Chlorine dioxide

Chlorine dioxide is a gas which is generated on site (from a 'stabilised' liquid form) and injected into the water system prior to filtration. Chlorine dioxide has been used for many years in Europe and there is increasing interest in its use in the USA.

Chlorine dioxide produces fewer by-products, particularly chloramines and is reputed to kill *Cryptosporidium* in addition to bacteria. However, it is corrosive to copper and will produce a chlorite and chlorate by-product. If the level of the former rises above 0.1 mg/L it is regarded as a danger to bathers.

Chlorine dioxide must not be used with ozone or an activated carbon filter since they can increase the chlorite build up. It is critical that the dosing of chlorine dioxide is accurately controlled, because excess dosing can quickly build up the chlorite to carcinogenic levels. Liquid chlorine dioxide complex is now being offered in Australia as a separate additive, but its efficacy and cost effectiveness has not been proven.

Chlorine via electrolyser

This process is used in salt water pools and requires a salt content of about $1/6^{th}$ of sea water. On-site electrolytic chlorine generators produce 'liquid chlorine' (sodium hypochlorite) from the circulating salt water. The sodium hypochlorite produced by the large generators is stored and closed with normal control equipment. One of the by-products of large chlorine electrolysis units is hydrogen gas. Adequate ventilation must be provided to avoid explosion or fire when using on-site generators.

Electrolytic chlorine generation is not really suitable for public swimming pools or spas. The swimming pool or spa water requires a salt content of around 4000 mg/L, which some bathers object to. The salt content also raises the total dissolved solid content to very high levels and this can effect water physics and chemistry.

Alternatively, in-line electrolytic cells can be used to generate sodium hyperchlorite. In-line electrolytic cells attract chemicals (predominantly calcium) from the water and this can interfere with balancing the water. Calcium levels in public swimming pools and spas must be held at between 80 to 200 mg/L to achieve balance. The continual attraction of the calcium content onto the plates puts the water out of balance. Reverse polarity ‘self cleaning’ cells are claimed to avoid chemical adhesion to the plates.

In-line electrolytic chlorine production cannot cover a sudden heavy bather load by increased production or dosing and these units are unsuitable on their own for sites that have sudden or erratic bather loads. If electrolytic in-line chlorine cells are fitted, it is essential that additional on-demand liquid chlorine dosing is available to supplement the cell production when sudden increased bather load occurs.

Bromine

To be useable, bromine must be in solid form and is usually combined with other chemicals. Bromine is available in liquid form but is highly volatile and hazardous.

Bromine is considered to produce more by-products and some are of the opinion that it is a less effective disinfectant than chlorine. Bromine in the form of BCMDH (sticks or tablets) has been proved to produce skin problems if prolonged exposure to the treated water occurs. Similarly, with sodium bromide systems, a skin irritant effect has been reported with frequent exposure to water containing

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sodium bromide. Combined bromamines seem to be as hazardous as combined chloramines, even though the bromamines are a good disinfectant. For light and sporadically loaded pools, solid bromine and sodium bromide, both producing hypobromous acid when activated in water, seem to be a reasonable disinfectant.

Sodium bromide

Sodium bromide is a compound of bromine and is available in a solid or non-hazardous liquid form. Therefore, it is easy to handle and store. It needs to be activated on site and has been used with sodium hypochlorite in Australia and with sodium and calcium hypochlorite in the UK and Europe. This system has shown to be an economical and effective treatment for indoor pools and spas in particular.

Sodium bromide and ozone

Sodium bromide solution is activated by ozone producing hypobromous acid. To do this, ozone is consumed rapidly and therefore destruction of bromine by-products is not as thorough as in the chlorine/ozone process.

A great number of by-products are produced in this process and if the pool is heavily loaded, the pool air quality can also become polluted.

Well designed systems using sodium bromide and ozone can be satisfactory for lightly loaded pools. The consumption of ozone at the dosing site is claimed to be sufficient to eliminate ozone content in the water returning to the pool. This is claimed to eliminate the need for a deozonator.

'Solid bromine'

In order to provide a safe chemical, bromine is combined with chlorine and hydantoin to form bromochlorodimethylhydantoin, or for convenience sake, BCDMH. Manufactured in tablet or stick form, the chemical needs to be dissolved by erosion in a suitable in-line feeder. When dissolved in water, it produces hypobromous acid and hypochlorous acid, which are both highly active disinfectants.

