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J. Que Hales, Editor

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Journal of the Swimming Pool and Spa Industry

The Journal of the Swimming Pool and Spa Industry (JSPSI) publishes papers on all aspects of the swimming pool and spa industry. Research, informative papers, bibliographies, book reviews, and symposia-in-print are presented for the general education of all technically minded individuals in the industry.

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Welcome!

Welcome to Volume 2 of the *Journal of the Swimming Pool and Spa Industry*. Many excellent publications are currently available in the pool industry, each designed for a different purpose and a different readership; from general to service to retail. As of yet, however, we are not aware of one seeking out and publishing purely technical material covering interests of the entire swimming pool and spa industry. This is the function of our journal – to publish that kind of material that is too technical for publishing in a trade magazine. Some existing technical journals publish, from time to time, articles which relate to our industry (such as the *Journal of the American Water Works Association*, *Ozone News*, *Vom Wasser*, or the *Journal of Applied Microbiology*) but they don't delve deep enough, much less exclusively, into the swimming pool and spa industry. There is a wealth of material available in the technical realm, from conventional water chemistry to plaster technology, from alternative sanitizers to alternative surfaces, from plastic performance to motor curves. Some of this material describes new research, some explains conventional wisdom in a technical manner not readily available or understood in the industry today. It is the intent of the *JSPSI* to assemble, edit, and publish this type of material, providing an open forum for education, discussion and debate.

The journal format is time-honored in the world of academia. *JSPSI* will not attempt to reinvent the format, but will be structured much the same as other existing journals. The following is a list of what we expect to include in issues:

Research Papers: A wealth of research is currently being conducted in the industry, and the primary purpose of this journal will be to provide a forum for the publishing of research findings. Published material is expected to detail completed projects, although some papers describing works in progress may be accepted. Papers will include documentation as needed, including chemical formulas, mathematical support, tables, illustrations, and references. This issue's articles on cyanuric acid chemistry, alkalinity dosages, and nanofiltration are examples of this type of paper.

Informative papers: Some areas of knowledge are well researched and understood in certain circles, but not in the general pool industry. For example, cement curing, metal ion and ozone activity in water, heater efficiency and emissions, motor performance curves, etc. are all well understood in selected circles,

but not to the industry as a whole. Informative papers will be printed which explain, at a technical level, these types of ideas for the education of those in the industry who are technically minded, but not yet exposed to that particular segment of knowledge. This issue's article on ozone is an example of an informative paper.

Annotated Bibliographies: When appropriate, annotated bibliographies will be printed. The purpose of this type of bibliography is to collect in one location as complete a listing as possible of documentation on a particular subject. Such listings may be useful in furthering research in a given area. Unlike a simple bibliography, which merely lists all of the publications containing the data, annotated bibliographies include paragraph-long descriptive or evaluative summaries after each citation, so that the reader knows what he may expect to find without having to locate and read each separate work. For example, annotations relating to the Saturation Index might look like this:

Cardall, John T. and Jonathan S. Powell Jr. "The Fallibility of the Langelier Index." *Pool News* (4 Aug. 1974): 40–43. [Cardall and Powell discuss the inappropriateness of applying the Langelier Index to swimming pools, and describe experiments which they conducted, refuting the validity of the index in the pool environment. They discuss some of the factors in the pool environment which interfere with the index.]

Hamilton, Jock qtd. in Paul Konrad. "Whose Numbers Tell the Story?" *Pool & Spa News* (10 Apr. 1989): 22–26. [Hamilton is quoted in this story as refuting the Langelier Index's appropriateness in swimming pools, and offering an alternate index (the Hamilton Index) which he claims sufficiently addresses the pool environment.]

Langelier, Wilfred F. "The Analytical Control of Anti-corrosion Water Treatment." *Journal of the American Water Works Association (AWWA)* 28 #10 (1936):1500–1521. [This is the original paper published on the saturation concept, which has since become known as the Langelier Saturation Index. Langelier is cited as an associate professor of sanitary engineering at UC Berkeley. The article contains formulas, tables, photographs, and references, as well as a history of study on saturation. The index is applied to municipal water piping systems. No mention is made to

possible swimming pool applications of the concept.]

Thomas, Jerome qtd. in Paul Konrad. "Whose Numbers Tell the Story?" *Pool & Spa News* (10 Apr. 1989): 22–26. [Dr. Thomas, successor to Dr. Langelier at UC Berkeley, is quoted in this article. He maintains that the Langelier Index "has no significance to open bodies of water – including swimming pools and spas."]

Book Reviews: Books relating to technical aspects of the swimming pool industry may be reviewed. Reviewers will be qualified, independent persons, who will evaluate books based on such factors as content, accuracy, and readability. This issue contains a book review as an example of this type of article, and we hope to review other books as they become available.

Letters to the Editor: Appropriate letters to the editor may be printed. Letters will be responses or rebuttals to material in previous issues of the journal, and must be technical in nature.

Short Technical Notes: Notes of a technical nature, but of short length may be included in this category. An example of a short technical note is the terminology note in this issue. Technical notes are typically accepted and sent to publication much quicker

than a paper, due to their brevity, and can therefore be useful under certain circumstances.

Abstracts: Each submission in the journal is preceded by an abstract (the summary/introductory paragraph in italics at the start of each paper). As articles pertaining to the swimming pool/spa industry appear in other journals, the abstract may be reprinted in this journal, to alert our readers to the appearance of the article.

Special Reports: These are reports which review research results of topical importance in a particular facet of the industry, and are usually commissioned in advance by the Editor.

