

Chemical Precipitation

9.1 INTRODUCTION

The main chemical processes used in water and wastewater treatment practice include

- (1) Chemical coagulation, which is used to remove colloidal material
- (2) Chemical precipitation, which is used in water treatment to reduce water hardness by precipitation of calcium and magnesium ions and, in wastewater treatment, to remove phosphate as a precipitate of calcium, magnesium or iron.
- (3) Oxidation/reduction reactions, which, in conjunction with precipitation, are used to remove metals from wastewaters.
- (4) Water stabilisation, which regulates water pH to bring its carbonate system to an equilibrium state.
- (5) Ion-exchange processes, which are used for water softening and demineralisation.

Chemical coagulation is discussed in Chapter 3, while ion-exchange is the subject of Chapter 10. The remaining chemical processes are discussed in this chapter.

The following physical elements are common to most chemical process systems:

- (a) chemicals storage and handling facilities
- (b) chemicals dosing systems
- (c) rapid mixing system
- (d) reaction vessel (generally agitated)
- (e) solids separation system

Storage and handling facilities depend to a large extent on (i) the form and quantity in which chemicals are purchased, i.e. whether in bulk, liquid, solid or powdered form, and (ii) the characteristics of the chemicals, i.e. whether corrosive, hygroscopic etc. It is important to note that the most widely used construction materials – steel and concrete – require special protection in a low pH environment. It is normal design practice to provide bunded surrounds to chemical storage tanks to contain accidental spillages.

Chemical processes may be operated on a batch or continuous basis. For continuous operation special dosing facilities are required. Dry feeders may be used for the continuous addition of non-hygroscopic chemicals in powdered form, while variable-stroke piston or diaphragm pumps are widely used for the continuous addition of solutions. Simple dosing facilities are adequate for batch process operations.

The mixing system must effect a uniform dispersion of the added chemical in the water or wastewater being treated. Mixing systems which may be used include conduit mixing (conduit velocity $> 1 \text{ m s}^{-1}$); pump mixing – where the chemical is injected into the suction side of the pump; and turbine, propeller or other impeller-type, high-speed mixing devices.

The size of the reaction vessel required depends on reaction kinetics. In general, process design should aim to optimise the reaction kinetics so that the desired reaction goes to completion in the minimum time. This often requires that the reaction pH has to be maintained at a fixed value by the addition of an acid (e.g. coagulation of protein, isoelectric pH 4.2) or alkali (e.g. precipitation of calcium and magnesium). Where precise control of pH is required the use of automated control systems is essential.

Chemical precipitates are separated by sedimentation, sometimes with the aid of prior coagulation.

9.2 PRECIPITATION PROCESSES

The extent of separation of a cation by precipitation depends to a large extent on the solubility of its precipitate, which is usually either a hydroxide, carbonate or phosphate salt. At the saturation or equilibrium concentration of these slightly soluble salts an equilibrium exists between the solute ions and the solid phase, e.g.



For which the equilibrium expression is

$$\frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{CaCO}_3]_s} = K \quad (9.2)$$

The activity of the solid phase is constant and hence the denominator in equation (9.2) can be combined with K:

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = K_{\text{sp}} \quad (9.3)$$

where K_{sp} is called the solubility product. Solubility product values for a number of slightly soluble salts relevant to the present discussion are given in Table 9.1. In the case of hydroxides, solubilities can be calculated directly from the appropriate K_{sp} value if the pH is known. For carbonates and phosphates the calculation of solubility is complicated by their reactions in solution.:



For which the equilibrium expressions are usually written in the form:

$$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_2 = 10^{-10.4} \quad (9.6)$$

Table 9.1 Solubility constants at 25 °C*

Solid	pK _{sp}	Solid	PK _{sp}
Fe(OH) ₃ (amorph)	38	BaSO ₄	10
FePO ₄	17.9	Cu(OH) ₂	19.3
Fe ₃ (PO ₄) ₂	33	PbCl ₂	4.8
Fe(OH) ₂	14.5	Pb(OH) ₂	14.3
FeS	17.3	PbSO ₄	7.8
Fe ₂ S ₃	88	PbS	27
Al(OH) ₃ (amorph)	33	MgNH ₄ PO ₄	12.6
AlPO ₄	21	MgCO ₃	5
CaCO ₃ (calcite)	8.34	Mg(OH) ₂	10.7
CaCO ₃ (aragonite)	8.22	Mn(OH) ₂	12.8
CaMg(CO ₃) ₂ (dolomite)	16.7	AgCl	10
CaF ₂	10.3	Ag ₂ CrO ₄	11.6
Ca(OH) ₂	5.3	Ag ₂ SO ₄	4.8
Ca ₃ (PO ₄) ₂	26	Zn(OH) ₂	17.2
CaSO ₄	4.59	ZnS	21.5
SiO ₂ (amorph)	2.7		

