

Lovibond® Water Testing

Tintometer® Group



Pool & Spa

Water Treatment and Analysis

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Pool & Spa Water Treatment and Analysis



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Foreword

Welcome to this edition of the
Lovibond® Handbook of Pool & Spa Water Treatment and Analysis.

This handbook is intended mainly as a practical guide for owners/operators to assist in the efficient operation of their pools and spas.

Our aim is to illustrate the basic principles of modern water treatment procedures and to explain in some detail the significance and affect of the chemicals currently used for disinfection, flocculation, pH adjustment and the maintenance of water balance.

The ever increasing demands made on pools and spas make the monitoring of the water quality an essential part of the treatment programme. These requirements are met by the Lovibond® range of water testing equipment. This is simple to use, is reliable and accurate and yet is cost effective. The second part of this handbook explains the Lovibond® test procedures in detail and provides useful advice on how to apply them.

This edition has been prepared by Dr. Robert Münzberg and revised by Martin Woelk, based on the dealings with our customers' problems and the consulting with other pool experts. Acknowledgement is made for the kind advice in this handbook by Mr. Geoff Shute, the retired Chief Chemist of the Tintometer Ltd., Amesbury, England and by Mr. Howard Gosling, Swimming and Spa Pool Water Treatment Advisor, Nether Compton, Dorset, England.

We have tried to provide the fullest information on aspects of water treatment and testing but realise that we cannot cover everything so we apologise if we have not included your particular application.

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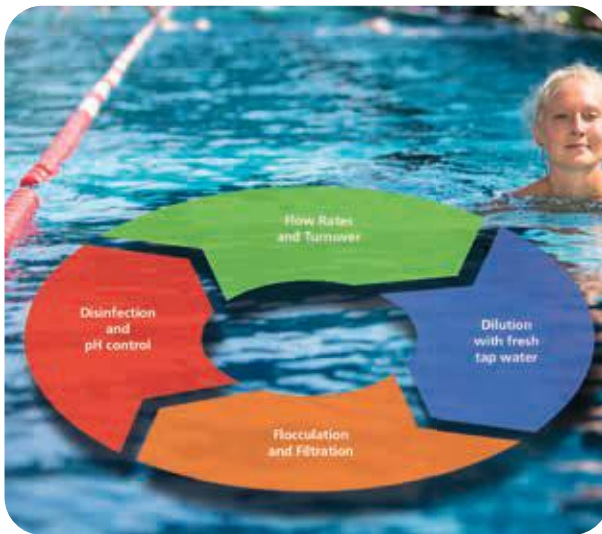


Swimming pool water treatment - the basics

The primary objective of pool water treatment is to maintain the water in a safe and pleasant condition for swimming. More specifically this objective can be summarised as needing to :

- keep the water free of pathogenic (harmful) bacteria
- keep the water free from growths of algae
- ensure the water is neither toxic nor irritating to swimmers
- prevent the formation of undesirable smells or taste in the water
- prevent corrosion of the pool surround, its fittings and equipment
- prevent scale formation in the pool, filter or pipework.

A simple diagram can illustrate the operation of a swimming pool even allowing for today's wide variety of treatment processes:



Flow rates and turnover

Pools become polluted at different rates. Generally the shallower the water the more bathers per cubic metre, and an open air pool has greater surface pollution than an indoor one.

Turnover is the number of hours it takes the filter to pass one complete volume of pool water. The calculation for this is :

$$\text{Turnover in hours} = \frac{\text{Pool capacity m}^3}{\text{Filter rating m}^3/\text{hr}}$$

The filter rating is the flow of water through it designed to achieve a specified degree of clarification, say down to 10 micron, or 0.01 mm, within a certain period. So each type of pool requires its own matched filter to develop a satisfactory turnover period.

As a general guide these are as follows :

| | |
|---------------------|---|
| 30 min – 1 hour | Paddling and waterslide splash pools, also Hydrotherapy pools |
| 30 min – 1.5 hours | Teaching pools |
| 10 min – 45 min | Leisure waters up to 0.5 m deep |
| 30 min – 1.25 hours | Leisure waters 0.5 to 1 m deep |
| 1 hour – 2 hours | Leisure waters 1 m to 1.5 m deep |
| 2 hours – 2.5 hours | Leisure waters over 1.5 m deep |
| 2.5 hours – 3 hours | Conventional public pools up to 25 m long with a 1 m shallow end. |
| 3 hours – 4 hours | Competition pools 50 m long |
| 4 hours – 8 hours | Diving pools. |

Hotel and Health Club pools may be able to have a longer turnover period than an equivalent public or leisure pool if there are strict limits on bather loads and the time the pools are used. The Design Bather Load should be known and enforced by operators at the entrance. Similarly, school pools may have been designed to have 'rest' periods between classes.

Dilution

Disinfection of the water and the filtration process will not destroy or remove all of the pollutants present.

A programme of dilution of the pool water with fresh water is desirable to reduce the build-up of pollutants from bathers and the by-products of the disinfection process.

To some extent dilution is carried out by the sheer nature of back washing the filter where the water flushed to drain must be replaced. Unfortunately this is not frequent enough to maintain the concentration of undesirable pollutants at an acceptable level.

Some pollutants can only be reduced by dilution – organic chloramines like chlorcreatinine for example, cannot be broken down by chemical means.

A useful guide as to volume required is **30 litres per bather per day in a public pool**, which should give benefits of lower levels of pollutants and hence reduce the use of the treatment chemicals themselves.

Filtration

The main purpose of the filter is to remove particulate matter and debris from the water. It strains out suspended solids down to sub-micron- size particles in order to maintain water clarity. It does not remove dissolved salts nor does it deal with micro-organisms.

The long established material for filters is sand and this is still preferred by many designers of large pools since it's use has been so well proven over 100 years.

Other types are : Cartridge filters

Zeolite mineral

Diatomaceous earth

Dolomitic filter material

The cartridge filter is a self-contained unit constructed of a synthetic fabric such as spunbonded polyester in a pleated format which is attached to a centre core within a cylindrical drum. This provides a large surface area for filtering in a very small confined space.

This type of filter is generally only used for small pools.

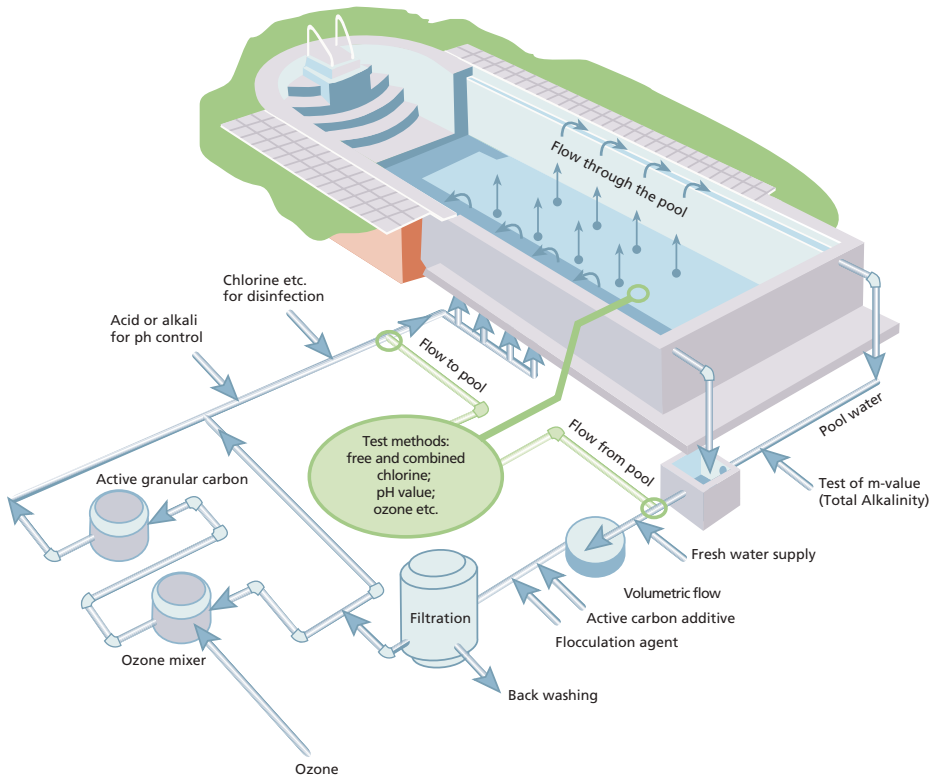
In both sand and zeolite filters, water is passed through the material under pressure. While passing through the sharp edged media, small particles of debris are trapped in the gaps, starting in the top layers.

Zeolite material is now growing in popularity over sand as it absorbs ammonia, gives good water clarity and can bring savings on chemical costs.

A gravity, vacuum or a pressure process occurs in a diatomaceous earth filter. Mesh bags are placed in a vessel usually under pressure and the diatomaceous earth is introduced into the system and settles on the mesh. Water passes through the now impregnated mesh and debris is collected as before.

Dolomitic filter material produces an alkaline reaction with the pool water and is used to stabilise the pH, particularly when chlorine gas is the disinfectant. Due to its composition there is a build up of calcium and magnesium bicarbonates in the water which increases its hardness and this contributes to the pH stabilisation. This process slowly uses up the dolomitic material and so at the appropriate time its level in the filter has to be topped up. The depth should usually be approximately 40 cm (15 ins) on top of the sand. Where Dolomitic Media is in a filter do not use Hypochlorite in the pool.

An advantage of this type of filter medium is its additional ability to filter out Iron and Manganese from the water.



Flocculation

Colloidal or finely suspended materials may not be trapped on the filter bed but continue to be circulated in the pool giving the water a cloudy appearance and reducing visibility for bathers.

This problem is more likely to occur in an outdoor pool due to the effect of the elements – wind and rain. The pool water is prone to collect windblown debris like dust, algae, spores, insects and footborne materials like soil and grit.

In order to remove this finely dispersed material the use of a flocculant is necessary. This is a chemical which is added to the pool water and which causes the particles to group together to form larger particles (flocs) which become big enough to be caught by the filter media and removed from the water. Following is a list of some of the more popular flocculants :

ALUM (aluminium sulphate)

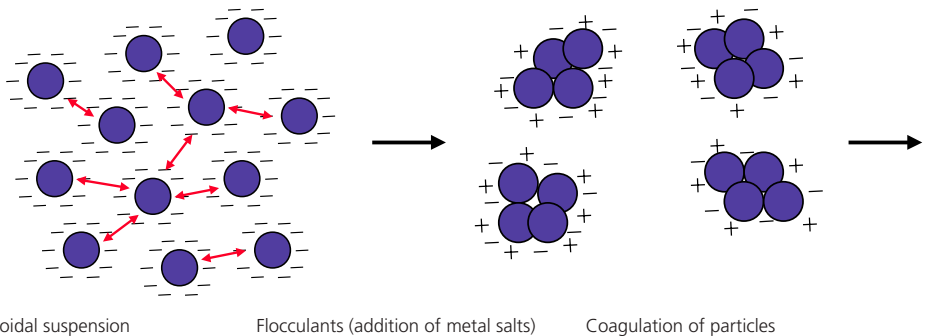
PAC (polyaluminium chloride or aluminium hydroxychloride)

PASS (polyaluminium sulpho silicate)

SODIUM ALUMINATE

IRONIII CHLORIDE HEXAHYDRATE

IRONIII SULPHATE



Chemically they all behave in similar ways by forming a gelatinous precipitate by hydrolysis.

