

# **TECHNOLOGY BRIEFING**

# PHOTO-CAT MULTI BARRIER WATER PURIFICATION





Industrial

Drinking Water

March 27, 2009

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Rev. March 19, 2008

# **EXECUTIVE SUMMARY**

This document is a comprehensive technical briefing on Photo-Cat technology. The document is designed to give intended users an understanding of the applicability, durability, capability, maturity and benefits of Photo-Cat technology in a variety of applications.

This document describes Photo-Cat's unique multi barrier protection capability, including its advantages and applicability in the following sectors: drinking water, water reuse, aquifer storage recharge, industrial process water and groundwater remediation.

The document also provides an overview of relevant Photo-Cat equipment installations and key pilot tests categorized by sector, since 1993.

Purifics is the oldest and most experienced vendor of Advanced Oxidation Processes, and is the only vendor of commercial photocatalytic processes, providing ceramic membrane systems since 1994.

This briefing is intended to communicate Photo-Cat's capability and to clarify misunderstandings and confusion with other technologies like  $UV/TiO_2$ , conventional polymeric membranes, UV/peroxide, and Peroxide/Ozone technologies.

In addition the document will identify certifications and standards used in manufacture, construction and assembly making Photo-Cat a Global Product.

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# **1 PRINCIPLES & ADVANTAGES OF THE PHOTO-CAT PROCESS**

Photo-Cat is a flexible water **PURIFICATION** technology that supports sustainable development, eliminates the need for chemical oxidants and provides the lowest life cycle cost when properly applied. It destroys organic pollutants in water, disinfects and kills biologicals, removes some metals and low nanometres size particles from water.

Photo-Cat technology is a photocatalytic oxidation and reduction process that utilizes a light activated titanium dioxide (TiO<sub>2</sub>) slurry catalyst. The Photo-Cat process is similar to other catalytic processes such as the catalytic converter on automobiles. The major difference in TiO<sub>2</sub> photocatalytic oxidation is that the TiO<sub>2</sub> catalyst uses light energy for activation, rather than heat energy, as is the case with conventional catalyst technologies. Photo-Cat is a low energy, ambient temperature and pressure process that utilizes a self cleaning ceramic membrane to recover the slurry. Essentially, the only input is electric power.

Photo-Cat is frequently referred to as an:

- Advanced Oxidation Process (TiO<sub>2</sub> Photocatalysis)
- UV Process
- A UF Membrane Process

It is the best of these water treatment technologies that is combined into the Photo-Cat process giving it unsurpassed multi barrier water purification capability that has been commercially applied since 1994. Photo-Cat is more accurately characterized as a **Photo-Catalytic Ceramic Membrane System**.

# 1.1 TiO<sub>2</sub> Photocatalysis

 $TiO_2$  photocatalysis uses the full spectrum of ultraviolet light to activate the  $TiO_2$  catalyst as opposed to the photons cleaving chemical bonds. The UV light photogenerates electrons into the conduction band of the catalyst semiconductor and positive "holes" at the surface of the  $TiO_2$ . When this occurs, the catalyst is in an activated state and four organic destruction pathways exist (both oxidative and reductive) as listed below.

1 & 2) The most typical oxidative pathway involves the reduction of oxygen, creating the <u>superoxide radical</u>. Subsequently, a water molecule or hydroxyl ion is oxidized at the positive hole and creates a <u>hydroxyl radical</u>. Both radicals, which are generated with one photon of light, readily oxidize the organic contaminants. Refer to the Aqueous Phase Photochemistry diagram below in Figure 1.

- 3) A third oxidative pathway is oxidation of the adsorbed organic contaminant directly at the <u>photo-generated hole</u> (which is denoted by the '+' shown in Figure 1). The oxidative power of the photo-generated hole is about 15% stronger than the hydroxyl radical.
- 4) The last degradative pathway is a reductive pathway via reduction by the <u>conduction band electron</u>. This degradative pathway is very efficient at destroying refractive organic contaminants that are resistant to the hydroxyl radical attack. An example of this treatment mode is the photocatalytic reduction of 1,3,5-trinitrobenzene (TNB) in the remediation of TNT contaminated water.



