Fate of Nitrogen Compounds in Swimming Pool Water

John A. Wojtowicz
Chemcon

Nitrogen compounds (ammonia, urea, amino acids, hippuric acid, creatinine, creatine, and uric acid) in urine and sweat from bathers are the principle source of swimming pool and spa contaminants. These nitrogen compounds cause problems in chlorine sanitized pools because they form combined chlorine compounds which are poor disinfectants compared to free chlorine because they do not hydrolyze significantly to hypochlorous acid. Nitrogen compounds must be oxidized because the combined chlorine compounds that they form are not only poor disinfectants but also are nutrients for bacteria and algae. Although ammonia is readily oxidized by breakpoint chlorination, organic nitrogen compounds are oxidized by chlorine at a much slower rate. Surprisingly, urea, which is the main nitrogen contaminant in pools, does not form combined chlorine and has no apparent effect on disinfection. However, its oxidation by chlorine can lead to ammonia derived chloramines. Ammonia derived chloramines are decomposed by sunlight and therefore should be less of a problem in outdoor pools.

Bather Contaminants

Studies have shown that bathers introduce between 20 and 30 mL of urine into swimming pool water (Gunkel and Jessen 1988). The urea introduced into swimming pools via urine ranges from 340 to 850 mg per bather. By contrast, sweat contributes only 37 mg of urea per bather. The main nitrogen compounds in urine are urea, ammonium ion, creatinine, amino acids, hippuric acid, uric acid, and creatine. Urea is the major constituent of urine, representing about 85% of the total nitrogen. By contrast, ammonia, which is often thought to be the main source of combined available chlorine (CAC) and chloramines in

swimming pools is only a minor contaminant, amounting to only about 4% of the total nitrogen.

Effect of Free and Combined Chlorine on Eye Irritation

Ammonia chloramines have been implicated in taste and odor problems in drinking water and also eye irritation in swimming pool water. Although ammonia chloramines are potential eye irritants at sufficiently high concentrations, the effect varies from insignificant for monochloramine to definite for trichloramine which is the main offender (White 1972 and Jandik 1977). The best defense against ammonia chloramines is regular shock treatment with a non–cyanurate chlorine–based sanitizer such as a hypochlorite, or chlorine gas. Free available chlorine (FAC) itself is not irritating to the eyes at concentrations below 20 ppm. Studies have shown that pH can also affect eye irritation (Mood et al. 1951).

Effect of Nitrogen Compounds on Combined Chlorine and Disinfection

The effects of the various nitrogen compounds on combined chlorine and on disinfection are summarized in Table 1. It is seen that urea, the major swimming pool/spa contaminant, is singularly conspicuous in that it does not form significant amounts of combined chlorine (Palin 1950) or affect disinfection (Fitzgerald and Der Vartanian 1967). Otherwise, it would make swimming pool disinfection extremely difficult, if not impossible. This indicates that urea does not form significant concentrations of chlorinated derivatives. However, urea has to be destroyed by oxidation because it is a nutrient for bacteria and algae and a source of ammonia chloramines. It is also seen that, by contrast with ammonia, the organic nitrogen compounds are oxidized slowly.

Oxidation of Nitrogen Compounds by Chlorine

Compound	Forms Combined Cl	Affects Disinfection	Rate Of Oxidation
Ammonia	Fast To Moderate	Fast To Moderate	Fast To Moderate
Amino Acids	Slow	Slow	Slow
Urea	Very Slow	Very Slow	Very Slow
Creatinine	Very Slow	Very Slow	Very Slow
Uric Acid	Very Slow	Very Slow	Very Slow

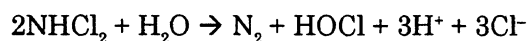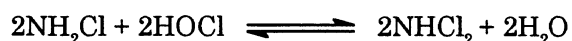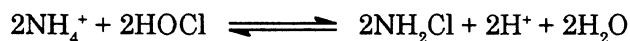## Table 1 – Effect of Nitrogen Compounds on Combined Chlorine and Disinfection

