



Designation: F1524 – 22

Standard Guide for Use of Advanced Oxidation Process for the Mitigation of Chemical Spills¹

This standard is issued under the fixed designation F1524; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide covers the considerations for advanced oxidation processes (AOPs) in the mitigation of spilled chemicals and hydrocarbons dissolved into ground and surface waters.

1.2 This guide addresses the application of advanced oxidation alone or in conjunction with other technologies.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* In addition, it is the responsibility of the user to ensure that such activity takes place under the control and direction of a qualified person with full knowledge of any potential safety and health protocols.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

D5745 Guide for Developing and Implementing Short-Term Measures or Early Actions for Site Remediation

E2081 Guide for Risk-Based Corrective Action

¹ This guide is under the jurisdiction of ASTM Committee F20 on Hazardous Substances and Oil Spill Response and is the direct responsibility of Subcommittee F20.22 on Mitigation Actions.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

E2616 Guide for Remedy Selection Integrating Risk-Based Corrective Action and Non-Risk Considerations

2.2 Federal and State Guidance Documents:

Guidance WQD-004 Advanced Oxidation Process (AOP) for the Oxidation of Microcontaminants. August 2017³

Proven Technologies And Remedies Guidance Remediation Of Chlorinated Volatile Organic Compounds In Vadose Zone Soil. California Department of Toxic Substances Control. 2010⁴

ERDC-TR-19-3. 2019 U.S. Army Corps of Engineers. Cross-Comparison of Advanced Oxidation Processes for Remediation of Organic Pollutants in Water Treatment Systems⁵

In Situ Remediation: Design Considerations and Performance Monitoring, Technical Guidance Document. New Jersey Department of Environmental Protection. October 2017⁶

Advanced Oxidation Processes (AOPs) For Destruction Of Methyl Tertiary Butyl Ether (MtBE -An Unregulated Contaminant) In Drinking Water. U.S. EPA. September 2004⁷

GAO-05-666 General Accounting Office. Groundwater Contamination: DOD Uses and Develops a Range of Remediation Technologies to Clean Up Military Sites. June 2006⁸

Technology Screening Matrix, Federal Remediation Technologies Roundtable. <https://frtr.gov/matrix/default.cfm>

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

³ Available from Oklahoma Department of Environmental Quality Department of Environmental Quality 707 N Robinson Oklahoma City, OK, 73102 <https://www.deq.ok.gov/>

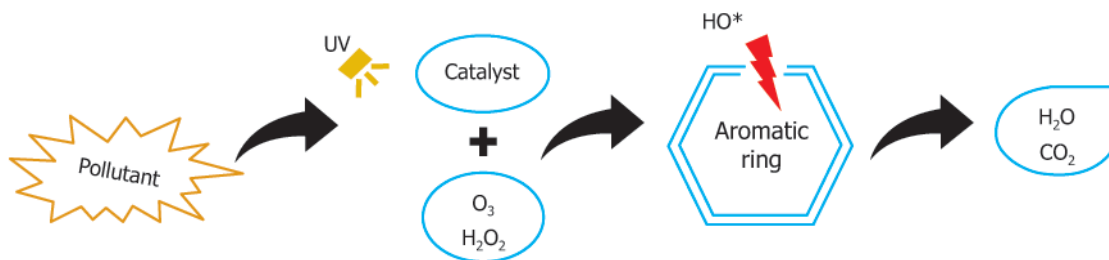
⁴ Available from California Department of Toxic Substances Control 1001 I Street, Sacramento, CA 95814-2828 <https://dtsc.ca.gov/>

⁵ Available from U.S. Army Corps of Engineers 441 G Street NW Washington, DC 20314-1000 <https://www.usace.army.mil/>

⁶ Available from New Jersey Department of Environmental Protection 401 East State Street, Trenton NJ, 08625. <https://www.nj.gov/dep/>

⁷ Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

⁸ Available from U.S. Government Publishing Office (GPO), 732 N. Capitol St., NW, Washington, DC 20401, <http://www.gpo.gov>.



Source: Amor, Carlos, et al. Application of Advanced Oxidation Processes for the Treatment of Recalcitrant Agro-Industrial Wastewater: A Review. *Water* 2019, 11(2), 205; <https://doi.org/10.3390/w11020205> (open access publication)

FIG. 1 Schematic Illustration of Hydroxyl Radical's Generation for the Degradation of Organic Pollutants

3.1.1 *advanced oxidation processes (AOPs)*—ambient temperature processes that involve the generation of highly reactive radical species and lead to the oxidation of waterborne contaminants (usually organic) in surface and ground waters.

