Operating Parameters to Minimize Emissions During Rotary Kiln Emergency Safety Vent Openings

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ABSTRACT

Certain designs of hazardous waste incinerator systems include emergency safety vents (ESVs). ESVs (also called dump stacks, vent stacks, emergency by-pass stacks, thermal relief valves, and pressure relief valves) are regarded as true emergency devices. Their purpose is to vent combustion gases directly from the combustion chambers to the atmosphere in the event of a failure of other system components. This is done for operator safety as well as to protect the incinerator and other downstream equipment from damage. ESVs are typically required for rotary kiln and hearth incinerators which process a portion of their waste load as bulk solids or contained liquids introduced continuously or in batch charges. Research has been performed at the U.S. EPA on a 73 kW (250,000 Btu/hr) rotary kiln incinerator simulator examining optimum settings of kiln operating parameters so as to minimize emissions during an ESV opening event. Experimental results are interpreted in the light of previous research results on transient "puffs." Mechanisms governing both the release of volatile matter during an ESV event and the subsequent pyrolysis and oxidation in the residual sorbent bed are identified. From a practical point of view, results indicate that alteration of operator-controllable kiln parameters during the onset of certain ESV opening events can have a significant effect on emissions of both organics and hydrogen chloride (HCl). A low air flow rate results in lower emissions of both organics and HCl. This hypothetical low air flow rate could possibly be equal to the flow rate induced by the natural draft coupled with air in-leakage. Rotational speed (RPM) appears to have slightly different effects on organics and HCl. Whereas emissions of HCl are minimized at a very low or non-existent RPM, emissions of organics exhibit a minimum at a low (but non-zero) RPM, with increasing emissions at both zero and high RPM. The use of a small afterburner to simulate an in-stack flare during an ESV event dramatically reduced organic emissions.

INTRODUCTION

In July 1990 a joint Environmental Protection Agency (EPA)/Occupational Safety and Health Administration (OSHA) task force was established to evaluate worker health and safety compliance at

select hazardous waste incineration facilities nationwide. Joint, unannounced inspections were conducted at 29 of the approximately 140 operating hazardous waste incinerators. These inspections focused on determining compliance with worker health and safety training requirements, accident prevention and emergency response requirements, potential worker exposure, and compliance with operational permits. The EPA/OSHA report (1) identified a number of violations of the standards and regulations, and noted the occurrence of a "significant number of waste feed cut-offs and emergency by-pass openings" at several of the facilities. One facility in particular reported 867 ESV events in a 6 month period. The report recommended that additional assessment of the cause and impact of waste feed cut-off and by-pass opening events be conducted. This recommendation was modified by the Agency's Hazardous Waste Incineration Permit Writers Working Group to include research examining the effect of incinerator operating parameters on the magnitude of organic and inorganic emissions during emergency safety (by-pass) vent (ESV) openings.

All hazardous waste incineration facilities must, as a condition of their Resource Conservation and Recovery Act (RCRA) permit, maintain automatic waste feed cut-off (AWFCO) control systems that stop waste feed to the incinerator whenever one or more continuously measured (or calculated) system variables drifts outside operating ranges specified by the permit. These system variables include combustion chamber temperatures, combustion gas flow rates or velocities, waste feed rates, and carbon monoxide emissions. AWFCO control systems are intended to prevent waste feed to the incinerator except during optimum conditions for its destruction. However, the EPA/OSHA report noted that several facilities routinely operate at conditions sufficiently close to their permit limits so that small variations in the system variables cause numerous AWFCOs. This is a concern because these frequent system upsets may increase emissions. Good combustion practice recommends continuous, steady-state operation to minimize emissions.

While all hazardous waste incinerators must include AWFCO control systems, only a subset include emergency safety vents (ESVs). ESVs are not usually required for liquid injection incinerators or other types of incinerators in which waste combustion stops almost immediately after waste feed is stopped. However, ESVs are common and typically required for rotary kiln and hearth incinerators which process a portion of their waste load as bulk solids or contained liquids introduced continuously or in batch charges (1). Waste in these types of incinerators may continue to be evolved from the solid phase inside the combustor and may burn for some time even after other waste and fuel streams have been shut off; for this reason, provisions are made to vent these gases in the event of an emergency. Unlike AWFCO control systems, ESVs (also called dump stacks, vent stacks, emergency by-pass stacks, thermal relief valves, and pressure relief valves) are regarded as true emergency devices. Their purpose is to vent combustion gases directly from the combustion chambers to the atmosphere in the event of a failure of other system components and should only be used under emergency conditions. This is done for operator safety as well as to protect the incinerator and other downstream equipment from damage. However, ESVs are typically located prior to air pollution control devices (APCDs); therefore, their emissions may contain large concentrations of acid gases, particulates, and toxic metals. Furthermore, the system upset and accompanying AWFCO which lead to any ESV event disrupt the primary flame and air flows and may produce poor combustion environments that are non-conducive to adequate organic destruction.

Rotary kilns represent one of the most common hazardous waste incinerator designs (2), and are uniquely versatile in that they allow solid and "containerized" liquid wastes to be charged in batch mode. Once inside the kiln, these solid wastes rapidly release volatile components into the gas phase where they react with the excess oxygen supplied from the kiln's combustion air sources. This rapid volatilization associated with the intermittent batch charge mode causes temperature and pressure excursions within the kiln as well as increases in the carbon monoxide, hydrocarbon, and particulate (soot) emissions. This phenomenon has been termed "puffing" and has been identified at sub scale and full scale by a number of research groups (3, 4, 5, 6, 7, 8, 9, 10). Under conditions where these normal puffing phenomena cause permit limitations to be exceeded, waste feed is automatically cut off until such time as all permit conditions are satisfied. However, as mentioned previously, AWFCO applies only to waste that hasn't yet been fed into the incinerator. ESVs may be activated during situations of poor operation which result in extreme conditions of high temperature or pressure and

which activate safety protocols designed for worker safety and protection of the kiln, afterburner, and APCDs from damage. This type of failure may be the result of feeding too much waste, a highly volatile waste, or a poor combination of wastes in individual charges. More often, however, ESV openings are the result of situations outside the operator's control including: loss of induced draft fan, loss of utilities (water, electricity), or failure of critical control circuits (11). However, the possibility of many of these contingencies may be minimized through improved design and engineering modifications and incorporation of redundant systems.

ESVs are typically short refractory-lined steel stacks containing closure devices that are normally closed. These closure devices may consist of a hinged lid with counterweight, a spring loaded lid, a rupture disk, or hydraulic, pneumatic, or electrical operating valves tied into control circuitry. ESVs are typically located near the exit of the secondary combustion chamber prior to the APCD inlet. However, some systems have them located at the primary combustion chamber (kiln) exit, before the secondary combustion chamber inlet. In the event of an ESV opening, even though the waste and auxiliary fuel burners are shut down, the waste remaining in the incinerator will undergo combustion and/or pyrolysis, with any oxygen supplied by air in-leakage due to the natural draft through the system. Draft is determined by stack dimensions, temperature gradient between the air inlet points and the exit of the ESV, and the size of the gaps in the system which allow in-leakage of air. This draft prevents the accumulation of potentially explosive gases within the combustion chambers, minimizes fugitive emissions from operator access areas, and diverts hot combustion gases to the atmosphere away from the APCD, thereby preventing equipment damage or operator injury. It also allows limited combustion to continue using air flow from natural draft. These vented gases may contain high concentrations of acid gases, particulates, toxic metals, undestroyed organics, and products of incomplete combustion (PICs).