The efficacy of BCDMH is not as reliant on pH as chlorine – it is nearly pH neutral. However, pH should be maintained at 7.2 to 7.8. The dimethylhydantoin content in the water should not be allowed to build up, but regular and correct backwashing and dilution should take care of this.

Medical research has indicated that some dermatological problems occur with bathers subject to prolonged exposure to higher temperature water in hydrotherapy pools and spas that are disinfected with BCDMH. It is not a problem with lower temperature water and infrequent users. Incorrect water management could also be a contributor to dermatological problems.

It is important to note that bromine products can create carcinogenic bromoforms. Some of these bromoforms can vaporise and affect pool air quality.

Non-halogen disinfectants

Ozone

There is no question that the use of ozone could be beneficial to the water quality of most public pools and spas (particularly indoor ones). In many cases there is a good argument for ozone being a compulsory inclusion. It has the capacity as a bactericide and viricide, to kill all viruses and bacteria in

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the water. It is also an excellent oxidiser and can reduce chloramines and other chemical compounds which interfere with good water chemistry and it will produce a clear atmosphere in pool and spa areas. Ozone generation on site using low-cost self-contained units has not been successful, due to problems with equipment design and lack of maintenance.

Even larger units have given problems because of poor design, inadequate training, lack of service indicators and maintenance. In one case, a venue removed a $100,000 ozone system and replaced it with a conventional liquid chlorine system. Later investigation revealed the real problem was lack of maintenance of the ozone system.

Ozone is a volatile, toxic, pH neutral gas which is aggressive, unstable and insoluble in water. It has a very short life cycle and great care must be taken to ensure the generation system is failsafe and ozone is not released to the atmosphere. For example, ozone in higher concentrations can erode the nasal membranes if inhaled in any quantity. There is therefore good reason to ensure warning, shutdown and failsafe devices are installed.

The production of ozone begins by compressing, cooling, dehumidifying and filtering air and feeding it through a very high voltage electrode gap of a corona discharge unit. Smaller units using UV tubes to generate ozone gas are manufactured, but as a rule they are too small for a public pool.

Ozone does not remain in the pool or spa water for long periods and therefore it has to be used with a residual disinfectant – chlorine or bromine. However, its disinfectant properties mean it becomes possible to operate the pool water at lower levels of free chlorine, with fewer resulting by-products.

Figure 37
Corona discharge ozone generators

Figure 38
Air preparation plant for ozone generation

Ozone – fullstream system

In a fullstream system, the ozone gas generated has to be drawn into a mixing chamber to ensure that no gas escapes and that it makes contact with the water flow from the pool or spa. A contact time of at least two minutes is necessary to ensure adequate action occurs between the ozone and pollutants, including bacteria. The mixing chamber is located after water filtration, so that particulates have already been removed.

In a recirculating system without a mixing chamber, the ozone contact time with pollutants is not initially as long as demanded for their complete destruction, but as the water continually recirculates, the ozone becomes effective by repeated contact.

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The reduction of combined chlorine by ozone is mainly through ozone's interference with chloramine production. As a result, the ozone assists in achieving breakpoint chlorination and removal of ammonia.

If there is any ozone gas remaining in water returning to the pool, it must be removed before reaching the pool or spa and before it is dosed with residual disinfectant. This is achieved by passing the water through an ozone removal system. This is usually an activated carbon filter, which also microflocculates the water and assists with particulate removal. Disinfectant is added, the pH adjusted and the water returned to the pool or spa. There is the possibility that the main filter medium can cultivate bacteria, since ozonisation and disinfection dosing takes place after the filter. It is critical that adequate filter backwashing procedures are adopted and regular filter water samples are microbiologically tested.

Ozone – slipstream system

Ozone can also be injected into the main hydraulic system and this is called a slipstream system. The ozone does not have the same contact time with all the pollutants, but its effect has been proved to be worthwhile.

Ozone generators of various capacities are used for slipstream injection. With the larger units it may be necessary to include an ozone removal system, an activated carbon filter or similar, before water is returned to the pool or spa.

