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INFO SHEET

Performance Through
Technology and Service

Delving into Pool Water Chemistry at Depth!

1. Introduction

Why is it important to routinely test pool water? The answer is simple: the state of water in a pool can be unpredictable and chaotic when it is not properly managed. The water itself is an unruly element. This liquid comes with a whole list of demands from the very day the tap is turned on. When water is added to a constructed hole in the ground, it will enter with either the need to consume or unpack. Immediate action is required to control the potential chaos coming from the very existence of water.

This is a combination of articles by leading people in the USA and AU pool industry and is designed to give added depth to your understanding of the issues seen most days, in pools everywhere.

2. Calcium

Calcium (Ca) is the primary ingredient water has a hankering for. When water is hungry due to lack of sufficient calcium, it goes on the hunt to find it. In a plaster or aggregate pool, it will seek its food in the material of the surface. Plaster and other cementitious surfaces have plenty of calcium. To keep the integrity of the surface, a minimum amount of a calcium additive, such as calcium chloride ($CaCl_2$), must be added. The minimum calcium to start must be 150 parts per million (ppm). To ensure this, a calcium hardness test is required.

Before adding any water to a newly surfaced pool, the source should be tested for calcium. One should never wait until the pool is filled before testing for calcium levels as it could lead to aggressive fill water taking calcium from the surface while the pool is being filled. There are startup systems which allow owners to add calcium as their pool fills to prevent any of it from being taken from the surface.

The ideal level of calcium for plaster pools (Pebblecrete and Marblesheen) is 350 ppm. For vinyl liner, painted and fibreglass, it is 250 ppm. If the pool is in a hard water area, the source should be tested first as well. Hard water contains high amounts of calcium.

This will unpack what it cannot hold in the form of a calcium carbonate ($CaCO_3$) scale, this makes it even more important to perform a calcium hardness test of source water before filling a pool.

3. Water Balance

Next comes water balance, and the two important tests for it are total alkalinity (TA) and pH.

Service professionals address TA first because it is the buffer for pH. Primarily, it acts as a buffer to prevent pH from decreasing while also slowing its increase. To obtain a true carbonate alkalinity reading, any amount of cyanuric acid (CYA) must be determined and considered as one-third of the TA reading. For example, a CYA reading of 60 ppm should be divided by three. The resulting number is then subtracted from the TA test, and the result is the true carbonate alkalinity.

For example, if a TA test results in 120 ppm and the CYA comes out as 60 ppm, then one-third of 60 ppm is 20 ppm. Subtracting the TA of 120 ppm minus CYA 20 ppm determines a carbonate alkalinity of 100 ppm.

A pH test is a measurement of the presence or lack of hydrogen in water.

Hydrogen lowers the pH, and it comes from the addition of pool acid—also known as hydrochloric acid (HCl). It is important to note the "H," which stands for hydrogen. Every time acid is added, hydrogen increases, which means the pH is decreasing. Lack of hydrogen causes the pH to increase.

One way to decrease hydrogen is by aerating the water. Forcing air into the pool water causes carbon dioxide (CO_2) to off gas and leave rapidly. When this happens, more hydrogen is consumed, and the pH goes up.

4. pH and more.

One should never wait until the pool is filled before testing for calcium levels as it could lead to aggressive fill water taking calcium from the surface.

Today's modern pools tend to run high on pH due to the increased aeration from negative edge, waterfalls, fountains, and various other water turbulence-prone features. The ideal pH level to achieve is 7.5. Minimising the time of running features which causes aeration and increasing acid can help as well.

It is important to maintain pH within pool standards. Some effects of allowing a **high** pH

(with pH over 7.8) are:

- Lack of disinfection
- Scale formation and metal staining
- Cloudy water
- Low oxidation-reduction potential (ORP)

HITCHINS TECHNOLOGIES PTY LTD ACN 119 448 501, **Postal:** PO Box 3186, Bonnells Bay NSW 2264, Australia
Phone: 1300 8879 20 Fax: 1300 8879 21 web: www.poolpaint.com.au Email: info@poolpaint.com.au

Contrastingly, **low** pH can lead to:

(with pH lower 7) are:

- Corrosion
- Etching of plaster
- Staining
- Damage to vinyl liner and fibreglass

TA and pH are two crucial tests that must be performed routinely. For the best results, service professionals should use a digital photometer to test.

5. Types of Chlorine

There are many sorts of chlorine present in pool water at any given time. When it comes to the efficacious treatment of the water, there are three main tests:

- Total chlorine (TC)
- Free chlorine (FC), which should range between 2 to 4 ppm
- Combined chlorine (CC), which should range between 0 to 0.2 ppm

Total chlorine (TC) test

TC is a measurement of both FC and CC. The test can indicate the presence of chlorine in the water, but it cannot tell how much FC or CC is present. Relying on a TC test when trying to maintain water quality is ineffective. An orthotolidine (OTO) test method for determining whether the water in the pool is safe or not is ineffective as well. OTO only indicates if there is chlorine present—it cannot determine what form of chlorine is most prevalent. Therefore, it is important to have a way to test for both TC and FC.

Free chlorine (FC) test

FC is the test experts focus on the most. It consists of two main constituents, hypochlorous acid (HOCl) and hypochlorite ion (OCl-). When chlorine is added to pool water, it creates HOCl. This molecule can kill 99 per cent germs and algae. Contact with water causes some HOCl to disassociate into hydrogen (H+) and OCl-, the latter is an ion with only one per cent ability to kill germs and algae.

Together HOCl and OCl- make up FC. The standard recommendation for FC is 2 to 4 ppm. The FC test measures both HOCl and OCl-; however, the test cannot tell the percentage of either in the water. Since the primary purpose for chlorine is to keep the water safe from germs and algae, the highest per cent of FC should be HOCl.

The most effective way to produce the highest per cent of HOCl is by maintaining the pH and temperature of the water. The lower the pH and water temperature, the more HOCl is produced, which is good. The higher the pH and water temperature, the less HOCl and more OCl- is produced, which is bad.

