

OBSERVATIONS ON THE USE OF MIXED OXIDANTS IN SWIMMING POOLS

Mechanisms for Lack of Swimmer's Complaints in the Presence of a Persistent Combined Chlorine Measurement

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SYNOPSIS

Evidence from reports in the technical literature, laboratory research, and operational experience with the *MIOX* mixed-oxidant solution (MOS) in swimming pool water strongly indicates that MOS causes steady oxidation of organic nitrogen compounds and organic chloramines, and rapid completion of the breakpoint reaction on inorganic –N– fragments from that oxidation rather than allowing accumulation of them (including volatile NHCl_2 and NCl_3) in the pool water, as is likely the case using chlorine (to wit, the common swimmer's complaints of "chlorinous" odors and burning eyes when bleach/hypochlorite is used for disinfection). This steady removal of organic nitrogen and rapid completion of the breakpoint reaction would be expected to cause the following beneficial effects, as have been noted by swimmers in and operators of virtually all pools using MOS as a replacement for chlorine for disinfection¹:

- Maintenance of an acceptable disinfection residual at lower doses of FAC as MOS than required using bleach;
- Nil production of chlorinous odors in air overlying the pool water and no burning eyes among swimmers;
- Reduction or elimination of the need to "shock" the water with excessive bleach/hypochlorite and/or persulfate to remove combined chlorine (the sum of chlorine as inorganic chloramines and organic chloramines)²;
- Elimination of shocking, as well as a reduction in the amount of draining and replacing pool water for management of combined chlorine concentrations causes a reduction in the rate of accumulation of Total Dissolved Solids (TDS) in the water and a reduction in costs associated with draining and replacing; and
- Improved clarity of the water both because the organic amine substrate would not be present in high enough concentrations to stimulate bacterial growth and disinfection activity is increased.

Better disinfection, although not as yet studied directly in pools, is also expected because: 1) the MOS has been shown in numerous studies to be a better disinfectant than chlorine alone; and 2) the bulk of the disinfection residual in the pool water is present as FAC not the combined chlorines (chloramines as both inorganic and organic).

¹ To date, more than 23 *MIOX* systems are in operation in the US alone treating over 44 separate pools of volumes ranging from 1200 gallon spas to 800,000 gallon Olympic pools.

² The experience of pool operators using *MIOX* MOS (replacing bleach/hypochlorite for disinfection) to date is that the need for "shocking" has been eliminated and that the combined chlorine accumulated in a day of heavy swimmer load is largely removed from the water overnight so long as the FAC as MOS residual is ≥ 2.0 mg/L.

Studies recently completed on two MOS-treated pools revealed three striking features:

1. Nitrate expressed as nitrogen (NO_3^- -N) concentrations do NOT accumulate in the MOS-treated pool waters, in contrast to literature reports on bleach-treated pools. This observation suggests a chemical mechanism for the degradation of organic nitrogen compounds by MOS that is different from that of bleach;
2. The accumulated Total Organic Carbon (TOC) concentrations from the Body Fluid Analog (BFA)ⁱ added continuously by bathers are MUCH lower than those reported in the literature for bleach-treated pools; and
3. The cause for persistent positive biases in the Combined Chlorine (CC) measurements, which are observed in some MOS-treated pools, is most likely slow degradation of some organic nitrogen (organic-N) components of the BFA. This results in small concentrations being observed (in the Total Kjeldahl Nitrogen analysis) at any time, and formation of organic chloramines – a persistent CC measurement arising from this mechanism is equivalent to a “*nuisance residual*”.

BACKGROUND

The MIOX-generated MOS has been used as a replacement for chlorine (as gas or bleach/hypochlorite) for disinfection treatment of swimming pools since the first installation at Longmont, CO in 1994. That early installation, while not successful for operational reasons, resulted nevertheless in reports that the pool operators and users were very pleased with the quality of the pool water. Complaints by swimmers of odors and burning eyes, prominent when chlorine (form of chlorine not fully specified but most likely bleach) was used, virtually ceased using MOS. As the numbers of pool installations worldwide has grown, similar glowing reports on the benefits of the MOS have been received repeatedly.

Some of the benefits of using MOS for disinfection treatment (replacing bleach/sodium hypochlorite) in swimming pool water were observed early and discussed at length by Bradfordⁱⁱ. The most common swimmer’s complaint – chlorinous odors, together with itchy dry skin and burning eyes – disappear within days of the introduction of MIOX MOS. The chlorinous odors are due, primarily, to volatile dichloramine (NHCl_2) and the burning eyes to volatile trichloramine (NCl_3), both created by the incomplete reaction of ammonia expressed as nitrogen (NH_3 -N) with FAC in route to complete breakpoint which releases the nitrogen as harmless N_2 gas. Commonly as well are observations in the chemistry of the pool water, lasting from several days to several 10’s of days, consistent with a model/hypothesis involving release of biofilms from the pool circulation system. Other improvements in the water follow, including dramatic increases in water clarity. These observations have been made in enough pools to have allowed development of expectations applicable to any pool starting MOS treatmentⁱⁱⁱ.

Beginning in 2002, Mr. Rick Dempsey, coauthor of this paper, the distributor for MIOX for recreational water applications in the US, and consultant (with over 12 years experience) on chemistry and operations to the commercial pool industry, reported these same observations with considerable quantitative detail added, plus additional observations, in his clients' pools when they replaced MIOX MOS for bleach/hypochlorite for disinfection.

Chemistry and Chemical Mechanisms

The chemical mechanisms responsible for these benefits are not completely clear. Part of the reason for this lack of clarity in knowledge stems from the fact that swimming pool maintenance

technology appears to have reached the point that some practices can best be described as “folklore”, that is practices for which the chemistry is either not well established, is sometimes misunderstood by the practitioner, or is not discussed in such comprehensive texts on the chemistry of disinfection as Faust and Aly^{iv} or White^v. Pool maintenance practices are generally straightforward, typically controlling the pH to a range of 7.2 – 7.6 and a disinfectant (chlorine) residual of no less than 2 mg/L (often an upper limit of 5 mg/L is set by a state regulatory agency). But in many cases when discussing maintenance practices with a pool operator it is unclear whether the disinfectant residual is as Free Available Chlorine (FAC) or as Total Chlorine (TC)³.