Aluminium-based compounds operate best at pH levels between 6.5 and 7.2 and iron salts between 6.5 and 7.5

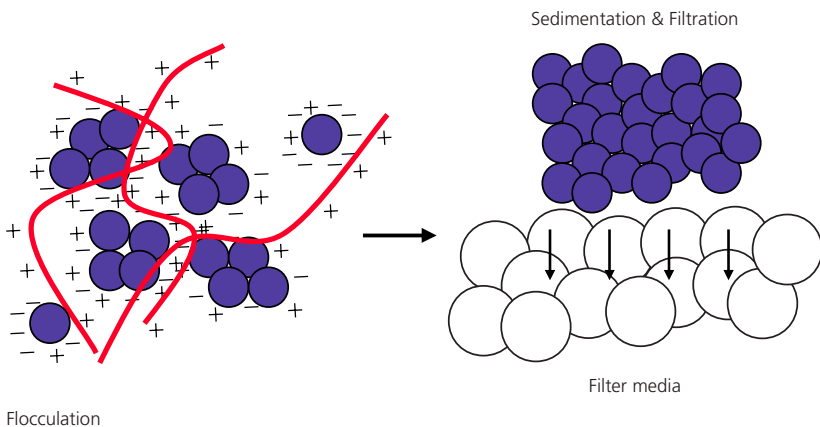
Iron salts however may leave an iron residual in the water which may cause staining, and so these are not now used on a large scale.

The most commonly used flocculants are the polyelectrolytes like PAC and PASS. As non-filterable water turbidity is usually caused by negatively charged particles these polyelectrolytes are cationic and attract the particles causing an increase in the floc size.

Cationic polyelectrolytes offer additional advantages as

- At the recommended dosage rates they are capable of flocculating living organisms such as algae and bacteria which would otherwise pass through the filter – the infectious cysts of *Cryptosporidium* and *Giardia* are small and resistant to disinfection.
- They produce a tough floc that is resistant to disintegration from the action of the pump impellor.

It should be stressed that flocculants must be used correctly at the recommended dosage rates and this is best achieved by dosing continuously by means of a dosing pump. Suppliers instructions must be followed.



Backwashing of Filters

With all types of filter there comes a time when it becomes loaded with debris and it is necessary to clean or backwash the filter bed.

The indication that this course of action is appropriate is when the pressure gauge on the filter shows that there is a pressure differential between the top of the filter bed and the bottom

Backwashing is the process of reversing the flow of water through the filter. This agitates the material and loosens the bed. The sharp grains collide with each other causing the collected debris to be flushed out to drain (waste).

This is the mechanism in sand, zeolite and dolomitic filters but in the case of diatomaceous earth filters the reverse flow not only removes the debris but the filter media itself. This then has to be replaced before filtration can again proceed.

Since cartridge filters cannot be backwashed they must be physically removed to be cleaned. They are flushed out, possibly with a garden hose to force debris off the surfaces, then cleaned with a strong solution of chlorine (about 100 mg/l) before being refitted for re-use. There are also proprietary chemical filter cleaners.

Water Disinfection

Disinfection, relative to swimming pool water, means essentially to

- keep the water free from potentially harmful bacteria.
- keep the water free from algae growths.
- ensure that the water is not irritating or toxic to the bathers.
- prevent the formation of undesirable smells or taste.

In other words it is safe and pleasant for bathers to swim in.

Disinfection is concerned with the destruction of micro-organisms – viruses, bacteria, algae, moulds and fungi. These exist in large numbers in our natural environment. The two important types as far as swimming pool water is concerned are bacteria and algae.

Millions of bacteria are present on the human body. Many are quite harmless but others cause illness and swimming pool water is an ideal medium for the passing of bacteria from one person to another.

By adding a disinfectant to the water, the pool operator is initiating a process which will hopefully destroy these bacteria as quickly as possible and hence minimise the risk of cross-infection.

Algae are natural forms of plant life and are present in all natural water courses – rivers, ponds, lakes etc. There are thousands of species in a diverse range of colours. The presence of algae in swimming pools is highly undesirable as algae growths turn the water cloudy and make the pool surfaces slippery and dangerous.

The disinfection process should be effective in controlling algae but supplementary chemicals called algicides are available for use in cases where they are difficult to remove.

In well managed and adequately disinfected pools, the spread of viral infections should not occur. Nasal and respiratory infections can be contracted by bathers in crowded areas; however, these are more likely to be caused by infected airborne droplets rather than contact with the pool water itself.

Two organisms which are particularly resistant to disinfection are the infective cysts of CRYPTOSPORIDIUM and GIARDIA. These are microscopic protozoa found widely in the natural environment, often in animals. They are responsible for diarrhoea and sickness and can be a problem in busy pools. Although resistant to disinfection they are larger than bacteria and therefore more susceptible to coagulation and hence removal by filtration.

Other pollutants are introduced into the pool water and these originate from the bathers as well. By far the most important are nitrogen compounds from body sweat and urine which, in the form of ammonia, react with some disinfectants to form potentially irritating by-products. Measures must be taken to remove these either by chemical means or dilution – this will be dealt with in more detail later.

Example: Legionella Pneumophila Bacteria



The average Legionella cell is 0.5 - 1.0 micrometer (μm) wide and 1.0 - 3.0 micrometers long. 1 micrometer (μm) = 1/1000 millimeter

Treatment Chemicals

Please note that all disinfectant chemicals used for Pools and Spas are specifically for that purpose and that normal household (e.g. toilet) cleaners are NOT suitable.

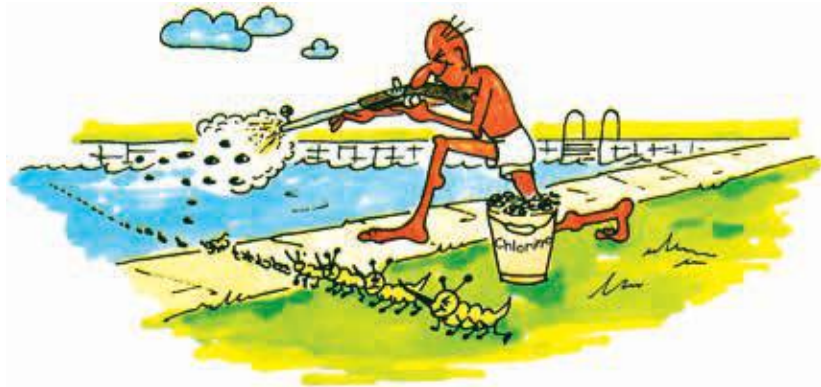
Chlorine Gas – anorganic

Liquified chlorine gas is the purest form of chlorine disinfection, it contains 100% of available chlorine.

When chlorine gas reacts with pool water it produces free available chlorine and hydrochloric acid. This process causes the pH of the water to fall to below pH2 – highly acidic-requiring the continuous and automated addition of alkali in the form of sodium carbonate (soda ash) or sodium hydroxide (caustic soda) to raise the pH again.

Chlorine gas is best suited for use in hard water areas where the natural hardness of the water helps to neutralise the acidity produced.

Chlorine gas must NEVER be used in residential pools.



Sodium Hypochlorite – anorganic

Sodium hypochlorite is by far the most popular of the disinfectants used in swimming pool water.

It is a pale yellowish liquid with the characteristic smell of household bleach. The commercial product contains between 10 and 15% of available chlorine which is considerably more than the domestic product.

Sodium hypochlorite is prepared by passing chlorine gas through a solution of sodium hydroxide under very controlled conditions. An excess of sodium hydroxide is left after the reaction to improve stability and this means that the solution has a very high pH – about pH 12.

Even under satisfactory storage conditions – in the dark and at cool temperatures – sodium hypochlorite decomposes slowly, liberating oxygen and losing its available chlorine content. Its pH however always remains high.

Some blended solutions are available which contain stabilising agents to retard decomposition. These are usually nearer the 10% available chlorine strength and although they are more stable they still gradually deteriorate due to heat, light etc. It is generally recommended that during summer months storage is limited to a period of one month in dark containers at temperatures as cool as possible.

Important note

Never add acid directly to sodium hypochlorite solution as this will cause the production of chlorine gas.

CAUTION: ALWAYS add chemicals to water. NEVER add water to a chemical as a violent action may occur.

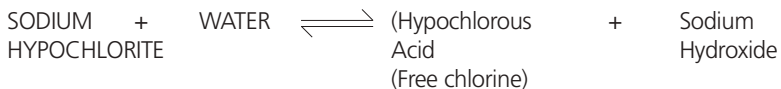
Although acid is necessary for pH correction it should be added to the pool gradually. In the case of hydrochloric acid (muriatic acid) it should be first diluted by adding to a plastic bucket or watering can with pool water then sprinkled over the surface.

With sodium hydrogen sulphate (dry acid) it should be dissolved in a plastic bucket or watering can of pool water then poured into the pool in different places.

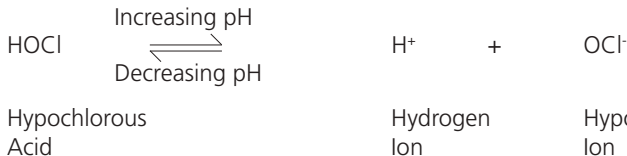
Alternatively sodium hypochlorite may be generated in situ by maintaining a high level of sodium chloride (common salt) in the pool water – usually 3.000 to 4.000 mg/l and passing some or all of it through an electrolyser. Natural sea water can also be used instead.

The system is not suitable for large pools but can be satisfactory for small pools with light bather loads as long as the electrolytic generation system can cope with fluctuations in conditions and maintain the recommended free chlorine residual.

The mechanism of sodium hypochlorite in pool water is as follows:



The proportion of hypochlorous acid produced depends on the pH of the pool water as it is subject to a reversible reaction thus:-



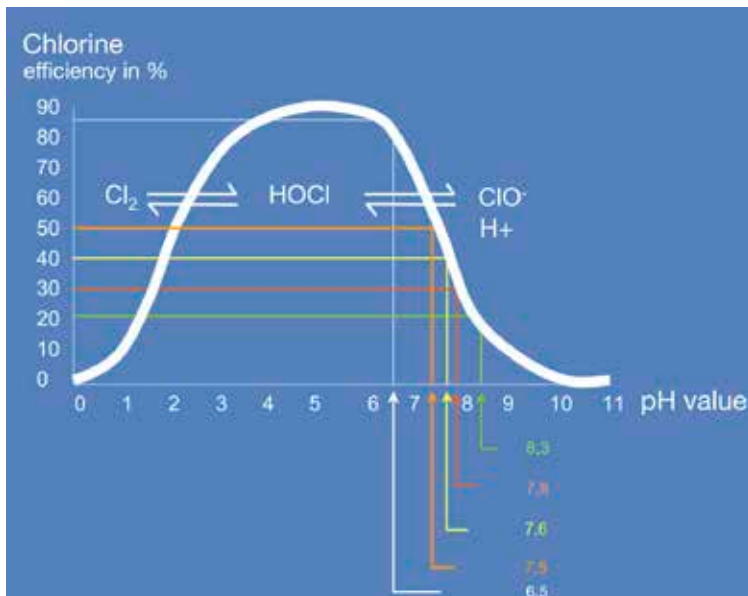
As the pH increases the reaction products are formed while the active HOCl predominates at lower pH values:

| pH | % HOCl | % OCl ⁻ | |
|----|--------|--------------------|----|
| | 5,0 | 100 | 0 |
| | 6,0 | 96 | 4 |
| | 7,0 | 75 | 25 |
| | 7,2 | 66 | 34 |
| | 7,5 | 49 | 51 |
| | 7,8 | 33 | 67 |
| | 8,0 | 23 | 77 |

As HOCl is the active form of the disinfectant and the OCl-ion has virtually no disinfecting power it would be ideal to run a pool at pH 5.0. Unfortunately this is not possible as this is an acidic condition and is unsatisfactory for both the pool plant and bathers alike.

The most satisfactory conditions exist between pH 7.2 and 7.5 when around 50% of the disinfectant is present as HOCl. It is comfortable for bathers and non-corrosive for the pool surround, its fixtures and fittings.

