COMPARISONS OF CHLORINE AND *MIOX* TREATED POOL WATER[1]

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TABLE OF CONTENTS

Topics

[1] This paper focuses on the *MIOX* water treatment. It was produced without any input from or consideration by the makers of the *MIOX* system. In a troublesome situation with which this writer was familiar, the *MIOX* solution was judged to be the best solution. To this day (11/28/2009) the MIOX system continues to offer swimming lesson clients *"sweet"* water.

1. Executive Summary

- ***The MIOX disinfectant system for swimming pool water is proposed as being superior to the chlorine-only disinfectant system.***
- ***The central problem is to have the various Health and Water agencies***
  - ***recognize the unique chemistry and effectiveness of MIOX in commercial instructional swimming pool environments,***
  - ***to alter the standards and tests of MIOX water to include accurate and valid assessments of that chemistry, and***
  - ***to monitor MIOX pools with these different tests and interpretations without misapplying chlorine-only valid tests and standards.***
- ***The MIOX water treatment produces an altered balance of organic and inorganic chloramines rendering the pool water "safer".***
- ***Common Health assessments of MIOX water could lead to false conclusions about water quality.***
- ***A compromise or modification of existing pool water assessment standards for MIOX treated pools is needed.***
- ***If the symptoms of bad water (the presence of inorganic chloramines) are not observed, further testing for the presence of chloramines is virtually a waste of resources.***
- ***The DPD$_3$ test does not distinguish between organic and inorganic chloramines making it invalid for assessing the effects of the MIOX system on pool water.***
- ***The absence of water odour (chloramines escaping into ambient air) and the absence of organic chloramines in the Health assessment results indicate false results.***
- ***A MIMs analysis has the greatest potential for yielding correct assessments of the level of presence of inorganic chloramines in pool water analyses.***
- ***To assure that test results are correct, a MIMs analysis should always be conducted in concert with other forms of residual chlorine analyses before declaring the status of MIOX disinfected water.***

2. A Brief History

A 40+ year-old swimming pool had functioned solely as a teaching facility. It needed updating and consideration was given to the water treatment method. Problems occasionally arose with Health Department testing of the chlorination process. Chlorination, had proven to be consistently troublesome in the teaching function. The traditional treatments often were distasteful and a source of complaints by clients.

The facility has one of the heaviest user demands on its limited pool size of any instructional pool in its state. A difficult challenge was always to keep water quality safe and acceptable using

traditional chlorine-only methods. While the "*old and tried*" chlorination method (chlorine usually is presented as sodium hypochlorite) has been effective and tolerated it has not been without problems. Chlorination has proven to be a health risk to some swimmers and staff (Rushall, 2005; Rushall & Weisenthal, 2003) and often produced obvious symptoms in swimmers including stinging eyes, retaining a chlorine smell after having left the facility, bleached hair and swim suits, skin irritations, degradation of tooth enamel, and coughing/wheezing as well as the strong smell of chlorine in ambient air. When pool water is in good condition it is clear, odourless, and taste-free; a condition now popularly described as being "*sweet water*". With chlorine-only treatment, pool water often cycles between being sweet and problematic. Quick treatments often involve dumping all the problem water and starting with a fresh pool, and superchlorination.

Better methods than chlorination for swimming pool sanitation now exist. They usually involve multiple-stage water treatment, some being more effective and some being more expensive than others. Of particular interest is the "*MIOX System*" (*MIOX*). *MIOX* uses a brine-tank sodium hypochlorite and mixed oxidants sanitising process. *MIOX* is considered to be superior to chlorine-only treatment because it sustains superior water quality and is more effective at removing dissolved solids. It produces a better and safer aquatic environment. *MIOX* has grown out of a world-wide acknowledged leadership role in water purification treatments. That technology has been modified for swimming pool water treatment and sanitation. Unfortunately, many Health departments have not kept up with this beneficial development.

After installing a *MIOX* water treatment in the instructional pool, it is the owners' opinion that it has produced the most sustained period of *sweet* water in memory.

- ***The MIOX disinfectant system for swimming pool water is proposed as being superior to the chlorine-only disinfectant system.***

3. A Problem

The maintenance of pool water quality is a critical responsibility of swimming pool operators. The monitoring of the effectiveness of water maintenance is the responsibility of several governmental agencies. Those agencies have standards and procedures that have been in place for many years.

The standards and procedures used normally are specifically set for chlorine-only pools. The chemistry of chlorination has a particular aetiology for which tests and standards have been devised and applied. However, the aetiology of *MIOX* is different, with some chlorine-valid tests and standards being invalid for evaluating its effectiveness in swimming pool sanitisation.

MIOX is considered an advancement in water treatment in comparison to the chlorine-only treatment in the particular circumstance of high-use instructional swimming pools. This has been the experience at the once-troubled pool, as well as in instructional and public pools in Japan, Hong Kong, and the USA.