Symposia-in-Print: These are collections of original research or informative papers, each individual paper being only about three to five pages in length, all held together by a unified theme. Subjects of forthcoming Symposia-in-print will periodically be announced in the journal. A Guest Editor will be assigned to head the project, and he will in turn invite authors active in the field of the symposium to submit papers, which then go through the normal editorial review procedure. Submissions by other authors not specifically invited are considered for inclusion on equal footing with invitees.

The people behind *JSPSI*:

Editor

The Editor of the *Journal of the Swimming Pool and Spa Industry* is J. Que Hales. He is currently employed by Pool Chlor, a residential gas chlorine chemical service firm. He has been in the pool industry since 1980, working first as a residential chemical technician, and then as the owner of a small independent cleaning, repair, and retail business. He has managed the Tucson office of Pool Chlor since 1985, and also functions as the Pool Chlor corporate computer systems manager and mailing operations manager. He studied English and Secondary Education at the University of Arizona. He is the co-author of several technical papers which have been reported on in various industry magazines. He has been a member of the Board of Directors of the National Association of Gas Chlorinators (NAGC) since its inception, and is currently the President of that organization. He is also Vice-President/President-elect of the Southern Arizona Chapter of the National Spa and Pool Institute (SAC-NSPI).

Editorial Advisor

The advisor to the editor on Journal management and editorial policy is Lyn Paymer of Association Services in Trabuco Canyon, California. Lyn is currently the Executive Director of a number of industry associations, including the National Plasterer's Council (NPC) and the NAGC.

Editorial Review Board

The Editorial Review Board is a group of volunteers who have agreed to read and referee submissions to the Journal. In order to maintain an objective, independent Journal, the Editor does not determine which submissions will be published and which ones will not. The Review Board, comprised of a wide selection of professionals in the publishing, technical, and service facets of the industry, performs a blind review, meaning that the Editor removes the cover sheet and other identifying text before the Board members see the submission. They then judge suitability based on sound scientific method, clarity, readability, pertinence to the industry and the Journal, etc. Each submission is reviewed by at least three individuals, two of whom must be Board members, and one of whom may be selected as needed from the industry at large for particular expertise on a specific subject. Board members do not know which other

members are reviewing a particular submission, and if a Board member chooses to abandon anonymity to contact a particular author for clarification, he/she will not compromise other reviewers (if known).

These Review Board members, along with the advisor to the editor, deserve our special thanks and appreciation. The *JSPSI* is a non-profit publication, and these individuals donate their time and efforts on our behalf. In subsequent issues they will be listed, but without full biographic information. We would like to take this initial opportunity, however, to introduce them (in alphabetical order):

C. Brent Cluff, Ph.D. did his undergraduate studies at Eastern Arizona College and the University of Arizona, received his BS and MS from the University of Arizona, and received his Ph.D. from Colorado State University. He is currently the owner/principal of Clean Water Products in Tucson, Arizona. He recently retired, after 32 years, from his position as an associate hydrologist with the University of Arizona.

Fernando del Corral, Ph.D. is a Research Microbiologist and is the Manager-Product Development, Recreational Water Research and Development Department at Buckman Laboratories, International. He studied at Southwest Baptist University (BS - Bacteriology and Chemistry), and the University of Georgia (MS and Ph.D. - Bacteriology). Dr. Corral is the author or coauthor of numerous publications, and has many patents, committee memberships, and professional association memberships to his credit.

Gerald Eckels is the principal of Kruger & Eckels, a Santa Ana, California-based manufacturer of swimming pool and spa controllers and meters. Formerly with Southern California Gas Company, he joined Kruger & Eckels in 1972. Kruger & Eckels provides custom engineered instrumentation that has been used in research, and distributes its products internationally.

Randy Golding, Ph.D. is a chemist at Tracer Research in Tucson, Arizona. Formerly a post-doctoral fellow at Lawrence Livermore Laboratories, Dr. Golding received his undergraduate degrees (BA - Education, BS - Chemistry) from Arizona State

University and his Ph.D. in Analytical Chemistry from the University of Arizona. He has consulted for a number of swimming pool chemical research projects.

Eric Herman was the Technical Editor for *Pool & Spa News* from 1989–1996. He was graduated from California State University at Fullerton with bachelor degrees in Journalism and English. Eric has published over 1000 articles, many of the technical in nature, in various publications, including *Pool & Spa News*, *Technical Resource Magazine*, and the *Sound and Video Contractor* trade journal.

Ron Jones has been in the swimming pool industry for 13 years, and was the Senior Research Scientist with BioLabs. He holds 3 patents, and has 7 pending on various water treatment applications, and does private consulting as Chemical Specialties in the areas of swimming pool and spa chemistry as well as industrial water treatment. He received a BS in Chemistry from the University of Georgia, and has served on the Chemical Treatment and Process Subcommittee of the NSPI.

Dave Knoop is the Applications Manager of Pool Products at Olin Research Center. He works with customers and consumers on product application issues, as well as being involved in field evaluation of new products. He has authored articles in both the trade press and the public media. Dave was graduated from the University of Wisconsin, with BS degrees in chemistry and biology. He is the former chairman and a current member of the NSPI's National Education Committee, which produces and administers the NSPI Tech program.

Doug Latta is the owner/principal of Aqua Clear Pools Inc. of Chatsworth, California. He studied at California Lutheran University (BA – Business) and California Coast University (MBA). He is a licensed swimming pool contractor, as well as a general building contractor in the state of California. He is a published author, and is the founding and immediate past president of the NAGC, a member of the board of the Swimming Pool Chemical Manufacturers Association, and the current president of the Swimming Pool Trades and Contractors Association, a California-based safety, education, and support association.

