Aquarius Technical Bulletin - No. 18

ORP Millivolts -

The Sensor for Measurement of Disinfection

Oxidising biocides such as gas or liquid Chlorine, Bromine and Ozone have been used for many years in potable water and swimming pools for disinfection.   In recent years both liquid bromine formulations and BCDMH bromine release biocides have proved to be very effective in control of bacterial levels in cooling water systems and in swimming pools.

Ozone is a very strong oxidising agent and its use in both cooling water systems and swimming pools is gaining ground.

ORP - *oxidation reduction potential* sensors, when coupled with differential inputs, high gain amplifiers and "ground reference" probes and microprocessor control circuitry, can provide for automatic control with dosage proportional to the disinfection demand.

These sensors can also provide for both high and low alarm signals, plus, via a computer, and all the data can be logged, to provide a hard copy record of the ORP millivolt levels maintained and verification of the levels of disinfection achieved.

Historically, control tests based on the DPD test method, and expressed in ppm Free Chlorine has been the widely accepted method of control of dosage. However the true performance criteria for disinfection level is Total Bacteria Counts or Heterotrophic Colony Counts.

The ORP sensor does **NOT** indicate actual Free Chlorine levels. Only when the pH is maintained at a constant value, see figure 1 below, does the straight line relationship between ORP and Free Chlorine apply.
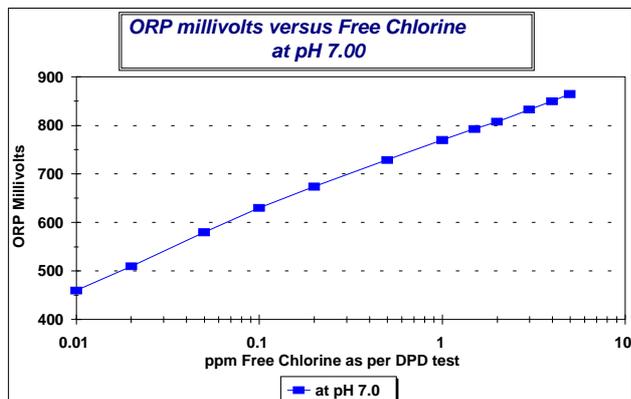
A paper presented to the American Cooling Tower Institute - TP92-08 [1] showed a relationship between ORP millivolts and Free Chlorine which varied when pH values changed between 7.00 and 8.00. As the majority of cooling water systems, and occasionally inadequately controlled swimming pools have pH values in the region of 8.5 to 9.0, we decided to investigate the ORP and free Chlorine relationship at these higher pH values.

This investigation was carried out on a recirculating water system fitted with carefully calibrated Aquarius, pH & ORP control systems, with data logging using Labtech Notebook.   A series of measurements for ORP millivolts and Free Chlorine residual were performed using a Hanna Model 95711 photometer, which utilises the DPD test method and is capable of reading from 0.01 to 2.50 ppm. as Free Chlorine.   The Free Chlorine levels were gradually increased and the corresponding millivolts were measured after steady state conditions, whilst the pH values were maintained constant at pH values of 7.0, 8.0 and 9.0 respectively.

The results are shown graphically on Figure 2 below, as the pH value is increased, higher levels of Free Chlorine are required to maintain the same ORP millivolt level, or at constant Free Chlorine levels the ORP millivolt output is reduced as pH values increase.

ORP millivolts versus Free Chlorine at pH values of 7.0, 8.0, 9.0

ORP millivolts versus Free Chlorine at pH 7.00
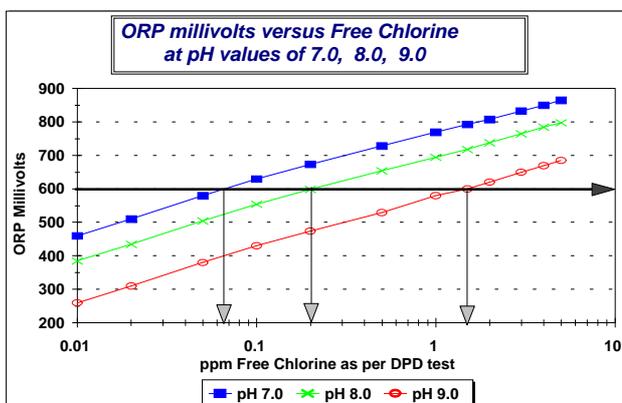
Note the straight line drawn on the graph above at 600 millivolts,
- at pH 7.00, the Free chlorine reading is 0.06 ppm,
- at pH 8.00, the Free chlorine reading is 0.20 ppm,
- at pH 9.00, the Free chlorine reading is 1.60 ppm.