Whilst the ozone input to the water volume is less that a full stream system, within a 24 hour turnover period, contact is made with the total water volume. The capital cost and plant room area for such a system is much less than a fullstream system.

Ozone – low dose systems

There is a minimum rate of dosing of ozone required for pool and spa water and the smallest effective ozone generator has a high capital cost. This makes it uneconomical for many smaller pools that might be found in swim schools, hotels, motels, apartments, clubs, or educational centres. A slipstream system would be ideal for smaller pools to combat water quality problems.

Small ozone generators have been produced for small volume pools and spas but they have proved to be inadequate in the ozone production rate and the quality of construction and are often supplied without de-ozonators. As ozone is such a highly effective method of controlling pool and spa water pollutants, it seems that the manufacture of a lower-cost suitably-sized ozone generator is called for.

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Figure 39-An ozone injection plan

Ultraviolet light (UV)

UV is used in Australia for purifying drinking water and overseas for disinfecting swimming pool water. It is useful in various combinations with other chemicals. The capital cost of installing a UV generator is much less than an ozone generator, but UV is nowhere near as aggressive or useful in destroying water pollutants. Apart from it's disinfectant properties, UV is useful in pool and spa water to assist in the breakdown of pollutants, including chloramines. There is a suggestion that UV slightly increases trihalomethanes. UV must be used with a residual disinfectant however, the use of UV does result in a slightly increased use of chlorine since some hypochlorous acid is decomposed by UV.

Recent Australian experience with UV used with high-pressure pre-coat filters and a chlorine residual disinfectant, have proved highly successful in reducing chloramines and water usage.

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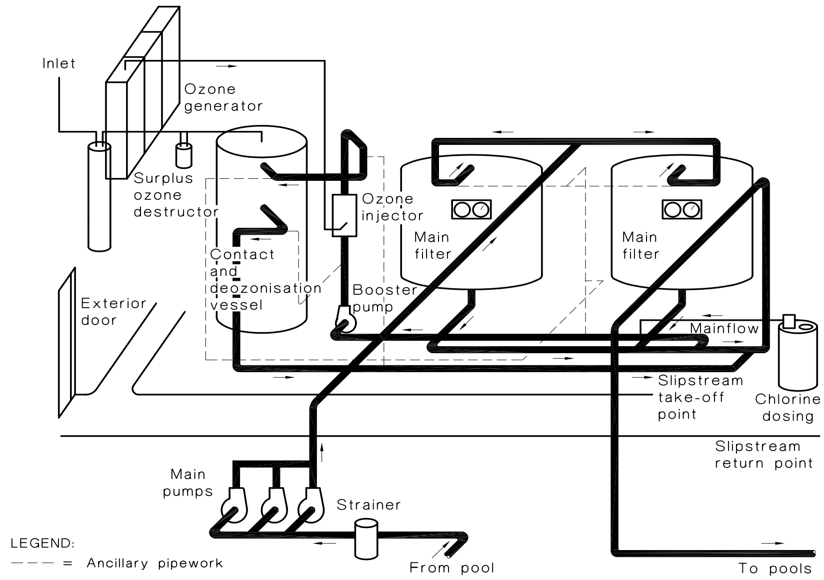

Figure 40-An ozone slipstream injection system

Figure 41-Ultraviolet generator

Ultraviolet (UV) – ozone

UV is used in conjunction with ozone in a slipstream process that can be retrofitted to existing systems. This process must also be used with a residual disinfectant – chlorine.

The use of UV radiation with ozone produces highly reactive hydroxyl radicals which are extremely powerful in breaking down chemical compounds, including chloramines.

The combined ozone/UV generator is plumbed into a diversion line of the hydraulic system, so that all pool or spa water is treated in a 24 hour period. The reported and observed benefits of lowering water pollutants, which results in very low combined chlorine and the production of a 'clear' atmosphere and the ability to use low free chlorine levels, is encouraging.

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Ultraviolet (UV)/sodium bromide/sodium hypochlorite

In pursuit of a lower capital outlay and lower maintenance cost system, UV is being used with other products. The UV, sodium bromide, sodium hypochlorite combination is being experimented with in the hope that water with a low residual disinfectant and low contaminant by-product is achieved. It is still too early to suggest it is successful.

