Ozone vs. Chlorine

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DEL Ozone, Inc.

In response to the many questions regarding ozone and chlorine reactions in swimming pool waters DEL has researched the subject and has the following to report.

Fact: Ozone's oxidizing potential is 2.07 vs. chorine's 1.49.

Fact: The apparent rate loss constant of ozone/chlorine 1.23.

Fact: The apparent rate loss constant of ozone/chloramine is 4.0.

This means that "Chloramine" in the water will reduce ozone more rapidly than "Free Available Chlorine" (FAC) will, though they both reduce ozone to some degree.

For example, in a "clean" water sample of pH 7 under continuous ozonation at 1 ppm the half-life for FAC is on the order of 20 minutes. Over this time about 0.7 ppm of ozone will be consumed by the reaction with chlorine (assuming an initial FAC concentration of 2.0 ppm).

These reactions are much too slow to interfere in disinfection reactions which usually complete within 1-2 minutes. Further, the existence of other contaminants for ozone to react with gives little or no time for the Cl - O_3 reactions to occur to any significant degree.

1. Ozone is incapable of reacting with HOCl at any significant rate.
2. Ozone reacts with hypochlorite ion, but not rapidly, to produce chlorate ion (23% yield) and chloride ion (77% yield).
3. Similarly, ozone does NOT react with HOBr but does react with hypobrimite ion to produce bromate ion (23% yield) and brimide ion (77% yield).

The pKa of HOCl/hypochlorite system is about 7.2 (meaning that at pH 7.2, half life of "free" chlorine is present at HOCl and the other half is present as hypochlorite ion). Assume that you start adding ozone. According to Hoigné et al., the hypochlorite ion slowly is destroyed. In turn, in order to maintain equilibrium, some HOCl dissociates to produce more hypochlorite.

Consequently, if one adds enough ozone to water long enough, eventually all of the chlorine will be converted into chlorate and chloride ions.

In a practical application such as a swimming pool there is a constant addition of contaminants for both ozone and chlorine to react with. There are also controls (ORP) that limit the amount of ozone being added to otherwise 'clean' water. Though it is possible and thus may occur under the right conditions the nature of the reactions and time required to complete them limit the action of ozone reducing chlorine in swimming pool water to a negligible amount.

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1. J. Hoigné and W. R. Haag, Reactions of Ozone with Cl and Br, Ozone Science and Engineering Vol. 6, pp. 103-114, (1985).
2. R. G. Rice, Rice International Consulting, Personal Communication, (1998).