At a pH of 7.5 and water temperature at 20 C (68 F), 55 per cent of HOCl is produced. At a pH of 8.0 and water temperature at 30 C (86 F), HOCl goes down to 24 per cent. Water temperature cannot always be controlled in the summer, which is good enough reason to run the pH slightly lower in the hot season. Pool owners can also produce 55 per cent HOCl in water with a temperature of 30 C (86 F), by adjusting pH down to 7.4.

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Combined chlorine (CC) test

CC is another way of saying chloramines. This chlorine is combined with contaminants in the water to form a nitrogen-bound chlorine. It is a poor disinfectant for pools and leads to irritating chlorine gas odours, particularly in indoor pools. Therefore, it is vital to test both TC and FC. By doing so, the level of CC in the water is determined. Subtracting FC from TC gives the number for CC in the pool. The ideal level of CC in pools is zero; the maximum acceptable level is 0.4 ppm. A more preferred level is no more than 0.2 ppm.

One test method used to measure both FC and CC down to 0.2 ppm is a FAS-DPD test. There is also a photometric test for determining TC, FC, and CC. For the safety of swimmers, and to keep algae from growing, it is vital to know what type of chlorine is dominant in the pool water.

6. Total Dissolved Solids (TDS) test

TDS is a test which is often overlooked but is key for the overall quality of pool water. The test is a measurement of all byproducts which have accumulated during the life of the water. Water is a great absorber and holder of micron-sized particulates, such as calcium, salts, phosphates, metals, and various other tiny solids. However, water becomes oversaturated from high TDS. When the level of solids reaches the point where water can no longer absorb, it starts doing the opposite.

This will occur by persistently cloudy water, scale formation, and decreased sanitiser efficiency. Testing for TDS routinely, or at least seasonally, is one of the most vital tests to perform.

While most standards do not give the maximum amount of TDS, it is recommended it should not exceed 1500* ppm over the start-up water. Should this occur, the efficiency of chlorine is reduced by 50 per cent. This means it will take 50 per cent more chlorine to properly sanitise the pool water. TDS tests are usually performed with electronic or digital meters, which are a worthwhile investment for any pool service provider.

(* Non salt water chlorinated pools)

Today’s modern pools tend to run high on pH (Alkaline) due to the increased aeration from negative edge, waterfalls, fountains, and various other water turbulence-prone features.

Some other tests that may prove beneficial in the management of pool water are nitrates, phosphates, and metal tests for copper or iron. Both nitrates and phosphates are two key nutrients for algae. Testing and managing of these key nutrients in pool water is vital to keep algae blooms from appearing at times when sanitiser levels may drift low. Tests which reveal the presence of metal are paramount, especially at start-up time, and the presence of any metal such as copper or iron should ideally be addressed with the use of a metal chelator or sequestering agent before sanitisers are introduced into the pool water. If metals are not removed or sequestered, staining can occur when sanitisers are added to the water or as a result of the pH drifting up or down.

All in all, it is crucial to be proactive in managing pools, and proper testing of both the pool and source water cannot be overstated.

From Terry Arko of Hasa Pool

7. Saltwater chlorinated pools

The salt used in swimming pools in Australia (and NZ) in conjunction with a saltwater chlorinator, is mostly from salt pans, where sea water is evaporated. The resultant crystals are usually washed, crushed and dried and bagged. They are sold in pool shops. This is NOT food grade salt.

The resultant sea salt is industrial grade and is acceptable for pools. Being a naturally occurring product, the sea water contains many inorganic elements and ions. Some are removed in the washing but not all. The composition includes ions of; chloride, sodium, magnesium, sulphate, calcium, potassium. Inorganic bromide, boron, strontium and fluoride, make up much of the rest. There are other compounds such as inorganic phosphorus, and nitrogen. Depending on other factors such as the effect of river floods and flows, underwater volcanic eruptions and the ocean currents and the locations of the sea water intakes for the salt pans, you can get a wide range of unknown compounds.

Fortunately, the sodium and the chloride are the most prevalent and are used to create the chlorine needed for water purity, via the electrolytic cell.
Here the salt water is electrically charged, and splits the salt molecules and generates chlorine, which provides the hygiene of the pool water. However, within the highly charged cell, other compounds are generated including calcium carbonate (scale) and other lesser compounds depending on the composition of the salt used in the pool.

Some of these "new" compounds, created as a byproduct of the generation of chlorine, are not very soluble. Over time, and as concentration increases with added salt and the variation in pool water chemistry and temperature, they drop out of solution. The water has lost its ability to keep this insoluble material suspended, it's lost its "buoyancy" in effect. This may happen gradually or even overnight. Often it seems when autumn gives way to winter and cooler water temperatures but will not be noted till springtime when getting the pool ready for the swimming season. It's usually evidenced by cloudy water, a whitish film on all – most wet pool surfaces and maybe a blotchy look over the surface with a whitish coloration. Rubbing the pool surface may create swirls of "chalk" dust in the water. It may also leave blotchy white stains in the splash zone and on surrounding pavers etc.

Treatment is not difficult if caught early but left untreated can create a very hard to remove residue on the pool surfaces.

Once noted it is best to consult your favourite pool shop for a flocculent. (flocking agent) Note there are 2 types, Aluminium Sulphate (Alum) and Synthetic Polymer. You can start with either and it may work or need a follow up treatment a week later with the other type, to finish the job. Follow directions for use carefully for effective results.
Keep an eye out for this situation coming back every now and then.

Back to basics: Choosing the right clarifier

Cleanliness and crystal-blue pool water is always the goal for a pool owner, and specialty retailers and service technicians strive to make sure an inviting pool is always achieved during the hot summer months.

Sometimes, however, events transpire that can create cloudy pool water. Therefore, it is imperative the cause of this water quality problem is properly diagnosed as it is crucial to solving the source of the cloudiness. In most cases, it is a result of improper filtration, insufficient water circulation or flowrate, and poor chemistry. Even early stages of algae growth can cloud the water.

