3. (Direct Chemical Oxidation)

(direct chemical oxidation: DCO) (<100°C) (aqueous-based process) . (peroxydisulfate anion: $S_2O_8^{2-}$) .

(sodium hydrogen sulfate) (ammonium hydrogen sulfate) .

peroxydisulfate 1 .

k_a 0.01 ± 0.005 min^{-1}

(Peroxydisulfate anion) SO_4^- .

DCO 80-100°C

PVC .

30 .

1. DCO

(Direct Chemical Oxidation: DCO) Lawrence Livermore National Laboratory (LLNL) MWFA (mixed waste focus area) . 100°C

( ) [1-8].

(sodium peroxydisulfate) (ammonium peroxydisulfate) . (sodium hydrogen sulfate) (ammonium hydrogen sulfate)

.   :

$$S_2O_8{}^{2-} + (organics) \Rightarrow 2HSO_4{}^{-} + (CO_2, H_2O, \text{inorganic residues})$$

(peroxydisulfate)

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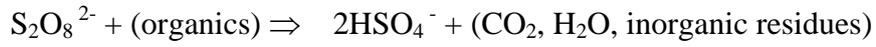
(ammonium peroxydisulfate)   (fluorine)   oxyfluorides

.

.

(working fluid)

.   ,   ,

,

.   (Peroxydisulfate)   (oxidation

potential)   .

(Teflon)   PVC

.

.   80-100°C

, PVC   140-180°C

24   (pyrolysis)

.

peroxydisulfate salts

(>80 C)

(strong charge transfer agent)   (sulfate radical

anion: SRA)   .
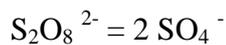
$$S_2O_8{}^{2-} = 2 \; SO_4{}^{-}$$ [1]

(organic molecular fragments),   (organic),

hydroxyl free radicals   Ag(II) and Co(III)   (high

oxidation states)   (peroxymonosulfate),

(hydrogen peroxide),   (nascent oxygen)

.   [1]

UV,   (transition metal ions),   (radiolysis)

(noble metals)   House [9], Menisci
[10]   Peyton   [11]   .

                                                                    $[S_2O_8^{2}]$ 1

                                                    .

        $d[R]/dt = - k_a [S_2O_8^{2-}]$ [2]

            [R] $[S_2O_8^{2-}]$ (L   ), k_a 0.01-
0.02 min $^{-1}$.

        1   (functional   group)
                    50 ppm   .
        1   SRA
                                                                            .

                                    SRA
                                        ,   .

Table I. Integral rate constants (equivalence based) for compounds with diverse functional groups at
            initial concentrations < 50 ppm.

Compound	M_w	n	$10^2 k_a$	Compound	M_w	n	$10^2 k_a$
	g/mol	eq/mol	1/min		g/mol	eq/mol	1/min
Urea	60.06	0	0.36	4-amino-pyridine	94.12	20	1.47
oxalic acid dihydrate	126.00	2	0.38	acetic acid	60.05	8	1.54
Nitromethane	61.04	8	0.63	sucrose	342.29	48	1.55
Salicylate-Na salt	160.10	28	0.73	Methylphosphonic acid	96.02	8	1.56
formic acid	46.03	2	0.73	2,2'-thiodiethanol	122.18	28	1.71
Triethylamine	101.19	36	0.76	1,4-dioxane	88.11	20	1.94
DMSO	78.13	18	0.79	ethylene glycol	62.07	10	1.95
DIMP	180.18	44	1.26	formamide	45.04	5	2.01
Na-EDTA	372.24	39	1.34	Na-lauryl sulfate	288.38	72	2.32
4-chloropyridine HCl	150.01	21	1.43				

*Conditions: T= 100°C; $[H_3PO_4]$= 0.0574 M; $[S_2O_8^{-2}]$ = 0.245 N; 0.3 cm^2 Pt wire catalysis.

1000/(T+273.16)

Figure 1. The domain of operation of DCO at T= 90-100°C falls on the extrapolated rate of formation of the sulfate radical anion. More concentrated organics are destroyed at higher rates than dilute organics (concentrations < 50 ppm), because of the accelerating effect of intermediate free radicals on peroxydisulfate activation.

DCO   Phosphorus group, sulfur group   amino nitrogen group
              oxyanion   (Ammonium   ion)
              (perfluorinated polymers: CFx)   . 100°C
                        , PE   PVC   .   SRA
                   pH=1   pH   pH
          . PCB
                        -   Cl⁻

                                         .

