Application of a Medium Pressure UV System for the Treatment of N-Nitrosodimethylamine (NDMA)

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Introduction

N-nitrosodimethylamine (NDMA) was first detected in 1990 as a problem pollutant in drinking water wells at levels as high as 3,000 ppt in Elmira, Ontario, Canada. The waste from a large chemical plant over many years had led to the contamination of the drinking water wells for the community. After extensive evaluation and testing, it was determined that UV photolysis was the most effective treatment method which led to the installation of a Calgon 270 kW Rayox® UV system in 1991. The system has been continuously treating water to this day. At about the same time, NDMA was found in the drinking water on an Indian reserve in Ontario, and a similar UV system was installed to remove NDMA from that water. Since then NDMA has been detected as a pollutant in ground waters, surface waters, industrial effluents and wastewaters in many jurisdictions. Many sources have been identified, including chemical plants that manufacture pesticides and herbicides, rubber manufacturing plants, rocket fuel manufacturing plants and wastewater treatment plants.

Recently there has been considerable concern in California about the detection of NDMA in drinking water feed wells at levels as high as 900 ppt. NDMA was found to be a carcinogen in animals and assessed as a Class 1 carcinogen by the USEPA. It is currently listed as a priority pollutant on the US EPA National Priorities List. California has set an “action level” of 20 ppt for NDMA and treatment systems are required to treat to the detection limit of 2 ppt.

NDMA is often produced as a byproduct in the industrial use of dimethylamine (DMA). DMA is a semi-volatile organic chemical that is soluble in water and has been commercially used for several decades. For example, from the mid 1950’s till April, 1976, it was manufactured and used as an intermediate in the production of 1,1-dimethylhydrazine, a storable liquid rocket fuel that contained approximately 0.1% NDMA as an impurity. In addition 1,1-dimethylhydrazine oxidizes to produce NDMA. DMA is also used for the inhibition of nitrification in soil, as a plasticizer for rubber and polymers, as a solvent in the fiber and plastics industry, an antioxidant, a softener of copolymers, and as an additive to lubricants. DMA is used in rubber processing where it reacts with nitrite to produce NDMA which can be present as a contaminant in the final rubber product.

N-nitrosodimethylamine is also present in many other products such as tobacco smoke and a variety of foods such as cheeses, soybean oil, canned fruit, various meat products, bacon, various cured meat, cooked ham, milk, fish and fish products, apple brandy, and other alcoholic beverages including beer.

NDMA is thermally stable in aqueous solutions, and conventional methods such as biological treatment, air stripping, and activated carbon are not effective for NDMA treatment. Since
NDMA is photochemically labile, advanced oxidation technologies, based on irradiation with ultraviolet (UV) light, have been promoted for the removal of NDMA in contaminated waters. Direct UV photolysis readily destroys the compound and has been used commercially for over 10 years for the treatment of NDMA in contaminated groundwater.

In direct UV photolysis, a high powered lamp emits UV radiation through a quartz sleeve into the contaminated water. The photons of light are absorbed by NDMA resulting in breaking of the N-N bond in the molecule. The destruction of NDMA is therefore dependent upon the amount of UV light which is applied to the contaminated water and the UV wavelengths emitted by the lamp.

**Advanced Oxidation Technology Treatment of NDMA**

The UV treatment of NDMA is an example of Advanced Oxidation Technologies (AOTs). AOTs are defined as generally those technologies in which highly reactive intermediates (e.g., hydroxyl radicals) are generated, which greatly accelerate oxidative degradation reactions but also include those in which direct photolysis of the target contaminant is involved.

Many of the AOTs are driven by the absorption of ultraviolet light, which can occur in many ways, including:

1. **UV Direct Photolysis**
   In this case, the contaminated water to be treated enters the UV reactor with no additives. The UV is absorbed directly by the pollutant leading to its degradation. The degradation of NDMA is a good example of this type of AOTs.

2. **UV/H₂O₂ Process**
   In this case, hydrogen peroxide (H₂O₂) is added to the contaminated water prior to the water entering the UV reactor. The UV is absorbed by the H₂O₂, causing its dissociation into hydroxyl radicals (•OH), one of the most powerful oxidizing agents known. The •OH radicals then attack and oxidize the pollutants.

