

The Design of Advanced Pool and Spa Water Treatment Systems

Using Catalytic Filtration Technologies (CFT)

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The design and application of novel and patented catalytic filtration technologies (CFT) will be presented towards the advancement of pool and spa water treatment systems. System designs to be presented include loop configurations as well as one-pass recycle / reuse / reclaim systems. Catalytic Filtration Technologies may become the next generation of water management and water treatment technologies, since they are a new science that can improve the technical and economic effectiveness of water treatment systems.

A catalytic filter is a porous separation device in which the filtration surface has been activated to produce novel oxidation chemistries. Current filters available to end users today are made from surfaces that are inert, or can break down in extreme environments; these current filters are therefore designated as 'passive filters'. Since catalytic filters can be manufactured from pore size ranges from reverse osmosis (molecular separations) through microfiltration (bacterial, parasitic, and bulk colloidal separations) regimes, CFT can be applied to a wide range of markets.

CFT can be applied to pool and water treatment systems in conjunction with current and future chemistries such as muriatic acid, algicides, ozone, ultraviolet radiation, halogens and chloramines, etc., to minimize pathogenic and organic contamination potentials.

CFT can increase the economic effectiveness of water treatment systems through the minimizing of operational costs such as filter replacement, chemical loading, and water replacement and disposal costs.

Background

The contamination of pool and spa water treatment systems by colloidal and dissolved organic matter is of critical concern (Tamminen 1996). Organic contaminants can be viewed as microorganisms, organic chemicals and chemical reaction products in pool and spa water treatment systems. These contaminants have the potential to create great health concerns in both public and private water treatment systems (Atlas 1984).

Microorganisms can be further broken down into parasites, bacteria and viruses (for the purpose of this discussion). Parasites such as Giardia, Cryptosporidium and Entamoeba are typically micron sized or larger. Large numbers of parasites can be detected in fresh water environments (Atlas and Bartha 1987). Since pools are typically open to their surroundings, animals infected with these parasites have the potential to come into direct contact with a pool or spa, contaminate it with the parasites, and can pass the risk of infection to humans. Parasites and algae have been well documented to be resistant to chlorination and UV treatment (Tamminen 1996), so their numbers must be monitored and controlled carefully. Pathogenic bacteria such as *E. coli* and *Staphylococcus sp.* have been documented to affect the health of otherwise healthy individuals (Lyght *et al.* 1961). Certain bacteria have the potential to form a biofilm or contamination layer on fixed surfaces that can pro-

tect or shield the pathogens from oxidizing chemicals such as hydrogen peroxide and chlorine (Glaze 1987). Poor system design can result in an overgrowth of the bacteria and greatly increase the risk of infection from using a contaminated pool or spa. Pathogenic viruses are as dangerous as influenza (flu, or the common cold) as well as polioviruses, and of course the viruses that can cause AIDS. Viruses do not require nutrients to survive; they attach themselves to a host cell, inject their genetic material into the cell and force the cell to become a virus factory (Atlas 1984). Examples of virus related human infections include 'swimmer's ear,' as well as infections of the nasal passages. Viruses are especially insidious in that they are typically smaller than one micron in size and have the potential to pass through typical filtration systems. The control of microbes in the pool and spa water treatment environment is therefore of critical concern to both the end user as well as the system designer.

Organic chemicals and chemical reaction products can include bacterial fragments (lipopolysaccharides), cellular plant fragments (humic acids), as well as organic compounds ranging from low molecular weight trihalomethanes up through high molecular weight plasticizing agents (Governal 1992). Although the short term effect of these organic contaminants can be far less critical than the near immediate health risks generated by microorganisms, one must consider the long term effects of repeatedly exposing the human body to potentially carcinogenic chlorinated reaction by-products. Although a discussion of health-related risks from chlorinated compounds is beyond the scope of this paper, literature exists that can show the potential for contamination of pool and spa water systems by chlorinated compounds (Dobbs and Cohen 1980). In summary, repeated long term exposure to chlorinated compounds have the potential to cause health concerns, and their use should be minimized.

Passive Filtration

The time honored method of controlling these types of contaminants has been primarily through pool and spa water treatment system designs that include some form of passive filtration technology (Smith 1988). For the purpose of this discussion, passive filter materials can include materials such as carbon, polymeric composites and/or some forms of stainless steel. These passive filtration technologies are widely used today under the more familiar names of Reverse Osmosis (molecular weight cutoffs around 300), Nanofiltration (molecular weight cutoff typically in the range of 1,000 to 6,000), Ultrafiltration (molecular weight cutoff range of 6,000 to 100,000), and Microfiltration (micron sized particle retention) (Schmitt and Snijders 1990). These classifications are therefore based on the pore sizes of the passive mem-

branes used. The filters used in the pool and spa industries (microfiltration regime) can remove contaminants through a size exclusion process and in some cases, electrostatic interaction with the surface membrane. Their goal is to remove contaminants without recontaminating the fluid with filter by-products.

