

MINIMIZATION OF TOXIC COMBUSTION BYPRODUCTS:  
REVIEW OF CURRENT ACTIVITIES

by

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## MINIMIZATION OF TOXIC COMBUSTION BYPRODUCTS: REVIEW OF CURRENT ACTIVITIES

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### ABSTRACT

In general, toxic combustion byproducts (TCBs) are the unwanted residues remaining in flue gases, combustion ashes, and wastewaters from the operation of an incineration or combustion facility. If a combustor is not well designed and operated, it may emit too high a level of TCBs. Categories of TCBs and some example constituents are as follows:

- (1) Acid gas:  $\text{HCl}$ ,  $\text{NO}_x$  and  $\text{SO}_2$ ;
- (2) Organics: Hydrocarbons such as dioxins and furans (PCDDs and PCDFs);
- (3) Particulates: Trace metals (conventional metals and radioactive metals) and soots;
- (4) Contaminants in ash; and
- (5) Contaminants in spent wastewater

Pollutants in Category (2) above are generally considered to be the products of incomplete combustion (PICs) in the field of hazardous waste incineration in the United States.

The issue of TCBs has been one of the major technical and sociological issues surrounding the implementation of incineration as a waste treatment alternative. Because of the complexity and controversy, EPA's Dr. C.C. Lee conceived of and initiated the International Congress on Toxic Combustion Byproducts (ICTCB) to provide a forum for scientists to discuss the issues of and controls for TCBs in 1989. This Paper focuses on the review of the 1989 ICTCB (the First ICTCB) activities. The 1991 (the Second) and 1993 (the Third) ICTCB activities will be reviewed at another time. The objective of these reviews is to discuss:

- (1) What have we learned from the ICTCB conferences;
- (2) What can we use from what we have learned; and
- (3) What improvement in the ICTCBs is needed.

### INTRODUCTION

The control of emissions of toxic combustion byproducts (TCBs) is "now" one of the major technical and sociological issues surrounding the implementation of incineration as a waste treatment alternative. The current RCRA regulation on "destruction and removal efficiency" has led to the unfortunate public misconception of incineration as a "landfill in the sky." As a result, the public has developed the so-called "NIMBY" (not in my back yard) attitude which makes the siting of an incineration facility extremely difficult.

National organizations have been established to campaign against incineration. Local communities often mobilize against it. It is ironic that incineration has often been selected to be the most effective technology to treat toxic waste, yet, it probably has maximum opposition from the public, compared to alternative technologies. While pollution prevention approaches have the potential to substantially reduce the quantity of hazardous waste generated, it is unlikely that it can be totally eliminated. Therefore, some hazardous waste will likely continue to be generated, as long as industry is continuously manufacturing products for human consumption. The question then becomes "Why not use one of the most effective and environmentally protective technologies (incineration) to dispose of these toxic wastes?"

One obstacle to the widespread adoption of incineration has been the issue of toxic combustion byproducts (TCBs). Categories of TCBs and some example constituents are as follows [Categories (2) and (3) contain the most critical components of concern]:

- (1) Acid gas: HCl, NO<sub>x</sub> and SO<sub>2</sub>;
- (2) Organics: Hydrocarbons such as dioxins and furans (PCDDs and PCDFs) [This Category is generally referred to as the products of incomplete combustion (PICs)];
- (3) Particulates: Trace metals (conventional metals and radioactive metals) and soots;
- (4) Contaminants in ash; and
- (5) Contaminants in spent wastewater

The authors began to write a series of TCB-related papers in 1988 to search for TCB solutions (Lee-7/88; 8/88; 4/90; 5/90; 11/90; 2/91; 4/91; 8/91). Then, EPA's Dr. C. C. Lee initiated the International Congress on Toxic Combustion Byproducts (ICTCB) in 1989 to provide a forum for scientists to discuss TCB issues.

#### THE THEME OF THE ICTCB

The theme of the First ICTCB and all those to follow was summarized in the Opening Remarks of the first ICTCB Chairman, EPA's Dr. C. C. Lee. His remarks are highlighted as follows:

- Need: To address the TCB issues. They cover the whole spectrum of issues ranging from TCB formation to controls, from regulation development to compliance and enforcement, from technology development to performance assurance, from the community right-to-know to public participation, etc.
- Scope: To encompass all waste incineration and fossil fuel combustion-related subjects. Both waste incineration and fossil fuel combustion have the same metals problems, similar chlorine-in-feed problems, etc.
- Approach: To provide a forum for all concerned parties to discuss issues and to develop answers.
- Output: To advance the understanding, development, and application of combustion/incineration and pollution control technologies for the reduction of risks from waste incineration and fossil fuel combustion operations.

## CHRONICLE OF EVENTS

- The First ICTCB was held at the University of California at Los Angeles (UCLA), August 2-4, 1989. Twenty four (24) presented papers were later selected, peer-reviewed and published in a special edition of the Combustion Science and Technology (CST) journal in Volume 74, Numbers 1-6, 1990 (CST90-pxx).
- The Second ICTCB was held at the University of Utah, Salt Lake City, Utah on March 26-29, 1991. Twenty eight (28) presented papers were later selected, peer-reviewed and published in a special edition of the Combustion Science and Technology (CST) journal in Volume 85, Numbers 1-6, 1992.
- The Third ICTCB was held at the Massachusetts Institute of Technology (MIT), Cambridge, Massachusetts on June 14-16, 1993. Similar to the First and the Second ICTCB, selected papers will be published in a special edition of the CST journal (probably in 1994).
- The Fourth ICTCB will be held at the University of California at Berkeley in the summer of 1995 (specific date will be selected in the near future). Those who wish for his/her name to be included in the future mailing list should contact EPA's Ms. Georgia Dunaway; her address is: U.S. EPA, Risk Reduction Engineering Laboratory, 26 West Martin L. King Dr. Cincinnati, Ohio 45268, telephone number 513-569-7650, fax number 513-569-7549.