              $Cl° + OH^- = Cl^- + OH°$

    SRA   SRA   mean free
path   .   peroxydisulfate
      SRA   ,
                                                                                        .

                                              PCB
                                              [12].
Dichloropropanol, ethylene glycol   phenol   ,

.

2. DCO

DCO   ,   ,

1992   Lawrence Livermore National Laboratory

.   2   15 kg/day (   )   DCO

LLNL

[13]. Acetic acid, formamide, ethylene
glycol, tributyl phosphate, trialkyl amines, kerosene, methyl chloroform, trinitrotoluene

,   ,   ,
PCB   , pentachlorophenol, ion exchange resins (DOWEX)

.

.

1. Peroxydisulfate   .

(hydrolysis)

CO_2

CO_2

.

pentachlorophenol   PCBs   DCO

.

2. Trichloroethane

scale-up   .

3. Non-cellulostic   debris

.

.

4.

CO_2 (

)   .

DCO   ,

chloride ion   .

5.   dioxins   furans

                                    .

6.

                    .

Figure 2. One of five, 2-m tall, 75-liter hydrolysis (or oxidation) vessels at LLNL's pilot-scale waste
treatment facility. Rapid hydrolysis of mixed-waste chloro-solvents to produce water-soluble
products was demonstrated here and in same scale laboratory systems (Figure 4).

3.

CSTR(continuously-stirred tank-reactors)

peroxydisulfate . bisulfate
sulfate ion

. recycle

,   ,

———————

DCO   LLNL   .

100°C

. LLNL   mixed-waste
1,1,1-trichloroethane (TCA)   150°C

(3).   3

CSTR   (4).

15 kg/day   (   ) DCO   LLNL

[13]. Acetic acid, formamide, ethylene glycol, tributyl phosphate, trialkyl amines,
kerosene, methyl chloroform, trinitrotoluene   ,

,   , PCB , pentachlorophenol, ion
exchange resins (DOWEX)

.

(scale-up)

(treatablility)   3,4

.

———————

.

,   .

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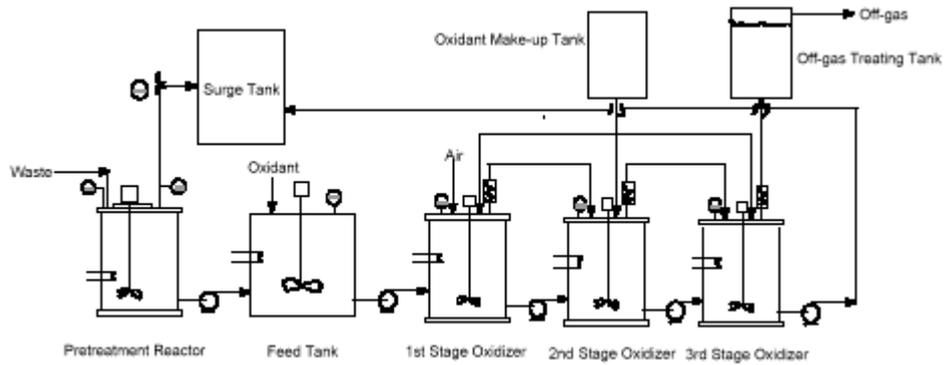
Figure 3. Schematic of pilot scale process tested at LLNL on wastes based on 1,1,1-trichloroethane (methyl chloroform). Pre-hydrolysis converts very volatile chlorinated solvents to water-soluble products, which are then oxidized at atmospheric pressure in a series of three CSTR's.
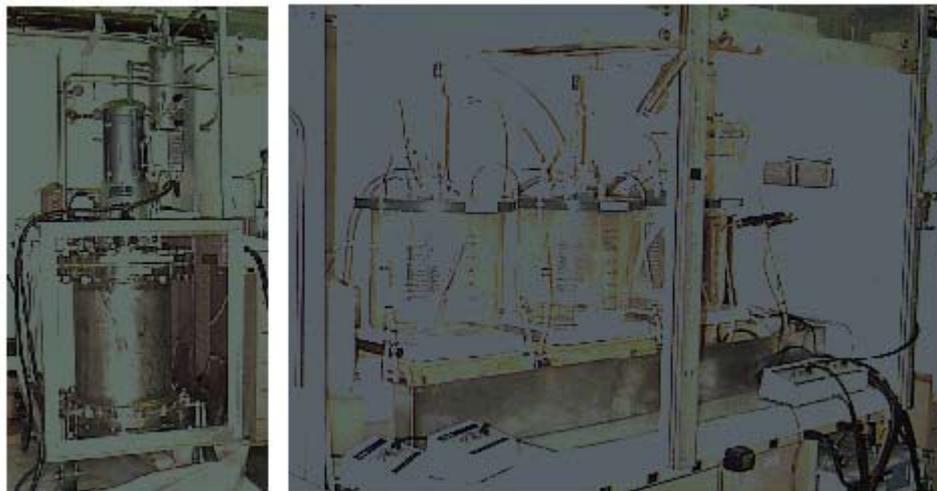
Figure 4. Pilot-scale laboratory unit used in destruction of trichloroethane (TCA) solvents 15 kg/day. The 60-liter hydrolysis vessel (left) converts TCA into water- oluble species, which are oxidized in a three-stage CSTR system (right). Data from this system is presented in Table 6.