Although passive filtration technologies are currently used throughout the world, they do so with a number of drawbacks. These well-documented drawbacks include (Meltzer):

- 1) Incompatibility of passive filters to withstand long term exposure to common non-specific oxidizing agents found in water treatment systems such as ultraviolet radiation (UV), ozone (O₃), and hydrogen peroxide (H₂O₂).
- 2) Particle shedding of the filters (pieces of the filter break off and recontaminate the water) throughout the filter's lifetime. Pulsing or the sudden changing of water pressure of the filters in typical water treatment systems can cause an increase in the particle generation rates of the passive filter, and the contamination level of the product water.
- 3) Frequent replacement of filters as per an annual / biannual maintenance schedule.
- 4) Plugging or the condition where excessive build-up of contaminants prevents water from flowing through the passive filter.
- 5) Microbial grow-through (pathogens, bacteria and viruses) is a phenomena that occurs when the microorganisms build up on a surface, maneuver through the filter media and exit the filter into the downstream environment.
- 6) The accumulation of microbes anywhere in a water treatment system can also result in biofilm formation and potentially allow the filter to act as a site to grow organisms.
- 7) Low molecular weight chlorinated compounds have a higher probability of permeating a passive filter than do large particles.

The Catalytic Filter

The Catalytic Filter process was invented to overcome the drawbacks or inherent limitations of passive filtration technologies. The goal of any catalytic technology is to activate the surface of, in this case, the filter through the deposition of a proprietary formulation of transition metals. Transition metals such as titanium, zinc, tungsten, tin and copper have the potential to strongly bond with a passive surface; the metals, in the presence of oxidizing agents such as ozone, UV radiation and hydrogen peroxide crack water into highly reactive short-lived radicals (U.S. 1994). These radicals are highly energetic and can easily break down organic contaminants in a water

treatment environment (Rice 1995).

The catalytic filter exhibits contamination removal characteristics including pore size exclusion (as per passive filtration technologies) and through direct oxidation of the contaminants to simpler compounds. In this way, the rate of contamination build-up on a filter surface decreases dramatically. A further benefit is derived from the decreased shedding of contaminating particles from the surface of the catalytic filter, as it is stable in the water environment. Microbial grow-through is virtually eliminated as the surface is hostile to the microbes; the rate of biofilm formation is decreased due to a decrease in available bacterial nutrients, and the aggressiveness

of the filter surface towards the microbes. The catalytic filtration technologies' abilities to remove contaminants from water is further enhanced when exposed to UV, ozone and hydrogen peroxide. A cleaner filter can increase the operational lifetime of the filter and require fewer changeouts over the lifetime of the pool or spa. The use of hydrogen peroxide, ozone, UV radiation and bromine can also reduce and potentially eliminate the use of chlorine in a treatment system.

Since the catalytic filter operates under an additional oxidative mechanism, a brief discussion of the chemistry of organic contamination oxidation in the pool and spa water environment is in order. As shown in Figure 1, ultraviolet radiation (shown as 'hv') can oxidize an organic contaminant "R" and liberate dissolved carbon dioxide gas, water and a simpler organic contaminant designated "R'". The oxidation process can continue with the release of simpler compounds, until the ultimate conversion of the or-

