



Engineering Bulletin

Chemical Oxidation Treatment

Purpose

Section 121(b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) mandates the Environmental Protection Agency (EPA) to select remedies that "utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable" and to prefer remedial actions in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants, and contaminants as a principal element." The Engineering Bulletins are a series of documents that summarize the latest information available on selected treatment and site remediation technologies and related issues. They provide summaries of and references for the latest information to help remedial project managers, on-scene coordinators, contractors, and other site cleanup managers understand the type of data and site characteristics needed to evaluate a technology for potential applicability to their Superfund or other hazardous waste site. Those documents that describe individual treatment technologies focus on remedial investigation scoping needs. Addenda will be issued periodically to update the original bulletins.

Abstract

Oxidation destroys hazardous contaminants by chemically converting them to nonhazardous or less toxic compounds that are ideally more stable, less mobile, and/or inert. However, under some conditions, other hazardous compounds may be formed. The oxidizing agents most commonly used for the treatment of hazardous contaminants are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide. Current research has shown the combination of these reagents or ultraviolet (UV) light and an oxidizing agent(s) makes the process more effective [1] [2] [3, p. 11]. Treatability studies are necessary to document the applicability and performance of chemical oxidation systems technology for a specific site.

Chemical oxidation is a developed technology commonly used to treat liquid mixtures containing amines, chlorophenols, cyanides, halogenated aliphatic compounds, mercaptans, phe-

nols, and certain pesticides [4, p. 7.76] [5, p. 7.42]. In lab-scale tests, chemical oxidation has been shown to be effective for chlorinated organics [6, p. 229].

This bulletin provides information on the technology applicability, limitations, a technology description, the types of residuals produced, site requirements, current performance data, status of the technology, and sources of further information.

Technology Applicability

Chemical oxidation effectively treats liquids that contain oxidizable contaminants; however, it can be used on slurried soils and sludges. Because it is a nonselective treatment, it is most suited to media with low concentrations of contaminants.

The effectiveness of chemical oxidation technology on general contaminant groups is shown in Table 1. Examples of constituents within contaminant groups are provided in "Technology Screening Guide for Treatment of CERCLA Soils and Sludges" [7]. This table is based on the current available information or professional judgement when no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiency achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatability was tested to show that, for that particular contaminant and matrix, the technology was effective. The ratings of potential effectiveness and no-expected-effectiveness are based upon expert judgement. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no-expected-effectiveness rating is given.

Chemical oxidation depends on the chemistry of the oxidizing agent(s) and the chemical contaminants. Table 2 lists selected organic compounds by their relative ability to be oxidized. Chemical oxidation has also been used as part of a treatment process for cyanide-bearing wastes and metals such

* [reference number, page number]

as arsenic, iron, and manganese [8, p. 4.4]. Metal oxides formed in the oxidation process more readily precipitate out of the treated medium.

The oxidation of some compounds will require a combination of oxidizing agents or the use of UV light with an oxidizing agent(s) [1][2] [3, p. 10]. An example of such a situation is polychlorinated biphenyls (PCBs), which do not

react with ozone alone, but have been destroyed by combined UV-ozone treatment [5, p. 7.48]. Enhanced chemical oxidation has been used at several Superfund sites [3][9].

Limitations

If oxidation reactions are not complete, residual hazardous compounds may remain in the contaminant stream. In addition, intermediate hazardous compounds may be formed (e.g., trihalomethanes, epoxides, and nitrosamines) [10][11, p. 190]. Incomplete oxidation may be caused by insufficient quantity of the oxidizing agent(s), inhibition of oxidation reactions by low or high pH, the strength of the oxidizing agent(s), the presence of interfering compounds that consume reagent, or inadequate mixing or contact time between contaminant and oxidizing agent(s) [12, p. 10.52]. It is important to monitor the concentrations of residual oxidizing agent(s), contaminants, and products to ensure a complete reaction has occurred. It may be necessary to monitor reaction conditions such as pH, temperature, and contact time to optimize the reaction. Determination of potential reactions and rates may be critical to prevent explosions or formation of unwanted compounds.