Short of requiring secondary treatment of these gases, it is unlikely that any operational modifications would totally prevent the release of the acid gases, inorganic particulates, and toxic metals. A major argument against requiring installation of flue gas cleaning equipment on an ESV is that it would defeat the purpose of the ESV as an emergency device. APCDs typically impose a significant pressure drop on the combustion gas stream, requiring induced draft (ID) fans to pull the gases through the APCD. In the event of an ESV opening, though, gases must be allowed fairly unrestricted access to the atmosphere in order to prevent safety problems, and the assumption that electricity will be present with which to operate the ID fans may not be valid. Another potential option is to spray water into the primary chamber to immediately quench all reactions in the event of an ESV opening. This option is not attractive either, since the resulting thermal shock could cause significant damage to the firebrick in the kiln.

Ideally, it may be possible, through simple operational modifications, to minimize the emissions of undestroyed organics, PICs, and organic particulates, and delay the rate of release of the acid gases and inorganic species, and thus their stack concentrations (thereby reducing dispersion), and promote toxic metal retention in the kiln ash, while not increasing risk to workers or damaging any equipment. It should be noted, however, that all operating parameters may not be controllable during all ESV events, such as those due to power outages.

Research has been performed at the U.S. EPA on a 73 kW (250,000 Btu/hr) rotary kiln incinerator simulator (RKIS) to address ESV issues related to rotary kiln incinerators. Specifically, this research examined optimum settings of kiln operating parameters so as to minimize emissions of PICs and HCl during a simulated ESV opening event (metals emissions were not within the scope of this project). Questions addressed by this research include:

1. Can emissions be reduced through changes in kiln rotation speed?

2. How are emissions dependent on the amount of air flow induced through the kiln by natural draft or auxiliary induced draft fans?

3. What are the advantages of using an emergency flare (firing non-hazardous auxiliary fuels) located near the ESV opening, to reduce emissions of organics?

These questions were posed, based on previous research experience on factors that influence the transient emissions of "puffs" during the batch incineration of containerized liquid wastes bound on sorbents (3, 4, 12, 13, 14, 15).

EXPERIMENTAL

Apparatus

The EPA RKIS has been described in detail previously (3, 4). It has been established that the 73 kW (250,000 Btu/hr) pilot-scale simulator exhibits the salient features of full-scale units with thermal ratings 20 to 40 times larger. The simulator matches the volumetric heat release, gas-phase residence time, and temperature profile of many full-scale units, and yet is flexible enough to allow parametric testing. A schematic drawing of the simulator is presented in FIGURE 1. Batch charges are introduced via a manually operated charging chute. A small afterburner consisting of an Eclipse model 51.5 MVTA (43.8 kW; 150,000 Btu/hr) is mounted at the base of the secondary combustion chamber. Although it was recessed and allowed only minimal contacting between the flare and the kiln effluent, this simulated an emergency flare mounted near the ESV opening. While operated during these tests, the simulated flare was lit prior to the introduction of the waste in the kiln, and kept on for the duration of the simulated ESV event.

The effluent from the RKIS (and all other research combustors at the RTP site) is ducted into a dedicated flue gas cleaning system (FGCS) consisting of a 1.1 MW (4,000,000 Btu/hr) afterburner,
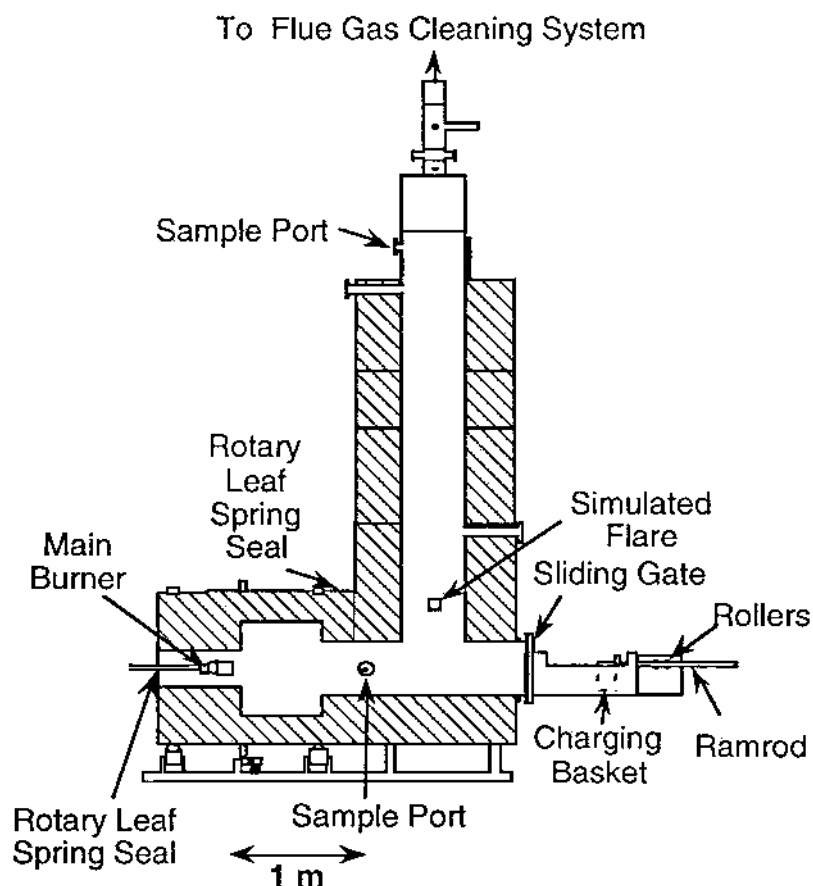

FIGURE 1. Rotary kiln incinerator simulator.

followed by a spray quench, baghouse, and wet scrubber. The presence of the FGCS enables extremely flexible operation of EPA's research combustors such as the RKIS, including simulations of extreme system failures (such as ESV opening events) without venting pollutants into the atmosphere. For all tests, the FGCS is only a cleanup system; measurements for this study were all made prior to the gases entry to the FGCS.

Measurements made on the RKIS are not intended to be directly extrapolated to full-scale units. It is, for example, very difficult to scale up some of the important gas-phase mixing phenomena from the simulator, where, for instance, stratification is not a factor, to a full scale unit, where stratification is known to be significant (7). The purpose of the simulator is to individually examine the fundamental phenomena that occur in full-scale units, and to gain an understanding of the qualitative trends that would be found in a full-scale rotary kiln. In no way should it be inferred that the concentrations of pollutants from this apparatus would be the same as those from full-scale units.

Approach

A response-surface experimental design (16) was used to reduce the number of tests required. This methodology permits determination, on the basis of one experiment involving a minimal number of trials, of an empirical relationship between the response (dependent) and the controlled (independent) variables in the experimental design. Data on the dependent variables are collected at low, intermediate, and high settings of the independent variables. The primary variables of interest (both dependent and independent) are listed in TABLE 1. Due to the fact that more than one independent variable is changed for each trial, the use of a response-surface experimental design does not easily allow the creation of two dimensional plots using actual data. The result is that data from all trials are used together in a regression analysis. Two dimensional plots may then be created from the regression model by examining the effect of varying one independent variable while holding all others constant.