## SPONSORING ORGANIZATIONS

The sponsoring organizations for the various ICTCBs are provided in Table 1.

TABLE 1. SPONSORING ORGANIZATIONS (Alphabetic Order)	ICTCB-		
	89	91	93
Coalition For Responsible Waste Incineration, Washington DC		x	x
EPA, Risk Reduction Engineering Laboratory, Cincinnati, Ohio	x	x	x
Gas Research Institute, Chicago, Illinois		x	x
Industrial Technology Research Institute, Hsin Chu, Taiwan			x
National Institute of Environmental Health Sciences, Research Triangle Park, North Carolina		x	x
National Science Foundation/Advanced Combustion Engineering Research Center, University of Utah		x	x

National Science Foundation/Engineering Research Center for Hazardous Substances Control, UCLA	x		
Northeast Hazardous Substance Research Center, Newark, NJ			x
Sandia National Laboratory, Livermore, California		x	x
Southern California Edison, Los Angeles, California		x	x

## SUMMARY OF THE FIRST CONGRESS

This Paper summarizes information presented at the 1989 ICTCB, the First International Congress. It provides the highlights of major areas/papers presented. The major areas are grouped under the following headings: (1) Overview; (2) Regulations; (3) Combustion systems; (4) Liquid combustion; (5) Solid combustion; (6) Metals emissions; (7) Organic emissions; (8) PAH and soot emissions; (9) Acid gas emissions; (10) Simulations and transport; (11) TCB control; (12) Monitoring, sampling and analysis; and (13) Risk assessment.

### Overview

J. Skinner, then Acting Deputy Assistant Administrator of EPA's Office of Research and Development, provided the Congress with a description of EPA's research and development direction. He indicated that the primary responsibility for technology innovation and development resides in the private sector. EPA's role is to stimulate and guide private sector development by identifying needs and by providing technical and logistical support where possible (ICTCB89-s1).

T. Oppelt, Director of EPA's Risk Reduction Engineering Laboratory, then provided EPA's mission. He said that EPA's mission must embody the concepts of risk prevention and reduction. These concepts involve a hierarchy of policy and technical tools that support national efforts to: (1) minimize the amounts of pollutants generated; (2) recycle or reuse pollutants; (3) control the materials or wastes that cannot be recycled or reused; and (4) minimize human and environmental exposures to any remaining wastes or pollutants. For many materials or wastes that cannot be prevented or recycled, he indicated that incineration will be the control technology of choice. He also indicated that substantial, continued research in improving the effectiveness of hazardous waste incineration, especially with regard to the importance of PICs and metals emissions, is required of EPA, academia, and industry to resolve the paradox which has arisen from the public's objection to the use of incineration technology --- in that the technology which often provides the greatest level of control (destruction) of toxic materials (incineration) often has the least amount of public support (ICTCB89-s4).

### Regulations

Environmental regulations are the driving forces for the protection of the environment. R. Holloway of EPA's Office of Solid Waste discussed his regulatory work aimed at the "Burning of Hazardous Waste in Boilers and Industrial Furnaces (BIF)" so that their emissions of TCBS can be controlled. The BIF rules were later published in the Federal Register, Vol. 56, No. 35, Thursday, February 21, 1991 and were codified in 40 CFR Parts 260, et al. In

brief, the BIF rules set standards to control the emissions of the following species from the operation of hazardous waste-burning BIFs (ICTCB89-sl):

- (1) Hydrogen chloride (HCl);
- (2) Carbon monoxide (CO) which is used as the surrogate to control PIC emissions; and
- (3) Metals including: (A) four (4) carcinogenic metals [arsenic (As); beryllium (Be); chromium (Cr); and cadmium (Cd)]; and (B) six (6) toxic metals [antimony (Sb); barium (Ba); lead (Pb); mercury (Hg); silver (Ag); and thallium (Tl)].

Almost parallel to the development of the BIF rules, the U.S. Congress passed the Clean Air Act Amendments in 1991. One of the key elements in the Amendments is the control of the 189 hazardous air pollutants (HAPs) from major sources (see Table 2 for the HAP listings). The main reason for providing this listing is to provide a reference so that if specific PICs have to be identified in the future, the HAP compounds can be used as the first step in the identification process.

### Combustion Systems

O. Smith, et al., of UCLA presented their work on the incineration of a surrogate (sulfur hexafluoride, SF<sub>6</sub>) in a low speed "dump" combustor. The paper shows that good SF<sub>6</sub> DREs, in some cases exceeding the detection limit of nearly six 9's, can be achieved (CST90-pl99).

