PROCESS DESCRIPTION

In a limestone contactor, water flows through a bed of crushed sieved limestone in a similar way as it would flow through a sand filter (Spencer, 2000). The pH of water that flows through the limestone bed will be adjusted until it nears equilibrium with calcium carbonate ($CaCO_3$(s)). The components of a contactor include a contact tank, limestone bed, inlet line, outlet line, overflow line, access lid (for closed system contactor only) and a flush outlet line (DeSouza et al., 2000).

There are two types of contactors: (i) open and (ii) closed system contactor. The former is exposed to the atmosphere and the latter is covered from the atmosphere. There are also contactors that are built in pressurized vessels (Stauder, 2002).

Limestone contactors are typically located at the end of the treatment train – after filtration, primary disinfection and chlorine contact (Spencer, 2000 and Benjamin et al., 1992). According to Spencer (2000) and Benjamin et al. (1992), by placing a contactor this way ensures the pH is maintained at a low level for effective chlorination. However, there are also contactors that are located after filtration and before chlorine addition (Stauder, 2002). Most of these contactors are located in Germany. The reason for placing the contactor before chlorine addition is because disinfection is not required in most limestone contactor plants in Germany especially if the plants are treating high quality deep spring water with very low turbidity (less than 0.1 NTU) and no or very low numberof coliforms (Stauder, 2003).

The SSP takes a side stream of unstabilized water and doses it with carbon dioxide (De Souza et al., 2000). The acidified CO_2-dosed side-stream then contacts a limestone bed, which will dissolve a considerable amount of $CaCO_3$, increasing alkalinity and calcium concentration in the water. Much of the remaining CO_2 is recovered by stripping with air and reused in the process whereas the stabilized side-stream blends with the main stream for full stabilization.

The Simplified SSP is similar to the SSP but excludes CO_2 recovery. In this process, there are two options that can be carried out after the acidified CO_2-dosed side-stream contacts with a limestone bed: (1) Strip CO_2 from the sidestream with no recovery, or (2) blend the sidestream and mainstream without stripping (De Souza et al., 2000).

The Spraystab I is intended for small groundwater systems that need to remove iron or manganese. It combines aeration, limestone stabilization and filtration in one tank (Mackintosh, De Souza and De Villiers, 2003). The raw groundwater is first aerated to strip excess carbon dioxide from water and dissolve oxygen in the water to be stabilized. Finally, the water flows through a dual media filter (top layer of hydro-anthracite and lower layer of filter sand). In the filter, the limestone fines and other insoluble matter such as iron and manganese flocs are removed.

The Spraystab II is intended for small groundwater systems that do not need to remove iron or manganese. It is similar to Spraystab I but excludes multi-media filtration and the water flows in the contactor in an upward direction (Mackintosh, De Souza and De Villiers, 2003). The raw groundwater is first aerated and then flows downward through a tube to the base of the limestone stabilization unit. Sludge and iron flocs (if iron is

present in the water) will be collected at the base of the unit. Then, the water is collected and uniformly distributed by a slotted pipe manifold system through the limestone bed in an upward direction to be stabilized.

(A) CHEMICAL REACTIONS INVOLVED IN LIMESTONE DISSOLUTION

In order to understand the reactions involved in a limestone contactor, one must understand the basic principles governing the carbonate system in natural water and its equilibrium with limestone. Natural water contains carbonate species such as aqueous or dissolved carbon dioxide ($CO_2(aq)$), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) (Snoeyink and Jenkins, 1980). In a limestone contactor, the concentrations of the dissolved carbonate species are driven toward chemical equilibrium with $CaCO_3$ by dissolving limestone. It is the interaction of these species that controls the pH in natural water (De Souza et. al., 2000) and can be undersaturated, in equilibrium or oversaturated with $CaCO_3$ although low pH and alkalinity waters here are undersaturated with $CaCO_3$.

The degree of $CaCO_3$ saturation of water is commonly calculated using the Langelier Index (L.I.). L.I. is the difference between the actual pH and hypothetical pH at equilibrium. Undersaturated water is represented by a negative value of L.I. and tends to dissolve $CaCO_3$ whereas oversaturated water is represented by a positive value of L.I. and tends to precipitate $CaCO_3$. Other procedures that can be used to determine the state of saturation of $CaCO_3$ include evaluating the Calcium Carbonate Dissolution Potential, Ryznar (Saturation) Index, general saturation index also known as disequilibrium index and Larson's Ratio (Schock, 1999b). Marble Test and the carbonate saturometer device can also be used and both operate on the same principle (Schock, 1999b).