TABLE 1. Variables of Interest.

Independent	
	Kiln Rotation Speed (RPM)
	Kiln Air Flow
	Presence/Absence of Simulated Flare
Dependent	
	Peak HCl Concentration
	Puff Magnitude (P)
	Selected Organic Compounds

The independent variables were selected based on the likelihood of their ability to be controlled by an incinerator operator in the event of an ESV opening, which may be caused by a failure of available utilities (e.g., electricity), operator error, or an equipment failure. Based on these variables, the test matrix listed in TABLE 2 was developed. It was desired that a 0.1 RPM case be performed. However, the drive motor on the RKIS developed problems and 0.44 RPM was the lowest attainable non-zero rotation speed. It was also desired that a 0.14 Nm^3/min (300 scfh) air flow case be performed, but due to the problem of air in-leakage, coupled with the safety consideration of operating the kiln at significant negative pressure conditions (-37.3 Pa) during these extreme system failure conditions, 0.42 Nm^3/min (900 scfh) was the lowest attainable air flow rate. The 0.28 Nm^3/min (600 scfh) leak rate is 13% of the total combustion air supplied during normal operation. This value may be a higher percentage than is found in full-scale rotary kilns, since the leak rate is a function of kiln circumference and kiln design, but the total gas flow through the kiln is increased with kiln volume.

Tests were performed according to the following test protocol: steady-state gas flow conditions in the rotary kiln were established and the system was allowed to attain thermal equilibrium at 870 °C (1600 °F) and 11 % oxygen at the kiln exit. Charges consisted of a mixture of 50% toluene (TOL) and 50% carbon tetrachloride (CCl4) by mass, with a total charge mass of 200 g, absorbed into 180 g of

TABLE 2. Test Matrix.

Test No.[1]	% Normal Air[2]	RPM	Simulated Flare	Other Samples
2	100[3]	0.5	on	-
3	89	0.44	off	-
4	63	0.5	off	-
5	63	0	off	-
6	20	0.44	off	-
7	33	0.9	off	-
8	78	0.9	off	-
9	63	0.5	off	-
10	63	0.5	on	-
13	100[3]	0.5	on	organics[4]
14	63	0.5	off	organics[4]
15	63	0.5	on	organics[4]

[1] Non-consecutive run numbers are due to tests done on polyethylene/polyvinyl chloride mix, and are not within the scope of this paper.

[2] 0.28 Nm^3/min (600 scfh) leak rate was assumed, based on material balance calculations.

[3] 2.17 Nm3/min (4600 scfh) combustion air; normal operation (baseline tests with main burner lit through entire event).

[4] Tedlar$^{\circledR}$ bag samples and detector tubes.

ground corncob, and placed in a 0.95 L (1 qt) cardboard container. A single charge was batch fed into the rotary kiln and, 10 s after feeding, the main flame was extinguished, and the desired air flow rate and RPM were established. Each test was repeated five times. After runs 1 through 12 were completed, certain test conditions were repeated to perform sampling for volatile organic compounds (VOCs). VOCs were sampled during the transient event. Only one test was performed at each condition for the VOC samples. In addition to the simulated ESV tests; baseline tests were performed, which were identical to the simulated ESV tests; however, the main flame was not extinguished. The purpose of the baseline tests was to compare the failure mode caused by extinguishing the main flame, to the normal operation of the RKIS run in batch mode.

In addition to the tests with TOL/CCl$_4$, tests at selected conditions were performed with a mixture of polyethylene (PE) and polyvinyl chloride (PVC), for the purposes of verifying that a viable simulation of an ESV opening could be performed without damaging the equipment or creating a safety hazard for personnel, and also to estimate operating ranges for the HCl analyzer. The PE/PVC tests, although included in the numbering scheme for these tests, are not included in the data analysis section, since an insufficient number of points were present on which to perform the regression analysis.

Gases were monitored with continuous emission monitors (CEMs) to measure oxygen (O$_2$), carbon dioxide (CO$_2$), carbon monoxide (CO), nitric oxide (NO), and total hydrocarbons (THCs) both before and after the kiln's secondary combustion chamber, as well as hydrochloric acid (HCl) at the kiln exit. On runs No. 13 through 15, grab samples were taken using a Tedlar$^{\circledR}$ bag to give semi-quantitative analyses of VOCs. VOCs were collected in Tedlar$^{\circledR}$ bags described in EPA Method 18 (17). The Tedlar$^{\circledR}$ bag samples were analyzed by gas chromatography/mass spectrometry by EPA Method 8240 (18).

In addition to the Tedlar$^{\circledR}$ bag samples, detector tube (Dräeger tube) samples were taken on runs No. 13 through 15, to qualitatively determine if diatomic chlorine (Cl$_2$) or phosgene (COCl$_2$) was present in the stack gases. It was postulated that the lack of the water vapor normally present from the main flame might lead to a hydrogen deficiency, which could cause the formation of species not normally present in stack gases. The detector tubes were set up so that stack gases would be drawn through them at the maximum possible rate, for the duration of the simulated ESV opening event.

Surrogate Performance Indicators

It is necessary, when comparing incinerator operating conditions, to use a reasonable basis for determining the performance of the incinerator. The RCRA mandates that all hazardous waste incinerators maintain a 99.99% Destruction and Removal Efficiency (DRE) of each principal organic hazardous constituent (POHC) contained in the waste. DRE is a costly analysis to perform, and takes weeks before the analytical results are delivered. What is needed for research purposes is a "quick and dirty" measurement of incinerator performance that takes into account emissions of all easily measurable organic pollutants.

AEERL has been working to develop an on-line performance indicator for combustors burning hazardous waste (14). In particular, this on-line performance indicator must be easy to use and inexpensive. Ideally, an on-line "PIC Monitor" would be useful but, to date, on-line continuous measurement of trace organics has not progressed outside the laboratory. Therefore, due to current technology limitations, any on-line performance indicator must use only measurement techniques available today at a reasonable price. The new proposed RCRA regulations may require monitoring of CO and/or THCs on a continuous basis in all combustors burning hazardous waste. It seems appropriate to use these analyzers as the starting point for an on-line performance indicator for research purposes.

A typical hazardous waste consists of many different compounds but, in terms of an ultimate analysis, any incinerable waste would contain carbon, hydrogen, nitrogen, oxygen, ash, and a host of other compounds, such as heavy metals, halogens, sulfur, phosphorus, and moisture. Since incineration is combustion, the preferred end products are CO_2 and water vapor. However, complete conversion is never achieved and, due to fluctuations in feed composition, heat content, or batch charging, transients can occur that have the potential to deviate from optimal combustion conditions. In this case, PICs are created, with the predominant PICs being CO, unburned volatile and semi-volatile hydrocarbons (possibly halogenated, oxygenated, or nitrogenated), and soot, possibly containing condensed non-volatile organic material. FIGURE 2 illustrates these phenomena. CO was measured with non-dispersive infra-red gas analyzers (Beckman Model 864). THCs were measured with a heated THC analyzer (Beckman Model 402) operated at 149 °C (300 °F). Soot was measured by weighing the filters in the THC analyzer before and after each test, and using the sample gas flow rate to calculate emission rates (assuming isokinetic sampling). The waste feed had minimal ash content, so it was a reasonable assumption to assume that all filter particulate was soot.