Michael Unhoch is a graduate from Illinois State University with a Degree in Chemistry. He has

over 20 years experience in the Pool and Spa Industry. He started while in High School as a service technician for the local public pool. He later had worked for a retail pool store and had his own service route. After graduating from college he spent four and a half years with PPG Industries Pool Products Group as a Chemist. In 1988 he became Technical Services Manager for Great Lakes Biochemicals. He joined ICI Americas' as a Development Chemist in the Pool Products Business and is currently a New Product Development Specialist in the newly formed Zeneca Pool Products Business.

R. Neil Lowry, Ph.D. is a graduate of the University of Western Ontario in Honors Chemistry and received his Doctorate in Inorganic Chemistry from Cornell University. Being in the pool industry since 1977, Dr. Lowry has published extensively in industry trade journals and holds an annual 3–day course on pool water chemistry. He is also a member of the NSPI's Chemical Treatment and Process Committee and has given several talks at past NSPI trade shows. Dr. Lowry is a consultant to governments and numerous corporations in the areas of label registration, chemical formulations, marketing and text writing. He was contracted by Agriculture Canada to standardize all pool chemical labels falling under the Pest Control Products Act of Canada. More recently Dr. Lowry created Spa Water Standards for commercial spas under the jurisdiction of the Ontario Department of Health.

Alison Osinski, Ph.D. has received degrees from the University of Maryland (Ph.D.), Florida International University (M.S.) and Hillsdale College (B.S.) in Physical Education with a specialty in Aquatics. She is actively involved with several national and regional aquatic organizations, and currently serves as an officer or advisory board member for many organizations, including the National Swimming Pool Foundation (NSPF), the Professional Pool Operators of America, and the International Association of Aquatic Consultants. Her experience includes past employment as a lifeguard, swim instructor, swim and crew coach, pool service technician, and university professor, prior to starting her consulting firm, Aquatic Consulting Services, in 1982. She is the author of over 65 publications, and is a frequent speaker at national aquatics conferences. She runs the "Swimming Pool Hotline" and has a regular column entitled "Information Please" in *Pool & Spa News*.

Rip G. Rice, Ph.D. is president of RICE International Consulting Enterprises, a consulting firm which was established in 1972. He is a cofounder of the International Ozone Association (1973), and is Editor-in-Chief of Ozone: *Science & Engineering* and *Ozone News*, which are the journal of the IOA, and its bimonthly newsletter, respectively. Dr. Rice has authored or coauthored many papers describing the chemistry of ozone with respect to pool and whirlpool water treatment, and prepared the final draft of the Recommended Code of Practice for Public Spas using Ozone for the National Environmental Health Association (June 1989). Since January 1992, Dr. Rice has been a member of the National Spa & Pool Institute (NSPI) Chemical Treatment and Process Subcommittee of the NSPI Technical Council.

Margis Robinson is the president of Memphis, Tennessee-based Bio-Chem Associates, Inc., a consulting firm specializing in swimming pool water chemistry-related problems, and the treatment of water and wastewater. He has been involved in the pool industry for over 22 years, and is the author of a book and also of articles in various trade journals. He was graduated from Samford University with a BS in chemistry, and has been professionally involved in many industries, including terms as technical director and project engineer of several space shuttle projects.

Kim Skinner is the co-owner of Pool Chlor, a chemical service firm with offices throughout the Southwest. He joined Pool Chlor in 1974. Kim has worked in the swimming pool industry for 25 years, and is a former manager of Skinner Swim Pool Plastering, Inc. of Sun Valley, California. He is the co-author of several technical reports on swimming pool water chemistry and plaster phenomena, which have been featured in articles in the trade press. A speaker and panelist at various trade conventions, Kim is also involved with the NSPI, the Chlorine Institute, and the NAGC.

John A. Wojtowicz currently works as a consultant, and is retired from his position as senior consulting scientist for Olin Corp. Seventeen of his 47 years of industrial experience were 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 dichloroisocyanurate. He holds over 55 patents and has published over 30 technical papers. His areas of expertise include swimming pool chemistry, manufacture and product and process development in hypochlorites and chloroisocyanurates, alternate sanitizers and sanitation systems (i.e.: ozone, hydrogen peroxide-UV, bromine, etc.), chloramines and bromamines, computer programming, and expert witnessing.

Sanitizer Chemistry Technical Symposium

March 1996 – Long Beach, California

A technical symposium on Sanitizer Chemistry was held in Long Beach in March of 1996. It was co-sponsored by the *Journal of the Swimming Pool and Spa Industry* and the Western Pool and Spa Show, with additional sponsorship by Fountainhead Technologies, Inc., Pool & Spa News, and Pool Chlor, Inc. The organizers and moderators of the symposium were Ray Denkewicz of Fountainhead Technologies, and Que Hales of *JSPSI* and Pool Chlor. Keynote remarks were made by Professor Charles Gerba, Ph.D. from the University of Arizona, and closing remarks were made by Dr. Pamela Bowden M.D. of the Centers for Disease Control. The papers presented at the symposium will appear in upcoming issues of the Journal, beginning with this issue. The following (in order of presentation at the symposium) are abstracts from all of the presentations:

Professor Charles Gerba, Ph.D. – University of Arizona

Dr. Gerba's keynote address focused on the area of microbiological concerns in swimming pools and spas. Dr. Gerba is a leading authority on disease-causing organisms and methods for their inactivation. Dr. Gerba has over 350 scientific publications to his credit, and is actively involved with the U.S. EPA on microbial issues in water.

