ROTARY KILN INCINERATION – COMBUSTION CHAMBER DYNAMICS*

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Summary

A multifaceted experimental and theoretical program aimed at understanding rotary kiln performance is underway. The overall program involves university, industry, and government participation and is broken into distinct sub-programs. This paper discusses in some detail the research effort performed to date in two of the sub-programs: full-scale *in situ* sampling and kiln-simulator experimentation. Full-scale *in situ* measurements are obtained from the Louisiana Division rotary kiln facility of Dow Chemical USA, located in Plaquemine, Louisiana. Summary results obtained from controlled experiments that were performed during continuous processing of carbon tetrachloride and preliminary results obtained during batch mode processing of toluene-laden sorbent packs are presented. Kiln-simulator data are obtained by using the facilities of the Chemical Engineering Department at the University of Utah. Recent kiln-simulator work, conducted in support of the full-scale measurements sub-program, has aided in providing an understanding of the results that have been obtained at the full-scale. Modeling efforts, conducted at Louisiana State University and the University of Utah, have concentrated on the development of realistic, fluid-flow and heat-transfer models, near-term chlorinated kinetic models and bed mass-transfer models to be incorporated into a global three-dimensional kiln-simulator model. The paper concludes with an overview of these modeling efforts.

Introduction

Rotary kilns were initially developed as process furnaces for treating cement, lime, dolemite, and similar products. Their adaptability to a wide variety of continuous process operations, however, has led to widespread use in many other applications. In particular, rotary kiln incineration has been used for over 20 years in the United States and Europe for destroying waste organics. This technology is now generally regarded as the preferred method of treat-

ment for many hazardous organic wastes; solids, sludges, and liquids can all be treated simultaneously with continuous mixing at high temperatures.

This paper reports on aspects of a cooperative effort among university, industry and government aimed at obtaining a better understanding of the rotary kiln process. The overall project is broken into distinct sub-programs including: (i) full-scale *in situ* sampling from an operating rotary kiln incinerator, (ii) kiln-simulator and bench scale experimentation to aid in the interpretation of full-scale results and characterization of bed evolution phenomena and (iii) development of realistic, near-term models. This communication presents a summary of the study to date including: data obtained from the *in situ* field measurements sub-program, results that are being obtained from the kiln-simulator sub-program in support of the *in situ* field measurements sub-program, and an overview of the modeling approach used to arrive at rotary kiln incinerator predictive capabilities.

Full-scale, *in situ* sampling sub-program

The focal point of this study is the unique opportunity to probe the flame zones of an operating industrial rotary kiln incinerator. The sub-program objectives, a description of the full-scale incinerator facilities, the procedures for sample collection and sample analysis, and detailed results from field tests during quasi-steady (that is, under conditions where the time constants for changes in operating conditions are large compared to the time constants for sampling) incineration of carbon tetrachloride (CCl_4) have been presented elsewhere [1–4]. A summary of these results, and initial batch-mode test results are presented here.

Overview

The overall goal of the program is to obtain a better understanding of the processes that occur during rotary kiln incineration, with a view toward improving kiln operation and design for hazardous waste destruction. *In situ* sampling from a full-scale incinerator is providing a unique insight into these processes that has not been possible before. Gas samples and temperatures are obtained during the operation of the incinerator facility at the Louisiana Division of Dow Chemical USA, located in Plaquemine, Louisiana, USA (hereafter referred to as the Dow facility). The 3.2-m ID and 10.7-m long kiln has a design capacity of 17 MW with an 800°C outlet temperature. The design capacity of the secondary combustion chamber is 7 MW with a 1000°C outlet temperature and 2-s minimum residence time.

Gas samples are drawn from locations inside the kiln (near the exit) and from the afterburner location through two, water-cooled probes. Samples are collected in gas bombs and analyzed by gas chromatographic (GC) techniques in the mechanical engineering analytical laboratory at Louisiana State Uni-

TABLE 1

Sampling history for full-scale *in situ* sampling program

Test No.	Date	Feed	Sample locations	Experimental protocol
1	5 Nov. 1986	CCl$_4$	Lower kiln and afterburner	Quasi-steady
2	10 March 1987	CCl$_4$	Lower kiln and afterburner	Quasi-steady
3	20 Oct. 1987	CCl$_4$	Transition and afterburner	Quasi-steady
4	25 Feb. 1988	CCl$_4$	Upper kiln, afterburner, and stack	Quasi-steady
5	12 April 1988	C$_6$H$_5$CH$_3$ on sorbent	Upper kiln, afterburner, and stack	Batch-mode

TABLE 2

Kiln operating conditions during full scale *in situ* sampling program

Test No.	Waste feed type	Turb. air activated	Waste feed rate (l/min)	Cl/H ratios		Firing rate (kW)	
				Kiln	AB[a]	Kiln	AB
2	CCl$_4$	No	6.8	0.25	0.18	3220	4050
		Yes	7.9	0.21	0.17	4100	4000
4	CCl$_4$	No	4.2	0.11	0.09	5050	3540
		Yes	4.2	0.09	0.06	5050	3550
5	C$_7$H$_8$	No	3.8[b]	–	–	3052	3820
		Yes	3.8	–	–	3050	3840

[a]Afterburner.
[b]Average of 19 liters every 5 minutes.

versity (LSU). Backup analysis on approximately every tenth sample is provided by Dow personnel. Continuous total hydrocarbon concentration (THC) measurements of the kiln-probe gas are recorded by a facility THC analyzer.

An overview of the five field tests that have been conducted to date is given in Table 1. The kiln operating conditions for three of these tests, for which data are reported here, are given in Table 2.

Summary of results from the carbon tetrachloride trial

The series of CCl$_4$ tests provide a developing picture of the kiln processes during quasi-steady state incineration. During these tests, natural gas/CCl$_4$/air were fired from an upper kiln burner and natural gas/air were fired from a lower kiln burner. Turbulence air, injected with a tangential orientation to improve bulk mixing, could be turned on or off as desired (Refs. 1–3 provide details of the kiln configuration).

The results of these tests are exemplified by the concentrations of high-level,

stable gases in samples taken from the kiln during tests 2 and 4, as shown in Fig. 1. Data from two sampling locations (lower and upper) are shown, and the results for each location are given both with and without the turbulence air activated. The coordinates of the sampling locations are given in Fig. 2.

In the absence of turbulence air, the oxygen (O_2) is at near ambient air level, carbon dioxide (CO_2) and methane (CH_4) concentrations are low, and no carbon monoxide (CO) is observed in the lower part of the kiln. These results caused concern regarding the probe integrity (potentially allowing introduction of ambient air into the gas samples) and/or massive infiltration of ambient air through leaks around the kiln, particularly adjacent to the charging equipment. Subsequent tests showed the probe to be leak free.

