Hypochlorous Acid: The Key to How Chlorine Kills

By Karllee Barton

No matter what chlorine disinfection system is used in a pool, the end goal of the technology is to produce free chlorine (FC). FC is made up of both hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-) (White 2010). It is generally accepted that HOCl is much better at killing microbes than OCl^-, and that HOCl is the primary disinfectant in chlorine-based pool and spa disinfection systems.

Why should we focus so much attention on HOCl instead of just FC?

How much more effective is HOCl than OCl^-? When disinfecting *E. Coli*, HOCl is 80 times more effective than OCl^- (White 2010). Likewise, most studies have found HOCl to be far superior to OCl^- as a disinfectant (White 2010). HOCl has a stronger oxidizing potential and more easily reacts with structures on the inside and outside of pathogens to kill them. (Mizozoe 2019). Understanding how HOCl inactivates pathogens, how it is formed and how much is in the water are powerful tools for making sure the water is properly disinfected.

How does HOCl kill pathogens?

Block (2001) discusses how researchers since 1904 have been studying chlorine disinfection and concludes that "the mechanism of this activity has not been fully elucidated, despite much research." Chlorine is a strong oxidizer that can react with a variety of microbe components, and so is capable of killing cells in a variety of ways. Simultaneous reactions can be occurring, with the reactions and reaction rates varying with concentration, time, environmental conditions, and cell type. Similar to blind men describing an elephant (Wiki 2020), researchers have reported the results of various aspects, but due to the complexity and detection limitations, each researcher is only seeing a small part of the whole picture. Following are some of the observations reported by researchers.

In bacteria, the cell wall and membrane act like the walls of a house, protecting the bacteria from harm. The outsides of these structures are negatively charged which tends to repel negatively charged OCl^-, however neutrally charged molecules, like HOCl, are not repelled. Data indicates that HOCl damages internal structures of bacteria at lower concentrations and can penetrate cell walls while leaving them intact. OCl^-, on the other hand, damages the cell wall prior to damaging internal structures. (Mizozoe 2019).

In viruses, the disinfecting power of chlorine is attributed to HOCl's ability to either (a) damage the genetic material inside the virus or (b) damage structures on the capsid, the outer shell of the virus, in such a way that renders the virus unable to pass its infectious genetic material (Maillard 1998).

More complex organisms like protozoan parasites (*Giardia lamblia* and *Cryptosporidium*) are less sensitive to chlorine. They form cysts that act like bigger and stronger walls than those of bacteria. It stands to reason that HOCl and OCl^- cannot as easily penetrate these walls. It takes much more chlorine and/or time is required to kill these organisms. It takes about 45 minutes for 1 ppm of free chlorine to inactivate 99.9% of *Giardia* and about 10.6 days for the same inactivation of *Cryptosporidium*.

How is HOCl formed?

When FC is in the water, OCl^- and HOCl exist in equilibrium. Chemically, the difference between the two molecules is the presence of a hydrogen ion (H^+). FC gets this H^+ from water (H_2O). Since pH is a measure of H^+, it governs how many H^+ are available to form HOCl. At a pH of about 7.5 there will be an equal amount of OCl^- and HOCl. Below this pH, there are more H^+, therefore more HOCl will form. At a pH of 7.2, 61% of the FC will be HOCl. Conversely, at a pH of 7.8, only 35% of the FC will be HOCl. With almost twice the amount of HOCl at 7.2, the water will have almost twice the disinfection power than it would at 7.8. The graph below shows how the equilibrium between OCl^- and HOCl varies over pH.