3.1.2 *inorganic foulants*—compounds, such as iron, calcium and manganese, that precipitate throughout a treatment unit and cause reduced efficiency by fouling the quartz sleeve that protects the lamp in photolytic oxidation AOP systems or the fibreglass mesh that is coated with TiO₂ in photocatalytic AOP systems.

3.1.3 *mineralization*—the complete oxidation of an organic compound to carbon dioxide, water, and acid compounds, that is, hydrochloric acid if the compound is chlorinated.

3.1.4 *photoreactor*—the core of the photoreactor is a UV lamp that emits light in the broad range of 200 nm to 400 nm wavelength range.

3.1.5 *radical species*—a powerful oxidizing agent, principally the hydroxyl radical, that reacts rapidly with virtually all organic compounds to oxidize and eventually lead to their complete mineralization.

3.1.6 *scavengers*—a term used for substances that react with hydroxyl radicals that do not yield species that propagate the chain reaction for contaminant destruction. Scavengers can be either organic or inorganic compounds.

3.2 Acronyms:

3.2.1 *AOP*—Advanced Oxidation Process

3.2.2 *COC*—Chemicals of Concern

3.2.3 *EPA*—U.S. Environmental Protection Agency

3.2.4 *GAC*—Granulated Activated Carbon

3.2.5 *UV*—Ultraviolet

4. Significance and Use

4.1 *General*—This guide contains information regarding the use of AOPs to oxidize and eventually mineralize hazardous materials that have entered surface and groundwater as the result of a spill. These guidelines will only refer to those units that are currently applied at a field scale level. The user should review applicable state regulations and guidance on the applicability of AOP (see California DTSC 2010, New Jersey DEP 2017, Oklahoma DEQ 2017).

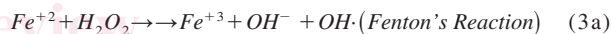
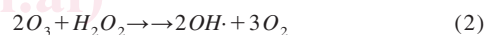
NOTE 1—Commercialization of AOP for the treatment of wastewater and process water is fairly mature. Several transnational companies offer mobile and large-scale processing units for the treatment of persistent

chemicals of concern. Standard Guides D5745, E2081, and E2616 may be useful. Fig. 1 illustrates the general AOP process.

Fig. 2 illustrates the range of AOP technologies.

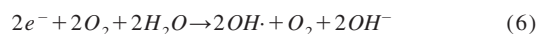
4.2 Oxidizing Agents:

4.2.1 *Hydroxyl Radical (OH)*—The OH radical is the most common oxidizing agent employed by this technology due to its powerful oxidizing ability. When compared to other oxidants such as molecular ozone, hydrogen peroxide, or hypochlorite, its rate of attack is commonly much faster. In fact, it is typically one million (10⁶) to one billion (10⁹) times faster than the corresponding attack with molecular ozone (Keller and Reed, 1991 (1)).⁹ The three most common methods for generating the hydroxyl radical are described in the following equations:



4.2.1.1 Hydrogen peroxide is the preferred oxidant for photolytic oxidation systems since ozone will encourage the air stripping of solutions containing volatile organics (Nyer, 1992 (2)). Capital and operating costs are also taken into account when a decision on the choice of oxidant is made (see NJ Dept. of Environmental Protection, 2017).

