

# WatPro

Water Treatment Simulator for Predicting Water Quality



## TECHNICAL REFERENCE

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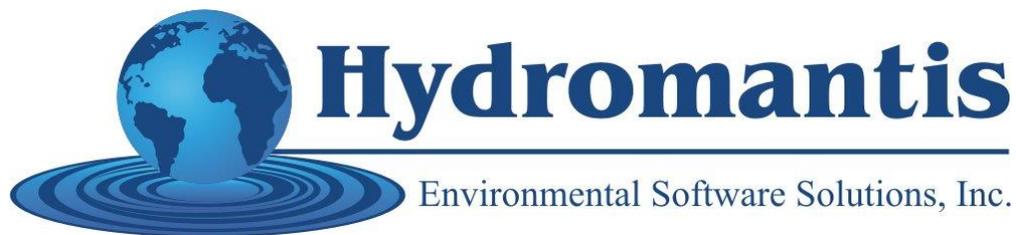
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# 1 Mathematical Models

This chapter of the WatPro manual presents the mathematical expressions used to model water quality. Many concepts are presented including inactivation of pathogens by various chemicals, formation of disinfectant by-products as a result of chemical addition and reduction of disinfectant concentrations through the system. A simplified order of operations used by WatPro is presented below.

- Initial reactions (e.g. chlorine interaction with ammonia)
- Ion balance (e.g. pH)
- Disinfectant concentration reduction (e.g. chlorine decay, chlorine dioxide consumption)
- Ion balance
- Inactivation by various chemicals (e.g. logarithmic reduction of *Giardia* cysts due to chlorine addition)
- Disinfectant By-Product formation (e.g. THM).

## 1.1 Inactivation

WatPro examines the reduction of *Giardia* and viruses, both by chemical disinfection (inactivation), and by physical removal, such as by filtration. WatPro considers the overall reduction of micro-organisms in a water treatment system to be the sum of the inactivations for each of the individual unit processes plus removal credits for filtration. The degree of inactivation is determined by the product of the disinfectant concentration (C) and contact time (t) and is referred to as the Ct value. The degree of inactivation by each disinfectant for given a Ct value is presented separately. Concentration and contact time are also discussed in separate sections.

### Inactivation Definition

Inactivation is based on species population (e.g. *Giardia* cyst, viruses) before and after disinfection according to the equation below.

$$\log \text{inactivation} = -\log_{10}\left(\frac{N}{N_0}\right)$$

where:

$N$  = concentration of microorganisms after treatment

$N_0$  = concentration of microorganisms before treatment

The percent inactivation of the species given the log inactivation can be determined from the inactivation expression and is presented below.

$$\% \text{ inactivation} = 100 - \frac{100}{10^{\text{loginactivation}}}$$

If a number of unit processes are connected in series, the overall inactivation of the system is the sum of the inactivations over all of the unit processes. If more than one disinfectant is present, the each disinfectant can be considered separately, and the overall inactivation is the sum of the inactivations at each unit process for each disinfectant. The inactivation for multiple unit processes and multiple disinfectants is presented below.

$$(\text{Overall Log Inactivation}) = \sum_{i=1}^m \sum_{j=1}^n (\text{Inactivation of Unit Process})_{i,j}$$

where:

$m$  : number of unit processes in series

$n$  : number of disinfectants

Unit Process <sub>$i,j$</sub>  : inactivation for  $i^{\text{th}}$  unit process with  $j^{\text{th}}$  disinfectant

### Inactivation Required as Indicated by the Surface Water Treatment Rule

Guidelines for disinfection are provided in the USEPA publication “Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources” (USEPA, 1991). This manual is often referred to as the Surface Water Treatment Rule and will be identified in future references as the SWTR.

The SWTR recommends that the inactivation requirements be based on the influent concentration of *Giardia* cyst concentration (daily average; geometric mean) (USEPA, 1991, section 4.4.2). The inactivation requirements based on influent *Giardia* concentrations, as used by WatPro, are presented in the table below. The SWTR recommends inactivation based on concentration ranges of <= 1, 1-10 and 10-100 cysyts/100L. Required inactivation for influent concentration in the ranges of 100-1000 and 1000-10000 cycsts/100L were obtained from USEPA (1992).

*Inactivation Requirements Used in WatPro*

<b>Giardia Cyst Concentration (Giardia/100L)</b>	<b>Recommended Giardia inactivation</b>	<b>Recommended Virus inactivation</b>
<= 1	3-log	4-log
>1-10	4-log	5-log
>10-100	5-log	6-log
>100-1000	6-log	7-log
>1000-10000	7-log	8-log

**Chlorine Inactivation**

*Chlorine Inactivation - Giardia*

Tables are provided in the SWTR (Appendix E, Tables E-1 to E-6, p. 185 - 187b) that relate the Ct value and the resultant log inactivation of *Giardia* cysts due to chlorine. Martin (1993) indicated that the SWTR treats *Giardia* inactivation due to chlorine for temperatures ranging from 0.5 to 5°C by the following relationship:

$$Ct = 0.36(pH)^{2.69} (C)^{0.15} (\text{inactivation})^1 (T)^{-0.15}$$

where:

Ct = free chlorine concentration (mg/L as Cl<sub>2</sub>) multiplied by the contact time t<sub>10</sub> (min) (mg min/L)

C	= free chlorine concentration (mg/L as Cl <sub>2</sub> )
inactivation	= logarithmic reduction in <i>Giardia</i> cyst concentration (--)
T	= temperature (°C)

This equation can be applied to temperatures greater than the 0.5 to 5°C range by applying the assumption (used in the SWTR) that there is a twofold decrease in Ct values every 10°C increase in temperature. To obtain an equation that can be used for all temperatures, Martin estimated Ct values at 5°C and applied the SWTR doubling assumption for every 10°C drop in temperature to come up with the following relationship that can be used for all temperatures.

$$Ct = 0.2828(\text{pH})^{2.69} (C)^{0.15} (\text{inactivation})^1 (0.933)^{(T-5)}$$

The equation can be rearranged so that given a Ct value, the *Giardia* cyst inactivation is calculated. The rearranged equation is presented below and is the form used by WatPro to determine the inactivation of *Giardia* cysts due to free chlorine.

$$\text{inactivation} = \frac{Ct}{0.2828(\text{pH})^{2.69} (C)^{0.15} (0.933)^{(T-5)}}$$

### *Chlorine Inactivation - Virus*

A table is provided in the SWTR (USEPA, 1991) (Appendix E, Table E-7, p. 188) that relate the Ct value and the resultant log inactivation of viruses due to free chlorine. The SWTR virus inactivation table for free chlorine is reproduced below.

Ct Values for Inactivation of Viruses by Free Chlorine

SWTR: Table E-7

Temperature (°C)	CT for Log Inactivation					
	2		3		4	
	pH		pH		pH	
	6 to 9	10	6 to 9	10	6 to 9	10
0.5	6	45	9	66	12	90
5	4	30	6	44	8	60
10	3	22	4	33	6	45
15	2	15	3	22	4	30
20	1	11	2	16	3	22
25	1	7	1	11	2	15

CT values in table have units mg.min/L

WatPro uses a polynomial interpolation of the SWTR tabular data. The maximum credit that WatPro applies is a 4-log reduction. Inactivation less than 2-log is extrapolated from the table.

**Chloramine Inactivation**

*Chloramine Inactivation - Giardia*

*Giardia* cyst inactivation due to chloramine is presented in the SWTR (USEPA, 1991) in a tabular format (Appendix E, Table E-12, page 190b). The SWTR *Giardia* cyst inactivation table for chloramine (Appendix E, Table E-12) is reproduced below.

Ct Values for Inactivation of *Giardia* Cysts by Chloramine

SWTR: Table E-12

Inactivation	Temperature (°C)					
	<= 1	5	10	15	20	25
0.5 log	635	365	310	250	185	125
1 log	1270	735	615	500	370	250
1.5 log	1900	1100	930	750	550	375
2 log	2535	1470	1230	1000	735	500
2.5 log	3170	1830	1540	1250	915	625
3 log	3800	2200	1850	1500	1100	750

values in table have units mg min/L

WatPro uses a polynomial interpolation of the SWTR tabular data. The maximum credit that WatPro applies to chloramine *Giardia* inactivation is 3-log reduction. Inactivation less than 0.5-log is extrapolated from the table. At very low temperatures and  $t_{10}$  values, the Ct values calculated can be very small, for example in the range of approximately 1 to 10 mg-min/L. These low values of Ct lie far outside of the range of values provided by the EPA table for *Giardia* inactivation. The interpolation procedure used in WatPro needs external boundary values to function correctly outside of the values in the Ct table. For this solution, WatPro has set supplementary external boundary conditions such that a Ct value of 0 corresponds to log inactivation of 0 for *Giardia*. The interpolation procedure can then range to values substantially less than Ct values in the EPA table.

### Chloramine Inactivation - Viruses

Virus inactivation due to chloramine is presented in the SWTR (USEPA, 1991) in a tabular format (Appendix E, Table E-13, page 191). The SWTR virus inactivation table for chloramine (Appendix E, Table E-13, page 191) is reproduced below.

Ct Values for Inactivation of Viruses by Chloramine

SWTR: Table E-13

Inactivation	Temperature (°C)					
	<= 1	5	10	15	20	25
2 log	1243	857	643	428	321	214
3 log	2063	1423	1067	712	534	356
4 log	2883	1988	1491	994	746	497

values in table have units mg min/L

WatPro uses a polynomial interpolation of the SWTR tabular data. The maximum credit that WatPro applies is 4-log reduction. Inactivation less than 2-log is extrapolated from the table. At very low temperatures and  $t_{10}$  values, the Ct values calculated can be very small, for example in the range of approximately 1 to 10 mg-min/L. These low values of Ct lie far outside of the range of values provided by the EPA table for virus inactivation. The interpolation procedure used in WatPro needs external boundary values to function correctly outside of the values in the Ct table. For this solution, WatPro has set supplementary external boundary conditions such that a Ct value of 0 corresponds to log inactivation of 0 for virus. The interpolation procedure can then range to values substantially less than Ct values in the EPA table.

**Chlorine Dioxide Inactivation**

*Chlorine Dioxide Inactivation - Giardia*

*Giardia* cyst inactivation by chlorine dioxide is presented in the SWTR (USEPA, 1991) in a tabular format (Appendix E, Table E-8, page 188). WatPro uses a polynomial interpolation of the SWTR tabular data. The maximum credit that WatPro applies is a 3-log reduction. Inactivation less than 0.5-log is extrapolated from the table. The SWTR *Giardia* cyst inactivation table for chlorine dioxide is reproduced below.

Ct Values for Inactivation of *Giardia* Cysts by Chlorine Dioxide

SWTR: Table E-8

Inactivation	Temperature (°C)					
	<=1	5	10	15	20	25
0.5 log	10	4.3	4	3.2	2.5	2
1 log	21	8.7	7.7	6.3	5	3.7
1.5 log	32	13	12	10	7.5	5.5
2 log	42	17	15	13	10	7.3
2.5 log	52	22	19	16	13	9
3 log	63	26	23	19	15	11

values in table have units mg.min/L

*Chlorine Dioxide Inactivation - Viruses*

Virus inactivation by chlorine dioxide is presented in the SWTR (USEPA, 1991) in a tabular format (Appendix E, Table E-9, page 189). WatPro uses a polynomial interpolation of the SWTR tabular data. The maximum credit that WatPro applies is a 4-log reduction. Inactivation less than 2-log is extrapolated from the table. The SWTR virus inactivation table for chlorine dioxide is reproduced below.

## Ct Values for Inactivation of Viruses by Chlorine Dioxide

SWTR: Table E-9

Inactivation	Temperature (°C)					
	<=1	5	10	15	20	25
2 log	8.4	5.6	4.2	2.8	2.1	1.4
3 log	25.6	17.1	12.8	8.6	6.4	4.3
4 log	50.1	33.4	25.1	16.7	12.5	8.4

values in table have units mg.min/L

## Ozone Inactivation

### Ozone Inactivation - *Giardia*

Ozone *Giardia* inactivation (Ct) tables are presented in the SWTR (USEPA, 1991) in Appendix E (p.189 and 190) and in Appendix O (calculating Ct for ozone). WatPro uses a polynomial interpolation of the SWTR tabular data. The maximum credit that WatPro applies to ozone for *Giardia* inactivation is 3-log reduction. For Ct values less than those indicated in the table, extrapolation of the data is conducted. For temperatures greater than 25°C, extrapolation of the data is conducted.

Ozone disinfection is only considered in the ozone unit processes. For other unit processes, the ozone concentration is assumed to be zero.

Ct values for Inactivation of *Giardia* Cysts by Ozone pH 6-9

SWTR: Table E-10

Inactivation	Temperature (deg C)					
	<= 1	5	10	15	20	25
0.5 log	0.48	0.32	0.23	0.16	0.12	0.08
1 log	0.97	0.63	0.48	0.32	0.24	0.16
1.5 log	1.5	0.95	0.72	0.48	0.36	0.24
2 log	1.9	1.3	0.95	0.63	0.48	0.32
2.5 log	2.4	1.6	1.2	0.79	0.60	0.40
3 log	2.9	1.9	1.43	0.95	0.72	0.48

values in table have units mg min/L.

### Ozone Inactivation - Viruses

Ozone virus inactivation (Ct) tables are presented in the SWTR (USEPA, 1991) in Appendix E (p.190) and in Appendix O (calculating Ct for ozone). WatPro uses a polynomial interpolation of the SWTR tabular data. The maximum credit that WatPro applies to ozone for virus inactivation is 4-log reduction. For Ct values less than those indicated in the table, extrapolation of the data is done. For temperatures greater than 25°C, extrapolation of the data is done.

Ozone disinfection is only considered in the ozone unit processes. For other unit processes, the ozone concentration is assumed to be zero.