*The equilibrium constant for the reaction $A_xB_y(\text{s}) \rightleftharpoons xA^{y+} + yB^{x-}$ is $K_{\text{sp}} = [A^{y+}]^x[B^{x-}]^y$;
 pK_{sp} = -log K_{sp}
 Source: *Snoeyink and Jenkins (1980)*

$$\frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = K_3 = 10^{-12.3} \quad (9.7)$$

Taking CaCO_3 as an example:

$$[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] \quad (9.8)$$

also

$$[\text{H}^+][\text{OH}^-] = K_w \quad (9.9)$$

The simultaneous solution of equations (9.3), (9.6), (9.8) and (9.9), together with the approximation that $[\text{OH}^-] = [\text{HCO}_3^-]$, produces the following equation:

$$K_2S^4 - 2K_2K_{sp}S^2 - K_wK_{sp}S + K_2K_{sp}^2 = 0 \quad (9.10)$$

where $S = [\text{Ca}^{2+}]$.

For a phosphate salt the corresponding equation is:

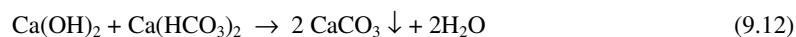
$$K_3S^4 - 2K_3K_{sp}S^2 - K_wK_{sp}S + K_3K_{sp}^2 = 0 \quad (9.11)$$

9.2.1 Precipitation of Ca^{2+} and Mg^{2+}

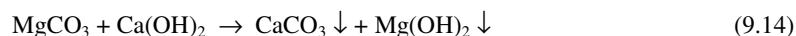
Ca^{2+} and Mg^{2+} are mainly responsible for causing 'hardness' in water. They precipitate soaps, hindering lather formation and may also cause the formation of a hard scale in hot water distribution systems and boilers. Water hardness is generally expressed as equivalent CaCO_3 in mg l^{-1} . Waters may be classified in hardness terms as follows:

0-100 mg l^{-1}	soft
100-250 mg l^{-1}	moderately hard
250-400 mg l^{-1}	hard
>400 mg l^{-1}	very hard

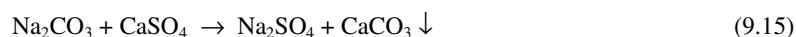
Ca^{2+} and Mg^{2+} can be precipitated in carbonate, hydroxide or phosphate forms. Carbonates and hydroxides are produced in the lime and lime-soda processes of water softening. On addition of hydrated lime ($\text{Ca}(\text{OH})_2$) to a hard water the following reactions occur:

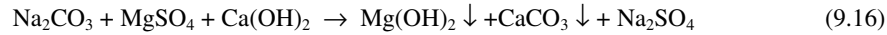


The solubilities of CaCO_3 and MgCO_3 at 20 °C are about 8.4 and 110 mg l^{-1} , respectively. In the presence of excess lime, MgCO_3 is converted to $\text{Mg}(\text{OH})_2$ which has a solubility of about 8.4 mg l^{-1} at 20 °C:



When Ca^{2+} and Mg^{2+} are associated with anions other than carbonates (non-carbonate hardness), precipitation can be effected by the addition of sodium carbonate:



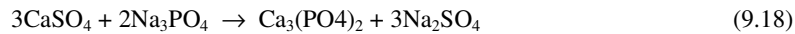
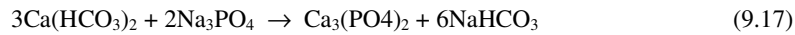


It is worthy of note that in the removal of hardness by the lime process the ion content of the water is reduced, while in the removal of non-carbonate hardness in the lime-soda process Ca^{2+} and Mg^{2+} are simply exchanged for Na^+ .

In theory, it should be feasible to reduce the hardness of water by chemical precipitation to a level corresponding to the solubilities of the carbonate and hydroxide precipitates produced, i.e. to a level of about 30 mg l^{-1} as CaCO_3 . In practice, however, the limiting concentration attainable is about 50-70 mg l^{-1} as CaCO_3 . This may be due to the formation of complex magnesium carbonates, which are more soluble than the hydroxide form.

Water softened by the lime or lime-soda processes are not stable and hence require pH adjustment, as discussed in section 9.3.

Sodium phosphate is also used as a precipitating agent for Ca^{2+} and Mg^{2+} ions. The resulting calcium and magnesium phosphates are less soluble than the corresponding carbonates and hydroxides ($<3.0 \text{ mg l}^{-1}$ as CaCO_3). The following are the relevant reactions:



Because phosphate is a relatively expensive precipitant, it can sometimes be used to best economic advantage in combination with lime and sodium carbonate when a water of very low hardness is required.

