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What Is Mixed Oxidant Solution?

MIOX Corporation, 23 November 2011

Summary

Despite years of field evidence demonstrating that mixed oxidant solution (MOS) is more effective than bleach in a variety of applications, identifying the specific oxidants in addition to free chlorine in MOS has been limited by the availability of analytical techniques capable of differentiating oxidant species. Now, however, recent laboratory data using a light-emitting analytical technique, chemiluminescence, strongly indicate the presence of both free available chlorine and trace amounts of **hydrogen peroxide** (H_2O_2) in freshly generated MOS.

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Mixed oxidant solution is made from brine (salt) and energy.

The MIOX® mixed-oxidant solution (MOS) is produced by electrolysis of sodium chloride (NaCl) brine in an electrolytic cell that has been optimized for disinfection efficacy. This solution exhibits microbial inactivation properties that are superior to bleach alone. In MOS, free available chlorine (FAC) is the primary analyzable oxidant constituent. However, the chemical produced from MIOX MOS generators shows demonstrable differences from bleach in both field and laboratory studies, indicating the presence of other oxidant species beyond FAC alone. The additional oxidant species in MOS are responsible for enhanced biocidal efficacy (demonstrated on a variety of microorganisms), as well as enhanced behavior in several chemical processes important in water treatment. **Figure 1** shows one example of the superior biocidal efficacy of MOS compared to sodium hypochlorite/bleach (NaOCl). There are several results published in the peer-reviewed literature that have demonstrated this superior efficacy.[1] Years of compiled field data also show differences.[2]

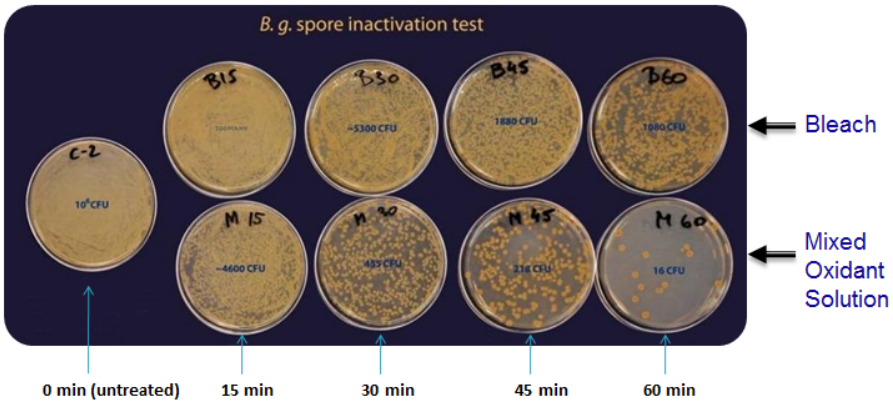

Figure 1: MOS is more effective than bleach.
Bacillus subtilis var. atrophaeus spores (ATCC No.: 51189) exposed to 5 mg/L FAC of MOS and NaOCl at pH 7.5. Exposure times: 15, 30, 45, 60 min

Analytical method limitations include FAC interference. A major obstacle to determining additional oxidant species present in MOS is the lack of analytical techniques for differentiating oxidants. Researchers continually improve oxidant analyses for FAC, ozone (O_3), hydrogen peroxide (H_2O_2) and chlorine dioxide (ClO_2).[3] Almost invariably, however, each of the methods is based on the total oxidizing capacity of the solution being analyzed and is readily subject to interferences from the presence of other potential oxidizing agents or intermediates from associated chemical reactions.[4] This is especially the case for analyzing additional oxidants in the presence of FAC.

Speciation research – ClO_2 and O_3 discounted and a growing body of evidence for H_2O_2 and/or other reactive oxygen species emerges. In 1994, Dowd[5] demonstrated the presence of a substantial systematic excess of oxidants over FAC alone in freshly-generated MOS produced at different brine flow rates. Methods included standard amperometric titration for FAC at pH 7 and a modification of the iodometric method at pH 2 in glacial acetic acid for total oxidants. While the nature and composition of the oxidants other than FAC was not identified, the method for total oxidants analysis suggested ClO_2, O_3, and H_2O_2 as possible components. The presence of ClO_2 and O_3 as analyzable components of the bulk produced MOS was discounted by subsequent research.[6]

By the 2000s, a growing body of evidence for H_2O_2 and/or other reactive oxygen species in MOS had emerged. The chemical and biocidal behavior of MOS, coupled with potentials measured at the anode of the electrolytic cell,

suggest the presence of other oxidants including reactive oxygen species (ROS). ROS are present in solutions of non-chloride brines electrolyzed under electrolytic conditions similar to those for producing MOS.[7] More recent research on the chemical species present in MOS using non-chloride brines has provided evidence that stronger oxidants than chlorine (likely ROS) are present in the solution. O_3, H_2O_2, and hydroxyl free radicals ($^{\bullet}OH$) were detected at the point of generation.[8] The longevity of each of these species in MOS is still not established, although that of O_3 and $^{\bullet}OH$ is expected to be short – milliseconds to seconds, explaining why no O_3 is detected in the bulk MOS. Literature data suggests that at higher pHs, such as those found in produced MOS, H_2O_2 has the potential to last hours to days in a chlorine matrix.