#### Ct Values for Inactivation of Viruses by Ozone

SWTR: Table E-11

Inactivation	Temperature (deg C)					
	<= 1	5	10	15	20	25
2 log	0.9	0.6	0.5	0.3	0.25	0.15
3 log	1.4	0.9	0.8	0.5	0.4	0.25
4 log	1.8	1.2	1.0	0.6	0.5	0.3

values in table have units mg min/L

### Potassium Permanganate Inactivation

The SWTR (Appendix F, Section F.2.6, p. 200) provides a description of potassium permanganate used as an oxidant in water treatment. It indicates that potassium permanganate may contribute to virus inactivation. The data presented in the SWTR are only provided as an indication of the potential of potassium permanganate as a disinfectant, and are not meant to be used as a basis for establishing Ct requirements. WatPro does not model potassium permanganate as a disinfectant.

## 1.2 Disinfectant Concentration

### Ozone Concentration

The value of the ozone concentration (C) used in the inactivation calculation (Ct) is dependent on how the concentration was obtained. If the ozone concentration represents the average of values throughout the depth of the tank, then this value can be used directly as the concentration. If the ozone concentration represents the effluent concentration from an ozone contactor cell, then this value must be modified depending on the configuration of the ozone contactor. The SWTR (USEPA, 1991, Table O-6, p.315) provides a table to determine the average tank ozone concentration based on the effluent concentration and the configuration of the contactor. This table is reproduced below. The table considers whether the contactor cell is the first in a series or not. For co-current and counter-current systems, a partial credit for inactivation is given dependent on the effluent residual ozone concentration.

Correlations to Predict Tank Ozone Concentration Based On Outlet Ozone Concentrations

SWTR: Table O-6 (p. 315)

	Flow Configuration			
	Turbine*	Co-Current	Counter-Current**	Reactive Flow
First Chamber*** (where O <sub>3</sub> added)	C = C <sub>out</sub>	partial credit <sup>α</sup>	partial credit <sup>α</sup>	not applicable
Subsequent Chambers (where O <sub>3</sub> added)	C = C <sub>out</sub>	C=C <sub>out</sub> or C = .5(C <sub>in</sub> +C <sub>out</sub> )	C = C <sub>out</sub> /2	C = C <sub>out</sub>

\* The turbine configuration is considered a complete mix system (O.1-5 p.291) and therefore the effluent concentration equals the tank concentration.

\*\* maximum ozone concentrations occur at the effluent.

\*\*\* used if O<sub>3</sub> is added or only effluent O<sub>3</sub> concentration is known or input into WatPro

α: partial credit: virus: 1-log inactivation credit if C<sub>out</sub> > 0.1 mg/L.

*Giardia*: 0.5 log inactivation credit if C<sub>out</sub> > 0.3 mg/L

The partial credit assumes that the tanks of the ozone contactor are the same size (O.3-8, p.315b).

For turbine addition of ozone, the tank is considered a complete mix system and therefore the effluent is the same as the tank contents. For a counter current system, the effluent concentration represents the maximum value. The water has been exposed to the ozone for the entire passage down the height of the tank. The average concentration in the tank (used as C, if available) is therefore less than the concentration of the water leaving this contactor cell.

For ozone contactor cells where ozone is not added but ozone concentrations are greater than zero, WatPro uses the effluent ozone concentration from the cell as the ozone concentration for the Ct calculation.

### Other Disinfectant Concentrations

For all disinfectants not discussed separately, the disinfectant concentration used in the inactivation calculation of Ct is represented by the unit process effluent concentration.

## 1.3 Contact Time

Three contact times are considered in WatPro;  $t_{10}$ ,  $t_{50}$  and  $t_{theta}$ . Each of the terms are defined below.

**$t_{10}$ :** Represents the time during which 90% of the water entering a tank remains in the tank. Put another way,  $t_{10}$  is the time in which 10% of the water entering a tank leaves the tank.

**$t_{50}$ :** Represents the time during which 50% of the water entering a tank remains in the tank.

**$t_{theta}$ :** Represents the time a particle of water would remain in the tank if the tank were a plug flow system (V/Q). For a plug flow system  $t_{10} = t_{50} = t_{theta}$

Uses for each of the contact times are described below.

$t_{10}$ : Used as the contact time for microbial disinfection

$t_{50}$ : Used as the contact time for DBP formation

$t_{theta}$ : Used as a reference time when comparing to a plug flow system. That is,  $t_{theta}$  represents the plug flow case.

If no tracer data are available, the ratios  $t_{10}:t_{theta}$  and  $t_{50}:t_{theta}$  have been assigned default values. For  $t_{10}:t_{theta}$ , the default ratio is generally a function of the tank baffling condition (i.e. ratios closer to one are associated with greater baffling). For  $t_{50}:t_{theta}$ , the default ratio is 0.7. If the  $t_{10}:t_{theta}$  ratio is greater than the  $t_{50}:t_{theta}$  ratio, then the  $t_{50}:t_{theta}$  ratio value is assigned the  $t_{10}:t_{theta}$  value. The WatPro default  $t_{10}:t_{theta}$  ratio as a function of tank baffling condition is identical to the SWTR (App C.2.3, p.149). The table below indicates the WatPro ratios.

Default Baffling Conditions in WatPro

Baffling Conditions	$t_{10}:t_{theta}$	$t_{50}:t_{theta}$
Un-baffled	0.1	0.7
Inlet Only	0.3	0.7
Inlet/outlet/intra-basin	0.5	0.7
Perforated inlet/intra basin	0.7	0.7
Plug flow	1.0	1.0

The above table applies for all unit processes except for channel, filtration, GAC and membrane. WatPro assumes that the channel and filtration unit processes have  $t_{10}:t_{theta}$  and  $t_{50}:t_{theta}$  ratios of 0.5 and 0.9, respectively. The GAC and membrane unit processes do not consider contact time.

## Tanks in Series

Hydraulically, unit processes can be described as either complete mix tanks, or plug flow tanks, or any hybrid of the two. In the tanks-in-series model, any flow through tank can be equated to a number of complete mix tanks in series. As the number of the tanks in series increases, the greater the tendency of the tanks to act like a plug flow system. The tanks-in-series method is useful when batch-system (i.e. plug flow) derived parameters are converted to a non-plug flow system. In order to estimate the number of tanks in series that can represent a system, the cumulative age distribution function (CSTRs-in-series model) is used. The cumulative age distribution function,  $F(t)$ , is reviewed by Teefy and Singer (1990) and Lawler and Singer (1993) and uses the summation expression presented below.

$$F(t) = 1 - \exp\left(-\frac{Nt}{t_{\text{theta}}}\right) \sum_{i=1}^N \left\{ \frac{1}{(i-1)!} \left(\frac{Nt}{t_{\text{theta}}}\right)^{i-1} \right\}$$

Where:

- $F(t)$  = cumulative age distribution; for  $t_{10}$   $F(t) = 0.1$
- $N$  = number of tanks in series
- $t$  = time in tank
- $t_{\text{theta}}$  = theoretical detention time of the tank

For  $t_{10}$ , the value of  $F(t)$  is 0.1. If the time,  $t$ , is the  $t_{10}$  value, then the ratio of  $t_{10}$  to  $t_{\text{theta}}$  can be evaluated for a given number of tanks in series. For a system with a given  $t_{10}:t_{\text{theta}}$  ratio, the number of tanks in series as indicated by solving the  $F(t)$  equation would lie between two whole numbers. In order to determine which number of tanks in series would represent the system, the mid-point value is used as the determining point. For example, if the number of tanks in series was actually between 2 and 3, but closer to 3 (more than half way between 2 and 3), 3 would be used. Based on this assumption, the table below was generated. This method was also used by USEPA (1992).

$t_{10}:t_{\theta}$	N	$t_{10}:t_{\theta}$	N
0 - 0.186	1	0.671 - 0.682	14
0.186 - 0.317	2	0.682 - 0.691	15
0.317 - 0.402	3	0.691 - 0.700	16
0.402 - 0.461	4	0.700 - 0.708	17
0.461 - 0.506	5	0.708 - 0.716	18
0.506 - 0.540	6	0.716 - 0.723	19
0.540 - 0.569	7	0.723 - 0.729	20
0.569 - 0.593	8	0.729 - 0.735	21
0.593 - 0.613	9	0.735 - 0.741	22
0.613 - 0.630	10	0.741 - 0.746	23
0.630 - 0.645	11	0.746 - 0.751	24
0.645 - 0.659	12	0.751 - 1	25
0.659 - 0.671	13		

Disinfectant decay, described separately in section 5.5, uses the tanks-in-series concept (parameters determined in batch experiments). Since inactivation uses only the  $t_{10}$  value, the tanks in series method is not required for inactivation.

## 1.4 Initial Disinfectant Demand

Following the addition of a disinfectant, a rapid decline in disinfectant concentration is typically observed. This initial uptake of the disinfectant is referred to as the initial demand. This section examines models that have been developed for estimating the initial demand. The models presented represent default models that are used if no other models are available. WatPro has the capability to be calibrated with respect to initial demand.

## Initial Chlorine Demand

From work conducted by Dharmarajah et al. (1991) an expression was derived for the instantaneous demand of chlorine by raw water. The expression, presented below, does not include initial chlorine demand due to ammonia.

$$C_{\text{instantaneous}} = \exp \left\{ -0.620 + 0.522 * \ln \left( \frac{\text{Dosage}}{\text{TOC}} \right) + 0.302 * \ln(\text{UV}_{254}) + 0.842 * \ln(\text{TOC}) \right\}$$

where:

Dosage = dosed chlorine concentration (mg/L as Cl<sub>2</sub>)

TOC = raw water TOC concentration (mg/L)

UV<sub>254</sub> = raw water UV absorbance at 254 nm; 1 cm pathlength (cm<sup>-1</sup>).

When determining the free chlorine concentration following the addition of chlorine the following expression is used.

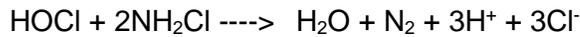
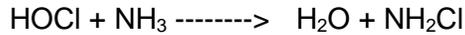
$$C_{\text{residual}} = C_{\text{dose}} - C_{\text{instantaneous}}$$

where:

C<sub>residual</sub> = the free chlorine concentration after the initial chlorine demand is considered

## Initial Chlorine Demand Due to Ammonia

When chlorine is added to water containing ammonia, monochloramine is assumed to form. If after all of the ammonia has reacted and there is still free chlorine present, the monochloramines react to form nitrogen gas. The assumed reactions are presented below. A similar approach was used by USEPA, 1992.



The initial chlorine demand due to ammonia is assumed to be instantaneous and is also assumed to occur before all other reactions.

### Initial Chlorine Dioxide Demand

In water treatment, dissolved organic matter and dissolved metals, such as manganese (II), react with  $\text{ClO}_2$  to create an instantaneous demand. The mathematical equation representing the consumption of chlorine dioxide (see Section on Disinfectant Decay) accounts for an initial demand of the disinfectant if the reaction time is 0 after the addition point. If the model detects a residual of chlorine dioxide in any process, the term for initial chlorine dioxide demand in the equation is voided.

## 1.5 Disinfectant Decay

When disinfectants are added to water, their concentrations have been observed to decline as a function of time. This section examines models that have been developed to determine the unit process effluent concentration based on the influent concentration. The models presented represent default models that are used if no other models are available.

### Chlorine Decay

Dharmarajah et al. (1991) presented chlorine decay curves based on batch experiments. It was observed that the decay curve could be represented by first or second order (by concentration) expressions depending on the time and ratio of the chlorine dose to initial TOC concentration ( $\text{Cl}_2:\text{TOC}$ ). The  $\text{Cl}_2:\text{TOC}$  ratios measured were 0.5, 1.0 and 1.5 and the calculated chlorine decay constants were  $k_1$ ,  $k_2$  and  $k_3$ , respectively. Each of the decay constant expressions are presented separately.

Cl <sub>2</sub> :TOC = 1.0, 1.5	second order decay	0 < t < 5 hrs	(k <sub>1</sub> )
	first order decay	5 < t < 120 hrs	(k <sub>2</sub> )
Cl <sub>2</sub> :TOC = 0.5	first order decay	0 < t < 120 hrs	(k <sub>3</sub> )

A first order batch equation has the form indicated below

$$\frac{dC}{dt} = -kC$$

where:

C = chlorine concentration (mg/L) at time t (hr)

k = decay constant (hr<sup>-1</sup>)

A second order batch equation has the form indicated below

$$\frac{dC}{dt} = -kC^2$$

In order to use the results of a batch experiment (equivalent to a plug flow system) for non-plug flow systems, a mass balance for a single CFSTR was developed. The resulting mass balance expressions are presented below.

$$\text{First Order: } C_{\text{out}} = \frac{C_{\text{in}}}{1 + kt_{\text{theta}}}$$

$$\text{Second Order: } C_{\text{out}}^2 (kt_{\text{theta}}) + C_{\text{out}} - C_{\text{in}} = 0$$

where:

$C_{out}$  = unit process effluent chlorine concentration (mg/L)

$C_{in}$  = unit process influent chlorine concentration (mg/L)

$k$  = decay coefficient ( $hr^{-1}$ )

$t_{theta}$  = theoretical detention time in the unit process ( $t_{10}$  used) (hr).

The second order equation is solved using the quadratic formula. The unit process is described using the tanks-in-series model, and the previous equations are applied to each of the tanks in series. The number of tanks in series is discussed separately in the contact time section.

$$k_1 = \exp \left\{ -2.44 - 1.57 * \ln \left( \frac{dosage}{TOC} \right) + 0.799 * \ln(UV_{254}) + 0.422 * pH \right\} / (dosage)$$

$$k_2 = \exp \left\{ -2.31 - 2.12 * \ln \left( \frac{dosage}{TOC} \right) + 1.27 * \ln(UV_{254}) + 0.471 * pH - 0.842 * \ln(TOC) \right\}$$

$$k_3 = \exp \left\{ -1.67 + 1.00 * \ln(UV_{254}) + 2.73 * \ln(TOC) \right\}$$

where:

dosage = dosed chlorine concentration (mg/L as  $Cl_2$ )

TOC = raw water TOC concentration (mg/L)

$UV_{254}$  = raw water UV absorbance at 254 nm; 1 cm path length ( $cm^{-1}$ ).

pH = pH after addition of chlorine (--).