Oil and grease in the media should be minimized to optimize the efficiency of the oxidation process. Oxidation is not cost-effective for highly concentrated wastes because of the large amounts of oxidizing agent(s) required.

Chemical oxidation can be used on soils and sludges if there is complete mixing of the oxidizing agent(s) and the oxidizable hazardous component in the matrix.

Ozonation systems generally have higher capital costs than those using other oxidizing agents because an ozone generator must be used. They must also have an ozone decomposition unit to prevent emission of excess ozone into the ambient air which further adds to the cost.

Although hydrogen peroxide is considered a relatively safe oxidant, proper storage and handling is required [5, p. 7.44]. The hydrogen peroxide reaction may be explosive when introduced into high-organic materials [11, p. 190].

The cost of generating UV light and the problem of scaling or coating on the lamps are two of the biggest drawbacks to UV-enhanced chemical oxidation systems. They do not perform as well in turbid waters and slurries because the reduced light transmission lowers the effectiveness [13].

Technology Description

Chemical oxidation is a process in which the oxidation state of a contaminant is increased while the oxidation state of the reactant is lowered. The electrons gained by the oxidizing agent are lost by the contaminant. An example of a common oxidation reaction is:

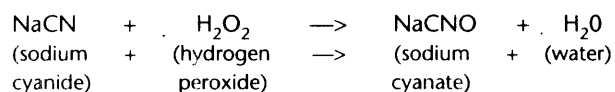


Table 1
Effectiveness of Chemical Oxidation on General Contaminant Groups for Liquids, Soils, and Sludges^a

Contaminant Groups		Liquids	Soils, Sludges
Organic	Halogenated volatiles	■	▼
	Halogenated semivolatiles	■	▼
	Nonhalogenated volatiles	■	▼
	Nonhalogenated semivolatiles	■	▼
	PCBs	■	□
	Pesticides	■	▼
	Dioxins/Furans	▼	□
	Organic cyanides	■	■
Organic corrosives	▼	▼	
Inorganic	Volatile metals	■	▼
	Nonvolatile metals	■	▼
	Asbestos	□	□
	Radioactive materials	□	□
	Inorganic corrosives	□	□
	Inorganic cyanides	■	■
Reactive	Oxidizers	□	□
	Reducers	■	▼

■ Demonstrated Effectiveness: Successful treatability test at some scale completed
▼ Potential Effectiveness: Expert opinion that technology will work
□ No Expected Effectiveness: Expert opinion that technology will not work
a Enhancement of the chemical oxidation process is required for the less easily oxidizable compounds for some contaminant groups.

Table 2
Selected Organic Compounds by Relative Ability to be Oxidized

Ability to be Oxidized	Examples
High	phenols, aldehydes, amines, some sulfur compounds
Medium	alcohols, ketones, organic acids, esters, alkyl-substituted aromatics, nitro-substituted aromatics, carbohydrates
Low	halogenated hydrocarbons, saturated aliphatics, benzene

In this reaction, the oxidation state of carbon in the sodium cyanide is increased while the oxidation state of each oxygen in the hydrogen peroxide is decreased.

Chemical oxidation is used when hazardous contaminants can be destroyed by converting them to nontoxic or less hazardous compounds. Contaminants are detoxified by actually changing their chemical forms. The process is nonselective; therefore, any oxidizable material reacts. The oxidizing agent(s) must be well mixed with the contaminants in a reactor to produce effective oxidation. In order for the oxidation reaction to occur, the pH must be maintained at a proper level; therefore, pH adjustment may be necessary [10][14].

Figure 1 shows a process flow diagram for a chemical oxidation system. The main component is the process reactor. Oxidant is fed into the mixing unit (1), then the reactor (2). Reaction products and excess oxidant are scrubbed prior to venting to the ambient air. The pH and the temperature in the reactor are controlled to ensure the reaction goes to completion. The reaction can be enhanced with the addition of UV light.