By utilizing time-integrated responses from process gas analyzers rather than instantaneous or averaged responses, it is possible to derive an indicator of the relative degree of local oxygen
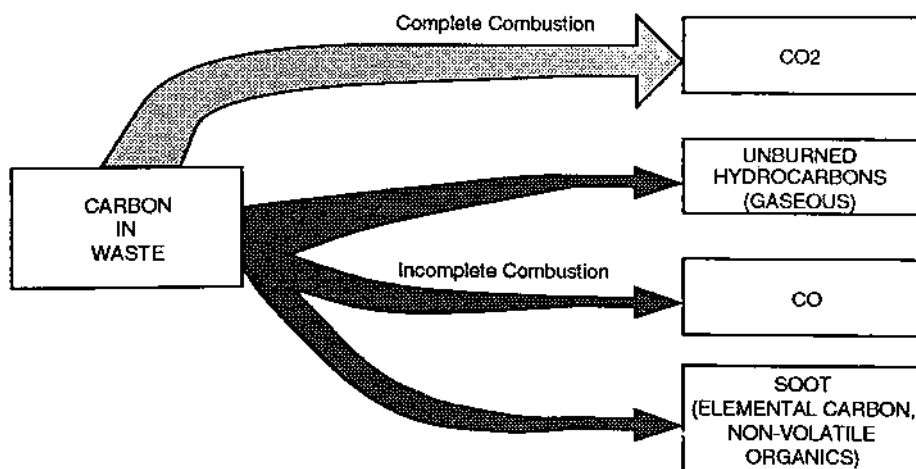

FIGURE 2. Fate of waste carbon.

starvation/poor combustion that waste material was exposed to while passing through the incinerator during a given measurement period. This performance indicator, called Puff Magnitude (P), is a quantity that is calculated using CO, THC, soot, and the estimated carbon content of the surrogate PIC species, then weighting these components according to their stoichiometric oxygen requirements. The three surrogate PIC fractions each forces different oxygen demands on the incinerator. For example, CO is a partially oxidized species, and requires less oxygen to become completely oxidized than, say methane. To take this into account, each of the surrogate PIC species can be summed and weighted according to the stoichiometric oxygen required to completely burn each component. P is expressed in units of moles O_2, and is defined as:

$$P = m_{thc}w_{thc} + m_{co}w_{co} + m_{soot}w_{soot} \qquad (1)$$

where m_{thc}, m_{co}, and m_{soot} represent the mass emission of THCs, CO, and soot, respectively, and w_{thc}, w_{co}, and w_{soot} are weighting factors based on the number of moles O_2 required to completely combust a given mass of each surrogate PIC species. For the purposes of calculating w_{thc} and w_{soot}, THC was assumed to be methane (CH_4) and soot was assumed to be elemental carbon.

P is an indicator of the relative degree of poor combustion that the waste is subjected to during the time that the measurements are taking place. P reflects the relative requirements for oxygen of the measured PIC components by reducing the contribution of partially oxidized species such as CO, and increasing the contribution of unoxidized species such as THCs and soot.

RESULTS

Based on the statistical experimental design, a regression analysis was performed on the data from the TOL/CCl4 tests, examining the effect of kiln air, RPM, and the simulated flare on total puff magnitude, and on the individual contributions of soot, CO, and THCs to total puff magnitude. Kiln air flow rate and RPM were found to be statistically significant variables determining the magnitudes of both PICs (as defined by P) and peak HCl concentration. The presence/absence of the simulated flare strongly affected PICs but, as would be expected, was not statistically significant regarding HCl, probably because the waste Cl was converted to HCl nearly quantitatively, and the amount of Cl that was incorporated into chlorinated PICs, though significant, was small relative to the total amount of Cl fed. Interestingly, it was found (during investigation of the statistically significant relationships between the dependent and independent variables) that the presence/absence of the main kiln flame was not a statistically significant variable in determining the magnitude of either PICs or HCl. This observation leads to the important suggestion that emissions that occur during an ESV opening event are similar in magnitude to emissions found at the kiln exit during the occurrence of a transient puff. Transient puffs can occur during routine kiln operation due to batch charging, but are normally destroyed while passing through the secondary combustion chamber. Although unexpected, this observation suggests that, as long as temperatures can be maintained in the kiln chamber during the ESV opening event, the observed high oxygen levels tend to offset the loss of the main flame.

Time Resolved Data

Previous work on transient emissions (puffs) from this rotary kiln involved experimentation with the gas flame in place. Under these conditions, puff magnitude and puff intensity increased with increased kiln rotation speed (14, 15) and with increased kiln temperature (4), but decreased with increased oxygen content in the primary flue gas (14). It has been shown that the most important phenomenon determining transient emissions was the release rate of organics from the sorbent pack, and how this depended on surface exposure rate (13).

The current situation examined has both similarities and differences from the base case described above. Some of these similarities and differences can be discussed with reference to FIGURE 3 which presents time-resolved traces of CO, CO_2, O_2, temperature, and THCs. In the first column are depicted time-resolved data obtained under normal baseline conditions (flame on); in the second column, the analogous data for the ESV (flame out) investigation at a kiln rotation speed of 0.5 RPM; and in the third column, the data for the ESV (flame out) investigation at a 0 RPM. The temperature
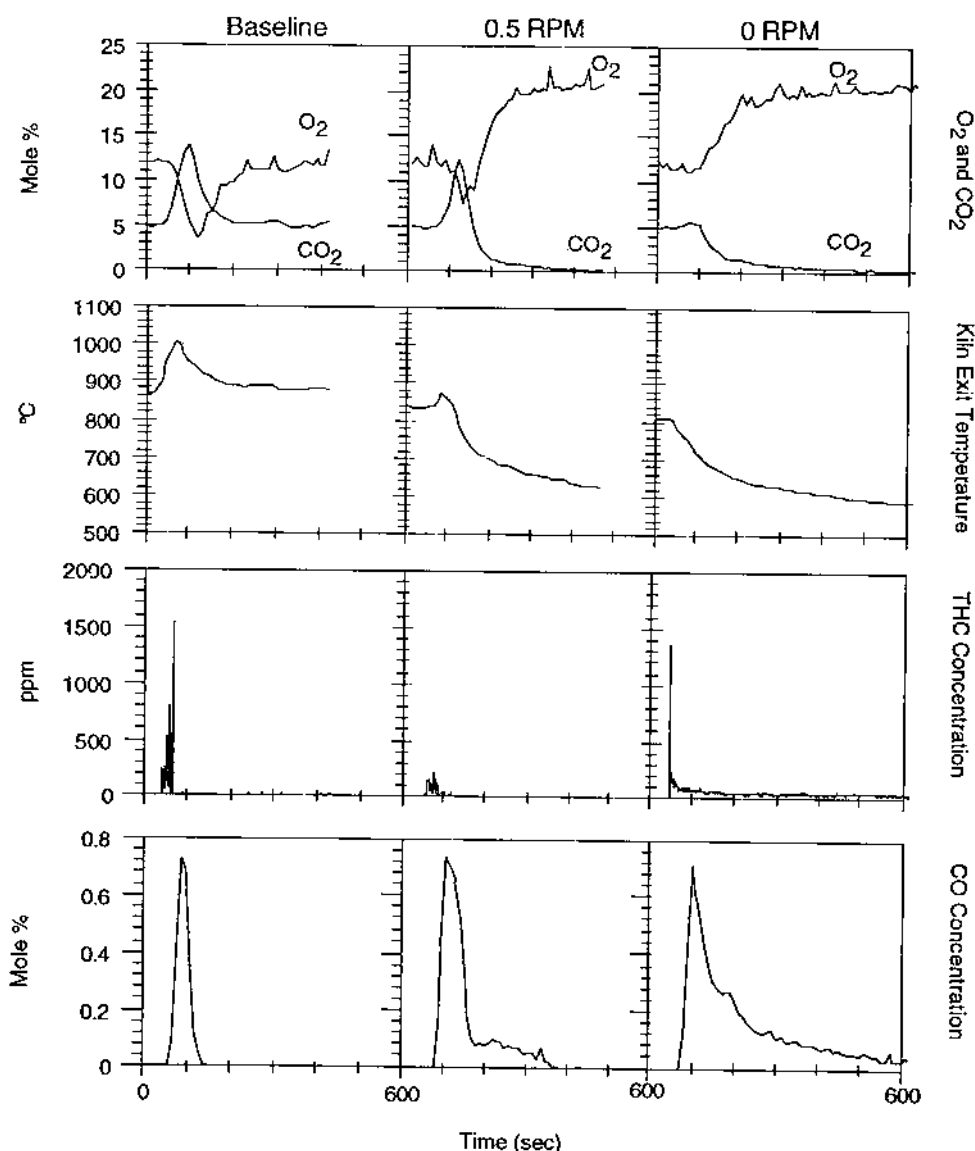
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FIGURE 3. Time-resolved traces of CO, CO_2, O_2, and THCs at three different conditions: Run 2; Baseline (with main flame), Run 4; 0.5 RPM (without main flame), and Run 5; 0 RPM (without main flame).