WatPro assumes that the default first order chlorine decay constant is represented by  $k_3$  and that the default second order chlorine decay constant is represented by  $k_1$ . Under WatPro default conditions, if the chlorine dose to TOC ratio is less than 0.5, the first order rate constant

is used and if the chlorine dose to TOC ratio is greater than 0.5, the second order rate constant is used. In addition, WatPro assumes that if chlorine is not dosed upstream of the unit process, and chlorine is present (e.g. raw water chlorinated elsewhere), then the influent chlorine concentration represents the chlorine dose concentration for determining the decay constants. If chlorine is not dosed at a unit process, then the dosage concentration for chlorine decay purposes is considered to be dosage at the last point of addition.

Calibration of the WatPro chlorine decay model is possible and is discussed in the Software Features Chapter.

### Chloramine Decay

Dharmarajah et al. (1991) presented chloramine decay curves based on batch experiments. USEPA (1992) used this data to determine decay coefficients. For contact times less than 10 hours, the decay curve was modeled by USEPA (1992) as an  $m^{\text{th}}$  order reaction and for times greater than 10 hours as a first order reaction.

A first order batch equation has the form indicated below

$$\frac{dC}{dt} = -kC$$

where:

C = chloramine concentration (mg/L)

k = decay constant ( $\text{hr}^{-1}$ )

An  $m^{\text{th}}$  order batch equation has the form indicated below

$$\frac{dC}{dt} = -kC^m$$

The order value  $m$  of the  $m^{\text{th}}$  order expression was determined by the following expression (USEPA, 1992).

$$m = 19.72 * [\text{NH}_2\text{Cl}]^{0.09768}$$

where:

$$[\text{NH}_2\text{Cl}] = \text{chloramine concentration (mole/L as Cl}_2\text{)}$$

In order to use the results of a batch experiment (equivalent to a plug flow system) for non-plug flow systems, a mass balance for a single CFSTR was developed. The resulting mass balance expressions are presented below.

$$\text{First Order: } C_{\text{out}} = \frac{C_{\text{in}}}{1 + kt_{\text{theta}}}$$

$$m^{\text{th}} \text{ Order: } C_{\text{out}}^m (kt_{\text{theta}}) + C_{\text{out}} - C_{\text{in}} = 0$$

The  $m^{\text{th}}$  order decay curve is solved iteratively. The unit process is described using the tanks-in-series model, and the previous equations are applied to each of the tanks in series. The number of tanks in series is discussed separately in the contact time section. The decay constants are presented below and were obtained from the USEPA (1992) source code.

$$k(\text{first order}) = 0.4235 * [\text{H}^+]^{0.2269} * (\text{TOC})^{-0.1872} * (\text{UV}_{254})^{0.3763}$$

$$k(\text{sec ond order}) = (1.86 * 10^{-12}) * [\text{H}^+]^{1.013} * (\text{TOC})^{1.0822} * (\text{UV}_{254})^{3.83} * [\text{NH}_2\text{Cl}]^{-25.31}$$

where:

[H <sup>+</sup> ]	= hydrogen ion concentration (mole/L)
TOC	= raw water TOC concentration (mg/L)
UV <sub>254</sub>	= raw water UV absorbance at 254 nm; 1 cm path length (cm <sup>-1</sup> ).
[NH <sub>2</sub> Cl]	= chloramine concentration (mole/L)
dosage	= dosed chlorine concentration (mg/L as Cl <sub>2</sub> ).

The calibration of chloramine decay is not currently available in WatPro.

### Chlorine Dioxide Consumption

The model for chlorine dioxide consumption is from the experimental work of Korn (1998) in bench-scale batch tests. The model is an empirically derived expression incorporating single parameters and two-parameter interactions.

The relationship for chlorine dioxide consumption derived by Korn (1998) is presented below.

$$\begin{aligned} \log(\text{chlorine dioxide consumed, mg/L}) = & \\ & - 0.482 + 0.338 \log(\text{pH}) - 0.0934 \log(T) + 0.455 \log(\text{ClO}_2\text{conc.} + 1) \\ & - 0.0288 \log(t + 1) + 0.162 \log(\text{NPOC} * \text{UV}_{254}) + 0.361 \log(T) * \log(\text{ClO}_2\text{conc.} + 1) \\ & + 0.258 \log(\text{ClO}_2\text{conc.} + 1) * \log(t + 1) + 0.336 \log(\text{NPOC} * \text{UV}_{254}) * \log(\text{ClO}_2\text{conc.} + 1) \\ & - 0.114 \log(\text{NPOC} * \text{UV}_{254}) * \log(T) \end{aligned}$$

where:

pH	= pH after chlorine dioxide addition (-)
T	= temperature (°C)
ClO <sub>2</sub> conc.	= initial applied chlorine dioxide concentration (mg/L)

t	= reaction time in the batch reactor (hr)
NPOC	= non-purgeable organic carbon (mg/L)
UV <sub>254</sub>	= raw water UV absorbance at 254 nm; 1 cm path length (cm <sup>-1</sup> )

While the Korn (1998) model is based on non-purgeable organic carbon (NPOC) measurements, the WatPro model uses the more commonly used total organic carbon (TOC) concentration in the equation in place of NPOC. If chlorine dioxide is present and more chlorine dioxide is added, WatPro considers the 'ClO<sub>2</sub>conc' term in the above equation to be the sum of the chlorine dioxide present at the addition point and the concentration added. The value 't' is considered, by WatPro, to be the theoretical detention time of the unit process.

Calibration of the chlorine dioxide consumption model is possible, and is discussed in the Software Features chapter.

### Ozone Decay

No default ozone decay function is available in WatPro at this time.

## 1.6 Disinfection By-Product (DBP) Formation

When disinfectants are added to water, by-products, from their reaction with constituents in the water, have been observed. This section examines models that have been developed to determine Disinfection By-Product (DBP) formation as a result of disinfectant addition.

### Disinfection By-Products from Chlorine

#### *Trihalomethane (THM) Formation*

The formation of Trihalomethane (THM) is assumed to occur as the result chlorine addition. The expression used to determine total trihalomethane (TTHM) formation is based on batch experimental work conducted by Amy et al. (1987) and is presented below.

$$\text{TTHM} = 0.00309(\text{UV}_{254} \cdot \text{TOC})^{0.440} (\text{Cl}_2)^{0.409} (t)^{0.265} (T)^{1.06} (\text{pH} - 2.6)^{0.715} (\text{Br} + 1)^{0.0358}$$

where:

TTHM	= total trihalomethane concentration ( $\mu\text{mole/L}$ )
$\text{UV}_{254}$	= water UV absorbance at 254 nm; 1 cm path length ( $\text{cm}^{-1}$ )
$\text{Cl}_2$	= chlorine dose at start of batch experiment ( $\text{mg/L}$ )
t	= reaction time in the batch reactor (hr)
T	= temperature ( $^{\circ}\text{C}$ )
pH	= pH after chlorine reaction (-)
Br	= bromide concentration in raw water ( $\text{mg/L}$ )

The expression was derived from a database where a chlorine residual was always present. WatPro assumes no THM formation if there is no free chlorine present. WatPro assumes that if chlorine is not dosed upstream of the unit process, and chlorine is present (e.g. raw water chlorinated elsewhere), then the influent chlorine is assumed to represent the chlorine dose concentration. As indicated previously in the contact time section, the reaction time, t, is considered to be represented by the  $t_{50}$  value for a unit process. This assumption is also made by USEPA (1992). If chloramines are present, the TTHM formation has been observed to be reduced compared to when only chlorine is present. As a result, a factor of 0.2 times the general TTHM equation is applied when chloramines are present (USEPA, 1992).

The units for the TTHM are expressed in  $\mu\text{mole/L}$ . Typically units of  $\mu\text{g/L}$  are desirable, however, the conversion using molecular weight is difficult because there are many compounds which comprise the TTHM. In order to facilitate the conversion, USEPA (1992) used the Amy et al. (1987) database to develop a model which describes the average molecular weight of the of the THM species formed during their experiments. The equation developed is presented below. The expression was obtained from the USEPA (1992) source code.

$$\text{AMW} = 105.32(\text{Br} + 1)^{0.4817} (\text{UV}_{254})^{-0.0892}$$

where:

AMW	= average molecular weight of THM species formed (g/mol)
UV <sub>254</sub>	= water UV absorbance at 254 nm; 1 cm path length (cm <sup>-1</sup> )
Br	= bromide concentration in water (mg/L)

Based on the database developed by Amy et al. (1987), USEPA (1992) developed equations for four components of the TTHM (chloroform, bromodichloromethane, chlorodibromomethane and bromoform). The equations are presented below, and were obtained from the USEPA (1992) source code.

$$\text{CHCl}_3 = 0.2776 (\text{UV}_{254} \cdot \text{TOC})^{0.6157} (\text{Cl}_2)^{0.3909} (t)^{0.2651} (T)^{1.1498} (\text{pH} - 2.6)^{0.7995} (\text{Br} + 1)^{-2.2336}$$

$$\text{CHBrCl}_2 = 0.8626 (\text{UV}_{254} \cdot \text{TOC})^{0.1773} (\text{Cl}_2)^{0.3090} (t)^{0.2706} (T)^{0.7201} (\text{pH} - 2.6)^{0.9253} (\text{Br})^{0.7223}$$

$$\text{CHBr}_2\text{Cl} = 2.574 \left( \frac{\text{UV}_{254}}{\text{TOC}} \right)^{-0.1843} (\text{Cl}_2)^{-0.0746} (t)^{0.2519} (T)^{0.5704} (\text{pH} - 2.6)^{1.3488} (\text{Br})^{2.0843}$$

$$\text{CHBr}_3 = 61.4 (\text{UV}_{254})^{0.6827} (\text{Cl}_2)^{-0.1757} (t)^{0.1096} (T)^{-0.0596} (\text{pH} - 2.6)^{1.8866} \left( \frac{\text{Br}}{\text{TOC}} \right)^{1.7921}$$

where:

UV <sub>254</sub>	= water UV absorbance at 254 nm; 1 cm path length (cm <sup>-1</sup> )
Cl <sub>2</sub>	= chlorine dose at start of batch experiment (mg/L)
t	= reaction time in the batch reactor (hr)
T	= temperature (°C)
pH	= pH after chlorine reaction (-)
Br	= bromide concentration in raw water (mg/L).

When calculating the speciated concentrations for THM, the TTHM is assumed by WatPro to be determined by the TTHM equation. The fraction of the TTHM for each speciated compound is determined by the ratio of the individual speciated compound to the sum of the speciated compounds.

WatPro calculates the concentrations based on the influent conditions for the unit process.

Calibration of the WatPro TTHM model is possible and is discussed in the Software Features Chapter.

### *Haloacetic Acid (HAA) Formation*

HAA formation is based on the AWWA Technical Advisory Workgroup's (TAW) work. The data were obtained from a series of batch experiments, 96 hours in duration, using water from eight facilities. The work is presented in USEPA (1992), and is used as the default model in WatPro. The speciated expressions used to determine HAA formation are presented below and were obtained from the USEPA (1992) source code.

$$\text{MCAA} = 1.634(\text{TOC})^{0.753} (\text{Br} + 0.01)^{-0.085} (\text{pH})^{-1.124} (\text{Cl}_2)^{0.509} (\text{t})^{0.300}$$

$$\text{DCAA} = 0.605(\text{TOC})^{0.291} (\text{UV}_{254})^{0.726} (\text{Br} + 0.01)^{-0.568} (\text{Cl}_2)^{0.480} (\text{t})^{0.239} (\text{T})^{0.665}$$

$$\text{TCAA} = 87.182(\text{TOC})^{0.355} (\text{UV}_{254})^{0.901} (\text{Br} + 0.01)^{-0.679} (\text{pH})^{-1.732} (\text{Cl}_2)^{0.881} (\text{t})^{0.264}$$

$$\text{MBAA} = 0.176(\text{TOC})^{1.664} (\text{UV}_{254})^{-0.624} (\text{Br})^{0.795} (\text{pH})^{-0.927} (\text{t})^{0.145} (\text{T})^{0.450}$$

$$\text{DBAA} = 84.940(\text{TOC})^{-0.620} (\text{UV}_{254})^{0.651} (\text{Br})^{1.073} (\text{Cl}_2)^{-0.200} (\text{t})^{0.120} (\text{T})^{0.657}$$

where:

MCAA = monochloroacetic acid (ug/L)

DCAA = dichloroacetic acid (ug/L)

TCAA = trichloroacetic acid (ug/L)

MBAA = monobromoacetic acid (ug/L)

DBAA = dibromoacetic acid (ug/L)

TOC = raw water total organic carbon (mg/L)

Br = bromide concentration (mg/L)

Cl<sub>2</sub> = chlorine dosage (mg/L)

t = time in batch reactor

UV<sub>254</sub> = water absorbance at 254 nm; 1 cm path length (cm<sup>-1</sup>)

T = batch reactor temperature (°C)

WatPro assumes the  $t_{50}$  value represents the reactor time  $t$ . This assumption was also made by USEPA (1992). The sum of the five (five) haloacetic acid species is determined by totaling their individual concentrations, and is denoted by HAA5. If chloramines are present, a factor of 0.2 is applied to each of the individual HAA species concentrations, similar to the approach used for TTHMS when chloramines are present (see Section 5.6.1.1)

Calibration of the WatPro model for HAA concentrations is possible and is discussed in the Software Features Chapter.