Common commercially available oxidants include ozone, hydrogen peroxide, hypochlorites, chlorine and chlorine dioxide. Treatment of hazardous contaminants requires a strong oxidizing agent(s), such as ozone or hydrogen peroxide. Ozone and combinations of ozone and hydrogen peroxide react rapidly with a large number of contaminants [3, p. 11]. Ozone has a half-life of 20 to 30 minutes at 20°C (68°F); therefore, it must be produced onsite. This requirement eliminates storage and handling problems associated with other oxidants.

Systems that use ozone in combination with hydrogen peroxide or UV radiation are catalytic ozonation processes. They accelerate ozone decomposition, thereby increasing the hydroxyl radical concentration and promoting the oxidation rate of the compounds of interest [3, p. 10]. Specifically, hydrogen perox-

ide, hydrogen ion, and UV radiation have been found to initiate ozone decomposition and accelerate the oxidation of refractory organics via the free radical reaction pathway [6, p. 228]. Reaction times can be 100 to 1000 times faster in the presence of UV light [11, p. 195]. Minimal emissions result from the UV-enhanced systems [15, p. 35].

Process Residuals

Residuals produced from chemical oxidation systems can include partially oxidized products (if the reaction does not go to completion) which may require further treatment. In some cases, inorganic salts may be formed [10]. Depending on the oxidizing agent used and the chlorine content of the contaminant, oxidation of organic compounds may result in the formation of HCl and NO_2 . Ozone and hydrogen peroxide have an advantage over oxidants containing chlorine because potentially hazardous chlorinated compounds are not formed [11, p. 187].

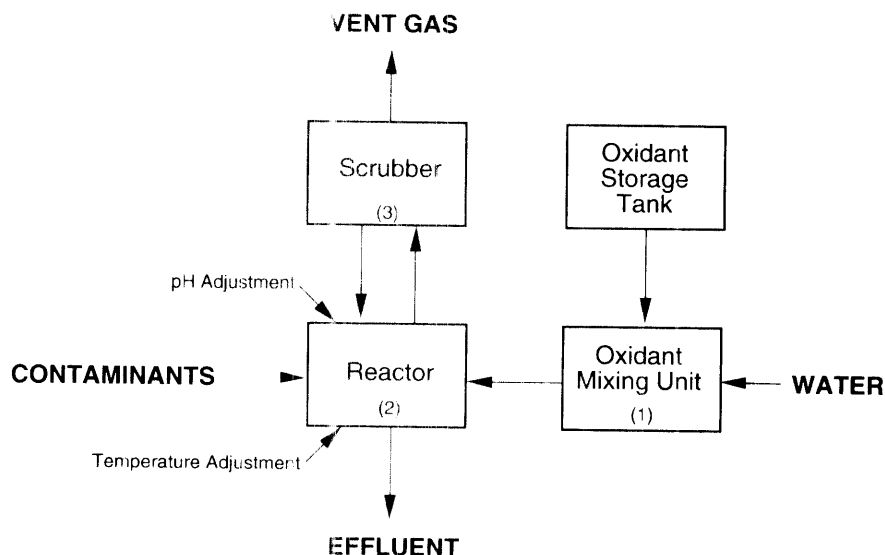
Acid gas control is required for reactions that produce HCl. Any precipitate formed has to be filtered out and may require additional treatment to comply with the appropriate regulations [10].

Site Requirements

Equipment requirements for oxidation processes include storage vessels, metering equipment, and reactor vessels with some type of agitation device. UV light may also be required. All the equipment is readily available and can be skid-mounted and sent to the site.

Ozone must be generated onsite because it is not practical to store. Other oxidizing agents require onsite storage and handling. A site safety plan would have to be developed to

Figure 1
Process Flow Diagram for Chemical Oxidation System



provide for personnel protection and special handling measures. Standard 440V, three-phase electrical service may be required depending on the reactor configuration. Water must be available onsite for cleaning and descaling operations, although the treated effluent might be used for this purpose. Water would also be needed for slurring soils and sludges. The quantity of water needed is vendor- and site-specific.

