

**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**

Polychlorodibenzo-p-dioxin  
and  
Polychlorodibenzo-furan  
Removal and Destruction

by S. Patel, M. D. Kaminski  
and L. Nuñez



Argonne National Laboratory, Argonne, Illinois 60439  
Operated by The University of Chicago  
for the United States Department of Energy under Contract W-31-109-Eng-38

**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**  
**Chemical Engineering  
Division**

Argonne National Laboratory, a U.S. Department of Energy Office of Science laboratory, is operated by The University of Chicago under contract W-31-109-Eng-38.

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor The University of Chicago, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Available electronically at <http://www.doe.gov/bridge>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from:

U.S. Department of Energy  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831-0062  
phone: (865) 576-8401  
fax: (865) 576-5728  
email: [reports@adonis.osti.gov](mailto:reports@adonis.osti.gov)

---

ANL-CMT-03/4

---

**Polychlorodibenzo-p-dioxin and Polychlorodibenzo-furan  
Removal and Destruction**

Stavan Patel and Michael D. Kaminski  
Chemical Engineering Division  
Argonne National Laboratory  
Argonne, IL 60439 USA

Luis Nuñez  
Physical Biological and Computing Sciences  
Argonne National Laboratory  
Argonne, IL 60439 USA

August 2003



## CONTENTS

	<u>Page</u>
1. INTRODUCTION.....	1
2. PHYSICAL PROPERTIES.....	2
3. LITERATURE REVIEW .....	2
3.1 Historic and Traditional Treatment Technologies.....	3
3.2 Emerging and Innovative Technologies.....	3
LITERATURE CITED.....	9
ACKNOWLEDGEMENTS.....	10

## FIGURES

1. Structures of PCDD and PCDF .....	2
--------------------------------------	---

## TABLES

1. Common Methods of Destroying Dioxin .....	2
2. Concentration of Furans and Dioxins in a Japanese Canal, Sample A.....	6
3. Concentration of Dioxins and Furans in a Japanese Canal, Sample B.....	6
4. Concentration of Dioxins and Furans in a Japanese Canal, Sample B (dioxins and furans are grouped as tetra-, penta-, hexa-, hepta-, and octa-substituted with chlorine) .....	7
5. Concentration of Contaminants in a Japanese Canal, Sample C.....	7
6. Concentration of Contaminants in a Japanese Landfill .....	7



# Polychlorodibenzo-*p*-Dioxin and Polychlorodibenzo-Furan Removal and Destruction

Stavan Patel, Michael D. Kaminski, and Luis Nuñez

## 1. INTRODUCTION

Dioxins are a group of about 200+ environmentally persistent chemicals that are formed as unwanted by-products of industrial manufacturing and burning activities. Specifically, dioxins or “dioxin-like” compounds comprise the chemical class of polychlorinated dibenzo-*p*-dioxins (PCDDs or CDDs), polychlorinated dibenzofurans (PCDFs or CDFs), polybrominated dibenzo-*p*-dioxins (PBDDs or BDDs), polybrominated dibenzofurans (PBDFs or BDFs), and polychlorinated biphenyls (PCBs). Dioxin-like refers to the similar chemical structure, physico-chemical properties, and toxic responses of these chemicals. These chemicals are hydrophobic and resist metabolism, resulting in bioaccumulation in fatty tissues of animals and humans. The major sources of dioxins include chemical and pesticide manufacturing, pulp and paper bleaching, burning of household trash, forest fires, and burning of industrial and medical waste products (Im et al. 2002).

There are 75 different dioxins, 135 different furans and 209 different polychlorinated biphenyls (PCBs). Only 7 of the 75 dioxins, 10 of the 135 furans, and 12 of the 209 PCBs have dioxin-like toxicity. These 29 different dioxins, furans, and PCBs all exhibit similar toxic effects caused by a common mechanism—binding to a particular molecule known as the aryl hydrocarbon or “Ah” receptor. The most widely studied of the dioxin or dioxin-like compounds is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), the most potent member of this family (Figure 1), which also has the greatest affinity for the Ah receptor. One key factor in toxicity is the number of chlorines in the molecule; those with three or fewer chlorines lack dioxin-like toxicity. Another key factor is where chlorines are attached. In dioxins and furans, it is critical for toxicity that chlorines be at the 2,3,7, and 8 positions. In PCBs, it is critical that the corresponding positions, which are 3, 3', 4, and 4', have chlorines. The chlorine number and position probably affect the toxicity of the molecules by changing their shapes, which in turn determines binding to the Ah receptor (Moriguchi et al. 2003).