Most presenters in this Session did not seek to have their papers submitted for CST peer-review publication. R. Seeker and C. Koshland, Editors of this CST edition (CST90-pi), summarized their (presenters) efforts as follows:

Mike Heap from the Energy and Environmental Research Corporation provided an overview of combustion systems and byproduct emissions. Robert Adrian from the California Air Resources Board presented results of extensive emissions testing from medical waste incinerators while Ed Lawless of the Midwest Research Institute provided an overview of EPA studies on hazardous waste incinerator emissions. Finally, Victor Engleman of the Science Applications International Corporation provided an overview of innovative incineration systems. Rubin of Carnegie Mellon University discussed evaluation models that allow an assessment of emissions of chemical substances.

### Liquid Combustion

J. Dalplanque, et al., of the University of California at Irvine presented the issues surrounding the numerical modeling of multicomponent droplets vaporization and combustion of hazardous liquid wastes (ICTCB89-s5).

J. Kramlich of the Energy and Environmental Research Corporation discussed bench-scale testing of a turbulent spray flame reactor. His work provided further understanding of characteristics such as spray quality, the stoichiometry impact on DRE, use of CO as an indicator of destruction efficiency, etc (CST90-pl7).

TABLE 2. HAZARDOUS AIR POLLUTANTS

CAS No. ORDER		ALPHABETIC ORDER	
50000	Formaldehyde	75070	Acetaldehyde
51285	Dinitrophenol(2,4-)	60355	Acetamide
51796	Ethyl carbamate (Urethane)	75058	Acetonitrile
53963	Acetylaminofluorene(2-)	98862	Acetophenone
56235	Carbon tetrachloride	53963	Acetylaminofluorene(2-)
56382	Parathion	107028	Acrolein
57147	Dimethyl(1,1-) hydrazine	79061	Acrylamide
57578	Propiolactone (beta-)	79107	Acrylic acid
57749	Chlordane	107131	Acrylonitrile
58899	Lindane (all isomers)	107051	Allyl chloride
59892	Nitrosomorpholine(n-)	92671	Aminobiphenyl(4-)
60117	Dimethyl aminoazobenzene	62533	Aniline
60344	Methyl hydrazine	90040	Anisidine(o-)
60355	Acetamide		Antimony compounds
62533	Aniline		Arsenic compounds (inorganic including arsine)
62737	Dichlorvos	1332214	Asbestos
62759	Nitrosodimethylamine(n-)	71432	Benzene (including benzene from gasoline)
63252	Carbaryl	92875	Benzidine
64675	Diethyl sulfate	98077	Benzotrichloride
67561	Methanol	100447	Benzyl chloride
67663	Chloroform		Beryllium compounds
67721	Hexachloroethane	92524	Biphenyl
68122	Dimethyl formamide	117817	Bis(2-ethylhexyl)phthalate (DEHP)
71432	Benzene (including benzene from gasoline)	542881	Bis(chloromethyl)ether
71556	Methyl chloroform (1,1,1-Trichloroethane)	75252	Bromoform
72435	Methoxychlor	106990	Butadiene(1,3-)
74839	Methyl bromide (Bromomethane)		Cadmium compounds
74873	Methyl chloride (Chloromethane)	156627	Calcium cyanamide
74884	Methyl iodide (Iodomethane)	105602	Caprolactam
75003	Ethyl chloride (Chloroethane)	133062	Captan
75014	Vinyl chloride	63252	Carbaryl

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CAS No. ORDER		ALPHABETIC ORDER	
75058	Acetonitrile	75150	Carbon disulfide
75070	Acetaldehyde	56235	Carbon tetrachloride
75092	Methylene chloride (Dichloromethane)	463581	Carbonyl sulfide
75150	Carbon disulfide	120809	Catechol
75218	Ethylene oxide	133904	Chloramben
75252	Bromoform	57749	Chlordane
75343	Ethylidene dichloride (1,1-Dichloroethane)	7782505	Chlorine
75354	Vinylidene chloride (1,1-Dichloroethylene)	79118	Chloroacetic acid
75445	Phosgene	532274	Chloroacetophenone(2-)
75558	Propylenimine(1,2-) (2-Methyl aziridine)	108907	Chlorobenzene
75569	Propylene oxide	510156	Chlorobenzilate
76448	Heptachlor	67663	Chloroform
77474	Hexachlorocyclopentadiene	107302	Chloromethyl methyl ether
77781	Dimethyl sulfate	126998	Chloroprene
78591	Isophorone		Chromium compounds
78875	Propylene dichloride (1,2-Dichloropropane)		Cobalt compounds
78933	Methyl ethyl ketone (2-Butanone)		Coke oven emissions
79005	Trichloroethane(1,1,2-)	108394	Cresol(m-)
79016	Trichloroethylene	95487	Cresol(o-)
79061	Acrylamide	106445	Cresol(p-)
79107	Acrylic acid	1319773	Cresols/Cresylic acid (isomers and mixture)
79118	Chloroacetic acid	98828	Cumene
79345	Tetrachloroethane(1,1,2,2-)		Cyanide compounds
79447	Dimethyl carbamoyl chloride	94757	D(2,4-), salts and esters
79469	Nitropropane(2-)	3547044	DDE
80626	Methyl methacrylate	334883	Diazomethane
82688	Pentachloronitrobenzene (Quintobenzene)	132649	Dibenzofurans
84742	Dibutylphthalate	96128	Dibromo(1,2-)-3-chloropropane
85449	Phthalic anhydride	84742	Dibutylphthalate
87683	Hexachlorobutadiene	106467	Dichlorobenzene(1,4-)(p)



