



Project Summary

Minimization and Control of Hazardous Combustion Byproducts

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Control of emissions of toxic organometallic compounds is one of the major technical and sociological issues surrounding the further implementation of incineration as a waste disposal alternative. A comprehensive review of the status of research concerning the emission of organic products of incomplete combustion (PICs) indicated that available full-scale data were insufficient in volume and quality to make firm conclusions. As enumerated below, several trends were identified that appeared to concur with scientific theory, and several deficiencies in fundamental knowledge and completeness of full-scale emissions data were observed.

PIC emissions are a natural consequence of the kinetically-limited thermal degradation of hazardous wastes. Comparison of PIC formation/destruction rates based on theory and nominal incineration conditions indicate that PIC emissions are always several orders of magnitude higher than predicted. This suggests that temporal or spatial excursions from these nominal conditions are occurring that are responsible for PIC emissions. Low temperatures due to quenching, residence time short circuits due to nonplug flow and/or unswept recesses, and locally high waste/oxygen concentration ratios due to poor microscale mixing or overloading are implicated as failure modes. Relative emission rates are controlled by failure conditions that

arise in post-flame regimes of full-scale systems.

Consideration of waste feed composition and the reported emissions suggested that a significant fraction of PICs that may have been emitted from full-scale facilities were not analyzed. Analysis of PIC emissions data from 17 full-scale facilities further suggested that the magnitude of PIC emissions correlated with the completeness of the sampling and analysis procedures.

A comprehensive rank-order statistical analysis of full-scale emissions data indicated that of the design and operational parameters evaluated, stack oxygen concentration and waste heat load exhibited the strongest correlation with various measures of PIC emissions. Regulatory surrogates for PIC emissions (CO and TUHC) and stack benzene and toluene concentrations exhibited only occasional correlation with various measures of PIC emissions.

Analysis of specifically identified emissions indicated that simple halogenated methanes, halogenated ethanes, halogenated ethenes, and nonhalogenated aromatic species were the most frequently observed and highest yield PICs. The high yields of the relatively fragile halogenated methanes and ethanes inferred that many of these PICs were formed downstream of the high-temperature zones of full-scale systems via radical-association reactions.



In conclusion, a series of design, operational, and regulatory implications for PIC control were presented. From the laboratory perspective, the urgent need for detailed studies of PIC characterization, yields, and emission mechanisms at elevated temperatures was emphasized. The benefits of interactions between laboratory-scale PIC studies, PIC toxicological studies, and sampling and analysis methods development for full-scale systems were also discussed.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Of all the issues surrounding waste disposal, the potential formation and emission of PICs from the thermal disposal of wastes is the most controversial. Much of the controversy is due to the lack of knowledge of PICs, the current regulation only addresses destruction and removal efficiency of principal organic hazardous constituents (POHCs) contained in the waste stream. This has led to the unfortunate public misconception of incineration as a "landfill in the sky".

It would seem that this important subject and controversy that has raged all through the 80's would be well researched and significant strides made towards answering key issues. However, we in reality know very little about PIC emissions. The purpose of this project was to define what we really know about PICs, what we think we know, and what we don't know. The reader is referred to the final report for a comprehensive analysis of theories of PIC formation and a thorough statistical analysis of pilot- and full-scale PIC emissions data. The project culminates with numerous implications for PIC emissions control.

Although every effort has been made to approach this subject scientifically and arrive at logical, factually-based conclusions, there will undoubtedly continue to arise nonfactual or even clearly incorrect statements concerning PICs. It is hoped that this report will at least serve to establish a framework for rational discussion of the issues surrounding PICs.

Theories of PIC Formation

There are only a few issues for which we have sufficient data that agree with scientific theory that will allow us to advance several theories about PICs. These theories are discussed below.

Theory 0—PICs are a Natural Consequence of Thermal Degradation of Toxic Wastes

This theory is so fundamental and obvious that it is designated as the Zeroth Theory of PIC Formation. From a scientific point of view, any product of the oxidative or pyrolytic degradation of a compound, other than the thermodynamically most stable end-products, should be included in the definition of a PIC. If we want to designate PICs of environmental concern where toxicity and concentration are factors, then we can define a new term: toxic, principal, product of incomplete combustion (ToP-PIC). The question is not whether PICs are emitted from hazardous waste incinerators, because they will undoubtedly be formed and emitted from any combustion source. The true issue is whether they are of environmental consequence, which is a very complex issue.