——————————

,

.

(   )   .

(thiosulfate)   .   DCO

.   ,

.

.

(   )

.   dioxin

furan   .

4.

1   m^3 200   kg/day

.   5N $k_a = 0.02\text{-}0.04$ min^{-1} .

CSTR   Scale   .

,

.

.

——————————

2

.   .

——————————

3   90°C   kerosene   .

.

————————————————————————

4

. peroxydisulfate

. CO_2

CO_2

.

<u>PCB</u>

5 PCB

.

PCB ,

. Pentachlorophenol DCO

. 2% PCB

[13].

<u>methyl chloroform</u>

6 2 (60L 3 15L

CSTR)

. 2

. pilot scale

(i.e., 15 kg-C/day) .

Table 2. Oxidation rates (scale factors) for compounds at high concentrations.

Compound	Rate, kg/m³-day	Percentage destroyed at rate
2,4,6-trinitrotoluene	132	>98.8
Kerosene	186	>99.97
Triethylamine	205	>98.8
Dowex	132	>99
Ethylene glycol	432	>99.93

Table 3. Oxidation of kerosene (predominately dodecane) at 90 °C.

Time, min	Oxidant added, Equivalents	Carbon determinations, ppm-Wt C	Residual Carbon, g-C	Destruction extent, %
0	0	59060	3.17	0
70	1.4	1.3	0.00073	99.97
140	2.8	0.27	0.00029	99.99

Table 4. Oxidation of Chloro-solvents by peroxydisulfate in sealed vessels.

Chloro-solvent	Extent of oxidation after 1 hour
Perchloroethylene	0.991
Trichloroethylene	0.996
methylene chloride	0.991
Chloroform	0.967
Perchloroethylene/chloroform mixtures (50%)	0.991

Table 5. Results of DCO treatment of low concentrations of PCBÕs (45 ppm Arochlor 1242) by oxidation in basic media, and by oxidation following hydrolysis pretreatment. Analysis is by EPA method 608; Analysis by Centre Analytical, Inc.; *corresponds to limit of detection. Values are in microgram/L (ppb).

Compound	Oxidation #1: Excess oxidant, 1 M NaOH 85-95°C for 1 hr Two samples		4.5 h hydrolysis, 100°C oxidation for 1 hr	48 hr hydrolysis, 100°C oxidation for 1 hr
monochlorobiphenyl	<0.65*	<0.5*	<0.5*	<0.5*
Dichlorobiphenyl	<0.65*	<0.5*	<0.5*	3.47
trichlorobiphenyl	<0.65*	<0.5*	<0.5*	2.37
tetrachlorobiphenyl	<1.3*	<1.0*	<1.0*	7.08
pentachlorobiphenyl	<1.3*	<1.0*	<1.0*	<1.0*
hexachlorobiphenyl	<1.3*	<1.0*	<1.0*	<1.0*
heptachlorobiphenyl	<1.9*	<1.5*	<1.5*	<1.5*
octachloro-biphenyl	<1.9*	<1.5*	<1.5*	<1.5*
decachlorobiphenyl	<3.2*	<2.5*	<2.5*	<2.5*

Table 6. Experimental and theoretical destruction of waste (base-hydrolyzed trichloroethane) in three-stage CSTR T = 90°C; V = 15 liters per vessel; flow = 0.10 liter/min; process model: rate = k_a [$S_2O_8^{2-}$]

Parameter	Experimental	Process Model
Concentration of waste input	0.11 M	(0.11 M)
CSTR #1 output	0.0061 M	0.00701 M
cumulative efficiency	94.45%	93.6%
CSTR #2	0.0006M	0.0005 M
cumulative efficiency	99.46%	99.59%
CSTR #3	0.0003M	0.00003 M
cumulative efficiency	99.76%	99.97%

5.