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CAS No. ORDER		ALPHABETIC ORDER	
87865	Pentachlorophenol	91941	Dichlorobenzidene(3,3-)
88062	Trichlorophenol(2,4,6-)	111444	Dichloroethyl ether (Bis(2-chloroethyl)ether)
90040	Anisidine(o-)	542756	Dichloropropene(1,3-)
91203	Naphthalene	62737	Dichlorvos
91225	Quinoline	111422	Diethanolamine
91941	Dichlorobenzidene(3,3-)	64675	Diethyl sulfate
92524	Biphenyl	121697	Diethyl(n,n-) aniline (n,n-Dimethylaniline)
92671	Aminobiphenyl(4-)	119904	Dimethoxybenzidine(3,3-)
92875	Benzidine	60117	Dimethyl aminoazobenzene
92933	Nitrobiphenyl(4-)	79447	Dimethyl carbamoyl chloride
94757	D(2,4-), salts and esters	68122	Dimethyl formamide
95476	Xylenes(o-)	131113	Dimethyl phthalate
95487	Cresol(o-)	77781	Dimethyl sulfate
95534	Toluidine(o-)	57147	Dimethyl(1,1-) hydrazine
95807	Toluene(2,4-) diamine	119937	Dimethyl(3,3'-) benzidine
95954	Trichlorophenol(2,4,5-)	534521	Dinitro(4,6-)-o-cresol, and salts
96093	Styrene oxide	51285	Dinitrophenol(2,4-)
96128	Dibromo(1,2-)-3-chloropropane	121142	Dinitrotoluene(2,4-)
96457	Ethylene thiourea	123911	Dioxane(1,4-) (1,4-Diethyleneoxide)
98077	Benzotrichloride	122667	Diphenylhydrazine(1,2-)
98828	Cumene	106898	Epichlorohydrin (1-chloro-2,3-epoxypropane)
98862	Acetophenone	106887	Epoxybutane(1,2-)
98953	Nitrobenzene	140885	Ethyl acrylate
100027	Nitrophenol(4-)	100414	Ethyl benzene
100414	Ethyl benzene	51796	Ethyl carbamate (Urethane)
100425	Styrene	75003	Ethyl chloride (Chloroethane)
100447	Benzyl chloride	106934	Ethylene dibromide (Dibromoethane)
101144	Methylene(4,4-) bis(2-chloroaniline)	107062	Ethylene dichloride (1,2-Dichloroethane)
101688	Methylene diphenyl diisocyanate (MDI)	107211	Ethylene glycol
101779	Methylenedianiline(4,4'-)	151564	Ethylene imine (Aziridine)

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CAS No. ORDER		ALPHABETIC ORDER	
105602	Caprolactam	75218	Ethylene oxide
106423	Xylenes(p-)	96457	Ethylene thiourea
106445	Cresol(p-)	75343	Ethylidene dichloride (1,1-Dichloroethane)
106467	Dichlorobenzene(1,4-)(p)		Fine mineral fibers
106503	Phenylenediamine(p-)	50000	Formaldehyde
106514	Quinone		Glycol ethers
106887	Epoxybutane(1,2-)	76448	Heptachlor
106898	Epichlorohydrin (1-chloro-2,3-epoxypropane)	118741	Hexachlorobenzene
106934	Ethylene dibromide (Dibromoethane)	87683	Hexachlorobutadiene
106990	Butadiene(1,3-)	77474	Hexachlorocyclopentadiene
107028	Acrolein	67721	Hexachloroethane
107051	Allyl chloride	822060	Hexamethylene-1,6-diisocyanate
107062	Ethylene dichloride (1,2-Dichloroethane)	680319	Hexamethylphosphoramide
107131	Acrylonitrile	110543	Hexane
107211	Ethylene glycol	302012	Hydrazine
107302	Chloromethyl methyl ether	7647010	Hydrochloric acid
108054	Vinyl acetate	7664393	Hydrogen fluoride (Hydrofluoric acid)
108101	Methyl isobutyl ketone (Hexone)	7783064	Hydrogen sulfide
108316	Maleic anhydride	123319	Hydroquinone
108383	Xylenes(m-)	78591	Isophorone
108394	Cresol(m-)		Lead compounds
108883	Toluene	58899	Lindane (all isomers)
108907	Chlorobenzene	108316	Maleic anhydride
108952	Phenol		Manganese compounds
110543	Hexane		Mercury compounds
111422	Diethanolamine	67561	Methanol
111444	Dichloroethyl ether (Bis(2-chloroethyl)ether)	72435	Methoxychlor
114261	Propoxur (Baygon)	74839	Methyl bromide (Bromomethane)
117817	Bis(2-ethylhexyl)phthalate (DEHP)	74873	Methyl chloride (Chloromethane)
118741	Hexachlorobenzene	71556	Methyl chloroform (1,1,1-Trichloroethane)