Onsite analytical equipment may be needed to conduct pH, oil, and grease analyses. Liquid and gas chromatographs

capable of determining site-specific organic compounds may be required for the operation to be more efficient and to provide better information for process control.

Performance Data

Performance of full-scale chemical oxidation systems has been reported by several sources, including equipment vendors. Some of the data presented for specific contaminant removal effectiveness were obtained from publications developed by the respective chemical oxidation system vendors. The quality of this information has not been determined; however, it does give an indication of the efficiency of chemical oxidation. Data on chemical oxidation systems at Superfund sites are discussed in the following paragraphs.

Ultrax International installed its system at the Lorentz Barrel and Drum Superfund site in San Jose, California. The system uses ozone and hydrogen peroxide with UV radiation to treat contaminated groundwater whose main contaminants were 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), and 1,1-dichloroethane (DCA). Demonstration of this system at the Lorentz site was also part of the Superfund Innovative Technology Evaluation (SITE) program. During the SITE testing, hydraulic retention time (reaction time), ozone dose, hydrogen peroxide dose, UV radiation intensity, and pH level were varied, as shown in Table 3, to assess the system's performance. The results of the testing are listed in Table 4 [3].

The system destruction efficiency averaged more than 90 percent of the TCE in the contaminated groundwater over the range of operating parameters. Destruction efficiencies for 1,1,1-TCA and 1,1-DCA increased when the ozone dosage was increased. During these runs, the destruction efficiency for

Table 3
Lorentz Barrel and Drum SITE Testing Parameters [3]

Run	pH	Time (min)	Ozone dose (mg/l)	H ₂ O ₂ dose (mg/l)	UV Lamps
1	7.2	40	75	25	all on
2	6.2	40	75	25	all on
3	5.2	40	75	25	all on
4	7.2	60	75	25	all on
5	7.2	20	75	25	all on
6	7.2	40	110	25	all on
7	7.2	40	38	25	all on
8	7.2	40	110	38	all on
9	7.2	40	110	13	all on
10	7.2	40	110	13	1/2 on
11	7.2	40	110	13	1/2 on
12	7.2	40	110	13	all on
13	7.2	40	110	13	all on

Table 4
Lorentz Barrel and Drum SITE Test Results (contaminated groundwater) [3]

Run	1,1,1-TCA			TCE			1,1-DCA		
	Influent ^a (µg/l)	Effluent ^a (µg/l)	% Removed	Influent ^a (µg/l)	Effluent ^a (µg/l)	% Removed	Influent ^a (µg/l)	Effluent ^a (µg/l)	% Removed
1	4.0	1.2	70	86.0	4.6	95	11.5	6.2	46
2	3.7	0.6	83	55.0	2.4	96	10.0	3.2	69
3	3.8	1.3	65	64.0	3.6	94	10.0	6.7	35
4	3.9	1.8	53	56.0	3.4	94	12.0	7.8	32
5	4.1	1.4	66	50.0	6.2	88	10.0	6.4	36
6	3.9	1.0	73	73.0	1.0	98	11.0	5.2	54
7	4.7	3.0	37	70.0	17.0	76	13.0	9.2	30
8	3.5	0.7	80	59.0	0.7	99	9.8	4.7	52
9	4.3	0.8	83	65.0	1.2	98	11.0	5.3	54
10	3.4	0.6	82	57.0	1.6	97	10.0	3.9	62
11	3.8	0.8	80	57.0	1.3	98	11.0	5.4	50
12	3.3	0.4	87	52.0	0.6	99	11.0	3.8	65
13	3.2	0.5	85	49.0	0.6	99	10.0	4.2	60

^a Mean Value

1,1,1-TCA was over 80 percent and almost 60 percent for 1,1-DCA. For a more detailed discussion, the reader should consult reference 3.

The Ultrox[®] system was also used to treat contaminated groundwater in Muskegon, Michigan. Before treatment, the TCE concentration was reported to be as high as 7 parts per million (ppm). The Ultrox[®] system has reduced effluent levels to under 2 parts per billion (ppb) [13, p. 90].