## Disinfection By-Products from Chlorine Dioxide

### *Chlorite Formation*

The model for chlorite formation is from the experimental work of Korn (1998) in bench-scale batch tests. The model is an empirically derived expression incorporating single parameters and two-parameter interactions.

The relationship for chlorite formation derived by Korn (1998) is:

$$\begin{aligned} \log(\text{chlorite conc. formed, mg/L}) = & \\ & - 0.346 - 0.070\log(\text{pH}) - 0.0253\log(\text{T}) - 0.597\log(\text{ClO}_2\text{conc.} + 1) \\ & - 0.136\log(\text{t} + 1) - 0.0038\log(\text{NPOC} * \text{UV}_{254}) + 0.293\log(\text{T}) * \log(\text{ClO}_2\text{conc.} + 1) \\ & + 0.393\log(\text{ClO}_2\text{conc.} + 1) * \log(\text{t} + 1) + 1.27\log(\text{pH}) * \log(\text{ClO}_2\text{conc.} + 1) \\ & + 0.67\log(\text{NPOC} * \text{UV}_{254}) * \log(\text{ClO}_2\text{conc.} + 1) - 0.1611\log(\text{NPOC} * \text{UV}_{254}) * \log(\text{t} + 1) \end{aligned}$$

where:

pH	= pH after chlorine dioxide addition (-)
T	= temperature (°C)
ClO <sub>2</sub> conc.	= initial applied chlorine dioxide concentration (mg/L)
t	= reaction time in the batch reactor (hr)
NPOC	= non-purgeable organic carbon (mg/L)
UV <sub>254</sub>	= raw water UV absorbance at 254 nm; 1 cm path length (cm <sup>-1</sup> )

While the Korn (1998) model is based on non-purgeable organic carbon (NPOC) measurements, the WatPro model uses the more commonly used total organic carbon (TOC) concentration in the equation in place of NPOC.

Calibration of the chlorite formation model is possible, and is discussed in the Software Features chapter.

### *Chlorate Formation*

The model for chlorate formation is from the experimental work of Korn (1998) in bench-scale batch tests. The model is an empirically derived expression incorporating single parameters and two-parameter interactions. The relationship for chlorate formation derived by Korn (1998) is:

$$\begin{aligned} \log(\text{chlorate conc. formed, mg/L}) = & \\ & - 1.99 + 0.62\log(\text{pH}) - 0.090\log(T) + 0.698\log(\text{ClO}_2\text{conc.} + 1) \\ & - 0.104\log(t + 1) + 0.046\log(\text{NPOC} \cdot \text{UV}_{254}) + 0.389\log(T) \cdot \log(\text{ClO}_2\text{conc.} + 1) \\ & + 0.346\log(\text{ClO}_2\text{conc.} + 1) \cdot \log(t + 1) + 0.486\log(\text{NPOC} \cdot \text{UV}_{254}) \cdot \log(\text{ClO}_2\text{conc.} + 1) \\ & - 0.119\log(\text{NPOC} \cdot \text{UV}_{254}) \cdot \log(t + 1) \end{aligned}$$

where:

pH	= pH after chlorine dioxide addition (-)
T	= temperature (°C)
ClO <sub>2</sub> conc.	= initial applied chlorine dioxide concentration (mg/L)
t	= reaction time in the batch reactor (hr)
NPOC	= non-purgeable organic carbon (mg/L)
UV <sub>254</sub>	= raw water UV absorbance at 254 nm; 1 cm path length (cm <sup>-1</sup> )

While the Korn (1998) model is based on non-purgeable organic carbon measurements, the WatPro model uses the more commonly used total organic carbon (TOC) concentration in the equation in place of NPOC.

Calibration of the chlorate formation model is possible, and is discussed in the Software Features chapter.

## 1.7 Alkalinity and pH

### Introduction to Alkalinity and pH

Both alkalinity and pH are affected by the addition of chemicals. Since varying one of the parameters will vary the other, both are simultaneously discussed.

### Definitions

#### Alkalinity

Alkalinity is defined as the ability of water to resist reductions in pH when acidic compounds are added. The alkalinity of natural waters results mainly from dissolved carbonates and, therefore, is measured in equivalence to calcium carbonate ( $\text{CaCO}_3$ ). Total alkalinity is the sum of the equivalent bicarbonate ( $\text{HCO}_3^-$ ), carbonate ( $\text{CO}_3^{2-}$ ), hydroxide ( $\text{OH}^-$ ) and minus the hydrogen ( $\text{H}^+$ ) ion molar concentrations (Sundstrom and Klei, 1979, p.321). The total alkalinity expression is presented below in Eq'n 1.1.

$$\text{Alkalinity} = [\text{HCO}_3^-] + 2 \cdot [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad \text{Eq'n 1.1}$$

where:

$[\text{HCO}_3^-]$  = concentration of bicarbonate ion [mole/L]

$[\text{CO}_3^{2-}]$  = concentration of carbonate ion [mole/L]

$[\text{OH}^-]$  = concentration of hydroxide ion [mole/L]

$[\text{H}^+]$  = concentration of hydrogen ion [mole/L]

The carbonate ion has a multiplying factor of two in the above equation since its ionic strength has an equivalence of two.

#### pH

The pH of a solution is defined as the potency of the hydrogen ion and allows the conversion from a hydrogen ion concentration to a simplified scale (Toon and Ellis, 1978). The expression for pH is described by the equation below.

$$\text{pH} = -\log([\text{H}^+])$$

where:

$$[\text{H}^+] = \text{molar concentration of hydrogen ion [mole/L]}$$

### *Mathematical Expressions*

Since a solution must be electrically neutral (or a current would flow), a balance in the solution must exist between the total charge of the positive ions and the total charge of the negative ions. Expressions for the positive and negative ions are presented in equations below in Eq'n 1.2 and Eq'n 1.3.

$$\sum(\text{positive ions}) = C'_b + [\text{H}^+] + 2 \cdot [\text{Ca}^{2+}] + [\text{CaOH}^+] + 2 \cdot [\text{Mg}^{2+}] + [\text{MgOH}^+] + [\text{NH}_4^+] \quad \text{Eq'n 1.2}$$

$$\sum(\text{negative ions}) = C'_a + [\text{OH}^-] + [\text{HCO}_3^-] + 2 \cdot [\text{CO}_3^{2-}] + [\text{OCl}^-] + [\text{ClO}_2^-] + [\text{ClO}_3^-] \quad \text{Eq'n 1.3}$$

where:

$$\Sigma(\text{positive ions}) = \text{sum of equivalence ion concentrations of negatively charged ions [mole/L]}$$

$$\Sigma(\text{negative ions}) = \text{sum of equivalence ion concentrations of positively charged ions [mole/L]}$$

$$C'_b = \text{sum of equivalence ion concentrations of positively charged ions not indicated in expression [mole/L]}$$

$$[\text{H}^+] = \text{concentration of hydrogen ion [mole/L]}$$

$$[\text{Ca}^{2+}] = \text{concentration of calcium ion [mole/L]}$$

$[\text{CaOH}^+]$	= concentration of calcium hydroxide ion [mole/L]
$[\text{Mg}^{2+}]$	= concentration of magnesium ion [mole/L]
$[\text{MgOH}^+]$	= concentration of magnesium hydroxide ion [mole/L]
$[\text{NH}_4^+]$	= concentration of ammonium ion [mole/L]
$C'_a$	= sum of equivalence ion concentrations of negatively charged ions not indicated in expression [mole/L]
$[\text{OH}^-]$	= concentration of hydroxide ion [mole/L]
$[\text{HCO}_3^-]$	= concentration of bicarbonate ion [mole/L]
$[\text{CO}_3^{2-}]$	= concentration of carbonate ion [mole/L]
$[\text{OCl}^-]$	= concentration of hypochlorite ion [mole/L]
$[\text{ClO}_2^-]$	= concentration of chlorite ion [mole/L]
$[\text{ClO}_3^-]$	= concentration of chlorate ion [mole/L].

WatPro determines ion concentrations for all of the specific ions indicated in the above expressions. If ions different than those indicated are added to the solution (e.g.  $\text{Na}^+$ ), their concentration is added to either  $C'_b$  or  $C'_a$ . For example, if sodium hypochlorite ( $\text{NaOCl}$ ) were added,  $C'_b$  would be increased by the sodium concentration added (assuming  $\text{NaOCl} \rightarrow \text{Na}^+ + \text{OCl}^-$ ). When a compound is added to water, the ionic balance in the system must shift so that electroneutrality of Eq'n 1.2 and Eq'n 1.3 is maintained. Under these conditions, the  $[\text{H}^+]$  (or the pH) is adjusted. If the pH is given (i.e.  $[\text{H}^+]$  can be determined) then the values of  $C'_b$  and  $C'_a$  are adjusted so that electroneutrality is maintained.

The molar concentrations for the identified ions will depend on the concentration of chemical added that produces the ion (e.g.  $\text{NaOCl}$ ) and the equilibrium concentrations for the ions in the solution. Ion equilibrium expressions used by WatPro are discussed in a separate section.

### *Ion Equilibrium and Solubility Expressions*

Ionization equilibrium expressions are used to determine the proportion of various forms of ions in the water. The solubility is used to determine when precipitate will begin to form in the water. Each of the equilibrium and solubility expressions are presented and are subsequently used in a later section. The equations are generally a function of temperature and are described by the USEPA (1992).

### Ionization Coefficient of Water

As indicated in the definition section, the pH of water is defined as the negative logarithm (base 10) of the hydrogen ion molar concentration. The equation for pH is reproduced below.

$$\text{pH} = -\log([\text{H}^+])$$

where:

$$[\text{H}^+] = \text{concentration of hydrogen ion [mole/L]}$$

The hydroxide ion concentration can be determined using the ion product of water and the hydrogen ion concentration.

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

where:

$$[\text{OH}^-] = \text{concentration of hydroxide ion [mole/L]}$$

$$K_w = \text{ion product of water [--]}$$

$$[\text{H}^+] = \text{concentration of hydrogen ion [mole/L]}$$

The ion product of water is reported to be a function of temperature (USEPA, 1992) and an expression to calculate it is presented below.

$$\text{Log}(K_w) = \frac{-4470.99}{T_k} + 6.0875 - 0.01706T_k$$

where:

$T_k$  = temperature (°K)

$K_w$  = ion product of water (at 25°C, the ion product is  $10^{-14}$ )

### Ionization Coefficients of Carbonate Species

The species considered for the carbonate ion include carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ). The sum of the ions is considered the aqueous carbonate ion concentration and is described by the expression presented below.

$$C_{\text{aq,CO}_3} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

where:

$C_{\text{aq,CO}_3}$  = total aqueous molar ion concentration of carbonate forms [mole/L]

The solution of the above expression is important since the alkalinity includes the bicarbonate and carbonate ion concentrations. The bicarbonate and carbonate ion concentrations are proportional to the total aqueous concentration of carbonate forms ( $C_{\text{T,CO}_3}$ ) and can be determined using the following expressions.

$$[\text{HCO}_3^-] = \alpha_{\text{HCO}_3^-} C_{\text{aq,CO}_3}$$

$$[\text{CO}_3^{2-}] = \alpha_{\text{CO}_3^{2-}} C_{\text{aq,CO}_3}$$

where:

$$\alpha_{\text{HCO}_3^-} = \frac{K_1 [\text{H}^+]}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2}$$

$$\alpha_{\text{CO}_3^{2-}} = \frac{K_1 K_2}{[\text{H}^+]^2 + K_1 [\text{H}^+] + K_1 K_2}$$

The equations used in the USEPA (1992) source code are presented below.

$$\log(K_1) = \frac{-3404.71}{T_k} + 14.8435 - (0.032786 \cdot T_k)$$

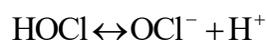
$$\log(K_2) = \frac{-2902.39}{T_k} + 6.4980 - (0.02379 \cdot T_k)$$

where:

$T_k$  = temperature (°K)

### Ionization Coefficient of Chlorine

Hypochlorous acid (HOCl) dissociates into the hypochlorite ion ( $\text{OCl}^-$ ) and the hydrogen ion ( $\text{H}^+$ ). The dissociation is presented below.



The ionization coefficient to describe ion equilibrium is presented below. Ion concentrations are expressed as moles/L.

$$K_{\text{HOCl}} = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]}$$

The ionization coefficient is calculated using the expression presented below and was obtained from the source code of USEPA (1992).

$$\ln(K_{\text{HOCl}}) = \frac{13800}{8.31441} \left( \frac{1}{293.15} - \frac{1}{T_k} \right) - 17.500$$

where:

$$T_k = \text{temperature (}^\circ\text{K)}$$

### Ionization Coefficient of Ammonia

Ammonia ( $\text{NH}_3$ ) combines with the hydrogen ion to form the ammonium ion. The equilibrium expression is presented below.



The ionization coefficient to describe ion equilibrium is presented below. Ion concentrations are expressed as moles/L.

$$K_{\text{NH}_3} = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$

The ionization coefficient is calculated using the expression presented below and was obtained from the source code of USEPA (1992).

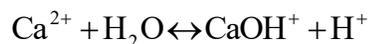
$$\ln(K_{\text{NH}_3}) = \frac{52210}{8.31441} \left( \frac{1}{293.15} - \frac{1}{T_k} \right) - 21.414$$

where:

$T_k$  = temperature (°K)

### Ionization Coefficient of Partly Dissociated Calcium Hydroxide

The dissociation for partly dissociated calcium hydroxide is presented below.



The ionization coefficient to describe ion equilibrium is presented below in Eq'n 1.4. Ion concentrations are expressed as moles/L.

$$K_{\text{CaOH}^+} = \frac{[\text{CaOH}^+][\text{H}^+]}{[\text{Ca}^{2+}]} \quad \text{Eq'n 1.4}$$

The ionization coefficient is calculated using the expression presented below and was obtained from the source code of USEPA (1992).