TABLE 2. HAZARDOUS AIR POLLUTANTS

CAS No. ORDER		ALPHABETIC ORDER	
119904	Dimethoxybenzidine(3,3-)	78933	Methyl ethyl ketone (2-Butanone)
119937	Dimethyl(3,3'-) benzidine	60344	Methyl hydrazine
120809	Catechol	74884	Methyl iodide (Iodomethane)
120821	Trichlorobenzene(1,2,4-)	108101	Methyl isobutyl ketone (Hexone)
121142	Dinitrotoluene(2,4-)	624839	Methyl isocyanate
121448	Triethylamine	80626	Methyl methacrylate
121697	Diethyl(n,n-) aniline (n,n-Dimethylaniline)	1634044	Methyl tert butyl ether
122667	Diphenylhydrazine(1,2-)	75092	Methylene chloride (Dichloromethane)
123319	Hydroquinone	101688	Methylene diphenyl diisocyanate (MDI)
123386	Propionaldehyde	101144	Methylene(4,4-) bis(2-chloroaniline)
123911	Dioxane(1,4-) (1,4-Diethyleneoxide)	101779	Methylenedianiline(4,4'-)
126998	Chloroprene	91203	Naphthalene
127184	Tetrachloroethylene (Perchloroethylene)		Nickel compounds
131113	Dimethyl phthalate	98953	Nitrobenzene
132649	Dibenzofurans	92933	Nitrobiphenyl(4-)
133062	Captan	100027	Nitrophenol(4-)
133904	Chloramben	79469	Nitropropane(2-)
140885	Ethyl acrylate	684935	Nitroso(n-)-n-methylurea
151564	Ethylene imine (Aziridine)	62759	Nitrosodimethylamine(n-)
156627	Calcium cyanamide	59892	Nitrosomorpholine(n-)
302012	Hydrazine	56382	Parathion
334883	Diazomethane	82688	Pentachloronitrobenzene (Quintobenzene)
463581	Carbonyl sulfide	87865	Pentachlorophenol
510156	Chlorobenzilate	108952	Phenol
532274	Chloroacetophenone(2-)	106503	Phenylenediamine(p-)
534521	Dinitro(4,6-)-o-cresol, and salts	75445	Phosgene
540841	Trimethylpentane(2,2,4-)	7803512	Phosphine
542756	Dichloropropene(1,3-)	7723140	Phosphorus
542881	Bis(chloromethyl)ether	85449	Phthalic anhydride

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CAS No. ORDER		ALPHABETIC ORDER	
584849	Toluene(2,4-) diisocyanate	1336363	Polychlorinated biphenyls (Aroclors)
593602	Vinyl bromide		Polycyclic organic matter
624839	Methyl isocyanate	1120714	Propane(1,3-) sultone
680319	Hexamethylphosphoramide	57578	Propiolactone (beta-)
684935	Nitroso(n-)-n-methylurea	123386	Propionaldehyde
822060	Hexamethylene-1,6-diisocyanate	114261	Propoxur (Baygon)
1120714	Propane(1,3-) sultone	78875	Propylene dichloride (1,2-Dichloropropane)
1319773	Cresols/Cresylic acid (isomers and mixture)	75569	Propylene oxide
1330207	Xylenes (isomers and mixture)	75558	Propylenimine(1,2-) (2-Methyl aziridine)
1332214	Asbestos	91225	Quinoline
1336363	Polychlorinated biphenyls (Aroclors)	106514	Quinone
1582098	Trifluralin		Radionuclides (including radon)
1634044	Methyl tert butyl ether		Selenium compounds
1746016	Tetrachlorodibenzo(2,3,7,8-)-p-dioxin	100425	Styrene
3547044	DDE	96093	Styrene oxide
7550450	Titanium tetrachloride	1746016	Tetrachlorodibenzo(2,3,7,8-)-p-dioxin
7647010	Hydrochloric acid	79345	Tetrachloroethane(1,1,2,2-)
7664393	Hydrogen fluoride (Hydrofluoric acid)	127184	Tetrachloroethylene (Perchloroethylene)
7723140	Phosphorus	7550450	Titanium tetrachloride
7782505	Chlorine	108883	Toluene
7783064	Hydrogen sulfide	95807	Toluene(2,4-) diamine
7803512	Phosphine	584849	Toluene(2,4-) diisocyanate
8001352	Toxaphene (chlorinated camphene)	95534	Toluidine(o-)
	Antimony compounds	8001352	Toxaphene (chlorinated camphene)
	Arsenic compounds (inorganic including arsine)	120821	Trichlorobenzene(1,2,4-
	Beryllium compounds	79005	Trichloroethane(1,1,2-)
	Cadmium compounds	79016	Trichloroethylene
	Chromium compounds	95954	Trichlorophenol(2,4,5-)

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CAS No. ORDER		ALPHABETIC ORDER	
	Cobalt compounds	88062	Trichlorophenol(2,4,6-)
	Coke oven emissions	121448	Triethylamine
	Cyanide compounds	1582098	Trifluralin
	Fine mineral fibers	540841	Trimethylpentane(2,2,4-)
	Glycol ethers	108054	Vinyl acetate
	Lead compounds	593602	Vinyl bromide
	Manganese compounds	75014	Vinyl chloride
	Mercury compounds	75354	Vinylidene chloride (1,1-Dichloroethylene)
	Nickel compounds	1330207	Xylenes (isomers and mixture)
	Polycyclic organic matter	108383	Xylenes(m-)
	Radionuclides (including radon)	95476	Xylenes(o-)
	Selenium compounds	106423	Xylenes(p-)

C. Law of the Princeton University presented an overview of liquid incineration phenomena and summarized important parameters which impact the performance of liquid-injection incinerators. The parameters discussed were: droplets (20-2000 microns), sprays, and the blending of wastes with different physical and chemical properties (CST90-p1).