In contrast, in the upper kiln, with turbulence air off, the level of O_2 is markedly reduced, and the levels of CO_2, CO and CH_4 are increased. Carbon tetra-
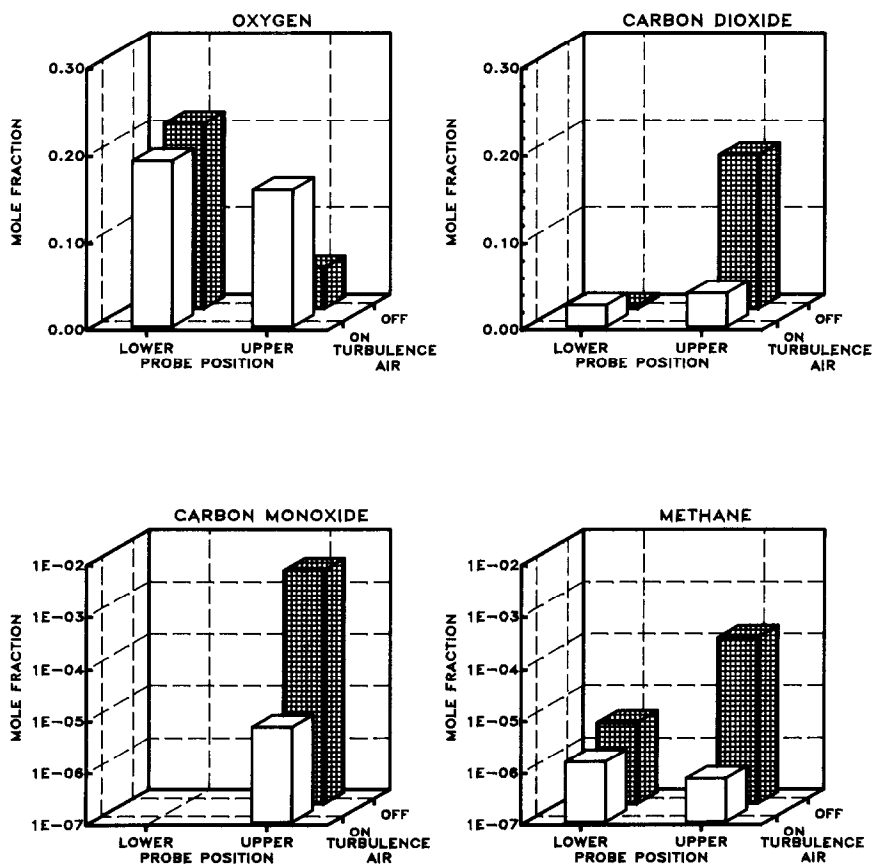

Fig. 1. Concentration of major stable species near the kiln-exit, showing the influence of sampling position and the activation of turbulence air. Reproduced with permission from [4].
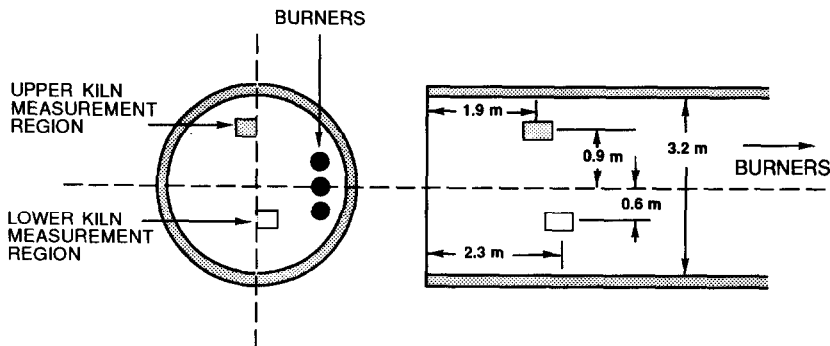
Fig. 2. Sampling locations near the kiln-exit used for the CCl_4 and $C_6H_5CH_3$ test results reported here. Reproduced with permission from reference [4].

chloride concentrations are below the detection limit in both the lower and upper regions of the kiln during turbulence air off operation. These results present a picture of the lower kiln, in the absence of turbulence air, as an un unreactive region dominated by combustion air and/or leak air. The upper kiln, on the other hand, appears to be a very reactive region. Recall that natural gas/CCl_4/air were fired from the upper burner but only natural gas/air were fired from the lower burner. The elevated level of CH_4 in the upper region suggests that CCl_4 quenched the methane combustion, as has been observed in related laboratory studies [5].

The activation of turbulence air reduces the concentration differences between the lower and upper regions of the kiln through bulk mixing. The appearance of CCl_4 at 1 ppm and 12 ppm in the lower and upper regions, respectively, indicates a reduction in CCl_4 destruction rates.

The concentration measurements are mirrored by temperature measurements, as shown in Fig. 3, where the probe temperatures are compared to temperatures measured by a fixed facility thermocouple located in the bulk gas flow region between the kiln and the afterburner. With respect to the fixed sensor, and with kiln turbulence air off, the temperature is reduced in the lower kiln and elevated in the upper kiln. Turbulence air, through elimination of thermal stratification, nearly eliminates these temperatures differences. The reduced temperature in the upper kiln explains the detection of CCl_4 in both the upper and lower kiln, i.e.,the reduced temperature reduces CCl_4 destruction rates.

Comparable results for bomb samples from the afterburner and the stack are shown in Fig. 4. Note that with the exception of CH_4, the effect of kiln turbulence air is greatly reduced. Recall that in the kiln, the highest concentrations of CH_4 were observed when the turbulence air was off. In contrast, no CH_4 was observed in the stack sample in the absence of turbulence air. One can also observe that the concentrations of the high-level gases in the after-
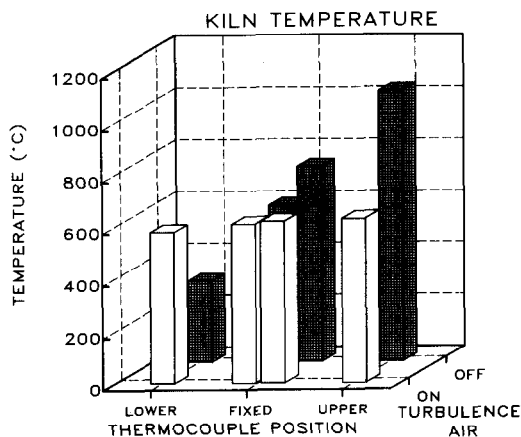
KILN TEMPERATURE

Fig. 3. Kiln temperatures measured by the probe thermocouple, showing the influence of probe location (see Fig. 2) and the activation of turbulence air. The middle towers give the temperatures measured by a fixed facility thermocouple. The leftmost towers correspond to the probe temperatures measured in the lower kiln and the rightmost correspond to the probe temperatures measured in the upper kiln. Reproduced with permission from [4].
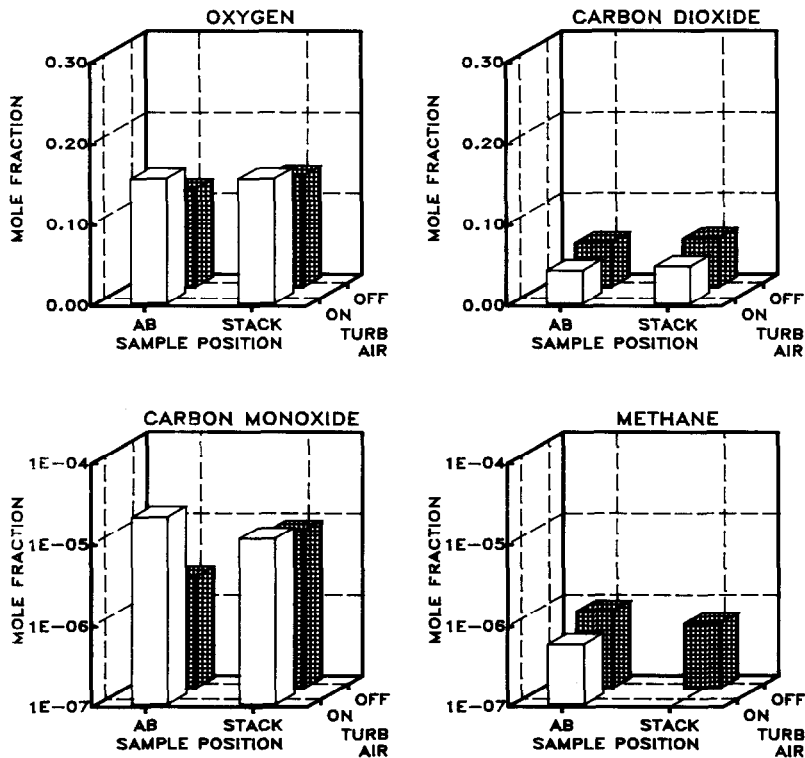