The distinction between FAC and TC is important because TC includes FAC and the so-called “combined chlorine” compounds which are chlorine reacted with an amine (nitrogen) group. The chloramines (predominantly NH₂Cl, but NHCl₂, and NCl₃ are often produced inadvertently) are used widely in potable water disinfection because they provide a disinfectant residual necessary to meet regulatory requirements and are weaker oxidants than FAC and therefore less reactive, forming less disinfection byproducts (Trihalomethanes or THMs). They provide some biocidal (disinfection) action but less than that of FAC. Chlorine in its various forms in potable and pool water also impart taste and odor. White⁵ (p. 395-396) notes that “[T]astes and odors [T&O] from the application of chlorine are not likely to occur from the chlorine compounds themselves up to the [concentration] limits listed below:”

Chlorine Compound	Threshold of T&O Complaint⁵	Henry’s Law Constant¹
Free Chlorine (HOCl)	20.0 mg/L	3.2 x 10 ⁻⁵
Monochloramine (NH ₂ Cl)	5.0 mg/L	3.4 x 10 ⁻⁴
Dichloramine (NHCl ₂)	0.8 mg/L	1.1 x 10 ⁻³
Nitrogen Trichloride (NCl ₃)	0.02 mg/L	0.33

Also listed in the table are the Henry’s Law constants (H) for the relevant forms of inorganic chlorine in pools under conditions typical for pools (pH ~ 7.5; Temperature ~ 28°C (~ 82°F))¹. The Henry’s Law constant (H) is the ratio of the concentration of the compound in the air above the water to its concentration in the water at equilibrium. As the volatility of the compound from the water rises, the numerical value of H also rises. Clearly the Threshold of T&O Complaints decreases with increasing volatility. Also, both Free Chlorine and Monochloramine have very low volatility, whereas Dichloramine and Nitrogen Trichloride would be considered highly volatile.

Faust and Aly⁴ (p. 105), however, note that NH₂Cl imparts a chlorine-like odor and flavor to potable water and NHCl₂ is associated with a swimming-pool-like, bleach-like taste and odor. Fortunately for the drinking water consumer, NH₂Cl, with its higher threshold of complaint due to taste and odor, predominates in potable water systems with NHCl₂ and NCl₃ forming only at pH’s less than about 7.0, which is lower than typical, and in chlorine dose to ammonia nitrogen

³ Awareness of the distinction between FAC, TC, and combined chlorine (CC) has grown considerably in recent years particularly within the commercial and municipal swimming pool community, and the regulatory agencies. Many county health departments are also aware of the key role of the CC measurement in pool management and public safety, and regulate pools on that basis.

(Cl/NH₃-N) ratios greater than about 10:1, which is much higher than the typical < 6:1 used in potable water treatment^{vi}.

The combined chlorine component of TC also includes chlorine reacted with the nitrogen groups of organic amines to form organic chloramines. The technical literature strongly indicates that the organic chloramines have nil disinfection capability. But at least a portion of these compounds detect as TC in standard wet chemical analyses⁴; thus their presence can easily mislead a pool operator into thinking he has adequate disinfectant residual and, thus, adequate disinfection, when in fact he does not.

While tastes and odors imparted by the organic chloramines are not discussed in recent texts, significantly from the standpoint of pool maintenance, White⁵ (p. 460) notes that high Cl/NH₃-N ratios (12:1) with high organic nitrogen compound concentrations in water forms NCl₃ which has a geranium-like odor, an odor that can be taken as chlorinous. Elsewhere White⁵ (p. 260) states that NCl₃ "...is characterized by its pungent, chlorine-like odor". And (p. 396) White⁵ notes that NCl₃ solubility in water is negligible, it will aerate with the slightest agitation, and at concentrations [in air] too low to get a response from the olfactory system, it will *cause the eyes to tear profusely*" [italics added by the authors].

Because chloramine formation is known to progress with increasing Cl/NH₃-N ratios from NH₂Cl to NHCl₂ to NCl₃ and finally to N₂ (the breakpoint), it is reasonable to expect that the nitrogen in organic amines, after being fragmented by oxidation, releasing inorganic –N– fragments to the water, reacts with chlorine in the same manner with progressive Cl/NH₃-N dose ratios. Thus a significant fraction of the total chloramines (responsible for the CC measured) present in swimming pool water may occur as NHCl₂ and, with increasing doses, as NCl₃ in the presence of high organic nitrogen (amine) concentrations and progressively higher Cl/NH₃-N dose ratios. Indeed, Hery and Hecht^{vii} showed that "...roughly 90% of the swimming pool atmosphere pollution by the chlorine species is due to nitrogen trichloride [trichloramine, NCl₃]" [note added by the authors].

In summary, the technical literature demonstrates chemical mechanisms for formation of at least two compounds by reaction of chlorine with organic nitrogen (amines) – NHCl₂ and NCl₃, – both of which have properties that are consistent with observations of pool users of objectionable conditions. Both have chlorinous, bleach-like odors and are volatile, slightly soluble in water, and NCl₃ causes tearing and irritation of the nose and respiratory tract at concentrations [in air] that are below thresholds of odor. Moreover, NHCl₂, NCl₃ and organic chloramines detect as TC (and CC) on commonly-used chlorine test kits but provide nil biocidal action.

CHLORINE (BLEACH) VERSUS MIXED-OXIDANT SOLUTION EFFECTS

Expected Chemistry in a Typical Pool Maintenance Scenario Using Chlorine (Bleach)

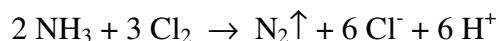
⁴ The fact that the chlorine in *organic* chloramines detects as CC in several analyses for FAC and TC – including the DPD colorimetric and DPD-FAS test commonly used in testing swimming pool waters – is well established and well known within the potable water treatment industry and the technical literature (for example see Gordon, et.al.⁶). This fact appears to be much less well known in the swimming pool industry – the instructions which accompany commonly used test kits do not note this effect although the technical staffs of the manufacturers of these test kits will readily explain it. Considering the abundance of organic–N compounds in the BFA, and the concentrations of organic–N compounds which would be expected to accumulate in a heavily-used pool, this lack of understanding of the chemistry of the major test method used for pool control is stunning.

In a typical pool maintenance scenario using bleach for disinfection, one would expect both organic amines and, with continuing chlorination⁵, organic chloramines, and inorganic –N– fragments (chlorinated as inorganic chloramines) from oxidative decomposition of organic amines to accumulate. As the Cl/NH₃-N dose ratio rises, NHCl₂ and NCl₃ are produced as discussed in the background text above. The presence of these compounds would be expected to lead at once to complaints of swimming-pool-like chlorinous odors and burning eyes, symptoms which are well documented in the technical literature as being associated with these compounds and typical of pools using bleach.