Alkyl biguanide with hydrogen peroxide

This is a biocidal disinfectant and there is no surety that all bacteria and viruses will be destroyed. It is not an oxidiser. The hydrogen peroxide is a good oxidiser and helps to produce clear water, but hydrogen peroxide as a disinfectant takes up to two hours to kill bacteria, compared with chlorine, which takes about three seconds. It is not suitable for public swimming pools and spas.

Super and Shock Chlorination

Super chlorination refers to a maintenance procedure where the free chlorine level is raised to 2 to 3 times the normal level. This can remove and prevent algae and biological film build up. Super chlorination can also be used as a method to reduce combined chlorine, notably the chloramines that can be responsible for objectionable odours and skin irritations. The procedure should be carried out when the pool is not in use, e.g. overnight. If chlorine levels are above regulatory requirements, then de-chlorination (e.g sodium thiosulphate or dilution) will be required before the pool can be used.

Shock chlorination goes further than superchlorination, elevating the free chlorine levels to up to 7 times the normal level. It is only carried out (being very wasteful of chlorine) in response to a major problem such as algal,. microbiological or turbidity.

These are industry procedures and are generally supported by regulatory authorities. However, there is some doubt as to the effectiveness of super chlorination in reducing the adverse effects of combined chlorine. The overdosing of chlorine will, at first, drop the combined chlorine level. However, the organic chloramines do not completely respond to super or shock chlorination, but simply push the original monochloramines to dichloramines and finally to toxic trichloramines - the real nasal and optical irritants. Further and regular super or shock chlorination will only promote and stabilise the trichloramines. Unless ozone or UV is used the combined chlorine (chloramines) will not be reduced. It is therefore paramount that other methods are used to reduce chloramines in halogen-only disinfected pools and spas.

There are now some alternative chemical treatments available as a substitute to chlorine 'shocking'- these are often termed 'oxygen based' or 'non chlorine shock' chemicals and they function by scavenging organics from the pool water. The effect of this will be to free up chlorine from the role of oxidising impurities and make it more effective as a disinfectant. Chloramine levels will drop once organics are removed from the pool water in this way, but 'non-chlorine shock' products will temporarily interfere with the combined chlorine readings of conventional test kits

Water balance

The term 'water balance' means the swimming pool water is in a state of equilibrium with respect to all relevant chemical compounds. Balanced water prolongs the life of a pool and its fittings, assists with preventing stains and improves bather comfort. If pool water has a low concentration of essential dissolved chemical components, it will try to obtain them by etching or eroding the pool surfaces and fittings. If the pool water has too high a concentration of dissolved chemicals, it will try to rid itself of

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the excess in the form of salt precipitates or deposits (scaling). Water balance is the key to maintaining continuously good water quality and providing conditions for maximum disinfectant and hydraulic system efficacy.

Langlier saturation index

Developed from a method that indicates the formation of scale (calcium carbonate) in boilers, W.L. Langelier in 1936 devised a measure referred to as the Langelier Saturation Index. The Langelier Saturation Index is reliant on specific chemical and physical factors. They are:

- calcium hardness
- total alkalinity
- pH
- water temperature
- total dissolved solids (TDS)

The Saturation Index is a measure that allows the common chemical and physical factors to be set at a level that creates the optimum water balance. Normally, adjustments are only made to calcium hardness, total alkalinity and pH.

The formula for calculating the water balance (Saturation Index) is: SI = pH + TF + CF + AF – SF

where:

SI = Saturation Index

pH = Actual pH

TF = Temperature factor

CF = Calcium factor

ATF = Total alkalinity factor

SF = (TD) Solids factor

The optimum Saturation Index point is zero. Values less than zero (-) indicate that the water is under saturated (with calcium and carbonates) and corrosive. Values greater than zero (+) indicate the water is over saturated and likely to scale. While 0 is the optimum value and should not be difficult to achieve, pools can be satisfactorily operated between -0.5 and +0.5. The most important issues are:

- to ensure the pH is maintained within the recommended range,
- that a disinfectant appropriate to the source water and pool use is chosen and its level is maintained,
- a close check is kept on alkalinity, and
- there are no obvious problems

then water balance as an issue becomes secondary.