Fig. 4. Concentrations of major stable species in the afterburner and stack, showing the influence of the activation of turbulence air.
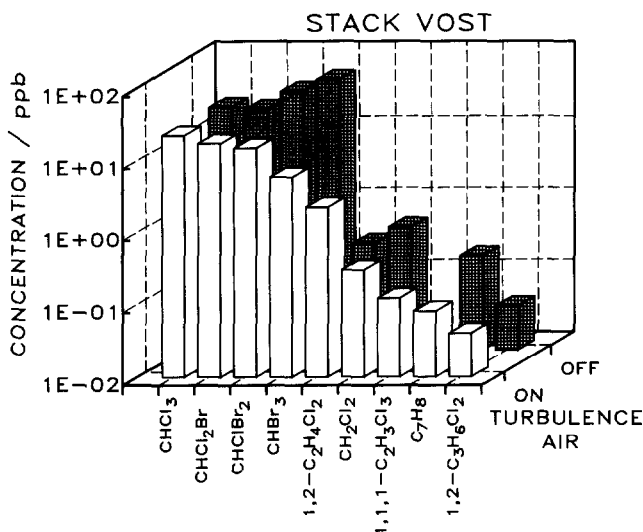
Fig. 5. Concentrations of minor stable species in stack VOST samples. Twelve compounds were detected; the nine most concentrated are shown here. Concentration is given in parts per billion (by volume).

burner show no simple systematic relationships to concentrations of the same gases measured locally in the kiln or to the average of the concentrations over the lower and upper sampling regions.

These results indicate that the pattern of temperature, concentration, and flow at the kiln exit does indeed affect afterburner and overall combustion performance, but that the effects are complex and as yet unkown. However, the large effects in the kiln, introduced by the activation of turbulence air, are smoothed and reduced by additional mixing and combustion in the afterburner.

Finally, volatile organic sampling train (VOST) measurements for low-level stable intermediates in the stack gas are shown in Fig. 5. Three of the measured compounds (C_6H_6, 1,1,2,2-$C_2H_2Cl_4$, and C_2HCl_3) were only detected in 1 of the 4 pairs obtained and hence are not presented in the figure. Note that CCl_4 was not observed at the detection level of 10 parts per trillion. The activation of turbulence air does not appear to systematically alter the concentrations of the compounds detected other than presenting the obvious diluting effect. The brominated and some of the chlorinated compounds are thought to be derived from the scrubber and quench water, which is drawn from the Mississippi river. In all cases, the measured destruction-and-removal efficiency (DRE) in the stack exceeded 99.99%.

Preliminary results for the toluene trial

For the toluene ($C_6H_5CH_3$) trial, 53-liter packs containing clay sorb (O_2SI montmorillonite clay, natural ground, kiln fired dried) and 19 liters of $C_6H_5CH_3$
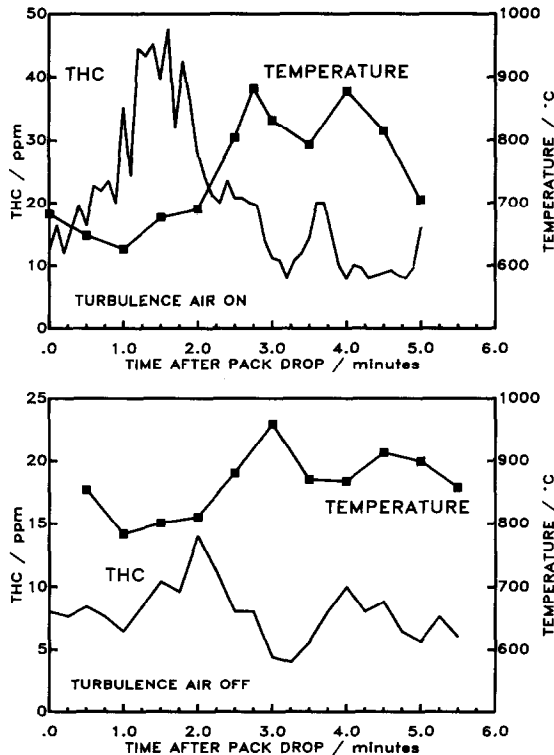
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Fig. 6. Temporal variations of temperature and total hydrocarbon concentration (THC) in the upper region of the kiln near the exit, with (upper) and without (lower) turbulence air activated. The solid lines connecting the temperature data points are intended only to show trends and to aid visualization. Reproduced with permission from [4].

(35 wt.%) were fed to the kiln in 5-minute intervals. For each of four packs, one sample was taken at progressive 30-second time intervals from 30 seconds up to two minutes. Samples were taken simultaneously from the upper region of the kiln near the exit (see Fig. 2) and from the afterburner.

For selected individual packs, the probe temperature was recorded at 30-second intervals for comparison to continuously recorded THC measurements. These results are shown in Fig. 6. With turbulence air both on and off, there is an initial decline in temperature, due to the pack loading procedure, followed by a rise to a peak at about three minutes, and a second peak at approximately four minutes. The THC measurement trends are roughly inverse to those of temperature. The effect of turbulence air is to accentuate the magnitude of the excursions, to reduce the temperature, and to elevate the THC level in the upper region of the kiln.

The peaks in the THC correspond to visual observations of luminous intensity in the kiln; periods of high THC correspond to a highly-luminous, particle-

laden flame that fills and totally obscures the kiln. Conversely, periods of low THC correspond to an elimination of kiln opacity. Kiln-simulator studies have shown that the first THC peak follows the initial decomposition of the pack and ignition of the $C_6H_5CH_3$ vapor. Eventually, the THCs are consumed in the flame and hence, the THC concentration decreases, and the measured temperature rises. These events are repeated as the kiln rotates and fresh bed surface is exposed.

Kiln-simulator sub-program

A comprehensive experimental program, using the pilot-scale facilities of the Chemical Engineering Department at the University of Utah, is being conducted by University of Utah and Louisiana State University (LSU) personnel. In particular, the experimental testing program is focussing on the evolution of selected components from within the pore structure of sorbent particles and the subsequent movement of the contaminant species through the particle and clumps of particles, ultimately to the surface of the kiln bed. This sub-program utilizes bench-scale equipment and also a unique kiln-simulator. The bench-scale programs and initial kiln simulator results have been discussed elsewhere [6–10]. This section of the paper presents recent results that were obtained from the kiln-simulator facility in direct support of the *in situ* field measurements sub-program discussed previously.

Overview

The overall goal of kiln-simulator study is to obtain data from an intermediate scale between the bench and full. Through careful interpretation, a greater understanding of the observed full-scale processes is being realized using the smaller, better controlled kiln-simulator device. In addition, these data are then being used to aid in the development and validation of mass transfer models.

The specific objectives of the kiln-simulator effort include:
• Helping to elucidate the complex phenomena observed in the full-scale testing.
• Evaluating the extent that kiln-simulators can be used to simulate full-scale rotary kiln incineration processes.
• Determining bed evolution rates. Rates are obtained from a controlled environment that approximates full-scale rotary kiln incinerators. Parametric studies are underway to determine the sensitivity of evolution rates to selected operational variables.