One problem is that *agencies' tests and standards that are valid for chlorine-only treated pools are partly invalid for MIOX treatments*.

When certain standards are surpassed with chlorination, immediate steps need to be taken to rectify the perceived problem or close the facility. In a commercial operation, such as that of a swimming school, either of those actions could require the facility to be closed at the

inconvenience of pupils and staff as well as disruption of commerce. The superior *MIOX* system is a preventative measure to avoid water problems and interruptions to business. However, if a chlorine-valid test result is applied invalidly to *MIOX* water treatment, instructional and commercial interruptions could be required with obvious effects.

- ***Therefore, the central problem is to have the various Health and Water agencies***
  - ***recognize the unique chemistry and effectiveness of MIOX in commercial instructional swimming pool environments,***
  - ***alter the standards and tests of MIOX water to include accurate and valid assessments of that chemistry, and***
  - ***monitor MIOX pools with these different tests and interpretations without misapplying chlorine-only valid tests and standards.***

4. A *MIOX* Idiosyncrasy

One major concern for the evaluation of water is the interaction of chlorine with ammonia. Since many pollutants of human origin contain nitrogen causing ammonia, swimming pools produce troublesome chloramines. It is important that chloramines be controlled. They often are required to be no more than 1 ppm in swimming pools when measured with the DPD3 test as part of the DPD Pool Test Kit.

However, there are two general types of chloramines produced in pool treatment systems. The DPD3 test does not differentiate the two (Shang & Blatchley, 2001), despite their having very different qualities. Organic chloramines (RNHCl) are not dangerous to pool users nor do they cause water quality to be degraded (National Center for Environmental Assessment, 1999). Inorganic chloramines are the problem chemicals. There are three types of inorganic chloramines, monochloramines (NH_2Cl), dichloramines ($NHCl_2$), and trichloramines (NCl_3). Depending upon the swimming pool environment, maintenance, and use, the mix of inorganic and organic chloramines varies (Lenntech, 2005).

The *MIOX* system includes extra oxidants as well as chlorine. The extra oxidants produce more organic chloramines than an equivalent chlorine-only treatment because of two factors:

- The chlorine part of the treatment produces both organic and inorganic chloramines in a normal manner.
- The additional *MIOX* part of the treatment produces additional organic chloramines [it works more effectively in removing more dissolved bodily solids] as well as breaking down inorganic chloramines into more organic chloramines (Bradford & Dempsey, 2005; National Center for Environmental Assessment, 1999).

Thus, in a chlorinated pool, the measurement of total chloramines would include a mix of harmless organic and dangerous inorganic chloramines. In a *MIOX* pool, the measurement of chloramines would include an elevated level of organic chloramines and a greatly reduced level of inorganic chloramines. This leads to the anomaly where a *MIOX* pool could yield a higher total of chloramines than a chlorine-only pool but would be safer for swimmers to use because of the increased organic and decreased inorganic chloramines.

- ***The MIOX water treatment produces an altered balance of organic and inorganic chloramines rendering the pool water "safer".***

Commonly, the standard assessment for total chloramines is 1 ppm with no differentiation between organic and inorganic chloramines. Apparently, this level is a conservative opinionated level determined quite some time ago. It is possible to achieve this level in chlorine-only pools by low user numbers and occasional superchlorination, the latter prohibiting pool use for some time. With *MIOX* pools, the added effectiveness of the integrated system increases the total chloramine level. A relatively high level in a *MIOX* pool (>1 ppm) indicates the system is working very well if the pool has very high use (it is removing a lot of dissolved solids). In moderate use *MIOX* pools, the level could be slightly above or below 1 ppm. In low-use *MIOX* pools, the level would be low and likely indistinguishable from a chlorine-only treated pool.

A regulating agency officer, using chlorine-only standards and assessments, would deduce invalidly that a high-use *MIOX* pool with a reading in excess of 1 ppm was in need of immediate rectification to reduce the level to <1 ppm. However, in low-use pools, the *MIOX* and chlorine-only pools would read similarly. It is this situational anomaly that could confuse the decision-making of an officer charged with the responsibility of monitoring swimming pool water health.

- ***Current Health assessments of MIOX water could lead to false conclusions about the Cross Street water quality.***

Consequently, to hold *MIOX* treated pools to the long-standing level of 1 ppm or less defeats the purpose of improving water quality in the heavy-use pools. A compromise or modification of existing pool water assessment standards for *MIOX* pools is needed.

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5. Measurement Difficulty

Water agencies often report no organic chloramines and high levels of monochloramines and dichloramines in water samples. The usual analytical procedure (amperometric titration) is fraught with pitfalls and potential errors and often leads to false conclusions (Shang & Blatchley, 2001). Some of the errors are warned in the *Standard Methods* manual (American Public Health Association, 1992).

