WET AIR OXIDATION — A TREATMENT MEANS FOR AQUEOUS HAZARDOUS WASTE STREAMS

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(Accepted December 1984)

Summary

Wet air oxidation (WAO) is a process in which dissolved or suspended oxygen-demanding components of a wastewater are oxidated at elevated temperature and pressure using an oxygen-containing gas such as air bubbling through the aqueous phase. In this paper the increasing use of WAO in detoxification of hazardous wastes is described. The cost of WAO is compared with that of incineration. Various present day applications of WAO are described in detail.

Introduction

Wet air oxidation (WAO) was developed in the mid-1940s as a way to recover vanillin from spent pulping liquor. Since the late 1950s, the process has been widely used to oxidize sewage sludge and for various industrial process wastewaters where energy and resource recovery were advantages. Since the early 1970s in many foreign applications and since the early 1980s in the U.S., the process has been applied to several hazardous waste applications. In total, 190 installations are in operation or under construction throughout the world. Commercal-scale WAO systems range in size from six gallons per minute to multiple units with an aggregate capacity of 3,000 gallons per minute or more.

WAO refers to the aqueous phase oxidation of dissolved or suspended oxygen-demanding components in a wastewater at temperatures usually in the 175 to 325°C range and at pressures sufficiently high to prevent excessive evaporation of water, generally between 300 and 3000 psig. The oxygen required by WAO reactions is provided by an oxygen-containing gas, usually air, bubbled through the liquid phase in a reactor used to contain the process, thus the term "wet air oxidation".

In most hazardous waste applications, WAO should be regarded as a pretreatment means. Conventional biological treatment often follows. The WAO process serves as means of detoxifying wastewaters by significantly reducing the concentration of hazardous compounds.

This article will further describe the process and describe current and potential hazardous waste applications.

The process

For any application, the equipment configuration is similar to that shown in Fig. 1. First, a stream containing oxidizable material is pumped to the system using a positive displacement high pressure pump. Air or pure oxygen is mixed with the feed liquid either before preheating or before the reactor where the oxidation takes place. Preheat is provided by exchange with hot oxidized effluent. For startup, or in cases where additional heating is necessary, indirectly applied steam or hot oil is used for additional preheating.

The oxidation occurring in the reactor raises the temperature of the mixture to the desired maximum. The oxidized reactor effluent, after being used to preheat the feed, is then cooled in an exchanger before its pressure is reduced through a control valve. Liquid and noncondensibles are disengaged in a separator drum and discharged separately.

The oxidation conditions chosen for an application depend on the treatment objectives. The key variables affecting the degree of oxidation are oxidation temperature and residence time. For waste sludge applications, where the objective is to break down the gelatinous nature of the sludge to improve dewaterability, treatment at 175—200°C for 5—20 minutes will yield sludges that can be dewatered to 40 to 60 percent solids. The oxygen demand of the sludge will only be reduced by 5—10 percent.

At higher temperatures and longer residence times, most of the chemical constituents in the wastewater are oxidized to carbon dioxide and water or low molecular weight oxygenated species.
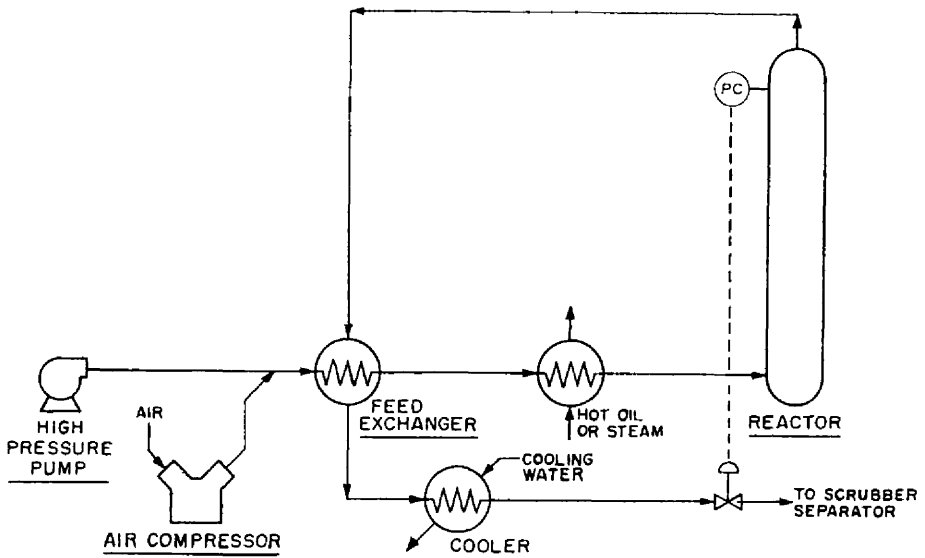

Fig. 1. Flowscheme.