Solarchem Environmental Systems installed its Rayox[®] enhanced oxidation unit at the Oswego, New York, Superfund site. This demonstration system, which uses UV radiation enhancement with ozone and hydrogen peroxide, treated collected leachate from a landfill site. Results of the testing are listed in Table 5 [9].

Peroxidation Systems' perox-pure[™] Organic Destruction process uses hydrogen peroxide and UV light to destroy dissolved organic contaminants. It has been used at a number of sites to reduce contaminants up to 90 percent. The perox-pure[™] has much lower effectiveness on aliphatic compounds, such as TCA, because they are not as reactive [15]. Table 6 is a partial list of contaminants treated and applications where the perox-pure[™] process has been used [16].

Table 7 lists performance data for several sites using the full-scale perox-pure[™] system [17] [18]. Most organics were reduced to extremely low levels by the perox-pure[™] treatment system at every site. At Site 1, the perox-pure[™] system, followed by an air stripper, was able to destroy 4 of the 6 organics below detection limits. It also eliminated over 90 percent of the air emissions as compared to the previous ar-

Table 5
Oswego Leachate Test Results [9]

<i>Volatile Organic Compounds (VOCs)</i>	<i>Inlet (ppb)</i>	<i>Outlet (ppb)</i>	<i>% Removed</i>
Methylene chloride (MeCl)	204	1	99.5
1,1-Dichloroethylene (DCE)	118	0	100
1,1-DCA	401	15.7	96
1,1,2-DCE	3690	14.9	99.6
1,2-DCA	701	109	85
1,1,1-TCE	261	3.1	98.9
Benzene	469	1.8	99.6
Methyl isobutyl ketone	47	2.2	95.8
1,1,2,2-Tetrachloroethane	344	4.2	98.8
Toluene	3620	3.9	99.9
Chlorobenzene	704	0	100
Ethylbenzene	2263	1.1	99.9
M-,P-Xylene	4635	1.3	99.9
O-Xylene	6158	2.4	99.9

rangement which used an air stripper followed by the perox-pure[™] system. At Site 5, the system was modified to pretreat the influent to remove iron and calcium. This resulted in no organics being detected in the effluent.

The Purus Inc. enhanced oxidation system was demonstrated on contaminated groundwater at Lawrence Livermore National Laboratory (LLNL). Benzene, toluene, ethylbenzene, and xylene (BTEX) levels were reduced from 5 ppm to as little as 5 ppb [19, p. 9]. The Purus system is also being used to treat

Table 6
Applications of perox-pure[™] System at Selected Sites [16]

<i>Location</i>	<i>Type</i>	<i>Contaminant</i>
CA	Groundwater	Tetrahydrofuran
CA	Leachate	Mixed organic acids
CA	Groundwater	TCE
CA	Groundwater	TCE, TCA, CCl ₄ , MeCl
MA	Dredge Water	PCBs
NH	Leachate	Ketones, VOCs
MD	Groundwater	TCE, perchloroethylene (PCE), TCA, DCE
MA	Groundwater	MeCl, TCA, dichloromethane (DCM)
CA	Municipal Water	Humic acid/color control
CA	Groundwater	TCE, PCE, TCA, DCE
WA	Groundwater	Pentachlorophenol
CO	Misc. Wastes	Hydrazine, DIMP
CO	Groundwater	Benzene, toluene, xylene (BTX)
CT	Bioeffluent	Chlorobenzene
CA	Groundwater	TCE, TCA, PCE, DCE
NY	Groundwater	TCE, DCE, PCE, TCA
CA	Groundwater	TCA, TCE
NY	Groundwater	TCE, DCE, DCA, TCA
PA	Effluent	Phenol
CA	Groundwater	BTX
PA	Effluent	Nitrated esters
NJ	Groundwater	TCE, DCE, PCE, MeCl
AZ	Groundwater	BTEX
TX	Effluent	Phenols, nitrophenols
MA	Groundwater	BTX
CO	Waste	Hydrazine
CA	Groundwater	TCE, PCE, BTX, TCA
AR	Groundwater	Acrylic acid, butyl acrylate
OH	Recycle	Bacteria, phenol, formaldehyde
LA	Groundwater	TCE, polynuclear aromatic hydrocarbons (PAHs)
AZ	Groundwater	TCE
UT	Effluent	Isopropyl alcohol (IPA), TOC, TCA, DCE, methyl ethyl ketone (MEK)
NJ	Effluent	Phenol
CA	Groundwater	TCE, PCE, DCE, TCA, MeCl, chloroform
CA	Effluent	BTX
CA	Groundwater	BTX
CA	Groundwater	TCE, Freon, MeCl, BTX
NC	Effluent	MeCl, phenol, PAHs