ADVANVCED TECHNOLOGY FOR THE NEW MILLENNIUM

The chemistry of chlorine solutions in water has reactions as follows :-

1. $NaOCl + H_2O = HOCl + NaOH$
   $HOCl \longleftrightarrow H^+ + OCl^-$
2. Bromine products react similarly to give
   $HOBr \longleftrightarrow H^+ + OBr^-$

The DPD test for Free Chlorine measures the total reaction ($HOCl \longleftrightarrow H^+ + OCl^-$) and contains buffers [2] to maintain the sample at pH 6.3 - 6.5, but the amount of HOCl which is present is pH dependant varying from 91% to 3% over the pH range 6.5 - 9.0, and as shown in the following table [3]

pH Value	Free Chlorine		Free Bromine	
	%HOCl	%OCl⁻	%HOBr	%OBr⁻
6.5	91	9	99	1
7.0	75	25	98	2
7.5	49	51	93	7
8.0	23	77	81	19
8.5	9	91	58	42
9.0	3	97	30	70

Technical literature shows that the HOCl & HOBr ions are the much stronger oxidising agents than are the OCl⁻ or OBr⁻ ions and that the HOCl & HOBr are both about 100 to 300 times more efficient in microbiological killing power or disinfection than are the OCl⁻ or OBr⁻ ions.

It is well known in cooling water treatment that 0.25 ppm Free Chlorine in a cooling system at pH 7.00 will maintain a Total Plate Count of 10^2 - 10^3 Colony Forming Units/ml (cfu/ml) and that the same 0.25 ppm in a system at pH 8.5 will reduce TPC's to 10^5 -10^6 cfu/ml.

Bromine based biocides have been used extensively in recent years because at the higher pH values in cooling water systems much more HOBr is available at these pH values to effectively kill bacteria.

At pH 8.5 only 9% of the chlorine added is available as HOCl, whereas 58% of the bromine is available as HOBr, so we can assume a much greater microbiological kill from bromine products at pH 8.5, on a concentration basis. This is amply supported by the many T.P.C. tests carried out on cooling water samples

In the treatment of swimming pools the pH is normally maintained between 7.4 -7.6 to balance the water's corrosivety and scaling tendency. This pH range also greatly assists the bacteria kill or disinfection rates as 50% of the chlorine added is available as HOCl ion at this pH.

As early as the 1960's, German and Swedish scientists [4,5] had shown *that the inactivation or kill rate of bacteria by oxidising agents was accurately predicted by ORP millivolt level* and that *it was not possible to formulate a relationship between bacterial kill rate and concentration of Free Chlorine*.

Also that **ORP millivolts, regardless of water quality, accurately predicts inactivation or kill rates of bacteria.**

If we return to Figure 2 and observe the line for constant ORP millivolts at 600 mV. and then calculate the amount of HOCl ion that would be available at the different pH values we can draw a remarkable conclusion, **ORP at 600 mV. = 0.046 ppm HOCl at the 3 different pH values,**

pH Value	ppm Free Chlorine	ppm HOCl	millivolts ORP
7.0	0.06	0.045	600
8.0	0.20	0.046	600
9.0	1.60	0.046	600

If we draw a similar line at 700 mV. and calculate the HOCl ion amount, the results are as follows

pH Value	ppm Free Chlorine	ppm HOCl	millivolts ORP
7.0	0.3	0.225	700
8.0	1.0	0.23	700
9.0	2.7	0.24	700