This report provides a short summary of technologies used to destroy or separate dioxins/furans from environmental samples. It is meant as a resource for developing a technology employing magnetic particles as an engineering vehicle for large-scale, cost-effective destruction of dioxins/furans in fresh waters or sludges/soils.

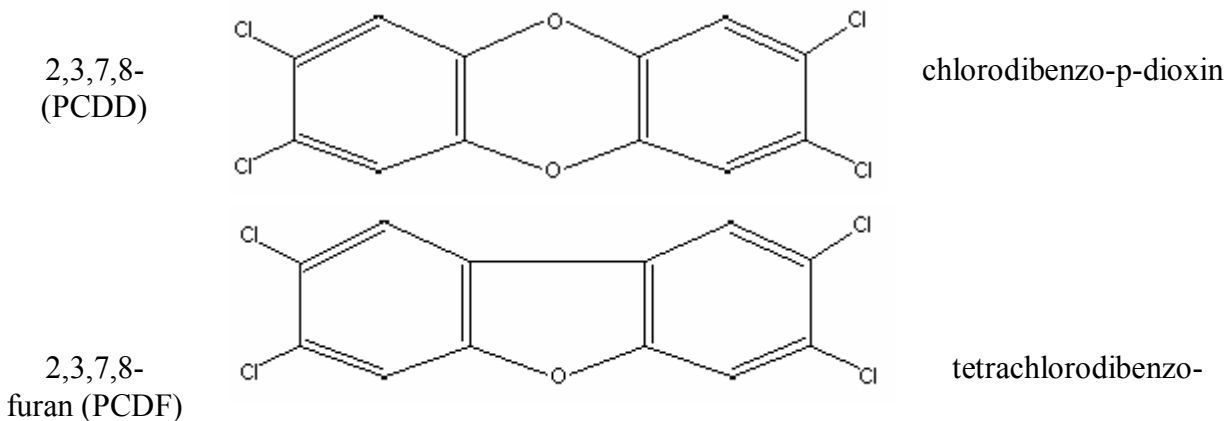


Figure 1. Structures of PCDD and PCDF

## 2. PHYSICAL PROPERTIES

A brief summary of the physical properties of dioxins is provided below (Kao 1999).

Molecular weight: 322 g/ mol. for a tetra substituted dioxin  
 460 g/mol. for an octa substituted dioxin  
 Solubility in water: 19.3 ng/L (very high solubility in organic solvents)  
 Melting point: 590 K  
 Vapor pressure at 298 K:  $7.4 \times 10^{-10}$  mm Hg  
 Partition coefficients for octanol/water:  $1.4 \times 10^6$

## 3. LITERATURE REVIEW

There are several methods of destroying dioxin (Table 1) and these are discussed in more detail in this section.

Table 1. Common Methods of Destroying Dioxin

Gas Phase	Hydroxyl radical reaction
	Direct photolysis
Particulate Phase	Wet and dry deposition
Liquid/Solid Phase	Photo degradation
	Solar decomposition (UV light)
	Photochemical degradation
	Mobile incineration (primarily for PCDD contaminated soil treatment)



### 3.1 HISTORIC AND TRADITIONAL TREATMENT TECHNOLOGIES

**Landfill Cap System and Deep Well Injection:** Most common forms of remediation technologies. Used to cover buried waste materials and to prevent contact with the environment, and to effectively manage human and ecological risks associated with a remediation site (Rahuman et al. 2000).

**High-Temperature Incineration:** High-temperature (870-1200°C) destructive method for *ex-situ* treatment of polluted soil. Soil is fed into an incinerator under high temperature and in the presence of oxygen, and contaminants are volatilized and combusted into innocuous substances. Destruction efficiencies of 99.9999% have been achieved (Rahuman et al. 2000).

