HOCL and OCL

A series of e-mail articles from the research group onBalance, May 2006

HOCl and OCl^- Update #1

What search words generate more hits to onBalance's Poolhelp.com website than any others? The phrase "HOCl and OCl^-". Although the relationship between chlorine and pH is one of the first things taught in most basic pool chemistry classes, a few misunderstandings occasionally get set in people's minds.

It is common to hear the comment in basic pool water chemistry classes that increasing pH makes chlorine less able to kill things, and that decreasing pH makes the chlorine better able to kill things. This is actually not exactly correct – although there is a reason that impression is acquired.

There is a pH-related effect on the speed at which a fixed concentration of total chlorine will do its job – but let's take a look at two specific scenarios that better illustrate how to better look at the issue.

First, when chlorine is added to water it forms (among other things) hypochlorous acid, or **HOCl – the most active, effective form of dissolved chlorine.** This same active ingredient is formed regardless of whether the chlorine was originally introduced to the water as tablet or powder, liquid or gas.

Then, depending on the pH of the water, some of the chlorine remains as HOCl, but a percentage dissociates, or splits into OCl^- and H^+.

When writing these equations in chemical form, double reverse arrows, or an equilibrium symbol is used, signifying that the conversion is dynamic and reversible. The effector of movement from right to left and left to right is pH:

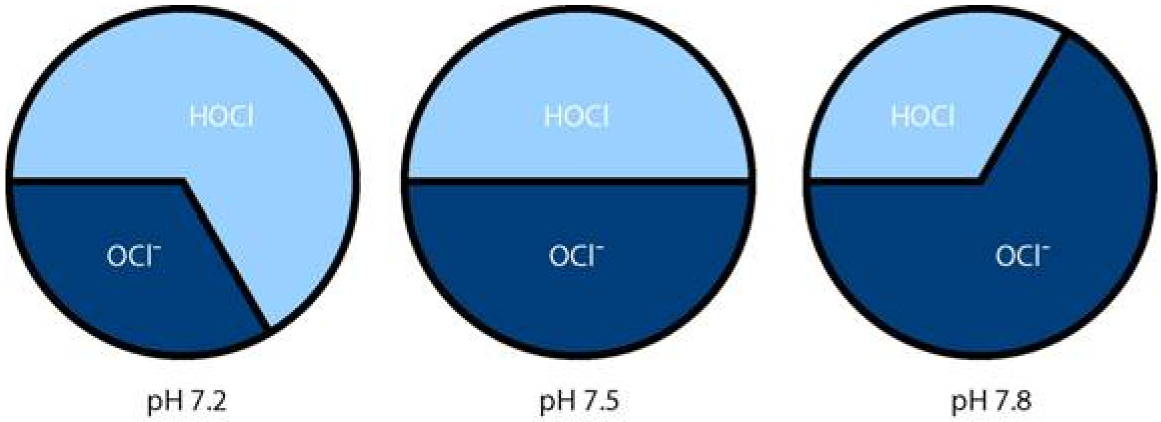
$$HOCl \rightleftharpoons OCl^- + H^+$$

OCl^- is a less active form of dissolved chlorine. It can still oxidize material, and "kill" pathogens, but it takes longer to do so. On the other hand, it is also a more stable version of dissolved chlorine.

HOCl and OCl^- Update #2

In the standard pool pH range of 7.2 to 7.8, a significant shift occurs in the ratio of HOCl to OCl^-. At 7.2, chlorine is essentially 2/3 HOCl and 1/3 OCl^-. At 7.5 the ratio is essentially 50:50, and at 7.8, it is essentially 1/3 HOCl and 2/3 OCl^-. Conveniently symmetric!

We could graphically demonstrate the relationship like this:



So which of these three examples shows chlorine that is better at its job? That is really a trick question – because it depends on other parameters that define the job…

Here is an example of why: When constantly feeding an acidic sanitizer into pool water, the "drift" or tendency is for the pH to drop from the sanitizer addition. So the operator may choose to target a pH of 7.8 in order to avoid ever drifting below an acceptable range.

If, however, the feeder was injecting a base sanitizer, he might choose to target 7.2 instead!

In which of these two scenarios is the water better sanitized?

(Hint: this is another trick question.)