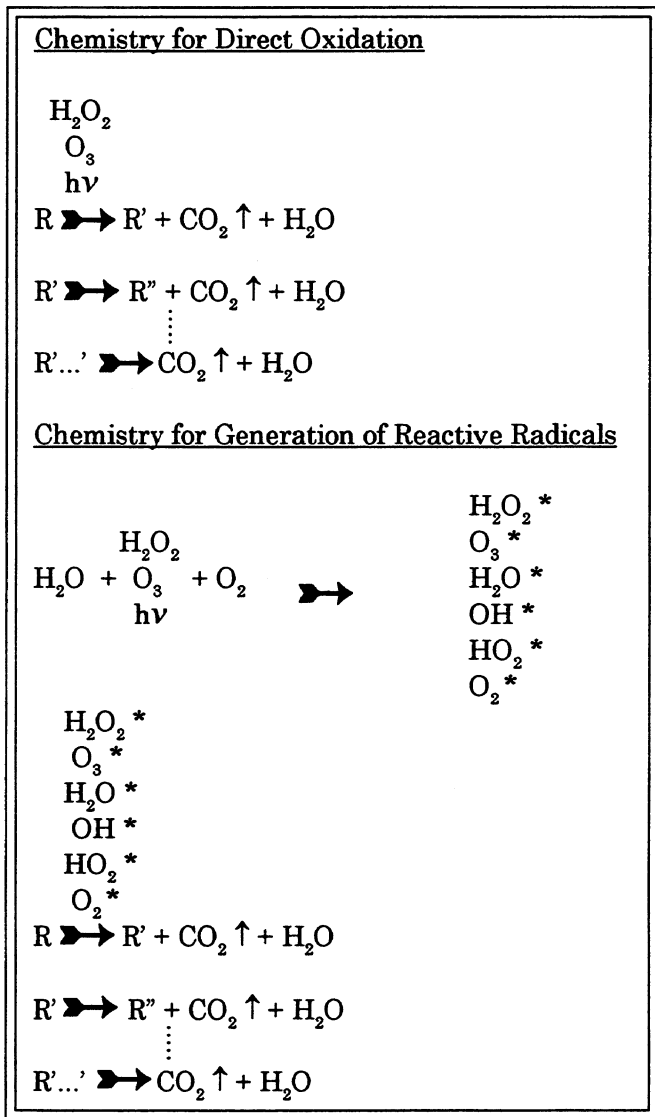
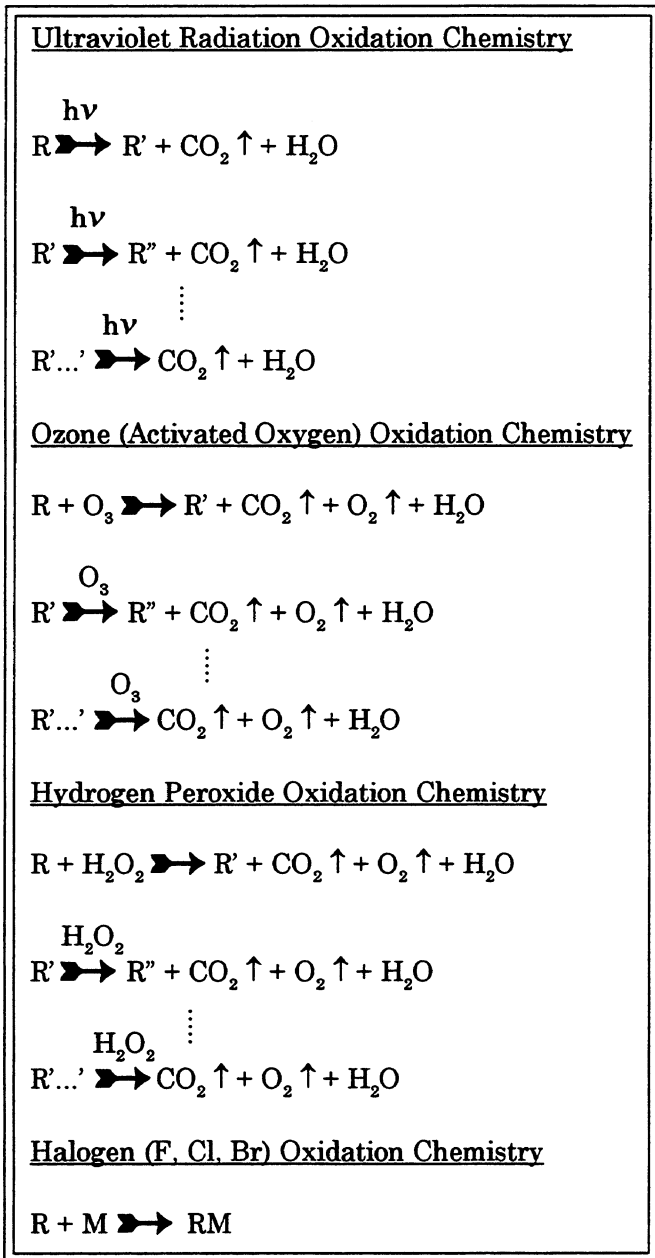


Figure 1 – Oxidation Chemistries for Organic Contaminant Removal

Figure 2 – Direct and Indirect Oxidation Mechanisms

ganic contaminant to dissolved carbon dioxide and water. Such complete conversion is rare and not typical of this environment. In actuality, the organic contaminant (which can include microbes) are broken down to stable or recalcitrant compounds that can then be trapped on a filter. The amount of residual remaining in the water can be measured as the total organic carbon or TOC and is usually represented as parts per million (ppm) or micrograms per liter (μg/l). Non-specific oxidizing agents such as ozone and hydrogen peroxide can oxidize organic contaminants to simpler compounds and usually result in a generation of dissolved oxygen as a reaction by-product.

As shown in Figure 2, the above reactions are examples of direct oxidation; a second pathway exists for the oxidation of organic contaminants in the water environment. This second chemistry results from the generation of reactive radicals from the existing water molecules by the oxidizing agents listed above. In this scenario, UV radiation, hydrogen peroxide, and ozone can individually or in combination interact with water molecules and produce highly energetic and short-lived reactive radicals. As shown in the Figure, radicals such as hydroperoxyl, ozonyl, hydroxyl, and superoxyl radicals have been established as having key roles in oxidizing even the most difficult organics down to simpler materials. The pathways are highly complex and diversified; the result, however, can be shown to consist mostly of carbon dioxide and water endpoints (oxygen can also be generated under certain conditions). Since the radicals are highly unstable, it is advantageous to accelerate their generation towards the destruction of the organic contaminants.

The catalytic filtration technology therefore uses two mechanisms to destroy organic contaminants. As shown in Figure 3, the direct oxidation pathway allows the combination of non-specific oxidizing agents such as hydrogen peroxide, ozone and UV radiation to oxidize the contaminants directly on the catalytic filter surface. The second mechanism is the acceleration of the generation of these highly reactive radicals (designated as "A*" in the Figure) from the water environment. This can be shown to be an indirect oxidation of organic contamination; the reaction is very fast and tends towards completion almost as quickly.

The catalytic filter is therefore more effective when exposed to the oxidizing agents that can be incompatible with current passive technologies. The result is purified water fed into the pool or spa from a highly effective contamination control system.