V. McDonell of the University of California at Irvine described the application of laser interferometry (optical scattering techniques) to the study of droplet/gas-phase interaction and behavior in liquid spray combustion systems. Three applications were presented: (1) the effect of swirl on the dispersion of droplets; (2) an assessment of spray symmetry; and (3) measurements in a reacting environment (CST90-p343).

#### Solids Combustion

G. Darivakis, et al., of MIT presented the pyrolysis and combustion behavior of polyethylene (PE) and polystyrene (PS). In the first stage of solids combustion, thermal decomposition transforms the starting material into two products that fuel oxidation: a solid (char) and volatiles. The latter have sufficient mobility and/or vapor pressure to separate from the decomposing substrate. The detailed dynamics of this separation process (devolatilization) determine the release rates, yields, compositions and heating values of volatiles, and thus impact ignition, flame duration, heterogeneous versus homogeneous combustion intensity, and emissions loadings, compositions, and toxicity. This paper quantified basic features of PE and PS devolatilization including the yields of total volatiles (total weight loss) and of condensibles (tars + higher molecular weight volatilizable material that solidifies at room temperature). Measurements were performed at temperatures and heating rates pertinent to solid waste incineration and to fires (CST90-p267).

P. Lemieux, et al., of EPA discussed the effect of oxygen augmentation on transient behavior in a rotary kiln. The study showed that physical processes controlling the release of waste from the sorbent material are greatly affected by the rotation speed of the kiln and the kiln temperature (CST90-p311).

T. Lester, et al., of the Louisiana State University described the repeatability of the transients resulting from the one-pack insertion of toluene/sorbent on the next insertion. Their study objective was to provide, for the first time, detailed information on the physical and chemical environments inside the high temperature zones of an operating industrial incinerator (CST90-p67).

J. Lighty, et al., of the University of Utah presented a study of transport processes in a rotary kiln during the desorption of organic and metallic contaminants from solids. As expected, lighter components desorb faster than the heavier hydrocarbons (CST90-p31).

#### Metals Emissions

R. Barton, et al., of the Energy and Environmental Research Corporation presented their computer model which can reportedly co-relate the trace metal emission mechanisms of waste combustors. The mechanisms include particle

entrainment, chemical speciation, chemical integrations, vaporization, condensation, particle coagulation and particle collection by flue gas cleaning equipment. The objective of the study was to assess the ability of waste combustion devices to control the emission of toxic metals (CST90-p327).

R. Flagan, et al., of the California Institute of Technology discussed the nature of pyrogenous fumes (fumes formed due to heat). The paper indicated that fume particles produced from vapors in high temperature systems are remarkably similar in structure, regardless of their composition or the details of the system in which they were formed (ICTCB89-s9).

S. Friedlander, et al., of UCLA discussed the needs for better understanding of aerosol formation, the chemistry of organic emissions, the processing of solid and liquid incinerator feeds, the modelling and control of combustion systems, gas mixing and turbulence and novel and advanced systems (ICTCB89-s4). He and his coworkers also presented their work on the control of fine aerosols in incineration processes (ICTCB89-s9).

N. Gallagher, et al., of the University of Arizona presented their work on the alkali metal (sodium and potassium) partitioning from pulverized coal combustion in a down-fired coal combustor. In all cases, sodium was enriched in the small particle size range, and was shown to form both a sodium-rich fume and an enriched surface layer around existing particles. (CST90-p211).

R. Quann, et al., of MIT presented their studies on the submicron particle formation as a function of coal types in a laboratory combustion furnace. When pulverized coal is burned, particles ranging in size from about 100 microns down into the submicron size may form and are composed primarily of oxides (and sulfates) of Si, Al, Fe, Ca, Mg, K and Na. The submicron particles, which may only comprise about 1 % of the total particle mass, are of the greatest concern, because they are of respirable size, are surface-enriched in toxic trace metals and are the least effectively captured by conventional electrostatic precipitators (CST90-p245).

### Organic Emissions

R. Barat, et al., of MIT and J. Bozzelli of the New Jersey Institute of Technology (NJIT) presented their work in which they used a turbulent, jet-stirred, toroidal combustor to study the inhibition of hydrocarbon oxidation by chlorine. This work provided an understanding of how this inhibition leads to flame instability and to PIC formation. The paper concluded that in the presence of chlorine, blowout of the flame occurs sooner (i.e., at a lower mass rate) after the onset of instabilities than in a comparable combustion environment without chlorine. The primary cause of this enhanced instability was an inhibition of CO burnout due to the consumption of OH radicals by product HCl. In addition, chain-terminating consumption of HO<sub>2</sub> radicals by Cl further inhibited CO burnout since HO<sub>2</sub> was a major source of OH in their testing system (CST90-p361).

H. Hagenmaier of the University of Tübingen in Germany presented the mechanisms of formation and decomposition of polychlorinated dibenzo-dioxin (PCDD) and -furan (PCDF) in incineration processes. The mechanisms include: (1) PCDD/PCDF are already present in the waste and are incompletely destroyed or transformed during combustion; (2) PCDD/PCDF are formed from structurally-

related compounds such as PCBs, chlorobenzenes, etc.; and (3) PCDD/PCDF are formed by de novo syntheses. This means that they are formed either from organochlorine compounds structurally not related to PCDD/PCDF such as polyvinyl chloride (PVC) or by incomplete combustion of organic matter in the presence of a chlorine source such as metal chlorides (ICTCB89-s8).