Brian C. Bokowy – BioLab

The Chemistries of Bromine for Pool and Spa Water Treatment

The bromination of pool and spa water has long been recognized as an effective method of sanitization and as an alternative to chlorine based sanitation systems. The chemistries of bromine sanitation and hypobromous acid are discussed with respect to pool and spa water treatment. The use of 1-Bromo-3-Chloro-5,5-Dimethylhydantoin is the most common method of bromination of pool and spa water. Most commonly referred to as BCDMH, 1-Bromo-3-Chloro-5,5-Dimethylhydantoin presents unique chemical and physical properties that make it an effective pool and spa sanitizer. The physical properties of BCDMH are discussed in addition to methods of product application. A description of bromine-ozone chemistries and their significance in pool and spa water treatment is also included.

Allen Clawson and Beth Hamil – DEL Industries

Corona Discharge Ozone Systems Application Guidelines for Commercial Pools and Spa Pools

Successful application of an ozone system on commercial pools and spa pools can only be accom-

plished when the following charter is maintained:

Install an ozone system that provides the highest oxidation and disinfection of water while ensuring that no ozone enters an area where humans, equipment, or the environment are endangered.

There are varied opinions on the best way to address ozone system and reaction tank sizing for commercial pools and spa pools. Historically, in the U.S., these guidelines have been vague or non-existent regarding the application of ozone on commercial pools and spa pools.

The paper presents basic system design and application with a complete set of guidelines from sizing formulas to safety issues.

Wolfram Hartwig, Ph.D. – Engineered Treatment Systems

To DIN or Not to DIN: Ozonation of Pool Water in Public and Commercial Pools

The German pool code, DIN 19643, is a comprehensive standard that regulates all aspects of pool design. It includes ozonation as part of the disinfection and treatment of the pool water. Compliance is mandatory in some, but not all, European states. Health officials and pool designers in many countries around the world, where ozonation is not covered by existing codes, have accepted DIN 19643 as a guideline.

The paper presents some of the basic design concepts of DIN 19643, with emphasis on the ozonation parameters. These are contrasted with U.S. designs, in process applications that employ pre-filter or post-filter injection and full flow or side stream ozonation. Results from several selected sites demonstrate the successful elimination of pool water problems. Recommendations include a list of suggested design dosages based on observations, and additional ozonation design criteria.

John Rafter – Fountainhead Technologies

Determination of Anti-microbial Synergy in the Monopersulfate/Silver Ion System

*The bactericidal effect of silver ions in solution has been known for centuries and used to that effect in medicine and water treatment. The disinfection rate of silver ions at low concentrations (less than 0.1 ppm) versus the sanitary index organism *E. coli* is significant but relatively slow. It has been established that a synergy exists between silver ions at low concentration and potassium peroxymonosulfate to enhance the rate of silver ion disinfection.*

Rip G. Rice, Ph.D. – Rice International Consulting Enterprises

Chemistries of Ozone for Municipal Pool and Spa Water Treatment: Facts, Fallacies, and Current Concerns

Ozone generated by ultraviolet (UV) radiation is used in North America for treating (mostly residential) spa and pool waters almost exclusively, while only a handful of North American municipal pools and spas are using ozone generated by corona discharge technology in accordance with well-established German teachings. On the other hand, several thousand European municipal swimming pools and spas are using corona discharge-generated ozone today at concentrations which cannot be generated effectively by UV radiation in quantities sufficient to perform simultaneous oxidation and disinfection.

To apply ozone efficaciously and cost-effectively for the treatment of municipal pool and spa waters, an understanding of its chemistry in water is essential, particularly with respect to those human-supplied contaminants and chemical additives encountered. The pertinent chemistries of ozone are discussed in this paper with respect to the major constituents of pools and spas it is likely to encounter. The numerous technological advantages of ozone generated by corona discharge versus UV radiation also are discussed, including the use of ozone to produce hypobromous acid in situ from bromide ion charged to the pool waters.

Several examples of North American municipal swimming pool installations using ozone according to European teachings are described. Also, current issues of interest in the ozonation industry will be discussed.

Jacques M. Steininger, D. Eng. Sc. – Santa Barbara Control Systems

Catherine Pareja, Eng. Tech. – Institut Universitaire Technologique de Nancy-Brabois, France

ORP Sensor Response in Chlorinated Water

Proper maintenance of pool or spa water requires careful monitoring of the pH and sanitizer levels. In the past, the sanitizer concentration was tested with OTO or DPD test kits. The advent of chemical automation in recent years has introduced the use of the ORP sensor to measure the Oxidation-Reduction Potential generated by the sanitizer in the water.

While many studies have shown that ORP measurements in pool and spa water are very effective in monitoring the activity of the sanitizer (chlorine, bromine or ozone), very little information has been presented on the response of the ORP sensor as a measuring instrument. In this study, the response time and reproducibility of commercially available ORP sensors were determined and compared to amperometric, colorimetric and DPD test kit measurements.

The effect of the Total Dissolved Solids concentration (TDS) on ORP sensor readings was determined for sodium Chloride (NaCl) concentrations between 0 and 3,500 ppm (mg/l). The ORP sensor response curves for chlorine concentrations between 0.2 ppm (mg/l) and 12.5 ppm (mg/l) and for pH values between 6.5 and 8.5 were redetermined under controlled laboratory conditions and compared with earlier published data.