Although HOCl is considered as being 'free chlorine', all colorimetric methods of analysis for this measure, the sum of the hypochlorous acid HOCl and hypochlorite ion OCl⁻.



Calcium Hypochlorite – anorganic

Calcium hypochlorite (cal hypo) is a stable alternative to sodium hypochlorite. Available commercially in granular form or as tablets it usually contains 65% of available chlorine, which is considerably more than sodium hypochlorite.

Cal hypo is not normally dosed by hand but rather it is dissolved in water and pumped into the pool circulation system automatically.

The tablets are placed in a feeder system through which the pool water flows, or alternatively placed in the skimmer baskets as in the case of domestic pools.

Regular use of cal hypo will increase calcium levels in the water which is beneficial in soft water areas. Concrete pools in these areas often suffer grout loss from between the tiles and sometimes the screed from behind the tiles due to the water having a 'calcium demand' and seeking out sources of calcium to help satisfy this.

Cal hypo is doubly beneficial in these cases as it both disinfects and helps to satisfy the calcium demand of the water.

In a hard water area with continued use of cal hypo, grout attack is unlikely but rather the risk of scale deposits on the sides of the pool and calcification of the filter is possible. Balanced water is very important here –see page 46.

Cal hypo is alkaline with a pH between 11 and 12 so acid is needed for pH correction in the pool.

The Total Dissolved Solids content of the water will also rise but not to the same extent as when using sodium hypochlorite.

Chlorinated Isocyanurates (stabilised chlorine) – organic

These are compounds of chlorine and cyanuric acid which are in world-wide use due to the fact that the cyanuric acid acts as a stabiliser in outdoor pools, reducing the chlorine loss due to the action of ultra violet rays from the sun.

Two compounds are available – sodium dichloroisocyanurate 'Di-Chlor' and trichloroisocyanuric acid 'Tri-Chlor'.

Di-Chloroisocyanurate (fast dissolving) – organic

This is a granular material containing about 60% of available chlorine. It is a highly soluble compound which makes it ideal for direct application to the pool. Furthermore it has an almost neutral pH which means it will not have an effect on the pH of the pool water.

When dissolved in water Di-Chlor produces hypochlorous acid (free chlorine) and cyanuric acid and it is important to monitor the latter as well as the free chlorine as it's concentration tends to build up in the pool water until a situation arises when chlorine – lock occurs –see page 47.

Tri-Chloroisocyanuric acid (slow dissolving) – organic

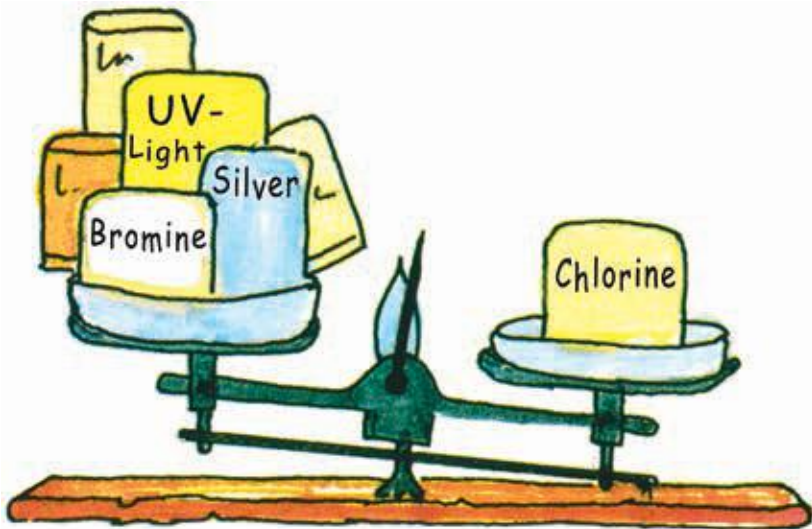
This contains about 90% of available chlorine and is normally supplied in the form of large tablets. It is not particularly soluble which makes it ideal for flow-through erosion feeders, floaters or in skimmer basket applications.

It has a low pH – about 3 which may require pH adjustment with pH-increasing chemicals like sodium carbonate (soda ash)

It produces hypochlorous acid and cyanuric acid in solution in a similar manner to dichlor and the same potential problem applies over the build-up of cyanuric acid.

As a general rule free chlorine residuals must be kept higher than with regular hypochlorites because with Di-Chlor and Tri-Chlor a reduction in the rate of kill of bacteria occurs with increasing concentrations of cyanuric acid. The level recommended depends on the cyanuric acid content as indicated in the table:

| Cyanuric acid mg/l | mg/l 30 | mg/l 50 | mg/l 70 | mg/l 90 | mg/l 100 | mg/l 130 | mg/l 140 | mg/l 160 | mg/l 180 | mg/l 200 |
|---|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Available free chlorine in relation to DPD 1 measurement (pH 7,5 ; t = 25 °C) | 45 ca. % | 33 ca. % | 28 ca. % | 14 ca. % | 12 ca. % | 10 ca. % | 9 ca. % | 8 ca. % | 7 ca. % | 6 ca. % |



Recommended values for domestic pools - EN 16713

| | Measure | Target |
|--------|-------------------------------|--|
| Daily | free chlorine | 0.3 - 1.5 mg/l anorganic chlorine 1.0 - 3.0 mg/l Chlore organique |
| | combined chlorine pH value | max. 0.5 mg/l 6.8 - 7.6 |
| Weekly | Cyanuric acid | max. 100 mg/l |

Bromine

Bromine has always been considered a disinfectant with similar properties to chlorine but in the context of swimming pool water treatment it is superior.

In chlorine treated water, by-products are often formed which cause eye irritation and sometimes offensive odours. These are, of course, the combined chlorines, the chloramines.

In bromine treated pools, although combined bromines are formed, the bromamines, eye irritation is virtually totally absent as these, unlike the chloramines, are good disinfectants with their activity almost being equal to free chlorine or free bromine.

The use of elemental bromine however is very uncommon as it is a heavy red liquid which is very corrosive and gives off pungent fumes. It's handling therefore requires very special precautions and consequently it is generally unsuitable for use in pool water treatment.

A safe alternative which is very popular world-wide is an organic compound which contains both bromine and chlorine molecules. This is 1-bromo-3-chloro-5,5- dimethylhydantoin (BCDMH).It is usually supplied in the form of tablets and contains 61% of available bromine and 27% of available chlorine.

BCDMH dissolves in the water to release both free bromine (hypobromous acid) and free chlorine (hypochlorous acid) and although the latter is also a disinfectant, the primary disinfectant in a pool treated with BCDMH is hypobromous acid) it kills bacteria and oxidises organic matter and in doing so 'spent bromine' is left in the water in the form of the bromide ion. The hypochlorous acid present regenerates this 'spent bromine' back to hypobromous acid and so the process continues. As a result the active disinfectant in a BCDMH treated pool is always hypobromous acid.

BCDMH does not require any special storage conditions other than 'cool and dry' and if this recommendation is followed it is a very stable compound .

A potential negative aspect on the use of BCDMH is that a small proportion of bathers develop an itch followed by a visible rash within 12 hours of exposure to water treated with this chemical. The problem is unusual in children and more common in bathers of say 50 years or more.

Ozone

Ozone is the most rapid disinfectant and most powerful oxidising agent available for water treatment. It is a highly active gas which reacts immediately on contact with bacteria or other contaminants and impurities found in swimming pool water.

Ozone is not a stable gas and it reverts quickly back to oxygen. This is why it has to be generated on-site and immediately introduced into the circulating pool water. The most efficient commercial production method is to pass dried air through a corona discharge ionising field.

Ozone is also a toxic gas and so any which is unreacted must be removed from the water, prior to its return to the pool, by means of a deozonising filter. This is normally activated carbon.

Commonly found bacteria like E Coli are killed up to hundreds of times quicker than with chlorine and even the highly infectious organism Cryptosporidium, which is resistant to high levels of chlorine, is destroyed by 3 mg/l of ozone in just one minute.

Ozone's powerful oxidising properties prevent the build up of undesirable and odour producing by-products of the chlorination of human-based organic pollution – monochloramine, dichloramine and nitrogen trichloride. It does this by breaking down the components of urine and sweat thereby removing the precursors of the chloramines etc.

Ozone also acts as a powerful flocculant and renders the use of additional, more conventional flocculants unnecessary. A noticeable beneficial effect of ozone treatment is consequently the exceptional clarity of the water.

In commercial pools, as all of the ozone has to be removed from the return water, chlorine has to be added post filter to maintain a residual in the pool itself to combat pollution. The level of chlorine is much less than would be required in a chlorine-only pool.

In residential pools ozone is sometimes the only source of purification and as the dose is much lower than that required by much larger pools, the water is not deozonated. Normally a long-life copper-based algicide is used to provide a back up and occasionally a little chlorine may be added after an extra contamination load, say after a pool party. "Safe practice" decrees that a disinfectant residual (chlorine or bromine) should be used at all times.

Active Oxygen = Peroxyde, Persulphate, MPS

This is the popular name for an alternative method of pool water treatment to the established compounds based on chlorine or bromine. Although compatible with both of these, even being used in conjunction with them, active oxygen is based on the strong oxidiser potassium monopersulphate. It is also referred to as potassium peroxymonosulphate or simply monopersulphate compound.

Potassium monopersulphate is a chemical which oxidises organic pollution without producing any of the irritating combined chlorine products. It is a white, granular free-flowing powder which is very soluble in water but it is acidic so pH correction of the pool water may be necessary.

It is sometimes used as the only oxidiser in private pools but here it has an accompanying special algicide which assists with the disinfection process.

In public pools it is mainly used as an alternative to chlorine when shock dosing is required. Using chlorine for this can often bring problems from increased levels of combined chlorine rather than a reduction in them. This is due to some organic chloramines not being destroyed by chlorine whereas the use of potassium monopersulphate will break them down by oxidation.

In addition to its use as a non-chlorine shock it is used as an oxidiser when a pool is being run on bromine as the primary disinfectant. Here it can be used with BCDMH to assist with the regeneration of the 'spent bromine' back to hypobromous acid.

Alternatively, as part of a two product disinfection system it is widely used with sodium bromide as the bromine donor. The potassium monopersulphate oxidises or 'activates' the bromide ion to bromine which rapidly forms the powerful disinfectant hypobromous acid. This, on reaction with pool water pollution is reduced to 'spent bromine' when the action of the monopersulphate oxidises it back to bromine. This process can be repeated continuously as long as there is sufficient oxidiser present.

Adequate and efficient filtration is essential when using potassium monopersulphate as pollutants and oxidised material must be removed from the water as soon as possible. Regular backwashing is necessary to prevent a build-up of organic pollutants within the filter bed. The use of a suitable flocculant may be beneficial.

An alternative oxidiser to potassium monopersulphate is liquid hydrogen peroxide . This works in a similar manner but being liquid is more difficult to handle and is less stable.

It is normally used in private pools only and is coupled to an automatic dosing and control system which ensures that the correct quantity of chemical is dosed.

The advantage of hydrogen peroxide is that the products of decomposition are oxygen and water thus not adding to the TDS level in the pool.

Biguande (PHMB)

PolyHexaMethylene Biguanide (PHMB) is a non-chlorine bactericide developed for use in private swimming pools. It is not recommended for use in pools fitted with an ozone device. Special versions exist for spa/hot tub use.

Although it does have some algistatic properties it must be used in conjunction with specific algicide to minimise the risk of the growth of the more robust strains of algae. Monthly oxidising with Hydrogen Peroxide is also required.

Many pool owners welcome an alternative to the established halogen treatments, although it must be emphasised that PHMB and chlorine are not compatible and should not be mixed in pool water. In fact, it is vital that all traces of chlorine in a previously chlorine treated pool must be removed before any PHMB is added; this is carried out using Sodium Thiosulphate.