E. Ritter, et al., of NJIT discussed their work on the thermal reactions of chloro- and dichlorobenzene in  $H_2$  and chlorobenzene in  $H_2/O_2$  mixtures in a tubular flow reactor between 835 and 1275°K. The study successfully illustrated the elementary reaction pathways leading to the formation of polychlorinated dibenzofurans (PCDFs) and dibenzodioxins (PCDDs) by adding oxygen atoms to a chlorinated biphenyl and a chlorinated dibenzofuran respectively (CST90-pl17).

D. Tirey, et al., of the University of Dayton Research Institute (UDRI) introduced their work on the thermal degradation of tetrachloroethylene ( $C_2Cl_4$ ) and ethylene ( $C_2H_4$ ) using a high-temperature flow reactor system. The study showed that  $C_2Cl_4$  has a propensity for formation of higher molecular weight aromatic species that is similar to that of its non-chlorinated analogue,  $C_2H_4$ . Acetylene ( $C_2H_2$ ) is the major product from  $C_2H_4$  degradation while hexachlorobenzene ( $C_6Cl_6$ ) is the major product from  $C_2Cl_4$  decomposition (CST90-pl37).

W. Tsang of the National Institute of Standards and Technology introduced a single-step reaction rate constant to aid in the understanding of the formation and destruction of chlorinated organic compounds. However, he warned that rechlorination is possible in the post-combustion region, when the surface temperature is low (CST90-p99).

R. Van Dell of the Dow Chemical Company presented a simplified computer flame model to predict the formation and destruction of soots and PICs in a laboratory thermal oxidizer (LTOX). Although the simple model adequately predicted flame temperature, diffusion velocity, soot yields and soot concentrations, the author indicated that refinement of the model was needed (CST90-p379).

#### PAH and Soot Emissions

R. Barbella, et al., of the University of Naples in Italy presented the optical and chemical characterization of carbon polymorphs formed during the spray combustion of hydrocarbons. Carbon polymorphs are a large variety of carbon structures resulting from the spray combustion of mixed saturated, unsaturated and aromatic hydrocarbons. The carbon polymorphs (which contain a larger number of carbon atoms than those contained in the original fuel) could represent toxic air pollutants since they include compounds such as substituted and unsubstituted polycyclic aromatic compounds (PACs) and larger aggregates of carbon atoms such as tar and soot (CST90-p159).

M. Frenklach of Pennsylvania State University presented his study on the formation of polycyclic aromatic hydrocarbons (PAHs) in chlorine-containing environments. PAHs are the precursors of soot and have been identified as carcinogenic and mutagenic. His study which showed that the presence of chlorine in hydrocarbon systems strongly promotes the formation of PAHs has concluded that: (1) the enhanced, chlorine-catalyzed degradation of POHC



molecules promotes the formation of aromatic ring compounds; and (2) the large concentration of Cl atoms accelerates the abstraction of aromatic H from stable PAH molecules, and activates them for further growth (CST90-p283).

J. McKinnon, et al., of MIT presented the soot formation mechanisms and the effects of chlorine. Chlorine is a known inhibitor of combustion and promoter of soot formation. The paper concluded that soot formation involves the growth of high molecular weight PAHs, the reactive coagulation of these heavy molecules, and mass addition from PAH and acetylene. These processes are opposed by oxidative and pyrolytic degradation, thus resulting in a competition which determines whether and to what extent any soot emission occurs (CST90-p175).

J. Mitchell, et al., of the University of Western Ontario presented the results of using additives to control soot formation. Additives can either enhance soot oxidation or inhibit soot agglomeration so that the soot particles remain small and thus are easily oxidized (CST90-p63).

### Acid Gas Emissions

M. Ravichandran, et al., of Cornell University discussed the chemical kinetic constraints placed on  $\text{NO}_x$  reduction by ammonia injection in both a perfectly stirred reactor and a plug flow reactor. The results indicated that  $\text{NO}_x$  reduction by ammonia injection in the case of incinerators would require more stringent process control and is likely to require higher amounts of  $\text{NH}_3$  and  $\text{H}_2$  to achieve  $\text{NO}_x$  reduction efficiencies comparable to what has been achieved in the case of utility boiler furnaces. One of reasons for this is that waste incinerators use more excess air than that of utility boilers (ICTCB89-s10).

### Simulations and Transport

G. Silcox, et al., of the University of Utah presented their study on the mathematical and physical modeling of rotary kilns with applications to scaling and design. The model study examined heat and mass transfer in an indirectly-fired rotary kiln, and mixing times in a slumping kiln bed. The design and operating study examined kiln length, solids residence time, solids feed rate, and feed moisture content. The effects of moisture were particularly important to both heat and mass transfer (ICTCB89-s10).

P. Smith, et al., of Brigham Young University presented their application of computational combustion simulations to full-scale pulverized-coal industrial furnaces and utility boilers. Heterogeneous and turbulent heat transfer aspects strongly influence the formation and decay of byproducts in practical coal combustion systems because many of the sub-processes resulting in combustion byproducts are highly temperature-sensitive and because the purpose of most furnaces is to extract energy from the flame (ICTCB89-s10).

### TCB Control

T. Brna of the U.S. EPA presented an overview of TCB control options which included: (1) in-furnace methods; and (2) post-combustion methods (CST90-p83).

M. Ho, of Union Carbide Industrial Gases, Inc. presented the method of oxygen enrichment to control the transient emissions from a rotary kiln; the method described was an in-furnace method (ICTCB89-s7).