It can be concluded that the ORP probe output is proportional to the concentration of HOCl ion.
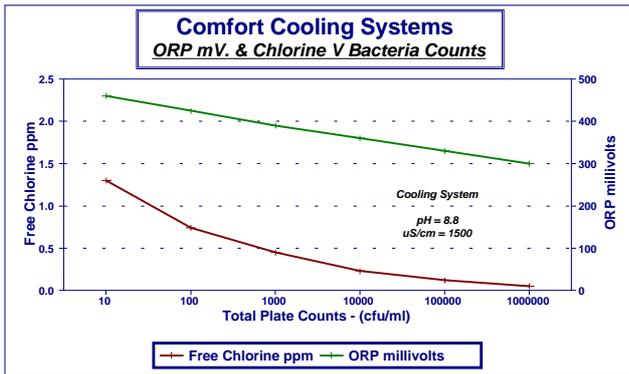
Based on above data we plotted ORP mV. against the calculated amount of HOCl present and similarly for ORP mV. versus HOBr. The results, see below, show good straight line relationships

ORP Control
Millivolts V. HOCl at 25 C
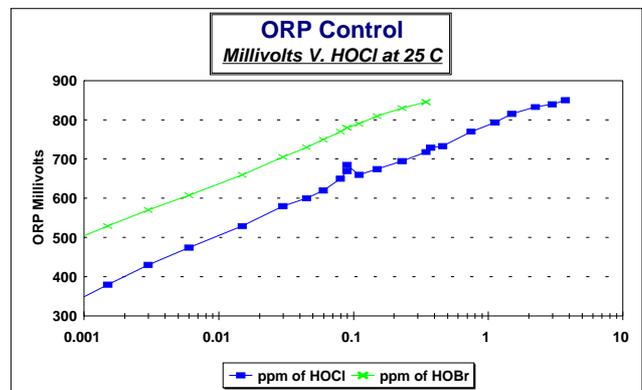
From the above data it is clear that the ORP sensor is responding to the much more powerful oxidising agents, From published technical literature, graphs have also been plotted of the Total Plate Count, e.g. poliovirus deactivation versus ORP mV. and from this data and water treatment experience **we should be able to "plug in" an ORP millivolt Set Point control value of 450 - 500 mV. on most cooling towers, and expect to maintain 10^2 -10^3 T.P.C and be able to disregard both pH value and pH adjustment.**

Average chlorine levels and ORP millivolts readings from a cooling water system, obtained over a lengthy period were plotted against Total Plate Counts to give the graph below. [6]

Comfort Cooling Systems
ORP mV. & Chlorine V Bacteria Counts

Cooling System
pH = 8.8
uS/cm = 1500

— Free Chlorine ppm   — ORP millivolts

Effect of Proportional Dosage
Primary School Pool - Wed 19/2/97

— ORP mV.   ▮ Chlorine Dosage

The chlorine demand of a cooling system varies with many things but essentially will vary with load, or the evaporation rate of the cooling system.

Due to the small volumes of water in most cooling systems there is no buffer for chlorine demand and dosage must be proportional to the varying demand if tight control of chlorine (or bromine) is to be maintained.

Swimming pools usually have large volumes and sufficient buffer volume for pH control, but the chlorine demand is essentially equal to the bather load.   It is very important to maintain disinfectant residuals especially when bathers are in the water but this is when chlorine is rapidly consumed.

The following graph was data logged from a Primary School pool **and demonstrates the absolute need for automatic control and proportional dosage if strict control on disinfection levels are to be continuously maintained.**

Chlorine Disinfectant Dosage
Primary School Pool - Wed 19/2/97

— ORP mV.   — Chlorine Dosage
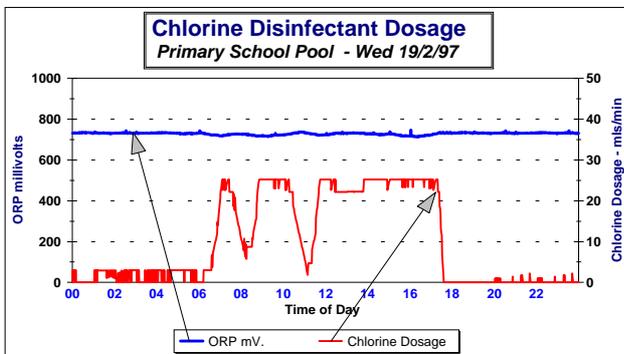
The above graph dramatically shows the increase in oxidant demand when bathers enter the pool at 06:30 a.m. and the absolute need for the dosage rate to dramatically and automatically increase (by a factor of 10 in this case) to maintain the desired level of disinfection when the bathers are in the water !.