Theory 1—PIC Emission Rates are Kinetically, Not Thermodynamically, Controlled

If an incinerator achieves thermodynamic equilibrium, then one only needs to know the elemental composition of the waste/fuel/oxidizer (air) feed system and the temperature to calculate the emissions from the system. For example, thermodynamically complete combustion or pyrolysis of a chlorinated hydrocarbon at 1800°F results in the formation of a few stable products, e.g., CO₂, H₂O, HCl, H₂, Cl₂, etc., and trace quantities of CO and organic byproducts (Eq. 1). Numerous calculations of PIC emission rates have been performed assuming an incinerator at equilibrium. These calculations typically demonstrate that observed PIC concentrations are at least 10 orders of magnitude greater than predicted based on equilibrium (Figure 1, Table 1).

Some have argued for rather vague concepts with little scientific basis or practical utility, such as PIC emissions being at "pseudo-equilibrium". Sufficient time is *not* available for equilibrium to be achieved, and PIC emissions are a function of time (i.e., kinetically controlled). Chemical reaction kinetics

undoubtedly play a large role in PIC formation. However, physical kinetics, such as vaporization and waste/air mixing, can also contribute to kinetically limited routes of PIC formation.

Theory 2—Deviation from Normal, Average Operating Conditions are Responsible for Most PIC Emissions

Modern, well-designed and managed incinerators operate at temperatures in excess of 1800°F, residence times greater than 2.0 s, and at least 50% excess air. Detailed elementary and global oxidation kinetic models consistently show that destruction efficiencies (DE's) for POHCs under these conditions are greater than 99.9999% for even the most stable compounds. Similar calculations for PICs result in yields < 0.000001 (Table 2, columns 3, 4, and 6).

Since the nominal operating range of incinerators precludes measurable POHC or PIC emissions, we are left with the conclusion that temporal or spatial excursions from the measured conditions are responsible for the observed emissions. These "failure modes" may be due to excursions in temperature (thermal), residence time (temporal), or oxygen concentration (mixing). As examples, a spatial, thermal-failure mode could be a cold gas boundary layer in a boiler whereas a temporal, thermal-failure mode would be a simple flameout. A spatial, residence-time failure could be deviation from ideal plug flow such that residence-time short circuits are possible. A temporal, residence-time failure could be loss of atomization pressure in a burner such that very large droplets are produced that do not vaporize until they have traversed much of the combustion chamber. A temporal, mixing failure could be poor waste/air micromixing on the molecular level due to flash volatilization, whereas a spatial failure could simply be poor burner placement or location of secondary air ports.

Hypotheses of PIC Formation

In addition to these theories that the preponderance of the data support, a body of qualitative and semi-quantitative laboratory and field data have led to certain observations concerning PIC emissions. We refer to these as partially verified hypotheses.