Further, environmental events such as wind or rainstorms, nearby plant life, and even swimmers bring undesirable contaminants into the pool water. With adequate sanitisation, oxidation, and proper water balance, many issues can be removed or avoided entirely. These tiny particles scatter readily and give water a hazy, murky appearance; however, having the client answer a few key questions can help ensure the right solution is used to solve the problem quickly and get the pool water looking crystal clear again.

Diagnosing the problem

If one notices cloudy pool water, the chemical balance needs to be tested. Low sanitiser residuals or a high pH can be the cause of the problem and it can be easily addressed. In fact, this is a common issue with saltwater pools, which often struggle with an elevated pH. As chlorine is created in the electrolytic cell, sodium hydroxide also forms and drives pH up. As a result, these pools may encounter water-clouding scale from either calcium carbonate or calcium phosphate if the pH is not addressed in a timely manner. Correcting the water chemistry might be sufficient to restore the pristine water but, in some cases, the filter just needs a little help.

When cloudy water is observed, the first thing to check is the filtration system. Some types, such as diatomaceous earth (DE) or cartridge, filter more efficiently than standard silica sand. Maintaining a proper flowrate is one of the most important facets to not only keep water clear, but to be sure sanitizer is adequately circulated throughout the pool.

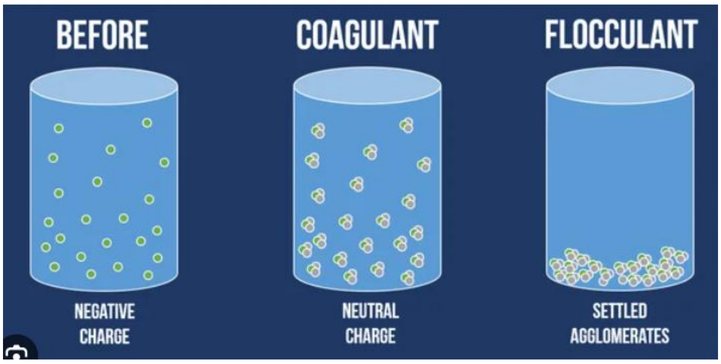
To check this, service techs must first inspect the filter pressure gauge to be sure it is working properly. Most pool filters will operate normally between 69 and 138 kPa (10 and 20 psi); therefore, it is important to verify it does not rise higher than 69 kPa (10 psi) above the normal operating pressure. If the pressure gauge is working properly, a service tech should place their hand in front of the pool return to feel the water pressure. If it feels weak, it is a good sign the filter should be inspected.

Something as simple as replacing or cleaning the filter media might be enough to re-establish the proper flowrate. If the issue does not appear to be related to a soiled or improperly working filter, it might just be the contaminants are too small for the sand, cartridge, or DE filter media to capture and, as a result, they keep getting circulated through the water. In the event of a cracked lateral or damaged filter manifold, filter media will recirculate back out and deposit onto the pool floor.

Treating with clarifiers

When pools are not equipped with skimmers, keeping the water clear will be quite difficult

If it has been determined there are no apparent issues with water balance or equipment, a service tech should consider using a clarifying agent. There are many options available in the water clarifier category, and with so many to choose from, making a decision can be overwhelming. In many cases, pool care experts such as dealers or service technicians are expected to be able to resolve these issues as quickly as possible. Understanding the technologies and chemistries available can help pool experts make the most informed recommendation for each particular water quality issue.



Most pool chemical companies commonly offer clarifiers that may either be synthetic or ‘natural’ polymeric coagulants. These popular clarifiers are positively charged, or cationic. Most of the cloudy water causing particulates have negative, or anionic, charges. Chitosan or synthetic polymer-based clarifiers help bind the microscopic particles together so they can form one large chain that can be captured by the filter. These typically have smaller treatment doses and are often used more for maintenance purposes than as a troubleshooter. Dosages of 29.5 to 59 ml per 20,000 L are the most common measurements one is likely to see. Polymeric clarifiers often require less physical maintenance than other methods may need and are good for pools that cannot be effectively vacuumed. These types of products often work best when the problem is observed early on. While effective and treatments are easy, some can take up to 48 hours to restore water clarity. Another drawback is that for some clarifiers, it is quite important for service techs not to over-apply the product. An overdose of a synthetic polymer can actually make a water-quality issue worse.

Maybe a flocculant is the right way to go.

Flocculants, typically an aluminium-based material such as aluminium sulphate (alum) or poly-aluminium chloride (PAC), work by bridging together large amounts of particulate to help them drop to the bottom of the pool to be easily removed by the vacuum. Flocculants are often poured directly down the skimmer, which enables it to be distributed throughout the pool quicker. Some require minor adjustments to the water’s chemical balance to maximise efficiency.

Flocculants are often useful after an algaecide treatment, and to remove dirt particles that have been blown into the pool after a major storm. They are also ideal for use in pools that have poor circulation, as flocculants, in many cases, have a much quicker turnaround since they often work overnight. Although they do require a bit of legwork for consumers or service technicians, flocculants show results in just a few hours. The major drawback with these is they are dependent on the type of filter the pool owner has (*e.g.* those that are able to be vacuumed to waste such as sand or some DE filters). Vacuuming such a large amount of debris through the filter can overload the media and, in some cases, even damage cartridges. Since vacuuming to waste will require water replacement, a flocculant may not be the right strategy in areas or times where water usage is restricted.

When should one try filter media?

Sometimes, the filter media itself is not sufficient in grabbing tinier particles. While sand filters are common and perfectly fine to use, this media is not as efficient in capturing smaller particle sizes that cartridge or DE filters can.

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In fact, cellulose and even DE can be highly efficient at clearing up a cloudy pool. Some cellulose products are modified to have a charge to enhance the ability of capturing particulate. These filtration aids are applied similarly to flocculants, down the skimmer to allow the product to form an additional layer atop the filter sand, DE, or cartridge. That said, a pool with at least one skimmer is critical to it working. These have a universal appeal, as they are not only useful in filtering out smaller organic debris, they can also capture surface staining metals such as copper, iron, or manganese. When these products are applied, they settle into a layer on top of the sand bed, providing another layer where debris can be captured. How much is applied depends on the square footage of the filter's filtration area. If either DE or cellulose is added to aid a sand filter, thorough backwashing is required once the filter pressure rises significantly. It is important for service techs to always read and follow label directions for the product, as well as manufacturer's directions for any equipment.