To calculate the saturation index, test results for pH, temperature, calcium hardness, total alkalinity and TDS are taken. Test results are then converted to the factors found in Table 11.

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Table 9- Saturation Index Factors

Temperature			Total Alkalinity		Calcium hardness		Total Dissolved Solids	
°F	**°C**	**TF**	**mg/L**	**AF**	**mg/L**	**CF**	**mg/L**	**SF**
32	0	0.0	5	0.7	5	0.3		
37	3	0.1	25	1.4	25	1.0	<1000	12.1
46	5	0.2	50	1.7	50	1.3		
53	12	0.3	75	1.9	75	1.5		
60	16	0.4	100	2.0	100	1.6		
66	19	0.5	150	2.2	150	1.8	1000 to 2000	12.2
76	24	0.6	200	2.3	200	1.9		
84	29	0.7	300	2.5	300	2.1		
94	34	0.8	400	2.6	400	2.2		
105	41	0.9	800	2.9	800	2.5	2000 to 3000	12.3
128	51	1.0	1000	3.0	1000	2.6		

Example:

The pH is 7.4
The temperature is 29°C so the factor is 0.7
The calcium hardness is 150 mg/L so the factor is 1.8
The total alkalinity is 150 mg/L so the factor is 2.2
The total dissolved solids is below 1000 mg/L 12.1
The SI is therefore 7.4 + 0.7 + 1.8 + 2.2 - 12.1 = 0.0

Table 10- Range of applicability for the Saturation Index

	Min.	**Max.**
PH	7.2	7.8
Total alkalinity mg/L	80.0	150.0
Calcium hardness mg/L	80.0	200.0
Temperature	25.0	40.0

The water balance nomogram in Figure 44 will quickly show that it is difficult to balance water with excessively high or extremely low calcium levels and total alkalinity levels. If total alkalinity is at a very high level to account for a low calcium level, it can hold the pH high and tax the pH reduction system. Similarly if total alkalinity is very low to account for a very high calcium level, difficulty will occur in stabilising the pH. It is therefore clear that calcium and total alkalinity should be maintained at the mid levels.

Ryznar Stability Index

More recently the ***'Ryznar Stability Index'*** (RSI), an industrial corrosion index primarily used in the water cooling tower industry, has been applied to commercial pools, particularly in the United States. RSI directly relates to the corrosive or scaling ability of the pool water. In some cases, pools operate with LSI values that indicate correct water balance, yet they often experience pool surface staining and the need for equipment repair and replacement. The RSI can be another tool that can help achieve the maximum life of the plumbing, mechanical and heating equipment.

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Table 11 — Water characteristics predicted by the Ryznar Stability Index

RSI Value	Tendency of Water
4.0 - 5.0	Heavy scale
5.0 - 6.0	Light scale
6.0 - 7.0	Little scale or corrosion
7.0 - 7.5	Corrosion significant
7.5 - 9.0	Heavy corrosion
> 9.0	Corrosion intolerable

The Ryznar Stability Index is calculated from the formula:

RSI = 2pHs - pH

Where

pH = Actual pH of the water

pHs = Calculated saturated pH (Calcium Carbonate saturation)

= Alkalinity factor + Calcium hardness factor + total solids at the temperature of the water

= SF – (AF + CF +TF)(Factors from Table11)

The Ryznar Stability Index range of 6.3 to 6.7 is good, with the optimum being 6.5.

Example:

A pool has the following characteristics—

- pH - 7.5
- Temperature - 28°C
- Calcium - 250 ppm
- "M" Alkalinity – 100 ppm
- TDS - 2000ppm

The pH of saturation (pHs) for this water is 7.5. The LSI is 0.0 and indicates balanced pool water. However calculating the RSI from the formula also gives a value of 7.5, which indicates (Table 13) corrosive conditions exist. As this would suggest the need to increase the calcium levels above the recommended range, the RSI should always be used in conjunction with other indicators to ensure overall chemical balance is maintained.

Cyanuric acid adjustment (CYA)

If cyanuric acid is used in the water, an adjustment may have to be made.

If the cyanuric acid level exceeds 50 mg/L and the total alkalinity level 100 mg/L, the following correction factor should be subtracted from the total alkalinity reading:

Cyanuric Acid concentration (mg/L) × Adjustment value from Table 14

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