



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

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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 *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 and health 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.

2. Terminology

2.1 Definitions of Terms Specific to This Standard:

2.1.1 *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.

2.1.2 *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 fiberglass mesh that is coated with TiO_2 in photocatalytic AOP systems.

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

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

2.1.5 *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.

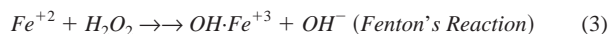
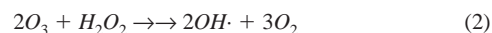
2.1.6 *scavengers*—a term used for substances that react with hydroxyl radicals that do not yield species that propagate the chain reaction for contaminant destruction. Scavengers can be either organic or inorganic compounds.

3. Significance and Use

3.1 *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. Since much of this technology development is still at the benchscale level, these guidelines will only refer to those units that are currently applied at a field scale level.

3.2 Oxidizing Agents:

3.2.1 *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 (10^6) to one billion (10^9) times faster than the corresponding attack with molecular ozone (1).² The three most common methods for generating the hydroxyl radical are described in the following equations:



3.2.1.1 Hydrogen peroxide is the preferred oxidant for photolytic oxidation systems since ozone will encourage the air stripping of solutions containing volatile organics (2). Capital and operating costs are also taken into account when a decision on the choice of oxidant is made.

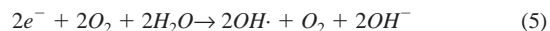
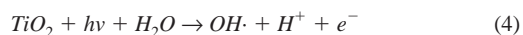
3.2.1.2 Advanced oxidation technology has also been developed based on the anatase form of titanium dioxide. This

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² The boldface numbers in parentheses refer to the list of references at the end of this standard.

method by which the photocatalytic process generates hydroxyl radicals is described in the following equations:



3.2.2 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. Since most of these lamps are proprietary, preliminary benchscale testing becomes crucial when dealing with these compounds.

3.3 AOP Treatment Techniques:

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

3.3.1.1 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.

3.3.1.2 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.

3.4 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.

4. Constraints on Usage

4.1 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.

4.2 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.

4.3 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).

4.4 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 situations where the inorganics are in a relatively low concentration (low parts per million), one would tend to lower the pH, while a higher pH would be preferable at the higher concentrations where the inorganics could be separated and removed.

4.5 System Fouling—Generally, inorganic foulants, such as iron, manganese, and calcium, in the ppm range, cause reduced flow, increased pressure and low performance of a treatment system. This phenomenon is common in most organic treatment units regardless of the mechanism employed. Pretreatment systems usually involve chemical addition (that is, pH adjustment) or membrane technology, or both, as they are generally the most economical and effective for inorganic removal. Preliminary benchscale testing is commonly used to determine the applicability and the cost-effectiveness of the different pretreatment systems.

4.6 Off-Gas Analysis—Organic analysis of the exiting gaseous stream will assist the operator in modifying system parameters to maximize system performance and efficiency. This technique is also beneficial during preliminary testing as it provides an indication of the AOP technology's ability to destroy the compounds as compared to simply stripping them from the water phase into the air.

4.7 Destruction Rate Constants—The reaction of the OH radical with organic compounds is largely dependent upon the rate constant. A list (3) of reaction rates for common contaminants is shown in Table 1.

5. Practical Applications

5.1 Emergency Situations—Advanced oxidation process (AOP) applications would normally follow containment and recovery of the waste stream in question. The time required for this primary stage should be sufficient for the AOP user to at least obtain the necessary background information on the contaminants in question. Benchscale confirmation testing is desirable, if time permits. Under no circumstances should AOP be used in a clean-up unless the manufacturer can supply data concerning testing on the same or similar chemical solutions.