#### Figure 1: Aqueous Phase Photochemistry

In all four degradation pathways listed above, organic contaminants are destroyed on the surface of the  $TiO_2$ . The light energy is used only as an energy source for catalyst activation. Consequently, photocatalytic by-products are controlled and consistent because the degradative pathways do not create organic radicals.

Table 1 lists the relative oxidative strength of various radicals and oxidizing species in relation to chlorine.

Oxidizing Species	<b>Relative Power</b>	
Photo-Generated Hole on TiO <sub>2</sub> *	2.35	
Fluorine	2.23	
Hydroxyl Radical *	2.05	
Atomic Oxygen	1.78	
Ozone	1.52	
Hydrogen Peroxide	1.31	
Permanganate	1.24	
Hypochlorous Acid	1.10	
Chlorine	1.00	

# Table 1: Relative Oxidizing Power Versus Various Oxidizing Species

\*Oxidizing Species Generated by Photo-Cat

This table is important to illustrate why Photo-Cat is the most aggressive technology for oxidizing organic contaminants, and the lowest cost solution.

#### 1.2 Photolysis

The photocatalytic process should not be confused with UV/H<sub>2</sub>O<sub>2</sub> or UV/O<sub>3</sub>, which are photolytic processes. Photolytic technologies generate hydroxyl radicals by using high energy photons to cleave the peroxide molecule: H<sub>2</sub>O<sub>2</sub> + UV  $\rightarrow$ 2°OH. The efficiency of this type of process is greatly reduced by the fact that in the range of 75% of the °OH recombine back to H<sub>2</sub>O<sub>2</sub> without accomplishing any work. Photolytic technologies typically use medium or high pressure lamps to generate the photons. Photolysis can also photolyze organic compounds directly, and can create random intermediates. Random intermediates are a concern.

#### **1.3** Principles of Photo-Cat – Understanding the Differences Between Other AOPs

Since the Photo-Cat does create hydroxyl radicals; it is referred to as an advanced oxidation process (AOP). Based on this generic classification, it is wrongly assumed that Photo-Cat suffers from the same problems and shortcomings of photolytic technologies such as UV/Peroxide, UV/Ozone and Ozone/Peroxide.

The biggest difference between these other technologies is in the way radicals are generated. The Photo-Cat uses a light-activated  $TiO_2$  catalyst to generate radicals,

and the powerful photocatalytic positive hole. These oxidizing species are the first and third strongest oxidizing species. The catalyst reduces the activation energy required to generate the radicals, thus reducing energy requirements.

Unlike UV/peroxide, which requires photons with sufficient energy to break chemical bonds, Photo-Cat only requires photons at a wavelength of less than 388nm capable of exciting electrons. This provides a high degree of freedom in selecting UV sources for the Photo-Cat, and allows Purifics to utilize the highest efficiency lamps, with the greatest lamp life (41% efficient with over 24,000 hour life).

Unlike ozone/peroxide technologies, Photo-Cat does not require chemical oxidants to create its radicals. The handling, hazards, and cost associated with ozone production and storage, are eliminated. Hydrogen peroxide has the same issues associated with it. This process is also prone to producing the toxin bromate in the treated water if the water has trace salinity causing bromide to be present.

In the Photo-Cat process, essentially all of the UV light is absorbed by the photocatalyst and is absorbed at the surface of the quartz-water interface. Photolysis reactions are eliminated, along with the issues associated with the production of random intermediates. The Photo-Cat system does not rely on transmittance of photons through the water. This makes the Photo-Cat process completely impervious to any type of absorbance issues, such as turbidity, high TDS, or colour. This ability also reduces complexity by eliminating pre-treatment, and provides greater overall efficiency. Unlike traditional UV/peroxide technologies which operate in laminar flow regimes, the Photo-Cat reactor is highly turbulent (Re as high as 40,000), which provides maximum mass transfer of contaminant,  $TiO_2$  and photons, providing optimum destruction efficiency.