Multi-functional products

There are many products that fall under a 'multi-functional' category such as oxidising agents, dual-action phosphate, or contaminant removers. Most pool water clarifier options are liquid, but contaminant removal technologies are also available in solid forms. Some of the liquid clarifiers might be highly concentrated and require pre-dilution, others can just be broadcast over the water surface, while others may recommend super chlorination. Often, chlorinating shock products may even contain built-in clarifiers to aid in filtration. Many service technicians even use water clarifiers as a part of their weekly maintenance. It is usually more cost-efficient to prevent problems rather than resolve them.

Phosphate levels increase over time, especially when it is present in the source water or after adding certain chelating/sequestering products. Other ways it can enter is through fertilizers, skin, dead bacteria, or even bather waste. In saltwater pools, cloudy water can form in scale-inducing environments where the saturation index is too high due to hard water, high pH, and high total alkalinity. While some believe orthophosphate is the cause of cloudy water, it is generally not the case. When orthophosphate is high in concentration, it can bind with calcium and create problem-causing calcium phosphate scale. While cloudy water is an unfortunate side effect, greater problems can present themselves. For example, scale formation on an electrolytic cell can be quite damaging. Phosphate remover can react very quickly in the water as the lanthanum reacts with calcium carbonate and calcium phosphate, forming an insoluble compound that can either be removed by the filter or vacuuming. Phosphate removers are also filtration aids and may contain additional components used to either enhance filtration from either a polymeric or polyaluminum clarifier, surfactants, and often enzymes to break down body oils. Most phosphate removers contain a lanthanum compound—either lanthanum chloride or lanthanum sulphate. As some of the phosphate is being removed via the filter, the clarifying agents in these multi-action products continuously aid other contaminants or tiny particles as well.

Pool type/structure

Water clarity can even vary based on a pool's design. Further, the number of returns, skimmers, and even the size of the filter in relation to the volume of water in the pool can be impactful. Above-ground pools come in many different variations, sizes, and shapes. Some types, for instance, will often use a one-size-fits-all pump and cartridge filter combination, one return, and sometimes, not even a skimmer. When pools are not equipped with skimmers, keeping the water clear will be quite difficult.

For some service techs, picking the right treatment for a cloudy pool can be overwhelming. However, when one is able to pinpoint the cause and take some of the pool's other 'quirks' into consideration, deciding on the appropriate treatment can be a breeze.

From Emily Johnson of BioLab Inc

8. It's all in the salt: why quality pool salt is better for your pool

From **Pool & Spa Magazine**, Wednesday, May 1, 2013

Different products impact pool water differently and finding the right combination of quality products is the key to maintaining a healthy pool. Salt is the primary ingredient in keeping saltwater pools healthy and operating effectively, but it's not as simple as adding any type of salt to your clients' pool water.

Salt is required for electrolysis to take place in the electrolytic chlorine generator (salt chlorinator) to produce chlorine that sanitises the water. The right amount of salt allows the salt chlorinator to produce enough chlorine to help keep the pool healthy and fight algae and other bacteria.

Using poor quality salts or putting in incorrect levels of salt into your pool (either too high or too low) can impact this process and damage salt chlorinator equipment. Some of the common problems associated with poor quality pool salts includes staining, scale and increased chlorine demand. Organic contaminants found in pool salts are the number one cause of common water problems like cloudy water or increased chlorine demand. Also, inorganic contaminants usually affect water clarity, dissolution rate and other water health factors.

What is good quality pool salt?

All salt crystals used for pools contain sodium chloride (NaCl), but it's the level and type of contaminants that are embedded within the salt crystals that determines its quality and this usually depends on where the raw material was originally sourced. In Australia, pool salt is produced in a number of ways including mining and mechanically or naturally evaporating it from saltwater lakes.

One of our major salt suppliers has solar salt fields on coastlines and large inland lakes in Queensland, New South Wales, Victoria and South Australia that rely heavily on a natural evaporative process to create salt. Cheetham Salt pumps seawater into shallow ponds and as the sun and the wind evaporate the water, the solution is slowly guided through a series of ponds and finally into a thick layer of salt on the crystalliser floor. It is then harvested, crushed, washed and screened into specific particle sizes and packaged to suit the needs of the end customer. Because the salt crystals have been crushed and refined, a lot of the impurities (or contaminants) are removed to ensure a high-quality product for pool use.

Identifying good quality pool salts

Sometimes pool salt with contaminants or impurities has characteristics that can be immediately recognised. These include shape and colour of the salt crystals and the impact they have on pool water when added. Below are some tips on how to identify poor quality pool salts.

• Finely crushed: pool salts should almost appear like table salt as this means they have been refined to remove impurities. It doesn't always mean the salt is 100 percent pure, but the processing and cleaning of the salt before it is packaged helps to remove contaminants.

• Irregular shape: chunky, irregular shaped salt crystals are usually a sign of salt with contaminants and impurities embedded within. Uniform cubic shape salt crystals are purer and make it a better choice for pools.

• Labels: professionals in the pool care industry should always use salt specifically produced for pools. Other types of salt can contain additives that affect the efficiency of the chlorinator.

• Colour of the salt: pool salt that is snow white in colour is better quality as it is more refined and purified. Off-white pool salt often indicates impurities and poor quality.

• Water discolouration: if by adding salt the colour of the pool water changes, this is a sign of inorganic contaminants such as metals being present.

Solving common water quality issues

Using poor quality salt in your pool can lead to staining and scaling on your pool surface. It can do the same to the inside of your pool equipment, thus increasing the wear and tear and lessening the lifespan of your equipment. Using a quality pool salt will lower the risk of these problems.