Technical Data

The effectiveness of the catalytic filter was proven to be extremely relevant to the pool and spa industry through one of the toughest testing envi-

ronments imaginable. Fundamental research and development was performed on a pilot scale ultrapure water treatment system that simulates a spectrum of water environments including waste water, potable water, and ultrapure water treatment systems (Governal 1992). The background levels of the total organic carbon (TOC) are measured in the part per billion range and the levels of bacteria are detected in the counts per liter range for this series of experiments. The system design and the water quality for these studies are therefore very representative of the largest scale present day electronics grade water systems. This environment has been proven to be extraordinarily aggressive towards existing passive filters as these filters are forced to remove trace contaminants while simultaneously having the potential to be exposed to non-specific oxidizing agents such as UV radiation, hydrogen peroxide and dissolved ozone.

The protocols used for these studies consisted of

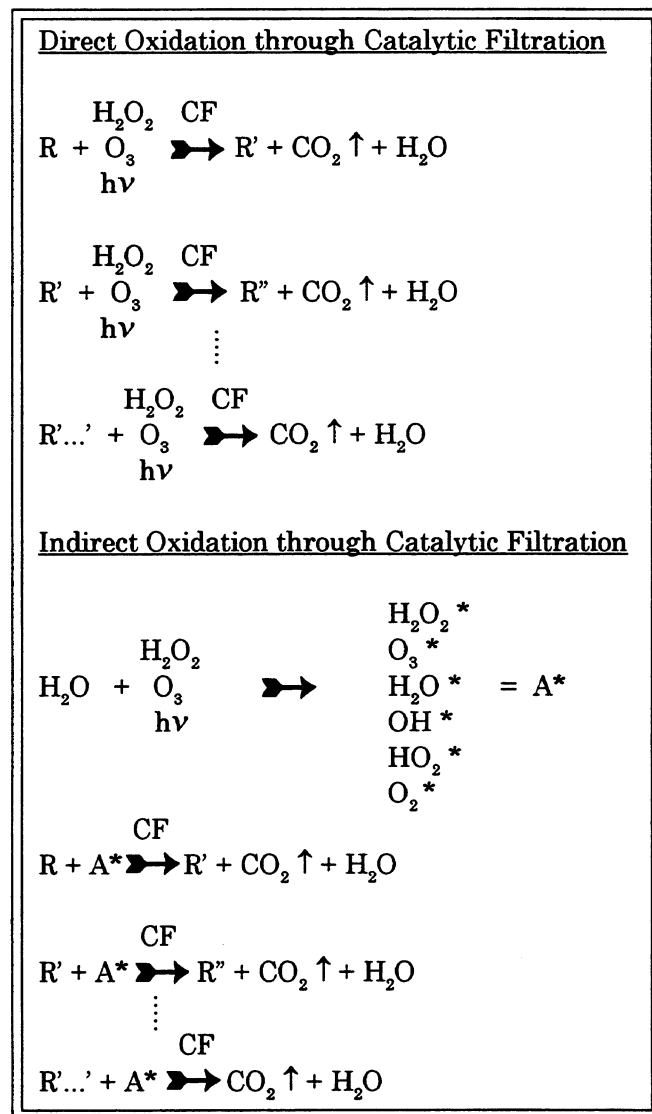


Figure 3 – Oxidation Mechanisms using Catalytic Filtration

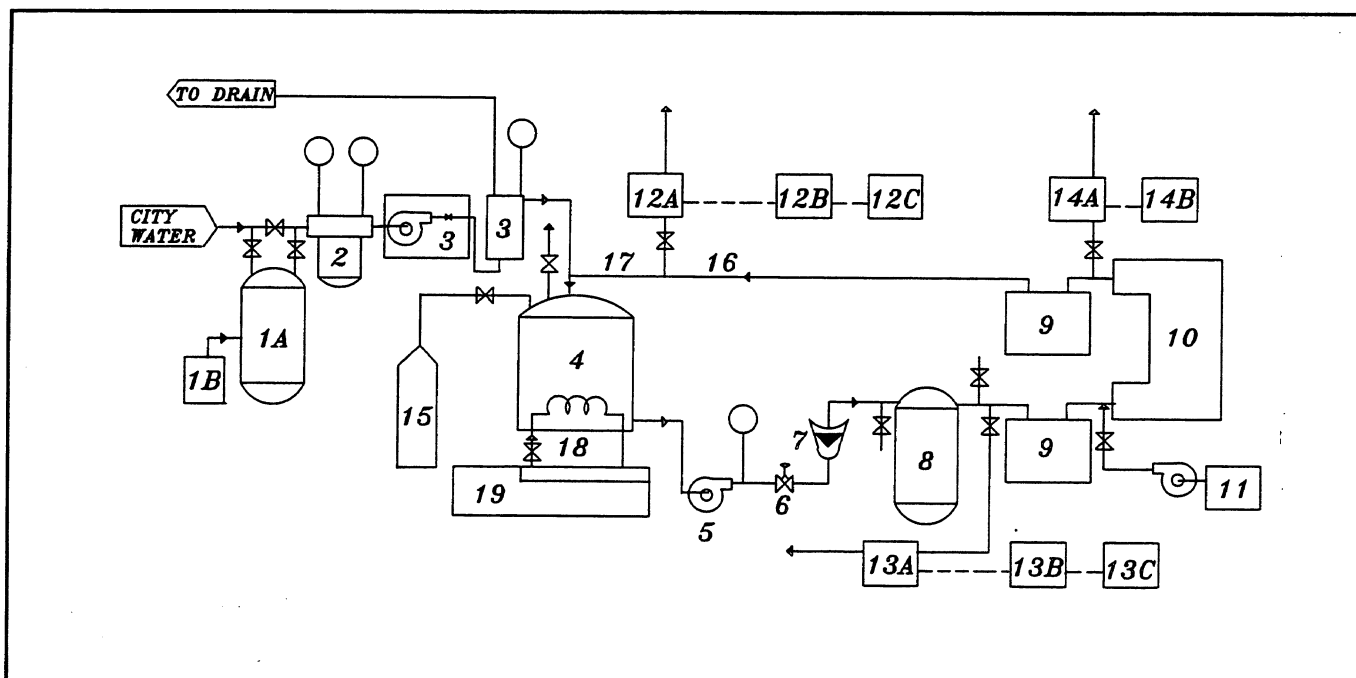