Pilot-scale rotary-kiln facility

The University of Utah rotary kiln-simulator is designed to characterize the processes that occur in a large-scale rotary-kiln incinerator. In particular, the system is configured so that the chemical composition and temperature of a

particular element of kiln charge can be followed as it moves through the kiln. Rotary kilns present a particularly difficult experimental scaling problem because of the radically different time constants associated with the overall process. The combustion reactions and molecular diffusion occur in a fraction of a second, the bulk-gas residence time may be fractional in minutes, and the solid-phase residence time may be as long as multiple hours. In the University of Utah rotary kiln-simulator, the travel of a given element of charge is translated into time. The simulator is, therefore, operated in a batch mode. By sampling the bed and product gas as a function of time, it is possible to follow the evolution and oxidation of material as it would occur during passage through an actual kiln. Details of the kiln facility have been given previously [7,10,11].

The 73 kW natural gas fired rotary kiln simulator is constructed in three refractory lined steel sections with the core of the main section sized at 0.61 m in diameter and 0.61 m long. A schematic of the kiln is shown in Fig. 7. The burner and main sections rotate from 0.5 to 2.0 rpm, and the exhaust section
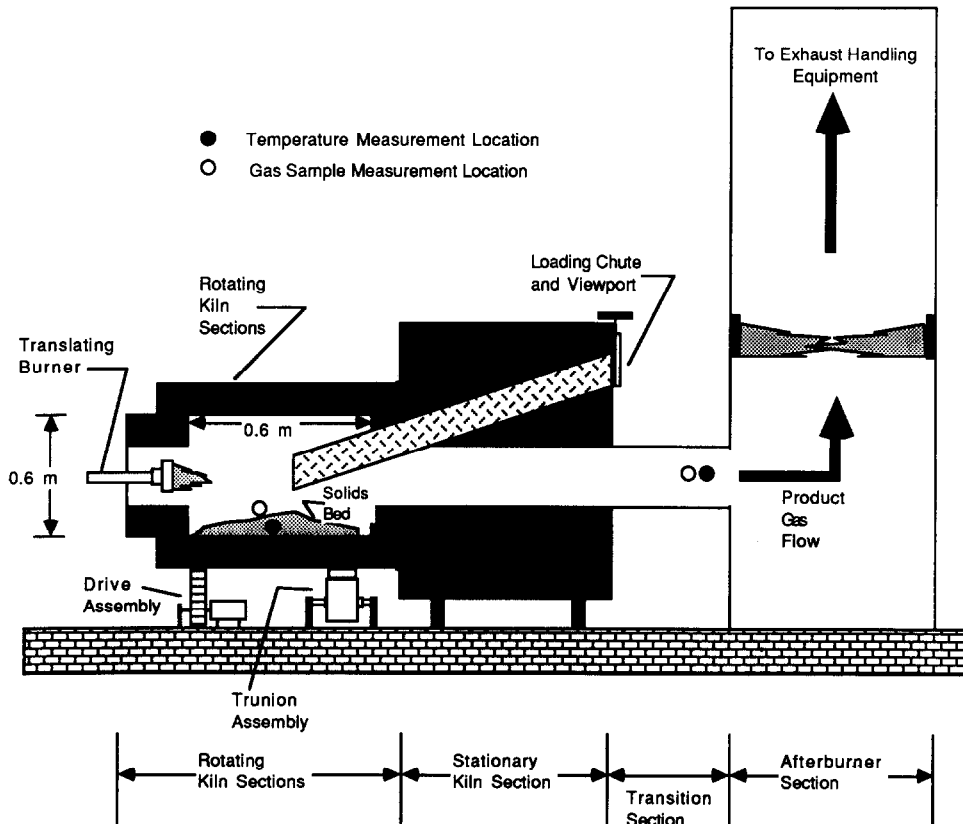
Fig. 7. The University of Utah rotary kiln-simulator.

remains stationary. A rear loading chute (a half pipe of 20 cm diameter) allows a charge of waste to be placed in the center of the main section of the kiln-simulator.

Batch samples of toluene-laden sorbent contained in large manila paper envelopes are used in this study (total charge size limited to 1.8 kg). The sorbent is identical to that used in the batch mode full-scale study discussed previously (test 5 in Tables 1 and 2). The toluene/sorbent mixtures are premixed to desired levels, loaded into the paper envelopes and introduced into the kiln. The kiln is operated typically at slightly sub-atmospheric pressures during loading. After charging, the loading chute is quickly retracted and a blast-gate valve, which serves as an airlock, is closed to prevent emission of combustion product gas into the laboratory. After passing through the exhaust section of the kiln, the combustion gases enter a transition section followed by an afterburner section, where further high-temperature gas processing occurs. Cooling coils maintain the rotary kiln shell, the transition shell and the afterburner shell at acceptable temperature levels.

Sampling system

Gas samples are obtained from within the rotary kiln-simulator and transition sections using quartz-lined sampling probes at the locations shown in Fig. 7. Continuous O_2, CO, CO_2, NO_x, and total hydrocarbon (THC) measurements are obtained by using a variety of dedicated instrumentation. In addition, sample gas is continuously withdrawn from the kiln transition section in a heated line and captured in a series of liquid impingers. Selected constituents are stripped from the gas stream and dissolved in the solvent, methylchloride (CH_3Cl). Gas chromatography/mass spectrometric (GC/MS) techniques are then used to determine a time-integrated measurement of constituent-breakthrough from the kiln and transition sections as shown in Fig. 7. A permanent visual record is also obtained for each series of experiments on VHS tape.

Kiln-simulator characterization studies

An objective of the initial testing program was to determine the appropriateness of this kiln-simulator as an aid in the study of full-scale rotary-kiln incinerator processes. The ability to make comparisons with the full-scale measurements sub-program, to the greatest extent possible, was highly desirable. To what extent such kiln-simulator devices accurately simulate full-scale processes has been an unanswered question. It is clear, however, that such facilities may represent valuable research tools if appropriate scaling can be achieved. Consider the data obtained from the full-scale, batch-load test (see Fig. 6, test 5 in Tables 1 and 2). Toluene evolution from the bed of the full-scale facility appears to be intermittent with distinct bursts superimposed on an otherwise declining evolution rate. Explaining this intermittent contaminant evolution behavior was very difficult based only on the full-scale data and

visual observations that were obtained. However, by accurately replicating the burst condition in the kiln-simulator a more complete picture of the full-scale processes is emerging.

An outline of the testing program that was conducted to characterize the kiln-simulator follows. Special attention is given to experimental reproducibility. Typical results obtained from the developed test program are then presented.

Initial characterization studies. The initial characterization work was primarily concerned in defining the test conditions which most closely simulate full-scale operation. Preliminary calculations indicate that simultaneous scaling of all important phenomena (bed motion, heat transfer, mass transfer, and chemical reactivity) was impossible. There are parameters, however, that can be accounted for.

From video tape data obtained during the *in situ* field testing sub-program, it was observed that the solids bed inside the full-scale facility exhibited a slumping motion (as compared to a sliding or rolling motion) during the test 5 run (see Tables 1 and 2). Bed motion studies performed in the Utah kiln-simulator demonstrated that a similar slumping motion could be realized over a wide range of kiln-simulator rotation rates and charge amounts.

