Phosphate Removal ...Revisted

by **R. Neil Lowry,** *Ph.D.*

The Canadian show issue of Pool & Spa Marketing magazine (Vol. 27, No. 7, pg. 57, Dec./03), featured an article written by R.Neil Lowry entitled, 'Phosphate Removal: We Have a Solution... But Do We Have A Problem?' A review of this article might be warranted before reading this follow-up article. With phosphate-removal products now a salient part of the present marketplace, an update of this topic appeared warranted by the editor of Hubbard Marketing & Publishing Ltd.

What Is Phosphate And Why Is It So Nasty? The phosphate mentioned in all phosphate-removal product literature is called inorganic phosphate or 'orthophosphate', having the formula:

$[PO_4]^{-3}$
Orthophosphate

It is a negatively charged ion called an anion with a triple charge. This anion is deemed 'nasty' as it is one of the nutrients required by micro-organisms for growth. Other forms of phosphate-containing chemicals that contain carbon chains are called organophosphates and normally are not employed as a growth nutrient.

What Are Micro-organisms? These are tiny living organisms that are only visible under a microscope (viruses are excluded). The human eye has a limited resolution of 40 μm (micron, 10^{-6} meters) while most micro-organisms are in the 0.5 to 2 μm range. The key micro-organism of interest to outdoor pool owners is algae. For simplicity, only green algae will be discussed here.

Explain Green Algae A Little More! Green algae are unicellular eukaryotes (containing a nucleus in its cell) and are photosynthetic (they contain chlorophyll and combined with sunlight and carbon dioxide, CO_2, produce carbohydrates and oxygen, O_2). They are abundant in fresh water either as fragments or in a protective spore (simplistically stated). In pools, 'Chlorella' is the main green algae to combat.

Algae can proliferate quickly and under the right conditions can become an 'algae bloom', giving a pool a turbid green colouration due to the billions of algae cells in the pool.

Definition Of A 'Growth And Limiting Nutrient': In order to grow green algae, this micro-organism requires the ever-present sunlight (ultraviolet rays), carbon dioxide and the following key growth nutrients: nitrogen, phosphorus and sulfur. If one of these nutrients is in a low concentration, it is called a 'limiting ingredient', that is, no longer present in adequate amounts to continue the growth of the algae. Adding a limiting nutrient will stimulate algae to resume growth until some other nutrient, or the same one, becomes limiting.

Examining Growth Nutrients: Of the three nutrients, sulfur appears in pools as the sulfate anion $(SO_4)^{-2}$ that can be readily utilized by algae. Pool chemicals such as sodium bisulfate (a pH reducer) or potassium monopersulfate are key sources of sulfur. However, it is either nitrogen or phosphorus that is the limiting nutrient as both are needed in large amounts. Algae use nitrogen found in nitrate $(NO_3)^{-1}$, ammonia (in the reduced form) or amine from proteins. In the pool environment, irrespective of the formation of combined chlorines, there is a constant input of nitrogen from bathers and the environment.

In contrast, orthophosphate appears to be the limiting nutrient in pools and fresh water sources. As is stated in one microbiological text, "low phosphate levels actually limit microbial growth in many aquatic environments".

Two Arguments That Orthophosphate Is The Nutrient Causing Algae Growth: A generation ago synthetic detergents for laundry use contained about 12 per cent phosphate 'builders'. These builders, by controlling pH, surface tension and other properties, enhanced the performance of detergents. Consequently, treated sewage water which did not remove phosphates would act as fertilizers for the growth of unwanted plant life (a process called 'eutrophication') when discharged into certain large bodies of fresh water. Lake Erie is often cited as an example of this. Removal of phosphate builders alleviated this problem.

The 2003 article in *Pool & Spa Marketing* on phosphate removal mentioned a serviceman employing TSP (trisodium phosphate) to lower calcium hardness, resulting in constant algae for the rest of the season. The constant level of orthophosphate, at a concentration beyond comprehension, readily nourished continued algae growth. This service individual never used enough chlorine to get ahead of this proliferation.

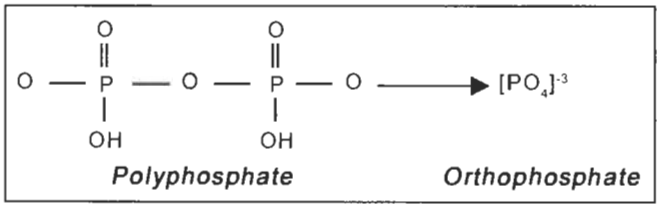
It certainly appears that citing phosphates as the limiting nutrient, and in excess being the key factor for growth of algae, stands on firm ground.

Where Do Phosphates In Pools Originate? Proponents and originators of phosphate-removal products previously searched at great lengths to explain the presence of phosphates in pools. Fertilizers and municipalities using phosphate-based chemicals to inhibit the corrosion of potable water piping were cited. One publication discusses phosphate-laden dust from the deserts of China, traveling 9,000 miles to fertilize the lush

forests of Hawaii. Shampoos and bather wastes are also mentioned. Use of cleaning agents such as TSP would also be a source. However, all these sources are rare or marginal when one realizes that hundreds of sequestering agent formulations used for calcium and stain control are phosphate-based.

