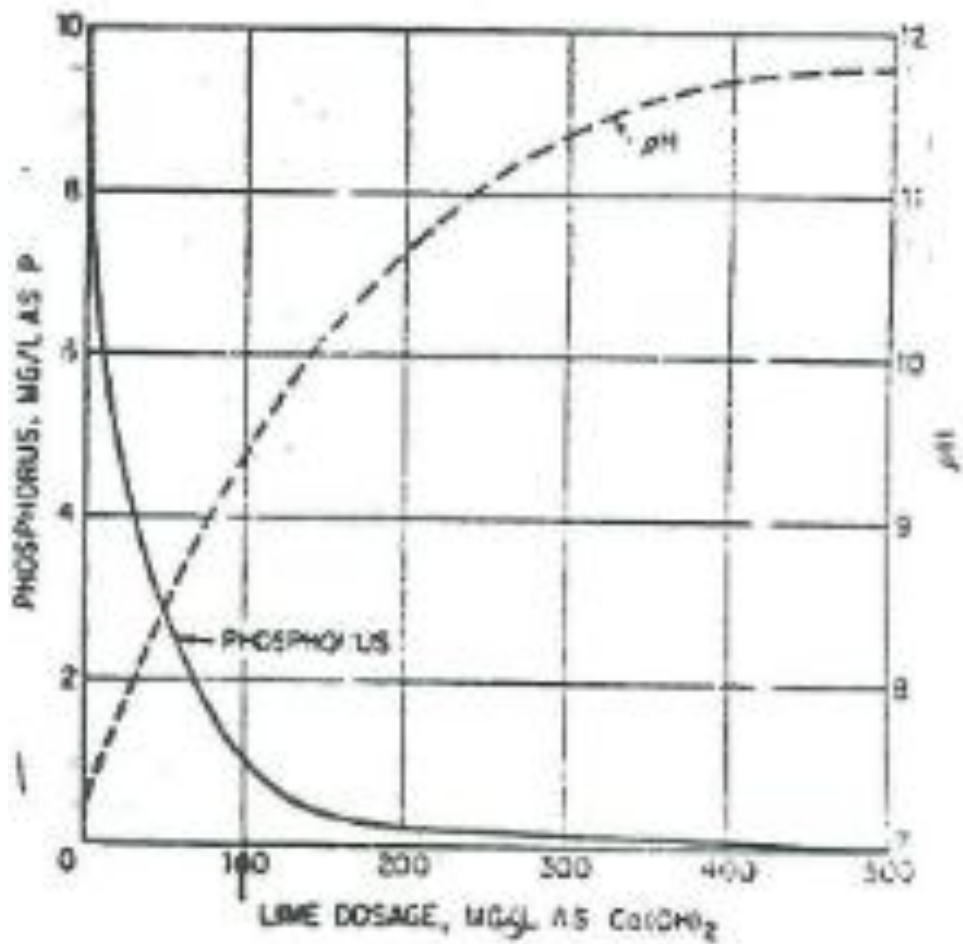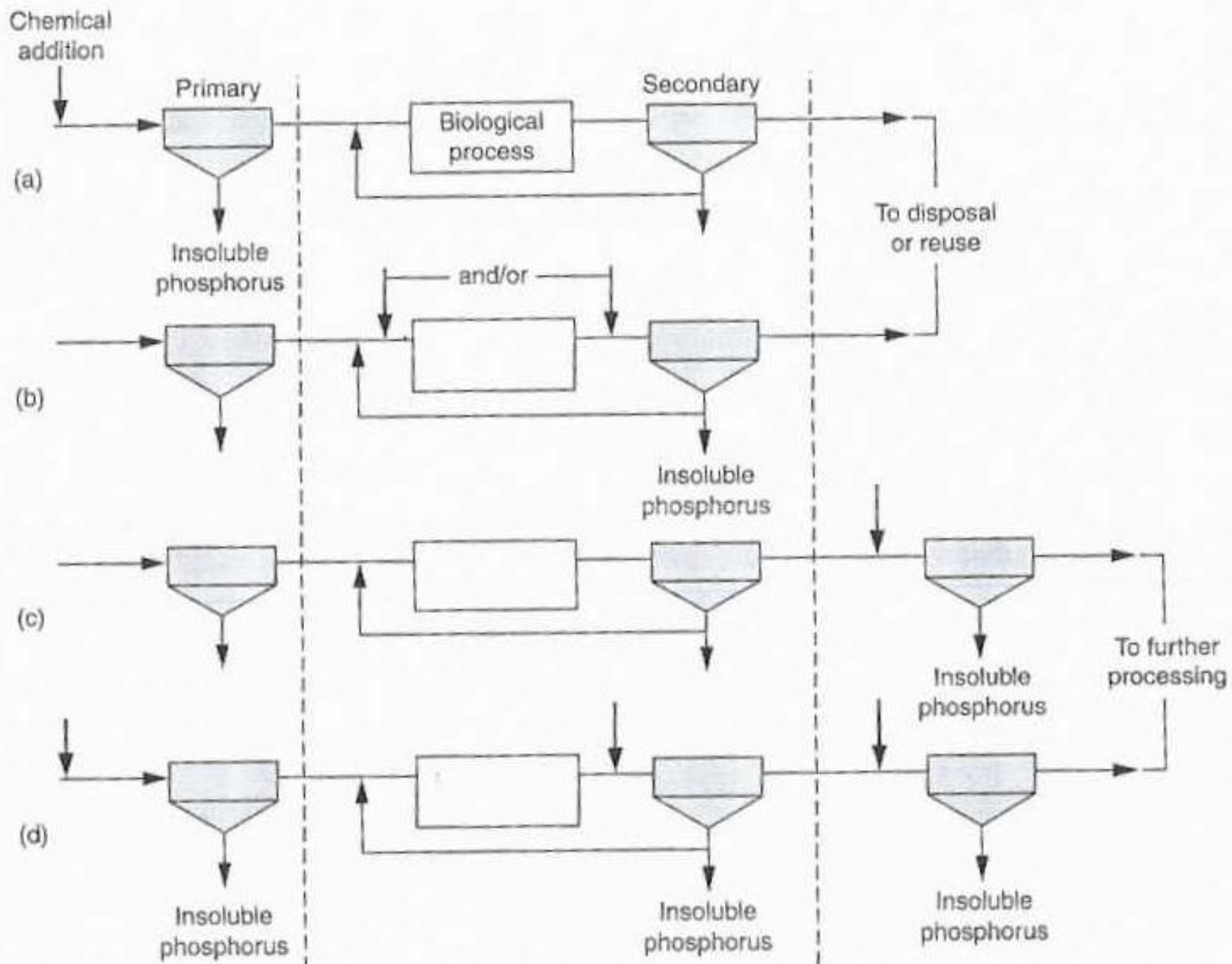
Figure 2-2 Lime coagulation of sewage.

