

## Research on Emissions and Mitigation of POP's from Combustion Sources

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### **ABSTRACT**

The environmental consequences of persistent organic pollutants (POP's) are of increasing concern due to the serious health effects on animals and humans including reproduction, development and immunological function. Several major classes of POP's, including polycyclic aromatic hydrocarbons (PAH's), chlorobenzenes, chlorinated dioxins and chlorinated furans, have been identified as products of incomplete combustion (PIC's) produced in trace levels in combustion systems. A wide variety of combustion processes, ranging from power plants, industrial boilers, industrial furnaces and incinerators, to home heating devices, are believed to be potential sources of POP's. Full-scale combustion facilities can be significant sources of POP's due to the large mass flow of flue gas released from a plant. Total emissions of POP's from small combustion devices, such as wood stoves and residential oil furnaces, can also be significant due to the large numbers of existing units near high population areas. It becomes increasingly important to understand the formation of POP's from different combustion processes to identify sources of POP's and to develop strategies for their prevention and mitigation. Research on POP emissions from combustion sources conducted by EPA is largely driven by the need for regulating the emissions of hazardous air pollutants as required by

Title III of the 1990 Clean Air Act Amendments and by the Resource Conservation and Recovery Act. This paper provides a summary of EPA's research on emissions and control of POP's from combustion sources with emphasis on source characterization and measurement, formation and destruction mechanisms, formation prevention and flue gas cleaning. Laboratory experiments conducted to examine the PAH emissions from a wide variety of combustion processes, ranging from pulverized coal utility boilers to wood stoves, have shown that they exhibit widely different emission characteristics. Waste incineration research conducted by the National Risk Management Research Laboratory, Air Pollution Prevention and Control Division (NRMRL/APPCD) has also shown that complex mechanisms, including physical mixing and chemical kinetics, are involved in the formation of chlorinated PIC's.<sup>1</sup> Research has also indicated that the formation of ultra-trace levels of chlorinated-dioxins and -furans in combustion/incineration processes includes the complex interaction of several factors including temperature, chlorine content and catalyst. The beneficial effect of sulfur and sorbents for dioxin formation prevention is demonstrated. This Laboratory's effort to develop and evaluate state-of-the-art technologies for on-line measurements of PAH's, volatile PIC's, dioxins and furans is also discussed. The promising potential of applying artificial-intelligence-based control systems for improving combustion processes operating conditions as a POP prevention approach is demonstrated.

## 1. INTRODUCTION

The wide distribution of persistent organic pollutants (POP's) in the environment has become a global issue of growing concern. International intentions to control such substances are expressed in the Washington Declaration made at the conclusion of a United Nations Environmental Program conference attended by environment ministers of 108 countries held in Washington, DC, during November 1995 [1]. POP's are long-lived organic compounds which survive long distance migration in the global environment and

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<sup>1</sup> NRMRL/APPCD was previously named the Air and Energy Engineering Research Laboratory (AEERL).

become concentrated as they move through the food chain with serious health effects on animals and humans including reproduction, development and immunological function. Much of the concern on POP's involves 12 chemicals or chemical classes, including polychlorinated biphenyls (PCB's), polychlorinated dibenzo-p-dioxins (PCDD's) and -furans (PCDF's), polycyclic aromatic hydrocarbons (PAH's) and pesticides such as DDT and chlordane.

Although the production and use of many of the anthropogenic chemicals which are considered as POP's, such as PCB's and dichlorodiphenyltrichloroethane (DDT), are banned in most developed countries, they are still widely distributed and used in developing countries. However, there are also POP's which are produced unintentionally as byproducts from combustion processes. Several major classes of POP's, including PAH's, chlorobenzenes, PCDD's and PCDF's, have been identified as products of incomplete combustion (PIC's) emitted at trace levels from various combustion systems. The development of control and mitigation strategies for POP's requires a better understanding of the major sources of these pollutants. It is very important to identify the industrial and residential combustion processes which may also be the potential sources of POP's. This paper summarizes EPA's research on POP emissions and control from different combustion sources.