3. **UV/TiO₂ process**
   This is a heterogeneous process is which UV is absorbed by titanium dioxide (TiO₂) particles added to the contaminated water. Hydroxyl radicals, generated on the surface of the TiO₂ particles, then attack and oxidize the pollutants in the water.

All of the above processes work to a varying degree of efficiency. If the pollutant(s) absorb UV strongly, the Direct Photolysis Process will likely be the most economic. If the pollutant(s) do not absorb UV, then the UV/H₂O₂ process is likely to be the most economic. Also, if further degradation of photolysis byproducts is of concern, then this process would be the optimum choice. The UV/TiO₂ process suffers from a low efficiency of production of hydroxyl radicals and is not competitive in most cases. However, if the pollutant is strongly adsorbed to the surface of the TiO₂, this process can be effective, especially at very low concentrations of the pollutant.
Figure 1 shows the absorption spectrum of NDMA along with the emission spectra of low- and medium pressure UV lamps.

![Absorption spectrum of NDMA and emission spectra of UV lamps](image)

There is a good overlap between the emission spectrum of the medium pressure UV lamp and the NDMA absorption spectrum, which indicates that medium pressure UV lamp technology would be more efficient than low pressure UV lamp technology. For this reason, almost all current industrial scale UV installations for the treatment of NDMA employ medium pressure UV lamps.

When NDMA absorbs a photon, the molecule may undergo a photochemical reaction in which the N-N bond breaks:

\[
(CH_3)_2N\text{NO} + h\nu \rightarrow (CH_3)_2N^\bullet + NO
\]

The dimethylamino radical ends up as dimethylamine (DMA) and the NO as nitrite (NO\textsubscript{2}^-), so that DMA and nitrite are the principal byproducts of the UV photolysis.

In some cases, hydrogen peroxide (usually 2-5 mg/L in drinking or ground water) is added to the contaminated water to be treated. This is done in cases where other contaminants (e.g., 1,4-dioxane) need to be removed. Now the UV is also absorbed by hydrogen peroxide, with the following destruction mechanism:

\[
H_2O_2 + h\nu \rightarrow 2 \cdot OH
\]

\[
\cdot OH + (CH_3)_2N\text{NO} \rightarrow (\cdot CH_2)(CH_3)N\text{NO} + H_2O
\]
The (•CH2)(CH3)N–NO radical undergoes a complex series of reactions, some of which involve reaction with O2, leading to the generation of smaller organic molecules (e.g., formic acid) and nitrate (NO3–). The hydroxyl (•OH) radical can also react with other organic contaminants (e.g., 1,4-dioxane) or dissolved organic matter.

**Figures-of-Merit for Advanced Oxidation Technologies**

The kinetics of the photochemical degradation of NDMA is first-order, meaning that the treatment time (or electrical energy consumed) required to degrade NDMA is the same for each order of magnitude degraded. For example, it takes the same amount of electrical energy to degrade NDMA from 10 ppb to 1 ppb as it does to degrade from 100 ppb to 10 ppb, and so on for every order of magnitude of degradation. For this reason, a Figure-of-Merit has been introduced referred to as the Electrical Energy per Order (EEO), defined as the amount of electrical energy (kWh) necessary to degrade a pollutant by one order of magnitude in 1000 US gallons of water.

The Electrical Energy per Order (EEO) figure-of-merit is easily calculated from knowing the electrical energy (in kWh) used to drive the AOT process per unit volume (e.g. per m³ or per 1000 US gallons):

\[
E_{EO} = \frac{\text{Electrical Energy (kWh/1000gal)}}{\log(C_i/C_f)}
\]

where \(C_i\) and \(C_f\) are the initial and final concentrations of the target pollutant. Figure 2 shows an example of the UV treatment of NDMA and illustrates how the \(E_{EO}\) is calculated.

Figure 2. An example of the UV treatment of NDMA. The horizontal dotted line represents the 1 log or 90% destruction of NDMA. The \(E_{EO}\) in this example is therefore 0.13-kWh/order/1000 gal.