Figure 4 – Schematic of the Ultrapure Water System

- 1a: Water softener
- 1b: Brine tank
- 2: Carbon bed; 3 micron filter
- 3: Reverse osmosis unit; Millipore RO15 with thin film polyamide membrane
- 4: PVDF storage tank with level control; 10 gallon capacity
- 5: PVDF Circulation pump; 7 gpm @ 20 psig
- 6: PVDF manual diaphragm valve; 0–7 gpm
- 7: PVDF Flowmeter
- 8: Polishing mixed-bed ion exchange tank
- 9: Catalytic filter
- 10: UV-254 and 185 nm; Aquafine SL-1
- 11: Ozonated water injection system
- 12: Analyzers
- 13: Analyzers
- 14: Analyzers
- 15: Nitrogen source and particle filter
- 16: Sampling valves; 316L EPSS
- 18: 316L EPSS Cooling Coils
- 19: Heat Exchanger

Analyzers*:

TOC analyzer: Anatel A-100

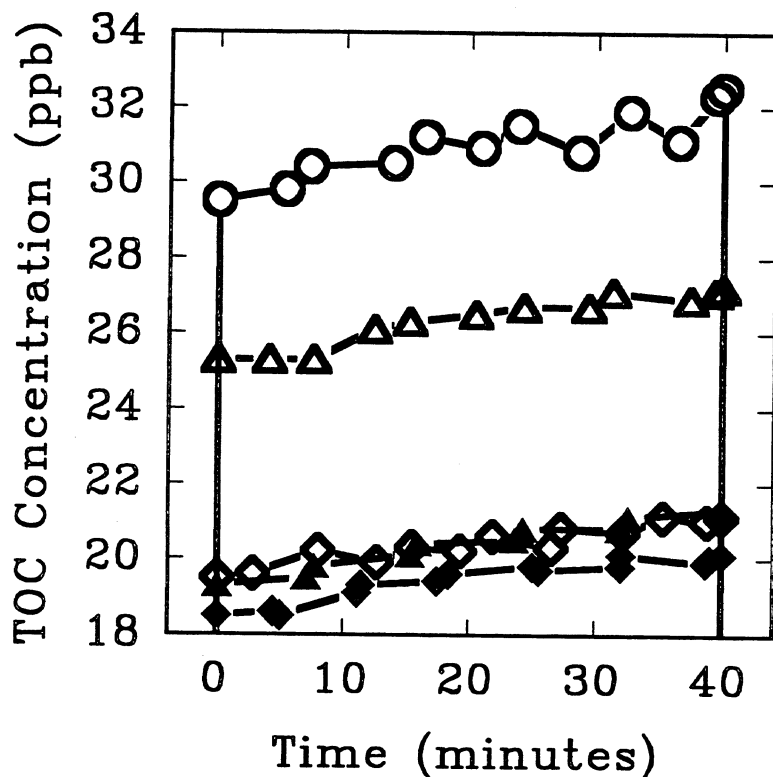
Resistivity meter: Martek MK-18

Dissolved ozone analyzer: Orbisphere 26501

Particle Counter: PMS HSLIS-M50

* – Each analyzer can be used at all sampling ports

Table 1 – List of Components in the Ultrapure Water Pilot System



- Input
- △ Passive Filter (75 Micron Pore Size)
- ▲ Catalytic Filter (92 Micron Pore Size)
- ◆ 50 ppb Ozone + Passive Filter (75 Micron Pore Size)
- ◆ 50 ppb Ozone + Catalytic Filter (92 Micron Pore Size)

Figure 5 – Profiles of TOC in the High-Purity Water System (The TOC is Composed of Background plus Humic Acids)