The high mixing rates obtained in the Photo-Cat reactor coupled with the honing ability of the  $TiO_2$  catalyst eliminates any fouling mechanisms on the quartz sleeves of the reactor. Thus, no wiper mechanisms are required, hence eliminating any cleaning requirements during the life of the system. The elimination of UV-quartz wipers reduces system complexity, cost, and the potential for a failure.

The Photo-Cat technology provides much greater degrees of freedom in comparison to other AOP technologies; elimination of  $H_2O_2$ , ozone, chemical oxidant storage, quartz wipers. Other degrees of freedom include the use of highest efficiency and longest life lamps, the greatest mass transfer reactor for optimal organic destruction, reduced energy requirements through the catalytic radical formation, two radicals generated per photon of energy, and no effects of UV absorption.

# The net effect is a 3:1 operating cost advantage of Photo-Cat versus other technologies.

# 1.4 TiO<sub>2</sub> Photocatalysis: Slurry Vs Fixed

Photo-Cat is a process that uses the  $TiO_2$  in a slurry form, and then effectively recovers 100% of the slurry in a continuous process. Other  $TiO_2$  processes have experimented with an immobilized or fixed  $TiO_2$ . Technically this process works but its commercial viability is very limited. Fixed  $TiO_2$  processes have unsolved issues for bonding, fouling, masking, mass transfer, durability and photon efficiency that at best give is an order of magnitude poorer performance than slurry photocatalysis.

# 1.5 Photo-Cat Materials of Construction

The Photo-Cat is constructed of quarts glass, stainless steel, ceramic, gaskets and electronics. Fabrication standards meet or exceed client's requirements. With the exception of a few valves and pumps Photo-Cat is essentially a solid state device. The result is a system that does not leach or corrode, has high reliably and proven durability in high cycle operations or sustained 24/7 duty.

# 1.6 UV Lamps

The Photo-Cat utilizes high efficiency low pressure UV lamps as the light source to excite the TiO<sub>2</sub>. The catalyst uses the full spectrum of the lamp from 360nm to 185nm giving a lamp UV efficiency of up to 41%. In addition the Photo-Cat lamp was developed in 1998 with a long life capability to operate reliably and durably from the freezing point of water to elevated ambient temperatures >40°C. Photo-Cat lamps have seen over 36,000 hours of operation at only 21% degradation. This key component of lamp life gives Photo-Cat its ability to support energy conservation and sustainable development.

# 1.7 Oxidation without Hydrogen Peroxide or Ozone

Photo-Cat utilizes dissolved oxygen to generate radicals. **No hydrogen peroxide or ozone is required** in the process. This eliminates the safety concerns related to handling these chemicals, and the costs associated with them.

Eliminating the need for hydrogen peroxide is extremely important for drinking water applications. First there is a real cost saving related to the elimination of hydrogen peroxide. First, there is a capital cost savings by eliminating the chemical storage requirement, and secondly the operating cost savings by not having to handle or consume it. Typical dosages for UV/peroxide systems in drinking water can range from 5-20ppm, and have to be added in excess. Typical peroxide consumption is very low, consequently, the majority of the peroxide is wasted and must be removed downstream using carbon or chlorine (which creates additional cost and complexity). Finally, there are undesirable **stabilizer compounds** (both inorganic and organic) **in peroxide**, which are very resistance to oxidation. Typical organic stabilizer compounds can be 8-hydroxyquinline, pyridine carboxylic acids,

tartaric and benzoic acids, and acetanilide and acetophenetidin compounds. Similarly, 1,4-dioxane was a stabilizer used in chlorinated degreasing agents

Ozone will create the carcinogen bromate ion in water that contains bromide, which is typically associated with water containing salt. Bromate is a toxin and is costly and expense to remove if not treated properly. The Photo-Cat will not generate bromate ion, and it will effectively reduce bromate ion back to benign bromide ion.

#### **1.8** The Proof is in the Test

The ultimate proof results from testing the actual water of concern so a comparison of the overall system efficiency can be performed. It is also prudent to fully understand the true O&M cost structure beyond simple power and chemical usage. Some technologies require expensive cleaning or components.