Michael J. Unhoch, Roy D. Vore, Ph.D., and Peter S. K. Lee, Ph.D.

Zeneca Biocides – Chemical Research and Development Laboratory

Stability of Swimming Pool/Spa Sanitizers: Comparative Chemical Stability of Polyhexamethylene Biguanide and Hypochlorous Acid

Proper hygienic conditions in swimming pools and spas are dependent on the maintenance of a minimum level of disinfectant. The two most common disinfectants in swimming pools are polyhexamethylene biguanide (PHMB) and chlorine (HOCl). The stability of PHMB and HOCl were compared over the range of temperature, pH, organic load, and sunlight that occur in typical pools and spas. The concentration of bioavailable PHMB was unaffected by temperatures between 39°F and 108°F, pH values between 6.2 and 10.0, and organic load. The quantity of the HOCl available for disinfecting purposes was significantly affected by shifts in temperature and pH. In the presence of ammonia HOCl was converted to less active chloramines. PHMB was not depleted under artificial sunlight levels that caused rapid depletion of HOCl. In practical terms, the PHMB concentrations should be monitored weekly and dosed when the active level falls below the recommended level of 6 ppm. The instability of HOCl mandates that testing and adjustments of levels be performed on a daily basis and, depending on which form and feeding system is used, maintained between 3 and 5 ppm.

John A. Wojtowicz – Chemcon

Relative Biocidal Effectiveness of Hypochlorous Acid and Chloroisocyanurates

Earlier laboratory studies showed that, although cyanuric acid stabilizes available chlorine against photochemical decomposition, it reduces the effectiveness (i.e.: deactivation/kill rate) of available chlorine as a disinfectant against bacteria such as E. coli and S. aureus. This was attributed to the formation of chloroisocyanurates which, although more stable to sunlight, were thought to be less efficient biocides than hypochlorous acid.

A determination of all thirteen equilibrium constants for the cyanuric acid–available chlorine system now allows calculation of the free hypochlorous acid as a function of pH and the concentrations of cyanuric acid and total available chlorine. Vapor–liquid equilibrium measurements on aqueous chloroisocyanurate solutions were in good agreement with calculated hypochlorous acid concentrations.

A computer program was employed to calculate the concentrations of hypochlorous acid as well as the

various chloroisocyanurates in the published experimental data on the effect of cyanuric acid on the kill time of bacteria by available chlorine. Statistical analysis was utilized to evaluate the relative efficiency of hypochlorous acid and chloroisocyanurates. It showed that killing/deactivation of bacteria was due essentially entirely to hypochlorous acid. Data for stabilized and unstabilized conditions gave similar results.

Although chloroisocyanurates are relatively ineffective biocides, they allow longer term disinfection in outdoor swimming pools compared to unstabilized available chlorine because they serve as a reservoir of hypochlorous acid – releasing it on demand via hydrolysis.

Pamela Bowden, M.D. – Center for Injury Prevention and Control, Centers for Disease Control

A closing perspective was offered by Dr. Pamela Bowden of the Centers for Disease Control, on issues involving the monitoring of outbreaks in swimming pool and spa waters.

Sanitizer Chemistry

A Technical Symposium

Phoenix Civic Plaza – Phoenix Arizona
Wednesday, November 20 1996

Co-sponsored by the National Spa and Pool Institute, Fountainhead Technologies, and the Journal of the Swimming Pool and Spa Industry

Organizers:

*Ray Denkewicz – Fountainhead Technologies
Professor Charles Gerba, Ph.D. – University of Arizona
Que Hales – Journal of the Swimming Pool and Spa Industry*

Moderators:

*Ray Denkewicz – Fountainhead Technologies
Carvin DiGiovanni – National Spa and Pool Institute
Que Hales – Journal of the Swimming Pool and Spa Industry*

The symposium is scheduled to begin at 8:00am, Wednesday November 20th, and conclude at 5:00 that evening. The room location is: Phoenix #16–17–18, North Lobby CC. The Symposium is approved for 7 hours of technical credit hours toward the NSPI Certified level. Proceedings of this Symposium will be available for purchase on audiocassette from the NSPI, and also in printed, bound format from the Journal. Additional information may be obtained from Que Hales at the office of the Journal (520–573–6696) or from Ray Denkewicz at Fountainhead Technologies (401–725–9990 ext. 13).

Keynote

Bill Kent, President

National Spa and Pool Institute

The Making of a Happy Pool

Anita Highsmith

Centers for Disease Control and Prevention

Monitoring Disease Outbreaks in Swimming Pools and Spas

Papers

(in order of presentation)

Dave Worley, Ph.D.

Auburn University

Novel N-Halamine Water Biocides

John A. Wojtowicz

Chemcon

An Updated Version of the Langelier Saturation Index

Roy D. Vore, Ph.D.

Zeneca Biocides

Michael J. Unhoch

The use of PHMB as a Sanitizer in Domestic Spas

Jacques M. Steininger, D. Eng. Sc.