J. Kilgroe, et al., of the U.S. EPA described the use of combustion control for limiting organic emissions (mainly chlorinated dibenzo-p-dioxins and -furans) from municipal waste combustors. The paper defined the concept of "good combustion practices (GCP)" as the set of conditions that minimize the emission of organic compounds. GCPs at that time included: (1) uniformity of waste feed; (2) adequate combustion temperature; (3) amount and distribution of combustion air; (4) mixing; (5) minimization of particulate matter carryover; (6) control of downstream temperature; and (7) combustion monitoring and control (CST90-p223).

R. Wood, et al., of the ASME Research Committee on Industrial and Municipal Waste presented methods to minimize combustion excursions from rotary kiln incinerators. The paper found that an operating kiln produces no significant combustion excursions from batch feeds when the minimum oxygen level at the outlet of the combustor is above 1% (ICTCB89-s7).

#### Monitoring, Sampling and Analysis

W. McClennen, et al., of the University of Utah presented a system for the on-line analysis of organic vapors by short-column (1 meter) gas chromatography/mass spectrometry (GC/MS) to monitor products from a thermal soil desorption reactor. The broad range of boiling points and polarities of the organic compounds in wastes mandates the use of sophisticated instrumentation for monitoring their production, evolution, and destruction. The short-column GC/MS can accurately measure the transient concentrations (30-60 second intervals) of a broad range of aromatic compounds. It can separate the organic vapors away from the major ambient atmospheric constituents and also provide some separation of isomers otherwise indistinguishable by MS. The mass spectrometer provides a rapid and sensitive method of compound identification (CST90-p297).

#### Risk Assessment

In the past, EPA's incineration standards such as the Destruction and Removal Efficiency (DRE), HCl and particulate requirements have been technology-based standards. The BIF rule incorporates risk assessment calculations into the requirements of the standard.

A. Smith, et al., of The University of California at Berkeley discussed the health risk assessment of incinerator air emissions incorporating background ambient air data. The emissions data used were supplied by Ogden Martin Systems, Inc. and were derived from stack sampling at a municipal waste incinerator located at West Babylon on Long Island, New York. Key compounds used for the risk assessment were PCDDs, PCDFs, lead and mercury. Human exposure was estimated for a lifetime average exposure of a hypothetical person living for 70 years, 24 hours per day, at the point of maximum annual average ground level concentration of emissions. The study concluded that the cancer risks attributable to air pollution emissions from a municipal waste incineration facility with modern air pollution equipment are below 1 in 100,000. (CST90-p51).

## WHAT HAVE WE LEARNED FROM THE ICTCB?

"A lot" is probably the most simple way to describe what we have learned from the information presented at the First ICTCB. The thirteen areas identified in the above-mentioned groups/summary are but a sampling. Each area has so much more information to offer. Using the area of metals emissions as an example, metals speciation research requires specialized knowledge to fully understand the mechanisms that influence which metals species goes to which effluent stream when metals are in the incineration/combustion environments.

## WHAT CAN WE USE FROM WHAT WE HAVE LEARNED?

The technical community has been searching for answers to the following questions:

- (1) Are significant TCBs actually being emitted from waste incinerators from an environmental risk standpoint and how much, quantitatively and qualitatively?
- (2) Why is the issue of TCBs still the focus of the public's concern, after so many years of research and after so many risk assessments have shown TCBs to be relatively benign (as long as appropriate pollution controls are incorporated into the incinerator design)?
- (3) Do other treatment technologies emit any unwanted reaction by-products (RBPs) and how much?
- (4) Is there any comparison between TCBs and RBPs? which are more harmful to human health and the environment?
- (5) Can scientists provide any data to relieve the public's fears or to overcome their "NIMBY" attitude?

Perhaps the ICTCBs may be able to provide answers to the above questions.

## WHAT IMPROVEMENT IS NEEDED?

Based upon the research topics/areas reviewed herein, the authors believe that the ICTCBs of the future need to emphasize such additional topics as:

- Performance assurance (to assure that a permitted system will perform to the degree required);
- Ash quality and its reuse or its ultimate disposal;
- The ultimate disposal of spent wastewaters from any air pollution control operations associated with incineration/combustion;
- Fugitive emissions;
- The public's involvement; and
- Health effects from environmental contaminations (this subject was included in the Second and Third ICTBPs).

The authors anxiously await the Fourth Congress --- see you at Cal-Berkeley!

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16. ABSTRACT In general, toxic combustion byproducts (TCBs) are the unwanted residues remaining in flue gases, combustion ashes, and wastewaters from the operation of an incineration or combustion facility. If a combustor is not well designed and operated, it may emit too high a level of TCBs.  The issue of TCBs has been one of the major technical and sociological issues surrounding the implementation of incineration as a waste treatment alternative. Because of the complexity and controversy, EPA's Dr. C.C. Lee in 1989 conceived of and initiated the International Congress on Toxic Combustion Byproducts (ICTCB) to provide a forum for scientists to discuss the issues of and controls for TCBs.  This Paper focuses on the review of the 1989 ICTCB (the First ICTCB) activities. The 1991 (the Second) and 1993 (the Third) ICTCB activities will be reviewed at another time. The objective of these reviews is to discuss: (1) What have we learned from the ICTCB conferences; (2) What can we use from what we have learned; and (3) What improvement in the ICTCBs is needed.		
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