#### **1.9** What is Water Purification?

Purification is a term that is often used inappropriately when describing water treatment: Webster's Dictionary defines Purification as "cleaning by getting rid of impurities". Current industry practice confuses chemical treatment as water purification which is not correct.



\*Applicable to certain metals only.

The Photo-Cat process is capable of all of the above types of purification with the exception of some metals and salt removal.

#### 1.10 RO Pre-Treatment

Photo-Cat provides a low molecular weight and sterile feed to RO and other salt removal processes ensuring their optimal performance. Photo-Cat is the only AOP

process that can be used upstream of an RO process because it will not harm the RO membrane.

### 1.11 Elimination of Granular Activated Carbon (GAC)

Photo-Cat is routinely applied to displace GAC for the removal of organic contaminants. Key advantages of the Photo-Cat is that it destroys the contaminant of concern, has a lower life cycle cost, which supports sustainable development and the reduction of green house gases. Photo-Cat over GAC eliminates legacy liability.

Photo-Cat also destroys organic contaminants that GAC has difficulty removing (ie. 1,4-dioxane, vinyl chloride, NDMA, etc.).

#### 1.12 Chemical-Free Drinking and Water Reuse Purification

Photo-Cat is a **Multi Barrier** water treatment technology used for the purification and protection of potable water. Photo-Cat has been used to purify water in a variety of potable water source protection and high purity process water applications. It is a highly developed technology that has been proven and demonstrated. Photo-Cat is a unique chemical-free process that removes chemical contaminants (EDCs), biological species, NDMA, viruses, oocysts, bromate, submicron particulate, and metals such as manganese, mercury, and iron.



Applying the low energy Photo-Cat process to potable water, its many benefits will significantly improve drinking water quality and reduce cost and complexity. Photo-Cat will purify ground / surface water and tertiary water to drinking water standards. Photo-Cat not only **removes or destroys difficult contaminants like cryptosporidium, giardia, 1,4-dioxane and EDCs;** it also improves the taste, color, and clarity of water while reducing odor. Photo-Cat has demonstrated success where other AOPs and membranes have failed, and documented sustained operational performance of greater than six log removal.

Photo-Cat is a single unit process that reduces the complexity of traditional potable water purification systems.

#### 1.13 What is Multi Barrier Protection in One Unit Operation

As shown in the Figure below, the Multi Barrier Protection of Photo-Cat combines the best of chemical-free **AOP** technology; with long life, wiper-free **UV**; and with maintenance-free **ceramic membranes** in a single unit operation.



With a host of benefits including superior water treatment capabilities, no quartz wipers, low lifecycle cost, negligible consumables, and simplicity, the Photo-Cat purification process represents an alternative to the costly and complex treatment methods currently on the market. Photo-Cat must not be confused with conventional AOPs and membrane technologies.

As a fully developed system that incorporates a plant-wide SCADA and control network, Photo-Cat represents a leap beyond traditional baseline technologies and providing a significant opportunity in capital and lifecycle cost reduction.

Photo-Cat truly minimizes waste and promotes sustainable development. In addition, Photo-Cat is capable of detecting and reporting changes in water chemistry. It is Photo-Cat's fully developed automation that also allows it to identify future service requirements.

Photo-Cat can be fully tailored to specific client needs. It can stand alone, or be integrated with existing operations to completely unify plant processes. For a fully operational Photo-Cat system, simply drop it in place and it is ready to run. Thus, Photo-Cat is ideal in situations where skill sets for operation and maintenance are limited.

#### 1.14 Photo-Cat Air Treatment

Photo-Cat is used in the purification in air when the air born contaminants are soluble, and can be transferred to the water phase by scrubbing or other methods. Once the contaminant has been transferred to the aqueous phase, the Photo-Cat destroys the organic contamination, and the water is sent back to the scrubber unit. This is common practise in removing explosives, alcohols, ketones, etc. in air.

### 1.15 Photo-Cat Ceramic Membrane System

Purifics has engineered **Ceramic Membrane Systems** since 1993. Today, Photo-Cat, with its physical ceramic barrier, is used in a variety of applications, including: the removal of particles down to 12 nm range with water flux in the range of  $3700 \ l/m2/hr$  @ 20 C, 1 bar (2200 gal/ft2/d at 15psi); with continuous integrity testing built into the process. The process will generate water with <0.1 NTU.