Scaling of the heat transfer phenomena (primarily convection and radiation) based on mathematical modeling of both the full-scale and kiln-simulator resulted in the choice of a 1.8 kg total charge. Although the full-scale work was conducted with a toluene loading of 35 wt.%, the recent simulator-scale work was limited to a 10 wt.% toluene loading. This limitation results primarily from the severity of the initial toluene evolution burst that has, at times, resulted in loss of the kiln-simulator afterburner flames, due to intense soot formation and the subsequent activation of the afterburner flame shut-down detection system, when the 10 wt.% toluene loading is exceeded.

A series of "container" tests was conducted to establish the influence of container type. The contaminated solid was loaded into cylindrical cardboard containers, heavy manilla paper envelopes, and thin plastic bags. The cardboard containers affected bed motion considerably. This occurs because, even at high temperatures, complete decomposition of the container may not occur until well into the run. Bed motion and hence, bed evolution, can therefore be drastically affected by the unpredictable decomposition of this type of container. Although undesirable for obvious experimental reasons, we note that this type of bed behavior has also been noted at the full-scale during processing of plastic pack containers. The thin plastic bags, conversely, decompose quickly in the high-temperature, kiln environment. Their use was not pursued, however, because of safety problems that surfaced during the loading procedure. The plastic actually decomposed too quickly. Large manilla envelopes performed quite satisfactorily as containers for this study. When compared with

the thick cardboard containers, the envelopes readily decomposed in the high-temperature, kiln environment in a reproducible manner. In contrast to the plastic bags, the envelopes provided superior structural stability and thermal resistance, so that safety considerations were met during preparation and loading procedures.

An over-fire bed air rake was installed in the kiln to provide uniform flame structure and to enhance bulk mixing (similar to that afforded the full-scale rotary kiln during turbulence-air operation). The rake was situated so that air flows parallel to kiln rotation and directly over the bed of solids. Addition of kiln over-fire air stabilized the flame, resulting from the toluene evolution, in a repeatable location within the kiln, and results in repeatable evolution characteristics. Perturbations due to loading chute removal and other small differences in loading techniques were less pronounced using the over-fire air rake. Visual observations also dramatically improved by using the over-fire air rake. Final envelope orientation within the kiln remains an important parameter, even with the use of the kiln over-fire air. Achieving reproducible envelope orientations is possible, however, exercising care during the loading procedure.

Data reproducibility. Typical reproducibility data for this kiln-simulator are presented in Fig. 8, where the temporal O_2 profiles as measured in the transition section are shown. Oxygen profiles are representative of the other data
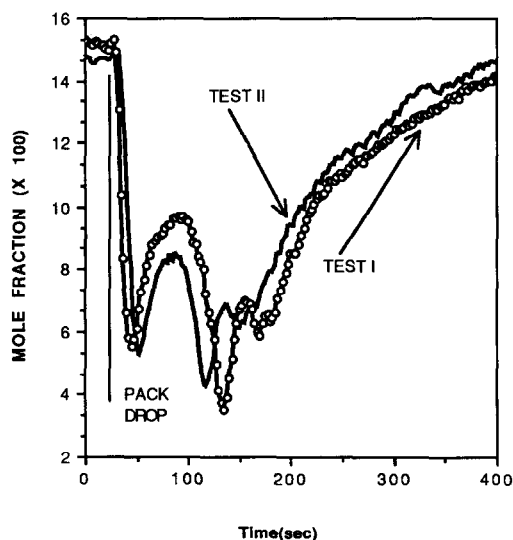

Fig. 8. Experimental reproducibility results for the kiln-simulator. Oxygen profiles for toluene-laden sorbent envelopes.

collected (CO, CO_2, etc.). The data presented are for sorbent (O_2SI montmo-rillonite clay, natural ground, kiln fired dried) contaminated with toluene (near the 10 wt.% level). The figure clearly demonstrates that, under carefully con-trolled experimental conditions, it is very reasonable to expect a high level of reproducibility in these experiments, even to the point of replicating the inter-mittent contaminant bursts noted in the full-scale studies. Such experimental precision is required since toluene evolution cannot be directly measured under the flame-mode conditions of this study and therefore must be inferred from other measured parameters (O_2, CO_2, CO, etc.).

Test matrix. Although a number of study parameters exist, two important test variables were targeted: kiln-simulator bulk temperature (as measured in the transition section – see Fig. 7) and kiln-simulator rotation rate. Tests were conducted at kiln-simulator rotation rates of 0.08, 0.3, 0.7 and 1.1 rpm, and bulk temperatures of 621, 677 and 732°C. All tests were conducted with tol-uene-laden sorbent charges. The initial excess kiln O_2, as measured at the tran-sition section (Fig. 7) was held constant (to the greatest extent possible) at 15 vol.% (dry basis). Flame-mode processing occurred during all of the tests except during excessive bed evolution periods (selected bursting events) when the kiln O_2 availability was suppressed and flame extinction resulted.

Kiln-simulator results

The data presented were obtained during eight experiments that were con-ducted at two kiln-simulator bulk temperatures (621 and 732°C) and four rotation rates each, as specified above. The over-fire air rake flow remained constant at 0.10 m^3/s. Profiles of the bulk O_2 and CO (as measured on a dry volume basis from the transition section – see Fig. 7) are shown in Figs. 9 and 10. Concentrations of benzene (C_6H_6) and toluene ($C_6H_5CH_3$) collected from the impinger trap are shown in Fig. 11.

Before discussing the specific results shown in the figures, a generic descrip-tion of a typical run is presented. After loading into the kiln-simulator, the manilla envelope decomposes. This may occur within 5–15 s, depending upon temperature and kiln-simulator rotation rate. Usually, the envelope ignites on the upper, exposed surface. As the envelope decomposes, the bed forms, filling the lower part of the kiln-simulator. The time for bed formation to occur is dependent upon the rotation rate of the kiln-simulator and varies from 10–60 s. As the envelope decomposes and the bed is exposed to the kiln environment, toluene evolves from the exposed surface in continuously declining manner with periodic bursts, corresponding to the bed slumping motion and the ex-posure of fresh bed surface, superimposed on the overall declining evolution rate. The toluene mixes with available O_2 and, at the temperatures of this study, ignites. Depending upon rotation rate, the evolution rate may over-whelm the ability of the kiln to supply oxygen, and flame extinction may result.
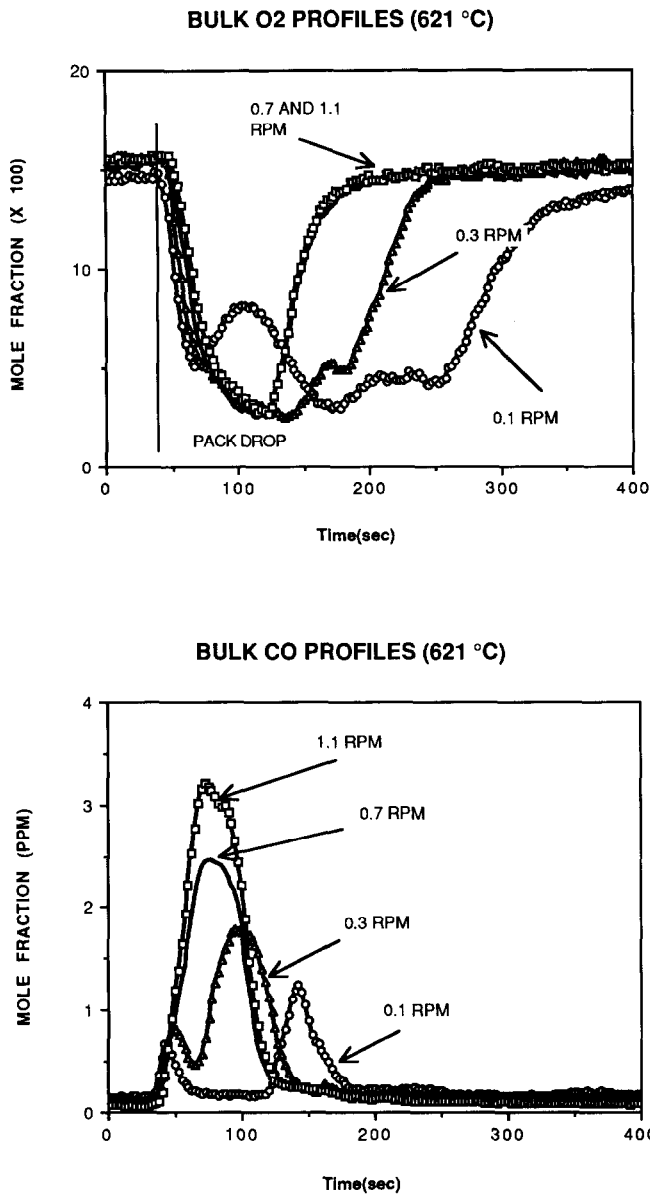
BULK O2 PROFILES (621 °C)