9.2.2 Precipitation of phosphorus from wastewaters

Phosphorus and nitrogen are the key nutrients that cause enrichment of natural water bodies giving rise to excessive growth of aquatic plants and plant-like organisms such as algae, a condition generally known as eutrophication. In most fresh waters phosphorus is the nutrient that limits growth because of its limited availability in the natural aquatic environment. Hence, the reduction of phosphorus to a low level is normally specified for wastewaters discharged into such sensitive receiving waters. This can be achieved by chemical precipitation and/or by enhanced biological uptake (see Chapter 12 for discussion of the latter).

The typical total phosphorus (TP) concentration in municipal wastewater varies from conurbation to conurbation but generally falls within the range $1.6\text{-}2.2 \text{ g d}^{-1}$ per person-equivalent (PE). Assuming a specific water consumption of $150 \text{ l PE}^{-1} \text{ d}^{-1}$, this corresponds to a wastewater concentration range of $10\text{-}15 \text{ mg l}^{-1}$. Wastewater phosphorus is present in domestic wastewater in orthophosphate, polyphosphate and organic phosphate forms, typically in the approximate ratio 5:4:1 (Snoeyink and Jenkins, 1980). Conventional wastewater treatment, including primary sedimentation and normal biological treatment, is unlikely to remove more than about 40% of the TP load, leaving a residual concentration in the typical range $6\text{-}9 \text{ mg l}^{-1}$. Hence, in circumstances where there is a requirement for the reduction of wastewater TP to a low level, say $1\text{-}2 \text{ mg l}^{-1}$ (discharge to sensitive waters), it is necessary to include a phosphorus precipitation step in the treatment system. The chemical precipitants used are hydrated lime, aluminium and iron salts.

The precipitant chemical may be added to the raw influent (pre-precipitation) or may be dosed into the mixed liquor in the aeration basin of an activated sludge process (simultaneous precipitation) or in a separate final stage of treatment (post-precipitation).

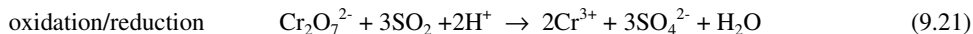
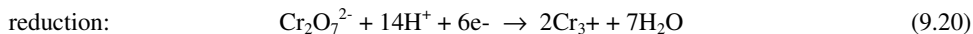
Precipitation as calcium phosphate is achieved by adding lime ($\text{Ca}(\text{OH})_2$) to the wastewater, raising the pH to about 10.5. The lime dose required to elevate the pH to this level is a function of the wastewater alkalinity and may be approximated as 1.5 times the alkalinity as CaCO_3 . Thus, the calcium dose is not stoichiometrically related to the phosphorus concentration. While lime is a relatively low-cost chemical, the disadvantages of the lime process are that it produces a large amount of sludge residue

and creates a too high pH for environmental discharge. While it would appear from the equilibrium solubility characteristics of calcium phosphates that a low phosphate concentration could be achieved at a pH value in the range 8.5-9.5, this has not been found to be feasible under typical wastewater process operating conditions.

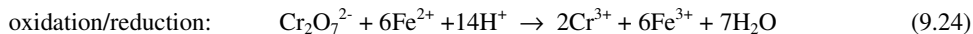
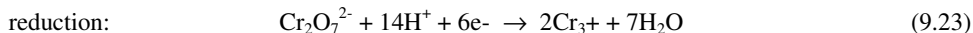
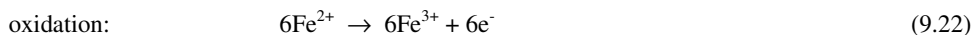
Iron and aluminium salts are used for phosphorus removal in both simultaneous and post-precipitation processes. Equilibrium analysis indicates that the minimum solubility of AlPO_4 is at about pH 6 and the minimum solubility of FePO_4 is at about pH 5. In practical wastewater applications the operating pH is likely to be well above these values and hence process performance in terms of residual TP is likely to adversely affected as the deviation of the process pH from the optimum pH increases. Operating experiences (Casey et al., 1978; USEPA, 1987) show that the theoretical solubility levels are not achievable in wastewater treatment processes at metal ion dose rates corresponding to the stoichiometric metal ion:phosphate ion ratio. It is found in practice that a metal ion addition of two to three times the stoichiometric requirement is necessary to reduce the effluent TP to the region of 1-2 mg/l. This excess over the stoichiometric amount is due to the simultaneous precipitation of metal hydroxide and the formation of soluble metal phosphate complexes. It is also important to note that the achievement of low effluent TP concentrations requires efficient removal of suspended solids. Each mg l^{-1} of dry effluent suspended solids in a biologically treated final effluent may increase the effluent TP concentration by 0.02 to over 0.04 mg TP l^{-1} (ATV, 2000).