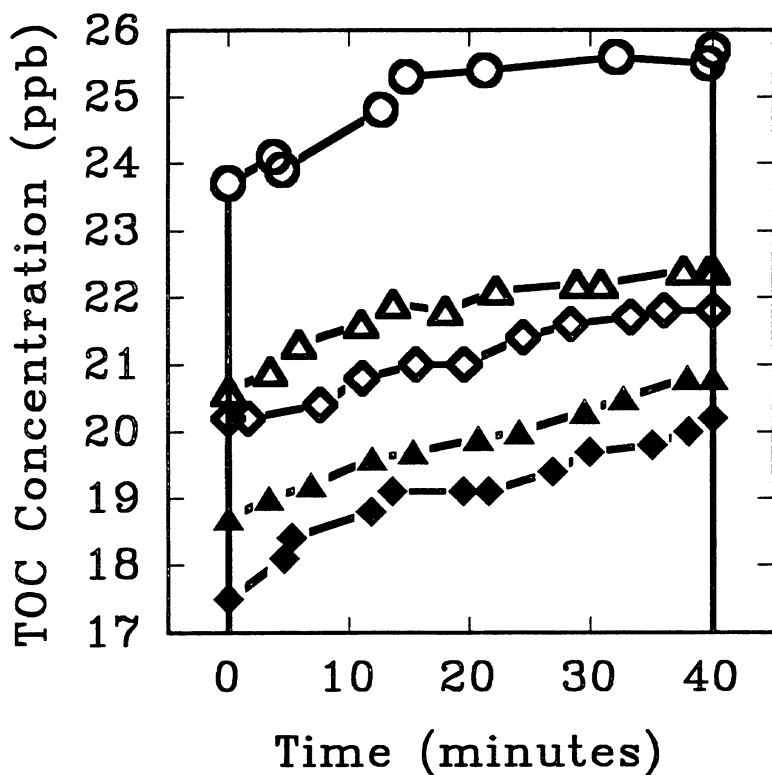
injecting trace amounts of representative and well defined organic contaminants into the pilot scale ultrapure water treatment system and, through the state of the art measuring devices, determining the capabilities of the catalytic filter to remove the contaminants independently, in combination with other water treatment operations including UV and ozone, and in comparison with a passive filter as is currently applied in water treatment industries (See Figure 4 and Table 1). Organic contamination in the high-purity water systems was provided in two primary forms. The first class of contaminant is the ill-defined background TOC level, which is representative of the levels of TOC found in most systems (Governal 1992). The second class of organic contaminant used in the study was the injection of model contaminants humic acids and bacterial lipopolysaccharides (LPS) as they have been shown previously to represent classes of organic contaminants found in pool and spa water systems (Rice 1995, Tamminen 1996); in each experi-

ment, 25 $\mu\text{g/l}$ (ppb) of each compound was injected into the system to show the effect of external loading on the water treatment component(s) being tested. TOC was injected into sample ports upstream of the water treatment system, and measured using an Anatel A-100 TOC analyzer (Boulder, CO) upstream and downstream of the system. The experiments were repeated using an untreated or passive filter to show the reactive effect of the catalytic filter in a variety of system configurations.

Figure 5 represents the results of injecting 25 parts per billion (ppb, $\mu\text{g/l}$) of the humic acids into the pilot system. As shown in the plot of TOC (as the sum of the injected Humic acids level and the background TOC) in ppb ($\mu\text{g/l}$) against time in minutes; the circles represent the amount of contaminant the unit operations are exposed to as a function of time and displayed an average value of approximately 31.5 ppb. The triangles represent the resulting TOC profile when the input function is treated by a system consisting of a 75 micron passive filter; as a result of this treatment, the average TOC value decreased to approximately 26.1 ppb. The filled triangles represent the action of a 92 micron catalytic filter in removing the contamination; the average TOC value was reduced, in this case, to 20.1 ppb. Note that when the catalytic filter was used in a similar sequence, the TOC level was substantially lower than the equivalent passive filter; this indicated that a greater amount of contamination was removed when the catalytic filter was used. The diamonds represent the action of the passive filter in removing the

organic contamination when assisted through the injection of 50 ppb ($\mu\text{g/l}$) dissolved ozone; the average TOC value after this type of treatment decreased to 20.2 ppb. The filled diamonds represent the action of the catalytic filter in removing the contaminant when assisted through the injection of 50 ppb ($\mu\text{g/l}$) dissolved ozone; the average TOC using this configuration was 18.6 ppb. In each case tested, the use of a catalytic filter showed superior TOC removal and was independent of dissolved ozone concentration.

Figure 6 represents the results of injecting 25 ppb ($\mu\text{g/l}$) of the bacterial cell wall fragments also known as Lipopolysaccharides (LPS) into the pilot system. As shown in the plot of TOC (as the sum of the injected LPS level and the background TOC) in ppb, ($\mu\text{g/l}$) against time in minutes; the circles represent the amount of contaminant the unit operations are exposed to as a function of time and displayed an average value of approximately 25.0 ppb. The triangles represent the resulting TOC profile when the



- Input
- △ Passive Filter (75 Micron Pore Size)
- ▲ Catalytic Filter (92 Micron Pore Size)
- ◇ 50 ppb Ozone + Passive Filter (75 Micron Pore Size)
- ◆ 50 ppb Ozone + Catalytic Filter (92 Micron Pore Size)

Figure 6 – Profiles of TOC in the High-Purity Water System (The TOC is Composed of Background plus LPS)

input function is treated by a system consisting of a 75 micron passive filter; as a result of this treatment, the average TOC value decreased to approximately 21.4 ppb. The filled triangles represent the action of a 92 micron catalytic filter in removing the contamination; the average TOC value was reduced, in this case, to 19.7 ppb. Note that when the catalytic filter was used in a similar sequence, the TOC level was substantially lower than the equivalent passive filter; this indicated that a greater amount of contamination was removed when the catalytic filter was used. The diamonds represent the action of the passive filter in removing the organic contamination when assisted through the injection of 50 ppb ($\mu\text{g/l}$) dissolved ozone; the average TOC value after this type of treatment decreased to 21.0 ppb. The filled diamonds represent the action of the catalytic filter in removing the contaminant when assisted through the injection of 50 ppb ($\mu\text{g/l}$) dissolved ozone; the average TOC us-

ing this configuration was 18.8 ppb. In each case tested, the use of a catalytic filter showed superior TOC removal and was independent of dissolved ozone concentration.