traces are as expected, and decay slowly with the flame shut off. Full-scale kiln temperatures may decay slower due to larger refractory masses. The oxygen profiles shown in the first two columns are similar, in that they both show comparable dips between 0 and 200 seconds, although for the base case the O_2 returns to its original value, while for the ESV case at 0.5 RPM, it subsequently climbs to 21%. For the 0 RPM ESV case, there is no dip discernible, and the concentration climbs to 21%. Time resolved THC traces are similar for the base case (column 1) and the ESV case at 0.5 RPM (column 2), but the 0 RPM case (column 3) shows only a single spike followed by no further activity. The CO traces also suggest a sharp initial peak only for the base case, but followed by a slow CO formation for the other two cases shown.

Insight into controlling mechanisms can be gained by interpreting these traces as follows. There are two regimes of waste processing and/or combustion that are applicable. When the flame is on, the

puff magnitude is determined largely by the volatile release rate, which is essentially governed by the surface (of the sorbent aggregate) exposed to a high temperature. The increased oxygen flow when the flame is off would appear to facilitate the partial oxidation of the released THC (which are decreased, compared to the base case) to CO (which is increased compared to the base case). When the flame is off, there is a second regime consisting of slow pyrolysis within the sorbent bed. Fewer organics are released as volatile hydrocarbons, possibly because the exposed surface has been cooled by the flow of fresh air. The greater the air flow rate, the faster the surface is cooled, the fewer volatiles are released directly, and the more are pyrolized to form carbonaceous compounds within the bed, over very long times (500 s). These carbonaceous species are ultimately entrained in the air flow, and are counted as soot. Different from the base case is, however, the fact that, while there, the soot is probably formed inside a gaseous puff; here, under ESV conditions, it is formed within the bed. In fact, data shown below support the idea that there are two sources for soot, with in-bed formation dominating at low RPM and high kiln air flows, and in-puff formation dominating at high RPM (rapidly exposed area) and possibly lower kiln air flows.

Emissions of PICs

Effect of Kiln Air Flow Rate

FIGUREs 4a and 4b illustrate the effect of kiln air flow rate on P (puff magnitude). Low air flow rates result in lower emissions of PICs. This phenomenon appears to be related to the fact that, even though only small amounts of air will enter the kiln after the burner is cut off, adequate oxygen levels may still remain in the primary combustion chamber due to the absence of the main flame and its associated oxygen demand and reduced waste volatilization rate. The ambient oxygen levels promote combustion and oxidation of the waste compounds remaining in the kiln. At low air flow rates, the thermal inertia of the kiln apparently maintains temperatures that are sufficiently high to sustain combustion. In addition, the likelihood of entrainment of unburned bed material is lower at lower air flow rates. As air flow rates increase, combustion reactions that might occur in the gas phase are quenched by the ambient air being forced into the kiln. Additionally, there is the possibility of greater entrainment of unburned bed material. Thus, it appears that a low, but non-zero, air flow rate through the kiln is advantageous during an ESV opening event. Depending on the rate of in-leakage in a full-scale kiln, sufficient air might be available through the natural draft generated from having the ESV being open to the atmosphere. If a particular system has a low air in-leakage rate, it might be more advantageous to allow some small level of combustion air to flow through the burner. When examining the effect of a simulated flare on organic emissions, the presence of the flare (as operated in this test equipment) dramatically reduces CO and THCs, but has little effect on the carbonaceous particulate. Soot is typically more difficult to burn out than CO and THCs.