Reductions in water clarity with time and bather load that often occur in swimming pools using bleach for disinfection may be due solely to the fact that biocidal activity does not increase with increasing chlorine dose, despite accumulation of organic chloramines. Indeed, biocidal activity may decrease because the organic chloramines provide nil biocidal activity, even though the TC concentration would appear to the operator to increase. Moreover, the organic amines are food substrate for bacteria. It would be expected that, as organic amines increase in concentration but biocidal activity stays constant or decreases, certain bacteria can find a niche in the pool water, develop into colonies, and contribute to loss of water clarity.

MIOX MOS and the Breakpoint Reaction

The MOS has been shown in laboratory^{viii} and subsequently in potable water systems in Texas^{ix} and in Iowa^x to oxidize ammonia (NH₃-N) and inorganic chloramines to nitrogen gas (N₂) at Cl/NH₃-N dose ratios lower than either the theoretical (7.6:1) or the practical (8 – 10:1; in fact, ratios as high as 15:1 have been reported to be used) ratios required to drive the breakpoint reaction



At the Fonda, IA water treatment plant¹⁰, for example, Cl/NH₃-N dose ratios as low as 5.2:1 as MOS caused a breakpoint-like reaction leading to complete loss of NH₃-N from the raw water. The most plausible chemical explanation for this effect is that the non-chlorine components of the MOS, rather than the chlorine, react preferentially with ammonia and chloramines causing loss of the ammonia as nitrogen gas but reduced (compared to chlorine alone) consumption of the chlorine.

While research on the chemical effect of the MOS on organic chloramines has not been performed as yet, it is hypothesized and expected that the MOS, which is known to be a stronger oxidant than chlorine alone, causes steady decomposition of the organic chloramines to inorganic –N– fragments rather than an accumulation of them in swimming pool water⁶. This steady

⁵ It is worth noting that in larger public swimming pools, the rate of chlorine dosing is often controlled by a pH/ORP (Oxidation-Reduction Potential) controller. The ORP sensor detects mostly the FAC component because the ORP of chloramines and organic chloramines is much lower than that of FAC. Thus, chlorine will continue to be added based largely on the FAC component regardless of the TC residual concentration. In home swimming pools, chlorine tends to be added continually also through use of solid calcium hypochlorite (Ca(OCl)₂) or High Test Hypochlorite (HTH) with minimal monitoring of the disinfection residual. In either case, the accumulation of organic chloramines scenario as discussed in text is likely to occur.

⁶ Another aspect of pool maintenance “folklore” that may be relevant to this discussion is that when pool water becomes cloudy and/or complaints of odor and burning eyes become frequent, it is common practice to “shock” the water with a large overdose of bleach. The chemical effect of the shocking would be oxidation of accumulated inorganic chloramines to nitrogen gas by the breakpoint reaction and, probably, oxidation of the accumulated

decomposition of organic amines to inorganic –N– fragments is followed (in the presence of FAC as MOS) by rapid completion of the breakpoint reaction, allowing little if any accumulation of the volatile, chlorinous-odor causing NHCl_2 and NCl_3 reaction intermediates. Such an effect would be completely consistent with other information and observations accumulated over 10-years of research and operational experience on the superior disinfection and chemical oxidation behavior of the MOS^{xi}.

Expected Chemistry in a Pool Maintenance Scenario Using MIOX MOS

A swimming pool maintenance scenario using MOS instead of bleach for disinfection would be expected to show the following features due to: 1) better disinfection; and 2) steady oxidation of organic chloramines to inorganic –N– fragments followed by rapid completion of the breakpoint reaction.

- Maintenance of an acceptable disinfection residual (both FAC and TC) at lower FAC doses than required using chlorine;
- Nil accumulation of volatile NHCl_2 and NCl_3 in the water and, as a result, no chlorinous odors in the air overlying the pool water and no burning eyes among swimmers;
- Dramatic reduction or complete elimination of the need to periodically "shock" the pool water with excessive bleach/hypochlorite and/or persulfate to remove combined chlorine;
- Better disinfection both because the MOS is a better disinfectant than chlorine alone and the bulk of the disinfection residual in the pool water would be present as FAC not the combined chlorines; and
- Improved clarity of the water both because the organic amine substrate would not be present to stimulate bacterial growth and disinfection effectiveness is increased.

STUDIES ON POOLS AND MODEL POOLS

Beginning in September 2004, the three pools at a Pool Complex in New Jersey using MOS for disinfection began developing a persistent CC measurement $\gg 0.2$ mg/L but **WITHOUT** the swimmer's complaints or other features normally associated with a high CC measurement – obviously the commonly-accepted quantitative correlation between the CC measurement and swimmer's complaints was **NOT** present using MOS. We attempted many times between September and November to eliminate the CC measurement by manipulating the operations of the pool, but to no avail. It was fairly clear, however, that some constituent in the water of the three pools was causing a persistent positive bias in the CC measurement (using the DPD-FAS test); literature research by Bradford identified several candidate constituents. In addition, experiments with the pools indicated that the constituent(s) causing the persistent positive bias in the CC measurement was being **ADDED** with the MOS rather than being created in the pool water, and that the constituent(s) also reacted with and was partially consumed by other constituents of the pool water – most likely these reactions are oxidation of organic material added in the BFA⁷. Samples from the three pools were collected and analyzed at a commercial water analysis laboratory; results reported in December 2004.

organic chloramines and chlorinated inorganic –N– fragments as well. The biocidal effect of shocking is obvious. The net result is, as would be expected, improved clarity of the water and cessation of swimmers' complaints.

⁷ The CC measurement would rise to >1.2 mg/L as the MOS dose increased then decline, trending to 0.4 - 0.6 mg/L as if any reaction stopped at a concentration of about 0.4 mg/L (as a CC measurement). The Oxidation-Reduction

Since it was uncertain what constituent(s) could be causing the persistent positive bias in the CC measurement, the objective of the analyses was to obtain as complete a chemical characterization as possible, given current analytical capabilities. As it seemed fairly certain at the time [later proved to be incorrect] that the constituent(s) of interest was an inorganic, and complete characterization of the organic compound composition is currently impossible, the focus was on inorganic cations and metals, and anions, plus a Total Organic Carbon (TOC) analysis to assess the TOC status of the pool waters relative to recent published findings.