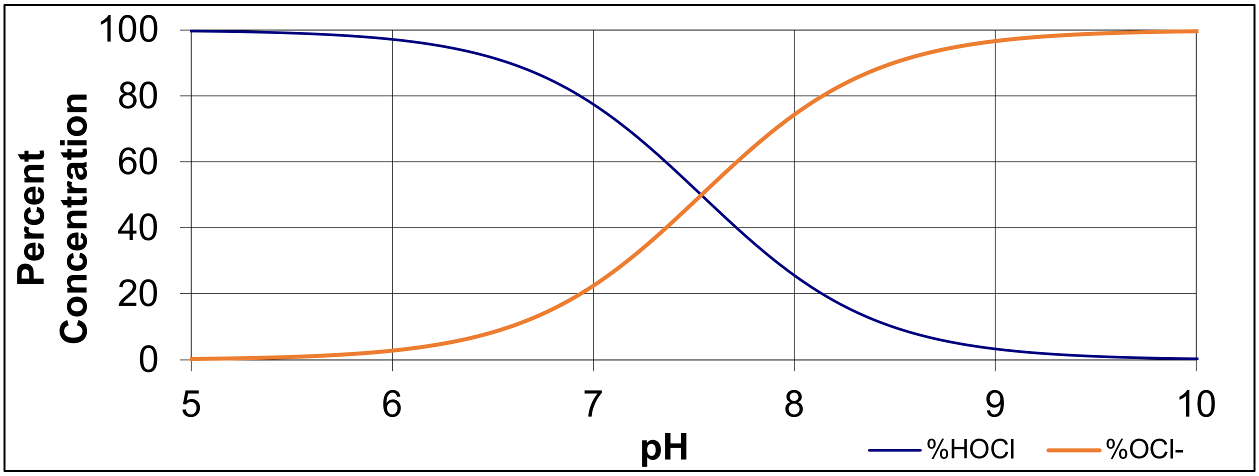

Figure 1: Relationship between pH, HOCl and OCl⁻

The following reactions describe how different chlorine products react with water (H_2O) to form FC:

- Chlorine gas: $Cl_2 + H_2O \rightarrow HOCl + HCl$
- Sodium hypochlorite: $\mathrm{NaOCl} + H_2O \rightarrow \mathrm{HOCl} + \mathrm{NaOH}$
- Calcium Hypochlorite: $Ca(OCl)_2 + H_2O \rightarrow 2\ HOCl + Ca(OH)_2$
- Isocyanurates:
  - dichlor: $NaC_3N_3O_3Cl_2 + 2\ H_2O \leftrightarrow 2\ HOCl + C_3N_3O_3H_2^- + Na^+$
  - trichlor: $C_3Cl_3N_3O_3 + 3\ H_2O \leftrightarrow 3\ HOCl + C_3N_3O_3H_3$

Isocyanurates present a special case when disinfecting with chlorine, because when dissolved they yield FC and cyanuric acid ($C_3N_3O_3H_3$, CYA, chlorine stabilizer). In the pool, FC binds to CYA in an equilibrium reaction. A relatively small concentration of CYA will stabilize a significant percentage of the FC in the pool, leaving very little HOCl for disinfection. The HOCl concentration in a pool starting with 1 ppm FC will decrease from 0.5 ppm HOCl to 0.02 ppm HOCl with as little as 20 ppm of CYA added to the water. With 100 ppm CYA, the same pool would have only 0.004 ppm HOCl. (These values were calculated with the following assumptions for water chemistry: 800 ppm TDS, pH 7.5 and temp. 77°F.)

Cyanuric acid helps to protect the FC residual from depleting too quickly due to decomposition caused by UV light found in sunlight. Because the reaction between FC and CYA is an equilibrium reaction, it is not permanent. As HOCl is depleted, it is quickly replaced by the chlorine reserve created by the stabilized chlorine. However, it is important to remember that molecules participating in reactions must collide for those reactions to occur. With less HOCl in the water, it takes longer for them to find the pathogens and react with them. This remains unchanged no matter how much chlorine is in reserve, even if it were an infinite amount. Operators of pools using CYA or isocyanurates must perform a balancing act of having enough CYA to protect FC residuals from the sun, but also keeping the HOCl concentrations high enough to maintain disinfection within the pool.

How much HOCl is in the water?

Understanding how much HOCl is in the water can be problematic for operators. To compound this issue, the industry standard methods for measuring FC (N,N-diethyl-p-phenylenediamine, or DPD methods) do not differentiate between FC and chlorine bound to CYA. HOCl can be calculated using the FC measured by DPD (DPD-FC), CYA concentration, pH, temperature and total dissolved solids (TDS). This paper uses the equations described in the 1974 paper by O'Brien et al. to determine HOCl concentrations. FC and CYA have the greatest impact on HOCl concentrations, followed by pH. With a few assumptions about the water chemistry, HOCl concentrations can be reasonably estimated using FC and CYA, using a ratio concept. If FC is increased relative to an increase in CYA, then the HOCl remains relatively consistent. Table 1 illustrates this concept assuming a pH 7.8, 77°F and 1000 ppm TDS. At the highest pH recommended for pools, 7.8, HOCl concentrations are lowest, and at the lowest pH recommended, 7.2, HOCl concentrations are higher. Tables 2 and 3 show HOCl concentrations at 7.2 and 7.8 for different ratios.

Table 1: HOCl Concentrations with Constant CYA to FC Ratio		
CYA	FC	HOCl
15	1	0.0234
30	2	0.0244
45	3	0.0247
60	4	0.0249
75	5	0.0250
90	6	0.0251
Assumptions: pH 7.8, 77°F and 1000 ppm TDS		

Table 2: HOCl for Different CYA to FC Ratios with Low pH		
CYA	FC	HOCl
0	1	0.6533
15	1	0.0314
20	1	0.0233
30	1	0.0154
45	1	0.0102
90	1	0.0050
Table 2: pH 7.2, 77°F and 1000 ppm TDS		

Table 3: HOCl for Different CYA to FC Ratios with High pH		
CYA	FC	HOCl
0	1	0.3212
15	1	0.0234
20	1	0.0175
30	1	0.0116
45	1	0.0077
90	1	0.0038
Table 3: pH 7.8, 77°F and 1000 ppm TDS		

How do we apply this towards disinfection?