Santa Barbara Control Systems

Chlorine and ORP Testing

The Journal of the Swimming Pool and Spa Industry

- Tom Seechuk** **LaMotte Company**
MPS Interferences in the DPD Method
- Bonnie Sandel, Ph.D.** **Olin Chemicals Research**
Chlorine Disinfection Chemistry
- Rip G. Rice, Ph.D.** **Rice International Consulting Enterprises**
Wolfram Hartwig, Ph.D. **Engineered Treatment Systems**
Potentials for Ozone to Control Cryptosporidium Oocysts in Pools and Spas
- Ed Lightcap** **DuPont**
Peroxygen Compounds as Oxidizers
- Bob Kulperger** **Natural Chemistry, Inc.**
Natural Enzyme Technology Applied to Pools and Spas
- Ray Kramer** **Eltech/Electrode Corp.**
Electrolytic Chlorine Generation
- Robert Gevernal, Ph.D.** **International Innovative Technologies**
The Design of Advanced Pool and Spa Water Treatment Systems Using Catalytic Filtration Technologies
- Carlos Enriquez** **University of Arizona**
Copper/Silver Ionization Disinfection
- Fernando del Corral, Ph.D.** **Buckman Laboratories**
Swimming Pool Algaecides
- Mary Costanzo** **BioLab, Inc.**
- Brian C. Bokowy**
Bromine and Ozone: Chemistry and Operational Challenges Encountered in the Treatment of Heavily Used Commercial Recreational Water Systems
- Allen Clawson** **DEL Industries**
Side or Slipstream Application of Ozone and Ozone Dosing for Commercial Swimming Pools
- Professor Charles Gerba, Ph.D.** **University of Arizona**
Enteric Virus Outbreaks in Swimming Pools

Call for Papers

Swimming Pool Surface Technology Technical Symposium March 5, 1997 Long Beach, CA

The *Journal of the Swimming Pool and Spa Industry*, the Western Pool and Spa Show, and the Swimming Pool Trades and Contractors Association (SPTCA) are excited to announce the second annual pool and spa industry technical symposium. The theme for this second technical symposium will include any aspects of plaster, paint, fiberglass, additives, and related chemistry of swimming pools and spas. Presentations on all aspects of these areas will be considered. Original, previously unpublished research will be presented with technical manuscripts considered for publication in the *Journal of the Swimming Pool and Spa Industry* (JSPSI).

This technical symposium will be held in conjunction with the Western Pool and Spa Show, a leading trade show boasting one of the largest and most inclusive educational programs in the pool and spa industry. The Western Pool and Spa Show will be held March 6–8, 1997. The technical symposium will be held March 5, 1997.

Initial commitments on papers accepted for presentation include research presentations on cement, aggregate, additives, and start-up chemistry. Both manufacturers and

service industry members are slated to contribute.

There is still room for several more papers. Abstracts may be sent to the *JSPSI* office (phone, fax, email, and address are listed on page 1 of this Journal).

The pre-registration cost for attending the symposium is \$45.00. Preregistration forms, as well as information on accommodations at the convention hotel, are available upon request from the *JSPSI* office, or from the Western Pool and Spa Show (800–787–7727). Entrance to the Western Pool and Spa Show exhibit hall is free of charge. The pre-registration cost for the traditional educational seminar series, along with the new contractor's educational seminars is also \$45.00, but a discounted pre-registration rate of \$70.00 is offered for those wishing to attend both the seminars and the symposium. Pre-registration is offered through February 15, 1997. Please note that the cost for non-registered admittance to the symposium is \$60.00.

A request form for pre-registration and show information is included on page 48 of this Journal.

Letters to the Editor

It is the policy of the Journal to publish appropriate letters to the editor. Letters will be responses or rebuttals to material in previous issues of the Journal, and must be technical in nature. The Editor reserves the right to edit such submissions as appropriate. Because of the length of time between issues, it is also the policy of the Journal to allow authors to respond immediately to letters commenting on their work.

Response to “Interesting Questions”

This is a response to some of the questions posed in the opinion paper of Ben Powell which appeared in Volume 1 Number 2, 1995.

pH Ranges (i.e., Eye Irritation) Since swimming pool water is a foreign environment to the eyes, it can cause eye sensations or irritation. Some people may be more affected than others since the pH of tears secreted by the lachrymal gland varies from 5.2 to 8.35 with an average of 7.4 (White 1972). Studies in an unstabilized indoor pool with a small bather load and low combined chlorine levels showed that eye irritation was somewhat less at pH 8 than at pH 7 (Mood *et al* 1952). Within the pH range 7–8, pH had a greater effect than available chlorine (≤ 0.5 ppm). Eye sensations included: stinging or smarting, tearing and watering, sensitivity to light, blurred vision, etc.

Of course eye irritation is strongly influenced by bather load and combined chlorine levels (i.e., chloramines). There is no doubt that chloramines can cause eye irritation, the effect increasing in the order: $\text{NH}_2\text{Cl} < \text{NHCl}_2 < \text{NCl}_3$ which correlates with the taste and odor threshold of these compounds shown in the table below (White 1972).

Compound	Taste and Odor Threshold, ppm
free av. Cl (i.e., HOCl + ClO ⁻)	20
monochloramine	5
dichloramine	0.8
nitrogen trichloride	0.02

Nitrogen trichloride is the most volatile of the inorganic chloramines and is the worst offender. It is a strong lachrymator that affects the eyes and mucous membranes. I have firsthand knowledge of the effects of NCl_3 having worked with it in the laboratory. The main source of nitrogen trichloride is not ammonia but urea, which is the main bather impurity in pools. Inorganic chloramines are less of a problem in outdoor pools because they are decomposed by sunlight. The absorptivities of chloramines at 300 nm are shown in the table below.