TABLE 1 Rate Constants for the Hydroxyl Radical

Compound, m	$k_M, \text{OH}\cdot, (10^{+9} \text{ m}^{-1}\text{s}^{-1})$
Benzene	7.8
Hydroperoxide Ion	7.5
Vinyl Chloride	7.1
Chlorobenzene	4.5
1-Butanol	4.2
Trichloroethane	4.0
Nitrobenzene	3.9
Pyridine	3.8
Toluene	3.0
Tetrachloroethane	2.3
Carbonate Ion	0.39
Dichloromethane	0.058
Bicarbonate	0.0085
Chloroform	~0.005
Carbon Tetrachloride	NR

TABLE 2 Typical Field Scale Results of AOP Field Trials

NOTE 1—MF – microfiltration
RO – reverse osmosis

Specific Compound	Flowrate	Concentration		Notes	Reference
		Initial	Final		
1,4 dioxane	19–114 L/min	100 ppm	<10 ppb	system able to reduce dioxane in raw or deionized water consistently	(1)
methylene chloride	19 L/min	130–730 ppb	3.1 ppb	high iron conc, prevented precipitation by maintaining pH at 3	(1)
trichloroethylene		9.7–19.9 ppm	0.4 ppb		
1,2 trans-dichloroethylene		6–12.5 ppm	<0.1 ppb		
vinyl chloride		10–1010 ppb	0.5 ppb		
chloroethane		10 ppb	<0.3 ppb		
nitrate esters, explosives	15 L/min	1000–5000 ppm	<1 ppm	systems tested with UV/H2O2, UV alone, and proprietary pretreatment for carbonate removal	(1)
trichloroethylene, benzene, chloroform, chlorobenzene, 1,2 dichloroethane	30 L/min	1.55 ppm 0.23 ppm 0.08 ppm 0.05 ppm 0.01 ppm	<5 ppb <0.8 ppb 0.04 ppm <1 ppb <2 ppb	pH adjustment, MF/UV/H2O2 system	(4)
benzene, toluene, xylene	23 L/min	1.22 ppm 0.47 ppm 9.29 ppm	<0.05 ppm <0.05 ppm <0.10 ppm	UV/H ₂ O ₂	(5)
ethylbenzene		0.59 ppm	<0.05 ppm		
n-nitrosodimethylamine	95 L/min	80 ppt	5 ppt	UV	(6)
cyanide	not available	6 ppm	2 ppm	sulphide and fluoride precipitated prior to treatment	(7)
dichloroethylene, dichloroethane benzene	batch, 5 minutes	0.5 ppm 5 ppm 3 ppm	ND ND 0.009 ppm	phenolics pretreated with proprietary reagent	(7)
trichloroethylene, dichloroethylene, vinyl chloride	26 L/min	30 000 ppb 20 000 ppb 500 ppb	0.4 ppb <0.1 ppb 0.5 ppb	adjusted pH <3 to prevent fouling of UV quartz	(7)
methylene chloride benzene toluene	batch	470 ppb 353 ppb 2740 ppb	1 ppb 1 ppb 4 ppb	UV/03/H2O2 at pH 10	(8)

5.1.1 Emergency Clean-Up Operation—For a spill, under emergency clean-up situations, the AOP technology user must do the following:

5.1.1.1 Monitor the feed, effluent, and off-gas stream analysis closely,

5.1.1.2 Monitor the feed flowrate and adjust accordingly,

5.1.1.3 Use holding tanks prior to discharge in order to buffer changes in discharge concentrations, and

5.1.1.4 Modify system parameters as necessary, based on the above conditions.

5.2 Non-Emergency Operation—Once the leachate or chemicals reach the groundwater, the critical period is over and rapid response is less effective. Preliminary testing and preparation can be performed by the mitigator prior to treatment.

Pretesting and manufacturers' information will determine the most appropriate operating conditions and the pretreatment required. This will not, however, reduce the importance of closely monitoring all aspects of the data. Sudden changes in feed concentrations could severely reduce the destruction rates.

5.3 Field Scale Results Using AOP Technology—Table 2 provides a summary of typical destruction capabilities achieved during photolytic AOP field trials conducted between 1988–1993.

6. Keywords

6.1 advanced oxidation; AOP; destruction; enhanced oxidation; hydrogen peroxide; hydroxyl radical; ozone; photolysis; titanium dioxide; ultraviolet

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