BULK CO PROFILES (621 °C)

Fig. 9. Continuous O_2 and CO variation versus kiln rotation rate for toluene-laden sorbent run at 621°C.

Heavy sooting generally occurs during and immediately before flame extinction. As the toluene evolution rate declines, the local O_2 availability increases and flames may again occur. Exposure of new bed surface, depending upon bed

BULK O2 PROFILES (732 °C)

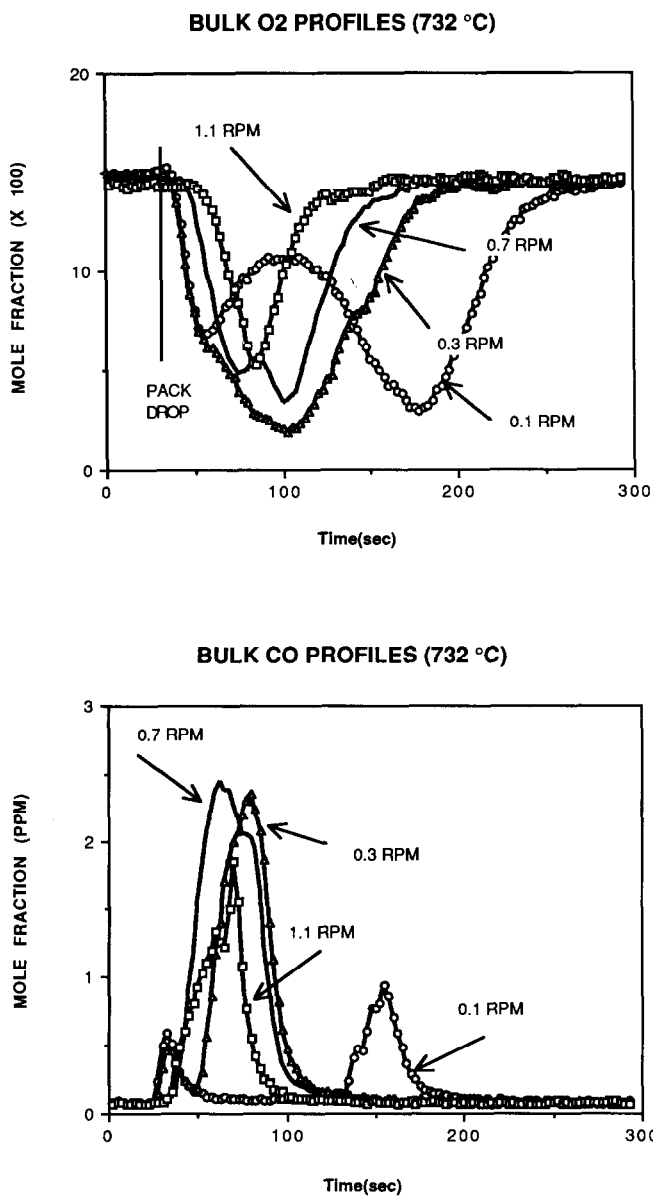

BULK CO PROFILES (732 °C)

Fig. 10. Continuous O_2 and CO variation versus kiln rotation for toluene-laden sorbent run at 732°C.

motion as influenced by rotation rate, may result in intermittent bursts of toluene and hence intermittent flames, as the overall toluene evolution rate decreases throughout the experimental time period.

The O_2 traces shown in Figs. 9 and 10 are an indicator of toluene evolution in the kiln during burning periods – not during intermittent burst conditions when there is insufficient O_2 to support flame-mode combustion. The CO trace is an indicator of the kiln's failure to provide sufficient O_2 for complete combustion during high toluene evolution rates. The impinger trap results (Fig. 11) provide a relative comparison of species breakthrough at the kiln exit during the entire evolution event.

The data show a general trend that increasing rotation rate leads to faster toluene evolution, as inferred from the O_2 and CO curves. This is clearest in the 621 °C data of Figs. 9 and 10. The CO trace implies that the overload becomes more intense (higher peaks) for higher rotations. The O_2 trace supports this inference by demonstrating a longer interval of moderate O_2 suppression for low rotation rates and much briefer suppression periods for higher rotation rates. Visual data support this also.

An exception to this general trend is observed in the 732 °C data. The CO trace shows a slight decrease in overload intensity at the highest rotation rate (compare the 1.1 rpm and 0.7 rpm runs). An initial hypothesis to explain this behavior is that the evolution rate is limited by surface heat up which, in turn, is influenced by rotation rate, bulk temperature, and soot production. At higher rotation rates, new surfaces are exposed for shorter periods between slumps. The fresh surface may be buried before it has been adequately heated, resulting in incomplete evolution while particles are exposed to the surface. Also at higher temperatures and rotation rates, the production of soot increases, resulting in radiation shielding for the bed surface. The overall results would be a lower initial evolution rate controlled by bulk temperature of the bed. Unfortunately this hypothesis does not explain why the phenomenon is absent in the 621 °C tests. Further experiments will be necessary to determine if the trend is real (as opposed to an experimental artifact) and, if real, the cause of this unexpected behavior.

Another observation can be made regarding the presence of multiple evolution events. These are most evident in the CO data for both temperatures presented. For low rotation settings there are two CO spikes separated by a substantial time interval. These peaks correspond to visual observations of the container breaking down, solids spilling out, and the initiation of the solids slumping motion. When a container is loaded into the kiln, it lands in the bottom center of the kiln floor, ignites, and exposes a pile of solids. At low rotation rates, a substantial period of time passes before the portion of the kiln wall in contact with the solids inclines enough to initiate slumping and the exposure of fresh surface, resulting in a second evolution burst. Increasing the rotation rate decreases the slumping delay and causes the two peaks to converge together until they are indistinguishable.