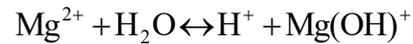
$$\ln(K_{\text{CaOH}^+}) = \frac{-72320}{8.31441 \cdot T_k}$$

where:

$T_k$  = temperature (°K)

### Ionization Coefficient of Partly Dissociated Magnesium Hydroxide

The dissociation for magnesium hydroxide is presented below.



The ionization coefficient to describe ion equilibrium is presented below in Eq'n 1.5. Ion concentrations are expressed as moles/L.

$$K_{\text{MgOH}^+} = \frac{[\text{MgOH}^+][\text{H}^+]}{[\text{Mg}^{2+}]} \quad \text{Eq'n 1.5}$$

The ionization coefficient is calculated using the expression presented below and was obtained from the source code of USEPA (1992).

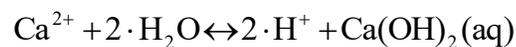
$$\ln(K_{\text{MgOH}^+}) = \frac{-65180}{8.31441 \cdot T_k}$$

where:

$T_k$  = temperature (°K)

### Solubility of Aqueous Calcium Hydroxide

The section examines calcium hydroxide in the solution. The dissociation for calcium hydroxide is presented below.



The ionization coefficient to describe ion equilibrium is presented below in Equation 1.6. Ion concentrations are expressed as moles/L.

$$K_{\text{Ca(OH)}_2(\text{aq})} = \frac{[\text{Ca(OH)}_2(\text{aq})][\text{H}^+]^2}{[\text{Ca}^{2+}]}$$

Equation 1.6

The ionization coefficient is calculated using the expression presented below and was obtained from the source code of USEPA (1992).

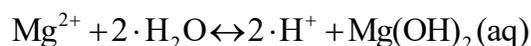
$$\ln(K_{\text{Ca(OH)}_2(\text{aq})}) = \frac{-159800}{8.31441 \cdot T_k}$$

where:

$T_k$  = temperature (°K)

### Solubility of Aqueous Magnesium Hydroxide

This section examines magnesium hydroxide in solution. The dissociation for calcium hydroxide is presented below.



The ionization coefficient to describe ion equilibrium is presented below in Eq'n 1.7. Ion concentrations are expressed as moles/L.

$$K_{\text{Mg(OH)}_2(\text{aq})} = \frac{[\text{Mg(OH)}_2(\text{aq})][\text{H}^+]^2}{[\text{Mg}^{2+}]}$$

Eq'n 1.7

The ionization coefficient is calculated using the expression presented below and was obtained from the source code of USEPA (1992).

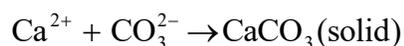
$$\ln(K_{\text{Mg(OH)}_2(\text{aq})}) = \frac{-159760}{8.31441 \cdot T_k}$$

where:

$T_k$  = temperature (°K)

### Solubility of Calcium Carbonate

This section examines the solubility of calcium carbonate and is used to determine at what point calcium carbonate precipitates from solution as a solid, and what are the resulting calcium and carbonate ions concentrations. The dissociation expression is presented below



The ionization coefficient to describe ion equilibrium is presented below in Eq'n 1.8. Ion concentrations are expressed as moles/L.

$$K_{\text{CaCO}_3(\text{solid})} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] \quad \text{Eq'n 1.8}$$

The ionization coefficient is calculated using the expression presented below and was obtained from the source code of USEPA (1992).

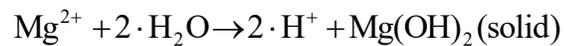
$$\ln(K_{\text{CaCO}_3(\text{solid})}) = \frac{12530}{8.31441} \left( \frac{1}{293.15} - \frac{1}{T_k} \right) - 19.111$$

where:

$T_k$  = temperature (°K)

### Solubility of Magnesium Hydroxide

This section examines the solubility of magnesium hydroxide and is used to determine at what point magnesium hydroxide precipitation from solution as a solid and what is the resulting magnesium ion concentration. The dissociation expression is presented below



The ionization coefficient to describe ion equilibrium is presented below in Eq'n 1.9. Ion concentrations are expressed as moles/L.

$$K_{\text{Mg}(\text{OH})_2(\text{solid})} = \frac{[\text{Mg}^{2+}]}{[\text{H}^+][\text{H}^+]} \quad \text{Eq'n 1.9}$$

The ionization coefficient is calculated using the expression presented below and was obtained from the source code of USEPA (1992).

$$\ln(K_{\text{Mg}(\text{OH})_2(\text{solid})}) = \frac{-113960}{8.31441} \left( \frac{1}{293.15} - \frac{1}{T_k} \right) + 38.78$$

where:

$T_k$  = temperature (°K)

### *System Mass Balances for Magnesium, Calcium and Carbonates*

The mass balances considered when examining pH and alkalinity include magnesium, calcium and carbonates. These mass balances are used to solve ion concentrations in both aqueous and solid phases. Magnesium is considered first, and then, since the calcium and carbonate mass balances are inter-related the calcium and carbonate mass balances are examined together.

#### **Magnesium Mass Balance**

The total mass of magnesium in the water is considered constant (unless physically removed or added to the system) and is the sum of the aqueous and solid phase masses. Since the mass can be normalized by the volume (i.e. concentration), concentration values are used to represent the mass balance. The total magnesium concentration is the sum of the aqueous and solid phase concentrations as indicated below.

$$C_{\text{total,Mg}} = C_{\text{aq,Mg}} + C_{\text{solid,Mg}}$$

Where:

$C_{\text{total,Mg}}$  = total magnesium concentration (mole/L)

$C_{\text{aq,Mg}}$  = aqueous phase magnesium concentration (mole/L)

$C_{\text{solid,Mg}}$  = solid phase magnesium concentration (mole/L)

The aqueous and solid phase concentrations are assumed to be the sum the ions indicated below in Eq'n 1.10 and Eq'n 1.11, respectively.

Eq'n 1.10

$$C_{\text{aq,Mg}} = [\text{Mg}^{2+}] + [\text{Mg}(\text{OH})^+] + [\text{Mg}(\text{OH})_2(\text{aq})]$$

Eq'n 1.11

$$C_{\text{solid,Mg}} = [\text{Mg}(\text{OH})_2(\text{solid})]$$

The ionization coefficient for aqueous magnesium hydroxide (Eq'n 1.7) is rearranged in the form indicated in Eq'n 1.12 (Equation A-50 in EPA (1992)).

$$[\text{Mg}(\text{OH})_2(\text{aq})] = \frac{[\text{Mg}^{2+}]}{[\text{H}^+]^2} K_{\text{Mg}(\text{OH})_2(\text{aq})} \quad \text{Eq'n 1.12}$$

The ionization coefficient for partly dissociated magnesium hydroxide (Eq'n 1.5) is rearranged in the form indicated in Eq'n 1.13 (Equation A-41 in EPA (1992)).

$$[\text{Mg}(\text{OH})^+] = \frac{[\text{Mg}^{2+}]}{[\text{H}^+]} K_{\text{MgOH}^+} \quad \text{Eq'n 1.13}$$

The ion concentration expressions in Eq'n 1.12 and Eq'n 1.13 are substituted in the aqueous phase expression (Eq'n 1.10). The resulting expression is presented below in Eq'n 1.14.

$$C_{\text{aq,Mg}} = [\text{Mg}^{2+}] + \frac{[\text{Mg}^{2+}]}{[\text{H}^+]} K_{\text{MgOH}^+} + \frac{[\text{Mg}^{2+}]}{[\text{H}^+]^2} K_{\text{Mg}(\text{OH})_2(\text{aq})} \quad \text{Eq'n 1.14}$$

Eq'n 1.14 is rearranged in the form indicated below in Eq'n 1.15 (Equation A-52 in EPA (1992)). Eq'n 1.15 is used if all of the magnesium is in the aqueous form.

$$[\text{Mg}^{2+}] = \alpha_{\text{Mg}^{2+},\text{Mg}} C_{\text{aq,Mg}} \quad \text{Eq'n 1.15}$$

The value for  $\alpha_{\text{Mg}^{2+},\text{Mg}}$  represents the fraction of the total aqueous phase magnesium concentration that is in the form of the magnesium ion ( $\text{Mg}^{2+}$ ). Its form is indicated below in Eq'n 1.16.

$$\alpha_{\text{Mg}^{2+},\text{Mg}} = \frac{1}{1 + \frac{K_{\text{MgOH}^+}}{[\text{H}^+]} + \frac{K_{\text{Mg}(\text{OH})_2(\text{aq})}}{[\text{H}^+]^2}} \quad \text{Eq'n 1.16}$$

The ionization coefficient for the solubility of magnesium hydroxide (Eq'n 1.9) is rearranged and presented in Eq'n 1.17.

$$[\text{Mg}^{2+}] = K_{\text{Mg}(\text{OH})_2(\text{solid})} [\text{H}^+]^2 \quad \text{Eq'n 1.17}$$

If a solid phase for magnesium exists (i.e.  $[\text{Mg}^{2+}] [\text{H}^+]^2 > K_{\text{Mg}(\text{OH})_2(\text{solid})}$ ), Eq'n 1.14 and Eq'n 1.17 are equated and the resulting equation is rearranged and presented in Eq'n 1.18.

$$C_{\text{aq},\text{Mg}} = \frac{K_{\text{Mg}(\text{OH})_2(\text{solid})}}{\alpha_{\text{Mg}^{2+},\text{Mg}}} [\text{H}^+]^2 \quad \text{Eq'n 1.18}$$

The total aqueous phase magnesium concentration can then be used to determine the solid phase concentration using Eq'n 1.19.

$$C_{\text{solid},\text{Mg}} = C_{\text{total},\text{Mg}} - C_{\text{aq},\text{Mg}} \quad \text{Eq'n 1.19}$$

## Calcium Mass Balances

The total mass of calcium in the water is considered constant (unless physically removed or added to the system) and is the sum of the aqueous and solid phase masses. Since the mass can be normalized by the volume (i.e. concentration), concentration values are used to represent the mass balance. The total calcium concentration is the sum of the aqueous and solid phase concentrations as indicated below in Eq'n 1.20

$$C_{\text{total,Ca}} = C_{\text{aq,Ca}} + C_{\text{solid,Ca}} \quad \text{Eq'n 1.20}$$

Where:

$C_{\text{total,Ca}}$  = total calcium concentration (mole/L)

$C_{\text{aq,Ca}}$  = aqueous phase calcium concentration (mole/L)

$C_{\text{solid,Ca}}$  = solid phase calcium concentration (mole/L).

The aqueous and solid phase concentrations are assumed to be the sum of the ions indicated below in Eq'n 1.21 (Equation A-45 in EPA (1992)) and Eq'n 1.22, respectively.

$$C_{\text{aq,Ca}} = [\text{Ca}^{2+}] + [\text{Ca}(\text{OH})^+] + [\text{Ca}(\text{OH})_2(\text{aq})] \quad \text{Eq'n 1.21}$$

$$C_{\text{solid,Ca}} = [\text{CaCO}_3(\text{solid})] \quad \text{Eq'n 1.22}$$

The ionization coefficient for aqueous calcium hydroxide (Equation 1.6) is rearranged in the form indicated in Eq'n 1.23 (Equation A-46 in EPA (1992)).

$$[\text{Ca}(\text{OH})_2(\text{aq})] = \frac{[\text{Ca}^{2+}]}{[\text{H}^+]^2} K_{\text{Ca}(\text{OH})_2(\text{aq})} \quad \text{Eq'n 1.23}$$

The ionization coefficient for partly dissociated calcium hydroxide (Eq'n 5.4) is rearranged in the form indicated in Eq'n 1.24 (Equation A-40 in EPA (1992)).

$$[\text{Ca}(\text{OH})^+] = \frac{[\text{Ca}^{2+}]}{[\text{H}^+]} K_{\text{CaOH}^+} \quad \text{Eq'n 1.24}$$

The ion concentration expressions in Eq'n 1.23 and Eq'n 1.24 are substituted in the calcium aqueous phase expression (Eq'n 1.21). The resulting expression is presented below in Eq'n 1.25.

$$C_{\text{aq,Ca}} = [\text{Ca}^{2+}] + \frac{[\text{Ca}^{2+}]}{[\text{H}^+]} K_{\text{CaOH}^+} + \frac{[\text{Ca}^{2+}]}{[\text{H}^+]^2} K_{\text{Ca(OH)}_2(\text{aq})} \quad \text{Eq'n 1.25}$$

Eq'n 1.25 is rearranged in the form indicated below in Eq'n 1.26 (Equation A-48 in EPA (1992)). Eq'n 1.26 is used if all of the calcium is in the aqueous form.

$$[\text{Ca}^{2+}] = \alpha_{\text{Ca}^{2+},\text{Ca}} C_{\text{aq,Ca}} \quad \text{Eq'n 1.26}$$

The value for  $\alpha_{\text{Ca}^{2+},\text{Ca}}$  represents the fraction of the total aqueous phase calcium concentration that is in the form of the calcium ion ( $\text{Ca}^{2+}$ ). Its form is indicated below in Eq'n 1.27.

$$\alpha_{\text{Ca}^{2+},\text{Ca}} = \frac{1}{1 + \frac{K_{\text{CaOH}^+}}{[\text{H}^+]} + \frac{K_{\text{Ca(OH)}_2(\text{aq})}}{[\text{H}^+]^2}} \quad \text{Eq'n 1.27}$$

A solid phase for calcium ( $\text{CaCO}_3$ ) will exist if the product of the calcium ion ( $\text{Ca}^{2+}$ ) and the carbonate ion ( $\text{CO}_3^{2-}$ ) is greater than the ionization coefficient for the solubility of calcium hydroxide. Since the carbonate concentration is also a function of the carbonate mass balance, the carbonate system must be considered before the carbonate concentration can be determined.