One way of using this information is to see the impact on disinfection based on the Chick-Watson model of disinfection. This model uses disinfectant concentration and time of exposure to predict the inactivation of pathogens. It is commonly used by drinking-water and waste-water professionals. The disinfectant concentration and time required for a particular reduction of pathogen is referred to as the CT value. The following formula can be used to determine the exposure time required to achieve a pathogen reduction using the CT value published in the technical literature and disinfection concentration:

Equation 1:

$$T = \frac{CT\ Value}{C}$$

Where,

T is the time of exposure in minutes to the disinfectant needed to achieve the desired reduction in pathogen.

CT is the concentration (C) multiplied by the time (T) required for disinfection. It is expressed in ppm*mins. This is calculated using experimental data where the reduction in pathogens is observed over time with a known concentration of disinfectant. The CT value is determined for a particular reduction in pathogens, usually expressed in $\log_{10}$ reductions. For example, a 3 $\log_{10}$ reduction would decrease a pathogen population of 1000 to 1. This is a 99.9% reduction in pathogens. When using CT values from the technical literature, Equation 1 assumes that the water conditions are equal to that of the water used in the published experiment; therefore the conditions known to affect the disinfection rate such as pH and temperature should be taken into account when using CT values.

C is the concentration of disinfectant in ppm.

Once the required exposure times are determined when CYA is not present, the time required for an equivalent reduction of pathogens can be predicted when it is. This can be done by by multiplying the time required to achieve a pathogen reduction when CYA is not present by the concentration of HOCl when it is, divided by the HOCl concentration present at the DPD-FC used to determine the exposure time. This is shown in the following equation:

Equation 2:

$$T_{CYA} = \frac{T_{DPD-FC} * C_{CYA\ HOCl}}{C_{HOCl}}$$

Where,

T_{CYA} is the predicted time, when CYA is present, to achieve an equivalent pathogen reduction when it is not.

$T_{DPD\text{-}FC}$ is the time required to achieve a pathogen reduction when CYA is not present. This is calculated using equation 1 and assumes the FC is measured using the DPD method.

$C_{CYA\ HOCl}$ is the concentration of HOCl, when CYA is present, at the DPD-FC used to determine $T_{DPD\text{-}FC}$. This is calculated using equations described in O'Brien et al. 1974.

C_{HOCl} is the concentration HOCl, when CYA is not present, at the DPD-FC used to determine the $T_{DPD\text{-}FC}$. This is calculated using the equations described in O'Brien et al. 1974.

Table 4 has been calculated using equations 1 and 2. The CT values were found from various sources (CDC 2012)(MAHC Annex). HOCl concentrations were calculated using pH and temperatures described in the sources. An assumption of 800 ppm TDS was made. As CYA increases, so does the time required to inactivate the pathogen. In the recreational water industry, there is not a consensus on a maximum inactivation time for any specific pathogen. There are many factors that can affect whether a person will get sick, including but not limited to dilution, how much pathogen it takes to get sick and path of transmission.

Table 4: Predicted Inactivation Times of Chlorine with CYA, minutes

	CYA, ppm	0	15	20	30	45	90
	DPD-FC, ppm	1	1	1	1	1	1
Pathogen	*Shigella sonnei**	0.5	10	13	20	31	61
	*Escherichia coli O157:H7***	<1	19	26	39	59	118
	*Noroviruses**	0.1	18	25	37	60	119
	*Legionella**	4	123	165	255	387	774
	*Hepatitis A***	20	383	516	784	1184	2369
	*Giardia***	45	862	1161	1763	2665	5329
	*Cryptosporidium***	15300	293119	394695	599461	906003	1812007

*CT_{FC} values used in calculations were taken from tables in the Effect of Chlorination of Inactivation Selected Pathogens (CDC 2012). ** CT_{FC} values used in calculations were taken from MAHC Annex 2018. White values are less than an hour. Yellow values are between 1 and 24 hours. Red values are longer than 24 hours.

Conclusion

No matter which chlorine product is used, ultimately the goal is to form FC and therefore HOCl to disinfect the water. Understanding how HOCl is formed, how it inactivates pathogens and how much is in the water are powerful tools for operators to disinfect pool and spa waters. Hopefully, this paper gives you a good understanding of how HOCl impacts disinfection.

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