Compound	Absorptivity L/mol/cm
monochloramine	25
dichloramine	293
nitrogen trichloride	165

Studies were carried out in which various solutions were added to a rabbit's eye (Jandik 1977). The results tabulated below showed no effect for free av. Cl up to 8 ppm, monochloramine up to 2 ppm, and monochlorourea up to 6 ppm. Definite irritation was observed at 20–30 ppm free av. Cl, 4 ppm monochloramine, and 10 ppm monochlorourea.

Sodium Bicarbonate and Alkalinity (i.e., Effect of Carbon Dioxide Loss on pH of Spa Water) The rate of CO_2 evolution is primarily a function of four factors which vary in the following approximate order: aeration > alkalinity > turbulence > temperature. The CO_2 loss rate can be reduced by:

Observation	Free Av. Cl, ppm	Combined Chlorine, ppm	
		Monochloramine	Monochlorourea
No reaction	0–8	0–2	0–6
uncertain reaction	16	3	
distinct irritation	20–30	4	10
strong irritation			12
very strong irritation		5	

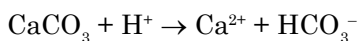
- eliminating or reducing the intensity or duration of aeration
- maintaining a low carbonate alkalinity (e.g., 50 ppm); although the amount of CO₂ in the water varies linearly with alkalinity at a given pH, the loss rate varies as the square of the alkalinity
- reducing the spa water temperature (not very practical)
- use of a buffer such as borate which will augment the buffering provided by cyanurate and carbonate alkalinity

Oxidation–Reduction Potential (ORP) Oxidation–Reduction Potential (ORP) is a measure of the oxidizing power of a sanitizer. Hypochlorous acid (the active biocide in pool water) has a greater ORP than hypochlorite ion which has a higher ORP than chloroisocyanurates or chloramines. The ORP decreases with increasing pH, cyanuric acid concentration, and combined chlorine. Studies have shown that the kill time of bacteria decreases with increasing ORP at a given pH (Steininger 1985).

Carbon Dioxide If CO₂ is added to pool water with adequate dispersion it will allow complete dissolution and will pose no more of a problem than generating CO₂ by addition of acid. Carbon dioxide is continuously evolved because pool water is maintained in a state of supersaturation with respect to carbon dioxide. The pool doesn't care how the CO₂ was added. The rate of evolution will simply depend on the concentration of CO₂ at a particular temperature, alkalinity, and turbulence.

Saturation Chemistry First of all the basic Langelier saturation index has not been modified for the pool industry. It is based on the same basic saturation index equation proposed by Langelier. The only modification has been the introduction of slightly different temperature and ionic strength corrections and factors for conversion of concentrations in mol/liter to ppm (Larson and Buswell 1942, Van Waters 1962). Langelier demonstrated the validity of his equation by treating various water samples from different sources with excess powdered calcium carbonate to saturate them followed by filtration and analysis. He found that the average calculated saturation index was very close to zero (i.e., –0.02).

The effect of carbon dioxide on calcium carbonate solubility is already taken into account in the derivation of the index which is based on the following overall reaction representing the dissolution of calcium carbonate:



At a given pH, the ratio of bicarbonate to carbon dioxide is fixed. Starting at a given alkalinity and pH, if the carbon dioxide concentration is changed, either

by evolution or by acid addition, the pH and the saturation index change accordingly.

The Langelier saturation index was originally developed for application to water in cast iron distribution pipes (Langelier 1936) which is an example of a closed system, meaning that no CO₂ is evolved. Although swimming pools are open systems and evolve CO₂, the CO₂ is replenished by periodic acid addition, preventing pools from equilibrating with the low levels of atmospheric carbon dioxide. At a given pH and carbonate alkalinity, swimming pools have the same concentration of dissolved CO₂ as a closed system.

John A. Wojtowicz, Consultant

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The Author Responds:

Mr. Wojtowicz's responses to the questions I raised are quite interesting. Under the topic of **pH ranges**, the information he provides extends the data I have, but tends to validate the interpretation I have made of my field experiences: pH, *per se*, is not a major factor in pool user eye irritation. The data he provides

on chloramine irritation, when correlated with data from Dr. A. T. Palin, published in a booklet by LaMotte, suggests that high pH levels may actually result in lower eye irritation. (Dr. Palin's data shows *both* NCl_3 and NHCl_2 persistent fractions occurring at pH levels up to 7.5 when water is chlorinated to breakpoint, but not remaining when the water is at pH 8.0.) His comments further seem to support my observation that high free chlorine levels (less than 10 ppm) are also not significant causes of eye irritation.

No doubt I'm missing something, but Mr. Wojtowicz's comments under **Sodium Bicarbonate** seem less than helpful. Granted, the problem of CO_2 (and more to the point, alkalinity loss) in spas can be reduced by lowering temperature and aeration. However, most spa users I know would not consider this a constructive change. I can remember one individual's response in particular (when Mr. Wojtowicz's suggestions were inadvertently implemented on his spa due to equipment malfunction). As best I can remember, he observed, somewhat less than calmly, that "if I'd wanted a damn pool, I would have bought a damn pool. When is my spa going to be fixed?" No doubt borates contribute to the stability of pH levels, but do they contribute maintaining a near neutral carbonate saturation level? Regarding using a starting point of bicarbonate levels of 50 ppm, I have not tried this. However, I have watched bicarbonate levels descend from 120 ppm to 40 ppm in a spa during one blower cycle (15 minutes).

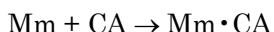
Regarding **Carbon Dioxide**, Mr. Wojtowicz provides guidelines for *avoiding* problems due to CO_2 use, but does not provide information on whether problems can actually occur. Current wisdom in the HVAC industry seems to point to CO_2 levels as a major component in IAQ (indoor air quality) problems. My question was whether real world systems, as actually installed and operated, are causing problems. My experience suggests that in some cases the answer is yes.