### Carbonate Mass Balance

The total mass of the carbonate species in the water is considered constant (unless physically removed or added to the system) and is the sum of the aqueous and solid phase masses. Since the mass can be normalized by the volume (i.e. concentration), concentration values are used to represent the mass balance. The total carbonate species concentration is the sum of the aqueous and solid phase concentrations as indicated below in Eq'n 1.28.

$$C_{\text{total,CO}_3^{2-}} = C_{\text{aq,CO}_3^{2-}} + C_{\text{solid,CO}_3^{2-}} \quad \text{Eq'n 1.28}$$

Where:

- $C_{\text{total,CO}_3}$  = total carbonate species concentration (mole/L)
- $C_{\text{aq,CO}_3}$  = aqueous phase carbonate species concentration (mole/L)
- $C_{\text{solid,CO}_3}$  = solid phase carbonate species concentration (mole/L).

The aqueous and solid phase concentrations are assumed to be the sum of the ions indicated below in Eq'n 1.29 and Eq'n 1.30, respectively.

$$C_{\text{aq,CO}_3^{2-}} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad \text{Eq'n 1.29}$$

$$C_{\text{solid,CO}_3^{2-}} = [\text{CaCO}_3(\text{solid})] \quad \text{Eq'n 1.30}$$

The concentration of the bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ) ions can be determined using the relations indicated in Eq'n 1.31 and Eq'n 1.32. The values for  $\alpha_{\text{HCO}_3}$  and  $\alpha_{\text{CO}_3}$  represent the fraction of the total aqueous phase carbonate species concentration for the bicarbonate and carbonate ions. Mathematical expressions for  $\alpha_{\text{HCO}_3}$  and  $\alpha_{\text{CO}_3}$  are presented in the section describing ionization coefficients for carbonate species.

$$[\text{HCO}_3^-] = \alpha_{\text{HCO}_3^-} C_{\text{aq,CO}_3} \quad \text{Eq'n 1.31}$$

$$[\text{CO}_3^{2-}] = \alpha_{\text{CO}_3^{2-}} C_{\text{aq,CO}_3} \quad \text{Eq'n 1.32}$$

The ionization coefficient for the solubility of calcium hydroxide (Eq'n 1.8) can be rearranged as indicated below in Eq'n 1.33.

$$[\text{CO}_3^{2-}] = \frac{1}{K_{\text{CaCO}_3(\text{solid})}} [\text{Ca}^{2+}] \quad \text{Eq'n 1.33}$$

### Coupling of Calcium and Carbonate Species Mass Balances

Since the solid component of the calcium and carbonate mass balances both contain calcium carbonate, the two must be combined in order to determine, if there is solid calcium carbonate present, the carbonate species concentrations. Since calcium carbonate is composed of a calcium ion and a carbonate ion, the number of calcium moles in the solid phase must be equal the number of carbonate moles in the solid phase. This relationship is expressed in Eq'n 1.34.

$$C_{\text{solid, Ca}^{2+}} = C_{\text{solid, CO}_3^{2-}} \quad \text{Eq'n 1.34}$$

where:

$C_{\text{solid, Ca}}$  = solid phase calcium concentration [mole/L]

$C_{\text{solid, CO}_3}$  = solid phase carbonate concentration [mole/L].

The calcium mass balance (Eq'n 1.20) and the carbonate species mass balance (Eq'n 1.28) expressions can be rearranged as indicated in Eq'n 1.35 and Eq'n 5.36.

$$C_{\text{solid, Ca}} = C_{\text{total, Ca}} - C_{\text{aq, Ca}} \quad \text{Eq'n 1.35}$$

$$C_{\text{solid, CO}_3^{2-}} = C_{\text{total, CO}_3^{2-}} - C_{\text{aq, CO}_3^{2-}} \quad \text{Eq'n 1.36}$$

$$C_{\text{solid, CO}_3^{2-}} = C_{\text{total, CO}_3^{2-}} - C_{\text{aq, CO}_3^{2-}} \quad \text{Eq'n 1.36}$$

$$C_{\text{total,Ca}} - C_{\text{aq,Ca}} = C_{\text{total,CO}_3^{2-}} - C_{\text{aq,CO}_3^{2-}} \quad \text{Eq'n 1.37}$$

Eq'n 1.37 is rearranged in Eq'n 1.38.

$$C_{\text{aq,Ca}} = -C_{\text{total,CO}_3^{2-}} + C_{\text{aq,CO}_3^{2-}} + C_{\text{total,Ca}} \quad \text{Eq'n 1.38}$$

In Eq'n 1.38 the total carbonate and calcium concentrations are known for an individual unit process since only their form will change. If carbonate or calcium is removed or added to the system, the totals can still be determined. Therefore, Eq'n 1.38 can be simplified if the aqueous phase calcium concentration ( $C_{\text{aq,Ca}}$ ) can be replaced with an expression containing the total aqueous carbonate.

The ionization coefficient for the solubility of calcium hydroxide (Eq'n 1.8) is the product of the concentrations for the calcium ion ( $\text{Ca}^{2+}$ ) and the aqueous carbonate ion ( $\text{CO}_3^{2-}$ ) and is reproduced below.

$$K_{\text{CaCO}_3(\text{solid})} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \quad \text{EQ'N 1.8}$$

The aqueous calcium ion concentration can be determined using Eq'n 1.26 and the aqueous carbonate ion concentration can be determined using Eq'n 1.32. The equations are reproduced below.

$$[\text{Ca}^{2+}] = \alpha_{\text{Ca}^{2+},\text{Ca}} C_{\text{aq,Ca}} \quad \text{EQ'N 1.26}$$

$$[\text{CO}_3^{2-}] = \alpha_{\text{CO}_3^{2-}} C_{\text{aq,CO}_3} \quad \text{Eq'n 1.32}$$

Eq'n 1.26 and Eq'n 1.32 were substituted in Eq'n 1.8 and rearranged as indicated in Eq'n 1.39 (Equation A-67 in EPA (1992)).

$$C_{\text{aq,Ca}} = \frac{K_{\text{CaCO}_3(\text{solid})}}{(C_{\text{aq,CO}_3})(\alpha_{\text{Ca}^{2+},\text{Ca}})(\alpha_{\text{CO}_3})} \quad \text{Eq'n 1.39}$$

Eq'n 1.39 is substituted into Eq'n 1.38 as indicated in Eq'n 1.40.

$$-C_{\text{total,CO}_3^{2-}} + C_{\text{aq,CO}_3^{2-}} + C_{\text{total,Ca}} = \frac{K_{\text{CaCO}_3(\text{solid})}}{(C_{\text{aq,CO}_3})(\alpha_{\text{Ca}^{2+},\text{Ca}})(\alpha_{\text{CO}_3})} \quad \text{Eq'n 1.40}$$

Eq'n 1.40 is rearranged as indicated in Eq'n 1.41.

$$\left(C_{\text{aq,CO}_3^{2-}}\right)^2 + \left(C_{\text{total,Ca}} - C_{\text{total,CO}_3^{2-}}\right)C_{\text{aq,CO}_3^{2-}} - \frac{K_{\text{CaCO}_3(\text{solid})}}{(\alpha_{\text{Ca}^{2+},\text{Ca}})(\alpha_{\text{CO}_3})} = 0 \quad \text{Eq'n 1.41}$$

Eq'n 1.41 can be solved for  $C_{\text{aq,CO}_3}$  using the quadratic rule.

### Effect of Chemical Addition on Alkalinity and pH

This section discusses the aqueous form of each of chemical which can be added in the treatment system, and if they affect the expressions for the ionic balance. The mathematical expressions, presented previously, used to represent the positive and negative ions in the water are reproduced below. For electroneutrality of the system, the sum of the positive ions must equal the sum of the negative ions.

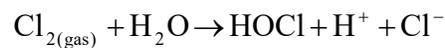
$$\sum (\text{positive ions}) = C'_b + [\text{H}^+] + 2 \cdot [\text{Ca}^{2+}] + [\text{CaOH}^+] + 2 \cdot [\text{Mg}^{2+}] + [\text{MgOH}^+] + [\text{NH}_4^+] \quad \text{EQ'N 1.2}$$

$$\sum (\text{negative ions}) = C'_a + [\text{OH}^-] + [\text{HCO}_3^-] + 2 \cdot [\text{CO}_3^{2-}] + [\text{OCl}^-] + [\text{ClO}_2^-] + [\text{ClO}_3^-] \quad \text{EQ'N 1.3}$$

### Disinfectant Chemical Addition

#### Chlorine

When chlorine is added to water, it is assumed to react to the form indicated below.



Chlorine is assumed to be added as mg/L as chlorine. In order to determine the molar addition of chlorine, the addition rate is divided by 1000 (to convert to g/L) and the molecular weight of  $\text{Cl}_2$  (g/mole). For each equivalent mole of chlorine gas added, one equivalent mole of the chloride ion is created ( $C'_a$  increases by one mole/L) and one mole of hypochlorous acid is generated (HOCl). Free chlorine is the sum hypochlorite ion ( $\text{OCl}^-$ ) and hypochlorous acid (USEPA, 1989, p.68) and WatPro does not distinguish between the two forms.

#### Sodium Hypochlorite

When sodium hypochlorite is added to water, it is assumed to react to the form indicated below.



Sodium hypochlorite is assumed to be added as mg/L, expressed as  $\text{Cl}_2$ . In order to determine the molar addition of sodium hypochlorite, the addition rate is divided by 1000 (to convert to units of g/L) and the molecular weight of chlorine (g/mole). For each equivalent mole of sodium hypochlorite added, one equivalent mole of the sodium ion is created ( $C'_b$  increases by one mole/L) and one mole hypochlorite ion is generated ( $\text{OCl}^-$ ). Free chlorine is the sum hypochlorite ion ( $\text{OCl}^-$ ) and hypochlorous acid (USEPA, 1989, p.68) and WatPro does not distinguish between the two forms.

## Chloramines

Chloramines are assumed to be added as mg/L expressed as  $\text{NH}_2\text{Cl}$ . In addition, chloramines are assumed to be introduced in the form of monochloramine ( $\text{NH}_2\text{Cl}$ ) and remain in this form in solution. As a result, the values of  $C'_b$  or  $C'_a$  do not change when chloramines are added. In order to determine the molar addition of chloramine, the addition rate of chloramines is divided by 1000 (to convert to units of g/L) and the molecular weight of  $\text{NH}_2\text{Cl}$  (g/mole).

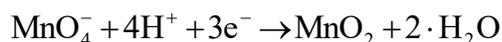
## Non-Disinfectant Chemicals

### Potassium Permanganate

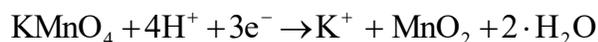
When potassium permanganate is added to water, it is assumed to react to the form indicated below.



One possible fate for the permanganate ion is for it to be reduced to manganese dioxide. The reaction forms the relatively insoluble manganese dioxide, as indicated by the USEPA (1992), is presented below.

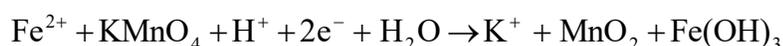


After combining the two previous equations, the following overall reaction is generated.



For the reactions considered, for each equivalent mole of potassium permanganate added, the value of  $C'_b$  increases by one mole per liter and  $C'_a$  decreases by three moles per liter.

If ferric ions ( $\text{Fe}^{2+}$ ) are present, it is assumed that the permanganate ion will oxidize them to the ferric ion form ( $\text{Fe}^{3+}$ ). The ferric ions can then precipitate as ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ). A possible overall reaction with ferrous ions present is presented below.

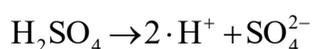


For the above reaction, for each equivalent mole of potassium permanganate added, the value of  $C'_b$  decreases by one mole per liter and  $C'_a$  decreases by two moles per liter. EPA (1992) assumes that ferrous is present and that the last equation represents actual conditions. WatPro also assumes this condition.

The manganese dioxide and ferric hydroxide are assumed to be insoluble. Potassium permanganate is assumed to be added as mg/L as  $\text{KMnO}_4$ . In order to determine the molar addition of  $\text{KMnO}_4$ , the addition rate is divided by 1000 (to convert to g/L) and the molecular weight of  $\text{KMnO}_4$  (g/mole).

### Sulfuric Acid

When sulfuric acid is added to water, it is assumed to react to the form indicated below.



Sulfuric acid is assumed to be added as mg/L. In order to determine the molar addition of sulfuric acid, the addition rate is divided by 1000 (to convert to units of g/L) and the molecular weight of sulfuric acid (g/mole). For each equivalent mole of sulfuric acid added, two equivalent moles of the sulfate ion is created (charge is two) and the value of  $C'_a$  is increased by two moles per liter.

### Sodium Hydroxide (Caustic)

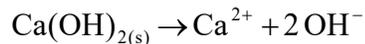
When sodium hydroxide is added to water, it is assumed to react to the form indicated below.



Sodium hydroxide is assumed to be added as mg/L as NaOH. In order to determine the molar addition of sodium hydroxide, the addition rate is divided by 1000 (to convert to g/L) and the molecular weight of NaOH (g/mole). For each equivalent mole of sodium hydroxide added, one equivalent mole of the sodium ion is created and the value of  $C'_b$  is increased by one mole per liter.

### Calcium Hydroxide (Lime)

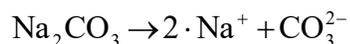
When calcium hydroxide (lime) is added to water, it is assumed to react to the form indicated below.



Calcium hydroxide is assumed to be added as mg/L as  $\text{Ca(OH)}_2$ . In order to determine the molar addition of calcium hydroxide, the addition rate is divided by 1000 (to convert to units of g/L) and the molecular weight of  $\text{Ca(OH)}_2$ . For each mole of calcium hydroxide added, the total calcium molar concentration ( $C_{\text{total, Ca}}$ ) is increased by one mole per liter. The values of  $C'_b$  and  $C'_a$  are not altered.