9.2.3 Reduction and precipitation of Cr^{6+}

Hexavalent chromium (Cr^{6+}) occurs in wastes from metal plating and anodising processes. The pH of such wastes is usually quite low and the Cr^{6+} concentration may be as high as 2% by weight. Removal is effected in a two-stage process, in which Cr^{6+} is first reduced to Cr^{3+} and then precipitated as a hydroxide. The reducing agents commonly used are sulphur dioxide (SO_2), ferrous sulphate (FeSO_4) and sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$). The following oxidation-reduction reactions occur:

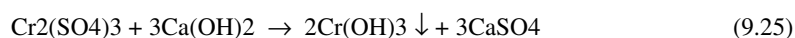


Reaction (9.21) is highly pH-dependent, being virtually instantaneous below pH 2.0. The reaction with metabisulphite is essentially the same as with SO_2 . When ferrous sulphate is the reducing agent used, the following reactions occur:

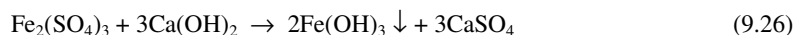


Reaction (9.24) is rapid below pH 3.0.

The trivalent chromium produced on reduction of Cr^{6+} is precipitated as a hydroxide on the addition of hydrated lime:



The ferric iron from reaction (9.24) is similarly precipitated:



9.3 CHEMICAL STABILISATION

In the context of water treatment, stability is generally taken to mean the existence of an equilibrium condition in respect of dissolved calcium carbonate, i.e. a stable water will neither deposit calcium carbonate in the distribution system nor will it take calcium carbonate into solution from the distribution system. When such a condition exists, equilibrium equations (9.3) and (9.6) apply:

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = K_{\text{sp}} \quad (9.3)$$

$$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_2 = 10^{-10.4} \quad (9.6)$$

Combining (9.3) and (9.6):

$$\frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{H}^+]} = K_{\text{sp}} / K_2 \quad (9.27)$$

or

$$\text{pH}_s = \text{p}K_2 - \text{p}K_{\text{sp}} - \log[\text{Ca}^{2+}] - \log[\text{HCO}_3^-] \quad (9.28)$$

where pH_s is the equilibrium pH corresponding to the Ca^{2+} and HCO_3^- concentrations in solution. The difference between the pH_s of a water and its actual pH is a measure of its instability and is sometimes called the Langelier saturation index (SI):

$$\text{SI} = \text{pH} - \text{pH}_s$$

In a fully stable water, SI is zero. When SI is positive the water is super-saturated and will deposit CaCO_3 ; when SI is negative, the water is under-saturated and will tend to take CaCO_3 into solution.

If the Ca^{2+} and HCO_3^- values are known, the value of pH_s can be calculated from equation (9.30), using the $\text{p}K_{\text{sp}}$ and $\text{p}K_2$ values given in Table 9.2.

		Table 9.2 Stability constants				
Temp. (°C)	5	10	15	20	25	40
$\text{p}K_{\text{sp}}$	8.09	8.15	8.22	8.28	8.34	8.51
$\text{p}K_2$	10.56	10.49	10.43	10.38	10.33	10.22

The influence of ion concentration on ion activity can be taken into account by modifying the constant values given in table 9.2 as follows (Fair et al., 1968):

$$\text{p}K_{\text{sp}} = \text{p}K_{\text{sp}}(\text{T}) - 4(\mu)^{0.5}/[1+3.9(\mu)^{0.5}] \quad (9.29)$$

$$\text{p}K_2 = \text{p}K_2(\text{T}) - 2(\mu)^{0.5}/[1+1.4(\mu)^{0.5}] \quad (9.30)$$

where T refers to temperature (°C) and μ is calculated as follows:

$$\mu \cong 2.5 \times 10^{-5} S_d, \text{ where } S_d \text{ is the total dissolved solids in the water (mg l}^{-1}\text{), or}$$

$$\mu \cong 4\text{H} - T_{\text{alk}}, \text{ where H is the total hardness (moles l}^{-1}\text{) and } T_{\text{alk}} \text{ is the total alkalinity (eq l}^{-1}\text{).}$$

Some natural waters of low hardness and alkalinity as well as coagulated waters and waters softened by the ion-exchange process may have a negative saturation index. This is corrected by raising the pH by

the addition of alkali chemicals such as lime ($\text{Ca}(\text{OH})_2$), soda ash (Na_2CO_3) or caustic soda (NaOH). Lime-softened waters, on the other-hand, have a positive saturation index and are equilibrated by the addition of an acid or CO_2 gas.

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Related reading

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