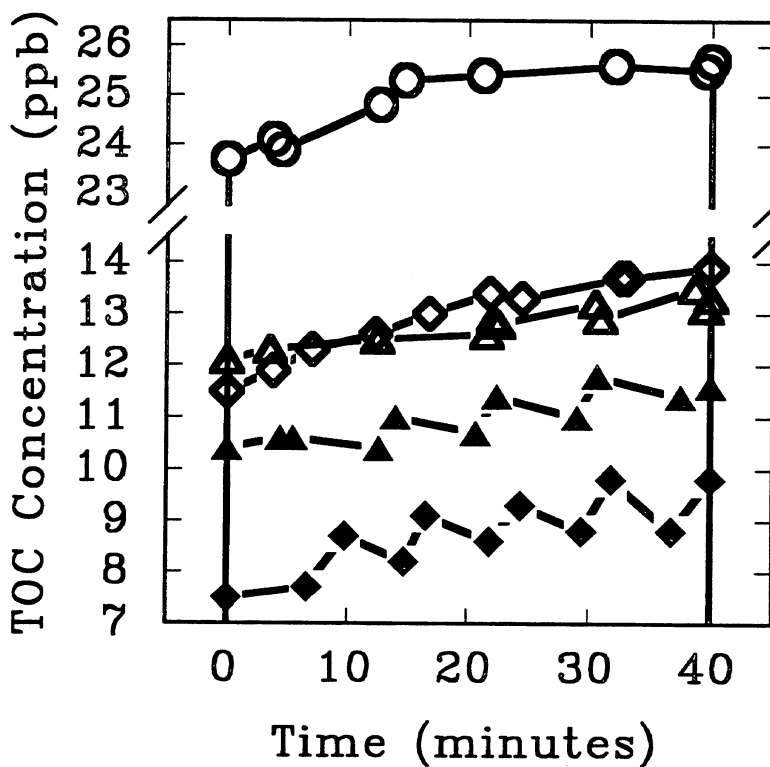
Figure 7 shows the plot of TOC against time when the filters are sequenced with the combination of UV and 50 parts per billion of dissolved ozone to remove both the background contaminants and the injected LPS from the water treatment system. The circles represent the input function and again show an average TOC value of approximately 25.0 ppb. The triangles show the effect of using the sequence of dissolved ozone, the passive filter and the UV sterilizer as a water treatment package to remove the contaminant and resulted in a decrease in the average TOC level to approximately 12.6 ppb. The filled triangles show the effect of using the sequence of dissolved ozone, the catalytic filter and the UV sterilizer as a water treatment package to remove the contaminant and resulted in a decrease in the average TOC level to approximately 11.0 ppb. The diamonds show the effect when a passive filter is situated downstream from the ozone / UV sequence and resulted in an average TOC value of approximately 12.6 ppb. The filled diamonds represent the action of the ozone / UV / catalytic filter sequence of unit operations in the removing of the TOC; in this case, the average contaminant level was reduced to approximately 8.6 ppb. The catalytic filter, regardless of sequence, proved itself to remove the organic contaminant at a faster rate than an equivalent passive filter.

In all cases and within every body of data tested, the systems incorporating catalytic filter technologies consistently and more effectively removed organic contaminants from water systems than conventional passive filter treatment systems.

System Designs

The sequences used in this system were designed to show the potential of the catalytic filters in comparison to passive filters in large scale applications for the pool and spa industries. As shown in Figure 8 (a), the water treatment system can be designed as an on-line injection of 50 ppb ozone alone or in combination with additional non-specific oxidizing agents such as hydrogen peroxide and bromine followed by the catalytic filter. Using this configuration, the catalytic filter can be continuously exposed to oxidizing agents and a bromine residual can be maintained in the product water.

Figures 8 (b) and (c) are chemical-free systems



- Input
- △ 50 ppb Ozone + Passive Filter (75 Microns) + UV
- ▲ 50 ppb Ozone + Catalytic Filter (92 Microns) + UV
- ◇ 50 ppb Ozone + UV + Passive Filter (75 Microns)
- ◆ 50 ppb Ozone + UV + Catalytic Filter (92 Microns)

Figure 7 – TOC Profiles in the Ultrapure Water System (Using Bacterial Lipopolysaccharides (LPS) Background TOC Included in the Data)

in which the catalytic filter acts as an activated strainer to treat the water in the presence of UV radiation; the UV oxidizer is used to reduce the amount of organic contamination that would then be discharged. A system like this could be used to drain a pool and discharge the water safely, or as a pretreatment step for water recycling.