### Sodium Carbonate (Soda Ash)

When sodium carbonate (soda ash) is added to water, it is assumed to react to the form indicated below.



Sodium carbonate is assumed to be added as mg/L as  $\text{Na}_2\text{CO}_3$ . In order to determine the molar addition of sodium carbonate, the addition rate is divided by 1000 (to convert to units of g/L) and

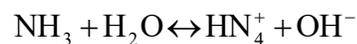
the molecular weight of sodium carbonate (g/mole). For each equivalent mole of sodium carbonate added, two equivalent moles of the sodium ion are created ( $C'_b$  increases by two moles/L) and the total carbonate molar concentration ( $C_{\text{total,CO}_3}$ ) is increased by one mole per liter.

### Carbon Dioxide

When one mole per liter of carbon dioxide is added to water, the total carbonate species concentration ( $C_{\text{total,CO}_3}$ ) assumed to increase by one mole per liter. The values of  $C'_b$  and  $C'_a$  do not change. Carbon dioxide is assumed to be added as mg/L as  $\text{CO}_2$ . In order to determine the molar addition of  $\text{CO}_2$ , the addition rate is divided by 1000 (to obtain units g/L) and the molecular weight of  $\text{CO}_2$  (g/mole).

### Ammonia

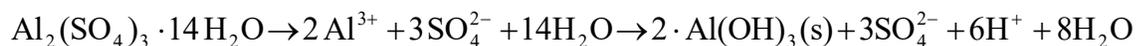
When ammonia is added to water, it is assumed to react to the form indicated below.



Ammonia is assumed to be added as mg/L as N. In order to determine the molar addition rate of ammonia, the addition rate is divided by 1000 (to obtain units of g/L) and the molecular weight of nitrogen. Since reaction for ammonia is considered reversible, the ammonia and ammonium ion concentrations are determined using the ammonia dissociation constant. The sum of the ammonia and ammonium concentrations is increased by the molar addition rate of the ammonia.

### Alum (Aluminum Sulfate)

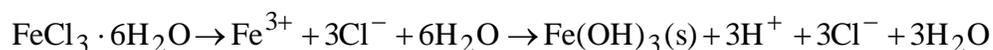
When alum is added to water, it is assumed to react to the form indicated below.



The aluminum ions are assumed to react with hydroxide ions to form an insoluble compound (aluminum hydroxide;  $\text{Al}(\text{OH})_3$ ). Alum is assumed to be added as mg/L as  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ . In order to determine the molar addition of alum, the addition rate is divided by 1000 (to obtain units of g/L) and the molecular weight of alum (g/mole). For each equivalent mole of alum added, three sulfate ions are created ( $C_a$  increases by six mole per liter).

### Ferric Chloride

When ferric chloride is added to water, it is assumed to react to the form indicated below.

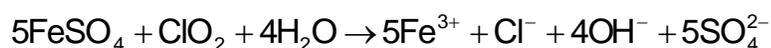


The ferric ions are assumed to react with water to form an insoluble compound (ferric hydroxide;  $\text{Fe}(\text{OH})_3$ ). Ferric chloride is assumed to be added as mg/L as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . In order to determine the molar addition of ferric chloride, the addition rate is divided by 1000 (to obtain units of g/L) and the molecular weight of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (g/mole). For each equivalent mole of ferric chloride added, three chloride ions are created ( $C_a$  increases by three mole per liter).

### Ferrous Sulfate

In WatPro, ferrous sulfate is added (in mg/L as ferrous sulfate) for removal of chlorine dioxide and chlorite ion (by-product when disinfecting with chlorine dioxide) although it does react with other compounds. It is not used in WatPro as a coagulant for TOC removal (see later section on TOC removal chemicals in this chapter). WatPro assumes that ferrous sulfate reacts with the following compounds in the specified order: chlorine dioxide, free chlorine, chlorite, oxygen.

When ferrous sulfate is added to water with chlorine dioxide present, it is assumed to react first with the chlorine dioxide, in the reaction presented below.



The resulting iron (III) species then reacts with water to form an insoluble compound (ferric hydroxide: Fe(OH)<sub>3</sub>).

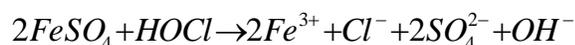


The overall reaction of ferrous sulfate with chlorine dioxide in water is:

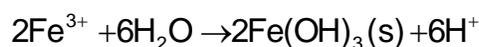


In order to determine the molar addition of ferrous sulfate, the addition rate in mg/L is divided by 1,000 (to obtain units of g/L) and the molecular weight of ferrous sulfate. For each mole of ferrous sulfate added, 0.2 moles (i.e., 1/5 in above equation) of chloride ion and 1 mole of sulfate ion (5/5 in above equation) are created. C<sub>a</sub>' increases by 2.2 moles per liter (i.e., 1\*0.2+2\*1).

If all chlorine dioxide has been consumed by addition of an excess of the iron (II) salt, the ferrous sulfate next reacts with any free chlorine present as indicated in the expression below.



The resulting iron (III) species then reacts with water to form an insoluble compound (ferric hydroxide: Fe(OH)<sub>3</sub>).

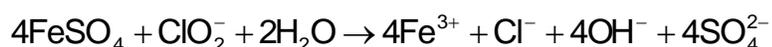


The overall reaction of ferrous sulfate with free chlorine in water is:



For each mole of ferrous sulfate added, 0.5 moles (i.e.  $\frac{1}{2}$  in above equation) of chloride ion and 1.0 moles (i.e.  $\frac{2}{2}$  in above equation) of sulfate are created ( $C_a'$  increases by 2.5 moles per liter, i.e.  $1 \cdot 0.5 + 2 \cdot 1$ ).

If all of the free chlorine has been consumed by the addition of an excess of the iron (II) salt, the ferrous sulfate next reacts with any chlorite present, as indicated by the reaction below.

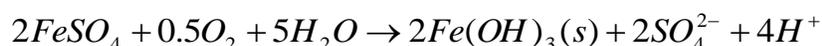


The resulting iron (III) species reacts with water to form an insoluble compound (ferric hydroxide:  $\text{Fe}(\text{OH})_3$ ). The overall reaction of ferrous sulfate with chlorite in water is:



For each mole of ferrous sulfate added, 0.25 moles (i.e.,  $\frac{1}{4}$  in above equation) of chloride ion and 1.0 mole ( $\frac{4}{4}$  in above equation) of sulfate ion are created ( $C_a'$  increases by 2.25 moles per liter, i.e.,  $1 \cdot 0.25 + 2 \cdot 1$ ), while 0.25 moles ( $\frac{1}{4}$  in above equation) of chlorite ion are removed.

If an excess of ferrous sulfate is added beyond the stoichiometric quantities of chlorine dioxide, free chlorine and chlorite, WatPro assumes that the ferrous ion is oxidized to the ferric ion, and the ferric ion reacts in water to form the insoluble compound ferric hydroxide. The model assumes that sufficient dissolved oxygen resides in the water for the reaction to proceed according to the form indicated below.

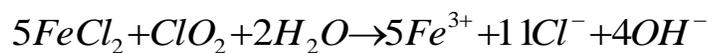


For each mole of ferrous sulfate added, after the chlorine dioxide, free chlorine and chlorite reactions have been satisfied, 1 mole (i.e.,  $\frac{2}{2}$  in above equation) of sulfate is created ( $C_a'$  increases by 2 moles per liter, i.e.  $2 \cdot (\frac{2}{2})$ ).

## Ferrous Chloride

In WatPro, ferrous chloride is added (in mg/L as ferrous chloride) for removal of chlorine, chlorine dioxide and chlorite ion (by-product when disinfecting with chlorine dioxide) although it does react with other compounds. It is not used in WatPro as a coagulant for TOC removal (see later section on TOC removal chemicals in this chapter). WatPro assumes that ferrous chloride reacts with the following compounds in the specified order: chlorine dioxide, free chlorine, chlorite, oxygen.

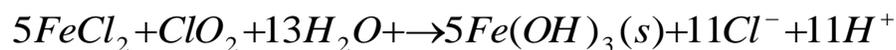
When ferrous chloride is added to water with chlorine dioxide present, it is assumed to react first with the chlorine dioxide, in the reaction presented below.



The resulting iron (III) species then reacts with water to form an insoluble compound (ferric hydroxide:  $Fe(OH)_3$ ).

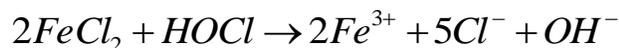


The overall reaction of ferrous chloride with chlorine dioxide in water is:

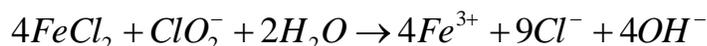


In order to determine the molar addition of ferrous chloride, the addition rate in mg/L is divided by 1,000 (to obtain units of g/L) and the molecular weight of ferrous chloride. For each mole of ferrous chloride added, 2.2 moles (i.e., 11/5 in above equation) of chloride ion are created, and  $C'_a$  increases by 2.2 moles per liter.

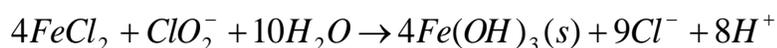
If all chlorine dioxide has been consumed by addition of an excess of the iron (II) salt, the ferrous chloride next reacts with any free chlorine present, as indicated by the reaction below:



If all free chlorine has been consumed by addition of an excess of the iron (II) salt, the ferrous chloride next reacts with any chlorite present, as indicated by the reaction below.

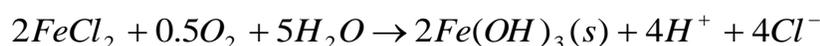


The resulting iron (III) species reacts with water to form an insoluble compound (ferric hydroxide:  $Fe(OH)_3$ ). The overall reaction of ferrous sulfate with chlorite in water is:



For each mole of ferrous chloride added, 2.25 moles (i.e., 9/4 in above equation) of chloride ion are created ( $C'_a$  increases by 2.25 moles per liter), while 0.25 moles (i.e. 1/4 in above equation) of chlorite are removed. Since chlorite is accounted for separately,  $C'_a$  increases by 2.25 moles per liter.

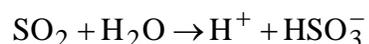
If an excess of ferrous chloride is added beyond the stoichiometric quantities of chlorine dioxide, free chlorine and chlorite, WatPro assumes that the ferrous ion is oxidized to the ferric ion, and the ferric ion reacts in water to form the insoluble compound ferric hydroxide. The model assumes that sufficient dissolved oxygen resides in the water for the reaction to proceed according to the form indicated below.



For each mole of ferrous chloride added, after the chlorine dioxide, free chlorine and chlorite reactions have been satisfied, 2 moles (i.e., 4/2 in above equation) of chloride are created ( $C'_a$  increases by 2 moles per liter).

## Sulfur Dioxide

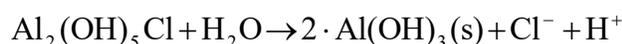
When sulfur dioxide is added to water, it is assumed to react to the form indicated below.



Sulfur dioxide is assumed to be added as mg/L as  $\text{SO}_2$ . In order to determine the molar addition of sulfur dioxide, the mass addition rate is divided by 1000 (to obtain units g/L) and the molecular weight of sulfur dioxide. For each equivalent mole of sulfur dioxide, one mole of hydrogen sulfite ion ( $\text{HSO}_3^-$ ) is created ( $C'_a$  increases by one mole per liter).

## Polyaluminum Hydroxychloride

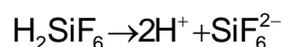
When polyaluminum hydroxychloride (80% basicity), also known as polyaluminum chloride or PACl, is added to water, it is assumed to react to the form indicated below.



An insoluble precipitate ( $\text{Al}(\text{OH})_3$ ) is assumed to form when PACl is added. For each equivalent mole of PACl added, one mole of chloride ions is created ( $C'_a$  increases by one mole per liter). PACl is assumed to be added as mg/L as PACl solution with the solution containing 35% by mass  $\text{Al}(\text{OH})_3$ .

## Hydrofluorosilicic Acid

When hydrofluorosilicic acid ( $\text{H}_2\text{SiF}_6$ ) is added to water, it is assumed to react to the form indicated below.



For each equivalent mole of hydrofluorosilicic acid, one mole of  $\text{SiF}_6^{2-}$  ion is created ( $C_a$  increases by two moles per liter). Hydrofluorosilicic acid is assumed to be added as mg/L as  $\text{H}_2\text{SiF}_6$  solution with the solution containing 25% by mass  $\text{H}_2\text{SiF}_6$ .

### Granular Activated Carbon

The addition of GAC is assumed not to affect the ionic balance or alkalinity.

### Membranes

The expressions used to determine the alkalinity effects of membranes is presented in USEPA (1992) and reproduced in this section.

$$\ln\left(\frac{\text{TH}_{\text{influent}}}{\text{TH}_{\text{effluent}}} - 1\right) = 13.1 - 0.0568 * (\text{recovery}) - 0.261 * \ln(\text{MWC}) * \ln(\text{TH}_{\text{influent}})$$

where:

$\text{TH}_{\text{influent}}$	= membrane feed water total hardness (mg/L as $\text{CaCO}_3$ )
$\text{TH}_{\text{effluent}}$	= effluent water total hardness (mg/L as $\text{CaCO}_3$ )
recovery	= ratio of membrane effluent water flow to feed flow (%)
MWC	= molecular weight cutoff for membrane (molecular weights greater than MWC do not pass through membrane)

The reduction in total hardness is assumed to be equally divided by the calcium and magnesium hardness (i.e. same removal fraction for Ca and Mg hardness).