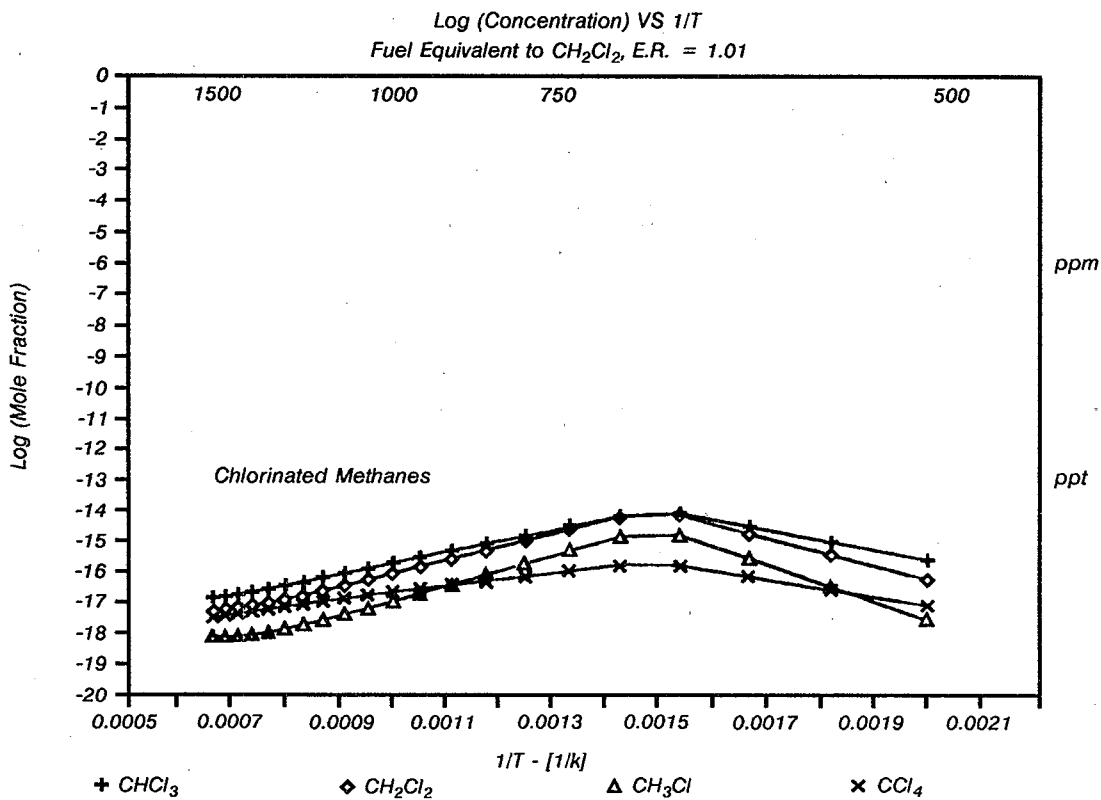
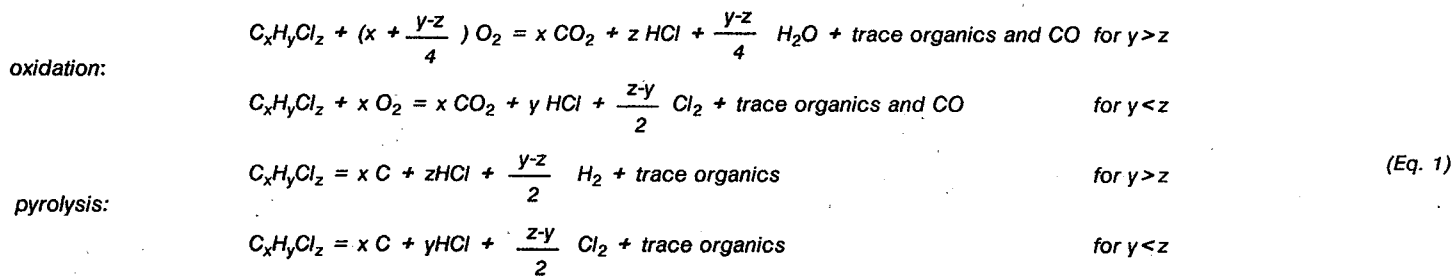


Figure 1. Equilibrium-predicted chlorinated methane concentrations over a temperature range of 500-1500° K (440-2240°F).

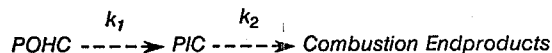
Table 1. Experimentally Measured and Equilibrium-Predicted POHC Concentrations from a Full-Scale Trial Burn (All values are in mole fraction)

POHC	Measured (Trial Burn)	Equilibrium Calculation (STANJAN)		
		2.65% O ₂	25% O ₂ Deficient	100% O ₂ Deficient
CCl ₂ H ₂	2x10 ⁻⁹	1x10 ⁻³¹	1x10 ⁻¹⁸	1x10 ⁻¹⁶
C ₇ H ₈	1x10 ⁻⁹	6x10 ⁻¹⁵⁶	1x10 ⁻³⁴	5x10 ⁻²³

Table 2. Kinetic Calculations of the Destruction Efficiency for PICs¹ for Various Flame and Post-Flame Reaction Conditions

POHC	PIC	Optimal Flame DE ²	Optimal Thermal DE ³	Thermal Failure DE ⁴	Overall (Optimal) DE ⁵	Overall (Failure) DE ⁶
1,1-Dichloroethane	Chloroethene	99.9999 +	99.9999 +	99.9997	99.9999 +	99.9999 +
Pentachloroethane	Tetrachloroethene	99.9999 +	99.9999 +	27.0164	99.9999 +	99.2702
Chlorobenzene	Benzene	99.9999 +	99.9999 +	92.2267	99.9999 +	99.9223

¹ PIC destruction calculations based on analytical solution of the following reaction scheme :



² DE calculated for optimal flame conditions ($T_f = 2780^\circ\text{F}$, $t_f = 0.1$ s).

