UV Advanced Oxidation For Potable Reuse In California

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On June 20, 2014 groundwater replenishment and recharge regulations were adopted in California. The California State Water Resource Control Board, Division of Drinking Water (DDW), has been reviewing groundwater recharge projects to ensure that they are in compliance with the recycled water regulations[2]. California Water Code §13561 states, "Indirect potable reuse for groundwater recharge means the planned use of recycled water for replenishment of a groundwater basin or an aquifer that has been designated as a source of water supply for a public water system". These types of indirect potable reuse projects are being considered by many public water systems due to drought and other factors.

The June 2014 regulations impose a number of requirements for groundwater replenishment and recharge projects (GRRP). These potable reuse regulations address the follow major topics:

(1) Enhanced wastewater source control programs,
(2) Multiple barrier treatment processes to provide:
    a. Pathogen log reduction of 12 for virus, 10 for Giardia and 10 for Cryptosporidium
    b. Chemical Contaminant reduction to meet primary, secondary and notification levels (NLs)[3]
    c. Constituents of Emerging Concern (CECs)
(3) Water quality and treatment process monitoring, and
(4) Provide full advanced treatment, including
    a. Reverse Osmosis (RO) and
    b. Advanced Oxidation Processes (AOP), for injection projects.

Full Advanced Treatment

Full Advanced Treatment is defined with specific requirements for design and operation of RO and AOP. For GRRP, no blending is required if 100% of the flow is treated via Full Advanced Treatment, including RO and AOP. Full Advanced Treatment is required for groundwater injection projects, but not for groundwater spreading projects. DDW requires multiple barriers for each type of contaminant. The treatment must be reliable, with backup/redundant processes, or other contingency plans, if there is a treatment failure. Together RO and AOP form a multiple-barrier treatment for many contaminants. As future regulations are adopted, Full Advanced Treatment will be specified for augmentation of surface water reservoirs and direct potable reuse.

Full Advanced Treatment is a set of processes designed to remove the organic chemicals, including CECs, that may pose a public health threat. Full Advanced Treatment starts with RO. RO permeate is ideal for UV AOP. RO removes 90 to 99% of most organic chemicals

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[2] https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/RecycledWater.shtml

[3] https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/NotificationLevels.shtml

and thereby produces water with an extremely high UV transmittance (UVT). Permeate will typically have a UVT greater than 98% for new RO membranes, decreasing over the life of the membrane to a UVT greater than 95% for RO membranes five years old or more. In simplistic terms, this means that RO permeate has such low absorbance at a wavelength of 254 nm, that the UV photons are mostly available for the AOP.

Most of the potable reuse projects in California use the addition of hydrogen peroxide just upstream of the UV to create hydroxyl radicals. However, a new option for AOP replaces the hydrogen peroxide with free chlorine, which also creates radicals that oxidize chemical compounds.

Nitrosamines

With enough energy, a very high dose of UV breaks the N-N bond and can thus be used to degrade nitrosamines, like NDMA. NDMA is known to be a toxic chemical of emerging concern. It does not readily adsorb or volatilize. As such, it cannot be removed by activated carbon and may travel easily through soils. RO is only able to remove approximately 50% of NDMA[4].

In the late 1990s, NDMA was found to be to be a drinking water contaminant in locations throughout the State of California, leading to the establishment of a NL. In 2000, NDMA was found in two Orange County wells associated with injection of treated wastewater associated with a groundwater replenishment projects. California has established the requirement that full advanced treatment must meet a level of 10 nanograms per liter (ng/L) for NDMA, which is the NL. Existing potable reuse projects in California are successfully operating AOP facilities for potable reuse that meet this objective.

UV alone is effective for reduction of nitrosamines, like NDMA, utilizing very high energy. In order to photolyze NDMA the energy required is approximately two orders of magnitude greater than that generally needed to disinfect the typical potable water sources for drinking water consumption. UV AOP is generally designed in terms of energy rather than UV dose, but experts have generally demonstrated that a dose of approximately 1000 mJ/cm^2 is necessary, which is ten times greater than the typical dose required for tertiary recycled water in California, which can be found in Table 1, NWRI UV Guidelines and are intended to inactivate enteric viruses rather than photolysis for AOP applications. UV AOP requires such a large amount of energy that it is able to claim a log removal of six for viruses, Cryptosporidium and Giardia.