Effect of Kiln RPM

The effect of kiln RPM on PIC emissions during an ESV opening was quite interesting, as is illustrated in FIGUREs 5a and 5b. Emissions of PICs were high at both the zero and at the high rotation cases, but exhibited a minimum at a value somewhere between the two. This differs from base case results with the main flame in place where minimum puff emissions occurred at the lowest RPM. The regression analysis used to create the curves indicates that this minimum is at around 0.4 RPM. However, as mentioned earlier, equipment problems made it impossible to achieve 0.1 RPM, the desired value for the low rotation case. The shape of the curve in FIGUREs 5a and 5b might well be different had data for 0.1 RPM been achievable. Notice that soot is the predominant PIC at the zero rotation case, both with and without the flare. It appears that, at the zero rotation case, the bed of waste in the kiln is not mixed, and tends to pyrolize in place, generating significant amounts of soot. As was reported previously (12, 13), the surface renewal processes that occur due to the rotation of the kiln are one of the primary mechanisms governing the rate of waste release from the bed. As rotation increases, the bed mixes and is better able to combust. At very high rotation speeds, the waste is released from the bed very rapidly and can produce high emissions due to inadequate oxygen
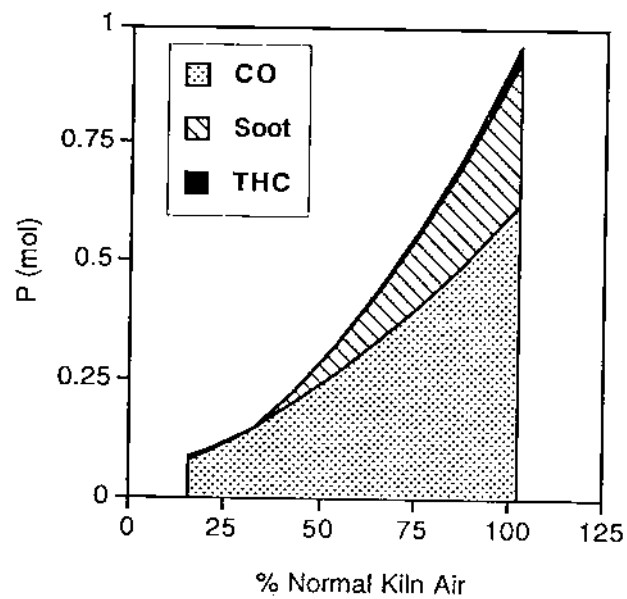
FIGURE 4a. Regression model predictions of the effect of kiln air flow rate on puff magnitude (P); without simulated ESV flare; RPM=0.5.
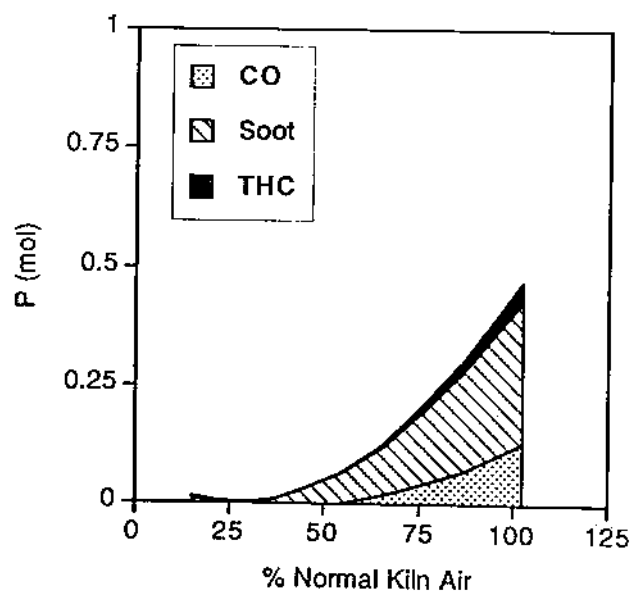

FIGURE 4b. Regression model predictions of the effect of kiln air flow rate on puff magnitude (P); with simulated ESV flare; RPM = 0.5.
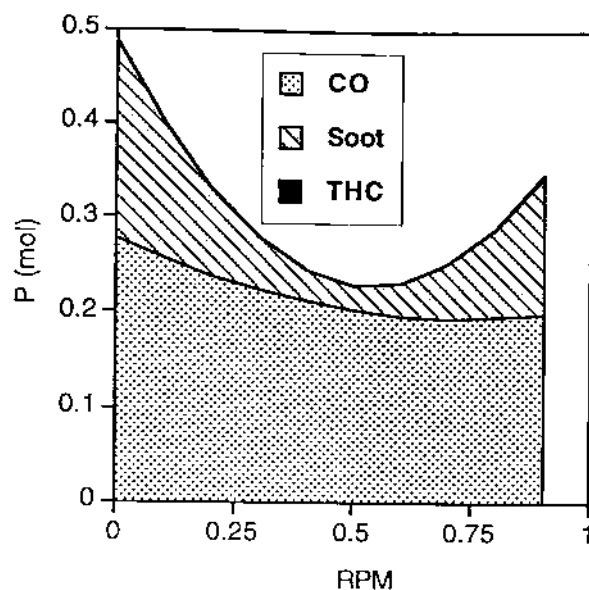
FIGURE 5a. Regression model predictions of the effect of kiln rotation speed on puff magnitude (P); without simulated ESV flare; kiln air = 0.94 Nm³/min (2000 scfh).
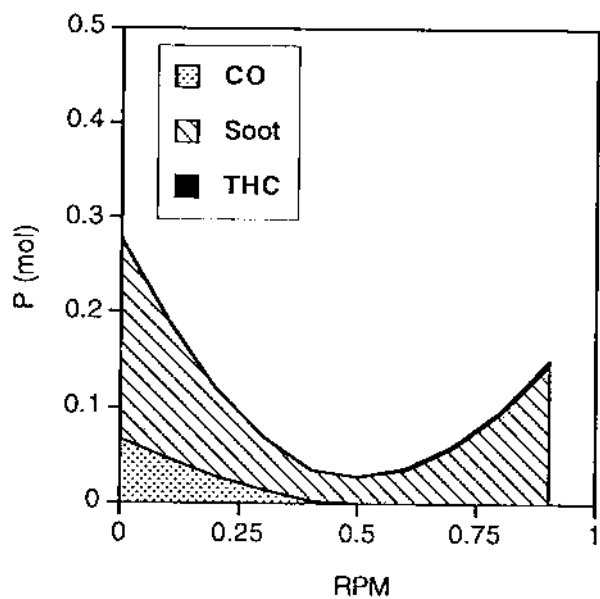

FIGURE 5b. Regression model predictions of the effect of kiln rotation speed on puff magnitude (P); with simulated ESV flare; kiln air = 0.94 Nm³/min (2000 scfh).

availability for transport. It would appear that, in the event of an ESV opening, a small, but non-zero rotational speed would be desirable to minimize organic emissions.

Emissions of HCl

Effect of Kiln Air

HCl emissions are indicative of waste combustion/release rates. HCl concentrations exhibited a maximum with respect to kiln air flow rate, as is shown in FIGURE 6. The decline in peak HCl concentration measured between 50 and 100 % normal kiln air flow rates is due primarily to dilution. The rise in peak HCl, between 0 and 50 % normal kiln air tracks the oxidation of the chlorinated waste compound and the release of HCl from the burning bed is a direct function of the rate of bed combustion. A low kiln air flow rate appears to moderate the combustion of the bed in the kiln, and thus, moderates the emissions of HCl. Increasing the air flow rate initially increases the rate of combustion, increasing the concentration of HCl in the stack. Eventually, though, increases in kiln air result in decreasing HCl concentrations because of dilution and possibly also because of quenching. Since it may not be a luxury for an incinerator operator to be able to force the flow of significant quantities of additional air to dilute the gases leaving the ESV, it seems prudent to take the course to allow minimal air in-leakage, and moderate the bed combustion, rather than dilute the flue gases, especially in light of the effect of kiln air on PIC emissions.