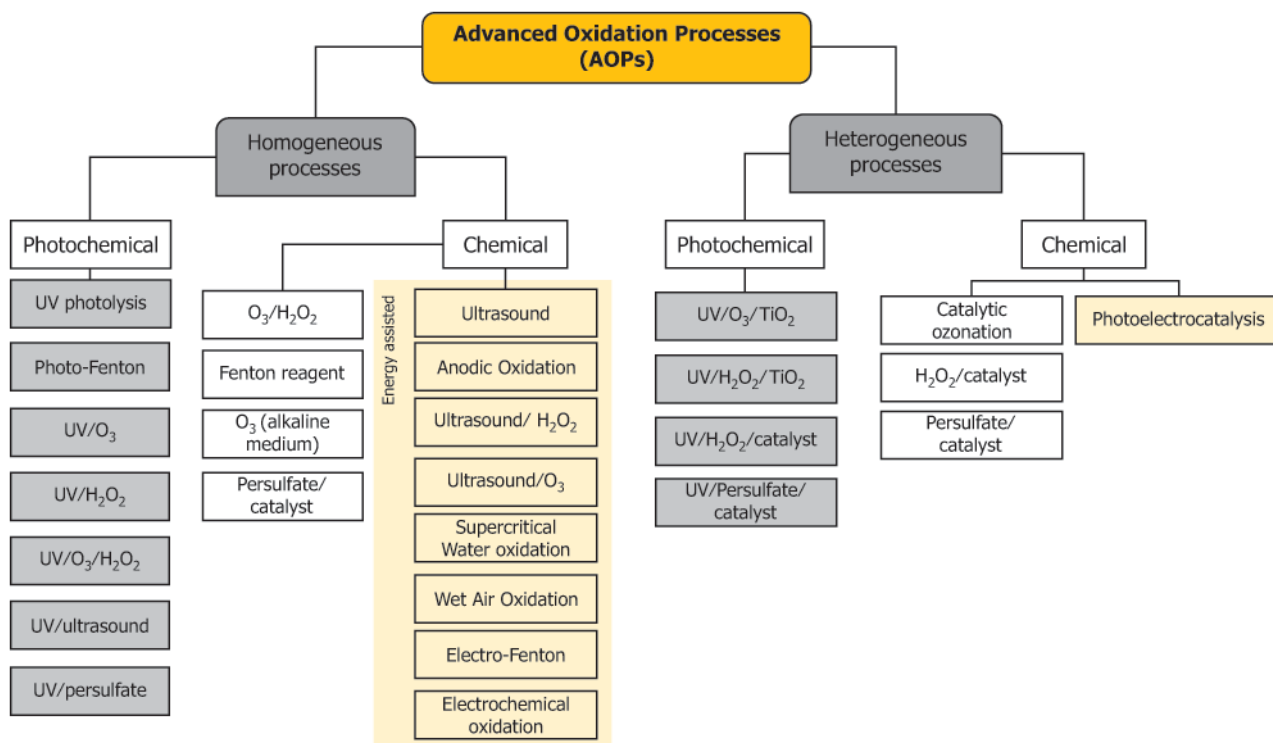
4.2.1.2 Advanced oxidation technology has also been developed based on the anatase form of titanium dioxide. This method by which the photocatalytic process generates hydroxyl radicals is described in the following equations:



4.2.2 *Photolysis*—Destruction pathways, besides the hydroxyl radical attack, are very important for the more refractory compounds such as chloroform, carbon tetrachloride, trichloroethane, and other chlorinated methane or ethane compounds. A photoreactor's ability to destroy these compounds photochemically will depend on its output level at specific wavelengths (see FRTR Technology Screening Tool).

4.3 AOP Treatment Techniques:

⁹ The boldface numbers in parentheses refer to the list of references at the end of this standard.



Source: Amor, Carlos, et al. Application of Advanced Oxidation Processes for the Treatment of Recalcitrant Agro-Industrial Wastewater: A Review. Water 2019, 11(2), 205; <https://doi.org/10.3390/w11020205> (open access publication)

FIG. 2 Examples of Advanced Oxidation Processes

4.3.1 Advanced oxidation processes (AOPs) may be applied alone or in conjunction with other treatment techniques as follows:

4.3.1.1 *Following a pretreatment step*—The pretreatment process can be either a physical or chemical process for the removal of inorganic or organic scavengers from the contaminated stream prior to AOP destruction.

4.3.1.2 *Following a preconcentration step*—Due to the increase in likelihood of radical or molecule contact, very dilute solutions can be treated cost effectively using AOPs after being concentrated.

4.4 *AOP Treatment Applications*—Advanced oxidation processes (AOPs) are most cost effective for those waste streams containing organic compounds at concentrations below 1 % (10 000 ppm). This figure will vary depending upon the nature of the compounds and whether there is competition for the oxidizing agent.

5. Constraints on Usage

5.1 *General*—Although AOPs are destruction processes, in order for compound mineralization to take place, the oxidation reactions must be taken to completion. In most cases, effluent analysis is the only method available to ensure this state. Some compounds are selective in their reactivity. For these reasons, preliminary bench-scale testing and literature searches on the predicted reaction mechanisms are essential prior to full scale

treatment (see the FRTR Technology Screening Matrix ITRC 2005, and GAO-05-666).

5.2 *Presence of Scavengers*—Scavengers, such as bicarbonate and carbonate, will adversely affect the ability of the oxidizing agent to react with the target compounds if these compounds are left as ions within the solution. Adjusting the pH of the solution will reduce this problem, however, the additional cost requirements must be balanced against the benefit received.

5.3 *Contaminant Identification*—The types of contaminants and their corresponding destruction rate constants will affect the overall system performance. In general, chlorinated aliphatics with carbon-to-carbon double bonds (unsaturated), degrade more quickly than chlorinated compounds with single bonds (saturated). In addition, refractory compounds such as carbon tetrachloride, chloroform, and other chlorinated methane compounds are quite resistant to degradation in the presence of the hydroxyl radical and should be destroyed photochemically (that is, UV alone).

5.4 *pH Adjustment*—Adjusting the pH of the solution prior to treatment may significantly affect the performance of the treatment. A feed solution at a pH of 9 will tend to cause precipitation of most inorganics, while a pH of 5 will cause them to remain in solution throughout the treatment process. In