



AQUADENE® BLENDED PHOSPHATE

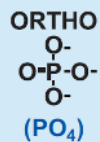
Chelation & Sequestration by Polyphosphates

INTRODUCTION

Today the most successful water treatment programs employ the use of blended poly/orthophosphates. The main benefits realized through phosphate treatment are; the control of corrosion, scale, iron and manganese. It's these wide ranging water treatment applications that make phosphate treatment a necessity for most municipal water systems. Therefore, today's municipal water managers must have a working understanding of the role phosphates play in a comprehensive water treatment program.

Chemically, phosphates are broken into two general categories that are defined by their chemical structure.

Both groups have molecular configurations and properties that allow them to perform specific chemical functions, which are used in a wide range of applications within various industries. The first is that of orthophosphate, which consists of one phosphorus atom bonded to four oxygen atoms.



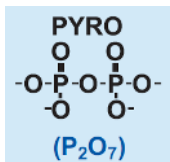
The function of orthophosphate in water treatment is that of a corrosion inhibitor, which is covered in detail in other Carus technical bulletins. For our present purposes, it is best to view orthophosphate as the basic building block for the more complex chemical category of polyphosphates.



POLYPHOSPHATES

Polyphosphates are units of orthophosphates (PO₄) linked together by common oxygen atoms. The resulting molecule is a linear or chain like structure. The chemical category of polyphosphates is subdivided into subgroups according to the length of each chain. The most basic of the groups is pyrophosphate, which is two orthophosphate groups linked together by a common oxygen atom.

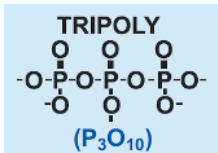
Triphosphate is next in the chemical series, containing three phosphate groups, again all bridged together by common oxygen atoms.

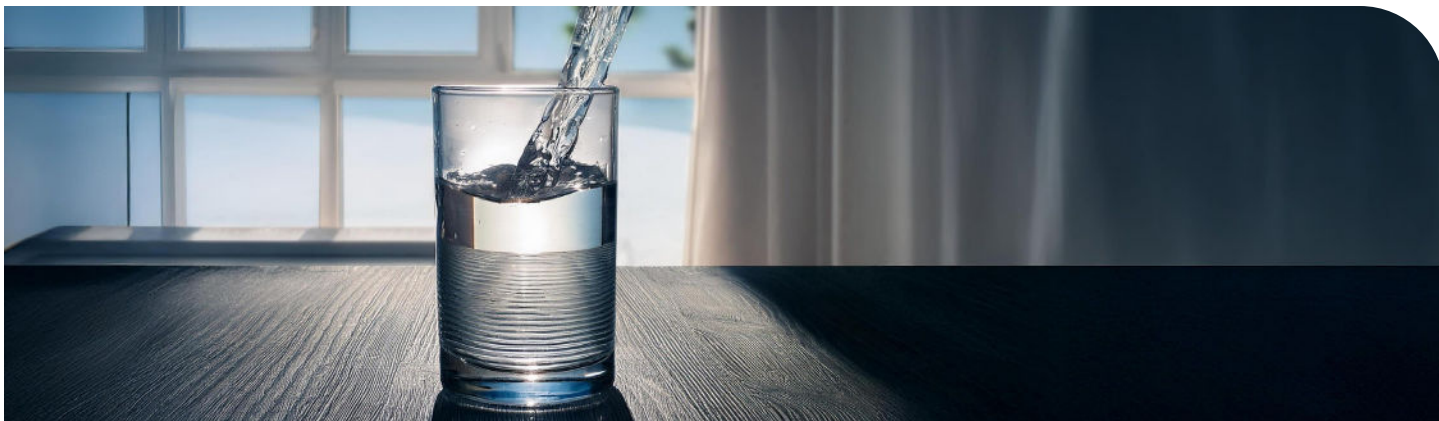


In our industry, all polyphosphates that have four or more chain lengths fall into a group known as hexametaphosphate. Typical technical grade hexametaphosphates have an average chain length of twelve or thirteen, depending on the manufacturer.

The term long chained hexametaphosphate refers to a grade having an average of twenty-one PO₄ groups. These longer chains are more expensive to produce and are used only in the higher quality blended phosphate products, such as Aquadene. The importance of this will become more apparent later in this discussion.

It is important to note that the unoccupied valences of the oxygen atoms, surrounding the phosphate chains in a dry state, can be filled with calcium, sodium and/or potassium. Calcium is generally not used in water treatment due to solubility problems. The elements that are present in the phosphate chains are determined during the manufacturing process.