Ceramic membranes have low lifecycle cost, essentially 100% duty, and sustainable flux. In addition, these ceramic membrane systems are fully automated, designed to meet boiler pressure vessel code for 150psi rating, and are not vulnerable to fatigue failure, abrasion, or chemical attack. Purifics' **ceramic membrane systems do not require cleaning, chemicals, replacements, or consumables.** Design life is 25 years.



0.4 MGD Membrane Size



1/4 MGD Membrane Size



Cross-Section of Ceramic Membrane

Ceramic Membranes are capable of operating over a wide temperature range from  $<0^{\circ}$ C to  $> 100^{\circ}$ C (extremes found in sea water and pressured water applications). The performance over this range is well understood and is primarily a function of fluid viscosity.

# **2 TREATMENT CAPABILITY FOR BIOLOGICAL SPECIES**

The Photo-Cat has demonstrated complete inactivation / removal of biological species. The following are data results from biological species used to challenge the Photo-Cat system. In a pilot test for Reuse water treatment (performed at the Sugar Creek WTP, Charlotte, NC) the Photo-Cat achieved >6.9 log removal of viruses, and > 5.3 log of coliform (both were 100% removed to the detection limit). This wastewater had a UVT of only 64%, however, Photo-Cat is not affected by UV absorbance. Photo-Cat has been proven effective in disinfection and oxidizing opaque fluids such as 40% starch slurry.

Photo-Cat not only disinfects contaminated water, it also kills bacteria, viruses, and oocysts such as e-coli and cryptosporidium. It is Photo-Cat's **Multi Barrier System** that eliminates Biologicals. Those Biologicals resistant to AOP & UV treatment can be filtered out by a physical ceramic barrier. This barrier provides a complete method of purification and protection for potable water. The advantage of a ceramic membrane barrier is its invulnerability to fatigue and other forms of failure.

The following sections provide additional biological inactivation data.



# 2.1 Inactivation Results for Cryptosporidium

#### 2.2 Bacteriophage Inactivation/Removal



#### 2.3 Photo-Cat Removal of Total Coliform in Tertiary Water



#### Reference: Carollo Engineers





#### 2.4 Photo-Cat Removal of MS2 (Virus) in Tertiary Water

Reference: Carollo Engineers

# **3 TREATMENT CAPABILITY FOR MICRO-CONTAMINANTS (EDCs)**

#### 3.1 Endocrine Disrupting Chemicals (EDCs)

An endocrine disrupting chemical (EDC) is a foreign chemical or substance which acts like a hormone in the endocrine system. The endocrine system regulates metabolism, growth, tissue function and effects moods.

The following micro-contaminants have been simultaneously tested at once using the Photo-Cat technology, with individual concentrations as high as 1,000 ng/L and were all effectively reduced.

#### Pharmaceuticals

Sulfamethoxazole (antibiotic) Atenolol (beta blocker) Trimethoprim (antibiotic) Iopromide (heart medication) Fluoxetine (Prozac) Meprobamate Dilantin (epilepsy medication) Carbamazepine Diazepam Atorvastatin (Lipitor) Benzophenone Primidone Gemfibrozil Diclofenac Naproxen (Aleve) Octylphenol Ibuprofen Ethynylestradiol (birth control pill)

#### **Personal Care Products**

Triclosan (Antibacterial soap) Musk Ketone

#### Hormones

Testosterone Progesterone Estrone Estradiol

#### **Other Chemicals**

Caffeine Atrazine (herbicide) TCPP (fire retardant) DEET (insect repellent) TCEP (fire retardant) Bisphenol A (plastics) BHA (food preservatives)





#### 3.1.2 Estrogenic Activity by Estradiol Equivalent Loss



### 3.1.3 Bromate Removal (provisional data)



#### 4/3/09

### **4 TREATMENT CAPABILITY FOR METALS & PARTICULATE**

The Photo-Cat has the ability to remove and recover on a sustained basis, the following metals: Fe, Mn, As, Hg, Pb, and Ag

The Photo-Cat also has the ability to break apart chelated metals, which allows the metals to be recovered.