Phosphorus Removal in Various Stages

- Addition of metal coagulants to wastewater can have a significant impact on the amount of sludge produced.
- There are a variety of chemical application points in the treatment scheme.
- The common addition points for metals in biological treatment plants are before the primary clarifier or before the secondary clarifier or during tertiary treatment.
- Some alternative treatment schemes are shown in the following slide.

Chemical addition

Primary

Biological process

Secondary

To disposal or reuse

Insoluble phosphorus

(a)

and/or

(b)

Insoluble phosphorus

Insoluble phosphorus

(c)

To further processing

Insoluble phosphorus

(d)

Insoluble phosphorus

Insoluble phosphorus

Insoluble phosphorus

During Primary Treatment

➢ Increases BOD and SS removal

➢ Least efficient use of salts. Therefore you have to add too much chemical.

➢ Fe and Al sludges are difficult to dewater.

➢ Results in sludge mass increases from 50 to 100% from the primary clarifier and an overall increase of 60 – 70% in the sludge mass produced by the plant.

During Secondary Treatment

➢ Lime cannot be used because of high pH.

➢ Overdose of Al or Fe salts may cause low pH and toxicity.

➢ Increases in sludge mass are 35 – 45% from the clarifier and 10 – 25% for the whole plant.

➢ These salts will also have an impact on sludge dewaterability.

Tertiary Treatment

➢ Highest capital cost because you need to have another sedimentation tank.

➢ Most efficient metal use. You use the least amount of chemical and produce the least amount of sludge.

➢ Lowest P in the effluent.

➢ Lime recovery is possible.

$$\text{sludge} \xrightarrow[\text{Recalcination}]{\text{Heat}} CaO + CO_2$$
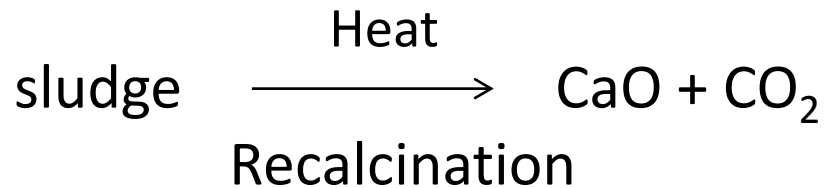
➢ Separate disposal of chemical precipitation.