The concentrations of benzene and toluene captured in the impinger trap are shown in Fig. 11. These measurements provide an indication of relative

Toluene and Benzene (621 °C)

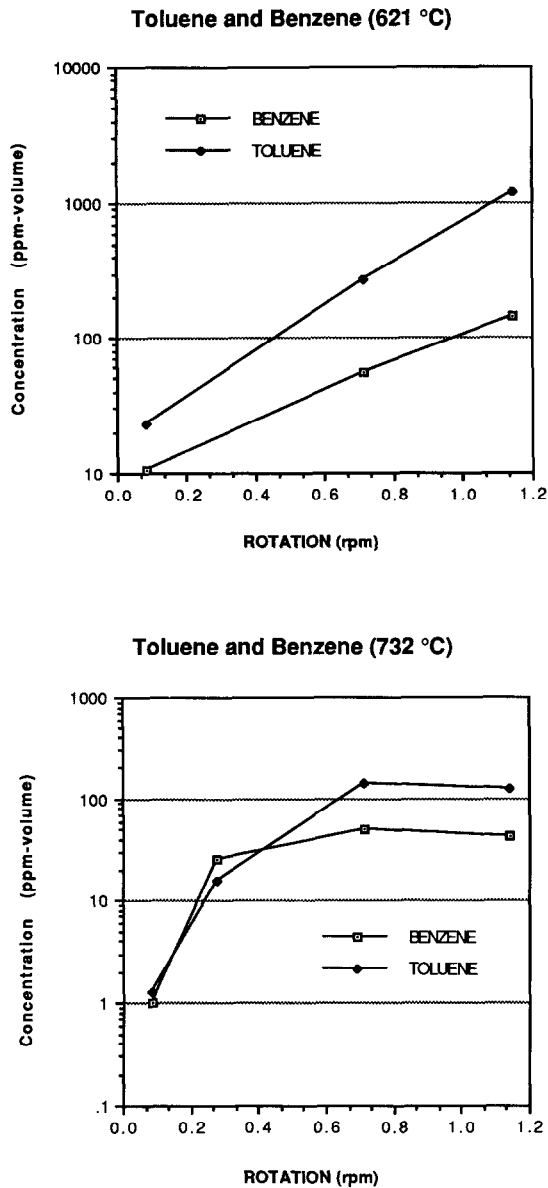**Toluene and Benzene (732 °C)**

Fig. 11. Toluene and benzene variation versus kiln rotation rate for toluene-laden sorbent runs at 621 °C and 732 °C obtained from the impinger train.

total integrated breakthrough of each species at the kiln exit. For brevity, only benzene and toluene have been included. However, similar data have been obtained for up to 7 other aromatic species (phenylacetylene, styrene, benzal-

dehyde, indene, and naphthalene). The toluene and benzene data corroborate the CO data. As the rotation rate increases, more waste is evolved than can be combusted and products of incomplete combustion, and even the waste, are observed to break through in increasing amounts. The data also show the unexpected decrease in overload magnitude at the highest rotation rate during the 732°C run.

The experimental results obtained demonstrate the utility of the kiln-simulator in helping to understand processes occurring at the full-scale. The influence of kiln rotation rate (hence, bed motion) on the evolution characteristics of this sorbent-contaminant matrix has been demonstrated. The intermittent bursting evolution behavior observed at the full-scale has been, at least in part, explained through careful interpretation at the kiln-simulator scale and is thought to arise primarily from bed motion. The kiln rotation causes the exposure of new bed surface which produces intermittent bursts of toluene.

The experimental results also show that increasing the rotation rate leads to faster toluene evolution. High rotation speeds can result in large peak CO and unburned hydrocarbon emissions from the kiln-simulator if the evolution rate is large enough that the resulting gas-phase combustion consumes all of the locally available oxygen. Benzene and 7 other aromatic hydrocarbons were found as products of incomplete toluene combustion (PIC's). Increasing kiln temperature had little effect on either the time delay before the peak evolution rate or the magnitude of the resulting peak CO concentrations.

Rotary-kiln numerical modeling – an overview

The long range objective of the modeling sub-program is to develop a predictive capability, based on fundamental considerations, for full-scale industrial rotary kilns. In view of the complex physical and chemical processes that account for the destruction of hazardous waste in a rotary kiln, the modeling effort has been subdivided initially into three major categories. These are:

- Modeling category 1: Three-dimensional (3-D) reactive flow-field simulation,
- Modeling category 2: Determination of suitable chemistry, and
- Modeling category 3: Modeling of the waste bed dynamics.

These categories describe the major phenomenological processes that occur in the kiln and, following successful completion, can be combined to yield a comprehensive computer code for the entire kiln incineration process. The first two categories are being are being investigated at LSU while the third is being pursued at the University of Utah.

A brief summary of the recent progress in each of the three categories is

discussed next. Additional details can be found in Morse [12], Miller et al. [13], Jang and Acharya [14], and Silcox and Pershing [15].

Modeling category 1: 3-D reactive flow-field simulation

A two-dimensional model (2-D) that incorporates turbulence, radiant and convective heat transfer, and global chemistry for chlorinated hydrocarbon combustion was developed initially to test basic assumptions, particularly those dealing with the chemical kinetics of chlorinated hydrocarbons. Since the chemistry of chlorinated hydrocarbons is not well understood, the 2-D model served as an expedient vehicle to examine several proposed kinetic schemes. It was also hoped that the 2-D results would provide qualitatively correct results that would be sufficient to guide future experimental work, and would allow some numerical experimentation without the consumption of vast quantities of computing time.

The idealized 2-D problem was visualized as a cross-sectional representation of a kiln with the principal differences being that both burners were assumed to be located on the symmetry plane of the kiln, not off-center as they are in the Dow facility. Since the principal difficulty has been the lack of a suitable kinetic model for CCl_4 destruction in a natural gas flame, initial calculations with the 2-D model were performed to focus on the kinetic model development.

As a first step, a model was developed, based on the assumption that the destruction rate of CCl_4 can be related directly to the destruction rate of CH_4 as follows:

$$d[CCl_4]/dt = (R \times M_{CCl_4}/M_{CH_4}) \, d[CH_4]/dt \qquad (1)$$

where R is the molar ratio of chlorine to hydrogen, and M is the molecular weight. The destruction rate of methane, $d[CH_4]/dt$ is obtained from the well-known mixing-limited eddy break-up model of Maghnussen and Hjertager [16]. Since, in this model, the reaction rate of CCl_4 is linked to an eddy break-up relation, it is assumed implicitly that the CCl_4 reactions are fast and that the kinetics are not important. Simple laboratory scale experiments of Valerias [17], Glassman [18] and Morse [12], however, indicate that kinetics are, in fact, important. Thus, it was expected that the destruction of CCl_4 would be over-predicted by this fast chemistry model, since the finite rate kinetics will "slow down" the destruction of CCl_4. Actual implementation of this model confirmed this. However, the CCl_4 destruction rate was predicted to be too fast with this underlying assumption and therefore this kinetic scheme was abandoned. Thus, a more realistic finite rate model for CCl_4 destruction is required.

The second kinetic model that was tested relied upon the assumption that the reaction rate is proportional to the square of the flame burning velocity, and therefore, actual flame data can be used to obtain an empirical relationship for the destruction rate of CCl_4 in a $CCl_4/CH_4/air$ flame in terms of $d[CH_4]/dt$ and the measured burning velocities in a CH_4 flame and in a $CCl_4/CH_4/air$

flame. In the present work, the burning velocity data of Valerias [17] were employed. Predictions with the second model appeared to be intuitively correct for a 2-D configuration, but differed considerably from the values measured in the actual (3-D) facility.

At this point, video tapes of the flames inside the full-scale rotary kiln were obtained, and it became apparent that the flow was highly 3-D in character, and that buoyancy had an important effect on the flow field. Therefore, initial expectations that the 2-D predictions would provide a qualitatively correct picture of the rotary kiln and would provide guidance to future experimental work appeared to be overly optimistic. Additional details of the 2-D predictions are given in Jang and Acharya [14].