Research on POP emissions from combustion sources conducted by the Air Pollution Prevention and Control Division (APPCD) of EPA's National Risk Management Research Laboratory (NRMRL) is motivated by the need for regulating the emissions of air toxic pollutants as required by Title III of the 1990 Clean Air Act Amendments (CAAA's) [2] and by the Resource Conservation and Recovery Act (RCRA) [3]. Title III of the CAAA's lists 189 compounds and compound classes and application of maximum achievable control technology (MACT) is required by any non-utility source that emits over 9,091 kg/year (10 t/year) of any one air toxic pollutant, or 22,727 kg/year (25 t/year) of total air toxic pollutants. PAH's, chlorobenzenes and PCDD's/PCDF's are among the classes of the 189 regulated air toxic pollutants which are also considered as important POP's. In addition, revised RCRA standards were proposed for hazardous waste combustors (hazardous waste burning incinerators, cement kilns and lightweight aggregate kilns) in April 1996 [4]. These proposed standards would limit the

PCDD/PCDF emissions to 0.2 ng International -Toxic Equivalency (I-TEQ)/dscm. Characterization of air toxic emissions from a wide range of sources and development of their control strategies have become an important part of the Agency's CAAA's implementation efforts. Research on dioxin emission prevention and control from hazardous waste combustion is very important to the Agency's RCRA regulation development.

## **2. POP EMISSIONS**

Characterization of organic air toxic emissions from combustion sources in general is much more difficult compared to that from chemical production facilities which involve predominately fugitive emissions of individual product compounds. Air toxic emissions generated by combustion, including the three major classes of POP's mentioned above, are typically contained in a complex mixture of organic compounds at trace levels. Because of large volumes of flue gas produced during the combustion process, even trace levels (ppm) of air toxic compounds in the flue gas can exceed the limits specified under Title III of the CAAA's. Due to a wide variety of combustion boilers that exist for utility, industrial, commercial and institutional applications across the country and because of the relatively small amount of information available characterizing organic air toxic emissions from these sources, research has been undertaken recently by EPA to provide such information.

### **2.1. PAH Emissions**

PAH's are among the most common PIC's found in combustion flue gases at trace levels. PAH's will likely be produced as a result of localized improper mixing of fuel and combustion air in a large size industrial combustor. A study was conducted by EPA to characterize organic air toxics emissions in the flue gases from the combustion of pulverized coal [5]. A small-scale combustor was operated under different conditions to simulate high excess air firing and nitrogen oxide (NO<sub>x</sub>) controls by combustion modifications of a utility boiler. Only a few organic air toxics were found above the

detection limits, with naphthalene as the only PAH identified from the tests. Results of the tests also indicate that total air toxics emissions from a large coal-fired utility plant are not likely to increase as a result of installation of combustion modifications for NO<sub>x</sub> control. In other research performed recently by EPA to determine the emissions levels of organic air toxics from combustion of various grades of oils, tests were conducted on a commercial fire tube package boiler running on fuel oil [6]. It was found that carbonyls dominated the trace organic emissions and PAH's constituted only minor components of the emissions.

The emissions of PAH's have been identified as the major pollutants emitted from residential combustion units in studies conducted by EPA. Large numbers of such units, including wood stoves, oil combustors and coal-fired furnaces, are operating in urban/suburban regions and their emissions may have serious impacts on indoor and ambient air quality. With collaboration of EPA's National Health and Environmental Effects Research Laboratory as part of the Integrated Air Cancer Project, we have conducted studies to characterize the organic emissions from different residential combustion devices. High levels of PAH's (0.7 g/kg wood burned) have been observed in EPA's wood stove research [7]. Some operating variables, such as wood species, stove type and altitude of the stove, were found to have a strong effect on PAH emissions, while burn rate has very little effect on PAH emissions. Pine was found to produce more PAH's than oak; conventional stoves showed higher PAH emission rates than those from a catalytic stove; and lowering the operating altitude of the stove from 825 to 90 m caused an increase in PAH emission rates. It was also found from this study that emissions from burning oak are less mutagenic than those from pine and emissions from the catalytic stove were more mutagenic than those from conventional stoves.

The organics emitted from residential heating furnaces have been found to be closely related to the chemical structure of the fuel burned in EPA's home heating fuels studies [8]. This is particularly true for wood and coal which contain mainly polymeric chemical structures where thermal cleaving during combustion accounts for a significant portion of the emitted organics. It was found that combustion of wood, which contains largely lignin and cellulose, produces mainly oxyaromatics and naphthalene accounts for almost all the PAH's in its emissions. The burning of coal, which contains fused ring structures,

produces emissions with three-, four- and five-ring PAH's, a class that includes benzo(a)pyrene and other known carcinogens. In the case of oil, the organic emissions contain mainly the unburned droplets of the oil itself, with substituted naphthalenes dominating the PAH emissions. Natural gas was found to be a clean-burning home heating fuel. Only a few PAH's with levels at least 100 times less than those emitted from wood stoves were identified in natural gas furnace emissions [9].

PAH's were identified as the most common pollutants produced from open burning of a wide variety of waste materials. Open burning is still widely practiced as a waste management method for several types of wastes, ranging from agricultural plastics to land-clearing debris. Because of concerns of their potential impacts on ambient air quality, EPA has undertaken a series of experimental studies to characterize the emissions from simulated open burning of waste materials. It was found that emissions produced from simulated open burning of agricultural plastic contain a complex mixture predominated by high molecular weight PAH's, only a minor fraction of which can be identified [10]. No mutagenic effects were found for the emissions as a whole; however, organic extracts of the particulate emissions contained mutagenicity comparable to that measured from wood stoves. In response to public concern over health hazards caused by the growing incidence of tire fires, EPA has conducted research to characterize the emissions generated from simulated scrap tire fires. It was found that the emissions contained mainly PAH's, which ranged from 10 to 50 g/kg of tire material burned and alkyl-substituted PAH's were the predominant PAH's identified [11]. EPA has also conducted a study to characterize the emissions produced from open burning of land-clearing debris, in order to assess the environmental risk associated with such land-clearing practice. Substantial emissions of a large number of pollutants including carbon monoxide (CO), fine particulate matter, volatile organic compounds (VOC's) and high molecular weight organics dominated by PAH's were observed from simulated open burning experiments [12]. Only 14 of the PAH's were identified, with a majority of PAH's only tentatively identified through searches of mass spectral libraries.

## **2.2. Formation of Chlorinated PIC's**

We are continuing our research to understand the formation and control mechanisms

associated with toxic organic pollutants from waste incineration, with emphasis placed on the emissions of chlorinated PIC's. Chlorocompounds are commonly contained in waste streams, which are difficult to destroy thermally during incineration with the resulting formation of chlorinated PIC's. Many of the chlorinated PIC's, such as chlorobenzenes, are toxic and also listed as a major class of POP's. Our research has focused mainly on PIC formation and control from rotary kiln incinerators. This particular incinerator design is very versatile and is widely used for treating industrial wastes in the form of liquids, sludges, or solids.

The secondary combustion chamber (SCC) is an important piece of control equipment for rotary kiln incinerators [13-14]. The SCC should be capable of destroying any unburned organic material that exits the primary combustion chamber due to rogue droplets, transients, quenching, or incomplete mixing. SCC's are also commonly used to combust liquid wastes that have high heating values. Design criteria in the past have been mostly limited to a time-temperature requirement, such as 2 s at 1000°C (1800°F). Although a time-temperature requirement is not written into the hazardous waste incinerator regulations as defined in the Resource Conservation and Recovery Act (RCRA), it appears to have been adopted as a criterion by regulators and the regulated community alike. A disadvantage of this "apparent" policy is that mixing, known to be of critical importance in incineration systems [15], is largely ignored and no economic incentives exist with which to improve afterburner designs, given that any new design would likely require a certain time-temperature profile before being allowed to be installed, even if such a design could meet required emissions limits with a much more compact configuration.

The emissions that the SCC must deal with generally result from some sort of system failure in the primary chamber, since steady-state operation of the primary chamber generally eliminates the need for an SCC. Liquid injection incinerators, for example, typically don't require an SCC. The failure modes that can cause elevated levels of organic compounds to enter the SCC include mixing failures, such as those caused by: poor microscale mixing intensities or poor macroscale mixing; poor atomization; flow stratification; batch charging and depletion of oxygen in the primary chamber; and reaction quenching, such as that caused by unburned material entering cold regions of

the combustion device, or by cold walls. Rotary kilns in particular exhibit high levels of flow stratification [16-18] and typically have some of their waste feed fed in batches and, as such, generally employ an SCC.

Part of the reason that a time-temperature requirement is used as a common SCC design criterion is that the effects of turbulence and complex chemical kinetics are not understood well enough to incorporate their use into the permitting process. It is very important, however, to work toward gaining an understanding of kinetics and mixing in incinerators, since it is possible to have excessive levels of PIC's even after having successfully met the necessary time-temperature requirement. EPA, in cooperation with the New Jersey Institute of Technology (NJIT) and Massachusetts Institute of Technology (MIT), has been performing research on a pilot-scale rotary kiln incinerator simulator (RKIS) to complement laboratory-scale research being performed at both of the previously mentioned academic institutions, with the ultimate goal of furthering the state-of-the-art of SCC design by incorporating gas-phase mixing and kinetic considerations into the design criteria, particularly in regards to chlorocarbon combustion. Initial pilot-scale experiments have consisted of system characterization tests.

In order to incorporate gas-phase mixing and kinetic phenomena into afterburner design, it is necessary to achieve several goals, including:

1. Development of reaction pathways and kinetic data for combustion of the principal organic hazardous constituents (POHC's) present in the waste, along with possible mechanisms of formation of PIC's from POHC decomposition products. Although mechanistic information is not available for complex compounds, mechanisms do exist for C1 and C2 chlorocarbon combustion [19]. Initial tests focused on combustion of carbon tetrachloride ( $\text{CCl}_4$ ) and methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), compounds for which kinetic mechanisms exist. Combustion of  $\text{CH}_2\text{Cl}_2$  results in levels of 1,2 dichlorobenzene and monochlorobenzene much higher than those found from  $\text{CCl}_4$  combustion. It may be possible that  $\text{CH}_2\text{Cl}_2$  can readily form chlorinated intermediate structures that are ring-growth precursors, resulting in direct formation of monochlorobenzene rather than from chlorination of benzene. Combustion of  $\text{CH}_2\text{Cl}_2$  produced higher quantities of

identified PIC's than combustion of  $\text{CCl}_4$ , particularly during fuel-lean combustion. Although  $\text{CCl}_4$  may be useful as a POHC due to its high thermal stability and provide a useful measure of a system's ability to meet the required 99.99 % destruction and removal efficiency (DRE), it may not challenge an incinerator's ability to produce or destroy PIC's.

2. Development of models that take into account macromixing and micromixing phenomena to aid in the scale-up of results from very small-scale experiments to pilot and full-scale systems. Kinetics and thermodynamics alone cannot account for emissions of PIC's from incinerators. Mixing must eventually be considered [20]. Initial tests have attempted to characterize the macromixing in the EPA's RKIS SCC using sulfur dioxide ( $\text{SO}_2$ ) as a tracer. By measuring residence time distributions (RTD's) in various portions of the SCC, it is possible to determine the unknown reactor volumes in a series of ideal reactors. These reactor volumes can then be modeled numerically using detailed reaction mechanisms [21].
3. Development of techniques to measure trace organic species or surrogates for trace organic species in the field, given that many of the advanced diagnostics available in a laboratory setting cannot easily be transferred to a field application. Semi-continuous measurement of key organic compounds can potentially be used to characterize the overall destruction of all hazardous trace organics of concern. Since POP's are frequently in the semi-volatile range of boiling points ( $>150^\circ\text{C}$ ) and thus more difficult to measure using existing monitoring methodologies, it is useful to find a surrogate compound for the POP's that is more easily measured than the POP of interest.

### 2.3. Dioxins

On-going research has been investigating the fundamental mechanisms behind formation of PCDD's/PCDF's, collectively termed 'dioxins'. Dioxins are formed in the post-combustion region from components of chlorine (Cl), unburned organics and catalytic surfaces. A complex interaction of surface-induced catalysis, organic ring structure formation and chlorination countered by destruction/dechlorination reactions can result in the formation and emission of dioxins and other chloro-organics The

synthesis reactions that lead to the formation of dioxins occur at temperatures ranging from approximately 200 to 600°C [22, 23]. They may be catalyzed by combustor deposits and by entrained and collected fly ash. These deposits can be composed of fly ash or sooty materials containing catalytic metals such as copper [24, 25]. With appropriate fly ash properties and operating temperatures, air pollution control devices such as electrostatic precipitators and fabric filters can act as chemical reactors that form dioxins and other chloro-organics[25].

While commonly associated with waste combustion, dioxin formation can also occur from burning coal, oil and wood. The mechanisms of formation are being studied at EPA to enable source-specific predictions and to develop pollution prevention strategies that discourage or prevent dioxin formation from occurring. Work at EPA has coupled mechanistic aspects related to the effect of different types of metal catalysts [26], the ability of Cl to chlorinate aromatic ring structures [27] and the role of catalysts in formation of the biaryl structure [28]. The effect of these interactive mechanistic parameters, along with combustor operating parameters, has been examined for their relationship with dioxin formation [29-30]. This work has shown on a combustor-specific basis that reduction of hydrogen chloride/chlorine (HCl/Cl<sub>2</sub>) concentration, completeness of combustion and/or increases in quench rate can reduce formation of dioxin.

Recent work has focused on the effect of sorbent injection technologies to remove Cl and thereby prevent formation of dioxins [31]. Research programs on two pilot-scale combustors have shown that injection of calcium (Ca)-based sorbents at moderately high temperatures has the effect of preventing formation of dioxins [29, 32]. This is likely to hold for all systems in which formation is Cl limited. This technology is the subject of two U.S. patents [33, 34] and is currently undergoing field demonstration in the U.S.

Another preventive strategy derived from mechanistic studies is the suppression of dioxin formation by the presence of sulfur (S) as SO<sub>2</sub>. The effect of SO<sub>2</sub> may relate to its effect on an important, catalytic chlorination reaction and biaryl synthesis [35] and/or its effect on gas-phase reactions with chlorinating compounds [36]. This SO<sub>2</sub> effect has been shown on a large pilot scale and is currently undergoing field demonstration. Results to date [30, 32] suggest significant (90%) suppression of dioxin formation across all congener classes at S/Cl ratios >1/1.

Upcoming work at EPA will undertake a mobile sampling program for dioxin emissions from heavy duty diesel vehicles. This work, part of EPA's Dioxin Reassessment effort, will provide important information in the effort to quantify dioxin sources in the environment. This effort is significant in that U.S. mobile sources, with the exception of a recently completed tunnel study (still in draft form), are entirely uncharacterized as potential dioxin sources. Further, it is possibly the first mobile sampling effort for diesel engine dioxins.

Another recently initiated program will be using isotopically labeled fuels to study the mechanisms and rates of formation. This work is geared toward discerning the critical pathways of dioxin formation and determining rate information for development of a global reaction model. Expected results will discern the importance of incomplete combustion (either gas phase or carbonaceous, solid phase) on supplying organic dioxin precursors and, thus, will be relevant to a wide variety of fuel types and combustors. This program is being designed with the assistance and advice of a team of international researchers and reviewers.

### **3. ON-LINE POP MEASUREMENT**

Part of the importance of determining what POP's are released from combustion systems is the measurement of those POP's. This creates a major technical challenge since many of the compounds of interest are present in very small quantities, plus are normally in the semivolatile boiling point range (>150°C), which partitions the organic compounds of interest between the gas phase and condensed phase (usually bound on particulate matter). This partition makes continuous measurement difficult. A useful approach to circumvent this limitation is to measure another, more easy-to-measure compound, that is a precursor to the POP of interest, or at least is a well-correlated indicator of not only the presence/absence of the POP, but also of the relative concentration of the POP in the stack. This concept of using a surrogate indicator has been used in current regulations of municipal waste combustors (MWC's). CO, for example, has been used as a useful surrogate for PCDD's/PCDF's in MWC systems; however, its usefulness as a surrogate

indicator breaks down in a system that is very well operated.

A potentially more useful approach is to measure a volatile organic precursor to the semivolatile POP's of concern. In a recently completed test program [37] at the U.S. EPA Incineration Research Facility (IRF) in Jefferson, Arkansas, several continuous emission monitors (CEM's) for measuring trace quantities of various organic and inorganic pollutants were tested. One of the CEM's tested was a dual-detector on-line gas chromatograph (GC) system developed by EPA/APPD in-house. This system consisted of a sample delivery system, a sample concentrator and a GC equipped with a flame ionization detector and an electron capture detector [38]. The IRF's rotary kiln incineration system was operated at conditions indicative of normal incinerator operation, while injecting varying concentrations of 10 VOC's that are usually found in incinerator stack gases as PIC's. Target VOC concentrations included low level (1-2  $\mu\text{g}/\text{m}^3$ ), medium level (10-20  $\mu\text{g}/\text{m}^3$ ) and high level (160-240  $\mu\text{g}/\text{m}^3$ ). Tests were performed to compare CEM results to the EPA's standard reference methods using a relative accuracy test audit protocol [39]. The EPA/APPD on-line GC performed successfully for most compounds at all concentration levels. Instrument sensitivities were sufficient to measure all 10 compounds at levels typically found in well-operated systems.

The high molecular weight PAH's are predominantly adsorbed on soot (carbon aerosols) due to their low vapor pressure at stack temperatures. Currently, PAH's are measured using a sampling train (EPA Modified Method 5, MM5) followed by solvent extraction and analysis using GC and mass spectrometry (MS) [40-42]. The measurement is time consuming and no real-time data can be obtained from such captive sampling techniques. EPA recently conducted tests to evaluate the application of a photoelectric aerosol sensor for on-line measurement of particle-bound PAH's in combustion flue gas. The PAH monitor works on the principle of photoionization of carbon aerosols. After being exposed to the ultraviolet (UV) light of the monitor, the carbon aerosols which have PAH molecules adsorbed on the surface pass through the monitor, then emit electrons and the resulting electric current is proportional to the particulate-bound PAH's. Initial tests of the PAH monitor for measuring emissions from burning tire-derived fuel in EPA's pilot-scale RKIS indicated that the monitor appeared to track transient operation of the combustor well [43]. The PAH monitor was also evaluated during a recently

completed test program, which gave excellent relative accuracy for measuring the three selected PAH's (naphthalene, phenanthrene and pyrene) at an intermediate concentration level [37]. Operating problems caused by the high moisture content of the combustion flue gas were experienced and the monitor's manufacturer is modifying the design of the instrument's moisture removal system.

A recent international research program has assisted in the development of Jet-REMPI™ (resonance-enhanced multiphoton ionization) as an analytical technique for monitoring extremely low concentrations of chlorinated dioxins. The DLR Jet-REMPI apparatus was tested in the EPA laboratories for its ability to detect chlorinated dioxins. This work [44] has detected spectra for a dichlorodibenzodioxin isomer and determined a detection limit of less than 30 ng/dscm. Identification work for more highly chlorinated isomers is currently underway. It is likely that suitable correlations between the lower chlorinated dioxin isomers and the more toxic, higher chlorinated isomers can be established, enabling Jet-REMPI to be used as a correlative monitor for dioxin toxic equivalency (TEQ) emissions.

#### **4. APPLICATIONS OF AI FOR COMBUSTION CONTROL**

The objective of this research [45] was to apply fuzzy logic artificial intelligence (AI) to control combustion systems, in particular the pilot-scale RKIS and its secondary combustion chamber (SCC) mentioned above. The mechanistic details of system response in a system such as the RKIS are complex and are not usually known *a priori*. However, a relatively small number of generic control rules based on operating experience can be linguistically stated and then translated into a fuzzy logic system for automatic control. The purpose of the control system in this case was to reduce emissions of PIC's from the RKIS, when significant transients were artificially imposed on the system by spraying liquid surrogate wastes into the RKIS based on a time-based algorithm.

Rotary kilns have the advantage of being flexible enough to handle a wide variety of waste streams in a wide variety of forms, including flammable liquids, aqueous streams,

sludges and whole drums. When a drum containing volatile material is fed into a rotary kiln, it ruptures and releases its contents into the hot kiln environment in a transient event that occurs over a short period of time. If the instantaneous stoichiometric requirements to combust the volatile waste are greater than the amount of oxygen being added to the kiln through the main burners or auxiliary air sources, then a plug of unburned material, called a transient "puff" leaves the kiln and must be dealt with by the SCC. The transient puffs include large quantities of soot, CO and organic compounds of both a volatile and semivolatile nature. Past experiments have shown high quantities of PAH's contained in transient puffs (46).

One possible control option is to equip the SCC with a system that can inject additional oxidizer in response to a puff leaving the kiln. This option has been shown to dramatically decrease the emissions of PAH's and other PIC's (35). If air is used as the oxidizer, then the downstream equipment, such as baghouses or scrubbers, must be sized to handle the increased volume of flue gases, based on maximum flow rates. If oxygen ( $O_2$ ) is used as the oxidizer, then the downstream equipment can be sized smaller; however, significant costs are associated with the use of pure  $O_2$ . A tradeoff is realized between increased capital costs and increased operating costs. If a means is available to maximize the efficiency of  $O_2$  usage, then  $O_2$  injection will become more economically attractive.

A series of experiments were performed to evaluate the effectiveness of fuzzy logic control schemes by injection of pure  $O_2$  into the SCC's afterburner. A statistically designed test matrix was repeated for each of four control schemes: no control, feedback control (based on stack  $O_2$ ) and two fuzzy logic control schemes based on CO and total hydrocarbon (THC) emissions at the kiln exit. Results were evaluated using a combined performance indicator that utilizes stoichiometrically weighted integrated emissions of CO, THC and soot at the inlet and outlet of the SCC. The following conclusions were observed:

- The speed of analyzer response is a significant hindrance to the effectiveness of any sort of process control for reduction of transients from incinerators.
- The feedback control tended to open the  $O_2$  valve all the way in order to attempt to restore the stack  $O_2$  to a level near the set point.

- The fuzzy logic control scheme was more effective than feedback in controlling transients of short duration.
- The fuzzy logic control scheme was significantly more efficient in its use of the injected oxygen, particularly where the transients were small.

## 5. CONCLUSIONS

Major classes of POP's including PAH's, chlorobenzenes and chlorinated dioxins and furans can be emitted from various combustion processes as unintentional and unwanted byproducts. Research has been conducted by EPA to study POP emissions from combustion sources, with emphasis on understanding the fundamental mechanisms which lead to POP emissions and identifying mitigation strategies for such emissions. Our research found that good combustion conditions achieved in well-operated industrial units in general prevent significant POP emissions. POP emissions result from complex interactions of a wide variety of physical and chemical mechanisms occurring in combustion systems. POP emission potentials strongly depend on the design and operating characteristics of the combustion units. The presence of fuel/waste components which contain difficult-to-destroy chemical structures in fuels/wastes also plays an important role for promoting POP emissions. Significant progress has also been made in our research on developing technologies for continuous monitoring and reducing POP emissions from combustion sources.

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