POLYPHOSPHATES (CONT'D)

The manufacture of polyphosphates involves two major chemical reactions. The first is a reaction between phosphoric acid (H_3PO_4) and the desired alkali to prepare the orthophosphate. In water treatment, the superior orthophosphate choice is sodium phosphate. The alkaline materials used in the process are sodium carbonate (Na_2CO_3) or sodium hydroxide ($NaOH$), which produce either mono or disodium orthophosphate. For example, the reaction for disodium orthophosphate would be:



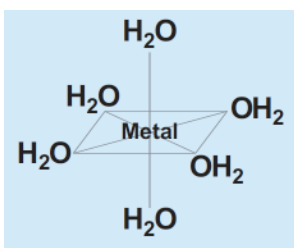
The second step is a calcination reaction to condense the orthophosphate into the desired polyphosphate. Polyphosphates may also be referred to as condensed phosphates. The name is derived from this reaction of which water is a by product. Our example here, would be the disodium orthophosphate being condensed into tetrasodium pyrophosphate.



We have looked at several different polyphosphates, all of which have been linear in their molecular structure. Linear polyphosphates are by far, the most commonly used polyphosphate in water treatment. The only exception to this would be Carus's use of an advanced cyclic phosphate material, which has a ring-like molecular structure. It is used in certain Aquadene formulations as a stabilizer and for other proprietary reasons, and it provides excellent benefits to the end user.

CHELATION - SEQUESTRATION

Multi-valent metal ions with positive charges such as Ca^{+2} , Fe^{+2} , and Mn^{+2} do not exist in a free state in a water solution. Instead, they are surrounded by water molecules and anions which "hydrate" the ionic species. Water molecules and more complex anions such as polyphosphates, when associated with metal ions in solution, are referred to as "ligands". These ligands are sub-grouped into categories determined by the number of sites available on the molecule to complex with the metal ions. Ligands with one site are known as "monodentate" from the Latin meaning one-toothed. Ligands with dual sites available to complex positively charged metal ions are known as "bidentate" (two-toothed). A ligand molecule with three complexing sites would be "tridentate". A good example of a ligand that has two sites would be sodium tripolyphosphate (STP). The number of polyphosphate's complexing sites are roughly proportional to the number of oxygen bridges present in the molecule.



CHELATION - SEQUESTRATION (CONT'D)

When a metal ion forms a complex with a bidentate ligand or higher, such as the above mentioned tripolyphosphate, a ring structure is formed. This ring structure may greatly change the physical/chemical properties of the metal ion. The name given to this ring forming reaction is "chelation". Chelation is from the Greek word "chelos", meaning claw. This word was chosen because the resulting molecular structure looks somewhat like a crab claw holding an object. During the chelation reaction, the ligand may be referred to as the "chelating agent". The resulting complex of ligand and metal ion is called the "chelate."



The chelate that is formed may or may not remain soluble. When the chelate remains water soluble and does not precipitate out, the process is called "sequestration". In the sequestration reaction, the chelate is stable and remains in solution. The terms sequestration and chelation are similar, but do not necessarily mean the same thing. Various factors such as temperature, pH, and the phosphate specie are just a few of the factors involved, which we will discuss, in determining the effectiveness of the sequestration process.

PHOSPHATE SPECIE

The theoretical chelation/sequestering capacity differs for each individual polyphosphate specie. The amount of chelant needed (for our purposes, the chelant will be polyphosphate) to complex a particular metal ion, can be calculated using stoichiometric equations. Using this information, a table can be constructed to show the different chelating/sequestering capacities of polyphosphates. Please note that the capacity for sodium hexametaphosphate (SHMP) is expressed in a range. This is because the hexametaphosphate is an umbrella term, covering the longer chained polyphosphates. The longer the chain, the more oxygen bridges present, therefore, the greater the theoretical chelating/sequestering capacities.

As stated earlier, when polyphosphates chelate/sequester a metal ion, the chemical properties of the metal ion can be greatly altered. The change in the chemical behavior of the chelate vs. that of the original metal ion can be quite beneficial. This is especially true with many well water sources that have high levels of iron and/or manganese. These two untreated metal ions have several undesirable effects, the most prominent being the resulting red and black waters which are formed.