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NDMA Installations

To date, virtually all high flow (> 1000 gpm) installations treating NDMA utilize medium pressure lamps inside a Rayox® Tower reactor. The Tower is a 48” diameter 316L SS vessel. The height of the Tower is dependent on the number of lamps required. From 6 to 36 lamps can be placed in a single Tower. The UV lamps are arranged horizontally in a criss-cross pattern spaced approximately 7” apart. Each UV lamp is a 20 kW high efficiency, medium pressure lamp. Inside the Tower, the UV light destroys NDMA by direct photolysis. This Tower design maximizes the efficiency of UV light utilization while minimizing the footprint required. NDMA absorbs UV light very strongly around 230 nm, where the UV output from the Rayox® medium pressure lamp is highest. A quartz sleeve separates each lamp from the water. The quartz sleeve is kept clean automatically by a patented air-actuated quartz cleaning mechanism that wipes the quartz surface at regular intervals. For some installations, there is a peroxide dosing system present where peroxide is added into a static mixer upstream of the Tower. The UV light photolyzes the hydrogen peroxide to generate hydroxyl radicals, which oxidize the 1,4-dioxane or other VOCs, present in the water. In this instance the NDMA is destroyed by hydroxyl radical oxidation in addition to direct photolysis.

Figure 3. Photograph of a 12 lamp Rayox® Tower with bottom entry and top exit.
Below are several installations treating NDMA with UV equipment provided by Calgon Carbon Corporation.

<table>
<thead>
<tr>
<th>Installation</th>
<th>System Type</th>
<th>Flow, USgpm</th>
<th>Influent NDMA, ppt</th>
<th>Effluent NDMA, ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suburban Water (Covina, CA)</td>
<td>1 x 15 Lamp Tower</td>
<td>3,000</td>
<td>90</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>LaPuente Valley Water District (LaPuente, CA)</td>
<td>2 x 12 Lamp Towers</td>
<td>2,500</td>
<td>900</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>GenCorp Aerojet (Sacramento, CA)</td>
<td>2 x 12 Lamp Towers</td>
<td>4,000</td>
<td>160</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>NASA (Whitesands, NM)</td>
<td>1 x 12 Lamp Tower</td>
<td>1,100</td>
<td>2,000</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Town of Elmira (Elmira, Canada)</td>
<td>270 kW Rayox® Tower</td>
<td>420</td>
<td>2,600</td>
<td>&lt; 140</td>
</tr>
<tr>
<td>Orange County Water (Orange County, CA)</td>
<td>2 x 15 Lamp Tower*</td>
<td>7,300</td>
<td>100-300</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>California Domestic Water (El Monte, CA)</td>
<td>1 x 18 Lamp Tower</td>
<td>5,000</td>
<td>100</td>
<td>&lt; 2</td>
</tr>
</tbody>
</table>

* Two separate installations.

Table 1. Partial List of NDMA Installations utilizing Rayox® Equipment manufactured by Calgon Carbon Corporation.

**Suburban Water (Covina, CA)**

One Calgon Carbon Rayox® UV Tower comprised of 15 lamps was installed at Suburban Water Systems in 1999. This system has continuously treated NDMA in ground water from approximately 90 ppt down to < 2 ppt. In the Tower, NDMA destruction occurs via direct UV photolysis with no peroxide added to the treatment system. This installation has received a California Department of Health Services operating permit.

**LaPuente Valley Water District (LaPuente, CA)**

Two Calgon Carbon Rayox® UV Towers in series, each comprised of 12 lamps, were installed at LaPuente in 1999. With NDMA analytical methods continuously improving and reporting limits being lower, a test was recently conducted in May 2001 to obtain an accurate $E_{EO}$ as shown in Table 2.

Four sets of samples were collected. The samples were analyzed by Southwest Research Institute (Pasadena, CA). The flowrate was set at 2,250 gpm for each test case. The number of lamps operating in the Tower was varied. The lamps used for this test were near the end of lamp life. It is expected that the $E_{EO}$ would be further decreased down to the 0.10 to 0.15 kWh/1000gal/order range with new lamps. The test conditions are shown in Table 2 below along with the $E_{EO}$.
<table>
<thead>
<tr>
<th>Lamps Number ON*</th>
<th>$E_{EO}$, kWh/1000gal/order</th>
</tr>
</thead>
<tbody>
<tr>
<td>3, 4, 5, 8 (Tower 1)</td>
<td>0.21</td>
</tr>
<tr>
<td>5, 8 (Tower 1)</td>
<td>0.16</td>
</tr>
<tr>
<td>5, 8 (Tower 1) and 5, 8 (Tower 2)</td>
<td>0.19</td>
</tr>
<tr>
<td>5, 8 (Tower 1) and 5, 8 (Tower 2)</td>
<td>0.21</td>
</tr>
<tr>
<td>5, 8 (Tower 1)</td>
<td>0.17</td>
</tr>
<tr>
<td>7, 8 (Tower 1)</td>
<td>0.16</td>
</tr>
</tbody>
</table>