**Clement Kilns:** At very high temperatures, the highly alkaline conditions in a Clement kiln are ideal for decomposing chlorinated organic waste. When operated properly, destruction of chlorinated compounds in Clement kilns can be >99.0% complete with no adverse effect on the quality of the exhaust gas (Benestad 1989).

**APEG Plus (glycolate dehalogenation):** Glycolate dehalogenation makes use of a chemical reagent called APEG. APEG consists of two parts: an alkali metal hydroxide (“A” in APEG) and polyethylene glycol (PEG). Sodium hydroxide and potassium hydroxide are the two most common alkali metals. The APEG process consists of mixing and heating the contaminated soil with the APEG reagent. During heating, the alkali metal hydroxide reacts with the halogen from the contaminant to form glycol ether and/or hydroxylated compounds and an alkali metal salt, which are water-soluble byproducts. This treatment chemically converts toxic materials to non-toxic materials (Tundo et al. 1985).

### 3.2 EMERGING AND INNOVATIVE TECHNOLOGIES

**Oxidation using Fenton’s Reagent:** PCDD is converted to a biodegradable compound using an oxidizing agent such as Fenton’s Reagent (hydrogen peroxide oxidation in the presence of ferrous ions,  $\text{Fe}^{2+}$ ) (Kao 1999).

**Dechlorination using Calcium Hydroxide:** Metal oxides are used to dechlorinate and destroy PCDD and PCDFs. Copper oxides have a stronger dechlorination effect than other metal oxides. Model fly ash containing  $\text{Ca}(\text{OH})_2$  exhibited the highest destruction potential, but a low dechlorination potential of dioxins (Webber et al. 2002).

**Hydrochlorination of Chlorinated Aromatic Environmental Pollutants to Alicyclic Compounds:** A combined Pd-Rh catalyst within a silica sol-gel matrix exhaustively detoxifies chlorinated aromatic pollutants not only by total removal of chlorine, but by the total reduction of the aromatic moieties to alicyclic rings. The reaction takes place under relative mild conditions of 80-100°C under 27 atm  $\text{H}_2$ . The immobilized catalyst is leach-proof in a variety of solvents and can be reused in several runs (Ghattas et al. 2003).

**Removal by Sorption Method using Polydimethylsiloxane Membranes:** PCDD is removed from milk without decomposition or denaturation of milk components by sorption onto hydrophobic polydimethylsiloxane (PDMS) membranes (Yoon et al. 2003).

**Decomposition using Vanadium Catalyst:** Titania-supported vanadium catalyst ( $\text{VO}_x/\text{TiO}_2$ ) showed the highest activity among all vanadium-based oxide catalyst for decomposition of chlorinated aromatic pollutants (Cho and Ihm 2002).

**Supercritical Oxidation:** Supercritical water oxidation is a high-temperature, high-pressure technology that uses the solubility properties of supercritical water in the destruction of organic compounds and toxic waste. Under supercritical conditions, with the addition of a proper oxidant (which may be either oxygen or hydrogen peroxide or a combination of both, or nitrate or any other oxidant) carbon is converted to carbon dioxide, hydrogen to water and chlorine atoms derived from chlorinated organic compounds to chloride ions (Environment Australia 1997).

**Electrochemical Oxidation:** An electrochemical cell is used to generate oxidizing species at the anode in an acid solution, normally nitric acid. These oxidizers and the acids then attack any organic compounds, converting most of them to carbon dioxide, water and inorganic ions at low temperature ( $80^\circ\text{C}$ ) and at atmospheric pressure (Rahuman et al. 2000).

**Solvated Electron Technology:** This technology neutralizes halogenated compounds by exposing them to free electrons in a solvated solution. Solvated solutions are prepared by dissolving base metals, usually sodium, but sometimes calcium or lithium into liquid anhydrous ammonia (Rahuman et al. 2000).

