

Chlorine improves UV-AOP efficiency in site-specific conditions

Several large potable water reuse facilities, including the Water Replenishment District of Southern California's Albert Robles Center for Water Recycling and Environmental Learning, are installing UV-oxidation systems that will use the UV-chlorine advanced oxidation process (AOP) instead of UV-hydrogen peroxide due to its lower cost and logistical benefits. **Adam Festger** and **Scott Bindner** of TrojanUV explain the conditions under which UV-chlorine AOP makes both practical and economic sense.

The challenges of ensuring sustainable drinking water supplies in Southern California, United States (US), have driven significant technological advancements in water treatment over the last two decades. Ultraviolet advanced oxidation (UV-AOP), a core process established at Orange County Water District's Groundwater Replenishment System (GWRS) in 2008, is one example. This installation continues to be the largest in the world for the removal of trace organics in advanced treated wastewater for potable reuse. The application of UV-AOP at the GWRS uses hydrogen peroxide (H_2O_2) to generate hydroxyl radicals that degrade organic contaminants present in the water.

Over the last ten years since the commissioning of the GWRS, other advanced wastewater treatment projects have also been developed with UV-AOP continuing to be a core treatment technology in process trains, along with advanced filtration methods such as microfiltration (MF), ultrafiltration (UF), and reverse osmosis (RO). Many of these advanced wastewater treatment projects look to maintain these same core treatment technologies with emphasis on improving efficiency while maintaining the mandated 0.5-log removal of 1,4-dioxane or equivalent treatment established by the California Water Resources Control Board's *Regulations Related to Recycled Water*. One developing investigation is whether the application of chlorine (i.e., bulk sodium hypochlorite, NaOCl, or gas chlorine) as an oxidant in place of H_2O_2 can improve UV-AOP cost efficiency in potable reuse.

Data from numerous pilot tests and a handful of full-scale investigations demonstrate that under the right conditions, UV-chlorine can lead to significant cost savings. But what are these conditions, and is UV-chlorine applicable at every potable reuse facility?

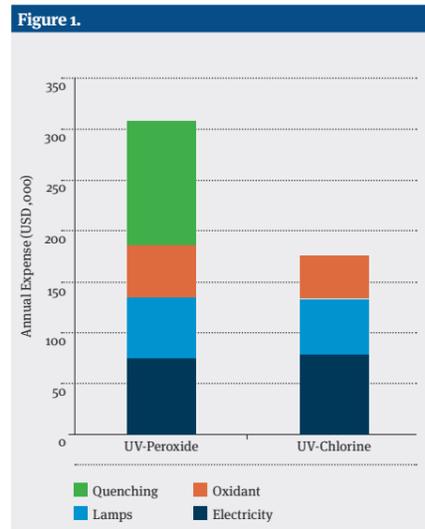
Under what conditions should a facility consider UV-chlorine versus UV- H_2O_2 ?

The performance of chlorine as an oxidizing agent has been evaluated through several pilot and full-scale installations (references available upon request). For the same mass-based concentration (i.e., milligrams per liter) considered in the UV-AOP, free chlorine absorbs more UV light at 254 nanometers (nm) than

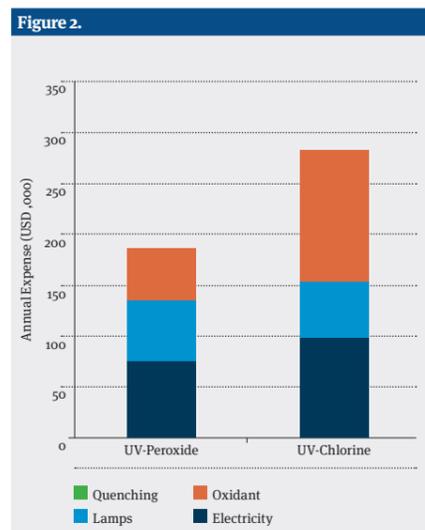
H_2O_2 and, as a result, can more efficiently be converted to the hydroxyl radicals ($\bullet OH$) that drive UV-AOP treatment. Depending on pH, free chlorine is present in water as hypochlorite ion ($-OCl$), hypochlorous acid (HOCl), or a combination of both species. While the $\bullet OH$ yield generated through H_2O_2 photolysis is pH-independent, given the pH-dependent speciation of free chlorine, the radical yield in UV-chlorine process depends on water pH. At 254 nm, the radical yield from HOCl photolysis is almost twice that generated from NaOCl photolysis.

On the other hand, the UV-AOP performance is negatively impacted by the oxidant (H_2O_2 or free chlorine) reactivity toward the generated radicals. H_2O_2 reaction with $\bullet OH$ is much slower than those of free chlorine species (hypochlorous acid, HOCl, and its conjugate base, $-OCl$). $-OCl$ demonstrates a very high affinity for generated $\bullet OH$ radicals, resulting in much higher radical scavenging capacity than both HOCl and H_2O_2 . At advanced water treatment facilities using RO membranes in their core treatment process, pH levels of between 5 and 6 are typically observed in RO permeate. At this pH, chlorine speciates preferably to HOCl. This is a favorable condition for the use of free chlorine as the oxidant in UV-AOP. Therefore, the lower scavenging potential of HOCl, together with the effects of wavelength-dependent molar absorption coefficient and higher radical yield, lead to higher treatment efficiency when HOCl is the dominant species in solution. Therefore, in pH, we arrive at the first criterion for UV-chlorine to be effective: that pH be less than approximately 6.0 to ensure that HOCl is the dominant species in solution.