PHMB is cationic and so acts as a flocculant in the pool. Backwashing of the filter more frequently is thus recommended.

Copper / Silver (Ionisation)

This is associated with electronic devices (ionisers) which generate copper and silver ions to provide disinfection in lightly-used private pools.

Silver is a well-known bactericide and copper an algicide and their use in pool water treatment is based on the ability to control their ions in solution.

An ioniser electrochemically generates silver and copper ions from a solid electrode composed of the two metallic elements. This is housed in a flow cell, through which the pool water passes.

The silver and copper ions are thus introduced into the pool and the capacity of the system is selected such that the desired level of the two metallic ions is built up in the water in a few days. The power output is then set to maintain the level, allowing for backwashing and bather load.

The charged silver and copper ions are potentially effective against bacteria and algae respectively, and working together are effective against a wide range of organisms.

The charged ions also have a flocculating effect, grouping dead micro-organisms and bacteria, which are then removed by the filter.

This process does not provide any mechanism of oxidation in the water and so it is advisable that a low level of a primary disinfectant be maintained. Recently, ionisers based on other minerals such as Zinc have been introduced, just using erosion rather than electrical action.

Ultra-Violet (UV)

Until fairly recently ultra-violet light (UV) water treatment was considered a relative newcomer to the business of disinfecting swimming pool water.

UV has been known to be effective in destroying bacteria and other micro organisms for nearly a century and has been used for the treatment of industrial and drinking water for nearly half that time.

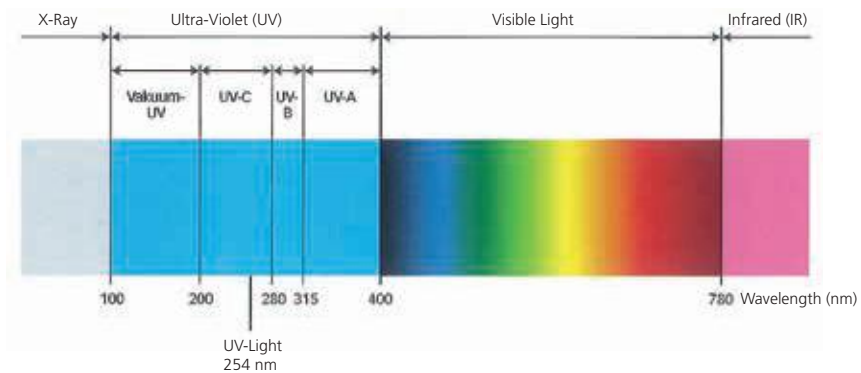
Ultra-violet light is generated by electric arcs, usually using a mercury vapour lamp. It exists in the part of the spectrum which is beyond the shortest wavelength visible to the human eye. It is most effective in the region between 240 nm and 280 nm, the so-called germicidal wavelength.

In swimming pools, UV breaks down chloramines and other organic compounds, like urea, by photo oxidation. Water temperature does not affect the process which means that the disinfection and chloramine reduction is equally efficient in unheated outdoor pools as well as warm leisure or hot hydrotherapy pools.

UV disinfection treats the full flow from the pool filters and provides protection against the problem of pseudomonas contamination of the filter bed.

A low concentration of a primary disinfectant is required to be added to the water to act as a residual disinfectant. This is usually chlorine and it should be used at the minimum possible level which may be as low as 0.5 mg/l free chlorine for a private pool, but adjusted so that algal growth is prevented from adhering to the pool surfaces. UV equipment will help control waterborne algae but is unlikely to have any effect on growing spores on the pool structure.

It should be noted that the disinfectant should be added after the UV treatment chamber to minimise the affect of UV light on the chemical.



Algicides

The appearance of algal growths in outdoor pools is an all too common nuisance. As well as being unsightly, they can prove to be dangerous if they make surfaces slippery. The pool water may turn cloudy and ultimately, if allowed to multiply unchecked, they can block filters or reduce their efficiency.

The most common cause of algal growths appearing is the failure to maintain an adequate free chlorine residual in the water at all times.

To prevent algal growth and to kill any existing algae there are two types of product in popular use, QAC's and Polymeric Copper compounds.

QAC or Quaternary Ammonium Compounds are effective at low concentrations (1 to 4 mg/l). They are also surface active agents and so at high concentrations they can cause foaming in the water.

Some QAC's create a demand on chlorine and bromine disinfectants and so the level of these in the pool should be raised several mg/l above normal before addition of the QAC to counteract this. It is thus important that some care is taken in their dosing into a pool.

Polymeric Copper or Chelated Copper is where copper is bound to an organic molecule for dosing which reduces considerably its toxicity to bathers but still enables it to be effective against algae. These types of product are often used as "winterisers" in private pools to prevent deterioration of the water while the pool is unused over the winter season.

Copper sulphate is no longer used as an algicide because as well as its toxicity it can cause problems with hair discolouration, and staining of pool surfaces, especially at pH values over 7.4.



Algal growths in outdoor pools

pH Control

The pH is a logarithmic scale, which ranges from 0 to 14.

A pH of 7.0 is neutral and if the value is above this, the water is alkaline i.e. it contains more alkaline components than acid components.

Conversely, if the pH value is below 7.0 it contains more acid components than alkaline components and is therefore acidic.

The optimum pH for swimming pool water is between pH 6.8 and 7.6 (EN 16713) for chlorine based disinfectants. This narrow target range is necessary for the disinfection process to be running efficiently, for the comfort of the bathers and for the general condition of the pool structure, its fixtures and fittings.

If the pH is too high (> 8.0) the effectiveness of the disinfection process is reduced, the water may become cloudy and scale formation can be promoted.

If the pH is too low (< 6.8) eye and skin irritation can occur and the pool fittings can be damaged by corrosion.

To avoid wild swings in the pH level caused by the addition of treatment chemicals it is necessary to maintain an acceptable level of ALKALINITY in the water. This is usually about 100 mg/l – see Balanced Water (page 46) and is made up of dissolved carbonates, bicarbonates and hydroxides. These have the effect of acting as a buffer to prevent large changes in pH upon the addition of acids or alkalis to the water.

The following chemicals are used for pH adjustment:

To raise the pH level

- Sodium Carbonate (Na_2CO_3) or Soda Ash, also called pH Plus. This has a pH of around 10 and will also raise the alkalinity of the water.
- Sodium Hydroxide (NaOH) or Caustic Soda.
This is very alkaline with a pH of 14 and must be handled with care. This will also raise the alkalinity of the water.
- Dolomitic Filter Material has the effect of raising the pH but it is not dosed separately as a chemical. It is included in the filter on top of the sand, and topping up is required at regular intervals, see Filtration section pages 8 and 9.

To lower the pH level

- Sodium Hydrogen Sulphate (NaHSO_4), Sodium Bisulphate or Dry Acid. Also called pH Minus.
This is a free flowing crystalline powder or granules which in solution has a pH of 1. It is normally dissolved in some water in a plastic container and then sprinkled around the pool. It also adds sulphate to the water.

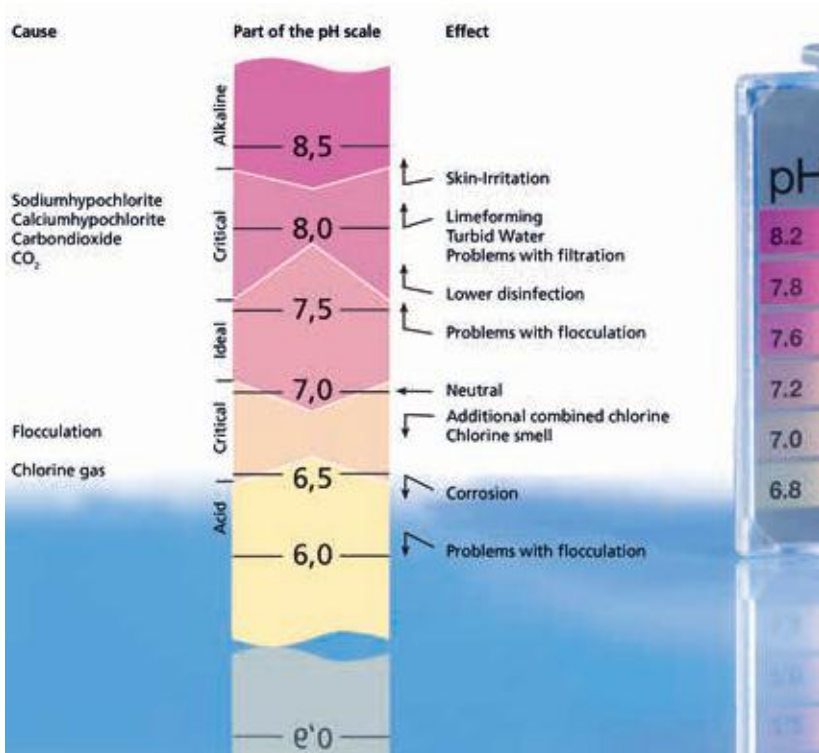
- Hydrochloric acid (HCl) also known as Muriatic Acid. This is an economical pH reducer but handling can be a problem, the concentrated acid (32%) is highly corrosive. Commercial grades should not be used as their iron content may be high and this could cause discolouration and cloudiness in the water. It is advisable to dilute the concentrated acid by adding to water in a plastic container before sprinkling it around the pool.

NOTE Always add acid to water, not the other way around.

- Carbon Dioxide (CO₂) this is a gas and therefore requires special injection equipment. When combining with the pool water, carbon dioxide forms carbonic acid which reduces the pH and also adds alkalinity to the water. This has distinct advantages in soft water areas where the natural alkalinity of the supply water is low, but in hard water areas it is not suitable as it will raise the alkalinity to unacceptably high levels. CO₂ works best at reducing pH value where the total Alkalinity of mains water is less than 150 mg/l as CaCO₃ and Hardness is less than 300 mg/l as CaCO₃.

In commercial pools pH adjustment is carried out as a continuous part of the treatment process through a metering pump. Dosing by hand as described above is only carried out in private pools where there is no alternative.

Causes and effects of pH values



Alkalinity

The alkalinity of a water is a measure of the alkaline salts dissolved in it – carbonates, bicarbonates and hydroxides. It should not be confused with pH which is a logarithmic scale indicating whether a solution is acidic, neutral or alkaline.

The higher the alkalinity the more resistant the water becomes to a change in pH value – it buffers the water (see section on pH control). An optimum level of alkalinity is required for a pool – usually around 100 mg/l measured as calcium carbonate CaCO_3 .

If however the alkalinity rises to over 200 mg/l it can make any pH adjustment difficult, and cause cloudiness in the water.

To raise alkalinity levels SODIUM BICARBONATE (NaHCO_3) is used. This has negligible effect on the pH of the water but it will add alkalinity.

Sodium carbonate (Na_2CO_3) on the other hand will raise the alkalinity but will also raise the pH.

Small regular adjustments of the alkalinity level are preferred to large doses at infrequent intervals.

To reduce the alkalinity, acid must be used. This is normally added to the deep end of the pool with the pump switched off so that the alkalinity is burned off rather than causing just a reduction in pH.

Calcium Hardness

Water supplies are often termed “soft ” or “hard” and this relates to their content of calcium and magnesium salts. A soft water will usually have less than 50 mg/l of these salts expressed as CaCO_3 . Hard water will contain over 300 mg/l as CaCO_3 .

Soft water will cause problems in swimming pools as it will have a “calcium demand” and seek out calcium from the pool structure. This is usually the tile grouting and even the painted concrete surface itself may not escape attack. This leaves gaps between the tiles and ultimately the tiles themselves may become dislodged due to erosion of the cement.