**Base-Catalyzed Decomposition:** Contaminated soil is dug and screened to remove debris and large particles, then crushed and mixed with sodium bicarbonate. This mixture is heated to  $200\text{-}400^\circ\text{C}$  in a rotary reactor. The heat separates the halogenated compounds from the soil by evaporation. The volatilized contaminants are captured, condensed and treated separately (National Research Council 1993). During trials in New Zealand, the solids residue was fed into the system, and this resulted in the reduction of the dioxin levels from an initial level of 1280 ppb toxic equivalent (TEQ) to a value below 0.1 ppb TEQ (Rahuman et al. 2000).

**Molten Metal Pyrolysis:** In this process, the molten metal acts as both the solvent and catalyst. Various industrial wastes are piped into a sealed bath of molten metal (typically iron) heated to  $2,400\text{-}3,000\text{ F}$ . The catalytic properties of the high-temperature metal break down the chemical compounds in the waste to their primary elements. These elements are extracted as gases, ceramics, and alloys by adding select chemicals and materials, such as oxygen and alumina. Dioxins and furans were reported as non-detectable in product gases at  $0.1\text{ ng TEQ/Nm}^3$  standard (Chanenchuk et al. 1994).

**Molten Salt Oxidation:** In this process, a bed of alkaline molten salt, usually sodium carbonate, oxidizes organic materials at a temperature of  $900\text{-}1000^\circ\text{C}$ . Any chlorine, sulfur, phosphorous, or ash products in the feed are converted to inorganic salts and retained in the salt bed. This

process cannot treat soils and other materials with a high content of inert materials (Schwinkendorf et al. 1995, National Research Council 1993).

**Plasma Arc:** In plasma arc treatment, directing an electric current through a low-pressure gas stream creates a thermal plasma field. Plasma arc fields can reach 5,000-15,000°C. The intense high-temperature zone can be used to dissociate waste into its atomic elements by injecting the waste into the plasma, or by using the plasma arch as a heat source for combustion or pyrolysis (Environment Australia 1997).

**Ultrasonic Technology:** Research at Argonne National Laboratory sought to develop an innovative ultrasonic detoxification process that could ultimately be used to detoxify contaminated soil and ground water at affected sites. Argonne was one of the first research organizations to systematically test ultrasonic technology on the detoxification of contaminated soil and ground water. Bench-scale batch and continuous flow systems were set up in the laboratory. The results of initial experiments confirmed that the ultrasonic detoxification can be used to reduce the concentrations of CCl<sub>4</sub> in water to less than 2 ppb and in soil to less than 1 ppb. A conceptual process design of an ultrasonic soil-detoxification system was completed. In addition to the destruction of organic compounds, this process is also potentially able to remove radioactive compounds from the soil matrix, and these metals can be subsequently recovered (Argonne National Laboratory 1997).

**Advanced Oxidative Process:** This process involves the use of O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub>, UV light, electrons, iron or other oxidizing compounds to degrade PCBs and volatile organic compounds. These oxidizing agents produce free radicals, which destroy organic matter (Oswego Environmental Research Center 1996).

Most of the technologies that have been developed until now deal with destruction of dioxins that are concentrated in a particular area, or with removing dioxins from soil or gas phases. It appears that not much work has been done to remove dioxins from rivers or canals in which the dioxin concentration is present in picogram-per-liter concentrations. Removing dioxins from a source such as a river is challenging because the toxin is present in such a small amount, and this particular toxin has very low solubility in water (0.2 ppb), which makes the toxin stick to the organic material at the water surface or to the bottom of the river in the sludge. Removal of such low concentrations of dioxins would require specificity in the removal technique, which would remove the dioxin from water without adding more harmful chemicals to the water stream.

Our group has received data on levels of furans and dioxins in canal streams and landfills in Japan (Tables 2-6). These data serve as a benchmark from which to evaluate specific separation/destruction technologies for low-level, large-scale contaminations.