Since a complete 3-D simulation of the reacting flow field appears to be necessary for realistic predictions, a 3-D code has been developed for this particular full-scale rotary-kiln incinerator. As a first step, the code was developed and tested for a laminar, isothermal flow by using the geometry of the actual facility. The code has been extended to include the effects of turbulence and radiation heat transfer. The next step is to include more realistic models for chlorinated hydrocarbon chemistry to describe the burning of CCl_4 in the CCl_4/CH_4/air flames in the kiln and to incorporate models for describing the bed behaviour including the dynamic mixing process in the bed, evolution and burning of the bed volatiles, and heterogeneous burning at the bed surface. These models are currently under development in companion effort, and are described next.

Modeling category 2: Determination of suitable chlorinated hydrocarbon chemistry

As noted earlier, more realistic chlorinated hydrocarbon chemistry is required to model the CCl_4/CH_4/air flame in the rotary kiln. Over the past several years, a considerable amount of work has been done at LSU toward this effort and considerable strides have been made in understanding the kinetics of chlorinated hydrocarbon combustion in laminar flat flames. Currently two routes to the development of simple, flame-based chemistry are being undertaken. First, the CCl_4/CH_4/air flame data of Morse [12] are being used to deduce a global, empirical single-step reaction model for CCl_4 destruction. Details of the method are given by Morse [12]. Basically, the flame profiles for CCl_4 and other major species are corrected for bulk diffusion of species in the flame, and the net reaction rates are deduced from the corrected profiles. Thus, a one reaction fit of the form

$$d[CCl_4]/dt = -k \exp(-E/RT)[CCl_4]^a[CH_4]^b[O_2]^c \qquad (2)$$

can be obtained where R denotes the gas constant, T the reaction temperature and k, E, a, b and c are empirical constants that are inferred from the net

reaction rate analysis. Clearly, this is simplistic, but it is believed that this form of the reaction rate expression will, at the very least, provide more realistic predictions for the destruction of CCl_4 than the two models described earlier with either infinitely fast kinetics or pseudo-kinetics based on laminar flame speeds.

A more rigorous approach is also being pursued with a flat flame computer model and detailed kinetic mechanism. The computer model iteratively solves the time-dependent equations until the steady state solution is asymptotically reached. From the detailed mechanism, a sensitivity analysis is used to identify the most important elementary reactions, and a reduced kinetic set is developed. This is an important goal since, compared to a detailed kinetic mechanism, a reduced set of equations is more amenable for incorporation into a 3-D turbulent reactive flow-field code. Considerable success has been achieved in modeling two $CCl_4/CH_4/air$ flames with Cl/H ratios of approximately 0.33. Details of this activity have been provided by Miller et al. [13]. As noted earlier, the development of a reduced set of equations is of critical importance. Based on the reaction-rate analysis results for the chlorinated hydrocarbon flames studied in the LSU flame laboratory, a preliminary quasi-global reaction mechanism has also been developed. The mechanism contains twenty-one reactions and nineteen chemical species. Although considerably more complex than the global one-step model, the reduced mechanism of 21 reactions offers some hope of being useful in a comprehensive incinerator code.

Modeling category 3: Modeling of the waste bed dynamics

The third component of the modeling studies is the kiln bed model which is being pursued at the University of Utah. The overall approach to bed modeling is summarized in Fig. 12. There are two submodels under development; a static

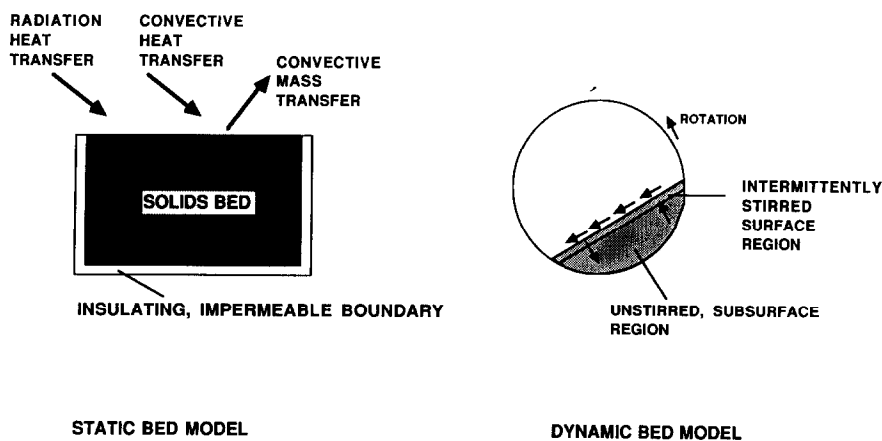STATIC BED MODEL   DYNAMIC BED MODEL

Fig. 12. Schematic of the overall approach to kiln bed modeling including static and dynamic compartments.

bed model and a dynamic bed model. The static bed model is 1-D in nature, describing the heat and mass transfer in a static bed of solid particles. This submodel includes heat transfer to the bed by radiation and convection, and mass transfer through the bed by diffusion and from the bed by convection. The governing equations for the static bed include a mass balance on individual particles, a mass balance on the bed, and an energy balance on the bed. The equations are solved simultaneously to predict the evolution rate from the bed.

Modeling for the dynamic bed just recently has started focussing on the complex slumping behavior of the bed. The bed behavior is represented by a two-compartment model that includes an intermittently stirred (dynamic) surface compartment and an un-stirred (static) subsurface compartment as shown in Fig. 12. The subsurface compartment feeds material to and receives material from the surface compartment in a circulating fashion. Considerable guidance will be obtained from the kiln-simulator and laboratory experiments as this model develops.

Two radiation heat-transfer models have been developed for use in the bed submodels. The first is a simple transient bed heating model that was developed in support of kiln-simulator studies, This model assumes that the gas and wall temperatures are uniform and known and that the bed can be treated by using a lumped capacity method. Heat transfer coefficients between the wall and the bed, and between the gas and the bed are estimated from Tscheng and Watkinson [19]. In addition to the transient model, a steady-state model, for non-isothermal kilns, is under development. This model is an extension of the work of Gorog et al. [20,21]. Here, the kiln is divided axially into zones. The different surfaces within a zone are characterized by their individual, isothermal temperatures. There are no radial temperature gradients in the gas or flame, although the flame and the gas surrounding it are at different temperatures. Radiation is permitted between the surfaces of immediately adjacent adjacent zones. The flame is also allowed to radiate to immediately adjacent zones. The highly non-linear equations that result from the energy balances are solved by successive substitution.

Closure

This study has been ongoing for three years. The work, funded by the U.S. EPA, involves the Louisiana State University, The University of Utah, and the Louisiana Division of Dow Chemical USA. The focal point of the research program has been the unique opportunity to probe the flame zones of an industrial rotary kiln incinerator to extract both temperature information and stable species concentrations as a function of position and operating conditions. Coupled with this has been laboratory work in small scale apparatus at Louisiana State University and the University of Utah and the development of a realistic computer code to model the physical and chemical phenomena

important to the destruction of hazardous waste in a rotary kiln. The end objective of the multifaceted project is the development of a rudimentary predictive capability, based on first principles, for the destruction of hazardous wastes, especially chlorinated hydrocarbons, in the complex environment of a rotary kiln. With such a predictive tool, it may be possible to assist industry in the design of rotary kiln incinerators that will not only exceed the operational capabilities of current units, but be more economical to operate. To date, no such capability exists.

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