* Lamp No. starts from 1, in succession, at the bottom of the Tower, with Lamp No. 12 at the top.

Table 2. Performance of LPVWD Rayox® Tower at 2,250 gpm

The system has continuously treated NDMA in ground water down to < 2 ppt. The treated water is used as drinking water for the community. NDMA destruction occurs via direct UV photolysis and hydroxyl radical oxidation with peroxide (approximately 3 ppm) added to the influent prior to UV treatment. With 4 lamps operating, the $E_{EO}$ is higher probably due to the fact that the effluent peroxide concentrations are at the detection limit with resulting analytical uncertainty. In addition to NDMA, the 1,4-dioxane in the ground water is also treated by the Tower. This installation has received a California Department of Health Services operating permit.

*GenCorp Aerojet (Sacramento, CA)*

Two Calgon Carbon Rayox® UV Towers operating in parallel, each comprising of 12 lamps, were installed at GenCorp Aerojet in 1999. The Towers were each sized on a maximum hydraulic flowrate of 7,500 gpm and an average treatment flowrate of 2,000 gpm. This system has continuously treated NDMA in ground water from approximately 160 ppt down to < 10 ppt. NDMA destruction occurs via direct UV photolysis and hydroxyl radical oxidation with peroxide added to the influent prior to UV treatment. In addition to NDMA, there is also TCE, DCE, and PCE in the groundwater stream which is treated by the Tower.

*NASA (Whitesands, NM)*

A series of in-house design tests utilizing a 1 kW bench UV reactor was conducted on a representative groundwater sample collected from the site in 1998. The results from the design test were used for full-scale system sizing. Subsequent pilot testing on-site using a 30 kW full scale reactor was performed to confirm the design basis for a 12 lamp Tower.

A 12 lamp Rayox® UV Tower is scheduled for installation in mid-2002 at the NASA Whitesands Missile Test Facility in New Mexico. This system was designed to treat NDMA from 2,000 ppt down to < 10 ppt at a flowrate of 1,100 gpm. In this installation, NDMA destruction occurs via direct UV photolysis with no peroxide added to the treatment system.
NDMA was first detected in 1990 as a problem pollutant in a groundwater drinking water source in Elmira, Ontario, Canada. The waste from a large chemical plant over many years had led to the contamination of the drinking water wells for the community. After extensive evaluation and testing, it was determined that UV photolysis was the most effective treatment method.

Three Calgon Carbon Rayox® skids, each comprising of three 30 kW reactors (90 kW total), were installed in the Town of Elmira in 1991. This system has continuously treated NDMA in the ground water from approximately 2,600 ppt down to < 140 ppt for surface discharge.

In 1998, the system was upgraded with an additional 180 kW of UV power to treat the additional wells brought on-line. The additional flow from the wells was 420 USgpm.

**Orange County Water District (Orange County, CA)**

A series of design tests utilizing a 1 kW medium pressure UV bench reactor were conducted on-site at the Orange County Water District. The results from the design test were coupled with Calgon Carbon’s in-house model to determine the full-scale Tower size. Two 15 lamp Towers were procured and installed by Orange County at two different sites. The “WF-21” Tower was used in conjunction with a peroxide dosing system to treat NDMA from a tertiary wastewater stream initially treated by RO. The second Tower was used to treat ground water from the Mesa Consolidated Water District’s (“MCWD”) Well No. 5, a potable water production well.

Both 15 lamp Rayox® UV Towers were installed in 2001 and have been successfully destroying NDMA since startup. The “WF-21” Tower was designed to treat NDMA from 300 ppt down to < 2 ppt at a flowrate of 3,500 gpm. The “MCWD” Tower was designed to treat NDMA from 100 ppt down to < 2 ppt at a flowrate of 3,800 gpm.