³ DE calculated for optimal post-flame conditions ($T_{pf} = 2300^\circ\text{F}$, $t_{pf} = 2.0$ s).

⁴ DE calculated for suboptimal post-flame conditions ($T_{pf} = 1340^\circ\text{F}$, $t_{pf} = 2.0$ s).

⁵ Overall DE based on 99% destruction of the waste experiencing flame conditions and 1% of the waste bypassing the flame but experiencing optimal post-flame conditions.

⁶ Overall DE based on 99% destruction of the waste experiencing flame conditions and 1% of the waste experiencing failure post-flame conditions.

Hypothesis 1—Flame Reactions Control Bulk or Absolute Emissions of PICs While Post-Flame (Thermal) Reactions Control Relative Emission Rates

This hypothesis is based on the reasonable assumption (Theory 2) that flame temperatures are high enough that any material experiencing nominal oxidizing flame conditions will be totally destroyed (POHCs and PICs) (Table 2, column 3). The small fraction of waste that somehow escapes the flame is responsible for PIC emissions. Since compounds fed as mixtures will

experience very similar destruction conditions, the relative thermal stability (oxidative or pyrolytic) of the escaping POHCs will determine their relative emission rates. In a similar manner, the propensity for formation of PICs and their stability under post-flame conditions will control their relative emission rates (Table 2, column 7). Since the bulk of the material is destroyed in the flame, operating and design parameters affecting the flame will control overall waste destruction efficiency. Post-flame conditions may, however, apparently control the relative DEs of POHCs and relative PIC yields.

There are, however, insufficient data on the range of temperature, residence times, and oxygen concentrations that can potentially exist in an incinerator flame to absolutely state that no PICs are emitted from the flame. Although a two-zone system seems to be conceptually useful, there is also a transition zone between the flame and post-flame zones where the distinction is blurred. In addition, differing vaporization rates of compounds can, in principle, result in not all species experiencing the exact same combustion conditions. Preliminary calculations suggest, however, that

droplet vaporization does not significantly affect relative DEs.

Hypothesis 2—Most PIC Emissions are the Result of Pyrolysis Pathways

This is essentially a narrowing of the focus of the failure mode concept presented as the second theory of PIC formation. Theoretical calculations concerning the oxidation of the most stable organic PICs indicate that temperatures below 1450°F for post-flame residence times of 2.0 s (Table 2, columns 5 and 7) or residence times less than 0.1 s, for post-flame temperatures of 2300°F are necessary for measurable PIC breakthrough. Since these temperatures are so low, it seems reasonable that pyrolysis pathways (which are much slower than oxidation reactions) may be responsible for a large fraction of POHC and PIC emissions. This hypothesis has been partially supported by comparison of actual versus predicted CO emissions. Since CO is only destroyed under oxidative conditions (primarily by OH), its stack concentration may be considered an indicator of the fraction of the incinerator that is acting as an oxidizer. Theoretical calculations indicate that CO levels should be on the order of a few ppb instead of the observed levels of 1 to 100 ppm, suggesting a significant fraction of the CO does not experience an oxidative environment. Full-scale emissions of undestroyed POHCs also agree best with a theoretical prediction of POHC stability based on pyrolysis kinetics.

Recent bench-scale experiments simulating the burning of plastics in a rotary kiln suggest that rapid thermal degradation results in a "transient puff" of hydrocarbons and chlorocarbons that can overload the system such that intimate waste/air mixing is not completed. Consequently, high concentrations of various PICs and soot are observed, apparently due to a transient pyrolysis condition.