Hazardous waste testing

Many bench studies have been performed and reported [5,6]. In most cases, destruction efficiencies exceeding 99 percent have been observed for compounds representing various categories of hazardous waste from the priority pollutant lists. Table 1 summarizes these results. Elevated temperatures, or the use of a soluble copper catalyst, increases the percent destruction.

Miller [7] also reported catalyzed wet air oxidation work for hazardous waste destruction. In his work, the level of destruction of toxic wastes was increased through the use of co-catalysts. Three compounds, Kepone, the PCBs in Aroclor 1254, and 1,2-dichlorobenzene, showed relatively poor destruction efficiencies.

These results, and those discussed by Randall [6], suggest the following observations about the susceptibility of various compound classes to destruction by conventional wet air oxidation:

* Inorganic and organic cyanide compounds are easily oxidized.
* Aliphatic and chlorinated aliphatic compounds are easily oxidized.
* Aromatic hydrocarbons such as toluene, acenaphthene, and pyrene are easily oxidized.
* Aromatic and halogenated aromatic compounds containing nonhalogen functional groups, e.g., phenols and anilines, are easily oxidized.
* Halogenated aromatic compounds without other nonhalogen functional groups, e.g., chlorobenzene and PCBs, are resistant to conventional wet air oxidation.

In addition to the specific oxidation data and general observations noted, the mixtures remaining after oxidation showed a 15 to 4000 fold reduction in toxicity [5].

Wet air oxidation vs. incineration

Generally, hazardous waste incineration is most economically used for waste streams containing high concentrations of nonaqueous organic materials. Wet air oxidation is used most economically for dilute aqueous waste streams containing levels of organic material that cannot be treated by conventional means.

In hazardous waste treatment applications, capital costs, as seen in Fig. 2, are generally higher than those for hazardous waste incineration. Capital costs generally depend on capacity, oxygen demand and severity of oxidation, all of which influence the choice of materials of construction.

Operating costs for wet air oxidation are generally lower than for incineration because less energy is required. Figure 3 shows the thermal energy requirement versus waste concentration for incineration and wet air oxidation. For more dilute waste streams, the energy demand for incineration is substantial. With incineration, it is necessary to supply not

TABLE 1

Bench scale wet air oxidation of pure compounds (from Randall and Knopp [5] and Randall [6]

Compound	Wet Air Oxidation Conditions	% Destroyed
Acenaphthene	275°C	99.99
	320°C	99.96
Acrolein	275°C	99.05
	320°C	> 99.96
Acrylonitrile	275°C	99.00
	275°C/catalyst	99.50
	329°C	99.91
Carbon tetrachloride	275°C	99.99
	275°C/catalyst	99.99
Chloroform	275°C	99.92
	275°C/catalyst	99.94
2-Chlorophenol	275°C	94.96
	275°C/catalyst	99.88
	320°C	99.86
Cyanide	275°C	99.96
2,4-Dichloroaniline	275°C	> 99.8
1,2-Dichloroethane	275°C	99.8
	275°C/catalyst	99.9
2,4-Dimethylphenol	275°C	99.99
	320°C	99.99
2,4-Dinitrotoluene	275°C	99.74
	320°C	99.88
1,2-Diphenylhydrazine	275°C	99.98
	320°C	99.98
Hexachlorocyclopentadiene	250°C	90.0
	275°C	98.2
	300°C	> 99.85
Malathion	200°C	99.87
	250°C	99.85
	300°C	99.97
4-Nitrophenol	275°C	99.60
	320°C	99.96
N-Nitrosodimethylamine	275°C	99.56
	275°C/catalyst	99.38
Pentachlorophenol	275°C	81.96
	275°C/catalyst	97.30
	320°C	99.88
Phenol	275°C	99.77
	320°C	99.97
Pyrene	275°C	00.995
	275°C/catalyst	99.997
Thiocyanate	275°C	> 99.98
Toluene	275°C	99.73
	275°C/catalyst	99.96

TABLE 1 (continued)