The graph of the "Effect of Proportional Dosage" shows the dose rates required to maintain the set level of ORP, and shows the absolute need for P.I.D. control on dosage.   The dosage rate needs to accelerate and de-accelerate with the demand caused by bather load.

Both graphs above are a good example of Data Acquisition - they were logged on site to our lap top computer, using the 4 -20 mA. outputs for pH and ORP values, plus the event outputs to record dosage rates, **via the BCMS optional outputs on the "Poolpac"**
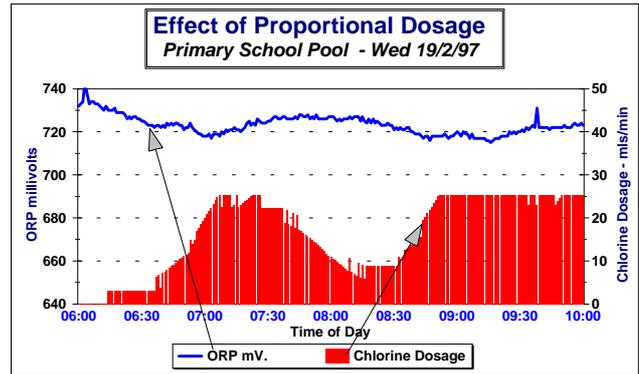
Data similar to this can be continuously logged as ASCII text files to on site PC computers, equipped with a suitable data acquisition card.

Graphs or Trend Charts may be produced from spreadsheets such as Quattro or Excel, and are extremely useful for trouble shooting, trend charting as above, or as a hard copy record of data on a minute by minute basis as defence in any "Duty of Care" or negligence claims.

Summary

It is only rarely that the dosage rates for pH and disinfectants are constant and can be controlled by simple metering or dosage pumps. Rather dosing must be on the actual demand from the particular system.

As demand usually varies widely it necessitates both automatic and proportional type dosage based on the system demand.

The accuracy of the control equipment is limited by the quality of information it receives from the sensor, thus it is imperative that the sensor can produce accurate readings in noisy industrial environments. High gain amplifiers, with differential inputs from the sensor and a "grounded reference" probe in close proximity is mandatory for accurate input.

To ensure continuity of accurate information it is essential to have a well designed manifold to house the sensors, with strainers for protection from system debris.

To obtain accurate information for data logging it is necessary to isolate the sensitive measuring instrument, from the noisy computer system and it is essential to have "loop isolated" outputs on analog signals.

Having accurate control also mandates a reliable dosage pump, magnetic type dose pumps are prone to "gas locks" due to gassing of commercial liquid chlorine solutions and air lock the pump head which requires manual bleeding and gives unreliable dosage. Peristaltic dose pumps particularly with NORPRENE tubing can reliably pump - gas, liquid or slurries, and have proven to be the pump of choice for reliable chlorine dosage up to 250 kPa. head pressure.

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Incorporation of a reliable flow sensor in the manifold ensures zero dosage under no flow conditions, and incorporation of chemical injection points in the manifold simplify plumbing, and provide for chemical dilution before it is introduced to the water system proper.

A control system having the above features, coupled with an understanding of the capabilities of the ORP sensor can dramatically improve the control of both pH and disinfection levels, with reduced chemical consumption, and more importantly improve the level of insurance against "Duty of Care" or negligence claims from the public on both swimming pools and on cooling water systems.