Table 2. Concentration of Furans and Dioxins in a Japanese Canal, Sample A

Polychloro-dibenzo furan	pg/L
2,3,7,8-TeCDF	42
1,2,3,7,8-PeCDF	160
2,3,4,7,8-PeCDF	270
1,2,3,4,7,8-HxCDF	370
1,2,3,6,7,8-HxCDF	480
1,2,3,7,8,9-HxCDF	35
2,3,4,6,7-HxCDF	1500
1,2,3,4,6,7,8-HpCDF	4600
1,2,3,4,7,8,9-HpCDF	640
OCDF	6200

Polychloro-dibenzo-p-dioxin	Pg/L
2,3,7,8-TeCDD	21
1,2,3,7,8-PeCDD	59
1,2,3,4,7,8-HxCDD	73
1,2,3,6,7,8-HxCDD	140
1,2,3,8,9-HxCDD	110
1,2,3,4,6,7,8-HpCDD	1700
OCDD	27000

Table 3. Concentration of Dioxins and Furans in a Japanese Canal, Sample B

Coplanar polychlorinated biphenyl	Pg/L
3,4,4',5-TeCB #81	29
3,3',4,4'-TeCB #77	530
3,3',4,4',5-PeCB #126	120
3,3',4,4',5,5'-HxCB #169	77
2',3,4,4',5-PeCB #123	83
2,3',4,4',5-PeCB #118	5400
2,3,3',4,4-PeCB #105	2600
2,3,4,5'5-PeCB #114	130
2,3',4,4',5,5'-HxCB #167	310
2,3',4,4',5,5'-HxCB #156	910
2,3,3',4,4',5'-HxCB #157	250
2,3,3',4,4',5,5'-HpCB #189	150

Table 4. Concentration of Dioxins and Furans in a Japanese Canal, Sample B (dioxins and furans are grouped as tetra-, penta-, hexa-, hepta-, and octa-substituted with chlorine)

PCDF	pg/L	PCDD	pg/L
TeCDFs	2000	TeCDDs	200
PeCDFs	4800	PeCDDs	570
HxCDFs	6900	HxCDDs	1500
HpCDFs	7800	HpCDDs	3300
OCDF	6200	OCDD	27000
TOTAL PCDFs	27700	TOTAL PCDDs	32570

Table 5. Concentration of Contaminants in a Japanese Canal, Sample C

Contaminant	mg/L
BOD	2,000
COD	4,000
SS	5,000

Table 6. Concentration of Contaminants in a Japanese Landfill

Contaminant	Concentration	Units
Tetrachloroethylene	20	mg/L
Trichloroethane	900	mg/L
Benzene	180	ppm/L
1,2-Dichloroethane	1500	mg/L

Dioxins and furans are only toxic when they are tetra-, penta-, hexa-, hepta-, and octa-substituted with chlorine. Mono, di, and tri-chlorine substituted dioxins and furans are not toxic. So, removing one chlorine atom from a tetra-substituted dioxin/ furan will make it non-toxic. However, the potential for chlorination of the treated waters by downstream activities is unknown. For example, if waters were partially dechlorinated by a treatment system, returned to the canal stream and then diverted to a water treatment plant for drinking water supplies, the chlorination process as a bacteriostat might promote the rechlorination and formation of toxic dioxins and furans from their non-toxic forms.