_____

(T<100 ₒC   )   DCO

,   .

,   ,   ,   ,

,   ,   ,   ,

,   ,   ,

.   ,

,   ,   (etching)

.   (Peroxydisulfate)

Ag(II)   (plutonyl

ion)   .

_____ .

90-100°C   1m^3

200 kg Carbon/day   .

(sulfate radical ion) SO^{4-}

(rate limiting step)   .

_____

DCO   peroxydisulfate

ion

.

2   .

.

6.

DCO(direct chemical oxidation:)

.

1. DCO

,   ,   ,

.

2.   ,   (scale-up)

   (scale-down)

           ,

.

3.

        . (

  (etching)

).

4. Peroxydisulfate

            sulfate

               .

5. 100°C

                        PCDD/Fs   (/   )

            .

6.   DCO

                        ,

                ,   ,   ,   ,

                    .

peroxydisulfate   (mediated chemical oxidant
couple)   Ag(I)/Ag(II), Ce(III)/Ce(IV), Co(II)/Co(III)

          .

          .

1. DCO

              .

2.   ,   ,

3.

References

1. John F. Cooper, F. Wang, J. Farmer, R. Foreman, T. Shell and K. King, "Direct Chemical Oxidation of Hazardous and Mixed Wastes" *(Proceedings. of the Third Biennial Mixed Waste Symposiu*m, American Society of Mechanical Engineers; Aug. 1995); Lawrence Livermore National Laboratory Report UCRL-JC-120141 March 28, 1995.

2. John F. Cooper, F. Wang, J. Farmer, M. Adamson, K. King and R. Krueger, "Direct Chemical Oxidation: Peroxydisulfate destruction of organic wastes," *Proceedings World Environmental Congress, International Conference and Trade Fair,* Page 219; London Ontario Sept. 17-22 1995.

3. F. Wang, J. F. Cooper, J. Farmer, M. Adamson and T. Shell, "Destruction of ion exchange resins by wet oxidation and by direct chemical oxidation--a comparison study," *Proceedings World Environmental Congress, International Conference and Trade Fair,* p. 206; London Ontario Sept. 17-22 1995.

4. John F. Cooper, Francis Wang, Roger Krueger, Ken King, Joseph C. Farmer, and Martyn Adamson, "Destruction of organic wastes by ammonium peroxydisulfate with electrolytic regeneration of the oxidant," LLNL Internal Report, September 1995. UCRL-121979 Rev 1 October 10, 1995.

5. John F. Cooper, Roger Krueger and Joseph C. Farmer, "Destruction of VX by aqueous-phase oxidation using peroxydisulfate: Direct chemical oxidation," (*Proceedings Workshop on Advances in Alternative Demilitarization Technologie*s, pp. 429-442; Reston VA September 25-7 1995; published by SAIC Aberdeen, MD)

6. John F. Cooper, Francis Wang, Roger Krueger, Ken King, Thomas Shell, Joseph C. Farmer, and Martyn Adamson, "Demonstration of omnivorous non-thermal mixed waste treatment: Direct chemical oxidation using peroxydisulfate," First Quarterly Report to Mixed Waste Focus Group, SF2-3-MW-35 October - December 1995; UCRL-ID-123193, February 1996.

7. John F. Cooper, Francis Wang Thomas Shell, and Ken King, "Destruction of 2,4,6-trinitrotoluene using ammonium peroxydisulfate," LLNL Report UCRL-ID-124585,

July 1996.

8. John F. Cooper, Francis Wang, Roger Krueger and Ken King, "Destruction of organic wastes with electrolytic regeneration of the oxidant," Proceedings Sixth International Conference on Radioactive Waste Management and Environmental Remediation, Singapore October 12-16 1997. UCRL-JC--121979 rev 2 July 1997.

9. House, D. A., Chem. Rev. 1961 62 185.

10. Minisci, F., , A.C., and Giordano, C.; Acc. Chem. Res.1983 16 27.

11. Gary Peyton, Marine Chemistry 41 91-103 (1993).

12. J. Richard Pugh, John H. Grinstead, Jr., James A. Farley, and James L. Horton Degradation of PCB's and atrazine by peroxydisulfate compounds," Proc. World Environmental Congress, International Conference and Trade Fair, London Ontario, September 17 1995

13. U. S. DOE., "Innovative Technology Summary Report: Direct Chemical Oxidation, An Alternative Oxidation Technology," September 1998.