The oxidation of nitrogen compounds by available chlorine (av. Cl) has been studied on a laboratory scale (Wojtowicz 1985). Ammonia is fairly rapidly oxidized with a 10–min decomposition of 38% at a stoichiometric molar dose ratio of av. Cl to nitrogen of 1.8. Bromide ion doubled the extent of decomposition to 77%. Doubling the dose ratio more than doubled the decomposition to 87%. Higher pH and the presence of cyanuric acid reduced the decomposition rate to a small extent. Amino acids reacted significantly slower with 60–min extents of decomposition in the 35–66% range. Urea and creatinine reacted much slower than the amino acids with 60–min extents of decomposition of only 7–8%. Although bromide ion increased the decomposition of urea and amino acids, it had little or no effect on decomposition of creatinine.

Breakpoint Chlorination

Mechanism – Breakpoint chlorination is the process by which combined chlorine compounds are oxidized. Breakpoint chlorination was initially practiced in treatment of drinking water to eliminate taste and odor (Griffin and Chamberlain 1941). Ammonia *per se* is not present in normal pool water because it reacts with hydrogen ions to form ammonium ion.
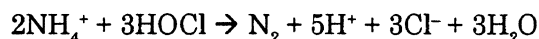
$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
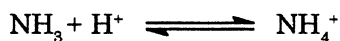
However, ammonium ion readily undergoes breakpoint chlorination. The reactions involved in breakpoint chlorination of ammonium ion are shown below.

$$2NH_4^+ + 2HOCl \rightleftharpoons 2NH_2Cl + 2H^+ + 2H_2O$$

$$2NH_2Cl + 2HOCl \rightleftharpoons 2NHCl_2 + 2H_2O$$

$$2NHCl_2 + H_2O \rightarrow N_2 + HOCl + 3H^+ + 3Cl^-$$

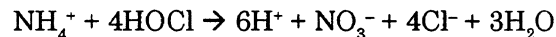Overall

$$2NH_4^+ + 3HOCl \rightarrow N_2 + 5H^+ + 3Cl^- + 3H_2O$$

In the first reaction ammonium ion reacts with hypochlorous acid (i.e., free chlorine) to form monochloramine. Monochloramine reacts with free chlorine to form dichloramine. Dichloramine is an unstable compound and it decomposes, its nitrogen content being oxidized to elemental gaseous nitrogen. The overall reaction shows that 1.5 mols of free chlorine are needed to oxidize one mol of ammonium ion. Some nitrogen trichloride is also formed, primarily beyond breakpoint. Nitrogen trichloride is fairly volatile and tends to escape into the atmosphere. It also undergoes slow decomposition by hydrolyzing back to $NHCl_2$.

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O$$
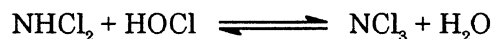
The reverse reaction is facilitated by hydroxide ion. The dichloramine that is reformed will decompose by the breakpoint mechanism. In addition to elemental nitrogen some nitrate is also formed in the oxidation of ammonium ion.

$$NH_4^+ + 4HOCl \rightarrow 6H^+ + NO_3^- + 4Cl^- + 3H_2O$$

The breakpoint mechanism shown above is an oversimplification, there are actually a total of 14 reactions involved (Jafvert 1985).

Chlorine Dosage – The two overall reactions in the breakpoint chlorination of ammonia nitrogen are oxidation to molecular nitrogen and nitrate ion with av. Cl to ammonia mol ratios of 1.5 and 4.0, respectively. Typically about 90% of the ammonia is oxidized to nitrogen and about 10% to nitrate. Thus, the average av. Cl to ammonia mol ratio is 1.75 compared to the theoretical 1.5. The chlorine dosage can be calculated from the equation:

$$c = n(71/14)r$$

Where: c = av. Cl dose (ppm)
       n = ammonia nitrogen (ppm)
       r = av. Cl/NH_3 molar dose ratio
      71 = molecular weight of chlorine
   14 = molecular weight of ammonia nitrogen

For the theoretical r value of 1.5, the chlorine dose is 7.6 ppm/ppm ammonia nitrogen, and for the typical actual r value of 1.75, the chlorine dose is 8.9 ppm/ppm ammonia nitrogen. If the ammonia is already in the form of monochloramine, then the calculated theoretical and actual chlorine doses are 2.5 and 3.8, respectively. Since the presence of organic matter increases the chlorine demand, the recommended chlorine dosage is 10 times the CAC (ANSI/NSPI 1992).

