Pool Chemistry Overview

Maintaining proper chemical balance in your pool water is the most important factor in ensuring the longevity of your pool equipment, liners, and fiberglass pools and steps. Testing your water on your own weekly or after major disruptions such as pool parties or heavy rain is important since it allows you to catch issues before they become a problem. You should get a test kit or strips which can test for chlorine, pH, alkalinity, and stabilizer since they are the most crucial chemicals to keep track of. It is also recommended to have your water tested by a professional monthly since many pool equipment manufactures will not honor warranties without records of regular water tests. The following information provides recommended concentrations of pool chemicals and some additional explanations for what the chemicals do, safety and storage concerns, and how to maintain the correct amount in your pool.

Recommended Ranges

Chlorine: 1.0-3.0 ppm (Pools with UV/ozone systems can go as low as 0.5 ppm)

pH: 7.2-7.8

Alkalinity: 80-150 ppm

Calcium: 200-400 ppm (fiberglass pools should keep this on the lower side of the range)

Stabilizer: 30-100 ppm

Metals: 0 ppm

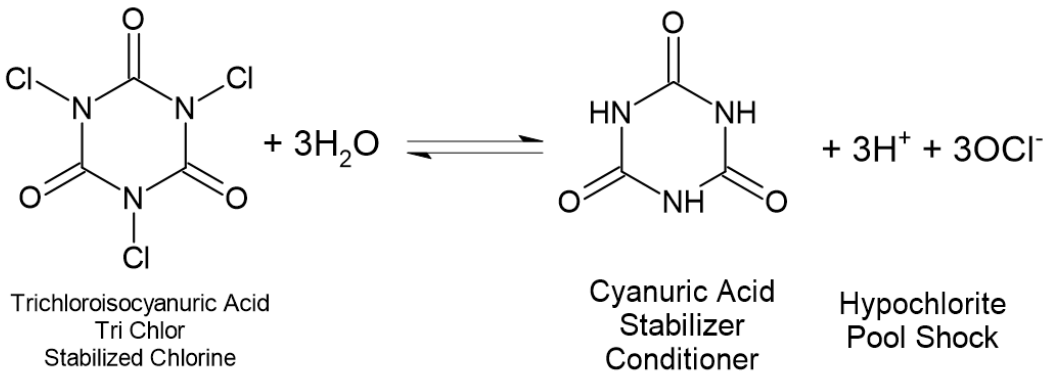
Chlorine

Chlorine is the main sanitizer for most swimming pools, and a major part of pool chemistry is making sure there is enough chlorine in your water to kill bacteria and algae in your water, but not so high that it damages your pool equipment or causes you discomfort. Chlorine is such an effective sanitizer because it is an unstable molecule that wants to perform oxidation reactions, so a lot of the chemistry around it is related to stabilizing it enough to keep it in your water.

Chlorine Terminology

- **Total Chlorine** – the total amount of all types of chlorine in the water
- **Free Chlorine** – the amount of chlorine that is free to sanitize the water
- **Combined Chlorine** – the amount of chlorine that has already sanitized something and is no longer capable of further sanitation

- **Trichlor** – stabilized chlorine that is found in chlorine tablets also known as Trichloroisocyanuric acid.
- **Shock** – non-stabilized chlorine also known as hypochlorite or bleach
- **Stabilizer** – molecule that stabilizes chlorine in water also known as Cyanuric acid or water conditioner.
- **Equilibrium** – an equilibrium reaction can go both forward or in reverse. Changing the amount of any of the products or reactants changes the equilibrium and the reaction will adjust to the new equilibrium by pushing the reaction either forward or reverse depending on what was changed.



The reaction equilibrium of stabilized chlorine in water

As hypochlorite is destroyed by UV light and heat or by sanitizing biologicals the equilibrium is shifted away from Trichlor and towards hypochlorite and stabilizer maintaining a consistent level of chlorine and acting as a slow release of sanitizer into the pool

How Chlorine Works

As stated above chlorine oxidizes molecules in order to kill microorganisms in your water. Stabilized chlorine acts as a place to store chlorine, so it remains in the water until it is needed. Since the reaction is in equilibrium, changes in the amount of any of the chemicals in the reaction moves the reaction either forward or back depending on which side of the arrow they are on. The hypochlorite binds to molecules particularly to the nitrogen found in bacteria, viruses, and bodily fluids. This generates chloramines which cause the distinct bad chlorine smell commonly found in public pools. Some of these

biproducts can also cause rashes. To counter this the pool will need to be shocked to further oxidize any remaining microorganisms in the water and refresh the pool with new hypochlorite.