- Cations/Metals – Method M201 (a version of EPA Drinking Water Method 200.8); ICP/MS broad scan metals;
- Anions – EPA Methods 300.0, 300.1 (BrO_3^-): Ion Chromatography; and L500 (ClO_4^-): Liquid Chromatography with quadrupole Mass Spectrometry (LC/MS/MS); and
- Total Organic Carbon – Standard Methods 5310C, UV persulfate digestion.

In addition, the director of R&D and the inorganic department manager at the analyzing laboratory examined the anion chromatograms for unquantified peaks [commercial analytical laboratories quantify only those peaks and constituents for which analytical standards have been established]. Significant unquantified peaks would have been investigated further by more specialized methods; however, although other peaks were noted, they were not quantitatively significant and a tentative identification was made, so no further investigation was conducted. The broad-scan metals analysis showed no unusual concentrations of metals and was dropped in later studies. Results of other analyses are discussed below.

A few months later, a similar occurrence of a persistent CC measurement (0.2 – 0.4 mg/L) but again *WITHOUT* the common swimmer's complaints appeared in a Swim School pool in North Carolina also using MOS for disinfection. A sample was collected in April 2005 and analyzed at the same laboratory for the same constituents (sans the broad-scan metals), plus a special-request Total Kjeldahl Nitrogen (the sum of ammonia ($\text{NH}_3\text{-N}$) and organic-N) which had been thought to be unimportant in the analyses of samples from the Pool Complex and had not been requested.

Results of the analyses of samples from the two facilities are listed below.

FACILITY		Pool Complex			Swim School
		Pool	Lap	Therapy	
Analyte	Units	166 kgal	20 kgal	1200 gal	190 kgal
MAJOR COMMON AND MINOR CATIONS					
Sodium (Na^+)	mg/L	130	230	300	370
Potassium (K^+)	mg/L	na	na	na	9.5
Lithium (Li^+)	mg/L	4.5	2.3	4.7	
Rubidium (Rb^+)	mg/L	0.021	0.018	0.022	
Calcium (Ca^{2+})	mg/L	98	63	57	88
Magnesium (Mg^{2+})	mg/L	1.7	1.2	3.1	3.0
Barium (Ba^{2+})	mg/L	0.0088	0.020	0.016	

Potential (ORP) reading tended to be invariant with the FAC, suggesting the presence of a separate reaction couple which strongly influenced the ORP measurement as a mixed-couple.

Strontium (Sr ²⁺)	mg/L	0.72	0.45	0.26	
MAJOR COMMON AND MINOR ANIONS					
Alkalinity (as CaCO ₃)	mg/L				90
Chloride (Cl ⁻)	mg/L	760	1200	1700	620
Sulfate (SO ₄ ²⁻)	mg/L	75	48	44	86
Nitrate (NO ₃ ⁻ -N)	mg/L	0.55	0.53	1.1	0.53
Phosphorus (P)	mg/L	0.11	0.11	0.32	
Bromide (Br ⁻)	mg/L	0.65	0.54	1.4	< 0.010
Bromate (BrO ₃ ⁻)	mg/L	0.14	0.21	0.22	0.032
Chlorite (ClO ₂ ⁻)	µg/L	< 10	< 10	< 10	< 10
Chlorate (ClO ₃ ⁻)	mg/L	19	28	56	23
Perchlorate (ClO ₄ ⁻)	µg/L	4.5	16	28	13
ORGANIC COMPOUNDS					
TOC	mg/L	13.6	14.8	35.2	9.32
Total Kjeldahl-N	mg/L				(0.058) ¹

¹ The regulatory required Method Reporting Limit (MRL) is 0.5 mg/L and that figure was shown on the official report. The value shown was obtained from the lab analyst; his lowest standard is 0.05 mg/L, and that was the Detection Limit.

Physical Characteristics and Bather Load Estimates for the Pool Complex

Currently estimates of bather loads are available only from the Pool Complex. Similar estimates from the Swim School are being developed; however, based on experience with swim schools generally, the bather load at the Swim School is expected to be similar to that of the Therapy Pool at the Pool Complex.

Function	Volume		Temperature	Bather Load
	Gallons	Cubic meters	°F	bathers/m ³ hr
Lap Pool	166,000	628.3	82	0.11
Therapy Pool	20,000	75.7	88 – 90	0.44
Spa	1,200	4.5	102 - 104	2.2

The bather loads are estimated based on the following assumptions:

- The volume of fluids discharged per unit time (hour) from each swimmer is a function of water temperature and swimmer activity – the temperature function alone is approximately 1 pint/hour at ~ 80°F, 2 pints/hour at ~ 90°F and 3 pints/hour at ~100°F and normal activity for that temperature, i.e. moderate lap swimming in the Lap Pool and swimming lessons of moderate activity in the Therapy Pool. These approximate volumes of body fluids are used as “equivalent bather” weighting factors as described below to normalize to published findings of pool chemistry as a function of bather loads.
- Swimming teams using the Lap Pool are exceptionally active, however – the “equivalent bather” is given a weighting factor of 2 consistent with the level of activity.
- Pool operation for 15 hour/day (0600 – 2100 hours), 7 days per week as a normal operation – all pools are closed from time to time for maintenance, of course.

Bather loads are estimated as follows: for perspective, a bather load of 0.5 bathers/m³ hr is considered *exceptionally heavy*.

POOL	TIME PERIOD	NO	DURATION OF SWIM hours	WEIGHT FACTOR	LOAD bath hrs/day	TOTAL bath hrs/day	BATHER LOAD bathers/m ³ hr
Lap	AM	100	1.5	1	150		
	PM	150	0.75	1	112		
	PM team	150	2.5	2	750	1012	0.11
Therapy	Day	250	1.0	2	500	500	0.44
Spa	Day	100	0.5	3	150	150	2.2

The chemistry of each pool is maintained within narrow limits of hardness and alkalinity by manual additions of chemicals when necessary. The pH is maintained in the range 7.4 – 7.6 by continuous monitoring and addition of acid (HCl) by pH controller. The FAC is maintained at about 2.0 mg/L ± by continuous ORP monitoring and addition of MOS (previously bleach). The controller can be programmed to increase the ORP set point at specific times to add more MOS (aka super MOS dosing) increasing the FAC; this operation is conducted often at night during off hours, allowing the excess FAC to be consumed by oxidation reactions and reach a concentration allowed for operation (typically ≤ 4 mg/L) by morning opening. FAC and CC measurements are made manually using the DPD-FAS drop-wise titration method several times during an operating day and the measurements used to adjust the ORP set point for MOS addition; the method has a sensitivity of 0.2 mg/L⁸.