It is advisable therefore that the calcium hardness of the pool water is established at the earliest opportunity and if necessary the concentration is raised to at least 200 mg/l as CaCO_3 by the addition of Calcium Chloride flake. This is a very soluble material and it should be noted that it will also add chloride ions to the water and will contribute to the Total Dissolved Solids content – see pages 28 and 45. High levels of calcium hardness (up to 1000 mg/l) have been known and as long as the water is Balanced –see page 48. It is not detrimental. Some suggestions are that it adds a sparkle and a deep blue colour to the water.

If it is required to reduce the level of calcium hardness the only way is to dump some of the water and top up with fresh, containing lower natural hardness.

The use of Dolomitic filter material –see page 9 will also add calcium ions to the water which will be a benefit in soft water areas.

Total Dissolved Solids (TDS)

Total Dissolved Solids is the sum of the dissolved compounds – hardness salts, treatment chemicals etc. in the water. It's importance has been recognised over recent years as giving an indication as to whether the pool is becoming saturated with chemicals in one form or another, and hence the length of time the water has been in the pool.

TDS is measured electronically as the conductivity of the water to which a factor is applied (usually about 0.7) to convert it to TDS in mg/l.

A popular recommendation for the maximum TDS in a pool is 1000 mg/l above the feed (mains) water. So if the feed water has a TDS of 400 mg/l, the maximum for the pool should be 1400 mg/l.

TDS can only be reduced by dilution and this must be carried out as a matter of priority if the water reaches the absolute maximum of 3000 mg/l, as at this level the water can be :

- salty to taste
- conductive – to produce corrosive conditions
- dull in appearance

Spa Pools (Hot Tubs)

A spa pool consists of a relatively small volume of warm water (35°C – 39°C) in which bathers sit as opposed to swim. It is often circular in design and constructed of acrylic or glass reinforced plastic (GRP) or of concrete.

The water is circulated inwards through nozzles set at frequent intervals around the perimeter and out through, main drains or skimmers. Alternatively the design may be of the overflow type in which the water flows into channels constructed around the outside of the shell. Even with this design, there will usually be a low suction point.

It is essential that the recirculating water is cleaned by an adequate filtration system and disinfected by an appropriate chemical treatment.

Most spas have some form of air injection system to create turbulence in the water, and this, with the increased temperature, can affect the efficiency of some of these treatments.

IMPORTANT: If there is water in a Spa, it must be treated and tested, even if no-one is using it, and records of this must be kept.

NOTE. A spa pool is distinguished from a Whirlpool Bath by the fact that the latter is drained and cleaned after each use. It has no filtration system and is not chemically treated.



Capacity and Bathing Load of Spa Pools

Each type of spa pool will have been designed to contain a maximum number of bathers at any one time. The recommendations are that a minimum surface area of 0.37 m^2 (4 sq ft) and a minimum of 0.25 m^3 (55 gallons) of water be provided for each bather.

It is also important to ensure that the maximum bathing load (number of bathers using the spa per hour) is not exceeded.

Filtration

The most efficient type of filter for a spa is the high rate sand filter. This can handle between 2 and 20 gallons of water per minute per square foot of filter area. A particle size for the sand of 0.40 to 0.55 mm and effective distribution is critical for proper operation of this type of filter.

Alternatively a Diatomaceous Earth (DE) filter system may be used – see Filtration page 9.

In both cases above, body oils and cosmetics removed from the bathers by the warm water accompanied by aeration, collect on the filter media. With sand filters, backwashing does not remove all of the oil coating and gradually all of the sand particles become coated, until oil passes straight through and a slight milkiness is imparted in the water. Regular, annual sand changes will prevent this from happening.

In domestic spas, cartridge filters are popular – see Filtration page 9. In these cases the fabric filaments become coated with oil until they are saturated, at which point the oils pass through, again imparting a slight milkiness in the water. The filter element is removed and cleaned with a proprietary cleaner after which it is suitable for re use.

Chemical Treatment

In a spa the increased temperature and turbulence causes chemical losses from the surface. Chlorine is more volatile, has a higher vapour pressure than say bromine and so is lost more rapidly. However it works faster than bromine and the response time after dosing is quicker. Bromine is often favoured despite this as it is more stable in hot water and is easier to handle – see Bromine page 19.

It is favoured particularly in light usage spas, whereas in heavily used facilities chlorine is more popular.

Spa water can gain combined chlorines very rapidly and the use of ozone is proving popular in keeping these under control. In addition ozone also acts as a flocculant so the overall effect is a very much improved water quality. Ozone is also used with bromine to give very efficient usage of the disinfectant – the ozone oxidises the spent bromine back to useful bromine.

UV treatment is also useful in spas. The continuous UV disinfection helps to ensure safe spa water by destroying bacteria and other organic pollutants, but a small residual of chlorine or bromine must be maintained in the water at all times.

Dosing Levels

As a general guide where chlorine-based disinfectants are used (without ozone), a free chlorine level of 3 to 5 mg/l should be maintained in the spa water.

In the case of bromine related disinfectants, a level of 4 to 6 mg/l of total or active bromine should be maintained.

Where ozone is used in addition to chlorination, free chlorine levels still need to be maintained above 1 mg/l and ideally between 2 and 3 mg/l to ensure adequate disinfection.

Water Balance (see also page 48)

If bather safety and comfort is to be guaranteed, water balance, as well as the correct level of disinfectant, must be maintained in spa water at all times.

The total alkalinity level is probably the most important parameter to control after the disinfectant.

When the air-blower is running, the spa water loses carbon dioxide causing the pH to rise, which in turn causes the alkalinity to fall. In medium to heavily used spas it is useful to have a programmable dosing pump to add regular amounts of sodium bicarbonate solution. This should maintain the alkalinity and in turn help stabilise the pH level.

Operational Criteria

Turnover rate for spas is expressed in minutes and is calculated from the following equation :

$$\text{Turnover rate (minutes)} = \frac{\text{Gallons of water in spa}}{\text{Flow rate in GPM}}$$

A proper turnover time is essential to ensure good water quality. A suggested ideal turnover time is less than 15 minutes for Residential and 6 minutes for Commercial Spas, even with light to moderate bather loads.

An industry standard in the UK requires that spa water is changed whenever the number of bathers equals half the spa capacity in gallons e.g. for a 500 gall (2.3 m²) spa, the water should be changed after every 250 users. For an average bathing load of 12 people per hour for 10 hours a day, this would mean dumping every 2 days. The filter backwashing usually coincides with water dumping since it takes most of the water to properly backwash the filter anyway. For Domestic Spas, we advise that there is full Water Replacement every 3 months no matter how little usage.

A system for continuous dilution of the water by means of a controlled valve to waste is useful and prevents water from becoming stale and over used – giving high TDS.

Although European Standards recommend 30 litres per bather this may not be practical and an easier system to work to would be a complete change of water every working day unless there is a very light bathing load.

Indicative parameters for domestic spas and hot tubs

| EN 17125 Parameter (extract) | Value |
|--|------------|
| pH-value | 6,8 to 7,6 |
| Free active chlorine (without cyanuric acid) in mg/l | 0,3 to 1,5 |
| Free chlorine used in combination with cyanuric acid in mg/l | 1,0 to 4,0 |
| Cyanuric acid in mg/L | max. 100 |
| Bromine in mg/l | 2,0 to 4,0 |



Water Testing Equipment and Methods

Notes on Sampling

It is very important that a representative sample of the pool or spa water is taken for analysis so

- always take the sample from the same place. This is generally best at the furthest point from the return to the pool of the freshly disinfected, filtered water.
- take the sample from approximately 300 mm below the surface and slightly away from the side of the pool.
- always rinse the sample container several times with the water before taking the sample for testing.

Colorimetric Analysis

This method of water analysis is by far the oldest and simplest way of determining the concentrations of anions and cations in water.

In its applications to swimming pool and spa water analysis it was established well over half a century ago that by adding a selective reagent to a sample of water a colour was produced, the intensity of which was proportional to the concentration of chlorine in the water.

Calibrated colour standards were produced, some in transparent plastic material, others in glass, against which the coloured test solution was matched to give the result of the analysis.

These two systems are still in use today with the plastic colour standards usually in the cheaper, less robust, test kits, while the glass colour standards tend to be in the better designed, professional kits developed for public pools and leisure complexes.

It is with this latter type, the chemically produced glass standards, which we at Lovibond® are primarily concerned and we have been producing these for the pool market for over 60 years at the Tintometer factory. Coupled with the well known Lovibond® Comparator the glass filter discs have been developed to suit changes in reagent types and formulations to give the greatest visual sensitivity in colourimetric water analysis.

The Lovibond® Comparator system has been continually updated and improved so that now it brings to the operator probably the best all-round features for accurate visual analysis :

- accurately calibrated glass colour standards, guaranteed non- fading even under extreme conditions.
- a Comparator unit which accepts discs, cassette-style, ensuring very perfect location every time and which has an in-built optical prism unit to bring the two fields of view – test solution and glass colour standard – adjacent to each other for accurate colour matching.
- a complete reagent system based on tablets. These have been shown to be the most reliable and consistent in reagent preparations.

An important point worth mentioning and often overlooked by operators is that for accurate results to be obtained when using this type of equipment, the correct lighting conditions should be used.

It is recommended that in the Northern Hemisphere, North daylight is used and in the Southern Hemisphere, South daylight. If these are not possible, or testing is being carried out during the hours of darkness, a Lovibond® Lighting Cabinet should be used – either portable or mains operated. These give a simulated daylight illumination and are preferred over ordinary tungsten or fluorescent lights which can cause errors.

Photometric Analysis

Modern technology has brought the field of electronics to pool water testing and the use of portable photometers is becoming widespread.

These are instruments which pass a beam of light through the coloured test solution onto a photodetector. The intensity of the light collected is then converted, by the microelectronics, into a value of concentration which appears in a digital display.

Hence, in this method of analysis, there is no colour matching for the operator to do, and providing the test procedure is followed exactly and some very important factors are noted, photometers can give very accurate test results.

These factors are :

- the correct type of reagent is used – special photometer grades of tablets are often specified.
- the reagent must be completely dissolved with no particles floating in the test cell.
- there must be no bubbles adhering to the inside walls of the test cell.
- the test cell must be dry on the outside with no finger marks on the glass.
- the cell compartment itself must be kept clean and dry.



Electrochemical Methods

Redox Potential (ORP)

Redox is a term for an electronic measurement to assess the state of balance between the oxidised and reduced states of a substance. In a pool, this is usually chlorine and the measurement is in millivolts (mV). The mV reading is known as the **redox potential**. It is not a measure of the concentration of the oxidised or reduced forms of the chlorine but indicates the state of the reaction.

An increase in the mV reading indicates an increase in the concentration of the oxidising substance (free chlorine) but the reading is not related directly to the free chlorine concentration.

Redox controllers are used only to give a qualitative estimate of free chlorine – a reading of around 700 mV would indicate approximately 1 mg/l – and so give a useful indication of how water quality is affected by bather load.

Redox response is not linear however and the response levels off rapidly above about 1.5 mg/l of free chlorine

Redox response is very sensitive to pH changes and unless the pH is finely controlled redox is very imprecise in control applications. The response of redox electrodes is relatively slow after start-up – often in the region of 20 minutes, so time must be allowed for the reading to stabilise.

When redox units are in operation, it is important that the electrodes are maintained and cleaned on a regular basis. To do this the electrode is taken out and impurities removed mechanically. The electrode must then be recalibrated using a special redox calibration solution, rinsed then replaced.

Manual testing of the pool water for free chlorine remains important.

Amperometric

This is form of electrochemical measurement and is concerned with the determination of the concentration of free chlorine as hypochlorous acid – as mentioned before this is the “active” form of free chlorine. Other methods measure both hypochlorous acid HOCl and hypochlorite ion OCl⁻.