How to Maintain Chlorine

- **Chlorine Tablets**

  Chlorine tablets provide stabilized chlorine for swimming pools. They are made to slowly dissolve in a chlorinator, floater, or skimmer and release the stabilized chlorine over time. Temperature and sunlight affect the stability of chlorine and how quickly the tablets dissolve, so it is important to monitor the amount of chlorine in the pool and adjust the settings on your chlorinator or the number of tablets you add to keep it within the recommended ranges. Typically, you will need less chlorine when its colder and more when it's warmer.

  When purchasing chlorine tablets try to find tablets that are 99% Trichlor. Tablets with a lower percentage of Trichlor usually have additives such as copper which build up and end up costing more to remove than you saved by buying lower quality chlorine. Brands that have "Blue" or "4 in 1"in their name tend to be the biggest culprits of this.

- **Salt Generator**

  Salt generators react Sodium Chloride (normal table salt) with water to generate hypochlorite and make hydroxide as a biproduct. This is great for the Evansville area because our water and rain tend to be acidic and the hydroxide generated by the salt generator neutralizes the acid meaning fewer pH corrections than with other sanitizing methods.
  As mentioned the chlorine generated by the salt generator is hypochlorite so to keep the chlorine in the water for longer, people with salt water systems will need to add stabilizer or run their generators at a higher setting to offset the more rapid chlorine destruction, this isn't recommended as this means the rather pricey salt cell will need to be replaced sooner.

- **Shock**

  Pool shock raises chlorine high above the normal amount of chlorine for a short time. This further oxidizes combined chlorine regenerating free chlorine and essentially destroying contaminants in the water until the pieces are small enough and chlorinated enough to become volatile and easily evaporate from the pool. You can buy shock in either a powder or dissolved in a liquid solution. Liquid acts more quickly than powder and is slightly less expensive than powder, however the powder stores better. Some pool stores also offer Dichlor shock. This

contains roughly 10% cyanuric acid and as a result repeated shocking using Dichlor can result in issues with high stabilizer.

- **Stabilizer**

  Stabilizer is cyanuric acid. Hypochlorite attaches to cyanuric acid to form Trichlor. Adding stabilizer pushes the reaction equilibrium towards Trichlor, keeping chlorine in the stable form more of the time preventing chlorine loss, however, it can become too high and keep too much of the chlorine in the stable form which means little of it is available to sanitize and the chlorine becomes much less efficient and can cause cloudiness.

  High stabilizer is a common problem in hotter climates such as Texas, Florida or southern California, but is rare in the Evansville area because frequent rain and winterizing the pool means that we tend to pump more water out than in a hot dry climate where pools can stay open all year. This helpfully keeps the cyanuric acid from building up to undesirable levels.

Chlorine Chemical Safety and Storage

- **Chlorine Safety** – Chlorine is a powerful oxidizer and environmental hazard, so try and avoid contact with both tablets and shock. If you accidentally get any on your skin thoroughly wash the affected area to avoid chemical burns. If any makes contact with your eye try and flush your eyes with fresh water in a sink or using a hose. When opening containers of chlorine such as buckets of tablets and shock or chlorinators turn your head away after it first opens and avoid breathing in the fumes as they can cause damage to your lungs. Chlorine can also damage clothing either by bleaching them or dissolving the fabric if its concentrated enough. It is a good idea to wear gloves and old clothes when handling chlorine. **NEVER MIX CHLORINE WITH ACID, IT MAKES MUSTARD GAS!** These are just recommendations on handling chlorine and first steps to take if you have an accident, read the safety information on the chemical's container and contact poison control for advice if you are exposed.
- **Chlorine Storage** – Chlorine in solid form, either as powder shock or tablets, should be stored in a cool dry area. If it becomes wet or gets above 90^{o} F it begins to degrade, however, if kept cool and dry it can remain potent for several years. Liquid shock should be used more quickly as it loses potency after several months. As an oxidizer chlorine will rust metals in areas where it is stored so that should also be considered when selecting a storage area.

pH

pH is used to measure of the acidity of pool water. Keeping your pH balanced is probably the single most important thing to do for your pool. The preferred range for pH in your pool is 7.2-7.8, which might sound like a very small range, but pH is in a logarithmic scale. This means a pH of 8 isn't just one more than a pH of 7 or even twice as high, but a full 10 times as high a pH of 7. Failure to maintain a balanced pH in your pool can lead to a wide range of issues; from reducing the efficiency of chlorine to destroying equipment or even causing chemical burns. It is easy to see why this is so important.

pH Terminology

- **Acid** – A chemical with a pH below 7, the lower the pH the more acidic the water
- **Base** – A chemical with a pH above 7, the higher the pH the more basic the water
- **Alkalinity** – In pool chemistry alkalinity is the concentration of carbonate in the water