Breakpoint Chlorination Plot – A breakpoint chlorination plot is shown in Figure 1. The horizontal axis shows the applied chlorine dose and the vertical axis the chlorine residuals. The data for a breakpoint plot is obtained by adding increasing amounts of chlorine to a series of samples of water each containing the same ppm ammonia nitrogen and analyzing for free and combined chlorine and ammonia nitrogen after a certain reaction period e.g., two hours as in this case. The region up to the hump primarily represents formation of monochloramine. Significant dichloramine forms after the hump and is accompanied by a decrease in both ammonia nitrogen and combined chlorine. At breakpoint (i.e., the dip) the process is essentially complete and further addition of chlorine results in formation of free chlorine. Small amounts of nitrogen trichloride form only beyond breakpoint.

Kinetics– The kinetics (i.e., the rates) of breakpoint chlorination have been studied (Saunier and Selleck 1985). The breakpoint reaction is fastest at about pH 7.5. For example, shock treatment (with 10 ppm FAC) of water containing 0.25 ppm ammonia nitrogen (1.3 ppm CAC), at pH 7.5 and 15–20°C, will oxidize 99% of the ammonia nitrogen in about 12 minutes.

Effect of Sunlight – The data on breakpoint chlorination presented thus far apply to indoor conditions. Actually the ammonia chloramines absorb ultraviolet light and thus are susceptible to decomposition by sunlight. The ultraviolet light absorptivity of the chloramines varies in the following order: $NHCl_2$ > NCl_3 > NH_2Cl. Actual experiments show that monochloramine is completely decomposed on exposure to sunlight for several hours (Wojtowicz 1985).

$$NH_2Cl + h\nu \rightarrow 1/3N_2 + 1/3NH_4^+ + 2/3H^+ + Cl^-$$
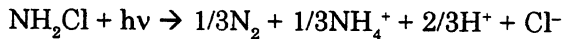
Where hv represents a photon of uv light. The above reaction shows that 67% of the ammonia nitrogen has been oxidized to elemental nitrogen. Based on their higher absorptivities, dichloramine and nitrogen trichloride should decompose even faster.

Effect of Organic Matter – The presence of organic matter has a significant effect on the typical breakpoint plot. The dip beyond the hump is much less pronounced because the organic chloramines oxidize at a much slower rate than ammonia.
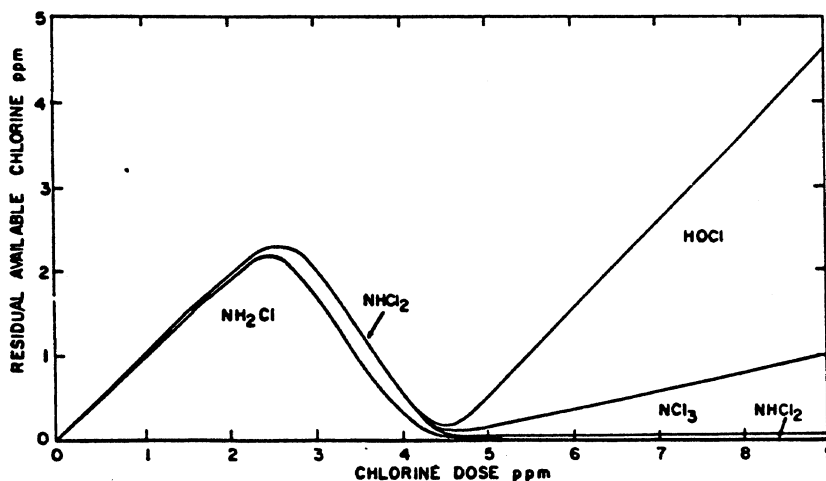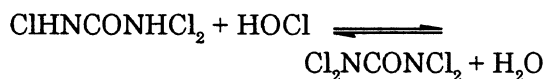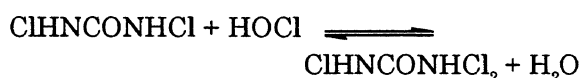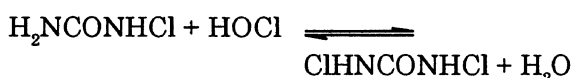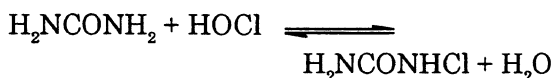