• Calcium scale: scaling can be identified by the visibility of white or grey chalky matter on pool walls, floors or equipment and if chlorine levels become difficult to maintain. It is perhaps the most damaging as it also affects the effectiveness and lifespan of the chlorinator. Scaling can also be hazardous for pool users, especially young children as it can be harsh on skin. Scaling can be treated and removed with diluted hydrochloric acid and, once it is removed, prevent it returning in the future by maintaining proper water balance.

• Staining: early signs of staining as a result of poor-quality pool salts can be identified by minor streaking on pool walls and discolouration of the water. Although it doesn't harm swimmers, scaling detracts from the overall appearance of the pool and ultimately damages it. Stains can usually be treated with products containing citric, absorbic or sulfamic acids. Removing dissolved stain-causing metals from pool salt can usually be accomplished with filter aids.

• Chlorine demand: when the amount of chlorine produced by the chlorinator can't overcome high levels of contaminants in the water, chlorine demand or "cloudy water" occurs. This can be caused by bather load or trees and plants debris and is also often caused when impure pool salt is first added to pool water. Cloudy water can be treated with filter aids and cleaning the pool filter.

• Slow dissolution: the amount of time and brushing needed to completely dissolve salt is an indicator of salt quality. If salt remains on the pool surface too long while it dissolves it may lead to weakening the plaster surface and cause staining and etching, so it's important to make sure that the salt is completely dissolved. Fine salt crystals generally dissolve faster and more effectively.

Maintaining a healthy saltwater pool

On top of choosing high quality pool salts, there are several other factors that affect the water health of a pool including maintaining the water balance and chemical balance to assist the pool equipment in processing the salt to chlorine and lengthen the lifespan of the equipment. A good quality salt chlorinator will also produce more chlorine for a longer period of time and ultimately have a longer lifespan.

It is also important to consider appropriate maintenance and treatment products without phosphates or sulphates for saltwater pools. Products containing sulphates and phosphates that are not formulated for salt water can cause scaling and early algae formation. Products to look out for are products that contain anti-scale and anti-stain agents which are proven to work in saltwater pools. Poolwerx has partnered with industry experts to maintain a high quality product that provide clients with the best treatment for their saltwater pools and guarantees a healthy and long-lasting swimming pool.

Some important points to take into consideration:

• Quality pool salt is a key factor in keeping saltwater pools healthy.

• Poor quality salt can produce several problems in a saltwater pool including staining, scale and increase in chlorine demand.

• Pool salt crystals can vary in shape and colour and quality can be immediately identified based on the impact of salt on pool water.

• Products to look out for are products that contain anti-scale and anti-stain agents which are proven to work in saltwater pools.

World Salt Production is currently 280 million tonnes per annum. China is the world's largest producer followed by the United States. Australian salt production is 12 million tonnes with around 90% exported. Salt around the world is produced by one of three technologies:

- solar evaporation of sea water or underground brine
- mining rock salt
- solution mining of underground salt deposits and subsequent evaporation.

Solar Salt is produced from either sea water or underground brine. The water or brine source contains a range of dissolved salts including common sodium chloride.

The ionic composition of sea water is as follows:

55.1%	Chloride (Cl^-)
30.6%	Sodium (Na^+)
7.7%	Sulfate ($SO4^{2-}$)
3.7%	Magnesium ($Mg2^+$)
1.2%	Calcium (Ca^{2+})
1.1%	Potassium (K^+)
0.4%	Bicarbonate (HCO^{3-})
0.2%	Bromide (Br^-)
0.1%	Borate ($BO3^{3-}$)

The input water (brine or groundwater) is pumped into evaporation ponds where water is evaporated through the action of the sun and wind. As the salt water or brine solution concentrates, it reaches a point where the dissolved salts start precipitating out of solution. The salt then crystallises out of solution based upon their solubility. Solar salt field operators manage the brine to ensure that a high proportion of the sodium chloride salt is deposited in crystalliser pans. The quantity of salt that can be produced varies based upon the input water concentration, area of ponds, evaporation and rainfall. The deposited salt is normally harvested annually.

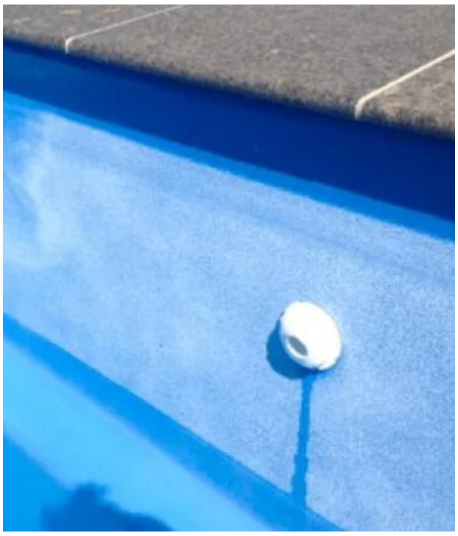
9. Analysing Three Types of Scale

Maintaining proper water balance is the key to keeping the pool water clear and surfaces scale-free. It is important to consider all forms of scale, but the focus should be on the one most likely to occur. Years of research, along with basic scientific principles, confirms that calcium carbonate usually is the primary culprit and should be the focus of pool professionals.

If calcium hardness is too high, precipitation can occur, which can cause cloudy water or scale on surfaces. The reason for placing an upper limit on calcium hardness is so that calcium-based minerals do not precipitate from solution.

It is important to distinguish between precipitation (or insolubility) and actual scale formation. Scale is adherence to a surface. Just because something precipitates or is somewhat insoluble does not mean that it will adhere. In addition, different types of scale have different crystal structures and their formation is influenced by different factors. While calcium carbonate is the most common, three types of calcium-based scale will be discussed. These include calcium carbonate, calcium phosphate and calcium sulphate.

Calcium carbonate scale



Calcium carbonate scale is driven by high pH. Other factors that contribute to its formation include high temperature (in part, because the carbon dioxide is more volatile) and high calcium or carbonate concentrations in the water.