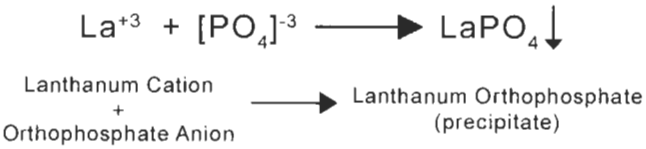
Phosphate-Based 'Sequestering Agents?' As stated in the original article on this topic, sequestering agents are used to prevent the precipitation or depositing of calcium (scale) and heavy metal salts (iron, copper, and manganese are called 'heavy metals' due to the high density of the elemental metal). Like many metals in the first transition series of the periodic table, these heavy metals produce highly coloured salts that can stain pool surfaces.

Pool water sequestering agents are, in the main, polyphosphate or phosphonic acid formulations, which as their name implies, are phosphorus-based. In pool water, in the presence of chlorine and sunlight, these products will hydrolyze over time and decompose into orthophosphates!



It is estimated that a pool on a regular regime of sequestering agents would accumulate levels of 1-3 ppm plus over the standard pool season. Most orthophosphates found in pool water originate from stain and scale control formulations.

Do These Phosphate-Removal Products Really Work? You bet! Phosphate-removal formulations contain a soluble salt of lanthanum (La), (lanthanum from the Greek meaning 'to lie hidden' – the first element of the rare earth series). In solution, lanthanum is a triple-charged cation (positively charged), La^{+3}. As shown earlier, orthophosphate is a negatively triple charged anion. Unlike charges attract and being triply charged means these two species bond strongly to each other and come out of solution (precipitate) as a very insoluble salt... hence the removal of orthophosphate.



From chemical tables, the solubility product of lanthanum phosphate is $[La^{+3}][PO4^{-3}] = 3.7 \times 10^{-23}$. Calculations show a concentration of 5.7×10^{-8} ppm (parts per million) orthophosphate remains soluble in the pool... hardly a trace!

If Sequestering Agents Produce Orthophosphates, Should They Not Be Avoided? If a pool owner had a backyard pond and added pool sequestering agents, the probability of aquatic plant and algae growth would increase due to eventual orthophosphate formation. The higher the dosage of such stain and scale control products, the greater chances of plant growth and eutrophication of the pond – a mini Lake Erie! Adding a phosphate removal product would avoid this problem. Phosphate-removal distributors state that levels of 125 ppb (parts per billion) or 0.125 ppm (parts per million) or below is an acceptable range for orthophosphate concentrations, whereas at 500 ppb or greater, algae blooms can proliferate.

Enough About Ponds, What About Pools? Here is where the phosphate-removal requirement will be challenged! Two arguments will be used.

1. Polyphosphate and phosphonic acid-based sequestering agents have been used in the pool industry for at least 30-plus years, while phosphate removal methods have been marketed for the past five years. What happened in the interim when phosphate-removal products did not exist? Were there thousands upon thousands of pools basking green in the sun? No! Why? It is because pools carry a residual of chlorine sanitizer. This stopped any algae growth, in spite of orthophosphate levels. As was stated by one pool chemical manufacturer, "...there were no phosphate removal products on the market until recently and with all the hype, how could we have survived in those days without them!"

2. Repeating a section of the previously cited 2003 article, in Dallas, Texas, at the November 2002, NSPI Show, Richard J. Muller, a microbiologist from BioLab USA (now Chemtura Inc.) stated that algae growth was non-existent at 30 ppm or 30,000 ppb of orthophosphate – a level not even approached by phosphate-based sequestering agent use! This is 60 times the stated level of 500 ppb orthophosphate cited as causing algae bloom! Mr. Muller also controlled algae with high orthophosphate level pools via an algaecide alone!

Conclusion: In the presence of normal levels of chlorine and/or algaecide, the levels of orthophosphate experienced in pools are irrelevant as is the need for phosphate-removal products.

Is There A Need To Defend The Use Of Phosphate-Based Sequestering Agents? Absolutely Not! Polyphosphate or phosphonic acid-based sequestering agents have been around much longer than any perceived phosphate problem. Their usefulness in preventing the formation of calcium scale and especially in scavenging stain-producing soluble heavy metals such as iron, copper and manganese, as well as removing and reducing the staining of pool surfaces, is well-known and deeply appreciated by pool operators and service personnel. Maintaining the required levels of sanitizer and/or algaecide avoids any problems from orthophosphate production and these sequestering agents will continue to maintain their position as effective stain and scale inhibitors.

What Is The Bottom Line?

1. Orthophosphates are the limiting growth nutrient for algae growth in pools.

2. The key source of orthophosphates in pools is from the standard stain and scale products used.

3. Phosphate-removal products will effectively remove orthophosphate from pool water.

4. In the absence of chlorine or algaecide maintenance, orthophosphates should be removed to avoid the enhancement of algae growth.

5. In the presence of recommended levels of chlorine sanitizer and/or algaecide, no algae will form irrespective of the levels of orthophosphate found in pools.

Reviewing these facts leads to the final conclusion... Phosphate-Removers... We Have A Solution But Do We Have A Problem? PSM

Dr. Lowry received his undergraduate Honours Chemistry degree from the University of Western Ontario and his doctorate degree in Inorganic Chemistry from Cornell University. He is the Canadian agent for Taylor Technologies of Sparks, Maryland. In addition to these responsibilities, he founded the Lowry School of Pool & Spa Chemistry in 1980.