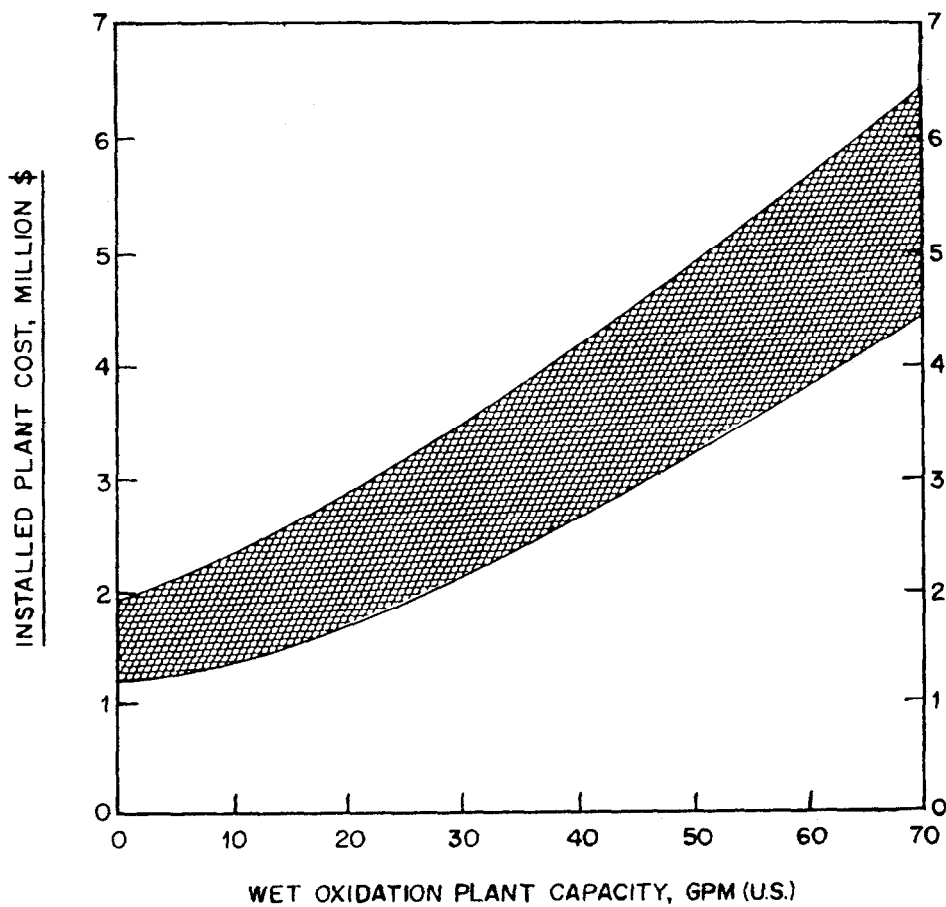| Compound	Wet Air Oxidation Conditions	% Destroyed
2,4,6-Trichloroaniline	280°C/catalyst	99.97
Kepone	280°C/catalyst	31.0
Aroclor 1254	320°C	63.0
	320°C/catalyst	2.0
1,2-Dichlorobenzene	275°C	2.98
	275°C/catalyst	32.2
	320°C/catalyst	69.11

Fig. 2. Installed plant costs vs. capacity of wet air oxidation units using air (1982). Figure is based on high pressure units; low pressure units will be substantially less.
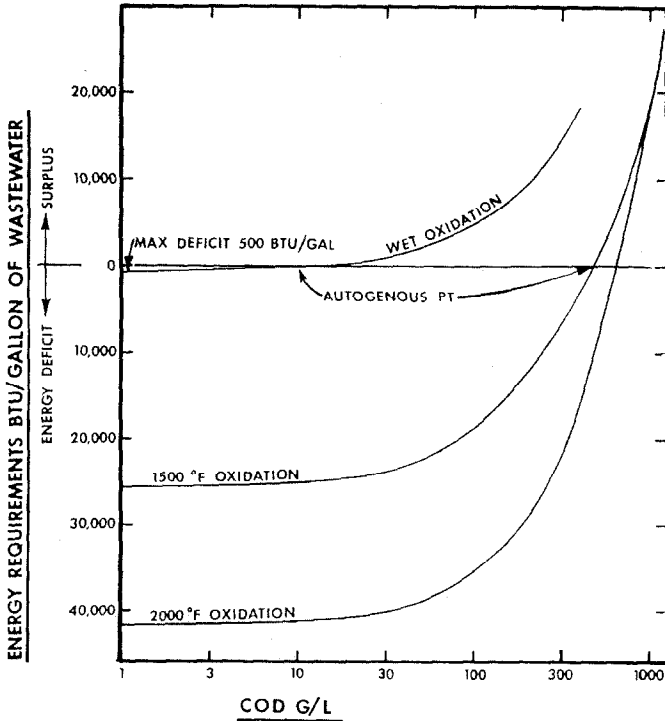
Fig. 3. Thermal energy requirements vs. organic content for both thermal oxidation and wet oxidation.