An increase in temperature causes increased molecular motion. This simply means that all the molecules move around much faster. Because the calcium and carbonate are moving faster, they are more likely to bump into each other causing them to form a bond.

Another side effect of increased temperature is a decrease on carbon dioxide (CO2) concentration. A decrease in carbon dioxide concentration will cause the reaction to move to the right which also promotes the formation of scale. Another way of looking at this is that higher temperature promotes dehydration.

An increase in pH causes bicarbonate ions (HCO3-) to dissociate. This means the bicarbonate tends to dissociate into hydrogen (H+) and carbonate (CO3-2). The higher availability of the carbonate ion makes scale more likely to form.

Lastly, the more calcium and carbonate that is available in the water, the more likely these are to come into contact with each other and form scale.

Calcium phosphate scale

It is important to remember that there is always a much higher level of carbonate than phosphate in pool water. Even in what some would consider a high phosphate pool (1,000 – 2,000ppb), it is still a very low level compared to carbonate. For example, 2,000ppb is only 2ppm. There is typically well over 100ppm of carbonate in the water. Because reactions are often “competitions” between two species, the one with the higher concentration tends to react faster. Of course, the use of a phosphate remover can drive the level lower, but it starts out very low compared to carbonate.

More importantly though, calcium phosphate scale is not driven by high pH because it is not part of the carbonate equilibrium. Calcium phosphate is not very soluble in water and a precipitate can form quickly. It is important to note again, however, that the formation of a precipitate does not necessarily mean that it will adhere (form scale). Listed below are the possible locations where precipitation, then adherence, could take place.

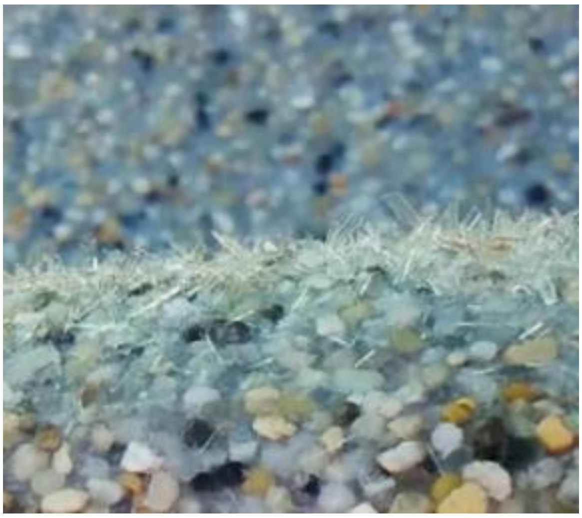
Main body of water — as mentioned, calcium phosphate is not very soluble and will precipitate fairly quickly. With the filtration system running, this material will usually be captured on the filter bed and removed with routine cleaning. It will be trapped in the filter easier if using a water clarifier. So, with proper filtration and filter cleaning, the precipitation in the bulk of the water is not really a problem as it never has a chance to settle out.

Heater — calcium phosphate will tend to deposit on warm surfaces. However, adherence also is affected by shear (or turbulence). Shear significantly reduces the chance for adherence. Because the most efficient heat transfer is with turbulent flow, the likelihood of calcium phosphate depositing on a heating element is low due to the high level of shear inside the heater.

Chlorine generator cell — calcium phosphate scale is not caused by high pH. Therefore, calcium phosphate is no more likely to form on a chlorine generator cell plate than anywhere else in the pool. There may be small amounts of calcium phosphate on cell plates, but analysis of dirty cells has confirmed that the vast majority of scale is, in fact, calcium carbonate.

Calcium sulphate scale

This type of scale is driven by the concentration of calcium and sulphate in the water.



Scientists use parameters such as solubility constants for specific compounds to predict which material is likely to stay in solution and which will precipitate. The solubility constant for calcium sulphate indicates that this compound is the least likely type of scale to form. In the unlikely scenario that the calcium and sulphate levels did reach the high concentration required, the precipitation process is different from that of calcium carbonate and calcium phosphate. In the case of calcium sulphate, the rate of crystal growth is extremely fast. So, the material “crashes out” of the water very quickly. Essentially, it’s an all or nothing process.

This is known as a super saturated solution, where crystal growth is faster than the initial crystal formation (nucleation). Once the water reaches the saturation point, it all falls out of solution. It is not a slow crystal growth process like other types of scale. For example, a pool operator would not see a slow build on a surface such as a chlorine generator plate, but rather all the material coming out of solution coating multiple surfaces all at once.

From Karen Rigsby Bio Lab USA

10. Understanding Calcium Hardness

Calcium hardness must be actively managed—along with pH and total alkalinity—to keep water in proper chemical balance. Current industry standards call for maintaining calcium hardness in the ideal range of 200–400 ppm in pools and 150–250 ppm in spas.

The Role of Calcium Hardness in Water Balance

While hardness in water consists of both calcium and magnesium salts ("total hardness"), only the calcium component is relevant in the water balance calculation for pools and spas. Called the Saturation Index (SI) formula, it considers the interrelationships of four chemical factors—calcium hardness; pH; total alkalinity, as corrected for the contribution of any cyanuric acid stabilizer in use; and, to a much lesser extent, the total dissolved solids level—plus one physical factor, water temperature. All but the mathletes among us use a water balance calculator like Taylor Technologies' Watergram® to do the number crunching involved. The value one arrives at reflects the water's degree of saturation with calcium carbonate.

When the SI value is zero, the water is properly balanced. Its calcium hardness, pH, and total alkalinity are acting in harmony with one another. When the SI is +0.5 or more, the unbalanced water is trending toward scaling, meaning conditions are right for calcium carbonate to come out of solution and deposit on surfaces as "scale." When the SI is -0.3 or less, the unbalanced water is trending toward corrosivity. Corrosive water attacks plaster, concrete, grout, and metal, resulting in etching, pitting, and surface stains and/or colored water caused by metal pulled out of piping, fittings, and equipment.