Some researchers have argued that upset pyrolysis conditions in full-scale incineration facilities actually result in lower PIC emissions. Other researchers, however, have shown that the high levels of soot that are formed may act as a reservoir for the PICs by surface absorption. Although air emissions may be mitigated by a high efficiency particulate control device, the total PIC yield and environmental burden is increased. The impact is simply shifted from the air to the land.

A significant number of cases exist, however, where emissions do not correlate with pyrolysis kinetics. In these instances, relative POHC and PIC emission rates may be facility specific. For example, very low temperature excursions may exist for which slower oxidation reactions can still contribute to emissions. Poorly atomized aqueous wastes could result in slow vaporization of water soluble species, resulting in a residence time failure.

Hypothesis 3—A Significant Fraction of the Observed PICs are Formed Outside the High Temperature Zones

A detailed study of the types of PICs emitted from full-scale hazardous waste incinerators, boilers, and kilns suggests that as high as 50% of observed PICs are likely formed by radical-radical and radical-O₂ association reactions (Table 3). These types of reactions are important as the system temperature is lowered because high activation energy unimolecular and radical-molecular reactions are not favorable. This may explain why thermally fragile PICs such as chloroform, 1,1,1-trichloroethane, and carbon tetrachloride are observed in the effluent of full-scale systems. In addition, it has been proposed and limited full-scale data suggests that formation of polychlorinated dibenzo-p-dioxins (PCDDs) is due to surface catalyzed reactions in the cool zones of the incinerator (i.e., transfer ducts, air pollution control devices).

Some studies, however, show evidence of analytical artifact whereas others suggest that volatile, fragile chlorocarbon PICs may be stripped from contaminated scrubber water. Both laboratory and full-scale research on the mechanism of PCDD formation is incomplete, and no quantitative study of gas-phase formation of PCDD from possible precursors has been performed.

Hypothesis 4—A Significant Fraction of Observed PICs are Due to Fuel/Waste Interactions

Analysis of full-scale data reveals that many of the observed PIC emissions are aromatic and polynuclear aromatic (PNAs) species, i.e., benzene, toluene, naphthalene, etc. These compounds are commonly observed in the effluent from most combustion devices. Further analysis, however, indicates that the presence of chlorine-containing wastes increases the emission of these species

as well as that of partially chlorinated hydrocarbons. Although chlorination of a stable hydrocarbon is kinetically unfavorable, chlorinated radicals may participate in condensation-type molecular growth reactions resulting in formation of chlorinated aromatic species and PNAs. Chlorine can also increase overall PIC emissions through the traditionally proposed effect of flame inhibition.

Not enough parametric full-scale studies have been performed to confirm the hypothesis, however. Although preliminary laboratory studies support this concept, the chemistry of chlorinated hydrocarbons and other hazardous materials is only beginning to be addressed.

Hypothesis 5—Carbon Monoxide and Total Unburned Hydrocarbons are Surrogates for PIC Emissions

From a scientific viewpoint, the emission rate of a surrogate should correlate (viz., have a statistically significant relationship through a continuous function) with the emission rate of a specific PIC or total PICs. From a regulatory viewpoint, it appears that a reasonable surrogate must only have a concentration greater than that of the PIC of interest such that, if the CO concentration is below a given level, the PIC will be below a given environmentally acceptable level.

The concept of CO as PIC surrogate arises from the fact that CO is more stable than any organic PIC. Total unburned hydrocarbons (TUHC) has been proposed as a PIC surrogate because TUHC, in principle, is the total of undestroyed POHC and organic PICs. Results of some full-scale tests indicate that CO and TUHC meet the regulatory definition of a surrogate for some PICs at some facilities. A statistically significant rank/order correlation between CO, TUHC, and various measures of PIC emissions was observed at a few sites. This is encouraging considering the limited range of conditions tested and the number of data points available.

The concept that the extreme stability (slow destruction kinetics) of CO makes it a suitable PIC surrogate is complicated by the fact that the concept does not recognize the formation kinetics of CO versus organic PICs. Under some failure conditions, PIC yields may be high whereas CO formation has yet to reach its maximum.

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C. C. Lee is the EPA Project Officer (see below).

The complete report, entitled "Minimization and Control of Hazardous Combustion Byproducts," (Order No. PB 90-259 854/AS; Cost: \$39.00, subject to change) will be available only from:

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