only the sensible heat and heat of vaporization of the liquid, but also sensible heat for vapors, combustion products, spent air and excess air up to a combustion temperature of between 1500 and 2500°F. With wet air oxidation, however, the only energy required is the difference in enthalpy between incoming and effluent streams. This value is typically 500 BTU/gallon for a waste low in organics, as opposed to 20,000 BTU/gallon for incineration. For a waste to become thermally self-sustaining in equipment of realistic size, a COD reduction of approximately 15,000 ppm is required with wet air oxidation. For incineration approximately 300,000 ppm of COD reduction is required.

A significant advantage of wet air oxidation is that there are minimal air pollution problems. Contaminants tend to stay in the aqueous phase. The small amount of gas that is discharged consists mainly of spent air and carbon dioxide. NO_x emissions are not observed because nitrogen compounds are converted to ammonia. Oxides of sulfur are not produced because sulfur compounds are converted to sulfate and remain in the liquid phase. Similarly, the chlorine from the oxidation of chlorinated compounds remains in solution as hydrochloric acid or salt. With hazardous waste incineration, expensive exhaust gas cleaning systems are required to remove particulates and acid gas.

Specific applications/case histories

Although it has been used in other applications for over 30 years, wet air oxidation has only recently been considered for treating hazardous waste.

TABLE 2

Zimpro wet air oxidation installations

No. of plants	Type of waste
109	Municipal sludge
29	Night soil
12	Carbon regeneration
7	Acrylonitrile
6	Metallurgical coking
6	Petrochemical
3	Paper filler
2	Industrial activated sludge
2	Pulping liquor
2	Hazardous waste
1	Paper mill sludge
1	Explosives, 3,4,5-T, malathion
1	Monosodium glutamate
1	Polysulfide rubber
1	Textile sludge
1	Chrome tannery waste
1	Petroleum refining
1	Misc. industrial sludges
186	

Table 2 lists wet air oxidation installations put in place by Zimpro Inc. Many of the industrial applications treat aqueous wastes that meet the RCRA definition of hazardous. Canney and Schaefer [9] summarize the results obtained at several typical operating wet air oxidation units.

Spent caustic
    Spent caustic is generated from the scrubbing of hydrocarbon gas streams for acid gas removal. pH and sulfide content generally make the waste toxic and high levels of organics create heavy loads for biological treatment. Several plants in the United States [10] and abroad use wet oxidation to detoxify this stream and reduce organic content prior to biological treatment. Data illustrating the sulfide destruction obtained when treating spent caustic scrubbing liquor are summarized in Tables 3 and 4.

Acrylonitrile
    Acrylonitrile production wastewaters contain high concentrations of cyanide as well as organic nitriles. These wastes generally have a COD in the

TABLE 3

Full scale wet air oxidation of ethylene plant spent caustic scrubbing liquor, Mitsubishi Petrochemical Co., Yokkaichi, Japan

Wet air oxidation conditions	
Temperature, °C	200
Flow, GPM	22
Residence time, min	60
Pressure, psig	500
COD	
Feed, g/l	7.5—15
Effluent, g/l	2.5—3
% Removal	67—80
Sulfide sulfur	
Feed, mg/l	1500—6000
Effluent, mg/l	0.3—0.8
% Removal	> 99.9

S.I. conversion: m³/d = GPM × 5.45
kPa = psig × 6.89

TABLE 4

Full scale wet air oxidation of olefins production spent caustic scrubbing liquor, Northern Petrochemical Co., Morris, Illinois

Wet air oxidation conditions		
Temperature, °C	177—260	315—320
Flow, GPM	15—23	18
Residence time, min	39—60	50
Pressure, psig	1900	1900
COD		
Feed, g/l	7.5	24.0
Effluent, g/l	3.0	0.8
% Removal	60	96.7
Sulfide sulfur		
Feed, mg/l	1000	9000
Effluent, mg/l	1	< 0.1
% Removal	99.9	> 99.9