The carbonate removal is assumed to be determined by the expression presented below.

$$\ln\left(\frac{C_{\text{total,CO}_3^{2-},\text{influent}}}{C_{\text{total,CO}_3^{2-},\text{effluent}}} - 1\right) = 5.88 - 0.00451 * \ln(\text{MWC})(P) - 0.0171 * \ln(\text{MWC})(\text{recovery}) \\ + 0.000082(P)(\text{recovery}) \ln(\text{MWC})$$

where:

$C_{\text{total,CO}_3^{2-},\text{influent}}$  = membrane influent total carbonate species concentration (mole/L)

$C_{\text{total,CO}_3^{2-},\text{effluent}}$  = membrane effluent total carbonate species concentration (mole/L)

P = membrane operating pressure (psi)

The alkalinity removal is assumed to be determined by the expression presented below.

$$\ln\left(\frac{\text{Alk}_{\text{influent}}}{\text{Alk}_{\text{effluent}}} - 1\right) = 7.50 - 0.421 * \ln(\text{MWC}) * \ln(\text{Alk}_{\text{influent}}) \\ + 0.00338 * \ln(\text{MWC}) * \ln(\text{Alk}_{\text{influent}}) * (P) \\ - 0.000145 * (P) * (\text{recovery}) * \ln(\text{MWC})$$

where:

$\text{Alk}_{\text{influent}}$  = influent alkalinity to membrane (mg/L as  $\text{CaCO}_3$ )

$\text{Alk}_{\text{effluent}}$  = effluent alkalinity from membrane (mg/L as  $\text{CaCO}_3$ ).

An iterative procedure adjusting the pH (i.e.  $[\text{H}^+]$ ) until the alkalinity calculated from the above equation equals the general alkalinity equation (Eq'n 1.1) is used to determine the resulting pH of the membrane effluent. The values for  $C'_b$  and  $C'_a$  are determined using the ionic balance expressions (Eq'n 1.2 and Eq'n 1.3)

## 1.8 Water Parameter Removal Mechanisms

A number of chemicals or unit processes are used in the water treatment industry to improve the quality of raw influent water. WatPro considers TOC and  $UV_{254}$  removal, with each described separately in this section.

### TOC removal

Removal of TOC by coagulants or process units (membranes) is discussed below. Allowance has also been made in WatPro for removal of TOC across filters, as described earlier in the Process Data Entry chapter.

### Alum

TOC reduction through the use of the coagulant alum is considered to only occur in the flocculator basin. For example, if alum were added several unit processes upstream of a flocculator basin, the TOC will only change at the flocculator basin.

An empirical relation for the removal of TOC through the addition of alum was developed by the USEPA (1992). The data collected and analyzed were based on three separate full-scale studies including seventeen treatment plants. The expression presented in the USEPA source code is reproduced below.

$$\ln(\text{TOC}_f) = -0.1639 + 1.159\ln(\text{TOC}_0) - 0.4458\ln(\text{alumdose}) - 0.06982\ln(\text{TOC}_0)*\ln(\text{alumdose}) \\ + 0.05666(\text{pH})*\ln(\text{alumdose})$$

where:

$\text{TOC}_f$	= final water total organic carbon (mg/L)
$\text{TOC}_0$	= raw water total organic carbon (mg/L)
alumdose	= alum dose (mg/L as $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ )
pH	= pH following the addition of alum

### *Ferric Chloride*

TOC reduction through the use of the coagulant ferric chloride is considered to only occur in the flocculator basin. For example, if ferric chloride were added several unit processes upstream of a flocculator basin, the TOC will only change at the flocculator basin.

An empirical relation for the removal of TOC through the addition of ferric chloride was developed by the USEPA (1992). The data collected and analyzed were based on bench and pilot-scale. The expression presented in the USEPA source code is reproduced below.

$$\log_{10}(\text{TOC}_f) = 0.316 + 0.891 \cdot \log_{10}(\text{TOC}_o) - 0.018 \cdot \log_{10}(\text{FeCl}_3 \text{ dose}) - 0.231 \cdot \left( \frac{1}{\text{pH}} \right)$$

where:

$\text{TOC}_f$  = final water total organic carbon (mg/L)

$\text{TOC}_o$  = raw water total organic carbon (mg/L)

$\text{FeCl}_3$  dose = ferric chloride (mg/L as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ )

pH = pH following the addition of chemical

### *Ferrous Sulfate*

In WatPro, ferrous sulfate is only added for removal of chlorine dioxide, free chlorine and chlorite ion, formed as a by-product when disinfecting with chlorine dioxide. WatPro does not incorporate any relationships for removal of TOC by ferrous sulfate.

### *Ferrous Chloride*

In WatPro, ferrous chloride is only added for removal of chlorine dioxide, free chlorine and chlorite ion, formed as a by-product when disinfecting with chlorine dioxide. WatPro does not incorporate any relationships for removal of TOC by ferrous chloride.

### *Polyaluminum Hydroxychloride Solution (PACl)*

WatPro assumes that PACl (basicity = 80; solution strength 35% by mass) has the same TOC removal capacity as alum. The dose of PACl is converted to an equivalent of alum and then the alum TOC removal expression is used. The conversion of PACl addition to an equivalent alum addition is done by multiplying the PACl addition rate (mg/L) by 0.35 (since PACl is considered a 35% solution) and the ratio of the alum molecular weight to the molecular weight of PACl ( $\text{Al}_2(\text{OH})_5\text{Cl}$ ).

### *Granular Activated Carbon*

The equation used to describe the sorption of TOC onto GAC is described by USEPA (1992) and reproduced below.

$$\text{TOC}_{\text{effluent}} = \left[ \frac{(\text{TOC}_{\text{influent}})^{n-1}}{1 + A e^{-rt}} \right]^{\frac{1}{n-1}}$$

where:

$\text{TOC}_{\text{effluent}}$	= TOC effluent concentration (mg/L)
$\text{TOC}_{\text{influent}}$	= TOC influent concentration (mg/L)
$1/n$	= Freundlich isotherm for TOC exponent
$r$	= derived function parameter
$A$	= derived function parameter
$t$	= time since last GAC reactivation (d)

and

$$r = 0.07426(\text{EBCT})^{-0.4289}$$

$$A = 0.7570(\text{EBCT})^{1.350}$$

where

EBCT = empty bed contact time in the GAC unit (minutes)

1/n = 0.316 (constant)

The values of 1/n, r and A used by USEPA (1992), represent the derived values from GAC tests conducted at one of three tested locations. The selected site had TOC removals in between the two other sites. Since the effluent TOC concentration is a function of time, the average effluent TOC over the life of the GAC (regeneration frequency) is used.

It is assumed that following the activated carbon unit, free chlorine and chloramine concentrations are zero. THMs and HAAs are assumed to be unaffected by the activated carbon unit (i.e. neither created nor destroyed).

### Membranes

The equation used to describe the removal of TOC by membranes is described by USEPA (1992) and reproduced below. The equation is the result of three sets of batch scale process evaluations.

$$\ln\left(\frac{\text{DOC}_{\text{influent}}}{\text{DOC}_{\text{effluent}}} - 1\right) = 0.986 + 2.59 * \ln(\text{DOC}_{\text{influent}}) - 0.385 * \ln(\text{MWC}) * \ln(\text{DOC}_{\text{influent}})$$

where:

DOC<sub>influent</sub> = membrane influent dissolved organic carbon (mg/L)

DOC<sub>effluent</sub> = membrane effluent dissolved organic carbon (mg/L)

MWC = molecular weight cutoff for membrane (molecular weights greater than MWC do not pass through membrane)

When determining membrane removal efficiencies, DOC is assumed to equal TOC.

## UV<sub>254</sub> Removal

Removal of UV<sub>254</sub> by coagulants or process units (membranes) is discussed below. Allowance has also been made in WatPro for removal of UV<sub>254</sub> across filters, as described earlier in the Process Data Entry chapter.

### Alum

UV<sub>254</sub> reduction through the use of the coagulant alum is considered to only occur in the flocculator tank. For example, if alum were added several unit processes upstream of a flocculator tank, the UV<sub>254</sub> will only change at the flocculator tank.

An empirical relation for the removal of UV<sub>254</sub> through the addition of alum was developed by the USEPA (1992) based on a database developed by the US EPA's Technical Support Division.

$$\ln(\text{UV}_{254f}) = -4.64 + 0.879 \ln(\text{UV}_{254o}) - 0.185 \ln(\text{alumdose}) + 0.564(\text{pH})$$

where:

UV <sub>254o</sub>	= raw water UV <sub>254</sub> (cm <sup>-1</sup> )
UV <sub>254f</sub>	= filtered water UV <sub>254</sub> (cm <sup>-1</sup> )
alumdose	= alum dose (mg/L as Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> *14H <sub>2</sub> O)
pH	= pH following the addition of alum

### Ferric Chloride

UV<sub>254</sub> reduction through the use of the coagulant ferric chloride is considered to only occur in the flocculator tank. For example, if ferric chloride were added several unit processes upstream of a flocculator tank, the UV<sub>254</sub> will only change at the flocculator tank.

An empirical relation for the removal of UV<sub>254</sub> through the addition of ferric chloride was developed by the US EPA (1992). The data collected and analyzed was based on bench and pilot-scale. The expression presented in the US EPA source code is reproduced below.

$$\log_{10}(\text{UV}_{254_f}) = 0.228 + 1.025 \cdot \log_{10}(\text{UV}_{254_o}) - 0.033 \cdot \log_{10}(\text{FeCl}_3 \text{ dose}) - 0.237 \left( \frac{1}{\text{pH}} \right)$$

where:

UV <sub>254<sub>f</sub></sub>	= final water UV <sub>254</sub> (cm <sup>-1</sup> )
UV <sub>254<sub>o</sub></sub>	= raw water UV <sub>254</sub> (cm <sup>-1</sup> )
FeCl <sub>3</sub> dose	= ferric chloride dose (mg/L as FeCl <sub>3</sub> *6H <sub>2</sub> O)
pH	= pH following the addition of ferric chloride

### *Ferrous Sulfate*

In WatPro, ferrous sulfate is only added for removal of chlorine dioxide and chlorite ion, formed as a by-product when disinfecting with chlorine dioxide. WatPro does not incorporate any relationships for removal of UV<sub>254</sub> by ferrous sulfate.

### *Ferrous Chloride*

In WatPro, ferrous chloride is only added for removal of chlorine dioxide and chlorite ion, formed as a by-product when disinfecting with chlorine dioxide. WatPro does not incorporate any relationships for removal of UV<sub>254</sub> by ferrous chloride.

### *Polyaluminum Hydroxychloride Solution (PACl)*

WatPro assumes that PACl (basicity = 80; solution strength 35% by mass) has the same UV<sub>254</sub> removal capacity as alum. The dose of PACl is converted to an equivalent of alum and then the

alum  $UV_{254}$  removal expression is used. The conversion of PACl addition to an equivalent alum addition is done by multiplying the PACl addition rate (mg/L) by 0.35 (since PACl is considered a 35% solution) and the ratio of the alum molecular weight to the molecular weight of PACl ( $Al_2(OH)_5Cl$ ).

### *Granular Activated Carbon*

The fraction of  $UV_{254}$  removed as a result of GAC is assumed to be the same as the fraction of TOC removed. This assumption is also made by US EPA (1992).

### *Membranes*

The fraction of  $UV_{254}$  removed as a result of membranes is assumed to be the same as the fraction of TOC removed. This assumption is also made by US EPA (1992).

### **Hardness Removal (Membranes)**

The equation used by WatPro to describe hardness removal across a membrane is described by USEPA (1992) and reproduced below.

$$\ln \left[ \left( \frac{TH_{in}}{TH_{out}} \right) - 1 \right] = 13.1 - 0.0568 * Recovery - 0.261 * \ln(MWC) * \ln(TH_{in})$$

where:

- $TH_{in}$  = feed water total hardness (mg/L as calcium carbonate)
- $TH_{out}$  = product water total hardness (mg/L as calcium carbonate)
- Recovery = fraction of influent water transformed into product water (%)
- MWC = molecular weight cutoff.

### Alkalinity Removal (Membranes)

The equation used by WatPro to describe alkalinity removal across a membrane is described by US EPA (1992) and reproduced below.

$$\ln \left[ \left( \frac{ALK_{in}}{ALK_{out}} \right) - 1 \right] = 7.50 - 0.421 * \ln(MWC) * \ln(ALK_{in}) + 0.00338 * \ln(MWC) * \ln(ALK_{in}) * Pr\ essure - 0.000145 * (Pr\ essure) * (Re\ cov\ ery) * \ln(MWC)$$

where:

- ALK<sub>in</sub> = feed water alkalinity (mg/L as calcium carbonate)
- ALK<sub>out</sub> = product water alkalinity (mg/L as calcium carbonate)
- MWC = molecular weight cutoff
- Pressure = operating pressure (psi)
- Recovery = fraction of influent water transformed into product water (%).

### Carbonate Removal (Membranes)

The equation used by WatPro to describe carbonate removal across a membrane is described by US EPA (1992) and reproduced below.

$$\ln \left[ \left( \frac{C_{total,CO_3^{2-},in}}{C_{total,CO_3^{2-},out}} \right) - 1 \right] = 5.88 - 0.00451 * \ln(MWC) * Pr\ essure - 0.0171 * \ln(MWC) * Re\ cov\ ery + 0.000082 * (Pr\ essure) * (Re\ cov\ ery) * \ln(MWC)$$

where:

- C<sub>Total,CO<sub>3</sub><sup>2-</sup>,in</sub> = feed water total carbonate concentration (mg/L as calcium carbonate)
- C<sub>Total,CO<sub>3</sub><sup>2-</sup>,out</sub> = product water total carbonate concentration (mg/L as calcium carbonate)

Pressure = operating pressure (psi)

MWC = molecular weight cutoff

Recovery = fraction of influent water transformed into product water (%).

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