HOCl and OCl^- Update #3

The question was "In which of these two scenarios is the water better sanitized?" If the total amount of chlorine was constant in both of these examples, the answer is that both of these are equally capable of addressing the same amount of chlorine demand. However, the one at pH 7.8 will take longer to do the job… and is more stable. And the one at 7.2 will do the job faster, but is more volatile. Either case could be good… depending on the pool's type and use.

What do we learn here? That it is better to say that lowering pH (without changing the total amount of chlorine) makes ***a greater percentage of the chlorine*** both faster and more volatile. And that raising pH (with constant total chlorine) makes ***a greater percentage of the chlorine*** both slower and more stable.

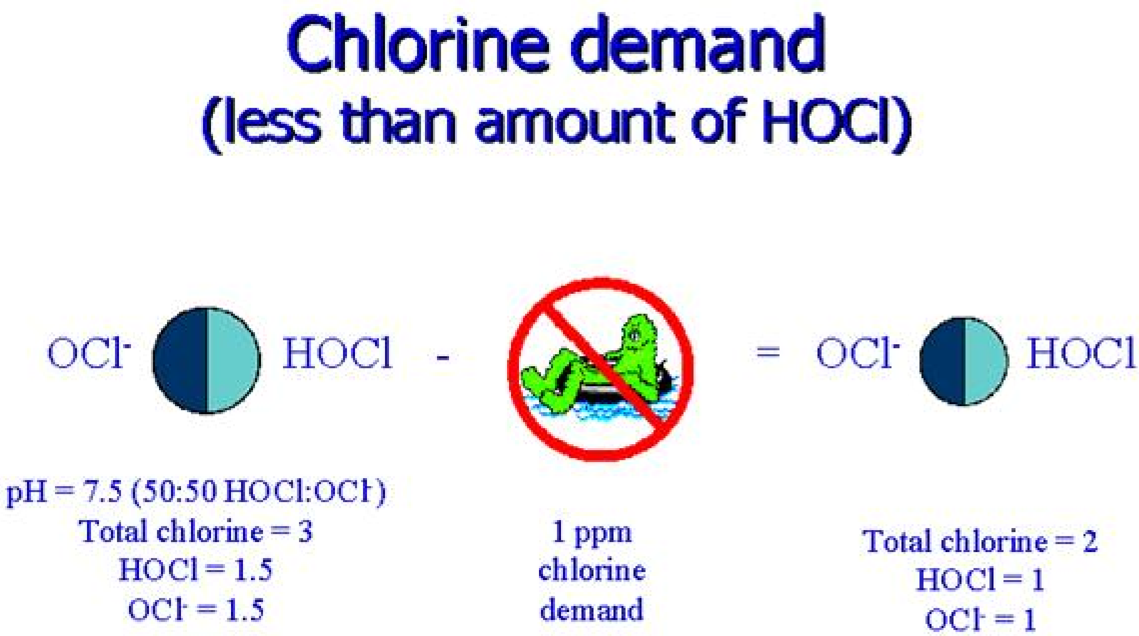
Then what if you decided that, for a particular pool situation, you wanted 2 ppm of faster killing HOCl? Here are three ways of accomplishing that goal:

(no picture)

What do we learn here? That you can have the **same amount** of "fast" HOCl in the water at **three different pH levels**. All you have to do to accomplish this is alter the total chlorine level! So it is actually inaccurate to simply say that "increasing pH makes chlorine less able to kill things" – especially if you don't also specify that the total chlorine remains constant.