If one assumes that the only aqueous species are H^+, OH^-, calcium and carbonate species, then reactions 1 to 7 take place when unstabilized water dissolves limestone in a closed system and reaches equilibrium.

Equation 1. Dissociation of Water

$$H_2O \Leftrightarrow H^+ + OH^- \qquad\qquad K_W = \{H^+\}\{OH^-\}$$

Equation 2. Dissolution of CaCO$_3$ from Limestone

$$CaCO_{3(s)} \Leftrightarrow Ca^{2+} + CO_3^{2-} \qquad\qquad Ksp = \{Ca^{2+}\}\{CO_3^{2-}\}$$

Equation 3. Formation of HCO$_3^-$

$$CO_3^{2-} + H^+ \Leftrightarrow HCO_3^- \qquad\qquad K_{a,2} = \frac{\{HCO_3^-\}}{\{H^+\}\{CO_3^{2-}\}}$$

Equation 4. Formation of H$_2$CO$_3$*

$$HCO_3^- + H^+ \Leftrightarrow H_2CO_3^* \qquad\qquad K_{a,1} = \frac{\{H_2CO_3^*\}}{\{H^+\}\{HCO_3^-\}}$$

Equation 5. Formation of CaCO$_3$^{o} Complex:

$$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3^o \qquad\qquad K = \frac{\{CaCO_3^o\}}{\{Ca^{2+}\}\{CO_3^{2-}\}}$$

Equation 6. Formation of CaOH$^+$ Complex:

$$Ca^{2+} + OH^- \Leftrightarrow CaOH^+ \qquad\qquad K = \frac{\{CaOH^+\}}{\{Ca^{2+}\}\{OH^-\}}$$

Equation 7. Formation of CaHCO$_3$$^+$ Complex:

$$Ca^{2+} + HCO_3^- \Leftrightarrow CaHCO_3^+ \qquad\qquad K = \frac{\{CaHCO_3^+\}}{\{Ca^{2+}\}\{HCO_3^-\}}$$

In reactions 1 to 7, activities rather than concentrations are used in expressing the corresponding equilibrium constants. This is due to increased electrostatic interactions between ions as concentration of ions in solution increases (Snoeyink and Jenkins, 1980). As a result, the activity of ions becomes less than their measured or analytical concentration. Several mass balances must also be met as follows.

Equation 8. Total Calcium Concentration

$$C_{T,Ca} = [Ca^{2+}] + [CaHCO_3^+] + [CaCO_3^0] + [CaOH^+]$$

Equation 9. Total Carbonate Concentration

$$C_{T,CO3} = [H_2CO_3^*] + [HCO_3^-] + [CaHCO_3^+] + [CaCO_3^o] + [CO_3^{2-}]$$

Equation 10. Charge Balance

$$2[Ca^{2+}] + [CaHCO_3^+] + [CaOH^+] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

Equation 11. Concentration Balance

$$C_{T,Ca} = C_{T,CO3}$$

Calculations for real waters soon become more complicated because of the presence of other species but the principles are the same. Realistically, computer softwares such as AQUACHEM, MINEQL, MINTEQ, STASOFT or custom programs are used. Both Letterman and Kothari (1995) and Schott (2003) have developed programs specifically for solving dissolution of limestone in contactors as discussed later.

(B) MATHEMATICAL MODEL OF LIMESTONE DISSOLUTION

As CaCO₃ dissolves from the limestone contactor media, particle size, bed depth, bed porosity, flow velocity and pressure drop change with time. It is important to make design choices for these variables since they affect the dissolution rate and recharge frequency. Letterman and Kothari (1995) and Haddad (1986) developed models of limestone dissolution rate that are sensitive to these variables and can be used for design. Haddad (1986) used Equation 12 and 13 to model the limestone dissolution process in a contactor operating at steady state.

Equation 12. Calcium Carbonate Dissolution Rate, r

$$r = k_o a (Ceq - C)$$

where:

r = Calcium carbonate dissolution rate (moles/cm².s).

Ceq = Equilibrium calcium ion concentration, moles/L.

C = Bulk calcium concentration, moles/L.

a = Area of $CaCO_3$ per unit volume of fluid, cm⁻¹.

k_o = Overall dissolution rate constant, cm/s.