Discussion of Analytical Results

Alkali Metal Cations (Na⁺, K⁺, Li⁺, Rb⁺)

Sodium (Na⁺) and potassium (K⁺) normally constitute the bulk of the alkali metal cations in a water sample. K⁺ is not detected by ICP so is not reported for the Pool Complex; the concentration seen in the Swim School sample is typical even of potable waters. The high concentrations of Lithium (Li⁺) reflect the use of lithium hypochlorite (LiOCl) to supplement MOS at the Pool Complex, and Rubidium (Rb⁺) is most likely a contaminant of both bleach (also used occasionally when MOS ran short) and LiOCl. Lithium concentrations are highest in the Lap Pool and the Spa, reflecting the tendency for LiOCl to be used more in those pools.

Alkaline Earth Metal Cations (Ca²⁺, Mg²⁺, Ba²⁺, Sr²⁺)

⁸ The measured ORP is known to be influenced by the major ion composition of the water (the effect of Cl⁻ is predicted theoretically, for example, as a 30 mV decrease per decade increase in Cl⁻ concentration and the ORP is observed to decrease as the Total Dissolved Solids (TDS) concentration increases) and dramatically influenced by the presence of both inorganic and organic chloramines; the ORP at a given measured FAC drops by several 10's of millivolts when cyanuric acid is added to the water to a concentration of a few 10's mg/L. During the startup period using MOS in fresh pool water, the ORP-FAC relationship initially approached that predicted theoretically in contrast to that observed using bleach; however, with continued MOS use without changing the pool water, the ORP measurement tended to be independent of the FAC, suggesting the increasing presence of a separate oxidation-reduction couple which tended to dominate the ORP, an effect on ORP from increasing TDS, or other factors not yet identified.

These four divalent cations are all detected as hardness. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) are typically the major components of hardness in waters; the smaller concentrations of barium (Ba^{2+}) and strontium (Sr^{2+}) probably arise as contaminants in the chemicals used for hardness adjustment.

Major Common and Minor Anions

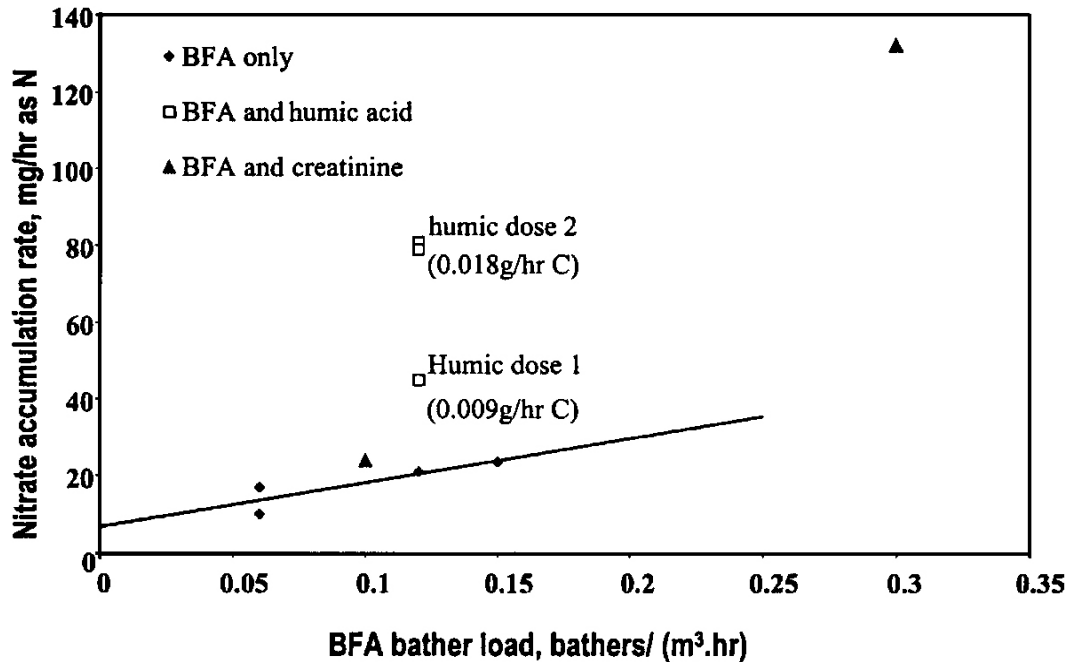
Chloride (Cl^-) is expected to be “conservative” in waters, i.e. in the absence of volatile losses of chlorine as Cl_2 or as the inorganic chloramines, it does not engage in reactions leading to net losses (the same may be said for chlorate (ClO_3^-) and perchlorate (ClO_4^-) discussed later). Because the major source of Cl^- in the pools is the NaCl in MOS, as well as in the other chlorine-based disinfectants used, the concentrations are expected to be proportional to the total MOS and other disinfectant doses since last draining. Any quantification of the proportionality to MOS dose exclusively, however, is confounded by the use of lithium hypochlorite (LiOCl) preferentially in the Lap Pool.

Sulfate (SO_4^{2-}) is normally expected to be “conservative” in waters as well except that it can engage in precipitation reactions, especially with Ca^{2+} to form gypsum (CaSO_4), leading to a net loss of both Ca^{2+} and SO_4^{2-} . Gypsum (CaSO_4) is one of the few compounds in nature showing reduced solubility with increase in temperature (a feature which causes gypsum scale formation in boilers). Thus the differences (decreases) in both Ca^{2+} and SO_4^{2-} from the coolest to warmest of the three pools of the Pool Complex may result from more precipitation of gypsum in the warmer pools, with the gypsum being removed in the filters.

Nitrate (as nitrogen, NO_3^- -N) is a curiosity the evaluation of which strongly suggests that there are different reaction pathways between the reactions of FAC as MOS and FAC as bleach (or LiOCl) with organic nitrogen compounds and ammonia. Judd and Bullock^{xiii} reported in their experiments with a model pool dosed with BFA at varying rates and holding the FAC (as bleach) at a concentration at $2.0 \pm \text{mg/L}$ that NO_3^- -N accumulated in the pool water to very high concentrations (15 mg/L was the highest observed) and accounted for 4 – 28% of the dosed amino nitrogen (both NH_3 -N and organic-N). Not unexpectedly, the rate of NO_3^- -N accumulation was found to increase with bather load as shown in the figure below (from Judd and Bullock (2003)).