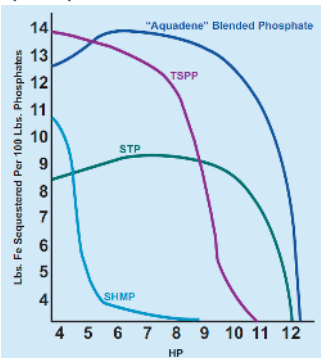
PHOSPHATE SPECIE (CONT'D)

THEORETICAL CHELATION CAPACITIES FOR POLYPHOSPHATES
CHELANT (with Formula & Mol. Weight)

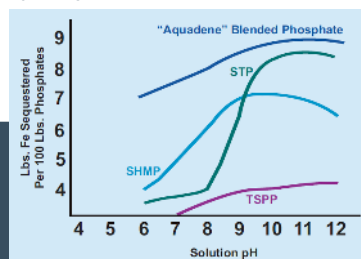
Metal Being Chelated (Automatic Wt.)	TSPP $\text{Na}_4\text{P}_2\text{O}_7$	TKPP $\text{K}_3\text{P}_2\text{O}_7$ (330)	STP $\text{Na}_3\text{K}_2\text{P}_3\text{O}_{10}$ (368)	SKTP $\text{Na}_3\text{K}_3\text{P}_3\text{O}_{10}$ (400)	KTP $\text{K}_3\text{P}_3\text{O}_{10}$ (448)	SHMP $\text{Na}_{n+2}\text{P}_n\text{O}_{3n+1}$ (n=6)(n=14) (675)(1490)
Ba (137.4)	1.9	2.4	2.7	2.9	3.3	4.9 - 10.8
Ca (40)	6.6	8.2	9.2	10.0	11.2	16.8 - 37.7
Fe (55.8)	4.8	5.9	6.6	7.2	8.0	12.1 - 26.6
Mg (24.3)	10.9	13.5	15.1	16.5	18.4	27.7 - 26.6
Mn (54.9)	4.8	6.0	6.7	7.3	8.2	12.3 - 27.1
Sr (87.4)	3.0	3.8	4.2	4.6	5.1	7.7 - 17.0

Iron and manganese ions are leached into the well water from the permeable rock strata that make up the aquifer. The richer the strata is in both these elements, generally the higher the metal ion concentrations in the water. The higher the concentrations of the iron and manganese ions (see graph 1), the more severe the problems will become. The resulting water can cause staining of porcelain plumbing fixtures, dishes and clothing, particularly when bleach is being used in the laundry. The inside of pipes become coated with oxides of iron and manganese, further lowering the water quality. The removal of iron and manganese ions is possible through elaborate, and very expensive filtration systems. Many times, especially in smaller water systems, this is not a feasible option. The financially sound and most simplistic solution to iron and manganese leaching is to use the NSF and EPA approved treatment method of AQUADENE® addition to the source water.

GRAPH 1
Sequestration of Iron
by Phosphates at 25° C



GRAPH 2
Sequestration of Calcium
by Phosphates at 25° C



pH

Polyphosphates as chelating agents have different pH profiles when it comes to their ability to sequester. For example, tetrasodium pyrophosphate (TSPP) will chelate more efficiently in lower pH environments, while sodium tripolyphosphate (STP) chelates more efficiently in the more alkaline environments. STP loses most of its ability to sequester at a neutral pH in contrast to TSPP which is less effective in more alkaline environments.

At a higher pH, polyphosphates will chelate the metal ion, however may not remain soluble. This can be especially pronounced when the wrong polyphosphates are used at an incorrect feed rate during a calcium sequestration application. The resulting chelate (tri-calcium phosphate) is insoluble and precipitates out of solution. This can cause the water operator several problems, most notably rendering the water filters to a non-functional state. All of the problems, including blocked filters, can be completely avoidable by using Carus' blended phosphate products. AQUADENE® products are chemically engineered to avoid such problems.

Another factor that needs to be taken into consideration when dealing with elevated or depressed pH environments is that of "hydrolysis" or "reversion". The terms refer to the chemical process in which all polyphosphates degrade into non-chelating orthophosphates. The speed of the process may vary due to many different physio-chemical factors, including polyphosphate specie. Depressed or elevated pH levels are major factors in speeding up this process of reversion. In other words, the longer a polyphosphate is exposed to extreme pH conditions, the less effective it will be as a sequestering agent.