MIOX has applied this commonly-understood principle that is observed in nature to analyzing the mixed oxidant solution. Laboratory data using chemiluminescence analytical techniques indicate the presence of H_2O_2 in MOS. Certain chemiluminescent reagents are known to emit light in reaction with NaOCl, but not with H_2O_2. Very strong chemiluminescence is produced, however, in reactions when bleach and H_2O_2 are present simultaneously.[10] The comparison of the reagent-mediated chemiluminescence of bleach and MOS in the pH range between 7.5 and 9 strongly suggests the presence of H_2O_2 and/or other reactive oxygen species in addition to FAC as hypochlorite (OCl^-) in MOS (see **Figure 2**).[9] Upon aging, the reagent-mediated chemiluminescent properties of MOS become gradually similar to those of bleach, which is also reflected in decreased biocidal efficacy compared to freshly generated MOS.

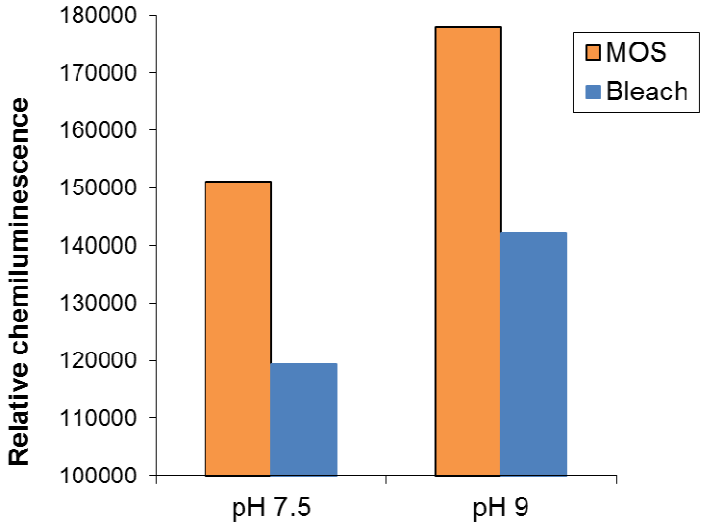

Figure 2: MOS in the presence of a chemiluminescence agent strongly suggests the presence of H_2O_2 and/or other reactive oxygen species not present in Clorox bleach.

Interestingly, the human immune defense system utilizes a similar strategy in which immune cells produce ROS at the sites of infection to kill bacteria. This is achieved when a chemical reaction occurs between NaOCl and H_2O_2.[10]

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[2] Bradford, W.L., 2006, "The Differences between On-Site Generated Mixed-Oxidant Solution and Sodium Hypochlorite" MIOX Corporation, www.miox.com.

[3] Standard Methods for the Examination of Water and Wastewater, 20th edition.

[4] **"**Disinfectant Residual Measurement Methods, Second Edition", AWWA Research Foundation; Prepared by Gilbert Gordon, Miami University; William J. Cooper, Florida International University; Rip G. Rice, Rice, Incorporated; and Gilbert E. Pacey, Miami University. 1992.

[5] Dowd, M.T., 1994, "Assessment of THM Formation with MIOX", Master's Thesis, University of North Carolina, Department of Environmental Sciences and Engineering, School of Public Health, Chapel Hill, NC.

[6] 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.

[7] Jeong, J., J.Y. Kim, and J. Yoon, 2006. "The Role of Reactive Oxygen Species in the Electrochemical Inactivation of Microorganisms", Environ. Sci. Technol., 40(19):6117-6122.

[8] Weinberg, H., S. Rodriguez-Mozaz, and A. Sykes, 2008, "Characterization of the Chemical Constituents of Mixed Oxidant Disinfection", Final Project Report, presented to MIOX Corporation by the University of North Carolina, Department of Environmental Sciences and Engineering, Chapel Hill, NC, 23 July 2008.

[9] Bajszar, G., 2008, "Co-Oxidation by Hypochlorite and Reactive Oxygen Species: Implications for Mixed Oxidant Solution Speciation", presented at MIOX Corporation, Albuquerque, NM 20 February 2008.

[10] Brestel, E. P. (1985) Biochem. Biophys. Res. Commun. 126:482-488.