Table 1
NWRI UV Guidelines[5]

[4] Mitch, W. A.; Sharp, J. O.; Trussell, R. R.; Valentine, R. L.; Alvarez-Cohen, L.; Sedlak, D. L. (2003). "N-Nitrosodimethylamine (NDMA) as a Drinking Water Contaminant: A Review". Environmental Engineering Science. **20** (5): 389–404. *doi:10.1089/109287503768335896*.
[5] Ultraviolet Disinfection Guidelines for Drinking Water and Water Reuse, Third Edition, August 2012, National Water Research Institute and Water Research Foundation http://nwri-usa.org/documents/UVGuidelines3rdEdition2012.pdf

UV dose	Application	Minimum UV transmittance
100 mJ/cm^2	Following non-membrane filtration	55%
80 mJ/cm^2	following membrane filtration	65%
50 mJ/cm^2	following Reverse Osmosis (RO)	90%

Advanced Oxidation of Organic Chemicals

UV AOP is effective for oxidization of organics that pass through the RO membrane. As stated before, RO is very effective at removing most organic chemicals. However, there are a few that are removed at less than 90%, due to factors such as low molecular weight (MW), including the following examples in Table 2 that have been detected in permeate at current GRRPs:

Table 2
Low Molecular Weight Chemicals Detected

Chemical	Contaminant Category	Use or Byproduct	MW
N-nitrosodimethylamine (NDMA)	Nitrosamine	Disinfection Byproduct	74
N-nitrosomorpholine (NMOR)	Nitrosamine	Disinfection Byproduct	116
1,4-dioxane	industrial chemical	solvent	88
Chloroform	Trihalomethanes	Disinfection Byproduct	119
Acetone	industrial chemical	solvent	58
Methyl isothiocyanate (MITC)	herbicide	soil fumigant for fungi and nematodes	73

While UV alone is effective on nitrosamines; it cannot photolyze 1,4-dioxane or other organics effectively. California regulations require demonstration of the effectiveness of the AOP. Currently, each GRRP has designed and demonstrated a 0.5-log reduction of 1,4 dioxane. The most common approach is the addition of three parts per million (ppm) of hydrogen peroxide upstream of high dose UV to create hydroxyl radicals in order to meet the requirement. It should be noted that the hydrogen peroxide dose and energy needed will depend on the water quality produced by each GRRP. Although hydrogen peroxide has been utilized effectively at most of the potable reuse project, a new alternative has recently been demonstrated. The City of Los Angeles Terminal Island groundwater injection project is designed with free chlorine at a minimum free chlorine dose of 2.0 mg/L and a UV dose of 920 mJ/cm^2 .

Constituents of Emerging Concern

Currently, more than 135,000,000 chemicals are registered with Chemical Abstract Services and more than 15,000 are added each day. CECs include a wide and diverse spectrum of potential contaminants. They are "potential" contaminants because they are currently unregulated, but may be considered for regulation in the future. They may or may not have public health concerns. Emerging contaminants include constituents such pharmaceuticals, endocrine disrupting compounds (EDCs), hormones, personal care products (PCPs), and other constituents.

In addition to treatment for regulated organics, UV AOP also oxidizes for chemicals that are not detectable and are unknown. By providing treatment to ensure that the levels for NDMA and 1,4-dioxane will be below the California NLs, experts assume that concern over CECs should be addressed. This was confirmed by a Science Advisory Panel on CECs recently[6]. Existing potable reuse projects in California are operating AOP facilities that are effective treatment for CECs.

Monitoring and Operations

Monitoring is needed to ensure protection of public health, including, but not limited to, the identification of appropriate indicator and surrogate constituents. There are various approaches regarding monitoring of UV to achieve microorganisms, regulated organic chemicals, and emerging contaminant control for potable reuse. Typically, UV processes are monitored using online UVT. Another surrogate, in the form of an operational parameter, is power or energy applied per flow. Additionally the dose of hydrogen peroxide or free chlorine must be controlled. Free chlorine analyzers are common in potable and recycled treatment, whereas analyzers for hydrogen peroxide are not available currently. The only current approach to monitor hydrogen peroxide addition is via calculations of the chemical injection pump. Since this approach is not precise, commissioning at full scale must demonstrate the 0.5-log reduction of 1,4 dioxane.

CECs are useful indicators of municipal wastewater and some are indicators of the effectiveness of the AOP process. Examples include NDMA, DEET, numerous pharmaceuticals, and 1,4 dioxane. California uses these type of indicators to demonstrate performance of UV AOP. For the first year of operations monthly sampling is required. Since after one year, existing potable reuse projects have demonstrated their effectiveness, the required monitoring can be reduced to quarterly. Disinfection byproducts may pass RO/AOP, but generally are detected in very low levels.

UV AOP is a complicated process for most operators. Proper start-up and on-going training should be provided initially and via continuing education. UV AOP requires timely and proper maintenance to properly operate within specifications and permit requirements.

[6] http://sccwrp.org/ResearchAreas/Contaminants/RecycledWaterAdvisoryPanel.aspx