S.I. conversion: m³/d = GPM × 5.45
kPa = psig × 6.89

TABLE 5

Full scale wet air oxidation of acrylonitrile wastewater, Asahi Chemical Co., Kawasaki, Japan

Wet air oxidation conditions		
Temperature, °C	250	
Flow, GPM	145	
Residence time, min	90	
Pressure, psig	1000	
COD		
Feed, g/l	37—	46
Effluent, g/l	15—	16
% Removal	60—	65
Cyanide		
Feed, mg/l	400—	900
Effluent, mg/l	< 0.1	
% Removal	>99.9	

S.I. conversion: m^3/d = GPM × 5.45
kPa   = psig × 6.89

range from 40—120 g/l. The normal means of treatment in the United States is deep well disposal. Five plants in Japan use wet air oxidation to detoxify this wastewater prior to biological treatment [11].

Table 5 shows the >99.9% destruction of cyanide in acrylonitrile wastewater.

Coke oven gas scrubbing

During the production of coke for steel making, a fuel gas is produced. This fuel gas is scrubbed to remove HCN and H_2S. Currently, wet air oxidation is being used at several plants to oxidize the toxics in the scrubbing liquor. In wet air oxidation, the sulfur components are converted to sulfate and nitrogen components are converted to ammonium ion. In this application, ammonium sulfate is recovered as a saleable byproduct. Table 6 shows typical oxidation data.

Herbicide production wastewaters

A Michigan specialty chemicals company has chosen wet air oxidation to detoxify production wastes [12]. Wet air oxidation is being used in place of off-site disposal. Oxidized effluent which is no longer toxic is being treated in the plant's biological treatment system. Table 7 shows the results of bench, pilot, and full scale operation and illustrates the detoxification capabilities of wet air oxidation as applied to one of the company's herbicide manufacturing wastes.

Commercial waste treatment

Casmalia Resources operates the only fully permitted, Class I (Hazardous Waste) landfill in California. New legislation in California bans the burial of liquid hazardous wastes. Wet air oxidation has been chosen as one of the methods to destroy those wastes.

TABLE 6

Full scale wet air oxidation of coke oven gas desulfurization waste, Tokyo Gas, Yokohama, Japan

Wet air oxidation conditions	
Temperature, °C	260
Flow, GPM	17.6
Residence time, min	60
Pressure, psig	1065
SCN⁻	
Feed, g/l	30
Effluent, g/l	0.3
% Removal	99
$S_2O_3^{2-}$	
Feed, g/l	26.5
Effluent, g/l	< 0.1
% Removal	>99

S.I. conversion: m^3/d = GPM × 5.45
  kPa = psig × 6.89

TABLE 7

Herbicide production waste wet oxidation, Bofors Nobel, Muskegon, Michigan

	Feed	Effluent	% Removal
Autoclave			
COD, g/l	29.9	11.1	62.9
Herbicide by-product, mg/l	219	1	99.5
Oxidation temp., °C	260		
Pilot			
COD, g/l	58.4	17.0	70.9
Herbicide by-product, mg/l	484	<5	>99
Reactor Temp., °C	243		
Full scale installation			
COD, g/l	78.2	34.8	55.0
Herbicide by-product, mg/l	735	<5—13.3	99.3—98.2
Reactor temp., °C	245		

Wastes for the unit at Casmalia Resources are screened by autoclave testing to insure treatability in the wet air oxidation unit. A listing of wastes screened and results obtained is given in Table 8. Tables 9 and 10 show the results for several specific classes of wastes processed.

TABLE 8

Autoclave tests — Casmalia Resources test conditions: 280°C, 1 h reactor residence time