Thank you, Ben Powell

Response to "Interference in Melamine-based Determination of Cyanuric Acid Concentration"

This is in regard to the technical note "*Interference in Melamine-based Determination of Cyanuric Acid Concentration*" in Volume 1, number 2, 1995.

The turbidimetric determination of cyanuric acid (CA) with melamine (Mm) is dependent on precipitation of the 1:1 complex melamine cyanurate ($\text{Mm} \cdot \text{CA}$) by the following reaction:



Ideally, the available chlorine (av. Cl) in the sample should be reduced with thiosulfate prior to precipitation since some of the CA is in the form of chloroisocyanurate.

When presenting analytical data, complete data should be provided. An entry such as "distilled water + 0.1g CA" does not tell me what the concentration of CA is. The volume of water used should be given in the table. Also the assay of the CA used should be given. Incidentally, 0.2g of Trichlor provides ~1.1 times the CA in 0.1g of CA.

There is a potential problem with addition of NaOCl to the test solution containing precipitated melamine cyanurate. Hypochlorite can react with both CA and Mm to form chlorinated derivatives which have different solubilities than CA or Mm. In addition NaOCl can oxidize cyanuric acid to CO_2 and N_2 (Carlson 1978). One drop (~0.05 mL) of 10% NaOCl can increase the pH and the av. Cl in the test solution to ~12 and 600 ppm, respectively. Since the method has been calibrated for unchlorinated CA solutions at mildly alkaline pH, this may affect the results. Although no effect was observed at 25 ppm CA, higher concentrations should also be tested.

I would suggest that sufficient NaOCl be added to raise the av. Cl to 10 ppm as in normal shock treatment before addition of melamine to oxidize any oxidizable materials that may be present that might potentially interfere followed by dechlorination with sodium thiosulfate. Alternatively, Oxone (potassium peroxy-monosulfate) could be used to oxidize potentially interfering water impurities.

The author suggests three possible causes for the observed interference: 1) ammelide (Ad) and ammeline (An) in cyanuric acid used as a pool stabilizer, 2) ammonia, and 3) chloramine. Cyanuric acid normally contains $\leq 0.5\%$ Ad + An, and typically ~0.1%. This percentage is too small to explain the observed interference. Furthermore, available chlorine converts ammelide and ammeline to cyanuric acid under swimming pool conditions (Castrantas 1962). In addition, ammelide and ammeline in CA are converted to Trichlor during Trichlor manufacture (Wojtowicz 1979).

Ammonia *per se* does not exist in typical swimming pool water. At pool pH ammonia forms ammonium ion. However, in the presence of chlorine it will form monochloramine if the chlorine concentration is below breakpoint. Neither ammonium ion nor monochloramine should interfere since they do not form a precipitate with melamine. Indeed, there is no correlation with the observed extent of interference and the concentration of combined chlorine. The Trichlor pools for which data are provided appear to be poorly maintained, three out of four pools have excessive combined chlorine levels (1.6–4.2 ppm). If ammonia or chloramine are suspected interferences, why

not analyze for CA after shock treatment of the pools? Trichlor pools require superchlorination or shock treatment just as hypochlorite treated stabilized pools do.

It is known that acidic compounds other than cyanuric acid, ammelide, and ammeline can also form precipitates with melamine, e.g., oxalic acid (Lipschitz *et al* 1945). Although various acidic compounds (e.g., uric acid, lactic acid, glucuronic acid, glycine, etc.) are introduced into swimming pool water by bathers via urine and sweat, their concentrations are not expected to be significant in a well maintained pool. However, in poorly maintained pools the opposite could be true.

All that has been established is that a lower reading is obtained if the test solution is treated with NaOCl solution. This does not prove that this procedure gives the correct CA concentration. In order to establish the correct cyanuric acid concentration, an independent method should be used such as liquid chromatography. The Analytical Services Department at Olin Corp., Cheshire, CT has an established method and the capability for doing this analysis.

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References

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The Author Responds:

Mr. Wojtowicz's response to my technical note is appreciated, and it does provide some interesting information. However, he seems to have either missed or not understood the nature of the note – the technical note was not intended to be a dissertation on cyanuric acid testing nor an exhaustive study of the testing aberration. It was a case where I, from a particular advantage of treating thousands of pools over decades of time with a specific test and treatment regimen, have observed a phenomenon which is consistent and peculiar. I have, through intuition, reason, trial and error discovered a make-shift field resolution to the problem, but wished to share the facts so far known with the rest of the industry in an attempt to identify the actual chemistry behind the aberration and to help develop a more permanent resolution, or at least a solid explanation. Since I am dealing with a field application, analytical equipment at Olin or any other laboratory is not practical or economically feasible, other than in developing a permanent resolution.

Incidentally, superchlorination of the sample previous to the addition of melamine does not work consistently – the addition of chlorine afterwards does. The resultant "adjusted" cyanuric acid level is consistent with the level found through normal use of the test a month or two later, after chlorination and superchlorination with a non-cyanurate chlorine.

If my note spurs any activity in this matter, my purpose has been accomplished. In light of regulatory pressures to limit the levels of cyanuric acid in municipal swimming pools and spas, and the unfortunate side effect of di- and trichlor (of not being able to add more chlorine without adding more of the vehicle – cyanuric acid) any assistance from the technical community will be appreciated.

Thank you, Doug Latta