Amperometric analysers form the basis of automatic controllers in large pools as they can accurately control the level of hypochlorous acid in the water. Further more the response time of the sensors is rapid ensuring a minimum of delay in adjusting the level of disinfectant.

Amperometric controllers are much more sensitive and prone to external interference than redox controllers. They actually measure a small current flow which is proportional to the number of chlorine atoms discharged at the operating electrode in the cell. Any changes in the conductivity of the water will affect this and in a spa pool particularly unless the important parameters of alkalinity and pH are controlled along with some form of continuous dilution, an amperometric system can become very unbalanced and inaccurate.

Chlorine

OTO (ortho-tolidine)

Ortho Tolidine (OTO) has been used as a colorimetric reagent for chlorine for many decades. It is simple to use and produces an instant yellow colour with chlorine. However, as knowledge was gained on the mechanism of the chlorine disinfection process and the fact that there is more than one kind of chlorine residual, the chemistry of OTO was examined:



- DANGER: POISON
- SEVERE SKIN & EYE IRRITANT
- CAUSES CANCER

Research suggested that when testing water samples at normal pool temperatures the result indicated by OTO was that for total residual chlorine i.e. free available chlorine plus combined chlorine (chlorine which has combined with ammonia to form chloramines).

Recently however, by far the most damning feature of OTO is its toxicity. In Europe in the 1970's its use became restricted when it was categorised within a group of aromatic amines which are suspected of being carcinogenic (causing cancer). Workers handling them since then have been subject to regular medical inspections and the use of OTO in the swimming pool industry has been actively discouraged – its use in many countries is prohibited.



REACH (European chemical legislation concerning the Registration, Evaluation, Authorisation & restriction of Chemicals) is mandatory legislation applying to all member states of the European Community. OTO has been classified to be a group 1B carcinogen. That means it is suspected to cause cancer and is listed in Annex XVII of the REACH regulation.

A listing in Annex XVII means any product that contains OTO (> 0,1 %) may only be sold in the EU to professional users for the purpose of research and development. Even then special safety requirements must be fulfilled.

DPD in accordance to EN ISO 7393-2 standard

The EN ISO 7393-2 standard outlines an established way of checking chlorine values by measuring changes in the depth of colour of DPD (N,N-dialkyl-1,4-Phenyldiamine). These changes are detected by visual colour comparison or photometric measurement. Generally, this is known as the DPD method for the analysis of free chlorine.

To ensure accurate results it is vital that the analysis is carried out correctly and in strict compliance with the ISO standard. What does this imply and how does this relate to commercially available DPD 1 products?

In effect, the ISO standard describes the fundamental components of chlorine determination with DPD:

- 1) A phosphate buffer ensures that the pH value of the sample remains constantly between 6.2-6.5 in order to ensure full colour development
- 2) DPD sulphate should be used as the indicator.
- 3) Potassium iodide is used as the secondary reagent for the determination of total chlorine.

Standardized determination

The standard sets out how these components must be produced as liquids and also covers the use of custom, ready-to-use reagents in the form of a powder or tablet. The preface to this standard explicitly highlights that, if the custom reagent does not follow these regulations, end results may vary. End users should therefore ensure that their chosen reagent has been produced according to the requirements of the standard.

For many years, the combination of a buffer and DPD (as DPD 1 reagent) and DPD (with potassium iodide as DPD 3 reagent) has established itself as an international standard due to its wide commercial availability.

In the market, DPD 1 and DPD 3 are used as liquid, tablet or powder reagents. To comply with the standard, the DPD reagents must ensure long durability and exact dosage with the addition of non-interfering additives. Producers of these reagents must guarantee that their products also meet the requirements of EN ISO 7393-2.



Titration shows differences

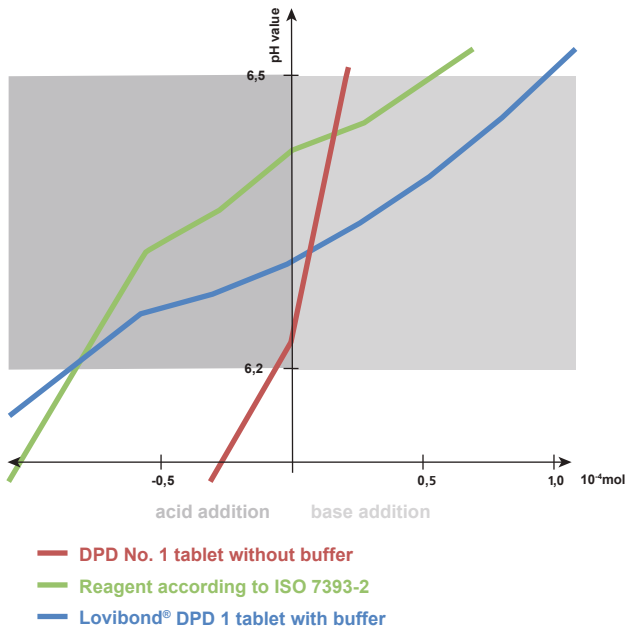
The titration curves of various commercially available reagents demonstrate whether or not the buffer system complies with the standard EN ISO 7393-2. The buffer is supposed to ensure a stable pH value for both acid and alkaline salt concentrations and, therefore, minimise incorrect measurements.

By adding acid or alkaline solution during a titration experiment the pH value is measured. The buffer ensures that any changes in pH value are minor. A steep curve, indicating a strong change of the pH value, indicates an insufficient buffer system.

Where insufficient buffer is indicated, incorrect measurement caused by slightly deviating pH values in the water is most likely to occur. Results are unreliable and do not comply with the requirements of the standard.

If a reagent can tolerate the addition of acid and alkaline solutions, the range for accurate chlorine determination is wider.

A missing buffer system is therefore a major quality defect and might lead to unreliable and incorrect results. End users are recommended to ensure their supply of DPD 1 reagent complies with International Standards.



DPD (N, N-dialkyl-1,4-phenylene diamine)

Thankfully a satisfactory, safe alternative to OTO was introduced in the late 1950's by Dr.A.T.Palin in England who found that the reagent NN Diethyl-p-Phenylene Diamine Sulphate could be used to selectively produce a colour with free available chlorine. We all know this reagent today as DPD and it has become accepted in many National and International Standards for drinking water analysis. It follows then that it is eminently suitable for monitoring swimming pool water.

The reagent itself is commonly available in three different forms: as a liquid, as a tablet or as powder.

With DPD in solution, care must be taken in storage as it deteriorates on exposure to light. In addition, it is only stable in acid solution, so a separate reagent consisting of an alkaline buffer solution must be used with it to ensure that the correct pH is produced in the test solution (6.2 - 6.5) for the full intensity of colour (red) to be developed.

The most popular form of the reagent with pool operators is when it is supplied in the form of tablets. These are packed in aluminium foil giving them a long shelf life, and this, together with production techniques ensuring accuracy in formulation, makes the product a most reliable and consistent test reagent.



Green chemistry

All Lovibond® reagents for Pool & Spa water testing are free from boric acid. The European Union (EU) has classified boric acid as a dangerous substance. The Lovibond® DPD No. 1 tablets also guarantee compliance with the buffering effect required by the standard.



Advantages of Tablet Reagents over liquids are:

- ease of handling
- ease of dosing – one per test
- long shelf life
- no storage problems



Liquids



Tablets



Powder

DPD test (mechanism)

There are two DPD tablets which are regularly used in swimming pool and spa water analysis:

- DPD No.1 – measures free available chlorine,
- DPD No.3 – used in conjunction with the No. 1 tablet and measures the total Residual Chlorine from which the combined chlorine is calculated.

Free Available Chlorine (sample preparation)

The DPD No. 1 tablet, gives a colour which is specific for free chlorine, and this colour is measured either colorimetrically or photometrically:

A clean test cell is rinsed with the water to be tested and is left empty.

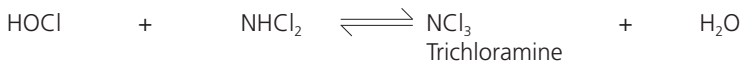
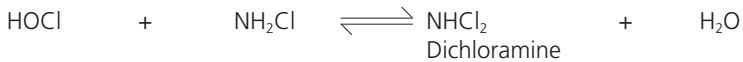
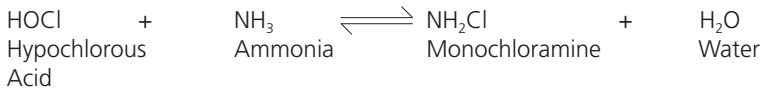
A DPD No. 1 tablet is added and crushed with a clean stirring rod. The water sample is then added and the cell is filled to the 10 ml mark.

The solution is mixed well with the stirring rod until the tablet has completely dissolved. The lid is put on the cell.

The colour must then be measured immediately to determine the free chlorine content of the water in mg/l (ppm).

Combined Chlorine (sample preparation)

This is the general name given to the derivatives of chlorine which are produced when free chlorine reacts with nitrogen compounds like ammonia and urea from bathers.



These are the products of the chlorine reactions which are responsible for most of the complaints from bathers of skin and eye irritation.

Trichloramine, more commonly called nitrogen trichloride, produced in the last reaction, is an unstable compound and being volatile comes off the surface of a pool as a gas with a nauseous odour. In addition, it is an extremely severe eye irritant. The chemical reaction does not proceed to completion at pH values above 5 so usually only very small amounts, if any are produced.

The two chloramines we are most concerned with are monochloramine and dichloramine. In the DPD test they are usually determined together using the DPD No.3 tablet :

The cell containing the dissolved DPD No.1 tablet – from the free chlorine test – is removed from the instrument and a DPD No. 3 tablet is added to it and mixed to dissolve with the stirring rod. The cell is allowed to **stand for 2 minutes** for complete reaction of the combined chlorine (monochloramine and dichloramine).

The cell is then replaced in the instrument and the colour is measured again. The result is total chlorine in mg/l.

To obtain the result for combined chlorine apply the following equation :

Combined Chlorine = Total Chlorine - Free Chlorine

Important Note : The DPD No.3 tablet contains potassium iodide which even in minute traces will cause a reaction from the combined chlorine present in the sample. It is essential that test cells and lids are thoroughly rinsed after using this tablet before another free chlorine test is carried out otherwise a false reading for free chlorine will be obtained.

To eliminate this problem some operators prefer to use separate cells for the free chlorine test and the total chlorine test, transferring the liquid from the free chlorine cell into another clean cell to which the DPD No.3 tablet is added, thus avoiding any iodide contamination of the first cell.

Interpretation of Results

The reading for free chlorine (HOCl and OCl^-) is the most important of all the pool tests. The general recommendation is for at least 1 mg/l of free chlorine to be present at all times in the water (more, if Cyanuric Acid is used: see page 17).

In addition it is also important that the ratio of the concentration of free chlorine to combined chlorine is at least 2:1. For example if the free chlorine concentration is 1.5 mg/l the combined chlorine concentration should be 0.75 mg/l or less.

In spa pools, with elevated temperatures, high turbulence and possible high organic loading from heavy usage, a free chlorine residual of 3 – 5 mg/l should be maintained.

In all cases it is desirable that the combined chlorine concentration should be below 1 mg/l if practically possible.

Bromine

The test for bromine is very similar to that for chlorine in that it uses the DPD No. 1 tablet.

Where it differs is that in the bromine test, the tablet not only responds to free bromine but also to any combined bromine – bromamines – which may be present. As discussed before, these compounds are good disinfectants in their own right, unlike the chloramines which have very little disinfecting power.

We therefore say that the DPD No.1 test is measuring total bromine or active bromine.

Levels of bromine as measured by the DPD No.1 tablet should be between 4 and 6 mg/l. This applies in pools as well as spas. The test procedure is as follows:

A clean test cell is rinsed with the water to be tested and is left empty.