The fact that the NO_3^- -N concentrations in the four pools were 1) very low compared to the concentrations accumulated in the Judd and Bullock¹² model pool despite extremely high bather loads, and 2) virtually invariant among the pools indicates that, using MOS, the load of organic-N from the BFA is ultimately discharged as nitrogen gas (N_2) through the breakpoint reaction of inorganic -N- fragments and NH_3 -N.

Nevertheless, the sharp contrast between the findings of these analyses and those of Judd and Bullock is clear indication of a different reaction pathway in waters treated with MOS compared to those treated with bleach. This, in turn, indicates the presence of at least one non-chlorine oxidant or catalyst in MOS not present in bleach.



Phosphorus (P) — the sources and chemical behavior of phosphorus are not known well enough at this time for any comment to be useful. However, the chemical form is probably orthophosphate (o-PO_4^{3-}) as H_2PO_4^- ; the lead chemist at the analyzing laboratory noted an indication of phosphate on the anion chromatograms but the concentrations were below the level of quantification (~ 0.2 mg/L as P).

Bromide (Br^-) and Bromate (BrO_3^-) — the presence of these constituents is expected; bromide is known to be present in the salt used for MOS generation and Gordon^{xiii} had noted the presence of small concentrations of bromate in the MOS generated by a small MIOX system, concluding that it was being produced by electrolysis in the MIOX cell from bromide in the salt. Occasional analyses of MOS treated potable waters containing Br^- have shown that MOS does not make BrO_3^- in the treated water at least to detectable concentrations and probably not at all.

Weinberg et.al.^{xiv} and more recently Brown, et.al.^{xv} reported bromate in bulk bleaches used for potable water treatment. Brown et.al. report concentrations of $0.244 - 0.310$ $\mu\text{g BrO}_3^-/\text{mg FAC}$ (MCL ≤ 10 $\mu\text{g/L}$). At these concentrations in bleach and given typical FAC doses for potable water treatment (~ 5 mg/L), BrO_3^- concentrations due to bleach disinfection are not likely to approach the MCL. However, in swimming pools which receive continual doses of FAC as MOS or as bleach, both Br^- and BrO_3^- concentrations would be expected to accumulate. The authors have inquired with the National Spa and Pool Institute/Association of Pool and Spa Professionals (NSPI/APSP) for guidelines or enforceable regulations on maximum BrO_3^- concentrations in pools; none have been issued, although the NSPI/APSP Recreational Water Quality Committee has recently discussed the accumulation of other constituents associated with disinfectants. For the moment at least, there appears to be no concern for BrO_3^- or other constituents in pools or other recreational waters.

Moreover, it is clear from the analysis of the Swim School sample that accumulation of Br^- and BrO_3^- can be virtually eliminated by using a low Br^- salt for MOS generation; the Br^-

concentration in the salt used at the Pool Complex was estimated at > 270 ppm (mg/kg) whereas that used at the Swim School was known to be < 100 ppm.

High concentrations of Br^- lead to dominance of $\text{Br}_2/\text{HOBr}/\text{OBr}^-$ as the disinfectant – so called, “bromine pools”. Inadvertent addition of Br^- into a bleach-treated pool under ORP control is also known to affect the ability of the ORP controller to prevent development of conditions typical of a “bromine pool”. Bromine pools are not known to develop chlorinous (or brominous) odors because the bromamines NHOBr and NBr_3 , analogous to the chloramines, have low volatility. However, the coauthor’s (Dempsey) experience is that bromine pools tend to require more chlorine because the $\text{Br}_2/\text{HOBr}/\text{OBr}^-$ forms are not as strong oxidants; the water takes on a cloudy, gray, dull-green appearance and swimmers complain of itchy skin and a condition (probably misnamed) known as “bromine rash”, all thought to be due to accumulation of bromamines (but possibly also due to accumulation of organic material and organic bromamines). These conditions require a chlorine or non-chlorine shock to remove. Operators tend to use more chlorine (as bleach) in bromine pools in order to maintain other features of the pool water, most notably water clarity. Dominance of disinfection by $\text{Br}_2/\text{HOBr}/\text{OBr}^-$ is known to occur at Br^- concentrations around 5 mg/L; there is little experience with the effects of Br^- at sub-mg/L concentrations on pool management.

It is reasonable to ask why, since BrO_3^- (and perforce Br^-) are also present in bleach, chemical behavior typical of a “bromine pool” is not regularly seen in bleach treated pools! The answer may be that bleach treated pools are typically drained much more frequently for control of CC and TDS than are MIOX MOS treated pools; thus the BrO_3^- and Br^- concentrations cannot build to the levels seen in these analyses. The experience to date in pools on which the coauthor (Dempsey) has consulted is that bleach treated pools are drained 4 to 6 times for each drain of a MIOX MOS treated pool because the driver to control CC is not present in the MIOX MOS treated pools. Instead they tend to be drained due to TDS buildup and for structural and piping maintenance. And the rate of TDS accumulation in MOS treated pools is also lower than in bleach treated pools because there is no need for shocking chemicals (excess bleach or persulfate) in MOS treated pools.

Chlorite (ClO_2^-), Chlorate (ClO_3^-), and Perchlorate (ClO_4^-) — The low (< 10 $\mu\text{g/L}$) chlorite (ClO_2^-) concentrations provide further verification that MOS does not contain chlorine dioxide (ClO_2).

The chlorate (ClO_3^-) and perchlorate (ClO_4^-) concentrations in the three pools of the Pool Complex increase in the same direction as the bather loads and the MOS dose. This is expected because MOS is known to contain small concentrations of both chlorate (~ 13 – 33 $\mu\text{g/mg}$ FAC) and perchlorate (~ 0.2 $\mu\text{g/mg}$ FAC). However, the concentration ratios between the pools are not the same for the two constituents – the chlorate concentration appears to be high relative to the perchlorate concentration in the Lap Pool. This apparent aberration is likely due to the use of LiOCl referentially in the Lap Pool; it is likely that LiOCl contains chlorate as a contaminant. The chlorate and perchlorate concentrations in the Swim School sample are like those of the Therapy Pool of the Pool Complex, supporting the expectation (to be confirmed) that the bather load at the Swim School is similar to that of the Therapy Pool.