Can damage from scaling water be reversed? By reducing the SI to around -1.0 for a short time (usually by lowering pH), some calcium deposits in the filter and circulation piping can be dissolved, and the water's flow may even remove chunks of loosened scale. But this will come at a price. A thin layer of the concrete surface of the pool may dissolve as well, and copper can be lost from piping and/or heat exchangers.

Damage from corrosive water cannot be reversed, only repaired by resurfacing the concrete and replacing piping. Colored water can be cured with a "metal out" product, or chelating agent, and some of these are reportedly successful at removing certain surface stains.

The Effects of High and Low Hardness

Specifically, water with high calcium hardness gets cloudy unless the alkalinity and/or pH are low enough to compensate. As mentioned, the excess calcium carbonate will precipitate as crusty, greyish white scale on surfaces, piping, and equipment. It's unsightly, can cause abrasions on users and snag bathing suits, and makes a good anchor for microorganisms. It will clog filters. When it builds up in piping, circulation is reduced, and pressure increases. Scaling is an especially acute problem in heaters because calcium's solubility is inversely proportional to temperature: As temperature increases, less calcium is able to stay dissolved. Scale on the pipes or coils acts as an insulator, slowing heat transfer. This makes it more expensive to heat the water. Over time, thick scale will cause a heater to fail.

Water with low calcium hardness will seek more by dissolving it from surfaces it comes in contact with that contain calcium, such as plaster, grout, and concrete decking. The late Dr. Neil Lowry, a well-respected instructor in our industry, preferred to call water with low calcium hardness "aggressive" rather than "corrosive" because the latter term implies the destruction of metals. The corrosiveness of unbalanced water, he would tell his students, comes from poorly maintained alkalinity and pH.

Calcium Hardness Too Low	Calcium Hardness Too High
• pitting of concrete pool surfaces	• cloudy water
• etching of plaster	• rough surfaces
• dissolving of grout	• clogged filters and reduced circulation through piping
• pitting of concrete pool deck	• heater inefficiency

Testing

To avoid damage to pools and spas from unbalanced water, test calcium hardness at least monthly.

Adjusting Hardness

You can raise water's calcium hardness easily by adding calcium chloride ($CaCl_2$). Two forms are sold: hydrated (77% strength) and anhydrous (100% strength). Each will generate heat when contact with water is made. Therefore, generally you are instructed NOT to pre-dissolve the calcium chloride in a bucket, but to broadcast it over the water's surface with the pump running. Adding calcium chloride in the hours before or after treating with soda ash (sodium carbonate) or baking soda (sodium bicarbonate) will result in cloudy water.

To decrease calcium hardness, you must partially drain the vessel and refill it with lower-hardness water. Unless pH and alkalinity are already low, however, it will often be more practical to adjust the Saturation Index by lowering these two factors through the addition of acid than to replace water. This would certainly be the case where drought has caused limits to be placed on water used for recreation.

From: Taylor Water Technologies LLC

WATER CHEMISTRY FOR CEMENT BASED ADHESIVES AND GROUTS IN TILED SWIMMING POOLS

Date: May 4th, 2020

INTRODUCTION AND SCOPE
The purpose of this bulletin is to provide an initial understanding of the effect some of the chemicals used in swimming pool water have on cement-based adhesives and grouts used with ceramic tile finishes. The traditional chemicals of concern are the Calcium based and the Sulphate based compounds that affect the mineralogy of the tile grouts and adhesives.
However, in recent times we have observed some unusual problems with cement-based grout in pools containing Magnesium Chloride (instead of normal salt – Sodium Chloride). We note also water treated with 'mineral salts' containing unusual trace elements.
While this bulletin is primarily related to tile finishes in immersed conditions, overflow and frequent wetting in the adjacent splash zones around pools may also show these effects.

CALCIUM HARDNESS
Hardness is said to be a measure of the Calcium and Magnesium dissolved in the water.
Pool water is said to be hard and non-aggressive when the Calcium level (expressed as Calcium Carbonate) exceeds, or can be maintained at over 200mg/L. In this situation Calcium is not leached from cement-based materials and the tile adhesives and grouts will remain in good condition.
Where the pool water has low (<90 mg/L) Calcium levels, it is said to be soft and aggressive towards cement-based materials. Calcium may be leached from the tile adhesives and grouts to such an extent that the grout is removed from joints between tiles and the tile adhesives may be weakened sufficiently to allow debonding of tiles.
High levels of Calcium may lead to lime scale (Calcium carbonate) deposits building up in the pool plumbing system. To prevent these deposits occurring, the pool water Calcium hardness levels have been recommended to be in the range 90 - 200 mg/L.

It has been noted that when the water has low Calcium hardness and low bicarbonate alkalinity levels, the pH value may still be high (indicating overall alkaline conditions) and the water is still aggressive to cement based products. This may be corrected by using a water treatment that adds Calcium salts to the water.

The chapter on Calcium hardness in GB65 - 1998 (see references) indicates that the water supply in most Australian cities is soft, except in Perth, Adelaide and some country areas. Melbourne water is said to be particularly soft. The importance of correctly maintaining the pool water chemistry should always include the Calcium and Sulphate chemistry.

THE SULPHATE EFFECT

The effects of soluble Sulphates on cement-based mortars and grouts are dependent on the Sulphate concentration. BS 5385.4 - 2015 states that the maximum permitted concentration of soluble Sulphates is 300 mg/L (expressed as SO_3 equivalent to 360 mg/L SO_4).

Sulphate weakens cement-based products by changing the original cement crystalline form to an expanded, mechanically weaker crystalline form. This leads to deterioration within the cement-based grouts as the expanded structure becomes more susceptible to chemical attack and physical stress.

Cement based products form strong bonds to the substrate and within adhesives and mortars by reacting (hydrating) with water and forming crystals that lock into the pores at the substrate (concrete) surface or interlock with each other in mortars and adhesives. These crystals may be considered as mechanical anchors and the bonding formed is very strong. Chemical alteration by the sulphates in the pool water changes these crystals to long thin needle-like shapes that are weaker than the original crystalline shapes.