HOCl and OCl^- Update #4

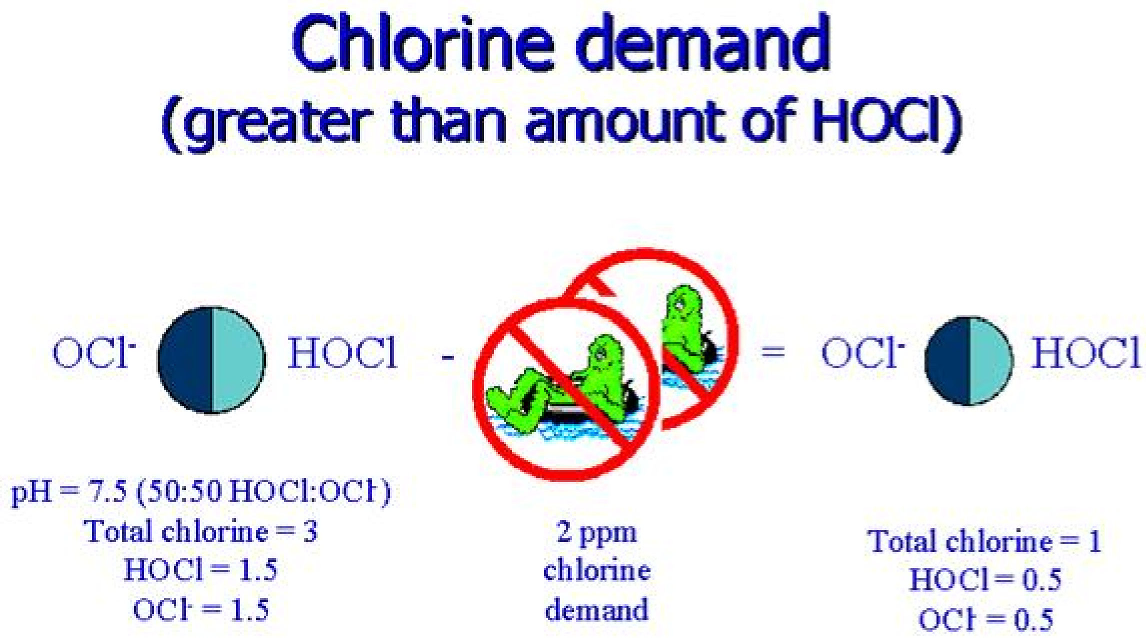
We mentioned earlier in this series that OCl^- can kill things – but slower than HOCl. Should we also assume that if you use up the HOCl then the OCl^- is the only thing left? Does the OCl^- stay that way?



Here we see that if we "use up" HOCl, there is still more HOCl! As long as there is still chlorine, the ratio of the two forms remains distributed as dictated by the pH… so if HOCl is consumed in a chemical process, OCl^- converts to HOCl (remember that equilibrium arrow?) to restore the pH-mandated ratio.

But what happens if there is **more chlorine demand** (represented in ppm) **than there is available ppm of HOCl?**

We could represent it like this:



In this example, some of the OCl^- may have done the work of meeting the chlorine demand… but it may also have been converted to HOCl first, which then did the job.

One industry educator used to say that this scenario couldn't happen – expecting OCl^- to do part of the job was like "sending foot soldiers in single file" – which he said would not work… the individual soldiers, one at a time, he said, would be defeated! But having sufficient HOCl to completely accomplish the job, he claimed, was like sending a solid front of foot soldiers against the enemy all at once, which he deemed effective.

This is incorrect for two reasons – first because OCl^- really is an oxidizer in its own right (albeit slower than HOCl), and secondly because as HOCl is consumed, the pH-mandated equilibrium is maintained by shifting OCl^- to HOCl, which can then do the job.

HOCl and OCl^- Update #5

How long does the OCl^- to HOCl shift take? Some chlorine experts have described it as "almost instantaneous".

We would probably call it "fast but still measurable".

If we look at a Ct chart*, for example, it shows that at pH 7, pH 7.5, and pH 8, it takes 37, 45, and 54 minutes respectively to get a 3 log reduction of Giardia cysts using a constant 1 ppm of chlorine at 25ºC. Some of that task may be accomplished with OCl^- but some of the time lag is from OCl^- shifting to HOCl and then "doing the job".

* "Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Sources" (AWWA, 1991)

The perspective that we would suggest is missing in some pool industry literature, therefore, is that when addressing the effect of pH on chlorine efficacy, it is more accurate to say that:

- Lowering pH (without changing the total amount of chlorine) makes ***a greater percentage of the chlorine*** become HOCl which is faster killing but more volatile.
- Raising pH (with constant total chlorine) makes ***a greater percentage of the chlorine*** become OCl which is more stable but slower acting.
- One can indeed change a target pH level but still maintain the same sanitizer speed by adjusting the total chlorine level.

It is not, however, correct to:

- Make a blanket statement that raising pH inherently makes chlorine a less able sanitizer/oxidizer – it merely changes its speed at a constant total chlorine and temperature, or makes no difference at all if the chlorine is also raised with the increase in pH.
- Make a blanket statement that lowering pH inherently makes chlorine a more able sanitizer/oxidizer – it merely changes its speed at a constant total chlorine and temperature, or makes no difference at all if the chlorine is also lowered with the decrease in pH.