TEMPERATURE

Temperature can effect the sequestering capacities of polyphosphates in much the same way that pH does. High temperature, over time, will cause the reversion of polyphosphates into orthophosphate to increase. As pointed out earlier, orthophosphates are non-chelating molecules. This non-ligand status is primarily due to the fact that orthophosphate (PO_4) is a single phosphate with no oxygen bridges, therefore having no ability to form the complex ring-like structure associated with chelation.

Through the use of pH and temperature tables, the half-life of a polyphosphate specie can be determined. An example would be the half life of pyrophosphate at pH of 7 and a temperature of 100° F, which would be 7,000 hours. These are particularly useful when engineering a blended phosphate product for municipal water systems. Your blended phosphate supplier must be able to provide you with technical data, such as ion chromatography, to assure that your blend of phosphates will address your specific needs.

SCALE-CONTROL

AQUADENE® phosphate blends attack unwanted metal ion problems at a molecular level through the sequestration process. The Fe²⁺ and Mn²⁺ ions are chelated by the polyphosphate components of AQUADENE. The resulting chelant remains in solution, and therefore is sequestered. The sequestered metal ion chemical properties are significantly changed by this process. The chemically adverse effects caused by the iron and manganese are immediately eliminated. Much of the existing damage, such as the oxide build up on the inner pipe wall, is reversed, and will be eliminated over time.

Source water that has high hardness levels also benefit by using AQUADENE blended phosphate products. Calcium and magnesium carbonates are the major components of hardness. Once again, the Ca and Mg metal ions are leached into the source water from surrounding rock and mineral formations. The metal ions precipitate out of solution as mineral carbonates of calcium and magnesium. These minerals form deposits throughout the water system, choking off pipes, sprinkler and shower heads. Once again, the solution is the safe, simple and cost-effective chemical addition of Aquadene.

The polyphosphates in AQUADENE acting as a ligand with the Ca and Mg ions (see graph 2) form a soluble chelant that no longer will form scale. In addition to the sequestering abilities of AQUADENE, the polyphosphate components, over time, actually remove the existing scale. The scale removal takes place at a molecular level. The chemical bonds that support the crystalline structure of scale forming minerals are disrupted, causing the scale to slowly dissolve.

WHY AQUADENE?

The process of sequestration is extremely important when it comes to water treatment. A water manager must be sure the company he is dealing with fully understands this sequestration process. The needs of a particular water system may be drastically different from other systems. Using a blend of polyphosphate that is not chemically tailored to a particular water can be ineffective and detrimental to the system's process. Therefore, companies which have only one or two products and recommend them for all water chemistries are not addressing the needs of different water qualities throughout the country. After all, it is a common understanding that all waters are not the same. Carus has over 100 NSF approved blends of phosphates, used across the country, as well as internationally.

THE QUESTIONS OF POLY/ORTHO PHOSPHATE RATIO

The most advantageous product for today's water manager's use is that of a blended poly/orthophosphate material. With a blend of both phosphate groups, not only do you get the sequestering benefits, you also maximize corrosion control in your system. (Corrosion control is discussed in depth in other Carus literature). The ratio of poly to ortho phosphate is important, and was pioneered and perfected by Carus over the last forty years. However, another important fact is specifically the choice of poly and ortho phosphates being used in the blend.

Are the specific phosphates being used in a particular phosphate blend, appropriate for your system? Are all 50:50 blends of poly orthophosphate the same? Is the least expensive phosphate blend the best approach to treating a public municipal facility? These are some of the questions which face water managers in our industry. We will attempt to answer these questions for you. Realizing that the safety of the community is foremost in our mind, proper product selection becomes critical. Some phosphate species are easier to produce and are more widely available, therefore making them less expensive to produce than other phosphates. As we discussed earlier, certain phosphates work better than others in different water chemistries. This means the least expensive product may not be the best suited for your water. Even though two products may have the same poly to orthophosphate ratio doesn't mean they are the same product. The use of more widely available and less expensive phosphates in your product can prove to be disastrous in terms of results, overall treatment costs and concern for public safety.

There have been several occasions where comparisons of products to Aquadene have been made. All Aquadene blended phosphate formulas are proprietary and are produced using methods that are unique to Carus LLC. Carus' blended phosphates are the "benchmark of the water treatment industry", and we take pride in using the finest phosphates available in the marketplace regardless of costs. We remain confident that our quality control of incoming phosphate raw materials continues to provide us with the finest product.

Please contact us directly for more information on Aquadene blended phosphate products, and realize the benefits of conducting business with Carus, a company with over 100 years of experience in the drinking water industry.



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