Where both low concentrations of Calcium compounds and high concentrations of Sulphates occur, the corrosion effect is accelerated.

ACIDITY

The pH is a measure of the acidity or alkalinity of pool water and the ideal value is 7.5 with the normal range between 7.2 and 7.8. The scale ranges from 0 to 14 where acidic conditions are indicated at low values below 7, and alkaline conditions are indicated by high values above 7. The value 7 is set at the reading of pure water, which is said to be neutral, neither acidic nor alkaline. The pH may vary in a pool with the effects being sore eyes or itchiness, accelerated corrosion and possibly scale formation, reduced effectiveness of Chlorine sanitisers and increased cloudiness of the water, especially when the pH is below 6.8 or above 8.5.

The importance of the pool water pH is that it is an indicator of the pool quality and how some of the pool chemicals will be acting. To raise the pH, the procedure is to normally add Sodium Carbonate or Bi-Carbonate, and to lower the pH, add Sodium Bisulphate or Hydrochloric Acid. Repeated additions of the Bi-Sulphate will lead to the chemical attack on the cement-based adhesives and grouts previously noted above. However low levels of Calcium in the pool water are not indicated by the pH readings as previously noted.

MAGNESIUM AND OTHER ELEMENTS

ARDEX has noted that in recent times some pools are treated with minerals other than common salt (i.e. sea salt) as the source of Chloride for the effective action of the electrolytic converters to generate free Chlorine. Whilst these treatments won’t affect polymer shell pools to our knowledge, the “jury is out” on the effect they can have on cementitious grouts and adhesives.

HITCHINS TECHNOLOGIES PTY LTD ACN 119 448 501, **Postal:** PO Box 3186, Bonnells Bay NSW 2264, Australia
Phone: 1300 8879 20 Fax: 1300 8879 21 web: www.poolpaint.com.au Email: info@poolpaint.com.au

Magnesium
One type of mineral treatment uses Magnesium Chloride instead of, or with Sodium Chloride (common sea salt). The issue with Magnesium relates to its chemical similarity to Calcium in terms of compounds formed. The Magnesium substitutes for Calcium in minerals which form the hardened cement paste matrix, and this change results in weakening of the material. It is a recognised situation, that Magnesium salts can damage cementitious containing materials such as concrete (e.g. Sumsian & Guthrie 2013, Darwin et.al. 2007, Cody et.al. 1996, Mather 1964) and we have noted that pools containing high levels of Magnesium Chloride appear to be linked with several recent instances of powdery cement-based grout. In lieu of this apparent situation we recommend that non-cementitious R Class grout materials are used in pools treated in this way.

Boron
We note also that pool water can be treated with water chemicals containing compounds of Boron, sometimes as a pH buffer at a concentration of less than 200ppm, but for other claimed reasons too. It also has properties for ion exchange and reducing water hardness. Otherwise, this is uncommon element in normal household environments, and is probably best known for uses as a disinfectant, wood preservative, fire retardant and insecticide. However, it is common in the nuclear industry, and literature related to the compounds of this element in the nuclear waste industry (e.g. Coumes et.al. 2009, Kim et.al. 1992) suggest that Boron compounds inhibit the cure of Portland cement-based systems for waste encapsulation. We know that improperly cured cement can have compromised properties, therefore in the absence of any hard data re pool issues, we would recommend cementitious materials used in pools treated in this way are well cured before any Boron containing material is added (i.e. at least 21 days dry cure as per AS3958).

Chlorine
This element is the water purification medium to keep the pool free of algae and other harmful organisms like bacteria. High levels of free Chlorine apart from being an irritant to swimmers, also can create changes in materials such as grouts. Particularly if coloured or pigmented grouts are used, the Chlorine bleaches the colour rendering the grouts a neutral whitish colour. Notably the grout above and below the waterline can end up being different shades or even appearing to be different colours.

RECOMMENDATIONS
The recommended water chemistry balance in pools with ceramic tile finishes using common water treatment (dry or tablet Chlorine, common salt, and water treated with UV or Ozone) is as follows:
Required
Total alkalinity range recommended 80 - 200 mg/L
pH range 7.2 - 7.8
Calcium Hardness range 150 - 200 mg/L
Sulphate range < 200 mg/L.
Other typical values
Chlorine (free) ~1-2ppm
Salt as Sodium Chloride (saltwater pools) ~4000-6000ppm

While these values may be slightly different to what many operators would regard as normal, we emphasise that these values are related to ceramic tile finishes that have been fixed (adhered) and grouted with cement-based products. The values given here are in the recommended ranges to prevent corrosion of the cement in the adhesives and grouts.

The Australian Standard references do include the information regarding the effects of the chemical compounds noted in this technical bulletin.
However, those standards also apply to other types of pool finishes and care must be taken to ensure that the appropriate range is used in tiled pools.
We would also advise that excessively high levels of Chlorine can have a negative impact on cement-based materials, and Brominated materials as used in spas are very aggressive and attack grouts and adhesives.

ADHESIVES AND GROUTS
This bulletin makes passing reference only to the types of adhesives and grouts that are suitable for use in swimming pools.
Essentially polymer fortified, cement-based adhesives and grouts are normally suitable and have been used successfully for many years. Increased durability has been achieved by replacing standard grey Portland cement with more Sulphate resistant, white cements; while the polymers used have increased bond strengths and resistance to turbulence in the water, as well as reducing the permeability of the adhesives and grouts. Reduced permeability reduces the flow of water through the cement-based adhesives and grouts hence slowing the effects of out of balance pool water.

From: Technical Bulletin TB143.005 ARDEX TECHNICAL SERVICES DEPARTMENT

Summary

This is but an introduction to a very complex and very dynamic situation. Basically, in pools (and spas) , water is always in a state of flux. Sometimes you are really challenged at every level, while many other pool owners have no issues.
Basically, it’s the “luck of the draw” as to where you and your pool are.
And when you are having issues reach out to knowledgeable pool shops or other professionals in the pool industry. There is a solution 99.9 % of the time, however you may need to dive in deep to find it.