6. Testing for Chloramines Level 1

The most obvious and reliable method for determining the presence of inorganic chloramines, particularly dichloramines, is direct observation. Chlorinated water does not smell or bleach without inorganic chloramines. An absence of pool odour indicates an absence of inorganic chloramines (National Center for Environmental Assessment, 1999). In the conduct of pool instructional programs, the absence of some or all of the following inorganic chloramine symptoms attests to the quality and safety of the water: no odour of "*chlorine*" in the air, no skin odour of "*chlorine*", no "*burning*" or itching eyes, swim suits and hair not bleaching, and no skin itch. It should be noted that "*pool smell*" in not caused by too much chlorine but is caused by escaping air-borne inorganic chloramines.

- ***If the symptoms of bad water (the presence of inorganic chloramines) are not observed, further testing for the presence of chloramines is virtually a waste of resources*** (Professional Pool Operators' Association, no date)**.**

7. Testing for Chloramines Level 2

As has been indicated above, the DPD3 test measures the total chloramines in pool water. With chlorine-only treatments in moderate- to low-use pools, the total can be below the cut-off point of 1 ppm. However, with *MIOX* water, the level can be higher in very high-use pools, the elevated level being caused by excessive inoffensive organic chloramines coupled with reduced inorganic chloramines. The common and current assessment procedures of swimming pools cannot make this distinction (Lenntech, 2005) and likely would incorrectly infer "*problem*" water in high use *MIOX* instructional pools.

- ***The DPD3 test does not distinguish between organic and inorganic chloramines making it invalid for assessing the effects of the MIOX system on pool water.***

The amperometric titration method of analysis for chlorine and chloramines has been questioned for its accuracy and validity of assessing chloramines in pool water (National Center for Environment Assessment, 1999; Shang & Blatchley, 2001). The major difficulty is that both forms of chloramines respond in a similar manner. The absence of water odour (chloramines escaping into ambient air) and the absence of organic chloramines in analyses could indicate false results. [Because solutions of organic and inorganic chloramines respond to these analyses as "*combined residual chlorine*" and because natural waters that contain high concentrations of ammonia form correspondingly high concentrations of combined residual chlorine, the terms combined residual chlorine and chloramines have become almost synonymous (National Center for Environmental Assessment, 1999).]

- ***The absence of water odour (chloramines escaping into ambient air) and the absence of organic chloramines in analyses could indicate false results.***

8. Testing for Chloramines Level 3

A recent form of analysis, membrane-introduction mass spectrometry (*MIMS*) is valid for quantifying inorganic chloramines (Donnermair & Blatchley, 2003). Shang and Blatchley (2001) used this form of analysis to verify the absence of residual inorganic chloramines in a water analysis after a DPD/FAS analysis had produced false positive results for defining a breakpoint chlorination curve. A *MIMs* analysis has the greatest potential for yielding correct assessments of the level of danger (the level of presence of inorganic chloramines) in pool water analyses.

- ***A MIMs analysis has the greatest potential for yielding correct assessments of the level of presence of inorganic chloramines in pool water analyses.***

To assure that test results are correct, a *MIMs* analysis should always be conducted in concert with other forms of residual chlorine analyses (DPD3 and the amperometric titration method) before declaring the status of *MIOX* disinfected water.

- ***To assure that test results are correct, a MIMs analysis should always be conducted in concert with other forms of residual chlorine analyses before declaring the status of MIOX disinfected water.***

9. Summary and Conclusions

The *MIOX* disinfectant system for swimming pool water is proposed as being superior to the chlorine-only disinfectant system. A vexing problem is to have the various Health and Water agencies i) recognize the unique chemistry and effectiveness of *MIOX* in commercial instructional swimming pool environments, ii) to alter the standards and tests of *MIOX* water to include accurate and valid assessments of that chemistry, and iii) to monitor *MIOX* pools with these different tests and interpretations without misapplying chlorine-only valid tests and standards. The *MIOX* water treatment produces an altered balance of organic and inorganic chloramines rendering the pool water "safer".

Current Health assessments of *MIOX* water could lead to false conclusions about instructional pool water quality. A compromise or modification of existing pool water assessment standards for *MIOX* treated pools is needed.

If the symptoms of bad water (the presence of inorganic chloramines) are not observed, further testing for the presence of chloramines is virtually a waste of resources. The DPD3 test does not distinguish between organic and inorganic chloramines making it invalid for assessing the effects of the *MIOX* system on pool water. The absence of water odour (chloramines escaping into ambient air) and the absence of organic chloramines in Health agency results indicate false results.

A *MIMs* analysis has the greatest potential for yielding correct assessments of the level of presence of inorganic chloramines in pool water analyses. To assure that test results are correct, a *MIMs* analysis should always be conducted in concert with other forms of residual chlorine analyses before declaring the status of *MIOX* disinfected water.

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