A DPD No.1 tablet is added and crushed with a clean stirring rod. The water sample is then added and the cell is filled to the 10 ml mark.

The solution is mixed well with the stirring rod until the tablet has completely dissolved and the lid is then put on the cell.

The colour produced is then measured to determine the concentration of total bromine in mg/l.

Although it is not strictly necessary to monitor the build-up of combined bromine on a day to day basis, it is a good idea to occasionally separate the total bromine into free and combined as, like with chlorine. It is desirable to have a ratio of free to combined of at least 2:1. This is carried out with the use of a DPD Nitrite tablet: Prepare a clean cell and crush a DPD No.1 tablet in the bottom of it – leave it empty of water.

Rinse out another cell, then fill to the 10 ml mark with water sample, and add a DPD Nitrite tablet.

Crush and mix to dissolve with a clean stirring rod.

Add the contents of the cell to the empty cell containing the crushed DPD No.1 tablet. Mix well to dissolve the tablet particles.

Measure the colour produced which gives the concentration of combined bromine in mg/l.

To obtain the concentration of free bromine subtract the result for combined bromine from that for total bromine.

pH-Value

As we have seen pH measurement and control is essential in any pool or spa to maintain the value within the desired range. For heavily used pools, the pH value should be measured continuously and adjusted automatically, for other pools it is sufficient to measure the pH value regularly and adjust it if necessary .

pH measurements in these cases are by colorimetric indicator and the one which is used world-wide is Phenolred.

This has a good colour change from yellow to red over the pH range 6.8 – 8.4 which makes it ideal for the monitoring of pool and spa water, which should be around the middle of this range.

Testing can be carried out with phenol red tablets or liquid, but in the case of the latter it is necessary to use a separate dechlorinating/debrominating liquid to prevent the disinfectant reacting with the indicator and changing it's colour. The tableted reagent has this dechlorinator/debrominator as an ingredient in the formulation. Phenol red in tablet form is also much more stable than the liquid and is easier to use:

A freshly rinsed cell is filled to the 10 ml mark and a phenol red tablet is added. This is crushed and mixed thoroughly to dissolve, using clean stirring rod.

The colour produced is matched either visually or in a photometer to give the pH value of the sample.

Note. If the colour produced is purple when testing a brominated water sample this is usually an indication that the bromine concentration is above 10 mg/l

For disinfectants based on chlorine to work properly and efficiently the pH value of the pool or spa water is critical. The normal recommendation is that the pH value should be maintained at between 6.8 and 7.6 (EN 16713).

For pools and spas using bromine-based disinfectants a wider pH range is acceptable – 6.8 to 7.8. This is due to the fact that the efficiency of the disinfection is maintained over this range.

Total Alkalinity

Alkalinity at levels below 50 mg/l may cause "pH bounce" which means large changes in pH value in response to changes in dosing levels of disinfectant and/or pH correction chemicals.

To prevent this, the level of alkalinity in a pool or spa should be based on the type of disinfectant in use :

| | |
|-----------------------------------|----------------|
| Chlorine gas disinfection | 180 – 200 mg/l |
| Sodium hypochlorite disinfection | 120 – 150 mg/l |
| Calcium hypochlorite disinfection | 80 – 120 mg/l |

To raise total alkalinity the addition of sodium bicarbonate is required – 1.5 kg per 50 m³ (11.000 gall) will raise TA by 15 mg/l..

If too high – over 200 mg/l - use sodium bisulphate – 2.4 kg per 50 m³ (11.000 gall) reduces TA by 20 mg/l.

ALTERNATIVELY

10 litres of 15% hydrochloric acid (muriatic acid) reduces TA by 20 mg/l.

The test for TA is quite straightforward using either liquid reagents in a drop test method or with tablet reagents in a tablet-count method.

In the liquid method a few drops of a colorimetric indicator is added to a measured volume of sample. Titrant is now added dropwise, until the indicator changes colour. The number of drops of titrant used are counted and a simple calculation gives the total alkalinity in mg/l as CaCO₃.

A much simpler method is to use Lovibond® Total Alkalinity tablets. These are added one at a time to a 50 ml volume of the pool or spa water. The colour produced initially is yellow which changes to bright red at the end-point. The number of tablets used is counted and the following formula is applied :

$$(\text{No of tablets} \times 40) - 20 = \text{Total Alkalinity in mg/l CaCO}_3$$

If more precision is needed the volume of sample can be doubled to 100 ml when the formula becomes :

$$(\text{No of tablets} \times 20) - 10 = \text{Total Alkalinity in mg/l CaCO}_3$$

Calcium Hardness

If the Calcium Hardness in a pool is below say 70 mg/l as CaCO_3 the water is likely to be corrosive to the pool structure and have a "calcium demand". Ideally the level should be raised to at least 200 mg/l by the addition of calcium chloride flake – 1.5 kg added to each 50 m³ (11.000 gall) of pool water will raise the calcium hardness by 20mg/l.

The test for the level of calcium hardness can be photometric but is more usually carried out by the tablet-count method :

Lovibond® Calcium Hardness tablets are added one at a time to a 50 ml volume of the pool or spa water. The colour produced initially is pink which changes to purple at the end-point. The number of tablets used is counted and the following formula is applied:

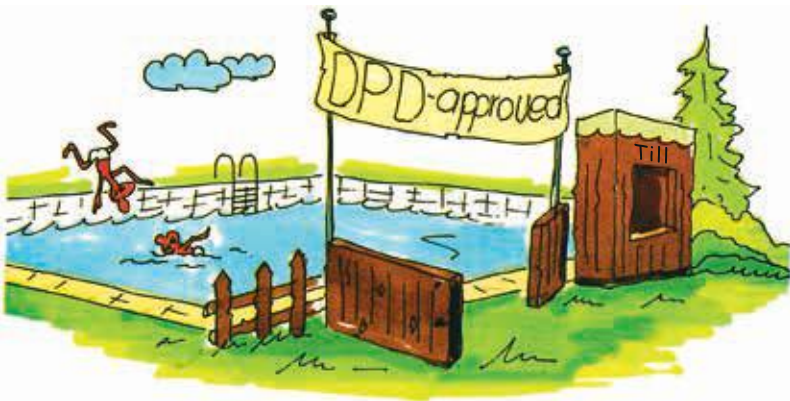
(No of tablets x 40) – 20 = Calcium Hardness in mg/l CaCO_3

Ozone

Ozone is a toxic gas and consequently in larger installations in particular, it must be removed from the water before it is returned to the pool after treatment.

However in spa pools, small amounts are generated to combat the oxidisable products which are produced – combined chlorines etc. which means that ozone rarely gets back into the spa itself. In any case the concentration of ozone in the atmosphere above spa pool water should not exceed 0.1 ppm.

The test for ozone in water can be carried out using the DPD method.



DPD Method for Ozone

- Ozone in the absence of residual chlorine or bromine:
Rinse a cell with sample and leave empty.
Add either [one DPD No.1 tablet and one DPD No.3 tablet], or (one DPD No. 4 tablet) and crush with a clean stirring rod.
Add the water sample to the 10 ml mark and mix gently with the stirring rod to dissolve the tablet(s).
Match the colour produced either colorimetrically or photometrically and record the reading as residual ozone in mg/l – call this reading A.
- Ozone in the presence of residual chlorine or bromine.
The above procedure is followed and the reading now corresponds to ozone plus total residual chlorine or bromine.
The second procedure is as follows;
Rinse the test cell thoroughly then fill to the 10 ml mark.
Add one DPD Glycine tablet, crush and mix to dissolve with the clean stirring rod.
Rinse a second cell with sample and then leave empty.
Add either [one DPD No.1 tablet and one DPD No.3 tablet], or (one DPD No. 4 tablet) and crush with the stirring rod.
Add to this cell the solution in the first cell and mix thoroughly to dissolve the tablet(s).
Match the colour produced either colorimetrically or photometrically and record the reading as total chlorine or bromine in terms of ozone in mg/l – call this reading B.
To obtain the ozone concentration subtract reading B from reading A.

Chloride

In pools running continuously on sodium hypochlorite disinfection, the build up of chloride can become a problem. In addition pH correction using hydrochloric acid (muriatic acid) will add chloride to the water.

High chloride levels can impart a salty taste to the water as well as giving poor colour and clarity. Levels are acceptable up to about 1000 mg/l and can be reduced by regular backwashing of the filters and/or adding fresh water.

Obviously the level of chloride will be a lot higher than 1000 mg/l for a pool running on salt for the electrolytic generation of chlorine. In this case the chloride concentration is about 2500 mg/l as Cl or 4000 mg/l as NaCl.

Testing for chloride is a simple procedure using Lovibond® Chloride tablets in a tablet-count method.

For a range of 0 – 1000 mg/l as Cl measure a 10 ml sample of water into a clean container and add about 40 ml of chloride-free water (deionised).

Add one Chloride test tablet and shake to dissolve. The solution will go yellow.

Continue adding tablets one at a time until the colour finally goes brown. Count the total number of tablets used and apply the formula:

$(\text{No. of tablets} \times 100) - 100 = \text{chloride in mg/l Cl}$

For a range of 0 – 5000 mg/l as Cl measure a 2 ml sample into a clean container and add about 40 ml of chloride-free water (deionised).

Add one Chloride test tablet and proceed as above. Finally apply the formula:

$(\text{No. of tablets} \times 500) - 500 = \text{chloride in mg/l Cl}$

To convert the result to mg/l sodium chloride NaCl multiply by 1.6.



Sulphate

It is becoming increasingly apparent that high sulphate levels can cause severe damage in concrete pools by attacking cement-based materials. In tiled pools sulphate attacks the tile grouting causing crumbling and expansion of the cement. This ultimately may result in tiles falling off the pool wall and floor.

Sulphate is introduced into the water from the use of sodium bisulphate (dry acid) for pH correction and from the use of aluminium sulphate as a flocculant. The problem is most likely to be found in heavily used pools using alkaline chlorine donors like calcium or sodium hypochlorite.

A maximum recommended level for sulphate in pool water is 360 mg/l. It can only be reduced by dumping some of the water and refilling with fresh.

A simple turbidimetric method is available for monitoring sulphate levels where a tablet reagent is added to the water sample in a special double-tube assembly. Any sulphate present will produce a cloudy solution which is measured by moving the inner tube until a black spot printed on its base just disappears from view. The result is then read off from a scale on the side of the outer tube.

This tube assembly is also used for the turbidimetric Cyanuric Acid test.

Cyanuric Acid (Stabilizer)

(see also page 17 & 18)

The presence of cyanuric acid in pool water results from the use of chlorinated isocyanurates as disinfectants – see page 17.

In the process of disinfection, the chlorine becomes used up but the cyanuric acid molecule remains, and over time can build up to such a concentration as to cause what is popularly known as Chlorine-lock in the pool.

Chlorine-lock usually occurs when the concentration of cyanuric acid in the pool water reaches levels of 150 mg/l and above. The water itself looks dull and lifeless and perhaps has a greenish tint and yet the DPD No.1 test for free chlorine still shows a good result – the water has become "over-stabilised" and the chlorine is locked in.

Hot weather and extended periods of drought with perhaps water rationing promote elevated levels of cyanuric acid in pools treated with chlorinated isocyanurates.

A level of 30 – 50 mg/l is satisfactory for stabilisation and should the level rise to above 100 mg/l it is advisable to reduce it by dumping some of the water and topping up with fresh.

It may be necessary to shock-dose the pool with free chlorine to kill any algae growth which may have appeared. In this case it is important to use either Sodium or Calcium Hypochlorite not more of the stabilised chlorine (Di-Chlor or Tri-Chlor).

A simple turbidimetric method is available for monitoring cyanuric acid levels; alternatively a low cost photometer is available which carries the test along with chlorine and pH.