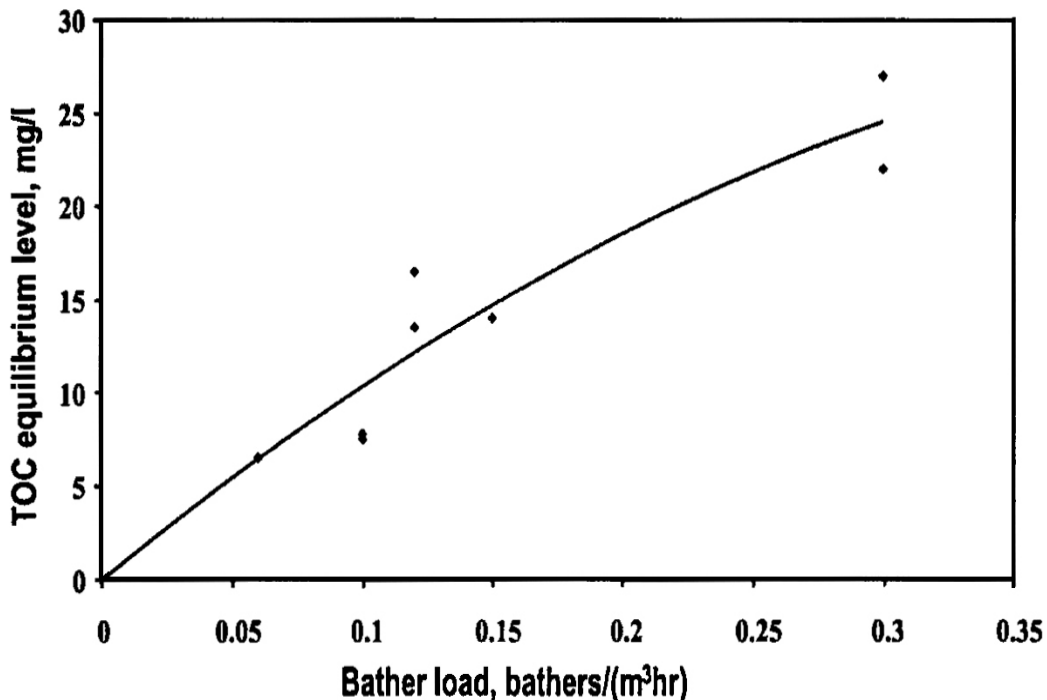
The last survey (known to the authors) of bleaches used for potable water disinfection showed chlorate concentrations ranging from 0.018 – 2.6 mg ClO_3^-/mg FAC, with a median of 0.11 mg/mg FAC^{xvi}; even the median concentration found in this survey is much greater than the

concentration range determined in MOS (0.013 – 0.033 mg/mg FAC). Despite the occurrence of chlorate in bleach, probably due to the absence of an EPA MCL for chlorate in potable waters, no concerns for the accumulation of chlorate in pools has been expressed by NSPI/APSP. Moreover, despite recent attention being devoted to perchlorate contamination of potable water supplies and the high likelihood that it is present in commercial bleaches as well, no MCL has been proposed, and no concern has been expressed by NSPI/APSP for the accumulation of perchlorate in pools.

Organic Compounds

Total Organic Carbon — Judd and Bullock¹² found that the Total Organic Carbon (TOC) concentration reached a maximum, or “equilibrium”, value as a function of the bather load in the pool, with the FAC concentration being held constant at 2.0 mg/L \pm as shown in the figure below (from Judd and Bullock).

This finding is counterintuitive; one would expect continued accumulation of TOC as a function of time at any given bather load. But the fact of a maximum concentration as a function of bather load suggests that the reaction between FAC and organic material at fixed FAC is a function of the organic concentration, i.e. as the organic concentration increases, the rate of reaction adjusts to balance the organic loading rate through the BFA. Mass action requires that the dose of FAC as bleach would have to increase as well with increasing BFA and increasing reaction rates; unfortunately, Judd and Bullock do not quantify the FAC as bleach doses. Moreover, the reaction between FAC and organic material leads to complete mineralization of the organic to CO₂ and H₂O; any fragments of organic material would have been detected as TOC.



The bather loads for the three Pool Complex pools applied to this figure would lead to the conclusion that the TOC observed in the Lap Pool (13.6 mg/L at a bather load of 0.11 bathers/m³ hour) is very close to that predicted in the figure, but that the TOC concentrations observed in the Therapy Pool (14.8 mg/L at a bather load of 0.44 bathers/m³ hour) and the Spa (35.2 mg/L at a

bather load of 2.2 bathers/m³ hour) are much lower than predicted in the figure; indeed the latter two bather load values are off the chart. Since the Therapy Pool and the Spa were treated almost exclusively with MOS, whereas the Lap Pool received LiOCl preferentially when MOS was in short supply, these results suggest that FAC as MOS is considerably more effective than FAC in any other form at decomposing organic material from the BFA. In addition, the Therapy Pool was subjected several times to overdosing with MOS overnight, and each time the excess FAC was consumed before the pool opened at 0530 the following morning (in some experiments, consumption of the excess FAC was complete within one hour). In the coauthor's (Dempsey) experience, this NEVER occurs using bleach for overdosing; the consumption of FAC as bleach requires much longer and the FAC remaining in the morning after overdosing with bleach the previous evening often exceeds the upper limit for opening and must be quenched with thiosulfate.

The TOC concentration in the Swim School sample was lower than that in any of the samples from the Pool Complex at a bather load expected to be like that of the Therapy Pool of the Pool Complex. However, the Swim School pool is not known to have been overdosed with MOS. Therefore, the MOS overdosing conducted in the Therapy Pool at the Pool Complex is likely to have been irrelevant to the TOC concentration observed there; i.e. the same total MOS dose would likely have been used with either regular maintenance of the FAC or with occasional overdosing at night. The conclusion is unencumbered — MOS maintained a MUCH lower TOC than did bleach (in the Judd and Bullock¹² model pool).

Total Kjeldahl Nitrogen (TKN) — unfortunately, no literature reports are available for comparison with the results discussed here. However, the TKN value of 0.058 mg/L in the Swim School sample seems remarkably low considering the predominance of organic amines (i.e. organic-N) in the BFA, and lower (by a factor of 28) than would be expected from the TOC concentration⁹. This finding strongly supports the conceptual model that MOS rapidly and preferentially attacks the organic-N compounds, reducing them to inorganic –N– fragments [the absence of swimmers' complaints in MOS-treated pools strongly suggests rapid discharge of the inorganic –N– fragments as N₂ through the breakpoint reaction as discussed earlier].