Effect of Kiln RPM

Increasing kiln rotational speed increased peak HCl concentrations, as illustrated in FIGURE 7. This result follows what would be expected both from intuition and past experimental work on puffs from this laboratory. Since the HCl concentrations are related to the rate of waste release from the bed, slowing the rate of waste release from the bed would result in lower peak HCl concentrations.
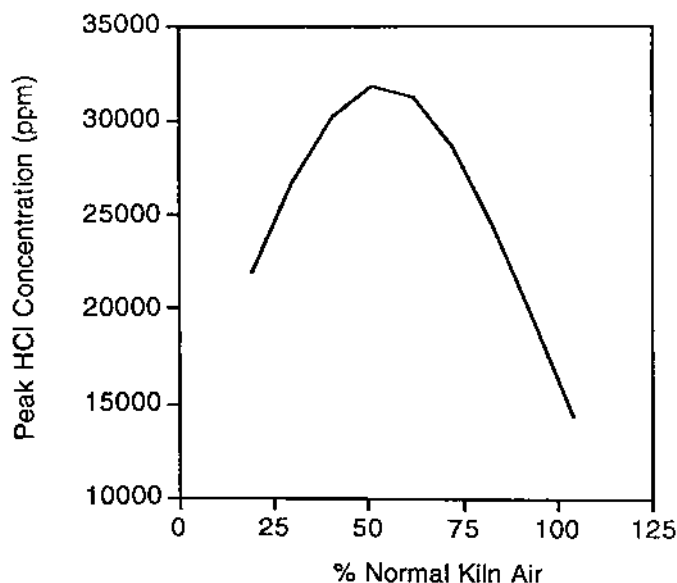

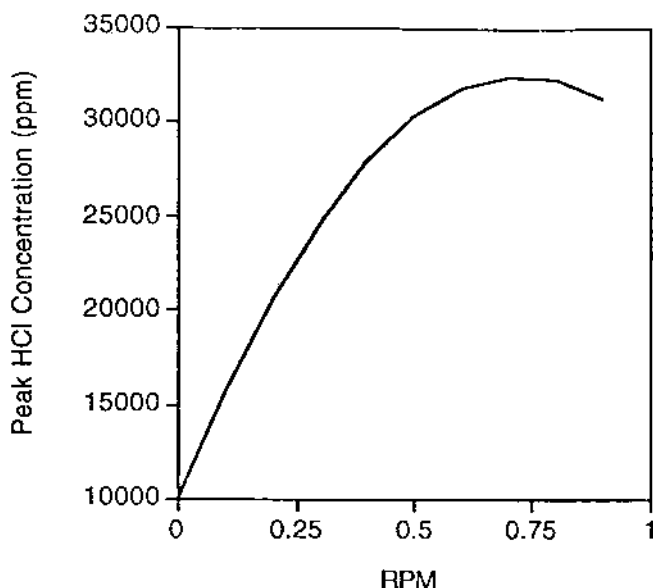FIGURE 6. Regression model predictions of the effect of kiln air on peak HCl concentrations; RPM = 0.5.

FIGURE 7. Regression model predictions of the effect of kiln RPM on peak HCl concentrations; kiln air = 0.94 Nm^3/min (2000 scfh).

Organic Samples

Proper quantification of transient emissions is difficult, since all standard EPA methods for PIC analysis require significant amounts of sampling time, and are best done over steady-state operation. Emissions from single transient events are difficult to sample and analyze. The samples from the Tedlar® bags and detector tubes, although not meant to be quantitative, do give some insight into what compounds might be formed during ESV openings. One concern about the potential differences for PICs generated during ESV openings is that there may be a lack of available hydrogen, since the water vapor generated from the main flame is no longer present. Since it is possible that the lack of hydrogen (and resulting hydroxyl radicals) could form species associated with hydrogen-deficient combustion conditions, such as those found when incinerating highly halogenated wastes, the investigators wanted to screen for easily identifiable PICs, and to examine the potential for the formation of diatomic Cl_2 or phosgene $(COCl_2)$, due to their toxic nature.

The detector tubes did not yield detectable quantities of either Cl_2 or $COCl_2$. Detection limits ranged from 187 to 575 ppm for Cl_2 and from 0.19 to 0.57 ppm for $COCl_2$. It is possible that sufficient hydrogen was present from the other materials in the bed to reduce these species below detection limits. In a full-scale system, the presence of water vapor from recently fed waste in the bed may provide sufficient hydrogen to minimize the emissions of Cl_2 and phosgene. This is especially true if a significant amount of moisture is present in the solid waste feed.

The Tedlar® bag samples yielded detectable quantities of some volatile organic species. The results from the Tedlar® bag analyses are presented in TABLE 3. Of particular note is the significant quantity of methylene chloride present in the samples. Presumably, this is a PIC formed from decomposition of CCl_4, which was detected as well. FIGURE 8 illustrates the total concentrations of identified VOCs from each run. A phenomenon of note is the concentration of detectable species emitted during run No. 13, which was a baseline test with the main burner lit for the duration of the run, and run No. 14, which was a test done under the simulated ESV opening conditions. The concentrations of VOCs from those two tests were the same order of magnitude. Run No. 13 simulated the transient puffs that can occur during normal kiln operation (5, 19), and which are normally dealt with by the incinerator's secondary combustion chamber and downstream flue gas

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TABLE 3. List of Compounds Identified from Tedlar® Bag Samples, ng/L.

Run No.	13	14	15
(1-Methylethenyl)-Benzene	ND	75	ND
1,1,1 Trichloroethane	10	ND	7.2
2-Chlorophenol	99	ND	84
2-Hydroxybenzaldehyde	31	ND	ND
Acetic Acid	70	123	ND
Acetone	76	ND	ND
Benzene	ND	29	ND
Benzothiazole	48	ND	ND
Carbon Tetrachloride	ND	25	14
Chlorobenzene	11	ND	3
Dichlorobenzene	ND	ND	ND
Ethylbenzene	ND	18	6
Methylene Chloride	1900	1100	6
Nitrophenol	ND	200	110
Phenol	52	320	42
Tetrachloroethene	ND	58	ND
Toluene	100	830	56
Trichloroethene	ND	7	ND
Xylenes	69	113	34

ND = not detected.

cleaning equipment. The fact that the magnitude of emissions during the system failure tests was similar to that of the emissions during normal operation, indicates that the poor combustion conditions generated from the extinguishment of the main flame are partially offset by the higher levels of oxygen present when the main flame is extinguished, provided that there is sufficient thermal inertia in the kiln and burning bed to maintain combustion for a period of time sufficient to combust most of the waste.
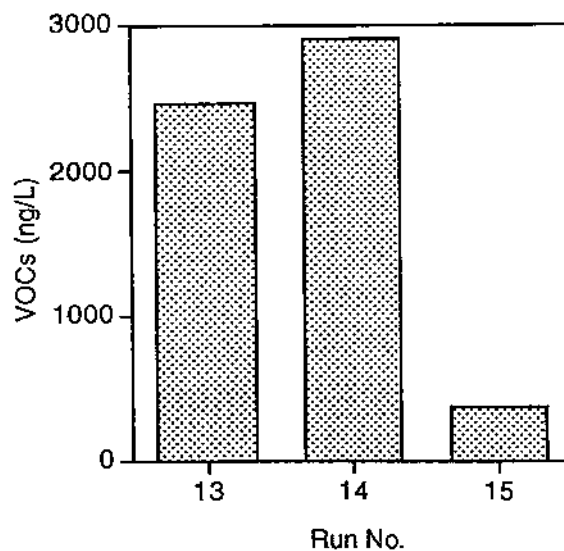

FIGURE 8. Total identified VOCs measured in Tedlar® bag samples.

The organic emissions leaving the ESV are not significantly different from those leaving the kiln under batch operation, other than the fact that, without a secondary combustion chamber present, high levels of organics potentially can be emitted directly into the atmosphere. As such, the use of an emergency flare near the opening of the ESV appears to be attractive, and would not impose a significant pressure drop on the gases leaving the ESV. The concentrations of organics found in run No. 15 (see FIGURE 8), which are much lower than those found in run No. 13 or 14, support this hypothesis as well. However, caution must be exercised when inferring the effect of an emergency flare from the simulated flare used in these tests. For example, the simulated flare in these tests did not provide significant flame contact with the kiln effluent. In addition, there may be safety issues when trying to operate a flare under conditions causing an ESV opening.