Figure 1 – Breakpoint Chlorination of Ammonia
pH 7.3–7.5, 0.5 ppm Ammonia N, 2 hour Contact Time (Palin 1950)

Oxidation of Urea by Chlorine

Nitrogen trichloride, nitrate ion, and nitrous oxide have been reported among nitrogen–containing products of oxidation of urea by chlorine (Samples 1959). The formation of elemental nitrogen is also expected.

Mechanism – Chlorination of urea can yield a total of four chlorinated derivatives.

$$H_2NCONH_2 + HOCl \rightleftharpoons$$
$$H_2NCONHCl + H_2O$$

$$H_2NCONHCl + HOCl \rightleftharpoons$$
$$ClHNCONHCl + H_2O$$

$$ClHNCONHCl + HOCl \rightleftharpoons$$
$$ClHNCONHCl_2 + H_2O$$

$$ClHNCONHCl_2 + HOCl \rightleftharpoons$$
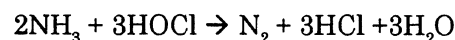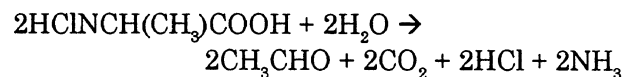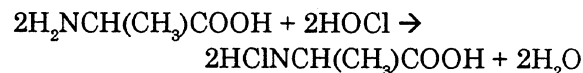$$Cl_2NCONCl_2 + H_2O$$

Appreciable concentrations of chloroureas probably are not formed since urea has been shown not to significantly affect disinfection by chlorine. To the extent that they do form, chlorinated ureas are a source of ammonia chloramines which will be released at a slow rate until all of the urea has been completely oxidized. For example, cleavage of the N–C bond in tetrachlorourea by hypochlorite ion will give one mol of nitrogen trichloride and one mol of dichloramine. The latter can decompose by the breakpoint mechanism. This mechanism is consistent with the observation that at pH 8, approximately one mol of nitrogen trichloride was obtained per mol of urea decomposed (Samples 1957).

Kinetics – The kinetics of oxidation of urea by chlorine has been studied (Palin 1950, Fuchs 1985, and Wojtowicz 1985). For shock treatment (10 ppm FAC) of water containing 1 ppm urea nitrogen, Palin's data indicate a urea half life of 99 hours, whereas Fuch's data indicate a shorter half–life of 47 hours. By contrast, the data of Wojtowicz indicates a much shorter urea half life of only 18 hours. If the urea nitrogen and av. Cl concentrations are doubled then the half–lives will be decreased by a factor of two.
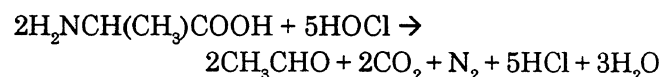
Oxidation of Amino Acids by Chlorine

Amino acids are oxidized by av. Cl during shock treatment. The reactions involved in oxidation of alanine are shown below. The initially formed chloram-

ine hydrolyzes giving an aldehyde, carbon dioxide, hydrochloric acid, and ammonia which is oxidized by normal breakpoint chlorination. The av. Cl demand is greater than that for ammonia because of oxidation of organic matter.