How pH works

Unlike chlorine where you are trying to keep a certain amount of it in the water, the goal for pH is to keep it from becoming either acidic or basic. To do this you simply add base if it becomes acidic or add acid if it becomes basic. Since most pools are outdoors and the pH can fluctuate widely based on rain, especially the acid rain we get in the Wabash and Ohio river valleys, it is helpful to keep a pH buffer in the water to prevent rapid swings in pH. The pH buffer we use for swimming pools is carbonate, which we call alkalinity. The carbonate will move through a series of equilibrium reactions when exposed to either acid or base which allow the pH to remain stable, however, it will eventually leave the water as carbon dioxide and need to be replenished. Interestingly these reactions at neutral pH generate carbonic acid (H_2CO_3) which is why carbonated drinks are so acidic and how high atmospheric carbon dioxide is acidifying the oceans and destroying coral reefs.

$$\mathbf{CO_2(g) + H_2O \rightleftharpoons CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO^-_3 \rightleftharpoons 2H^+ + CO^{2-}_3}$$

The equilibrium reactions of carbonate (alkalinity) with water

How to maintain pH

- **High pH**

  If your pH becomes too high, you will need to add acid. Typically, people use either hydrochloric acid (aka muriatic acid) as a liquid or sodium bisulfate (partially deprotonated sulfuric acid, also called pH down) as a powder.

  When your pH is too high it can lead to cloudy unsanitary water since chlorine is less effective at high pH. Other common issues are dry skin after swimming or foamy bubbles on the water's surface. This is caused by the high pH converting oils such as tanning oils and natural skin oils into soap through the process of saponification.

- **Low pH**

  If your pH becomes low, you will need to add base to neutralize the acid. To raise pH people commonly use sodium carbonate (also called pH up or soda ash) or sodium bicarbonate (also known as Alkalinity Up and baking soda). Typically, you would use pH up if just your pH is low and use Alkalinity Up if both pH and alkalinity are low.

  Low pH is the most common chemical issue in swimming pools and leads many issues. Chlorine efficiency decreases at low pH just as it does with high pH, which can lead to cloudiness and unsanitary water. Acidic water will cause corrosion to any metal it contacts in and around the pool and it's equipment leading to premature failure of affected pieces. Low pH also breaks bonds in plastic and vinyl equipment which makes them brittle and more likely to break. The most common reason people need to replace their liner early is because of damage from extended periods with low pH water. If you have a heater on your pool low pH will dissolve the copper in the heating manifold ruining the heater and adding a lot of copper to the water which can cause further issues discussed in the metals section. Finally, if the damage to the pool itself isn't a good enough reason to avoid low pH, swimming in acidic water can give you itchy skin, rashes, burning eyes, damaged hair, or even chemical burns if it's low enough.

- **Alkalinity**

  As mentioned in the Low pH section, Alkalinity Up is commonly used to treat both low pH and low alkalinity. The reason for this is both pH Up and Alkalinity Up are very similar molecules and can be converted into each other depending on the environment they are in. They both are bases and both raise alkalinity, but they differ in how much they raise each. The reason for this is the pH sodium bicarbonate (Alkalinity Up) is around 8.5 whereas the pH of Sodium Carbonate (pH Up) is around 11.5. Since pH is a logarithmic scale this means pH up is around 1000 times as

basic as alkalinity up. When people hear this, they think "Why buy Alkalinity Up if pH Up raises pH so much more?" Well, this doesn't tell the whole story. Sodium Carbonate's molecular formula is Na_2CO_3 giving it a mass of around 106g/mol and sodium bicarbonate has a molecular formula of $NaHCO_3$ giving it a mass of 84g/mol meaning you get around 130% as many molecules per pound with the bicarbonate vs the carbonate. You also get a lot more carbonate with alkalinity up meaning it raises your alkalinity much more than pH Up does.

pH Chemical Safety and Storage

- **Neutralization** – If there is an acid or base spill or if you are disposing of old chemicals, you can neutralize them with household chemicals. For acids use baking soda and for bases use vinegar. The neutralization reaction is the same one that is frequently used for school science fair volcanoes and will release heat and gas so do not do it in an enclosed area. After the bubbling stops you will be left with salt water which can be dumped down a drain or swept up.
- **Acid Storage** – Acids should be stored in a cool dry place away from any chlorine tablets or shock. **NEVER MIX CHLORINE WITH ACID, IT MAKES MUSTARD GAS!**
- **Acid Safety** – Both liquid and powder acids can cause severe chemical burns so gloves and eye protection are recommended when handling and you should avoid contact with skin.
- **Base Storage** – Alkalinity up and pH up should be stored in a cool dry place.
- **Base safety** – Both pH up and alkalinity up are mild eye irritants so be careful about getting them in your eyes.