The Photo-Cat also has the ability to remove particulate down to the 20nm range, which is the current limit of testing.



#### 4.1 Iron Removal from Drinking Water Vs pH

#### 4/3/09

### **5 LABORATORY RESEARCH & DEVELOPMENT**



**Photo-Cat L -** A unique tool for research and teaching of photo chemistry, controls, mass and heat transfer related to water purification & their technical attributes.

#### Affiliated Research

**Arizona State University** (Water Quality Center): 2007 Dr. John Crittenden Ph.D. P.E. N.A.E., Dr. Paul Westerhoff, PhD, PE, Dr. Morteza Abbaszadegan, Ph.D.

- DBP and DBP Precursor destruction
- Quantifying disinfection, EDC removal and disinfection by-products removal
- Photocatalytic inactivation of viruses using titanium dioxide nanoparticles and low-pressure UV light
- Elimination of Disinfection By-Products (DBPs) Using Photo-Cat technology

#### Southern Nevada Water Authority: 2007

Shane Snyder Ph.D., Mark J. Benotti Ph.D., Ben Stanford Ph.D.

- Validation of Bromate destruction
- Investigating destruction of EDC's

#### **University of Western Ontario**: 2007

Sohrab Rohani, Ph.D., P.Eng., F.C.I.C.

• Water Splitting for Hydrogen Generation and Photocatalytic Application of TiO<sub>2</sub> nanotube arrays

Dr. Paul Charpentier

• Hydrogen Generation from Renewable Waste Product Streams Using Supercritical Water Oxidation

### **University of Toronto**: 2006

Anni Luck

• "UV/TiO<sub>2</sub> for Drinking Water Treatment: Concurrent Degradation of 1,4-Dioxane and Removal of Iron and Manganese" presented at the Water Quality Technology Conference

#### Advanced Concepts and Technologies: 2006

• Detection & Destruction of Toxic & Hazardous Contaminants

#### Fanshawe College, London ON: 2005, 2006

• Academic Research & Training

#### University of Florida (Environmental Sciences-Commercial Space Technology

Center- ES CSTC): 2004

• Advanced Life Support

# 6 PHOTO-CAT MODELS

#### 6.1 Drinking Water & Water Reuse Systems

6.1.1 <u>0.25-0.5 MGD Photo-Cat System</u>



6.1.2 <u>1.5-6.75 MGD Photo-Cat System</u>



- 6.2 Industrial Process Water & Ground Water Remediation Systems
- 6.2.1 <u>DL Model: 2.5-50kW</u>
- 6.2.2 DDL Model: 50-100kW





6.2.3 <u>Mobile Verification Systems</u>



#### 6.3 Multi-Pallet Systems

#### 6.3.1 Industrial Multi-Pallet System: >100kW 6.3.2 Municipal 30 MGD System



#### 6.4 Certifications

Photo-Cat Technology is available in a number of design certification requirements and can be built to meet or exceed the requirements of CSA CAN3-Z299.3-85 for QA/QC.

#### 6.4.1 Boiler & Pressure Vessel Certification

Photo-Cat systems have been built to the ASME standard B31.1 for operating pressures up to 150 psi. The Photo-Cat is also available in Class 6 to Nuclear certification.

#### 6.4.2 <u>NSF & FDA</u>

The Photo-Cat system is certified to NSF/ANSI 61. Essentially all components in the Photo-Cat are FDA certified components when ever possible and applicable.



#### 6.4.3 Processing Explosives & Energetics

Photo-Cats have been built to process TNT and Nitro-glycerine. This involves essentially a food grade design similar to specification 7.3.2 with some additional safeguards. Photo-Cat can also be build to specification as high as CLASS 1 DIV 1.

#### 6.4.4 <u>Global Standards</u>

Photo-Cats have been built to the requirements of a number of different electrical standards. In addition the components of Photo-Cat can be found in countries around the globe which comply with local standards and from a spares perspective are readily available.