Waste	Parameter	Feed	Effluent	% Removal
Spent caustic	COD, g/l	40.0	7.5	81.3
	Total phenols, mg/l	5350	66	98.8
	Sulfide, mg/l	382	< 1	> 99.7
Acid distillate	COD, g/l	40.1	5.8	85.5
Alkaline solvent	COD, g/l	39.8	7.5	81.2
	Total phenols, mg/l	840	20	97.6
Cyanide plating	COD, g/l	17.1	3.2	81.3
	Cyanide, mg/l	6910	120	98.3
Metal finishing Cyanide	COD, g/l	40.4	6.0	85.1
	Cyanide, mg/l	5090.0	36.0	99.3
Cyanide plating	COD, g/l	40.2	8.6	78.6
	Cyanide, mg/l	20960.0	234.0[a]	98.9
Pesticide rinsate	COD, g/l	11.3	3.6	68.1
	Organic N, mg/l	701.0	56.0	77.7
Cadmium plating	COD, g/l	11.3	3.6	68.1
	Cyanide, mg/l	12980.0	52.0	99.6
Solvent still Bottoms	COD, g/l	43.9	8.6	80.4
	BOD, g/l	21.3	6.3	70.4
	BOD/COD	0.49	0.74	—
Rocket fuel waste Mixture	COD, g/l	45.1	1.8	96.0
Cyanide Wastewater	COD, g/l	29.6	10.4	64.9
	Cyanide, mg/l	33160.0	185.0	99.4
Pesticide wastes	COD, mg/l	1640.0	450.0	72.6
	BOD, mg/l	15.0	208.0	—
	BOD/COD	0.01	0.46	
Pesticide	COD, g/l	5.38	0.85	84.2
	BOD, g/l	1.81	0.725	53.0
	BOD/COD			

[a]During continuous operation of a full scale unit, oxidized product contained less than 7 ppm cyanide or > 99.96% destruction.

TABLE 9

Wet air oxidation demonstration of Gulf Oil spent caustic wastewater

Wet air oxidation conditions: Oxidation temperature, 515°F (268°C); Nominal residence time, 113 min; Waste flow rate, 5.3 GPM; Compressed air flow rate, 190 SCFM; Reactor pressure, 1610 psig; Residual oxygen concentration, 3.7%

Sample description	Composite influent raw waste	Composite effluent oxidized waste
COD, g/l	108.1	11.6
COD reduction, %	–	89.3
Total phenols, mg/l	15510	36
Total phenols reduction, %	–	99.77
Total sulfur, mg/l	3580	3090
Sulfate sulfur, mg/l	570	2910
Organic sulfur[a], mg/l	3010	180
Organic sulfur reduction, %	–	94.0
Sulfide sulfur, mg/l	< 1.0	< 1.0
pH	13.0	8.3
Total solids, g/l	88.6	59.7
Total ash, g/l	57.1	50.2
Volatile solids, g/l	31.5	9.5
DOC, mg/l	–	3680
Soluble chloride, mg/l	1510	550
Soluble fluoride, mg/l	4.4	1.3

[a]Organic sulfur = Total sulfur minus sulfate sulfur.

Other applications

Metal recovery. Many heavy and precious metals are held in plating and other solutions because of cyanide complexes or chelating agents such as EDTA (ethylenediaminetetraacetic acid). In order to remove these metals from solution, it is necessary to destroy the complexing or chelating agent. Wet air oxidation has shown excellent results in bench and pilot scale testing for this application.

Radioactive contamination clean-up. In this application, metal complexing solutions are used to wash or clean spill contaminated areas. The radioactive materials are held in solution by the complexing agent. To concentrate the waste, it is again necessary to destroy the complexing agent. Since these are dilute aqueous solutions, wet oxidation could again be an effective technology.

Conclusion

Wet air oxidation is finding new applications in detoxification of hazardous wastes. Testing and full scale operation has shown wet air oxidation to be an effective means of treating those wastes too dilute to economically

incinerate yet too toxic to biologically treat. As greater effort is made to end the landfilling of liquid toxic wastewaters, the use of wet air oxidation as an effective, economical treatment technology will continue to expand.

TABLE 10

Wet air oxidation demonstration cyanide wastewater class

Wet air oxidation conditions: Oxidation temperature, 495°F (257°C); Nominal residence time, 80 min; Waste flow rate, 7.5 GPM; Compressed air flow rate, 190 SCFM; Reactor pressure, 1220 psig; Residual oxygen concentration, 7.1%

Sample description	Composite influent raw waste	Composite effluent oxidized waste
COD, g/l	37.4	4.2
COD reduction, %	–	88.8
Cyanide, mg/l	25390	82
Cyanide reduction, %	–	99.7
DOC, mg/l	14710	1710
DOC reduction, %	–	88.4
pH	12.6	9.0
Total solids, g/l	135.3	91.2
Total ash, g/l	112.9	77.4
Volatile solids, g/l	22.4	13.8
BOD_s, mg/l	–	603
Soluble chloride, mg/l	–	773
Soluble fluoride, mg/l	30	29

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