Nevertheless, the presence of TKN at 0.058 mg/L is sufficient to explain the presence of a persistent CC measurement. The –N– moiety in the organic-N compounds of the BFA would be expected to be fully chlorinated with one chlorine atom for each –N– moiety at a Cl/N mass ratio of 5:1, and additional chlorines (up to 2) may attach to each –N– moiety in the presence of abundant FAC in the water (as is the case for properly operated swimming pools). Therefore, a measured CC concentration of 0.3 – 0.6 mg/L (0.058 x 5 or 10) would be expected to have been observed in this water sample; in fact, the measured CC concentration at the time the sample was collected was ~ 0.4 mg/L.

A persistent CC measurement in the absence of chlorinous odors from volatile dichloramine (NHCl₂) and trichloramine (NCl₃) is commonly considered a “*nuisance residual*”. This

⁹ The expected molar abundance of carbon, nitrogen, and phosphorus in organic material is the well-known Redfield Ratio – C₁₀₆N₁₆P (the molar abundance of –N– to –C– is actually higher in the organic material of the BFA, but use of the Redfield Ratio is sufficient to make the argument). Therefore, the mass of organic-N per unit mass of Total Organic Carbon (TOC) would be expected to be approximately this molar ratio multiplied by the ratio of the molecular weights of N and C, i.e. (16/106)(14/12), or ~ 0.176 N/C. Using this evaluation, the TKN concentration would be expected to have been 1.64 mg/L (0.176 x 9.32 mg/L (TOC)).

evaluation strongly suggests that nuisance residuals are due to organic-N compounds found in the BFA which are slower than others to fragment.

Geographical (and possibly temporal) variations observed in the occurrence of a persistent CC measurement in the absence of chlorinous odors (the nuisance residual) in MOS-treated pools cannot be explained at this time. However, it is likely that they are related to the composition of the BFA and, given geographical and seasonal variations in diet, geographical and temporal variations in the composition of the BFA, should they be shown to occur, would not be surprising.

ⁱ Judd, S.J. and S.H. Black, 2000, “Disinfection By-Product Formation in Swimming Pool Waters: A Simple Mass Balance”, *Wat. Res.*, 34(5):1611-1619.

ⁱⁱ Bradford, W.L., 2004, “Some Benefits of the Use of Mixed Oxidants in Swimming Pools: Speculation on Chemical Mechanisms for Lack of Swimmer’s Complaints Using Mixed-Oxidant Solution”, Los Alamos Technical Associates, Inc., Los Alamos, NM, 20 January 2000, last updated 02 January 2004.

ⁱⁱⁱ Bradford, W.L. and R. Dempsey, 2004, “General Observations and Expectations on Startup of MIOX”, Los Alamos Technical Associates, Inc., Los Alamos, NM, and Simply Water, LLC, Houston, TX, 29 April 2004.

^{iv} Faust, S.D. and O.M. Aly, 1998, *Chemistry of Water Treatment*, Second Edition, Ann Arbor Press, Chelsea, MI, 581 pp.

^v White, G.C., 1992, *The Handbook of Chlorination and Alternative Disinfectants*, Third Edition, Van Nostrand Reinhold, New York, NY, 1308 pp.

^{vi} Gordon, G., W.J. Cooper, R.G. Rice, and G.E. Pacey, 1992, *Disinfection Residual Measurement Methods*, Second Edition, AWWA Research Foundation and American Water Works Association, Denver, CO, 889 pp.

^{vii} Hery, M. and G. Hecht, 1998, “Occupational Exposure to Chloramines in Swimming Pools and Vegetable Processing Plants”, presented at the 2nd *International Conference on Pool Water Quality and Treatment*, March 4, 1998, Cranfield University, Bedfordshire, UK.

^{viii} Bradford, W.L. and R.I. Cisneros, 1995, "Oxidation of Ammonia in Aqueous Ammonia Solutions Using the MIOX Mixed-Oxidant Solution at Chlorine Concentrations Near Stoichiometric Equivalency with Ammonia Nitrogen", Los Alamos Technical Associates, Inc., Los Alamos, NM, LATA/MX-95/0015

^{ix} Daniel, E., 1995, “Pilot Study/Engineering Report for ‘MIOX On-Sight [sic] Mixed Oxidant Generator for Cash Water Supply Corporation’”, Cash Water Supply Corporation, Greenville, TX, July, 1995.

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- ^x Kuehl, N.R., 2000, “Mixed Oxidant Ammonia Removal Pilot Project”, presented at the 25th Annual Conference of the Iowa Rural Water Association, Kuehl and Payer, Ltd., Storm Lake, IA.
- ^{xi} Bradford, W.L., 1998, “The Differences Between On-Site Generated Mixed Oxidants and Sodium Hypochlorite”, Los Alamos Technical Associates, Los Alamos, NM and MIOX Corporation, Albuquerque, NM, last updated 9 January 2004.
- ^{xii} Judd, S.J. and G. Bullock, 2003, “The Fate of Chlorine and Organic Materials in Swimming Pools”, *Chemosphere*, 51:869-879. [also presented at the Aquatic Health Conference, 2-4 October 2004, Atlanta, GA]
- ^{xiii} Gordon, G.L., 1998, “Electrochemical Mixed Oxidant Treatment: Chemical Detail of Electrolyzed Salt Brine Technology”, prepared for the U.S. Environmental Protection Agency, National Risk Management Laboratory, Cincinnati, OH, May 1998.
- ^{xiv} Weinberg, H.S., C.A. DelComyn, and V. Unnam, 2003, "Bromate in Chlorinated Drinking Waters: Occurrence and Implications for Future Regulations", *Environ. Sci. Technol.*, 37(14):3104-3110.
- ^{xv} Brown, R.A., D.A. Cornwell, and M.J. MacPhee, 2004, “Trace Contaminants in Water Treatment Chemicals: Sources and Fates”, *J. Am. Wat. Wks. Assoc.*, 96(12):111-125.
- ^{xvi} Bolyard, M. and P.S. Fair, 1992, "Occurrence of Chlorate in Hypochlorite Solutions used for Drinking Water Disinfection", *Environ. Sci. Technol.*, 26(8): 1663-1665.