Other Chemicals

Calcium

Calcium, also called water hardness, is the measure of how much ionic Calcium is in your water. Low calcium can cause metals to leach from pool equipment causing premature failure. High calcium by contrast can leave chalky calcium scaling around the water line or calcium buildup in your plumbing, or equipment. The Evansville Tri-state area tends to have high calcium levels, but not outside the recommended range, so most people don't end up needing to add calcium locally. People with fiberglass pools should pay close attention to their calcium level since high calcium can deposit in the fiberglass causing permanent scaling which can only be removed by resurfacing of the pool which is very costly and can result in damage to the structure. Calcium can be increased by adding calcium chloride or decreased using descaling or calcium sequestering chemicals.

Metals

Many people assume that when hair and swimwear turn green after swimming it is a result of algae, however, the source is actually copper. When copper oxidizes (rusts) it turns green, and it is this rusted copper that is causing the green staining. Think of old pennies or the Statue of Liberty. Luckily getting excess metals in your water is fairly rare, when using high quality chemicals. Usually the source of metal in pool water is low quality chemicals, filling with high metal well water, or occasionally from pools with heaters that have had low pH for an extended period of time. If you begin getting yellow or brown stains, green hair and clothing, or water turning brown after a shock, you likely have high metals. There are treatments that can easily remove the metal from the water, but stains are harder to get rid of and usually they are the first indication you have that something is wrong. So, if you are using low quality chemicals keep in mind that they might cause permanent staining to white goods or liners and may end up costing you much more than you saved buying a cheaper chemical.

Algaecide

Algaecides are solutions which are designed to kill algae. There are two types of algaecides: preventatives and killers. Preventatives prevent algae from growing in the first place and killers kill existing algae. Preventative algaecide can also kills already existing algae, but not as effectively as treating with an algae killer. When looking for a preventative algaecide bigger is usually not better. Low quality algaecides especially those that come in gallons instead of quarts typically, have a large amount of copper in them. Be careful with these cheap copper filled algaecides, because they often cost you more to fix the problems they cause than you saved by buying them over a higher quality algaecide.

Phosphate/Nitrate/Nitrite/Ammonia

Phosphates, nitrates, nitrites, and ammonia are compounds found in fertilizers and most living things. They tend to build up over time as they are difficult to remove from water and can cause many problems once they have gotten to a high concentration. Commonly they find their way into pools from nearby farms, home gardens or even fertilized yards. However, they can also build up from decaying organic matter (dead leaves or small animals) that are allowed to decompose in the pool. Small amounts of nitrate can also enter pool water from the air via the nitrogen cycle (air is almost 80% nitrogen). Another common source of ammonia and nitrates is from urine. When these chemicals build up they tend to bind with chlorine keeping it from sanitizing the water and as you might imagine since they are

commonly found in fertilizer and algae is a plant, they can act as a nutrient source for the algae leading to massive algae blooms. As far as treatment goes if you have a large amount of all three in your water the cheapest option is usually to drain a large portion of the pool water and replace it with fresh water. If you just have a phosphate issue there are many phosphate removing treatments, though they tend to be expensive. Ammonia can be removed by repeated shocking, but you need to be careful how rapidly you add the shock since it can damage pool liners and equipment if the concentration gets too high. Nitrates and Nitrites are salts, so they are almost impossible to remove by chemical treatments. There are nitrate treatments for aquariums but scaling them up to pool sized volumes would cost thousands of dollars, so it's more cost effective to just drain and dilute the pool water. The good news is it's rare to have just nitrates and nitrites so when you dilute the water to remove the nitrates you will also be removing any phosphate and ammonia from the pool at the same time.

Common Reasons for Cloudy Water

1) High combined chlorine (will show up in a professional water test)
2) Low chlorine (will show up in a professional water test)
3) High stabilizer (will show up in a professional water test)
4) High calcium (will show up in a professional water test)
5) Microorganisms (usually during or after an algae bloom)
6) High ammonia, phosphates or nitrates (usually not tested for unless there is a persistent problem, but most pool stores can test for them)
7) Dirty, contaminated or old filter medium (sand and DE filters need to be regularly backwashed to maintain efficiency and cartridge filters need regular cleaning, infrequent maintenance will lead to the pool becoming cloudy. Eventually all filters will become aged and begin to lose functionality and need to be replaced to keep the pool clean.
8) Infrequent cleaning. Pretty self-explanatory, but if you don't clean the pool very often it will get dirty.