The turbidimetric test is as follows;

The tablet reagent is added to the water sample in a special double-tube assembly. Any cyanuric acid present will produce a cloudy solution which is measured by moving the inner tube until a black spot printed on its base just disappears from view. The result is then read off from a scale on the side of the outer tube.

Total Dissolved Solids (TDS)

The Total Dissolved Solids content of pool and spa water is a measure of the total quantity of solid material dissolved in it.

In mains water this comprises of hardness and other natural salts and the level will depend on the source of supply, but is within the region of 50 – 500 mg/l

The TDS level will gradually increase in a pool due to evaporation and concentration of hardness salts, impurities introduced by the natural elements, wind and rain, and the chemicals added to the water as part of the treatment process – chlorides and sulphates for example.

The real value of TDS measurement is that it can indicate whether too many chemicals have been added as a result of heavy bather load or lack of dilution and the water is becoming "stale".

It should be monitored by comparison between the pool and the mains feed water to the pool. TDS should ideally not be allowed to rise more than 1000 mg/l above the feed water, up to a maximum of 3000 mg/l

Should it become necessary to reduce the TDS level, this is carried out by replacing some of the water in the pool with fresh water. In some pools a satisfactory TDS level can be maintained by regular backwashing of the filters.

Measurement is by electronic meter which is really taking a conductivity reading of the water and applying an internal factor to display the TDS in mg/l.

Balanced Water (Langelier Index)

When a water is in balance, it is said to be neither corrosive nor scale-forming. In other words, it will not deposit a layer of calcium scale neither will it dissolve an existing layer of scale.

For most well run pools, the water will be in balance if the pH value is kept within the recommended range, but other factors should be taken into account which can affect the condition of the water. These are the total alkalinity, the calcium hardness, the TDS content and lastly, the temperature of the water. The concentration of chlorine or bromine do not appear in the Balanced Water Calculation. The formula for determining whether the water is balanced was developed by Langelier in the 1930's, hence the result after applying this is often called the Langelier Index or the Langelier Saturation Index or simply the Balanced Water Calculation.

Why is the balance so important? Because if it is not correct, corrosion and erosion are possible.

There are 3 main causes of corrosion and erosion;

- Galvanic attack
- Aggressive water
- Low calcium hardness.

Galvanic attack occurs when two or more dissimilar metals are in close proximity in a water environment (pool or spa) which contains high levels of chemical salts or TDS. The presence of chlorides encourages the water to be more conductive. To prevent this the TDS can be reduced or the level of calcium hardness raised so that a thin layer of scale is laid down to inhibit the metal's efficiency as an electrode. Lower levels of chlorides will prevent the water from acting as an electrolyte.

Low calcium hardness will often result in the loss of grout around the tiles, as the water tries to satisfy its need for calcium.

It is necessary therefore to maintain the TDS at sensible levels (ideally no more than 1000 mg/l above the feed water) and yet maintain an adequate level of calcium hardness in the water (around 200 mg/l minimum).

The formula for calculating the Langelier Index is as follows :

$$\text{pH} + \text{Temperature factor} + \text{Alkalinity factor} + \text{Calcium Hardness factor} - \text{TDS factor}$$

And is applied using the table below to obtain the factors from the actual test results for Total Alkalinity, Calcium Hardness and TDS.

| Temperature | | T.F. | Calcium Hardness mg/l as CaCO ₃ | C.F. | Total Alkalinity mg/l as CaCO ₃ | A.F. | Total Dissolved Solids mg/l | Factor |
|-------------|-----|------|--|------|--|------|--------------------------------|--------|
| °C | °F | | | | | | | |
| 0 | 32 | 0.0 | 5 | 0.3 | 5 | 0.7 | 0 | 12.0 |
| 3 | 37 | 0.1 | 25 | 1.0 | 25 | 1.4 | - | - |
| 8 | 46 | 0.2 | 50 | 1.3 | 50 | 1.7 | 1000 | 12.1 |
| 12 | 53 | 0.3 | 75 | 1.5 | 75 | 1.9 | - | - |
| 16 | 60 | 0.4 | 100 | 1.6 | 100 | 2.0 | 2000 | 12.2 |
| 19 | 66 | 0.5 | 150 | 1.8 | 125 | 2.1 | - | - |
| 24 | 76 | 0.6 | 200 | 1.9 | 150 | 2.2 | 3000 | 12.25 |
| 29 | 84 | 0.7 | 250 | 2.0 | 200 | 2.3 | - | - |
| 34 | 94 | 0.8 | 300 | 2.1 | 300 | 2.5 | 4000 | 12.3 |
| 41 | 105 | 0.9 | 400 | 2.2 | 400 | 2.6 | - | - |
| 53 | 128 | 1.0 | 600 | 2.35 | 800 | 2.9 | 5000 | 12.35 |
| - | - | - | 800 | 2.5 | 1000 | 3.0 | - | - |
| - | - | - | 1000 | 2.6 | - | - | 6000 | 12.4 |

In practical terms an Index Value in the region of zero to + 0.3 is considered satisfactory i.e. a low positive result, which indicates that the water can lay down a thin layer of protective scale.

| Example: | Langelier calculation: |
|-----------------------------|------------------------|
| pH = 7.5 | 7,5 |
| Temperature = 29 C° (84° F) | f 0,7 |
| Total alkalinity = 100 | f 2,0 |
| Calcium hardness = 300 | f 2,1 |
| TDS = 1100 | subtract: f 12,1 |
| | Total = + 0,2 |

A high Total Alkalinity is no compensation for a low Calcium Hardness. Each parameter should be within its recommended range.

Additional Water Balance Considerations

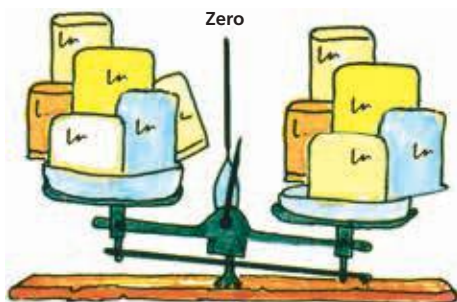
- In soft water areas where the constant addition of calcium is necessary to maintain a calcium level above the minimum, it could be advantageous to use calcium hypochlorite as the chlorine donor in order to obtain the calcium in addition to the chlorine from this product.

Also where the natural total alkalinity is low, the use of carbon dioxide gas for pH correction with calcium hypochlorite would be advantageous to produce an increase in the total alkalinity.

- In hard water areas where it may be difficult to reduce total alkalinity and pH to the recommended range, the use of hydrochloric acid (muriatic acid) may be necessary and it may be appropriate to operate with a total alkalinity of around 140 – 150 mg/l.

- Balance = Corrosive

- Low pH
- Low Alkalinity
- Low Calcium Hardness
- Low TDS
- Low Temperature



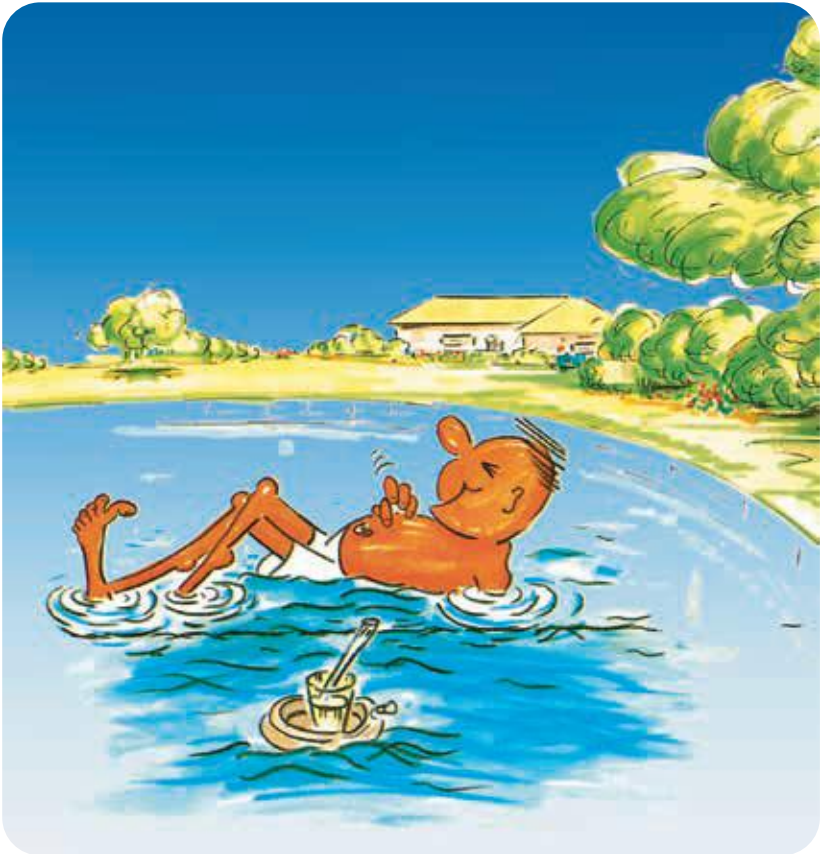
+ Balance = Scale Forming

- High pH
- High Alkalinity
- High Calcium Hardness
- High TDS
- High Temperature

Operational Problems

| Problem | Possible cause | Treatment |
|---|---|--|
| Pool water going green | No stabilizer in pool – sunlight dissipating disinfectant | Check disinfectant level and add stabilizer if necessary |
| | OR | |
| | High Cyanuric acid level (Chlorine lock) | Dilute with fresh water to reduce cyanuric acid to recommended level |
| Algal growth in pool | Inadequate disinfectant level | Ensure disinfectant level is adequate throughout pool – use algicide |
| Water dull - lifeless | TDS too high (High chloride level) | Check and reduce TDS by dilution if necessary |
| | High Cyanuric Acid level (Chlorine lock) | Check and reduce cyanuric acid if necessary |
| Salty taste in water | TDS too high | Check and adjust by dilution |
| | High Chloride level | Check and adjust by dilution |
| Cloudy water | Heavy bather load overloading the filtration system | Reduce bather load check filters |
| | High pH | Check and adjust pH |
| | High Alkalinity | Check and adjust Alkalinity |
| Signs of erosion of grout between tiles | Calcium Hardness too low | Check and adjust |
| | pH too low | Check and adjust |

| Problem | Possible Cause | Treatment |
|---|--|--|
| | High Sulphate level | Check and reduce to 360 mg/l if necessary |
| pH erratic | Low Alkalinity | Check and adjust |
| pH difficult to adjust | High Alkalinity | Check and reduce if necessary |
| Complaints of Smarting eyes and skin irritation | pH outside recommended range | Check and adjust pH |
| | Free chlorine low Combined Chlorine too high | Check and adjust Check and adjust by dilution |
| | Allergy to disinfectant | If individual try another Pool with different disinfectant |
| pH difficult to adjust | High Alkalinity | Check and reduce if necessary |



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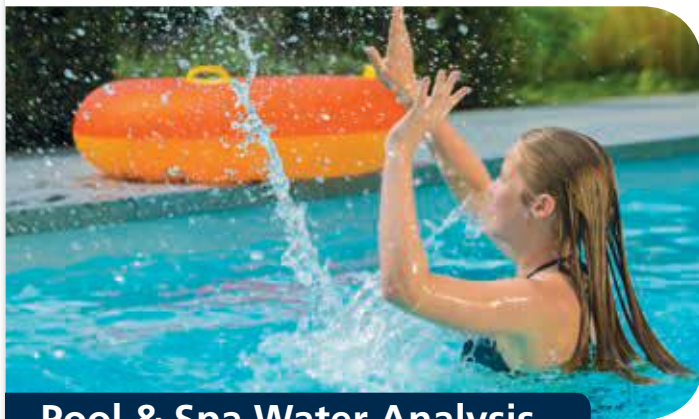


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