## LITERATURE CITED

- Argonne National Laboratory. 1997. "Ultrasonic Soil and Groundwater Cleanup," Document No. 585-003, Argonne National Laboratory Programs and Capabilities database (<http://www.anl.gov/LabDB2/Current/Int/H585-text.003.html>).
- Ayres, D. C. 1981. "Destruction of Polychlorodibenzo-p-Dioxins," *Nature* 290(5804), 323-324.
- Benestad, C. 1989. "Incineration of Hazardous Waste in Clement Kilns," *Waste Management and Research* 7, 351.
- Chanenchuk, C., A. Protopapas, and G. Alexopoulos. 1994. "Catalytic Extraction Process Application to Chlorinated Waste Streams," presented at I&EC Special Symposium, American Chemical Society, Atlanta, Georgia, September 19-21.
- Cho, C. H., and S. K. Ihm. 2002. "Development of New Vanadium-Based Oxide Catalyst for Decomposition of Chlorinated Aromatic Pollutants," *Environmental Science and Technology* 36(7), 1600-1606.
- Environment Australia. 1997. "Appropriate Technologies for the Treatment of Scheduled Wastes," Review Report Number 4- November 1997, [www.government.gov.au](http://www.government.gov.au).
- Ghattas, A., R. Abu-Reziq, D. Avnir, and J. Blum. 2003. "Exhaustive Hydrodechlorination of Chlorinated Aromatic Environmental Pollutants to Alicyclic Compounds," *Green Chemistry* 5(1), 40-43.
- Im, S. H., K. Kannan, J. P. Giesy, M. Matsuda, and T. Wakimoto. 2002. "Concentrations and Profiles of Polychlorinated Dibenzop-Dioxins and Dibenzofurans in Soils from Korea," *Environmental Science and Technology* 36(17), 3700-3705.
- Kao J. 1999. "Treatment of Dioxin Contaminated Soils by Oxidation and Bioremediation Technologies," National Sun Yat-Sen University, Institute of Environmental Engineering, Kaohsiung, Taiwan.
- Moriguchi, T., H. Motohashi, T. Hosoya, O. Nakajima, S. Takahashi, S. Ohsako, Y. Aoki, N. Nishimura, C. Tohyama, Y. Fujii-Kuriyama, and M. Yamamoto. 2003. "Distinct Response to Dioxin in an Arylhydrocarbon Receptor (AhR) – Humanized Mouse," *Proceedings of the National Academy of Sciences* 100 (10), 5652.
- National Research Council. 1993. "Alternative Technologies for the Destruction of Chemical Agents and Munitions," National Academy Press, Washington, D.C.
- Oswego Environmental Research Center. 1996. State University of New York, Oswego, New York.

Rahaman, M. L. Pistone, F. Trifiro and S. Miertus. 2000. "Destruction Technologies for Polychlorinated Biphenyls (PCBs)," International Center for Science and High Technology, United Nations Industrial Development Organization, Pure and Applied Chemistry, Trieste, Italy.

Schwinkendorf, W., J. McFee, M. Devarakonda, L. Nenninger, F. Fadullon, T. Donaldson, and K. Dikerson. 1995. "Alternatives to Incineration: Technical Area Status Report," prepared for the Mixed Waste Integrated Program, U.S. Department of Energy, Office of Technology Development, Washington, D.C., April.

Tundo P., S. Facchetti, W. Tumiatti, and U. Fortunati. 1985. "Chemical Degradation of 2,3,7,8-TCDD by Means of Polyethyleneglycol in the Presence of a Weak Base and an Oxidant," *Chemosphere* 14 (5), 403-410.

Webber R., K. Nagiq, J. Nishino, H. Shiraishi, M. Ishida, T. Takasuga, K. Konndo, and M.Hiraoka. 2002. "Effects of Selected Metal Oxides on the Dechlorination and Destruction of PCDD and PCDF," *Chemosphere* 46 (9-10), 1247-1253.

Yoon, B. O., S. Koyanagi, T. Asano, M. Hara, and A. Higuchi. 2003. "Removal of Endocrine Disruptors by Selective Sorption Method using Polydimethylsiloxane Membranes," *Journal of Membrane Science* 213 (1-2), 137-144.

## **ACKNOWLEDGEMENTS**

This work was supported by the U. S. Department of Energy under Contract W-31-109-Eng-38.



Distribution for ANL-CMT-03/4

Internal (Printed and Electronic Copies):

Michael Kaminski (5)  
Luis Nuñez

Carol Mertz  
Stavan Patel

George Vandegrift

Internal (Electronic Copy Only):

M. R. Hale, TIS  
D. Lewis  
J. I. Sackett

External (Electronic Copies Only):

M. A. Buckley, ANL Library-E

E. Sackett, ANL Library-W

Chemical Engineering Division Review Committee Members:

H. U. Anderson, University of Missouri-Rolla, Rolla, MO

C. L. Hussey, University of Mississippi, University, MS

M. V. Koch, University of Washington, Seattle, WA

V. P. Roan, Jr., University of Florida, Gainesville, FL

J. R. Selman, Illinois Institute of Technology, Chicago, IL

J. S. Tulenko, University of Florida, Gainesville, FL