air streams from air stripping of groundwater and vacuum extraction of soils under the SITE emerging technology program at LLNL.

Other case studies have shown greater than 99 percent destruction of the pesticides DDT, PCP, PCB, and Malathion with ozone/UV radiation [4, p. 7.67].

Technology Status

Chemical oxidation is a well-established technology used for disinfection of drinking water and wastewater and is a common treatment for cyanide wastes. Enhanced systems are now being used more frequently to treat hazardous streams.

This technology has been applied to Resource Recovery and Conservation Act (RCRA) wastes and has been used on Superfund wastes [7]. In 1988, chemical oxidation was listed in the Record of Decision at Lorentz Barrel & Drum in San Jose, California and Southern Maryland Wood, in Hollywood, MD. In 1989, chemical oxidation was listed at Sullivan's Ledge in New Bedford, Massachusetts; Bog Creek Farm in Howell Twp., New Jersey; Ott/Story/Cordova Chemical in Dalton Twp., Michigan; Burlington Northern in Somers, Montana; and Sacramento Army Depot in Sacramento, California.

Operating costs can be competitive with other treatment technologies such as air stripping and activated carbon. However, oxidation is becoming a more attractive option because the contaminants are destroyed rather than transferred to an-

Table 7
Full-Scale perox-pure™ Performance Data [17][18]

<i>Location</i>	<i>Contaminant</i>	<i>Influent (µg/l)</i>	<i>Effluent (µg/l)</i>
Site 1 Source of influent not reported	MeCl	30	1.5
	1,1-DCA	42	BDL
	1,2-DCE	2466	BDL
	1,1,1-TCA	1606	1218
	TCE	1060	BDL
	PCE	3160	BDL
Site 2 Concentrated Wastewater	Hydrazine	1,200,000	<1
	Monomethyl Hydrazine	100,000	<10
	Unsymmetrical dimethyl Hydrazine	1,500,000	<10
	Nitrosodimethylamine	1,500	<0.02
	Chlorinated Organics	75,000	<1
	Pesticides/Herbicides	500	<1
Site 3 Contaminated Groundwater	1,2-DCE	6.2	BDL
	TCE	66.3	BDL
	Chloroform	2.1	BDL
Site 4 Source of influent not reported	MeCl	600-800	33
	1,1,1-TCA	200-400	26
	1,2-DCE	50-250	<1
Site 5 Contaminated Groundwater	Benzene	7,600	ND*
	Toluene	24,000	ND*
	Chlorobenzene	8,800	ND*
	Ethylbenzene	3,300	ND*
	Xylenes	46,000	ND*
Site 6 Contaminated Groundwater	MeCl	903	11
	1,1,1-TCA	60	6

Detection Limits not Reported

BDL = Below Detection Limit

ND = Nondetected

* With Pretreatment

other media. Operating costs for mobile chemical oxidation systems have ranged from \$70 to \$150 per 1,000 gallons of water treated [8, p. 4.5]. Operating costs for the Ultrox® enhanced system have varied dramatically from \$0.15 to \$90/1000 gallons treated, depending on the type of contaminants, their concentration, and the desired cleanup standard. The greatest expense for this system is the cost of electricity to operate the ozone generator and UV lamps [13, p. 92].

EPA Contact

Technology-specific questions regarding chemical oxidation may be directed to:

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