**California Domestic Water Quality (El Monte, CA)**

An 18 lamp Calgon Carbon Rayox® UV Tower was recently installed at the California Domestic Water Company with startup performed on October 2001. This system was designed to treat NDMA in drinking water from approximately 100 ppt down to < 2 ppt. The treatment plant has been providing water to its consumers with < 2 ppt NDMA since startup. NDMA destruction occurs via direct UV photolysis. Although peroxide is not required for treatment, a standby peroxide dosing system has been provided should the need arise to destroy trace VOCs in the water.
Looking Ahead

Medium pressure (MP) lamps have been commercially used and proven in more than ten years of NDMA treatment. Recently, low pressure (LP) lamps have gained interest in this area as an alternative for MP lamp systems.

There are three major differences between LP and MP lamps.

- LP lamps operate at a lower power than MP lamps
- LP are more UVC-light efficient than MP lamps
- MP lamps are polychromatic while LP lamps are monochromatic

A medium pressure lamp on the Rayox® Tower uses 20 kW of power while a low pressure lamp uses about 90 W. The UVC light efficiency of a MP lamp on the Tower is about 25%, while typical UVC light efficiencies associated with LP lamps range between 35-40%. UVC light is defined as the percentage of the input electrical power that a lamp emits between 200 and 280 nm. UVC light production is important because these are the wavelengths at which NDMA and hydrogen peroxide absorb UV.

Since LP lamps have a higher UVC efficiency than MP lamps, there would be a corresponding lower electrical operating cost in using LP lamps for NDMA treatment. However, with a LP system, there are significantly more lamps (1,500 vs 12 for a typical installation) so there is a higher cost for labor in lamp change out. As opposed to a MP Tower with continuous quartz cleaning, there is also the increased cost of labor for manual quartz cleaning with the higher number of lamps in a LP system. In a LP system, the electrical re-pumping costs are significant as the reactor is usually unpressurized and the water must be re-pumped to the distribution system. Since the Tower was designed to be a pressurized vessel, there are no associated re-pumping costs.

With the compact and simple single-vessel Rayox® Tower design, a much smaller footprint is realized. This translates into a lower cost for installation compared to that of a channel-type, gravity-fed, low pressure reactor with a multitude of racks for lamps and ballasts. A low pressure system with more lamps, quartz and ballasts would typically entail a higher capital investment than a medium pressure system. In addition, an overhead monorail, an acid cleaning tank, a pump to re-pump the water to distribution, a wet-well, and a building to house the LP system must be supplied. Indirect costs such as heating and maintenance for a larger building should also be factored in when comparing systems.

Summary

Medium pressure (MP) lamps have been commercially used and proven in more than ten years of NDMA treatment. Almost all current industrial scale UV installations for the treatment of NDMA employ medium pressure UV lamps. Medium pressure UV systems are far more cost effective over low-pressure systems when comparing the overall lifecycle operating and installed capital costs for a project. While economics are a big determinant in system selection, other factors such as footprint, number of existing installations, reliability, and ease of maintenance must be included in the selection criteria. While satisfying all these
factors over a low pressure system, the Rayox® Tower, with its high efficiency medium pressure UV lamps has been shown to achieve optimal performance for NDMA destruction with the lowest overall lifecycle project costs.

Calgon Carbon Corporation (CCC), headquartered in Pittsburgh, Pennsylvania, is a global leader in services and solutions for making air and water cleaner and safer. As a leading firm in ultraviolet water treatment applications, Calgon Carbon has over three hundred commercial UV installations throughout the world. Our UV division specializes in the design, manufacture and sale of ultraviolet systems for drinking waters, groundwaters, and industrial wastewaters. CCC’s corporate goal is to maintain its position of leadership through extraordinary commitment to research and development, excellence in design, quality-centered manufacturing, and customer-oriented service.

More information on Calgon Carbon’s products is available on line at www.calgoncarbon.com.

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Acknowledgements:

Thanks to Keith G. Bircher and Mike Matuszewski of Calgon Carbon Corporation for their review and edits to this article.
References:


