

FUNDAMENTAL CRITERIA FOR THE BETTER DESIGN OF SECONDARY COMBUSTION CHAMBERS

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INTRODUCTION

The major concern regarding organic emissions from hazardous waste incineration systems is the formation of products of incomplete combustion (PICs). The toxic and, possibly, mutagenic character of these compounds represents one of the major problems to public acceptance of incineration as a safe waste disposal technology. Ongoing studies at MIT, sponsored by the US EPA Northeast Hazardous Substance Research Center (NHSRC), have shed light on the mechanisms of formation and emission of PICs, showing that the formation of PICs is highly dependent upon the local ratio of fuel and oxidant, and their amount and composition are sensitive to both turbulent mixing and chemical kinetic constraints.

A recent critical review on incineration science and technology, presented as a plenary lecture at the XXV International Symposium on Combustion by J.O.L. Wendt of University of Arizona, has clearly encouraged the scientific community to focus on turbulent mixing, rather than kinetics alone, in order to reach the goal of controlling and minimizing PIC emission from incinerators [1]. Also, it has shown that PIC emissions are closely related to transient phenomena (as rogue droplets formation caused by poor atomization, formation of puffs in kilns, fluctuations in feed rate and composition, etc.) which lead to failure modes tied to incomplete mixing. The current approach followed at MIT during the NHSRC-sponsored project thus seems to be very promising in giving a correct interpretation of the complex mechanisms involved in PIC formation, and in providing useful application of combustion science to incineration technology.

METHODOLOGY

The experimental facility has been designed to simulate the conditions in actual incinerator systems. It consists of a Toroidal Jet-Stirred Combustor (TJSC), which simulates the primary chamber of an incinerator, followed by a Plug Flow Reactor (PFR), as shown in Fig. 1. The hot combustion products from the TJSC are directed into the PFR, which represents the secondary combustion chamber, through a flow straightener. Mean flow velocities in the PFR range from 20 to 30 m/s for reacting flow.

An injector positioned at the PFR entrance allows injection of a selected species (oxidant, hydrocarbon, or chlorocarbon) directly into the PFR. The PFR injection system, and its turbulence intensity and chemical system, allow one to investigate the combined effects of turbulent mixing and chemical kinetic inhibition on PIC emissions. The experimental system is operated at high enough velocities to yield a Reynolds number corresponding to turbulent flow.

The PFR is equipped with optical access for application of a laser Rayleigh scattering diagnostic, leading to the definition of temperature probability density functions (PDFs) at a given location along the PFR axis. A water-cooled probe is used for sampling of the combustion gases whose concentrations are determined by gas chromatography/mass spectrometry.

Modeling of the experiment has been carried out using the Linear Eddy Model approach [2]. A semi-quantitative model coupling detailed chemical kinetics in homogeneous conditions with the interpretation of the effects of mixing constraints has also been developed. Furthermore,

use of CHEMKIN/SENKIN codes to investigate the temperature/time equivalence ratio history of the chemical system allows the selection of the most interesting conditions to be tested in the experimental facility.

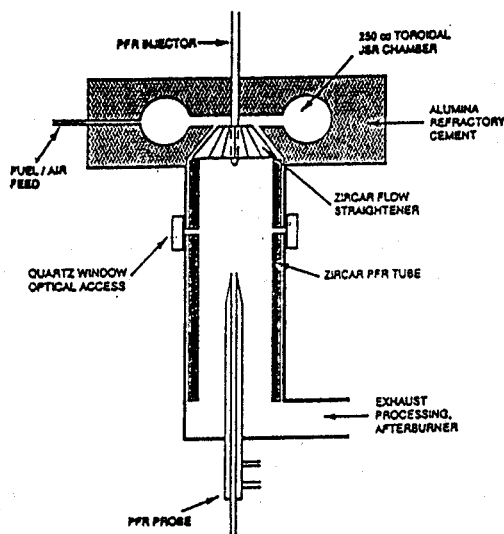


Figure 1. Schematic of the TJSC/PFR experimental system

RESULTS

The evolution of PDFs obtained by applying the Rayleigh scattering diagnostic technique shows evidence of mixing constraints in the PFR (Fig. 2).

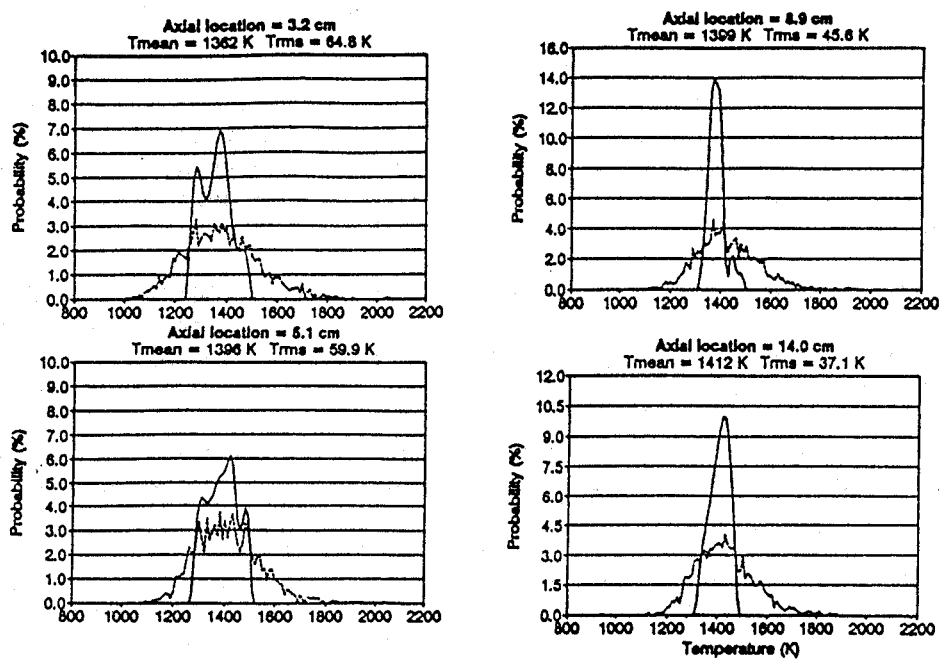


Figure 2. Temperature PDFs evolution for CH₃Cl injection in the PFR ($\phi = 1.25$)

The evolution of the turbulent system can be characterized by the decay of the fluctuating component of the injected material concentration distribution (in non-reacting conditions) with the distance from the injection point:

$$\sigma^2(x) = \sigma^2(0)\exp[-(1/\chi_d)x] + C$$

where σ^2 is the variance in the distribution, x is the distance from the point of injection, χ_d is the characteristic distance describing the approach of the concentration distribution to uniformity, and C is a constant which is determined experimentally. The mixing distance can be related to the mixing time τ_d , and to turbulence quantities such as the turbulent dissipation rate, ε , and the integral scale, L . Calculations made in order to obtain χ_d as a function of ε and L for the experimental conditions tested (injection of CH_3Cl in a N_2 baseline flow) gave a value of $\chi_d = 0.6$ cm, which is in good agreement with the value of $\chi_d = 0.7$ shown by the experimental trend.

Stable species concentration measurements were made along the length of the PFR, i.e., for different residence times. For example, as shown in Fig. 3, benzenes and chlorinated benzenes have been observed when methyl chloride was injected for an overall fuel-lean condition. Since aromatic compounds are only formed under pyrolysis conditions (high local value of the equivalence ratio ϕ) this indicates mixing controlled PIC formation (no aromatic compounds are produced when CH_3Cl is injected into the well-mixed environment of the TJSC) [3].

Research activities at MIT under the NHSRC program have thus proven evidence of mixing constraints in incinerator environments, whose interaction with the chemistry of the system is twofold. First, mixing constraints have the effect of decreasing the extent of reaction by delaying molecular mixing, compared to the case of a premixed environment. Second, they cause a distribution of the values of the local equivalence ratio (ϕ), compared to the theoretical ϕ value. Some of the high values of ϕ will result in pyrolytic pockets that can lead to the detection of species that would not otherwise be formed, and to a difference in concentrations of species which have a strong non-linear dependence on ϕ , compared to the conditions occurring in a completely mixed flow field.

The scale-up of the experimental and modeling activities has been achieved through collaboration between MIT, New Jersey Institute of Technology (NJIT) and EPA-Combustion Research Branch (CRB) by application of the experimental and modeling studies to the EPA-CRB's pilot scale facility, with emphasis on the secondary combustion chamber of the 73 kW rotary-kiln incinerator (Fig. 4).

Experimental results obtained from tests in which a dopant (CCl_4 and CH_2Cl_2) was injected in the secondary combustion chamber have confirmed the laboratory-scale results about PIC production and equivalence ratio history [4], encouraging the research groups to carry out an ongoing complementary test program.

An approach for the definition of a failure mode diagnostic system for application to practical incineration systems has also been developed. Experimental and modeling results have highlighted the possibility of a relationship between the PIC speciation measured in the exhaust and the kinetic and/or mixing failure mode that has led to the emissions. The strategy for the implementation of the diagnostic system is based on the presence of species, and on the value of selected ratios, which are sensitive to variations in operating parameters. For example, species having a strong non-linear dependence on the equivalence ratio, such as aromatics and soot which are produced above a critical ϕ , can provide insights on the mixing history. Figures 5 and 6 show the expected trend of selected ratios between species versus equivalence ratio as obtained by computer simulation of a perfectly mixed combustion environment.

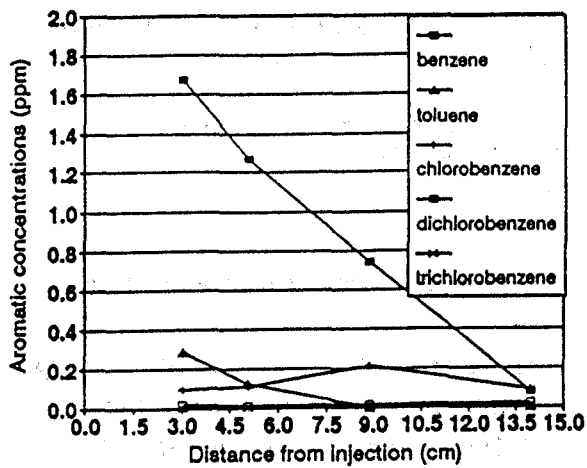


Figure 3. Concentration of aromatic species in the PFR ($\phi = 0.75$)

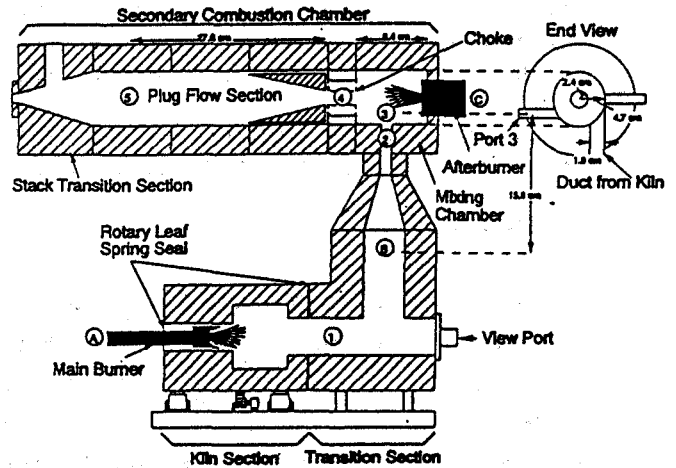


Figure 4. Schematic of the EPA-CRB pilot scale incinerator facility

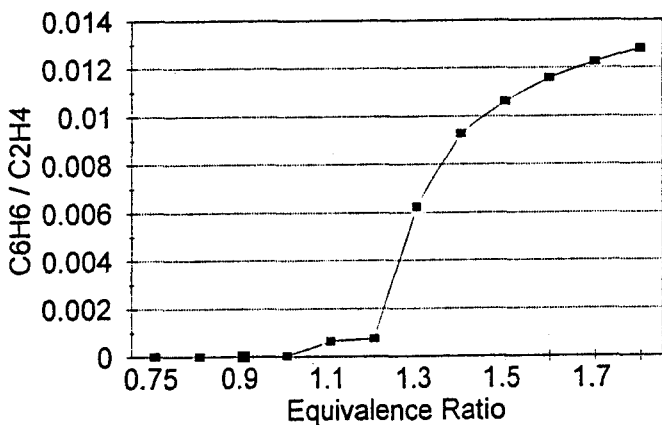


Figure 5. Evolution of C6H6/C2H4 ratio vs. ϕ

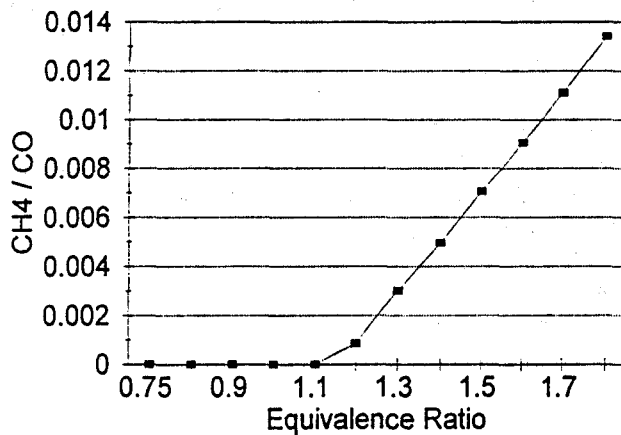


Figure 6. Evolution of CH4/CO ratio vs. ϕ

CONCLUSIONS

Experimental results have indicated effects of both incomplete mixing and chemical constraints on the formation of PICs. Evidence of mixing controlled PIC formation is given by the presence of species like aromatics, chlorinated aromatics, and high molecular weight species, in the exhaust gases. These species should not be formed under perfectly mixed conditions. The distribution of the value of the equivalence ratio is the most critical indicator in the interpretation of the effects of mixing constraints. Hence, evolution of species showing a strong non-linear dependence on the equivalence ratio provides insights on the mixing history in the incinerator.

The correct interpretation of exhaust composition data can lead to the development of a failure mode diagnostic for practical incinerator systems based on the detection of species which have a strong non-linear dependence on ϕ (as well as on other selected parameters). A

feed-back control system based on the presence of selected species in the gases leaving the secondary combustion chamber can be used to adjust the practical devices (air injectors, fuel and air flow controls, etc.), and quickly restore the optimal operating conditions.

Application of the results to the EPA-CRB's incineration facility plays a major role in transferring the research findings into practical industrial application.

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KINETICS OF METAL LEACHING FROM HEAVY METAL CONTAMINATED SOILS

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INTRODUCTION

The evaluation of the rate and extent of heavy metal leaching from contaminated real waste site soils is an important aspect in the design of soil washing processes. Although the technology of soil washing is well established in Europe, until recently it had been demonstrated only on a pilot scale in the United States. In January 1992, the first full scale soil washing system in the United States started operation at the King of Prussia Technical Corporation Superfund site at Winslow Township, New Jersey (1). Of the 498 Records of Decision published through 1991, only 18 specified soil washing as the primary remediation technology. Currently, models that may yield design information are not available and the soil washing technology is at an empirical level of development. This goal of this project was to develop a deterministic model to describe the kinetics of metal leaching from contaminated soils. Specific objectives of the project were to: 1) experimentally measure leaching kinetics under acidic conditions from real waste site soils, 2) determine through numerical simulation the fate and interactions of the various contaminant phases during the washing process, and 3) identify the rate controlling steps and gain insight into design and operational aspects of the washing process. The focus of the study was on Pb contaminated soils.

METHODOLOGY

BET analyses were conducted on the soil samples by a contract lab to obtain soil surface area, pore volume and pore diameter data. Sieve analyses (ASTM Method D422-63) were performed to obtain particle size distribution data from which the geometric mean was calculated and used for model simulations. A standard acid digestion procedure (EPA Method 3050) was conducted on soil samples to determine total Pb content.

A sequential extraction method developed by the DuPont Corporate Remediation Group (2) was used to determine the distribution of Pb in various geochemical phases. This technique was developed specifically for Pb contaminated soils. Soil samples were air dried and only material passing through a #10 sieve (2 mm mesh size) was used for analysis by sequential extraction. Pb was partitioned into the following ten fractions: 1) water soluble; 2) exchangeable; 3) Ag-displaceable; 4) carbonates; 5) Mn oxides; 6) organic; 7) amorphous Fe-oxide; 8) crystalline Fe-oxide; 9) sulfides; 10) residual. For modeling purposes, it was assumed that fractions 1, 2 and 4 form the easily leachable phase, and fractions 3 and 5 through 8 constitute an adsorbed phase. Phases 9 and 10 form the residual phase and were assumed to be immobile, even under strongly acidic washing conditions.

Bench scale soil washing experiments were performed to obtain kinetic data during acid washing of soils in a batch reactor system under vigorous mixing. pH was carefully controlled throughout the