A second criterion required for UV-chlorine to make economic sense is that levels of ammonia entering the UV-AOP system must be low. The use of upstream RO membranes, while promoting optimum pH levels for UV-AOP with free chlorine, also carries a disadvantage in cases where chloramines are used to prevent RO membrane fouling. To generate chloramines, NaOCl is typically dosed together with ammonia prior to MF and RO. Any unconverted ammonia mostly passes through the RO membranes and is subsequently converted to chloramines through exposure to the NaOCl used to generate



Cost comparison between UV-peroxide and UV-chlorine advanced oxidation in a situation where pH is low (<6), ammonia entering the UV-AOP is low (≤ 0.25 ppm NH_3-N), and quenching of residual H_2O_2 is required.



Cost comparison between UV-peroxide and UV-chlorine advanced oxidation in a situation where pH is low (<6) but ammonia entering the UV-AOP is relatively high (1 ppm NH_3-N), and quenching of residual H_2O_2 is not required.



Above: UV advanced oxidation is a core process at the Orange County Water District's Groundwater Replenishment System. This application of UV-AOP uses hydrogen peroxide to generate hydroxyl radicals that degrade organic contaminants present in the water.

Left: UV advanced oxidation will be a core process at the Water Replenishment District of Southern California's Albert Robles Center for Water Recycling and Environmental Learning, which is currently under construction. In this application of UV-AOP, the conditions at the site made the use of chlorine as the oxidizing agent a better choice when compared to traditional hydrogen peroxide. Photos provided by TrojanUV

free chlorine for UV-AOP. This, in addition to presenting a free chlorine demand at the dosing point prior to the UV-AOP system, generates chloramines that reduce the UV transmittance (UVT) of the water, increase hydroxyl radical scavenging demand, and reduce the overall performance of the UV-AOP system, leading to higher operating costs. Therefore, in order to avoid dosing large amounts of NaOCl and to maintain efficiency of UV-chlorine, ammonia levels need to be minimized.

Consider the case where just 0.25 parts per million (ppm) of free ammonia (NH_3-N) is present when NaOCl is dosed upstream of the UV system, which leads to an additional 1.25 ppm of NaOCl to be dosed to overcome the demand and leads to a reduction in UVT of 1.5 percent due to the formed monochloramine. This outcome impacts the design of the UV-oxidation system by increasing the required size of UV-AOP. Some facilities that don't fully denitrify can have large amounts of ammonia entering RO (e.g., up to 30 or 40 ppm). These facilities are not good candidates for UV-chlorine AOP, as this ammonia demand could not be overcome cost effectively.

The third condition governing whether or not UV-chlorine makes sense is related to the site-specific need to quench residual H_2O_2 . In applications where chlorine residual is needed in transmission lines, residual H_2O_2 would need to be quenched, as only 10 percent to 20 percent of dosed H_2O_2 is consumed in the UV-

H_2O_2 system. Often, this residual is quenched with chlorine but presents a challenging and potentially expensive post-treatment step. An example application where chlorine residual would be required is in a direct potable reuse facility in which treated water is sent to the headworks of the drinking water facility. Regrowth must be prevented in the transmission line, and therefore quenching of residual H_2O_2 would be required. This is a general criterion for considering UV-chlorine: it makes sense when quenching of residual H_2O_2 would be required.

To illustrate, consider a 30.3-million liter (8-million gallon) per day advanced wastewater treatment facility using MF, RO, and advanced oxidation. This facility could save more than US\$100,000 in annual operating costs by using NaOCl instead of H_2O_2 . As shown in Figure 1, these savings are primarily due to the lack of a quenching step, which would otherwise be needed when using H_2O_2 . Further, additional indirect cost benefits can also be considered such as the reduction of the number of chemicals on site. NaOCl, for instance, is generally used for multiple applications at an advanced treatment facility. Therefore, it can be a more convenient solution to expand the scope of any existing NaOCl dosing strategy for use in UV-AOP rather than incorporate an additional chemical such as H_2O_2 . Conversely, if ammonia is high (in this example, 1 ppm NH_3-N), driving UVT down and presenting chlorine demand,

and if H_2O_2 residual quenching is not required, the cost of UV-chlorine can be significantly higher than UV- H_2O_2 (Figure 2).

The Water Replenishment District of Southern California is currently constructing The Albert Robles Center for Water Recycling and Environmental Learning, which will use the core processes of UF, RO, and UV-AOP in advanced wastewater treatment for potable reuse. This is a facility for which UV-chlorine makes sense. For example, the District will approach the ammonia issue by implementing a strict maximum ammonia concentration of 0.1 ppm NH_3-N entering the UV-AOP system as well as having the amount of ammonia required for RO maintenance routinely monitored to ensure that levels passing through the RO do not exceed the 0.1-ppm limit. The facility will use UF/RO and will therefore have a low pH. Finally, quenching of residual H_2O_2 , if UV- H_2O_2 were to be implemented, would be required.

In summary, improving UV-AOP efficiency with chlorine as the oxidant is possible and dependent on site-specific circumstances. Today's advanced treatment facilities are being constructed to take advantage of the cost savings offered by UV-chlorine by controlling ammonia and ensuring that pH remains below 6. These considerations can lead to significant cost savings in the final treatment step of a full advanced treatment facility.