Acknowledgements

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2. Hanna Instruments -1997 Catalogue - page 45.
3. Ronald, D. (1985) - "Chlorine Measurement & Terminology Explained" - PACE June 1985
4. Lund, Ebba (1963) " Oxidative Inactivation of Poliovirus" University of Gothenberg and the Virological Department of Municipal Laboratories, Gothenberg, Copenhagen 1963
5. Carlsen, Sven (1968) "Evaluation of Disinfecting Effect of Swimming Pool Water by Redox Potential" Inst. Wasser, Germany 1968
6. Confidential data from an operating cooling water system provided to Aquarius Technologies P/L - 1996

Author

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ORP millivolts versus Free Chlorine in Swimming Pools at pH 7.5

Aquarius Technologies Pty Ltd ORP millivolts versus pH value
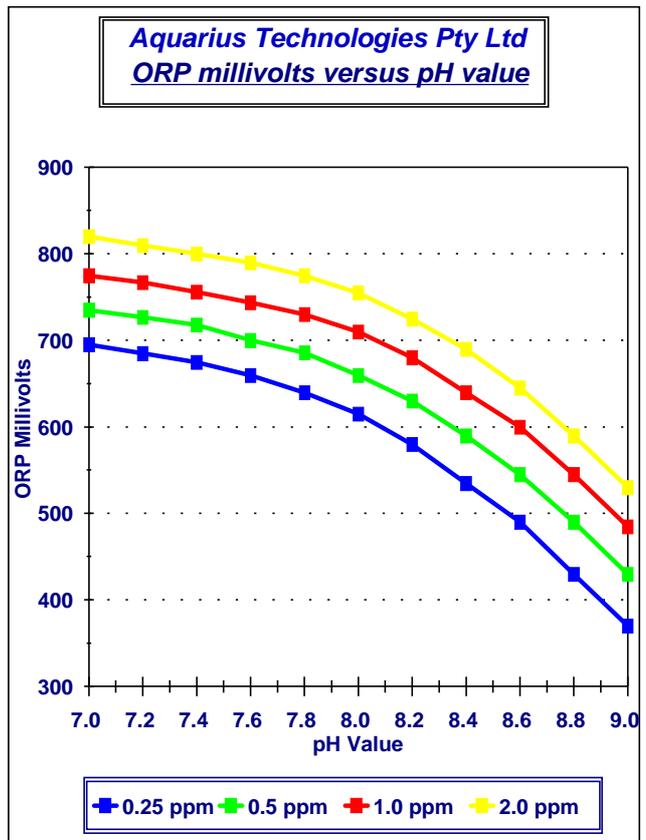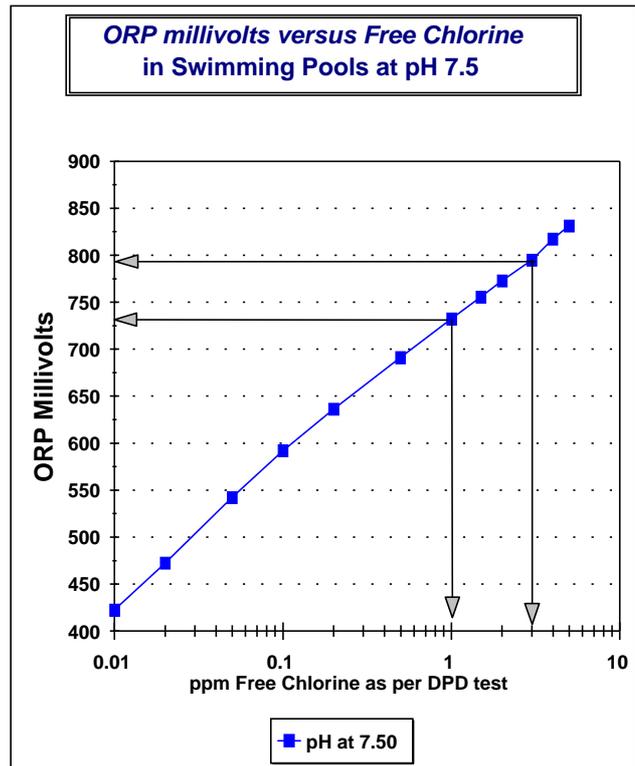
Typical ORP millivolts levels versus Free Chlorine (DPD method) on cooling water systems