Equation 13. Continuity Equation

$$N_D \frac{d^2C}{dZ^2} - \varepsilon \frac{dC}{dZ} + r\theta = 0$$

where:

N_D = Axial dispersion number, dimensionless.

Z = Depth, dimensionless.

ε = Porosity of limestone particles, dimensionless.

θ = Mean fluid residence time, sec.

Using equations 12 and 13, Letterman, Haddad and Driscoll (1991) developed a steady-state model that relates the depth of limestone required in the contactor to the desired effluent water chemistry, influent water chemistry, limestone particle size and shape, bed porosity, water temperature and superficial velocity (Equation 14).

Equation 14. Substitution of Equation 12 into 13

$$\frac{C_{eq} - C_{bL}}{C_{eq} - C_{bo}} = \exp\left\{ -\frac{k_o a L \varepsilon}{U_s} + \left(\frac{k_o a L \varepsilon}{U_s}\right)^2 N_D \right\}$$

where:

C_{bo} = Calcium concentration in the influent of a contactor, moles/L.

C_{bL} = Calcium concentration in the effluent of a contactor, moles/L.

L = Overall depth of a contactor, cm.

U_s = Superficial velocity of fluid, cm/s.

N_D = Axial dispersion number, dimensionless.

This model assumes that the rate of dissolution is controlled by two resistances that act in series: a surface reaction that controls the release of calcium from the solid and a mass transfer resistance that controls the rate of calcium transport between the solid surface and the bulk solution (Letterman and Kothari, 1995). Based on this kinetic model, Letterman and Kothari (1995) developed a computer program called DESCON. It can be downloaded from http://web.syr.edu/~rdletter/software.htm. It is used to facilitate the design of limestone contactors and will be discussed later in this module.

(C) FACTORS AFFECTING CaCO₃ DISSOLUTION RATE IN A LIMESTONE CONTACTOR

Dissolution of limestone increases pH, alkalinity and dissolved inorganic carbon (DIC) of water and depletes the amount of limestone in a bed (Haddad, 1986). As the amount of limestone lessens over time, the bed depth and contact time will also be reduced. In a poorly designed contactor, dissolution takes less time for the limestone to reach the recharge level and it needs to be refilled more frequently. This will not only affect the contactor performance but also the operating cost. Therefore, it is important to know the factors affecting dissolution rate of limestone before designing a contactor in order to ensure its long-term performance. Generally, the dissolution rate of limestone is affected by the physical and chemical properties of water and limestone as discussed below.

1. Physical and Chemical Properties of Water:

1.1. Extent of $CaCO_3$ undersaturation:
Water can dissolve limestone only if it is undersaturated with respect to $CaCO_3$. Higher dissolution rates occur with waters that are more undersaturated (Van Tonder et. al., 1997; Striebel et. al., 2002).

1.2. DIC content:
DIC is the sum of all carbonate containing species. It is represented by C_{T,CO_3} as shown in Equation 9. If the concentrations of complexes are assumed to be negligibly small, the DIC concentration is the sum of $H_2CO_3^*$, HCO_3^- and CO_3^{2-} concentrations. DIC content governs the equilibrium of the carbonate system and the level of $CaCO_3$ saturation. It affects the dissolution rate because it affects the extent of $CaCO_3$ undersaturation.

1.3. Temperature:
Limestone dissolution rate increases as the temperature of water increases (Cox, 1930; Letterman, 1995; Spencer, 2000). Rickard and Sjoberg (1983) also found that the overall dissolution rate constant is a complex function of temperature.

1.4. Ionic strength:
Rickard and Sjoberg (1983) demonstrated an ionic strength dependence of calcite dissolution rates in their study. In general, solubility of salts increases with increasing ionic strength (Snoeyink and Jenkins, 1980). Since ionic strength is used to calculate the activity coefficients of each carbonate species in water, it also affects the activities of species in equilibrium and dissolution kinetic equations.

1.5. Iron content:
A study conducted by Maree et. al. (1992) on using limestone in neutralizing acid mine water reveals that the efficiency of $CaCO_3$ stabilization process is strongly influenced by the acid mine water's iron content. They found that Fe(II) inhibits the dissolution rate due to precipitation of Fe(II) on the limestone surface. However, this may not necessarily occur with surface waters since typical iron content in surface waters is much lower and the pH is much higher than in acid mine water.

2. Physical and Chemical Properties of Limestone:

2.1. Limestone content:
There are several types of minerals that can be considered as limestone and used as a media in a contactor. These include marbles, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). In Germany, half-burnt dolomite ($CaCO_3.MgO$) and porous calcium carbonate ($CaCO_3$) are used (Stauder, 2003). According to Letterman (1995), media with the highest calcite and lowest dolomite content has the highest initial rates of dissolution. When dolomite was used, he found that the calcium carbonate

component of the dolomite dissolved faster than the magnesium carbonate component. A similar result was reported by Plummer and Busenberg (1982) (Letterman, 1995). Laboratory tests conducted by Menendez et. al. (2000) using limestone to neutralize acidic mine drainage also showed that the higher the $CaCO_3$ content in the stone, the higher the dissolution rate. The same result was also obtained in a study conducted by Letterman (1995) where the overall dissolution rate constant decreased by approximately 60% as the calcite content decreased from 0.92 to 0.09 g $CaCO_3$ per gram stone.

2.2. Particle size:

According to Rickard and Sjoberg (1983), Erga and Terjesen found that the rate of calcite dissolution is proportional to the surface area per unit volume of media. Smaller media sizes have a larger surface area exposed to the water, resulting in higher dissolution rates compared to the larger media sizes (Cox, 1930; Santoro et al., 1987; Maree et al. 1992; Du Plessis et al., 1994; Menendez et al., 2000).

2.3. Presence of impurities:

Benjamin et al. (1992) recommended that the type of limestone to be used in a contactor should be of high calcium limestone with minimum impurities. Impurities in limestone include iron, aluminum and silica. According to Letterman (1995), presence of silica only reduced the effective surface area of limestone but did not appear to cause a reduction in the dissolution rate of the calcite surface. However, aluminum and iron content of the stone reduced the overall dissolution rate.

Haddad (1986) also found that as limestone dissolved from the stone, the rate of dissolution decreased because a residue layer consists of insoluble impurities (such as silica, alumino-silicates and aluminum and iron oxides/hydroxides) is formed and remains on the surface. As the layer thickness increases, the rate of transport of calcium ion from $CaCO_3$ surface to the bulk solution decreases (Letterman, 1995).

(D) MODELING THE SSP AND SIMPLIFIED SSP

The dissolution of gaseous CO_2 into the aqueous phase depends on the relative CO_2 concentration in the two phases, surface area at the gas / liquid interface and mixing energy within the aqueous phase (De Souza et al., 2000). In addition, the temperature, pressure and ionic strength of the system also play important roles in the CO_2 dissolution. The recovery of excess dissolved CO_2 from the aqueous phase is affected by the difference in CO_2 concentration in the aqueous and gaseous phases, the surface area at the gas / liquid interface and pressure of the system.

PRO/II (manufactured and distributed by Simulation Sciences, Inc.) was initially selected by CSIR to model the SSP (De Souza et al., 2000). It modeled unit processes involved in the SSP such as feed generation, CO_2 addition/dissolution and $CaCO_3$ addition/dissolution but not the CO_2 stripping from the sidestream. Another model was later developed called SSP-MOD program. This program was developed from a model

used to describe the Simplified SSP. However, unlike the Simplified SSP, STASOFT 4 and WATCHEM cannot be used to model the SSP since they do not provide a mechanism for gas recycling. Therefore, JAVA was used to develop modules that model the various unit operations (such as CO_2 stripping, recovery and subsequent recycling) and a steady state mass balance in the SSP. The SSP-MOD program allows multiple runs using multiple input ranges and produce output that can be exported to MSExcel for graphical representation.

The model used to describe the Simplified SSP was developed using JAVA and STASOFT 4 package. STASOFT 4 package is an aquatic chemistry calculation package that consists of two programs called STASOFT 4 and WATCHEM. STASOFT 4 can be used to model the Simplified SSP since gas recycling is not required. WATCHEM is a user input program. This model produces output that can be customized and imported into MSExcel for graphical representation. Multiple runs can be conducted using this program. The following variations can be used in a single run:

a) Varying the sidestream/mainstream blending ratios.
b) Stripping CO_2 to the atmosphere before or after blending.
c) Operating with or without CO_2 stripping.
d) Adding various buffers such as lime, sodium hydroxide and sodium carbonate.