Figures 8 (d) and (e) show the combination of the chemical pretreatment system and the UV / catalytic filter unit operation. This level of treatment would be recommended for public pool and spa applications in which a large load of contamination would be expected to be treated to maintain water quality.

Note that in each case shown in Figure 8, at no time is chlorination required to maintain water quality. A chemical residual can be maintained in the pool through the use of a non-chlorinated compound. One such possibility may be through the use of bromine or brominated compounds (Rice 1995).

Conclusions

The purpose of this article is to introduce catalytic filtration technologies to the Pool and Spa Industry. This report is not a claim that these new catalytic filter technologies make every other passive filter technology immediately obsolete. It does, however, serve notice to the pool and spa industry that a revolutionary technology is on the horizon.

In all cases tested, the catalytic filtration technologies removed even trace organic contaminants from water treatment systems more effectively than conventional passive filter dependent products and systems; this resulted in purer and safer water for multiple applications at lower costs.

The design of new systems using catalytic filtration can result in water that is purified without the use of chlorine or chlorinated chemicals. This will reduce the amount of carcinogenic chlorine related compounds formed during the water treatment process.

As we look forward, the ultimate goal of these innovative technologies is to provide the purest water applicable for the end user at a fair price. This can be accomplished by replacing any existing product and system that uses less effective passive filters with catalytic filtration technologies.

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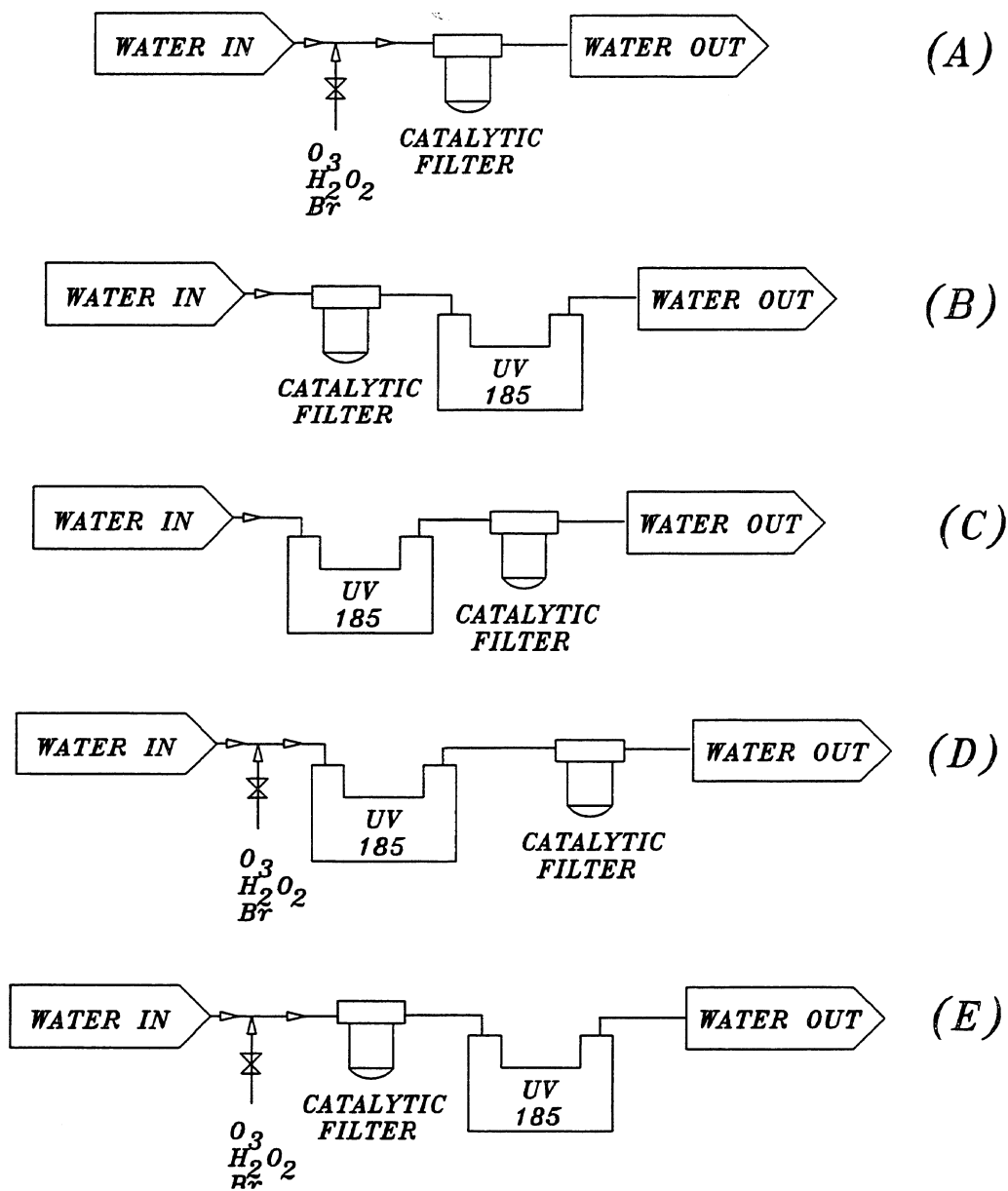


Figure 8 – System Designs Using Catalytic Filtration Technologies

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