$$2H_2NCH(CH_3)COOH + 2HOCl \rightarrow$$
$$2HClNCH(CH_3)COOH + 2H_2O$$

$$2HClNCH(CH_3)COOH + 2H_2O \rightarrow$$
$$2CH_3CHO + 2CO_2 + 2HCl + 2NH_3$$

$$2NH_3 + 3HOCl \rightarrow N_2 + 3HCl + 3H_2O$$

Overall:

$$2H_2NCH(CH_3)COOH + 5HOCl \rightarrow$$
$$2CH_3CHO + 2CO_2 + N_2 + 5HCl + 3H_2O$$

The acetaldehyde in the above reaction can be oxidized further to acetic acid consuming additional chlorine.

$$CH_3CHO + HOCl \rightarrow CH_3COOH + HCl$$
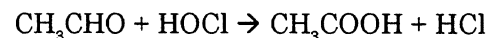
## Oxidation of Creatinine and Creatine

Creatinine and creatine are closely related compounds. Dehydration of creatine yields creatinine. Creatinine and creatine are oxidized by av. Cl to oxalic acid, carbon dioxide, water, hydrochloric acid, nitrogen, and methyl amine. Oxalic acid and methylamine can be oxidized further to carbon dioxide and water.

creatinine

creatine
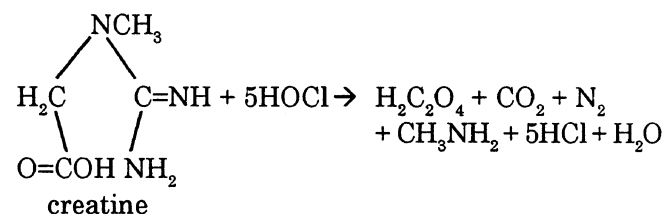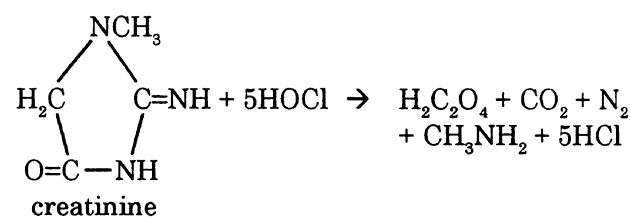
Oxidation of Uric Acid

Uric acid is oxidized by av. Cl to carbon dioxide, nitrogen, hydrochloric acid, and water. Mesooxalic

acid forms as an intermediate product and is oxidized to carbon dioxide and water.

$$C=O + 9HOCl \rightarrow 5CO_2 + 2N_2 + 9HCl + 2H_2O$$

uric acid
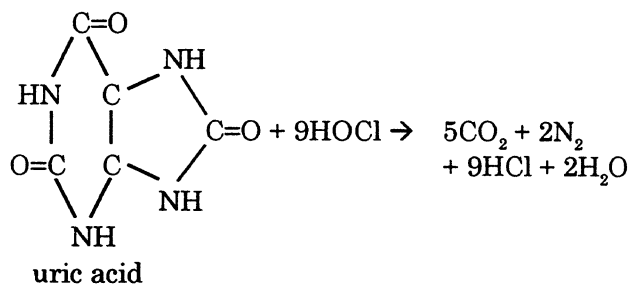
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About the Author

Now retired, **John A. Wojtowicz** was a senior consulting scientist for Olin Corp. Seventeen of his 47 years of industrial experience was spent in the swimming pool chemical area and primarily involved swimming pool chemistry and process and product research on calcium hypochlorite, trichloroisocyanuric acid, and sodium dichloro-isocyanurate. He holds over 55 U.S. patents and has published over 40 technical papers. He is currently a chemical consultant (Chemcon) residing at 3266 N. 151st Drive, Goodyear, AZ 85338, phone/fax #602–535–8851. His areas of expertise include swimming pool chemistry, manufacture and product and process development in hypochlorites and chloroisocyanurates, alternate sanitizers and sanitation systems (ozone, hydrogen peroxide–UV, bromine, etc.), chloramines and bromamines, computer programming, and expert witnessing.