CONCLUSIONS

Tests were performed on a bench-scale rotary kiln incinerator simulator to examine operating parameters that can be manipulated in the event of an ESV opening, in order to minimize the impact of emissions from the open ESV on personnel near the incinerator. The effect of these parameters on emissions of HCl and organics was examined. Organics were measured using both surrogate performance monitors (CO, THCs, and soot) and semi-quantitative analysis of gaseous grab samples. Conclusions are as follows:

- Emissions of PICs can be reduced by using a low air flow rate (perhaps the flow rate achieved through normal air in-leakage and the natural draft caused by the ESV opening) and a low, but non-zero kiln rotation speed.

- Emissions of HCl can be minimized by using a low air flow rate and low kiln rotation speed. The addition of an emergency flare near the opening of the ESV appears to be very effective in reducing the emissions of organic compounds.

- Qualitative analysis of organic emissions indicates that emissions of Cl_2 and phosgene do not appear to be a problem, even in the absence of the excess of water vapor normally provided by the primary flame.

- It appears that the concentrations of the organic PICs emitted during an ESV opening are comparable to those emitted from the rotary kiln (prior to secondary combustion) during normal batch mode operation, due to the higher levels of oxygen present in the kiln during the ESV opening event.

Further studies examining phenomena associated with ESV openings could involve closer examination of the effect of rotation on PICs, emissions of metals, and emissions of certain organic species of interest, such as dioxins and furans. These results have not been confirmed on any full-scale system and should be used accordingly.

ACKNOWLEDGMENTS

DISCLAIMER

The research described in this article has been reviewed by the Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. The contents of this article should not be construed to represent Agency policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

REFERENCES

1. U.S. EPA - OSHA Joint Task Force, (1991) "Evaluation of Compliance with On-Site Health and Safety Requirements at Hazardous Waste Incinerators."

2. Oppelt, E.T., (1987) Incineration of Hazardous Waste A Critical Review., *J. Air Poll. Cont. Assoc.*, **37**, p. 558.

3. Linak, W.P., J.D. Kilgroe, J.A. McSorley, J.O.L. Wendt, and J.E. Dunn, (1987a) On the Occurrence of Transient Puffs in a Rotary Kiln Incinerator Simulator I. Prototype Solid Plastic Wastes, *J. Air Poll. Cont. Assoc.*, **37**, p. 54.

4. Linak, W.P., J.A. McSorley, J.O.L. Wendt, and J.E. Dunn, (1987b) On the Occurrence of Transient Puffs in a Rotary Kiln Incinerator Simulator II. Contained Liquid Wastes on Sorbent, *J. Air Poll. Cont. Assoc.*, **37**, p. 934.

5. Wood, R.W., (1987) Eastman Kodak Company Rotary Kiln Performance Testing, *Proceedings on Rotary Kiln Incineration of Hazardous Waste*, p. 105, Baton Rouge, LA.

6. Wood, R.W., R.E. Bastian, J.M. Osborne, A. Sigg, and J.D. Wilson, (1989), "Measurement and Control of Combustion Excursions from Rotary Kiln Incinerators," *82nd Annual Meeting Air and Waste Management Assoc.*, 89-2.7.

7. Cundy, V.A., T.W. Lester, A.M. Sterling, A.N. Montestruc, J.S. Morse, C.B. Leger, and S. Acharya, (1989a), "Rotary Kiln Incineration III. An In depth Study - Kiln Exit/Afterburner/Stack Train and Kiln Exit Pattern Factor Measurements During Liquid CCl_4 Processing," *J. Air Poll. Cont. Assoc.*, **39**, 944-952.

8. Cundy, V.A., T.W. Lester, A.M. Sterling, A.N. Montestruc, J.S. Morse, C.B. Leger, and S. Acharya, (1989b), "Rotary Kiln Incineration IV. An In depth Study - Kiln Exit, Transition and Afterburner Sampling During Liquid CCl_4 Processing," *J. Air Poll. Cont. Assoc.*, **39**, 1073-1085.

9. Cundy, V.C., A.M. Sterling, T.W. Lester, A.L. Jakway, C.B. Leger, C. Lu, A.N. Montestruc, and R.B. Conway, (1991a) "Incineration of Xylene/Sorbent Packs. A Study of Conditions at the Exit of a Full Scale Industrial Incinerator," *Environ. Sci. Tech.*, **25**(2), 223-232.

10. Cundy, V.A., C. Lu, C.A. Cook, A.M. Sterling, C.B. Leger, A.L. Jakway, A.N. Montestruc, R. Conway, and T.W. Lester, (1991b), "Rotary Kiln Incineration of Dichloromethane and Xylene: A Comparison of Incinerability Characteristics Under Various Operating Conditions," *J. Air Waste Manage. Assoc.*, **41**, 1084-1094.

11. Emergency Safety Vent Subcommittee of the ASME Research Committee on Industrial and Municipal Wastes, (1991), "Incinerator Emergency Safety Vents."

12. Wendt, J.O.L. and W.P. Linak, (1988) Mechanisms Governing Transients from the Batch Incineration of Liquid Wastes in Rotary Kilns, *Combust. Sci. and Tech.*, **61**, p. 169.

13. Wendt, J.O.L., W.P. Linak, and P.M. Lemieux, (1990) "Prediction of Transient Behavior During Batch Incineration of Liquid Wastes in Rotary Kilns," *Haz. Waste & Haz. Mat.* **7**,1, p. 41.

14. Lemieux, P.M., W.P. Linak, J.A. McSorley, J.O.L. Wendt, and J.E. Dunn, (1990) "Minimization of Transient Emissions from Rotary Kiln Incinerators," *Combust. Sci. and Tech.*, **74**, pp. 311-325.

15. Lemieux, P.M., W.P. Linak, J.A. McSorley, and J.O.L. Wendt, "Transient Suppression Packaging for Reduced Emissions from Rotary Kiln Incinerators," *Combust. Sci. & Tech.*, **85**, 1-6, p. 203, 1992.

16. Hicks, C.R., (1973) *Fundamental Concepts in the Design of Experiments*, 2nd ed., Holt, Rinehart and Winston Inc., New York, NY.

17. Method 18, "Measurement of Gaseous Organic Compounds Emissions by Gas Chromatography," in Title 40 Code of Federal Regulations Part 60, Appendix A, U.S. Government Printing Office, Washington, DC, 1991.

18. Method 8240, "Gas Chromatography/Mass Spectrometry for Volatile Organics," in Test Methods for Evaluating Solid Waste, Volume IB: Laboratory Manual Physical/Chemical Methods, EPA-SW-846 (NTIS PB88-239223), 3rd ed., U.S. Environmental Protection Agency, Washington, DC, 1986.

19. Bastian, R.E. and R.W. Wood, (1987) Eastman Kodak Company Chemical Waste Incineration Organic Compound Destruction, *Proceedings on Rotary Kiln Incineration of Hazardous Waste*, p. 80, Baton Rouge, LA.